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Short communication

Sonochemical synthesis of size-controlled mercury selenide nanoparticles

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Abstract

A novel sonochemical method for preparation of mercury selenide has been developed based on the reaction of mercury acetate and sodium selenosulfate in an aqueous system at room temperature. Different complexing agents were used to control the particle size. X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were used to determine the phase, purity, size and morphology of the products. The results showed that the HgSe nanoparticles with different sizes could be obtained in the presence of complexing agents.

Keywords: Mercury selenide; Sonochemistry; Nanoparticles

1. Introduction

Recently, there has been an increased interest in the synthesis and characterizations of mercury selenide because it has a unique combination of properties which makes it *a candidate* material for detailed investigations of solid state phenomena [1,2] and its electrical properties leads to the wide applications in optoelectronic technology including photoconductive photovoltaic, IR detector, IR emitter, tunable lasers and thermoelectric coolers [3,4]. Conventional methods for the preparation of mercury chalcogenides include solid-state reaction [5], reaction of metal cation with hydrogen chalcogenides in aqueous solution [6], molecular precursor method [7], etc. Solid-state reaction usually requires elevated reaction temperature and the reaction is not easily controllable. For reaction of metal cation with hydrogen chalcogenides in aqueous solution, the hydrogen chalcogenides are gaseous and highly toxic. As for molecular precursor methods, the vapor phase precursor of organometallic compounds is very difficult to obtain. Many scientists are still exploring new, safe, simple routes to mercury chalcogenide semiconductors with the goal of using milder experimental parameters and avoiding toxic precursors.

During the past years a number of new methods for preparing mercury chalcogenides have been reported. Chemical bath deposition was found to be a convenient, mild and economical method for the preparation of mercury chalcogenide thin films including mercury(II) selenide [8,9]. A liquid ammonia route has been used to synthesize metal chalcogenides at room temperature [10]. But in this method, very toxic metallic mercury was employ and the product obtained was amorphous. Li et al. reported a direct conversion route to nanocrystalline mercury selenide [11] using mercury oxide and selenium powder as material sources and the ethylenediamine as solvent. The reaction is conducted at room temperature but the time lasted over 6 h and the product has large size.

Ultrasound has become an important tool in material science in the recent years and has been used in preparation of metal chalcogenides [12–16]. Because of the unique reaction effect [17,18] of the ultrasound irradiation, this method has a rapid reaction rate, controllable reaction conditions and the ability to

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Table 1
Relation between complexing agents and particle sizes

Sample No.	Complexing agent	Average size estimated by Debye–Scherrer formula (nm)	Size observed in TEM images (nm)
a	No	> 100	> 100
b	Ethylenediamine (0.5 mol l^{-1})	30	30–40
c	Ammonia (0.5 mol l^{-1})	20	18–25
d	TEA (0.200 mol l^{-1})	10	7–9
e	TEA (0.133 mol l^{-1})	15	10–12
f	TEA (0.067 mol l^{-1})	20	12–15

The total volume of the solution is 100 ml.

form nanoparticles with uniform shapes, narrow size distributions and high purity.

In this paper, we report a sonochemical method for the preparation of mercury(II) selenide nanoparticles based on the reaction between mercury acetate and sodium selenosulfate in an aqueous system. The products obtained are well-dispersed and the nanoparticles are of small sizes. We found that different complexing agents and different concentrations can be used to control the particle size.

2. Experimental

All the reagents used were of analytical purity. In a typical procedure, an aqueous solution of $Hg(CH_3COO)_2$ in the presence of complexing agents was mixed with 0.2 M Na_2SeSO_3 solution in a 150 ml round-bottom flask to give a final concentration of 20 mM $Hg(CH_3COO)_2$ and 20 mM Na_2SeSO_3 and the total volume of the solution was 100 ml. 0.2 M Na_2SeSO_3 solution was prepared by stirring 0.2 M Se and 0.5 M Na_2SO_3 at ca. 70 °C for 24 h [19]. Then the solutions were irradiated with a high-intensity ultrasonic horn (Xinzhi Co., China, Ti-born, 20 kHz, 60 W cm^{-2}) under ambient air for 30 min and black precipitates were obtained. After cooling to room temperature, the precipitates were centrifuged, washed by distilled water and acetone in sequence, and dried in air. The complexing agents used were triethanolamine (TEA), ammonia solution and ethylenediamine (en), respectively. The preparation conditions and results are listed in Table 1. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

The powder XRD patterns were recorded on Shimadzu XD-3A X-ray diffractometer (Cu Kα radiation, $\lambda = 0.15418$ nm). Transmission electron micrographs (TEM) examinations were carried out on a JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV. XPS measurements were carried out by employing ESCALAB MK II X-ray photoelectron spectrometer, using non-monochromatized Mg Kα X-ray as the excitation source.

