Synthesis, characterization, and photoluminescence properties of HgSe nanoparticles using a novel mercury precursor by the sonochemical method

Mahdiyeh Esmaeili-Zare · Masoud Salavati-Niasari

Received: 21 July 2014/Accepted: 20 November 2014 © Springer Science+Business Media Dordrecht 2014

Abstract In this paper, we report the synthesis and characterization of novel mercury selenide (HgSe) nanoparticles by sonochemical method. The HgSe nanoparticles have been prepared using [N,N'-bis(salicylaldehydo)ethylenediamine] mercury(II), [Hg(salen)] complex, as a novel precursor. The effects of the different capping agents, such as sodium dodecyl-benzene-sulfonate, polyethylene glycol, and polyvinyl pyrrolidone on the particle size and morphology of the samples have been investigated. The effect of different parameters, such as: temperature, power of irradiation, and reducing agent were also examined. These nanoparticles were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, photoluminescence, X-ray energy dispersive spectroscopy, and Fourier transform infrared spectroscopy.

Keywords Sonochemical synthesis · Mercury selenide · Surfactant · Complex precursor · Optical properties

Introduction

In recent years, there has been an increasing interest in semiconductors with nanosized dimensions in light of being widely studied because of its appropriate application in industry [1, 2], especially in the field of cadmium and zinc chalcogenide. Nevertheless, possibly due to the toxicity of mercuride, only a small number of reports relating to the synthesis of mercury chalcogenides nanoparticles are discovered. In those reports, some researchers prepared Hg (S, Se, Te) nanoparticles at room temperature [3, 17–19] while others prepared mercury

Institute of Nano Science and Nano Technology, University of Kashan,

PO Box 87317–51167, Kashan, Islamic Republic Iran

M. Esmaeili-Zare · M. Salavati-Niasari (🖂)

e-mail: salavati@kashanu.ac.ir

selenide thin layers on transparent polyester sheets by means of chemical bath deposition [4]. While being concerned with how to synthesize chemical materials fast and conveniently, they found it a real challenge. The sonochemical method can be used for solving this problem. It is a quick, synthetic method for many chemical reactions. Ultrasound has become an important tool in material science in recent years and has been used in the preparation of novel nanomaterials such as graphene nanosheets [20, 21]. Because of the unique reaction effect of the ultrasound irradiation, this method has a rapid reaction rate, controllable reaction conditions, and the ability to form nanoparticles with uniform shapes, narrow size distributions, and high purity.

Organic molecules containing imine groups have been interesting to inorganic chemists because these types of molecules are suitable ligands for transition metals and have found utility in a broad range of applications. Schiff base metal complexes have been widely studied because of their appropriate application in industry, and as antibacterial, anticancer, and herbicidal [5]. Salen ligands are tetradentate, consisting of two imine nitrogen and two phenolic oxygen donors that coordinate in the basal plane of the metal ion, and are readily prepared from the condensation of a salicylaldehyde and a diamine.

We have been interested in the synthesis of metal selenide and metal sulfide nanoparticles using new inorganic precursors, taking profit of the tools of organometallic chemistry [6–9]. Using the novel precursor can be useful and can open a new way for preparing nanomaterials to control nanocrystal size, shape, and distribution of the particle size.

The present work describes the synthesis of HgSe nanoparticles using sonochemical method. For this approach [N,N'-bis(salicylaldehydo)ethylenediamine] mercury complex was selected as a new precursor for the first time. Therefore, in this paper, we report on the HgSe nanoparticles using the sonochemical method.

Experimental

Materials and physical measurements

Sodium dodecyl sulfate (SDS: 99 % purity) was purchased from Merck, polyethylene glycol (PEG600, 1L = 1.3 kg, Merck), sodium dodecyl-benzene-sulfonate (SDBS: 88 % purity, Merck), poly vinyl pyrrolidone PVP-K40- (C₆H₉NO) *n* (n = 40) (99 % purity, Sigma-Aldrich), ethylenediamine (99 % purity, Merck) selenium tetra chloride (Merck) and mercury acetate (98 % purity, Merck) were used for synthesize of different morphology of the nanoparticles. All the chemicals were of the analytical grade and were used without further purification. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 100 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. XRD patterns were recorded by a Philips X-ray diffractometer using Ni-filtered Cu-K α radiation. Scanning electron microscopy (SEM) images were obtained on a LEO instrument. Transmission electron microscope (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The compositional analysis was done by energy-dispersive X-ray (EDX, Kevex, Delta Class I). Photoluminescence (PL) measurement was studied on a Perkin-Elmer fluorescence spectrophotometer.

