Synthesis and Characterization of Different Polymer Capped Zinc Selenide Nanoparticles by Hydrothermal Method

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ABSTRACT

Different polymer capping ZnSe nanoparticles have been synthesized by hydrothermal method. Polyvinyl alcohol (PVA), Chitosan and Carboxy methyl cellulose (CMC) are used as capping agent to stabilize the ZnSe nanoparticles. The resulting nanomaterials have been characterized by X-ray diffraction, Atomic Force Microscope (AFM), High resolution transmission electron microscope (HRTEM) and UV-Vis absorption spectrum. The particle size was estimated from broadening of XRD peak using Scherrer's formula and band gap energy of the material was also calculated from the UV-Vis absorption spectrum of the sample.

Key words: Nanoparticle, Zinc Selenide, XRD, Hydrothermal method, Capping agents.

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1.INTRODUCTION

Nanostructured materials can be utilized in fabricating novel active devices with improved functionalities. The discipline of Nanoscience and nanotechnology has recently become one of the most important areas of knowledge encompassing various scientific disciplines including physics, chemistry, biology and engineering. Nanoscience is concerned with the study of the unique properties of matter at its nano level and exploits them to create novel structures, devices and systems for different uses. Particles having size less than 100 nm are generally called nanoparticles. These have strikingly different properties due to their small size and thus are found useful in many applications. The ability to measure and manipulate matter on the nanometer level is making possible a new generation of materials with

enhanced mechanical, optical, transport and magnetic properties. Polymers are a large class of materials consisting of many small molecules called monomers that can be linked together to form long chains. Polymers consist mainly of identical or similar units joined together. A small molecule which combines each other to form a giant molecule and the process itself is known as polymerization. Because of the extraordinary range of properties of polymeric, they play an essential and ubiquitous role in everyday life [1, 2]. Nanostructured II–VI semiconductors have been studied very intensively in recent times due to their industrial implementation in nanoelectronic devices. The synthesis of semiconductor nanoparticles has attracted much interest due to their size-dependant properties and great potential in several applications such as nonlinear optics, photoelectrochemical cells, heterogeneous photocatalysis, optical switching and single electron transistors [3-10].

Zinc Selenide is often called II-VI semiconductor and also it is an intrinsic semiconductor with a band gap of about 2.70 eV at room temperature. ZnSe is one of the most typical and important crystalline materials for both application and research [11]. The ZnSe nanoparticles have wide-ranging applications in laser, optical instruments, etc. because it has a wide band gap (2.69 eV) and transmittance range (0.5–22 m), high luminescence efficiency, low absorption coefficient and excellent transparency to infrared [12-14]. Polyvinyl alcohol (PVA) has an excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and nontoxic. It has high tensile strength and flexibility. PVA is fully degradable and is a quick dissolver. PVA has a melting point of 230°C and 180-190°C for the fully hydrolyzed and partially hydrolyzed grades respectively [15]. Chitosan is a linear polysaccharide, produced usually by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimps etc). Due to its special structure containing many functional groups such as aminyl or hydroxyl [16-18]. Carboxylmethyl cellulose (CMC) or cellulose gum is a cellulose derivative with carboxymethyl groups (-CH_2-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. Cellulose derivatives have been relatively underutilized in the bioengineering field [19-21]. In this research the ZnSe nanoparticles were prepared by using a conventional hydrothermal method. The intrinsic properties of the resulting samples were studied by XRD, AFM, HRTEM and UV-Vis spectral techniques and results are reported.

2. MATERIALS AND METHOD

2.1. Preparation of polymer solutions:

The PVA solution was prepared by adding 1 g of PVA into 50 ml of deionised water and heated at 90^{o}C for 1 hour under constant stirring to obtain a viscous transparent solution. The chitosan solution was prepared by dissolving 1 g of chitosan in 100 ml of deionised water under constant stirring at room temperature. CMC solution was prepared by1.5 g of CMC in 100 ml of deionised water under constant stirring at room temperature.

