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List of research papers published in the journals notified on UGC Care list during 2018-23

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Pure red luminescence and concentration-dependent tunable emission color from europium-doped zinc sulfide nanoparticles

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ABSTRACT

Nano-sized Eu³⁺-doped ZnS particles were prepared by chemical precipitation method using polyethylene glycol as capping agent. The structural and morphological studies of ZnS:Eu³⁺ nanoparticles were carried out using X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). XRD results show that ZnS:Eu³⁺ nanoparticles have a cubic structure for all Eu³⁺ concentrations. Dependence of doping concentration on the photoluminescence (PL) of ZnS:Eu³⁺ nanophosphor was studied for excitations at 395 nm and 465 nm. At 395-nm excitation, emission colors of ZnS:Eu³⁺ nanophosphor lie in blue, green, yellow, and red regions of chromaticity diagram for different doping concentrations. But for all doping concentrations we got red emission when the excitation wavelength was 465 nm and the color purity was 92% for 0.03 M doped sample.

1 Introduction

The present day scientific and technical awareness in nano-sized semiconductor crystals is originated from the view of production of new materials with novel optoelectronic properties. Semiconductor nanophosphors have the opportunities for property modification and applications due to color purity, luminescence quantum efficiency, high optical gain, and photostability arising from the large surface-tovolume ratio and quantum confinement effect [1–8]. Continuing the work of Bhargava et al. [1] on ZnS:Mn, ZnS nanoparticles doped with different rare earth metal ions and transition metals ions (e.g., Ni, Tb, Cu, Co, Ag, and Au) have been prepared using a variety of synthesis methods and studied their properties [9–13]. The narrow peaks in the excitation and emission spectra are characteristic features of the rare earth ions and their relative intensities provide information about its local environment and point

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group symmetry [14]. Since the trivalent europium exhibit intense sharp emissions due to ${}^{5}D_{0}-{}^{7}F_{i}$ transitions (j = 0-6) from the excited ${}^{5}D_{0}$ state to the *j* levels of the ground state ${}^{7}F_{j}$, Eu^{3+} is the most exciting dopant among the rare earth metal ions. Since its 4f orbital is shielded by outer orbitals which declines its coupling with the nearby ligands the emissions are stable and sharp. The interaction of the rare earth ions with the electric field and the magnetic field component of the light lead to electric and magnetic dipole transitions. With respect to an inversion center the electric dipole operator possesses odd transformation properties under inversion. Hence intra-configurational electric dipole transitions like 4f-4f transitions are forbidden. The transitions such as the ${}^{5}D_{0}-{}^{7}F_{1}$ transition has magnetic dipole character and even transformation properties under inversion and hence the transitions between these states are allowed [15].

Since the ionic radius of Eu^{3+} is large (0.95 Å) in comparison with Zn^{2+} (0.74 Å) the incorporation of Eu^{3+} in the ZnS lattice is difficult and hence Eu^{3+} locates on the surface or trapped in the matrix. Normally the Eu³⁺ ions are well isolated in the ZnS matrix and hence the energy transfer is not possible. Besides this, the charge imbalance and higher coordination of Eu³⁺ ion make it difficult to incorporate them in ZnS. In the past few years, Eu³⁺-doped ZnS nanoparticles have been synthesized by various researchers using different techniques [16–22]. ZnS:Eu-based AC thin film electroluminescent device for white emission has been reported [23]. In all these reports intensity of PL emission in the blue region due to ZnS host is greater than intensity of transitions between the Eu³⁺ energy levels. In some cases there is evidence of energy transfer from ZnS host to Eu^{3+} , but the characteristic emissions due to Eu³⁺ are either very weak or not clearly observed. Here, we report a low-temperature cost-effective chemical precipitation technique for the synthesis of PEG (polyethylene glycol)-capped ZnS:Eu³⁺ nanoparticles with different Eu³⁺ concentrations and their structural and optical properties. We observed the synergistic effect of host sensitized and localized luminescence.

2 Experimental

Nano-sized ZnS:Eu³⁺ was synthesized by chemical precipitation method using zinc acetate, europium acetate [Eu(CH₃COO)₃], and sodium sulfide [Na₂S]. For the synthesis, solvent used was the mixture of deionized water and ethanol in 1:1 ratio. ZnS:Eu³⁺⁻ nanoparticles with Eu concentration of 0.01 M, 0.02 M, 0.03 M, 0.04 M, and 0.05 M have been precipitated from a mixture of acetates of zinc and europium with sodium sulfide in 1:2 M ratio of Zn:S. To the above solution PEG was added with constant stirring at 70 °C. The precipitate thus obtained was washed many times with water-ethanol solution. Afterward, the filtrate was dried for 11 h at 80 °C to get PEG-capped ZnS:Eu nanoparticles. The same procedure was used to prepare the undoped ZnS nanoparticles.

Bruker AXS D8 Advance X-ray diffractometer was used for the X-ray diffraction (XRD) studies. Morphology and compositional analyses of the prepared samples were carried out by JEOL JSM 6390 LV scanning electron microscope with EDS (energy-dispersive analysis) attachment. Varian Cary 5000 UV-Vis-NIR spectrophotometer was used for diffuse reflectance spectral (DRS) studies. FTIR analysis was done by Shimadzu IR Affinity-1 spectrophotometer. Photoluminescence (PL) spectra of the samples were taken with Horiba Fluromax 4C research spectrofluorometer.

3 Results and discussion

3.1 Structural and morphological study

The structure of the obtained undoped ZnS and doped ZnS:Eu³⁺ ($x \mod \%$) ($x = 1, 2, 3, 4, \mod 5$) nanoparticles was determined by XRD (X-ray powder diffraction). The XRD patterns (Fig. 1a) of ZnS and Eu-doped ZnS nanoparticles show a single phase having three diffraction peaks consistent with (111), (220), and (311) diffraction planes of cubic ZnS (JCPDS file No. 65-0309). Eu doping in ZnS has not altered the actual phase and no trace of secondary phase was observed, indicating high purity of the samples. The intensity of the diffraction planes increases with increase of Eu concentration indicating improved crystallinity. This may be due to the presence of zinc vacancies in the host lattice. Europium

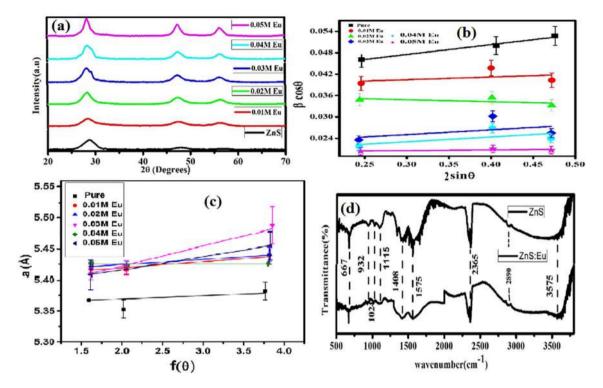


Fig. 1 a XRD, b W-H plot, c N-R plot, and d FTIR spectra of ZnS:Eu nanoparticles

atoms occupying empty zinc sites contribute to diffraction intensity. From the diffraction peaks, the grain size was estimated using Scherrer equation [24]. The reduced grain size and the strain which cause the broadening of diffraction peaks were calculated from the Williamson–Hall (W–H) method. By this method the crystallite size and the lattice strain [25] are calculated using the relation,

$$\beta\cos\theta = \frac{0.9\lambda}{D} + 2\xi\sin\theta$$

where β is the FWHM of the diffraction peak, λ is the X-ray wavelength, θ is the Bragg's angle, and ξ is the lattice strain. The W–H plot of the synthesized samples is given in Fig. 1b. The lattice strain and the crystallite size are obtained from the slope and from the intercept value of the plot. The mean grain size obtained from the Scherrer equation and W–H plot and the lattice strain are tabulated in Table 1. Using the Bragg equation [24], the lattice constants of the ZnS:Eu³⁺ (*x* mol%) (*x* = 1, 2, 3, 4, 5) nanoparticles were calculated (see Table 1). The accurate values of lattice constants can be determined using Nelson–Riley (N–R) plot (Fig. 1c), and the plot between calculated lattice constants from XRD pattern and the error function [25] is given by,

$$f(\theta) = \frac{1}{2} \left[\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right].$$

The lattice constants of the doped samples (Table 1) are greater in comparison with the undoped sample due to the change in ionic radius of the Eu³⁺ ion (0.95 Å) and Zn²⁺ ions (0.74 Å). A shift in diffraction angle toward left can be observed on doping which is also due to this mismatch in ionic radius. Williamson and Smallman relation, $\delta = \frac{1}{D^2}$ [20], was used to calculate dislocation density (δ), and it is given in Table 1.

Figure 1d depicts the FTIR spectra of ZnS and ZnS:Eu³⁺ nanoparticles. Since PEG have absorptions peaks similar to primary alcohol they consist of bending and stretching vibrations corresponding to C–H bending, C–O stretching, C–C stretching, and C–H stretching [26]. The spectral band in the region 3575 cm⁻¹ is due to the stretching vibration of OH group [26]. The stretching mode around 2890 cm⁻¹ was due to methylene group in PEG. The bending vibration of –CH₂ was seen at 1408 cm⁻¹ [27]. The C–C stretching mode is seen at 938 cm⁻¹ [26]. The spectral band at 1024 cm⁻¹ and 1115 cm⁻¹ are derived from the C–O stretching mode [26, 28]. The

Eu ³⁺ concentration	Crystallite size, D (nm)	Lattice parameter calculated (Å)	Lattice parameter by N-R plot (Å)	Strain $(\xi) \times 10^{-3}$	Dislocation density (δ) × 10 ¹⁷ /m ²	Band gap (eV)
ZnS	3	5.367	5.343	8.6	1.16	3.73
ZnS:Eu ³⁺ (0.01 M)	3	5.417	5.368	9.7	0.84	3.61
ZnS:Eu ³⁺ (0.02 M)	4	5.432	5.374	11.5	0.62	3.60
ZnS:Eu ³⁺ (0.03 M)	5	5.440	5.376	19.6	0.80	3.56
ZnS:Eu ³⁺ (0.04 M)	6	5.430	5.407	21.2	0.34	3.50
ZnS:Eu ³⁺ (0.05 M)	7	5.425	5.397	28.0	0.22	3.48

 Table 1 Structural parameters of ZnS and ZnS:Eu³⁺ nanoparticles calculated from XRD

band at 667 cm^{-1} is due to the ZnS stretching vibrations [10].

The crystallite size and morphology of ZnS: Eu^{3+} (0.03 M Eu^{3+}) nanoparticles were analyzed by TEM technique (Fig. 2). The particles are distributed with less aggregation and size of particles range from 3.5 to 7 nm with maximum number of particles at size 5 nm (Fig. 2a). Inset of Fig. 2a is the particle size distribution and the average particle size is 5.8 nm. The SAED (selected area electron diffraction) diagram (Fig. 2b) shows fine-crystallized diffraction

pattern with a central halo and concentric rings. These rings are indexed to the reflections from $(1\ 1\ 1)$, $(2\ 2\ 0)$, and $(3\ 1\ 1)$ planes ensuring the cubic phase of the ZnS:Eu³⁺ nanoparticles. HRTEM image of ZnS:Eu³⁺ given in Fig. 2c shows that the lattice spacing is around 0.28 nm, consistent to the (111) plane spacing of cubic ZnS indicating the nanoparticles grow preferentially along the [111] direction.

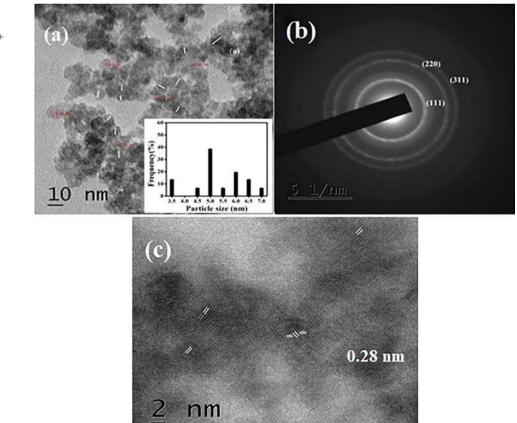


Fig. 2 a TEM image, **b** SAED pattern, and **c** HRTEM image of ZnS:Eu³⁺ (Eu³⁺ = 0.03 M) nanoparticles (inset particle size distribution)

3.2 Diffuse reflectance analysis

Diffuse reflectance spectroscopy (DRS) was used (Fig. 3a) to study the optical properties of the ZnS:Eu³⁺ nanocrystallites synthesized at different doping levels. Absorption spectra (Fig. 3b) were plotted using Kubelka–Munk function,

$$F(R) = \frac{k}{s} = \frac{(1-R)^2}{2R},$$

where k, s, and R represent the absorption, scattering, and the reflection coefficients. It is seen that the absorption edge of ZnS:Eu³⁺ samples gets red shifted in comparison with undoped sample and the shift increases with the increase of doping concentration. The band gap energy was calculated from the DRS studies by plotting energy (hv) vs. [F(R)hv]² and extrapolating the linear portion of the graph (Fig. 3c) onto the energy axis. For pure ZnS sample the band gap is greater than bulk (3.54 eV) due to confinement effects. On doping, crystallite size increases and band gap decreases which can be attributed to size effects. But it goes below that of bulk ZnS as the doping concentration increases above 3 at.% although the crystallite size is small. Hence this may be due to the formation of band tails or shallow defect levels within the band gap [28].

3.3 Photoluminescence study

Figure 4a elucidates the dependence of Eu³⁺ doping on luminescence of undoped and Eu³⁺-doped ZnS nanoparticles at an excitation wavelength of 395 nm. This corresponds to the $^{7}F_{0}$ - $^{5}L_{6}$ transition of Eu³⁺. For undoped ZnS nanoparticles, this excitation is to some defects near the band edge and the observed blue PL emission consists of an asymmetric broad emission due to the convolution of emissions from point defects such as sulfur vacancies and zinc interstitials in the lattice [29]. On doping, the characteristic emissions of the Eu³⁺ ions at 591, 616, 644, 696, and 747 nm due to $^{5}D_{0}$ - $^{7}F_{i}$ (j = 1 to 6) transitions of 4f⁶

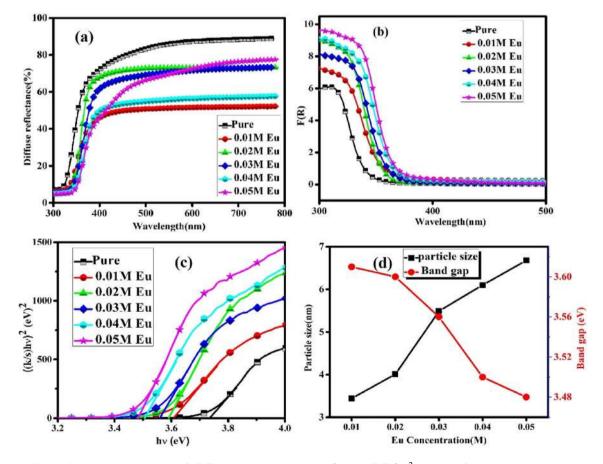
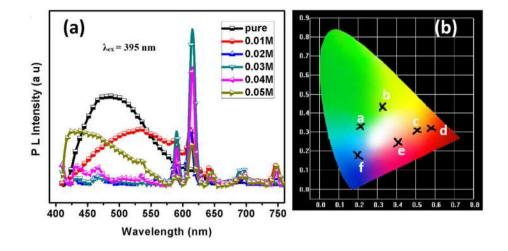


Fig. 3 a Diffuse reflectance spectra (DRS), b F(R) vs. wavelength plot, c (hv) vs. $(F(R)hv)^2$ plot, and d variation of band gap and particle sizes with doping concentration for the ZnS:Eu³⁺ nanoclusters

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Fig. 4 a PL spectra and **b** chromaticity diagram of pure and Eu³⁺-doped ZnS nanoparticles for an excitation of 395 nm



configuration were also observed. When Eu³⁺ ion inhabits the sites without an inversion center, electric dipole transitions are allowed but magnetic dipole transitions are forbidden [30]. The emissions at 616, 696, and 747 nm belong to electric dipole transition and that at 591 nm belongs to magnetic dipole transition [30, 31]. The emission at 747 nm is forbidden and results from medium j mixing. The emission at 644 nm caused by ${}^{5}D_{0}-{}^{7}F_{3}$ transition is forbidden for both electric dipole and magnetic dipole transitions and it is made possible through *j* mixing by crystal field potential [32]. Various interpretations were given to the less intense green emission band seen in ZnS:Eu³⁺ nanoparticles. This green emission at 534 nm in $ZnS:Eu^{3+}$ may be due to the occurrence of some self-activated luminescent centers, possibly due to elemental sulfur species on the surface of ZnS [33].

As the doping concentration is increased we can clearly observe a suppression of blue emission due to the ZnS host and an enhancement in yellow and red emissions due to Eu³⁺ ions up to 0.03 M sample. This is due to energy transfer mechanism from the defect level in ZnS to ${}^{5}L_{6}$ level of Eu $^{3+}$. Here the excitation is at 395 nm corresponding to which there is a defect level in ZnS host and an energy level in Eu^{3+} ion (⁵L₆) as evident from the excitation spectra of pure ZnS and $ZnS:Eu^{3+}$ (Fig. 6). So resonance energy transfer is possible from defect level in host to ${}^{5}L_{6}$ level of Eu³⁺. We can infer that the high luminescence intensity in 0.03 M sample is due to the synergistic effect of energy transfer from host and direct excitation in Eu^{3+} ions in ZnS lattice. For 0.04 M sample there is a reduction in intensity of emissions from Eu³⁺ levels due to concentration quenching as a result of energy transfer between Eu^{3+} ions as they become closer.

Thereafter, at 0.05 M concentration of Eu^{3+} , blue emission due to host reappears which means that energy transfer from host to activator is reduced. A shift in the broad blue emission due to ZnS can also be observed which is due to change in band gap and concentration of defect states in the lattice. Overall emission color changes depending on the relative intensities of blue, green, yellow, and red emissions. Points in the chromaticity diagram lie around the white region from bluish green to red and then to blue as the doping concentration is varied from 0.01 to 0.05 M (Fig. 4b). Red emission is obtained for 0.03 M Eu^{3+} concentration.

Figure 5a represents the PL emission spectra for an excitation of 465 nm corresponding to ⁷F₀-⁵D₂ transition in Eu³⁺. It exhibits all Eu³⁺ emissions similar to the excitation at 395 nm except the broad emission due to ZnS host. In this case also red emission intensity is maximum for 0.03 M concentration of Eu^{3+} . For higher concentrations, spacing between the Eu³⁺ ions decreases and hence its pairing causes the chance of energy transfer. Hence the excitation energy is shared among the Eu³⁺ ions, resulting in quenching of emission intensity. Overall emission color is red for all the samples and it is represented by the chromaticity diagram (Fig. 5b). Chromaticity coordinates of all samples for excitations at 395 nm and 465 nm are listed in Table 2. For 0.03 M and 0.04 M Eu³⁺-doped samples chromaticity coordinates lie very close to that of CRT red phosphor (0.65, 0.35).

The shortest distance between adjacent Eu^{3+} ions to bring about the concentration quenching called critical distance (R_c) can be calculated by the equation [34].

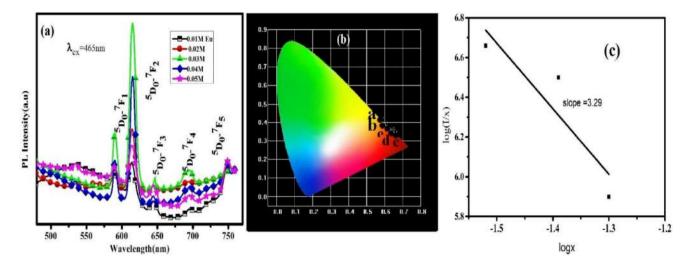


Fig. 5 a PL spectra of ZnS:Eu nanoparticles for different Eu³⁺ concentrations ($\lambda_{ex} = 465$ nm), b chromaticity diagram, and c logx vs. log*I*/x plot

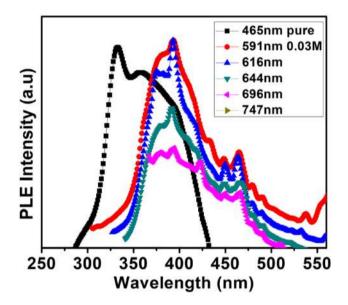


Fig. 6 PLE spectra of ZnS at 465 nm and ZnS: Eu^{3+} (0.03 M Eu^{3+}) for different emission wavelengths

$$R_{\rm c}=2\bigg[\frac{3V}{4\pi Nx_{\rm c}}\bigg]^{\frac{1}{3}},$$

where *V* and *N* are the volume and number of cations in the unit cell and x_c is the critical concentration. For ZnS, *V* = 155.37 Å, *N* = 4, and $x_c = 0.03$. So for Eu³⁺ ions in ZnS:Eu³⁺ the critical distance is about 13.5 Å. But the exchange interaction is valid only for critical distance R_C less than 5 Å. Hence, concentration quenching in PL intensity in the ZnS:Eu³⁺ nanoparticles is due to multipole–multipole interaction.

Table 2 CIE color coordinates of $ZnS:Eu^{3+}$ nanoparticles for different Eu^{3+} concentrations

Eu ³⁺ concentration (M)	Color coordinates				
	$\lambda_{\rm ex} = 395 \text{ nm}$	$\lambda_{\rm ex} = 465 \ \rm nm$			
0	(0.21, 0.33)	(0.33,0.44)			
0.01	(0.21, 0.33)	(0.58, 0.42)			
0.02	(0.51, 0.31)	(0.6, 0.39)			
0.03	(0.58, 0.32)	(0.65, 0.34)			
0.04	(0.41, 0.25)	(0.64, 0.35)			
0.05	(0.2, 0.18)	(0.64, 0.36)			

According to the Dexter's theory nature of multipolar interaction among the activators ions [35, 36] is calculated using the relation

$$\frac{I}{x} = k \left[1 + \beta(x)^{\frac{N}{3}} \right]^{-1}$$

where *I* is the intensity of PL emission with doping concentration (*x*), *k* and β denotes constants of host matrix and *N* represents the nature of interaction and it is equal to 6 for dipole–dipole interaction, 8 for dipole–quadrupole interaction and 10 for quadrupole–quadrupole interaction, respectively. From the slope of the graph of log(*x*) against log(*I*/*x*) (Fig. 5c), *N* can be calculated. In this case slope of the graph = -3.29 = -N/3, i.e., $N \sim 9.87$. It shows that the energy transfer that leads to concentration quenching phenomena of Eu³⁺ ions is due to quadrupole-quadrupole interaction.

In order to recognize the performance of ZnS:Eu³⁺ nanoparticles as red phosphors it is necessary to know the colour purity of the synthesized samples. It is the weighted average of the x, y coordinates comparative to the CIE white illuminant and the coordinate of the wavelength which is dominant, can be calculated using the equation [37].

Colour purity =
$$\frac{\sqrt{(x_{\rm s} - x_{\rm i})^2 + (y_{\rm s} - y_{\rm i})^2}}{\sqrt{(x_{\rm d} - x_{\rm i})^2 + (y_{\rm d} - y_{\rm i})^2}} \times 100\%,$$

where (x_i, y_i) and (x_s, y_s) is the CIE coordinates of the white illuminant and the corresponding sample and (x_d, y_d) is the co-ordinate corresponding to the dominant wavelength. The calculated values of colour purity for ZnS:Eu³⁺ (0.03 M) nanoparticles is 92%.

In order to understand luminescence mechanism in doped ZnS nanoparticles excitation spectra is also taken (Fig. 6). Pure ZnS shows excitation peaks at 333 and 361 nm and a shoulder peak at 395 nm. The peak at 333 nm corresponds to the excitation to conduction band edge whereas the peaks at 361 and 395 nm are due to some intrinsic defects. When monitoring the excitation spectra of ZnS:Eu (0.03 M) nanocrystallites for different emission wavelengths (Fig. 6) the excitation spectra are almost similar. It contains the distinguishing excitation peaks of the Eu³⁺ ions related to the straight excitation from the ground level to higher excited levels of the doped Eu³⁺ ions. The main excitation peaks are observed at 395, 465, 414 and 535 nm. The extreme peak at 395 nm corresponds to the 7F₀-5L₆ and the excitation peaks at 465 nm and 414 nm are due to $7F_0-5D_I$ (J = 2, 3) transition. The peak at 535 nm is attributed to $7F_1$ -5D₁ transitions of Eu³⁺ ions [38, 39].

4 Conclusion

In summary ZnS doped with different europium concentrations have been synthesized using a simple chemical precipitation method with PEG as capping agent. Different emission colours have been obtained on exciting ZnS:Eu³⁺ nanophosphor at 395 nm for different doping concentrations. For the excitation wavelength of 465 nm the emission colour is red and comparable with the CRT coordinates, at a doping concentration of 3 at.%. Obtained results from PL analysis showed that present ZnS:Eu³⁺ phosphor

have potential applications for lighting and display phosphors.

Author contributions

All authors contributed equally to the conception, design and analysis. Material preparation and data collection were done by KRB. Original manuscript was prepared by KRB and TAS. Supervision of the work and review and editing of manuscript were done by EIA.

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The authors have not disclosed any funding.

Data availability

The raw/processed data of this work will be made available on request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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WHAT EXPLAINS IPO UNDERPRICING IN INDIA?

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Abstract

This research article examines the initial return of 120 IPOs listed on the National Stock Exchange during the five-year period from April 2015 to March 2020 and the factors explaining initial return. Compared to the previous studies which concentrates only on the returns on the listing day, this paper considers the return on 5th day of trading also, in order to test the consistency of initial return. The results of the study clearly indicate the under-pricing of IPOs and the existence of 'Winners Curse' in the Indian stock market. It also found that the average initial return is substantially increasing on the 5th day of listing. The study found significant association between subscription rates and level of under-pricing on the listing day as well as on the fifth day, in line with the previous empirical findings.

Keywords: under-pricing, initial return, market adjusted average return, subscription rates

Introduction

Underpricing literally mean selling or offering something lower than its original value. In the capital market underpricing implies the positive closing of a scrip on the listing day (compared to issue price) in a stock exchange. Among the common anomalies discussed in IPO literature, underpricing is the prominent one. Under-pricing is evident in all markets, both developed and emerging. Most of the studies concentrated on U S market and all reported considerable amount of underpricing with different magnitude for different time periods. Underpricing from the point of view of issuers, is an opportunity cost. Researchers argue underpricing as an indirect compensation to underwriters (Loughran & Ritter, 2002). They also argue that issuers are not worrying about the money left on the table because of the sudden increase in their personal wealth (prospect theory). Another reason could be the superior knowledge advantage of the investment banker over the issue firm that cause to underprice the issue (Baron, 1982). There are well established empirical findings for underpricing in various capital markets around the world. In India, initial underpricing had been documented by various researchers. [See (Dhamija & Arora, 2017; Krishnamurti & Kumar, 2002; Madhusoodanan & Thiripalraju, 1997; Ranganathan & Saraogi, 2021; Shah, 1995)]. Unfortunately, there are few studies that concentrates on under-pricing with comprehensive set of variables and the survival of initial return up to 5 days of listing except studies conducted by (Puri, 2012; A. K. Singh & Kalra, 2019) in India who found initial returns on listing day and on subsequent critical days. In this study we examine the initial under-pricing and the 5th day return on Indian capital market and measure the relationship of average initial returns with some important determinants such as subscription rates, firm's age and issue size.

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Degree of under-pricing and its causes in the U. S Market

The reasons explaining underpricing include asymmetric information models of (Baron, 1982) and (Rock, 1986) where the former explains disproportionateness of information between the issuing firmand investment bankers and the latter explains this asymmetry between Informed and uninformed investors. (Michaely & Shaw, 1994) reports the relation between underwriters' reputation and the degree of underpricing and supportsasymmetric information hypothesis of Rock. Jay R Ritter (Ritter, 1991) documents the short run and long run performance of IPOs with specific hypothesis and reported thatlong run under performance and initial underpricing are inversely related.(Jain & Kini, 1994)examined the difference in working efficiency of firms when they become public from private. Their study found no substantial evidence to establish relationship between degree of underpricing and post issue performance rather reported decrease in the Market to Book ratio, Price Earnings Ratio and EPS after the IPO.

Studies from emerging markets and from India

The short run underpricing is a common phenomenon in emerging market as well.(Hermin & Murhadi, 2015) found significant relationship between underpricing and auditor's reputation, underwriter's reputation and return on equity among the IPOs listed on Stock Exchange during 2004-14 with 204 samples in Indonesia. In the study of French IPO market, Aissia and Hellara (Aissia & Hellara, 2019) examined the leverage and idiosyncratic volatility of IPO firms and report that industry and macro-economic variables are the important predictors of IPO underpricing. Rakibul Islam studied the existence of underpricing theories in Bangladesh stock market in explaining the reasons for underpricing and the predictive power of variables (R. Islam, 2014). (Adjasi et al., 2011) finds a significant underpricing of Nigerian market at 43.1%. In Pakistan, (Mumtaz et al., 2016) found robustness of variables used for explaining underpricing. They found only 6 significant variables out of 15 and the study supports the investors sentiment theory but no significant relationship to explain ex ante uncertainty. In a recent study, (Ahmad-Zaluki & Badru, 2020) found significant relationship between underpricing and the intended use of IPO proceeds in the prospectus in Bursa Malaysia.In India, studies which report wide spread underpricing in India include (Bansal & Khanna, 2012; Hawaldar et al., 2018; Pande & Vaidyanathan, 2007; Sahoo & Rajib, 2010; Seth et al., 2019) and they tried to establish the relationship of different explanatory variables with the underpricing. (Sabarinathan, 2010) examined the Indian IPO market during 1993 to 2009 and found significant changes in IPO firms include the offer size, firm size (in terms of post issue paid up capital), the method of pricing, firm's age, type of Industry and intended stock exchanges for listing. Anchor investor's role in underpricing has documented by (Kumar & Sahoo, 2021). This study tries to fill this gap by concentrating on the following objectives.

- To measure the initial returns of Indian IPOs on the day of listing and on the 5th day of listing on NSE.
- To examine the factors explaining initial performance of IPOs, specifically, Issue size, Age of the firm, and the Overall subscription rate.

Materials and methods

The study focuses on examining the initial return of IPOs listed on National Stock Exchange during the five-year period from April 2015 to March 2020 and the factors explaining initial return. The closing share prices of companies are elicited from the official website of National Stock Exchange (NSE) (https://www1.nseindia.com) which are also supplemented with information available on the website https://www.chittorgarh.com. For collecting data of firm's age and issue details like issue sizeand oversubscription rate, we referred the prospectus and also use the information supplemented

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by NSE and Chittorgarh. The data were compiled and arranged using M S Excel in proper form. For data analysis, we use EViews 9.0 software.

Year	Total Number of mainstream IPOs Listed on NSE	Included in Sample	Excluded	Sample (%)
2015-16	24	20	4	16.67
2016-17	28	26	2	21.67
2017-18	45	41	4	34.16
2018-19	20	18	2	15.00
2019-20	15	15	0	12.50
Total	131	120	11	100

Table1. Year	• wise details of nu	mber of companie	es listed on NSE	2 during 2015-2020
		move of company		

Source: www1.nseindia.com and compiled by the authors.

Variables and Hypothesis Development -Dependent variable- Underpricing (MAAR)

In line with previous literatures (A. Ljungqvist, 2007, Krishnamurti & Kumar, 2002)Market Adjusted Average Return (MAAR) on listing day is taken as a measure of under-pricing.

The process of computing the value of dependent variable (MAAR) is:

First, the return on security i is calculated:

$$RRi = P1 - P0 / P0$$

Where,

 $RRi = Absolute \ return \ of \ i^{th} \ share \ (Bruson, 2019)$

 P_1 = Closing share price on the listing day

 $P_0 = Offer \ price \ of \ the \ security$

Secondly, Market return (Mi) (Nifty 50 as benchmark) for the corresponding date of the IPO issue for each security is computed (closing value of Nifty on the listing day and Nifty on Offer closing day).

 $Mi = (M_1 - M_o)/M_o$

$$MAAR = \{(1 + RRi/1 + Mi) - 1\} * 100\}$$

Where, MAAR = Market Adjusted Average Return.

Dependent variable- Market Adjusted Average Return on 5th day of listing (MAAR₅)

The above same procedure is followed for computing 5^{th} Day RR (RR5) and Fifth Day Market Adjusted Average Return. (MAAR₅)

Independent Variables

The Average return (*MAAR*) is regressed across 3 Independent Variables, the firm's age, issue size and subscription rate. To make standardisation and to avoid heteroskedasticity, the values of all independent variables were converted into their natural log.

Firm's Age

In many previous literatures (Vetsuypens & Muscarella, 1989), (Clark, 2002), (Boehmer & Ljungqvist, 2004), (Bansal & Khanna, 2012); the 'firm's age' is taken as the time gap (in years) between the year of founding of the company and the year of IPO issue. Older the company, assuming good popularity and track record, lesser is the chance for information asymmetry, leading to

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less chance for under-pricing. Hence, there is an inverse relation between these two variables. Hence the null hypothesis can be stated as:

Hypothesis 1: *There is no significant relationship between Firm's Age and the level of underpricing* **Issue size**

The log values of *Issue size* are used as an independent variable. Studies show that large sized issues have lower underpricing as the number of bidders (prospective investors) will be high (Beatty & Ritter, 1986), (Megginson & Weiss, 1991),(Bansal & Khanna, 2012)(Chhabra et al., 2017; Dhamija & Arora, 2017). Therefore, an inverse relationship is expected between *degree of under-pricing* and *issue size*.

Hypothesis 2: *There is no significant relationship between issue size and the level of under-pricing* **Oversubscription rate**

Oversubscription rate represented in the model by the log (*the number of times the issue is subscribed in terms of offer size*), is used as another IV to explain the level of underpricing. Oversubscription indicate the investor's demand to new securities (Dhamija & Arora, 2017). So, a direct relationship is anticipated between oversubscription and level of under-pricing.

Hypothesis 3: There is no significant relationship between overall subscription rate

and the degree of under-pricing.

Hence, the regression model is:

 $MAAR = \alpha + \beta_1 lnissuesize + \beta_2 lnsubsc + \beta_3 lnage + \varepsilon i \dots (1)$

Where,

MAAR= Market Adjusted Average Return

lnissuesize = Log of size of issue

lnsubsc = Log of overall subscription rate (Number of times)

lnage = Log of firm's age

 $\varepsilon i =$ Error term.

Similar to above, hypothesis for establishing relationship between $MAAR_5$ with the three independent variables are:

Hypothesis 4: There is no significant relationship between Firms Age and the Market Adjusted Average Return on day 5(MAAR₅)

Hypothesis 5: There is no significant relationship between Issue size and the Market Adjusted Average Return on day 5(MAAR₅)

Hypothesis 6: There is no significant relationship between overall subscription rate and the Market Adjusted Average Return on day 5(MAAR₅)

Hence the regression equation is:

 $MAAR_5 = \alpha + \beta_1$ lnissuesize $+ \beta_2$ lnsubsc $+\beta_3$ lnage $+ \varepsilon i \dots \dots \dots (2)$ Where:

MAAR₅= Market Adjusted Average Return on 5^{th} day of Listing.

Independent variables as explained above)

Empirical results and discussion

Descriptive statistics

The difference between Raw Return (RR 15.94 %) and the Market Adjusted Average Return (MAAR) (16.07%) is only negligible at 0.13%. Other research studies also point towards similar findings Loughran &Ritter, 2002and Beatty&Ritter, 1986 (Beatty & Ritter, 1986). This is also in line with the findings of Hawaldar et al (Hawaldar et al., 2018) who reported the difference as attributable to stringent measures imposed by SEBI with respect to listing delay. Similarly, the Raw Return is 21.07% and MAAR is 21.26% on 5th day of listing. These findings underpin the under-pricing in Indian IPOs during 2015 to 2020. However, the level of initial under-pricing during this period is

(All

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much lesser compared to the findings of (Shah, 1995) which reported an initial under-pricing of 105.6% during 1991 to 1995.

Initial return on Listing Day and on the 5th Day

The year wise comparison of data revealed that underpricing was lowest in the year 2018-19 and the highest initial return was during the year 2016-17. The poor initial performance of IPOs during 2018-19 was mainly attributable to the increased volatility in the Indian capital market along with other markets in the world. (SEBI Annual report 2018-19, pp.no.65

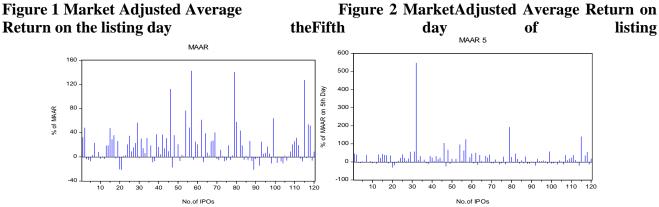


Figure shows the variability of returns of various IPOs during the study period. Among the IPOs 67.5% (81 IPOs) are under-priced (return >0) and 39 (32.5%) are overpriced (return<0). The average under-pricing for the period is 16.07% and 21.26% respectively.

Test of Year wise Initial returns

In order to test the statistical significance of year wise initial returns and the whole period returns (significantly different from zero or otherwise), t test is being used.

All the't' values are significant except in the year 2018-19 means that the MAAR and MAAR₅ in all the years are significantly different from zero. This finding is consistent with all of the previous studies which shows significant average underpricing in Indian Capital market.(Bansal & Khanna, 2012; A. K. Singh & Kalra, 2019)

Multiple Regression Results- MAAR

The Raw Return (RR) and Market adjusted Average Return (MAAR) on the listing day and 5th day was regressed with all the three independent variables. Since the difference between RR and MAAR is negligible, in line with previous literatures, this study reports only MAAR on the listing day and MAAR on 5th day of listing.

Since the data are cross sectional, the residuals are tested for homoscedasticity and multi collinearity. The result using Breusch-Pagan-Godfrey Test shows heteroskedasticity among residuals and the presence of collinearity (Uncentered VIF >10) in the case of *Firm Age* and *Issue size*. Therefore, Whites Heteroscedasticity Consistent standard errors for Estimation, which is BLUE (Best Linear Unbiased Estimate) is used. The result of regression is presented in Table3

Table 2 Wultiple Regression Results- WAAK					
White heteroskedasticity-consistent standard errors & covariance					
Variable	Coefficient	Std. Error	t-Statistic	Prob.	
С	5.221880	16.09707	0.324399	0.7462	
LNISSUESIZE	-1.120868	2.123964	-0.527725	0.5987	
LNSUBSC	12.01806	1.399211	8.589168	0.000*	
LNAGE	-3.222722	2.039387	-1.580241	0.1168	
R-squared	0.528180	Mean dependent v	ar	16.06956	

Table 2 Multiple Regression Results- MAAR

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Adjusted R-squared	0.515977	S.D. dependent var		29.40867
Prob(F-statistic)	0.000000	Wald F-statistic	2	28.21190
Prob(Wald F-statistic)	0.000000			

Out of the 3 IVs, only the subscription rate is significant (0.000). Therefore, the H_3 : There is no significant relationship between overall subscription rate and the degree of under-pricing", is not accepted at 5 % level of significance. This result is in line with the findings of (Rock, 1986; P. Singh & Kumar, 2008). It can be inferred that there is a strong positive relationship between the overall Subscription rate and the level of initial under-pricing.

Category	No. of	Percentage	Average Mean	MAAR-	MAAR-
	sample		subscription in	Listing	5 th Day
			no. of times	Day	%
			(Median)	%	
Under-priced	81	67.5	51.17	27.13	35.76
-			(32.05)		
Over-priced	39	32.5	4.22	-6.91	-8.85
			(1.9)		
Total	120	100			

Source: Secondary data compiled by authors. *Median values are shown in parenthesis.

For better understanding, the data was bifurcated into two sets; one set representing the underpriced issues and the other, the overpriced (Table 4). Out of the total sample of 120 IPOs, 81 IPOs (67.5 %) are under-priced and the average subscription rate of under-priced IPOs is 51.17 times of offer size whereas, that of over-priced IPOs (32.5%) is 4.22 times of offer size. Whereas, the initial return in under-priced section on listing day and 5th day of listing is 27.13% and 35.76% respectively and for overpriced section, the respective negative returns were -6.91% and -8.85%. Similar inferences were found in several international research studies(Rock, 1986; Vong &Trigueiros, 2009). Accordingly, there are two categories of investors, informed and uniformed. Informed investors will be crowded across the when the issues are good and they do not invest in bad issues since they have better information about the future growth prospects of the company. Whereas, the uninformed investors fail to recognise good issues and bad issues (Rock, 1986). The informed will get majority of good issues and the uninformed will get smaller portions in good issues and larger portion in bad issues and they will lose in terms of first day return, popularly referred to as "winners curse". Thus, higher subscription is found in case of underpriced issues than those of overpriced issues. These resultsunderlined the findings of Hong Kong IPOs (Vong &Trigueiros, 2009).

Relationship of Firm Age and Issue size with the level of under-pricing

The study analysed the relationship of *Firm Age and Issue size* with the level of under-pricing. Table 3 shows that firm's age is inversely related with the degree of under-pricing (t value -3.222722), even though not significant. This expectation of a inverse relationship between age and degree of underpricing is consistent with (Vetsuypens & Muscarella, 1989) ,(P. Singh & Kumar, 2008)and (Bansal & Khanna, 2012, 2013) but contradict to the findings of (Islam et al., 2010) they found a significant positive relationship between *Firm's age* and the level of under-pricing in Bangladesh market. Even though the sign is negative, there is no evidence of significant relationship between level of under-pricing and *issue size*, which is also contrary to the findings of (Islam et al., 2010).

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The model has overall significance at 5% (F, 0.0000) and the adjusted R^2 is 0.516 indicates that 51.6 % of the variability in level of underpricing in Indian IPO market is explained by issue size, firm age and subscription rate. This finding supports the theory of *ex ante uncertainty* as we could not predict the IPO returns with 100% accuracy. The uncentered VIF for Age and Issue size (Uncentered VIF is 17.24 and 33.03 respectively) is comparatively smaller. Besides, White heteroskedasticity-consistent standard errors and covariance for estimation makes the model valid.

It is found that the MAAR₅ (21.26 %) is higher than that of the MAAR on the listing day

Table 4 Multiple Regression Results-MAAR5						
Variable	Coefficient	Std. Error	t-Statistic	Prob.		
С	45.52696	34.44890	1.321579	0.1889		
LNISSUESIZE	-3.147644	4.245138	-0.741470	0.4599		
LNSUBSC	13.76931	2.795305	4.925869	**0.0000		
LNAGE	-12.16847	6.719193	-1.811001	*0.0727		
R-squared	0.198445	Mean dependent var		21.26017		
Adjusted R-squared	0.177715	S.D. dependent var		58.62788		
F-statistic	9.572874	Durbin-Watson stat		2.045561		
Prob(F-statistic)	0.000011					

Consistency of Under-pricing on the Fifth Day (MAAR₅)

(16.06%). A multiple regression was run to identify the factors explaining the MAAR on 5th day.

The analysis show that **Subscription rate** is the most significant factor explaining initial return on the 5^{th} day of listing (Table 5). The null hypothesis 6 rejected at p value 0.0000 which is highly significant at 5% level. This result sheds some light on the continuous demand of the shares from the investors who are ready to buy shares even on the 5^{th} day of listing as indicated at the time of floating through high oversubscription rate. The**Firm's** *Age*is negatively related with level of under-pricing and is significant at 10%. Our results failed to accept null hypothesis 4 at 10% and are consistent with many previous studies which have reported inverse relationship between initial returns and firm's age (P. Singh & Kumar, 2008).Similar to the regression results of MAAR on listing day and in line with previous literatures, there is anegative relationship between level of underpricing and the *issue size* [see (Madhusoodanan & Thiripalraju, 1997)]. Even though the sign is negative, the null hypothesis 5 is accepted and concluded that there is no significant relationship between level of under-pricing and *Issue size*.

The residuals are checked for heteroscedasticity and the null hypothesis is accepted and concluded that residuals are Homoscedastic. The model has overall significance at 5 % (Since F test-P value is 0.00) and the adjusted R^2 is 0.178 indicates that 17.8 % of the variability in MAAR5 is explained by the independent variables.

Conclusion

The empirical evidence of IPO underpricing is an international phenomenon. The present study focused on examining the initial return of IPOs listed on National Stock Exchange during the five-year period from April 2015 to March 2020 and the factors explaining initial return. Apart from the previous studies which concentrates only on the returns on the listing day, here, the return on 5th day of trading is also taken into consideration in order to test the consistency of initial return just after listing. The initial under-pricing is 16.07 % and MAAR on 5th Day is 21.26 %. The observed level of underpricing in this study is lesser than the findings of most of previous studies which were done in pre- book building era and this could be attributable to the stringent measures by SEBI to reduce

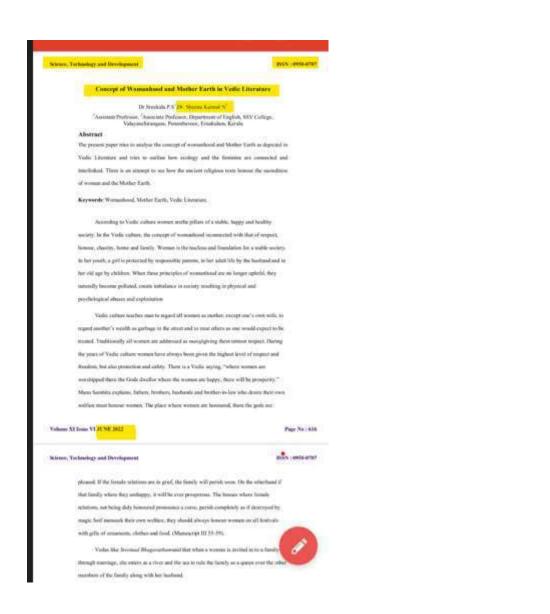
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information asymmetry. The under-priced issues were oversubscribed substantially when compared with the average overpriced IPOs. The results of the study clearly indicate the underpricing of IPOs and the existence of 'Winners Curse' in the Indian Capital market. It is found that the average initial return is substantially increasing on the 5th day of listing, therefore, the investors will be benefitted if they wait to exit from their investment on the 5th day of listing rather than on the listing day. Above all, the association of subscription rates and level of under-pricing is highly significant, on the listing day as well as on the fifth day, in line with the previous empirical findings. Further research on Indian capital market needs to be made by including more industry related and emerging market factors to shed more lighton the capital market anomalies.

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DISCOVERING THE ROOT OF EXISTENCE IN SHASHI DESPANDE'S *ROOTS AND SHADOWS*

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Abstract

Women's struggles in the context of contemporary Indian society, to find and preserve her identity as wife, mother and most important of all, as human being is Shashi Deshpande's major concern as a creative writer, and this appears in all her important stories. This is truly applicable to her novels as well. Our society considers women as ideally sympathetic, gentle, warm, passive and dependant. Domestic life and the work patterns evince the concept that women should be subordinate to and dependent on men. Through the character of Indu, in Roots and Shadows, Shashi Deshpande has very exquisitely portrayed the inner struggles and sufferings of the new class of Indian women, who have raised many questions regarding modern women who are tooted and shaped by the Indian customs but influenced by the Western wold.

Key words: Identity, Existence, Root, Realization

The emergence of women novelists in Indian English literature took place as early as the last quarter of the nineteenth century. But it was only after independence, that they could make solid contribution to Indian English fiction. The post-independence period, has brought to the forefront a number of noted women novelists who have enriched Indian English fiction by a creative release of feminine sensibility. The woman has been the focus of many literary works in this period and the major writers who have achieved recognition in the last decade of the 20th century are Kamala Markandaya, Nayantara Sahgal, Ruth Prawer Jhabvala, Anita Desai, Shashi Deshpande and the life through the eyes of women writers, one gets a glimpse of a different world till now not represented in literature. Women, who were treated as second class citizens were assigned their due place in these writings.

Shashi Deshpande is one of the famous contemporary Indian novelists in English. Deshpande's novels deal with the image of women in general. The writer with most sustained achievement in feministic fiction, has to her credit eight novels, six collections of short stories, and four children's books. Her writing is clearly a part of Indian literature, and emerges from her rootedness in middle class Indian society. G.S. Amur aptly remarks: "Women's struggles in the context of contemporary Indian society, to find and preserve her identity as wife, mother and most important of all, as human being is Shashi Deshpande's major concern as a creative writer, and this appears in all her important stories"(SD,Tlo,10)This is truly applicable to her novels as well. Our society considers women as ideally sympathetic, gentle, warm, passive and depended. Domestic life and the work patterns evince the concept that women should be subordinate to and dependent on men.

The protagonist of *Roots and Shadows* is a young woman who has rebelled against her authoritarian and traditional joint family. This work comes out with its feministic approach in Indu's, the protagonist's, exploration into herself. Indu left home as a teenager to study in a big city, and is now a journalist, she has married the man of her choice. But she realizes that her freedom is illusory; she has exchanged the orthodoxy of the village home for the comforts of the smart youngest of the city, where material well-being has to be assured by sacrificing principles, if necessary. She returns to the family home after an absence of twelve years when her great aunt, a childless widow dies, leaving her wealth to Indu. As the heroine takes charge of her legacy, she comes to realize the resilience of the village woman she had dismissed as weak.

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Indu traverses the road of self-realization and her destination is the point of comprehension of the mystery of human life. The struggle of such women gives shape and meaning to their individual existence in a sexist society. According to Deshpande, no amount of theorizing will solve women's problems- especially in the Indian context. Through Indu, in *Roots and Shadows*, a woman's attempt to assert her individuality and freedom is depicted. This work can also be called as a novel which explores the inner struggle of Indu, who represents a set of modern women who are educated and are very much in contact with the society, dealing with the critical problems like love, sex, marriage, settlement and individuality.

The story of this novel revolves around Indu. She broke away from her family out of resentment and married for love in order to assert her freedom. The four generations of the family lived together in the ancestral house built years ago by Indu's great-grandfather. It was an ancient family over which Akka ruled like an inconsiderate tyrant, ruthless and dominating. She was so dominating that she could reduce Kaka to a "red-faced stuttering school boy by her venomous tongue", even after he had become a grand-father. Living in the family was so close and so entangled with one another that if anyone moved, the other was bound to get hurt. Therefore, an undercurrent of tension was always present even during times of great rejoicing. There were intrigues, jealousies, rivalries and malicious words. Thus there were many diverse conflicts

The conflict between individual freedom and social obligation is evident mainly in the character and destiny of Indu. Her life functions simultaneously as the story of an individual as well as an institution. The institution to which she is actively related is the joint family system. The institution of marriage also figures significantly in the novel. Indu is engaged in a quest for freedom and self-identity. Her quest is at first frustrated by her joint family and later by her marriage with Jayant. Right from her childhood, Indu had seen that women

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occupied a secondary place in the family. As a child she had been told to be obedient and unquestioning, as a girl she had been told to be weak and submissive. When she had gathered the courage to ask why, she had got the answer that this was the only way a female could live and survive. She is forced to accept everything, even defeat, gracefully and her intelligence was only a burden for her and she is not supposed to think. Indu, finds dominant Akka and her family, a great hindrance to achieve her goal. When at college, Akka did not let her meet boys and cultivate friendship with them.

Women like Mini, Indu's cousin, are always involved in the fetishes of traditions and home hold work. They have no other option but to remain satisfied with the things provided. Even Akka herself represents another facet of deprived womanhood. She is the youngest sister of Indu's grandfather. Akka returns to her parental home as a rich widow after the death of her husband. At the age of twelve she got married and became a victim of the evils of patriarchal practices. Her soul of child withers away when she has had to tolerate the scathing and bestial sexual advances of her husband. Indu gathers all these from Narmada – Atya. Akka's personality gets changed when her husband faces a stroke .Now Akka learned the technique of domination. She knew that the world was made up of two types of people, the powerful and the weak and the powerful always ruled the weak.

Women are toned or conditioned to merge their aspirations and desires with those of their family. The instance of Mini before her, makes Indu understand that the very objective of educating a girl child was not to give her an independent stand but to get a good match. Later she leaves home and marries Jayant, a man of her choice .She leaves her parental house and enters the house of her husband to achieve freedom and completeness but soon realize the futility of her doings and decisions, "Jayant and I.....I wish I could say we have achieved complete happiness. But I cannot fantasize" (Deshpande 14). She continues, "This is my real sorrow that I can never be complete in myself. Until I met Jayant I had not kown it....that was

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somewhere outside me, a part of me without which I remained incomplete. Then I met Jayant and lost ability to be alone" (Deshpande 34). It appears that marriage has taught her the lesson of deception, "Her desire to assert herself had driven her from affection to hypocrisy" (Deshpande 33). Indu herself feels "I had learnt to reveal to Jayant nothing but what he wanted to see... I hid my response as if they were bits of garbage" (Deshpande 41).All these touching facts of losing her identity into her husband's, frightens her. Gradually Indu found that Jayant had not only expected her to submit but had also taken her submission for granted. She, unaware of it, submitted herself to him step by step on the altar of love. When she met the reality, she found that it was not love but an adjustment, as she never wanted strife in her married life .She bears everything only to show her victory over her parents. Indu resented all this suppression. She had sworn that she would never be a hypocrite and so she had been rebellious since birth. She had thought that womanhood was a beautiful world, but it was thrust upon her so brutally and harshly that she had received a rude shock and started resenting the fact that she was a woman.

The novelist presents a veritable state of women in which modern women are bound to live between tradition and modernity is revealed through Indu. She mocks the very word 'love', "I love a book, a word, or a sari, a curry, a child, a man" (Deshpande 97).The experience that love has no place in her life and drives her to the extreme stance of seeing only stratagem and betrayal, all around . She feels how sex becomes an emblem of power and authority. Marriage proves to be another trap and woman feels like a caged animal. Thus she willingly surrendered herself to Jayant even before he pressurized her to do so. She who had considered herself to be so independent, intelligent, clever and so proud is not seen anywhere. She who had set out to reform Indian womanhood has fallen into the trap waiting for her. She even wanted to get off leaving Jayant and living alone for that seemed to be the only way of becoming herself. Indu felt uneasy not only about her marriage but also about work too. What her editor said and what was acceptable to the public did not matter her. But she had not voice there too. When she voiced her doubts, Jayant answered that one person cannot change the whole system, therefore, there was no point in making herself an object of ridicule. It also worried Indu to realise that she had deserted her family only to become a part of success oriented patriarchal society. Of course she now belonged to the smart young set but was often depressed. She regrets that she had left her family for this hypocritical life. Her mother had died giving birth to her, but the family had never let her feel a motherless child. She felt that her wish to assert herself had stemmed from hypocrisy and assurance.

Akka is the eldest and the guardian of the family. She does not approve of Indu's marriage with Jayant. Nor do the family members dare approve and invite them. Akka believes that love marriage does not work. Love marriage could involve different castes and perhaps different languages. Kaka is also afraid of Akka and does not invite Indu. She marries Jayant who belongs to a joint family but prefers and moves to a nucleus family. Later on Indu moves back to the joint family as she has been made an heir to Akka's family. Financial power is very crucial in a joint family. When Indu feels unhappy with her conjugal life she is made heiress to the whole property. Thus she gets an opportunity to be away from Jayant. It was after ten years since she left her family. Jayant discouraged her decision. However, it was only when she reached her parental home that she realised how much it meant to her. She felt so comfortable and so much at home that she realised where she belonged to. As she is alone in Akka's house, she develops an intimate relationship with Naren. But soon she wished that she had listened to Jayant's advice and not come back. This was a very huge and unwanted responsibility for Indu as she had always wanted to be completely detached and not involved with the family.

Indu found herself in an unenviable position for there were so many people and all of them wanted her to do different things. Some of them are Narendra Atya, who had been widowed in her childhood, Sunanda Atya who had an irresponsible and jobless husband and the like. Finding herself in a state of dilemma Indu was tempted to follow Jayant's advice, who had written her that there was no need to be involved in other people's problem. As all the possibilities were going through her mind, she had the opportunity to reconsider her relationship with her husband. At the same time she was greatly attracted to Naren. He was also attracted to her and she gave herself to him twice, but the very next day her mind was in turmoil of matters of sin, crime, right and wrong. But she does not take love making as a sin or crime. Later she feels ashamed of herself and tells Naren, "...When you tried me, I thought... this is Jayant. So that's all I'm Naren. Not a pure woman. Not a too faithful wife. But as an anachronism. A woman who loves her husband too much, too passionately and is ashamed of it" (Deshpande 192).

She is also ashamed of herself for not being a virgin woman. Therefore, she hates her womanhood. After realizing her failure in married life, she looks down upon marriage as a trap, "A trap? Or a cage? ... a cage with two trapped animals glorifying hatred at each other" (Deshpande 67). This sheds a light on Indu's awareness of her autonomy and realization that she is a being, and not a dependent on her husband. Jayant never tried to understand her feelings. Thus there is no real communication between them, "Love, that's a word I don't really understand. It seems to me an overworked word... sometime I wonder if I will leave him.... the only way in which I can be, myself, my whole self again" (Deshpande 97). Because of this thought, instead of leaving Jayant, she goes back to him with the vain hope that things will change the situation "... go back to Jayant. What kind of a life can you build on a foundation of dishonesty.... Now I would go back and see that home could stand the scorching touch of honesty? Nevertheless, I knew I would not tell Jayant about Naren and me" (Deshpande 205). According to Jasbir Jain, Indu's "... adulterous relationship does not lead to a sense of guilt, instead it liberates the psyche from false restrictions" (Deshpande 15-16). But this is not fair. We cannot agree with Jain's theory of "liberating the psyche from false restriction" because how can anyone bring in the physical relationship with someone other than the husband as a liberation of psyche from false restriction. Then if men also start thinking like this there will not be any respect to the institution of marriage.

Indu's profession, namely writing, after marriage too was one that she undertakes to support her family expenditure as she got married without parents' permission. She expresses her on writing thus, "I no longer have any desire to mould people, to change them, to reform society. There is only one thing I know I can do... I can write..." (Deshpande 15). By this she asserts that she has no desire in reforming the society through her writings. While in the process of writing too she feels tired and wants to abandon it. Indu's failure in all these fields shows that she is dishonest in her endeavours. She is always in a chaotic state of psyche and combating with circumstances to reach final solution. According to Indu, one should listen to the dictates of one's own conscience and be true to oneself in speech and action. But unfortunately, she herself had failed to do so either for fear of failure or some other reason. She wanted to show her family that her marriage was a success and she had lied and compromised all along losing her identity. Indu who had proudly thought that she would never pretend had actually pretended before Jayant by not revealing her whole self to him, thereby wronged to Jayant, Naren and herself too. Indu had believed firmly that she should be detached and will not be involving in any unnecessary matters. But her relation with Naren revealed her concept to be wrong. She realized that Jayant would be shattered if she were to reject him, unlike Naren. Naren remains unaffected by Indu's rejection because he was a totally detached person, he was no body's husband or lover and he loved music to such an extent that he could completely lose himself in it. This made Indu realise that love was not a

restricting but a uniting bond and life meant depending, on each other. The only way in which she could bring harmony in her married life was to stop pretending and to reveal her whole self, her weakness and strength, her virtues and vices.

The author employs the technique of withdrawal as a tool for self-realisation for her protagonist. Indu withdraws away from her suffocating life situations. Unable to adjust to the social demands on her she attempts a temporary psychological as well as sociological withdrawal. This renders her freedom and ensures a place for her in both family and the society. All of a sudden Indu's vision becomes clear and she knows what she has to do. Now she realizes that Akka had been a pillar of strength, rather than an interfering old woman as she perceived. She has chosen Indu as her heiress because she believed that Indu was capable of showing the same indomitable courage and strength. Whatever freedom she wanted, Indu had to find within the bounds of her obligations and responsibilities and within them one is free to do what one wants.

Through the character of Indu, Shashi Deshpande has very exquisitely portrayed the inner struggles and sufferings of the new class of Indian women, who has raised many questions regarding modern women who are tooted and shaped by the Indian customs but influenced by the Western world. In ancient times, Indian woman was hailed as 'Pativrutha' or 'Sati' and now she is a changed person. Now she is aware of her conscience, her quest, her identity, her place and role in the family and society. Indu represents such a woman. The society can either reject and condemn her or encourage and co-operate with her in efforts to establish a new image. Shashi Deshpande generally as the female protagonist and employs a kind of stream-of-consciousness techniques. Almost all her novels deal with crisis in the heroine's life. Through the protagonists' consciousness-raising voice, struggling to assert her femininity, the author gets to the root of existence and gives vent to a kind of female subjectivity which refuses to reconcile and identify herself with the patriarchal and male-

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dominated society. *Roots and Shadows* reflects the turmoil of modern existence with its divergent demands and pressures by delineating the crisis of human personality and human relationships. This is confined within the parameters for home and family.

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Indian Culture - A Noble Ideal of Universal Love

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Abstract: The objective of this extract is to go through of the some of the reflections on our great Indian culture. We often hear the phrase "Indian Culture". But when we speak of that, certainly we do not have in mind the details of our culture. We have a vision, a view point which is unique to Indian culture. It is a culture which rejects narrow mindedness. Indian culture means sympathy and compassion. It adores the heart as well as the intellect. Mother earth is the one who forgives all our wrongs to her. She is very generous. Indian culture tell us that the earth is like our mother and should not be neglected at any cost..

