

Synthesis and Characterization of CMC capped ZnIn₂Se₄ Nanoparticles

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ABSTRACT: The development of rapid and reliable processes for the synthesis of nanomaterials is of great importance in the field of nanotechnology. The synthesis of nanoparticle such as metals, semiconductors and ceramics is carried out by using both physical and chemical methods. In recent times, a solvothermal method has been described for the preparation of the nanoparticles. Our aim is to prepare the carboxy methyl cellulose (CMC) capped zinc indium selenide (ZnIn₂Se₄) nanoparticles by the solvothermal method from zinc chloride, indium chloride and selenium dioxide. CMC, a non toxic biopolymer is used as capping agent to stabilize the nanoparticles. The resulting material is analysed by instrumental studies, viz., XRD, SEM, TEM and UV-vis spectroscopy. The particle size and band gap energy could be tried out, which would enhance the research works that depends on semiconductor and superconductivity materials.

KEYWORDS: Nanomaterials, Nanotechnology, Solvothermal, Semiconductor and Carboxy methyl cellulose.

I. INTRODUCTION

Semiconductor nanocrystals with high quality and narrow size distribution have been the object of intensive scientific and technological interest [1–9]. They exhibit outstanding optical, electronic, thermal and magnetic properties that are different from the bulk materials due to their quantum confinement effects and size dependent photoemission characteristics [10–16]. Recently, a ternary compound of II-III-VI group attracts many researchers due to their applications in optoelectronic devices and solar cells [17-19]. Zinc indium selenide is a kind of n-type ternary chalcogenide semiconductor of type A^IB^{II}₂C^{IV}₄, where A=Zn, Cd or Hg, B=In or Ga and X=Se, S, Te [20]. The direct energy gaps of this crystal have 1.82 eV at room temperature [21]. 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 [22].

Semiconductor nanoparticles stabilized by polymeric back bone have been synthesized over the past decade due to their excellent mechanical, optical, and optoelectronic properties [23]. In this work, Carboxy methyl cellulose is selected as the capping agent. Capping agents are used to arrest the growth of nanoparticles and to stabilize them from aggregation. They also modify the structural, morphological and optical properties of nanoparticles. In the present paper, ZnIn₂Se₄ nanoparticles are synthesized by using solvothermal method and carboxy methyl cellulose (CMC) as capping agent. This paper is organized as follows; The structural, Morphological and Optical properties of synthesized nanoparticles are presented in the 'Results and Discussion' section in detail, followed by a 'Conclusion' section. In this 'Method' section, we give a description of materials and synthesis method of ZnIn₂Se₄ nanoparticles with the capping agent.

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II. MATERIALS AND METHODS

2.1. Preparation of polymer solutions:

The carboxy methyl cellulose solution was prepared by dissolving 1.5g of CMC in 100ml of deionised water under constant stirring at room temperature.

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

In a typical synthesis, $ZnCl_2 \cdot 2H_2O$ (AR), $InCl_3$ (absolute, AR) and selenium dioxide (SeO_2 , AR) were added to 90 ml polymer solution 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 $180^\circ C$ for about 12 h and then cooled to room temperature naturally. The precipitate was collected, washed with absolute ethanol and distilled water in sequence for several times, then dried at $60^\circ C$ for 4 h and the powders were collected for characterization [24].