Synthesis of [Hg(salen)] complex

N,N'-bis-salicylidene-1,2-ethylendiamine; H₂salen; (3.7 mmol) was dissolved in 100 ml methanol; then 100 ml of mercury(II) acetate (0.037 M) was added to the above solution under stirring. Triethylamine (1 ml, 7.2 mmol) was added and the mixture was heated at 80 °C for 1 h. The mixture was filtered, and the yellow precipitate was washed with methanol and dried in a vacuum oven. The melting points of H₂salen ligand and corresponding mercury complex were measured to be 168 [10] and 260–270 °C, respectively. The higher melting point of the complex is considered to be due to the higher symmetry and thus more stability of the complex rather than the initial ligand.

Preparation of HgSe nanoparticles

We dissolved 0.2 g of [Hg(salen)] in 100 ml of propylene glycol (PG). Then, 0.1 g SeCl₄ was added to the solution under ultrasonic irradiation for 7 min. The solutions were then irradiated with an ultrasonic horn for 30 min and added drop-wise N_2H_4 ·H₂O. The black obtained precipitate was centrifuged, washed by distilled water and methanol, and dried in vacuum oven at 60 °C. Preparation of HgSe nanoparticles under different conditions is listed in Table 1.

Results and discussion

The XRD pattern of the HgSe is shown in Fig. 1. All of the reflections of the pattern can be indexed to the standard peak of the pure cubic phase of HgSe, which is in suitable agreement with the reported data (JCPDS No. 73-1668, a = b = c = 6.0720 Å). The patterns of the obtain samples 3, 6, 11, and 12 in different condition (effect of surfactant, temperature, ultrasonic power, reducing agent) are shown in Fig. 2a–d, respectively, which have appropriate agreement with the reported JCPDS. This revealed that the HgSe has a single phase cubic structure. The crystallite size measurements were also carried out using the Scherrer equation [11],

$$Dc = \frac{K\lambda}{\beta\cos\theta}$$

where β is the breadth of the observed diffraction line at its half intensity maximum, *K* is the so-called shape factor, which usually takes a value of about 0.9, and *k* is the

Sample no.	Effect	Surfactant	Temperature (°C)	Time (min)	Ultrasonic power (W/cm ²)	Reductant	Section
1	Surfactant	_	25	30	60	N ₂ H ₄ ·H ₂ O	Fig. <mark>5</mark> a
2		SDBS	25	30	60	$N_2H_4 \cdot H_2O$	Fig. 5c
3		SDS	25	30	60	$N_2H_4 \cdot H_2O$	Fig. <mark>5</mark> d
4		PEG 600	25	30	60	N_2H_4 · H_2O	Fig. <mark>5</mark> e
5		PVP 25,000	25	30	60	$N_2H_4 \cdot H_2O$	Fig. 5f
6	Temperature	-	50	30	60	$N_2H_4 \cdot H_2O$	Fig. <mark>6</mark> a
7		-	70	30	60	N_2H_4 · H_2O	Fig. <mark>6</mark> b
8	Time	_	25	15	60	N_2H_4 · H_2O	Fig. <mark>6</mark> c
9		-	25	45	60	$N_2H_4 \cdot H_2O$	Fig. <mark>6</mark> d
10	Ultrasonic power	-	25	30	40	N_2H_4 · H_2O	Fig. 7a
11		_	25	30	50	N_2H_4 · H_2O	Fig. 7b
12	Reducing agent	-	25	30	60	KBH_4	Fig. <mark>8</mark> a
13		-	25	30	60	Zn	Fig. <mark>8</mark> b
14	Sonication	-				$N_2H_4{\cdot}H_2O$	Fig. 9

Table 1 Preparation of HgSe under different conditions



Fig. 1 XRD pattern of the HgSe nanoparticles (No. 1)

wavelength of X-ray source used in XRD. The estimated crystallite size is about 15 nm.

FT-IR spectrum of the [Hg(salen)] precursor is illustrated in Fig. 3. The broad band at 3,428 cm⁻¹ is assigned to O–H bonds of hydration water. The peaks at 2,922 and 3,050 cm⁻¹ are responsible for the aliphatic and aromatic C–H bonds, respectively. The absorption at 1,615 cm⁻¹ is due to the C=N vibration. In addition, the peak at 1,438 cm⁻¹ is due to the C=C stretching mode. The peak at 757 cm⁻¹ is





assigned to bending mode of the phenyl group γ (=CH) and two peaks located at 1,146 and 1,178 cm⁻¹ corresponding to the phenolic C–O bond.

