PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 1, 01PCN09(3pp) (2012)

Simple Synthesis of Mercury Sulfide Nanstructures Via a One-Step Method

P. Ghaderi-Sheikhiabadi, M. Salavati-Niasari

Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317–51167, I. R. Iran

(Received 06 June 2012; published online16 July 2012)

High-quality and high-yield rod-like HgS dendrites with cubic structure was synthesized by a wet chemical route, without using any surfactant and organic solvents at 180°C for 5 h, by using $Hg(NO_3)_2.H_2O$ and thioglycolic acid (TGA) as starting reagents. The obtained HgS with different morphologies and sized were characterized by FT-IR, SEM, TEM, EDX, and XRD. The morphology of HgS nanostructures could be changed from rod-like dendrites to nanoparticles by only decreased temperature reaction to 110°C. The optical absorption results showed that HgS is considered as an important material in the field of optoelectronics

Keywords: Nanostructures, Mercury Sulfide, Hydrothermal, Semiconductors.

PACS numbers: 78.66.Db, 68.37.Lp

1. INTRODUCTION

HgS usually crystallizes in two forms: the cubic phase (b-HgS, metacinnabar) and the hexagonal phase (a-HgS, cinnabar). Recently, nanocrystalline chalcogenides are relatively scarce due to the high toxicity problem of mercury. Nevertheless, HgS is an useful material with wide application in many fields such as ultrasonic transducers, image sensors, electrostatic image materials, and photoelectric conversion devices [1, 2]. Also HgS is promising material for catalysts and infrared detectors, because of its narrow gap bond [3]. So far, various morphologies and architectures HgS nanostructures have been reported, such as nanoparticles [4, 5], tube-like particles [6], star-shape [7], rod-like particles [8]. Many efficient techniques were developed for preparing HgS, mainly two-step procedure at ambient temperature [2], sonochemical method [5], microwave method [6], Langmuir–Blodgett (LB) method [9], solid-state reaction at high temperatures [10], sol–gel procedure [11], gas reaction and so on. Yang and co-workers has recently developed a mild hydrothermal route to synthesize metal sulfides using of thioglycolic acids (TGA) as nontoxic template [12], and it reveals that TGA acts as an oriented growth reactant during above process. Herein, we present a one-step hydrothermal method which is milder, simpler, more practical, and environmentally friendly method than other methods. The trick in hydrothermal synthesis of HgS nanostructures presented here is the using of TGA as a sulfur source and stability agent which was previously used as the stability agent to prevent the chalcogenide nanocrystals from aggregating [13, 14].

2. METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

In a typical synthesis 1.46×10^{-3} mol $Hg(NO_3)_2.H_2O$ solution was puddled with 2.9×10^{-6} mol TGA solution at ambient temperature and under magnetic stirr. When solutions is dissolved together, the precipitate appeared because Hg^{+2} reacted with TGA to from complex ions $(HgS)_m(HgSCH_2COOH)_k^+$ in aqueous solution. The resulting homogeneous solution was transferred to a 250 ml Teflon-line stainless steel autoclave. The autoclave was sealed and maintained at 180°C for 5 h in a digital temperature controlled oven. The complex ions could be decomposed to form HgS at high temperature and pressure. After thermal treatment the resulting black precipitate was washed with distilled water and absolute ethanol to remove the possibly remaining any impurities, and finally dried before characterization.

SEM images were obtained on Philips XL-30ESEM equipped with an energy dispersive.

3. RESULTS AND DISCUSSION

The IR spectra (no reported in this article) of the HgS obtained at 180°C for 1 h exhibit many differences from the pure TGA, which should be due to the ordered alignment and regular conformation of TGA molecules in the precursors, while in liquid-state TGA the orientation and conformation of the molecules are randomized due to thermal perturbation. From the result of FT-IR analysis, it is suggested that the organic component - CH_2COOH should exist in the composite [15]. We believe that these results, the whole process can be expressed as follows;

$$HSCH_2COOH + Hg^{+2} \rightarrow HgHS^+ + CH_2COOH^+$$

$$HgHS^+ \rightarrow HgS + H^+$$

$$mHgS + kHSCH_2COOH + kHg^{+2} \rightarrow$$

$$\rightarrow (HgS)_m(HgSCH_2COOH)^{+k} + kH^+ \rightarrow HgS$$

Series of reaction parameters were investigated for a better understanding of the crystal growth mechanism. When the molar ratio of reactants is near the stoichiometric ratio (1:1), rod-like HgS dendrite produced (Fig. 1a). For the dendrites of HgS, when the molar ratio of reactants increased to 1:2, 1:4 and 1:6 cannot cause the further increase of their size but lead to the destruction of dendritic patterns and three patterns nanoparticle, flower-like and rod-like HgS particle formation (Fig. 1b, c and d).

