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Structural characterization of chemically synthesized CdSe nanoparticles

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ABSTRACT

CdSe nanoparticles were prepared at room-temperature via direct reaction between $Cd(NO_3)_2$ and Na_2Se in the presence of cetyltrimethyl ammonium bromide (CTAB) used as a capping material. The nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-Visible absorption spectrum, Fourier transform infrared (FT-IR) spectroscopy, Raman scattering, differential scanning calorimetry (DSC), differential thermal gravimetric (DTG) and heat stage X-ray diffraction (HS-XRD).

Analysis of the obtained data reveals the precipitation of defective zinc blende CdSe nanoparticles of size about 11 nm in diameter. A blue shift in the optical gap, from 1.71 to 1.82 eV, has been observed for the absorption spectrum of the synthesized CdSe nanoparticles, as an indication of quantum confinement effect. The zinc blende phase is enhanced upon annealing above the melting of Se (220 °C) as is transformed into a better order and stable wurtzite structure upon further heating. More than one melting point has been recorded for the CdSe nanoparticles referring to different ranges of particle sizes (7:25 nm). A value of 810 °C characterizes the melting point of the predominant size (11 nm) of the CdSe nanoparticles.

1. Introduction

Nanoparticles have been investigated intensively in the past two decades because of their size-dependent properties and the possibility of arranging them in micro (and nano) assemblies [1–3].

Selenides have been widely used as thermoelectric cooling materials, optical filter, optical recording materials, solar cells, superionic materials, biological sensor and laser materials [4–6]. Nanoparticles of selenide semiconductors were attracting the attention due to their brilliant prospects. In particular, nanostructures of CdSe have received considerably more attention due to its great fundamental, experimental and applied interests. Indeed, CdSe nanocrystals are useful in understanding the phenomenon of quantum confinement effect as are used in the fabrication of devices like PV cells, lasers, TFTs, Light-emitting diodes and other nanoscale devices [7].

In the past few years, there have been several reports on the synthesis of CdSe nanoparticles. CdSe nanoparticles were successfully synthesized by organometallic approach [8–10]. Such a procedure requires expensive chemicals and resulting in the production of small amounts of colloidal nanoparticles. Besides, the nanoparticles prepared in organic phase are insoluble in water, and, therefore, cannot be directly applied in bio-systems. The synthesis in aqueous phase is an alternative method for the preparation of nanoparticles. Compared with organic phase synthesis, aqueous synthesis exhibits good reproducibility, low toxicity and inexpensive; besides that the products have excellent water-solubility, stability and biological compatibility [11,12]. In literature, few reports were found about the synthesis of nanoparticles such as CdS [13,14] and CdSe [12,15] in water phase.

Therefore, our attention in the present paper became focused on developing a relatively cheap, yet effective, method for achieving of the CdSe nanoparticles. This has been done via a direct reaction between $Cd(NO_3)_2$ and Na_2Se in the presence of cetyltrimethyl ammonium bromide (CTAB), which is used as a capping agent. The structural characterization of the synthesized material is accurately considered.

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2. Experimental

2.1. Synthesis

Typically, 4.96 g of $Cd(NO_3)_2 \cdot 4H_2O$ {Riedel-de Haën, 99%} and 2.5 g of CTAB {PARK-Scientific Limited, 99%} were dissolved in 100 mL of re-distilled water under stirring at room-temperature (RT~25 °C). In another flask, 2 g of Na_2Se {Alfa Aesar, 99.8%} was dissolved in 100 mL of re-distilled water, and then added to the former solution while stirring; i.e.,

$$Cd(NO_3)_2 + Na_2Se \rightarrow CdSe + 2(Na_2NO_3)$$

Once the reaction took place, the solution was filtered, washed several times (5–10 times) by re-distilled water, and left in a dark and dry place till complete dryness.

2.2. Measurements

The structure and the phase changes of the synthesized CdSe sample were examined by BRUKER D_8 ADVANCE heat stage X-ray diffraction (HS-XRD) using CuKα ($\lambda = 0.15406$ nm), at a power of 1600 W (40 kV and 40 mA). For heat stages, heating rate at 60°/min was used.

Transmission electron microscope (TEM), type 1230 JOEL, operating at power = 100 kV has been used for data collection. For obtaining the TEM images, the as-prepared sample was dispersed in absolute ethanol ultrasonically and then the colloid was dropped onto Cu-grids coated with amorphous carbon film and dried.

UV-visible spectrum of the as-prepared sample was recorded using Bio-Cary50 Model spectrophotometer in the wavelength range 300–900 nm. The sample was suspended in re-distilled water, which has been used as a blank in setting up the base line. A quartz cell has been used as a sample container.