The FT-IR spectra of the obtained samples 3, 6, 11, and 12 in different condition (effect of surfactant, temperature, ultrasonic power, reducing agent) are shown in Fig. 4a–e. HgSe has no absorption peak in the range of $4,000-400 \text{ cm}^{-1}$ so these spectra show that products do not have major IR-active impurity.

It was found that the sonochemical reactions occur within the interfacial region, forming nanocrystals due to very high quenching rate experienced by the products. Several factors influence the acoustic cavitation such as low vapor pressure, high surface tension, and high sound speed. The influence of the capping agent, temperature, time, ultrasonic power, and reducing agent type on the as-prepared HgSe nanoparticles were investigated (Figs. 5, 6, 7, 8–9). The nanoparticles in the absence of the capping agent (Fig. 5a) with grain diameter about 15–30 nm have acceptable distribution. Ultrasonic irradiation creates bubbles, which produces high temperature and energy after decomposition. This process provides an appropriate amount of energy for formation of HgSe nanoparticles. TEM image of the assynthesized HgSe nanoparticles is shown in Fig. 5b to determine the particle size of the product. The shape of the obtained products are quasi-spherical with dimensions about 15–30 nm.



Fig. 3 FT-IR spectrum of the Hg(salen) precursor



Fig. 4 FT-IR spectra of the samples 2, 3, 6, 11, and 12

With exchange of the capping agent from SDBS to SDS, PEG and PVP in the presence of hydrazine as a reductant, the nanoparticles show dense agglomeration and an increase in the particle size (Fig. 5c–f, Scheme 1). It has been reported that the presence of capping molecule (such as PEG and PVP) can alter the surface energy of the crystallographic surface, and promote the anisotropic growth of nanocrystals and therefore we can see this trend in the case of HgSe [12]. By using ultrasound irradiation, the formed bubbles collapse, resulting in the generation of high-speed microjets with very high velocity, which these microjets can generate HgSe nanoparticles [10].



Fig. 5 a SEM, b TEM images of the as-prepared HgSe in the absence of capping agent (No. 1), SEM images in the presence of: c SDBS (No. 2), d SDS (No. 3), e PEG (No. 4) and f PVP (No. 5)

The effect of the reaction temperature and time on the morphology of the products was also investigated (Fig. 6). With increasing the reaction temperature from 25 (Fig. 5a) to 50 °C (Fig. 6a), the particle size of the nanoparticles increased, but with enhancement temperature to 70 °C (Fig. 6b), the size and agglomeration of the nanoparticles decreased, which may be due to an increase in diffusion rate of bubbles in nucleation region affecting the reactant concentration. Reaction time effect on the morphology of the nanoparticles, in absence of the capping agent, was examined (Fig. 6c, d). By increasing the reaction time from 15 (Fig. 6c) to 30 min (Fig. 5a), the size of the obtained nanoparticles was decreased. With enhancement of the reaction time to 45 min (Fig. 6d), morphology and size of the samples



Fig. 6 SEM images of the prepared HgSe in the presence of hydrazine: **a** at 50 $^{\circ}$ C (No. 6), **b** at 70 $^{\circ}$ C (No. 7), **c** at 25 $^{\circ}$ C for 15 min (No. 8) and **d** at 25 $^{\circ}$ C for 45 min (No. 9) of sonication

changed and agglomeration of the nanoparticles increased, which is consistent with Oswald ripening.

Figure 7 shows the SEM images of the obtained samples at various powers. It can be observed that with enhancement of the power from 40 (Fig. 7a) to 50 W (Fig. 7b), the size and agglomeration of the nanoparticles increase. It was found that when PG was selected as a solvent, the reaction proceeded smoothly at the power of 40 W. By increasing the ultrasound power to 60 W (Fig. 5a), the agglomeration of nanoparticles break down and the size of HgSe nanoparticles decrease. Results show that at higher powers, nucleation stage overcomes the growth stage and smaller particles will be achieved.

It might be noted that the final temperature and pressure reached after the collapse of the bubble is proportional to the ultrasonic power. If the ultrasonic power was increased, the extent of the collapse of the bubble would be greatly increased, leading to a higher temperature and pressure accordingly, which would enhance the effect of ultrasonic chemical reactions as a whole. Due to the viscosity of PG, forming a cavity will require a much higher threshold than water. That might be one of the reasons why ultrasonic power is lower in water systems than in PG systems. The implosive collapse of bubbles in PG solvent would result in higher temperature and pressure than in aqueous solvents. Taking this into account, PG is an excellent solvent for sonochemical reaction [13].



