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# Mercury selenide nanorods: Synthesis and characterization *via* a simple hydrothermal method

Mehdi Bazarganipour<sup>a</sup>, Minoo Sadri<sup>b</sup>, Fatemeh Davar<sup>c</sup>, Masoud Salavati-Niasari<sup>a,c,\*</sup>

<sup>a</sup> Department of Inorganic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, P.O. Box 87317-51167, Iran
<sup>b</sup> Department of Chemistry, College of Science, Bu-Ali Sina University, P.O. Box 4135, Hamadan 65174, Iran
<sup>c</sup> Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P.O. Box 87317-51167, Iran

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#### ABSTRACT

HgSe nanorods have been synthesized through a simple hydrothermal reduction approach. The nanorods formed were  $\approx$ 45 nm average diameter and  $\approx$ 3 µm nm in length. X-ray diffraction characterization suggested that the product consists of cubic phase pure HgSe. The as-prepared products were also characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). An X-ray energy dispersive spectroscopy (EDX) study further confirmed the composition and purity of the product. The synthesis procedure is simple and uses less toxic reagents than the previously reported methods. The results showed that the capping agent CTAB (cetyltrimethylammoniumbromide) plays a crucial role in the process. Other factors, such as the reaction time, temperature, different capping agent and the reductant type also have an influence on the morphology of the final products to some extent.

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#### 1. Introduction

Over the last twenty years, a great deal of work has gone into understanding the properties of matter at the nanometer scale. One class of mesoscopic system receiving a lot of attention is colloidal semi-conductor quantum dots (QDs) or nanocrystals (NCs) [1–4]. Progress in this area has benefited from the dynamic interplay between advances in synthesis, optical characterization and theory [5]. Despite this synergy, a major bottleneck in this field has traditionally been the availability of high quality, crystalline samples with narrow size distributions, high photoluminescence efficiencies and controlled surface chemistries. II–VI materials, in particular, have led to new opportunities for a better understanding and to utilize the size-dependent optical and electrical behavior of QDs [6,7] as a result of the discovery in the early 90s by Murray and others that one could make high-quality QDs through the thermolysis of pyrophoric organometallic reagents [8,9].

Prior to these advances, however, analogous examples of high quality II–VI nanocrystalline compounds could already be found in small clusters of zinc and cadmium chalcogenides of precise molecular weight. These clusters represent the molecular limit of QDs and are also some of the first examples of colloidal nanoparticles. They contain less than 100 atoms and typically lie in the size range between 1 and 2 nm.

\* Corresponding author at: Department of Inorganic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, P.O. Box 87317-51167, Iran. Tel.: +98 361 591 2383; fax: +98 361 555 2935.

In the case of II-VI mercury chalcogenides, very little work exists to date on either clusters or QDs, although interest in these materials abounds. Bulk mercury chalcogenides are semi-metals widely used in infrared sensing applications. Alloys of Hg compounds ( $Hg_{1-x}Cd_xTe$ , for example) are particularly important systems because of the wide range of tunable optical, electrical and magnetic properties, achieved through compositional tuning (x)of this material, from pure semi-metallic Hg (S, Se, Te) to narrow gap  $Hg_{1-x}Cd_x$  (S, Se, Te) and ultimately to wider gap semiconductor Cd (S, Se, Te). At the same time, such material tunability can also be explored by making QDs or clusters of these compounds, exploiting well-known quantum confinement effects that occur when the physical size of the NC is smaller than the bulk exciton Bohr radius. Furthermore, the ease of compositional tuning suggests that a similar parameter space can be investigated, not only through size, but also through composition, with the creation of ternary mercury chalcogenide QDs/clusters leading to tunable absorbing and emitting species spanning anywhere from the visible into the far-infrared. Such compounds have potential use as visible/infrared fluorescent tags, lasing/amplifying elements at 1.3 and 1.55  $\mu$ m, and in remote sensing applications [10].

The existing mercury chalcogenide NC syntheses that have been reported largely deal with solvothermal or solvent-based approaches for making these compounds. These approaches entail sonochemistry [11], microwave-assisted heating [12,13] and the thermolysis of common mercury precursors [14,15]. Other methods make use of metal ion impregnated Langmuir Blodgett films [16] or other restricted environments such as vesicles [17] or sol-gel networks [18] to grow HgS QDs. Recently, the hydrothermal method





E-mail address: salavati@kashanu.ac.ir (M. Salavati-Niasari).

