Aqueous synthesis of CdO nanoparticles under ultrasonic waves and evaluation of their structural, morphological and optical properties

N. S. JAVAN*, Y. AZIZIAN-KALANDARAGH[a], A. KHODAYARI[b]
Physics Department, Miyaneh Branch, Islamic Azad University, Miyaneh, Iran
[a]*Department of Physics, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran*
[b]*Department of Chemistry, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran*

$Cd(OH)_2$ nanocrystals were prepared by inducement of ultrasonic waves using aqueous solutions of cadmium acetate and sodium hydroxide in presence of 5 mmol 3-Mercaptopropionic acid (3-MPA) as a capping agent. After thermal treatment at 250 ^oC during 1 hour, $Cd(OH)_2$ nanocrystals transforms to CdO regime. The X-ray diffraction (XRD) studies display that the products are well crystallized in the form of cubic structure. Scanning electron microscope (SEM) images reveal that the product consisting of sphere nanocrystallites of about 30-50nm diameter, which aggregated in the form of polydispersive clusters. Optical measurements indicate a direct band gap of about 3.4 eV. There was observed a blue shift of about 1.1 eV, in comparison to its bulk value due to quantum confinement effects of electrons and holes.

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1. Introduction

Semiconductor nanocrystals reveal size dependent physical and chemical properties due to confinement of their charge carrier wave functions in small volume [1-7].

Quantum confinement effect in semiconductor nanocrystals becomes important when the radius of semiconductor nanocrystals become near, equal to or smaller than its Bohr exciton radius. These nanocrystals exhibit size quantization effects such as a blue shift in energy gap of semiconductor materials and etc [8-12]. Due to these unusual properties, semiconductor nanocrystals have been proposed for fabrication of various optoelectronic devices. Among the family of oxide semiconductors, cadmium oxide is an important candidate for the fabrication of optoelectronic devices, because of its interesting electronic and optical properties such as high carrier mobility and transparency [13-18]. In particular, CdO is promising for the fabrication of solar cells, sensors, transparent electrodes and photodiodes [18-22]. The tunability of the optical properties of semiconductor nanocrystals by controlling their size may provide an opportunity for fabrication of new semiconductor materials with desirable conditions. There are different deposition techniques for preparation of semiconductor CdO thin films such as spray pyrolysis [23-26], ultrasonic spray pyrolysis [27], pulsed laser deposition[28] sol-gel[29,30], reactive evaporation[31-32], MOCVD [33-36], sputtering [37-40], and solution growth [41,42], there are only very little reports available on the preparation of the CdO nanostructures as free standing powder[43-50]. It is one of the main goals of technologists to obtain high quality materials under simpler conditions and using safer precursor. Generally, most of above mentioned methods require high temperature and the use of highly sensitive toxic solvents.

Previously ultrasonic irradiation has been used extensively to fabricate novel nanomaterials [51-57]. Physical and chemical effects of ultrasonic waves for fragmentation to small particles and acceleration of reaction and for preparation of new materials with desirable properties have been observed. These effects originated from acoustic cavitation that is, the formation, growth and collapse of bubbles in a liquid-solid phase. The extremely high temperatures (>5000K), pressures (>20mPa), and cooling rates ($>10^{11}Ks^{-1}$) are obtained upon the collapse of the bubble. This high cooling rate hinders the organization and crystallization of the products [58-64]. In this paper, for the first time, we describe a synthetic method for preparation of CdO nanocrystals by a simple ultrasound-assisted process. We have chosen this method because of its advantages, such as easier composition control, low toxicity, better homogeneity, low processing temperature, easier fabrication of plenty nanoparticles, lower cost, and possibility of using high purity starting materials. In this paper we also report annealing effect on the optical and structural properties of CdO nanocrystals.

2. Experimental details

2.1 Materials

The starting materials for the preparation of CdO nanocrystals were Cadmium acetate dihydrate ($C_4H_6CdO_4.2H_2O$ extra pure), Sodium hydroxide (NaOH

extra pure), 3-Mercaptopropionic acid (3-MPA), absolute ethanol and deionized water. All chemicals were obtained from Merck and directly employed without purification.