Keywords: Indian culture

I. INTRODUCTION

Culture is the sum total of man's thoughts, expressions and actions. Hindu culture is understood from the Vedas, Ithihasas, Puranas etc. Consideration for the feelings of others, for the rights of others and for the faults of others are the highest marks of culture and without this man would be uncultured. Indian culture has tried to build an intimate ties with animals, birds, trees and shrubs. Indian culture has given to all these a loved place in the human family. Man's power is limited. But Indian culture teaches man to use that limited power in the best possible way. It is not in our power to care for all the animals in nature. We cannot have a loving relationship with every single animal in nature. But let us at least create bonds of affection with some of the animals.

In man's moral philosophy, the whole of creation should be considered, whether animate of inanimate. If man cares only for the human species, he would be on the same level of animal's and birds. Man will prove supreme in creation only is he loves and looks after non-human creation, only if he establishes a close relationship with non-human nature. The real greatness of man lies in his being able to say that he loves everything in nature, rather than in his ability to destroy the rest of creation. The cow, in our traditional culture, is not merely regarded as an object of utility. It is true that in the beginning man saw the cow's importance mainly because of the numerous ways in which she can be useful.

But once a cow enters our courtyard she becomes a member of our family. Indian culture does not recommend that cows and bullocks, when they became old, should be sent off the butcher. The cow gave us an abundant supply of milk for ten or fifteen years. She produced oxen who plough our fields and do their jobs for us. If we abandon such a cow because she has now grow old, would be sheer ingratitude. Man does not live by utility alone. He has noble feelings which give value to his life. If we kill our loftier feelings with the weapon of utilitarianism, our worth as human beings will be reduced to zero that is our tradition teaches us and we must always remember this.

In the cultural tradition of India, the cow is to be regarded as a member of the family. We set aside a portion of food for the cow before beginning our meal. Serve the cow first and then eat : such is the practice. Through cow we worship all the other animals. Homage to cow is considered as homage to the entire animal kingdom. The cow is omnipresent in Indian culture. But now we know that the modern man due to their slavery, ignorance or poverty treats them in a brutal way and our life had become mechanical. Just as we can establish a relationship with the entire animal kingdom through the cow, we have to come close to birds too. With our limited strength we may not be able to relate to all birds of the entire world.

But we do remember the few species of birds that dwell near our houses. Before starting our meals we used to welcome crows and gives them a few crumbs of food in the past. Crows and sparrows are part of our surroundings and we remember them often. As an example we may notice how the grandmothers used to feed their younger one's calling the birds and giving them too a share of the food. The crows and sparrows in whose company our children grow up surely deserve our gratitude. By beckoning them we can express our interest in the entire kingdom of birds. Much value is given to birds in Indian culture. Peacock, kokil, parrot etc were our favorite birds and we used to give their names to our children. The relationship such birds and their masters is an example of the deep longing of the human soul to establish close kinship

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with the rest of creation. Trees, shrubs, creepers, grass and reeds -- like animals and birds - are bought into intimate relationship with man. Such has been the Indian cultural tradition. It is obvious that man cannot look after the whole of the vast vegetative world. That is the function of the clouds in the sky.

But we do make an arbour for the tulsi plants. We look upon tulsi plant as a representative of the vegetation. we worship tulsi plant, we water it before other plants in the garden. To remember tulsi is to remember all other shrubs and plants. In our culture we see a deep love for bushes, climbers and creepers. If we look at the poetical dramas of Kalidas, we can see this love expressed in many ways. Shakuntala arranges the marriage of a mango tree with atimukta creeper. In our great epic Ramayana, Rama was banished into the forest for twelve years. But to him, life in the forest was not as an ordeal.

Ram preferred the creepers and arbours of the forest to his marble palace in Ayodhya. He loved forests and groves. The moment we think of Rama, the image of Panchavati comes before us. Rama, Sita and Lakshmana spent many happy days in the shade of giant banyan trees in the Panchavati ashram. Sita planted trees around the little thatched hut where they lived. She fetched water from Godavari river to water them. We have ascribed human feelings and sensations to trees and shrubs. In the summer, a sun-shade is built over the tulsi plant toprotect it from the heat. We abstain from plucking flowers and fruits in the evening, after dark. It is also customary not to dig grass after dark. The feeling is that trees and shrubs are asleep at night so we should not disturb them in their sleep.

In this way, Indian culture has created for man an affectionate relationship with animals and birds, trees, shrubs and creepers. It is assumed that animals, birds and trees are not only alive but are also endowed with consciousness and feelings. They are born, and they die. They experience both pleasure and pain. Such is the Indian way of looking at life in general. When we see a river, greet her. We are indebted to rivers in many ways so worship them. Worship mountain because it is covered with vegetation which sustains us, that is what our tradition says. We addresses rivers as mothers. Their life-giving water sustains us. We may be able to do without m other's milk, but not without the water offered to us by Mother River.

The entire creation teaches us Advaita. The clouds give away all their water, the trees give their fruits, the rivers their moisture, the flowers their fragrance the sun and the moon give their light. Their message is: whatever exists is for everyone, let every thing be enjoyed together. The stars in the firmament are for everyone. The life-giving breeze that God gives us are for one and all. But man builds walls of separation and marks out his own property. And the earth, the greatest of all. Mother Earth is the one who forgives all our wrongs to her. She is very generous. we prick her with our ploughshares and she comes with corn foe us. We throw rubbish upon her we jump and dance upon her body. But Mother Earth does not get angry. She forgives all her children, Indian culture tells us that the earth is like our mother and should never be neglected. In our mythology, the earth is visualized as wearing the dress of ocean. The sun, the Moon and the stars are the flowers with which she adorns her hair. She has a garland of flowers with which she adores her neck. The mythical serpents, Sheshanaga and Vasuki, are considered as her anklets on her feet. Getting up in the morning, we apologize to Earth for the disrespect we would be showing her throughout the day and for trod on her. With boundless love for the whole of creation, animate and inanimate expressing gratitude towards all, we begin our day. Such is our Indian Culture. Let us attune ourselves to its music. Let us try to understand the ideal of this culture, its goal, its intention and its longing. We may carry forward into the future the great vision of our ancestors who created this culture.

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UNDERSTANDING THE NARRATIVE STRUCTURE IN CALL OF LIFE: FACING THE MASS EXTINCTION Dr. Sheena KaunaUN, Associate Professor, SreeSankaraVidyapeetorn

College, Valayanchirangara, Perumbavoor, Kerala

Tania John, Assistant Professor, Department of English, Aquinas College, Edacochin, Kerala

Abstract

The media has become an indispensable part of human life as a result of modernization. Now is the time of participatory media, which is a type of communication in which the audience can actively participate in the process of gathering, reporting, analysing, and transmitting content.Participatory culture transforms media consumption into the creation of new writings. In today's culture, the media plays a positive role in raising public awareness, disseminating information, and presenting people's perspectives on various issues. All processes of change that are media- induced across time are included in our notion of mediatization. The purpose of this study is to demonstrate how the documentary film *Call of Life: Facing the Mass Extinction* affects social change by urging people to take action. It is the first feature film to look into the mounting threat of biodiversity loss to Earth's life support systems. It considers how our cultural and economic structures have allowed this prodicament to arise, continue to perpetuate it, and even dictate our response to it, as well as the causes, scope, and potential implications of the mass extinction.

Keywords: Ecology, visual narratives, narrative structure, econarratology,

There is no denying that we live in a time when digital content is shared at an ever-increasing rate, often without adequate recognition or pay for the creative producers and organisations that help impire new ideas. The insights into how content creators, educators, curators, and archivists approached the subject of media arts at the turn of the century give us pause to examine the field's future directions. The basic rules of storytelling apply equally to docamentary and narrative fiction, namely: story, conflict, structure, and character. The factor that differentiates the characters from their objectives is conflict. There must always be an adversary in a conflict, which might be nature, as in the case of the selected documentary. Through interviews with leading scientists, psychologista, historians, and others, it looks beyond the immediate causes of the crisis to consider how our cultural and economic systems, as well as deep-scated psychological and behavioural patterns, have allowed and continue to reinforce the situation, and even determine our response to it. "Call of Life" depicts the story of a crisis that affects both the environment and human nature, posing a greater threat than anything bumans have ever faced.

The use of mass media to disseminate information tends to cause a shift and has an impact on shaping community life patterns. Information, interpretation, instruction, bonding, and diversion are all purposes served by the mainstream media. The media alters public perceptions and how people should interact with the world in a subtle but effective way. The media can engage constructively in socio-scientific challenges by analysing a wide range of real-world issues and basing scientific knowledge on these realities. Global warming, genetic engineering, animal testing, nuclear testing, deforestation practises, and environmental difficulties are examples of such issues in today's globe. In comparison to the other subgenres, the film has global appeal due to the addition of dubbing or subtitles that translate the dialogue into other languages.



There was string to the

DALT CONSCIOUNNESS IN THE POEMS OF MEENA KANDAKAMY

as Kalmal N., Associate Professor, Department of English, Sent Sci-

Alterna, Kandanamy's peritry is a perfait example of a implanting prompt against the starse Kandanamy's peritry is a perfait example of a implanting prompt against the starse framework of the starse in the starse in the starse starse in the starse security provide a starse of a starse starse and measurements that the dalits have had to endore. Her work hadameentally calls on a star atom a the starse with her brack ground. Yet, after reviewing the historical context of her are, the starse is a fact that some of them areas simple and universal. These poems are made of her are, the starse is a fact that some of them areas simple and universal. These poems are made of her are, the starse is a fact that some of them areas simple and universal. These poems are made of her are, the starse is a fact that some of them areas simple and universal. These poems are made of her are, the starse is an area of a start both the brack ground. Yet, after reviewing the historical context of her are, the starse is an a clubber and particular starse is and more secret a surround the dalit. The Dalits is started on an a clubber interpretation. However, some of the dalitand dalit permitting, who are well as tripte marginalization. However, some of the dalitand dalit permitting and the secret is started accessible or legal, the previously interported isociation that by the dait. The poems of a Canton made accessible or legal, the previously interported isociation that by the dait. The poems of the factories with an through in this article, as are how she depintualitic consciousness, dimension, and a consciousness is the dait. The poems of the factories with a thing article, as are how she depintualitic consciousness, dimension, who accession and a start. The poems of the factories is the dait. The poems of the factories is the dait.

Leared: Dulit Consciousness, descrimination, segregation, marginalization, above

1. Introduction

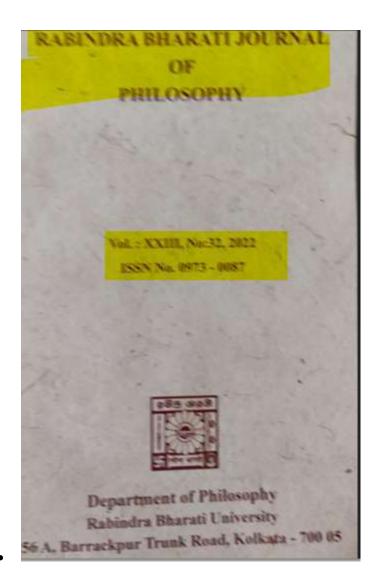
time Kardmany is one of the multidimensional faces that is marging in the costsurpt cary India sing a Loglish. She is a poet, empyint, interpreter, journalist, and activists to tensionally uses her den to represent the underprivileged classes of the society. She has some the advances of the down community in her constant battle against the dominant change. Kandacany is well emound The courseposes appendix in uttacking the hegemonic framework of the patrianchal and racin society. We excent to a neglected travelling class and learns about the minimum problem and received society, when then through the learn of a weener's activity, presenting a neglected on to three, and when providently, and her own blogs. *Touch*, her must well-known collections of poetry with a minimum by Kanada Das, was published in 2006 and ignicity gained wideoperal archem as an excellent "A

3.9. Using by Dalits is particularly bedian, since it amorphed from a shady social structure that has personal a long time in this country. Instant of hence a story about pecers, facises, and aerials, Dalit writing must the real reality. The Judian Constitution has about their induces percents, but Dalit must be real reality. The Judian Constitution has about the backdop. "Dalit writing" is may us a part of academics shows that these practices percell is the backdop. "Dalit writing" is many that emerges as an outbard against casteriors. There have been more compositions on these more that emerges as an outbard against casteriors. There have been more compositions on these more that emerges, by mutarrow writers arrows field, such Suraj Daddy Chashas, Hama and backarso in Tamil, Urmila Passet, Ont Prakash Valmilit, Mohan Das Naimishamy, w Marshe and multipating on the factor in Hindli. As a result, a well organized sufficience of Dalit writeness exist solary Mama. Station in Tamid, Urmida Pawar, Oni Prakinit Valnitis, Monan Dar Nannellarly, in Marate and Statya Baraanti in Hindi. As a result, a well-organized collection of Data servings exist suday Messa-missiony is one among them and her worthing in the result of the years of strangele the Datas have had being Kandasamy is a champion for Datits, but her works go much beyond that. They also defined being kookal freedom, the class and station system, and, surprisingly, address everyday issues while "bridge accurate the class and station system."

king strong emotions in the readers.

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BINDRA BHARATI JOURNAL OF PHILOSOPHY SN 0 A READING OF THE FEMALE PSYCHE IN ANITA NAIR'S LADIES COUPE

pr. Sheena Kaimal N., Associate Professor, Department of English, Ster Soniara Videore Valayanchirangara, Ernakoulam, Kerala, Indi

Abstract. Contemporary Indian women's yearning for individuality in a society where men are in there is expressed by Anita Nair in her novel, Laulies Coupe. The interior identities of the female charge it are cleverly investigated psychologically. By tempering their ladylike sensibility and characters are insight, Nair penetrates deeply into the inner payche of the depressed wanters and draw and their concerns, which are primarily caused by the psychological and localized doparties in a Both the outside world and the family have oppressed women for centuries, and Anna Naar's Later Coupe is rife with quests for discovering the inherent personality of the women. Marriage remains a local necessity where women seek security as well as respectability in men. Anna Nair has tentation in her works about the advent of a woman writer who might reveal more mysteries about propiers personalities and take the readers on a great exploration journey. These books have the power to challenge the small world. In this article, there is an attempt to demonstrate how Anita Nair tries to explore and delve deep into the inner psyche of women.

Krywords: Female psyche, inner psyche, interior identities, inherent personality, psychological imight

Introduction: Anita Nair is a novelist, short-story writer, essayist, journalist, and artist from Kerala Among her works are The Better Man, Ladies Coupe, Mistress, Lessons in Forgetting, Idris, and Aphahet. Soup for Loveraetc. She has also authored a number of poems. She has written a number of essays, and Malabar Psyche, a book of poetry. In addition to writing the screenplay for the film adaptation of her novel, Lexnons in Forgetting, she has also participated in two plays, received the Public Film Grant in 2013; and written two plays herself. Also, she was given the Crosssord Prize and a Sahinya Akademi grant. Her works have been translated into 31 different languages and published all over the world. The experimental writing and mentoring initiative she directs is called Anita's Loft.

Ladies Couper, Anita Nair's second book, was released in 2001 and has been translated into more than 25 languages throughout the world and it ranks among the top five books of 2002, according to ernes. The tile of the book draws attention to demonstrate how women are treated in Indian culture, possibly because it is thought that a woman can be safer alone in an all-ladies' compartment or a hus on an excursion. Indian women enjoy this type of preferential treatment; there is a "women just line" at the licket counter, "a ladies special bus," or, in this case, "a ladies coupe." Because Indian society firmly believes that a woman cannot survive without a man's insurance, the existence of these amenities

The plot of the novel, Ladies Coupers centered on the five women Margaret Shanit, Januki, Prabha Devi, Shank and the novel of the novel of the novel of the second Sheeta, and Marikolamthu. Then there is also Akhilandeswari, a middle-aged Brahmin moman whe is Victure K country. visiting Kanyakumari to find inner peace and to prepare her mind for the independence of a soman Aklula is Akhila is looking for a solution to her age-old question of whether a woman needs a man to complete be or of the her or if she can remain single and be content as they all discuss their personal experiences. All of the tomaining women's descriptions of their contacts with men, are unfavorable. This demonstrates that they can accept find to their contacts with men, are unfavorable. This demonstrates that they can accept find to total. can never find fulfillment or happiness in their interactions with them. It finally becomes apparent that tack never find fulfillment or happiness in their interactions with them. It finally becomes apparent that

tach person is unique and that only the person experiencing an issue can find a solution. It is erucial to bok at work to be a solution of the person experiencing an issue can find a solution. It is erucial to look at women's psychology in order to understand the problems that women encounter-Despite the fact that this portrayal of ladylike sensibility is mostly made through the projection of the souther here. conflict between social conventions and personal support for opportunity. Ladies Coope is a very

Vol. : XXIII, No:32, 2022

Education and Society (Flater affit metric) If GC Care Journal Vid-44, Inne-3, Na-43, July September, 2020 THE COLONIZED TERRAIN OF THE BODY: A READING OF MANULA PADMANABILAN'S MARKETY

Marena Kaimal N, Assistant Professor, Department of English, SSV College, Valayanshirangara, Korata, India, shornakannala if genal com

Abstract This activate looks at how the play Harrow represents the environment of provident to ten-important and made controls environment in the gaps left by the Transplane human in a workfield financial practice that interfore the interactivity development of individuals, transplane that cash a service public bookers. The play dimensions the influence of deparity that distinguishes that (in) human exchange between well, frequents from a septodiscing equation (development and development and development excited, the new participants as the trade. The latter two their body parts and organs in return for each, in the promotionial discourse, this is contained on the version of the body. Securitar on the other worldwide memory turning turns, transplant issuiries involves the complex discologement of addividual and pack media and namials of gettic borders.

Keywords: Transplant Tourism, Capitalism, New Imperialism, Colonization, Terrain, Body

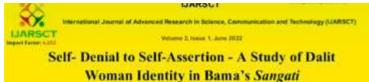
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ni and Society (विश्वान arth समाव) arv Journal: Vol-44, Issue-X, No.-43, July-September: 2020 (UGC Care Journal)

right. In the dealt camps of The Second Great War, where captives had no case to their own bodies and were denied the essential right to life, so well to the rights of perturbity and expansion one more instance of bodies imprisoned with practically on polynear opportunity.

1 2. Review of Linerature Organ transplantations in Itelia is represented by the Transplantation of Haman Organ Ari which was passed by the Indian Performent in 1994. The 'setting of a util organ' was determin aniardul by the THOA, but it allows for exceptions with authorizations given by the Approval Communitys. In the event that between and receiver were associated in our Offsta allowed ways — an parents, youngstern, stillings, or sponses — THOA 'considered the transplantation of kidneys from



Dr. Shrena Kaimal N. WWW officer, Valoyan him

Abstract: The paper attempts to analyze Bana's Sungeti and tries to find out love Bana asserts the identity of Dalit momen through her mercutive. The study focusion on Songast as a literary expression o restrictive and posteries and how the vertice portuges the journey of the Dalit women from the handship faced from the denial of the soft in the exercises of their identity.

Keywords: Self-Denial, Self-Assertion, Dulla Woman Mentity, etc.

1 INTRODUCTION

EXTRODUCTION Dalii fiterature is ni expression of the Dali encodencement of the rights and justice of the Dalis. Musi of their writings are their own experiments, straggles and sufferings, in forms of literature like portro, autobiographine, doer attrice, novels, street plays etc. Alek Mukherjee attests, "There is tri it generates, service, volumes, international and coefficie, competitions for survival, drankermoses and datth" (11) is the weeks of M. F. Edite, "The voucleus lower store here, the worklalses from a work laws?", igid, in Devisagament 13) Dali women, site genebally begin to produce literature which portrayed the sufferings and humiliation they had faced. They have tried to express their comessions

Interative which portrayed the edifferings and humilitation they had faced. They have tried to express their consciounness through their literary expressions. The Dath forminist believe that situation which is typical to any firminist resources is yet to buil the Dath woman as an equal sister. Women who beliesg to the upper cates have not considered Dath women as equal. Dath woman have been transed wowen than the way men have been tracted. Dath forminies can thus be doubled us a "discussed of discontent" and "splittical difference" from the main stream that finding firminies to be doubled or and adjusted base firminist's begrenowy which privileges mainstream hulian women, but also the begrencey of all Dath trens. It recalls the joint and multiple operations of casts and graded faced by the Dath woman. Dath firminies calculates the Witterney. of Dalor seman from the privileged upper name seman and ordebutes their identity, strongth, labour, and realistness. Women, all over the world and repectally in the Third World coantities have had to face so many difficulties and line Dalor somen it has been a tough task. The Dalor women are adjusted to two types of solpagatane, of their gender as well as of

suscept it has been a tongh baik. The Dalit suscept the Dalits. Dalit suscept to two types of solngarism, of their generic at world as of their zante. A Dalit suscept that message the Dalits. Dalit suscepts there also have the courage to voice the attreties against from. The time has come for front to pipping their also the data of their generic and their posterior and resistance to the investigation from. The time has come for front to pipping their also the data of their posterior and they have come out with literary works in the linens of books which have been to a gener texture anothering pipkes, that depied the sufferings day have faced. The provincent aroung them are Shanabal Kandoh. Linnala Passar. P. Strukansi, hally Kandoh, Chenda, Oryannak, 'Qida Cheirpoga, Banas en, Belang a Taral, Dalit Chenitan yearsan, Banas is able to septence to patient intensition of the women to face community. Bates also the constraint Shanas, Banas is able to septence that are arealistic who have to face works the non-basis again and the sector and arealistic and there have a sector repetience by the Dalit Christian works on Taral Node. She solongaroothy work two recer awards, *Sumgari* (1994) and Faceward (2002) along with tran arollesistion of doet nation, *Konsubralinane* (1994) work Ory Tarane Evene awards, *Sumgari* (1994) and Faceward (2002) along with tran arollesistion of short mixers, *Konsubralinane* (1994) and Ory Tarane Evene awards). Turning (2002) along with two autoentions of short anteres, Researcheduces (2009) and Ors Tarrine Evolution (2002). The paper attempts to analyse Huma's Alongost which they is interest-quite the morginalization and hamilation experiment by the Dulit women inside and outside their loose study and community. The strangthe and oppressions which the Dulit warners have had to indicate a term of the study experiment by the women of the momentanes society. Dulit women have had the field could be addressed when these regretions of the women of the momentanes society. Dulit women have had the field could be addressed about their regretion of the moment of the momentanes society. Dulit women momentanes among the Dulit sinteneous down their regrets and justice.

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The Storming of Sorayu M. - Interrogating the Denial of Identity for Women Dr. Sheves Kantal N., Associate Professor, Department of English, SSV College, Valayanchinngara, Ernakstan, Keells

shownak simaln i gmail com

ABSTRACT

The research paper entitled "The Suming of Scenard M - Interrugating the Denial of Identity for Weaton" probes time the way Soraya, the Utle character is denied identity and voice in the religious postiarchal Sourc of from The religious fundamentations join the State and adopt an officit paramethal states which redefines the words of the Divine against the woman and silence her. The publics condition of the woman who is isonarced to death by storing makes the readers to question the notices of divine platice, morality, sexuality and gender relations.

Key worsts Denial, James, Identity,

Violence against sectors is not a new or recent phenomenon. History of scores's opprecision shows that partiarchy has often singlift the help of religions and has mining Scoretores to silence women and their rights. Holy Words are often being misinterpreted or result whenever the dominant 'aelf' wants in subordinate the 'other' in terms of gender and sexuality. There is often the convergence of the power of the State and religion. The State machines the authenty of religious patriarchy to exert in dominance. Feminist voices have often operatored the patriarchal exception interpretations of Scorptiare.

Trials on women based on religious patriarchy can be seen through all the ages. The so called religious authorizes whenever exerted their feodal power have always demanded purity and subservence on the part of women. They have also sought the help of the State to exert their authority. Whenever the State becomes begemonic, the rulers have sought the help of religion too. So the oppression of women always depends on a hierarchical structure constructed by the State as well as the religion. Religious study with the help of the State are marrated brangh many literary works. In England, during the Middle Ages, women were panished by accusing them of hereny and during the early Modern Tra, women who stood against the authoritots have here executed in the name of writheraft. Soraya's story of injustice which happened in Iran in the 1980s is also an exercise of power both by the religion as well as the State.

The Sonong of Soroyar M, written by Freidoune Sahebjam, atticulates the injuntcen and bardships which the women of Iran have faced from the oppressive begenome. Share with the help of patriarchal construction of meanings for the Holy Texts. The write narrates the terrible real life of a thirty five year old Iranian woman. Sonoya, who has been stoned to death for having Seen disloyal to her bashband. The accuration has been fake and has been made hy her worksand Ghoeban Ali in order for him in marry a young gift. To get rul of Soraya (as be dial sot want to pay for her) Ali conspires with the Mullah and the Mayor of the village. Ali lireatens the Mullah and says that he will expose the pair life of the Mullah.

Soraya is compelled to take care of Hashem, a widower. Later she is accused of adultery with Hashem. The widower is also a perfect accomplice for the hegemonic patriarchal powers chiefs dictate the norms and rules. There is no one other than her aunt Zahra, to support Soraya num her powerless situation. It is Zahra who later details the story to Sabebjam. Soraya has ad to undergo hard trials and is eventually sentenced to death by storing. This story of

NIU International Journal of Human Rights ISSN: 2394-0298 Volume 95(V), 2022 43

AT INAL OF THE AMATIC SOURTY OF MUMBAL ON

ARAVIND ADIGA'S THE WHITE TIGER: THE VORCE OF THE SUBALTERS

Dr. Sheena Katmid N. Associate Parliance, Dep

Abstract

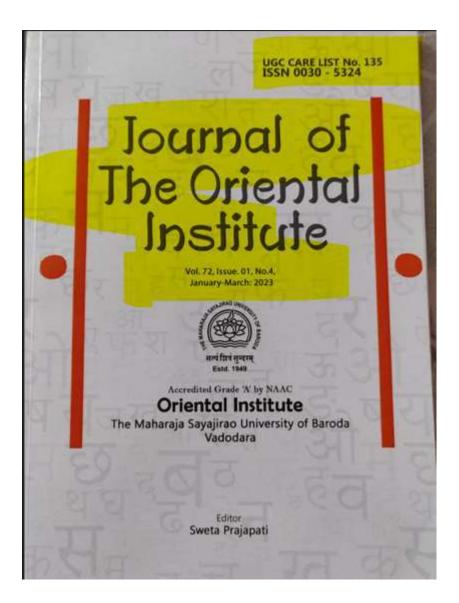
Abstract in his fact sovel. The White Tiger (2008), Aravind Adiga—a notable representative of Indian writing in English—has successfully brought anomian to the problem of the marginalized and the softerprivileged its has made an effort to impress upon his sodience the significance of the marginalized or underclass in the development of India. Adiga is attempting to draw attaction to the fact that the marginalized or underclass in the development of India. the development of India. Addga is astrompting to drive attantion to the fact that the adheberes can talk at since, by depicting the protagonist in an ariginal way, as he underpose a transformation from a village completion to a citized because annual through the use of Manduavellian stranges. Adiga since to explanate the room subaltern concentrations for the besefit of solution people. But she depicting the paragonist, Baltimi Halwai, going through a great deal of difficulty and transform before finally uncertains in the solutions in a depicted in Adiga's Indian society in order to understand the admitty of the subaltern class in *The White Toger* from the standpoint of posterolonial dialoctics.

Keywords: Sobalters Consciousness, Marginalized, Underprivileged, Identity, Postcolonial Dialecture

Introduction

The title of the text under consideration, The White Tiger (2008) alliades metaphocically to the manuformation of the colonial oppressed dominanted into the oppressively analysis manuformation in a water picture. In 10th the tale of Balram Halwai, who is oppressed or dominanted and the significant events that shape the transevork of the novel, beginning in the liftle town of Laxmangarh in the remote ladin state of backhard and moving on to Delhi and Bangalore. The beginning power inposed by the oppression who shape and control the life of the dominated, powerless people, is portuged in the newel. The depiction of the subalterius and their opposition to regain their electry and minus is shown in Adigu's work, in their efforts to move from the periphery to the centre. The movel is serious in the episodary form and for this Adiga explains the reason ble this

form and for this Adiga explains the reason blue this. Since the story contains actual mutder, he is smable to share with a myone as a result, he need only shares it alone. The inspending presence of a significant foregoing permuts has no consider his nation and society, as it does with all Indiani who are preoccupied to colonial legacy, perhaps) with the outsider's gate. He therefore convertes about himself and his notion as the sechasion of his room. (The Bonder Tisse, April 6, 2000) Adiga places the downtrodden, the marginalized and the lower class of society, as the consider meta-instruction in The White Tiger. It is the rale of the other, of the marginalized, victuating group which is denied equality and, as a result, is labelled as being underprovidegal. Due to their social standage incial, religions, or economic status, they are strateled wither to monther group. The "indertism," as incial, religions, or economic status, they are strateled with devices and alorigates, manuface, and the Madiga calls it, is portrayed to highlight the structure of the devices and alorigates, manuface, and yours subordinate class in Indian society, where the lower class, tribes and alorigate, depicts he puny, them, subordinate class in Indian society, where the lower class, tribes and alorigates, manuface, and workers about the store, and small businessmen are all quashed in one way or number. Adiga depicts here, the puny, them about the class in Indian society, where the lower class, triber and aborgoon, manufiles, and workers, labourers, and small businessmen are all quashed in one way or mother. Adapt depicts the point, branes, and humilitation of the underprivileged in the context of an advanced capitalist society in *The White* and flumilitation of the underprivileged in the context of an advanced capitalist society we are in *Toper*. Through the representation of a subordinate figure who stants for his class and others who are in *Toper*. Through the representation of a subordinate figure who stants for his class and others who are in "perpetual slavery," an attempt has been made to "lister to the quiet wince of history" in this indy.



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THE SEARCH FOR IDENTITY IN KIRAN DESAFS THE INHERITANCE OF LOSS

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ABSTRACT

The Inheritance of Loss by Kiran Desai presents three different ways of cultural identification, which this study aims to examine. The novel concentrates on three distinct types of cultural identification in various spatiotemporal situations through three intersecting plotlines. Judge Jennibhai, whose cultural identity has been profoundly influenced by the imperialist ideology during the British colonization of India, is a prime example of the first type of cultural identification, which is permeated with a sense of foreignness. Jennibhai renounces his Indianness and sticks to English cultural identification for Biju, a young immigrant and undocumented worker in several New York restaurants, is on the question of cultural authenticity in the diasporic environment. Biju pushes cultural authenticity. The third mode focuses on the cultural identification journeys of Sai and Gyan. Gyan, Sai's muths tutor, embodies the ambition to transcend limited intornalism much as Sai, Jennibhai's granddaughter, does. Sai and Gyan both suggest the possibility of crossing boundaries.

Keywords: Identity, Cultural Identification, Authenticity, Cultural Boundaries, Crossing Borders,

INTRODUCTION

The Inheritance of Loxi, Kiran Desai's second book, spans almost five decades from the colonial past in the 1930s to the globalized present in the 1980s. It does this by weaving three crossing plot strands into its narrative. The tale of the retired judge Jernabhal Patel, who is cut off from his Indian cultural roots and dwells in the aftermath of British colonization, is one plot. When his granddaughter Sai shows him to Cho Oyu, a run-down mansion in the Himalayas where he lives alone, Jernubhai becomes engrossed in memories of his boyhood days, during the British colonization in the first part of the 20th century. Another main character in the novel is Biju, an undocumented immigrant who makes his home in the New York restaurant basements. The deplorable poverty in New York and the news reports about political unrest in Kalimpong make Biju to give up his unrealized dream of living in America. Biju, the son of the judge's cook, sets out for the dreamland after much difficulty, only to discover that the voyage there is also a trip back to the "imaginary" home country. The other plot centres on the political unrest, especially the Gorkhaland Movement in Kalimpong, as well as the dispute between Sai, the Judge's granddaughter, and Gyan, a Nepali living in Kalimpong. Through the points of view of Sai and Gyan, the story emphasizes how the younger generation is unhappy with the current state of affairs.

The Inheritance of Loss maps three types of cultural identity through the interwoven story threads. Jemubhai's cultural identification is first marked by a sense of foreignness, which denotes being non-Indian or, more specifically, being English. Technically, anything that is from a foreign country is said to be foreign, but the word "foreign" carries both racial and cultural connotations. In order to appear foreign, Jemubhai had to adopt a non-Indian cultural identity. Surprisingly, the feeling of selfabjection is entwined with the experience of foreignness. By developing his cultural identity during the colonial era, Jemubhai shows how colonial interpellation transforms the colonized person into an inferior subject. As a result, Jemubhai creates his identity as a foreigner in his own country to deny

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Accelerator functionalized nanosilica for vulcanization efficiency and thermal resistance of SBR

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ABSTRACT

A simple and efficient method is developed to incorporate nanosilica (NS) into styrene-butadiene rubber (SBR) without using any coupling agents. Sodium isopropyl xanthate modified nanosilica (SIPX-NS) is homogeneously dispersed into SBR to give a better filler-rubber interaction. The SIPX-NS accelerates sulphur vulcanization leading to excellent mechanical properties for SBR composites. An obvious improvement in overall properties of SBR by the incorporation of nanosilica modified with a vulcanizing accelerator is showcased in this work. This brings new opportunities for the rubber composites with high-performance applications. The tensile strength and thermal stability of SBR 6SIPX-NS composite has been improved by 53% and 11 °C respectively compared to SBR gum composite. © 2022 Elsevier Ltd. All rights reserved.

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1. Introduction

The elastomer composite technology is in a paradigm shift as silica occupies the place of carbon black. The environmental and economic advantages of silica technology overcome the difficulty in processing of rubber with silica. It also minimises the use of expensive coupling agents. The easy incorporation of silica in the elastomeric composites without the use of coupling agents will lead to a quantum leap in the elastomer composites technology in future. Nanosilica has several properties like strong adsorption, surface activity, unsaturated valence bonds and electron tunnelling [1]. However, silica particles tend to agglomerate because of high surface energy [2]. Besides, abundant hydroxyl groups present on nanosilica surface result in hydrophilic nature and that causes incompatibility with elastomers [3–6]. To facilitate the interface bonding between polymer chains and nanosilica particles, silica modification is essential [7]. Different methods used for silica modification include chemical, thermal, electrochemical methods and also treatment with coupling agents [8–11]. Among the coupling agents, silane coupling agents are mainly used in rubber industry

* Corresponding author. *E-mail address:* pdileep84@gmail.com (P. Dileep). in order to get better dispersion of silica in rubber composites. The reinforcing efficiency of silica is enhanced by the reaction of functional groups present on silane coupling agents with rubber and silica [12]. Silane coupling agents can act as good *in-situ* modifying agents because of its ability to toughen the filler-polymer matrix *via* the development of covalent bonding between SBR and nanosilica particles [13,14].

In this work, the reinforcement effect of sodium isopropyl xanthate (SIPX) modified nanosilica on SBR composites is studied in detail. Thermal characteristics of pristine and modified nanosilica SBR vulcanizates were evaluated by TGA. The variations in chemical interactions of SBR vulcanizates were assessed from the crosslink density.

2. Experimental

2.1. Materials

Emulsion grade SBR (24% styrene content) was purchased from Reliance Industries, India. Nanosilica of 520 m²/g. surface area was synthesized in our laboratory [15] and modified using SIPX by a refluxing method [16]. Commercial grade of sulphur (S), Tetramethylthiuram disulphide (TMTD), N-cyclohexyl-2-benzothiazole

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sulphenamide (CBS), styrenated phenol (SP), stearic acid, and Zinc oxide (ZnO) were used. Toluene and diethylene glycol (DEG) were purchased from Merck Specialties Private Limited, India.

2.2. Methods

2.2.1. SBR/nanosilica composites preparation

The SBR/nanosilica compounds were prepared as per ASTM D 3184 standard on Thermo Haake Polylab for 8 min at 70 °C. Mastication of SBR was carried out for 3 min and then ZnO, stearic acid, nanosilica and DEG were added. After three minutes, CBS, TMTD and sulphur were added. The mixing was continued for another two minutes to obtain a homogeneous dispersion of ingredients. After thorough mixing, the compound was sheeted out 5 times in a laboratory mixing mill and finally at a nip gap of 3 mm. This compound was kept for maturation for one day at room temperature before moulding. The formulation of SBR mixes are shown in Table 1. Our previous work showed that the SBR composite with 5phr nanosilica (SBR 5NS) loading [15] provides better performance. Hence in this work accelerator modified nanosilica varied from 5 phr to 7phr. The compounds were moulded at 160 °C and 150 kg/cm² pressure at optimum cure time in a hydraulic press with 1 feet platen size.

2.3. Characterization methods

The microstructure of tensile fractured surfaces was analyzed by JOEL (Model JSM 8390 LV) scanning electron microscope. TA instruments (model Q-50) Thermogravimetric Analyser was used to perform the thermogravimetric analysis. The cure characteristics of rubber compounds were determined on Rubber Process Analyser (RPA 2000) as per ASTM D 5289. Instron make Universal Testing Machine was used for the stress-strain analysis of samples according to ASTM D 412. ASTM D 624 standard was used to measure tear strength of composites. The hardness of samples were measured using Durometer (Shore A type) as per ASTM D 2240. Bariess make DIN abrader was employed for abrasion loss analysis as per ASTM D 5963. Densimeter was used to determine the specific gravity of composites as per ASTM D 297. Compression set of vulcanizates was studied as per ASTM D 395 standard. Goodrich flexometer, Dynisco, USA was used to determine the heat buildup analysis as per ASTM D 623. ASTM D 7121 standard was used to measure the rebound resilience using Dunlop Tripsometer. Swelling of the samples were studied using toluene as solvent. Flory-Rehner equation was used to calculate the crosslink density of the vulcanizates [17].

3. Results

3.1. Cure parameters of SBR nanocomposites

Fig. 1 shows the cure behaviour and Table 2 shows the cure parameters of SBR nanocomposites. According to Mathew *et al.* [18], the cure parameters of the nanocomposites are influenced by the concentration and surface nature of silica. From Fig. 1, the

 Table 1

 Formulation of SBR mixes.

1	

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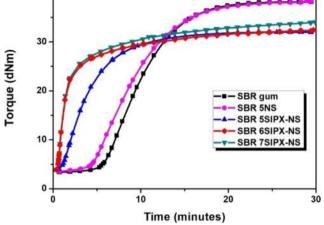


Fig 1. Cure characteristics of SBR composites.

Table 2	
Cure parameters of SBR composites.	

40

Sample name	TS ₂ (Minutes)	T ₉₀ (Minutes)	$M_{H}-M_{L}(dNm)$
SBR gum	5.85	15.52	34.81
SBR 5NS	4.55	14.99	34.2
SBR 5SIPX-NS	1.30	10.27	28.18
SBR 6SIPX-NS	0.64	9.64	28.53
SBR 7SIPX-NS	0.64	9.92	30.09

optimum cure time and scorch time of SBR 5NS composite showed higher value owing to the absorption of curatives by nanosilica particles. However, both the scorch and optimum cure value for SBR SIPX-NS composites are lower than SBR 5NS composites. This is due to the adsorbed accelerator molecules of SIPX over the silanol hydroxyl groups on nanosilica after the modification, which enhances the accelerating effect of vulcanization. Ismail *et al.* suggested that an increase in the filler concentration causes a decrease in scorch time due to the higher amount of heat development during mixing [19]. Lower scorch time of SBR SIPX-NS composites indicates its poor processability. Maximum torque (M_H), a measure of crosslink density and polymer-filler interactions increases linearly with SIPX-NS addition.

3.2. Stress strain properties

High interfacial interaction as well as uniform dispersion of SIPX-NS have a significant influence on the mechanical properties of SBR composites. Fig. 2 shows the dependence of tensile strength on filler content. The maximum tensile strength is attained for SBR 6SIPX-NS composite compared to other SBR composites. This is due to better filler-rubber interaction. Higher loading of nanosilica causes poor filler-rubber interaction due to silica aggregation [20]. Higher concentration of nanoparticles causes its agglomeration, which reduces the stress transfer within the composite and

Ingredients ^a (phr) ^b	Mix Names						
(p)	SBR Gum	SBR 5NS	SBR 5SIPX-NS	SBR 6SIPX-NS	SBR 7SIPX-NS		
NS SIPX-NS	0 0	5 0	0 5	0 6	0 7		

^a SBR 100, ZnO 5.0, stearic acid 1.5, DEG 10% of filler, SP 1.0, TMTD 0.2, CBS 0.8 and sulphur 2.0 were similar to all formulations.

^b Parts per hundred rubber.

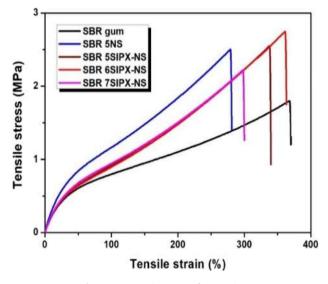


Fig. 2. Stress strain curves of composites.

leads to the reduction in tensile strength [21]. Where as at lower concentration (5SIPX-NS), the filler content is not sufficient to reinforce the SBR matrix. SBR 6SIPX-NS shows an increase of 53% and 10% respectively in tensile strength than SBR gum compound and SBR 5NS composite.

Table 3 indicates tensile strength, elongation at break, modulus at 200% and tear strength of SBR vulcanizates. As the filler concentration increases, the elongation at break subside as the non-deformable nanosilica particles restricts the mobility of the polymer chains [22]. The improvement in tear property and modulus at 200% elongation with silica loading indicates the reinforcing effect of nanosilica. Dispersion of nanosilica, its size and concentration are the key factors that influence modulus and tensile property of SBR vulcanizates. There is no significant changes in modulus at 200% elongation for SBR 5NS and SBR/SIPX-NS composites. Increase in SIPX-NS concentration does not affect the modulus of the composites due to its better dispersion and interaction with SBR matrix. The tear strength increases with increasing SIPX-NS concentration in SBR matrix. This results also supports the cross link density of the SBR/SIPX-NS composites [23].

3.3. Other mechanical parameters

Table 4 indicates the mechanical properties of all vulcanizates. The hardness of SBR nanocomposites increases with filler concentration. This is related to the rise in cross link density [24] and modulus of composites. SBR 7SIPX-NS showed maximum hardness because of the increase in rigidity of the modified filler. The abrasion loss of SBR vulcanizates is presented in Table 4 column 3. The results showed that abrasion loss decreases with nanosilica concentration. Abrasion loss is evaluated as a function of volume loss [25]. Rubber vulcanizate's abrasion resistance depends on factors such as surface activity, filler size, structure, and rubber filler inter-

Table 3			
Tensile and tear p	roperties	of SBR	composites.

actions [26]. The abrasion resistance of composites is controlled by their modulus and friction coefficient [15]. Vulcanizates with better abrasion resistance possess a lower friction coefficient and higher modulus. Also, a composite with uniform filler dispersion have superior wear property compared with non-uniform filler dispersion. Lower abrasion loss of SBR SIPX-NS composites is due to the uniform dispersion and interaction of filler in the SBR matrix, which enables better service life of the composite.

The compression set resistance depends on the capability of the structure to recover from a continuous forced strain. The dynamic compression set percentage and compression set percentages are increasing marginally with SIPX-NS concentration as silica filler is considered as a non-resilient material [27]. When the modulus of composites increases, the polymer chain mobility is restricted even after the applied stress is removed. This shows that there exists a direct relationship between modulus and compression set values. Heat buildup is the measure of heat dissipated throughout the cyclic deformation [28]. The rise in heat build-up of vulcanizates with filler concentration leads to fatigue failure and poor mechanical properties [29]. Heat build up of SBR 5SIPX-NS composite is lower than that of unmodified nanosilica composite due to the reduced friction of uniformly distributed SIPX-NS particle in the SBR matrix. The rebound resilience reduces with the increase of SIPX-NS content as silica is a non deformable material. There is no substantial difference in rebound resilience and heat build-up values of SBR 5NS and SBR SIPX-NS composites because the modification of the filler improves the dispersion in the SBR matrix.

3.4. Morphology of SBR nanocomposites

Fig. 3 shows the SEM images of tensile fractured surfaces of SBR 5NS and SBR 6SIPX-NS nanocomposites. Fig. 3(a) indicates the nonuniformly dispersed nanosilica in SBR with higher agglomerates due to the hydrogen bonding between surface silanol groups [30]. Nanosilica agglomerates were reduced after the modification as the silanol hydroxyl groups were reacted with SIPX [31]. Hence the SIPX-NS particles were uniformly dispersed in the SBR matrix at a nanoscale level as shown in Fig. 3(b). Homogeneous distribution of filler materials into the matrix increases the overall performance of the composites while the non-homogeneous dispersion of the fillers decreases the characteristic properties by creating stress concentrated spots [32].

3.5. Thermal characteristics of composites

Fig. 4 shows the TG and DTG curves of SBR gum, SBR 5NS and SBR 6SIPX-NS composites. All these samples showed a two-step degradation. In TG curves, the first weight loss at 150–250 °C is due to the degradation of small molecular additives and unstable crosslinking agents. The second degradation in the temperature range of 300–500 °C is due to the degradation of SBR [33]. Table 5 represents the thermal degradation characteristic data of SBR vulcanizates. The onset degradation temperature of SBR gum and SBR 5NS is 357 °C, whereas for SBR 6SIPX-NS the T_{on} is increased to 11 °C. The 50% degradation temperature (T₅₀) increases to 5 °C for SBR 6SIPX-NS composite. The thermal degradation of SBR com-

Sample name	Tensile strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)	Tear strength (N/mm)
SBR gum	1.81 ± 0.10	369 ± 11	1.1 ± 0.05	34.90 ± 0.9
SBR 5NS	2.51 ± 0.15	280 ± 17	1.5 ± 0.10	43.62 ± 1.2
SBR 5SIPXNS	2.56 ± 0.10	339 ± 08	1.5 ± 0.08	41.71 ± 1.4
SBR 6SIPXNS	2.76 ± 0.14	360 ± 14	1.5 ± 0.03	45.94 ± 1.5
SBR 7SIPXNS	2.23 ± 0.16	291 ± 08	1.5 ± 0.06	46.15 ± 1.8

Table 4

Mechanical properties.

Sample name	Hardness (Shore A)	Abrasion loss (cc)	Compression set (%)	Dynamic compression set (%)	Rebound resilience (%)	Heat build up (°C)
SBR gum	43 ± 1	0.28 ± 0.01	25.6 ± 0.2	2.3 ± 0.1	65 ± 1	16 ± 2
SBR 5NS	44 ± 0.5	0.26 ± 0.02	28.4 ± 0.1	4.65 ± 0.1	55 ± 2	30 ± 1
SBR 5SIPX-NS	45 ± 1.0	0.24 ± 0.05	29.7 ± 0.25	6.5 ± 0.2	57 ± 1	27 ± 2
SBR 6SIPX-NS	46 ± 0.5	0.23 ± 0.01	34.91 ± 0.17	7.2 ± 0.2	56 ± 1	32 ± 1
SBR 7SIPX-NS	46.5 ± 0.5	0.21 ± 0.01	35.48 ± 0.2	7.1 ± 0.3	55 ± 1	33 ± 1

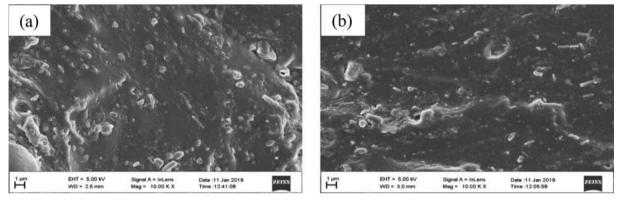


Fig. 3. SEM image of tensile fractured surfaces (a) SBR 5NS (b) SBR 6SIPX-NS.

posites altered based on nature and type of metal ion, xanthate concentration *etc.* [34]. Lower xanthate concentration has no substantial effect on the thermal characteristics of SBR SIPX-NS com-

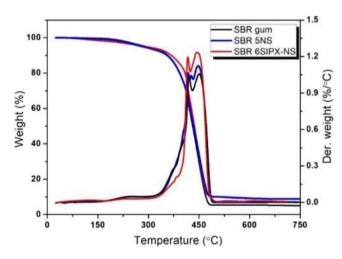


Fig. 4. TG and DTG curves of SBR gum, SBR-5NS and SBR 6SIPX-NS composites.

Table 5

Thermal degradation characteristics.

Sample name	Onset degradation temperature (T _{on} , °C)	Temperature at 50% degradation (T ₅₀ , °C)	Residue at 750 °C (%)
SBR Gum	357	431	5.06
SBR 5NS	357	434	8.8
SBR 6SIPX-NS	368	436	9.02

Table 6

Cross link density of SBR composites.

posite. Because of lower potential energy of SBR surface, higher temperature forces the nanosilica to move on to the composite surface that produce SBR-nanosilica char which acts like a thermal obstruction for saving SBR from further disintegration [35].

3.6. Solvent barrier properties of composites

The cross link density was determined by a swelling method. When vulcanized rubbers are immersed in solvents, they swell to equilibrium degrees [36]. The cross link density is influenced by rubber filler interaction and chemical crosslinks of vulcanizates [37]. The cross link density of SBR nanosilica composites are presented in Table 6. The swelling ratio slowly decreases with increasing SIPX-NS content. Uniformly distributed SIPX-NS particles in the SBR matrix restricts the solvent transport and hence an increase in cross-link density of SBR SIPX-NS composites [38].

4. Conclusion

SBR composites with nanosilica (5phr) and SIPX modified nanosilica (5–7 phr) were prepared. Improved cure and mechanical properties were obtained for the composite containing 6SIPX-NS. TGA of SBR 6SIPX-NS showed an 11 °C increase in onset degradation temperature. SEM analysis revealed improved rubber-filler interaction in SBR composite with 6 phr modified nanosilica. Modification of nanosilica with SIPX showed improved crosslink density.

CRediT authorship contribution statement

P. Dileep: Conceptualization, Methodology, Visualization, Investigation. M.P. Poornima: Data curation, Resources. Sinto

Sample name	SBR gum	SBR 5NS	SBR 5SIPXNS	SBR 6SIPXNS	SBR 7SIPXNS
Cross link density (10 ⁻⁵ mol/g)	12 ± 0.15	13 ± 0.1	13 ± 0.1	14 ± 0.05	14 ± 0.1

Jacob: Supervision, Writing – review & editing. **John P. Rappai:** Reviewing and editing. **C.D. Midhun Dominic:** Data curation, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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NARRATIVE, HISTORY AND FICTION IN THE LAST MUGHAL: THE FALL OF A DYNASTY, 1857 BY WILLIAM DALRYMPLE

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Abstract

History, the term despite its apparent innocence and simplicity eludes a clear-cut definition. In the conventional sense history means the events which happened sometime in the past. But history cannet be reduced into mere past events, dead and buried, rather it is a growing entity, a dynamic process, a continuum which has its origin in a bygone time, continues and influences the current period and stretches out into a forthcoming tomorrow. One thing which is more difficult than giving a fitting definition to history is the process of transforming it to a coherent narrative. Historiography or writing of history is therefore a complex process that demands a great degree of objectivity as it provides a standpoint from which significant events are observed and analyzed. The complexity arises when the writer of history cannot dispense with subjectivity in the interpretation of outwardly objective facts. In such a dead lock situation the writer of history chooses subjective interpretive methods and this accounts for the interface between history and literature, more precisely fiction. Fiction and its different techniques including the process of narration, narrative elements, characterization and other tropes have often been used by historians for constructing 'histories' and authors of literary works use historical facts in fictional works to produce alternative histories. Postmodern historical theorists like Hayden White have insisted on writing history using the method of fiction. For the postmodern fiction writers, history is an indispensable element in their works. A host of other emerging historians resort to writing history in the garb of fiction. A number of hybrid forms like historical fiction, fictional history, historiographic fiction and many others have cropped up from this lawful liaison between fiction and history. Yet another genre of writing which is fiction and history simultaneously is on the rise in contemporary Indian literary topography. This paper is an attempt to analyze this new genre, its idiosyncratic features and possibilities based on the celebrated work The Last Mughal: The Fall of a dynasty, Delhi, 1857 by William Dalrymple.

Key words- history-facts- objectivity- fiction-reality- subjectivity- narrative- historiography.

History, Objectivity and the idea of Narrative:

History in the traditional sense plainly means events that happened sometime in the past and the way it is recorded and preserved. Though apparently innocent this definition hides a number of real issues. What is 'past' then and how can anyone draw a demarcating line between past and present? And which is the best method that could be adopted to record those events which are generally considered as 'factual' and to preserve them for futurity? The question of where does this time period of past end and present begin is a perplexing one of rhetorical nature for anyone pondering over it. At one point it is past at the next moment it has become present and it is then stretched out into future leaving its mark upon all the intermittent episodes.

Another major challenge that a writer of history in his / her effort to preserve these vital events. confronts is to find an ample method for documenting them without tampering its factuality¹.

Factuality refers to the state of being real or truthful. The concept of factuality in a narrative, both literary and historical is a complex one and it may give rise to questions of ontological and Journal of Kavikulaguru Kalidas Sanskrit University, Ramtek

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Gender and Livelihood Patterns in the Context of Migrant Women Labourers to Kerala

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Navas M. Khadar* & Sudhakaran K.M.**

Abstract

According to the Kerala Economic Review 2021, unemployment in Kerala is 10 per cent, compared to the national average of 4.8 per cent. In 2013, a report of the Labour Department of Kerala showed that 2.5 million non-state workers worked in Kerala, which is suffering from the same level of unemployment. In the enumeration of non-state workers in Kerala, only males engaged in development work in cities are included. But women migrant workers working in rural areas are not included. Many migrant women workers work in small businesses, hotels, factories, brick-making units, agriculture, and as domestic helps. Women migrant workers do not get enough consideration in the academic setting where various studies of migrant workers in Kerala are being conducted. It is doubtful whether the constitutional provisions and associated policy directives on discriminating against workers based on gender are implemented among unorganized workers. Since the 1990s, there have been major changes in Kerala's labourer situation, mainly a lack of skilled and unskilled labour and widespread migration from Kerala to the Gulf countries. Studies are being done about the wage exploitation faced by migrant workers in Kerala. But most of it is done in large manufacturing units, or among workers engaged in direct employment. The conditions of male dominance in the field of work also exist among migrant workers. Even the government lacks a clear vision of women's work or their sufferings in the industry. The fact that agents in Kerala operate brothels using migrant workers as middlemen suggests a more tangible form of exploitation.

In the new migration situation in Kerala, the presence of women workers is increasing. A large section of interstate workers find employment in informal sectors like brick kiln industry, the construction sector, beauty parlours, the plantation sector, garment industry, plywood manufacturing units, and other fields. Migrant women workers who previously came only with their families are now coming alone in search

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of work. There are many women workers in Kerala today who work within and outside the scope of the interstate worker act of 1979. They are constantly subjected to exploitation and human rights violations in society and at work. This paper presents the human rights violations in the everyday experiences of migrant women workers who live in precarious living and working conditions.

Key Words: Labour Force, Interstate Women Migration, Gender Exploitation, Human Rights

Methodology

According to the Planning Board's estimate for 2021, there are 28 lakh to 34 lakh migrant workers in Kerala. It was also mentioned that most migrant workers (28 per cent) live in Ernakulam district. According to the official figures of the Government of Kerala, the total number of migrant workers in Kerala is 5,16,320. The largest number (1,15,053) of migrant workers reside in Ernakulam district. If we look at the number of female migrant workers, according to the data of the Kerala Govt., Ernakulam district has the highest number of female migrant workers (9986). Therefore, Ernakulam district was chosen for the study of women workers. In the first phase of the investigation, pockets of migrant women workers were found in 84 panchayats of Ernakulam district, and out of that, Vengola, Kizhakkambalam, Rayamangalam, Sreemulanagaram, Aikaranad, Asamannur, Kaladi, Kumbalangi, Ramamangalam panchayats and Perumbavoor Municipality were selected for data collection for writing this article. This article is written by taking currently published research reports, articles and government regulations as secondary data.

Migration to Kerala: Changing Trends

Even before the independence of India, the first group of people had arrived in Kerala. According to studies of the Tamil migrant population that arrived in South Travancore and North Malabar in the 1940s for agriculture, Kerala is a good migration ground. During the period when agriculture was given priority, those who came for agricultural work were later made permanent residents of Kerala. As with post-independence migration, migration to Kerala was motivated by a desire for a better job. The period 1950–60 marks the history of the migrant population who arrived for brickyard work, carpentry, and plantation work. That is what the history of people who migrated from Karnataka and Andhra Pradesh to Wayanad suggests. Even after 50 years, they are still living in Kerala as a migrant population, which can be understood as an unsolved problem in governance. The 1970s were a period that saw a huge increase in migration to Kerala. When the youth of Kerala migrated to the GCC countries on a whim, all the traditional sectors of Kerala faced awful shortage of workers. In the 1970s, migration to various sectors such as agriculture, fishing, factory work, goldsmithing, construction, and carpentry intensified. Most of the migrants came from the states of Tamil Nadu, Andhra Pradesh, Karnataka, and Maharashtra.

As part of the industrial revolution and neo-liberal policies, various factories sprang up in many parts of the country. There were changes in the pattern of migration. Migration from rural to urban areas has increased significantly. New industries started in Kerala. More jobs were created in the manufacturing sector, and the Assam Deforestation Act revitalised the Kerala timber industry. Changes in immigration arrival states have occurred since 2000. According to the 2011 census, the interstate workers coming to Kerala were earlier from Tamil Nadu, Karnataka and Andhra, but now they are coming from Assam, Bengal, Bihar and Haryana. This shift in migration also led to changes in the arrival of women. Women who used to come only with their husbands are now looking for work on their own. They go to work alone at different workplaces. They try to live together and tend to earn more money.

This research paper explores the phenomenon of migration to Kerala, a state in South India, and its impact on the state's social, economic, and cultural landscape. The study highlights that migration to Kerala has been prevalent for centuries and is motivated by factors such as agriculture, industries, and employment opportunities. The Tamil migrant population arrived in South Travancore and North Malabar in the 1940s for agricultural work, leading to the formation of a migrant population that still exists in Kerala today. Post-independence, migration to Kerala was motivated by a desire for better job opportunities, with the youth of Kerala migrating to the Gulf Cooperation Council (GCC) countries. Changes in the economy brought about changes in migration patterns, with migration from rural to urban areas increasing significantly.

The study also highlights the impact of migration on gender relations. Women who used to come only with their husbands are now looking for work on their own, leading to the emergence of new forms of female labour that challenge traditional gender roles in Kerala. However, migration also poses challenges to migrants, including discrimination and social exclusion. The study emphasizes the need for the state government to provide basic amenities to migrants and ensure that they are not exploited by employers. Overall, migration has played a significant role in shaping the social, economic, and cultural landscape of Kerala. While it has enriched the cultural diversity of the state, it has also challenged traditional ways of life and raised issues of citizenship and marginalisation. The study calls for a comprehensive approach to migration that addresses the needs of migrants and promotes their integration into the local society.

Interstate Women Migration

One particular group of migrants that has gained significant attention in recent years is women migrants who migrate from other Indian states to Kerala. The state has a long history of migration, both internal and external. The first wave of migration to Kerala was from the neighbouring state of Tamil Nadu, followed by labour migration from other parts of India and the Middle East. According to the 2011 Census, Kerala had a total population of 33.4 million, of which 2.2 million were migrants from other states.

Interstate women migration to Kerala has been on the rise in recent years. Women from states like West Bengal, Odisha, Assam and Bihar migrate to Kerala in search of better employment opportunities, higher wages and better living conditions. According to a study conducted by the Centre for Development Studies in Thiruvananthapuram, the number of interstate women migrants in Kerala increased from 1.5 lahks in 2001 to 5.5 lakh in 2011. The study also found that women migrants were concentrated in the construction, hospitality and domestic work sectors.

Although academic studies have addressed the migrant worker issue, the women workers are found often excluded from such studies. The research gap in this study is that this article about women migrant workers is being made invisible. According to a study conducted by the Kerala Institute of Labour and Employment (KILE) (2020), for which they interviewed 536 migrant women, most women are reluctant to come out. Women from Tamil Nadu, Assam, Odisha, Jharkhand and Bengal are among the first to arrive from other states. Discussions, studies, and academic research on migrant workers currently tend to visualize only male workers. Even in studies of migrant workers, women migrant workers are exploited and excluded. Within the slums, the physical presence and labour contribution of women are not acknowledged, and government policies and academic research that are aimed at them, fail to bring to light the real facts. This article attempts to study the status of migrant workers in Kerala.

The KILE (2020) report indicates that the vast majority of women migrant workers to Kerala are young and a quarter of them are illiterate. According to the information obtained from the fieldwork, female migrant workers are mostly found in the plantations, fishing sector, and textile manufacturing. Apart from this, they are also actively engaged in work in beauty parlours and hotels, and also as domestic workers. The number of migrant women workers working in plywood and plastic manufacturing sectors, and brickyards is also relatively high.

The primary reason for interstate women's migration to Kerala is economic. Women from other states come to Kerala in search of better job opportunities and higher wages. The minimum wage in Kerala is higher than that in most other states, making it an attractive destination for migrants. The state's construction and hospitality sectors also provide employment opportunities that are not available in their home states. Another factor driving women's migration to Kerala is social. Women from states with more conservative and patriarchal societies come to Kerala to escape gender-based discrimination and violence. Kerala is known for its progressive social policies, and women migrants feel safer and more secure in the state.

The information about the inflow of female migrant workers gathered from fieldwork on the arrival of women workers in Kerala is shared here. Migrant women come to Kerala mainly in five ways. This does not include students who come to study.

