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PHOTOCATALYTIC ACTIVITY OF POLYMER CAPPED METAL OXIDE NANOPARTICLES

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Abstract:

In the present study, the photocatalytic activity of polymer capped zinc oxide nanoparticles. Cellulose is used as polymer. The obtained polymer capped nanoparticles were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) with EDX, Transmission electron microscopy (TEM), Fourier Transform Infrared spectroscopy (FTIR) and UV-visible absorption spectroscopy measurements. The XRD result indicated that the zinc oxide nanoparticles are highly crystalline, having the hexagonal wurtzite crystal structure. The average size of the synthesized nanoparticles is 40.2nm. The photocatalytic acitivity of the polymer capped zinc oxide nanoparticles were also analysed.

Keywords: Polymer, Congo red, Nanoparticles, Zinc oxide, Photocatalytic activity.

Introduction:

Nanoscience is the study of structures and molecules on the scales of nanometers ranging between 1 to 100 nm [1]. It encompasses a wide range of disciplines, including physics, chemistry, biology, engineering, and materials science. They typically range in size from a few to several hundred nanometers. These nanoparticles exhibit unique physical, chemical, and

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optical properties compared to their bulk counterparts, owing to their high surface area-to-volume ratio and quantum size effects. Zinc oxide itself is a wide-bandgap semiconductor with various applications due to its optical, electronic, and catalytic properties [1]. When synthesized at the nanoscale, ZnO NPs possess enhanced surface reactivity and optical properties, making them valuable in a wide range of applications. Thus, nano-ZnO has the potential to be used in gas sensors, surface acoustic wave (SAW) devices, photocatalyst for the degradation of waste water pollutants, catalysts, semiconductors, varistors, piezoelectric devices, UV photodiodes, UV-shielding materials, rubber, medical and dental materials, pigments and coatings, ceramic, concrete, antibacterial and bactericide, and composites [2–8]. Several research groups have reported on the synthesis of ZnO micro/nanostructures with varying shapes using different methods in the past years. Among these techniques are sputter deposition [9], ion beam-assisted deposition [10], laser ablation [11], hydrothermal method [12], sol-gel method [13-14], chemical vapour transport and condensation [15, 16], thermal evaporation [17], metal organic chemical vapour deposition [18], and electrochemical deposition [19-20]. In our research previous work, we have reported the synthesized and characterization of cellulose capped zinc oxide nanoparticles [21]. The present study aims to synthesize cellulose capped zinc oxide nanoparticles via precipitation method and photocatalytic acitivity of the nanoparticles. Cellulose, as one of the most abundant biopolymers, has many merits like biodegradability, biocompatibility and low cost. The polymer capped zinc oxide nanoparticles is used to dye degradation.

2. Materials and Methods:

2.1. Synthesis of polymer capped zinc oxide (ZnO) nanoparticles:

The capping agent cellulose is dissolved in 100 ml of distilled water and stirred at 90oC for one hour and then cooled to room temperature. 2.8754 g of $ZnSO_4.7H_2O$ (0.1M) was dissolved in 100 mL of distilled water. Meanwhile, Cellulose solution was prepared and was added to $ZnSO_4.7H_2O$ (0.1M) solution. Then 1.6802 g of $NaHCO_3$ (0.2 M) was prepared separately and was added drop wise into the above solution under constant stirring. After being stirred at room temperature for 2-3 hours, the as formed precipitates were filtered, washed with

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distilled water and ethanol and finally dried in hot air oven at 80oC to get cellulose capped zinc oxide nanoparticles [22].

2.2. Characterization of the polymer capped zinc oxide nanoparticles:

Nanoparticles are generally characterized by their size, morphology and surface charge, using such advanced microscopic techniques as X-ray Diffraction (XRD), scanning electron microscopy (SEM) with EDAX, transmission electron microscopy (TEM), FTIR and UV-Visible absorption spectroscopy.

