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A microwave assisted heating method for the rapid synthesis of sphalerite-type mercury sulfide nanocrystals with different sizes

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Abstract

A novel method for the preparation of sphalerite-type HgS (β -HgS) nanocrystals by microwave irradiation is reported in this paper. Mercury acetate and thiourea were used as mercury source and sulfur source, respectively. It was found that the HgS with different average crystal sizes from 8 to 23 nm were obtained by using different solvents. The products were characterized by powder X-ray diffraction, transmission electron microscopy, electron diffraction, X-ray photoelectron spectroscopy, energy-dispersive X-ray analysis and UV–Visible absorption spectroscopy. The probable mechanism of the formation of β -HgS nanocrystal is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been much interest in the synthesis and physical characterization of nanocrystalline metal sulfide semiconductors in the recent years [1–5]. Mercury sulfide is a useful material and is widely used in many fields such as ultrasonic transducers [6,7], image sensors [8], electrostatic image materials [8] and photoelectric conversion devices [6–8]. However, up to now, only a few references have reported the preparation of the

mercury sulfides because of the toxicity of mercury. Some methods for the preparation of nanocrystalline mercury sulfides have been reported in the past few years. Preparations of the HgS thin film by chemical bath deposition method have also been carried out by some researchers [9,10]. Zeng and his co-workers prepared HgS with controllable morphologies by a solvothermal method [11]. Both hexagonal and cubic phase of nanocrystalline HgS can be synthesized via this method, but the crystal sizes of the products are relatively large. Li et al. reported an oxide direct conversion route to trigonal-type HgS (α -HgS), using mercury oxide and sulfur powder as starting materials and ethylenediamine as solvent. The reaction was carried out at room temperature, and

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the reaction time lasted over 5 h [12]. Gedanken et al. applied ultrasound irradiation to prepare nanocrystalline HgS. They also chose sulfur powder as sulfur source and ethylenediamine as solvent, but the reaction time was reduced to 1 h [13].

Microwaves are electromagnetic waves containing electric and magnetic field components. The electric field applies a force on charged particles as a result of which the charged particles start to migrate or rotate. Due to the movement of charged particles further polarization of polar particles takes place. The concerted forces applied by the electric and magnetic components of microwaves are rapidly changing in direction, which creates friction and collisions of the molecules. Claimed effects of microwave irradiation include thermal and non-thermal effects [14]. Microwave irradiation as a heating method has found a number of applications in chemistry. The microwave synthesis, which is generally quite fast, simple and efficient in energy, has been developed and is widely used in the fields such as molecular sieve preparation [15,16], radiopharmaceuticals [17,18], the preparation of inorganic complexes and oxide [19–21], organic reactions [22–24], plasma chemistry [25], analytical chemistry [26] and catalysis [27]. The applications of microwave irradiation in the preparation of nanocrystalline particles have been reported in recent years [28–36]. Microwave irradiation has shown very rapid growth in its application to material science due to its unique reaction effects such as rapid volumetric heating and the consequent dramatic increase in reaction rates, etc. A variety of articles have also shown how rapid heating rate can be harnessed to produce binary and tertiary solid-state compound [20,37–39]. Compared with conventional methods, microwave synthesis has the advantages of short reaction time, small particle size, narrow particle size distribution and high purity.

Finding fast and efficient methods to produce nanocrystalline particles and realizing the control over the crystal size are new challenges to synthetic chemists and material scientists. This paper presents a novel method for the preparation of β -HgS. The microwave irradiation technique is applied to prepare the nanocrystalline β -HgS particles, and

the reaction time was greatly reduced to only 10 mins. β -HgS nanoparticles with different crystal sizes were successfully prepared by choosing different solvents. It is found to be a fast, convenient, mild, energy efficient and environmentally friendly route to produce the nanocrystalline HgS particles with controllable sizes in only one step.

