Structural, compositional and optical characterization of water soluble CdS nanoparticles synthesized by ultrasonic irradiation

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Nanostructure CdS particles have been successfully prepared by chemical reaction of cadmium acetate ($C_4H_6CdO_4.2H_2O$) as a Cd^{2+} ion source and thiourea (H_2NCSNH_2) as a S^{2-} ion source in aqueous media with inducement ultrasonic irradiation at room temperature and normal laboratory conditions. This simple and one step preparation can be considered as a green synthesis. The obtained particles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and UV-Vis spectrophotometer. XRD pattern reveals that the CdS nanoparticles formed are highly pure and are crystalline in nature with cubic structure. SEM images shows that the product consists of spherical nanocrystallites of about 20nm which aggregated in the form of polydispersive. Energy dispersive X-ray analysis (EDAX) shows that the proportion of cadmium to sulfur is neatr to Cd:S=1:1, showing that the product is almost stoichiometric. Optical measurements indicate a direct band gap of about 4.69 eV. There was observed a blue shift of about 2.29 eV, in comparison to its bulk value due to quantum confinement effects of electrons and holes.

1. Introduction

Quantum confinement effect in semiconductor nanocrystalline materials are known to make their novel optical and electrical properties significantly different from those of the bulk materials or single atoms. These nanocrystals have unique electronic and optical properties because of their small size and extremely large surface to volume ratio that have potential applications in a number of areas [1-7]. Among the II-VI semiconducting chalcogenides, CdS is one of the most important material with a direct band gap of 2.4eV at room temperature, owing to its applications as photocatalyst [8], nonlinear optical material [9-11], in solar cells [12-13], gamma and X-ray detectors [14-15], photocatalytical solar energy stockings [16], and in display devices [17-18]. The nanoparticles of CdS have been synthesized by various routes including chemical bath deposition [19], ionic [20] and electrochemical reactions [21] growth in polymer matrix using SILAR method [22], irradiation technique using gamma-[23] and UV- irradiation[24] solvothemal routes [25] and those embedded in glass matrix [26]. As to these methods mentioned above, it is very difficult to obtain pure nanoparticles, because some of these reactions require some special conditions such as high temperature, using sensitive precursors, toxic capping agents and templates. Providing the above conditions are difficult and people are encountered with dangerous materials and in most cases the yield of the products are very low. Our attempt is to obtain high quality materials under normal laboratory conditions and using safe precursors at room

temperature using sonochemical method. Sonochemistry is driven by acoustic cavitation, formation, growth and implosive collapse of bubbles in liquids irradiated with high intensity ultrasound waves. During cavitation, bubble collapse produces intense local heating (5000 K), high pressures (>20MP), and very short lifetimes. These transient, localized hot spots drive high-energy chemical reactions [27-30]. Previously, the sono-chemical method has been applied to the synthesis nanoparticles in non aqueous media [30-35]. Herein, we report a facile and novel route to synthesize CdS nanoparticles at room temperature by an ultrasonic irradiation between cadmium acetate and thiourea in aqueous media. The advantage of this process is that it is a cheap, simple and efficient method for producing nearly monodisperse nanoparticles. The main difference and advantage of this synthesis is to use distilled water as a green solvent and washing agent to produce high quality CdS nanoparticles without another impurity and without toxicity. In this article a formation mechanism of CdS nanoparticles is proposed and some of their optical, structural and compositional properties are investigated.

2. Experimental details

2.1. Materials

Cadmium acetate ($C_4H_6CdO_4.2H_2O$, extra pure), thiourea (H_2NCSNH_2, Purity ≥ 99%), sodium hydroxide (NaOH, extra pure), tartaric acid ($C_4H_6O_6$, Purity ≥ 99.5%)

were purchased from Merck and used without further purification. Double distilled water was used as a solvent and washing agent.

2.2. Instruments

Optical absorption studies were carried out using a UV-Vis spectrophotometer (Shimadzu, Model 1650, Japan). The structural characterization of nanoparticles was carried out by analysis of XRD pattern, using a philips X pert X-ray diffractometer of Cu K_α radiation (λ=1.54 Å). Morphology and compositional investigations of samples were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray analyses (EDAX) employing an LEO 1430VP apparatus with 15 and 18 accelerating voltages respectively.