2.2. Synthesis of different polymer capped Zinc selenide nanoparticles:

In order to synthesis different polymer capping ZnSe nanostructure materials by hydrothermal route, Zinc chloride [0.2M $ZnCl_2$], Aqueous ammonia [25% NH_3], Selenium dioxide [0.1N SeO_2], Polyvinyl alcohol [PVA], Chitosan and Caroxy methyl cellulose [CMC]. The PVA, Chitosan and CMC act as polymer capping agent. A 20 ml amount of 0.2M $ZnCl_2$ aqueous solution was mixed with 20 ml of ammonia solution(25% NH_3) under continuous stirring then 20 ml of PVA solution and SeO_2 (0.1N) were added into the mixed

solution. The pH is 9 using sodium hydroxide solution. After one hour of stirring, the resulting reaction mixture was transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and maintained in an electric oven at 180^{o}C for two hours and then cooled to room temperature. The precipitates were carefully collected and washed with deionised water and absolute ethanol several times and then dried. The same procedure was repeated for the synthesis of chitosan and CMC capped ZnSe nanoparticles by replacing the PVA solution with chitosan and CMC polymers respectively.

3. RESULTS AND DISCUSSION

3.1 XRD analysis:

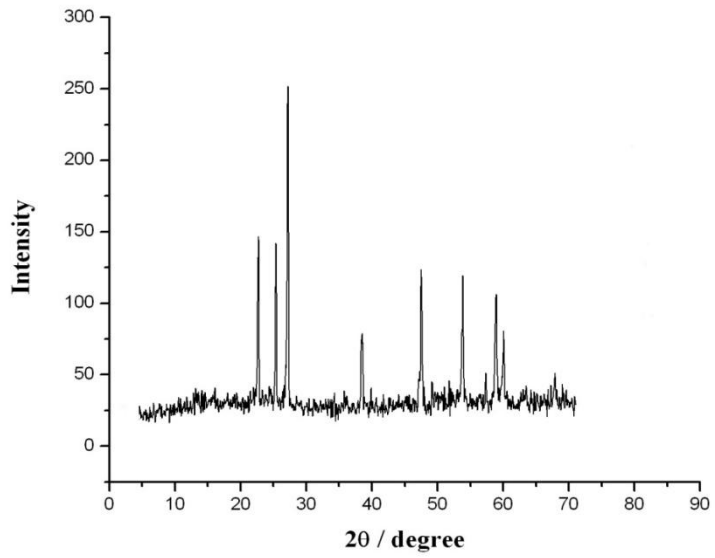

Fig 1.a: XRD pattern of PVA capped ZnSe nanoparticle

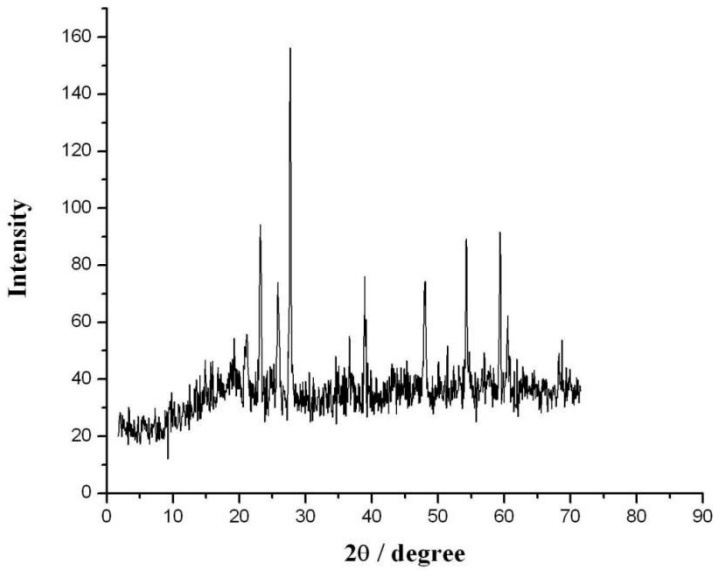

Fig 1.b: XRD pattern of Chitosan capped ZnSe nanoparticle

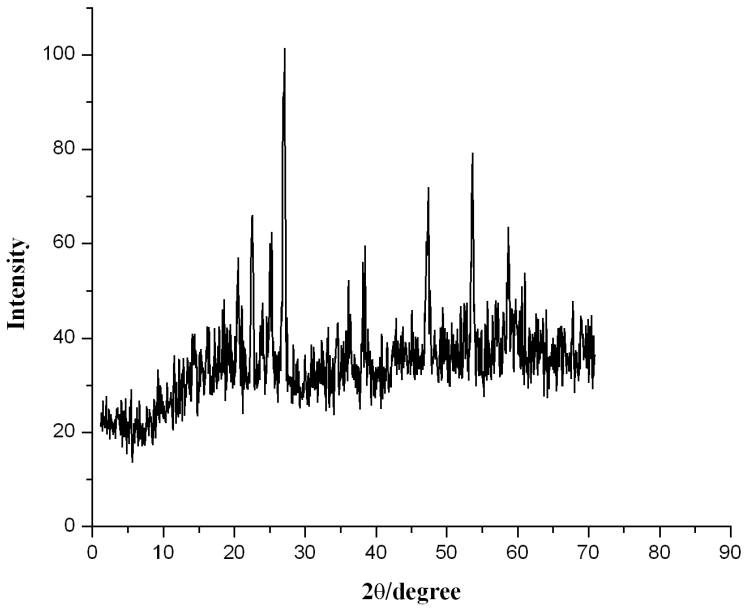

Fig1.c: XRD pattern of CMC capped ZnSe nanoparticle

The XRD pattern of different polymers capped ZnSe samples are shown in Figures(1.a, 1.b, 1.c). From these figures, the characteristics peaks located at 2θ= 23.45, 25.56, 27.23, 49.87^o and 53.6^o are corresponding to (100), (002), (101), (112) and (311) planes respectively. These peaks match well with the peak of hexagonal (wurtzite) crystal structure. Similar result have already reported by Hernandez *etal*[22]. The size of the nanocrystallites was estimated using Debye-Scherrer formula.

$$D = 0.9\lambda / (\beta\cos\theta)$$

Where D is the average crystallite size, λ is the wavelength of incident X-ray, β is the full width half maximum (FWHM) of X-ray diffraction expressed in radian and θ is the position of the diffraction peak in the diffractograms. The particle size was obtained in the above there XRD pattern as 34.8nm, 34.81nm and 17.4nm respectively.