2. Experiment section

2.1. Materials

All the reagents were of analytical purity, and were used without further purification. N,N-dimethyl formamide (DMF) and tetrahydrofuran (THF) were purchased from Shanghai Chemical Reagent Factory (China). Absolute ethanol and rubenic acid were purchased from Nanjing Chemical Reagent Factory (China). Thiourea was purchased from Suzhou Jincheng Chemical Reagent Factory (China). Thioacetamide (TAA) was purchased from Jiangsu Taicang Chemical Reagent Factory (China). Mercury acetate was purchased from Guangzhou Chemistry Reagent Factory (China). Distilled water was used in the experiments.

2.2. Instruments

A microwave oven with 650 W power (Sanle General Electric Corp. Nanjing, China) was used in our experiments. A refluxing system was connected with the microwave oven.

The X-ray powder diffraction (XRD) patterns were recorded on Shimadzu XD-3A X-ray diffractometer (Cu K_{α} radiation, $\lambda = 0.15418$ nm). Transmission electron micrographs (TEM) and electron diffraction patterns (ED) were obtained by employing JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV. The surface of the products was detected by X-ray photoelectron spectra recorded on ESCALAB MK II X-ray photoelectron spectrometer, using non-monochromatized Mg K_{α} X-ray as the excitation source. EDAX measurements were performed on the PV9100 instrument.

Shimadzu UV-3100 photospectrometer was used to record the UV–Visible absorption spectra of the as-prepared particles.

2.3. Preparation of β -HgS nanoparticles

In a typical procedure, 1.6 g $\text{Hg}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 0.5 g thiourea were added in 50 ml solvent. Absolute ethanol (EtOH), tetrahydrofuran (THF), distilled water, N,N-dimethyl formamide (DMF) and 20% DMF aqueous solution were chosen as solvents respectively. The mixture was placed in the microwave reflux system and the reaction was performed under ambient air for 10 min. The microwave oven followed a working cycle of 6 s on and 24 s off (20% power). Then a great amount of black precipitate occurred. After cooling to room temperature, the precipitates were centrifuged, washed with distilled water and absolute ethanol, and dried in the air. The final products were collected for characterizations.

3. Results and discussion

3.1. XRD, TEM, XPS and EDAX studies

The XRD patterns (Fig. 1) show that the products obtained are the cubic phase HgS. The

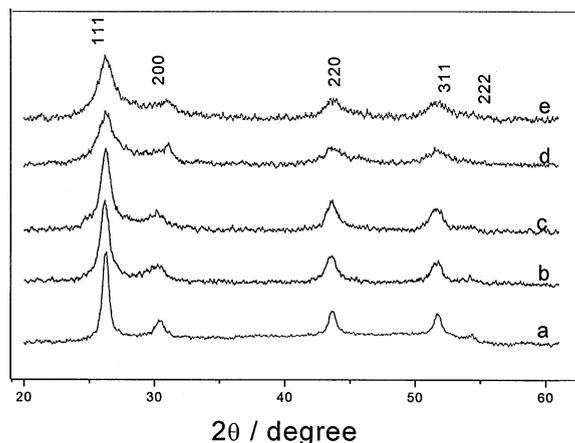


Fig. 1. The XRD patterns of the HgS prepared in different solvents: (a) DMF; (b) H_2O ; (c) 20%DMF– H_2O ; (d) THF; (e) EtOH.

peaks are corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2), which matches literature pattern for β -HgS [40]. The broadening of the peaks indicates that the crystal sizes are small. The average crystal sizes of the particles are estimated by Debye–Scherrer formula [41] from the XRD patterns. In different solvents, the as-prepared particles are of different average sizes according to the half peak-width.

The TEM images (Fig. 2a–e) show the sizes and morphologies of the nanocrystals. It is apparent that the nanocrystals are spherical. The average sizes are in the range of 8–23 nm. They are in good agreement with those estimated by Debye–Scherrer formula from the XRD patterns. The results are shown in Table 1.

