Synthesis and characterization of CdSe semiconductor nanoparticles by ultrasonic irradiation

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Abstract

Cubic CdSe nanoparticles have been prepared using cadmium acetate dihydrate ($C_4H_6CdO_4 \cdot 2H_2O$) as a Cd^{2+} ion source and sodium selenosulfate (Na_2SeSO_3) as a Se^{2-} ion source with the aid of ultrasound irradiation in normal laboratory conditions at room temperature (27 °C). Scanning electron microscope (SEM) images display that the product consists of nanocrystallites of about 20 nm which aggregated in the form of polydispersive nanoclusters with dimensions in the range of 150–200 nm. X-ray diffraction analysis exhibits that the particles are excellently crystallized. Energy dispersive X-ray spectroscopy (EDX) measurements further confirms the formation of purely CdSe nanoparticles and average atomic percentage of Cd to Se is about 52:48; showing that the product is almost stoichiometric. UV–visible absorption spectroscopy of the as prepared nanoparticles shows the presence of direct transition with energy band gap of about 2.02 eV. Comparing to 1.74 eV, corresponding to its bulk value, a blue shift of about 0.28 eV is detected which is understood as a quantum size effect, due to confinement of electron and hole in a small volume.
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1. Introduction

Semiconductor nanoparticles have attained considerable interest during past decade in many different scientific disciplines [1–5]. The properties of matter changes profoundly as the length scale of the particles become comparable to the excitonic Bohr radius. The resultant is a quantum confinement effect where the electronic energy levels becomes discrete and leads to band gap broadening, increase in oscillator strength and reduction in the radiative recombination of carriers from few nanoseconds to few picoseconds [6,7]. The synthesis of binary metal chalcogenides of groups II–VI semiconductors in a nanocrystalline form has also been growing area of research due to their important non-linear properties, luminescent properties, quantum size effect and other physical and chemical properties [8].

Cadmium selenide is one of the groups II–VI compounds which encounters an extensive range of applications in optoelectronic devices, such as photoelectrochemical cells [9–11], photoconductors [12,13], thin film transistors [14], gamma ray detectors [15], large screen liquid crystal display [16], etc. Many approaches have been suggested for synthesis of this group semiconductor crystallites or nanocrystallines, such as gas-phase reaction between the elements or its compounds and gaseous H_2Se [17], solid state reaction [18], chemical bath deposition [19] and pyrolysis of single source precursors [20]. Generally, all these reactions require high temperature (500 °C) and the use of toxic and highly sensitive precursors. Parkin and co-workers [21], reported a direct combination of elements in amine for the synthesis of metal chalcogenides. However, the obtained products ZnE and CdE (E = S, Se or Te) were X-ray amorphous and needed to be crystallized at above 300 °C. Bandaranayke et al. [22], reported a method for synthesis of CdE crystallites using aqueous solution precipitation from Na_2E and $CdCl_2$ followed by thermal annealing at high temperature. Subsequently, a thermal solvent method was studied [23] and many main groups and transient metal chalcogenides have been prepared through this method [24–27]. However, this method still needs relatively high temperature or high pressure and long reacting time (several hours to days). Our attempt is to obtain high quality materials under moderate conditions and using safe precursors at a relatively low temperature. The sonochemical method has been

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extensively used to generate novel materials [28–31]. Recently, CdSe films were deposited by pulse electrodeposition with and without ultrasonic waves and their structural and optical properties have been studied [32,33]. Chemical effects of ultrasonic waves for acceleration of chemical reaction and for the synthesis of new materials with unusual properties have been observed. In this paper, we present a new method to prepare cubic CdSe nanoparticles using cadmium acetate as a cationic source and sodium selenosulfate as an anionic source with the help of ultrasound irradiation in normal laboratory conditions at room temperature (27 °C).

2. Experimental details

2.1. Materials

Cadmium acetate dihydrate ($C_4H_6CdO_4 \cdot 2H_2O$ extra pure), Se powder (purity $\geq$ 99%), sodium hydroxide (NaOH extra pure), sodium sulfite (Na_2SO_3 extra pure) Tartaric acid ($C_4H_6O_6 \geq$ 99.5%), thiophenol (C_6H6S purity > 98%) and absolute ethanol were obtained from Merck and directly employed without purification.