3. Results and Discussions:

3.1. XRD Analysis:

The XRD pattern show perceptible peaks of cellulose capped zinc oxide nanoparticles at 31.9^{o}, 34.5^{o}, 36.3^{o}, 47.5^{o}, 56.7^{o} and 62.9^{o} corredponds to (100), (002), (101), (102), (110) and (101) planes. The resulting spectrum's indexed peaks match very well with bulk zinc oxide's (JCPDS code no. 36-1451), indicating that the synthesised nanoparticles possess a highly pure wurtzite hexagonal structure. The presence of a noticeable broadening of the diffraction peaks indicates that the materials being synthesised are in the nanoscale range. Scherrer's equation has been used to calculate the average particle size from the full width at half maximum (FWHM) of the diffraction peaks. It has been measured that the size of zinc oxide nanoparticles is 40.2 nm. The XRD pattern indicates that the polymer does not change the structure of the ZnO crystal. It can be concluded that the polymer only adsorbs on the face of the ZnO particles as a covering layer and does not involve the crystal lattice. The crystalline size of the ZnO particles (D) is evaluated according to the Debye–Scherrer equation, $D = K\lambda/(\beta\cos\theta)$, where K is the scherrer constant, λ the X-ray wavelength, η the peak width of half maximum, and θ is the Bragg diffraction angle.

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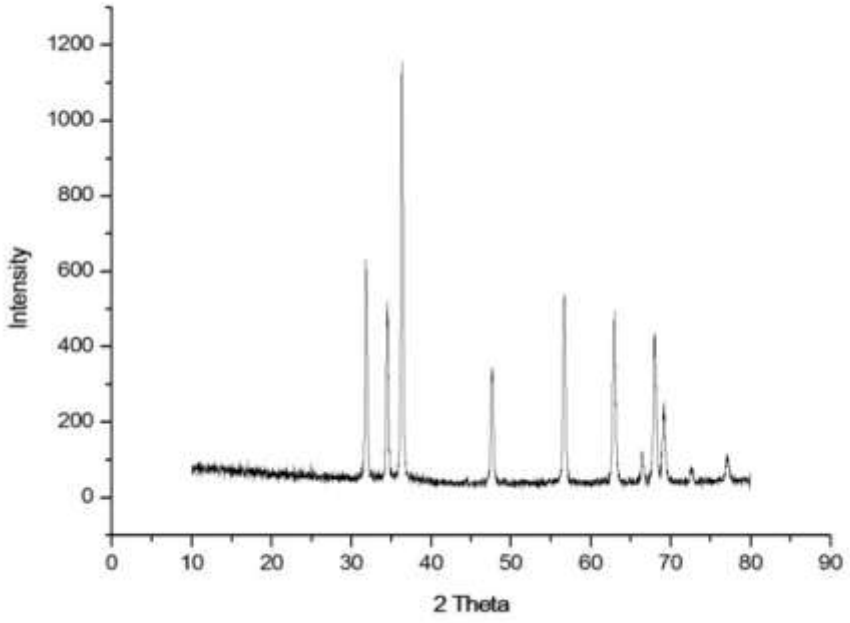

Fig.1. XRD Spectrum of Cellulose capped ZnO nanoparticles

3.2. SEM with EDAX Analysis:

Using a scanning electron microscope, the surface morphology of the synthesized cellulose capped zinc oxide nanoparticles was determined. It is evident from this material (Fig. 2) that the cellulose capped zinc oxide nanoparticles are nearly evenly distributed throughout the polymer matrix. However, because of its larger specific surface area and hydrophilic nature, ZnO aggregates were also observed in some locations. Figure 3 shows the EDAX spectra of polymer capped zinc oxide nanoparticles. The EDX spectrum exhibits distinct peaks for zinc and oxygen, and the results showed the formation of zinc oxide nanoparticles.