- 1. Those arriving due to marriage
- 2. Those that come with the help of relatives
- 3. Those arriving at the contractor's discretion
- 4. Those who reach out through community organisations
- 5. Those arriving alone.

Female migrant workers who come to Kerala due to marriage later turn to work. The arrival of women workers in Kerala began with the migration of Tamil people to Kerala. In the 1950s and 1960s, Tamil male labourers migrated to Kerala along with their wives. Their main occupation was domestic work, plantation work, and working in plantation areas. In the 1990s, migration from North Indian states to Kerala increased, stemming the flow of migration from South Indian states. As such, their wives started arriving with the men who had migrated to Kerala.

They moved away from domestic work and started working in manufacturing units. During this time, women began to do the same jobs as men. The number of women workers who come with their relatives is increasing exponentially. Migrant women come with both men and women. Reports (Resmi, 2009) indicate an increase in sexual harassment among women, accompanied by men. During the fieldwork in the area of 'Vallam' in Kerala's Ernakulam district it was discovered that some sanctuaries are operating in this area where women have been engaged as sex workers and majority of the them had come with their relatives for work in Kerala.

Women migrant workers in many manufacturing units have been classified as contractors under the 1979 Act. It was learned that they started working within 15 days of their arrival in Kerala. Based on interviews with the women working in the plywood sector, it was understood that the principal employer is providing accommodation for them. But unsanitary living conditions and substance abuse are causing them various health problems. Indian Journal of Politics and International Relations

The migration facilitated by community organisations came to light after the police jeep attack at Kitex Garments company at Kizhakkambalam gram panchayat in Ernakulam district on December 26, 2021. During the Christmas celebrations there, a section of the workers of the company, under the influence of alcohol assaulted the policemen, who came to control the noisy partying following a complaint registered by the locals, and set the police jeep on fire (Shajan 2023). The police have arrested all the accused in connection with the incident. From newspaper reports after their arrest, it was understood that all the accused were converted Christians. To understand the truth of this, ten women working from the company were selected for interviews (finding and interviewing them was very difficult). All of them had identified that they were part of a special community organisation. This type of migration is also common in the plywood industry pockets in Kerala. In the fieldwork, we realised that people belonging to the Muslim community were getting jobs in the plywood sector quickly.

The number of women coming to work alone is increasing. Those who come with the aim of seeing Kerala have been provided accommodation by their friends. Through interviews, we understood that those who have passed the 10th Class are the ones who have reached the state this way. Among the solo entrants there were some aspirants looking for professional jobs. And they work in beauty salons, spas, baji shops, and *paan* shops.

Interstate women migration presents both challenges and opportunities. One of the important challenges is the lack of social support systems. Migrant women often face discrimination and exploitation, and the absence of social networks exacerbates their vulnerability. They are also at risk of physical and sexual abuse, and their access to justice is limited. However, interstate women migration also presents opportunities for the state. Migrant women contribute to the state's economy by working in low-skilled sectors, and their remittances provide a significant boost to their home state's economy. The influx of migrants also brings diversity to Kerala's society, enriching its cultural fabric. The state government should work towards creating a conducive environment for migrant women, which includes access to education, healthcare and legal aid. Additionally, there is a need for greater awareness and sensitivity towards the rights of migrant women and the contribution they make to society.

The Health of Women Migrant Workers

In-depth interviews with women migrant workers based on their work, living conditions, and health systems were conducted as part of this study. In the study conducted in Ernakulam district, based on talking to 100 women from 10 workplaces,

it was understood that most of the migrant women do jobs without mental satisfaction. Among those who spoke directly, women in the age group of 18 to 40 faced health-related problems. The important reason for these health-related problems is that they do not have clear knowledge about health and hygiene. Vaginal and sexually transmitted diseases are becoming more common in women, but non-hospitalization exacerbates the problem. Talking to migrant women who suffer from malnutrition, it becomes clear that they have been malnourished since childhood. Lack of rest in non-time-bound work in Kerala worsens their health condition.

The health issues of migrant women workers do not appear to be generally discussed. The Interstate Migrant Workmen Act (1979) clearly states the requirements to be followed by the contractor or employer in the living arrangements of migrant workers. But when we saw their real condition, we realized that 60 per cent of the contractors were not providing the basic facilities. The Migration Act applies to all migrant workers. But when we see their current working methods, it becomes obvious that they are working without any consideration for women workers. The contractors often fail to address the problems of women suffering from menstrual problems and assume that they will somehow cope with it. The main reason why these issues have not yet been addressed is the lack of space for menstrual hygiene practices in the areas they work in and the lack of research on these at the workplace level. As a result, it is critical to conduct health awareness programmes for female migrant workers in their institutions.

Kerala's Labour Department and Local Self-Government system do not collect accurate information about the status of women in the workplace. The lack of specific social security schemes for migrant workers at the panchayat level (Khadar, 2020) can also be considered a fundamental shortcoming. The Department of Labour puts the total number of migrant women workers at 26,516 (Labour Commissionerate 2023). But the actual facts are not in agreement with the government's estimates based on fieldwork. However, the Kerala Planning Board Report (2021) provides figures that are more realistic.

The living conditions of women migrant workers in Kerala are often substandard. They are often forced to live in cramped spaces, such as small rooms or dormitories, with minimal or no ventilation. This can lead to respiratory problems and other health issues. Lack of access to clean drinking water and sanitation facilities further exacerbates the problem, making them prone to infections. The work environment of women migrant workers can also be hazardous. In many cases, they are employed in industries such as construction, manufacturing or agriculture, which involve physical labour and exposure to chemicals and other harmful substances. This puts them at risk of occupational hazards such as musculoskeletal disorders, skin problems and respiratory diseases. In addition, women migrant workers often Indian Journal of Politics and International Relations

face challenges in accessing healthcare. They may not have health insurance or may not even be aware of the healthcare facilities available to them. Even if they do have access to healthcare, language barriers and cultural differences can make it difficult for them to communicate their health concerns effectively.

Women migrant workers in Kerala are often employed in low-paying jobs with long working hours. They may work in industries such as construction and hospitality, or as domestic worker, where they are paid lower wages than their male counterparts. They may also be forced to work overtime without compensation, which can lead to exhaustion and burnout. In many cases, women migrant workers do not have job security or access to social protection. They may be employed on a contract basis, which means that they can be dismissed at any time without any notice or compensation. This lack of job security can lead to stress and anxiety, which can have an impact on their mental and physical health. Women migrant workers in Kerala also face discrimination and harassment at workplaces. They may be subjected to verbal abuse, sexual harassment, or exploitation by their employers or colleagues. This can lead to a hostile work environment, which can have a significant impact on their well-being and productivity. The health and job conditions of women migrant workers in Kerala are a cause for concern. These women are vulnerable to a range of health problems due to their living conditions and the nature of their work. It is important for the government, employers, and civil society organisations to work together to address these issues. Measures such as providing access to healthcare, improving living conditions, and enforcing labour laws can help protect the health and well-being of women migrant workers. In addition, efforts to promote gender equality and prevent discrimination and harassment can help create a more inclusive and supportive work environment for these women.

Application of Labour Force and Social Conditions

Migrant women workers are employed in Kerala at a higher rate than indigenous women workers (Anjali, 2016). In India, women who migrate after marriage are found to have increased their access to employment by 10 per cent (Neetha, 2019). Studies indicate that migrant women workers arriving in Kerala are getting physically abused at workplaces due to overwork, restless work, and sexual harassment (Resmi, 2009). An industry employs a disproportionate number of female workers compared to the number of male workers. Therefore, Prasad (2017) indicates, in his work that is based on the information found through fieldwork, it is the employer who ignores them and pretends not to see them. In Kerala, we have seen the struggle for the rights of women workers at workplaces. The struggles for the rights of women workers, such as the sit-in strike, were successful to some extent through organised movements. But not a single labour organisation is ready to address the problems

of migrant women workers in Kerala in an organised manner. Working long hours without rest, working on roads in extremely hot and humid weather, working at places where there is no place to sit or rest, and not being able to conduct proper health check-ups are all can be considered a violation of human rights. Through the field visit, we have been convinced that it is imperative that the employer and the local self-government bodies jointly organise medical camps at workplaces every month to study and address the health problems being faced by women workers, and it is also necessary to educate women workers about their rights and sensitise them to the exploitative nature of the workforce under the leadership of the Labour Department.

Wage discrimination at workplaces is a major problem being faced by women workers. Even indigenous women workers do not get the same wages as men for doing the same work. In this social situation, the demand for justice for migrant women workers comes from a human rights perspective. The Payment of Wages Act (1936), the Minimum Wages Act (1948), and the Equal Remuneration Act (1976) exist in India, but the fact that those laws still fail to protect the migrant women workers can be seen as a denial of rights.

One of the major issues being faced by women migrant workers in Kerala is low wages. Most of these women work in the informal sector and are paid meagre salaries. This is mainly due to the fact that they are not covered under any labour laws and are not entitled to any benefits such as paid leave or health insurance. In addition, they are often subjected to long working hours and are not provided with proper working conditions, which further exacerbates their vulnerability.

Another major issue faced by women migrant workers in Kerala is the lack of social protection. They are often subject to various forms of abuse, including physical and sexual abuse. Despite this, many of them are afraid to report such incidents, as they fear retaliation from their employers. In addition, they are often denied access to basic amenities such as healthcare and education, which further perpetuates their vulnerability. Moreover, women migrant workers in Kerala also face various forms of discrimination based on their gender, caste and ethnicity. They are often treated as second-class citizens and are subjected to various forms of harassment and violence. This is especially true for women from marginalised communities, who face multiple layers of discrimination based on their gender, caste and economic status.

The application of labour laws and social conditions in the context of women migrant workers in Kerala are complex issues that require a multifaceted approach. It is important to address the systemic issues that lead to the exploitation of these women, including the lack of social protection, the absence of labour laws, and the

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prevalence of discrimination based on gender, caste and ethnicity. Moreover, it is important to provide these women with access to basic amenities such as healthcare and education and to empower them with the knowledge and skills required to demand their rights and fight against exploitation. Only then can we create a more equitable and just society, where women migrant workers are treated with dignity and respect.

Migrant Female Workers and Social Security Programmes

The issue of migrant female workers and social security programmes in Kerala is complex and multifaceted. While Kerala has made significant strides in providing social security to its citizens, including migrant workers, there are still significant gaps in the system, particularly in the context of female workers. One of the key challenges being faced by migrant female workers is access to social security programmes. Many migrant workers, particularly those working in the informal sector, may not be aware of the various programmes available to them or may face language and cultural barriers that prevent them from accessing these programmes. This can leave them vulnerable to exploitation and abuse, particularly in situations where they are working without legal documentation.

Even when migrant female workers are aware of social security programmes, they may face additional barriers to accessing them. Another key issue is the lack of adequate protection for migrant female workers at workplaces. This can include issues such as wage theft, discrimination, and sexual harassment. Without adequate protections in place, migrant female workers may be hesitant to report abuses, particularly if they fear retaliation from their employers.

Overall, while Kerala has made progress in providing social security to its citizens, more needs to be done to ensure that migrant female workers are not left behind. This may include increasing awareness on social security programmes among migrant workers, providing additional support to help them access these programmes, and strengthening workplace protections to prevent abuse and exploitation. Additionally, there may be a need to re-evaluate the design of social security programmes to ensure that they are accessible to all workers, regardless of their background or employment status.

There are currently three schemes for migrant workers in Kerala. Interstate Migrants Welfare Scheme (2010), Awas Health Insurance (2017) and Apna Ghar (2019). All three of these schemes are for the entire population of migrant workers in Kerala. But only one-third of its total beneficiaries are females. According to the Kerala Labour Commissioner, women account for less than 7 per cent of the total Awas health insurance enrollees in Kerala.

In other words, it has to be understood that the registration system is malecentric or that government officials have failed to draw women to registration processes. Apna Ghar Scheme is a dormitory housing scheme for migrant workers. Discrimination against women begins with dorm registration. A total of 1,140 beneficiaries are living in the dormitory accommodation facility, which has already started functioning at Kanjikode and Kinalur. But the fact that there is not even a single migrant woman worker among them is proof of the marginalisation of women in the scheme. Apna Ghar is only available to migrant workers in industries located in Kanjikode and Kinalur. The reason why women workers are not getting the benefit of this government scheme should be subjected to further studies.

Conclusion

The participation of women migrant workers in the labour force in Kerala has been on the rise in recent years. However, the government's estimation of less than seven per cent of female migrant workers living in Kerala is incomplete and unsatisfactory. The data collection process does not adequately include migrant women workers, making them invisible in official statistics. This exclusion highlights the urgent need for better representation and inclusion of migrant women workers in the data collection process.

Furthermore, the labour sector in Kerala does not follow the legal provision of equal pay for equal work in the case of women workers. Women migrant workers are subjected to harsh working conditions, unsanitary accommodation, and sexual exploitation at their workplaces, which, in turn, violate their basic human rights. These issues are prevalent not just in Ernakulum district but in all the 13 districts of Kerala. Therefore, it is imperative that efforts be made to extend this study's findings to all the districts in Kerala to help understand and address the situation.

It is also necessary to scale up awareness programmes on health among migrant women workers. The local self-government bodies and principal employers should work together to make health and hygiene accessible to all women at work and organise medical camps for the purpose. This step will help migrant women workers access medical facilities and provide them with basic healthcare services.

The exclusion or non-consideration of women migrant workers in government schemes are contrary to the Constitutional values. Kerala's employment situation heavily relies on migrant workers, and women workers are often marginalised and excluded from employment and social status. Therefore, the government must take proactive measures to make women workers more aware of exploitation and human rights violations.

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In conclusion, women migrant workers are an integral part of Kerala's labour force, and their contribution is invaluable. However, their exclusion from official statistics and data collection processes is a matter of great concern. Addressing the issues of unequal pay, miserable working conditions, and human rights violations is essential to ensure the protection and well-being of women migrant workers. The government should take proactive steps to improve the situation and create a more inclusive and equitable environment for all migrant workers in Kerala.

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THE IMPACT OF LIBERALIZATION, PRIVATIZATION AND GLOBALIZATION [ICLPG-2021]

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GENDER BASED DISCRIMINATION AND ROLE OF GENDER BASED DISCRIMINATION

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ANAGH

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Introduction

"Any distinction, exclusion or restriction made on the basis of sex which has the effect or purpose of impairing or nullifying the recognition, enjoyment or exercise by women, irrespective of their marital status, on the basis of equality of men and women, of human rights and fundamental freedoms in the political economic, social, cultural, civil or any other field." (United Nations, 1979. Convention on the Elimination of all forms of Discrimination Against Women'. Article 1)

The United Nations Organisation the concept of gender discrimination in the above mentioned manner. This definition relates discrimination on the basis of gender, and it is consequent exclusions, restrictions etc. This definition lays emphasis on the fact that discrimination of any kind of the basis of gender, sex, and its relation to womanhood vis-à-vis- direct or indirect - is taboo and should be eliminated from the social network once and for all for peaceful coexistence in a society. It is not the factor of gender or sex or other matters that carries importance. A persons's book of life becomes meaningful and complete only when the chapters inherent in this book become meaningful, fruitful, useful and purposeful. For this purpose the actions concerned are to be goal oriented, necessitated by a purpose. There should be no

deviation from this action. The imposition of gender and related discriminatory activities result in violation of human right which is most unwarranted as envisaged in the Article 1 of theUnited Nations' 'Convention on the Elimination of all forms of Discrimination Against Women' (CEDAW) of 1979.

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The term discrimination is not merely confined to the people in the society, it is inherent directly or indirectly in the laws and legislations passed in the light of the same. On cursory analysis of the definition by UN as cited above, it is to be mentioned that the definition has laid importance on two genders viz male and female respectively. It is clear that the other genders inclusive of the society has not been given due consideration. Discrimination can stem from both law (de jure) or from practice (de facto).

De jure discrimination: The same is the case with the laws, legislations, etc. enacted in the light of the concept of gender discrimination. It is evident that the concept of gender discrimination still persists in this society despite several enactments, deliberations and researchers, etc. conducted on the topic.

For eg: In some countries, the law states that women (citizens) who marry foreign men lose their citizenship and/or property rights. On the other

நகினத் தமிழாய்வு (பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்) 3-5 ஜீன், 2021 – சிறப்பிதழ் (ISSN: 2321-984X) hamizh Research (A. Quarterte Internet John (ISSN: 2321-984X) Modern Thamizh Research (A Quarterly International Multilateral Thamizh Journal) 3 to 5 June, 2021 - Appiulagie (ISSN: 2321-984X) Three Days Multi-Disciplinary International Multilateral Thamizh Journal) 3 to 5 June, 2021 - Special Issue (ISSN: 2321-984X) Three Days Multi-Disciplinary International Multilateral Thamizh Journal) 3 to 5 June, 2021 - Special Issue (ISSN 202021) Organized by P.G. & Research Department of Webinar On "The Impact of Liberalization, Privatization and Globalization [ICLPG-2021] Organized by: P.G. & Research Department of History, C. Abdul Hakeem College (Autonomous), Melvisharm, Ranipet District, Tamilnadu

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Evolution of Film as a Source of History

- Dr. Sebastian Joseph

Associate Professor and Research Guide, PG Dept. of History, UC College, Aluva, Eranakulam, Kerala. - RadhikaLal Assistant Professor, Dep. Of History, SSV College, Valayamchirangara.

Summary :

From the outset, historians have a deep scepticism towards the notion that films can be considered as historical evidences. The time has come to seriously contest this approach of the historians towards films. Historians generally considered early historical films as breaches. If they ever associated with films, it was as if they were masters of historical facts. They immensely trusted at the immortality of raw historical facts.

Keywords: Historical writing, Postmodern, Evidence, Historical Films

Introduction :

The traditional paradigm of history writing is often associated with the legacy of the Greco-Roman school at a time when the discipline was engaged in history writing based on hearsay accounts from those who witnessed great events, especially wars. Political history was the main focus in their writings and other aspects though mentioned at some points, were subordinated to political events. When Herodotus stressed on truthful enquiry, Polybius looked at the utilitarian purposes and Cicero stood for literary and rhetorical genres. In the Hellenistic period, the notion of history as a factual account and a literary genre (or a mode of writing) prevailed. The word 'historia', both in Latin and Greek, refer to 'a literary genre with its rules and styles, canons of greatness

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and social utility'. In the Roman Age, there was a shift in function of history from pure enquiry to a higher level of philosophy. Dionysius of Halicarnassus asserted that 'history is philosophy from examples.' In the period of the Roman Empire, the emphasis again shifted to literary truth and factual information. Also history began to be seen as an account of the past.

The Church and the Jewish historiography stressed on moral values than literary truth. In the period of later Roman Empire, facts began to acquire prominence than fiction. The Greeko-Roman philosophy's metaphysical doctrine of substance was challenged by the Christians doctrine of creation, which stressed that only God is eternal and everything else has been created by God. Historical process came to be the working out of God's purposes. Christian philosophy was also, universal, providential, apocalyptic and periodized. The Greeks saw history as story whereas the Latin Christians stressed on literary truthfulness. The Christian historiographers saw history as a collective past of the selected people, who were not non- Christians. The rhetoric nature of history was strengthened.

In the European Middle Ages, 'historia' referred to 'narrative works of art, saints' lives, part of the Bible, the literal sense of scriptural texts, liturgical offices, epic poems, other texts and objects.' Though 'truth' was the prime factor, 'truth' itself had diverse meanings.

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Ecological Imperialism in the Hills of India : The Case of Munnar

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The establishment of British Empire in India is akin to the appropriation of the aboriginal resources and tribals of India. The natural resource base of India acted as a laboratory to the Western science and technology. While political imperialism followed ecological imperialism in all other colonies of Britain, the vice versa was their strategy in India. But the hill stations of India witnessed the same plan of action as that in the other colonies, i.e., ecological imperialism was succeeded by political imperialism. The archived and textualised past of Munnar, fragmented and well organised in forms of original records and secondary reflections is a veritable source of understanding for analysing the history of Munnar. The imperial gaze of the English, individual and collective subjected the pristine landscape for an extensive and rigorous scrutiny of the Empire resulting in the reconfiguration of the native landscape in the way of making it a garden, tea garden suitable for the exploitative networks of plantation industry and its commercial agents. The paper specifically examines the ways in which the British imperialism crept into the hills of Munnar and appropriated the nature and life of Munnar

Ecological Imperialism :

Alfred W Crosby in his book, Ecological Imperialism: The Biological Expansion of Europe, 900-1900, argues that European conquestoverUnited States, Argentina, Uruguay, Australia, Canada and New Zealand was constituted by not only military, technology and

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economy, but also through a process called, ecological imperialism. Crosby calls these lands as Lands of Demographic Takeover. 'There has been four categories of organisms that helped Europeans to expand: (1) human beings (2) animals closely associated with human beings- desirable animals like horses, cattle and undesirable animals like rats (3) disease causing pathogens (4) weeds. 107 The vast areas of forests and pastoral lands in the Lands of Demographic Takeover were inundated by animals and plants from the Old World, i.e. Europe. The Europeans were accompanied or preceded by their domesticated animals, and these animals adapted o the new environment faster than their masters and their number grew rapidly. 109 Wherever the Europeans settled, the pathogens they carried created epidemics of smallpox, measles, influenza and tuberculosis. They also brought with them weeds that hindered the growth of native plants and even outgrew them. The demographic takeover of the colonies was facilitated not only by humans and gunpowder alone, but also by various aggressive and opportunistic animals, pathogens and weeds also

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Taking the case of India alone, Europeans arrived in India, not for a demographic takeover, but for trade only. Later, under favourable circumstances, they took over the administration, polity and economy of India. The arrival of European animals, plants and pathogens only succeeded humans. So India, as a whole, is not a place where the concept of Ecological

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ORIGINAL PAPER



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Abstract

Accelerator functional character was introduced on nanosilica by chemical reaction of sodium isopropyl xanthate (SIPX) with nanosilica (NS). Functional characteristics of nanosilica were confirmed by elemental analysis, thermogravimetric analysis, and infrared spectroscopy. This SIPX functionalized nanosilica (SIPX-NS) incorporated natural rubber (NR) composites were used to evaluate the dispersion of silica in rubber and also the interaction between rubber and filler. The finely dispersed SIPX-NS particles in the NR matrix are revealed from the morphological analysis. Subtle changes in the surface chemistry of silica had a profound influence on dispersibility in the NR matrix. NR 4SIPX-NS composite showed an increase in tensile strength by 10%, flex crack initiation resistance by 13%, tensile strength retention by 16% and cure time reduced by 2 min relative to those of NR 3NS composite. This simple, efficient and cost-effective surface modification of silica improved the vulcanization efficiency and mechanical performance of NR composites and has great potential in the fabrication of high-performance polymer composites.

Keywords Nanosilica - Surface modification - Sodium isopropyl xanthate - Thermal conductivity - Flex crack resistance

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Formation and photoluminescence of ZnS:Tb nanoparticles stabilized by polyethylene glycol

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Keywords: Nanoparticles Phosphor X-ray diffraction Photoluminescence Chromaticity coordinates

ABSTRACT

ZnS nanoparticles doped with 1 mol.% of Tb have been prepared at 70 °C by simple chemical precipitation method using poly ethylene glycol (PEG) as capping agent. The synthesized nanoparticles have been analysed using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL) and UV–Vis absorption spectroscopy. From X-ray diffraction analysis, it was found that nanostructured ZnS:Tb particles exhibited cubic structure with an average crystallite size of 2.75 nm. Room temperature photoluminescence (PL) spectrum of the doped sample exhibited broad emission in the visible region with multiple peaks at 395 and 412 nm due to ${}^{5}D_{3} \rightarrow {}^{7}F_{6}$ and ${}^{7}F_{5}$ transitions and 492, 536, 600, 653 and 680 nm due to ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$, ${}^{7}F_{5}$, ${}^{7}F_{4}^{7}F_{1}$ and ${}^{7}F_{0}$ transitions. © 2020 Elsevier Ltd. All rights reserved.

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[6]. The trivalent terbium metal ion has 4f⁸ electronic configura-

tion in ground state and $4f^7$, $5d^1$ electronic configuration in the

excited state. After the absorption of energy, the excitation hap-

pens and intraelectronic transitions take place from $4f^8$ to $4f^7$ 5d¹. When terbium ion comes to its 7F_i ground level from 5D_4

and ⁵D₃lowest excited levels, the characteristic f-f emission tran-

sitions takes place. The green emission produced from ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition in Tb provides a four-level laser system with a lower

threshold pump power compared with that of Er³⁺ ions makes

the Tb a promising ion for green lasing applications. Besides, Tb

doped phosphors are environmentally friendly and more energy

saving than mercury-containing fluorescent lamps [7–9]. Thus,

terbium doped phosphors are appropriate for many technological

applications like fluorescence lamps, cathode ray tubes, field

emission displays and for many others [10-14]. Considering the

wide applications of Tb doped materials, in this work we report

the synthesis of 1 mol% Tb doped ZnS nanoparticles by the chem-

ical precipitation method using poly ethylene glycol (PEG) as capping agent and its characterization by the X-ray diffraction (XRD),

Fourier transform infrared spectroscopy (FTIR), UV-vis and PL

1. Introduction

Researchers have been taking enormous interest to synthesize semiconductor nano materials because of their size-dependent optoelectronic properties. Zinc sulphide (ZnS) is an important II-VI semiconductor material with remarkable optical properties due to its wide optical band gap of ~3.65 eV. The ZnS nanomaterials are non-toxic, with high temperature stability, chemical stability and exhibit good biological compatibility. Due to wide band gap ZnS is a suitable host material for the doping of RE and transition metal ions. ZnS doped with these optically active luminescent materials finds its applications in displays, LEDS, lasers, etc. [1–4]. It is known that ZnS doped with the rare-earth elements could be more valuable in amending the luminescence properties of ZnS due to their special 4f-4f intra-shell transitions. Hence ZnS nanocrystals doped with various RE ions can be used in producing efficient phosphor materials with a range of colors in red, blue, and green [5]. Therefore, the development of rare-earth activated luminescent materials has been the subject of wide research recently. Among the rare earth elements trivalent terbium ion (Tb) is well recognized as the highly competent green phosphor

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spectroscopy.





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2. Experimental

ZnS:Tb nanoparticles were prepared by chemical precipitation method using zinc acetate $[Zn(CH_3COO)_2]$, terbium nitrate [Tb $(NO_3)_3$] and sodium sulphide $[Na_2S]$ with 1:2 M ratio of Zn:S. The solvent used for the preparation was the deionized water- ethanol mixture of equal volume. The PEG (1 ml) was added in the above solution with constant stirring at 70 °C. The obtained precipitate was washed with de-ionized water–ethanol mixture for several times and filtered. Finally, the filtered powders were dried for 11 h at 80 °C and grinded to obtain PEG capped ZnS:Tb nanoparticles

The X-ray diffraction studies of the sample was carried out on Bruker AXS D8 Advance X-ray diffractometer. The absorption spectrum of the sample was recorded with a UV–Vis spectrophotometer (Shimadzu UVPC 2401). Shimadzu spectrophotometer was used for the FTIR analysis. The PL properties of the sample were measured using Horiba Fluromax 4C research spectrofluorometer with xenon lamp as the excitation source.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD pattern of Tb doped ZnS nanoparticles which shows major reflections from (111), (220) and (311) planes of the cubic phase ZnS nanoparticles as per JCPDS data file No: 65–0309 The average size of the nanocrystallites was estimated from the line broadening of the XRD peaks using Debye –Scherrer's equation [15],

$$d = (.9\lambda)/(\beta \text{Cos}\theta) \tag{1}$$

where D is the average diameter of the nanocrystallites, λ is the wavelength of the Cu-K α (1.5405 A°) radiation, β (in radian) is the full width at half maximum (FWHM) and θ is the Bragg angle. The average crystallite size of PEG capped ZnS:Tb nanoparticles was found to be 2.75 nm. The lattice parameters of cubic zinc blend were determined using the relation

$$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}$$
(2)

where d_{hkl} is the interplanar separation corresponding to Miller indices h, k, and l. The value of lattice parameter for ZnS:Tb nanoparticles was found to be a = b = c = 5.367 A° which is less than the bulk for which lattice parameter is 5.400 A°. An error function, f (θ) was introduced by Nelson and Riley for the determination of correction in lattice parameter (a) given by [16]

$$f(\theta) = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$
(3)

From the NR plot [Fig. 1(b) f (θ) versus calculated lattice constant values], the corrected lattice parameter is calculated as 5.342A°.

The diffraction line broadening caused by the strain and small crystallite size were analyzed using Williamson-Hall (W-H) method. The W–H plot for the ZnS:Tb is shown in Fig. 1(c). The relation used for the calculation of lattice strain and crystallite size [17,18] is

$$\cos\theta = \frac{k\lambda}{D} + 2\xi\sin\theta \tag{4}$$

where ξ represents the lattice strain and other parameters have the same meaning as in Scherrer's eqn. From the W–H plot, the average lattice strain and crystallite size were found to be 0.0099 and 3.2 nm, respectively.

3.2. Optical studies

Fig. 2 shows the FTIR spectrum of the ZnS:Tb nanoparticles. The spectrum has been recorded in the $400-4000 \text{ cm}^{-1}$. It is used to recognize the functional groups or adsorbing species existing on the surface of the nanoparticles and enable us to notice the molecular impurities. The spectral bands between 500 and 690 cm⁻¹are related to Zn-S stretching vibrations [17,19]. The peak at 970 cm^{-1} is due to C-H bending or due to the C-C vibration, related to the interaction between ZnS:Tb and PEG [17,19]. The C-O stretching and O-H bending frequencies are found at 1028 cm^{-1} and 1577 cm^{-1} [20]. The band centered at 1200 cm^{-1} originates from C- O- C bands of PEG [21]. The intense peak at 1419 cm⁻¹ was related to the C–O–H bending [18]. The spectral bands at 2120 cm^{-1} and 2348 cm^{-1} can be assigned to the C-H stretching vibration [17,22]. The broad peak in the range of 2500-3600 cm⁻¹ is attributed to the stretching vibration of -OH group which indicate the presence of adsorbed water on the ZnS surface [20].

UV–Vis absorption spectrum of the ZnS:Tb nanoparticles is given in Fig. 3. We could find that the absorption region is from 300 to 400 nm and the direct band gap energy (E) is calculated from the Taucplot(shown in inset of Fig. 3, a plot of $(\alpha h\nu)^{1/2}$ versus photon energy (hv)) using the relation

$$\alpha h \upsilon = A (h \upsilon - E_g)^n \tag{5}$$

where A is a constant, α represents the absorption coefficient and n = 1/2 for the allowed direct band gap. It can be seen from the Tauc

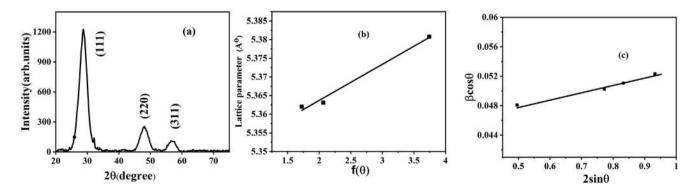


Fig. 1. (a) XRD pattern and (b) Nelson and Riley plot (c) Williamson-Hall plot of ZnS:Tb nanoparticles.

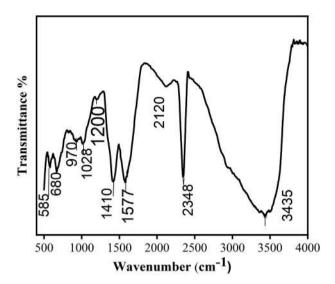


Fig. 2. FTIR spectrum of ZnS:Tb nanoparticles.

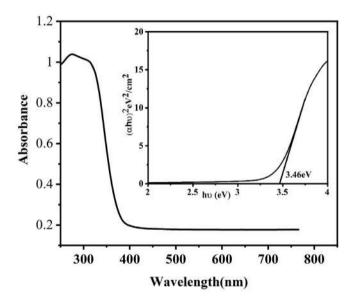


Fig. 3. Absorption spectrum of ZnS:Tb nanoparticles [Inset Tauc plot].

plot that the band gap of ZnS:Tb is 3.46 eV by extrapolating the linear region of the plot to the x- axis.

The room-temperature photoluminescence (PL) spectrum of ZnS:Tb nanoparticles recorded with an excitation wavelength of 370 nm is shown in Fig. 4(a). This spectrum consists of a broad emission band in the range of 470-575 nm. The recombination of electron-hole pairs at defect sites leads to the change in the local charge distribution, which modifies the equilibrium bond length and affects strong vibrational transitions, produces a broad emission band in the PL spectrum. It consists of several bands associated transitions from the ⁵D₃ (blue emissions) and ⁵D₄ (greenred emissions) levels to the ${}^{7}F_{1}$ multiplets. The emission peaks at 395, 412,492, 536 and 600 nm correspond to ${}^{5}D_{3} \rightarrow {}^{7}F_{6}, {}^{5}D_{3} \rightarrow {}^{7}F_{5}$ ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ and ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ transitions [23–27]. The peaks at 653 and 680 nm which are rarely reported, are due to ⁵D₄ \rightarrow ⁷F₁and ⁵D₄ \rightarrow ⁷F₀ transitions of the trivalent Tb ions [7] Among them, the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ band is responsible for the green emission. Since this green emission dominates overall emissions, it is called hypersensitive transition and its intensity is influenced by the nature of the surrounding environment. Hence his band finds applications in green lasers and optical amplifiers [28]. Photoluminescence excitation (PLE) spectrum is a useful method to investigate the electronic transitions of materials with high sensitivity compared to absorption measurements. Fig. 4 shows the PLE spectra of the ZnS:Tb for the emission wavelength at 535 nm (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition). The spectrum peaks at 332 nm(${}^{7}F_{6} \rightarrow {}^{5}D_{1}$), 358 nm (${}^{7}F_{6} \rightarrow {}^{5}L_{9}$, ${}^{5}D_{2}$, ${}^{5}G_{5}$), 388 nm (${}^{7}F_{6} \rightarrow {}^{5}D_{3}$), 412 nm(${}^{7}F_{5} \rightarrow {}^{5}D_{3}$), 449 nm $({}^{7}F_{5} \rightarrow {}^{5}D_{3})$, 466 nm $({}^{7}F_{3} \rightarrow {}^{5}D_{4})$, 490 nm $({}^{7}F_{6} \rightarrow {}^{5}D_{4})$ respectively [29].

To evaluate the effectiveness of ZnS:Tb phosphor to be used in light sources, CIE chromaticity coordinates are calculated. The calculated colour coordinates for the emission spectra are (0.38, 0.42) [Fig. 4(c)]. From CIE coordinates it is found that characteristic light from the ZnS:Tb ions is greenish-yellow.

4. Conclusion

Terbium doped zinc sulphide nanophosphor with average crystallite size 2.75 nm was prepared by chemical precipitation method using polyethylene glycol as stabilizing agent. On near band edge excitation, the sample exhibited greenish-yellow emission with high intensity so that it can be further explored for several luminescence applications.

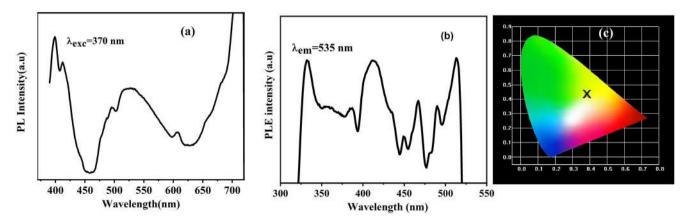


Fig. 4. (a) PL & (b) PLE spectrum (c) CIE Chromaticity diagram for the nanocrystalline ZnS: Tb.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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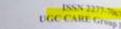
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ASPORA AND CULTURE IN JHUMPA LAHIRI'S INTERPRETER OF MALADIES

SHODHASAMHITA

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This study seeks to comprehend how a dissporie framework affects multicultural identity with reference to Interpreter of Maladies by Jhumpa Lahiri. A diasporie identity gives a writer in exile, who is working outside of national burders more self-assurance. They enjoy more freedom because of their diasporie positions in the U.S. Britain, and other nations with established, assimilating societies. This study will investigate this theme by analysing interpreter of Maladies by Jhumpa Lahiri. The majority of the short stories in Jhumpa Lahiri, Interpreter of Maladies deal with the issues of identity faced by Indian Americans who are caught between they Indian origin and American culture. The crisis is manifest in their unremitting struggle to preserve, to integrate and to adjust. The collection is open to postcolonial studies since it deals with the ambivalence, marginality, and in-betweenness of the displaced Indian Americans.

Keywords: Diaspora, Culture, Identity, Multicultural, In- betweenness.

1. INTRODUCTION

L1. About Jhumpa Lahiri

Jhumpa Lahiri, who was born in London, and her Bengali parents relocated to Rhode Island when she was a small girl. Lahiri notes that despite spending more than thirty years in the country, her parents still feel that they are emotionally exiles, and she also has experienced conflicting expectations growing up.

One of her special talents that have drawn in a large audience is her capacity to portray the voices of numerous distinct characters and to convey the oldest cultural tensions in the most direct way. Lahiri is a migrant and diasposic writer because she is the offspring of Indian immigrants and also travels across borders when she leaves England, where she was born, to become a citizen of the United States. She examines the Indian dissport in her work and develops a narrative that exposes the ambiguity of the identity and the concepts of cultural difference within the dissporte context.

2. OBJECTIVE:

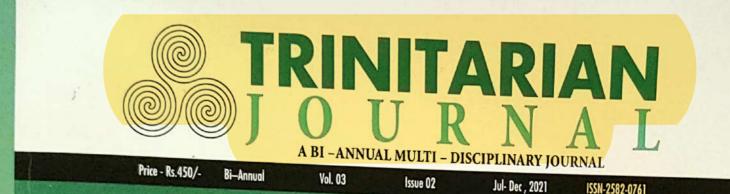
The main objective of this paper is to examine Diaspora and Culture in Jhumpa Lahiri's Interpreter of Maladies

2.1. Interpreter of Maladies

The nine short stories in Interpreter of Maladies explore the issues of identity, immigrant experiences, cultural differences, but the store of the differences, love, and family. The majority of the individuals are Indians or Indian Americans, and their adividual tales together provide a powerful portrait of the Indian Duaspora. Her storytelling work is

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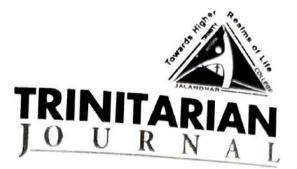


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OCCUPATIONAL STRESS MANAGEMENT DURING COVID PANDEMIC

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ABSTRACT

Occupational stress results from various interactions of the worker and the environment of the work they perform their duties. Location, gender, environment, and many other factors contribute to the buildup of stress. Job stress results from the interaction of the worker and the conditions of work. Views differ on the importance of worker characteristics versus working conditions as the primary cause of occupational stress. Some stress is normal. In fact, it is often what provides us with the energy and motivation to meet our daily challenges both at home and at the workplace. Stress in these situations is the kind that helps us "rise" to a challenge and meet our goals such as deadlines, sales or production targets, or finding new clients. Some people would not consider this challenge a type of stress because, having met the challenge, we are satisfied and happy. However, as with most things, too much stress can have negative impacts. When the feeling of satisfaction turns into exhaustion, frustration or dissatisfaction, or when the challenges at work become too demanding, we begin to see negative signs of stress. In this juncture occupational stress related problems are more complex particularly in the covid 19 pandemic situations. So the investigator here tries to introduce a guiz adapted from the Canadian Mental Health Association of Ontario to identify employees stress levels and suggest some mental fitness tips to overcome occupational stress.

Keywords: Occupational stress, EAP programmes, Mental health

INTRODUCTION

Occupational stress is stress involving in workplace. Fear of job redundancy, layoffs due to an uncertain economy, increased demands for overtime due to staff cutbacks act as negative stressors. Employees who start to feel the "pressure to perform" can get caught in a downward spiral of increasing effort to meet rising expectations with no increase in job satisfaction. The Covid 19 pandemic augment the situations more serious. The relentless requirement to work at optimum performance takes its toll in job dissatisfaction, employee turnover, reduced efficiency, illness and even death. Absenteeism, illness, alcoholism,

TRINITARIAN JOURNAL



JAC: A Journal Of Camposition Theory 155N 10731-6755 UNDERSTANDING THE STRESSORS AMONG STUDENTS AND THEIR PERCEPTION AND ATTITUDE TOWARDS ONLINE EDUCATION Dhanya.S. Research Scholar, Post Graduate and Research Department of Commerce, Maharaja's College, Ermikulum, Kerala Dr. Reshmill, Assistant Professor, SSV College, Valayunchirangara, Ernakolum, Kerala ABSTRACT The main purpose behind conducting the muly is to analyze the various arecenes a students and their perceptionand attitude unservity online education. During COVID-19 educational tostitutions shifted to virtual platforms to conduct online classes. The study has been underwisen among college studentswith reference to Ernskulum Denvice A sumple comprises of 125 students under the age of 18-26 and those who attended online classes has here characters for colleges or random basis in the Ernakalam Dimerct. The data collected through online survey using a structured governmenter. The findings of the study revealed that restricted maches student interaction is the key challenge faced while adopting online education. The study also revealed that there is no gender difference in the matter Jactor while adopting online education. High fee structure is the key challenge the andersy faced in offline method of education. Frequency, Preventage, Independent Sample -1 nen. were used for the analysis. Results of the study will be helpful for educational institutions as well as trachers to get bitter understanding about the key challenges faced by tradents while adopting online education, that contributing invarids the effectiveness of quality education. **KEYWORDS** Online, Offline Education, COVID-19, CollegeStudent's, VirtualPlatforms, Stress 1.1 INTRODUCTION Education helps to develop the personality, thoughts and to get good status in the society Information and Communication Technology (JCT) is becoming a fast changing and renewing technology in education sector. Hall, in cited in (Smart & Cappel, 306) noted that Volume XIV, Inne XII, DECEMBER 2021 Page Not 34



Impact of Employee Involvement on Organizational Effectiveness in the Banking Sector in Kerala

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ABSTRACT

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Reywords: Engilisyw Intelsement. Degantantional Effectiveness

NTRODUCTION

One of the groatest underlying across in the success of failure of any generation is the power of its people, and took well that power is facused towards meeting the organization's objectives. It is a correston knowledge that every basisness againstation depends on its effective incriming of human resources. The prostance of this factor its due to its unique finarcientistics. Like, this is the only resource which is able to produce an surpragrouter than its input. All companies operate on the strengths and weaknesses of their employees. Even in a fully automated factory employees have to design, maintain, and openie the systems that create output. Organizations that can tap the strengths of their people will be strengter and more competitive than those that cannot (Cooper, 2011). Organizations that regard people as autoastorms or mere cogs in a velocal will rever realize their full potential. In the long raw, such companies' melliciencies attract competitive (han those the mangement philosophy changes, they will disappear. Employee involvement is a process for mangerial decision-making and improvement activities appropriate to their levels in the organization. Since McGragor's Theory Y first brought on managers the idoa of a participation managers the idoa of a participation instragers and special activities such an quality of work. Iffer (QWL) programs (Band, 2004).

programs (Band, 2004). There is at the end of the day only one thing that differentiates one company from another-its people. Not the product, no service establishments, and the processtor secret ingredients, ultimately any of these can be duplicated. The Japanese have always recognized this and it is one of the ransons for their success in world markets they place tremendom value on the

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MULTICULTURAL IDENTITY IN JHUMPA LAHIRPS THE NAMESAKE

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Abstract

The cultural differences in Jhumpa Lahiri's novel The Namesake are highlighted in this ensay. One of the main themes in literature today is the disparity between cultures. It deals with cultures, primarily those characters who adopt new cultures and encounter difficulties assimilating into the host culture. The difficulties of assimilating into another culture are primarily caused by cultural disparity. The character of Ashima Ganguali, who settles in Massachusetts, and how she lived her life while living abroad are highlighted in Lahiri's The Namesake. The character of Ashima Ganguali is thus depicted in this paper as the problem of cultural disparity. The Namesake not only dramatizes the Diaspora conflicts that immigrants experience as a result of coming into contact with a completely foreign culture, but it also looks at a conflict between two generations of a migrant family. In addition, this paper paves the way for future scholars to analyze Jhumpa Lahiri's The Namesake in the contexts of migration, alienation, parental love, identity exploration, and other related topics. Keywords: Cultures, Disparity, Identity, Diaspora, Migration

1. INTRODUCTION

Jhumpa Lahiri's novel The Namesake tells the tale of how race, culture, and inheritance affect a person's outlook on life. The text details the diasporic experiences of the main characters, the Bengali newlyweds Ashoke and Ashima, who have moved to America to start a new life. The newlyweds are allowed to learn new national laws. Ashima moved from India to America with no knowledge of the place, but she soon realized how much she missed her family back in India. Because of the climate change, she struggles. Ashima struggled to adapt to the climatic conditions because India had different weather conditions, but in America, it was too cold and snowy. She spends the majority of her time daydreaming about her childhood home and the things she used to do there, while keeping track of "the Indian time on her hands" which in Calcutta is ten and a half hours ahead. Ashima tries to prepare Bengali food at home, even though people in America adhere to different kinds of culture and cuisine. She felt lonely there during her pregnancy and gave birth to her son there alone, far from her family in America. She would be looked after by her family if she were to reside in India. Once the baby's name has been given, the new parents are permitted to leave the hospital. They finally gave their son the name Gogol and left the hospital. Gogol likes his name at first but later tries to change it to Nikhil. After the birth of Gogol and Sonia, Ashima learned how to go shopping and attended parties that American-based Indians had invited her to.

The author of the novel, The Namesake Jhumpa Lahiri was born in 1967 to Indian parents in London. She later relocated to the US to continue her studies and spent some time there. Despite having extensive knowledge of India, she has only occasionally visited her parents' country. She visited India as a tourist when she was younger, she has never lived there. Her debut book, Interpreter of Maladius, is a compilation of short stories with themes related to Indian-American identities and Diasporas. According

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	1	Interrogating Gender Norms- A Reading of Jereena's Oru Malayah Hijadayude	
		Athmakatha Paper ID:IIMJAH2103003 Sheena Kaimal N.	
		Paper 1D 100 Art 2105005 Sheetia Kanna N. Assistant Professor and Head	
		Department of English	
		Sree Sankara Vidyapeetom College	
		e-mail:sheenakaimaln@gmail.com	
		Abstract	
		The present paper attempts at an analysis of the autobiography of a transgender woman named	
		Jereena who has had to undergo severe trials and tribulations in her life because of her transgender A_{C}	416/6

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A Study about Constraints Of Small Rubber Growers In Kottayam District Of Kerala State

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Abstract

This project represents the various constraints faced by Small Rubber Growers In Kottayam District Of Kerala State. Kerala has a long tradition in the cultivation of Plantation Crops. India is a Country where agriculture directly shapes the daily lives and hopes of the majority of people. The Rubber plantations occupy 0.4 Percent of the Gross cropped areas and Contribute 0.19 Percent to the National GDP. One who grows Rubber is known as Rubber Growers. For the purpose of the study one who registered in the Rubber Producers Society is considered as Rubber Growers.

Key Words : Agriculture, Constraints of Small Rubber Growers, Rubber

1. INTRODUCTION

Kerala has a long tradition in the cultivation of Plantation Crops. The plantation sector comprising Rubber, Tea, Coffee, Cardamom is the highly cash-rich segment within the agricultural sector in Kerala. The State accounts for 45percent of the total and under plantation crops to the country and together Account for 28 percent of the net cropped area of the State. Nearly 14 lakhs families are dependent on the Plantation Sector for livelihood. Rubber is the most critical , strategic and versatile raw material in the modern world.Demand and Prices of Rubber positively linked to

economic growth. The Low Prices will have a critical bearing on planting and replacing decisions and future availability of Natural Rubber (NR) The Indian Rubber Plantations sector is dominated by small holding, which accounts for almost 93 percent of the total Rubber Production in the country.

2. LITERATURE REVIEW

Shahul Hameedu (2014) In an article stated that India is one of the largest producers and consumers of Natural Rubber. Natural Rubber is used extensively in many applications and products.

Giridhara Gowda K And Suresh Ramana Mayya (2016) in their findings from a survey of Rubber Planters of Dakshina Kannada District of Karnataka. stated that the calculated value of significantly In Harvesting Cost between different regions = 8. 011. The table value of F at 5 percent level of significance 5.14. The calculated value is more than the Table Value and hence the Null Hypothesis is rejected which leads us to conclude that there is significant difference in the harvesting cost in different regions.

Kobayashi, Et Al. (2014) In their study indicated that additional water use reduces discharges from the basin of its storage. Variations in transpiration of Rubber Plantation with age and over the seasons have been reported from Central Cambodia.

3. Objectives of the Study

- > To identify the constraints faced by Small Rubber Growers
- > To suggest measures to overcome the problems of Rubber Growers

4. Research Methodology

The researcher interviewed a total of 459 sample members. For determining the constraints of rubber growers the Overall Sample respondents have has

been covered under three categories. viz 107 Respondents under upto 2 acres category;209 Respondents under 2.1 to 4 acres category, and 143 respondents above 4 acres category. The constraints are analysed with Garrett ranking technique and the computed mean scores. Primary data has been collected by conducting direct interviews using structured questionnaires.

Secondary data collected from books, journals and the internet.

5. Analysis

Analysis is done on the basis of Garett ranking technique and computed mean scores. It is also done according to the landholding size of sample respondents

5.1 Analysis of Constraints Experienced by the Members

T 11	1
Table	
ruore	1

Religion	Up To 2 Acres	2.1 to 4 Acres	Above 4 Acres	Total		
Yes	65	137	92	294		
	(60.7)	(65.6)	(64.3)	(64.1)		
No	42	72	51	165		
	(39.3)	(34.4)	(35.7)	(35.9)		
Total	107	209	143	459		
	(100.0)	(100.0)	(100.0)	(100.0)		

Experience of constraints sample members

It is understood from Table 1 that 60.7 per cent of up to 2 acres category members, 65.6 percent of 2.1 to 4 acres category members, and 64.3 percent of above 4 acres category members have experienced the constraints from Rubber Producers Societies while producing rubber. Overall the constraints are experienced by 64.1 percent of members. It is evident from the study that out of 459 members, 165 members constituting 35.9 per cent have not experienced any constraints from the Rubber Producers Societies.

Further in this study, an attempt is made to analyze the experiences of constraints faced by the small rubber growers whale producing rubber. The constraints were categorized into poor input distribution, poor technical assistance, poor financial assistance, poor storage facility, political influence and other constraints. The constraints experienced by the members of Rubber Producers Societies are analysed with the help of Garrett's ranking technique. The ranks assigned to each constraint by the sample members were converted into percent by using the following formula:

Percent position = $\underline{100(Rij-0.5)}$

Nj

Where

Rij= Rank given by the jth member for the ith constraints

Nj= Number of reason ranked by the jth member

The percent position of each rank thus obtained was converted into scores by referring to the table given by Garett. The scores of all respondents for each constraint was then added together and divided by the number of respondents experiencing that particular constraint. The mean scores of each constraint thus arrived and ranks were allotted. This procedure is adopted for all three types of landholdings. The results are explained in the following tables.

$5.2\ \mathrm{Constraints}\ \mathrm{Experienced}\ \mathrm{by}\ \mathrm{the}\ \mathrm{up}\ \mathrm{to}\ 2\ \mathrm{acres}\ \mathrm{category}\ \mathrm{members}\ .$

Table 2

Constraints	Mean Score	Rank	No. Of Members Responded	Percentage To Constraints Experienced(92)
Poor input distribution	50.08	iv	53	81.54
Poor technical assistance	56.11	111	51	78.46
Poor financial assistance	57.23	1	61	93.84
Poor storage facility	56.76	11	58	89.23
Political influence	41.28	vi	52	80.00
Other constraints	41.33	v	49	75.38

Results of Garrett's ranking	technique of	f up to 2 acres	category members'	constraints
------------------------------	--------------	-----------------	-------------------	-------------

The results given in Table 2 reveal that the most important constraint experienced by the up to 2 acres category members in rubber production is 'poor by poor storage facility' (mean score = 56.76) and 'poor technical assistance' (mean score = 56.11). These constraints have been ranked second and third respectively and the percentage of response is 89.23 and 78.46 percent. The other constraints such as poor input distribution, other constraints and political influence have been ranked fourth, fifth and sixth respectively.

5.3Constraints Experienced by 2.1 to 4 acres category Members

Results of Garrett's ranking technique of 2.1 to 4 acres category members' constraints							
Constraints	Mean Score	Rank	No. Of Members Responded	Percentage To Constraints Experienced(137)			

Table 3

.

Poor input distribution	56.50	11	101	73.72
Poor technical assistance	49.11	111	94	68.61
Poor financial assistance	59.32	1	122	89.05
Poor storage facility	48.93	lv	86	62.77
Political influence	41.93	vl	84	61.31
Other constraints	44.54	v	85	62.04

Table 3 exhibits the final results of the Garrett's Ranking technique of 2.1 to 4 acres category members. The constraints experienced were responded to by more than 60 percent of members. The study points out that the most important constraint experienced by the members is 'poor financial assistance' which scored a mean score of 59.32. Based on this mean score, the first rank has been assigned to this constraint. Next to this, the constraint 'poor input distribution' got a mean score of 56.50 and ranked in the second position. The third rank has been assigned to the constraint 'poor technical assistance' which has a mean score of 49.11.

5.4 Constraints Experienced by the above 4 acres Category Members

Table 4

Results of Garrett's Ranking Techniques of above 4 Acres Category Members' Constraints

Constraints Mean Score	Rank No. Of Members Responded	Percentage To Constraints Experienced(92)
---------------------------	-------------------------------------	---

Poor input distribution	55.95	11	84	91.30
distribution				

Poor technical assistance	53.00	lv	79	85.87
Poor financial assistance	56.92	1	86	93.48
Poor storage facility	53.74	111	81	88.04
Political influence	39.63	Vl	77	83.70
Other constraints	45.03	v	74	80.43

The results shown in table 4 highlight that the most important constraint experienced by the above 4 acres category members in rubber farming is poor financial assistance with a mean score of 56.92. These constraints have been responded to by 93.48 percent members. Thus first rank has been secured by this constraint.it is followed by poor input distribution and poor storage facility. The computed mean score is 55.95 and 53.74 respectively and ranked second and third respectively. The percentage of responses to these constraints are 91.30 and 88.04. The other three constraints are placed in the order of priority based on the mean score.

5.5 Analysis of consolidated views of constraints experienced.

Consolidated views of learn-wise analysis				
Constraints	Up To 2 Acres	2.1 To 4 Acres	Above 4 Acres	
Poor input distribution	lv	11	11	
Poor technical assistance	111	111	lv	
Poor financial assistance	1	1	1	
Poor storage facility	11	lv	111	
Political influence	vl	Vl	vl	
Other constraints	v	V	v	

 Table 5

 Consolidated views of team-wise analysis

From table 5 it is clear that the constraint poor financial assistance has been experienced as the first constraint by all landholding category members.

6. Findings

1 Poor financial assistance has been experienced as the first constraint landholding category member

2) The constraint, poor storage facility has been considered as the second constraint by 'upto 2 acres' Category members and same was ranked as third by the 'above 4' acres category and fourth by '2-1 to 4 acres' category memberi respectively.

3) The '2.1 to 4 acres' category and 'above 4 acres' category members ranked constraint 'poor input distribution' as the second and it is ranked as fourth by the 'up to 2 acres' category members.

4) Regarding the constraint poor technical assistance The Up To 2 Acres and 2.1 to 4 Acres category members experienced as their third choice and above 4 acres category members considered it as their fourth choice.

5) All the sample respondents irrespective of their land ranked the constraints, Viz other constraints and political influence, as their fifth and sixth ranks respectively.

7. Conclusion and Recommendations

The researcher comes to the conclusion that the majority of respondents feel that the Rubber Producers Societies are not fully assisting the members towards their financial requirements. Hence they pointed out the constraint 'poor technical assistance' as their first constraint. Much attention is needed from the rubber Producers societies towards this constraint for further improvement in future.

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A study on Occupational Stress of IT employees with special

reference to Ernakulam District

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Abstract

Since the IT industry depends on knowledge workers, they may be considered as the' raw material' of the industry. While several problems affect the workforce in the IT industry, stress has emerged as the most significant problem, causing the employees to underperform and thereby leading to productivity loss. This study takes a close outlook at the stress-related issues facing the employees working in various IT companies and analyses the factors responsible for the same.

Keywords; IT employees, occupational stress,

1. Introduction

The IT industry accounted for 8% of India's GDP in 2020. Exports from the Indian IT industry are expected to increase by 1.9% to reach US\$ 150 billion in FY21. In 2020, the IT industry recorded 138,000 new hires. India is the topmost offshoring destination for IT companies across the world. Having proven its capabilities in delivering both on-shore and off-shore services to global clients, emerging technologies now offer an entire new gamut of opportunities for top IT firms in India. The industry is expected to grow to US\$ 350 billion by 2025 and BPM is expected to account for US\$ 50 55 billion of the total revenue.

The Indian IT industry has been steering the growth of the Indian economy in the past decade, unlike any other industry by generating jobs, pushing up exports, increasing FDI, creating wealth, thereby boosting the forex reserves, and also by other visible and invisible ways. This sterling performance of the IT industry was largely on account of its human resources. This industry has also been much affected by the pervasive forces of globalization and by the persistent growth of information technology. These changes have in turn affected the way firms compete and specifically the way they are managed. The increased complexity of global competition has exerted tremendous pressure on workers and thus imposed considerable stress on them. Thus, job stress becomes a common problem

faced by employees in many organizations today. It affects employee's mental and physical health and in the long run, affects the company's performance. This study attempts to identify the sources of stress and its prevalence among employees in the IT industry in Ernakulam District.

2. Literature Review

In the eighteenth and nineteenth centuries, stress is denoted as "force, pressure, strain, or strong effort', with reference now also to objects but still primarily to a person or person's organs on mental power (Hinkle, 1973). Continued and prolonged stress may result in fatigue, anxiety, tension and extreme irritability. If severe and prolonged it will result in exhaustion and may cause depression and anxiety (Seyle, 1946). Later studies of stress indicate more of a person-fit environment rather than biological effect of stress as indicated by Seyle .

Stress is seen as a dynamic condition in which an individual is confronted with an opportunity, constraints or reward related to what he or she desires for which the outcome is perceived to be both uncertain and important. Mc Grath (1970) defines stress as a perceived substantial imbalance between demand and response capability, under conditions where failure to meet demand has important perceived consequences. It is also the closest to the popular 'person environment fit' formulation by French (1974). Stress is always mistaken as bad, and negative. It must be noted that it also has a positive value. It is an opportunity when it affects potential gain (Boswell et al, 2006). Positive stress may result in stimulating and enhancing work performance. Excessive stress may result in negative effects and hence affect the worker's health and work performance. This directly affects the company's performance. A small amount of stress may positively encourage workers to work harder. Excessive stress may result in negative effects. Stress is also associated with constraints and demands. Constraints are forces that prevent individuals from doing what they design, where damage and to loss of something designed. Two conditions are important for potential stress to become actual stress (Schuler, 1980). There must be uncertainty over the outcome and outcome must be important.

3. Objective of the Study

The general objective was to investigate the effect of job characteristics and the organizational working environment on the employee's stress in the BPO industry. The specific objectives of the study are :

- 1. To identify how prevalent is the stress among managers and executives
- 2. To study the major sources of stress among managers and executives

3. To find the stress dimensions contributing to stress in the industry

4. Research Methodology

Primary data were collected from 60 respondents(including 22 managers and 38 executives) from 10 various IT companies located in Ernakulam district through random sampling.56 respondents representing a 94% response rate have been obtained. The secondary data were collected from books, journals, and websites.

5. Analysis

The research objective of the study was to provide an insight into the causes of stress among employees in the BPO industries in the Ernakulam district.

5.1 Profile of Respondents

Most of the respondents are in the age group of 31 to 40 (34%) and 41 to 50 (31%). Among the respondents, the highest gender group is male which stands at 60.4% compared to females at 29.6%. On ethnicity, 64.2% of the respondents are postgraduates compared to graduate 26.4%. Further, most of the respondents are married with or without children. The total married respondent stands at 58.50% (Married without children at 13.2% and married with children at 45.3%, this total up to 58.5%)Majority at least 10 years of working experience (at 35.8%) and at least 3 to 6 years of length of services in the same company.

5.2 Reliability

The Cronbach's Alpha reliability test shows a score of 0.7 and the coefficients across the variables, and since the figure is considerably high, the data is then reliable for analysis.

5.3 Table No 1 : Respondents' feeling of stress

	Energy energy	n ana anta ao
Item	Frequency	percentage
Strongly disagree	2	3.77
Disagree	11	18.87
Neither agree or disagree	25	41.51
agree	19	32.08
Strongly agree	2	3.77
Total	58	100

Overall I find my present job stressful

Source: compiled from field survey

Table 1 illustrates that 41.51% of the respondents neither agree nor disagree. However, by comparing the two total figures of agreement and disagreement, we noticed the overall perception of stress is high (35.9% agree that job is stressful compared to 22.7 disagree.

