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An easy route to synthesize superfine *meta* cinnabar (β-HgS) semiconductor nanoparticles and their optical properties

Amir-Reza Judy-Azar, Sajjad Mohebbi *

Department of Chemistry, University of Kurdistan, P.O. Box 66175-416, Sanandaj, Iran

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ABSTRACT

A facile decomposition reaction was successfully developed to synthesize superfine β-HgS nanoparticles in single step process under mild condition. This report describes the use of thioglycolic acid as both reducing and stabilizer agent to produce superfine nanoparticles and no secondary chemical reducing agent is required. Semiconductor nanoparticles show novel optical properties due to the large number of surface atoms and/or the three-dimensional confinement of electrons. Decrease in particle size changes the order of confinement of the electrons and the electronic structure of the solid state. The optical properties and quantum-confined effect of the β-HgS nanoparticles are confirmed by the ultraviolet-visible (UV–vis), DRS analysis and photoluminescence analysis. Diffuse reflectance spectroscopy shows the large blue shift of band gap for as-synthesized nanoparticles toward bulk state.

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1. Introduction

Semiconductor chalcogenides nanoparticles have attracted considerable attention due to their size-dependent properties and their novel electronic and optical properties arising from quantum confinement effects comparable to the corresponding bulk materials [1–3]. Semiconductor materials of II–VI groups play an important role in areas of modern science and technology, such as photovoltaic cells, light-emitting diodes (LEDs), electroluminescence devices, photo-detectors, catalysis, and sensors [4]. One of the most important semiconductor compounds of II–VI groups is HgS that possesses excellent optoelectronic properties in the infrared region and can be used in ultrasonic transducers, electrostatic image materials and photoelectric conversion devices [5–7] etc. Semiconductors of II–VI groups such as CdSe, CdS and ZnS nanocrystals have been extensively prepared and studied due to their relatively simple synthesis and distinct particle size dependent on optical properties [8], but to date because of the toxicity of mercury there have been few reports on HgS nanocrystals synthesis.

When the crystalline size is in the range of nanometer and comparable to that of the a_B, the nanocrystal can be considered as a "particle in a box" that leads to the manifestation of quantum size effects (QSEs) [9]. These QSEs are responsible for the observation of novel properties such as band gap widening [10]. Bulk HgS exists in two forms, the wide band gap α-HgS (trigonal, $Eg=2.0$ eV) and narrow band gap β-HgS (zinc blend, $Eg=0.5$ eV) which are technologically important materials and between them, β-HgS treats like a semi-metal [11] which is considered as an infrared sensor material such as InAs, [12] InSb, [13] PbSnTe, [14] and HgCdTe [15]. In the past decade variety of synthetic techniques have been developed for the synthesis of metal sulfide II–VI semiconductors nanocrystals such as sol–gel processing [16], reverse micelles [17], chemical bath deposition [18], sonochemical method [19], microwave irradiation [20], hydrothermal and solvothermal routes [21,22] and biomimetic method [23].

However, finding a new and efficient method for preparation of WBG semiconductors still is one of the most challenging issues. In this paper, we are going to report a simple and one pot reaction to synthesize superfine β-HgS semiconductor nanoparticles with novel optical properties.

2. Experimental

Synthesis of HgS nanoparticles: In a typical procedure, 2 mmol (0.62 g) mercury (II) nitrate monohydrate was added to 10 ml thioglycolic acid and the mixture was stirred for ten minutes. The mixture was heated to 70 °C. Then the color of solution slowly turned gray and finally to dark brown. The mixture was stirred and heated at the same temperature for 10 min to let the reaction be completed. The obtained black powder separated by centrifuge and washed with double distilled water and finally dried in a vacuum oven at 50 °C for 5 h.

X-ray diffraction (XRD) analysis was performed using Bruker D and Advance X-ray powder diffractometer with graphite

* Corresponding author. Tel.: +98 871 6624133; fax: +98 871 6660075.
E-mail addresses: smohebbi@uok.ac.ir, sajadmohebi@yahoo.com (S. Mohebbi).

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monochromatized CuKa1 radiation ($k=1.5406$ Å) and the beta filter was used. To obtain three dimensional photographs from surface of the produced nanoparticles AFM analysis were carried out using solver pro AFM model. To determine the morphology of Meta cinnabar nanoparticles transmission electron microscopy (TEM) images were taken on JEOL JEM-1210 Using copper grid as sample holder. Fourier transform infrared (FT-IR) spectra were recorded on FT-IR Nicolet 6700, using KBr plates and EDAX analysis was carried out by NEW XL30 144-2.5. To investigate the optical properties of as-synthesized NPs, UV–vis measurement was carried out by Varian model Cary 1E UV–visible spectrophotometer. Also, UV–vis diffuse reflectance spectra (DRS) were recorded on MPC 2200 Shimadzu and photoluminescence spectroscopy was recorded on Perkin-Elmer LS-55.

3. Result and discussion

To study the crystalline structure of produced nanoparticles, XRD analysis was carried out at room temperature. The mean crystallite size diameter (D) of the HgS nanoparticles was estimated by Scherrer's equation: $D=(0.9\lambda/B\cos\theta)$ where λ is the wavelength of X-ray, B is the full-width at half maximum (FWHM) and θ represents the diffraction angle at a certain crystal plane.

Fig. 1(a) shows the XRD patterns of the nanoparticles. All the peaks can be indexed to face centered-cubic β-HgS. The most intense peaks at $2\theta=26.428^\circ$, 30.591°, 43.917°, 51.911°, and 54.233° correspond to (111), (200), (220), (311), and (222) planes, respectively which matches well by NBS card 6-261 for cubic zinc blende phase β-HgS. The sizes of nanoparticle were determined in the range of 30 nm.