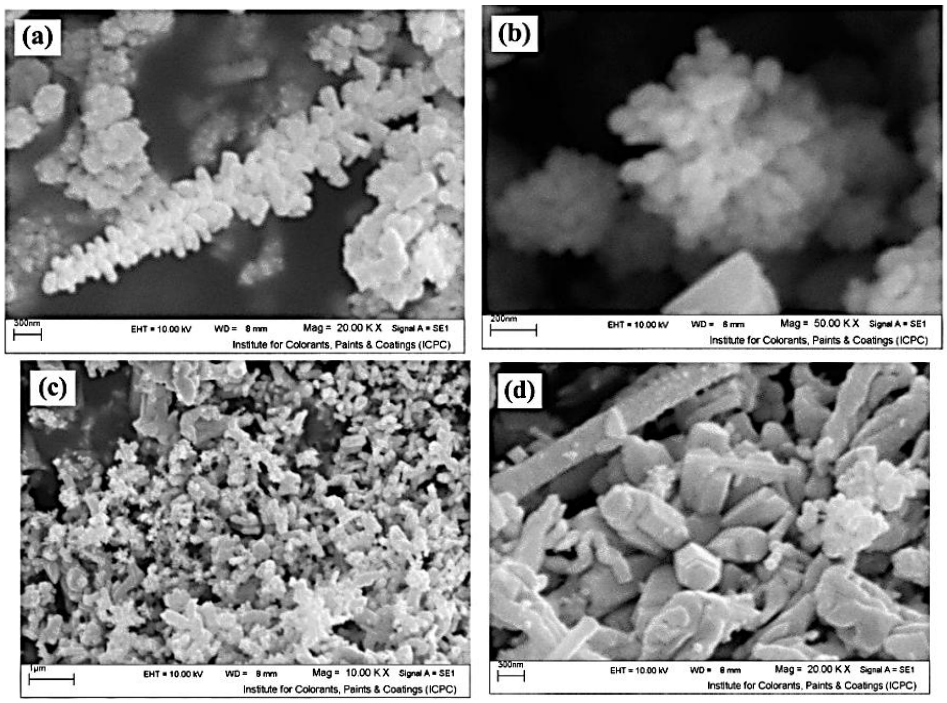

Fig. 1 – SEM images of HgS samples obtained at 180 °C for 5 h with atomic ratio of Hg:S: (a) 1:1, (b) 1:2, (c) 1:4, and (d) 1:6.