5.4 Sources of Stress

Sources	Mean	Standard deviation
Unrealistic objectives	3.29	1.002
Time pressure and deadlines	3.21	0.981
My relationship with my colleagues	3.11	1.126
Unsympathetic boss	3.00	0.935
Interpersonal relations	2.97	0.993

Table No 2 : Sources of stress

My relationship with my subordinates	2.89	1.019
Performance related compensation	2.89	1.079
Taking my work at home	2.89	0.934
Incompetent boss	3.21	0.854

Table No 2 shows the "Unrealistic objectives" have a higher mean score of 3.29 followed by "Incompetent Boss" at 3.21 and "time pressure and deadline" at 3.21. The high mean scores reflected negative perceptions and thus these are the main sources of stress to the respondents in the organization. All other factors of stress have a score value ranging from 2.89-3.11 which affects negativity.

Competition among organizations requires every firm to pursue innovations and find new technology, and thus necessitate management to construct new planning and improve objectives. Sometimes, the changes could be unrealistic. These changes can make the current employee skills and experiences obsolete in a short time and thus this innovation is a threat to many people and causes them stress. There is also the issue of organizational leadership which represents the managerial style of the organization's senior executives. Some leaders do not acquire the expertise, skills, nor the right knowledge to assist them in making good decisions. This could create cultures of fear, anxiety, and tension among the subordinates and consequently, stress. There is also the issue of task and role demands of the organization on the personal job. It includes the design of the individual job, working conditions, and the physical work layout. An excessive demand causes stress to the worker. At times, the individual is given more jobs than he or she can perform.

5.5 Predictors of Stress

The stepwise multiple regression analysis was used to test the relationship of overall stress level as dependent variables and the job and organizational climate characteristics as the independent variables. From the analysis, as shown in table no.3, only 5 dimensions have been entered into the regression equation. They are adaptability, job security, conflict, support, and integrity. These 5 dimensions explained the variability in the overall stress level of employees. Nevertheless, by looking at the R-square value, all these factors when taken

into consideration explained 25.7% of the variability in the level of stress.

	Factors of stress	Sig*	Beta
A	Integrity	0.001	-0.441
В	Conflict	0.000	0.229
С	Job security	0.005	0.320
D	Adaptability	0.008	0.218
Е	Support	0.039	0.161

Table No 3 : Predictor for Stress

*p<0.05

From Table No 4, it can be concluded that stress are inversely related to integrity (Beta= -0.441) and positively related to conflict (Beta=0.229) ,to job security (Beta=0.320), adaptability (Beta=0.218) and support (Beta=0.161). The beta value closest to one would present the strongest correlation. In this study, the Beta for stress relationship with integrity is highest, which implies that as integrity increases, stress would be reduced. Other predictors, however, have a lower correlation with stress.

6.Major Findings

1. Most of the respondents are in the age group of 31 to 40 (34%) and 41 to 50 A(31%). Among the respondents, the highest gender group is male which stands at 60.4%.

2. Table 1 illustrates that 41.51% of the respondents neither agree nor disagree. However, by comparing the two total figures of agreement and disagreement, we noticed the overall perception of stress is high (35.9% agree that job is stressful compared to 22.7 disagree compared to females at 29.6%.

3.From Table 2, "Unrealistic objectives" have a higher mean score of 3.29 followed by "Incompetent Boss" at 3.21 and "time pressure and deadline" at 3.21. The high

mean scores reflected negative perceptions and thus sources of stress to the respondents in the organization.

4.From Table 4, it can be concluded that stress are inversely related to integrity (Beta= -0.441), positively related to conflict (Beta=0.229) ,to job security (Beta=0.320), adaptability (Beta=0.218) and support (Beta=0.161). The beta value closest to one

would present the strongest correlation. In this study, the Beta for stress relationship with integrity is highest, which implies that as integrity increases, stress would be reduced. Other predictors, however, have a lower correlation with stress.

7. Conclusion and Recommendations

The research objective of the study was to provide an insight into the causes of stress among employees in the BPO industries in the Ernakulam district. Overall the study indicated that 35.85% of the respondents feel they are stressed at work. The main sources of stress were unrealistic objectives, the issue of the incompetent boss, time pressure, and deadlines. From the study, the five major predictors of stressors found in the BPO industries are support, adaptability, job security, conflict, and integrity. These are all the potential elements affecting job stress. In addition, integrity has an inverse relationship and the highest correlation towards stress. To stay competitive and cost-effective, the management in the BPO industry has to be sensitive towards employee's perceptions. In the era of hypercompetitiveness, every effort should be made to maximize our resources to stay competitive.

Human resources are one of the strategic company resources which can help a company to move ahead of others. Individuals, particularly organizational leaders need to take initiative to learn about themselves and their careers, to pick up new skills, develop self-motivation and acquire the expertise needed to make decisions. The breakdown of integrity among employers and employees can be a major cause of stress if not carefully monitored.

On the societal level, there is a need to make society and organizations more humane and caring. More emphasis should be on fitting organizations to people and not the other way round. A company should provide greater economic security and psychological security in the form of training in survival skills in today's fast-changing society. In terms of adaptability, stress management advice at the organizational level may help the reduction of stress to a tolerable level. Person-environment misfits can be corrected either by placement, appraisal, and training or job redesign, enlargement, and rotation at the organizational level. The ultimate hope of this study is to help the BPO industry to grow within the context of an enhanced level of competitiveness brought about by the forces of globalization and advancement in information technology. It is hoped that the findings in This study can create awareness as well as help companies develop strategies for the development of their human resources.

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Significance of Supernatural Creatures in Hindu Mythology

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Supernaturalism is perhaps the broadest classification of religious practices encompassing any belief system dealing with supernatural forces. Supernaturalism asserts the existence of forces beyond human comprehension that frequently interfere for better or worse in human affairs.

Some supernatural creatures have good aspect which is related to Divine Beings usually called Gods and Goddesses. There are also Demigods. Some others have evil aspect. They are ghosts, demons and vampires. All these supernatural creatures never fade from popular awareness. Even though their form may vary, they seem to be embedded in our consciousness. They appear repeatedly in literature around the world, in movies, advertisements, video games and modern books.

Sreemad Bhagavatham is considered to be one of the Mahapuranic texts of Hindu literature. It consists of many stories renowned in Hindu tradition. It focuses on the incarnations of Lord Vishnu particularly human form. ie Sreekrishna, who established the rule of dharma and moral order through his several supernatural incarnations. Supernatural deeds of Lord Krishna in Sreemad Bhagavatham teach us to live in harmony with nature to keep ecological balance.

Ancient Hindu battles depict great heroes, demons, celestial weapons and beings, magic and the supernatural. Wars are waged with the purpose of upholding *Dharma* over *Adharma*. The major Hindu Gods often engage in war either in the form of Avatars or in their form. They and many Hindu heroes use *astra*, celestial weapons, with fearsome supernatural power, to aid them in battle.

Sreemad Bhagavatham is the most complete and authoritative exposition of Vedic knowledge covering everything from the nature of the self to the origin of the universe. It is the literary incarnation of God. It is meant for the ultimate good of all people. The purpose of this fifth Vedam is to encourage one to understand that one is not an independent entity but a part of a universal body that depends on many supernatural forces.

Lord Krishna is the greatest hero of all times. In the long history of the world there has been no equivalent to such a great hero like Sree Krishna in India or even elsewhere on this Earth. Sreemad Bhagavatham delineates His supernatural power. Before the birth of Sree Krishna His parents were kept in jail by the king Kamsa. But the moment Krishna was born, the doors of the jail suddenly opened and was safely shifted to *Gokulam*.

Lord Krishna performed innumerable supernatural things during His incarnation. Lord Vishnu enters this world in different *yugam* in different form to restore balance whenever his presence is needed.

Mother Earth once burdened as she was too many sinners, could bear the pain no more. She assumed the form of a cow and approached Lord Vishnu and told him how much she was suffering on account of the *adharmam* which was rampant. The sinful kings were polluting her. Vishnu consoled her and has decided to take a human form and name. He has decided to live on the face of the earth till her troubles are over. Lord Vishnu incarnated as Sree Krishna in the form of human being to destroy the callousness in wicked men and transform them into pure men without asking any weapon.

At the very beginning of His life on the earth, SreeKrishna left the city of Madhura in order to live in the forest with the cowherds. Krshna spent His childhood among the twelve forests of vrindavan. The trees were His friends. SreeKrishna brought forward the cows and played on His flute through the forest of Vrindavan which was full of flowers, vegetables and pasturing grass. There were chirping birds, clear water and lakes with water that could relieve one of all fatigues, sweet flavoured breeze always refreshing the mind and body.

One day in summer season Krishna along with the cowherd boys, cows, and calves went to the bank of the river Yamuna as usual to graze the cattle. Since summer was very severe all boys, cows and calves became very thirsty. All began to drink the water of the river Yamuna. But all of them fell down unconsciously because the river was polluted with the poison of

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the great snake Kaliya. Krishna glanced mercifully at them. At time all regained their consciousness. Thus they were rescued by Krishna.

16th chapter of 10th scandham brings into light that Krishna purified the water of Yamuna by driving away the great serpent Kaliya, which was very poisonous, to the island Ramanakam. The water of Yamuna became vain on account of this poison. Even if a bird happened to pass over the river, it would fall down and die as a result of this severe poison emanated from the mouth of Kaliya. Most of the trees and creepers around the lake dried up on account of the poisonous atmosphere. Immediately Krishna climbed up a big kadamba tree grown on the bank of Yamuna and jumped in to the lake. Kaliya actually wanted to bite Krishna. But Krishna jumped, moved and danced around all the hoods. He performed *Kaliyamardhanam*. Thereby the serpent became very tired and lost its strength. Heavy blood oozed from the mouth. Krishna ordered kaliya to leave this lake and go to the island *Ramanakam*.

Tenth *scandham* chapter 18 depicts the protection of cowherd boys and cows from the forest fire by Krishna. Once the cowherd boys were engaged in playing in the forest vrindavan. Some boys along with cows entered the forest known as Isikatavi. Then they saw fire engulfing the forest. They were enveloped by forest fire which was very ferocious and all of them could not escape from this situation. Krishna with His mystic power swallowed up all the blazing fire and protected them from this threatening danger.

Sree Krishna inspires Vasudevar, His father, to exchange Him with the daughter of maharaja Nandagopar at gokul. By his influence the door keepers fall asleep and the doors are opened automatically. Vasudevar carries the child Krishna across the river Yamuna. It was raining with mild thunder. River Yamuna gave way for Vasudevar to cross and Ananthanaga followed him with hoods opened to shelter them from rains. Vasudeva reaches gokulam and replaces Krishna with the daughter of Nandagopa. Thereafter come back and bound his legs with iron shackles as before.

When SreeKrishna turns three months old, mother Yasotha perform uthana ceremony. She was busy with the uthana ceremony and put his child Krishna to a bed under a handcart, which contained vessels full of milk and curd, in the courtyard at gokul. After sometimes Krishna woke up and demanded mother's milk. Yasotha didn't hear His cry. when no one notices, He angrily kicked the cart with His little legs and overturned the handcart scattering the various utensils here and there. The gopis and gopas were struck with wonder. They could not believe this wonderful phenomenon.

SreeKrishna had supernatural powers right from the day He was born. He was born with full powers and all these powers were used to set things right. During His child hood, one day, mother Yasotha saw in His mouth the whole Universe including the sky, higher planetary system, earth, sun, moon, fire, air, seas, mountains, rivers, forests and all kinds of living entities. Yasotha became astonished and afraid. Another incident was that the playmates of Krishna complained Yasotha that Krishna has eaten mud. Yasoyha came and asked Him to open His mouth wide. Krishna opened His mouth and showed the entire Universe in His mouth.

During His childhood while SreeKrishna was playing with cowherd boys, a demon called Bakasura assumed the form of a gigantic duck and swallowed Krishna. SreeKrishna became hot like fire inside the mouth of the demon and made the demon throw Him out. There after holding the two ends of the beak of the duck, Krishna stretched the mouth of the duck, split it and killed the demon.

In the 10th scandham chapter 25 SreeKrishna told villagers that they were farmers and should do their duty and concentrate on farming and protection of their cattle. They were suggested not to conduct sacrifice for natural phenomenon. They therefore did not proceed with the special pooja. Indra became angry when offering of sacrifice for him was stopped. He poured the rain incessantly for seven days. They could not tolerate the worst situation of incessant rain. The inhabitants approached Krishna to rescue them from the wretched atmosphere. Abruptly Krishna lifted the Govardhana Hill easily on the little finger of his left hand as picking up a mushroom by a child to protect all the inhabitants under this umbrella. Thereby He has got the name *Govardhanadhari*.

Once after observing the *dwadashi vrata* king Ambreesh was about to break his fast. Just then sage Durvasav reached there. The king requested his distinguished guest to have food with him. Durvasav accepted the invitation and went off to the river for morning ablutions. Only twenty minutes were left for breaking it. The king wetted his lips with a few drops of water purified with tulsi leaves. Durvasav became angry and created a demon to kill him. SreeKrishna killed Kritiya using His supernatural weapon *Sudarshanachakram*.



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Lord Vishnu is willing to assume any form or shape for the welfare and well-being of His dear devotees. When His people become the victims of distress, tyranny and torture, Lord Vishnu descends to the Earth in diverse manifestations and incarnations in order to destroy sin, ignorance and devilish forces from the face of Mother Earth.

An asura named Hayagreeva was causing great sufferings to the whole world. Vishnu has decided to free the world of his menace. He intended to destroy all such perverse people by a deluge. The whole world was covered with water. As man would be very weak in water and unable to do much in order to do good, He had taken the manifestations of fish to fulfil his purposes.

The world had lost many precious things in the great flood. To get precious things Lord Vishnu resolved to churn the Ocean of Milk. During the churning Vasuki lost its grip on the mountain. The mountain Mandhara began to sink. Mahavishnu incarnated in the form of *Koorma* and reached there to lift it up and held it in that position.

The demon Hiranyaksha hid the world in the bottom of the sea. Hiranyaksha was proud of his strength. Hiranyaksha started searching for lord Narayana to fight with him. Lord took the form of Varaha with terrible curved tusks thousands of miles long came out of Brahma's nostril. The Varaham grew very fast and became a gigantic figure. *Varaham* plunged in to the ocean looked for and found Mother Earth. He then lifted earth on His tusks and began swimming upwards. *Varaham* killed the asura and placed Mother Earth in her original place. He killed the evil force and saved the mankind and the earth from its tyranny.

Hiranyakashipu prevented people from doing good deeds on the earth. He has decided to annihilate good people. He began torturing and killing the pious and saintly. Nobody can tolerate his atrocities. He became arrogant and forgot the Supreme Power pervades the Universe. He was a man of *adharmam*. To annihilate this callous man from this Universe in order to maintain ecological balance Lord Vishnu incarnated in the form of Narasimham. The end of *Narasimhavatharam* is to destroy wicked thoughts of man and to lit the good thoughts in man's mind to make the man the owner of good thoughts. Mahabali was the mightiest of emperors. He was Lord of earth and heaven. Nobody dared to oppose his will. He ruled his subjects kindly and well, but made them rely on themselves and not on dharma or karma. The Vedas were neglected, religious rites were not performed and men cared only for their pleasures. Everyone had some food and material comforts. People led a gay and carefree life. If it goes on, the world will sink in to materialism. It is necessary to save the world from Mahabali. So Lord Vishnu descended down in to the world as Vamana to maintain dharma and reinstate order.

The world was once overburdened with kings and warriors who were fighting with each other and creating disturbance. The Prithvi was overburdened by *adharmam*, corruption and the Brahmin and the Vedas began to disappear. The duty of the rulers of society is to protect religious principles. When they failed to do it they became burden on the land. There had no happiness in the society ruled by such men. Lord Vishnu incarnated as Parasurama as the son of Jamadgni to annihilate these fighting men.

Lord Vishnu took the opportunity to be born as SreeRama in the world to achieve His three-fold ends namely to ride men of fear, mostly of fear of the rakshasas, to show men by His own rule how a land should be ruled and to show men a unique and unforgettable ideal of monogamy by the love of Rama and Sita for each other.

If the number of callous persons is increased on the earth, it will increase burden on the earth. Mother Earth could not tolerate the burden and atrocities committed by these callous persons. Balarama supported SreeKrishna to alleviate the burden on the earth by annihilating these wicked men. Balarama subdued a wicked man by name Pralamba and killed him. Lord Balarama dragged and brought the Yamuna river in hundred streams with the tip of his plough to fertilize the land and for irrigation.

The incarnation of SreeKrishna is said to be Poornavatharam. Aim of His incarnation was to complete all the things which cannot be completed by human beings. At the end of *Kali yugam*, when *adharmam* is predominant and vice has the upper hand and virtue has disappeared and men have become demons, sunk in every form of debauchery, vice and wickedness are eagerly destroying one another, Lord Vishnu will incarnate again as *Kalki*, the son of Brahmin chief in order to reinstate *dharmam*. He will travel everywhere on the earth with a sword in hand riding on his horse Devadatha and kill all the bad. Good people will be purified by the dust rising from horse's hooves.

His astonishing, supernatural and miraculous activities were for the establishment of permanent peace for the turmoil world. '*Loka samastha sughino bhavandhu*'.Thus *Avatharam* is a descent of God for the ascent of man. Lord Vishnu descends on the earth with supernatural powers to keep up the harmony of the universe. The works done by the avathars and their teachings produce a benign spiritual influence on human beings. It comes to reveal the divine nature in man and Copyright to IJARSCT DOI: 10.48175/IJARSCT-2854 252 www.ijarsct.co.in



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makes him rise above the petty materialistic life of passion and egoism. Many avathars have discharged one function, but SreeKrishna has carried out many supernatural activities. That is why SreeKrishna is called *Poorna Avatharam*.

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Important Female Characters in the Ramayana: Their Relevance in the Modern Society

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The Ramayana, written and composed by Valmiki, is one of the greatest works of literature in the history of ancient India. It has survived the test of time, and still continues to be one of the most critically acclaimed works of all generations. The characters in Ramayana are seemed to be inspirational figures in all our lives. Rama, Sita, Lakshmana and Hanuman epitomize all the virtues that should be present in all human beings in the planet to achieve the state of continual peace.

Sree Rama was about to be crowned as emperor.Narada arrived and reminded Rama that his sole work in this incarnation was to kill the asuras and bring peace in the universe.Sree Rama replied that he was aware of the purpose of his incarnation. Devas approached SaraswathyDevi and requested her to go to Ayodhya and enter the tongue of Mandhara.

In AyodyaKandamMadhara made her appearance with three bends on her body. She,crooked and very cunning with her talk, climbed the stairs of the palace and observed the streets of Ayodya decorated and the people incelebration mood. There she got the news that tomorrowSree Rama is going to be crowned as king. She got disillusioned and thought of her position in the palace. At once She rushed to the palace of Kaikeyi and informed her of the coronation ceremony of Rama.Kaikeyi actually delighted so much.She took a necklace from her neck and gave to Mandhara. But Mandharacontinuosly scoldedKaikeyi and compelled her to think of the steps to stop the coronation. But Kaikeyi replied that Rama was the dearest to her. She loved Rama more than Bharatha and Rama loved her more than Kausalya. Not an unpleasant word camefrom him.He was the darling of the people and did only what was right.Mandharastarted to inject venom in to the mind ofKaikeyi. She argued thatby birth Rama is the eldest and had the right to the throne. If it happened



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SAL UNCERTAINTY IN CHITRA BANERJEE DIVARAKUNPS THE MISTRESS OF SPICES

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convert is a loaded and complicated concept. It has a polyvocal sense since it comprises various of a particular locale. The effects of "cultural dislocations" on the lives of the immigrants are themen in Diasporn literature. The topics of representation, personality, and sociocalizeral be discussed through the purview of diasporic studies. Being a worker herself, Chitra the discussed through the purview of diasporic studies. Being a worker herself, Chitra bedarant is one of the important voices in the American mainstream composition. The broakaroni is one of the important voices in the American mainstream composition. The broakaroni is one of the important voices in the American mainstream composition. The broakaroni ranslator for India. In a personal family set up, tightly associated with social, calaeral, the novels written by Divakaroni deal with the experiences of the immigrants in the US. She broakaroni translator for India. In a personal family set up, tightly associated with social, calaeral, the novels written by Divakaroni deal internationality has repeatedly come up to highlight how preserve their native culture despite the dominating and the contradicting culture of the other barrees of Spaces depicts immigrants who encounter cultural difficulties in an alien land, while barrees of Spaces depicts immigrants who encounter cultural difficulties in an alien land, while barrees of the host country.

Caltural Uncertainty, immigrants, Diasporic Literature, cultural traditions, native culture.

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aling to the novelist and filmmaker Robert Alan, "Cultural differences should not alienate us from anther, but rather cultural diversity gives an aggregate strength that can aid all of mankind." As a cohere is important to society and humanity. It also embodies the character and traditions of history puple has its own traditions and ways of life. The definition of culture according to Zimmermann's at a follows: "Culture is the traits and knowledge about a certain gathering, language, religion, as scial customs, music, and arts." Sometimes, due to prejudices, culture and custom generate havoc gommunities. Some immigrants have discounted their own cultural heritage due to cultural action.

singn country during the postcolonial era, the eastern migrants have had to deal with many cultural new. One of the main areas in postcolonial writing, dealing with the cultural tensions, is dissperie ing It displays the hybrid nature of immigration. The present study aims to study in detail. Chitra me Divakaruni's *The Mistress of Spices* which deals with the theme of diasporie identity and cultural fee. This masterwork emphasises immigration conflicts in western nations, particularly the US. The of spices, implies the preservation of the extensive cultural heritage of India. The characters in the state of spices.

specially the protagonist Tilo, embodies the soul of India. The migrate from their own local land to some other unfamiliar land in search of opportunities and overy. Almost all immigrants, whether willing or reluctant, go through the agony and pangs of the new land and its way of life because their new 'universe' seems to be (as James Gleick area) "unpleasant, not adjusted, scabrous, not smooth". In any event, they encounter a cultural clash they land on foreign terrain. The ancient cultural and ethnic personalities of the immigrants are in they due to the cultural collision.



Greener approach towards the synthesis of titanium dioxide nanostructures with exposed (001) facets for enhanced visible light photodegradation of organic pollutants

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ABSTRACT

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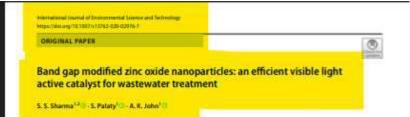
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Green chemistry is considered as an effective alternative for the conventional chemistry in the perspective of environmental sustainability. The principles of green chemistry can be applied to the field of nanotechnology especially for the synthesis of nanomaterials. In the current work, we have demonstrated an eco-friendly and inexpensive plant-mediated green method for the synthesis of valible light active titanium dioxide (FiO) nanoparticles with exposed high-energy [001] facets using the leaf extrast of *Cloronalacu (Urunt*. The synthesis ed nanoparticles were analyzed using UV-Vis spectroscopy, X-ray diffraction (XEO), FTR spectroscopy (OFS), and high-ensolution transmission electron spectroscopy (IRTEM), fitadies showed that phytochemicals present in the plant extrast act as both reducing agent and capping agent in the synthesis. The photo-analytic activity of the synthesized materials uses determined by analyzing the photodegradation of four different dyes such as methylene blue, fach-size, crystal violet, and rhodamine (G. All the dyns showed more than 85% degradation in 180 min. What compared with the chemically synthesized materials the green synthesized protectallytic activity. The superior photocatallytic performance of the sample is mainly attributed in the presence of defect and on-existence of [001] and [101] facets.

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Abstract

Abstract The use of photocatalysis in wasterwater transment using low cost photocatalyst plays a sitial role in flowarting the migma of water pollution. In this work, we report synthesis of netal- and non-metal-doped zinc uside (ZaO) nanostructures via solid state, solvent and surfactant-free microwiser-ansisted thermal decomposition method. BRTEM images confirm the formation of highly crystalline nanosof morphology in the case of solarm-doped ZuO. The photocatalytic activity of the synthesized marples initially associed by the degradation of methylerer blue noder visible light limitation suggests that SZO-3 (15 wfs No-doped) with admitable degradation rate (95% in 180 nan with append rate constant of 1.89 × 10⁻² min⁻²) and tenacious photostability envisages its potential applications in water treatment processes. The condescence of admission, while light and catalyst resulted in a solar and catalyst in 60 min. and catalyst resulted in augmented degradation (98.5%) in 60 min.

Reywords: Somophotocutalysis - Water treatment - Doped zinc oxide nanostructures - Band gap engineering

Introduction

Over the last decade, remainders around the globe have been thriving to address the water pollution resulting from the accumulation of motions organic dyes from numerous industries. The decomposition of organic dyes in efficient water by semiconductor-mediated catalysis by utilizing altrasonic by semiconductor-mellated catalysis by utilizing attraction irradiation and photocatalysis is at the forefront among the diverse methods (Qi et al. 2017; Horman et al. 2018; Lino et al. 2018; Neuroratha et al. 2018; Zhou and Fu 2018). Zhou oxide (ZhO) nanoparticles play a prominent role in photo-catalysis on well an structuralitysis, and its competence is an good as or better than the extensively used photocatalysis, tramma distuide (TrG₃). ZeO has paramount importance in advance utilizing due to its combustic modulus languation. in photocatalysis due to its synthesis methods by which its morphology, crystal structure and optical properties can be tailound to extend the visible light absorption (Chen et al.

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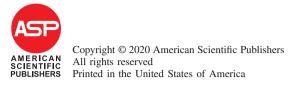
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2017; Alam et al. 2018; Dun et al. 2018). Despite the admirable traits of nano-ZnO such as high photosensitivity, vesattle and low core synthesis methods, photocaralysis suffers limitations such as high recombination rate of charge carriers and limited absorption in the visible light range (Kumur et al. 2015; Basadi et al. 2010). Various strungies have been et al. 2015, Basadi et al. 2018). Various strategies have been employed to servectione the limitations of 2200 photocatalyst inch as doping with metals and non-metals, coupling with other semiconductors and carlon structures forming heleno junctions, enciding the defences and explorating the exposed crystal facets, etc. (Yang et al. 2013; Raza et al. 2016; Feng. nt al. 2017). The wide spread methods commonly employed for synthesizing nano-ZnO include sol-gel process, hydrothermal or solvothermal processes, microwave and soto-chemical synthesis, precipitation, thermal decomposition, mechanochemical processes, etc. (Hameed et al. 2015; Wa et al. 2017; Histh and Ting 2018).

Among the various methods employed, thermal decom-position method can be profitably explosited for synthesizing nano-ZnO structures without the use of additional solvents or structure-directing agents. Several studies have proved that engineering the band gap of ZnO by incorporating dopart ions in the crystal lattice facilitates better visible light absorption as well as reduces the recombination rate of charge carriers perking up the photocatalytic activity (Virek et al. 2017; Rahimi and Yazdani 2018). In order to lower the

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Effect of Dopant Precursor Solutions on the Structural and Optical Properties of ZnS:Cu Nanophosphors

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Nanoparticles of ZnS doped with Cu (ZnS:Cu) were prepared at room temperature by wet chemical method without any capping agent using two dopant precursor solutions-aqueous: (i) Copper acetate [ZnS:CA] and (ii) Copper nitrate [ZnS:CN] solutions. The characterization of the samples was carried out for the structural, surface morphological and optical properties. XRD analysis results revealed the formation of cubic structure ZnS:Cu particles with an average size of 2.5 nm. From diffuse reflectance spectral (DRS) studies the band gap was found to be higher than bulk due to quantum confinement effect. In Photoluminescence (PL) spectra a sulphur vacancy related blue emission around 432 nm and a green emission from the recombination between the shallow donor level and the t_2 level of Cu were observed. The ZnS:CN nanoparticles showed enhanced luminescence property compared with that of ZnS:CA nanoparticles.

Keywords: Nanophosphors, Capping Agents, Photoluminescence, Stress.

1. INTRODUCTION

Transition and rare earth metal ions doped ZnS nanoparticles are used as prominent phosphor materials for display, lighting, sensors and lasers. It is well known that among the transition metal ions Mn can be incorporated into nano ZnS host in large proportions without altering the crystal structure. Hence, studies on the growth and optical properties of ZnS:Mn have been conducted by several researchers. Because of its excellent luminescence properties, bulk ZnS:Cu phosphors are also well-studied luminescent materials. Since CuS precipitates earlier than ZnS during the synthesis, studies of nano ZnS:Cu have not been carried out as widely as ZnS:Mn nanoparticles. Most of the synthesis methods of nanophosphors with capping agents or surfactants cause undesirable luminescence centers; subsequently the PL emission process becomes more complex. Hence, it is advantageous to attain efficient PL emission from uncapped nano ZnS:Cu. Many researchers reported the PL emission of ZnS:Cu nanoparticles in different ways [1-4]. In our present work, for the excitation wavelength of 340 nm, we have observed the two emissions-blue emission around 432 nm

and green emission around 522 nm. This paper discusses the preparation of uncapped ZnS:Cu (ZnS:CA and ZnS:CN) nanocrystals from two dopant precursor solutions by wet chemical method and has been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), diffuse reflectance spectroscopy and photoluminescence (PL) techniques.

2. MATERIALS AND METHODS

2.1. Chemicals

Zinc acetate $[Zn(CH_3COO)_2, Spectrum Reagents, 98\%]$, copper acetate $[Cu(CH_3COO)_2, Sigma Aldrich, 99\%]$, copper nitrate $[Cu(NO_3)_2, Sigma Aldrich, 99\%]$ and sodium sulphide $[Ns_2S, Merck]$ were used as received, without additional purification.

2.2. Synthesis

Two different dopant precursor solutions viz; aqueous copper acetate and aqueous copper nitrate solutions were attempted for the preparation of ZnS:Cu nanocrystals. These nanoparticles were synthesized by wet chemical method similar to our previous work [5]. In the procedure, 25 ml of 0.0005 M dopant precursor solution was added

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to 25 ml of 1 M zinc acetate $[Zn(CH_3COO)_2]$ solution, under strong stirring. 25 ml of 1 M Na₂S solution was introduced into the above solution and then the mixture solution was stirred for 20 minutes. The resulting white colloidal suspension was filtered and the obtained precipitate was washed with distilled water and dried at 70 °C. Following the same procedure, ZnS:Cu nanoparticles for 0.001 M Cu was also prepared.

The phase and structure of the synthesized samples were identified with X-ray diffraction (XRD) patterns, recorded by Bruker AXS D8 advance X-ray diffractomter with Cu (1.5405 Å) as X-ray source. Morphological analysis was carried out using scanning electron microscopy (SEM) with EDS attachment using Jeol model JSM 6390 LV. Diffuse reflectance measurements of dry powders were performed for energy gap determination, using Varian Cary 5000 UV-Vis-NIR spectrophotometer with a spectral bandwidth of 2 nm. FTIR analysis was done in the range of 4000–400 cm⁻¹ by Fourier transform infrared spectrophotometer (Shimadzu). Horiba Fluromax 4C research spectrofluorometer with a 150 W ozone free xenon lamp was used for Photoluminescence (PL) studies.

3. RESULTS AND DISCUSSION 3.1. Structural Characterization: XRD, SEM and

FTIR Analysis Figure 1(A) shows the XRD patterns of ZnS:Cu nanoparticles synthesized at room temperatures with 0.001 M of copper nitrate [ZnS:CN] or copper acetate $Cu(CH_3COO)_2$ [ZnS:CA]. The three broaden diffraction peaks in the XRD patterns indicate nanocrystalline nature and correspond to the lattice planes (111), (220) and (311) of the cubic zinc sulphide structure (JCPDS file No. 65-0309). The shoulder peaks on the diffraction peak corresponding to (111) plane in the ZnS:CA sample are due to the formation of CuS (JCPDS File No. 831463). The grain size measurements were carried out from the full width at half-maximum of the three main peaks of XRD pattern using Scherrer formula $D = 0.9\lambda/\beta\cos\theta$, where D is the average grain size, β is the half peak width at full maximum (FWHM), λ the wavelength of the Cu-K α used and θ is the glancing angle. The strain and crystallite size were calculated by Williamson-Hall (W-H) method by which $\beta \cos \theta = k\lambda/D + \xi \sin \theta$, where k = 0.9 known as the crystallite shape constant and other parameters have

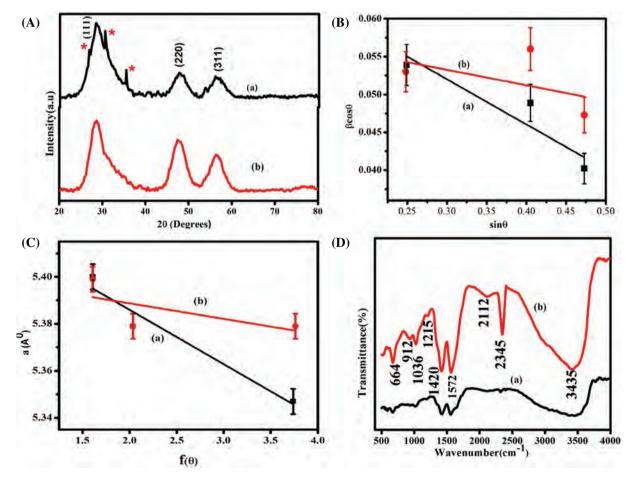


Figure 1. (A) X-ray diffractogram (*denotes CuS phase) (B) Williamson-Hall plot (C) Nelson-Riley plot and (D) FTIR spectra of nanostructured ZnS:Cu—(a) ZnS:CA and (b) ZnS:CN.

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the same meaning as in Scherrer equation [6]. The slope (ξ) of the plot of sin θ versus $\beta \cos \theta$ (Fig. 1(B)) gives the average internal strain, and from the intercept $0.9\lambda/D$ the crystallite size can be determined. The mean crystalline domain size calculated from Scherrer equation and W-H plot have been estimated to be around 2.4 nm and 2.6 nm for ZnS:CA and ZnS:CN respectively. The lattice strains were found to be -0.05611 and -0.01756 for ZnS:CA and ZnS:CN respectively. Here the negative sign shows compressive strain in the samples. Since the samples were in cubic phase, the lattice parameters were calculated using the relation, $d_{hkl}^2 = a^2/(h^2 + k^2 + l^2)$ where d_{hkl} is the interplanar separation corresponding to Miller indices h, k, and l. The corrected values of lattice parameters can be determined using Nelson Riley plot (N-R plot). The N-R curve (Fig. 1(C)) is plotted between the calculated 'a' for different planes and the error function, $f(\theta) =$ $1/2[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$. The stress and strain that are developed during the crystal formation leads to changes in lattice parameters from the bulk counterpart. The intrinsic stress developed during the formation of nanoparticles was calculated using the relation [7] $\varepsilon = Y(a - a_o)/(2\eta a_o)$, where Y is the Young's modules of ZnS (75 GPa), a_o is the bulk lattice parameter (0.5400 nm), a is the lattice constant measured from the XRD and η is the Poisson's ratio which is 0.28 for ZnS. Using Williamson and Smallmans relation $\delta = 1/D^2$, dislocation density in the samples was determined [8]. The calculated values of grain size (D), lattice parameter (a), dislocation density (δ), stress and strain (ξ) are given in Table I below.

FTIR spectra (Fig. 1(D)) of the samples were recorded in the wave number range 400–4000 cm⁻¹. However, the spectra were identical and the bonds were strong in the sample ZnS:CN. The vibrational frequencies of the various bonds present in the materials can be assigned by observing the peak position in the spectrum (Table II, below).

In order to analyze the image morphology and the composition of the materials, the synthesized doped nanoparticles were examined by SEM and EDAX. The shape and size distribution of the synthesized nanoparticles were characterized by SEM image (Figs. 2(a) and 3(a)).

In fact, because of the agglomeration, particles could not be distinctly visualized and hence exact calculation of the size of particles using SEM images was somewhat difficult. But, as is clear from the SEM images, the formed particles of ZnS:CA are small in comparison with the ZnS:CN

 Table I.
 Structural parameters of ZnS:Cu nanoparticles calculated from XRD.

Sample	Mean crystallite size (D) nm	a _{calculated} (Å)	a _{corrected} (Å)	Strain (ξ)	Stress (ε) ×10 ¹² N/m ²	Dislocation density (δ) $\times 10^{17}$ /m ²
ZnS:CA ZnS:CN	2.4 2.6	5.375 5.383	5.432 5.40	$-0.0561 \\ -0.0176$	$-0.62 \\ -0.42$	1.7 1.6

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Table II. IR peaks and their assignments.

Wave number (cm ⁻¹)	Assignment
1036	Zn–S vibration [9, 10]
664	Zn–OH bending mode [11]
3435	O-H stretching mode [12, 13]
1572	C=O stretching modes [14]
1215	C–O stretching [15]
1420	C-O-H bending [16]
2345	C–H vibration [17, 18]
912	Out-of-plane band due to O-H stretching [19]

particles. The EDX spectra of both samples exhibit the peak related to elemental Cu and (Figs. 2(f) and 3(f)) confirmed the composition of elements (Zn, S and Cu) in the samples. From the elemental maps it appears that Zn, S and Cu maps correlate exactly. The concentration of copper in the ZnS:CA and ZnS:CN samples are 2.46 at.% and 2.34 at.% respectively. But the Cu/Zn ratio in both samples is almost equal to 0.033 and 0.032 for ZnS:CN, ZnS:CA respectively.

3.2. Optical Characterization: DRS and PL Spectroscopy

From the diffuse reflectance spectra (Fig. 4), the absorbance was calculated using the Kubelka-Munk function $F(R) = (1-R)^2/2R = k/s$, where k and s are absorption and scattering coefficients [20, 21]. The optical absorption spectra of the two ZnS:Cu samples obtained from the diffuse reflectance values are shown in Figure 5(a). It can be seen from the figure that the two samples show sharp absorption edge at 330 nm which reflects the approximate band gap of nanoparticles.

The exact band gap energy values was determined using the conventional method of extrapolating the straight line portion of the $h\nu$ versus $[(k/s)h\nu]^2$ plot to k/s = 0(Fig. 5(b)). The band gap thus obtained for ZnS:CA and ZnS:CN are 3.76 and 3.74 eV. There is a blue shift in band gap values in comparison with the bulk value of 3.65 eV which may be attributed to quantum confinement effect. Based on this, the band gap of nanocrystallites is given by Brus equation [22],

$$E^* \approx E_g + rac{h^2}{8R^2} \left\{ \left[rac{1}{m_e}
ight] + \left[rac{1}{m_h}
ight]
ight\} - rac{1.8e^2}{4\piarepsilon_0arepsilon_r R}$$

Where E_g is the band gap of the bulk, m_e and m_h are electron and hole effective masses and R is the radius of nanoparticles. Substituting E_g , m_e , m_h and ε_r the above equation reduces to

$$E^* \approx E_g - \frac{0.3}{R} + \frac{1.5}{R^2}$$

The calculated particle radii are 2.57 and 2.74 nm for ZnS:CA and ZnS:CN respectively.

To find out the effect of dopant solution on luminescence, we have recorded the room temperature PL

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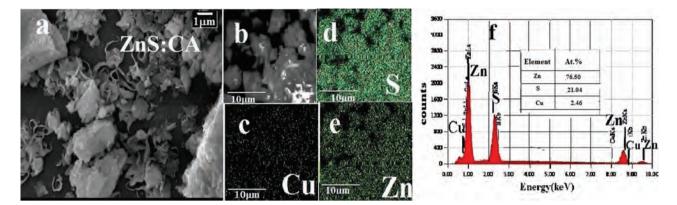


Figure 2. (a) SEM, (b-e) EDS maps and (f) EDS spectrum of ZnS:CA with 0.001 M of Cu²⁺.

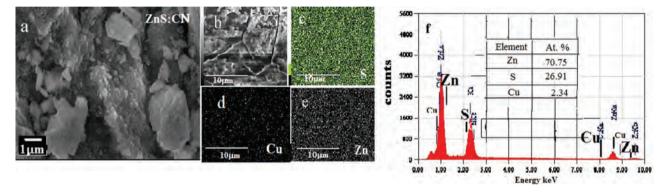


Figure 3. (a) SEM, (b-e) EDS maps and (f) EDS spectrum of ZnS:CN with 0.001 M of Cu²⁺.

emission spectra of the two ZnS:Cu samples—[ZnS:CA] and [ZnS:CN], synthesized for two Cu concentrations of 0.0005 M and 0.001 M at an excitation wavelength of 340 nm, as shown in Figure 6(A). It was found that PL emission of ZnS:CN sample (Figs. 6(A(c and b))) is more intense than that of ZnS:CA (Figs. 6(A(a and b)))

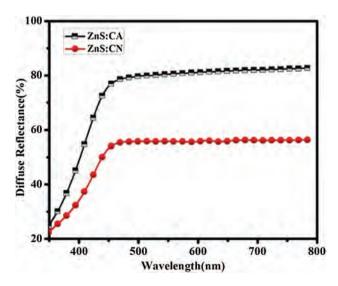


Figure 4. Diffuse reflectance spectra of ZnS:Cu nanoparticles—ZnS:CA and ZnS:CN.

for both Cu concentrations. For the doping concentration of 0.001 M Cu, the emission is 7 times more intense than that of ZnS:CA. Even though the amount of Cu in ZnS:CA (2.46 at.% by EDAX) is more than that of ZnS:CN (2.34 at.%), the Cu/Zn ratio in ZnS:CN (0.033) and ZnS:CA (0.032) are almost equal. But in ZnS:CA, the majority of the Cu ions are not incorporated in ZnS host lattice by replacing the Zn ions and hence the luminescence centers of Cu²⁺ ions are not formed but leads to the formation of CuS. Therefore the decreased intensity in ZnS:CA is due to CuS formation which is confirmed by its peaks in XRD pattern. The PL emission spectra of both samples (Fig. 6(A)) consist of a broad emission band in the range 450-550 nm. Due to the broad and unsymmetrical nature of PL spectra, they are deconvoluted and it was found that both the samples have similar peaks. In the broad region, the PL spectrum of ZnS:CN (Fig. 6(B)) consists of two emissions, one blue emission at 432 nm and other green emission around 526 nm. For the ZnS:CA sample PL spectrum on deconvolution (Fig. 6(C)) gives these emissions at 438 nm and 515 nm. The blue emission around 432 nm is due to the ZnS host and can be ascribed to the recombination of electrons at sulphur vacancy donor level with holes trapped at the zinc vacancy acceptor level [23]. The green emission observed in ZnS:Cu nanocrystallites can be assigned to the recombination of delocalized shallow donor level related to sulphur

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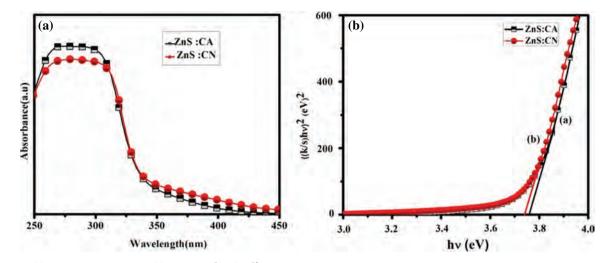


Figure 5. (a) Absorption spectra and (b) $h\nu$ versus $[(k/s)h\nu]^2$ plot of ZnS:Cu nanoparticles—ZnS:CA and ZnS:CN.

vacancy with the 't₂' level resulting from the splitting of $3d^9$ ground state of Cu²⁺ in the band gap of ZnS [24]. The emission peak of green emission in nano ZnS:Cu gets red shifted from the bulk ZnS:Cu for which this emission

was found to be at 500 nm. This may be due to the shift in energy levels of Cu impurity arising from nanoparticles formation. For the ZnS:CN nanoparticles in addition to Cu related green emission, a red emission around 640 nm

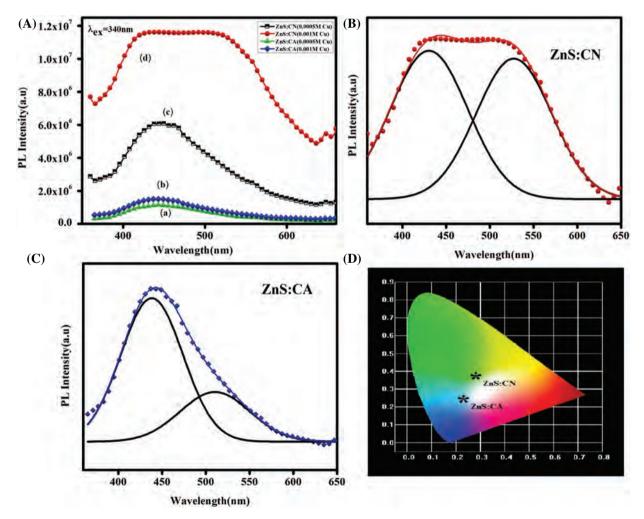


Figure 6. (A) Photoluminescence spectra ($\lambda_{ex} = 340$ nm) for 0.0005 M and 0.001 M of Cu of (a and b) ZnS:CA and (c and d) for ZnS:CN, (B and C) the individual components of PL spectra of ZnS:CN and ZnS:CA by deconvolution and (D) CIE diagram.

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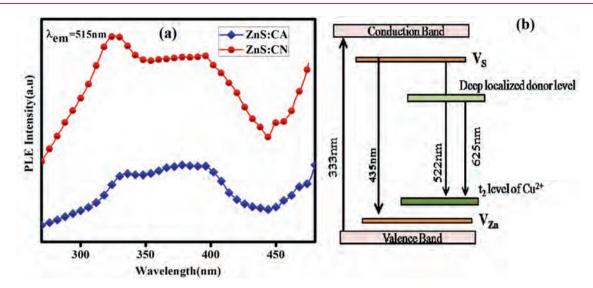


Figure 7. (a) PLE spectra ($\lambda_{em} = 515$ nm) of ZnS:CN and ZnS:CA and (b) schematic energy level diagram showing all emissions.

was also observed. For the bulk ZnS:Cu this red emission was reported and can be assigned to the recombination of deep localized sulphur vacancy donor level and t_2 level of Cu.

Figure 7(a) shows the excitation spectra of ZnS:CA and ZnS:CN for the emission wavelength of 515 nm. The spectra are identical. This high-energy band with peak around 332 nm corresponds to the ZnS band-toband transition. The other low-energy bands around 390, 445 nm corresponds to the absorption of defect levels. Based on the PL results obtained, the schematic energy level diagram is given in Figure 7(b). Here V_{Zn} , V_s stand for zinc and sulphur vacancies. To evaluate the performance of Cu doped ZnS on luminescence emission, CIE coordinates are calculated. We obtained CIE coordinates, x = 0.23 and y = 0.25 for ZnS:CA and x = 0.27 and y = 0.36 for ZnS:CN. The overall emission colour is green and bluish white for ZnS:CN and ZnS:CA (Fig. 6(D)) respectively.

4. CONCLUSION

Cu doped ZnS nanoparticles were prepared through wet chemical method using two dopant precursor solutionsaqueous copper acetate and copper nitrate solutions. The ZnS:CN nanoparticles exhibited better luminescence property compared to ZnS:CA nanoparticles and the overall emission colour is green. The results of PL studies presented here show that ZnS:Cu nanophosphor is a green phosphor when the Cu source is copper nitrate and it can be used for display applications.

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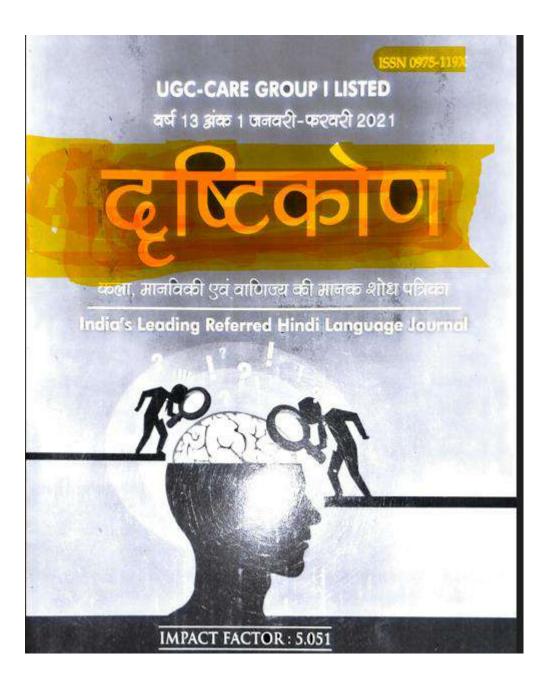
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सहायक आजसा जार रवाया में है। वे एक दूसरे से आंधान और संबद्ध है। मानव प्रकृति जेर पर्यवरण व के एकति, पर्यावरण, समाज और संस्कृति एक दूसरे के महत्वपूर्ण अंग है। वे एक दूसरे से अधिन अंगत दत है इसलिए अपने तक सोधित प्रकृति, पर्यावरण, समाज और संस्कृति एक इसरे के महत्वपूर्ण और है। व एक पूसर से जीवन प्रकृति दत है इसलिए अपने तक सीवित सका लेता है एव प्रकृतिक तत्व ही मनुष्य जीवन का कारण, आधार और ऊर्जा यनते हैं। मानव जीवन प्रकृति दत है इसलिए अपने तक सीवित सका लेता है एव प्रकृतिक तत्व ही मनुष्य जीवन का कारण, आधार और उन्हों यनते हैं। यानव जीवन प्रकृति दत है इसलिए जेपने तक लेता है एव प्राकृतिक तत्व ही मनुष्य जीतन का कारण, आधार और ऊजा बनत ह। मागन प्राय संबंधों का सूत्र स्थापित होने लगा जे करन रह नहीं सकता चुकि प्रकृति जीवन के केन्द्र में है। कालांतर में प्रकृति और मनुष्य के बीच लगातार संबंधों का सूत्र स्थापित होने लगा जे करन रह की सकता चुकि प्रकृति जीवन के केन्द्र में है। कालांतर में प्रकृति और मनुष्य के बीच लगातार संबंधों का सूत्र स्थापित होने लगा। प्रकृति के बाह क्य नहों सकता चुकि प्रकृति जीवन के कोद में है। कालांतर में प्रकृति और मनुष्य क बाय रागाण मानव इसके साथ जुड्ते गए जिसके फलरस्वरूप समाज का श्वरूप निर्मित होने लगा साथ ही संस्कृति भी पनपने लगी। प्रकृति के बाह त्या द भानव इसके साथ जुड्ते गए जिसके फलरस्वरूप समाज का श्वरूप निर्मित होने लगा साथ ही संस्कृति के अंतरंग और बाह्य माधने ह णनव इसके साथ जुड़ते गए जिसके फलस्वरूप समाज का स्वरूप निामत हान लगा लाग है। जुड़ाव के एहसास ने उसे सामाजिक, आधिक एवं सांस्कृतिक सरेवना के लिए आधार प्रदान किया। प्रकृति के अंतरंग और बाद्य सध्यों के श्रे का जुड़ाव के एहसास ने उसे सामाजिक, आधिक एवं सांस्कृतिक सरेवना के लिए आधार प्रदान किया। प्रकृति के अंतरंग और बाद्य स जुडाव के एहसाम ने उसे सामाजिक, आधिक एवं सांस्कृतिक संरचना के लिए आपार अधा भया आवासऔर जीवन मूल्यों की आर अग्रस क के बुडाव के फलस्वरूप मनुष्य सामृहिक बनता गया एवं आजीविका, खानपान, वस्त्र अलंकार, आवासऔर जीवन मूल्यों की आर अग्रस के बुडाव के फलस्वरूप मनुष्य सामृहिक बनता गया एवं आजीविका, खानपान, वस्त्र अलंकार, आवासऔर जीवन मूल्यों की आर अग्रस के बुढाव के फलरवरूप मनुष्य सामूहिक बनता गया एवं आजाविका, खानपान, परंत करती और प्रकृति के योग से रवित होता गया। रक्त रक्ष को सभ्यता तक पहुंच गया। मानव एकऔर अपनी जरूरत के साधनों को रचता गया दूसरी और प्रकृति के योग को पर्यावरण कहा ज्या को सभ्यता तक पहुंच गया। मानव एकऔर अपनी जरूरत के साधनों की रचता गया दूसरी और अजैविक कारकों के योग को पर्यावरण कहा को सभ्यता तक पहुंच गया। मानव एकआर अपना जरूरत क साधना का रचना त्या के अर्जविक कारकों के योग को पर्यावरण का। जन तम प्रांतकिया में उसने प्रकृति पर भी प्रहार किया। प्रकृति, प्राणो, वनस्पति जैसे जैविक और अर्जविक कारकों के योग को पर्यावरण का। जन नग गकवा म उसने प्रकृति पर भा प्रहार किया। प्रकृति, आणा, जातीया बयपन से ही मनुष्य उसके प्रति प्रतिक्रिया व्यक्त करने के साथ-सव उसके प्रयोकरण एक समग्र सांस्कृतिक, भौगोलिक और सामाजिक तत्व है। बयपन से ही मनुष्य उसके प्रति प्रतिक्रिया व्यक्त करने क स्वांकरण एक समग्र सांस्कृतिक, भौगोलिक और सामाजिक तत्व है। जयपन स्वांध का अपने प्रयावरण के प्रति भावनात्मक जयपन रयावरण एक समग्र सारकृतिक, भागालक आर सामाभक जर्भ हा ने गया। व्यक्ति का अपने पर्यावरण के प्रति भावनात्मक बुहाव एव हे अनुकूल हालने और अपने को उसके अनुकूल ढालने की प्रक्रिया में जुड़ गया। व्यक्ति का अपने पर्यावरण के प्रति भावनात्मक बुहाव एव हे ल अनुमूल डालने और अपने का उसके अनुमूल डालने का प्राक्रणा ने उप के कारण बनती है। पर्यावरण से व्यक्ति को अस्मित मो बुझे रहे है रहती है और किसी पर्यावरण विशेष का अंग होने की अनुभूति उसके आनंद का कारण बनती है। पर्यावरण से व्यक्ति को अस्मित मे रहता हे ओर किसा प्रयोवरण विशय का अग होन का अनुमूछ उसके प्रथम प्रयोवरण के संपर्क और प्रतिक्रिया में आता है और आतीक व्यक्त के व्यक्तित्व और पर्यावरण का भनिष्ठ संबंध है। उसका बाह्य व्यक्तित्व निरंतर प्रयोवरण के संपर्क और प्रतिक्रिया में क स्वाकतन आर पयावरण का भानफ सबभ हा उसका बाह जातमान राजात स्वाप्ति, अनुभूति, चिंतन, व्यवहार आदि को जानने कलिए उसक रक्षेत्र क मनोविज्ञन पर गहरा प्रभाव डालता है। किसी व्यक्ति को अभिरुपि, अवस्थिति, अनुभूति, चिंतन, व्यवहार आदि को जानने कलिए उसके रक्षेत्र क भगावसान २१ १००८ प्रभाव ठालता २१ किस व्यक्त के अवैविक कारकों तक सीमित न रहकर मानव व्यक्तित्व पर भी प्रभाव डालत है। सांक्षेत्र डालने की जरूरत होती है। इस प्रकार पर्यावरण जीवक अवैविक कारकों तक सीमित न रहकर मानव व्यक्तित्व पर भी प्रभाव डालत है। सांक्षेत्र

में किसी भी प्रकार के असंतुलन का प्रभाव मानव मनोविज्ञान पर भी असर करता है। मानव सामाजिक प्राणो होने के बाते सामाजिक पर्यावरण उसके लिए अत्यंत प्रमुख बन जाता है। भारत के प्राचीन ऋषियों ने राष्ट्र एवं भिन्न हे। नागव रागा गण अन्य छान क गाव राग्या पर व प्रायों के अंदर उपस्थित एकरूपता को खोज कर उसके आधार पर मनुष्य को वैयक्तिक तथा समास क का सुदृढ् बनाने के लिए नानारूपात्मक पदार्थों के अंदर उपस्थित एकरूपता को खोज कर उसके आधार पर मनुष्य को वैयक्तिक तथा समास क समाजिक पर्यावरण को स्वस्थ और पवित्र रखने के लिए मानसिक पर्यावरण और बौद्धिक पर्यावरण का गठजोड़ अत्यंत महत्वपूर्ण है। वब रे इंदे टोक रहते हैं तब तक सामाजिक पर्यावरण भी ठीक ही रहता है। जब इनमें उतार-चढ़ाव आता है तो सामाजिक पर्यावरण बिगड़त है- पर्नम्ह क अंतर्गत सन में उठतेवाले विचार, शडदोष, भावना आदि आते हैं जिसके असंतुलन का सीधा असर मन पर पड्ता है और मन निरमेश कर दे⊞ असमर्थ हो जाता है। इसे मानसिक पर्यावरण प्रदूषण कहा जा सकता है। जब मन काम करने में असमर्थ होता है तो इसका असर बुद्धि प व्हा बोद्धिक पर्यावरण भी विगडता है।

अद्यतन समाज अर्थ केन्द्रित हो गया है। वह सब कुछ अर्थ के तराजू पर तोलता है और अर्थ उसे भौतिक सुख प्रदान करता है। अत्र मौत्र व त्रलाश हो जोवन का लक्ष्य बना हुआ है। भोगों को प्राप्ति को जीवन का एकमात्र मुल्य मान लिया जाता है जिसके फलस्वरूप मुखवरो बंक जन्म हुआ है जो प्रकृति के संसाधनों को दुहकर उत्पादन करता है, बाजार में बेचता है और रापत करता है। मांग और खपत में समोकल स्वोत्त लगता है। मांग के साथ खपत और खपत के साथ मांग बढ़ती ही रहती है और उसके साथ पर्यावरण की क्षति और सामाजिक पारिस्थिति 💷 शुरू होता है। योग्यता और सफलता को, भोग के लिए साधनों को जुटाने के सामर्थ्य से नापा जाने का जमाना आ पहुंचा है। इस पश्मित देन सुख शांत को उपलब्धि को परिभाषा ही बदल गई। हमारे समाज में जहां भोग और योग का समन्वय हुआ करता था,आज पश्चिम को पंत्वी पकड मजबूत की और हमारो नई पीड़ी को सुख-सुविधा, भोग, हिंसा, उन्माद, विवेक शून्यता आदि से प्रेरित अपसंस्कृति की ओर धडेत दि कारण समाज में तैतिक मूल्यों की गिगवर देखी जाती है। भारतीय समाज में एक समय भूमा का सुख था जो प्रकृति पर निर्भर था। अब का प्रायगण तब्दी भावन जिल्ला में स्वी के लेगा के के लोग है। भारतीय समाज में एक समय भूमा का सुख था जो प्रकृति पर निर्भर था। अब का पृथिव्याः वालां भावना विलुप्त हो गयी है। केवल दोहन की योजनाएं बाकी हैं। मनुष्य और प्रकृति का रिश्ता भोग को वस्तु और उपग्रेस क कर रह गया है। यह एक तरह से बाजारू रिश्ता है जिसपर आत्मीयता और सामाजिकता का कोई भाव ही नहीं है। इस तरह के संबंध विश्व मानसिक और बौद्धिक पर्यावरण पर अगर पहा है जिसपर आत्मीयता और सामाजिकता का कोई भाव ही नहीं है। इस तरह के संबंध विश् मानसिक और बौद्धिक पर्यावरण पर असर पड़ा है जिसका सीधा प्रभाव सामाजिक पर्यावरण पर दिखाई देने लगा है। इम आज झि की सामाजिक संस्कृति और पर्यावरण की ओर अगरप को को के जाने के जाने के जाने के सामाजिक पर्यावरण पर दिखाई देने लगा है। इम आज झि की सामाजिक संस्कृति और पर्यावरण की ओर अग्रसर हो रहे हैं उसमें स्वार्थ, व्यक्तिवाद, धनलिप्सा और प्रतिस्पर्धा के तत्व *काम का रहे हैं। विव* विचार और जीवन दर्शन इसमें अपनी अपनी अपनि प्रसिक्त विश्व के सिल्ली की की की की स्वार्थ के तत्व काम का संस्कृत विचार और जोवन दर्शन इसमें अपनी अपनी भूमिका निभा रहे हैं। किसी भी प्रदूषण से पहले मानसिक प्रदूषण होता है। मन हमारे अंदर होक्सी है, वही कमें और जान का केंद्र है। एन जन प्रतिष्ठ जेन के देने किसी भी प्रदूषण से पहले मानसिक प्रदूषण होता है। मन है, वहीं कमें और ज्ञान का केंद्र है। मन जब प्रदूषित होता है तो विचारों में दूषित भावनाएं उत्पन्न होती है। मनुष्य की मानवीधता नष्ट हे हो है। (1352)

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Facile synthesis of nitrogen doped carbon dots from waste biomass: Potential optical and biomedical applications

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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Jackfruit peel Tamarind peel Hydrothermal synthesis N-CDs Cyototoxicity	We report a facile, one-pot hydrothermal synthesis of surface passivated, nitrogen doped carbon dots (N-CDs) from jackfruit peel and tamarind peel precursors. The synthesized N-CDs emit strong excitation dependent fluorescence in the blue region. The samples illustrate exciting quantum confined optical properties. Graphitization of N-CDs is identified by X-ray diffraction. Surface functionalization is confirmed by FT-IR studies whereas nitrogen doping by X-ray photoelectron spectroscopy. The average size of synthesized N-CDs estimated from transmission electron images is 6.4 nm and 5.3 nm for jackfruit peel and tamarind peel precursors respectively. Quantum yield of N-CDs from jackfruit peel (13.04%) is higher than that from tamarind peel (6.13%). Appreciable anti-cancerous activity of the as-prepared carbon dots could be detected with DLA tumour cells extracted from mice. The work proposes an innovative design to yield blue luminescent carbon dots with high quantum

yield from biowaste, providing a green and sustainable alternative to traditional carbon sources.