Fig. 7 SEM images under different powers of ultrasound: a 40 W (No. 10) and b 50 W (No. 11)



Fig. 8 SEM images of the products with different reducing agents: a KBH4 (No. 12) and b Zn (No. 13)

Fig. 9 SEM image of the sample No. 14



With using strong reducing agents such as KBH_4 and hydrazine hydrate, a large number of nuclei was created and further growth of the nuclei was limited. As a result, many small particles were obtained (Figs. 5a, 8a). Reduction in the presence of Zn proceeds only two dimensionally (Fig. 8b). In this experiment, the reaction that takes place using a chemical reducing agent is the reduction of Se source to form Se^{2-} ions that subsequently react with Hg^{2+} ions to form HgSe.



Scheme 1 Schematic diagram illustrating formation of the HgSe nanoparticles

For investigating of the sonication effect on the morphology of the products, the blank reaction was performed without ultrasound irradiation. Aggregated nano-structures are formed in the absence of sonication (Fig. 9). An advantage of using ultrasound irradiation is that it yields smaller particles and the result shows a growth in the particle size without ultrasound method.

Figure 10 shows the proton nuclear magnetic resonance (¹H-NMR) spectrum of the complex precursor. The multiple peaks appeared at the chemical shifts of 6.8–7.6 ppm is attributed to the aromatic protons. The sharp peaks appeared at 8.6



Fig. 10 ¹H-NMR spectrum of the [Hg(Salen)] precursor

and 3.9 ppm could be assigned to the proton of HC=N group and N- CH_2 , respectively.

The probable formation process of HgSe nanoparticles under ultrasound waves (US) in propylene glycol can be summarized as follows [14, 15]:

$$Hg(salen) + OHCH_2CH(OH)CH_3 \xrightarrow{US} Hg^{2+} + salen^{2-}$$
(1)

$$SeCl_4 + OHCH_2 CH(OH)CH_3 \rightarrow Se^{4+} + 4Cl^{-}$$
(2)

$$OHCH_2 CH(OH)CH_3 \xrightarrow{US} H^{-} + HOCH^{-}CH(OH)CH_3$$
(3)

$$\mathrm{H}^{\cdot} + \mathrm{H}^{\cdot} \rightarrow \mathrm{H}_{2}.$$

Then N_2H_4 H_2O is reacted with Se⁴⁺, obtained from solutions of SeCl₄, giving rise to HgSe nanoparticles:

$$Se^{4+} + N_2H_4H_2O \xrightarrow{US} Se^0 + N_2 + 4H^+ + H_2O$$

$$\tag{4}$$

$$\mathrm{H}_2 + \mathrm{Se}^0 \to \mathrm{Se}^{2-} + 2\mathrm{H}^+ \tag{5}$$



Fig. 11 a EDS pattern, b room-temperature photoluminescence spectrum, and c diffuse reflectance spectrum of the HgSe nanoparticles (No. 1)

Table 2 Characterization comparison of band gap of HgSe nanostructures with other similar works

Band gap (eV)	Method	References
1.55	Emulsion	Liu et al. [24]
0.78	Electrodeposition	Mahalingam et al. [25]
1.65 (without voltage) and	Solvothermal method	RangaRao and Dutta [26]
1.72 (at 700 V)		

$$\mathrm{Se}^{2-} + \mathrm{Hg}^{2+} \to \mathrm{Hg}\mathrm{Se}.$$
 (6)

Energy-dispersive spectroscopy (EDS) analysis was employed to determine the composition of the HgSe nanoparticles (Sample No. 1). As shown in Fig. 11a, the EDS clearly identifies that the nanoparticles are composed of Hg (at.% 51.24 %) and Se (at.% 48.76 %); they should therefore be attributed to HgSe and further confirm the purity of products. Room temperature PL spectrum of the HgSe nanoparticles (Sample No. 1) with excitation at 257 nm is shown in Fig. 11b. A very broad peak centered at 302 nm (4.109 eV) is shown in the PL spectrum. The band gap energy of the bulk HgSe crystal E_g is -0.24 eV [16], therefore, the band gap energy of the as-synthesized HgSe nanoparticles is blue shifted compared to bulk sample. The large blue-shift in the optical band-gap observed for this sample compared to bulk mercury selenides can be attributed to strong confinement



Scheme 2 Quantum confinement is responsible for the increase of energy difference between energy states and band gap

(Table 2. Characterization comparison of band gap of HgSe nanostructures with other similar works).