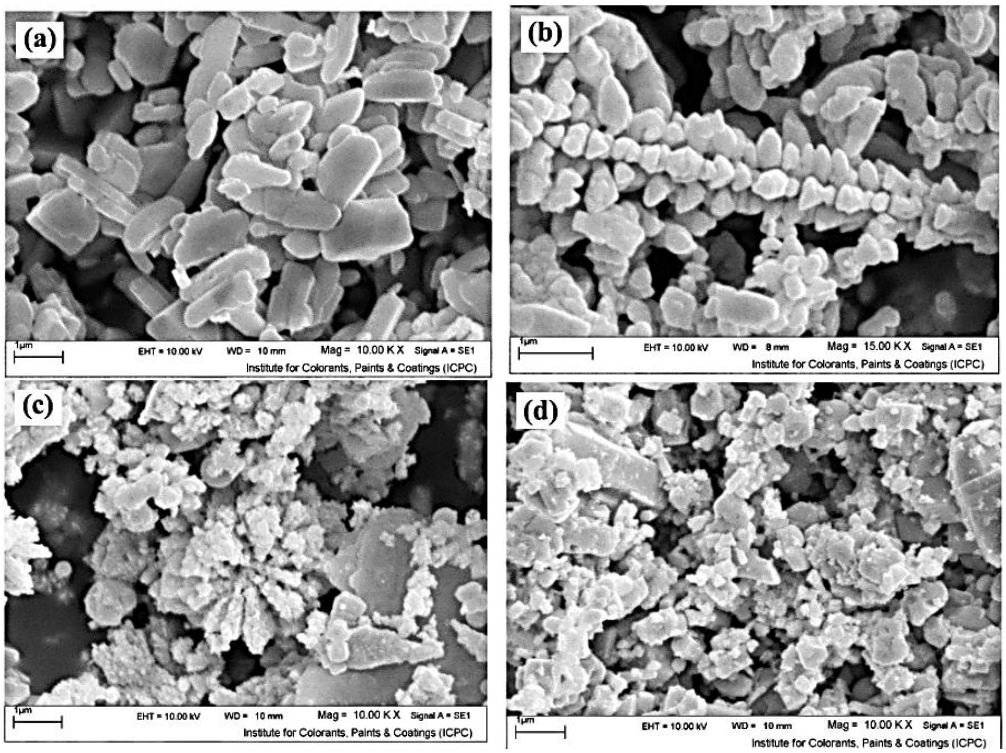

Fig. 1 – SEM images of HgS samples obtained to using $Hg(NO_3)_2$-H_2O and TGA with atomic ratio of Hg:S is 1:2 at 5 h for: (a) 150 °C, (b) 110 °C, (c) sample obtained with atomic ratio of Hg:S 1:2 at 180 °C for 18 h.and (d) 24 h

The flower-like structure were presumed to be the intermediate states of particle to dendrite transition. The dendrietes formed through the crystallization of the aggregates that fused gradually into one crystal. The XRD pattern (no reported in this article) can be indexed as cubic HgS with calculated lattice parameters of a = 5.851 Å, which agree well with the reported values for HgS (JCPDS Card No. 06-0261) [4, 6]. By the use of Debye-Scherrer equation crystallite sizes of products were estimated and results indicated: 39.9 nm. If the reaction proceeds at 150°C, more dendrites can be found (Fig. 2a) When the raw materials react at 110°C for 5 h, no there is any dendrites patterns (Fig. 2b) For the preparation of HgS irregular structures, the crystallization time should be prolonged up to 18 and 24 h (Fig. 2c and d).

4. CONCLUSIONS

In summary, we report a simple convenient and efficient method for the morphology control (nanoparticle, rod-like, and dendrites) of HgS by a hydrothermal method in the ranges of 110-180°C for 5-24 h. Mercury sulfides are promising materials for catalysts and infrared detectors when coated with Rh or used alone.

ACKNOWLEDGEMENTS

Authors are grateful to Council of University of Kashan for providing financial support to undertake this work.

REFERENCES

1. N. Tokyo, *Appl. Phys.* **461**, 4857 (1975).
2. S.S. Kale, C. D. Lokhande, *Mater. Chem. Phys.* **59**, 242 (1999).
3. A. M. Fernandez, M.T.S. Nair, P.K. Nair, *Mater. Manuf. Process* **8**, 535 (1993).
4. D.Z Qin, X.M. Ma, L. Yang, L. Zhang, *Nanopart. Res.* **10**, 559 (2008).
5. M. Kristl, M. Drofenik, *Ultrason. Sonochem.* **15**, 695 (2008).
6. M. Shao, L. Kong, Q. Li, W. Yu, Y. Qian, *Inorg. Chem. Commum.* **6**, 737 (2003).
7. X. Changqi, Z. Zhicheng, Y. Qiang, *Mater. Lett.* **58**, 1671 (2004).
8. J. Zhang, Z. Chen, Z. Wang, N. Ming, *Mater. Res. Bull.* **39**, 2241 (2004).
9. C. Zylberajch, *Synth. Met.* **27**, 609 (1988).
10. O. Toshikazu, S. Yoshio, N. Susumu, *Jpn. Appl. Phys.* **9**, 840 (1970).
11. M. Guglielmi, A. Martucci, *Sol-Gel. Sci. Technol.* **11**, 229 (1998).
12. H. Zhang, D. Yang, S. Li, Y. Ji, X. Ma, D. Que, *Nanotechnology* **15**, 1122 (2004).
13. M. Salavati-Niasari, M.R. Loghman-Estarki, F. Davar, *Alloy. Compd.* **475**, 782 (2009).
14. M. Salavati-Niasari, D. Ghanbari, F. Davar, *Alloys. Compd.* **492**, 570 (2010).
15. M. Salavati-Niasari, M.R. Loghman-Estarki, F. Davar, *Chem. Eng.* **145**, 346 (2008).
16. L. Wu, Y. Wu, W. Lü, *Physica E* **28**, 76 (2005).

.