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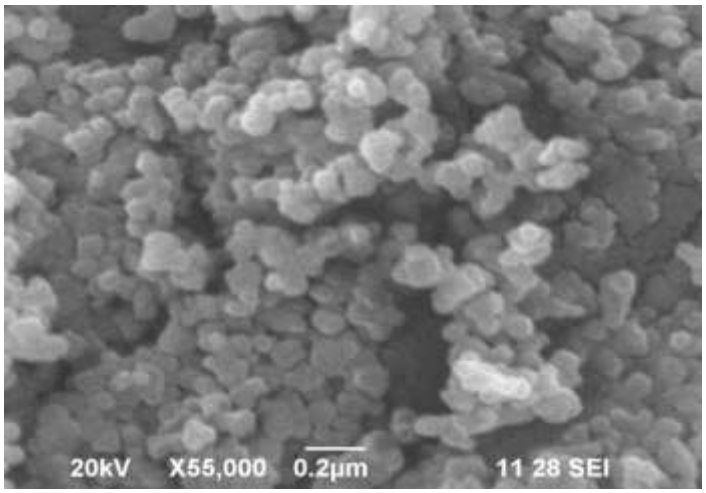

Fig.2. SEM image of Cellulose capped ZnO nanoparticles

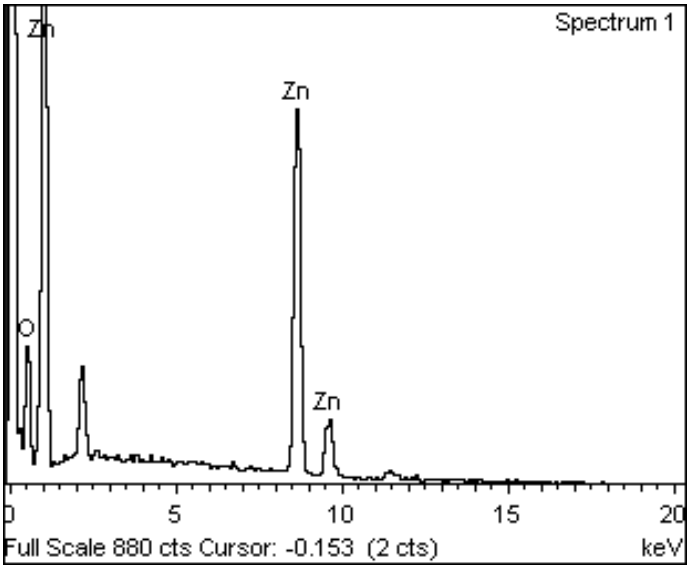

Fig.3. EDAX image of Cellulose capped ZnO nanoparticles

3.3. TEM Analysis:

Transmission electron microscopy is used to measure particle size. The TEM image of the cellulose capped zinc oxide nanoparticles showed spherical shaped metal oxide nanoparticles are distributed within the size range of 30-50 nm. The formation of metal oxide nanoparticles is confirmed by the TEM image.

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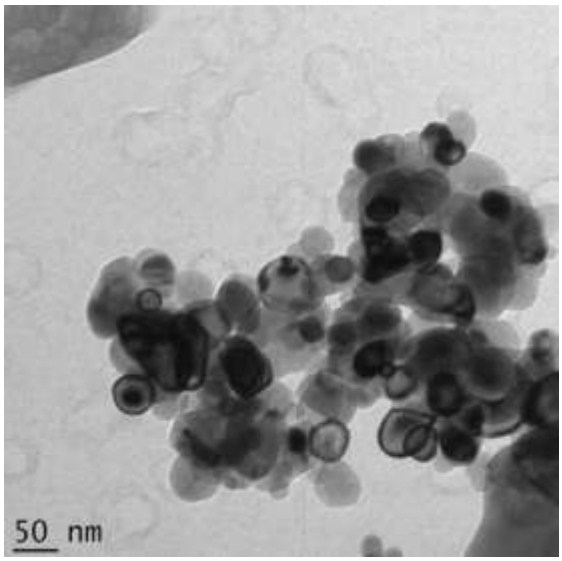

