PHOTOCATALYTIC ACTIVITY OF POLYMER CAPPED TERNARY SEMICONDUCTOR NANOPARTICLES

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Abstract: *In this work, we report the, optical, structural morphology and photocatalytic activity of Chitosan capped zinc indium selenide nanoparticles, which have been synthesized by solvothermal method from zinc chloride, indium chloride and selenium dioxide. Chitosan is acted as capping agent. The nanoparticles were characterized using XRD, SEM with EDAX, TEM and UV-Vis absorption spectroscopy. The synthesized nanoparticles have rhombhohedral crystal structure according to XRD pattern. The SEM revealed that the nanoparticles were uniformly distributed on the surface. The TEM microscopy confirmed that the $ZnIn_2Se_4$ nanoparticles were spherical in shape. The ranges of diameter of these nanoparticles are from 30 to 50 nm. In addition, photocatalytic degradation of Congo red in aqueous solution was performed using Chitosan capped zinc indium selenide nanoparticles under the illumination of visible light.*

Keywords: *Nanoparticles, Congo red, Zinc indium selenide, Solvothermal, Chitosan*

1. INTRODUCTION

Semiconductor nanocrystals with high quality and narrow size distribution have been the object of intensive scientific and technological interest [1-9]. Recently, a ternary compound of II-III-VI group attracts many researchers due to their applications in optoelectronic devices and solar cells [10]. Zinc indium selenide is a kind of n-type ternary chalcogenide semiconductor of type $A^{I}B^{II}{}_2C^{IV}{}_4$, where A=Zn, Cd or Hg, B=In or Ga and X=Se, S, Te. The direct energy gaps of this crystal have 1.82 eV at room temperature. The preparation of ZIS with a defective chalcopyrite structure has attracted much attention both for fundamental and for applied research. The defect in this compound arises from some percentage vacancies of Zn sites and naturally disorder is created which causes the appearance of a large number of electronic levels in the energy gap both very close to bottom of the conduction band and in the mid gap region [11]. In the present work, photocatalytic activity of zinc indium selenide nanoparticles are synthesized by using solvothermal method and chitosan used as capping agent. In our previous paper, we reported the structural, morphological and optical band gap determination of polymer capped zinc indium selenide nanoparticles [12].

2. MATERIALS AND METHOD

2.1. Preparation of polymer solutions

The chitosan solution was prepared by dissolving 1g of chitosan in 100 ml of 1% of acetic acid under constant stirring at room temperature.

2.2. Synthesis of chitosan capped Zinc Indium Selenide ($ZnIn_2Se_4$) nanoparticles

In a typical synthesis, $ZnCl_2.2H_2O$ (AR), $InCl_3$ *(absolute, AR)* and selenium dioxide (SeO_2, AR) were added to 90 ml polymer solution (Chitosan) at room temperature with the molar ratio of 1:2:4 under vigorous stirring to form a homogeneous solution. Then the obtained solution mixture was transferred into a Teflon-lined autoclave of 100 ml capacity. The autoclave was sealed and maintained at 180°C for about 12 h and then cooled to room temperature naturally [12].

2.3. Measurement of Photocatalytic Activity

The photocatalytic activity of the polymer capped zinc selenide nanoparticles and zinc indium selenide nanoparticles were evaluated by photo degradation of an aqueous Congo red (CR) textile dye. The experiment was carried out in a cylindrical double walled hollow photoreactor with water circulation facility. A visible lamp was placed inside the reactor. The catalytic experiments were carried out with 100 mL solution of CR [5×10^{-5} M] and 20 mg of the catalyst under constant stirring. About 3 mL of the aliquot solution was withdrawn at predetermined time intervals from the reaction mixture, centrifuged and the decrease in absorbance value was measured. A control experiment was carried out under identical experimental condition using commercial CR without catalyst.

$$\%\ \text{Decolourization} = [(\text{Co} - \text{C}) \div \text{Co}] \times 100$$

Where,
C_0, is the initial concentration of dye solution and
C, is the concentration of dye solution after photocatalytic degradation.