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has also been reported to prepare metal chalcogenide nanostructural materials, which has the potential advantages of relatively low cost, high purity and controlled morphology [19–24].

In this work, we report on HgSe nanorods prepared by the simpler hydrothermal method, and compare the difference in the nanostructure of HgSe synthesized with a different reductant type.



Fig. 1. XRD of HgSe prepared in the presence of  $KBH_4$  as the reductant and CTAB as the capping agent at 180 °C for 12 h.

#### 2. Experimental

#### 2.1. Materials and physical measurements

All of reagents and solvents were purchased from Merck (proanalysis) and were dried using molecular sieves (Linde 4 Å). XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation. Scanning electron microscopy (SEM) images were obtained on a Philips XL-30ESEM equipped with an X-ray energy dispersive detector. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV.

### 2.2. Nanostructured HgSe prepared by the hydrothermal method

 $Hg(NO_3)_3$ - $H_2O$  and SeCl<sub>4</sub> were used as the simple precursors in the hydrothermal synthesis. The precursors, with a stoichiometric ratio of Hg:Se (0.45:0.45 mmol), were put into a Teflon-lined autoclave. The autoclave was then filled with water up to 80% of its volume (100 ml capacity). After adding sufficient KBH<sub>4</sub> (0.2 g) as the reductant, and CTAB (cetyltrimethylammoniumbromide) (0.15 g) as the capping agent, the autoclave was sealed immediately and heated to 180 °C for the synthesis reaction. After reacting for 12 h, the autoclave was cooled down to room temperature naturally. The obtained precipitates were separated by centrifugation, washed with deionized water followed by ethanol three times, and dried at 100 °C under vacuum for 24 h. The structure and morphology of the HgSe powders were characterized by XRD and TEM.



Fig. 2. SEM images of HgSe prepared in the presence of (a) CTAB, (b) PEG 20000, (c) SDBS as the capping agent and (d) TEM images of HgSe prepared in the presence of CTAB as the capping agent and KBH<sub>4</sub> as the reductant at 180 °C for 12 h.

#### 3. Results and discussion

The composition of the as-prepared product was determined by XRD (Fig. 1). All peaks in the patterns correspond to the reflections of cubic phase HgSe [space group:  $\bar{F}43m$  (216)], with lattice constants a = 6.0720 Å (JCPDS 73-1668). No remarkable diffractions of other phases, such as selenium, mercury or their other compounds, can be found in Fig. 1, indicating that a crystalline HgSe phase has been formed after the synthesis for all samples. The broadening of the diffraction peaks indicates that the samples are nanosized. The average particle size of the sample is about 23 nm, estimated through the Scherrer formula.

Meanwhile, the influence of the capping agent, reductant type, time and temperature were investigated on the as-prepared HgSe nanorods (Figs. 2–5). The morphology and size of the assynthesized products were characterized by SEM and TEM. With exchange of the capping agent from PEG 20000 (0.15 g) to SDBS (sodium dodecyl-benzene-sulfonate) (0.15 g), and PEG 20000 in the presence of KBH<sub>4</sub> as a reductant, the nanostructures show dense agglomeration and the particle size increased (Fig. 2a–c). In fact, these nanostructures appear to be polycrystalline agglomerations of crystallites. The morphology of the resulting nanostructure was examined by TEM. From the TEM image (Fig. 2d), HgSe nanostructures with an average diameter of 25 nm were observed.

Fig. 3 reveals the reductant type effect on the morphology of the nanostructure in the presence of CTAB as a capping agent. In this study, the reductant plays a key role in the morphology of the HgSe

nanorods. In the presence of  $N_2H_4$  (0.1 ml) as the reductant, rodshape is the preferential morphology (Fig. 3a). Meanwhile, in the presence of Zn (0.08 g) as the reductant, particles are the preferential morphology (Fig. 3b).

Strong reductants such as  $KBH_4$  and  $N_2H_4$ , in combination with stirring rapidly, created a large number of nuclei and further growth of the nuclei was limited. As a result, many small particles were obtained. Reduction in the presence of Zn proceeds only twodimensionally, i.e., at the interface of the Zn powder with the metal cation solution. The rate of reduction is further limited by the mass transport of the metal cation solution to the Zn surface. Therefore, depletion of metal cations near the interface might occur. As a consequence of the rate and surface area limitations, crystal growth is favored over nucleus formation, with the result of larger particles [25].