Fig. 2f is a selected area electron diffraction (ED) picture of the as-prepared HgS nanoparticles using water as the solvent. The ED measurements show that the product is polycrystalline. The diffraction rings correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively, which is in accord with the XRD pattern.

The wide XPS spectrum of sample D is shown in Fig. 3. The C1s peak lies at 285.5 eV, which should be corrected to 284.6 eV. All the other peaks are corrected accordingly. No peaks of impurity are observed, indicating the high purity of the product. Fig. 4a and b show the high-resolution XPS spectra of Hg(4f) and S(2p), respectively. The two strong peaks taken for the Hg region at 100.9 and 104.95 eV are assigned to the Hg(4f) binding energy. The peaks measured in the S energy region detected at 162.2 and 163.3 eV are attributed to the S(2p) transitions. The ratio of Hg and S is calculated to be 56.6:43.4.

The EDAX pattern for the HgS prepared in water also shows the presence of Hg and S peaks with an average atomic ratio Hg:S of 56:44, which is in good agreement with the XPS results. This result points out that the surface of the sample is rich in Hg.

3.2. Optical properties

The UV–Visible absorption spectrum of 11.06 mg HgS nanoparticles (sample A) dispersed in 100 ml ethanol is shown in Fig. 5a. On the

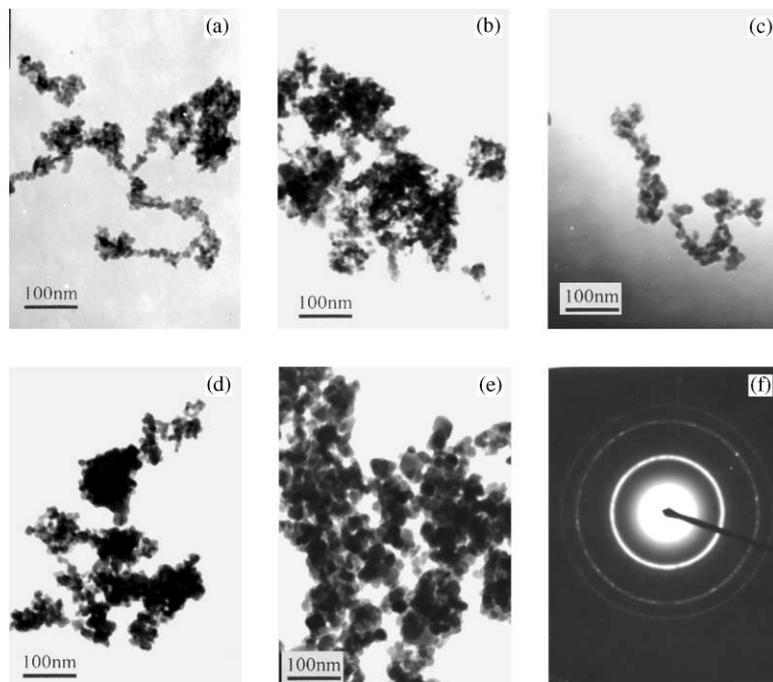


Fig. 2. The TEM images of the HgS nanoparticles prepared in different solvents: (a) in EtOH; (b) in THF; (c) in 20% DMF (d) in H₂O; (e) in DMF; (f) ED picture of HgS (prepared using water as solvent).

Table 1

Average diameter of the particles prepared in different solvents estimated by Debye–Scherrer formula and from TEM microphotograph

	Solvent	Debye–Scherrer formula (nm)	TEM (nm)
Sample A	EtOH	8	8–9
Sample B	THF	10	8–10
Sample C	20%DMF–H ₂ O solution	13	11–13
Sample D	H ₂ O	14	11–14
Sample E	DMF	23	20–24

spectrum, a broad absorption peak whose center is at about 360 nm is observed. An estimate of the optical band-gap is obtained using the following equation for a semiconductor:

$$\alpha(\nu) = A(h\nu/2 - E_g)^{m/2},$$

where α is the absorption coefficient and m equals 1 for a direct transition. The energy intercept of a plot of $(\alpha E_{\text{phot}})^2$ versus E_{phot} yields E_g for a direct transition (Fig. 4b) [42]. The band-gap energy of the nanoparticles was calculated to be 2.48 eV by direct transition method from the UV–Visible

absorption spectrum, which is 0.48 eV larger than that of bulk HgS ($E_g = 2.0$ eV) [9]. Light absorption leads to an electron in the conduction band and a positive hole in the valence band. In small particles they are confined to potential wells of small lateral dimension and the energy difference between the position of the conduction band and a free electron, which leads to a quantization of their energy levels. The phenomena arise when the size of the particles becomes comparable to the de Broglie wavelength of a charge carrier. The increase in the band-gap of the as-prepared HgS

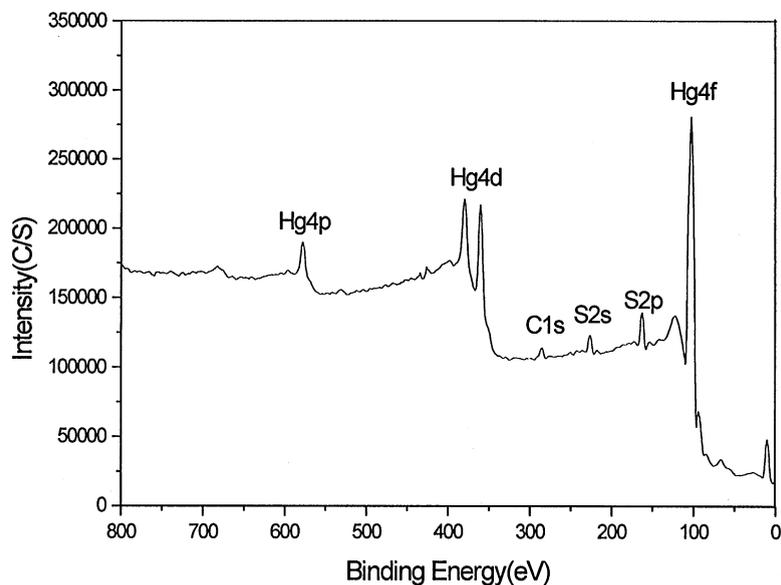


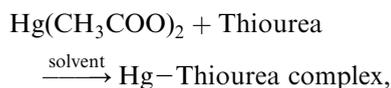
Fig. 3. The wide XPS spectrum of the as-prepared HgS using water as solvent (sample D).

nanoparticles is the indicative of size quaternization effects [43].

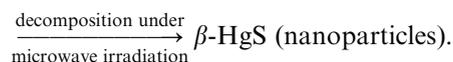
3.3. Probable mechanism

We also carried out experiments by using other materials as sulfur source in the preparation of the nanocrystalline HgS particles. It was found that when thioacetamide and rubeanic acid were used to replace thiourea, the products have the similar size and morphology. The effects of reaction time on the formation of the HgS nanocrystals were also investigated. The HgS nanocrystals were formed after exposed in the microwave irradiation for about 5 min, and after 10 min the reaction was completed. If the reaction time was prolonged to 30 min, the size and morphology of the products did not change.

The probable mechanism can be described as below:



Hg–thiourea complex



Firstly, the strong complex action between Hg^{2+} and thiourea (thioacetamide or rubeanic acid) leads to the formation of Hg–thiourea (Hg–thioacetamide or Hg–rubeanic acid) complexes. Secondly, the complexes undergo a decomposition process under the microwave irradiation. Thiourea reacts with Hg^{2+} , Ag^+ and Bi^{3+} and other metal ions to form complexes [44]. These complexes have the ability to decompose at suitable temperature and pressure to produce metal sulfides. Popov et al. reported the preparation of the Bi_2S_3 by thermal decomposition of Bi–thiourea complex [45]. Yu et al., have reported the solvothermal decomposition process of Bi–thiourea complex in polar solvents which produced Bi_2S_3 nanowires [46]. In our experiments, the HgS nanocrystals are the products of the decomposition of the Hg–thiourea (Hg–thioacetamide or Hg–rubeanic acid) complexes by microwave irradiation.