1. Introduction

Appropriate food waste management has a vital role in environmental, economic and social existence to a great extent. It is of paramount importance to transform this waste into valuable products thereby managing environmental pollution (Sarswat and Fre, 2015) and (Tripathi and Ranjan, 2015). Proper treatment of food waste is a relevant solution of disposal issues; also provide a platform for many inventions in agriculture, biomedicine and industry (Himaja et al., 2014). Generally, fruit peels are produced in huge quantities on food processing but are devoid of any economic value. They are valuable resources in material chemistry owing to their low cost, effortless processing conditions, abundant and easy availability. When fruits are consumed or transformed into value added products, their peels can also be utilized for sources of active compounds on account of their good fibre content. When these peels are carbonized, it results not only in carbon dot core, but also hydrophilic functional groups such as carbonyl, and hydroxyl. These functional groups being excellent chelating ligands, improves the optical and physicochemical properties, contributing to various applications in sensing and biomedical fields (Praneerad et al., 2018). Jackfruit (Artocarpus heterophyllus) belongs to the family of Moraceae. As the major fraction of the jackfruit is discarded as peel, it can be altered into a value added product. It contains cellulose, crude fiber and starch and is rich in different polar functional groups such as hydroxyl and amino groups (Ranasinghe et al., 2018). Tamarind (*Tamarindus indica*) belongs to the family of Fabaceae. Tamarind peel is easily crackable, brittle shell of tamarindus indica that is abundant as a by-product from tamarind pulp industry. It consists of hydroxyl and amide groups which may preferably assist in value added chemicals (Kumar et al., 2012).

In the last decade, various protocols have been developed for the fabrication of nanomaterials from natural precursors. Green methodologies are receiving much attention than conventional strategies due to the lesser impact on environment. Comparing chemical and physical synthetic techniques, green strategies provide simple, easy, relatively reproducible, cost effective, efficient and eco-friendly routes which may be performed at ambient conditions. These methods reduce the poisonous impacts of conventionally integrated nanoparticles to a greater extent. Hydrothermal treatment turned out to be the best among them considering the ease of manipulating reaction conditions (Chan et al., 2018). Carbon dots are an emerging subclass of zero dimensional nanoparticles that consists of a carbon core functionalised by different groups at the surface. They are characterised by quasi-spherical morphology composed mainly of amorphous carbon with sp² hybridised structure and size less than 10 nm (Niu et al., 2017). They exhibit

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attractive physicochemical properties such as tunable photoluminescence, functionalizability, low toxicity, dispersibility and multicolour emission associated with excitation, biocompatibility. These extraordinary features may be derived from either carbon core or the functional groups at the surface (Xu et al., 2004). These properties make a prominent impact on research pertaining to biosensors, biolabeling, catalysis, photovoltaics and photo electronics. Metal based inorganic semiconductor quantum dots widely used in the last decade owing to their unique property of quantum confinement effect have restricted use nowadays due to the presence of toxic metals such as Hg, Cd and Pb as their constituents. The recently emerged carbon dots are superior to quantum dots in view of photobleaching, facile surface functionalization, low toxicity and chemical inertness (Hardman, 2006). The process of doping can appreciably enhance the optical properties of C dots by incorporating hetero atoms like nitrogen and sulphur into their internal structure. As a result, high quantum efficiency can be achieved by creating novel functionalities. Nitrogen is the most preferred element in doping on account of the high resemblance with carbon in electronic structure and size. Incorporation of nitrogen can be attained either during synthesis by opting nitrogen containing precursors or post synthetic functionalization methodologies (Xu et al., 2016). Among the numerous protocols for the synthesis of carbon dots, hydrothermal treatment is considered to be the most efficient and convenient method as it involves facile instrumentation technique and high atom economy. This eco-friendly, nontoxic and cost effective method has a further advantage that it does not require any post synthetic surface passivation. Hydrothermal synthesis of CDs from bio sources like honey (Yang et al., 2014), water hyacinth (Paul and Kurian, 2020), milk (Wang and Zhou, 2014), sweet potato (Shen et al., 2017), papaya (Wang et al., 2016) are reported.

Herein we describe the use of cost-free food waste as a novel carbon source for the synthesis of carbon dots. Jackfruit peel and tamarind peels were selected as carbon source in the current research work considering the low cost and surplus local availability. The method demonstrates the recycling of environmental waste for eco-friendly nanomaterial synthesis with potential biomedical applications. Present day research prefers natural molecules as remedy for cancer as chemotherapy affects host cells in addition to the chronic and delayed toxicities in vital organs (Kavya et al., 2013). Natural products having anticancerous activity with good antioxidant potential and minimum host cell toxicity are of exceptional value in the current situation.

2. Materials and methods

2.1. Synthesis procedure

Dichloromethane was obtained from Sigma Aldrich, Germany. Jackfruit peel and tamarind peel collected locally were cleaned, dried and powdered. About 5g of jackfruit peel/tamarind peel was dispersed in 50 ml deionized water and the mixture was heated in a 100 ml Teflon-lined stainless steel autoclave at 180 °C for 12 h. The dispersion obtained was filtered through a Whatman filter paper, followed by washing with dichloromethane and centrifugation at 3000 rpm for 15 min. The unreacted materials got separated in the organic layer and the N-CDs were collected from the aqueous layer through centrifugation at 12,000 rpm thrice for 20 min. The brown coloured solution of as-prepared carbon dots was stored at 4 °C.

2.2. Characterisation

UV–Vis double beam spectrophotometer (Varian, Cary 5000) was used to record UV–Vis absorption spectra. The fluorescence measurements were done by a fluorescence spectrometer (Fluoromax 4- Horiba Instruments, Japan). The scan speed of the measurement was 240 nm/ min. Photoluminescence was studied by exciting the material in a range of 320–420 nm with an increment of 20 nm. An FTIR spectrometer

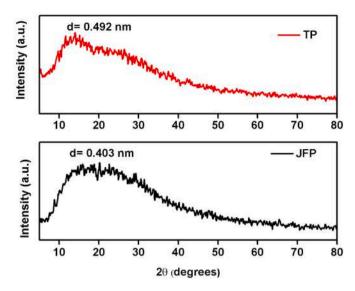


Fig. 1. XRD patterns of N-CDS from JFP and TP.

(Thermo Nicolet, Avatar 370) was used to study the Fourier Transform Infrared spectra for the analysis of functional groups. The morphology of the samples was investigated by TEM (Jeol/JEM 2100). ImageJ software was used to calculate the average particle size by selecting 50 particles. X-ray diffraction analysis was performed to analyse the crystallinity as well as phase purity of the samples. The colloidal particles were drop coated onto a glass plate. After drying, X-ray diffraction patterns were analyzed using a Bruker D8 ADVANCE with 2 θ scanning mode in the range 5-80⁰ at a step interval of 0.02⁰ with counting time of 5s per point. The surface chemical analysis was obtained with an X-ray photoelectron spectrometer (Axis Ultra, Kratos, UK).

The fluorescence quantum yield of the prepared samples was calculated by a relative method using equation (1) by comparing the PL intensities and absorbency values against quinine sulphate (0.1M H_2SO_4 , QY = 0.54) taken as reference (Kumar et al., 2017).

$$Q_{CD} = Q_{R} (I_{CD}/I_R) (A_R/A_{CD}) (\eta^2_{CD}/\eta^2_R$$
(1)

where "Q" is the quantum yield, "I" is the measured fluorescence intensity, "A" is the absorbance at excited wavelength, " η " is the refractive index. The subscript "R" represents the reference sample and "CD" represents carbon dots.

2.3. IN-VITRO cytotoxicity studies

Trypan blue exclusion method in which Dalton's Lymphoma Ascites cells (DLA) from the peretonial cavity of mice was used for the evaluation of anticancerous activity of N-CDs. The tumour cells were washed with Phosphate Buffer Saline. Different concentrations of carbon dots (50 μ g/ml, 100 μ g/ml, 150 μ g/ml and 200 μ g/ml) from two sources, jackfruit peel and tamarind peel were made using dimethyl sulfoxide (DMSO). Viable tumour cell suspension was added to the tubes containing various concentrations of carbon dots. Cell suspension without N-CDs was taken as the reference. Incubation was done at 37 °C for 3 h 0.1 ml of trypan blue was added and tested on a haemocytometer. By counting the stained and unstained cells, we can determine the cell viability. Equation (2) gives the cytotoxicity of the synthesized N-CDs.

$$% \text{ cytotoxicity} = \frac{\text{Number of dead cellsNumber of dead cells}}{+ \text{ Number of living cells}}$$
(2)

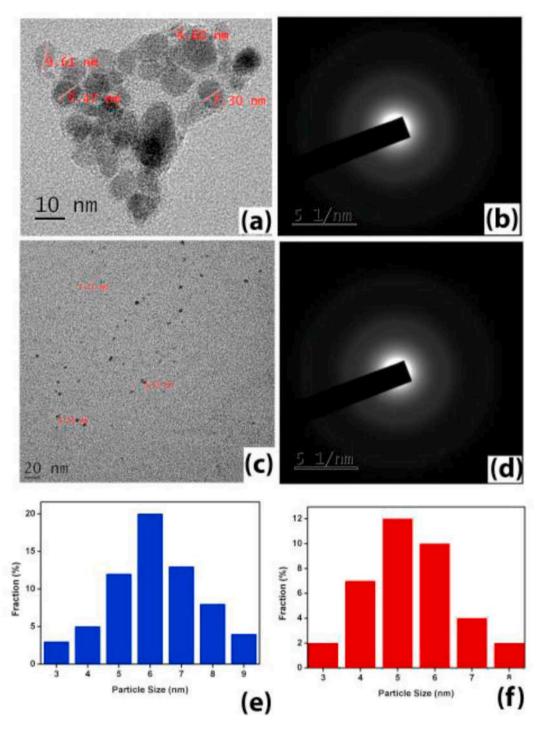


Fig. 2. (a) TEM image of N-CDs from JFP (b) SAED pattern of N-CDs from JFP (c) TEM image of N-CDs from TP (d) SAED pattern of N-CDs from TP (e) Size distribution histogram of N-CDs from TP.

3. Results and discussion

3.1. Characterisation of N-CDs

Recording X-ray diffraction pattern of a sample has many applications like qualitative phase analysis, quantitative phase analysis and study of preferred orientation. XRD profile of samples obtained from jackfruit peel (JFP) and tamarind peel (TP) are represented in Fig. 1. Sample from JFP depicts a single broad peak centred at 22° whereas sample from TP gives a sharper peak centred at 18°. These peaks could be assigned to (002) diffraction pattern of graphitic carbon (Han et al., 2016) and (Shen et al., 2017) suggesting a predominantly disordered amorphous graphitic structure of carbon dots (CDs). Bragg's equation was used to calculate the d spacing of the CDs with respect to the 20 position of (002) plane. The interlayer spacing was 0.403 nm and 0.492 nm for JFP and TP respectively, which is larger than that of graphite (0.34 nm). The enhancement in interlayer distance may be due to oxygen containing groups and introduction of further defect sites through N-doping in the lattice (Mewada et al., 2013) and (Yin et al., 2013) (see Fig. 2).

The surface morphology and size of the as-synthesized carbon dots was obtained from Transmission Electron Microscopy (TEM). TEM

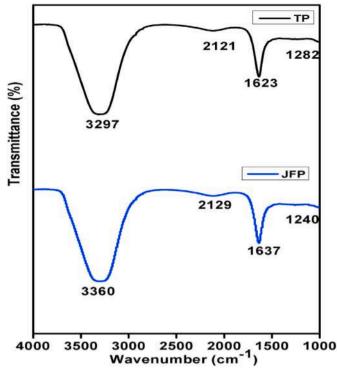


Fig. 3. FT-IR spectrum of N-CDs from JFP and TP.

images reveal well dispersed, quasi spherical structures without apparent aggregation. The particles are heterogenous in size, varying from 3 to 9 nm. Amorphous nature of CDs is confirmed by the lack of lattice fringes in the SAED pattern, in agreement with the XRD results. From the statistical particle size distribution estimated using Image-J software, the average size of carbon dots is found to be 6.4 nm and 5.3 nm for jackfruit peel and tamarind peel respectively.

The functional group present on the surface improve the stability, dispersibility and hydrophilicity of the CDs (Carolan et al., 2017) and (Chen, 2016). FT-IR spectrum of CDs from jackfruit peel shows a prominent absorption band at 3360 cm⁻¹, that can be assigned to N–H/O–H stretching vibration (Fig. 3). The characteristic absorption bands at 2129 cm⁻¹ and 1637 cm⁻¹ can be ascribed to N=C=N stretching and C=O stretching respectively suggesting that the obtained CDs are nitrogen doped (Jiang et al., 2015) and (Prathumsuwan et al., 2018). The band at 1240 cm⁻¹ denotes the presence of C–O–C stretching. These groups confirm the presence of hydroxyl and acid moieties on the surface (Gedda et al., 2016). CDs from tamarind peel also shows presence of similar groups from FT-IR spectrum.

Surface elemental analysis by X-ray photoelectron spectroscopy shows that carbon (283.6 eV), oxygen (529.5 eV) and nitrogen (397.6 eV) are present in the samples (Fig. 4). In the expanded XP spectrum of C (1s), the band can be de-convoluted into two major binding peaks at 284.5eV and 288.3eV, which can be assigned to the C=C, C=O functionalities over the surface of the N-CDs. The N(1s) band of carbon dots contain four major peaks at 399.4, 398.3, 400.3 eV and 401.4 eV which indicate the presence of the C–N–C, O=C–N, graphitic C–N and N–H moieties respectively. On de-convoluting the high-resolution spectrum of O(1s), two binding peaks at 531.3 eV and 532.4 eV, due to the existence of sp² C=O and sp³ C–O/C–OH groups are detected. The surface analysis results confirms the functionalization of CDs with hydroxyl (–C-OH), carboxyl (–C=O) and amine (C–NH₂) groups, suggested by the IR results (Xu et al., 2017). A slight variation in the nitrogen content that

Table 1

Percentage of carbon, oxygen and nitrogen in N-CDs from JFP and TP.

Peak	JFP (%)	TP (%)
C1s	59.9	64.6
O1s	36.2	30.2
N1s	3.9	5.2

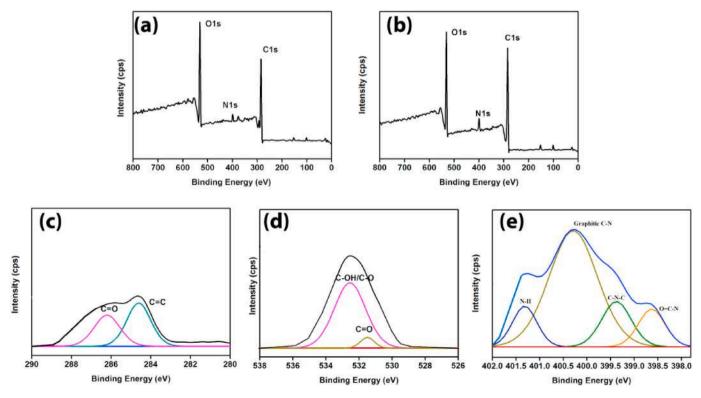


Fig. 4. (a) Wide XPS spectrum of N-CDs from JFP (b) Wide XPS spectrum of N-CDs from TP (c) C1s spectrum (d) O1s spectrum (e) N1s spectrum.

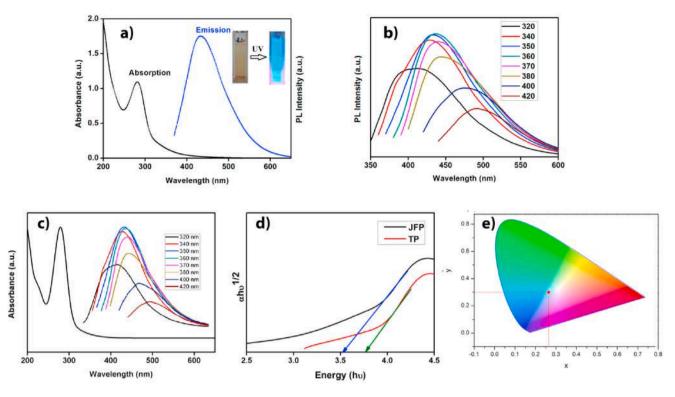


Fig. 5. (a) UV–Visible absorption spectrum, PL emission and the digital image of N-CDs from JFP (b) Fluorescence emission spectra of N-CDs from JFP at different excitation wavelengths from 320 nm to 420 nm. (c) UV–Visible absorption spectrum and PL emission of N-CDs from TP (d) Band gap of N-CDs from JFP and TP (e) CIE diagram of N-CDs from JFP.

can be attributed to the precursor is noticed (Table 1).

UV-Visible absorption and photoluminescence (PL) investigations were done to study the optical characteristics of N-CDs. The synthesized N-CD solution, brownish in colour under daylight, shows intense blue fluorescence under UV excitation (inset of Fig. 5a). The absorption peak around 280 nm in the UV-Visible spectra is due to carbonic core center and can be attributed to the π - π * electronic transition of C–O groups of N-CDs. The surface state of the molecules may have trapping of excited state energies which may help in attaining strong fluorescence. In addition, it is found that the blue emitting N-CDs exhibit excitation dependent photoluminescence as shown in Fig. 5b. The excitation at 350 nm develops a strong PL emission at 430 nm. When the excitation wavelength is increased from 320 nm to 420 nm, the emission peak is red shifted from 410 nm to 510 nm. Generally, the relationship among carbon core and the surface chemical groups determines the fluorescence behaviour (Zhu et al., 2012). The oxygen functionalities and defects have crucial roles in the photoluminescent property, in addition to quantum confinement effect. Also, upon stabilising the surface energy traps in N-CDs result in fluorescence. The strong photoluminescence may also be the result of emissive traps of the nitrogen doped surface (Zhang and Chen, 2014). Abundant active sites offered by the electron rich nitrogen atoms plays a prominent role in excitation dependent PL behaviour of the N- CDs (Wang et al., 2017) and (Wu et al., 2019).

UV–Visible spectroscopy can also throw insight to the band strength or band gap energy. The indirect optical energy gap (Eg) can be calculated from Tauc plot using equation (3) (Sharma and Bhogal, 2017).

$$(\alpha h \upsilon)^n = C(h \upsilon - Eg)$$
(3)

where α is the absorption coefficient, hv is the energy, C is the proportionality constant and Eg is the energy gap. N is an index with values ½, 3/2, 2 and 3 depending on the nature of electronic transition. Energy gap can be calculated by extrapolating the linear portions of $(\alpha hv)^{1/2}$ V hv. Blue and green lines show the extrapolation for N-CDs from jackfruit peel and tamarind peel respectively (Fig. 5d). The corresponding band

gap for N-CDs from JFP and TP is 3.52 eV and 3.77 eV respectively. Electronic structure of N-CDs is size dependent. Various functional groups existing on the surface of N-CDs also contribute to the band gap. Carolan et al. produced nitrogen doped carbon dots from citric acid and ethylenediamine using atmospheric pressure microplasma. The band gap values obtained were 2.2, 2.56, 2.67, and 2.7 eV for increasing concentrations of ethylenediamine. The paper reports increase in band gap with nitrogen content (Carolan et al., 2017). The band gap obtained in this work is slightly larger than reported values but in accordance with the explanation given by Carolan et al., as N-CDs from TP has greater nitrogen content than that from JFP. Also, the value is comparable with the highly efficient photocatalyst, TiO₂ (3.2eV).

Photo stability is another important parameter which plays prominent role in various applications. The photostability of as-prepared N-CDs was investigated by continuously irradiating under a UV lamp of 365 nm for 2 h. PL data from different excitation wavelengths provide the quality of blue light emission as identified from the 1931 CIE (x, y) chromaticity co-ordinates. Fig. 5e shows the chromaticity diagram of N-CDs from jackfruit peel demonstrating the CIE colour parameters. The parameters relating to excitation wavelengths 300 nm, 320 nm, 350 nm and 370 nm are (0.24, 0.29), (0.25, 0.30), (0.26, 0.29) and (0.24, 0.28) respectively. At all excitation wavelengths, The CIE co-ordinates correspond to blue light, indicating that the aqueous solution of N-CDs emit blue light under UV irradiation. N-CDs from tamarind peel provide a similar data (Joseph and Aji, 2016). The quantum yield of carbon dots is greatly influenced by various synthetic methodologies, surface passivation, element doping and precursors. The quantum yield of the N-CDs obtained from jackfruit peel is found to be 13.04% and 6.13% from tamarind peel, which are quite higher than previous reports (Mehta et al., 2015) and (Liu et al., 2012).

3.2. IN VITRO cytotoxicity studies

The present study analyzes the in-vitro anticancerous activity of N-

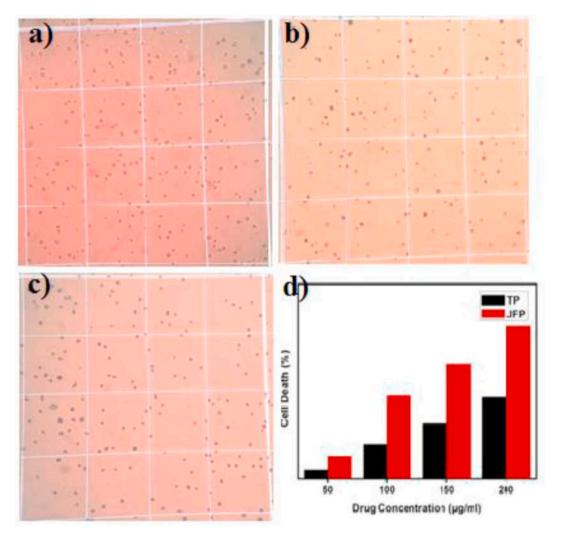


Fig. 6. (a) Image of live cell before insertion of N-CDS (b) Image of cells after addition of 200 µg/ml of TP (c) Image of cells after addition of 200 µg/ml of JFP (d) Graph showing the comparison of cell viability of TP and JFP.

CDs in DLA tumour bearing mice. Swiss albino mice were selected and the cells were maintained in vivo by intraperetonial inoculation. When tumour cells are transformed, DLA cells were aspirated using saline. Four different concentrations (50 μ g/ml, 100 μ g/ml, 150 μ g/ml and 200 $\mu g/ml)$ of N-CDs were opted for the analysis. Image of the live cells before applying the drug is shown in Fig. 6a. The live cells remain intact and the dead cells turned into blue colour of trypan blue (Thavamani et al., 2014) and (Kanagamania et al., 2017). N-CDs treatment resulted in distinct morphological changes and significant decline in the number of viable cells (Fig. 6b, c and d). A higher concentration of N-CDs from both sources kill most of the cancer cells as they are stained blue and is confirmed that N-CDs exhibit significant anti-proliferative activity against tumour cells. At a concentration of 200 µg/ml of N-CDs from JFP, there are no viable cells as shown in Fig. 6c. JFP shows a better cytotoxic activity than TP as the cells completely die at a concentration of 200 μ g/ml of JFP (Fig. 6c). TP could destroy only 60% at 200 μ g/ml. Almost 40% of the cells are still alive in case of N-CDs from TP. This proves that the anticancerous activity is more predominant with N-CDs from jackfruit peel compared to tamarind peel. This is the first report on the activity of N-CDs against DLA tumour cells. Similar investigations have been done over silver nanoparticles which utilize a silver precursor like silver nitrate for the synthesis. When compared with silver nanoparticles, in the present work N-CDs are completely derived from waste biomass which implies a cost effective nanomaterial synthesis against DLA tumour cells from mice.

4. Conclusions

In summary, we hereby took the advantage of utilizing waste materials, jackfruit peel and tamarind peel for the preparation of carbon dots. The work combines a green synthetic strategy with promising photoluminescent properties. The optimised reaction conditions could generate size tuned carbon dots possessing a fine degree of graphitization with inherent nitrogen doping. Fluorescence is enhanced by the functionalization of nitrogen and oxygen containing groups. The asprepared N-CDs exhibit good quantum yield and excellent solubility without any surface passivation. In vitro cytotoxicity studies against DLA tumour cells reveal the application of natural biomaterials against cancer cells. The antitumour activity may be due to remarkable antioxidant potential. The eco-friendly production of fluorescent N-CDs opens up broad application prospectus in the realm of biological field due to their multifunctional ability.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Recent trends in the use of green sources for carbon dot synthesis–A short review



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ABSTRACT

Carbon dots, a class of zero dimensional nanomaterials have recently emerged as excellent candidates for versatile applications such as bioimaging, catalysis, sensing and drug delivery. They possess outstanding optical properties, low toxicity, high biocompatibility, and require simple low-cost synthesis methods. Both top-down and bottom-up approaches have been developed for the synthesis since its discovery. Various techniques such as laser ablation, chemical and electrochemical oxidations, thermolysis and sonolysis of carbon precursors have been reported for the synthesis of these key materials. Recently, the attention has been shifted to the synthesis of carbon dots from eco-friendly sources like biomass especially waste biomass as well as other waste, as these precursors provide a partial solution for the mitigation of the omnipresent problem of waste management. This review presents an overview of the various methods and precursors used in the synthetic strategies of carbon dots, with emphasis on green synthesis.

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1. Introduction

Carbon dots (CDs), a relatively emerging member of carbon material family was first reported in 2004 [177]. These materials, whose size ranges less than 10 nm, are composed mainly of amorphous carbon along with nanocrystalline regions of sp² hybridized graphitic carbon. The unique structure and size suggest tunable chemical, physical, optical and electronic properties. They exhibit low toxicity, unique luminescence properties, high water solubility, thermal stability, chemical inertness, and ease of functionalisation. These multifaceted properties make them perfect nanomaterials in numerous fields such as biolabeling, optical sensing, drug delivery, biosensing, energy conversion and catalysis [200]. In addition to their novel properties, easy synthesis from numerous available carbon sources including organic and inorganic materials have attracted the attention of material scientists worldwide. Studies imply that size and surface state have a predominant role in determining the properties. Numerous attempts prove that synthesis as well as post treatment techniques have significant role in tailoring the nature and properties of CDs [22,133].

The main constituents of carbon dots are carbon, hydrogen and oxygen. The synthesis route often determines the proportion of

* Corresponding author. *E-mail address:* mk@macollege.in (M. Kurian). these elements in CDs [165]. Doping with hetero atoms like nitrogen, sulphur and phosphorus improves the properties to a great extent. For example, CDs show photoluminescence with tuneable colours ranging from blue to red on hetero atom doping and the synthetic techniques as well as internal structure of these materials determine the basis for this tuneable emission [101,166]. To an extent, the fragmented graphitic structure and presence of functional group on the surface forms the basis of photoluminescent and electron transfer property [92]. Core and surface electronic states of carbon dots plays a prominent role in the creation of electronic acceptor levels whereas the nature of the surface groups governs their hydrogen bonding capacity which in turn affects the photoluminescence. Also, it has been reported that it is possible to synthesize functionalized carbon dots in a single step and is beneficial in being fluorescent without any doping. They are fit for chemical modification and surface passivation. [124].

Carbon dots have several interesting properties such as excellent optical and electrical properties, biocompatibility, high quantum yield, superior photostability, low toxicity, low cost and exceptional productivity. ([179]. They are slowly replacing semiconductor quantum dots based on toxic heavy metals in invitro studies. Also, they are catalytically active due to their superior ability in transfer. Han et al. introduced an electrochemical etching technique to fabricate well dispersed and uniform carbon quantum dots of average diameter 5 nm. They demonstrated the competence

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Fig. 1. Properties of carbon dots.

of carbon quantum dots to act as effective catalysts in aldol condensation reaction under visible light [60] The properties can be greatly improved by several modifications on CDs. Embedding CDs in host matrices improved the luminescent properties like thermally activated delayed fluorescence and room temperature phosphorescence [82]. Supporting CDs on MoS₂ layers changed the energy level configuration and visible light absorption. Separation and transfer of photogenerated charges greatly improved resulting in the increased production of photoinduced charges thereby enhancing the photocatalytic activity [83]. Han et al. reported an electrochemical synthesis of carbon guantum dots and a hydrolytic method for CDs/SiO₂ porous nanocomposites. Suppression of catalyst aggregation and promotion of catalyst stability are performed by the SiO₂ beads. These porous nanocomposites exhibited high catalytic activity for selective oxidation of cis-cyclooctene under the irradiation of visible light [59]. An overview of the advantages of carbon dots is presented in Fig. 1.

2. Synthesis routes for carbon dots

There are numerous methods for the synthesis of carbon dots that may or may not require tough, stringent or expensive preparation steps. Carbon dots were first synthesised by an arc discharge method. Recently, nitrogen-doped carbon nanoparticles similar to carbon dots were synthesised by Wang et al. by a non-thermal plasma source based on magnetically stabilized gliding arc discharge method [159]. Chemical oxidation, hydrothermal carbonisation, ultrasonic methods, microwave assisted synthesis, solvothermal method, laser ablation technique, thermolysis, atmospheric plasma-based synthesis and electrochemical method are some among them. Different synthesis techniques offer opportunities for tuning the size and constituent elements of carbon dots and thereby the properties. Though the purpose of the present review is to consolidate the greener carbon precursors that could be used for the production of CDs, a short description of some of the commonly employed synthesis techniques is detailed in this section.

Laser ablation is a facile and rapid technique for preparing carbon dots in which carbon target is irradiated by a laser. But the energy consumption is high and quantum yield is low in this method. Also, it is an expensive method which cannot assure control over the size of the nanoparticle [41,106,136]. Hu et al. studied the effect of laser pulse width on size and morphology of carbon dots. They could verify that the pulse width had a huge effect on the nucleation and growth of synthesized particles [72].

In chemical oxidation, carbon precursor is oxidised by a strong oxidant to carbon dots. It is comparatively an easy technique to produce carbon dots in large scale manner. But, lack of homogeneity in the size distribution of resulting particles is a serious disadvantage faced by this method [158]. The role of size and surface states of carbon dots in optical properties and photoluminescence has been investigated. Varying the concentration of HNO₃ used for oxidative refluxing could decide the size of the synthesized particle and selective reduction with NaBH₄ alters the surface states [73].

Carbon dots of high purity and yield with controllable morphology and size can be produced by electrochemical oxidation. But it is of restricted use as the technique involves complicated processing steps. [37,186]. The various electrodes used are graphite rod, carbon fibre and carbon paste. Liu et al. reported electrochemical synthesis which uses graphite electrode as the working electrode, a platinum foil as counter electrode and an Ag/AgCl as reference electrode. They produced CDs with an average diameter of 4.0 \pm 0.2 nm that could be used for the sensing of Fe³⁺ ions in tap water [87].

Ultrasonic energy has been widely used for carbon dot synthesis because of the simplicity of the process, low cost and lack of secondary pollution [79,123]. Wu et al. synthesised amine decorated CDs through an ultrasonic method from graphite rods. The resulting CDs were useful in cobalt (II) ions detection in real samples and nucleic acid sensing in biological cells [174]. Carbon dots, derived from citric acid, urea and poly(ethylene glycol) by ultrasonic processing have been used as lubricant. The lubricating action was attributed to the carbon core and small size, providing a rolling effect [62].

A facile and economic synthesis is offered by microwave method which demands only a short reaction time [57]. Size controllable particles with high yield can be expected in this simple technique, though it is high energy demanding. Also, the technique suffers from the limitation of uncontrollable reaction conditions [65]. A mixture of citric acid and Citrus japonica were carbonised by microwaves to produce biocompatible luminescent carbon dots for biological applications [So et al., 2018].

Solvothermal method especially hydrothermal method is by far the well utilised and common technique for the synthesis of simple, doped and supported carbon dots [16,88,134]. It involves chemical reaction in a solvent like water in a sealed pressure vessel. The advantages of this method are environmental friendliness, relatively mild operating conditions, one-step synthetic procedure as well as good dispersion in solution. As a result, a wide variety of precursors such as aloe [180], papaya [167], apple juice [97], water hyacinth [113], cornstalk [135] and milk [170] have been used for the synthesis of CDs using hydrothermal method. It is an efficient method in terms of its cost effectiveness and ease.

A cost effective solvent free synthesis can be done by thermal decomposition, though the resulting particles lack homogeneous distribution of nanoparticles [24]. Despite several advancements in the field of CDs synthesis, use of stringent reaction conditions, toxic precursors and post synthetic steps for surface passivation are often complicates the process and hinder their widespread applications. Majority of the reports have obvious disadvantages like expensive equipment, use of corrosive chemicals, nonhomogenity of resulting nanoparticles and hence are not economic. [94].; [108,164]. Easier and low-cost synthesis techniques as well as use of eco-friendly precursors have been tried by various research groups [80,114,144]. This review aims at providing an exhaustive list of the various eco-friendly carbon precursors that have been used for the synthesis of CDs. Emphasis is given to the use of var-

ious biomolecules, bio organisms, food waste as well as other industrial wastes such as plastics and sludge. The work presented here offers a perspective on the future technical trends for the development of CDs and CD based materials profitable in applications.

3. Synthesis from green sources

Several synthetic and natural carbon containing substances have been used as precursors for carbon dot synthesis. Conventional bottom-up and top-down methods for the synthesis of carbon dots led to complicated economic and environmental issues due to the requirement of large amounts of toxic solvents, hazardous organic molecules, expensive precursors and high energy. Therefore, considerable efforts have been made to develop green route of synthesis with less harmful precursors.

3.1. Biomass as carbon dot precursors

Biomass refers to the biodegradable fraction of products, waste and residues of biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste (European Directive 2009/28/CE, 2009). It excludes organic materials such as fossil fuels which was formed by geological processes into substances such as coal or petroleum. Biomass valorisation has grown significantly in recent years due to social responsiveness and sustainability-based policies for the conservation of the environment [81,155].

Biomass has been increasingly used as a green source for the synthesis of carbon dots in recent times [9,10,96,183]. It contains various organic substrates such as carbohydrates, proteins, alkaloids, carotenoids etc. Almost all fruits and vegetables as well as commonly found plants have been tried as carbon precursors with varying degrees of success. Atchudan et al. synthesised nitrogen doped carbon dots with average size 5±2 nm from Chionanthus retusus fruit extract by hydrothermal carbonisation. The interlayer distance of these nitrogen doped carbon dots was found to be 0.21 nm from transmission electron microscopic images. These particles exhibited high fluorescence properties, low cytotoxicity and substantial selectivity towards Fe³⁺ ions [12]. Silver ions could be sensed by the carbon dots synthesised from the green plant, broccoli by a hydrothermal method. These blue luminescent water-soluble carbon dots were utilized as potential probe for detection of silver ions through photoluminescence quenching [11]. Highly fluorescent nitrogen and sulphur co-doped carbon dots were synthesised by the photochemical oxidation of carbohydrates in vegetables by Romero et al. [126]. A highly selective and sensitive strategy for the determination of one of the most poisonous ions, Hg²⁺ using carbon quantum dots fabricated via one pot hydrothermal method from apple juice was carried out by Yue et al. [188] TEM images demonstrated their well dispersed spherical shape having an average diameter 2.80.4 nm and the presence of sp² graphitic carbon. These water-soluble carbon dots when compared with other fluorescent materials like glutathione-capped CdS, and CdTe quantum dots had remarkable efficiency in Hg²⁺ determination. In a thought-provoking work, nitrogen-doped carbon dots were synthesized from grass by hydrothermal method. Photocatalytic activity of the resulting particles was tested in the degradation of Acid Blue, Acid Red, Eosin Y, Eriochrome Black T, Methyl orange and Methylene blue dyes. They also served as efficient adsorbents for Cd^{2+} and Pb^{2+} ions from water [128].

In many a case, different variations of the same precursor were tried by various research groups with varied results, illustrating the importance of synthesis methods and conditions. For example, lemon has been chosen by various researchers for the synthesis of CDs [63,68,130,132,139]. Highly water soluble quasi spherical nanoparticles with average size of 5.8 nm were obtained from lemon juice by hydrothermal method which could be used as fluorescent probe in cell imaging [148]. Red-emitting carbon dots that exhibit excitation-independent emission at 631 nm with a high quantum yield of 28% in water have been synthesized by heating an ethanol solution of pulp-free lemon juice. The resulting CDs with an average diameter of 4.6 nm exhibited low cytotoxicity and good photostability, allowing them to be used as luminescent probes for in vitro an in vivo bioimaging and light-emitting diodes [39]. Magnetic Fe₃O₄/CDs have been synthesised from grape fruit, lemon, turmeric extracts using magnetite as capping agents in a hydrothermal method. These particles could be used as a nontoxic photoluminescence sensor for detecting Escherichia coli bacteria [4]. Formamide solution of pulp-free lemon juice yielded CDs that exhibited photoluminescence emission at 704 nm with high quantum yield of 31% in water and an average size of 5.7 nm. The intense near-infrared emission of these CDs was attributed to their surface states, which in turn are modulated by both the particle size and amount of nitrogen doping. They could be used as fluorescent probe for in vitro and in vivo bioimaging due to their photostability and low cytotoxicity, [40]. Hoan et al. also synthesised highly luminescent carbon dots from lemon juice by a simple one-pot hydrothermal method at different temperatures, time, ageing of precursors, and diluted solvents to control the luminescence of C-dots. The synthesised C-dots had strong green light emission with quantum yield in the range of 14- 24%, suggesting potential applications in optoelectronics and bioimaging. [2019] CDs have also been prepared from lemon and onion biomasses using one-step microwave-assisted carbonization method. These CDs displayed excellent water solubility and quantum yield of 23.6%. Fluorescent resonance energy transfer between the CDs and riboflavin could be achieved with CDs acting as donor and riboflavin as acceptor allowing the development of an accurate and fast analytical method for the determination of riboflavin in multivitamin/mineral supplements [103]. Lemon juice has also been used in conjunction with glycerol for the synthesis of carbon dots that exhibited quenching of emission by nitrobenzene and Hg²⁺ ions. Electrostatic attraction plays a major role in the interaction with Hg²⁺ ions whereas the quenching mechanism involves predominantly static and dynamic quenching. [45] Carbon dots synthesized by a simple hydrothermal method using lemon juice as carbon precursor showed potential applications in labeling and detection of molybdenum ion (Mo^{6+}) to a detection limit as low as 20 ppm [67]. Meanwhile, carbon dots synthesised by the hydrothermal treatment of lemon juice at 240 °C were found to emit bright green luminescence. They could be used for detection of ion V^{5+} in water and serum to a limit of 3.2 ppm even with interference by high concentrations of other metal ions [66]. Watersoluble, nitrogen-doped, fluorescent carbon quantum dots consisting of a ring type moiety in the centre surrounded by graphitic network was synthesised from lemon juice and ammonia by hydrothermal treatment. These particles could act as efficient fluorescent probe for selective detection of Fe³⁺ with a detection limit of 140 ppb. The extremely low detection limit was attributed to the static quenching in addition to dynamic quenching [102]. In situ reduction of Ag⁺ and Au³⁺ ions was done with CDs prepared by carbonization of lemon extract in a one-pot microwave assisted technique within 6 min. The synthesized pristine C-dots, Ag/C-dot and Au/C-dot nanohybrids colloidal solutions exhibited bright photoluminescence (PL) at ~515 nm with significant quantum yield of 48.3%, 46.2%, 62.2% and PL emission lifetime of 3.6 ns, 9.4 ns and 9.0 ns respectively. These C-dots-based nanohybrids exhibited no signs of cytotoxicity in colon cancer cell lines and were easily internalized for fluorescence bioimaging [Sajid et al., 2019]. Transition metal ion (Co²⁺, Fe²⁺, Mn²⁺ and Ni²⁺) doped carbon dots were synthesised by microwave method with citrus lemon as the carbon source. These water soluble, tiny carbon dots with average size 3.2 ± 0.4 nm were found to be promising nanoprobes for bioimaging [127].

Similar to citrus lemon, garlic also has been tried as a green source for the synthesis of CDs by various research groups. Photostable, water dispersible and blue fluorescent emitting nitrogen and sulphur doped carbon dots were synthesised by Zhao et al. through hydrothermal synthesis using garlic as precursor. The as prepared CDs exhibited outstanding biocompatibility, excellent optical properties and radical scavenging activity which prove them to be amazing materials in bioimaging [198]. Garlic was used by Sun et al. also to synthesize carbon dots. N content and formation of C-N and C=N were critical to improve the quantum yield. Quenching the fluorescence of the CDs in presence of Fe^{3+} ion made these CDs a luminescent probe for selective detection of Fe³⁺ ion [145]. Luminescent garlic carbon dots with superior photostability are synthesized via microwave assisted heating. The garlic dots are biocompatible, have low toxicity and can be used as benign theranostic nanoparticles for bioimaging with efficient antioxidative effects towards macrophages [184].

Comparatively rarer and unlikely bio resources also have been used as carbon precursors for carbon dots. For example, pork has been used carbon source to prepare CDs that acted as efficient sensors in the determination of uric acid in human serum and urine samples [196]. In a similar vein, tobacco was used by Miao et al. [99] for the synthesis of bright-blue fluorescent carbon dots. These particles could be used for distinguishing the three tetracyclines on a test strip. Feng et al. used silkworm chrysalis as the natural carbon source for the microwave assisted synthesis of CDs that could be used in bioimaging [53]. Several reviews are available in literature in this area and hence in the present review, not much importance is given to the use of plants and plant extracts [32,98,131]. Instead, the review focus on the recent trends in the synthesis of CDs from other resources such as food and other wastes, bio active molecules and micro-organisms.

3.2. Micro-organisms as carbon dot precursors

Microorganisms have been used as biofactories for the green synthesis of several nanomaterials such as metal nanoparticles like Ag, Au etc. [93] and metal oxides like ZnO and Cu₂O, MgO, [50]. The method is time saving, eco-friendly, and hence is treated as a safe production method that minimize waste. Recently, several micro-organisms such as yeast, bacteria and algae have been used as green precursors for the synthesis of carbon dots [74,194]. For example, mushroom fungus has been used as a carbon source in an environment friendly synthesis procedure. Sensitive assay of hyaluronic acid and hyaluronidase could be done on human urine samples [185]. Bacillus cereus in a one-step hydrothermal process yielded CDs that act as a sensitive sensor for p-nitrophenol detection with a detection limit of 0.11 μ M. The CDs exhibited excellent biocompatibility, high photostability, multicolour fluorescence emission properties and low or no biotoxicity [191]. In another study, N doped carbon dots with average size of 4. \pm 2.0 nm were synthesised using rhizobium from soy as the carbon and nitrogen source by a hydrothermal method. These particles exhibited excellent fluorescence and were used for the determination of chlortetracycline hydrochloride with a detection limit of $0.254 \,\mu\text{M}$ [193]. Biomass of Lactobacillus plantarum could be converted to fluorescent CDs with low cytotoxicity by a one-step hydrothermal carbonization which exhibited potential applications in biofilm treatment [86]. On using penicillin G as the carbon source, the synthesised CDs exhibited aggressive antibacterial activity against Staphylococcus aureus, E. coli (DH5a), MDR E. coli and Methicillin-resistant Staphylococcus aureus [137].

Diverse varieties of algal biomass have been used by different scientists in an attempt to create CDs with diverse applications. The mineral nutrients in biomass were found be important for the composition, crystallinity, dispersion and photoluminescence properties of CDs produced. [192]. Zhang et al. used Nannochloropsis algae biocrude oil as a precursor for synthesing N and S doped CDs. The synthesised samples exhibited potential application of CDs for bioimaging in plant cells [190]. N and S co doped CDs were prepared hydrothermally from bloom-forming green alga Dunaliella salina. The obtained CDs with an average particle size of 3.2 ± 0.5 nm could be used for algal imaging, scavenging of 1, 1diphenyl-2-picrylhydrazyl and hydroxyl radicals, selective detection of Fe(III), and visible light-induced photodegradation of methylene blue and methyl violet [84]. On using eutrophic algal blooms as the carbon source, highly luminescent CDs of average particle size \sim 8 nm with high photostability, luminescence stability in different environments, low cytotoxicity, and excellent cell permeability could be synthesised [121]. In an interesting study, Plácido et al. used microalgae biochar as the carbon source. The resulting CD fluorescence was stable over a wide range of pH and resistant to photo-bleaching. making them suitable as fluorescence probes. These particles could be used as a transducer for detecting heavy metal ions in aqueous systems [115].

Carbon dots synthesised by a hydrothermal pyrolysis of Saccharomyces cerevisiae yeast could be used for the sequential detection of manganese(VII) and L-ascorbic acid in tap water, river water, and medicinal herb samples with satisfactory results [56]. Fluorescent carbon dots with photoinduced bactericidal functions and bio-imaging in bacterial viability assessment were synthesized from beer yeast. The CDs with high quantum yield possessed high negative zeta potential (-41.7 mV) and low cytotoxicity and hence could be used as an efficient dye for bacterial viability evaluation [54]. Wu et al. synthesised CDs from yeast extract in a high yield of 65.8%. These nanoparticles when doped on polyvinyl alcohol could act as fluorescent shape memory material [173]. Ji et al. synthesised fluorescent carbon dots (from yeast Cryptococcus podzolicus 5–2 by hydrothermal synthesis method. These nanoparticles exhibited excellent biocompatibility with multicolour fluorescence emission properties and could be used for bioimaging and detection of Ag(I), 2,4-dinitrophenol and 4-nitrophenol [76].

3.3. Carbon dot synthesis from bioactive molecules

In recent times various bio active molecules have been widely tried by researchers worldwide in order to reduce the severity of the synthesis conditions as well as to synthesise particles with exceptional properties [2,89,96]. Niu et al. synthesised uniform, spherical nitrogen doped carbon dots of average size 8 nm by one pot hydrothermal carbonisation of alanine and ethylene diamine. These biocompatible and low cytotoxic CDs were used as sensitive sensors for determining dihydronicotinamide adenine dinucleotide [104]. A microwave assisted strategy using L- ascorbic acid as the carbon precursor and β -alanine as the nitrogen dopant produced carbon dots of quantum yield 14%. These photoluminescent, less cytotoxic carbon dots were used as staining probe for imaging of HeLa and MDCK cells. [49]. Pyrolysis of D glucose and L aspartic acid resulted in fluorescent, highly biocompatible carbon dots which are capable of targeting C6 glioma cells. The in vitro and in vivo studies paved the way for a promising ability of these carbon dots to target brain glioma with high selectivity [201].

Phosphorus and nitrogen co-doped carbon dots synthesised from adenosine disodium triphosphate exhibited bright blue fluorescence on exposure to UV illumination. These CDs were proven to be excellent probes for cellular imaging [Zheng et al., 2017]. Deoxyribonucleic acid (DNA) yielded CDs with efficient internalization in pathogenic fungal cells, negligible cytotoxicity, good PL

Table 1

Synthesis methods and applications of carbon dots from bio active precursors.

Precursor	Synthetic method	Size (nm)	Applications	Reference
Citric acid, urea and thiourea	Microwave	10	Sensor for iodide and Hg ²⁺	[147]
Citric acid and ethylenediamine	Refluxing	3	Cell imaging and sensing	[168]
Urea and malonic acid	Hydrothermal	2-3	Detection of picric acid	[52]
Citric acid and thiourea	Hydrothermal	4-6	Sensing of uric acid	[169]
Ascorbic acid	Refluxing	3.20 ± 0.72	Flourescent probes	[77]
Citric acid and cystamine dihydrochloride	Hydrothermal	1.3 - 2.3	multicolour bioimaging	[25]
Folic acid	Hydrothermal	4.5 ± 1.0	Detection of Hg ²⁺ ions	[189]
Vitamin B1	Hydrothermal	3.2	Detection of Fe ³⁺ ions	[175]
Gelatin	Hydrothermal treatment	1.7	Bioimaging agent	[85]
Dopamine	ultrasonication	<10	Detection of Fe ²⁺ ions	[91]
Albumin	Hydrothermal	<10	Bio imaging of human breast cancer Bcap-37 cell	[69]
Thymidine	Hydrothermal method	<10	Detection of Cr (VI)	[100]
Hyaluronic acid and citric acid	Hydrothermal method	<10	Detection of Fe ³⁺ ions and folic acid	[172]
Collagen	Hydrothermal	<10	Nanophotonics	[95]
Urea and ethylenediamine tetra acetic acid	Solvothermal in ethylene glycol solvent	<10	Fe ³⁺ ion and apoferritin detection	[61]

stability, and high biocompatibility. They could be used as nanotrackers in microbial studies and for detection of dopamine [109]. Nucleobases such as adenosine, cytidine, thymidine or guanosine were used as nitrogen sources along with citric acid for the synthesis of CDs. Multiple metal ions, like Cu^{2+} and Hg^{2+} ions could be detected and quantified using these CDs. Guanosine derived CDs showed maximum efficiency [202]. Chakraborty et al. prepared Fe²⁺ doped carbon dots from haemoglobin precursor and used them for hydrogen peroxide sensing and pro-drug activation [21]. Other biomolecules reported for CD synthesis and the potential applications of the resulting particles are tabulated in table 1.

Recently, bioactive molecules such as drugs have also been used to synthesise CDs. Aspirin, a common anti-inflammatory medication was used to synthesize CDs through a one-step microwaveassisted method. These nanoparticles showed excellent cellular imaging and anti-inflammation properties. [178]. Jiaosanxian, a traditional Chinese medicine used for dyspepsia therapy was used for the preparation of carbon dots with an average diameter of 4.4-6.4 nm. These CDs were effective in regulating blood sugar indicating its potential use as a hypoglycaemia agent. They also exhibited sensitivity of fluorescence response to Cr(VI) [143]. Carbon dots derived from procaine drug exhibited biomarker function and anticancer activity. The particles were synthesized by condensing procaine, citric acid and ethylenediamine via hydrothermal synthesis [197]. Surface passivated CDs were obtained from curcumin by a hydrothermal method. These particles exhibited rapid free radical scavenging ability and could be used as optical nanoprobes and for biolabeling [108]. Fluorescent carbon dots were prepared from vancomycin, an antibiotic by a hydrothermal treatment. These particles when loaded with flutamide were prospective candidates for imaging and drug delivery in cancer cells [42]. A well-known antibiotic aminosalicylic acid was used as the precursor to produce bright carbon dots of average diameter 6 nm. The as-prepared particles were found to be biocompatible, less cytotoxic and could act as efficient sensors of Fe³⁺ ions in living cells [140].

3.4. Carbon dot synthesis from waste biomass

Management of waste biomass as a result of population growth and the ever-increasing need for the production of horticultural products is a major challenge to be addressed. Now a days, the attention has been shifted from biomass to waste biomass for the production of value-added products in mild experimental conditions. Waste biomass constitute a sustainable and cheap source of raw materials that can be considered as an effective and potential alternative feedstock for the preparation of carbon dots [17,18]. Water soluble highly fluorescent, blue emitting carbon quantum dots of size 3–5 nm were prepared from coconut shell by hydrothermal method. Since the carbon precursor is an agricultural waste, the preparation proceeded through a cost effective and eco-friendly method. These CDs could be utilized as fluorescence based pH sensor as they were sensitive over a range of 4-11. They were biocompatible and found applications in cancer treatment [27]. A large scale synthesis of water soluble carbon nanodots with size approximately 4nm from food waste derived sources was reported by Park etal. The presence of oxygen containing groups on their surface makes them highly water soluble and their outstanding photostability and low cytotoxicity promises their immense applications in biomedical imaging [112]. Lignocellulosic waste was used for preparing fluorescent carbon dots by a microwave assisted reaction. Their exceptional physicochemical properties suggested various potential applications [125]. Low-temperature carbonization of watermelon peel yielded CDs of particle sizes ~ 2.0 nm, strong blue luminescence, acceptable fluorescence lifetime and good stability. These particles showed potential for high-performance optical imaging probes in cells [203]. Magneto fluorescent CDs synthesised from chitin from waste crab shell and doped with Gd³⁺, Mn^{2+} , and Eu^{3+} showed excellent potential as a T_1 contrast agent in MRI. They could also be used as diagnostic probes and theranostic agents [187]. An overview of the waste biomaterials that have been reported in literature as carbon dot precursors is given in table 2.

3.5. Synthesis of carbon dots from other waste materials

Synthesis of carbon dots from waste is a much researched subject recently as it contributes greatly to solid waste management [64,156]. For example, clotted cream on thermal carbonisation yielded CDs of average size 6.6 nm. These particles when coated with Pd nanoparticles showed high catalytic activity for the Heck and Suzuki coupling reactions [38].

Value added utilization of sewage sludge was done by converting the organic compounds contained in it to CDs with microwave irradiation. Quantum yield of 21.7%, higher than the most values of waste-derived CDs was obtained. Further, these CDs were sensitive and selective sensor for para-nitrophenol [71]. Carbon dots of average size 17.5 nm were prepared by a microwave-assisted reaction catalysed by a solid acid catalyst from the primary sludge of pulp and paper industry [125]. In an interesting work, waste black toner ink was carbonized in a muffle furnace at \sim 600 °C followed by oxidation to functionalized iron-oxide nano-carbons. These particles were effective in the photocatalytic degradation of Congo Red dye in sunlight [129]. Carbon dots could be synthesised from waste paper also by solvothermal method. The prepared CDs could be easily used to prepare anti-counterfeiting ink and fluorescent flexible film [111]. Hydrothermal treatment of waste paper and urea was found

 Table 2

 Synthesis conditions and applications of waste biomass derived carbon dots.

Source	Synthesis Method	Size	Applications	Referenc
Crab shells	Sonochemical	<10 nm	Theranostic applications	[35]
Fish scales	Hydrothermal	<10 nm	Environmental and clinical Fe ³⁺ analyses	[195]
Shrimp shells	Calcination	<10 nm	Detection of chromium(VI) ions	[149]
Prawn shells	Hydrothermal	4 nm	sensing probes for Cu^{2+} detection	[55]
Sugarcane bagasse	Hydrothermal carbonization	1.8 nm	cells	[44]
Sugarcane bagasse char	Hydrothermal	7.5 nm	Drug carrier for acetaminophen	[28]
Sugarcane bagasse	Chemical oxidation	5 nm	Bio-sensor, bio-imaging and drug delivery	[150]
·····	KOU shamiaal astivation	10	applications	[[]]]
Sugarcane bagasse	KOH chemical activation	<10 nm	Adsorbent for naphthalene	[51]
Palm shell powder	Hydrothermal	<10 nm	Fluorescence probe for nitrophenols	[141]
Owarf banana peel	Hydrothermal	<10 nm	Detection of Fe ³⁺ ion and bioimaging	[13]
Drange pericarp	Hydrothermal	<10 nm	Nano-biotechnology	[43]
Drange waste peels	Hydrothermal carbonization	<10 nm	Photocatalyst for degradation of naphthol blue-black azo dye	[120]
Pineapple peel	Hydrothermal	<10 nm	Quantification of Hg ²⁺ , electronic security devices and as memory element	[153]
Aloe peel	Hydrothermal carbonization	<10 nm	Electrode for dye-sensitized solar cells and super capacitors	[160]
anana peel	Hydrothermal	5 nm	Bioimaging	[14]
Mangosteen peel	Pyrolysis	$\sim 2-15 \mathrm{nm}$	Fluorescent probes	[14]
Dried lemon peel	Hydrothermal	$\sim 2-15$ him < 10 nm	Determination of carmine	
				[142]
Wheat straw	Hydrothermal	<10 nm	Detection of F^- and cellular imaging	[90]
Chickpea peel	Pyrolysis	7.0 nm	Bioimaging	[138]
Sugarcane bagasse, garlic peels, taro peels	Ultrasonic wet chemical oxidation	<10 nm	Sensing of fluoride ions	[19]
Drange peels	Hydrothermal	$2.9\pm0.5\text{nm}$	Optical switching devices, bio-scanning, bio-imaging	[146]
Citrus fruit peels	Sand bath assisted method	<10 nm	Biological labels for cellular imaging	[58]
Cassava peels	Hydrothermal	<10 nm	Bioimaging and metal ion and salt biosensing	[119]
Drange peels	Hydrothermal	10 nM	Cr(VI) detection	[162]
Grapefruit peel	Hydrothermal	<10 nm	Sensitive detection of p53 protein in biological fluid	[176]
Banana peels	Hydrothermal	<10 nm	Biosensing, electronics, catalysis	[107]
	Charring	<10 nm	Photodegradation of crystal violet	
Bitter Apple peels .emon peel	Hydrothermal	<101ml 1–3 nm	Detection of Cr ⁶⁺ ions, photodegradation of	[3] [152]
		10	methylene blue	[00]
Apple seeds	Pyrolysis	<10 nm	Detection of 4-nitrophenol, bioimaging	[23]
Duck blood	Hydrothermal	<10 nm	Detection of glucose	[171]
Duck breasts	Roasting	2.59–1.95 nm	Bio imaging	[29]
Sugar beet pulp, grape marc, tomato peels and seeds, olive pomace	Hydrothermal	<10 nm	Production of biofuel	[20]
Date kernel	Hydrothermal	<10 nm	Probe for Zoledronic acid drug in human serum and cellular imaging	[8]
Allium sativum peel	Oxidative pyrolysis	<10 nm	in vitro biomarker	[34]
ychee exocarp	Hydrothermal	<10 nm	nanoprobe for cancer cells	[181]
Mango peel	Pyrolyzation with oxygenolysis	2–6 nm	Cellular labeling on A549 cells, detection of Fe ²⁺ ions	[78]
Chicken egg shell membrane	Hydrothermal	<10 nm	Probe for base pair selective DNA recognition	[117]
Dairy waste whey	Pyrolysis	<10 nm	Sensor selenite	[36]
ea residue	Chemical oxidation	<10 nm	Imaging of yeast cells, detection of tetracycline	[30]
lea leaf residue	Oxidative pyrolysis	<10 nm	Sensor for gefitinib	[71]
Vaste tea extract	Hydrothermal	<10 nm	Sensor for CrO ₄ ²⁻ , Fe ³⁺	[26]
Passion fruit shells	Hydrothermal	<5 nm	Fluorescent probe	[182]
Dil palm empty fruit bunches	Hydrothermal	3.4 nm	Detection of Cu^{2+}	[1]
Rice husk	Thermal carbonization	<10 nm	Detection of Sn(II)	[105]
Spoiled milk	Hydrothermal	<10 nm	Sensing of Cr ⁶⁺ ions	[15]
Naste tea leaves, peanut shells	Hydrothermal	<10 nm	Biomarker	[204]
Papaya waste	Hydrothermal	<10 nm	Detection of Cr (III), Cr (VI)	[116]
Naste tea residue	Pyrolysis in controlled condition	<10 nm	Detection of free chlorine	[47]
Rice husk	Hydrothermal	4–5 nm	Detection of alcohol vapors	[151]
Durian peel	Pyrolysis	10 nm	Dopants for electrodes in supercapacitor	[118]
Tender coconut waste	Hydrothermal	<10 nm	Detection of ETA in urine and water	[48]
Cat feed stock waste	Hydrothermal carbonization	<10 nm	Fluorescence probe to Fe^{3+} ion detection	[40]
Pseudo-stem of banana plant	Hydrothermal	<10 nm	Probes for multi-coloured imaging of HeLa and MCF-7 cells	[5] [154]
Spent coffee grounds	Solvent-free carbonization	2.1-3.9 nm	Fluorescent probes for Fe ³⁺ ions	[30]

to yield N doped CDs with strong blue-green luminescence. These particles with good optoelectronic properties could be fabricated into broadband photodetectors by incorporating ZnO nanorod arrays [161]. Cellulose waste papers were converted to CDs by a microwave method assisted by ionic liquids [75]. Waste kitchen chimney oil was used to prepare CDs which exhibited excellent optical properties, superior biocompatibility, and water solubility. These particles with an average size of 1-4 nm could sense Fe³⁺ ion in a wide range of concentration with a detection limit of 0.18 nM [33]. Fluorescent carbon dots of size 5 nm could be prepared from kerosene fuel soot by acid treatment. They could be used for the selective and sensitive detection of explosives like picric acid and metal ions like Cu^{2+} and Fe^{3+} [157]. Candle soot also has been used as carbon precursor for the preparation of CDs by oxidation process. These particles displayed ability for the detection of mercury (Hg (II)) and iron (Fe (III)) metal ions. Net surface negative charge of the CDs played an important role in the sensor action and binding efficiency towards metal ions [110].

Plastics and polymers pose great threat to the environment due to their non-biodegradable nature and the huge quantities that are discarded as waste after use. Conversion of plastic waste into value added products is a prime area of research to environmental scientists worldwide. Waste polyethylene terephthalate or PET could be converted to fluorescent carbon dots by air oxidation followed by hydrothermal treatment in aqueous H₂O₂ solution. The particles exhibited unique photoluminescence properties and were used for the detection of ferric ion (Fe^{3+}) [70]. Another common polymer waste, polystyrene also was converted to nitrogen-doped CDs. The materials with unique photoluminescence properties could be used for the sensitive detection of Au^{3+} ions [122]. Polypropylene plastic waste has also been converted to CDs by heating near its melting point. The potential applications include photocatalysis, bioimaging and sensing in optoelectronic materials. [6]. Polyurethane foam, another plastic that is usually discarded as waste after its use also could be converted to N doped CDs by pyrolysis. The carbon dots with high quantum yield exhibited superior selectivity towards Ag⁺ ions with a detection limit of 2.8 μ M [31]. Water soluble fluorescent nitrogen doped carbon dots were synthesised from polyacrylamide by hydrothermal method. The resulting particles were used for the selective detection of one of neurotransmitter, dopamine. Zhao et al. demonstrated that these carbon dots exhibited a linear graph between flouresence quenching and dopamine concentration in the urine sample with high selectivity [199].

