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Synthesis and Characterization Studies of ZnSe Quantum Dots†

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ZnSe quantum dots have been synthesized by wet chemical, template free process by zinc acetate and elemental selenium powder in presence of ethylene glycol, hydrazine hydrate and a defined amount of water at 90 ºC. The product was in strong quantum confinement regime, having yield as high as 50 %. The transmission electron microscopy (TEM) image indicated that the particles were well dispersed and spherical in shape. The X-ray diffraction (XRD) analysis showed that the ZnSe nanoparticles were of the cubic structure, with average particle diameter of *ca.* 3.50 nm. The FTIR characteristic indicates that the N_2H_4 molecule has intercalated into the complex and formed a molecular precursor.

Key Words: Reflux method, ZnSe, Quantum dots, Quantum confinement, Semiconductor, Blue shift.

INTRODUCTION

Chemically synthesized nanostructures and their assembly are of fundamental importance due to their unique dimension dependent properties and their potential applications as building blocks in nanoelectronics, nano-optronics, nanosensors and actuators and in biology[1-15]. Recently much interest has been aroused in the preparation and assembly of semiconductor quantum dots due to their narrow and intensive emission spectra, continuous absorption band, high chemical and photo bleaching stability, processability and surface functionality. There is a wide range of very efficient light emitting quantum dots, which can be synthesized both in organic or as aqueous solutions[16-24]. ZnSe is an important II-VI, *n*-type, direct band gap semiconductor has attracted considerable attention due to its applications in light-emitting diodes, photo-detectors and full colour display[25-28]. The wide band gap (bulk band gap 2.7 eV) of ZnSe and significantly large binding energy (21 meV)[29], make this an ideal choice as an inorganic passivation shell for a variety of semiconductor core/shell nanocrystals, in order to improve the stability and emission properties of the semiconductor core nanocrystals with relatively narrow band gap and for efficient room temperature exciton devices with improve temperature characteristics[30-33]. ZnSe is also attractive host for the formation of doped nanocrystals[34-36]. Several novel applications have been presented which require size, shape and phase control of ZnSe nanostructured materials[37-40]. Hines *et al.*[30], reported a high temperature organometallic synthesis route, similar to that used for CdSe nanoparticles for producing monodispersed ZnSe nanoparticles. Recent reports[41,42] on solvothermal or hydrothermal synthesis of hollow ZnSe microspheres also broaden the way to synthesise ZnSe nanoparticles.

Aqueous synthesis of ZnSe nanoparticles using zinc perchlorate has also been reported[43-45]. Reiss *et al.*[42] have reported the synthesis of ZnSe nanoparticles in non-coordinating solvent (octadene) *via* direct reaction of zinc stearate with selenium. Sharp absorption features were observed and the luminescence could be tuned in the range 390-440 nm. However, the synthesis was carried out at high temperature of *ca.* 300 ºC using toxic chemicals like tri octyl phosphine. We report here a simple route which neither makes use of any toxic chemicals nor requires high temperature to produce monodispersed, highly luminescent ZnSe nanoparticles showing sharp absorption edges.

EXPERIMENTAL

Highly pure zinc acetate (99.9 %) and selenium (99.999 %) purchased from Central Drug House, New Delhi and Hi Media Laboratories, Mumbai and used without further purifi-

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cation. Ethylene glycol and Hydrazine hydrate of analytical grade purchased from Merk, Germany and used as received.

Characterization techniques: A Perkin Elmer Lamda 20 UV-VIS spectrophotometer was used to carry-out absorption spectra in the 300-700 nm wavelength range, while room temperature photoluminescence (PL) spectra were recorded on a Perkin Elmer LS 55 luminescence spectrometer. XRD measurements of the samples were performed using a Bruker aXS D8 advanced diffractometer with CuK_α radiation (λ = 1.5406 Å) operated at 40 kV and 40 mA. A Philips CM120 BIOTWIW at 80 K was used for TEM measurements and a Perkin Elmer spectrum one FT-IR spectrometer with universal ATR sampling accessory was used for the FT-IR spectra.