The formation of uniform nanosized particles demands a uniform growth environment, and

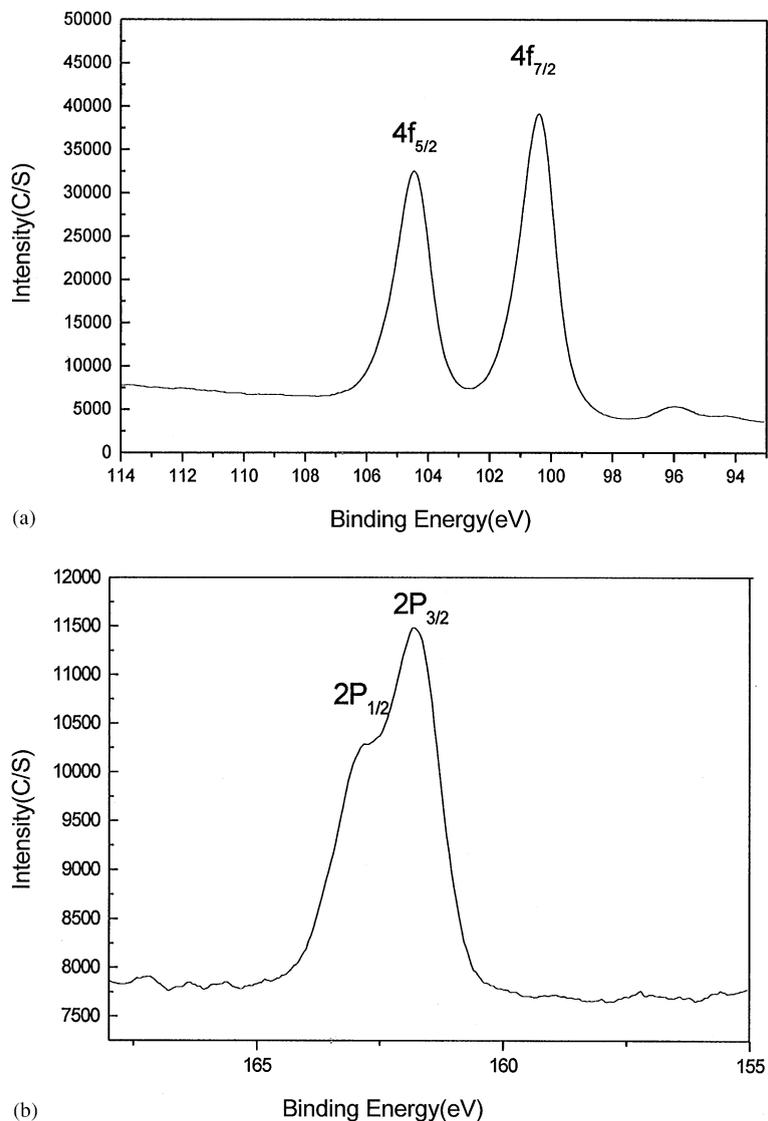


Fig. 4. The high-resolution XPS spectra taken for the Hg and S region of HgS (sample D): (a) Hg(4f); (b) S(2p).

microwave heating affords this. With microwave irradiation of reactants in polar solvents, temperature and concentration gradients can be avoided, providing a uniform environment for the nucleation [36]. During the process, Microwave not only provided the energy for the decomposition of the complexes, but also greatly accelerated the nucleation of the HgS and depressed the straightforward growth of the new-

born HgS nuclei due to the intense friction and collisions of the molecules created by the microwave irradiation. It was found that solvents played a critical role in the formation of the products. In different solvents, the properties of the complexes, the collision rate between the reactants molecules, the heating rate of reaction and the temperature of reaction were different. As a result, nanocrystalline HgS particles with different sizes were obtained.