Fig. 1(b) shows the energy dispersive X-ray analysis of HgS nanoparticles. As shown, strong peaks for Hg and S elements are found in the spectrum with the stoichiometric ratio of nearly 1:1. Also EDAX analysis shows that there is no any additional peak related to impurities in synthesized nanocrystals.

The chemical state of the as-synthesized nanoparticles surface was characterized by FT-IR spectroscopy. Fig. 2 shows the typical IR spectra of the thioglycolic acid (TGA) and β-HgS NPs after washing and drying in vacuum. The broad peak in FT-IR spectrum of HgS around 500–1000 cm^{-1} may indicate to Hg–S vibration.

As a complementary and useful method for initial surface investigation of as-synthesized nanoparticles, atomic force microscopy (AFM) was carried out at room temperature. About 0.0001 g of nanoparticles was sonicated in 40 ml water and then one drop of solution was placed on a glassy lamella. The lamella was dried in oven at 80 °C. The 2D and 3D images of AFM with area of $8\,\mu m\times 8\,\mu m$ are represented in Fig. 3. As it is seen, the nanoparticles have a uniform surface and initial approximation of the nanoparticles size is about 40 nm. Another point taken from the AFM images is that the produced nanoparticles are spherical that is further confirmed with transmission electron microscopy.

TEM images of the separated nanoparticles are shown in Fig. 4. The sample for TEM photographs was prepared by spray technique method. As it is observed, nanoparticles are spherical and their sizes are corresponding to XRD results. The superfine nanoparticles have mean diameters of approximately 2–10 nm.

Optical properties of HgS nanoparticles: To obtain information about optical properties of superfine β-HgS nanocrystals, UV–vis absorption analysis was carried out at room temperature and the corresponding spectrum is shown in Fig. 5a. The threshold of the absorption at 213 nm is obvious blue shift as compared with the bulk β–HgS that is attributing to the quantum confinement effect of β-HgS superfine nanoparticles.

Further confirmation for the nature of HgS as a wide band gap semiconductor was carried out by UV–visible diffuse reflectance (DRS) and photoluminescence analysis (PL) that is shown in Fig. 5 (b–d). The band gap energy (Eg) was calculated by the following equation [24]:

$$\alpha(\nu)=A\left(\frac{h\nu}{2}-Eg\right)^{m/2} \quad (1)$$

where A is constant, $\alpha(\nu)$ is the absorption coefficient and Eg is the band gap. For a direct transition $m=1$, and a plot of $(\alpha E_{phot})^2$

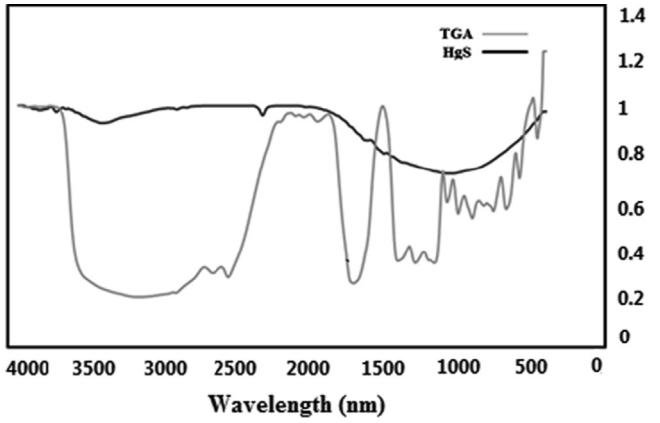

Fig. 2. FT-IR spectra of thioglycolic acid (a) and as-prepared HgS nanoparticles (b).

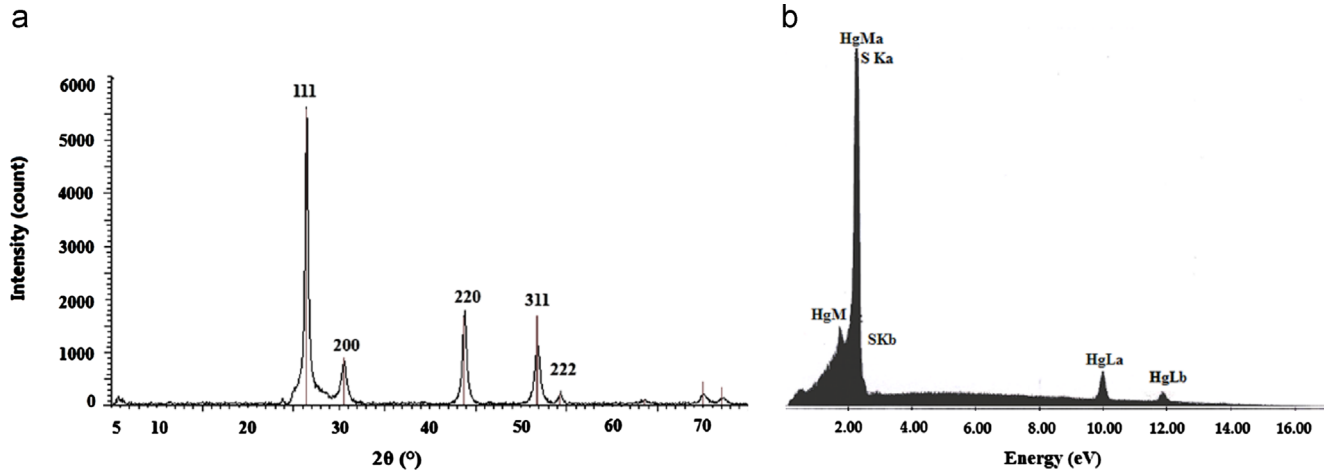

Fig. 1. XRD pattern (a) and Energy dispersive X-ray diagram (b) of as-prepared β-HgS nanoparticles.

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