In continuation, the effect of reaction time on the morphology of the nanorods, in presence of CTAB as the capping agent, was investigated (Fig. 4a and b). By increasing the reaction time from 6 to 24 h, the nanorods break down and there is dense agglomeration.

The effect of the reaction temperature on the morphology of the nanorods, in the presence of CTAB as the capping agent, was also investigated (Fig. 5a and b). On increasing the reaction temperature from 100 to  $150 \,^{\circ}$ C, nanorods were gradually constituted (Table 1).

X-ray energy dispersive spectroscopy (EDS) analysis measurement was used to characterize the chemical composition of the products (Fig. 6). The results for HgSe in the presence of  $KBH_4$  as



Fig. 3. SEM images of HgSe prepared in the presence of CTAB as the capping agent and (a)  $N_2H_4$  and (b) Zn as the reductant.



Fig. 4. SEM images of HgSe prepared in the presence of CTAB as the capping agent and N<sub>2</sub>H<sub>4</sub> as the reductant at 180 °C for (a) 6 h and (b) 24 h.



Fig. 5. SEM images of HgSe prepared in the presence of N<sub>2</sub>H<sub>4</sub> as the reductant and CTAB as the capping agent at (a) 100 °C and (b) 150 °C for 12 h.

 Table 1

 The reaction conditions for each chemical system used.

Section	Capping agent	Reductant	Temperature (°C), time (h)
Fig. 2a	СТАВ	KBH4	180, 12
Fig. 2b	PEG 20000	KBH <sub>4</sub>	180, 12
Fig. 2c	SDBS	KBH4	180, 12
Fig. 3a	CTAB	$N_2H_4$	180, 12
Fig. 3b	CTAB	Zn	180, 12
Fig. 4a	CTAB	$N_2H_4$	180, 6
Fig. 4b	CTAB	$N_2H_4$	180, 24
Fig. 5a	CTAB	$N_2H_4$	100, 12
Fig. 5b	CTAB	$N_2H_4$	150, 12

## HgMa SeLb SeLa ntensity (a.u.) HaLa SeKa Sekh 2.00 4.00 6.00 8.00 10.00 12.00 14.00 15.00 KeV

Fig. 6. EDS spectrum of HgSe prepared in the presence of  $KBH_4$  as the reductant and CTAB as the capping agent at 180  $^\circ C$  for 12 h.

the reductant and CTAB as the capping agent at 180 °C for 12 h show that there exist only the elements Hg and Se, and the atomic ratio of Hg to Se in different areas is always 49.7:50.3, which indicates the pure HgSe phase in the rods. In addition, neither N nor C signals were detected in the EDS spectrum, which means no solvent or capping agent exists in the rod crystals.

In comparison to other similar works, illustrated in Table 2, our method is simple and has low cost and can be scaled-up. Also, we

Table 2		
Characterization comparison of H	Se nanorods with	other similar works.

Method	Precursors	Size	Morphology	Ref.
Chemical	Hg(NO <sub>3</sub> ) <sub>2</sub> ,	Thickness of	Thin film	[26]
Thermal	Na <sub>2</sub> SeSO <sub>3</sub> Cycloocteno-	0.8 µm Particles size	Nanoparticle	[27]
decomposition	1,2,3-	less than		
	mercury acetate	20 1111		
Sonochemical	Mercury acetate	Mainly 30– 40 pm	Nanoparticle	[28]
Sonochemical	Mercury nitrate, Se powder	Approximately 18 nm in size	Nanoparticle	[29]

have used non-toxic precursors and solvent. With this route, we have applied various capping agents and reductant types, which is rare in the preparation of HgSe nanorods. The sizes of the HgSe nanorods seem more convenient than in similar works.

#### 4. Conclusion

In summary, this work has demonstrated a new approach for the controllable growth of HgSe nanorods *via* reductant exchange (Table 1). This route to HgSe nanorods is simple, convenient and effective, and holds potential for the large-scale synthesis needed for commercial applications. Most important of all, this new approach can yield a rod-like morphology of HgSe directly, without mechanical crushing and sieving as is need for a solidified melt, which may result in enhanced thermoelectric properties being exhibited.