2.2. Instruments

Morphology and structure investigations were performed using the LEO 1430VP scanning electron microscope (SEM) with 15 and 18 kV accelerating voltages. The purity and elemental analyses of the products were obtained by EDX on the same LEO 1430VP instrument with accelerating voltage of 20 kV. The sample used for SEM and EDX observations were prepared by relocating the particles, which at first was dispersed in ethanol, on a glass substrate bound to SEM stage. After allowing the evaporation of ethanol, the particles on the stage were coated with a thin layer of gold and palladium. The x-ray diffraction (XRD) pattern of products were recorded on Philips X pert X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å) employing scanning step size of $0.02° \, s^{-1}$, in 2θ range from 15° to 70°. UV–visible absorption spectra of the sample were recorded employing a double beam, Shimadzu, 1650 spectrometer, Japan, applying quartz cuvettes of optical path length 1 cm.

2.3. Preparation of CdSe nanoparticles

For preparation of CdSe nanoparticles, 10 ml of 0.2 M aqueous solution of cadmium acetate dihydrate ($C_4H_6CdO_4 \cdot 2H_2O$) was mixed with 10 ml of 0.2 M aqueous solution of tartaric acid ($C_4H_6O_6$) to form a complex and was use as cationic precursor solution. Then sodium selenosulfate ($Na_2Se \, SO_3$), as the anionic precursor solution containing Se source, was prepared by dissolving 0.25 g Se powder in 50 ml of 1.1 M aqueous solution of sodium sulfite (Na_2SO_3) by magnetically stirring for 4 h at 80 °C applying a reflux column system. After stirring, all the selenium powder was dissolved and the transparent solution was allowed to be cooled to the room temperature. The pH of this solution brought to 9 by addition of NaOH. Then 10 ml of the anionic and 20 ml of the cationic precursor solutions were added in a

flat bottom flask and mixed slowly and the color of the mixture gradually changed from milky to orange within 15 min. Then 1 ml of 0.05 M thiophenol in absolute ethanol was added to the resultant mixture and was irradiated by ultrasonic waves for 1 h at room temperature. Ultrasonic irradiation was achieved using Dr. Heilscher high intensity ultrasound processor UP200H Germany (0.3 cm diameter Ti horn, 200 W, 23 kHz). The titanium tip of the horn was immersed directly in the reaction solution which was in 100 ml borosilicate flat bottom flask. Then the solution was centrifuged for 10 min at revolution rate 0f 4000 rpm and washed with absolute ethanol for several times. After washing, the color of the as prepared nanoparticles was orange.

2.4. Reaction mechanism

The formation of the CdSe nanoparticles involves the following steps. The cationic precursor solution releases Cd^{2+} ions from [Cd (tartaric acid)]$^{2+}$ as:

$$[Cd \, (tartaric \, acid)]^{2+} \rightarrow Cd^{2+} + tartaric \, acid. \tag{1}$$
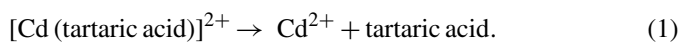
In the anionic precursor solution, sodium selenosulfate hydrolyzes to give Se^{2-} ions as:

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^- \tag{2}$$

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-} \tag{3}$$
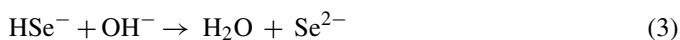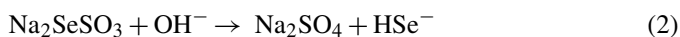
When the cationic precursor solution containing Cd^{2+} ions and the anionic precursor solution containing Se^{2-} ions are brought together, the following reaction take place to form CdSe nanoparticles:

$$Cd^{2+} + Se^{2-} \rightarrow CdSe \tag{4}$$

The role of thiophenol is to cap the particles preventing them from coagulation.

3. Results and discussion

3.1. Morphology and structure

The composition of the products was studied by energy dispersive X-ray spectroscopy (EDX) and is depicted in Fig. 1. The curve exhibits the presence of Cd and Se peaks with an average atomic percentage ratio of 52:48, which is rich in cadmium. Other peaks in this figure correspond to gold, palladium and silicate which are due to sputter coating of the glass substrate on the EDX stage and were not considered for elemental analysis of Cd and Se.

The XRD pattern of the nanoparticles is depicted in Fig. 2. The peaks can be classified to (1 1 1), (2 2 0) and (3 1 1) plains and is associated with cubic CdSe (JCPDS-ICDD Copyright 1999, file No. 19-0191). The peaks are broadened, indicating that the sizes of the particles are small.