3. RESULTS AND DISCUSSION

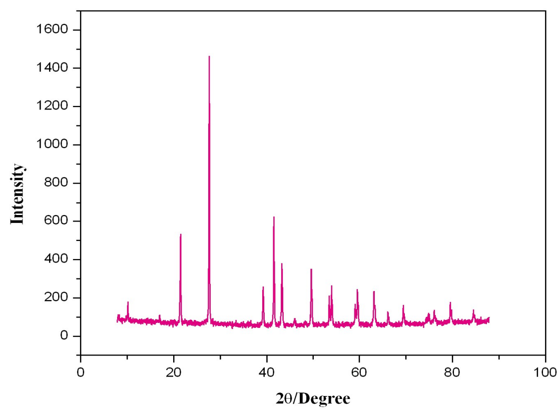

Fig.1. XRD Spectrum of Chitosan capped $ZnIn_2Se_4$ nanoparticles

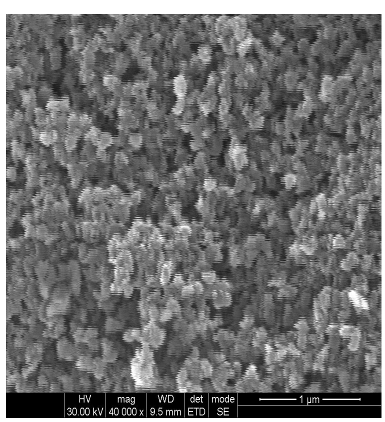

Fig.2. SEM image of Chitosan capped $ZnIn_2Se_4$ nanoparticles

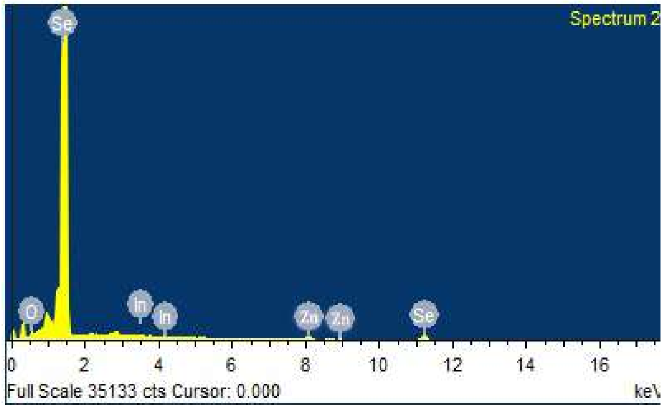

Fig.2.a. EDAX image of Chitosan capped $ZnIn_2Se_4$ nanoparticles

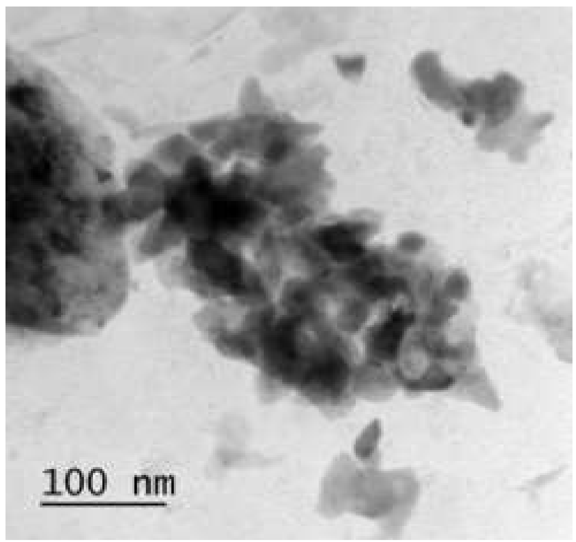

Fig.3. TEM image of Chitosan capped $ZnIn_2Se_4$ nanoparticles

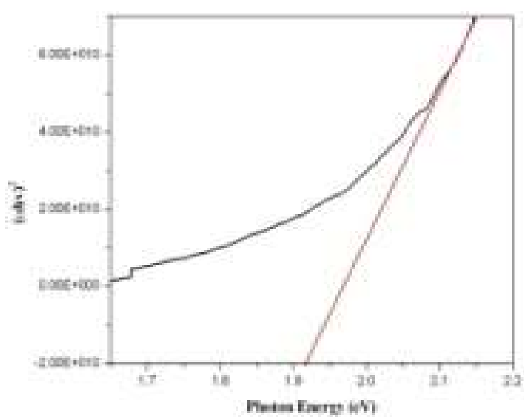

Fig.4. Band gap of Chitosan capped $ZnIn_2Se_4$ nanoparticles

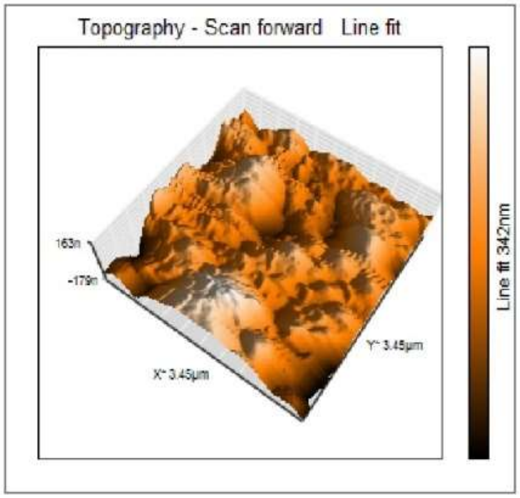

Fig. 5. AFM 3D image of Chitosan capped Zinc Indium Selenide ($ZnIn_2Se_4$) nanoparticles