Fig.4. TEM image of Cellulose capped ZnO nanoparticles

3.4. UV Analysis:

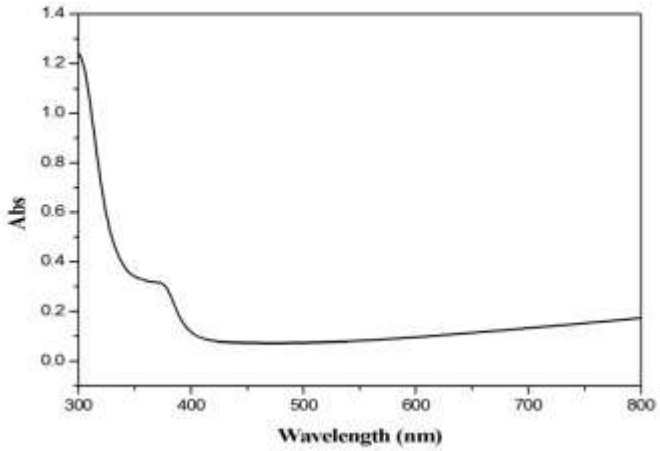

Fig. 5. UV-Vis spectrum of Cellulose capped Zinc oxide nanoparticles

Figure 5 shows the UV-vis spectrum of the cellulose capped ZnO nanoparticles that were synthesized. The simple synthetic process of cellulose capped ZnO nanoparticles production is confirmed by the prominent absorption peak found at 370 nm. When comparing the excitonic absorbance of the produced polymer capped ZnO NPs (370 nm) to that of the bulk ZnO (373

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nm), there was a noticeable blue shift. Furthermore, the characteristic peak was the only peak seen in the spectrum, indicating that the ZnO NPs are very pure.

3.5. FTIR Analysis:

Figure 6 shows the results of the FTIR examination of the polymer capped ZnO nanoparticles. The development of polymer capped zinc oxide nanoparticles is confirmed by the primary peaks below 500 cm^{-1} that is seen and corresponds to Zn-O. The bond seen at 2360 cm^{-1} is caused by the CO_2 molecule in the air, this peak is associated with the asymmetric strectching vibration of the CO_2 molecule. It can be observed in sample containing CO_2 or in spectra taken in environment, whereas the peaks at 1380 cm^{-1}, 1097 cm^{-1}, and 1032 cm^{-1} correspond to the symmetric stretching of the C-O bond. The stretching vibration of O-H groups is shown by the characteristic band at 3450 cm^{-1}. The cellulose capping of ZnO nanoparticles is confirmed through FT-IR spectroscopy, which suggests that a monomolecular layer on ZnO nanoparticles surface be formed.

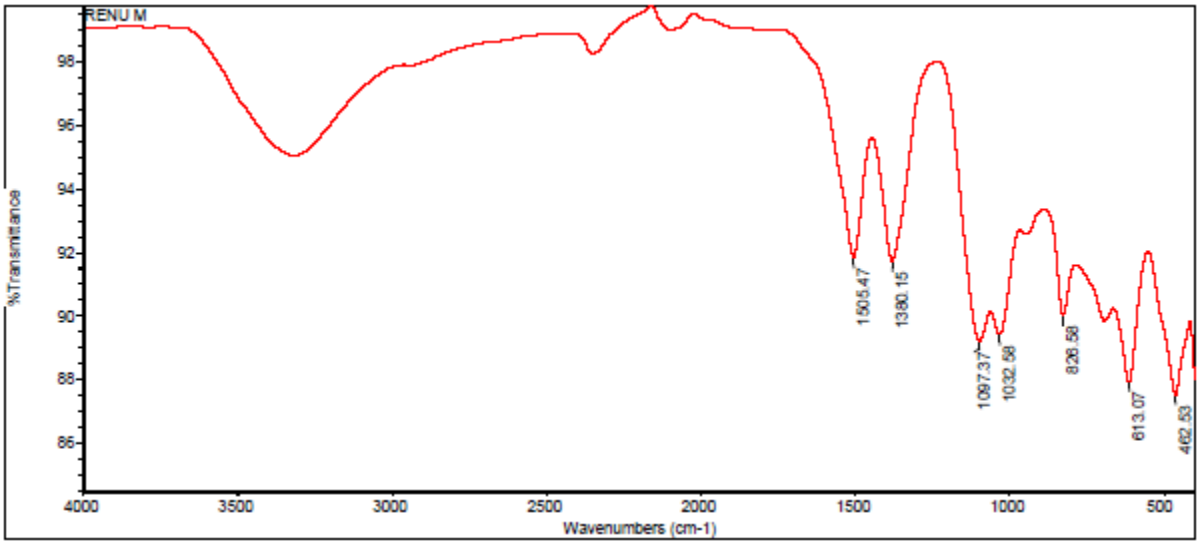

Fig.6. FTIR image of Cellulose capped ZnO nanoparticles

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3.6. Photocatalytic activity of cellulose capped Zinc oxide nanoparticles in presence of UV light irradiation:

3.6.1. Effect of Contact time:

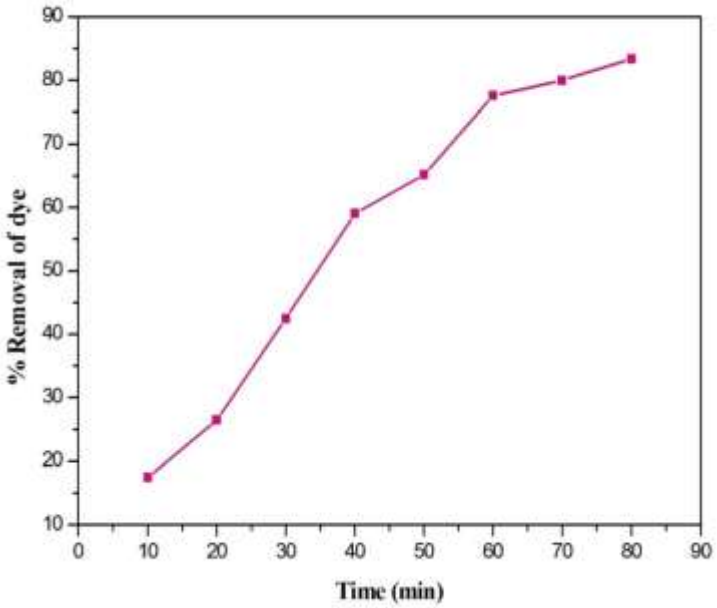

Fig.7. Effect of contact time

The rate of removal of congo red dye is shown in figure.7. for UV light irradiation. The extent of removal of CR dye by cellulose capped zinc oxide nanoparticles was found to be increased, reached a maximum value with increase in contact time. The equilibrium time was found to be 80 minutes for UV light irradiation. This may be due to with increase in irradiation time, dye molecules. Catalysts has enough time to take part in photocatalytic degradation process and hence percentage of degradation increased. As in shown these figures, desorption occurred after saturation. Therefore, considering technical and economic aspects, a contact time of 80 min for UV light irradiation was chosen for dye removal from aqueous solution by the adsorbent. The results of experiments showed that the photocatalytic degradation of CR dye obey apparently pseudo first order kinetics and the rate expression is given by the following equation,

$$\ln (C_o/C_t) = k_t \quad \text{---------- (5)}$$

Where,

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C_o = initial concentration of dye solution

C_t = final concentration of dye solution in various time interval

3.6.2. Effect of Dosage:

The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl and superoxide radicals. When the concentration of cellulose capped catalyst increased from 10 mg to 20 mg, the percentage removal of dye was also increased. The trend for this behavior is given in Fig.8.