2.3 Synthesis

The preparation method in this work was similar to our work for preparation of CdSe nanoparticles, that has been published recently [35]. For synthesis of CdS nanoparticles, 10 ml of 0.2 M aqueous solution of cadmium acetate ($C_4H_6CdO_4.2H_2O$) was complexed with 10 ml of 0.2 M aqueous solution of tartaric acid as a cationic precursor so that the pH value of mixture were 5. Then 10 ml of 0.2 M aqueous solution of thiourea (H_2NCSNH_2) was prepared as an anionic precursor. The pH value of this solution was 10. Then 20 ml of cationic and 10 ml of the anionic precursor solutions were added in a round bottom flask and the mixture was exposed to ultrasound irradiation for 1 h at room temperature under normal laboratory conditions. The color of the mixture changed gradually from milky to yellow. 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 horn was directly immersed in the reaction solution. The temperature of the solution was increased to ~65 °C. After cooling to room temperature, the solution was centrifuged for 10 min at rotation rate of 4000 rpm and washed by distilled water and ethanol for several times. An yellow precipitate is obtained at the end of the process. The particles which were dispersed in ethanol were transferred on microscope glass slide and allowed to be dried in the air at room temperature.
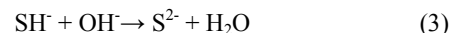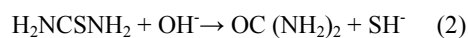
2.4. The reaction mechanism of CdS nanoparticles

The formation process of CdS nanoparticles are proposed as follows:
The cationic precursor solution releases Cd^{2+} ions from [Cd(tartaric acid)]$^{2+}$ as:

$$[Cd(tartaric\ acid)]^{2+} \rightarrow Cd^{2+} + tartaric\ acid \qquad (1)$$
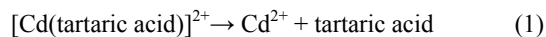
In the anionic precursor solution, thiourea hydrolysis occurs and give S^{2-} ions according to:

$$H_2NCSNH_2 + OH^- \rightarrow OC\ (NH_2)_2 + SH^- \qquad (2)$$

$$SH^- + OH^- \rightarrow S^{2-} + H_2O \qquad (3)$$

Finally the CdS nanoparticles are formed by combination of Cd^{2+} with S^{2-} ions as:

$$Cd^{2+} + S^{2-} \rightarrow CdS. \qquad (4)$$

3. Results and discussion

Energy dispersive X-ray analysis (EDAX) technique has been used to derive the quantitative information on the as prepared product and the pattern is shown in Fig. 1. The average percentage of Cd and S are to be 54 and 46 respectively. Other peaks in this figure correspond to palladium, gold and silicate which are due to sputter coating of palladium and gold on the glass substrate placed on the EDAX device and were not considered for elemental analysis of Cd and S.
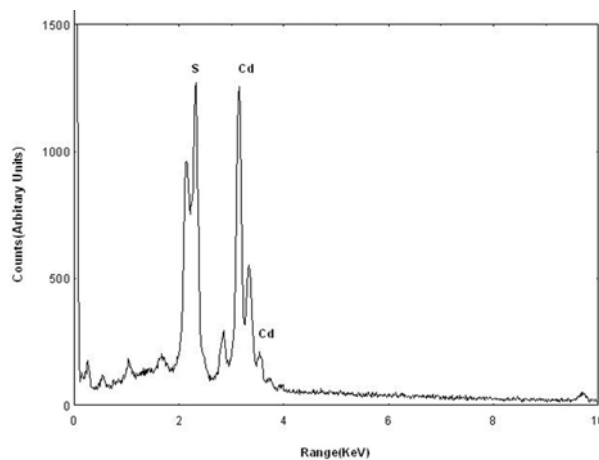

Fig. 1. EDAX pattern of the as prepared samples.

The XRD pattern of CdS nanoparticles is exhibited in Fig. 2. The CdS nanoparticles formed are highly pure nanocrystallites in hexagonal (wurtzite type) structure (JCPDS-ICDD, copyright 1999, file no 41-1049) The three diffraction peaks correspond to (002), (110) and (201) planes. The peaks are broadened indicating the size of particles are very small. The crystallite size of CdS nanoparticles was calculated using Debye-Shcerrer's formula [36]:

$$L=0.9\lambda/\beta cos\theta \qquad (5)$$

Where L is the crystallite size, λ is the X-ray wavelength used (λ=1.54 Å, β is the full-width at half-maxima (FWHM) of the prominent peak and θ is the diffraction angle corresponding to the peak. In the case of spherical crystallites, the relation between L and D, the