The XRD pattern of different chitosan capped $ZnIn_2Se_4$ nanoparticles were shown in fig.1. For the sample a major peak is observed at about 27.17 and its equivalent inter-planar spacing is of 3.279 Å which corresponds to reflection from (112) plane of rhombhohedral system. This indicates that the nanocrystalline in nature. It coincides with the Zeyada et.al report [13]. In SEM with EDAX spectrum, it is seen that the lot of polymer capped nanoparticles are spherically shaped grains are distributed on the surface of the nanoparticles in fig.2.a. The EDAX spectra indicated well defined peaks corresponding to Zn, In and Se in addition to O (fig.2.b). TEM (fig.3) is revealed that the nanoparticles were mainly spherical in nature with few of them irregular shape. The diameter of spherical zinc indium selenide nanoparticle with an average size is 40 nm - 55 nm. The band gap was found to be 1.91 eV for chitosan capped $ZnIn_2Se_4$ nanoparticles. The band gap figure is shown in fig.4. Surface topological features of chitosan capped zinc indium selenide nanoparticle as observed under 3D AFM is shown in Fig. 5. The micrograph is at 3.45 µm × 3.45 µm. It might be used to investigate the surface roughness, RMS value and particle size of the nanoparticle. The micrograph illustrate that the substrate are entirely covered with grains of different size.

The experiments showed that degradation was completed nearly within 30 min. It was observed that decolorization and photodegradation increased with increase in the irradiation time. The kinetics of photodegradation was found that the degradation reaction of CR under the catalysis of chitosan capped zinc indium selenide nanoparticle basically obeys to the first order reaction kinetics. The increase in the degradation efficiency of CR with increase in the amount of catalyst may be due to increase in the active sites available on the catalyst surface for the reaction. The increase in the degradation efficiency of CR with increase in the amount of catalyst may be due to increase in the active sites available on the catalyst surface for the reaction. Initial concentration of dye is generally noted that the degradation rate increases with the increase in dye concentration to a certain level and a further increase in dye concentration leads to decrease the degradation rate of the dye [14-15].

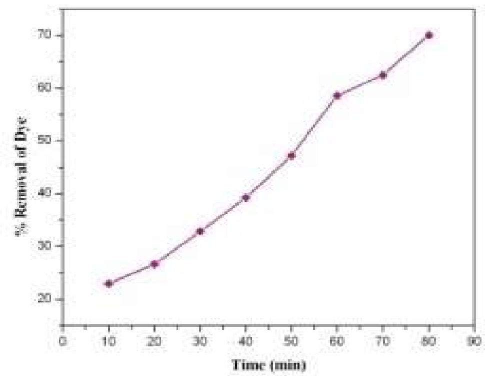

Fig. 5. Effect of Contact time in presence of visible irradaiation

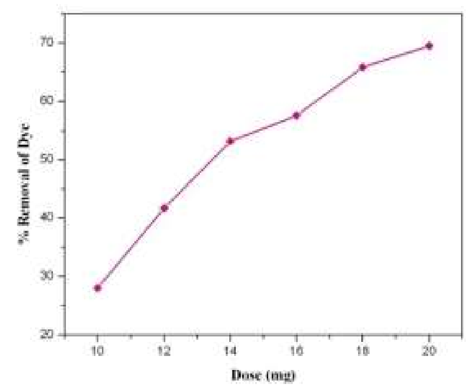

Fig. 6. Effect of Dosage in presence of visible irradaiation

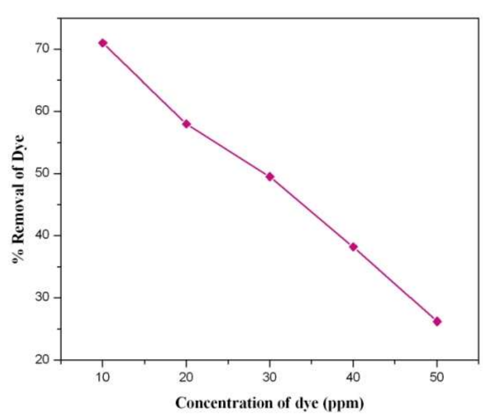

Fig.7. Effect of initial concentration of dye in presence of visible irradaiation

4. Conclusion

The Chitosan capped zinc indium selenide have rhombhohedral crystal structure according to XRD pattern. SEM analysis revealed that the spherically shaped grains are distributed on the surface. The EDAX spectra indicated well defined peaks corresponding to Zn, In and Se. The band gap energy of these nanoparticles is 1.91 eV (Chitosan). These values are higher than that of bulk zinc indium selenide (1.82 eV) nanoparticles and the material is blue shifted, when compared with bulk zinc indium selenide. AFM image might be used to investigate the surface roughness, RMS value and particle size of the nanoparticle. The micrograph illustrate that the substrate are entirely covered with grains of different size.The percentage removal of congo red was analyzed with different experimental parameters such as contact time, dosage. Based on the analysis, the resulting materials are to be very useful in water treatment.