4. Conclusions

In this review, we have described the recent advances in the synthesis of carbon dots, focusing on newer precursors. The use of renewable, inexpensive, and green resources not only meets the urgent need for large-scale synthesis of CDs, but also promotes the development of sustainable management.

However, considering the recent progress in the green synthesis of carbon dots, certain points need to be noted. First, most of the present synthetic procedures have been done on a laboratory scale. Large scale production of CDs using these precursors have not been conducted in most cases and as a result, it is still to be known whether the prepared samples would exhibit the unique properties exhibited in the lab scale preparation. If large scale production from green sources is realised, it will have a great impact from the economic and environmental points of view since CDs are one of the most sought for materials in many applications. Second, the comprehensive understanding of the crystallization is essential for the design of CDs with versatile optical properties. The mechanism of multiphoton fluorescence and up-conversion emission is still unclear, and further research is needed to elucidate this phenomenon. Similarly, surface chemistry, particle size and aspect ratio, among other properties, have critical influence on the performance of CDs in energy and engineering materials. Third challenge is the synthesis of long wavelength emissive CDs as most of the research works point towards the absorption wavelength and emission wavelength in the ultraviolet/ visible region, which is too short for most biomedical applications. UV light disrupts important molecules such as DNA and proteins, thereby limiting the biomedical and catalytic applications. NIR light is preferred over UV/visible light because it penetrates deep into tissues and has low biological toxicity.

Thus, the use of a more environmentally friendly method to prepare high-quality CDs is still an urgent question waiting to be solved. However, based on the pace of carbon dot research worldwide, in the future, we can expect the advent of more facile and robust synthetic routes and creative applications to better realize the potential of the increasingly important CD materials. Further, combination of various green synthesis techniques is also necessary to overcome a balance of competing aspects during the synthesis.

Declaration of Competing Interest

There are no conflicts of interest to declare.

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Microwave assisted green synthesis of silver nanoparticles for optical, catalytic, biological and electrochemical applications

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ABSTRACT

Plant-derived nanoparticles have multi-functionalities owing to their ecological origin and biocompatible nature. A novel and stable silver nanoparticle (AgNP) was reported here using *Cyanthillium cinereum* (*C. cinereum*) as a reducing as well as capping agent by rapid microwave-assisted green method. The synthesized nanoparticles revealed their crystalline and spherical nature with an average size of 19.25 \pm 0.44 nm in HR-TEM analysis. The excitation of electrons from occupied d-bands to states above the Fermi level while employing photoluminescence studies of AgNP indicated their awesome optical properties. Rapid decomposition of dangerous organic dyes like methylene blue and fuchsine in the catalytic presence of AgNP was evidenced from simple UV–visible spectral analysis. *In vitro* antioxidant potential assessed by DPPH assay indicated an IC₅₀ value of 40.80 \pm 0.14 µg/mL for the new AgNP. A substantial control on the growth of pathogenic bacteria such as *Staphylococcus aureus* and *Klebsiella pneumonia* can be achieved by synthesized nanoparticles as demonstrated by the well diffusion method. AgNP was also functioned as a non-enzymatic electrochemical sensor with a sharp oxidation peak with peak potentials at 0.366 V and it has a wide application as a bio sensor in neurobiology especially in the detection of neurotransmitters like dopamine with high sensitivity.

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KEYWORDS

Cyanthillium cinereum; AgNP; photoluminescence; biosensor; carbon paste electrode

Introduction

Nanotechnology is an emerging area which has shown an unprecedented growth that embrace diverse applications [1,2]. This technology mainly employs the use of particles with the dimensions of 1–100 nm [3]. Nanomaterials have its usefulness in diverse fields such as electronics, biomedical, biotechnology and therapeutics. In the technology arena, silver nanoparticles (AgNPs) occupy a significant position among various nanoparticles, owing to its cost-effectiveness, nontoxic and eco-friendly nature [4]. Bactericidal and bacteriostatic properties contribute towards its use as antimicrobial agents [5,6].

The properties of nanoparticles depend mainly on its shape, size and surface area which was inherently influenced by its mode of synthesis and tentative conditions [7]. Physico-chemical methods are the most common way for the synthesis and stabilization of metal nanoparticles. Chemical methods employed includes sonochemical [8,9], electrochemical [10], colloidal [11] and thermal decomposition methods. Separate agents are required for the synthesis and also for the maintenance of their stability [12]. Green synthetic methods gain much significance owing to their non-toxic, sustainable and green reductants and surfactants which eliminate the over use of hazardous chemicals [13–15]. It is cost effective, uses

non-toxic renewable materials, employs low temperature, and hence considered to be more environment friendly. Silver nanoparticles are synthesized through green process mainly employing various parts of plants such as leaf [16], stem [17], fruit [18], bark [19], shells [20], roots [21] and flowers [22] as a reducing agent. Green synthetic method is known to generate particles with reasonably good morphology and stability.

Silver nanoparticles differ from all other metal-based nanoparticles in its unique optical, electrical and biological properties and wide application in bio sensing, catalysis, imaging, drug delivery and also in cancer treatment [23]. It was reported that the green synthesized AgNPs using leaf extracts of Azadirachta indica [24], Manilkara zapota [25], Rosa brunonii Lindl [26], Jatropha curcas [27], etc. showed excellent antibacterial activity owing to its high surface area to volume ratio [28,29]. Green synthesized AgNPs are approved as efficient catalysts for photocatalytical degradation of organic pollutants [30-33]. Microwave synthesized AgNPs from bio-waste (banana leaves) extract are polydispersed in nature and exhibit prominent antibacterial activity. These particles fight against lung cancer and breast cancer cells by endorsing inhibition of cell migration and proliferation on low concentrations [34]. The monitoring of thiol and protein adsorption as well as the bioaffinity can be examined using the silver-nanoparticles-on-plastic sensors [35].

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There are various reports on photocatalytic and bactericidal effects of nanocomposites. Co₃S₄-SnO₂/PVPCS composites work better than ${\rm SnO}_2$ nanoparticles, and ${\rm Co}_3{\rm S}_4{\rm -}{\rm SnO}_2$ nanocomposites in lidocaine degradation and photocatalysis. This composite also showed a good antibacterial effect against Staphylococcus aureus, and Escherichia coli and showed antifungal effect against Candida albicans [36]. Likewise, Cr₂O₃/cellulose composites showed an efficacy in photo-degradation of crystal violet and bactericidal effect against Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Streptococcus pyogenes [37]. There are also reports on efficacy of CuS/polyvinyl alcohol-chitosan (CuS/PVACS) in photo-degradation with malachite green solutions in which 96.51% of malachite green was found to be degraded by CuS/PVACS upon UV-irradiation in 60 min. CuS/ PVACS was also evaluated for its antibacterial activity against gram positive and gram negative bacteria in which the nanocomposite has shown bacteriostatic behaviour versus Escherichia coli, Pseudomonas syringae, Staphylococcus aureus, and Streptococcus pneumonia [38]. Silver sulphide-magnesium oxide/graphene oxide (Ag₂S-MgO/GO) nanocomposite synthesized via sol-gel/ultrasound method showed the highest rate of photo-degradation of rhodamine B (RhB) under UV light (98.8%) and visible light (64.8%) owing to the enhanced charge transfer efficiency via decreasing band gap amount; reduced e/h + recombination of MgO with the Ag₂S crystal and an enhanced removal efficiency with the supported on grapheme oxide. This showed a good antibacterial and antifungal activity against Bacillus vallismortis, Escherichia coli, Aspergillus flavus and Trichoderma viride [39]. AgO, CoO, CdO nanoparticles and AgO-CoO-CdO heterometal oxides synthesized by the chemical method showed a substantial degradation of dye and also showed good antibacterial effect against Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa and B. cereus [40]. Silver-platinum (Ag-Pt) nanoparticles synthesized using the Crocus sativus L. plant ethanolic extract, showed highest antioxidant properties compared to the Ag nanoparticles and ascorbic acid (AA) and demonstrated the substantial antimicrobial and cytotoxic activities against pathogenic microbes and MCF-7 breast cancer cell line. The environmental chemistry analysis depicts that methyl orange can be degraded from water by catalytic degradation process with sodium borohydride (NaBH₄) [41].

Cyanthillium cinereum (Less.) H. Rob. (Asteraceae) commonly called as little ironweed has been consistently known for its medicinal properties and also get its recognition in the Ayurveda's [42]. This plant has possessed excellent antibacterial, antiviral, analgesic antipyretic and anticancer activities [43,44]. The current work reports the synthesis of AgNPs via eco-friendly green route microwave-assisted synthesis utilizing the leaf extract of Cyanthillium cinereum as the reducing as well as stabilizing agents. The formation of AgNPs at different concentrations and also their stability at different intervals of time were evaluated using UV-vis spectroscopic technique. The obtained nanoparticles were properly characterized using XRD, FE-SEM and TEM techniques. The antioxidant property of the noble metal nanoparticles could be evaluated using 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay. The ecological importance of the AgNPs was assessed in the

degradation of polluting organic dyes and thus proved to be a material of immediate relevance in the contemporary era. The *in vitro* antibacterial scopes of the AgNPs were also tested. Optical properties and electrochemical properties as sensor for the detection of dopamine (DA) were evaluated.

Materials and methods

Materials

All the chemicals used were of analytical grade. Silver nitrate (AgNO₃; 99.8%), methylene blue, fuchsine and NaBH₄ were purchased from Merck India Ltd. (Bengaluru, India).

Preparation of plant extract

Fresh and healthy leaves of *Cyanthillium cinereum* (*C. cinereum*) were collected and washed well with distilled water and dried in air. Then, 25 g of dried leaves were cut into small piece and boiled with 200 mL of deionized water taken in a round bottom flask fitted with water condenser for 20 min. It was cooled and filtered using Whatman No 1. filter paper. The plant extracts thus obtained were stored at 4° C in refrigerator and used as a reducing agent within two days.

Synthesis of silver nanoparticles

Ten millilitres of the plant extract was added to 100 mL of the varied concentrations of aqueous $AgNO_3$ solution (1 M to 1 mM) at a ratio of 1:10 (v/v). The resulting mixture was continuously stirred and subjected to microwave irradiation in an oven operating at a power of 800 W and frequency 2450 MHz until the solution changed its colour. The bioreduction of Ag^+ ions to Ag0 was monitored by analysing samples at 3, 4, 5 and 6 min intervals of reaction time using UV-vis spectrophotometer [45]. The synthesized nanoparticle was then dispersed in double distilled water and centrifuged. The separated particles were dried and used for further analysis.

Characterization of silver nanoparticles

The absorption spectra of the synthesized nanoparticles were analysed using Shimadzu UV-1800 spectrophotometer (Kyoto, Japan) at a wavelength of 300-700 nm [46]. XRD measurement was made on a Bruker AXSD8 advanced powder X-ray diffractometer (Billerica, MA). Cu-K α (λ = 1.54 Å) radiation was used as the X-ray source (40 kV, 35 mA) and 2θ range from 2 to 800 and the scanning rate used was 0.05°/s. The XRD sample was prepared by drop coating the nanoparticle solution on a glass slide followed by drying under ambient condition. The mean particle diameter of AgNP was calculated from the XRD pattern according to the line width of the plane, reflection peak using Scherrer formula. $D = 0.9\lambda/\beta \cos \theta$ where D is the average crystalline domain size perpendicular to the reflection planes, λ is the X-ray wavelength; β is the full width at half maximum (FWHM) and θ is the diffraction angle [15]. HR-TEM images were recorded using JEOL JEM-2100 microscope (JEOL Ltd., Tokyo, Japan) to analyse the size and

shape of nanoparticles [13]. To find out the excitation and emission maxima for the AgNPs, prescan was performed using fluorescence spectrometer (Fluoromax 4-Horiba Instruments, Kyoto, Japan) which recorded the spectra with a scan speed of 240 nm/min with excitation slit width of 5 nm and emission slit width of 5 nm.

Catalytic degradation

The AgNPs synthesized were used for the removal of organic dyes, causing ecological pollution. For analysing the degradation reaction, two prominent cationic dyes methylene blue and fuchsine were used. Two millilitres (0.08×10^{-3} M) of the dye, 0.5 mL of freshly prepared NaBH₄ (0.06 M) and 0.5 mL of AgNP-*Cinereum* (0.02 mg/mL) were taken in a quartz cuvette of 1 cm path length. The UV-vis absorption spectra of the reaction mixture were recorded at definite intervals of time in the range of 200–700 nm. Complete disappearance of the colour in the reaction mixture was the direct indication of the degradation of the dye. The kinetics of the reaction was scanned by measuring the absorbance at specified wavelength for both the dyes. A control reaction was also setup

without nanoparticles to ascertain the dye degradation is brought about by nanoparticles.

Antioxidant capacity using the DPPH assay

The antioxidant activity of the synthesized nanoparticles was evaluated based on their ability to trap DPPH radical. Ascorbic acid is used as a positive control. AgNP without DPPH was used as blank. Colloidal solution of AgNP (2 mL) and 0.1 mM DPPH solution in ethanol (2 mL) were mixed and shaken vigorously for 2 min. The solution was incubated in the dark at room temperature for 30 min followed by absorbance reading at 517 nm using UV–vis. Results were conveyed as percentage reduction of the initial DPPH absorption in relative to the control. The inhibition ratio can be calculated according to the equation:

Inhibition ratio (%) = {
$$(A_0 - A_c)/A_0$$
} × 100

where A_0 is the absorbance of the control and Ac is the absorbance at the addition of the analytical sample.

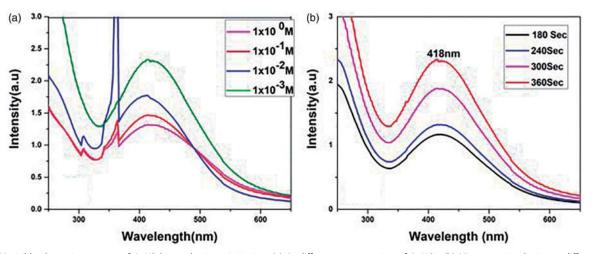


Figure 1. UV-visible absorption spectra of AgNP biosynthesis optimization. (a) At different concentration of AgNO₃. (b) Microwave irradiation at different intervals of time.

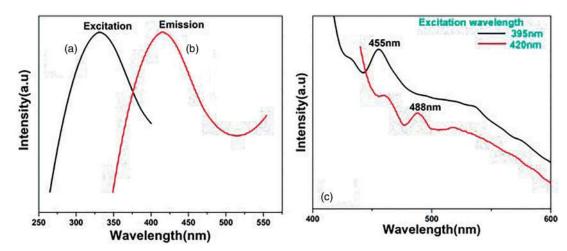


Figure 2. Photoluminescence excitation spectrum of Ag NP (a) excitation centred at 332 nm and (b) emission at 416 nm. (c) Emission spectrum of Ag NP: excited at 395 nm and 420 nm.

Antibacterial evaluation

The antibacterial activities of AgNP were carried out by well diffusion method [47]. For that, a nutrient agar medium plate was prepared, sterilized and solidified. After solidification, bacterial cultures both Gram-positive bacteria *Staphylococcus aureus* (*S. aureus*) and Gram-negative bacteria *Klebsiella*

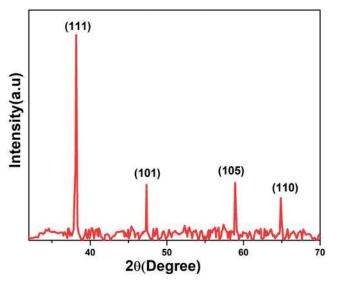


Figure 3. XRD pattern of AgNP.

pneumoniae (K. pneumoniae) were swabbed on these plates. The wells were made on the plates and AgNPs solution (10 mg/mL) along with positive and negative controls was loaded in the wells. It was then kept for incubation at 37 °C for 24 h. Zones of inhibition for control and AgNP were measured. Repeat the experiment thrice and mean values of zone diameter were presented.

Electrochemical analysis

Cyclic voltammetry (CV) was chosen as a primary mode for the development of non-enzymatic DA sensor with carbon paste electrodes (CPEs) modified with AgNP as working electrode in a three-electrode electrochemical setup using Metrohm Autolab potentiostat/galvanostat (model no. PGSTAT302N). The modified electrode was prepared by dropping 4.0 µL of the nanocomposite suspension onto precleaned CPE and dried at room temperature. The electrochemical measurements were carried in electrochemical cell system by successive voltammetric cycles (130 cycles, potential range from -0.30 to 0.95 V versus Ag/AgCl (3.0 mol L⁻¹ KCl) in 0.1 mol L^{-1} NaOH solution). After the optimized procedure of the electrochemical measurements, the CPE/AgNP was evaluated for the DA determination which was carried out by differential pulse voltammetry (DPV).

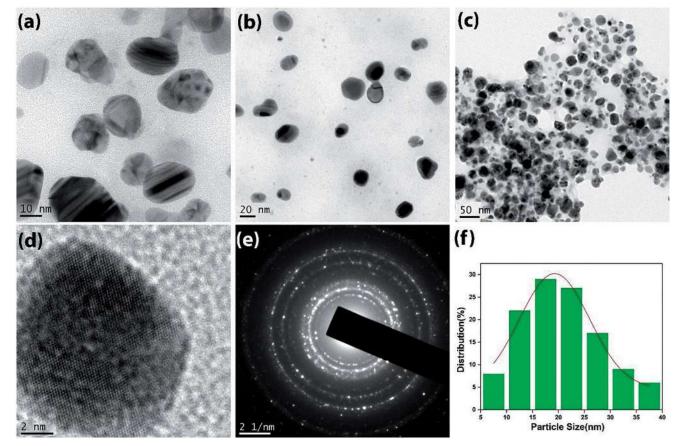


Figure 4. Transmission electron microscopic images of AgNP. (a–c) Images under diverse magnifications, (d) HR-TEM image of AgNP, (e) SAED pattern of AgNP and (f) particle size histogram.

Results and discussion

UV-vis spectra analysis

Primarily, the formation of AgNPs was confirmed by observing the colour change of AgNO₃ solution. With the addition of *Cyanthillium cinereum* leaf extract to the AgNO₃ solution, a steady change in colour from colourless to dark brown was observed, which was further confirmed by UV–vis spectroscopy [48]. The intensity of extremely symmetric single-band absorption with peak maxima of surface plasmon resonance (SPR) peaks for AgNP [49] synthesized at different concentration of AgNO₃ solution was analysed (Figure 1(a)) and found that a concentration of about 1×10^{-3} M AgNO₃ was adequate for the synthesis of AgNP [50]. Also, the absorption spectrum using the precursor 1×10^{-3} M AgNO₃ was verified at different intervals of time such as 180 s, 240 s, 300 s and 360 s [51] (Figure 1(b)) and observed that at a maximum of 360 s is enough for the complete formation of AgNP where there is a broad absorption peak at 418 nm and after a specific irradiation interval of 360 s coagulation of AgNP makes it difficult to analyse it by spectral data. The size and shape of the particles, in nearby dielectric medium and the

Table 1. Comparative study	on the particle size and	property analysed for AgN	synthesized from various sources.

S. no.	Plant source	Particle size	Ref.	Property analysed
1	Menthapiperita (Lamiaceae) extract	90 nm	[56]	Antibacterial activity
2	Caralluma tuberculata extract	32 nm	[57]	Antioxidant and antibacterial property
3	Citrus paradise extract	52 nm	[58]	Catalytic degradation of toxic dyes
4	Origanum vulgare L. extract	48 nm	[59]	Microbicidal activities
5	Mussaenda erythrophylla leaf extract	50–80 nm	[2]	Catalytic degradation
6	Aegle marmelos extract	60 nm	[60]	Capping effect
7	Tephrosia purpurea leaf extract	20 nm	[61]	Antimicrobial activity
8	Terminalia bellirica fruit aqueous extract	20.6 nm	[62]	Catalytic and antibacterial applications
9	Holarrhena antidysenterica (L.) Wall. bark extract	32 nm	[63]	Larvicidal activity
10	Cyanthillium cinereum leaf extract	19.25 nm	This work	Catalytic degradation, antioxidant capacity, antibacteria evaluation and electrochemical responses

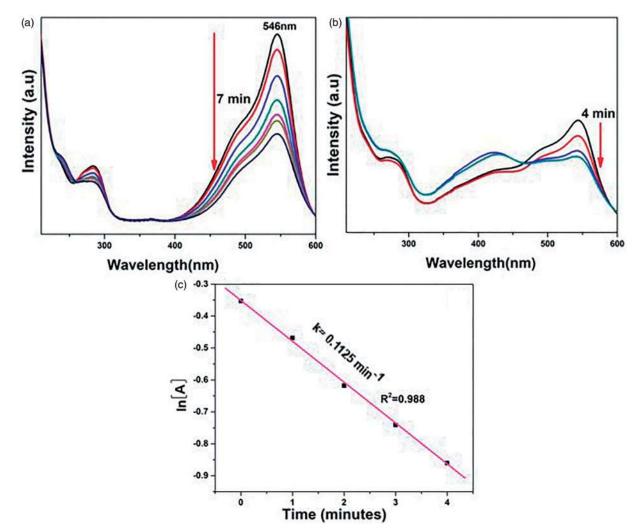


Figure 5. UV-vis absorption spectra measured at 1 min intervals for the degradation of fuchsine. (a) In the absence of AgNP. (b) In the presence of AgNP. (c) Kinetic plot (In[A] verses time).

accumulation of nanoparticles affect the SPR peak of AgNP [52].

Photoluminescence study

Photoluminescence occurs in noble metals due to an excitation in the electrons from occupied d bands to states above the Fermi level. The emission spectrum of synthesized AgNP is dependent on the excitation wavelength [53,54]. Ensuing the electron-phonon and hole-phonon scattering processes lead to energy loss and finally a photoluminescent recombination of an electron from an occupied sp band with the hole [14,53]. Photo excitation of AgNP at excitation wavelength of 332 nm (Figure 2(a)) produced a very intense fluorescent emission peak at 416 nm (Figure 2(b)), while excitation at 395 nm and 420 nm produced fluorescence emission peak at 455 nm and 420 nm respectively with reduced intensity (Figure 2(c)). For AgNPs, the luminescence emission arises as a result of electron-hole recombination processes, i.e. the electron from sp conduction band above the Fermi level and hole from d-band below the Fermi level [52-54].

XRD analysis

The results obtained from XRD analysis of biosynthesized AgNP was very intense and sharp and it confirms its crystalline structure [55] (Figure 3). The existence of strong peaks at $2\theta = 38.16^{\circ}$, 47.33° , 58.91° and 64.88° belonged to the presence of (1 1 1), (1 0 1), (1 0 5) and (1 1 0) planes (JCPDS file no. 04-0783) (Bragg's reflection), respectively, and confirmed the crystalline and face centred cubic (FCC) structure of AgNP [48].

TEM analysis

The morphological and crystallographical information of the synthesized AgNP was obtained from the TEM analysis. Figure 4 represents the microscopic images (a–c) of spherical AgNPs at different magnifications. The lattice fringes and atomic columns of nanosilver were clearly seen from the HR-TEM image (d). Elastic scattering of electrons on AgNP produced the bright spots (e) in the selected area electron diffraction (SAED) pattern, which indicates that particles are highly crystalline in nature [15]. The distribution of the particles' size of synthesized AgNP was shown in the histogram (f) and the particle size is in between 5 and 40 nm with an average size of 19.25 ± 0.44 nm. Also from Table 1, it is clear that the present study emphasizes on the synthesis of very small AgNPs with enhanced property as comparing to others, which is discussed in this work.

Catalytic degradation

The catalytic activity of plant derived AgNP was investigated using the degradation reactions of fuchsine and methylene blue using NaBH₄. These dyes were selected for our study

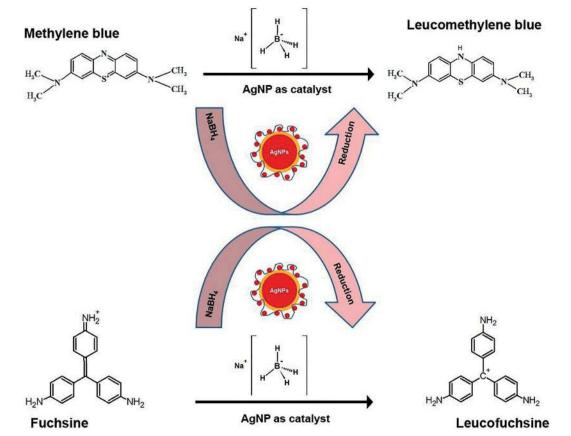


Figure 6. Time-dependent UV-vis spectra for the removal of methylene blue. (a) In the absence of AgNP. (b) In the presence of AgNP. (c) Kinetic plot (In[A] verses time).

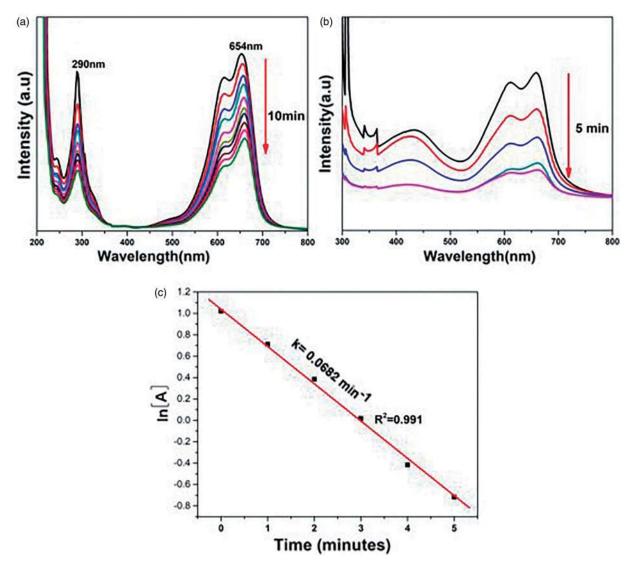


Figure 7. The mechanism of reduction of methylene blue and fuchsine by NaBH₄ in the presence of AgNP.

Table 2. Antioxidant activity of aqueous leaf extracts, AgNP and ascorbic acid (standard) showing scavenging % of extracts and IC_{50} value in C. cinereum.

S. no.	Samples	Concentration (µg/mL)	Scavenging ability (%)	IC ₅₀ value (μg/mL)
1	C. cinereum	12.5	16.01 ± 0.05	74.05 ± 0.05
		25	25.36 ± 0.02	
		50	40.31 ± 0.10	
		100	55.76 ± 0.09	
		200	74.24 ± 0.01	
2	Synthesized AgNP	12.5	27.41 ± 0.09	40.80 ± 0.14
		25	39.62 ± 0.03	
		50	51.33 ± 0.07	
		100	68.22 ± 0.50	
		200	84.33 ± 0.02	
3	Ascorbic acid (standard)	12.5	30.33 ± 0.09	35.52 ± 0.12
		25	41.23 ± 0.03	
		50	54.25 ± 0.07	
		100	71.31 ± 0.30	
		200	88.69 ± 0.11	

because its absorption maximum does not overlap with the SPR band of AgNPs [26]. Fuchsine or rosaniline hydrochloride is a magenta dye with chemical formula $C_{20}H_{19}N_3$ ·HCl. The UV-vis absorption spectrum of an aqueous solution of fuchsine shows peaks at 292 nm and 546 nm. The reduction of

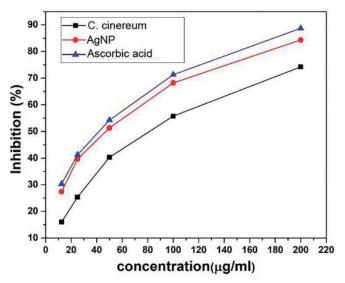


Figure 8. Dose-dependent antioxidant potentials of *C. cinereum* and AgNP assessed by the DPPH assay.



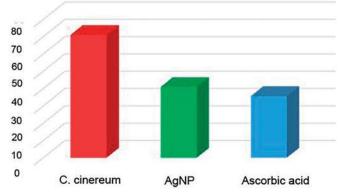


Figure 9. $\rm IC_{50}$ values for antiradical analysis of C. cinereum and AgNP in comparison with ascorbic acid.

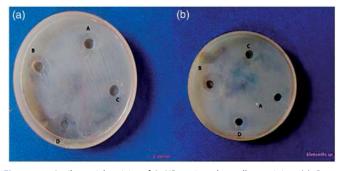


Figure 10. Antibacterial activity of AgNP against the well containing: (a) Grampositive bacteria *Staphylococcus aureus* (*S. aureus*) and (b) Gram-negative bacteria *Klebsiella pneumoniae* (*K. pneumoniae*). A: double distilled water; B: streptomycin; C: *Cyanthillium cinereum* extract; D: AgNP.

fuchsine into leucofuchsine can be followed spectrophotometrically by monitoring the absorption maximum at 546 nm. Comparing Figure 5(a,b), it is clear that when AgNP was added to the reaction mixture containing both fuchsine and NaBH₄, the intensity of the peak at 546 nm began to decrease continuously with the passage of time. The kinetic studies were performed by ln[A] versus time graph (Figure 5(c)). Rate constant determination proved a pseudo-first order kinetics with respect to the concentration of the dye [64].

Methylene blue is a cationic thiazine dye which shows its UV-vis absorption peaks at 290 and 654 nm with hump at 612 nm due to $\pi \to \pi^*$ and $n \to \pi^*$ transitions [28]. The reduction of methylene blue into its colourless form is schematically represented in Figure 6 [65,66] and further analysed by spectrophotometer using Figure 7(a,b) to monitor the absorption maximum at 654 nm. The kinetic plot of ln[A] versus time graph Figure 7(c) verifies that it follows a pseudo-first order kinetics.

Antioxidant capacity using the DPPH assay

The excellent free radical capturing power of phyto-fabricated AgNP and the plant extract was tested by DPPH method. The percentage radical scavenging activity (RSA) was measured and results are shown in Table 2. The RSA increased in a dose-dependent manner of the tested samples and plant extracts (Figure 8). The recorded scavenging ability for the lowest concentration of the synthesized AgNP

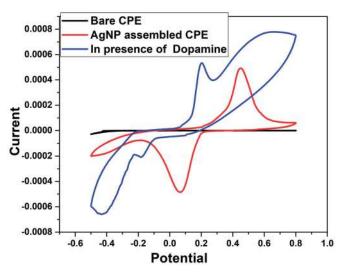


Figure 11. Typical 3D cyclic voltammograms for the (a) bare-CPE (b) and AgNP assembled-CPE. (c) In the presence of dopamine.

 $(12.5 \,\mu\text{g/mL})$ was 27.41 ± 0.09 and this scavenging ability was increased to 84.33 ± 0.02 , when concentration was increased to 200 $\mu g/mL$ (average IC_{50} - 40.80 \pm 0.14 $\mu g/mL$) (Table 2). However, the scavenging ability was recorded for aqueous leaf extract at lowest concentration 16.01 ± 0.05 (12.5 µg/mL) and when concentration was increased the scavenging ability was 74.24 ± 0.09 (200 µg/mL) (Table 2) with average IC₅₀ value, $74.05 \pm 0.05 \,\mu$ g/mL. The IC₅₀ values of the synthesized nanoparticles are comparable with that of standard antioxidants having the IC₅₀ value, $35.52 \pm 0.12 \,\mu$ g/mL (Figure 9). These results corroborate well with the previous reports on antioxidant property shown by the phyto-fabricated AgNP using various plant extracts depending mainly on the methemployed the preparation ods in of nanoparticles [14,26,28,46].

Antibacterial evaluation

The in vitro antibacterial activity of green synthesized AgNP against the common pathogenic bacteria both Gram-positive bacteria Staphylococcus aureus (S. aureus) and Gram-negative bacteria Klebsiella pneumoniae (K. pneumoniae) was assessed by the well diffusion method in which circular inhibition zone was formed around the well impregnated AgNP [67]. A maximum zone was recorded as 1.6 cm for S. aureus and 1.9 cm for K. pneumoniae when treated with AqNP. No zone of inhibition was observed for the plant extract alone (Figure 10). The efficacy of AgNP in inhibiting the growth of pathogenic bacteria is attributed to its ability to enter the cell and bind to various bacterial cellular components [68]. Inside a cell, the nanoparticles would interfere with the bacterial growth and signalling pathway by modulating tyrosine phosphorylation of putative peptide substrates critical for cell viability and division [69]. A nanoparticle can interact with DNA, inside a bacterium and thus losing its ability to replicate which may lead to the cell death [51,68]. Growth of gramnegative bacteria was more profoundly affected by the AgNP than that of the gram-positive organisms since the interaction between such nanoparticles and the cell wall of

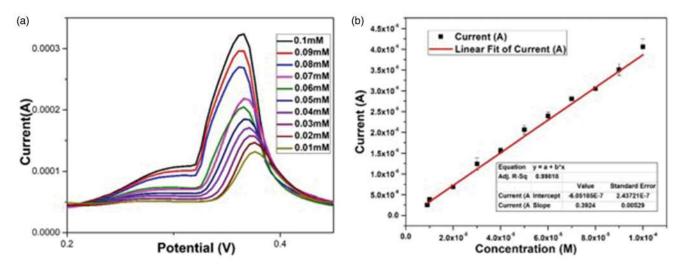


Figure 12. (a) DPV responses of the AgNP-CPE for the detection of different concentrations of dopamine (from 0.01 mM to 0.1 mM) in PBS (pH 6.8). (b) The corresponding linear calibration plots of stripping peak currents in optimized experimental conditions.

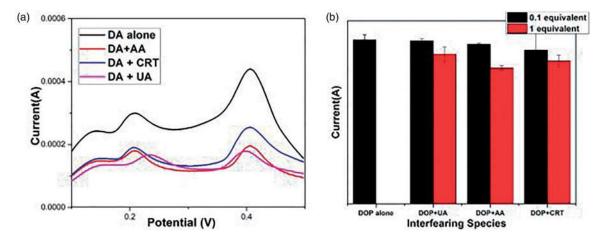


Figure 13. DPV curves corresponding to 0.1 mM dopamine (a) in the presence of uric acid (UA), ascorbic acid (AA) and creatinine (CRT). (b) Bar plots depicting the effect of interferents on DPV.

bacteria would be facilitated by the relative abundance of negative charges on the gram-negative bacteria [69] which was again confirmed from our results.

Electrochemical responses

The electrochemical performance of DA having 1×10^{-3} M concentration at the CPE was investigated by CV (Figure 11) in 0.1 mol L^{-1} PBS (pH 6.5) at 20 mV s⁻¹. Even though bare CPE does not show an oxidation or reduction peak, AgNP assembled CPE showed an anodic peak (0.45 V) which could be attributed to the oxidation of Ag to AgO. Further scanning the potential towards more negative values indicated a peak around 0.06 V which could be ascribed to the reduction of AgO to Ag [70]. Due to the high surface area of AgNPassembled-CPE, there is a significant enhancement in the peak currents that helps to increases the electro-catalytic activity of the electrode [71]. Using AgNP modified CPE, a distinct redox couple for DA was observed with large increase of current height and shifting [72] of the anodic peak potential to 0.21 V and cathodic peak potential to -0.178 V. Hence, it could be inferred that AgNP modified

electrode is recommended for the detection of DA since it makes a significant change in potential.

Sensitivity and selectivity analysis

The differential pulse voltammetric (DPV) technique was carried out to determine the electrocatalytic sensitivity of DA using AgNP-assembled-CPE. The individual electrocatalytic oxidation of DA at the AgNP modified electrode was investigated in 10 mL buffer solution (pH 6.8) at a scan rate of 50 mV/s by varying the concentrations. The results showed that analytes are oxidized and show a well-defined and distinguishable sharp oxidation peaks with peak potentials at 0.366 V. With increase in the concentration of analytes, the anodic peak current increases [73] (Figure 12) with a correlation coefficient (R^2) of 0.998 indicating that analytes have been oxidized by the active AgNP modified electrode [71,74].

The backbone parameter for evaluating the selectivity is the performance of non-enzymatic DA sensors in the presence of known interferents. During the quantification of DA level, the interferents including uric acid (UA), AA and creatinine (CRT) are found in human blood serum. The interfering effect on adding 1 equivalent of UA, AA and CRT which can be compared with 0.1 equivalent DA at the specified potential were determined and the results were found. Figure 13(b) indicates that even in the presence of interfering species the DA having a concentration of 0.1 equivalent shows a significant current using AgNP supported electrode suggesting the high selective nature of the developed DA sensor [75,76].

Conclusions

Plant mediated microwave synthesis offers a green and nontoxic synthetic pathway for AgNPs. The AgNPs obtained were well characterized via UV-vis, XRD and TEM analyses. It is clear from the various spectroscopic and imaging analyses, AgNP was found to be crystalline and spherical in shape with an average size of 19.25 nm Their biological significance was proven by DPPH radical scavenging assay which indicated an IC_{50} value of $40.80 \pm 0.14 \,\mu$ g/mL. The progress of degradation of environment polluting dyes was monitored in situ via UV-vis spectroscopy without light irradiation. Also the AqNP shows effective antibacterial activity against Staphylococcus aureus (S. aureus) which is gram positive and Klebsiella pneumoniae (K. pneumoniae) which is gram negative having a zone of inhibition of 1.6 cm and 1.9 cm respectively which is very close to the standard streptomycin. Moreover, the AgNP modified CPE shows excellent electrocatalytic activity towards DA detection with high sensitivity and with a correlation coefficient (R^2) of 0.998 which imparts its application as a non-enzymatic sensor for DA. The present research highlights the potential application of multifunctional nanoparticles for environmental protection due to their catalytic capacities.

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. This article does not contain any studies with animal subjects.

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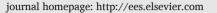
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Highly luminescent ZnS:Mn quantum dots capped with aloe vera extract

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ABSTRACT

This study demonstrates the optical properties of ZnS:Mn²⁺ qquantum dots synthesized by simple and eco-friendly chemical precipitation method using aloe vera (AV) extract as the stabilizing agent. The nanoparticles have been characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, diffuse reflectance spectroscopy (DRS), photoluminescence (PL) and time-resolved PL spectroscopy. Increase in band gap energy with decrease in particle size was observed from DRS studies due to quantum confinement effect. Dominant yellow emission was observed from characteristic ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ transitions of the Mn²⁺ions in the ZnS:Mn/AV nanoparticles. The results provide insight to the quantum confinement effect that occur and how it affect decay life time of the ZnS:Mn²⁺/AV nanoparticles.

1. Introduction

Among the nanoscale materials, ZnS is a wide band gap II-VI semiconductor (3.68 eV) with remarkable optical properties. Special attention is given to transition metal ion doped ZnS nanoparticles which find

its applications in LEDS and lasers owing to their optoelectronic properties [1–6]. Among the transition metals, Mn has attracted much attention because of its luminescence intensity, biocompatibility, and bioimaging capability [6-8]. Our previous work focused on luminescence properties of white light emitting ZnS:Mn nanocrystals prepared without any capping agent [9]. Because of less size controllability and particle agglomeration various chemical based capping agents, complexing agents, etc. were used in the synthesis of ZnS:Mn nanocrystals with controllable size distribution and less aggregation [10-13]. The capping agents provide surface passivation and thus minimize the electronic trapping capabilities of surface defects, resulting in higher photoluminescence intensity [14,15]. Since these chemicals are highly toxic, synthesized nanoparticles are not useful in medical or biological applications. The synthesis and optical characterization of water dispersible, ZnS:Mn nanocrystals capped with L-Valine, L-Cysteine, histidine, arginine, methionine and chitosan have already been reported earlier [16-19]. Various bioactive components of aloe vera have effective antibacterial, anti-inflammatory, antioxidant, and immunomodulatory effects that promote both tissue regeneration and growth. Therefore in this work we used aloe vera as the capping agent to reduce cytotoxicity problems of ZnS:Mn nanocrystals, a major limitation in biomedical application. T. Muralikrishna et al. used aloe vera to cap the gold nanoparticles [20]. The biomolecules present in the plant extracts stabilizes the growth of nanoparticles, thus leads to the decrease of surface energy and prevent them from further aggregation [21,22]. Methanol extract of aloe vera gel consists of coumarins, alkaloids, tannins, steroids, quinines, anthraquinones, phenols, resin, glycoside

and carbohydrate as analysed by phytochemical screening and it provides surface passivation of ZnS:Mn nanoparticles prepared by chemical precipitation method. We have reported the biocompatibility and antibacterial property of these ZnS:Mn/AV quantum dots [23]. The observed pure yellow emission of aloe vera capped ZnS:Mn (ZnS:Mn/AV) finds potential applications in the advance of luminescence devices. Besides, the measurement of fluorescence decay time is an important parameter to realize the influence of host on energy levels of dopants and mechanism of energy transfer. It was reported [24-26] that the lifetime of yellow emission of Mn^{2+} in ZnS: Mn^{2+} nanoparticles is of the order of milliseconds. The shortening of lifetime of ZnS:Mn nanocrystals from milliseconds to nanoseconds based on quantum confinement induced ligand-TM hybridisation theory is also reported [27]. In this work we have measured life time for the yellow emission of Mn^{2+} in ms and ns range. We report the optical properties of aloe vera capped biocompatible ZnS:Mn quantum dots (ZnS:Mn/AV) with controlled size and enhanced luminescence for possible use as nanoscale fluorescent probes in pharmaceutical and biomedical field.

2. Experimental

25 ml of 0.01 M manganese chloride solution in methanol was added dropwise to 25 ml of 1 M zinc acetate solution in methanol and stirred well.2.5 ml of 2 mg methanol extract of AV dissolved in 10 ml methanol was added to the above solution and the whole mixture was stirred magnetically at 70 °C. Later 25 ml 1 M solution of sodium sulphide in methanol was added to this solution and stirring is continued for 20 min keeping temperature at 70 °C. The obtained precipitate was filtered and washed with methanol several times. Finally, the filtered powder was dried for 15 h at 70 °C and ground to obtain ZnS:Mn/AV nanoparticles. Following the same procedure, ZnS:Mn²⁺nanoparticles without AV was also prepared.

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The synthesized samples were structurally characterised by FTIR spectroscopy using Shimadzu spectrophotometer and transmission electron microscopy (TEM) using JEOL 3010. Varian Cary 5000 UV–Vis–NIR spectrophotometer was used for DRS measurements. Chemical composition of the samples was determined by inductively coupled plasma (ICP) (ICP–1000IV, Shimadzu) analysis. The photoluminescence measurements were performed at room temperature using Horiba Fluoromax 4C research spectrofluorometer. Life time measurements were carried out using Fluorocab from M/s Horiba with spectra LED 390 nm and nano LED 340 nm as excitation sources.

3. Results and discussion

3.1. TEM analysis

Fig. 1(a&b) shows the TEM and selective area electron diffraction (SAED) images of uncapped ZnS:Mn nanoparticles. From the TEM images the particle size obtained for the uncapped nanoparticles is 4.5 nm. The SAED pattern Fig. 1(b) consists of a central halo with three concentric broad rings which correspond to the reflections from (1 1 1), (2 2 0) and (3 1 1) planes of cubic zinc blende phase. Fig. 1(c&d) shows the TEM and SAED images of capped ZnS:Mn nanoparticles which show monodispersed almost spherical nanoparticles with less aggregation and particle size 2.2 nm.

3.2. FTIR analysis

FTIR spectra of AV, ZnS:Mn and ZnS:Mn/AV Fig. 2 were recorded in the range 400–4000 $\rm cm^{-1}.~In$

the FTIR spectra of AV, uncapped and capped ZnS:Mn samples the prominent absorption peaks and their assignments are given in the Table 1.

In AV the broad absorption band in the range of 3000–3400 cm⁻¹ is characteristic of -C-H, -N-H or -O-H stretching that comes under aldehydes, alkanes or aromatic group containing phenols, tannins, quinines, glycosides, alkaloids etc. The absorption peak at 1641 cm⁻¹ can be attributed to alloin, the most important aloe vera gel component belonging to anthraquinone glycoside [33].The absorption band positioned at 1411 cm⁻¹is likely due to C–H or C–O or C–OH groups of esters and phenols [14]. All phytochemicals listed above are present in the methanol extract and experimentally proved by preliminary phytochemical screening.

Absence of peak in the range 2222–2260 cm⁻¹ corresponding to C \equiv N stretching bands indicates that the extract didn't possess nitrile compounds which are toxic components found in many plant species as cyanogenic glycosides. All the peaks in ZnS:Mn²⁺/AV are present in ZnS:Mn sample except the peaks at 2970 and 1106 cm⁻¹ which are present in capped ZnS:Mn. The peaks at 2970 cm⁻¹ which is at 2950 cm⁻¹ in AV and 1106 cm⁻¹ indicate the coordination of ZnS:Mn with the AV. The additional and the intense IR peaks in

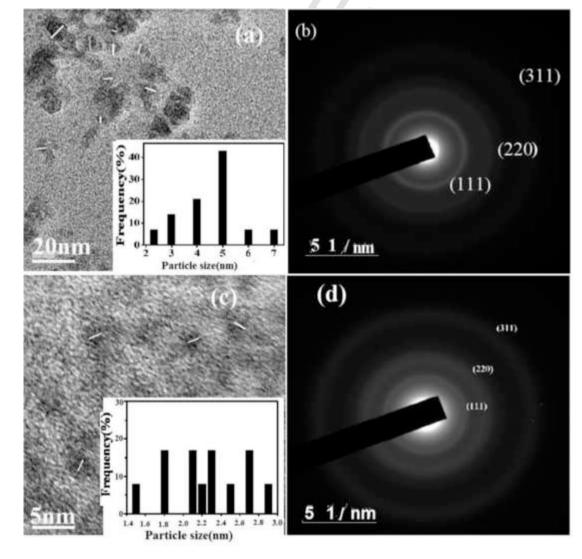


Fig. 1. (a)&(b) TEM&SAED pattern of uncapped ZnS:Mn and (c) & (d)TEM&SAED pattern of ZnS:Mn/AV nanoparticles[insets correspond to particle size distributions].

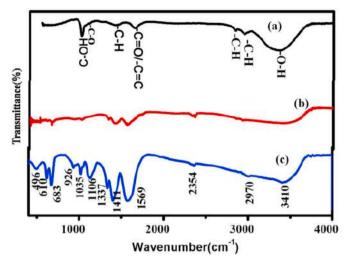


Fig. 2. FTIR spectra of (a) AV (b) ZnS:Mn and (c) ZnS:Mn/AV quantum dots.

Table 1

Prominent absorption peaks and their assignments in AV, ZnS:Mn and ZnS:Mn/AV quantum dots.

Absorption peaks (cm $^{-1}$)	Assigned vibrations	Samples involved
496, 610, 683	Zn-S stretching (corresponding to	ZnS:Mn/AV &
	sulphides) [31]	ZnS:Mn
926	Mn–S vibration [31]	ZnS:Mn & ZnS:Mn/
		AV
1025-1035	C-H vibrations [29]	AV, ZnS:Mn/AV &
		ZnS:Mn
1106	C-O stretching [30]	AV, ZnS:Mn/AV
1337, 2354	C=O stretching or microstructure	ZnS:Mn/AV &
	formation [31]	ZnS:Mn
1411	symmetric bending of C-H [14]	AV, ZnS:Mn/AV &
		ZnS:Mn
1569	C=O stretching [32]	ZnS:Mn/AV &
		ZnS:Mn
1641	C=O stretching [33]	AV
2875	C–H stretching [28]	AV
2970	C–H bending [28]	AV & ZnS:Mn/AV
3000-3400	N–H, O–H stretching [31,33]	AV, ZnS:Mn/AV & ZnS:Mn

ZnS:Mn²⁺/AV nanoparticles confirm that aloe vera is attached to the surfaces of ZnS:Mn²⁺ nanoparticles.

3.3. Optical characterization

The diffuse reflection spectroscopy Fig. 3(A)was used to study the absorption characteristics of the prepared samples. From DRS spectra absorption coefficient are obtained by using Kubelka Munk function given by $F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}$ where R, k, s are the reflection, absorption and scattering coefficients. The band gap energy can be calculated by extrapolating the linear part of $\{(k/s)h\nu\}^2 vs h\nu$ graph to the energy axis at k/s = 0 as shown in figure Fig. 3 (B). The corresponding E_g values for ZnS:Mn²⁺/AV and ZnS:Mn²⁺ nanoparticles are 4.96 eV and 4.03 eV. The absorption peak observed below band gap in ZnS:Mn²⁺/AV quantum dots is due to excitonic absorption. When the radius of a nanocrystal becomes comparable to the Bohr exciton radius of its bulk counterpart, quantum confinement effect brings out major changes in its opto-electronic properties.

Since the radius of ZnS:Mn/AV and ZnS:Mn²⁺ quantum dots (determined from TEM studies) are smaller than Bohr exciton radius (2.5 nm) the particles are in strong confinement regime. Based on quantum confinement effects, the band gap energy of nanocrystallite in strong confinement regime according to Brus equation is

$$E^* = E_g + \frac{h^2}{8R^2} \left\{ \left[\frac{1}{m_e} \right] + \left[\frac{1}{m_h} \right] \right\}$$

where E_g is the band gap of the bulk, m_e and m_h are the effective masses of electron and hole. Substituting $E_g=3.54$ eV, $m_e=0.34~m_0,~m_h=0.23~m_0$ in equation the radius of quantum dots obtained are 1.4 nm and 2.36 nm in the case of ZnS:Mn/AV and ZnS:Mn^{2+} nanophosphors respectively.

Photoluminescence emission spectra of synthesized samples recorded at room temperature for an excitation wavelength of 340 nm is given in Fig. 4. From the recorded spectra it is clear that the two samples exhibit two manganese related yellow emissions. The blue emission at 440 nm is the self-activated emission of defects [34]. When Mn²⁺ ions are doped into the ZnS host lattice, the strong interaction between the s-p electrons of ZnS and the 3 d^5 electrons of Mn $^{2+}$ ions takes place and the prohibited transition of ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ within 3d shell of Mn^{2+} become partially permitted. Hence an intense yellow emission around 590 nm resulting from ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ transition of Mn^{2+} ion is produced [35–37].For ZnS:Mn²⁺ nanoparticles, larger part of the Mn²⁺ ions are at surface sites and take up axial or lower symmetry sites and reduces the growth of ZnS host nanoparticles. The increased yellow emission intensity of ZnS:Mn nanoparticles is a direct outcome of fast energy transport of the excited electron hole pairs of the ZnS host into the dopant ion, following a proficient and quick radiative recombination of Mn d-electron.

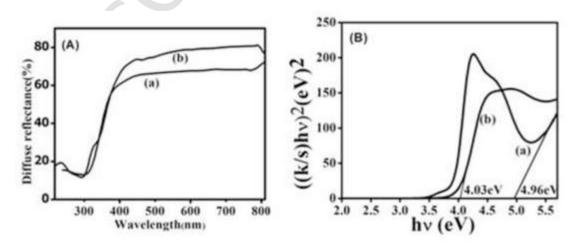


Fig. 3. (A) Diffuse reflectance spectra & (B) {(k/s)hv}² V hv plots of (a) ZnS:Mn/AV and (b) ZnS:Mn quantum dots.

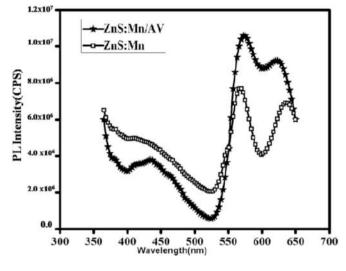


Fig. 4. PL emission spectra ($\lambda_{ex} = 340$ nm) of ZnS:Mn/AV& ZnS:Mn quantum dots.

There are reports [14,15,38] for the enhanced photoluminescence in capped ZnS:Mn nanoparticles in comparison with that in uncapped sample. AV act as passivator to reduce the surface defects and promotes radiative probability through the Mn^{2+} ions and hence in ZnS:Mn/AV, intensity of yellow emission becomes ~1.4 times of that in uncapped ZnS:Mn quantum dots. Mn^{2+} ions located at different sites in the ZnS lattice resulted in different luminescence properties [39,40]. Luminescence intensity due to impurity sites is inversely proportional to cube of the radius of particle [41]. Thus particle size reduction due to AV capping is another reason for increase in PL intensity.

It was reported that the yellow emission band around 590 nm is the result of superposition of four emissions, emission with λ_{max} at 557 nm due to tetrahedral cubic lattice, Mn^{2+} ions near dislocation or point defects give rise to λ_{max} at 578 nm, λ_{max} at 600 nm due to Mn^{2+} in octahedral interstices and λ_{max} at 635 nm is related with the formation of α -MnS [42,43]. In our case ZnS:Mn show only the emissions with peaks at 575 and 625 nm which are due to Mn^{2+} ions near dislocation or point defects and due to the formation of α -MnS. Because of size dependent phonon coupling and change in crystal field strength these emissions are shifted slightly for the capped particles.

To understand the origin of emission spectra, a study of its excitation spectra is needed, from which few important information about the luminescence mechanism can be obtained. Using Ligand field theory and Tanabe-Sugano diagram for the Mn^{2+} d⁵ level, the different possible electronic transitions accountable for the emissions in Mn^{2+} ions is explained [44].The PLE spectrum (Fig. 5 (a)) shows five excitation peaks in the wave length region of 380–510 nm. These absorption peaks are at 393, 430, 465,480 and 491 nm and due to the direct excitation transitions of Mn^{2+} . Five excitation bands around 390, 430, 475, 498, and 535 nm of Mn^{2+} are reported in bulk ZnS:Mn crystal [44–47]. Hence

the absorption bands at 393, 430, 465, 480 and 491 nm in the synthesized ZnS:Mn nanoparticles corresponds to the ${}^{6}A_{1}$ (${}^{6}S$) $\rightarrow {}^{4}E$ (${}^{4}D$), ${}^{6}A_{1}$ (${}^{6}S$) $\rightarrow {}^{4}T_{2}$ (${}^{4}D$), ${}^{6}A_{1}$ (${}^{6}S$) $\rightarrow {}^{4}T_{2}$ (${}^{4}D$), ${}^{6}A_{1}$ (${}^{6}S$) $\rightarrow {}^{4}T_{2}$ (${}^{4}G$) and ${}^{4}E$ (${}^{4}G$), ${}^{6}A_{1}$ (${}^{6}S$) $\rightarrow {}^{4}T_{2}$ (${}^{4}G$) and ${}^{6}A_{1}$ (${}^{6}S$) $\rightarrow {}^{4}T_{1}$ (${}^{4}G$) transitions within 3 d⁵ configuration of Mn²⁺. The band with peak at 318 and 358 nm may originate from the absorption of light by the ZnS host or due to the higher excited levels of Mn²⁺. In the present study, observed absorption peaks are shifted slightly from the reported observations and can be ascribed to the change in the local structures in the region of Mn luminescent centers in ZnS:Mn²⁺ nanoparticles.

CIE (Commission International d'Eclairage) coordinates calculated from the measured PL emission spectra are (0.42, 0.38) and (0.48, 0.40) for $\text{ZnS:}\text{Mn}^{2+}$ and $\text{ZnS:}\text{Mn}^{2+}/\text{AV}$ as shown in chromaticity diagram (Fig. 6). It shows that the overall emission colour of ZnS:Mn/AV is yellow while that of uncapped ZnS:Mn nanoparticles is pale yellow.

The lifetime decay dynamics (Fig. 7) of $\text{ZnS:Mn}^{2+}/\text{AV}$ and ZnS:Mn^{2+} nanocrystals for the emissions at 575 nm and 625 nm were performed. The decay plots are well fixed by third order exponential equation $I(\tau) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$ where $\tau_{1,}$ $\tau_{2,}$ τ_{3} represent the decay times of the PL emission and A_1 , A_2 , A_3 represent the relative weights of the decay components at t = 0. Based on the parameters the average decay time (τ) of Mn was calculated by the following equation [48] and they were found to be in ms range (Table 2).

$$=\frac{A_{1}\tau_{1}^{2}+A_{2}\tau_{2}^{2}+A_{3}\tau_{3}^{2}}{A_{1}\tau_{1}+A_{2}\tau_{2}+A_{3}\tau_{3}}$$
(3)

It has been known that ZnS:Mn nanoparticles have a short life time in the ns range and a long lifetime in the ms range [49–53]. Hence we also performed the decay dynamics using nano LED 340 nm as excitation source (Fig. 7(C)) and the decay curve is well fitted by using a single exponential decay function. There are lifetimes in ms range for Mn emissions at 575 nm and 625 nm. Among these shorter components is assigned to the ⁴T₁ lifetime of a surface bound Mn ion and longer is assigned to the ⁴T₁ lifetime of a lattice bound Mn impurity. For the emission at 625 nm, lifetime in ns range also exists. The lifetime determined are 0.5 and 1.76 ns for the ZnS:Mn/AV and ZnS:Mn nanoparticles. By performing single quantum dot fluorescence decay studies, it has been suggested that the same emission center exhibits different decay times [54]. But this short lifetime belongs to the tail of the blue emission of ZnS emission. The decay time of ZnS:Mn nanoparticles in ns range and ms range have been contradictorily reported [49-53,55-58]. The conflicting results from these previous reports show that the decay dynamics of the Mn ion in ZnS lattice is still an unresolved issue. By transient absorption as well as emission decay kinetic profiles, Jae Hun Chung et al. [50] also reported that all the nanosecond luminescence decay components of ZnS:Mn nanoparticles are from defect related ZnS host rather than from Mn ions. Mn related emission decays with dual time constants in ms range. Among these ms range lifetime components the fast component results from surface bound Mn ions, while the slow one from the lattice bound Mn ions. The better spin-orbit coupling and vi-

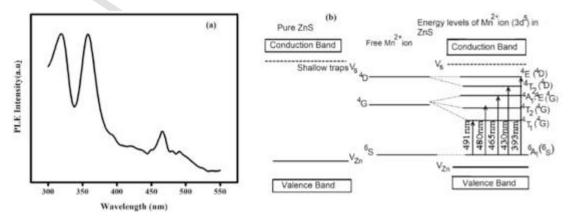


Fig. 5. (a) Excitation spectra ($\lambda_{em} = 590$ nm) and (b) schematic representation of the PL excitation in ZnS:Mn/AV quantum dots.

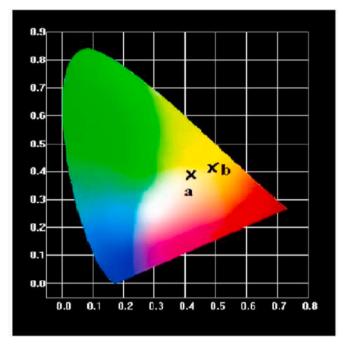


Fig. 6. CIE chromaticity diagram. The Points (a) and (b) correspond to PL emissions of $\rm ZnS:Mn^{2+}$ and $\rm ZnS:Mn^{2+}/AV$ nanoparticles.

bronic coupling with the vibrational motions of coordinated species of the surface bound Mn and the lower binding symmetry cause the enhancement in the transition strength hence resulting in the life time shortening of the exterior Mn ions. For ZnS:Mn/AV reduced particle size leads to the fractional increase of surface-bound Mn ions resulting in the shortening of overall luminescence lifetime. Similar results have been reported in recent times in the case of ZnS: Mn nanocrystals by Tuan et al. [59].

4. Conclusion

In this paper we have demonstrated a new strategy for the green synthesis of ZnS:Mn quantum dots in the strong confinement regime using aloe vera as capping agent. A blue shift is observed in the band gap of capped particles due to size effects in nanoregime. ZnS:Mn/AV quantum dots with strong yellow emission and good monodispersivity find application in medical research related to imaging.

CRediT authorship contribution statement

K.R. Bindu: Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **S. Ajeesh Kumar:** Formal analysis, Investigation. **M. Anilkumar:** Formal analysis, Investigation. **E.I. Anila:** Conceptualization, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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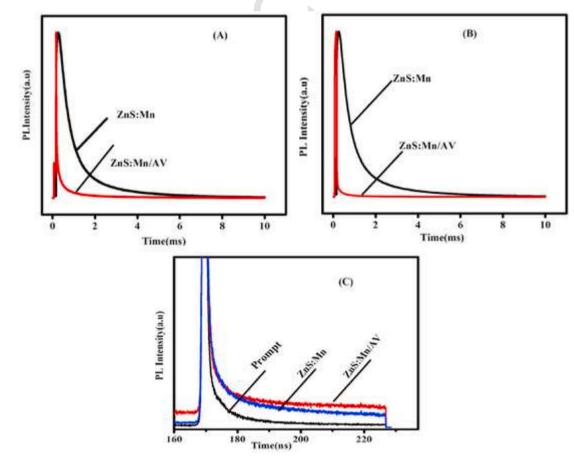


Fig. 7. PL decay curves of ZnS:Mn and ZnS:Mn/AV nanoparticles for emissions at (A) 575 nm, (B) 625 nm with decay time in milliseconds and (C) decay curves at 625 nm with decay time in nanoseconds.