III. RESULTS AND DISCUSSION

3.1. XRD analysis:

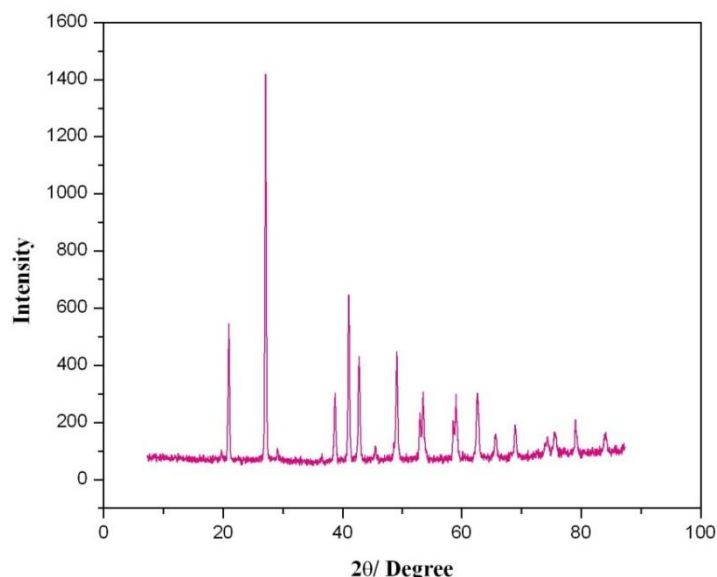


Figure.1. XRD pattern of CMC capped $ZnIn_2Se_4$ nanoparticles

Structural analysis of the CMC capped $ZnIn_2Se_4$ nanoparticles was carried out using $Cu-K\alpha$ radiation having wavelength 1.5406 \AA . XRD patterns were recorded by varying diffraction angle (2θ) from 10 to 100. Fig.1. shows a major peak is observe at about 27.17 and its equivalent inter-planar spacing is of 3.279 \AA , which corresponds to reflection from (112) plane of rhombohedral crystal structure and lattice constant $a=4.05 \text{ \AA}$ and $c=52.29 \text{ \AA}$ [25-26] suggesting the formation of $ZnIn_2Se_4$ nanoparticles. The peak of broadening at a lower angle is more meaningful for the calculation of particle size. The mean crystallite size (D) of nanoparticles was estimated by using the Scherrer formula (Scherrer 1918) using (112) reflection from the XRD pattern as follows.

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$$D = \frac{0.9\lambda}{(\beta \cos\theta)} \text{ ----- } 1$$

Where λ , β and θ are the X-ray wavelength of the radiation, the full width at half maximum of the diffraction peak and the Bragg diffraction angle, respectively. The evaluated crystalline size is found to be 49 nm.

3.2. SEM analysis:

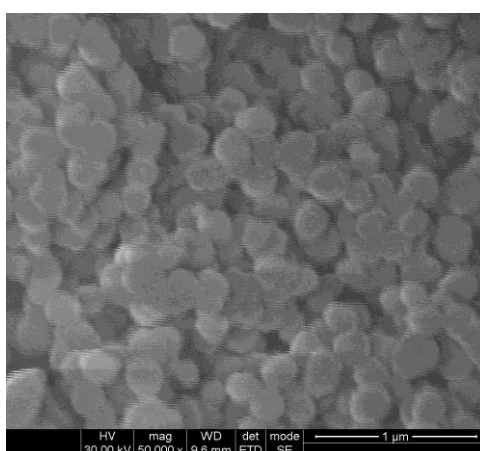


Figure.2. SEM image of CMC capped ZnIn₂Se₄ nanoparticles

The surface morphology of the synthesized CMC capped ZnIn₂Se₄ nanoparticles was examined by SEM micrographs and shown in figure.2. with magnifications of 58.44 Kx and 34.03 Kx, respectively. The micrographs revealed that the samples had the uniformity; homogeneity and a sphere like particles were distributed on the polymer. It is evident that the SEM micrographs shows rhombohedral crystal structure of the synthesized CMC capped ZnIn₂Se₄ nanoparticles.

3.3. TEM analysis:

The obtained ternary semiconductor nanoparticles are further characterized by transmission electron microscope. The shape and size of the sample is investigated using TEM analysis. Figure.3. represents the TEM micrograph of CMC capped ZnIn₂Se₄ nanoparticles, confirming that the nanoparticles are nearly spherical and they are different in size. The ranges of diameter of ternary semiconductor nanoparticles are from 30-50 nm. It may be noted that the size of CMC capped ZnIn₂Se₄ nanoparticles estimated from TEM is in good agreement with particle size calculated from the XRD analysis.

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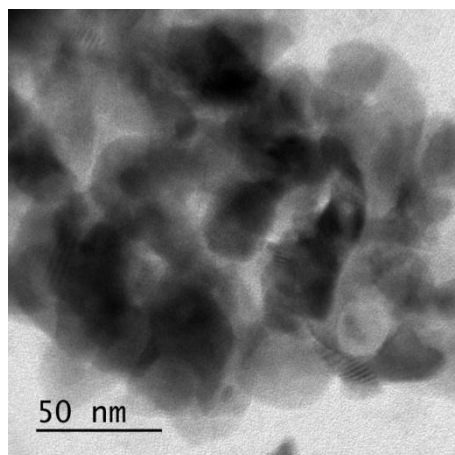