5. References:

1. *Murray, C.B., Norris, D.J., Bawendi, M.G., "Synthesis and Characterization nearly monodispersive CdE (E=Sulphur, Selenium, Tellurium)semiconductor nanocrystallites", J. Am. Chem. Soc. Vol. 115, Issue 19, pp. 8706-8715, 1993.*
2. *Weller, H., "Colloidal semiconductor Q-Particles: Chemistry in the transition region between solid state and molecules", Angew. Chem., Int.Ed. Engl. Vol. 32, pp. 41-53, 1993.*
3. *Manna, L., Scher, E.C., Alivisatos, A. P., "Synthesis of soluble and processable Rod-, Arrow-, Teardrop-, and Tetrapod-Shaped CdSe nanocrystals", J. Am. Chem. Soc, Vol. 122, Issue 51, pp. 12700-12706, 2000.*
4. *Rogach, A.L., Talapin, D.V., Shevchenko, E.V., Kornowski, A., Haase, M., Weller, H., "Organization of matter on different size scales: Monodisperse Nanocrystals and their superstructures", Adv. Funct. Mater. Vol. 12, pp. 653-664, 2002.*
5. *Wang, X., Zhuang, J., Peng, Q., Li, Y., "A general strategy for nanocrystal synthesis", Nature, Vol. 437, pp. 121-124, 2005.*
6. *Ma, W., Luther, J. M., Zheng, H., Wu, Y., Alivisatos, A.P., "Photovoltaic devices employing ternary PbSxSe1-x nanocrystals", Nano Lett, Vol.9, Issue 4, pp. 1699-1703, 2009.*
7. *Ruberu, T.P.A., Vela, J., "Expanding the One-Dimensional CdS-CdSe composition landscape: Axially anisotropic CdS1-xSex nanorods", ACSNano, Vol. 5, Issue 7, pp. 5775-5784, 2011.*
8. *Ruberu, T.P.A., Albright, H.R., Callis, B., Ward, B., Cisneros, J., Fan, H., Vela, J., "Molecular control of the Nanoscale: Effect of Phosphine –Chalcogenide Reactivity on CdS-CdSe Nanocrystal composition and morphology", ACS Nano, Vol. 6, Issue 6, pp. 5348-5359, 2012.*
9. *Thompson, M.J., Ruberu, T.P.A., Blakeney, K.J., Torres, K.V., Dilsaver, P.S., Vela, J., "Axial Composition Gradients and Phase Segregation Regulate the Aspect Ratio of Cu2ZnSnS4 Nanorods", J. Phys. Chem. Lett, Vol. 4, pp. 3918-3923, 2013.*
10. *Alagumuthu, G., Anantha kumar, T., "Synthesis and Characterization of CMC capped $ZnIn_2Se_4$ Nanoparticles", International Journal of Innovative Research in Science, Engineering and Technology, Vol. 5, pp. 178-183.*
11. *Luengo, J., Joshi, N.V., "Composition dependence of the energy gap of ZnxMn1-xIn2Se4 and optical absorption spectroscopy", Mater. Lett, Vol. 26, pp.47-50, 1996.*
12. *Alagumuthu G, Anantha kumar T, Structural, Morphological and Optical band gap determination of Chitosan capped $ZnIn_2Se_4$ nanoparticles, Nanoscience and Nanotechnology: An International Journal, vol. 5, pp. 41-45, 2015.*

13. *H.M. Zeyada, M.S. Aziz, A.S. Behairy, Structure Formation and Mechanisms of DC Conduction in Thermally Evaporated Nanocrystalline Structure $ZnIn_2Se_4$ Thin Films, Physica B. 404 (2009) 3957-3963.*
14. *Saquib, M & Muneer, M 2003, 'TiO_2-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions', Dyes Pigments, vol. 56, no. 1, pp. 37–49.*
15. *Sakthivel, S Neppolian, B Shankar, MV Arabindoo, B Palanichamy, M & Murugesan, V 2003, 'Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2', Solar Energy Material and Solar Cells, vol. 77, no. 1, pp. 65-82.*