3.2. AFM analysis of different polymer capped ZnSe nanoparticles:

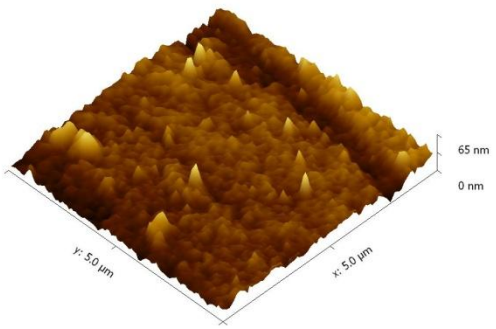

Fig 2.a: AFM 3D image of PVA capped ZnSe nanoparticle

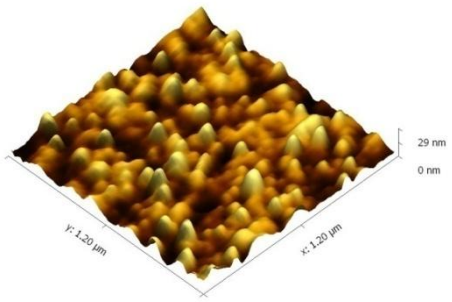

Fig 2.b: AFM 3D image of Chitosan capped ZnSe nanoparticle

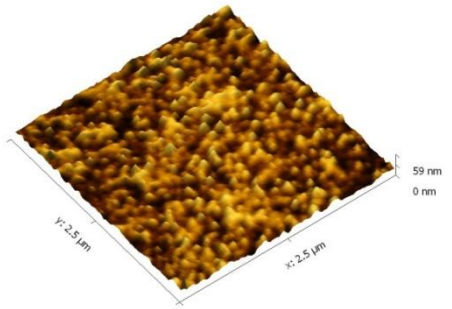

Fig 2.c: AFM 3D image of CMC capped ZnSe nanoparticle

Atomic microscopies an important tool to observe the surface morphology. It provides two and three dimensional images of the sample surface. Surface topological features of different polymer capped ZnSe samples as-observed under AFM 3D is shown in figures 2.a, 2.b and 2.c. The sample exhibit an uniform surface with cone like grains covering the ZnSe surface can be seen for all samples. The surface roughness, RMS average value and heights were determined by AFM analysis. The surface roughness was found to be in the range of 1.97 µm to 2.32 µm. The surface roughness of the samples was increased in the presence of different polymer capping agent due to the presence of functional groups. The average crystallite size of the sample was 34.7nm, 35nm and 17.5nm which has good agreement with the XRD results. AFM observations showed uniform distribution of ZnSe particle in polymer matrix with nanometer regime.

3.3. HRTEM analysis of different polymer capped ZnSe nanoparticles:

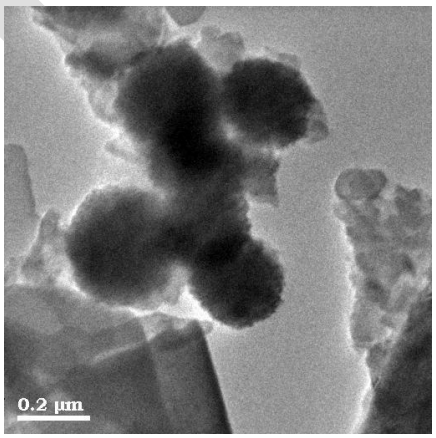

Fig 3.a: HRTEM image of PVA capped ZnSe nanoparticle

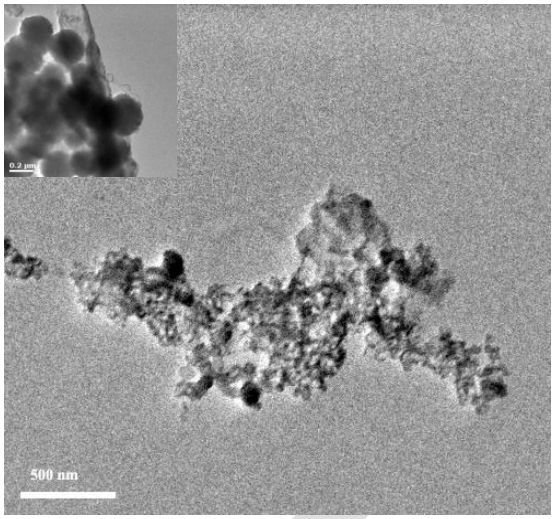

Fig 3.b: HRTEM image of Chitosan capped ZnSe nanoparticle

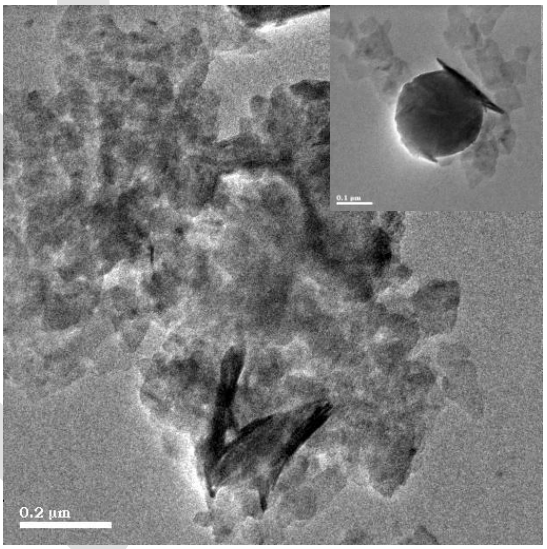

Fig 3.c: HRTEM image of CMC capped ZnSe nanoparticle

Figures 3.a, 3.b and 3.c show the HRTEM image of different polymer capping ZnSe nanoparticles. These HRTEM images indicating the monodispersed spherical crystallite. The nanoparticles are clearly well identified and no effective aggregation of bulk particle is formed. From the HRTEM image, these are observed that polymers are play an important role in enhancing the disperse property of ZnSe nanoparticles.There are report on the capping mechanism of polymers in growth process of ZnSe nanoparticle and also the influence polymers dosage in tailoring the shape and size of the ZnSe nanostructures.