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#### References

- S.V. Gaponenko, Optical Properties of Semiconductor Nanocrystals, Cambridge University Press, New York, 1998.
- [2] M. Salavati-Niasari, M. Bazarganipour, F. Davar, J. Alloys Compd. 489 (2010) 530.
- [3] M. Salavati-Niasari, M. Bazarganipour, F. Davar, J. Alloys Compd. 499 (2010) 121.
- [4] M.D. Archer, A.J. Nozik, Fundamentals and Applications of Quantum-confined Structures. Nanostructures and Photoelectrochemical Systems for Solar Photon Conversion, Imperial College Press, London, UK, 2008. pp. 147–208.
- [5] A.D. Yoffe, Adv. Phys. 51 (2002) 799.

- [6] D.L. Klein, R. Roth, A.K.L. Lim, A.P. Alivisatos, P.L. McEuen, Nature 389 (1997) 699.
- [7] W.U. Huynh, J.J. Dittmer, A.P. Alivisatos, Science 295 (2002) 2425.
- [8] C.B. Murray, D.J. Norris, M.G. Bawendi, J. Am. Chem. Soc. 115 (1993) 8706.
- [9] J.E. Bowen Katari, V.L. Colvin, A.P. Alivisatos, J. Phys. Chem. 98 (1994) 4109. [10] M. Kuno, K.A. Higginson, S.B. Oadri, M. Yousuf, S.H. Lee, B.L. Davis, H.
- M. Kuno, K.A. Higginson, S.B. Qadri, M. Yousuf, S.H. Lee, B.L. Davis, H. Mattoussi, J. Phys. Chem. B 107 (2003) 5758.
   J. Zhu, S. Liu, O. Palchik, Y. Koltypin, A. Gedanken, J. Solid State Chem. 153
- (2000) 342.
- [12] H. Wang, J.-R. Zhang, J.-J. Zhu, J. Cryst. Growth 233 (2001) 829.
- [13] X.-H. Liao, J.-J. Zhu, H.-Y. Chen, Mater. Sci. Eng. B 85 (2001) 85.
- [14] Y. Li, Y. Ding, H. Liao, Y. Qian, J. Phys. Chem. Solids 60 (1999) 965.
- [15] J.-H. Zeng, J. Yang, Y.-T. Qian, Mater. Res. Bull. 36 (2001) 343.
- [16] D.J. Elliot, D.N. Furlong, F. Grieser, Colloids Surf. A 155 (1999) 101.
- [17] B.A. Korgel, H.G. Monbouquette, Langmuir 16 (2000) 3588.
- [18] M. Guglielmi, A. Martucci, J. Fick, G. Vitrant, J. Sol-Gel Sci. Technol. 11 (1998) 229.

- [19] M. Salavati-Niasari, F. Davar, M.R. Loghman-Estarki, J. Alloys Compd. 494 (2010) 199.
- [20] M. Salavati-Niasari, A. Sobhani, F. Davar, J. Alloys Compd. 507 (2010) 77.
- [21] M. Salavati-Niasari, D. Ghanbari, F. Davar, J. Alloys Compd. 492 (2010) 570.
- [22] M. Salavati-Niasari, M. Bazarganipour, F. Davar, A. Amini Fazl, Appl. Surf. Sci. 257 (2010) 781.
- [23] M. Salavati-Niasari, D. Ghanbari, F. Davar, J. Alloys Compd. 488 (2009) 442.
- [24] M. Salavati-Niasari, G. Hosseinzadeh, F. Davar, J. Alloys Compd. 509 (2011) 134.
- [25] A. Trifonova, M. Wachtler, M.R. Wagner, H. Schroettner, Ch. Mitterbauer, F. Hofer, K.-C. Möller, M. Winter, J.O. Besenhard, Solid State Ion. 168 (2004) 51.
- [26] P.P. Hankare, V.M. Bhuse, K.M. Garadkar, S.D. Delekar, I.S. Mulla, Mater. Chem. Phys. 82 (2003) 711.
- [27] N. Singh, K.R. Patil, P.K. Khanna, Mater. Sci. Eng. B 142 (2007) 31.
- [28] T. Ding, J.-J. Zhu, J.-M. Hong, Mater. Lett. 57 (2003) 4445.
- [29] M. Kristl, M. Drofenik, Ultrason. Sonochem. 15 (2008) 695.