2.2 Instruments

The X-ray diffraction (XRD) analysis of the products was carried out on an Italstructures (MPD3000) instrument operating at 40kV and a current of 30mA with Cu*K*α radiation (λ=1.54^{o}A). The surface morphology of samples was analyzed by scanning electron microscope (SEM), LEO 1430VP with 15 kV accelerating voltage. The samples used for SEM observation was prepared by recoating the particles which at first was dispersed in ethanol, on a glass substrate bound to SEM stage. After annealing and allowing the evaporation of ethanol, the particles on the stage were coated with a thin layer of gold and palladium. Diffusive reflectance spectra of the sample were recorded employing a double beam, Shimadzu, 1650 spectrometer, Japan, applying quartz cuvettes of optical path length 1cm.

2.3 Preparation of CdO nanoparticles

The preparation procedure of CdO nanoparticles is as follows: 30 ml of aqueous solutions of cadmium acetate and sodium hydroxide of concentration 0.2M was prepared separately. These two solutions are mixed well and were put in a 100ml round bottom flask. Then the mixture solutions were exposed to a high intensity ultrasound processor, Dr. Hielscher, UP 200H, Germany (0.3 cm diameter Ti horn, 200W, 23 kHz) at room temperature for 2 hours. During irradiation, 5mml of 3-MPA were added to the mixture. In this step adding 3-MPA would cap the dissolved zinc acetate colloids by the help of ultrasonic irradiation. At the end of the reaction, a great amount of milky precipitates were obtained. After cooled to room temperature, the precipitates were centrifuged, washed by deionized water and ethanol in sequence and dried in the vacuum. Post annealing treatment was applied for thermal oxidation and well crystallization of the product at temperatures 250^{o}C for 1 hour. Formation of CdO nanocrystals can be proposed employing the following reactions:

$$Cd(CH_3COO)_2 .2H_2O + 2NaOH \rightarrow Cd(OH)_2 + 2Na(CH_3COO) + 2H_2O$$

$$Cd(OH)_2 \xrightarrow{250\,^{o}C} CdO + H_2O$$

The samples were collected for characterizations using XRD, SEM and UV-Vis spectrophotometer techniques.

3. Results and discussion

The sizes and morphology of the as-prepared products were studied by SEM images with 50Kx magnification and are shown in Fig. 1a-b. The results show nanoparticles have been constructed in sphere shape with averages sizes between 30-50nm which collection of this particles can produce polydispersive clusters with average cluster sizes between 80-300nm for $Cd(OH)_2$; Fig. 1 (a). The SEM image show that averages size in almost same amount with average cluster sizes between 100-400nm for CdO; Fig. 1 (b), that enlarge of cluster size due to heat treatments and increase of agglomeration.

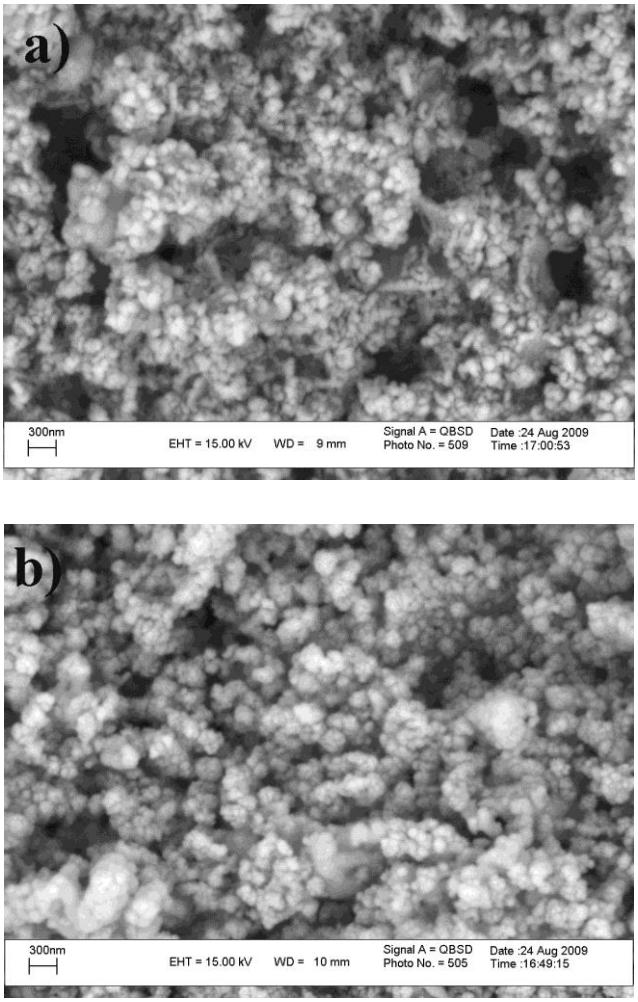

Fig. 1a-b. SEM image of the as-prepared sphere shape, a) $Cd(OH)_2$ and b) CdO nanoparticles.