diameter of crystallite, is given by L= (3/4) D. The average particle size of CdS was found to be 5.8 nm.
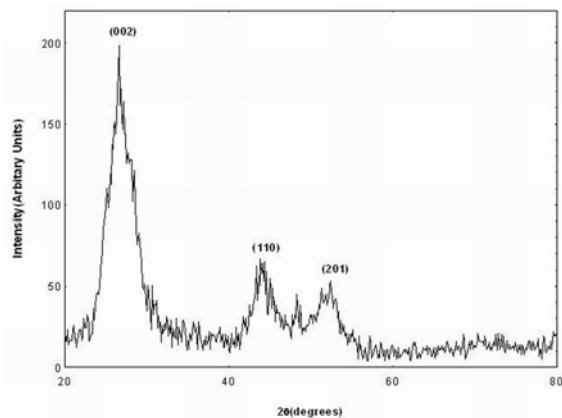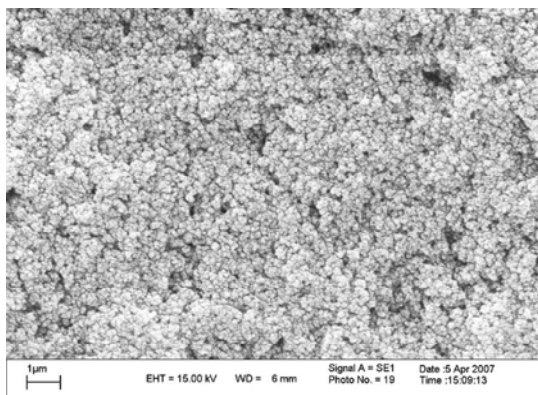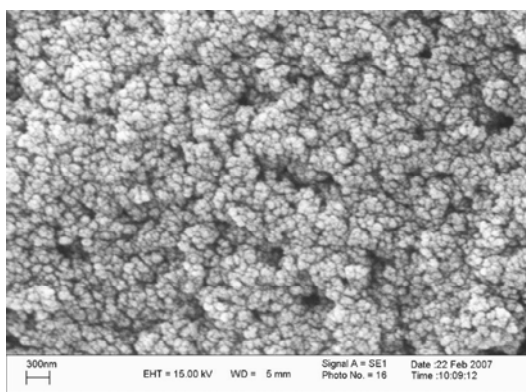

Fig. 2. XRD pattern of the as prepared CdS nanoparticles.

Fig. 3(a) and (b) show the SEM micrograph of as-prepared CdS nanoparticles at two different magnifications 25 k and 60 k, respectively. It is clear from figures that the product is aggregated to form highly monodispersed spherical nanoclusters of about 20 nm in diameter.

a

b

Fig. 3(a) and (b), SEM images of the sample.

Fig. 4 shows the Uv-Visible absorption spectrum of as prepared CdS nanoparticles. The absorption peak is observed at 241 nm which corresponds to a band gap of 4.69 eV. Comparing to 2.41 eV of bulk CdS, it shows a huge blue shift of about 2.28 eV has been observed; indicating the particles are extremely small and the blue shift corresponds to the confinement of electrons and holes in an extremely small volume of space. A weak bend observed in 480 nm indicates the existence of bulk crystals in solution. Our results in this research are unique compared to the previous results obtained in our group [37].
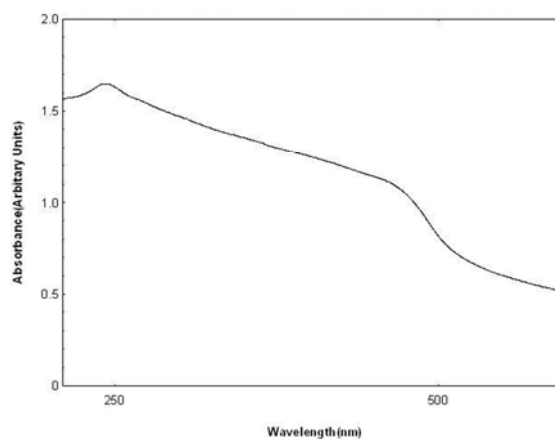

Fig. 4. UV-vis absorption pattern of the as prepared CdS nanoparticles.

To get more confirmation, the size of nanoparticles is calculated in the frame of the effective mass approximation. According to this approximation, the band gap of semiconductor nanocrystal considered as a sphere with radius R is given by:

$$E_g(R) = E_g(bulk)+[h^2/8 \mu R^2]-1.78e^2/(\varepsilon R) \quad (6)$$

where $E_g(R)$ is the band gap value of the nanoparticles, $E_g(bulk)$ is the band gap value of the bulk material, h is Plank's constant, e is electron charge, R and ε are the radius and the dielectric constant of the CdS and $\mu=m^*_e m^*_h/(m^*_e+m^*_h)$, where m^*_e and m^*_h are effective masses of electrons and holes, respectively [38-40]. Thus, the calculated particles size is 1.03 nm, which value is in good agreement with the results obtained from XRD and with admissible resolving power limit observed from SEM images.

4. Conclusions

CdS nanoparticles have been successfully prepared through the reaction of cadmium acetate with thiourea by ultrasonic irradiation in aqueous media, which is considered as green solvent, at normal laboratory conditions. XRD, EDAX and SEM investigations show

that the products are highly pure CdS nanoparticles with hexagonal crystal structure. The percentage ratio of Cd to S is 54:46 indicates an almost stoichiometric compound. The ultrasonic irradiation method is fast, not expensive and the product can be obtained under ambient conditions. Extremely small CdS nanoparticles induce a huge blue shift of 2.28 eV in band gap corresponding to its bulk value. This confirms the confinements of electrons and holes in extremely small volume of space.

Acknowledgements

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