3. Results and discussion

3.1. Results of characterizations

The peaks in the XRD patterns (Figs. 1 and 2) are corresponding to (111), (200), (220), (311) and (222),

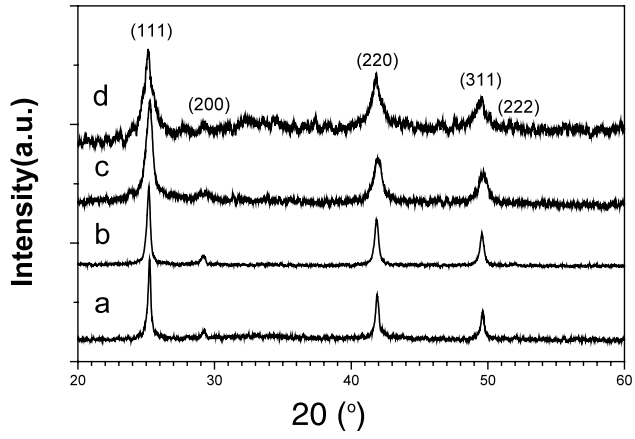

Fig. 1. XRD patterns of HgSe nanoparticles using different complexing agents: (a) without any complexing agent; (b) en; (c) NH_3; (d) TEA (0.2 mol l^{-1}).

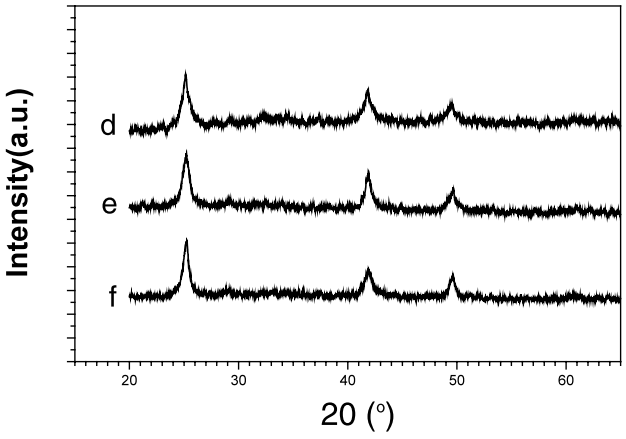

Fig. 2. XRD patterns of HgSe nanoparticles prepared in the presence of different concentration of TEA: (d) 3 g TEA; (e) 2 g TEA; (f) 1 g TEA.

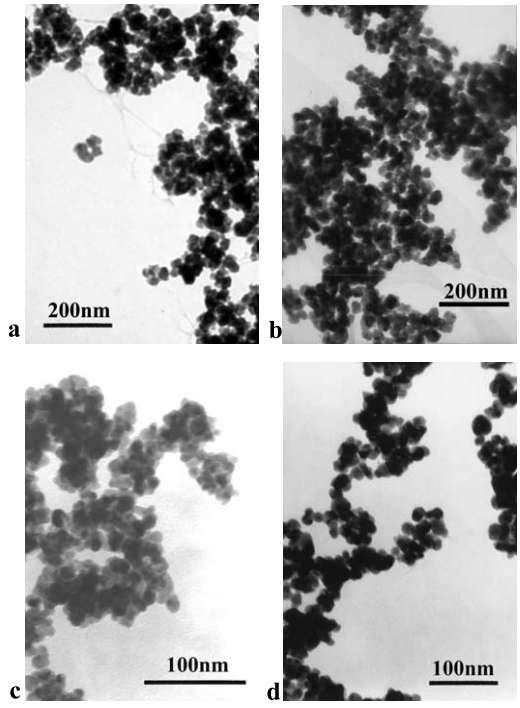

Fig. 3. TEM images of HgSe nanoparticles prepared in the presence of different complexing agents: (a) ethlenediamine; (b) NH_3; (c) TEA (0.200 mol l^{-1}); (d) TEA (0.133 mol l^{-1}).

which matches literature pattern for cubic HgSe (JCPDS, No. 15-456). The average sizes of the particles are estimated by Debye–Scherrer formula from the XRD patterns. The as-prepared particles obtained by using different complexing agents are of different average sizes (Fig. 1). Fig. 2 shows the patterns of the HgSe particles prepared in the presence of different concentrations of TEA. TEA as a complexing agent can effectively control the HgSe particle sizes than more other complexing agents such as en and ammonia. Experiments indicate that high TEA *concentrations lead* to small particles. The results are shown in Table 1.

The TEM images (Fig. 3a–d) show the sizes and morphologies of the products. The well-dispersed particles exhibit spherical shape. The average sizes of the products are in good agreement with those estimated by Debye–Scherrer formula from the XRD patterns. The results are shown in Table 1.