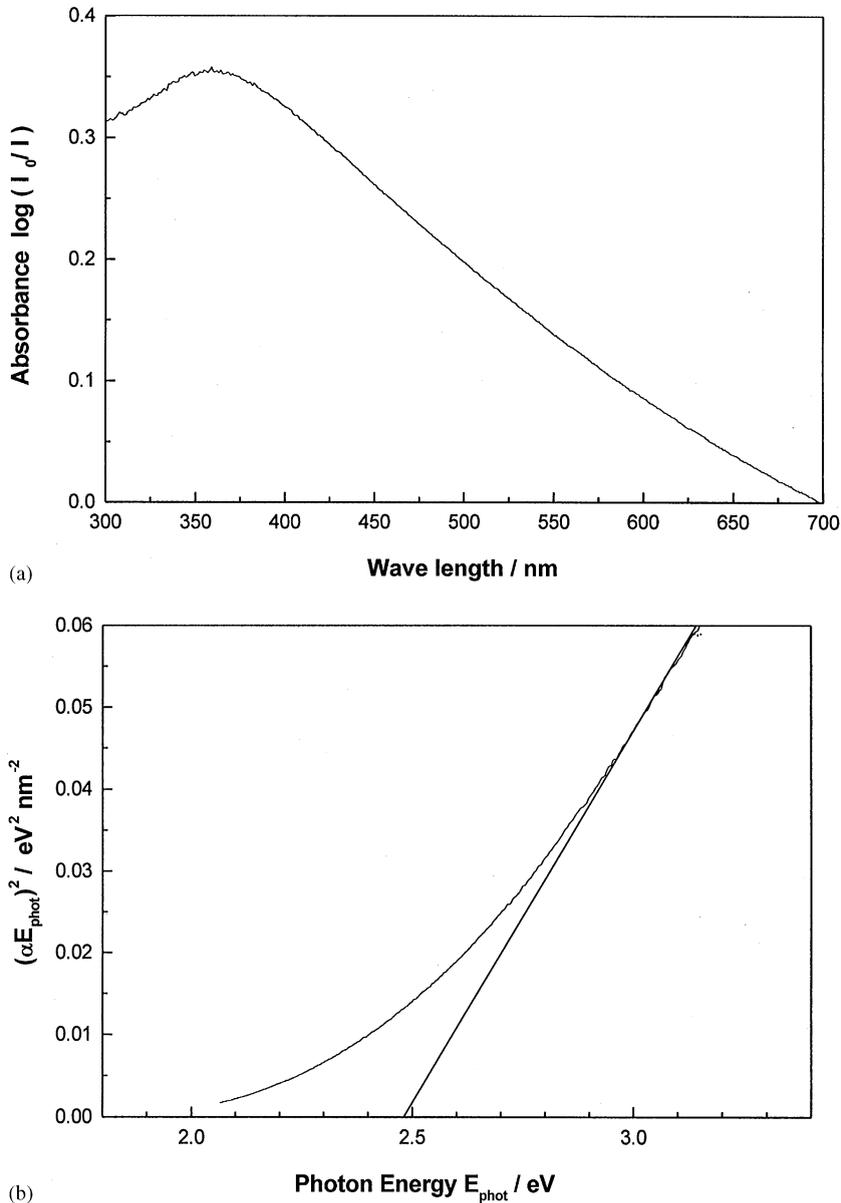


Fig. 5. (a) The UV–Vis absorbance spectrum of HgS nanoparticles prepared in EtOH (sample A) (in EtOH suspension); (b) Plots of $(\alpha E_{\text{phot}})^2$ versus E_{phot} for direct transitions.

4. Conclusion

In summary, the size-controlled synthesis of sphalrite-type HgS (β -HgS) nanocrystals has been reported by microwave irradiation. It was found to

be a convenient, mild and efficient route to the synthesis of the nanocrystalline HgS particles with controllable sizes. Further studies may extend the method for the preparation of other nanocrystalline metal sulfides.

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