Fig. 2a-b shows the XRD pattern of the as-prepared) $Cd(OH)_2$ and annealed CdO nanoparticles. Several peaks corresponding to diffraction of hexagonal $Cd(OH)_2$ and cubic CdO appear in the Fig. 2a. This clearly proves polycrystalline nature of the as-prepared product. In the Fig. 2b (111), (200), (220), (311) and (222) peaks related to cubic CdO crystalline phase (JCPDS file no. 31-228, 01-1049). The broadness of the peaks indicated that the size of nanoparticles is reasonably nanocrystalline in nature.

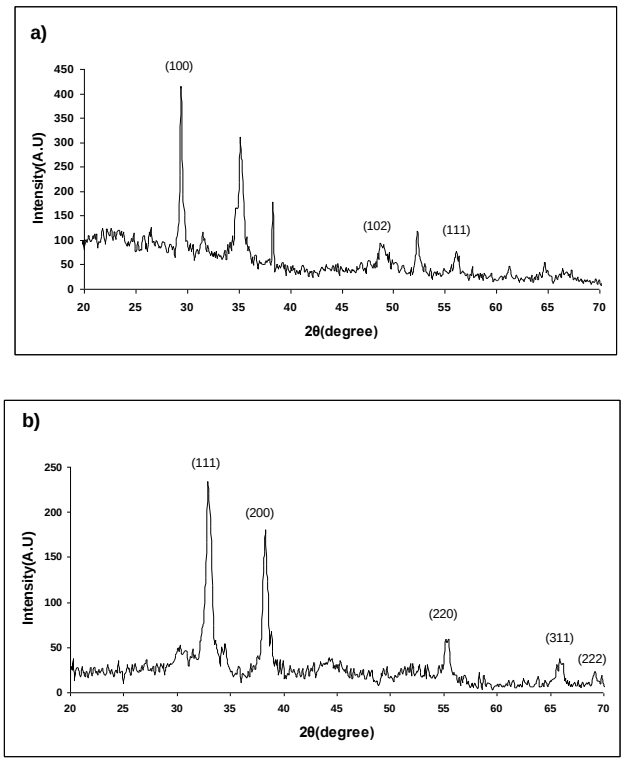

Fig. 2a-b. XRD pattern of the as-prepared nanoparticles, a) $Cd(OH)_2$\CdO and b) CdO.

Fig. 3 shows the Diffusive reflectance spectra of the annealed CdO nanoparticles recorded in the spectral range 300–650 nm. The absorption peak is observed at 361 nm which corresponds to a band gap of 3.4 eV. Comparing to 2.3 eV of bulk CdO, a blue shift of about 1.1 eV has been observed; indicating the particles are small and the blue shift corresponds to the confinement of electrons and holes in an extremely small volume of space.

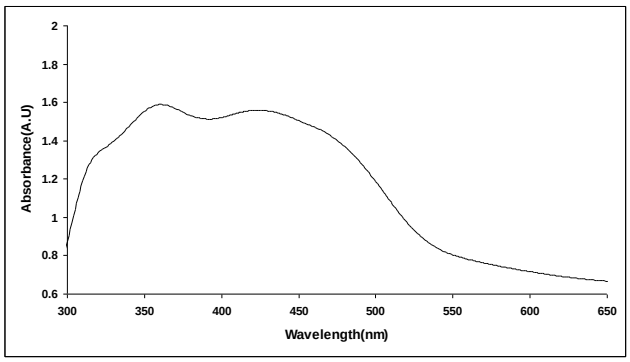

Fig. 3. Diffusive reflectance spectra of the annealed CdO.

4. Conclusions

In summary, we have successfully prepared CdO nanoparticles by an ultrasonic-assisted method. SEM images show that the formed CdO nanoparticles are of spherical shape with the average length from 40 to 60nm which aggregated in the form of clusters with various cluster sizes. The result from the analyses of XRD patterns confirms the crystallinity and also the purity of the prepared samples. The optical band gap value was estimated to be 3.4 eV, which show a blue shift in band gap energy of about 1.1 eV has been observed.

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*Corresponding author: nsj108119@yahoo.com