In order to achieve more confirmative information, Debye–Scherrer formula [34]:

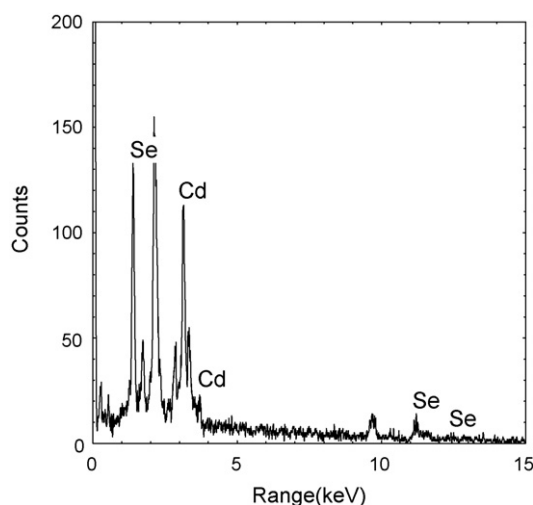$$L = \frac{0.9\lambda}{B \cos \theta}$$

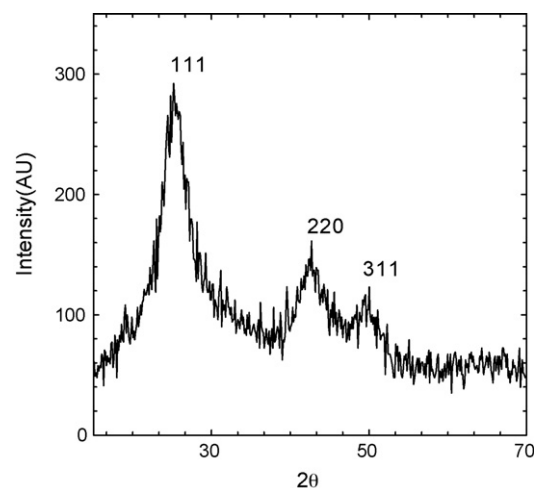Fig. 1. EDX spectrum of the as prepared CdSe nanoparticles.

Fig. 2. XRD pattern of the as prepared CdSe nanoparticles.

has been applied to calculate the size of the nanoparticles. Here, L is the coherent length, λ the wave length of X-ray radiation, B the full-width at half-maxima (FWHM) of the prominent peak and θ is the angle of diffraction. In the case of spherical crystallites, the relation between L and D, the diameter of crystallite, is given by $L = (3/4)D$. The value of L obtained from XRD pattern is 4.28 nm. So the corresponding crystallite size of nanoparticles obtained in this way is 5.73 nm.

In order to further elucidate the size and the crystal structure of the nanoparticles, SEM image was taken at different magnifications and is shown in Fig. 3A–C. An overview of images show
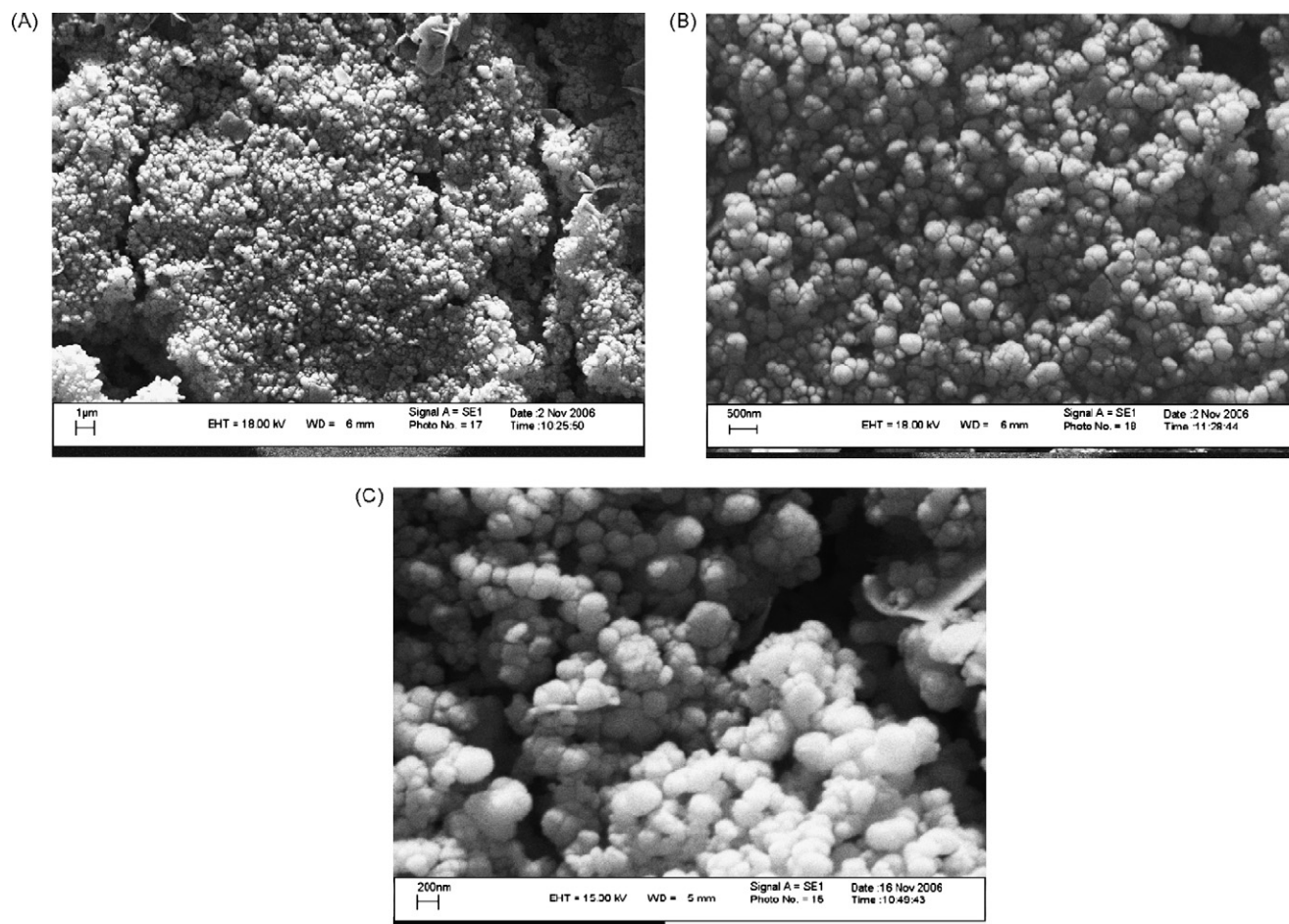