Quantum confinement is a change of electronic and optical properties when the material sampled is of sufficiently small size, typically 10 nm or less. The band gap increases as the size of the nanostructure decreases (see Scheme. 2). Specifically, the phenomenon results from electrons and holes being squeezed into a dimension that approaches a critical quantum measurement, called the exciton Bohr radius. A stronger confinement leads to a larger separation of the energy levels; as a result, a higher energy is required to promote an electron from the valance band to the conduction band.

Conclusions

HgSe nanoparticles were successfully prepared by a facile sonochemical method at room temperature. Using the surfactants and high temperatures is not necessary for this synthesis. SEM, TEM, XRD, ¹H-NMR, FT-IR, and PL techniques were used to characterize the structure and purity of the HgSe nanoparticles. The influence of different parameters such as capping agent, temperature, power of irradiation and reducing agent type on the morphology of the product was also examined. HgSe is one of the very interesting II–VI materials to be investigated for its applications in optoelectronic technology including photoconductive photovoltaic, IR detector, IR emitter, tunable lasers, and thermoelectric coolers [22, 23].

Acknowledgments The authors are grateful to the council of University of Kashan for their unending effort to provide financial support to undertake this work by Grant No. (159271/242).

References

- 1. S. Gorer, G. Hodes, J. Phys. Chem. 98, 5338 (1994)
- 2. S.A. Empedocles, J. Phys. Chem. B 103, 1826 (1999)
- 3. L.Q. Li, H.W. Liao, H.R. Wang, J. Mater. Chem. 9, 2675 (1999)
- 4. B.B. Pejova, M.Z. Najdoski, I.S. Grozdanov, S.K. Dey, J. Mater. Chem. 9, 2889 (1999)
- 5. P.G. Cozzi, Chem. Soc. Rev. 33, 410 (2004)
- 6. M. Salavati-Niasari, A. Khansari, F. Davar, Inorg. Chem. 362, 4937 (2009)
- 7. A. Sobhani, M. Salavati-Niasari, Mater. Res. Bull. 47, 1905 (2012)
- 8. M. Salavati-Niasari, N. Mir, F. Davar, J. Alloys Compd. 493, 163 (2010)
- 9. F.S. Sangsefidi, M. Salavati-Niasari, M. Esmaeili-Zare, Superlattices Microstruct. 62, 1 (2013)
- 10. A.A. Khandar, B. Shaabani, F. Belaj, A. Bakhtiari, Polyhedron 25, 1893 (2006)
- R. Jenkins, R.L. Snyder, Chemical Analysis: Introduction to X-ray Powder Diffractometry (Wiley, New York, 1996), p. 90
- L.S. Cavalcante, J.C. Sczancoski, M. Siu Li, E. Longo, J.A. Varela, Colloids Surf. A Physicochem. Eng. Asp. 396, 346 (2012)
- 13. T. Ding, J.J. Zhu, J.M. Hong, Mater. Lett. 57, 4445 (2003)
- 14. M. Esmaeili-Zare, M. Salavati-Niasari, A. Sobhani, Ultrason. Sonochem. 19, 1079 (2012)
- 15. M. Esmaeili-Zare, M. Salavati-Niasari, D. Ghanbari, High Temp. Mater. Process. 32, 157 (2013)
- 16. C.Y. Moon, S.H. Wei, Phys. Rev. B 74, 045205 (2006)
- 17. S.K. Mehta, S. Kumar, S. Chaudharya, K.K. Bhasina, Nanoscale 2, 145 (2010)
- 18. N. Srinivasan, S. Thirumaran, S. Ciattinib, RSC Adv. 4, 22971 (2014)
- 19. X. Liu, R. Liu, Y. Tang, L. Zhang, X. Houab, Y. Lv, Analyst 137, 1473 (2012)
- 20. A. Gedanken, Ultrason. Sonochem. 11, 47 (2004)
- 21. K. Krishnamoorthy, G.S. Kim, S.J. Kim, Ultrason. Sonochem. 20, 644 (2013)
- 22. R.K. Willardson, A.C. Beer, *Semiconductors and Semimetals*, vol. 16 (Academic Press, New York, 1981)
- 23. K. Singh, S.S.D. Mishra, J. Ind. Chem. Soc. 76, 104 (1999)
- 24. L. Liu, Q. Wu, Y. Ding, H. Liu, B. Zhang, Colloids Surf. A Physicochem. Eng. Asp. 240, 135 (2004)
- T. Mahalingam, A. Kathalingam, C. Sanjeeviraja, R. Chandramohan, J.P. Chu, Y.D. Kim, S. Velumani, Mater. Charact. 58, 735 (2007)
- 26. A. RangaRao, V. Dutta, Sol. Energy Mater. Sol. Cells 95, 1050 (2011)