The wide XPS spectrum of sample d is shown in Fig. 4a. No peaks of any impurity are observed, indicating the high purity of the product. Fig. 4b and c show the high-resolution XPS spectra of Hg(4f) and Se(3d), respectively. The two strong peaks for the Hg region observed at 100.2 and 104.3 eV are assigned to the Hg(4f) binding energy. The peak measured in the Se energy region detected at 54.1 eV is attributed to the Se(3d) transitions. The ratio of Hg and Se is calculated to be 1.1:1.

3.2. Discussions

The effects of high-intensity of ultrasound result from acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquids which generates transient temperatures of ~5000 K, pressures of ~1800 atm and cooling rates of 10^{10} K S^{-1}. The extreme conditions of sonification are favorable for many reactions in liquid and liquid-solid mixture [20]. During sonochemical processes, $H^{\bullet}$ and $OH^{\bullet}$ radicals are formed [21]. The mechanism of the sonochemical formation of HgSe nanoparticles is probably related to the radical species generated from water molecules by the absorption of the ultrasound energy. The probable reaction mechanism can be explained as follows:

$$H_2O \rightarrow H^{\bullet} + OH^{\bullet} \quad (1)$$

$$2H^{\bullet} + SeSO_3^{2-} \rightarrow Se^{2-} + H_2SO_3 \quad (2)$$

$$Hg(TEA \text{ or } NH_3 \text{ or en})_n^{2+} + Se^{2-} \rightarrow HgSe + n(TEA \text{ or } NH_3 \text{ or en}) \quad (3)$$

$$nHgSe \rightarrow (HgSe)_n \quad (4)$$

In this process, the in-situ generated $H^{\bullet}$ would react with $SeSO_3^{2-}$ to form Se^{2-} ions that rapidly combine with $Hg(TEA \text{ or } NH_3 \text{ or en})_n^{2+}$ ions to give HgSe nuclei. The release of Se^{2-} is a continuous process that makes these new-born nuclei grow gradually into lager particles. The complexing agents play an important role in the formation of HgSe nanoparticles. The different complexing agents and the concentration of complexing agent can affect the nucleation rate of HgSe, which leads to the formation of HgSe nanoparticles with different sizes.

4. Conclusions

In summary, a convenient sonochemical method has been successfully established to prepare mercury selenide nanoparticles and it is found that using different complexing agents or changing the concentration of the complexing agents can control the particle sizes. This method has been proven to be a convenient, mild and energy efficient route. We can also prepare other metal chalcogenide semiconductor nanoparticles by this route.

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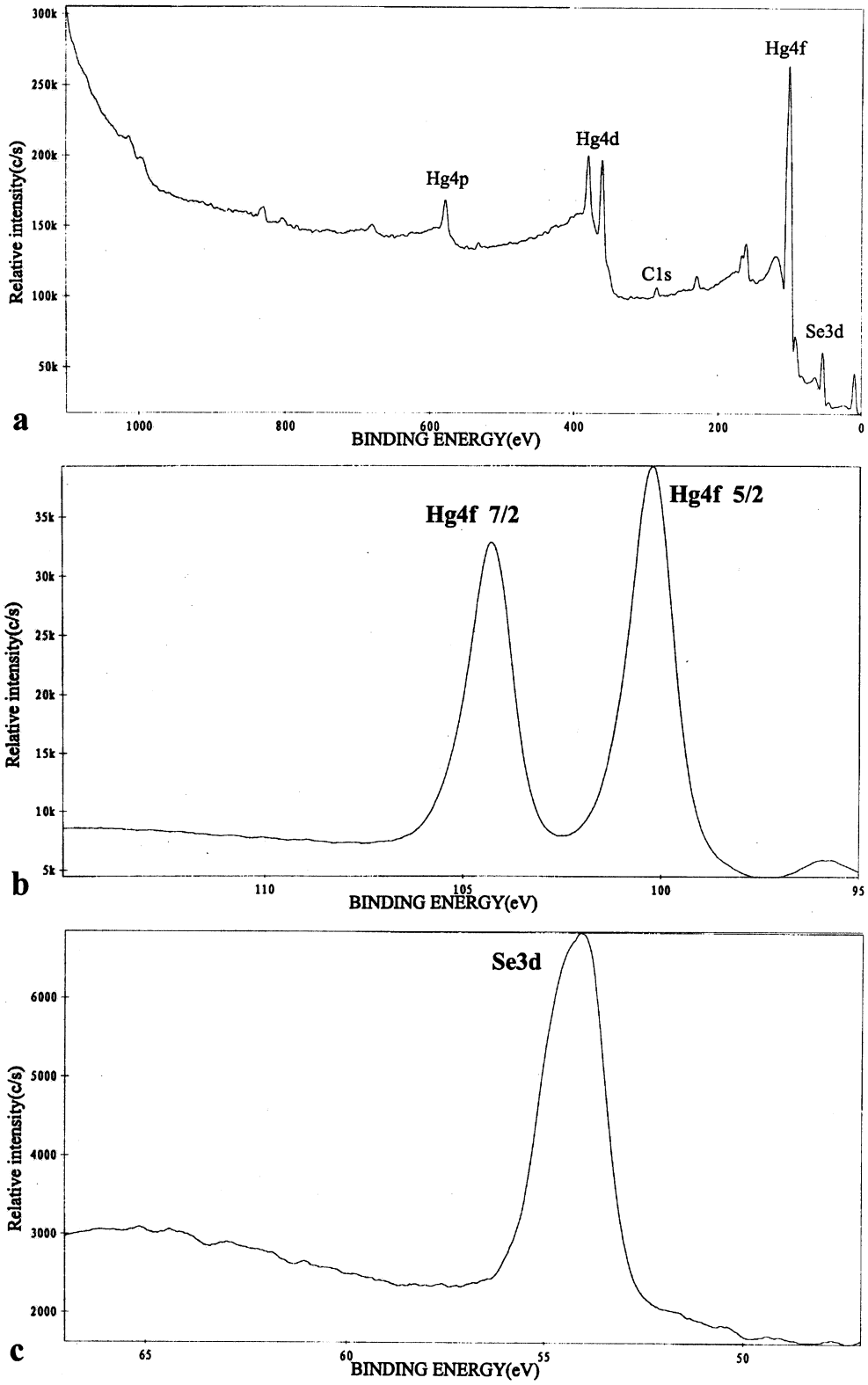