3.4. UV-Vis absorption spectroscopy:

UV-Vis absorption spectrum of different polymer capping ZnSe nanostructure materials is shown in Fig. 4.a, 4.b and 4.c. It is a useful absorption characterization to analyze nanomaterials. The UV-Vis spectral analysis was carried out between 200nm and 800nm. These figures show the absorption spectrum of ZnSe nanostructure materials prepared with surfactants PVA, Chitosan and CMC. The absorption spectroscopy is very useful to calculate the optical band gap (E_g)with the help of the following equation

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

Where k is constant, E_g is the optical band gap and n is a constant equal to 1 for direct band-gap semiconductors. The plot of (αhν)2 vs. hν is shown in **Fig. 5**. Extrapolating the straight line of this plot for zero absorption coefficient it gives the direct band gap of nanostructure materials which is shown in **Fig. 5.**

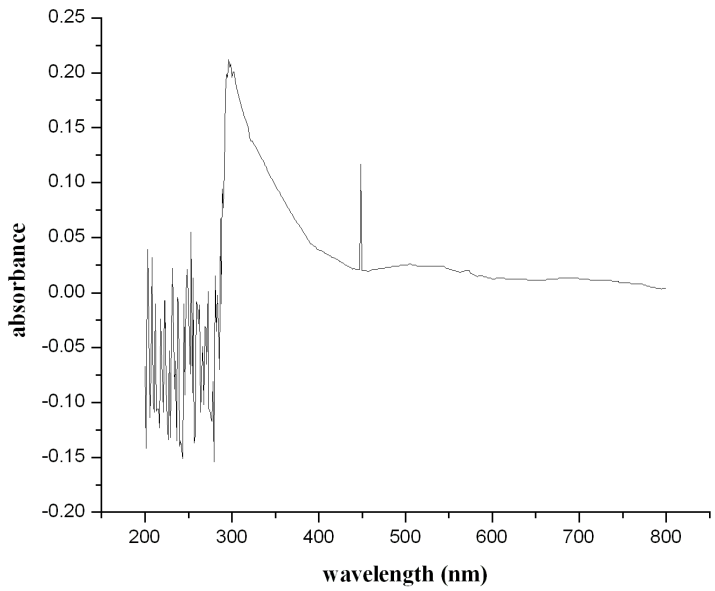

Fig 4.a: UV-Vis absorption spectrum of PVA capped ZnSe nanoparticle