Synthesis of ZnSe nanoparticles: A typical procedure for synthesis of ZnSe quantum dots is as follows. In synthesis 1.2 g zinc acetate and 0.818 g elemental selenium was taken with deionized water, ethylene glycol and hydrazine hydrate in the volume of 5:3:2, respectively in a 200 mL capacity conical flask. Then the solution was refluxed at 90 ºC for 5 h. Finally, the yellowish precipitates were collected and washed with anhydrous ethanol and hot distilled water for several times, then dried in vacuum at 50 ºC for 6 h.

RESULTS AND DISCUSSION

In the present work, Se source was derived from the reduction of Se by N_2H_4. These highly reactive Se can be easily converted into Se^{2-}, which results in a high monomer concentration. In the initial step, hydrazine hydrate complexes with metallic Zn^{2+} and forms the transparent soluble complexes solution, which effectively decreases the concentration of Zn^{2+} and avoids the precipitation of $ZnSeO_3$, thus providing a more homogenous solution environment for the reaction. Se^{2-} is released slowly and interacts with surplus N_2H_4 to form the molecular precursor immediately. The reaction could be described as follows:

$$2Se^{2-} + 4N_2H_4 + 2Zn^{2+} \rightarrow 2ZnSe{\cdot}N_2H_4 + \downarrow 3N_2 + \uparrow 6H_2O$$

$$ZnSe{\cdot}N_2H_4 \rightarrow ZnSe + N_2H_4$$

XRD Analysis: X-Ray diffraction pattern of the as prepared ZnSe sample is shown in Fig. 1. All the diffraction peaks in this pattern can be indexed to cubic structure. Which is in very good accordance with the JCPDS card No. 01-088-2345 for ZnSe (a = b = c= 5.670 Å). The several peaks of cubic phase of ZnSe have been obtained due to diffraction form (1 1 1), (2 2 0), (3 1 1) and (3 3 1) planes of ZnSe. Two peaks of $ZnSeO_4{\cdot}H_2O$ have also been obtained in the diffraction data. The information on the particle size (D) of ZnSe quantum dots has been obtained from the following Debye -Scherrer relations:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where β is the full-widths-at-half-maximum (FWHM) of the diffraction peaks.

FTIR Analysis: As prepared sample was characterized by FTIR analysis and the corresponding spectrum is shown in Fig. 2. The broad peak at 3402 cm^{-1} and the weak peak at 2384 cm^{-1} are assigned to O-H characteristic vibrations resulting from all small quantity of $ZnSeO_4{\cdot}H_2O$ on the sample.