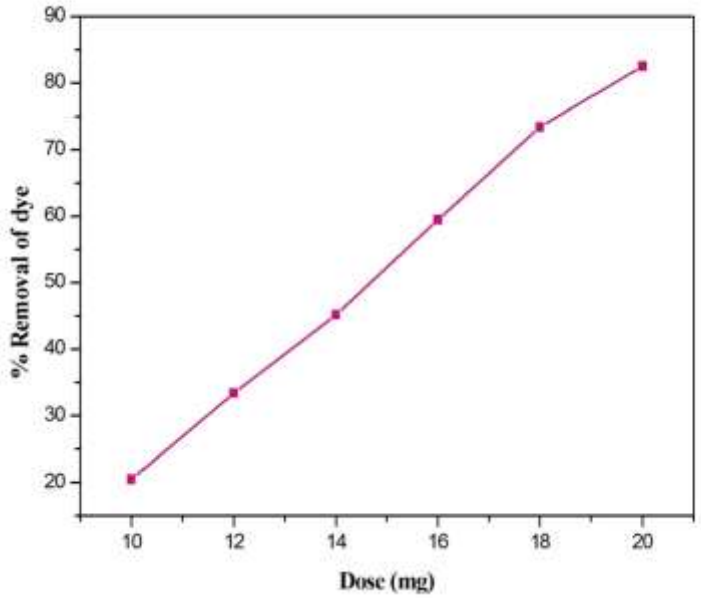

Fig.8. Effect of Dosage

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3.6.3. Effect of initial concentration of Congo red dye:

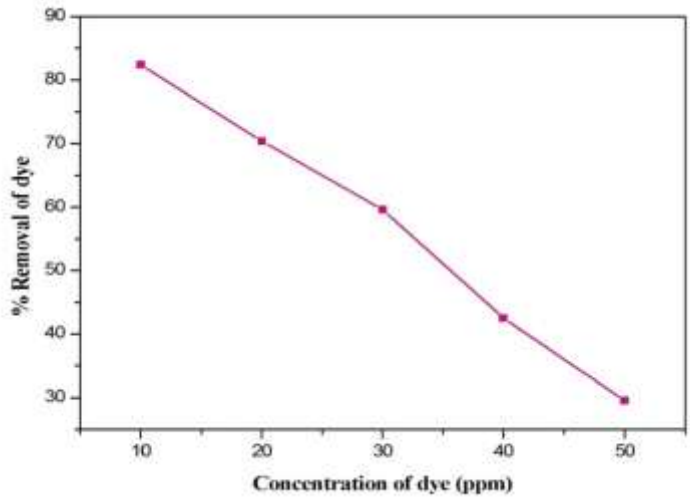

Fig.9. Effect of Initial concentration of dye

The effect of initial concentration of the dye on the rate of dye degradation was performed by varying the initial dye concentration from 10 ppm to 50 ppm with constant catalyst loading and the results are reported in Fig. 9. for UV irradiation. The observed results reveal that the initial concentration influences the rate of degradation of the dye. When the dye concentration increases from 10 ppm to 50 ppm, the rate of degradation decreases because of the number of dye molecules that are adsorbed at the surface of the catalyst. The photon entering path is reduced by the adsorbed dye molecules. This proves that the rate of decolourisation and degradation decreases considerably with increase in dye concentration.

4. Conclusion:

Cellulose was used as the capping agent in the successful preparation of polymer capped zinc oxide nanoparticles. The resulting nanomaterial was characterised by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX), Transmission electron spectroscopy (TEM), X-ray diffraction (XRD) and UV-Visible absorption spectroscopy. The nanomaterial have wurtzite hexagonal structure. Scherrer's equation has been used to determine the average particle size based on the XRD characterisation. The average size of the polymer capped zinc oxide nanoparticles is

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40.2 nm. The spherical shaped metal oxide nanoparticles are shown by TEM analysis, which is distributed within the size range of 30-50 nm. The FTIR and UV-visible absorption spectroscopy indicated the formation of zinc oxide nanoparticles. The percentage removal of congo red was analyzed with different experimental parameters such as contact time, dosage and initial concentration of dye. Hence, cellulose capped zinc oxide nanoparticles acts as an excellent photocatalyst in for degradation of dyes from textile industries.

References:

1. T. Anantha kumar, S. Malathi, C.V. Mythili, M. Jeyachandran, Structural, Morphological and Optical Properties of Zinc Oxide Nanoparticles by Polymer Capping, International Journal of ChemTech Research, 2018,11; 48-57.
2. Xiong M, Gu G, You B, Wu L. Preparation and Characterization of poly(styrene butylacrylate) latex/nano-ZnOnanocomposites. J. ApplPolym Sci., 2003, 90; 1923-1931.
3. El-Kemary M, El-Shamy H, El-Mehasseb I. Photocatalytic degradation of ciprofloxacin drug in water using ZnO nanoparticles. J. Lumi., 2010,130; 2327-2331.
4. Moezzi A, McDonagh A-M, Cortie MB. Zinc oxide particles: synthesis, properties and applications. Chem. Eng. J., 2012,185-186; 1-22.
5. Schmidt-Mendel L, MacManus-Driscoll JL. ZnO nanostructures; defects and devices. Mater.Today., 2007, 10; 40-48.
6. Ma X-Y, Zhang W-D. Effects of flower-like ZnOnanowhiskers on the mechanical, thermal and antibacterial properties of waterborne polyurethane. Polym. DegradStab., 2009, 94; 1103-1109.
7. Li YQ, Fu SY, Mai YW. Preparation and characterization of transparent ZnO/epoxy nanocomposites with high-Uv shielding efficiency. Polym., 2006, 47;2127-2132.
8. Li YO, Yang Y, Fu SY. Photo-stabilization properties of transparent inorganic UV-filter/epoxy nanocomposites. Compos. Sci Technol., 2007, 67;3465-3471.
9. W. Chiou, W. Wu, and J. Ting, "Growth of single crystal ZnO nanowires using sputter deposition," Diamond and Related Materials, 2003, 12, 10-11; 1841–1844.
10. W. Li, D. S. Mao, Z. H. Zheng et al., "ZnO/Zn phosphor thin films prepared by IBED," Surface and Coatings Technology, 2000, 128-129, 1; 346–350.

ISSN PRINT 2319 1775 Online 2320 7876

 UGC CARE Listed (Group -I) Journal Volume 10, Iss 12, 2021

11. Y. Sun, G. M. Fuge, and M. N. R. Ashfold, "ZnO/Zn phosphor thin films prepared by IBED," Chemical Physics Letters, 2004, 396, 1–3; 21–26.
12. Z. R. Dai, Z. W. Pan, and Z. L. Wang, "Novel nanostructures of functional oxides synthesized by thermal evaporation," Advanced Functional Materials, 2003, 13, 1; 9–24.
13. L. E. Greene, M. Law, J. Goldberger et al., "Low-temperature wafer-scale production of ZnO nanowire arrays," Angewandte Chemie—International Edition, 2003, 42, 26; 3031–3034.
14. S. E. Ahn, J. S. Lee, H. Kim et al., "Photoresponse of sol-gelsynthesized ZnO nanorods," Applied Physics Letters, 2004, 84, 975; 5022–5024.
15. K. Keis, E. Magnusson, H. Lindstrom, S. E. Lindquist, and A. Hagfeldt, "A 5% efficient photoelectrochemical solar cell based on nanostructured ZnO electrodes," Solar Energy Materials and Solar Cells, 2002, 73, 1; 51–58.
16. D. Voss, "Condensed-matter physics: switch-hitter materials tantalize theorists," Science, 2001, 292, 5524; 1987–1990.
17. M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, "Catalytic growth of zinc oxide nanowires by vapor transport," Advanced Materials, 2001, 13, 2; 113–116.
18. W. Lee, M. C. Jeong, and J. M. Myoung, "Catalyst-free growth of ZnO nanowires by metal-organic chemical vapour deposition (MOCVD) and thermal evaporation," Acta Materialia, 2004, 52, 13; 3949–3957.
19. Y. C. Wang and M. H. Hon, "Preparation of nanosized ZnO arrays by electrophoretic deposition," Electrochemical and Solid-State Letters, 2002, 5, 4; C53–C55.
20. M. J. Zheng, "Fabrication and optical properties of large-scale uniform zinc oxide nanowire arrays by one-step electrochemical deposition technique," Chemical Physics Letters, 2002, 363, 1-2; 123–128.
21. S. Malathi, T. Anantha kumar, C.V. Mythili, R. Jeba Sherin, Synthesis and characterization of polymer capped metaloxide nanoparticles, 2021, 8, 9; 81-86.
22. Sudha M, Senthilkumar S, Hariharan R, Suganthi A,Rajarajan M. Synthesis, Characterization and study of Photocatalytic activity of surface modified ZnO nanoparticles by PEG capping. J. Sol-Gel Sci. Technol., 2013, 65; 301-310.