A Fourier transform infrared (FT-IR) spectroscopy and Raman measurements were carried out using FT-IR Raman JASCO (6300 Type A).

The differential scanning calorimetry (DSC) curves were recorded using SETARAM analyzer (Labsys^{TM} TG DSC1) with heating rates of 5–10°/min in the temperature range: RT-1000 °C. Differential thermal gravimetric (DTG) curve was recorded using Shimadzu analyzer (model DTG-60/60A) with a heating rate of 10°/min.

3. Results and discussion

3.1. XRD analyses

The XRD pattern of the as-prepared CdSe sample is shown in Fig. 1. The figure shows that the intensity of the characteristic diffraction lines is rather low as accompanied by a relatively high background pattern. This indicates that the diffraction pattern of Fig. 1 exhibited a poor crystalline structure. Here, the pattern is characterized by the presence of three groups of diffraction lines.

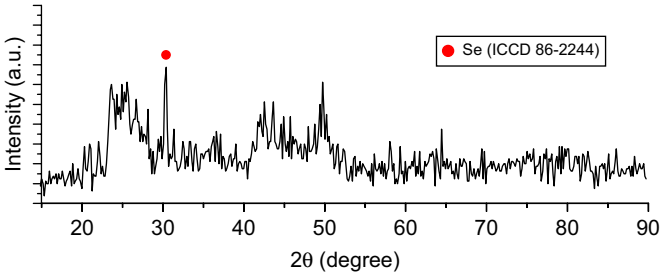

Fig. 1. XRD pattern of the as-prepared CdSe nanoparticles.

These groups lie over the area of what is called a stepped-hump in the corresponding amorphous phase. In other words, these angular ranges correspond to numerous lattice directions or atomic planes of high scattering power in the respective crystalline forms. The stepped-hump areas roughly occupy the angular ranges: (21:37), (37:46) and (46:54) in 2θ for the first, second and third step, respectively. These three steps have their respective maxima at about 26°, 43° and 50°.

Identification of the observed diffraction peaks in Fig. 1 declares the presence of CdSe zinc blende structure (see the ICCD Card no. 19-0191). However, such a diffraction pattern is considered to be a defective crystal structure. This is due, mainly, to the appearance of the three-stepped-hump together with the appearance of a clear selenium peak. The Se peak appeared at $2\theta = 30.358°$, attributed to the (1 0 1) plane, which is the preferred orientation of the Se hexagonal structure. This was concluded by referring to the ICCD Card no. 86-2244.

In fact, the presence of a Se peak in the synthesized CdSe sample could be attributed to the possibility of forming H_2Se during the dissolution of Na_2Se in accord with the following equation:

$$Na_2Se + H_2O \rightarrow NaOH + H_2Se$$

Hence, the presence of H_2Se in an aqueous NO_3^- media enhances the formation of pure Se.

The average crystalline size, that was determined from the half-width of the diffraction peaks using the Debye–Scherrer equation, was approximately 5 nm in diameter for the CdSe nanoparticles, while it was about 55 nm for Se nanoparticles.

3.2. TEM observation

Fig. 2 presents TEM images of the size distribution of the as-prepared material. The left image, shown in Fig. 2(a), focuses on the Se particles. This photo shows the existence of Se nanoparticles with sizes lying in the range 40:80 nm, while most of them have size of about 60 nm. The other image, shown in Fig. 2(b), focuses on CdSe nanoparticles. It can be concluded from this photo that the particle size ranges from 7 to 25 nm, while most of them have a size of about 11 nm.

3.3. UV–visible absorption spectrum

The most dramatic property of semiconductor nanoparticles is the size evolution of the optical absorption spectra. In this respect, Fig. 3 shows the absorption spectrum of the nanoparticles of CdSe. The figure shows that the recorded spectrum exhibits an absorption edge having its onset at ~685 nm. This corresponds to an energy gap of ~1.82 eV. The edge is assigned to the optical transition of the first excitonic state. Generally, the wavelength of the exciton absorption *band* decreases with decreasing the particle size as a result of quantum confinement of the photo-generated electron–hole pairs.

In fact, the value of the energy gap, estimated from Fig. 3, reflects a considerable blue shift relative to the absorption band edge of bulk CdSe (725 nm and 1.71 eV), [16]. The grain size of semiconductor nanoparticles can be determined using Brus equation [17]

$$E_g^{nano} - E_g^{bulk} = \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_o r} - 0.248E_{Ry}^*$$

where E_g^{nano} and E_g^{bulk} are the respective nanoparticles and bulk energy band gaps, r is the radius of the particle, m^*_e & m^*_h are the reduced masses of the conduction band electron and valence band hole in units of electron mass, ε_o is the vacuum permittivity, ε is