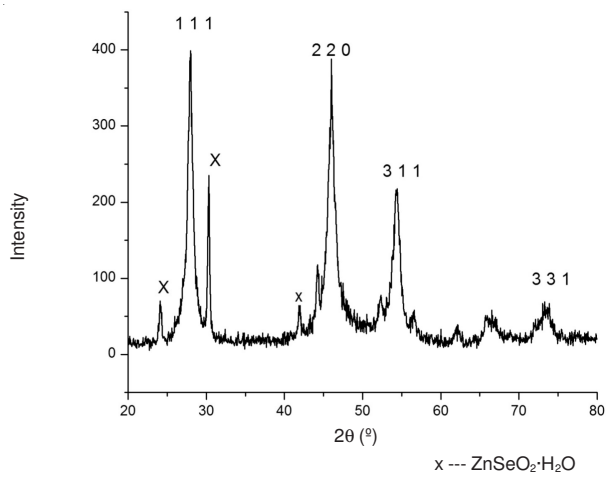

Fig. 1. X-Ray diffraction pattern of ZnSe sample

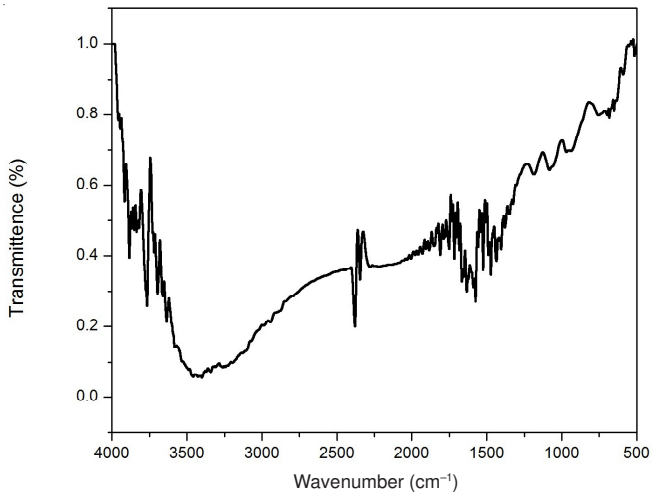

Fig. 2. FT-IR spectrum of ZnSe sample

The sharp peak at 2379 cm^{-1} corresponds to N-H stretching vibration band and the shift toward lower frequency compared with hydrazine may result from the interaction of N_2H_4 with zinc ion and regular periodic structure of molecular precursor. The NH_2 scissor and twist band appears at 1584 and 1561 cm^{-1}, respectively. Sharper and stronger peaks indicate weaker interaction ordered arrangements of hydrazine molecules existing in the precursors. All IR characteristic indicates that the N_2H_4 molecule has intercalated into the complex and formed a molecular precursor.

Optical analysis: The optical properties of ZnSe quantum dots are dependent on the size and the shape of the quantum dots. The optical properties of ZnSe quantum dots were characterized by UV-VIS absorption and the result is shown in Fig. 3. There is a obvious shoulder peaks in the UV-VIS absorption spectrum and the corresponding onset at 330 nm which can be assigned to the band gap and the second excited state within each crystallite, respectively. The absorption spectra of ZnSe quantum dots were studied without taking into account the reflection and transmission losses. The band gap energy, E_g, of ZnSe quantum dots was found to be 3.14 eV that showed the 'blue shift' of 0.44 eV from standard bulk band gap at room temperature (E_g = 2.7 eV). It is well-known that the reaction conditions such as heating time, temperature, kinds and amount

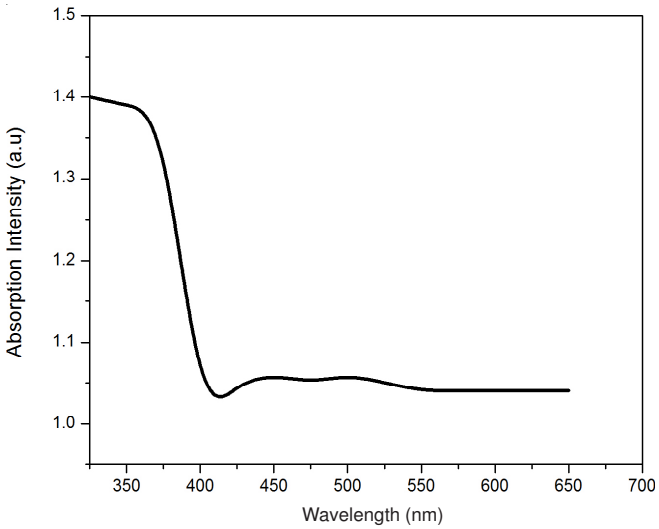

Fig. 3. Absorption spectra of ZnSe sample

of reagents have effect on the morphology and size of the products in the processes. The room temperature photoluminescence spectrum centered at 387 nm of as prepared ZnSe quantum dots excited at 230 nm is shown in Fig. 4 which is attributed to the recombination of excitons and the UV- blue emissions at *ca.* 410 nm that results from the recombination of a photon-generated hole with a charge state of the specific defect.