Fluorescence lifetime data of ZnS:Mn and ZnS:Mn/AV.

nS:Mn and ZnS:Mn/AV.		
	Average	Average

Sample	Emission	at 625 nm		Average Lifetime (τ) ms	Emission a	at 575 nm		Average Lifetime (τ) ms	Emission at 625 nm (τ) ns
	$\tau_1(ms)$	$\tau_2(ms)$	$\tau_3(ms)$		$\tau_1(ms)$	$\tau_2(ms)$	$\tau_3(ms)$		
ZnS:Mn ZnS:Mn/AV	0.91 0.65	2.9 2.8	0.37 0.19	1.64 1.86	0.84 0.55	2.7 2.5	0.36 0.16	1.68 1.57	1.76 0.5

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Full length article

Optimized synthesis temperature and doping concentration of copper in zinc sulphide nanoparticles for green emission

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ARTICLE INFO	A B S T R A C T				
<i>Keywords:</i> Nanoparticles Optoelectronic properties Photoluminescence	Photoluminescence (PL) of copper doped zinc sulphide (ZnS:Cu) nanoparticles synthesised with different Cu concentrations and at different synthesis temperature have been investigated. These ZnS:Cu nanoparticles were synthesised without any capping agent by simple chemical precipitation method. So as prepared Cu doped ZnS nanoparticles are then characterized by using scanning electron microscopy (SEM), Transmission electron mi- croscopy (TEM), X-ray diffraction (XRD), photoluminescence (PL) and diffuse reflectance (DRS) spectroscopy. The optical properties of the ZnS:Cu nanoclusters are investigated in detail. Four emissions bands consisting of surface state emission (blue), Cu blue, green and red emissions which are both sensitive to the synthesis tem- peratures and dopant concentration are observed. The determination of the CIE colour coordinates from PL				

1. Introduction

Semiconductor nanoparticles have attracted more attention in the recent decades due to their novel optoelectronic properties. The structural and optoelectronic properties of semiconductor nanoparticles differ from those of their corresponding bulk form due to quantum confinement effects. Aong the II-VI semiconductors, Zinc sulphide has a a direct band gap of 3.65 eV for cubic zinc blende and 3.77 eV for hexagonal wurtzite. On account of unique fundamental properties ZnS has been found diverse applications such as display technologies, luminescent devices, sensors, solar cells, biological devices, etc. [1–3]. The extensive designing and engineering of ZnS allows it to be widely and effectively used in diverse applications such as transparent conductors, UV photodetectors, luminescent devices, and catalysis [4-6]. Among the doped ZnS nanoparticles ZnS:Mn and ZnS:Cu nanoparticles are prominent phosphorescence materials. Since the solubility of Cu²⁺S is less than ZnS Cu²⁺S precipitates earlier than ZnS during the synthesis. Hence the incorporation of Cu²⁺ ions into the ZnS lattice is not easy compared to the doping of Mn²⁺ ions [7]. For this reason studies on ZnS: Cu nanocrystals have not been done widely like ZnS:Mn nanoparticles. ZnS doped with Cu has been explored as an excellent candidate for developing high-performance transparent conductive materials (TCMs) which can be seen everywhere in our daily life such as light-emitting

[8-10].In recent years various efficient optoelectronic devices uses ZnS-CuS nanocomposite films as p-type TCM [11]. Besides, Cu has been specifically used for doping ZnS to produce luminescent materials with emission bands in the range of 420-600 nm. Coming to luminescence properties of Cu doped ZnS crystals there are two familiar emission bands, namely green and blue bands. Besides these emissions UV, red and IR emissions were also reported in bulk Cu doped ZnS [12]. For ZnS: Cu nanoparticles, the emission spectra reported by various groups were quite different the emission of ZnS:Cu nanoparticles becomes a debating topic [13-18]. In our present work we have observed the three emissions of Cu²⁺- blue emission at 468 nm, green emission at 522 nm and weak red emission at 625 nm. To our knowledge in ZnS:Cu nanoparticles any two of these emissions were reported only. Similarly there are reports to tune this dual emission by changing the quantity of Cu ions added or by passivating the surface of the quantum dots with different inorganic or organic surfactants or by different synthesis methods like solid state reaction method, solvothermal method, colloidal method, electro spinning, etc [9,12,19–26]. The use of the expensive, environmentally toxic materials as capping agents may cause unintentional luminescence centers and hence the energy transfer mechanism in luminescence turns to be complex. Hence it is advantageous to get intense, tunable color emission from ZnS:Cu nanoparticles without using any capping agent

diodes (LEDs), smartphones, solar cells, display technologies, etc.

emission spectra confirms tunable color emission by varying the Cu concentration and synthesis temperature.

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through any simple method. Besides in order to get better nano phosphors it is important to realize the effect of the synthesis temperature and Cu concentration on the particle size and optical characteristics mainly photoluminescence of ZnS:Cu nanoparticles. The value of best possible Cu concentration for obtaining efficient green emission of Cu in ZnS nanoparticles is controversial [20,27,28]. We have determined the optimized Cu concentration for obtaining maximum Cu related green emission as 0.001 M of Cu and thereafter it quenches. We have also discussed the emission characteristics along with structural characteristics of 0.001 M of ZnS:Cu (at which PL intensity is maximum) nanoparticles synthesised at different temperatures and optimized the synthesis temperature for obtaining maximum intensity of green emission. All the known synthesis methods were carried out with different capping agent and no systematic investigation on the effect of doping concentration and synthesis temperature on the structural, optical properties were carried out on uncapped ZnS:Cu nanoparticles. During the synthesis, it was observed that the colour of the ZnS:Cu sample synthesised was significantly changed by increasing doping percentage and became darker as the amount of Cu was higher. Such observable and major changes show that the concentration of Cu added may affect some other optical properties. Here we studied the effect of synthesis temperature and concentration of copper added during the synthesis on the spectroscopic and crystallographic properties ZnS:Cu nanoparticles.

2. Materials and methods

ZnS:Cu nanoparticles have been prepared by chemical precipitation technique without any capping agent, similar to our previous work [29]. Cu doped ZnS have precipitated from a mixture of zinc acetate [Zn (CH₃COO)₂] and copper nitrate [Cu(NO₃)₂] with sodium sulphide [Na₂S] in water in ratio of 1:1 for Zn:S. The precipitate thus formed was filtered, washed with distilled water and dried by keeping in a hot air oven at 70 °C for 16 h. In this way five samples were synthesised at room temperature with different Cu (0.0005, 0.001, 0.002, 0.003 & 0.004 M) concentrations. The same procedure was also followed for the synthesis of all the ZnS:Cu nanoparticles at 50 °C, 70 °C and 90 °C keeping Cu concentration (0.001 M) same.

The synthesised samples were structurally characterised by AXS D8 Advance X-ray diffractometer and transmission electron microscopy (TEM) using JEOL 3010. Scanning electron microscopy (SEM) with EDS attachment (Jeol model JSM 6390 LV) is used for morphological analysis. Diffuse reflectance measurements of dry powders were recorded using Varian Cary 5000 UV–Vis–NIR spectrophotometer to determine energy gap. Horiba Fluromax 4C research spectrofluorometer was used for Photoluminescence (PL) studies.

3. Result and discussions

3.1. Structural characterization

In order to get the effect of Cu concentration in the final nanostructure of the synthesised nanoparticles, XRD measurements of ZnS:Cu nanoparticles were performed.

Fig. 1(a) and Fig. 2(a) show the XRD patterns of ZnS:Cu nanoparticles synthesised at room temperature with the different concentrations (0.0005, 0.001, 0.002, 0.003, 0.004 M Cu) of Cu and at different (0.001 M Cu) synthesis temperatures. The reflections from (111), (220) and (311) planes are in well matched with standard JCPDS file No. 65-0309 which confirms the cubic crystal structure of ZnS. The grain size measurements were carried out using Scherrer formula and Williamson-Hall (W–H) method [30,31]. With the increase in Cu concentration the diffraction peaks becomes broad indicating reduction in grain size. With increase in temperature (0.001 M Cu) no significant change in the XRD pattern was seen, indicating of the effective doping of Cu ions into ZnS host lattice. The results (Table 1) show that the grain size is decreased with Cu^{2+} concentration. Similar results were seen for the $ZnS:Cu^{2+}$ nanocrystals synthesised by S. Muthukumaran et al. [32]. For higher concentration of Cu, XRD pattern consists of impurity peaks which may be the phase of CuS. The average crystallite sizes at different synthesis temperature (Table 2) indicates that however there is no marked variation in grain size at lower synthesis temperature, a higher synthesis temperature results in large grain size. The strain in the crystal structure is obtained from the slope of the W-H plot (Table 1). Besides, the microstructure parameters like dislocation density (δ) and lattice constant were also determined from the XRD patterns. The lattice parameter is calculated by using the formula $d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}$ where d_{hkl} the interplaner distance related to Miller indices h, k, and 1 and 'a' the lattice parameter. Since the ionic radius of Cu^{2+} (0.073 Å) is less than that of Zn^{2+} (0.074 Å) the Cu²⁺ ions doped into the ZnS matrix may lead to the compression of the unit cell volume supporting the observed compressive strain consequentially the decreased lattice parameter of the crystals than the bulk for which lattice parameter is 5.400 Å. With increase in Cu concentration the lattice constant decreases from 5.393 to 5.31 Å indicating the replacement of Zn^{2+} by Cu^{2+} . The reduced lattice constants of ZnS:Cu nanoparticles synthesised at room temperatures, 50 °C and 70 °C may be due to the compression of the unit cell volume (compressive strain). But as the temperature is high (at temperature of 90 °C) it leads to the expansion of the unit cell volume of the doped sample resulting in an improved lattice constant (5.398Å) confirmed by positive strain. Dislocation density (δ) in the synthesised ZnS:Cu samples was calculated using the Williamson and Smallmans relation [33]. The intrinsic stress developed during the formation of nanocrystallites is determined using the relation [34], $\varepsilon = \frac{Y(a-a_0)}{2\eta a_0}$ where Y be the Young's modules of ZnS (75 GPa), a₀ the bulk lattice parameter, a the lattice constant calculated from the XRD and η is the Poisson's ratio which is

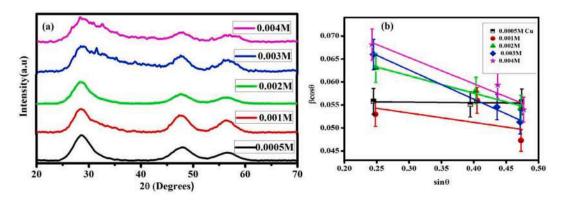


Fig. 1. (a) XRD pattern and (b) Williamson-Hall plot of ZnS:Cu nanoparticles with different Cu concentration (0.0005-0.004 M).

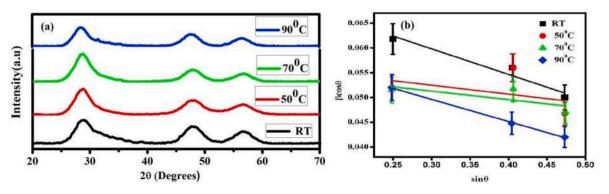


Fig. 2. (a) X-ray diffractogram and (b) W-H plot of ZnS:Cu nanoparticles (0.001 M Cu) nanoparticles. synthesised at different temperature.

Table 1

Crystallite size, lattice parameter, stress, strain and dislocation density of ZnS:Cu nanoparticles with different Cu concentration.

Cu concentration M	Mean Crystallite size (D) nm	Lattice constant (a) (Á)	Stress (ε) X10 ⁹ N/m ²	Strain (ξ)	Dislocation density (δ) x $10^{17}/m^2$
0.0005	$2.531{\pm}0.001$	5.393	-0.17	-0.001	1.56
0.001	$2.502{\pm}0.012$	5.383	-0.42	-0.018	1.6
0.002	$2.170{\pm}0.002$	5.380	-0.49	-0.037	2.1
0.003	$2.121{\pm}0.002$	5.324	-1.80	-0.063	2.2
0.004	$1.750{\pm}0.006$	5.316	-2.08	-0.066	3.2

Table 2

Crystallite size, lattice parameter, stress, strain and dislocation density of ZnS:Cu nanoparticles synthesised at different temperature.

Synthesis Temp.	Mean crystallite size (D) nm	Lattice constant (a) (Á)	Stress (ε) X10 ⁹ N/m ²	Strain (ξ)	Dislocation density(δ) $x10^{17}/m^2$
RT	$2.503{\pm}~0.004$	5.383	-0.42	-0.018	1.95
50 °C	$2.61{\pm}0.01$	5.370	-0.74	-0.012	1.25
70 °C	$2.651 {\pm}~0.006$	5.373	-0.67	-0.010	1.00
90 °C	$3.001{\pm}~0.001$	5.398	-0.05	0.014	1.29

0.28 for ZnS. The average grain size (D) calculated from Scherrer eqn. and W–H plot [Fig. 1(b)&Fig. 2(b)], lattice parameter (a), dislocation density (δ), stress, and strain (ξ) of ZnS:Cu nanoparticles are recorded in Tables 1 and 2

Fig. 3 (a) and 3(b) show the TEM image and the selected area electron diffraction (SAED) pattern of ZnS:Cu (0.1 mol% Cu) nanoparticles. In the TEM image, it can be observed that this powder sample is composed of agglomerated nanocrystals of size ranging from 2 to 4 nm.

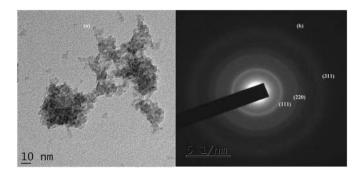


Fig. 3. (a) TEM & (b) SAED pattern of ZnS:Cu for 0.001 M of Cu^{2+} .

The SAED pattern exhibits rings instead of spots due to the random orientation of crystallites which relate to diffraction from different planes of the nanocrystallites. The three diffraction rings in the SAED patterns correspond to the $(1\ 1\ 1)$, $(2\ 2\ 0)$, and $(3\ 1\ 1)$ reflections, confirming the cubic zinc blende structure.

Fig. 4(a) shows the SEM image of ZnS:Cu (0.1 mol% Cu) nanoparticles. It consists of particles of irregular shapes. The composition analysis done by EDAX is shown in Fig. 4(b). It shows that Zn, S and Cu are present and 2.34 at.% Cu is detected for above said sample.

3.2. Optical characterization: DRS and PL spectroscopy

Fig. 5(a) shows the diffuse reflection spectra of ZnS:Cu nanoclusters measured by diffuse reflection techniques. From the diffuse reflectance values the absorbance was obtained by applying the Kubelka-Munk function $F(R)=\ \frac{k}{s}=\frac{(1-R)^2}{2R}\ ,\$ where k and s are absorption and scattering coefficient. The absorption spectra thus obtained from the diffuse reflectance values are shown in Fig. 5(b) and it shows that in the visible region (400-800 nm) ZnS:Cu nanoparticles have no absorption. Due to the quantum confinement effect arising from nanoparticles the absorption edge which is in the range of 300-330 nm are blue shifted from the bulk (345 nm). With the change of Cu concentration a minor change in absorption edge is observed and it corresponds to a change in band gap energy of ZnS:Cu nanoparticles with Cu concentration. Band gap energy of ZnS:Cu nanoparticles are then calculated from the plot of $\{(k/s)h\nu\}^2$ vs $h\nu$ by extrapolating its linear portion on $h\nu$ axis at k/s = 0 [Fig. 5(c)]. As seen in figure, the band gap of the ZnS:Cu nanoclusters varies from 3.97 to 3.55eV with Cu²⁺ doping. It is worth to observe that even though the grain size decreases with doping concentration the band gap is found to be decreasing. This red shift in band gap with decrease of grain size is attributed to band tailing effect. The dopant Cu ions produces distinct energy states in the band gap of the ZnS. At high doping these local levels can overlap to form a band and merge with the conduction band or valence band, resulting in the contraction of band gap. Such a red shift in ZnS:Cu²⁺ nanorods where doping concentration varies from 0.2% to 0.4% is observed by Baoyou Geng et al. [35]. They explained that when Cu ions reside in the Zn²⁺ sites in the host lattice, the Zn–Cu–S ternary coordination is formed; hence the band gap will depends on the ratio of Zn and Cu ions. The decrease of band gap with concentration may also be due to the CuS formation because the energy gap of CuS is smaller than that of ZnS.

Fig. 6 (a) & (b) gives the reflection and absorption spectra of ZnS:Cu (0.001 M Cu) nanoclusters synthesised at different temperatures. The band gap changes from 3.74 to 3.64 eV [Fig. 6(c)] with temperature. Due to the increase in the size of the nanocrystallites with temperature, the band gap gets red shifted. The variation of particle size and band gap energy with increasing doping concentration and with synthesis temperature is given in Fig. 5(d) and Fig. 6. (d).

Since the dopant Cu ions produces intermediate energy levels below the excitonic levels of host nanocrystals, its addition changes the

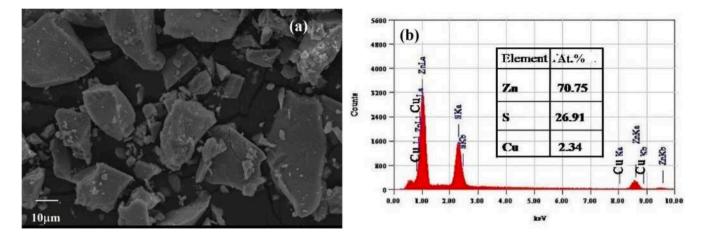


Fig. 4. (a) SEM & (b) EDS spectrum of ZnS:Cu for 0.001 M of Cu^{2+} .

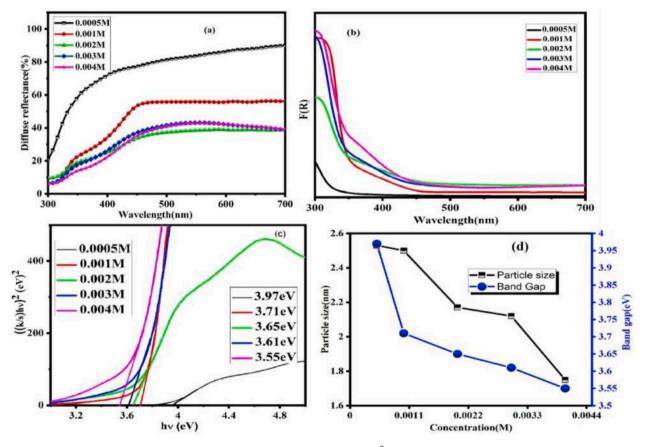


Fig. 5. (a) Diffuse reflectance spectra, (b) Plot of F(R) Vs wavelength, (c) the plot of $\{(k/s)h\nu\}^2$ versus $(h\nu)$ and (d)Variation of band gap energy and particle sizes with Cu concentration of ZnS:Cu nanoclusters synthesised at room temperature.

photophysical relaxation process. Hence to find out the effect of amount of Cu added on luminescence we have recorded PL emission spectra of the ZnS:Cu²⁺ for the excitation wavelength of 380 nm and are shown in Fig. 7(A). For all ZnS:Cu samples the emission spectra are quite similar and have similar emission peaks which indicates that the blue-green emission is the consequence of copper luminescence centers present in the ZnS matrix. All the samples show three emission bands-weak blue and red emissions centered at 415 nm and 625 nm and other broad emission in the range 450–600 nm having shoulders around 475 nm and 522 nm similar to the previous results in ZnS:Cu nanocrystallites [15, 36–38]. By Gaussian curve fitting [Fig. 7(B)] this broad emission is deconvoluted in to two emission peaks one at 475 nm and the other around 522 nm.

Due to the increased surface to volume ratio of nanoparticles the Cu ions both at substitution sites and interstitial sites can be more near the exterior region, mainly for small doping concentrations. Hence for low doping concentrations blue or green emission related to Cu can be dominant. The green emission in ZnS:Cu nanocrystals (~522 nm) is red shifted in comparison with green emission (500 nm) in bulk ZnS:Cu. Such a red shift is observed in the photoluminescence emission (PL) spectrum of nanomaterials [39–42]. It is known that Cu²⁺ ion has 3 d⁹ electronic structure of tetrahedral symmetry. On doping in to ZnS lattice, it replaces Zn²⁺ and 3 d⁹ ground state of Cu divided into lower lying 'e' levels and higher lying 't₂' levels [43]. Hence for Cu doped ZnS

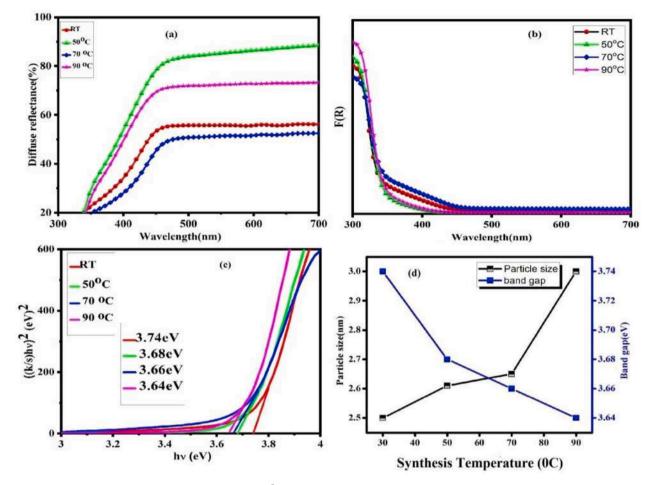


Fig. 6. (a) DRS (b) Plot of F(R) versus wavelength & (c) $\{(k/s)h\nu\}^2$ vs $(h\nu)$ plot and of ZnS:Cu nanoclusters synthesised at different temperature (d)Variation of particle size and band gap with synthesis temperature.

nanoparticles, researchers reported different emission bands. For example, Xu et al. [44] reported blue emission at 460 nm and green emission at 507 nm. But Khosravi et al. observed this green emission at 480 nm [39]. Huang et al. reported a blue PL emission band at 415 nm [14]. However for bulk Cu doped ZnS five emissions - blue, green, red, UV and IR emission were observed [12]. In our work the blue (475 nm) and the green emission (522 nm) are due to the transition from the conduction band edge and the shallow defect state to the t₂ state of Cu very close to the value observed by Xu et al. [15]. The red emission at 625 nm which is rarely observed in ZnS:Cu nanocrystallites is due to the transition between a deeply localized defect level related to S vacancy and t₂ state of Cu²⁺. But this red emission was observed in ZnS:Cu bulk material [43,45]. The possible emission centers in nano materials are associated with the surface or lattice imperfections or local impurities and usually inclined to many conditions like crystallinity, particles size, doping conditions and surface states of nanoparticles [46]. The blue emission observed at 415 nm is characteristics of ZnS and it is ascribed to the transition between the S vacancy and the valence band [47]. At higher Cu concentration an extra emission component at 445 nm, arising from the trap state emission of ZnS related with native zinc vacancy was observed [19]. Even though there is no change in the peak position of PL emissions for all samples the relative intensity significantly varies with concentration. At 0.001 M of doping concentration Cu²⁺ related green and red emission intensity is maximum but ZnS emission at 415 nm is minimum showing competent energy transfer mechanism between Zn²⁺ and Cu²⁺. In many II-VI semiconductors intensity of green emission is found to be decreased with the increase in concentration of the dopant. There are only few reports on the concentration quenching effect of

green emission in Cu^{2+} doped ZnS nanoparticles [19,27,28,48]. Since the synthesis is carried out in different conditions the optimum Cu^{2+} concentration for maximum green emission intensity is different. M. Kuppayee et al. [49] reported that in ZnS:Cu the PL intensity increases with Cu²⁺ concentration and optimum Cu concentration for maximum intensity is 0.4% above which quenching in the luminescence intensity takes place. W.Q.Peng et al. have reported optimized doping concentration of 1.0 at. % Cu [19]. Jayanthi et al. reported the maximum PL intensity for the doping concentration of 0.0001 M and Muthukumaran [32] found an optimum Cu²⁺ concentration of 0.01 M %. In these reports the synthesis is carried out only in the presence of capping agent. But in our case where the synthesis is carried out without capping agent, it is found that copper related green emission is maximum when the Cu²⁺ concentration is 0.001 M. Therefore, we can conclude that the optimum Cu concentration to get maximum green emission from ZnS:Cu nanoparticles is 0.001 M beyond which PL intensity is decreased. Since the quenching of the green emission band suggests the presence of CuS phase which reduces the amount of copper ions that perform as optically energetic luminescence centers in ZnS:Cu. It is confirmed by XRD studies which shows impurity peaks at higher doping concentrations and supported by dark gray colour of the samples with increase of doping concentration. The enhancement and quenching of red emission also takes place with that of green emission. Quenching of red emission may be due to the Cu-Cu pairs in the ZnS:Cu lattice. On increasing the doping concentration additional Cu luminescence centers are set up in the lattice and hence the excitation energy is transferred from one Cu^{2+} ion to its nearest \mbox{Cu}^{2+} ion by a nonradiative transition. So the concentration quenching of red emission can be ascribed to the existence of Cu^{2+} pairs.

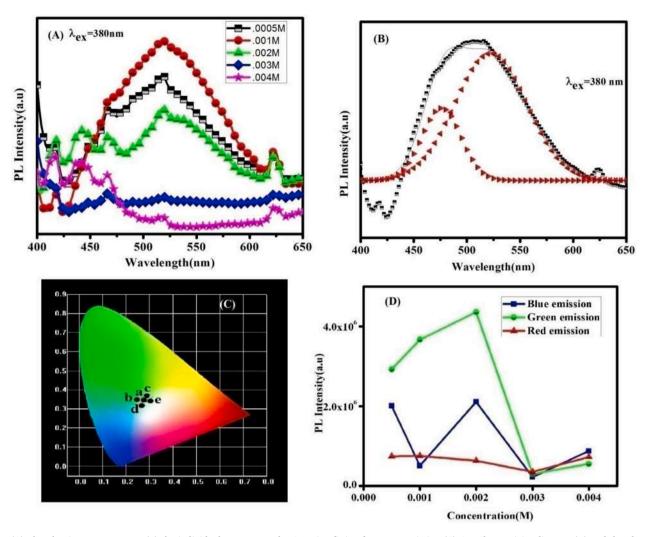


Fig. 7. (A) Photoluminescence spectra (B) the individual components by Gaussian fitting for green emission (C) CIE Chromaticity diagram (D) and the plot of the intensity of emission as a function of Cu concentration for the nanocrystalline $ZnS:Cu^{2+}$ synthesised with different Cu concentration.

Emission spectra of ZnS:Cu nanoparticles for different synthesis temperatures are shown in Fig. 8(A). For all samples the emission spectra are quite similar and have similar emission peaks. As given in Fig. 8(B), with increasing temperature, the host emission at 415 nm also increases but decreases at 90 $^\circ \mathrm{C}$ at which intensity of red emission is maximum indicating energy transfer mechanism is efficient. But the intensity of the PL emission related to copper gets enhanced at temperature of 50 °C there after the intensity of this emission is decreased continuously with temperature rise. This may be due to the charge trapping mechanism by which at 50 °C charge carriers trapped at the defect levels become free at the conduction band and give rise to the Cu²⁺ related PL emission. Hence the intensity of emission related to Cu is increased with temperature rise and as the trapped sites become vacant, the PL intensity decreases [50]. It may be also due to the formation of CuS. A plot of Cu²⁺ concentrations and synthesis temperature versus PL intensity of Cu-blue, green and red band emissions is given Fig. 7(D) and 8.(D). In order to understand the nature of the emission bands in ZnS:Cu nanoclusters, its excitation spectra [Fig. 9] is recorded for two emission wavelength 475 and 522 nm at room temperature. When monitoring the emissions of ZnS:Cu nanocrystals at 475 or 522 nm both the excitation spectra are almost same, consisting of three peaks. The highest energy band having maximum around 332 nm corresponds to the transition from band to band and equal to the band gap of ZnS: Cu^{2+} (3.74 eV), signifying that the energy is wrapped up by the ZnS host itself. The low energy bands with the peaks around 378 and 394 nm correspond to the excitation of impurities [14]. Based on the energy level structure [Fig. 9] PL mechanism can be described. Here V_s stands for sulphur vacancy. Due to the absorption of UV photons by the ZnS host nanoparticles the electrons gets excited to the conduction band from the valence band. The recombination of these electrons trapped by shallow defect level related to S and t_2 level of the copper leads to radiative transition resulting in the emission of green light at 522 nm. The transition between the shallow defect level and the ground state results in the emission of 415 nm. The emission at 475 nm originates from the transition between the conduction band and the Cu²⁺ impurity. For intra band excitation, the possibility of transition of excited states through dopant related energy levels is greater than the direct recombination with electrons in the ground level, the emission related to dopants is more powerful than host emission.

Since the emission of ZnS:Cu nanoparticles consist of the surface defect emission of host (blue emission) and dopant related emission (green and red color), a tunable colour output is obtained by changing the doping level added. Hence to assess the performance of ZnS:Cu nanoparticles to be used as phosphors in display devices, evaluation of the CIE color coordinates are most useful. The calculated CIE coordinates for Cu doped samples for different synthesis temperatures and for different Cu^{2+} concentration is given in Table 3. From Fig. 8(C), it is clearly seen that at the lower temperatures (RT & 50 °C) emission color is green. Similarly the color coordinates can be tuned from green to bluish white [Fig. 7(C)] by controlling Cu doping concentration showing

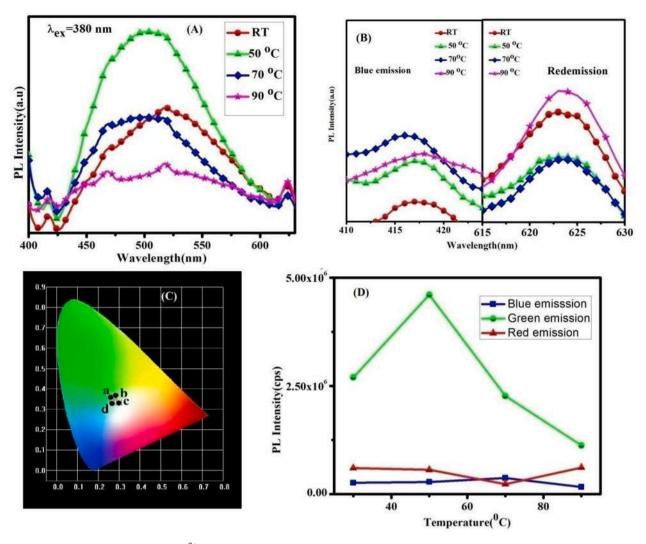


Fig. 8. (A) Photoluminescence spectra of ZnS:Cu²⁺ nanoparticles synthesised at different temperatures showing all emissions, (B) Emissions in the blue and red region of ZnS:Cu nanoparticles in magnified form (C) CIE diagram (a,b,c & d corresponds to CIE coordinates of ZnS:Cu nanoparticles synthesised at RT, 50 °C, 70 °C and 90 °C and (D) Plot of the intensity of emissions Vs synthesis temperature for the nanocrystalline ZnS:Cu.

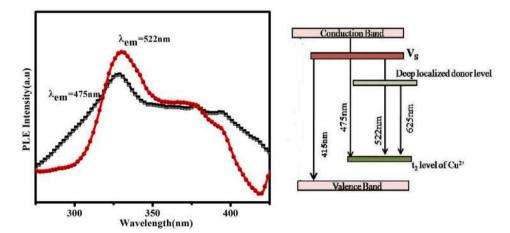


Fig. 9. PL excitation spectra and schematic energy band diagram showing the emissions in $ZnS:Cu^{2+}$ nanoparticles.

its extensive applications in the colour tunable optoelectronic strategies.

4. Conclusion

In this work ZnS:Cu nanoparticles for different Cu concentration and at different synthesis temperature were synthesised by chemical

Table 3

Showing CIE color coordinate with different synthesis temperature and Cu concentrations in nanocrystalline ZnS:Cu.

Concentration	Colour coordinate (x, y)	Temperature	Colour coordinate (x, y)
0.0005 M	(0.28, 0.35)	RT	(0.26, 0.36)
0.001 M	(0.26, 0.36)	50 °C	(0.28, 0.36)
0.002 M	(0.29, 0.36)	70 °C	(0.30, 0.34)
0.003 M	(0.27, 0.33)	90 °C	(0.27, 0.33)
0.004 M	(0.30, 0.35)		

precipitation method without any capping agent in water medium. The photoluminescence properties of ZnS:Cu nanoparticles are studied in detail. In addition to the blue emission of ZnS, ZnS:Cu²⁺ nanoparticles have three emissions, blue (475 nm), green (522 nm) and red (625 nm), which are attributed to the transition between conduction band, shallowly and deeply trapped electron with the t₂ levels of Cu²⁺. The optimized Cu concentration for maximum green emission intensity is 0.001 M. For ZnS:Cu nanoparticles (0.001 M Cu) the maximum green emission intensity is observed for the sample synthesised at 50 °C thereafter intensity is decreased. The colour tuning of the emission from the ZnS:Cu nanoparticles are evident from the calculated chromaticity coordinates and finds their applications in optoelectronic devices.

CRediT authorship contribution statement

K.R. Bindu: Formal analysis, Methodology, Writing - original draft. E.I. Anila: Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Abstract: The word carbohydrates can be traced back to Germans, who called them "Kohlen hydrates". It was then termed carbohydrates in English. 'Carbo' means that they contain carbon, 'hydr'means that they contain hydrogen and the third part of the name 'ate' mean that they contain oxygen. The ratio of hydrogen atom to oxygen atoms is 2:1. Carbohydrates are actually the organic compounds that are important for body functions. Carbohydrates are much abundant in plants, rather than in animals. Animals utilizes carbohydrates in the form of food. Muscle hypertrophy is an important factor for athletic performance. This study attempts to detailed discussion on importance of carbohydrates in muscle hypertrophy.

Key words; sports nutrition, carbohydrates, muscle hypertrophy

INTRODUCTION

"Nutrition may be defined as the sum total of the process by which the living organism receives and utilizes the food materials necessary for growth, maintaince of life, enhancing metabolic process, repair and replacement of worn out tissues and energy supply" (Z S C Okoye). sports nutrition research started in 1960's at Ball state university under direction of Dr David Costil.Sports nutrition is the study and practice of nutrition and diet as it relates to sports performance. It deals with the nutrients such as vitamins, minerals, carbohydrates, fats and protein. Carbohydrates are the polyhydroxy aldehydes or ketones or these are the compounds which on acidic hydrolysis give polyhydroxy aldehydes or ketones. They contain carbon, hydrogen and oxygen molecule. Carbohydrates are classified in to three categories, monosaccharides, oligosaccharides and polysaccharides. The main difference between the type of carbohydrates is actually the difference between their chemical composition. Compared to complex carbohydrates, simple carbohydrates have smaller chain of chemical composition. Muscle hypertrophy is an increase and growth of muscle cells and it is achieved through physical exercise. There are two types of muscular hypertrophy, myofibrillar and sarcoplasmic muscle hypertrophy.

OBJECTIVES OF THE STUDY

- To discuss functions of carbohydrates in terms of muscle hypertrophy. \geq
- \triangleright To discuss importance of carbohydrates in muscle hypertrophy.

STATEMENT OF THE PROBLEM

Carbohydrates are important fuel for physical exercise. The purpose of this study was detailed discussion on importance of carbohydrates in muscle hypertrophy and discussing the functions of carbohydrates in terms of muscle hypertrophy.

REVIEW OF LITERATURE

Amy R Lane et.al (2010, April) found influence of dietary carbohydrate intake on the free testosterone: cortisol ratio, response to short term intensive exercise training. William J Kraemer et.al (2017) found recovery responses of testosterone, growth hormone and IGF-1 after resistance exercise. Moller N Jorgensen J.O(2009) found effects of growth on glucose, protein and lipid metabolism in humans. M Wholever T.M, Br J Nutr. (2000 March) found dietary carbohydrates and insulin action in humans. Alghannan A F et.al (2016) found influence of post exercise carbohydrates protein ingestion on muscle glycogen metabolism in recovery and subsequent running exercise. Ivy J L et.al (2002) found influence post exercise carbohydrate, protein ingestion in subsequent running exercise. Classey J. L et.al (2001) found abdominal visceral fat and fasting insulin are important predictors of 24-hour GH release independent of age, gender, and other physiological factors.

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DISCUSSIONS

Discussions on importance of carbohydrates in muscle hypertrophy

Carbohydrates are the most abundant organic molecule in nature and primary source of energy in humans. General formula of carbohydrates are Cn(H2O). sugars are simple forms of carbohydrates. polysaccharides such as starch and fibre are complex forms of carbohydrates. The smallest carbohydrates are monosaccharides such as glucose and fructose. These compounds which do not break down in to simpler compounds on hydrolysis. The body breaks down most sugars and starches in to glucose. Sports persons rely carbohydrates for sustained energy, preventing fatigue and enhancing athletic performance.

Strength is an important component for athletic performance. Strength is highly improved through resistance training. Muscle cross section (muscle size), muscle fiber spectrum, coordination, energy supply, body weight and psychic factors directly affected muscle strength, so muscle hypertrophy is an important factor for sports performance. Mainly athletes achieved muscle hypertrophy through resistance training. isometric, isotonic and isokinetic resistance training improves muscle hypertrophy. Progression of training and proper nutrition also helps to improve muscle size. Sarcoplasmic muscle hypertrophy and myofibrillar muscle hypertrophy are two types of muscle hypertrophy. Myofibrillar muscle hypertrophy increases strength and speed and activates contractor muscle. Sarcoplasmic muscle hypertrophy increases energy storage and endurance and activates glycogen storage in muscles. The energy for muscle hypertrophy is primarily obtained through the breakdown of phosphogens (ATP-CP). The amount of phosphogens stores is therefore important for strength performance. Testosterone production, human growth hormone, immune system, cortisol and IGF-1 production directly influenced on muscle hypertrophy.

Protein sparing is the process by which the body derives energy from sources other than protein. Protein sparing effect helps to protect muscle proteins. According to classical studies of Munro (1964) administration of carbohydrates has a protein sparing effect in the fasting subjects, whereas fat does not have this effect. In this process body take glycogen for energy instead of breaking down muscle tissue for energy. Combination of carbohydrates with protein supplements produces greater anabolic response than protein alone.

Muscle is harder to build due to lower testosterone levels in athletes. For adult men and women regular resistance exercise are key to building and keeping muscles. Testosterone is an androgen. testicles produced large amount of testosterone in men, as well as small quantities produced by the adrenal gland in both men and women. The pituitary gland control testosterone production. Pituitary gland produces luteinizing hormone or LH. Which stimulates testicles and create more testosterone. Carbohydrates are essential for testosterone production. Studies shows that high carb and low protein diet improves free testosterone levels and low carbohydrates diet increases cortisol level (stress hormone). Cortisol negatively affected muscle hypertrophy and increases muscle catabolism.

Insulin is an important hormone in human body and also called the evil storage hormone. Insulin is released by pancreas, mainly related to intake of carbohydrates and insulin that causes cell to absorb glucose from the blood and used it for energy. Insulin helps to regulate blood sugar level by assisting the cells that absorb sugar from blood stream and it is a very powerful muscle building hormone, it shuttles glucose and amino-acids to the cells. Insulin act like a stimulator of muscle hypertrophy and it is an anabolic stimulus for muscle proteins. Insulin directly stimulate the cellular pathway in the muscle that regulate muscle growth and triggers sodium ion and potassium ion pump to allow amino-acids to enter and be turned in to protein. Also helps to promote blood supply towards muscles it helps to reach more oxygen and nutrients into muscle.

Growth hormone is a protein hormone and secreted by cells called somatotrophs in the anterior pituitary gland.HGH helps to growth and metabolism. The HGH stimulate the liver and other tissues to secrete IGF-1. IGF-1 is a key player in muscle growth. It stimulates both the differentiation ad proliferation of myoblasts. It also stimulates amino acid uptake and protein synthesis in muscle cells. Growth hormone show anti-insulin activity, supresses the abilities of insulin to stimulate uptake of glucose in peripheral tissues. Exercise, nutrition, sleep and stress affected production of growth hormone. Insulin and HGH mutually regulate the secretion of each other. The balance between

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insulin and HGH is associated with substrate and energy metabolism, but in case of protein metabolism they synergistically act each other. Research suggests that insulin may dicate the secretion of HGH.Consistent increase in insulin level prevent HGH production and reducing the level of HGH in body. In case of obesity, insulin is high and lower levels of HGH leads to further build-up of fat and affect muscle hypertrophy. Along with directly affecting insulin production excess sugar intake enhances weight gain and obesity, which also affect HGH levels.

"A new study shows that, following muscle injury, certain immune cells produce a protein called GDF3 that enhances formation of new muscle cells" (Laszlo Nagy. D, PhD, genomic control of metabolic program). Exercise is a form of stress and more vigorous physical exercise develops more physiological and biochemical changes in human body. Prolonged strenuous physical exercise challenging immune system and causes immune-depression. Consuming carbohydrates immediately after strenuous exercise also helps to restore immune function. This is especially important in situations where the recovery duration between the two consecutive exercise sessions in short, which is often the case for athlete (Dr Oliver Neubaver). Intake of carbohydrates during or immediately after exercise reduces exercise related immuno-depression and helps the body to recover. Well balanced diet helps to maintain immune function following longer duration physical exercise.

CONCLUSION

Carbohydrates are neutral chemical compounds and produced 4 calories of energy per gram energy. Humans stores carbohydrates in the form of glycogen and uses this nutrient for energy. Carbohydrates play key role in the metabolism of amino-acids and fatty acids. Intake of carbohydrates are important for immune function, testosterone production and also controls production of stress hormone cortisol. Production of Insulin directly related to intake of carbohydrates. Elevated insulin level may reduce HGH production.HGH is an important hormone for muscle hypertrophy. Insulin and glucagon ensure that cells throughout the body, and especially in the brain have a steady supply of blood sugar. Reduction in sugar intake also leads to an increase in HGH production.

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HERDING BEHAVIOUR, AND THE EFFECT ON INVESTMENT DECISIONS OF RETAIL INVESTORS

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ABSTRACT

ABSTRACT Financial markets are significantly influenced by unions factors like changes in economic, legal and political processes that occur in an economy. Neuertheless, the most vital factor is the investor's reaction and perception. From the investor's point of even, investment decision making process is dependent on the proceeding of the breaster, which can be called as investor investment. This research aims to report the reacench of individual investor's settlemente, exposedly herding behaviour in a historical perspective. This research paper is intended to ancover the consister's psychology in investment decision making facturing on the investor's rationality by explaining factors that affect th investment decision. This research factors on the herding behaviour of the investor and its effect on the investm decision making of the retail investors inErnabulan District

Keywords: Investor, Investor Sontiments, Investment, Investment duction making, perception, retail investor INTRODUCTION

In general, irrational behavior is considered behavioral bias. Behavioral biases are irrational beliefs about behaviors that may unconsciously influence our decision-making process. They are generally thought to be divided into two - emotional biases and cognitive hiases. Both biases are usually the result of prejudice in the choice of one thing over the other. In general, cognitive prejudices include decision-making based on principles that may or may not be exact. Emotional biases usually occur spontaneously on the basis of an individual's personal feelings at the time the decision is taken For a long time, everyone assumed that traditional finance theory was correct, because it states that investors think rationally and make conscious decisions; based on different emotional reactions or using economic models

However, after a number of investigations, it has been noted that human decisions often depend on their nature, intuitions and habits, cognitive or emotional bias hidden deep in the back of one's mind Individual investors are faced with more rational decision-making issues than institutional investors. (Ahamed, 2013)Small investors may not have all the relevant data for rapid and logical decision-making. People are unique creatures of financial behavior and, in different situations; they make

decisions in their own way, not just in accordance with traditional financial rules. Investment decision-making processes based on forecasting and the knowledge of market participants are becoming increasingly unrealistic in the current global finan market. The main reason for savings is to cover post-retirement expenses and also to acquire wealth. And the investment is targeted at the excess of money after meeting the individual's expenses.

In finance and economics, behavioral bias refers to a tendency to make decisions that result in rational financial decisions due to faulty cognitive reasoning or emotionally influenced reasoning. Behavioral biases can have an effect on financial market participants' behavior and decisions. By understanding behavioral bias, financial market participants may be able to moderate or adjust to bias and, as a result, improve economic outcomes. Individual investment natterns depend on various factors, such as economics, personal and emotional conditions, etc. Due to the changes in these conditions, there is also a change in individual investment patterns and decisions. 1.1 OBJECTIVES OF THE STUDY PRIMARY OBJECTIVES:

I) To determine the emotional biases that affect the investors decision on various investments

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സാഹിത്വത്തിലെ പ്രദേശം ഭാവനകൾ

മലയാളസാഹിത്വത്തിൽ ദൃശ്വവും അദ്ദശ്വവുമായി നിലനിൽക്കുന്ന പ്രാദേശികസംസ്കാരത്തെ പഠനവിധേയമാക്കുന്ന ലേഖനങ്ങൾ.

වුණුSæno

- 06 വീണ്ടെടുക്കേണ്ടുന്ന പ്രദേശങ്ങൾ എ.സി. ശ്രീഹരി
 - മലപ്പുറത്തിന്റെ അറബി, അറബി-മലയാളപാരമ്പര്യം ഡോ. അസീസ് തരുവണ
- 30 സമകാലികകഥയിലെ പ്രദേശങ്ങൾ ഡോ. വാസുദേവൻ വി,
- 43 പൊന്നാനിക്കളരിയുടെ സാംസ്കാരികഭൂമിക ഡോ. ഫസീല ടി.എ.

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- 53 <mark>'ഭൂത'ഭാവനകളുടെ സ്ഥലരാശി</mark> ഡോ. അനൂപ് വി.
 - എരി: ദേശവും പാത്രനിർമ്മിതിയും സൗമ്യ സി.എസ്.
 - കുട്ടനാടിന്റെ പ്രാദേശിക ചരിത്രമാനങ്ങൾ: തകഴിയുടെ 'കയറി'ൽ ഗീതു ദാസ്
 - പ്രദേശനിർമ്മിതിയുടെ സാംസ്കാരികവിനിമയങ്ങൾ 'ഐതിഹ്യമാല'യിൽ ഡോ. നെത്തല്ലൂർ ഹരികൃഷ്ണൻ

വിശുദ്ധജന്മങ്ങൾ: ദേശഭാവനയുടെ ഭാഷ്യങ്ങൾ ഹരിത കെ.

നായ്പോൾ രചനയിലെ കരീബിയൻ ദേശസംഘർഷങ്ങൾ അബ്ദുൾ സമദ് കെ.

ഡോ. അനൂപ് വി.

'<mark>ഭൂത'ഭാവനകളുടെ</mark> സ്ഥലരാശി

propose the following definition of the nation: it is an imagined political community-and imagined as both inherently limited and sovereign. It is imagined because the members of even the smallest nation will never know most of their fellow-members, meet them, or even hear of them, yet in the minds of each lives the image of their communion Communities are to be distinguished, not by their falsity/genuineness, but by the style in which they are imagined.... Finally, [the nation] is imagined as a community, because, regardless of the actual inequality and exploitation that may prevail in each, the nation is conceived as a deep, horizontal comradeship. Ultimately, it is this fraternity that makes it possible, over the past two centuries for so many millions of people, not so much to kill, as willing to die for such limited imaginings."

-Benedict Anderson

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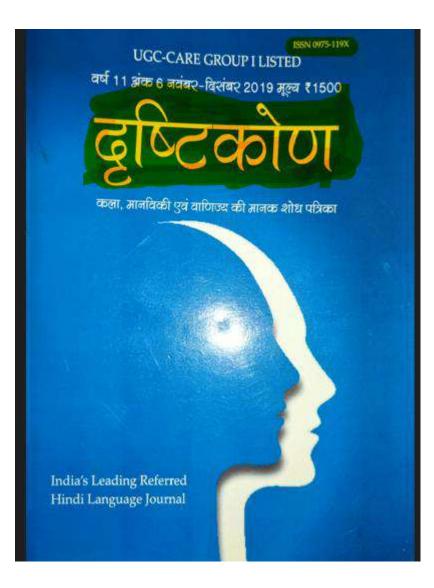
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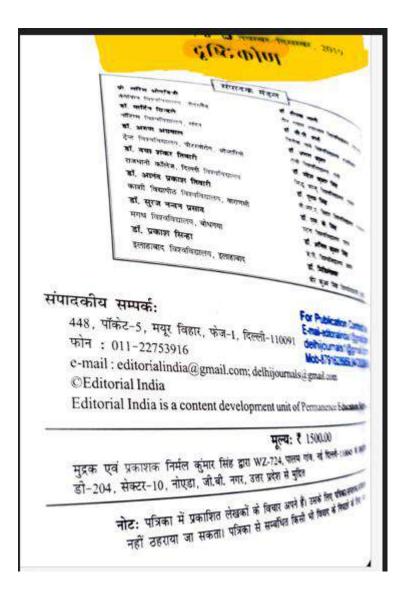
Politics of identity and history of community-based politics in Kerala

Sudhakaran K.M.

In the early twentieth century, Kerala society witnessed radical changes in the socio-economic and political realms. The advent of capitalism, colonial modernity, and various other ideologies and movements that emerged in different parts of the world created a diverse consciousness among the major sections of society. It was reflected in some of the reforms of the then rulers to improve the conditions of the subjugated sections of the society. The First World War and the post-War developments that unfolded in many parts of the world also generated diverse forms of consciousness within the national movement and the society at large. People who gained modern education from prominent communities with varying degrees of social consciousness exerted some influence on the way of thinking and formed new social alliances within the society. It was reflected in the formation of alliances between and among the major communities developed mainly against the existing special rights and positions enjoyed by the upper caste Hindus. These alliances then fought for their rightful share in government services, free access to the general public, and equal and equitable treatment by the authorities as enjoyed by the caste Hindus. Their modes of struggle were as peaceful and constitutional as submitting petitions and memoranda for more rights and privileges in society. The repercussions of the alliances helped the major political parties of the twentieth century, the subsequent formation of governments, and the strengthening of democratic alliances after Indian independence.

Coalition politics is an inevitable part of parliamentary politics. As society is divided into different castes and religious groups, sectarianism has gained a lot of importance in coalition politics. The caste/religious interests dominate within political parties and serve as the key to sectarianism. The decision to enter or leave the coalition is always taken within small internal circles based sometimes on communal balancing. The value and commitment to ideology in such agreements,







भूषम गरेत के विश्वमास लग , अपगण्यांद का परिष्कृत और त्रिकांसत रूप संस्कृति है। संस्कृति राज्य संस्कृत के 'सम' उपमर्ग इसक कु' धातु के जुड़ने से बना है जिसका अर्थ है परिष्कृत कार्य। प्रतिर्थन के आदाण्याई के अनुस्कर संस्कृति शिण्याचा है के उसने शब्दार्थ को अपेका शब्दों का भाषार्थ प्रत्रण करना चाहिए को विशेष और व्यापक है। संस्कृति के अंगर्गत मतुब्ध की भाषा, आबज रहेंत- रिवाल, दर्शन, तान, साहित्य, कतल, मुल्द, व्यवस्था तथा जोवन होती, धार्थिक अनुष्ठान, पर्व, त्योहत संस्था ब्राह्य का संस्थार, एक दूसरे के प्रति दृष्टिकोण और इनसे जुड़ी सार्ग चौरेत व्यापक है। संस्कृति का अंगर्गत मतुब्ध की भाषा, ब्राह्य का संस्थार, एक दूसरे के प्रति दृष्टिकोण और इनसे जुड़ी सार्ग चौरे का जोतन ही है। सार सब सिल्डर एक विशिष्ट जीवन-ब्राह्य बस्ता है जिसे संस्कृतिक घरोठर कहते हैं। विश्वमा और यूल्य चेतना पर संस्कृति का गडरा प्रमाय पहला है। गण्ड, रंग की बास वे इसका गठा प्रमाय बंध है। संस्कृति को परिभाषा सर मंतिपर विशिष्यम ने दुस प्रकार ने हैं। प्रयत्न द्वारा करा मंत्र-तेत बास वे इसका गठा प्रमाय बंध है। संस्कृति को परिभाषा सर मंत्रियर विशिष्य यात्रन प्रकृति है । प्रवत्न, कुला लेति, विधि, यौरिय, र्यति का बास्त इसकार प्रता है। दिदी साहत्य कोश के अनुसार संस्कृति तथा प्रचायों को संस्कृति महा जात है। ' एमप्यरिसिंह दिनकर के अनुसार संसकृति का अर्थ मनुष्य कांभोठते कि प्रदेश तथा अंग विश्वम साध्य दे इस आदि में होत्र का स्थल, स्थल लेति, विधि, यिति। तिवह सास्तवेश रहता है। दिदी साहत्य कोश के अनुसार संसकृति तथा व्यापाये के। संस्कृति कहा जात है। ' एमप्यरिसिंह दिनकर के अनुसार संस्कृति का अर्थ मनुष्य कांभोतरी विकास और उसकी नित्रिय साध्यक्रों को संयोहम जातीत है।' इन प्रकार कई विद्वनों का संपन्न हो गईक है । इजागी प्रसाद द्विपी के अनुसार संस्कृति का पित्रम साध्यक्रों को सार्गम परियाति है। इन्हा को संस्कृति का प्रत्रम हो गईक है । इजागी प्रसाद द्विपी के अनुसार संस्कृति का पिकास साध्यकों को सार्गनम संस्तरिय संस्थ अनुष्य के निरंतर संपर्भ हो क्राइ इं सं संस्कृति को परिपाधित किया है। संस्कृति का विश्वम साध्यकों की संसतिय संस्र स्वाय के अत्यत्य संस्त हो प्रहल से से संस्कृति को परिपाधित किया है। संस्कृति का पिकास साध्यकों को संस्वता स्वरति से से सर्व हो के अनुस्य के निरंस स

चलतेद संस्कृति में वैचारिकता का अति महत्वपूर्ण स्थान है। चुकि संस्कृति का संबंध मनुष्य के आंतरिक विचारों से है. यह एक अत्वुंची प्रक्रिया है के मानव को कर्श्वमुखी बनाती है। संस्कृति ही हमारे संस्कृति का परिष्कार करती है और मानव. संस्कृति क इस ति उसको सांस्कृतिक चेतना को विभिंत और प्रवल करता है। सांस्कृतिक चेतना से ही हमारी संस्कृति वास्तविक रूप में बहते है। सांस्कृतिक चेतना मनुष्य को, संस्वर, अपने आचरण में दिखाने को प्रेरित करती है। यह व्यक्तिगत होते हुए भी सम्मिद्यन का ने नेती है। सात्रांच संस्कृति चेटियक संस्कृति है और इसको सांस्कृतिक चेतना का मूलभूत आभर वसुधेत कुटुवकम को भावना है करते बजुवेद भी पुष्ट करता है। 'वेन्द्रसन् प्रश्नपत्रित पृष्टा सद्। यह विरत करती है। सात्र स्वर्थक होते है और उसको सांस्कृतिक चेतना का मूलभूत आभर वसुधेत कुटुवकम को भावना है करते बजुवेद भी पुष्ट करता है। 'वेन्द्रसन् प्रश्नपत्रित पूरा सद्। यह विरत भवति एक नोडम्।। हमारी संस्कृति से स्वर्थ स्वर्थ के द्वार कराई है। 'वेन्द्रसन् प्रश्न प्रयानविति पृष्टा सद्। यह विरत भवति एक नोडम्।। हमारी संस्कृति से स्वर्थ स्वर्थ के द्वार काई प्रेयत्व स्वर और अधीतिक स्वरार पर। मीतिक स्वर्थति मूर्व वस्तुओं से संधेश्वर होती है और उसका सरोका स्वर्थ के द्वार काई में खस्तुओं से होतत है। अधीतिक संस्कृति में सभी तत्य अत्रते है जिसका स्वरूप अभूर्य होता है जैर उनका सरोका स्वर्थ के द्वार काई में संस्वर्ध से प्रयोत , तृत्य आदि। पातीय संस्कृति में साम्मृतिक चेतना स्वरूप अभूर्य होतो है जैर उनका सरोका कि तो तर्त है और इसके द्वार हमें आरत के आध्योत्यक संस्वर्ध के वाणी देने का चेका चितना है। पाततीय संस्कृति को सबसे बड़ी विश्वरा उसकी धार्मिक बर्ड है। स्वर्थ के आध्योत्यक विश्वन को वाणी देने का चेका वित्यक सरीका सत्ती को। यह अकृव्य स्वित हो पर बढ़वा प्रसात्र कहा है। भारतीय संस्कृति में झडा, आप्रा के दिवा को चोचित करता है। परम तत्व ब्रह्य विश् व्य क्य क स्वर्ड वही खित्यकरता है। भारतीय संस्कृति में सडा, आप्रा को एकता को चोचित करता है। परम तत्व ब्रह्य विश् बायत है 9 और वही वहा हिवयत्वर्त एव जगत का रत्यमी है।' इसी सत्त की सर्वत ''' अनुभूर्यि प्रत्वकररव ही जोवन का पम लख्य बेव यह वह

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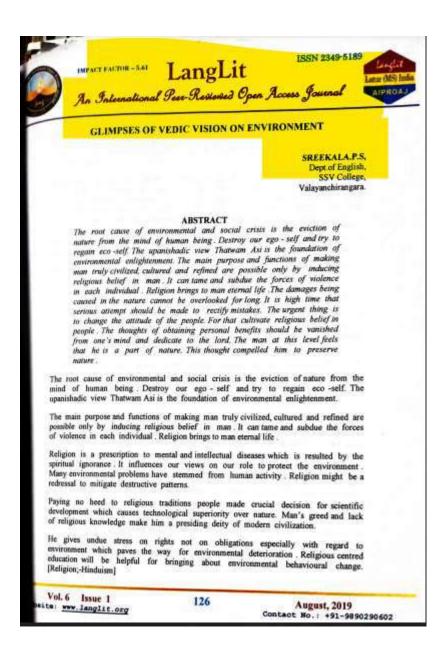
Teachings of Sreemad Bhagavatham on Environment

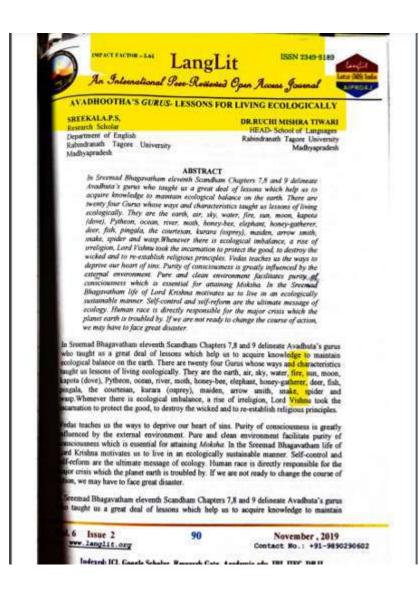
Sreekala.P.S. Lecturer, Dept of English, SSV College.

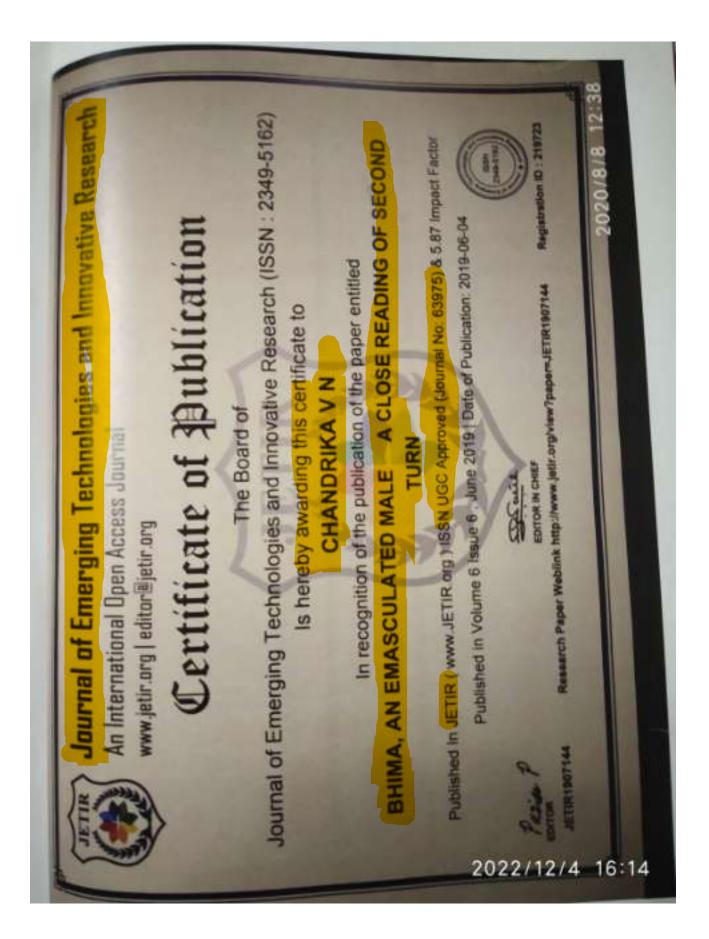
Today, the entire mankind is facing a crisis, perhaps the greatest crisis in human history. There is a unrest all over the world. Chaos is spreading and the world is threatened with a moral collapse. There is no respect for mankind. People do not realize the mankind. People do not realize the importance of human values. Man's life is cheaper than anything else in the world today. People have forgotten the sancity of man. The result has been conflicts, chaos, and confusion, oppression, exploitation and subordination all over the world. The bigger nations are trying to swallow-up smaller nations. In order to achieve this end, they sometimes indulge in wars in which there is a massacre of human lives. The solution to these problems lies in spiritual evolution. This is the only way to save mankind from the present catastrophe. Man should have the sense of spirituality which is the only solution of the present day problems.

Sreemad Bhagavatham can instill spiritual knowledge in to the minds of the people. It can rescue the world from this desperate crisis. The only solution for the present day problem is to make the people aware of Vedams and religious scriptures. Our ancestors had indepth belief in God. On the contrary modern man is like the king Venan who is arrogant and not pious. He has done everything without pleasing God. Hi attitude and behaviour are the root causes for all his problems. Man should develop a religious attinut towards the environment and save our planet and humanity.