Figure.3. TEM image of CMC capped $ZnIn_2Se_4$ nanoparticles

3.4. Optical properties:

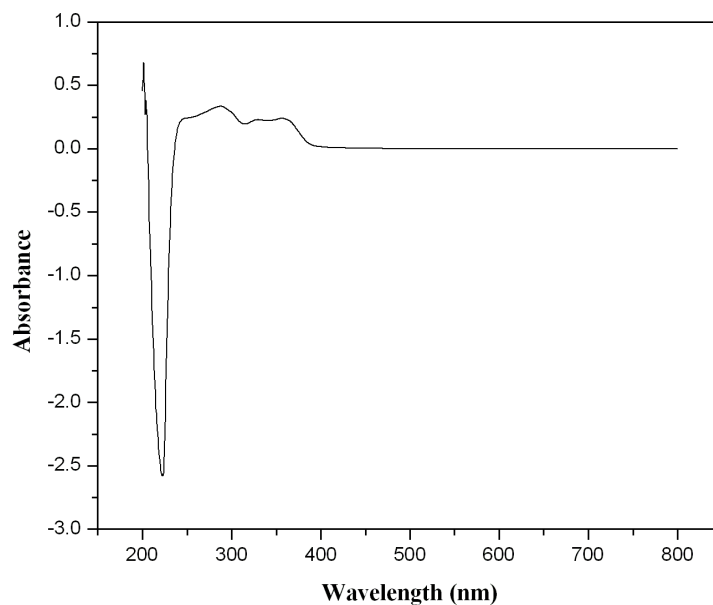


Figure.3. UV-vis absorption spectrum of CMC capped $ZnIn_2Se_4$ nanoparticles

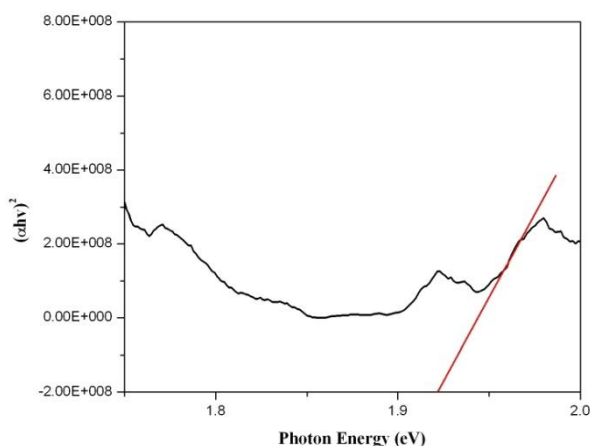


Figure.4. Band gap energy of CMC capped ZnIn₂Se₄ nanoparticles

The optical property of CMC capped ternary semiconductor sample is dependent on the size and the shape of the nanoparticles. The optical properties of CMC capped ZnIn₂Se₄ nanoparticles samples were characterized by UV-vis absorption and the result is shown in Figure.4. The absorption data were analysed using the classical relation for near edge optical absorption of semiconductor.

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \text{-----} 2$$

Where $h\nu$ is the photon energy. E_g the optical band gap. A and n are constants; where n is 2 for direct gap semiconductor and $1/2$ for indirect semiconductor. The variation of $(\alpha h\nu)^2$ versus $h\nu$ is linear at absorption edge which confirmed direct band gap transition in ZnIn₂Se₄ nanopartilces. Extrapolating the straight-line portion of the $(\alpha h\nu)^2$ versus $h\nu$ for zero absorption coefficient value gives E_g . The band gap energy of E_g of ZnIn₂Se₄ sample is found be 1.92 eV respectively that showed the blue shifts of 0.1 eV respectively from standard bulk band gap at room temperature ($E_g = 1.82$ eV). The absorption edge shifted towards shorter wavelength in comparison to the 1.82 eV band gap of bulk material. The blue shift in the absorption spectra is caused by polymer capping. Capping agent plays a very important role in this material [27-28].

IV. CONCLUSION

In summary, CMC capped Zinc indium selenide nanoparticles had been prepared by solvothermal method. The formation of CMC capped ZnIn₂Se₄ a nanoparticle was confirmed by XRD, SEM, TEM and UV-vis spectroscopy. The synthesized nanoparticles have rhombohedral crystal structure according to XRD pattern. The SEM revealed that the nanoparticles were uniformly distributed on the surface. The TEM microscopy confirmed that the ZnIn₂Se₄ nanoparticles were spherical in shape. The range of diameter of this nanoparticles are from 30 to 50 nm. The band gap energy of CMC capped ZnIn₂Se₄ nanoparticles found to be 1.92 eV and higher than that of bulk band gap of ZnIn₂Se₄ due to the polymer capping. In this investigation, a blue shift observed in the absorbance optical studies. This method is considered to be simple method for synthesise of polymer capped ternary semiconductor nanoparticles for wide range of application such as solar cells, modern electronics and electrooptical devices.

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