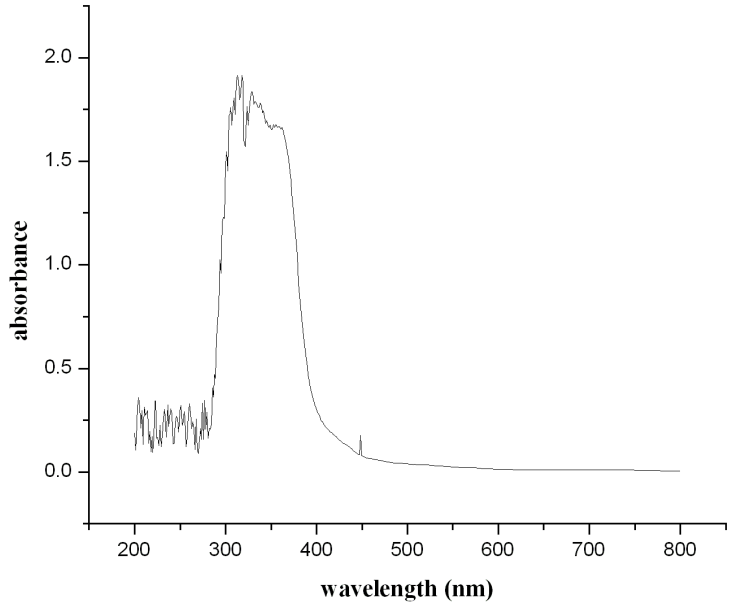

Fig 4.b: UV-Vis absorption spectrum of Chitosan capped ZnSe nanoparticle

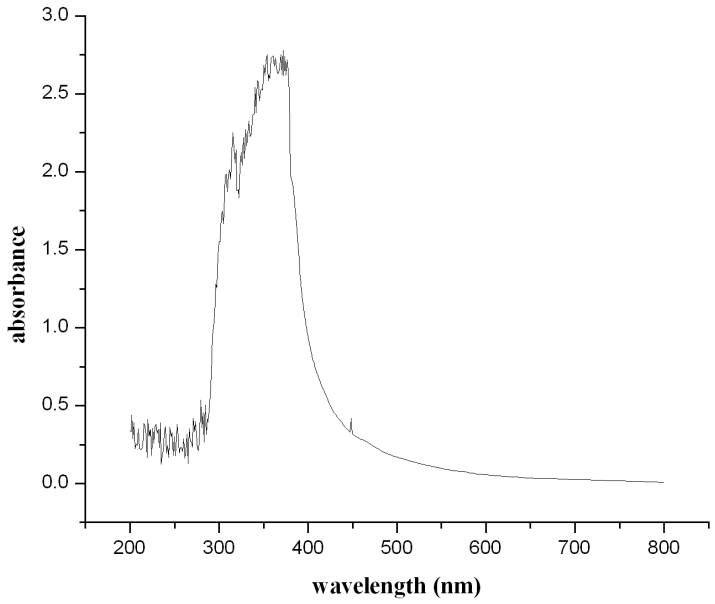

Fig 4.c: UV-Vis absorption spectrum of CMC capped ZnSe nanoparticle

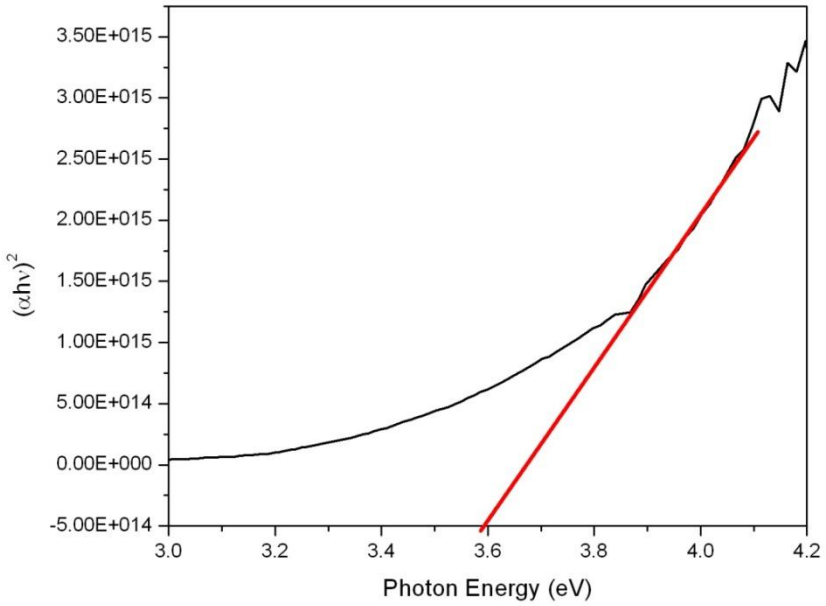

Fig 5.a: Band gap energy of PVA capped ZnSe nanoparticle

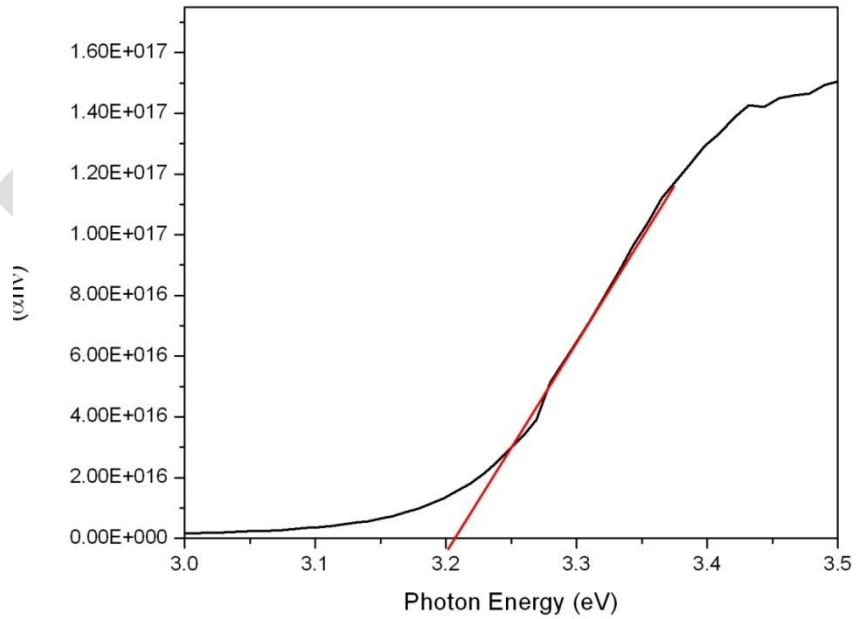

Fig.5.b: Band gap energy of Chitosan capped ZnSe nanoparticle

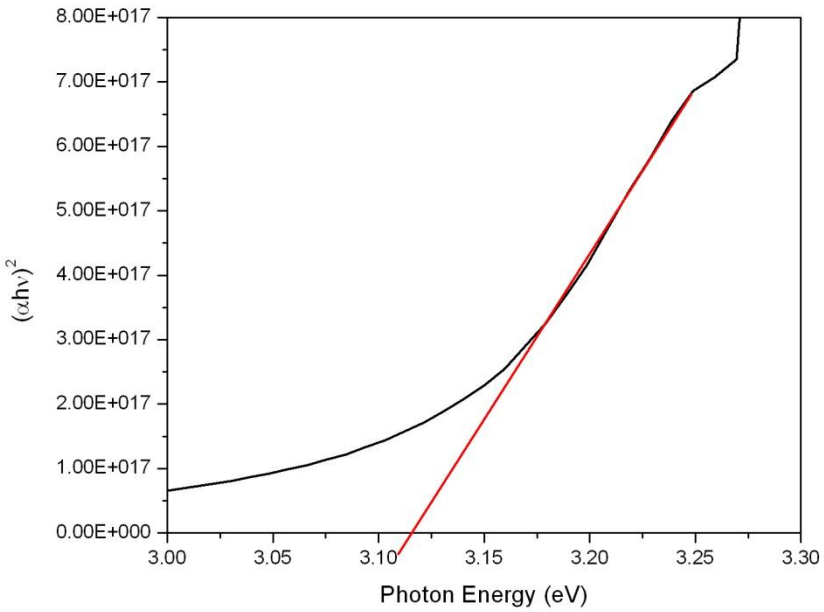

Fig 5.c: Band gap energy of CMC capped ZnSe nanoparticle

The absorption band gap edge was shifted to 296 nm and the corresponding band gap is 3.6 eV for PVA capped ZnSe nanomaterials, which is shown in Fig. 5.a. Where as in Fig.5.b the onset of the absorption edge at about 360 nm corresponds to the band gap of 3.2 eV for chitosan capped ZnSe nanomaterials and Fig. 5.c shows the absorption edge at about 390 nm corresponds to the band gap energy of 3.1 eV for CMC capped ZnSe nanomaterials. Which is higher compared to bulk ZnSe band gap 2.7 eV. Thus it is clear from the optical absorption study that the capping of ZnSe with different capping agent modifies the band gap of ZnSe nanomaterials and the sample is blue shifted when compared with the bulk ZnSe. The blue shift might be caused by nanosize effect and structural defect of nanomaterials.

CONCLUSION

Different polymer capping ZnSe nanoparticles have been prepared by the hydrothermal method. The polymers are used as capping agent to stabilize the ZnSe nanoparticles. These nanoparticles are confirmed by XRD, AFM, HRTEM and UV studies. The XRD studies showed that the ZnSe nanoparticles exihibit hexagonal crystal structure. Band gap energy of ZnSe nanoparticles was around 3.1eV – 3.6eV for different polymer capped nanoparticles, which is higher than that of bulk ZnSe nanoparticles indicate the capping agent modifies the band gap energy of the nanoparticles. The nanoparticles could find use in solar cells, in modern electronics and electrooptical devices.

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