Fig. 3. (A) SEM image of the as prepared CdSe nanoparticles at magnification of 10k. (B) SEM image of the as prepared CdSe nanoparticles at magnification of 30k. (C) SEM image of the as prepared CdSe nanoparticles at magnification of 60k.
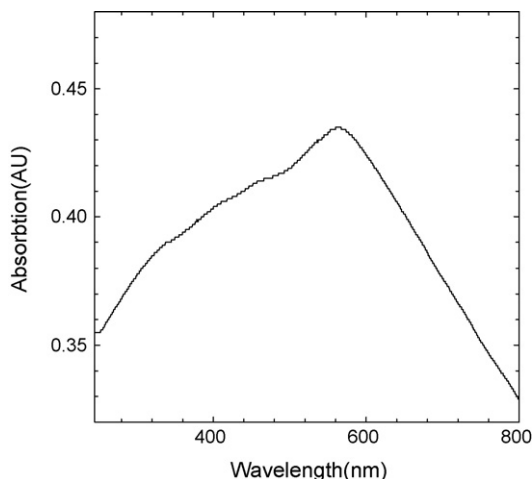
Fig. 4. UV–visible absorption spectrum of the as prepared CdSe nanoparticles.

the product consists of spherical nanocrystallites of about 20 nm in diameter aggregated in the form of polydispersive nanoclusters of approximately spherical shape with sizes in the range of 150–200 nm.

UV–visible spectrum of as prepared CdSe nanoparticles is shown in Fig. 4. In order to quantify the absorption edge or identifying the band gap of the as prepared nanoparticles, the plot shown in the figure was first converted into energy scale (electron volt) and then differentiated. This gives the maximum rate of change in absorption spectrum of nanoparticles or band gap. The band gap of CdSe nanoparticles obtained in this way is about 2.02 eV corresponding to absorption at the wavelength of ~563 nm in Fig. 4. If it is compared to 1.74 eV reported for the band gap of bulk CdSe [35], a blue shift of about 0.28 eV can be observed which is due to nanometer-sized particles.

4. Conclusion

A novel and simple procedure for preparation of CdSe nanoparticles using ultrasonic waves has been described. The product is nanocrystallites in cubic structure, of about 20 nm which aggregated in the form of polydispersive nanoclusters with sizes in the range 150–200 nm. The elemental analysis of the product confirms the formation of purely CdSe nanoparticles with average atomic percentage ratio of about 52:48; showing that the product is almost stoichiometric. UV–visible absorption spectroscopy of the as prepared nanoparticles reveals a blue shift of about 0.28 eV which is understood as a quantum size effect due to confinement of electron and hole in a small volume.

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