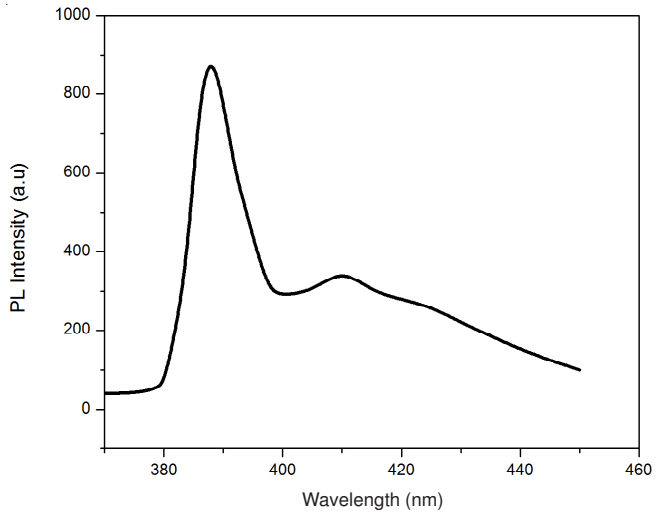

Fig. 4. Photoluminescence spectra of the ZnSe sample at room temperature

TEM Analysis: Fig. 5 shows the TEM images and particle size distribution of ZnSe nanoparticles. The image showed that the particles were well dispersed, small and spherical in shape. The particles are in the range 2.3-4.2 nm with mean particle diameter of 3.3 nm and standard deviation (σ) of 0.562 nm indicating broad size distribution. This is in accordance with the XRD result.

Conclusion

Nearly monodispersed ZnSe nanoparticles were successfully synthesized in aqueous solution of hydrazine hydrate and ethylene glycol at 90 ºC within 5 h, free from any hazardous element and surfactant or template. The advantages of this method are its simplicity, low cost and efficient which takes

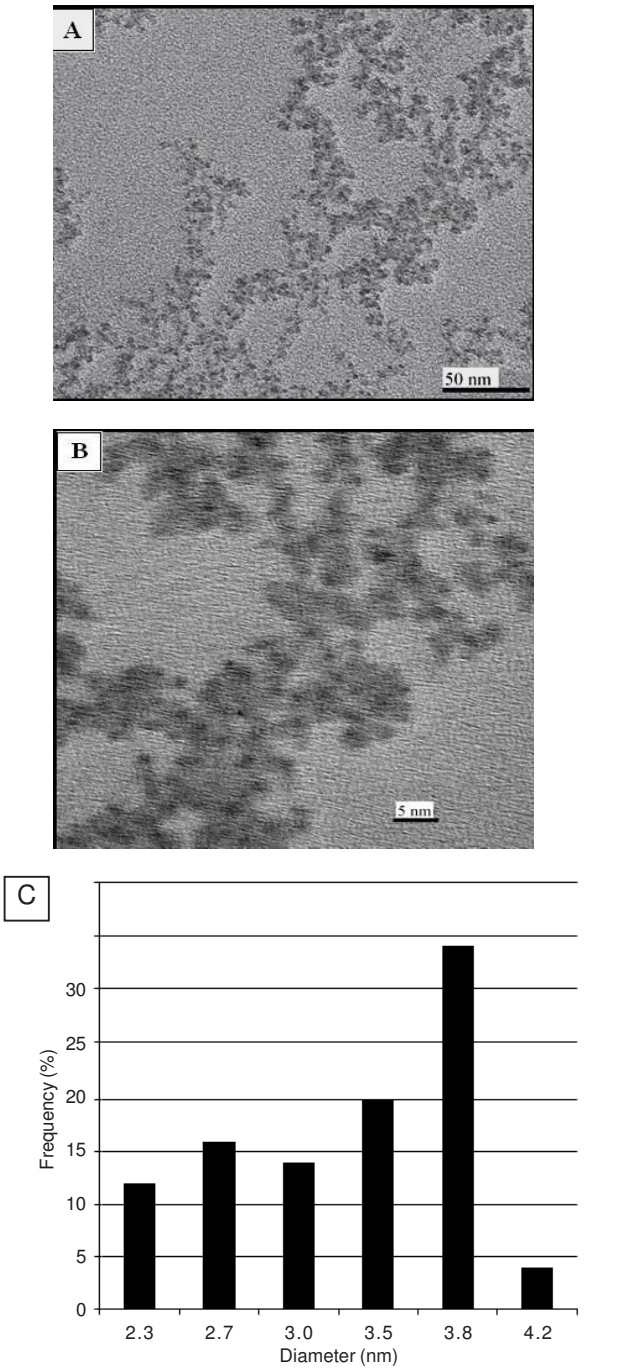

Fig. 5. TEM images (A and B) and particle size distribution (C) of ZnSe quantum dots

place within a short period of time and under ambient environmental conditions. The selenide nanoparticles can be used in many applications such as luminescent probe, biomedical labelling, catalysis, food and pharmaceutical industry and many other possible applications. This method can be extended for the preparation of other functionalized water soluble selenide nanoparticles.

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