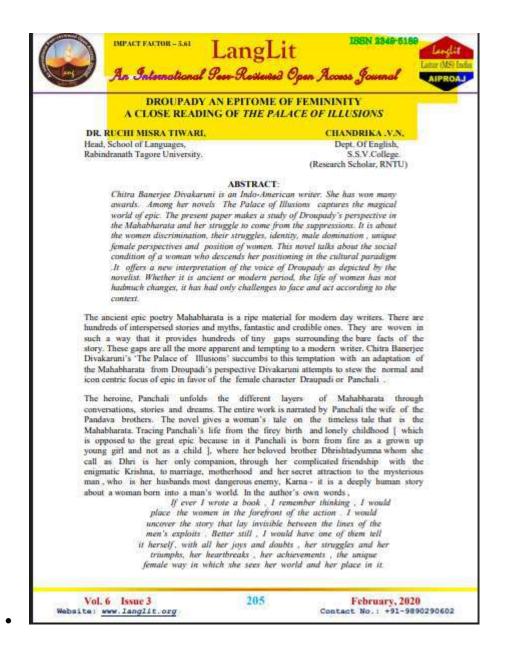
Sreemad Bhagavatham brings out the concent that a man cannot survive alone and he can







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Maharwetha Devi is widely acknowledged as one of India's foremost writers. Here mechant, powerful, satiric fiction has won her recognition in the form of Sahitya Academy (1979) and Jnapith (1996) awards, amongst several literary honours. She was also awarded the Padmasree in 1986 for her activist work amongst apposessed tribal communities. In recent years she has come to be recognized in the Western world as the spokesperson for the under-privileged and for women Maharwetha Devi's 'Draupadi' is presentation as a revisionist text where she attempts	6.
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N-doped photoluminescent carbon dots from water hyacinth for tumour detection

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ABSTRACT

Early diagnosis of life intimidating diseases such as cancer could drop down the mortality rate to a great extent. Carbon dots, being fluorescent materials hold a promising impact on the field of biomedicine. Herein, we report a single step, facile hydrothermal method for the synthesis of surface passivated, water soluble, spherical, fluorescent nitrogen doped carbon dots (N-CDs) from water hyacinth. From FT-IR and Raman Spectroscopic studies, surface functionalization was identified and nitrogen doping was confirmed by X-ray photoelectron spectroscopy. Optical properties were investigated by UV-Visible spectrophotometer and Fluorescence spectrometer and found that maximum fluorescence peak is located in the UV region. Amorphous nature of N-CDs was identified by X-ray diffraction. High resolution Transmission Electron Microscopy was used to study the morphological characteristics. The average size of N-CDs was found to be 6.2 nm. Anti-cancerous activity of the as-prepared carbon dots was examined against DLA tumour cells extracted from the peretonial cavity of mice and these tumour cells were not able to withstand at the increased concentration of carbon dots. The findings of our study prove the multifunctional ability of carbon dots to serve as optical probes in bioimaging applications.

Selection and peer-review under responsibility of the scientific committee of the International Conference on the Science and Technology of Advanced Materials.

1. Introduction

Waste biomass is a widely distributed, readily available, ecofriendly carbon source featuring magnificent natural properties. They are inexpensive precursors for green synthesis of nanomaterials and contribute towards recycle technology and sustainable material synthesis, substituting toxic chemicals [1]. The mounting waste generated worldwide is a prominent ecological burden for the society and its disposal and reuse is not effective in spite of stringent regulations [2]. So utilising biomass as a raw material for nanomaterial synthesis can be regarded as a sustainable alternative to tackle the troubles associated with global pollution.

Carbon dots are zero dimensional spherical particles less than 10 nm in diameter composed of amorphous carbon along with nanocrystalline regions of sp^2 hybridised graphitic structure [3,4]. Their unique structure offers them tunable chemical, physical, optical and electronic properties. These multifaceted

properties make them perfect nanomaterials in numerous fields such as biolabelling, optical sensing, drug delivery, biosensing, energy conversion and catalysis [5]. Although semiconductor quantum dots were identified to be good nanomaterials owing to their optical characteristics, they have restricted use due to their toxicity as well as environmental hazards. Low toxicity, high biocompatibility and fluorescent property of CDs from agricultural waste make them superior over conventional toxic heavy metal based quantum dots [6]. There are numerous protocols for the fabrication of CDs involving both synthetic and natural precursors. Among these strategies, hydrothermal treatment is the most efficient as it is cost effective, easy and less time consuming. Hydrothermal synthesis of CDs from a variety of sources like papaya [7], sweet potato [8], milk [9], orange juice [10], honey [11] apple juice [12] have been reported.

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Herein we report the synthesis of CDs via hydrothermal treatment from water hyacinth (WH), a waste biomass found near riverside. The significance of the work lies in the use of a carbon source that might become a severe threat for aquatic life.

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2. Experimental section

2.1. Materials and synthesis

Water hyacinth was collected locally and washed thrice with water and air dried. They were crushed to make fine powder and sieved. Dichloromethane (CH₂Cl₂, 99.5%) was purchased from Sigma Aldrich. Whatman filter paper 1 (90 mm), All chemicals were of analytical grade and used without further purification. Deionized water was used throughout the experiment. N doped carbon dots were synthesized by a one-pot hydrothermal method as illustrated by Fig. 1. In this typical synthesis procedure, about 5 g of water hyacinth was dispersed in 50 ml of deionized water with stirring and the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h, followed by cooling to room temperature. The obtained black dispersion was filtered through a Whatman filter paper and the filtrate was washed with dichloromethane to remove unreacted raw materials. It was then centrifuged at 3000 rpm for 15 min and the aqueous layer was collected and again centrifuged at 12,000 rpm thrice for 20 min. The brown coloured solution of N doped carbon dots was stored at 4 °C for further characterisation.

2.2. Characterisation techniques

The UV-Vis double beam spectrophotometer (Varian, Carv 5000) was used to study the absorption behaviour of the prepared carbon dots. 200–800 nm was set as the scanning range with a step size of 0.5 nm. The fluorescence behaviour and photoluminescence (PL) was studied by exciting the material in a range of 320-420 nm with an increment of 20 nm. The fluorescence spectrometer (Fluoromax 4-Horiba Instruments, Japan) recorded the spectra with a scan speed of 240 nm/min with excitation slit width of 5 nm and emission slit width of 5 nm. An FTIR spectrometer (Thermo Nicolet, Avatar 370) was employed to study the Fourier Transform Infrared spectra and analyse the functional groups around the range 4000-500 cm⁻¹. Raman spectrum was obtained using Bruker RFS 27: Stand alone FT-Raman Spectrometer in the scan range 50-4000 cm⁻¹ with a resolution 2 cm⁻¹. The synthesized carbon dots were properly diluted with distilled water and put onto the non shining side of the TEM grids. After proper air drying, images were taken by TEM (Jeol/JEM 2100). 30 particles were selected from images and average particle size was calculated using ImageJ software. Powder X-ray diffraction pattern was analyzed using a German Bruker D8 ADVANCE XRD with 20 scanning mode. The X-ray photoelectron spectrum (XPS) was obtained with an X-ray photoelectron spectrometer (Axis Ultra, Kratos, UK).

2.3. In-vitro cytotoxicity studies

The test compound was studied for short term in vitro cytotoxicity using Dalton's Lymphoma ascites cells (DLA). Cell viability was determined by trypan blue exclusion method. The tumour cells aspirated from the peritoneal cavity of tumour bearing mice were washed thrice with PBS. Viable cell suspension (10⁶ cells/0.1 ml) was added to three tubes containing different concentrations of carbon dots from three sources. Dimethyl sulfoxide (DMSO) was used as the solvent for preparing various concentrations of carbon dots. Phosphate Buffer Saline (PBS) was used to make up the volume to 1 ml. Only cell suspension was taken in control tube. These assay mixture were incubated for 3 h at 37 °C. Then the cell suspension was mixed with 0.1 ml of 1% trypan blue and kept for 2–3 min and loaded on a haemocytometer. Dead cells take up the blue colour of trypan blue whereas the live cells remain intact. The number of stained and unstained cells was counted separately.

% cytotoxicity =
$$\frac{\text{No. of dead cells}}{\text{No. of live cells} + \text{No.of dead cells}} \times 100$$

3. Results and discussion

The optical properties of N-CDs were studied by UV–Visible absorption as well as photoluminescence studies. The formation of fluorescent N-CDs is indicated by ultraviolet illumination at 365 nm as they show strong blue emission which could be easily observed with the naked eye (Fig. 2). The inset shows photographs of CDs under visible (left) and at ultraviolet illumination at 365 nm (right). It can be seen that there is an absorbance peak at 280 nm in the UV–Visible absorption spectrum typically assigned to the $\Pi - \Pi^*$ transitions of the carbon core [13]. Also, it may be due to the trapping of excited state energy of the surface states which results in strong fluorescence [14].

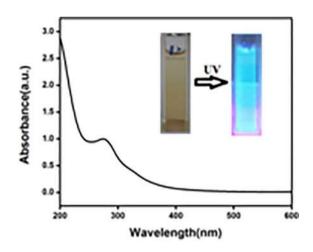


Fig. 2. UV-Visible absorption spectrum and the digital image.





The N-CDs exhibited a strong PL emission at 430 nm when excited at 340 nm (Fig. 3(A)). The emissive traps of the nitrogen doped surface are assumed to be the reason for this strong fluorescence [15]. Moreover, the fluorescence of N-CDs is excitation dependent and it changes with the excitation wavelength as seen in Fig. 3(B). The electron rich nitrogen atoms could offer more active sites and excitation dependent PL behaviour could be related to the different surface states of the N- CDs [16]. FTIR spectrum was characterised to study the functional groups as shown in Fig. 4. The broad peak at 3310 cm⁻¹ could be ascribed to the O-H stretching

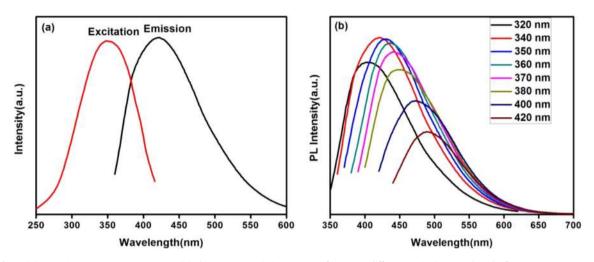


Fig. 3. (A) PL emission, excitation spectrum, (B) Fluorescence emission spectra of N-CDs at different excitation wavelengths from 320 nm to 420 nm.

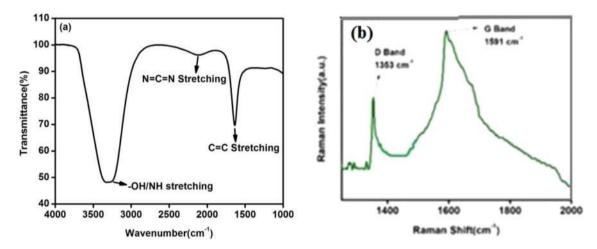


Fig. 4. (A) FT-IR Spectrum, (B) Raman Spectrum.

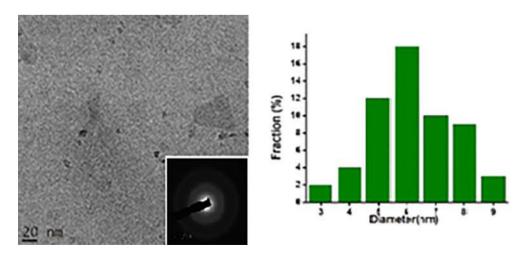


Fig. 5. TEM images of N-CDs from WH; Inset - SAED pattern. (B) Size distribution of CDs.

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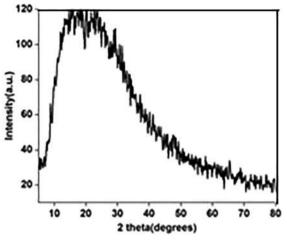


Fig. 6. XRD Pattern of N-CDs.

vibrations of carboxylic acid. The characteristic absorption bands at 2130 cm^{-1} and 1634 cm^{-1} can be assigned to N.C.N stretching and C.C stretching respectively. Therefore the presence of acid and hydroxyl moieties can be inferred on the surface of the synthesized N-CDs [17]. Fig. 4(B) shows the Raman spectrum of the synthesized N-CDs. The spectrum illustrated two different bands at 1363 and 1591 cm⁻¹ that corresponds to sp² carbon (G band) and the disordered graphite band of carbon atoms (D band) respectively. The peak intensities denote the presence of defective carbon structures which could explain the fluorescent properties [18].

The size and nature of the as prepared N-CDs was characterised by HRTEM. Well dispersed, uniform shaped, spherical N-CDs of average diameter 6.2 nm without apparent aggregation were identified by TEM images (Fig. 5) [19]. The size varies from 3 to 9 nm and the mean size was determined by imageJ2 software. The lack of lattice fringes indicates the amorphous nature of N-CDs. The XRD profile depicted in Fig. 6 exhibits a broad peak at 21° is assigned to (0 0 2) diffraction pattern of graphitic carbon confirming the disordered amorphous graphitic structure [19]. So N-CDs could be identified as amorphous spherical nanoparticles from XRD results along with HRTEM data (Fig. 7).

XPS spectra show three peaks at 283.7 eV, 529.7 eV and 397.7 eV corresponding to C1s, O1s and N1s respectively. The high resolution XP spectrum of C (1 s) was de-convoluted into four major binding peaks at 284.5, 285.4, 286.5, 288.1 eV assigned to the C.C, C–H/C–OC, C–N, C.O functionalities over the surface of the CDs. The N (1s) spectrum of N-CDs contain three major peaks at 399.5, 398.5 and 400.6 eV, which indicate the presence of the C–N–C, O-C–N and N–H moieties on the surface of the CDs. The high resolution spectrum of O (1s) was de-convoluted into two binding peaks at 531.0 and 532.15 eV, due to the existence of O-C and HO-C/O-C groups. Therefore, the surface analysis results suggested that the CDs has been functionalized by hydroxyl (–C–OH), amine (C–N–C) and carboxyl (–C=O) groups [14].

Different concentrations $(20 \ \mu g/ml, 50 \ \mu g/ml, 100 \ \mu g/ml$ and $200 \ \mu g/ml)$ of N-CDs were taken for cytotoxicity studies and the result is depicted in Fig. 8. Pie diagram is plotted with N-CDs concentration against cell death. It can be inferred that as the concentration of CDs increases, the cancer cells are not able to withstand

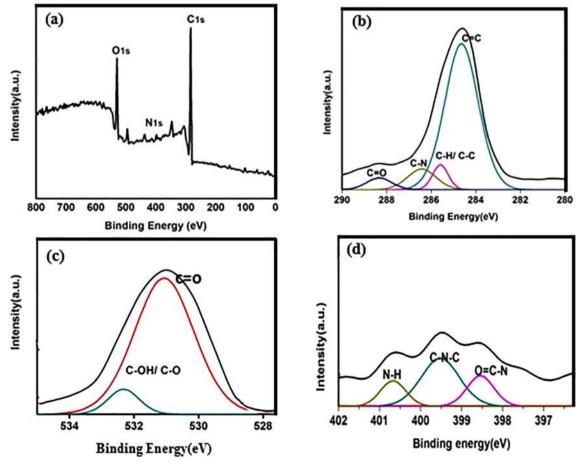
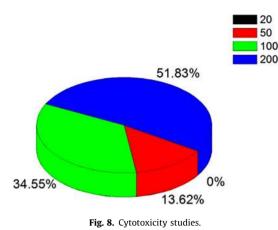


Fig. 7. (A) XPS spectra of N-CDs ((B) C1s spectra (C) O1s spectra (D) N1s spectra.

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resulting in subsequent death. This paves a way for N-CDs to act as an efficient drug against cancer cells.

4. Conclusions

We have developed a simple, eco-friendly and efficient method for the synthesis of nitrogen doped carbon dots from water hyacinth through hydrothermal strategy. To the best of our knowledge, this is a cost effective novel synthesis from natural waste like water hyacinth. Nitrogen doping as well as surface functionalization were identified by FT IR and XPS techniques. Amorphous nature and size were confirmed by HR TEM and XRD. The synthesized carbon dots emitted highly fluorescent blue light in the ultraviolet region and an excitation dependent photoluminescence was obtained. Cytotoxic studies confirmed the drug action of the prepared carbon dots against DLA cancer cells.

CRediT authorship contribution statement

Anju Paul: Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft. Manju Kurian: Conceptualization, Funding acquisition, Project administration, Resources, Software, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Facile synthesis of silver nanoparticles using Azolla caroliniana, their cytotoxicity, catalytic, optical and antibacterial activity

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ABSTRACT

In this study, eco-friendly synthesis of silver nano particles was achieved by a novel, facile route using *Azolla caroliniana* extract which act as a capping as well as reducing agent. Different synthetic parameters and the optical properties of the synthesized AgNPs was also studied. The characterization of synthesized AgNPs was carried out by Ultraviolet–Visible (UV–Vis) spectroscopy, Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction studies (XRD), and Transmission Electron Microscopy (TEM). TEM studies verified that the AgNPs formed have crystalline nature and spherical shape with an average diameter of 23 nm. The cyclic voltammetry profile of AgNPs modified electrode in NaOH depicted prominent redox peaks evidencing an impressive electrochemical response. The AgNPs shows high catalytic activity towards reduction of Crystal Violet and Fuchine which are highly polluting organic compounds. In addition to that the prepared AgNPs exhibited strong antibacterial activity against the tested microbes and also exhibits in vitro cytotoxicity against lymphoma ascites cells. © 2020 Elsevier Ltd. All rights reserved.

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1. Introduction

Nanotechnology gains much interest in modern life with its wide application in various sectors like electronic, biomedical, agricultural, food, cosmetics etc. [1,2]. Nano particles can be synthesised by countless methods such as physical, chemical, photochemical and biological method [3]. Among these green synthesis of nano particles using plant extract gains much interest due to its clean, nontoxic and eco-friendly nature. Of all the metal nanoparticles silver nano particles are having catalytic, optical, antibacterial, electrical as well as anticancerous activity [4,5].

Azolla caroliniana, also called as mosquito fern, is a moving, aquatic fern. It can also be used for the production of hydrogen fuel and also for the reduction of ammonia volatilization which convoys the application of chemical nitrogen fertilizer [6,7].

Synthetic dyes used in various industries such as textile, paper, food, cosmetics and pharmaceutical fields are pollutants [1,8]. The discharge from these industries results in environmental pollution

and also hazardous to the growth of living beings [9]. Fuchsine and crystal violet are the prominent organic dyes used in textile industries. Even though there are reports on silver and gold nanoparticles which shows the ability to degrade various organic dyes, there have been no attempts made till date to study the degradation of Fuchsine or rosaniline hydrochloride, a magenta dye with chemical formula $C_{20}H_{19}N_3$ ·HCl [10,11]. In-vitro anticancer properties inherent in the prepared silver can be tested against lymphoma ascites cells [12]. Electro chemical response of the silver nano particles found various application and also used as a biosensors for glucose detection [13] and have been widely employed as a tool for diabetes mellitus control due to its rapid response, accurate, selective and low cost per analysis.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical grade. Silver nitrate (AgNO3; 99.8%), Crystal Violet, Fuchsine and Sodium borohydride (NaBH₄) were purchase from Merk India Ltd.

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2.2. Methods

2.2.1. Preparation of Azolla caroliniana extract

Green fresh leaves of *Azolla caroliniana* (5 g) were collected and washed thoroughly in running tap water followed by double distilled water to remove any dirt particles adhering to it. These were taken in a round bottom flask fitted with water condenser and boiled for 20 min with 100 ml of double distilled water. It was cooled filtered through Whatman No. 1 filter paper. The extract thus obtained was stored at 4 $^{\circ}$ C [14].

2.3. Biosynthesis of silver nano particles

For the microwave-assisted synthesis of silver nano particles, 75 ml of 1 mM AgNO₃ solution was taken in an Erlenmeyer flask. To this 0.5 ml *Azolla caroliniana* extract diluted to 10 ml was added and stirred well. This was placed in a domestic microwave oven (IFB Solo 20PM1S) operating at a power of 800 W and frequency 2450 MHz and was subjected to microwave irradiation for 420 s [2]. Upon microwave irradiation, the colour of the reaction medium changed into brown due to nanoparticle formation. The formation of silver Nano particles (AgNP- Caroliniana) was monitored using a UV-vis spectrophotometer. The synthesised nano particles can then be dispersed in double distilled water and centrifuged. The separated particles were dried and were used for further analysis.

2.4. Characterization

UV-vis spectral analysis was carried out using a Shimadzu UV-1800 spectrophotometer [15]. FTIR spectrum was recorded on a Perkin Elmer-spectrum two spectrophotometer with ATR attachment which helps to identify the biomolecules responsible for the synthesis of nano particles. XRD measurement was made on a Brucker AXSD8 advanced powder X-ray diffratometer. Cu-Ka $(\lambda = 1.54 \text{ Å})$ radiation was used as the X-ray source (40KV. 35 mA) and 20 range from 2 to 800 and the scanning rate used be 0.05°/s. The XRD sample was prepared by drop coating the nanoparticle solution on a glass slide followed by drying under ambient condition. The mean particle diameter of AgNPs was calculated from the XRD pattern according to the line width of the plane, reflection peak using Scherrer formula. D = 0.9 λ/β Cos θ Where D is the average crystalline domain size perpendicular to the reflection planes, λ is the X-Ray wavelength; β is the Full Width at Half Maximum (FWHM) and θ is the diffraction angle [9,12]. HR-TEM images were recorded using JEOL JEM-2100 microscope to analyse the size and shape of nano particles [16].

2.5. Electrochemical response

The electrochemical response of the AgNPs was studied using cyclic voltammetric (CV). The CV was recorded with AgNPs modified Carbon Paste Electrode (CPE) was carried out in Metrohm Auto lab Potentiostat/Galvanostat (Model No. AUT87141) furnished with NOVA 2.1 software. An electrochemical setup containing modified carbon paste electrodes as working electrode, Pt wire can be used as a counter electrode and Ag/AgCl reference electrode is used for recording CV [13,17]. Carbon paste prepared by thorough mixing graphite powder and paraffin oil (weight ratio of 70:30) was packed in a clean glass tube. Silver wire was inserted into carbon paste for electrical contact. The carbon paste electrode surface was modified by drop casting 10 μ L of the AgNPs to get AgNPs/CPE [17].

2.6. Catalytic degradation of organic dyes

The investigation of the reductive degradation of organic dyes (Crystal Violet, Fuchsine) using NaBH₄ in presence of nanocatalyst was monitored with the help of UV Visible spectrophotometer.2 ml of 0.08×10^{-3} M solution of the dye and freshly prepared NaBH₄ solution (0.06 M, 0.5 ml), and the synthesized noble metal nanoparticles (0.02 mg/mL, 0.5 ml), were taken in the quartz cell [18]. The UV–vis. absorption spectra of the reaction mixture were recorded at definite intervals of time in the range of 200–700 nm [1]. Complete disappearance of the colour of the reaction medium was the direct indication of taking off of the dye. A control experiment was also conducted without using nanoparticles.

2.7. Cytotoxicity studies

Invitro cytotoxicity of the test compound was studied using Daltons lymphoma ascites cells (DLA). The tumour cells enunciated from the peritoneal cavity of tumour bearing mice was washed with PBS or normal saline. Cell viability determined using trypan blue exclusion method. Viable cell suspension $(1 \times 10^6$ cells in 0.1 ml) was added to tubes containing various concentrations of AgNP-Caroliniana, and the volume was made upto 1 ml using phosphate buffered saline (PBS) [19,20]. Control tube was prepared only using cell suspension. The assay mixture was incubated for 3 h at 37 °C and cell suspension was mixed with 0.1 ml of 1% trypan blue and kept for 2–3 min. It was then loaded on a haemocytometer. Dead cells take up the blue colour of trypan blue whereas live cells do not take up the dye. The number of stained and unstained cells were counted separately [20].

$$\% \text{ Cytotoxicity} = \frac{\text{No of dead cells} \times 100}{\text{No. of live cells} + \text{No. of dead cells}}$$

3. Results and discussion

3.1. Visual and UV-vis spectra analysis

Upon microwave irradiation, at various intervals of time the color of the reaction mixture gradually changes from colorless to yellowish brown. The main attraction of microwave synthesis is that it yields small, uniform sized nanoparticles in much lesser reaction time. The speedy consumption of starting materials reduces the formation of agglomerates in microwave assisted methods and provides nanoparticles with narrow size distribution. The first evidence for the formation of AgNP is obtained from the change in color of the reaction mixture.

The reduction of Ag⁺ was monitored at different intervals of time and was confirmed using UV–Visible spectrophotometer Fig. 1(a) and it is clear that an intense peak at 413 nm Fig. 1(b) indicates the formation of silver nanoparticles [15]. The synthesised particles shows an absorption band in the UV–vis region due to the surface plasmon resonance [3,21] of metal nano particles which gives information about the size and shape of the particles The phytochemicals present in the leaf extract act both as a reducing and stabilising agent for the synthesis of AgNPs [17,22].

3.2. FT-IR spectrum

The identification of the possible functional group involved in the reduction and stabilization of green-synthesized AgNPs can be achieved by the FT-IR spectroscopy. The FT-IR spectrum of plant extract and synthesised nanoparticles are shown in Fig. 2(a) and (b) respectively [3]. The broad band appearing at about 3272 cm^{-1} is due to the O–H stretching vibrations of various phe-

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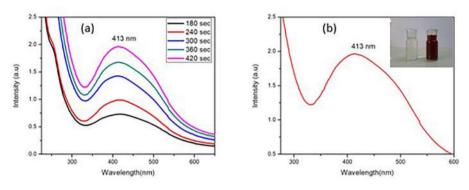


Fig. 1. (a) Formation of AgNP at different intervals of time (b) Intense peak by microwave irradiation for 420 s.

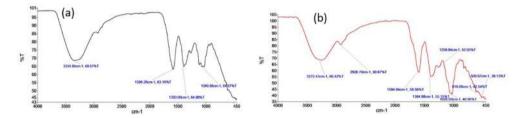


Fig. 2. (a) FT-IR spectrum of the Azolla caroliniana plant extract (b) FT-IR spectrum of AgNP-caroliniana.

nolic compounds present in the leaf extract. The peak at 2926 cm⁻¹ is characteristic of aliphatic C-H stretching vibrations. The moderately strong band at 1594 cm⁻¹ could be assigned to C=C stretching vibrations of aromatic ring [2,20]. The peak at 1384 cm⁻¹ may be O-H bending vibrations. The strong peak at 1026 cm⁻¹ corresponds to C-O stretching vibrations of phenolic groups. In addition, the peak at 616 cm⁻¹ is a characteristic of aromatic ring. Even though the FT-IR spectra of the plant extract and AgNP-Caroliniana are more or similar, the various absorption peaks in the spectrum of the plant extract are more intense than that of AgNP-Caroliniana. In the spectrum of AgNP-Caroliniana, we can see some minor variations in the position of several peaks with the first peak corresponds to the absorption caused by the O-H stretching vibration has shifted from 3334.86 cm⁻¹ 3272.43 cm⁻¹, peak of C-C stretching shifted from 1586.26 cm⁻¹ to 1594.94 cm^{-1} , peak of 1393.00 cm^{-1} to 1384.88 cm^{-1} indicative of O–H bending. A new peak at 2926.00 \mbox{cm}^{-1} has appeared in the FT-IR spectrum of AgNPs indicating C-H vibrations, which suggest the possible formation of silver nano particle as these shifts in the frequencies of absorption has been reported to be associated with the formation of AgNPs in which plant extracts were used as the reducing agents [3,11].

3.3. X-Ray diffraction (XRD) analysis

The biosynthesized silver nanostructure by using *Azolla caroliniana* extract was further demonstrated and confirmed by the characteristic peaks observed in the XRD image of silver [1,5]. The XRD pattern (Fig. 3) thus clearly shows that the Ag-NPs are crystalline in nature .The intense peaks at 2θ values 28.57° , 31.87° , 46.067° , 65.43° corresponds to $(2\ 1\ 0)$, $(1\ 1\ 3)$, $(2\ 0\ 0)$ and $(2\ 2\ 0)$ plane, Bragg's reflection based on the fcc structure of silver [9,23].

3.4. TEM analysis

The micrographic images of the synthesised silver nano particles were shown in Fig. 4. From the TEM images it is clear that the synthesised particles are of spherical [14] in shape and are distributed without any agglomeration. The diffraction rings in SAED

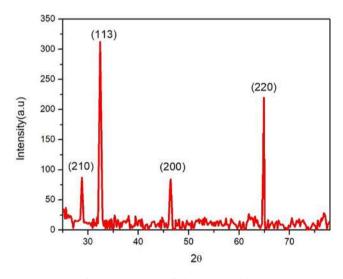


Fig. 3. XRD patterns of silver nanoparticles.

(Selected Area Electron Diffraction) pattern of TEM studies verified that the AgNPs formed have crystalline nature [2].The average particle size is around 23.6 ± 8.18 nm.

3.5. Electrochemical analysis

Here we compared the electrochemical response of the AgNPs modified CPE with bare CPE by analysing the CV in 0.1 M NaOH solution [13]. The AgNPs modified electrodes show significant development in current response compared to bare CPE. In the CV curve of the AgNPs/CPE Fig. 5(a) (red curve), all prominent peaks corresponding to particular redox transitions of metallic silver to silver oxide were observed [17,24].

The properties of AgNP modified electrodes and the catalytic activity of the synthesized material act as modifier and are assessed using the reaction of the Glucose/Gluconic acid redox

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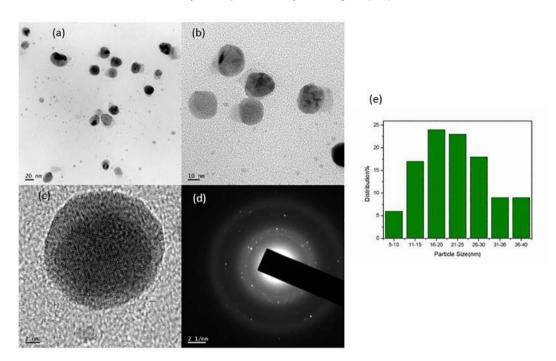


Fig. 4. HRTEM images of silver nanoparticles: (a-c) at different magnification, (d) SAED pattern. The image (e) shows the particle size distribution of sample.

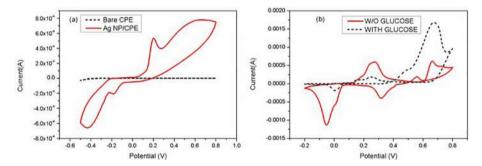


Fig. 5. (a) CV of AgNPs modified CPE (red solid curve) and bare CPE (black dotted line) recorded in 0.1 M NaOH against Ag/AgCl reference electrode and, Pt as a counter electrode at a scan rate of 50 mV s - 1 (b) Cyclic Voltammograms obtained from -0.2 V to 0.8 V in 0.1 mol L⁻¹ NaOH in presence (red solid curve) and absence of glucose (black dotted curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

couple reaction [24]. The electrode was previously, cycled 130 times until a steady and stable current is obtained. The oxidation of Ag to Ag₂O shows an anodic peak (0.38 V) followed by the formation of AgO (anodic peak at 0.73 V). The reduction of AgO to Ag₂O shows a cathodic current peak (0.37 V) and further scanning of the potential toward more negative values a peak around 0.02 V can be attributed to the reduction of Ag₂O to Ag. An increase in anodic current was observed (at 0.62 V) upon glucose addition. Based on cyclic voltammetry results and previous reports, the mechanism of observation can be explained by electrochemically. Formation AgO at 0.73 V (first step) which chemically reacts with glucose yielding Ag₂O and glucolactone. Glucolactone (second step) is chemically oxidized by Ag₂O resulting on Ag regeneration. While potential remains positively enough, silver is promptly reoxidized to Ag₂O on the reverse scan at 0.62 V promoting an increase in voltammetry signal related with presence of glucose. Therefore the current signal obtained at 0.62 V is proportional to glucose concentration [17].

ible spectrophotometer [21,25]. This characteristic absorption value which does not overlap with the SPR band of silver nano particles was used to trail the photocatalytic degradation process [4,8,25]. Comparing Fig. 6(a) and (b) it is clear that when AgNP was added to the reaction mixture containing both crystal violet and NaBH₄, the intensity of the peak at 586 nm began to decrease continuously with time.

The catalytic activity of AgNP-caroliniana was also investigated using the degradation reactions of Fuchsine using NaBH₄ [26]. The absorption maximum of this dye also does not overlap with the SPR band of silver nano particles. The UV–vis absorption spectrum of an aqueous solution of fuchsine shows peaks at 292 nm and 532 nm. The reduction of fuchsine into leuco fuchsin can be followed spectrophotometrically by monitoring the absorption maximum at 532 nm. Comparing Fig. 7(a) and (b) it is clear that when AgNP was added to the reaction mixture containing both fuchsine and NaBH₄, the intensity of the peak at 532 nm began to decrease continuously with time [21].

3.6. Degradation of organic dyes

Crystal Violet (also known as Basic Violet 3) a typical triphenylmethane dye shows a maximum wavelength at 586 nm in UV-vis-

3.7. Antibacterial studies

Here we have investigated the invitro antibacterial activity of the synthesized Ag NPs against the common pathogenic bacteria

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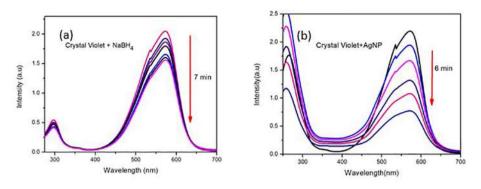


Fig. 6. UV-vis absorption spectra measured at 1 min intervals for the degradation of Crystal Violet (a) In the absence of AgNP-caroliniana and (b) In presence of AgNP-caroliniana. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

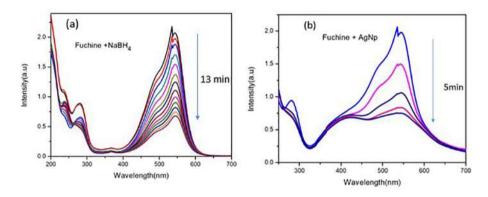
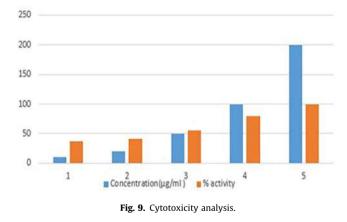


Fig. 7. UV-vis absorption spectra measured at 1 min intervals for the degradation of Fuchsin (a) In the absence of AgNP-Caroliniana and (b) In presence of AgNP-caroliniana.

both Gram-positive bacteria Staphylococcus aureus (S. aureus) and Gram-negative bacteria Klebsiella pneumoniae (K. pneumoniae) [4,27]. From Fig. 8 it was observed that silver nanoparticles possessed a higher degree of microbial inhibition as that of a positive control, Streptomycin and hindered the growth of both gram positive and gram negative microorganisms.

3.8. Cytotoxicity studies

Using the histogram (Fig. 9) we can compare the concentration at which AgNP-caroliniana shows 100% anticancerous activity [19,20]. Different concentrations of AgNP-caroliniana was added to the lymphoma ascites cells and the activity of the product was observed. A minimum of 200 μ g/ml is required for 100% activity [23].



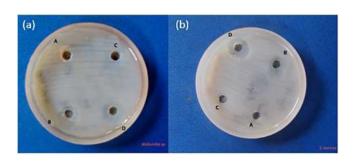


Fig. 8. Showing the antibacterial activity of AgNP-caroliniana against the well containing (a) Gram-positive bacteria Staphylococcus aureus (S. aureus) and (b) Gram-negative bacteria Klebsiella pneumoniae (K. pneumoniae) A = Double distilled water, B = Streptomycin, C = *Azolla caroliniana* extract D = AgNP-caroliniana.

4. Conclusions

In the present work we have synthesised silver nano particles using a novel microwave assisted technique where the *Azolla caroliniana* extract act as a reducing as well as capping agent. The formation of silver nanoparticle by green route opens the new avenues over chemical routes because of its cost effective and ecofriendly nature. Also it is found that synthesised nano particles are effective catalysts for the degradation of organic dye pollutants and shows an excellent electrochemical response towards glucose. Also the AgNP-caroliniana shows effective antibacterial activity against Staphylococcus aureus (S. aureus) which is gram positive and Klebsiella pneumoniae (K. pneumoniae) which is gram negative and also shows cytotoxicity against lymphoma ascites cells, leads to go high potential uses in biological application.

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CRediT authorship contribution statement

V.N. Anjana: Data curation, Writing - original draft, Software, Visualization, Investigation, Validation, Writing - review & editing. **Ebey P Koshy:** Conceptualization, Methodology, Supervision, Software, Validation, Writing - review & editing. **Beena Mathew:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Polyaniline doped with transition metal acid and naphthalene sulphonic acid-effect on electrical properties and photocatalytic activity

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Repeareds polyanting, molybels acid, # naphthalane subplease acid, deductive properties, photosizally/se activity

Abstract

PAPER

To study the effect of dopant type and dopant concentration on the properties of Polyaniline, a transition metal acid and an organic subplassic acid were selected. Polyaniline with these different dopant concentrations (0.01 M, 0.05 M and 0.1 M) of each acid were prepared by chemical oxidative polymerisation using Ammonium persulphate as oxidant at 0 $^{\circ}C$ -5 $^{\circ}C$. The morphology of the samples obtained was characterized by Field Emission Scanning Electron Microscopy (FESEM), structures were analyzed using Fourier Transform Infrared Spectroscopy (FTIR), optical properties by UV-viable spectroscopy and Photohaminescence spectroscopy. Dielectric property measurements reveal that organic sulphonic acid doped polyaniline exhibited high value of conductivity and dielectric constant than transition metal acid doped polyaniline. The samples with higher values of conductivity were selected for photocatalytic degradation study of Methylene blue under visible light irradiation. The higher degradation rate of 70.59% obtained from photocatalytic activity measurements reveals that organic sulphonic acid doped polyaniline is a better photocatalyst than transition metal acid doped one.

1. Introduction

Among the class of conducting polymers, polyaniline (PANI) remained nique on account of its easy and e Among the class of conducting polymers, polymiline (PANI) remains unsigne on account of its easy and deconstruical synthesis methods, interesting redux chemistry, distinctive doping? (adoping properties. Several methods have been reported for synthesizing polymiline such as chemistal oudaritie polymerination, electrochemical polymerination, interfacial polymeniation, remains polymerination, template - free method etc. [1-3]. The maphodalogy and properties of polyasoline differ depending on the synthesis method, nature of originaris and nature of dopants. Among the various factors occorrolling the morphology and properties of polymelia and uncentration of dopants. Among the various factors occorrolling the morphology and properties of polymiline, nature and uncentration of dopants. Among the various factors occorrolling the morphology and properties of polymiline, nature and uncentration of dopants. Among the various factors occorrolling the morphology and properties of polymiline, nature and uncentration of dopants and some a faccinating area of research for the polyment two docades [4, 3]. The various types of dopants reported till due include inorquatic acids (HC3, H, SO, H, JPO, HCHO, HBF4), orquine familiand and with -SO-H, orquine acids such around to train the acids (HC3, H, SO, H, JPO, HCHO, HBF4), and acids and carbon misorabes [5–6]. The morphology of polymiline acids (HC3, H, SO, H, JPO, M, JPO, JPHF4), and and acid to the some trained to the trained to the polymiline acids (HC3, H, SO, H, JPO, JPH74). polyaniline can be takined to monotolies, nanofibres, self-assembled nanotroctures and even to dendrific structures by altering the dopont structure and dopart/andine ratio (%-11). The present work investigates the effect of changing dopart type and dopart concentration on the photocatalytic activity and didectric properties of polyaniline.

2. Experimental

2.1. Materials and methods

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The Changing Scenario of Kathakali on Modern Stage

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Abstract

Kathakali has undergone many changes through different phases of transition. The major changes are in the areas of themes elements of stage in the process of on stage editing or manodharma and different constituents of Abhinaya including the Rasas. These changes have been made in in order to suit the requirements of modern stage and cater to the sensibilities of modern day viewer.

KEYWORDS: Temple classical dance, Naatyasasthram, Geethagovindam, Percussion Instruments, Abhinaya

Introduction

Nowadays Kathakali encounters several problems in its production and presentation from its emergence on the modern stage century's back. This is a vital condition of its transition from the traditional theatre to the contemporary stage. As classism defines, there is no ancient or perfect art, which should not be opened to refinement of technique or adaptation to the new context. The art Kathakali has synthesized the finest points of Indian histrionics and the power and vigour of the culture of the people. The very dynamism of this tradition is its capacity to change and adapt. Even though Kathakali went through many vicissitudes for the last few centuries, its inner viability and adaptability to keep itself as a vibrant and living form of cultural expression remains unchanged. In the Kerala Kalamandalam, Malayalam poet Vallathol Narayana Menon brought about a few changes by way of stream living certain aspects of its technique and interpretations as a part of the renaissance of the art in the late thirties. The veteran Gurus in different parts of Kerala followed the same throughout Kathakali's history. The emphasis that these attempts are done by those who have had a deep and sympathetic understanding of the art or who have been well-versed in its complex technique.

Phases of Transition.

In Kathakali, the matter is that in what matter the changes are to be brought about. To make an attempt convincing on the contemporary stage should be accompanied by a serious effort to understand its nature and purpose. The transition of any great classical art demands this. For example, Bharatha in the Natyasasthra, which traverses the whole gamut of dramaturgy, emphasizes the norms of appreciation by the patrons along with laying down the canons of Natya and the accomplishments of the artists. As Kathakali represents a distinct, evolved classical tradition, any change which is effected in order to fit it on the modern stage should be effected from within the tradition. For example, the 'Noh' and 'Kabuki' (the comparable dramatic traditions in Japan) have successfully adapted themselves to a stage which has been evolved to suit their special requirements.

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तौटपत्रिका में निर्धारित सारे पद अवैर अनुदान प्राप्त नहीं होता है। रचनाव	ानिक हैं। इसे किसी सर गर के विचारों से सम्पादव	कारी अथवा गैर-सरकारी संस्था 5 का सहमत होना अनिवार्य नहीं ^{है}



लो दलक को हिन्दी कहानी अपनी अलग पहचान बनाए हुए है। वह हुनेन उत्त-हलका के दलके की हिन्दी कहानी अपनी अलग पहचान बनाए हुए है। वह हुनेन उत्त-दलकान के दल्किय में अपना स्वस्तित करते हैं कि कहानी का उपजीया देनदिन किन्दन को किन्दने से जोको है और साबित करते हैं कि 'अब कहानी व एक साथ में अपनी है। क्याकार उदय प्रकार का कहना है कि 'अब कहानी व एक साथ में बन्द न्यूपी है। क्याकार उदय प्रकार का कहना है कि 'अब कहानी व एक साथ में बन्द न्यूपी है। क्याकार उदय प्रकार का कहना है कि 'अब कहानी व एक साथ में बन्द न्यूपी है। क्याकार अदय प्राणिक आदि के तरव भी मौजूद होने। इसकि कि न्यूपी के किन्दी और अनुमव का हिस्सा हो चुके है।' क्या के किन्दी और अनुमव की किन्दीनियों में आम जनता का यथाये प्रथान

स्वताज कर किन्द्रमा और अनुमव का हिस्सा हा मुफ हा हमरे रुवमते की जिन्द्रमा और अनुमव का हिस्सा हा मुफ हा वप्रयास सकत देमबद की कहानियों में आम जनता का यथाये मुखरित हुए । वप्रयास सकत देमबद की कहानियों में आम जनता का यथाये मुखरित हुए । वनता का वबार्थ है जो सामाजिक विषमताओं, विसंगतियों और विरूपताओं से बुद्ध रुव वर्त्ताकरियों जीवन में विशेषकर मानव चेतना में बदलाव ले आयी। यह बदलव आउ हे ल्लीकरियों जीवन में विशेषकर मानव चेतना में बदलाव ले आयी। यह बदलव आउ हे ल्लीकरियों जीवन में विशेषकर मानव चेतना में बदलाव ले अप निरंतर बदलता जा रहा है। स्वत्त के कारण मानवीय प्रथार्थ और अनुमव का रूप निरंतर बदलता जा रहा है। हा के कारण मानवीय प्रथार्थ और अनुमव का रूप निरंतर बदलता जा रहा है। कहा के कारण मानवीय स्वयार्थ और अनुमव का रूप कहा में कारण स्वर्भ तक होने लगे। युग के साथ-साथ शोषण की नीति भी बदलों का मानवाधिकन संस्वर्भ तक होने लगे। युग के साथ-साथ शोषण की नीति भी बदलों का मानवाधिकन संस्वर्भ के प्रशं में अपने पेर जमाने शुरू किए। इसका प्रमुख जयन देवन कहाने में कार अधुनिक दर्शन ने अपने पेर जमाने शुरू हिए।

नां दत्तक बी कहानी में प्रधातध्यता को प्रमुखता दी गई। इस दर्शक के स्टन समाठेक स्विति और वास्तविकता के बीध खड़ी है। भूमण्डलीकरण के औजार पूँजी हेंद्रेव न इस-घटन और प्रीदांगिकी के विकास ने मनुष्ध की नियति बदली। इसके साथ हे उसक मननेकल के प्रसार से हमारे अर्जित संस्कारों, संस्कृति और मूल्य का विघटन हुआ। तथ है प्रतिबतीयां राजनैतिक परिवंतन, राजनीतिओं-माफिया और पूँजीपतियों के गठबंधन सब्द अतकवाद आदि के विस्तार ने मानव जीवन और उसकी कहानी को बदला। राजनैतिक ज् ज़्यावर्तवरण ने अपनी नैतिकता और मूल्य परिवंतन करने के लिए मनुष्य पर दब्ध इत अधिकारों के नाम पर मानवाधिकारों के उल्लंघन ही ज्यादा होते रहे है। सरकार इत अन-ज वित-बिना कंदल कागजी रह गई।

रेली परित्वतियों के रहते मनुष्य हाशिए पर आ गया। उसका अस्तित्व खतरे ने पड़ व ह कहानेकात की पहली लिता बनी हाशिये पर होने मानव जीवन को केन्द्र में लने हैं। होने उन्होंने कई प्रकार की प्रयुखियों का प्रयोग आरंभ किया।

गानगणिकार मानव के अधिकारों का प्रायाग आरम किया। एक है नाल अधिकार सित्रयों के अधिकार, अनुसूचित जाति–जनजाति अधिकार कई प्रका है। पिकार विद्यार्थियों के अधिकार आदि। इस प्रपन्न में हमने अधिकार, स्त्रियों के अधिकार जाति–जनजाति बीठ-जनजाति के अधिकार आदि। इस प्रपन्न में हमने अधिकार, स्त्रियों के अधिकार वित्र-जनजाति के अधिकार, आम जनता का अधिकार आदि को नवें दशक की का^{त्री है।} जियार करने की कोशिश की है।

बाल अधिकाले -	A
वन्बर 1989 को परित	नी घोषणा संयुक्त राष्ट्र महासभा में 20 नवम्बर 1959 में की ^{चं की} किया गया। इसके अनुसार बच्चों को जीने का अधिकार, ^{दिकार ह} ै
	अन्या गया। इसके अनुसार बच्चों को जीने का अधिकार,

भार परना को जीवकार गरिमा के साथ अधिकार के दीना के दिना के जान भारत स्थापन की अधिकार गरिमा के साथ अधिकार के दीना की दीना भारत की जीवकार सादि दिसा गया है। इन साथ के होने हुए से देखे की दिना के बना भारत कि साथ प्राय की दिने हैं। स्थाप स्थापन की हैंग की देखा का की



Pricing and Performance of IPOs in India- A Critical Review

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ARTICLE DETAILS

ABSTRACT

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Keywords

IPOs, Winners curse, under pricing, signaling theory

Initial public Offers (IPOs) become the most popular way of raising finance in India. A Lot of studies has been conducted on various aspects of IPOs, i.e., Valuation and pricing of securities and performance of these securities after listing. Literatures are also available regarding the factors affecting the pricing and performance of securities. Various theories/hypothesis explains the reasons of under pricing of IPOs such as Winners curse hypothesis, Signaling theory, Information gathering theory etc. In this paper an attempt is made to critically review the studies done on the subject of IPOs in India as well as abroad.

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1. Introduction

Public issue can be classified into Initial Public Offer (IPO) and Further Public Offer (FPO). An Initial Public Offering (IPO) is a company's first offering of equity to the public in its life. Any further issue of securities is called Follow on Public offer or further public offer .Initial public offers are considered as the good source of finance by the enterprises. But from the investors point of view, they need to get adequate return for their investment.

The valuation, pricing and performance of shares of companies making initial public offer are of interesting topics among academicians and research scholars. The whole theories regarding IPOs can be classified in to three broad heads, namely:

- 1. IPO Valuation
- 2. IPO pricing
- 3. Performance of these securities in share market.

A lot of literatures, both empirical and conceptual, are available in each area of Initial Public Offers in different parts of the world. In this paper I am trying to analyse the empirical studies related with basic propositions and theories of capital market, specifically IPOs around the world. The literature available for IPO pricing and performance are abundant in number.

1.1 Objectives

The main objective of this paper is to study the literatures available in the area of Initial Public Offers in India and abroad.

1.2 Methodology

Various literatures on IPOs were collected from Journals and from the websites of publishers. A descriptive analysis is used for the presentation of the studies.

1.3 Limitations

Literatures on IPOs are abundant in number. But in this paper only ten studies are incorporated. So various phenomenon are left unaddressed.

2. Review of Literature

Numerous studies have been done in the world on the subject of Initial Public offers in various aspects such as Valuation, pricing, performance etc. The present study focused on reviews pointing on the performance of Initial Public offers.

Rock's model (Rock, 1986) presented the cause of under pricing of IPOs, the phenomenon popularly known as Winner's Curse. This hypothesis also known as asymmetric information theory. His argument depends on the existence of two groups of investors, one who have the knowledge about the true value of the firm and the other who are completely unaware about the true value of the firm. The informed investors are cognizant about the future prospect of the firm and will ready to buy only when the issue is underpriced. Whereas the uninformed investors don't have any knowledge about the under pricing and overpricing of issues and therefore they cannot differentiate the issues. If the new shares are priced at the expectations of informed investors, they will buy in IPOs, otherwise they restraint from the market. The uninformed investors, due to lack of knowledge will subscribe to issues and get negative initial returns. So the offering firm must under price the shares in order to guarantee that the uninformed investors buy the issue.

For the explanation of the model, he had made the following assumptions:

- The informed investors have perfect information about the future value of the new issue and they cannot borrow securities or short sell. (Because they cannot sell their private information.
- 2. Informed demand, I is no greater than the mean value of the shares offered ,v/Z
- 3. Uninformed investors have homogenous expectations about the distribution of v/
- 4. All investors have the same wealth.

Rock's model was for firm's commitment offerings, but can be generalized for other types of offerings also. This model

provides a basic explanation for the question why new issues are underpriced?

- Information Gathering theory- (Benveniste & Spindt, 1989) It stated that underpricing is a way to convince informed investors to disclose private information about the demand for shares in the preselling phase. In the IPO market, lead Managers consult clients before setting offer price in the prospectus. Lead managers may intentionally underprice IPOs, to attract more and more clients. The demand information is gathered during the pre-selling phase , which form the basis of pricing the issue. So the merchant bank play game with many of their large clients.
- Jay R Ritter (Ritter, 1991) documents the performance of IPOs in the short run and long run with specific hypothesis. Earlier, many studies have documented two anomalies in respect of IPO pricing and performance. (1) The short run under pricing phenomenon, and (2) The hot issue market. He added a third phenomenon in his study which states in the long run, these IPOs are overpriced or underperform in relation to the bench mark returns. Studying the sample of 1526 IPOs went public in the US during 1975-84. he found that major IPOs are underperformed compared to benchmark. His study reveals that the Initial Under pricing and the long run underperformance are negatively correlated.
- R Michaely and Shaw (Michaely & Wayne, 1994) studied the empirical implications of several models of IPO under pricing. Their study was consistent with Rock's winner's Curse hypothesis. Their results show that the IPOs underwritten by reputable investment banks experience significantly less under pricing and perform better in the long run. Again their result does not support the signaling theories explaining the reason of IPO under pricing.
- Shah (Shah, 1995) studied 2056 IPOs during the period from January 1991 to May 1995 and stated 105.6% excess return above the Offer price. Moreover he also reported that the IPO stocks outperform the market in first 200 days and then the shares underperform in 400 days.
- Purnanandam & Swaminathan (Purnanandam & Swaminathan, 2002) studied the valuation of IPOs and in their paper explained which is not consistent with the asymmetric information model. The study reveals that the median IPO is overvalued at the offer price over the long run. Taking a sample of more than 2000 IPOs during 1980-1997, they concluded that IPOs are overvalued and earn return more than that of undervalued IPOs on the first day of listing ,but the long run return will be much less than the underpriced IPOs. This overvaluation is common among different types of industries. Here to determine whether an IPO is overvalued or undervalued, they have used the 'fair value' concept which is related with the firm's

fundamentals. For the study, they had used the industry peer comparison /Industry peer multiples for the valuation. To choose industry peers, they consider sales, EBITDA, and profit margin of industry peers. Their results are not consistent with the Traditional asymmetric theories of Rock (1986) and other advocates, rather they consistent with the behavioral theories of IPOs.

- Regarding Indian IPO performance another study was done by Krishnamurti (Chandrasekhar & Kumar, 2002) which describes the institutional arrangements of the public issue process of IPOs in India. Based on the satisfied criteria, they analysed 386 IPOs which opened for subscription between July 1992 and December1994. Their study provides empirical evidence of the widespread under pricing and relates them to potential factors. The major factors are the lack of a formal mechanism for measuring the extent of demand from potential investors, the regulatory restrictions on pricing of new firms without a track record and the actual opening date of the public issue
- Study made by Loughran and Ritter (Ritter & Loughran, 2004) confirms the increase in number of under pricing of issues in US. They tried to explain the causes of increased under pricing attributable to different reasons. Changing risk composition, a realignment of incentives, and a changing issuer objective function. Major reason is attributable to previous latent agency problems between underwriters and issuing firms. Another may be the changes in the composition of the companies going public. They confirmed that the increase in valuations over time has caused issuers to be more complacent about leaving money on the table. But it is true that the degree of under pricing changed
- Francisco Santos (Santos, 2010) documents the connection of IPO under pricing and long term underperformance of the firm. He explained the long term under performance in two ways, i.e. In the first, the firm which makes IPO during low under pricing period would be less underperformed/no underperformance in the long run and in second way, if the company made its IPO during high under pricing period, the degree of under pricing will be higher. His evidence shows that the investor's sentiments in High under pricing firms will be higher. These results are consistent with a story in which low quality firms, in periods in which the average under pricing in the market is high, try to exploit investor's sentiment by going public during high underpriced periods.
- Bhatia & Singh (Bhatia & Singh, 2018) made a study which analysed the long run performance of 438 initial public offerings offered during June 1992 and March 2001. The result shows that firms with least issue size have performed better than firms with greater issue size. The results of the determinants of long run performance of IPO shows that initial return,

negative effect on the aftermarket returns.

issue size and market condition have significant and

	1		at a glance	
Author(s)	Year	Title description	Features/ Variables	Major findings
Kevin Rock	1986	Why IPOs underpriced	Firm commitment offering-	Under pricing due to information asymmetry.
Benveniste and Spendt	1989	How investment bankers determine the offer price and allocation of new issues	use of indications of interest from client by the investment bankers to price and allocate new issues	lead Managers consult clients before setting offer price in the prospectus.Lead managers may intentionally underprice IPOs,to attract more and more clients
Jay R Ritter	1991	The long run performance of Initial Public offerings	3 anomalies 1.Short run underpricing 2.Hot issue market 3.Long run under performance.	The Initial Under pricing and the long run underperformance are negatively correlate
R Michaely and W.H Shaw	1994	The Pricing of Initial Public Offerings: Tests of Adverse Selection and Signalling theories	Does not support the signaling theories	Consistent with winner's curse hypothesis
Shah A	1995	The Indian IPO market: Empirical Facts	stated 105.6% excess return above the Offer price	Support under pricing in India
Purnanandam & Swaminathan	2002	Are IPOs underpriced?	Return Comparing fair value and market value of shares	IPOs are overpriced with respect to their fair value
Chandrasekhar, Krishnamurti; Kumar, Pradeep	2002	The Initial Listing Performance of Indian IPOs	386 IPOs which opened for subscription between July 1992 and December1994	1)lack of a formal mechanism for measuring the extent of demand from potential investors,2) the regulatory restrictions on pricing of new firms without a track record and 3) the actual opening date of the public issue
Loughran and Ritter	2004	Why has IPO under pricing changed over time?	Reasons for IPO under pricing Patterns of IPOs in the U.S	 Changing issuer objective function. changes in the composition of the companies going public Incentives.
Francisco Santos	2010	IPO under pricing and Long Term Under performance	Establishes relationship between IPO under pricing and long un underperformance	Investors sentiments and under pricing have positive relationship and firms try to exploit this sentiments.
Shikha & Balwinder	2018	Long Run Performance of Initial Public Offerings in India	long run performance of 438 initial public offerings offered during June 1992 and March 2001. from Secondary data	 Firms with least issue size have performed better than firms with greater issue size Initial return, issue size and market condition have significant and negative effect on the aftermarket returns.

Table 1 Reviews at a glance

Source: Compiled from Secondary data

3. Conclusion

Under pricing is a most documented phenomenon in the academic area of Initial Public Offerings. Beyond the explanation of basic hypothesis such as Winners Curse and Information Gathering, well documented studies done by the

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Corporate Social Responsibility Compliance by the Listed Companies in Kerala

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ABSTRACT

The introduction of the Corporate Social Responsibility Clause in the Companies Act, 2013 was actually the rise of a new era in the corporate giving. The inclusion of mandate CSR in the Act can be seen as an effort taken by the government to establish equality in the society we live in. Many companies had addressed the rising societal demands in their own ways voluntarily and the state with most literate and educated public is not an exception. It can be observed that almost all the top companies in Kerala have responded to this call in a very positive way. Each of the companies in Kerala had tried to devise the implementation of CSR in unique ways. The objective of the study was to make an assessment of the CSR activities of the Kerala based listed companies during the year 2016-17. The study was aimed at attaining a proper understanding about the CSR initiatives and implementation by the major Companies in Kerala.

The CSR activities of the selected companies were compared with the CSR clause in the Companies Act and different rules related to CSR to assess the compliance level of these companies. The study proved that all the eligible Kerala based listed companies were doing CSR in 2016-17. Majority of them had framed a CSR policy the main area of CSR implementation was education. The company which had spent the maximum amount on CSR during the year 2016-17 was Kitex Garments Limited.

Keywords: Corporate Social Responsibility, Companies Act 2013, CSR Policy, CSR Committee, Kerala based listed companies.

INTRODUCTION:

Corporate Social Responsibility – this can be considered as the most discussed, criticized and substantiated concept of the era. It deals with the business of the business which is beyond financial numbers. People, precisely called as stake holders are demanding more and more from the corporate houses. The need for practices like corporate social responsibility, corporate governance can be attributed to the growing expectations of the people around business.

There is a saying that "with power, comes the responsibility" and the history portrays that the business community had always shown a concern for the society. It can be seen that the reference to a concern for social responsibility appeared in the early 1930s and 40s. It was suggested in a poll conducted by the Fortune Magazine in 1946 among the business executives that they have developed a taste for social concern and responsibility. Bowen (1953) stated that the business people should assume the responsibility that is desirable in terms of the objectives and the values of the society. It is evident that 1960s marked a significant growth in the efforts for formalising the concept of CSR. Also there were views against the concept of CSR. The one which became popular was by Milton Friedman in 1970 in an article in Newyork Time Magazine and it said that the social responsibility of business is to increase its profits.

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Corporate Social Responsibility Practices and Response of Customers: An analysis

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Abstract

The Corporate Social Responsibility value of any company depends on the stake holder reaction. How the stake holders perceive and response to the CSR activities of a company can highly influence the benefits they want to reap like increased customer patronage, employees with organisational commitment etc. It is always important from the point of view of companies to understand what and how the customers feel about the CSR of the Company. Stakeholders make use of CSR to make inferences about the values upheld by a company and how the company respond to the needs of the stakeholders. So it is very important from the point of view of the company to understand what the customers know about CSR, how they know about it and how it is perceived by them. The objective of the study is to understand the awareness and perception of the customers about corporate social responsibility. The study will focus on understanding the awareness and perception of customers and how it will affect their buying behaviour. Data will be collected from 50 individuals by administering a questionnaire. The study will be conducted in Ernakulum District. Customers will be chosen by convenient sampling method.

KEYWORDS: Corporate Social Responsibility, Customer Awareness, Customer purchase Intention, Customer Behaviour, Customer Loyalty

I Introduction

Corporate Social Responsibility is perceived to be the activities to ensure sustainability in the environment it operates. Sustainability is the base of the concept of corporate responsibility. But there can be situations where the corporate responsibility activities of the companies become not sustainable. It happens when the stakeholders do not value the CR activities of the company and properly reward the companies. The importance of stakeholders in the sustainable existence of business has become a prerequisite.

The change in the attitude of the stakeholders towards business and their activities is very visible now days. The Corporate Social Responsibility value of any company depends on the stake holder reaction. How the stake holders perceive and response to the CSR activities of a company can highly influence the benefits they want to reap like increased customer patronage, employees with organisational commitment etc. Stakeholders make use of CSR to make inferences about the values upheld by a company and how the company respond to the needs of the stakeholders. So it is very important from the point of view of the company to understand what the customers

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