Fig. 4. (a) Wide XPS picture of HgSe nanoparticles; high-resolution XPS picture; (b) Hg4f; (c) Se3d.

References

[1] P.P. Hankare, V.M. Bhuse, K.M. Garadkar, A.D. Jadhav, Mater. Chem. Phys. 71 (2001) 53–57.
[2] J.G. Broerman, Phys. Rev. 183 (1969) 54.
[3] R.K. Willardson, A.C. Beer, Semiconductors and Semimetals, vol. 16, Academic Press, New York, 1981.
[4] K. Singh, S.S.D. Mishra, J. Ind. Chem. Soc. 76 (1999) 104.
[5] T. Ohmiya, Y. Suge, Jpn. J. Appl. Phys. 9 (1970) 840.
[6] I.K. Taimini, Anal. Chim. Acta 12 (1995) 519.

[7] M.L. Steigerwald, C.R. Sprinkle, J. Am. Chem. Soc. 109 (1987) 7200.
[8] P. Pramanic, S. Bhattcharya, Mater. Res. Bull. 24 (1989) 945.
[9] B.B. Pejova, M.Z. Najdoski, I.S. Grozdanov, S.K. Dey, J. Mater. Chem. 9 (1999) 2889.
[10] G. Henshaw, I.P. Parkin, G.A. Shaw, J. Chem. Soc. Dalton Trans. (1997) 231.
[11] Y.D. Li, Y. Ding, H.W. Liao, Y.T. Qian, J. Phys. Chem. Solids 60 (1999) 965.
[12] J.J. Zhu, Yu. Koltypin, A. Gedanken, Chem. Mater. 12 (2000) 73.
[13] B. Li, Y. Xie, J.X. Huang, Y. Liu, Y.T. Qian, Chem. Mater. 12 (2000) 2614.
[14] M.M. Mdleleni, T. Hyeon, K.S. Suslick, J. Am. Chem. Soc. 120 (1998) 6189.
[15] G.Z. Wang, Y.W. Wang, W. Chen, C.H. Liang, G.H. Li, L.D. Zhang, Mater. Lett. 48 (2001) 269.
[16] R. Kerner, O. Palchik, A. Gedanken, Chem. Mater. 13 (2001) 1413.
[17] K.S. Suslick (Ed.), Ultrasound: Its Chemical, Physical and Biological Effects, VCH, Weinheim, Germany, 1988.
[18] K.S. Suslick, S.B. Choe, A.A. Cichowlas, M.W. Grinstaff, Nature 353 (1991) 414.
[19] S. Gorrer, A. Albu-Yaron, G. Hodes, J. Phys. Chem. 99 (1995) 16 442.
[20] K.S. Suslick, D.A. Hammerton, R.E. Cline, J. Am. Chem. Soc. 108 (1986) 5641.
[21] K. Okitsu, Y. Mizukoshi, H. Bandow, Y. Maedu, T. Yamamoto, Y. Nagata, Ultrasonics Sonochem. 3 (1996) S249.