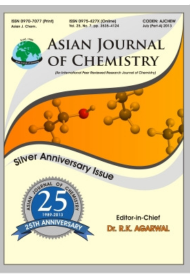
Asian Journal of Chemistry; Vol. 25, No. 11 (2013), 5904-5906

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13240



Synthesis of Nano-Structured HgS by Sol-Gel

LEILA KHARGHANIAN[1] and ALI MOGHIMI[2,*]

[1]Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2]Department of Chemistry, Varamin (Pishva) Branch, Islamic Azad University, Varamin, Iran

Corresponding author: E-mail: alimoghimi@iauvaramin.ac.ir

(*Received*: 26 May 2012; *Accepted*: 16 April 2013) AJC-13364

The main focus is laid on the sol-gel synthesis is opening a wide window toward nano-scopic metal sulfides with remarkable properties different from that of crystalline metal sulfides. Nanocomposites HgS/SiO_2 has been prepared by the sol-gel method starting from methyltriethoxysilane (MTEOS) precursors as the SiO_2 sources and mercaptopropyltrimethoxysilane (MPTMS) as the capping agent. The average diameter of HgS particles in the nano-composite materials can be controlled by the cadmium concentration and thermally treatment. The dried gel was treated at increasing temperatures, The crystallinity, shape and size of the metal sulfide nanocrystals were investigated by X-ray diffraction and transmission electron microscopy. The result indicates that the formation and the stability of the mercury sulfide phases are strongly affected by the precursors used as the mercury sources.

Key Words: Nano-structured Hg sulfides, Mercury sulfide in silica matrix, Sol-gel, Properties.

INTRODUCTION

In recent years there has been an increased interest in the use of nano-composites for different applications because it is easier to achieve homogeneity in thin layers with such materials. Among the nano-composite processing techniques, sol-gel process is one of the technologies for the development of nanostructure materials, thin layer coating, nanopowders, fibers and thin films because the method can produce high homogeneity at low synthesis temperatures[1-3].

Significant variations in the properties of these materials, which can differ greatly from the components in their pure form or from composites in which both of the phases have macroscopic dimensions. Nanostructure materials developed *via* sol-gel process have been used for a variety of applications. These applications include for electrically conductive applications, holographic memory and protective coatings[4-9].

Semiconductor nanocrystals in transparent media have received a large attention due to their promising applications in nonlinear optics and optical switches. In the other hand due to their small size and large specific surface area, nanoclusters exhibit electronic and optical properties that are different from those of bulk semiconductors. For a semiconductor crystal, electronic excitation consists of a loosely bound electron-hole pair (*i.e.* exciton), usually delocalized over a length much longer than the lattice constant. Thus one can prepare white mercury sulfide (HgS) instead of orange bulk HgS and yellow-brown lead sulfide (PbS) instead of black bulk PbS.

The sol-gel method has revealed the formation of the HgS nanoparticles in organic polymers or in silica matrixes[10-12]. Such organic-inorganic hybrids prepared by sol-gel process show unique mechanical properties such as high ductility, low elastic modulus and high mechanical strength[13]. The porous amorphous matrices, within which nanostructures are developed, play an active role in determining their physical properties in addition to providing a means of particle dispersion. It provides the sites for nucleation of the cadminm sulfide particles and minimizes their aggregation[14,15]. It is well known that the structure and composition of nanosulfides formed by sol-gel method depend on the preparation condition, the nature of the precursors, the ion source and pH. The properties of the hybrid materials could be tuned through the functionality or segment size of each component[16].

Siloxanes doped with semiconductor nanoparticles have been prepared by a method that combines sol-gel and colloidal chemistry. A relatively simple method has been set up with the specific goal of depositing doped HgS in siloxane matrice.

EXPERIMENTAL

Sulphide nanoparticles were produced by reaction of metal acetates and nitrates in methanol with thioacetamide (CH_3CSNH_2), and control of particle size was achieved by using mercaptopropyltrimethoxysilane (MPTMS) as the capping agent and methyltriethoxysilane (MTEOS) as the silica precursor. The reaction of mercuric acetate with thioacetamide is already quite fast at room temperature and the product is the corresponding sulphide. Immediately after the addition of thioacetamide the methanol solution of the mercury acetate turns white, yellow and rapidly evolves to orange give a precipitate which accumulates on the bottom of the reaction vessel. If mercaptopropyltrimethoxysilane is added to thioacetamide and then to the mercury acetate solution the liquid remains colourless for some seconds, then slowly turns white and changes colour at a rate and to an extent that is inversely proportional to the value of the MPTMS/thioacetamide molar ratio. In fact, the use of mercaptopropyltrimethoxysilane as a capping agent allows one to obtain a narrower size distribution.

A silica solution was obtained by mixing methyltriethoxysilane (MTEOS) in ethanol together with water and HCl The relative molar ratio of each chemical in the sol is MPTMS: EtOH:H_2O:HCl = 1:3:6:5. The use of methyltriethoxysilane as precursor reduces stresses developed during drying and allows one to obtain thicker films without cracks[17].

After stirring mercury acetate and mercaptopropyltrimethoxysilane for 40 min at 60 ºC, thioacetamide (5 mol %) was added dropwise and silica solution was added to the mixture and was vigorously stirred for 0.5 h.

Then, the HgS-siloxane mixed gel were further treated with the hydrothermal processing at the temperatures of 120 ºC for 12 h. The resultant dried solid was heated to 550 ºC at the heating rate of 1 ºC/min and then calcined at 550 ºC in air for 6 h.

Micro-structural characterization was carried out in a transmission electron microscopy (TEM) To determine crystalline phases of the nanocomposite XRD patterns were obtained by the powder method. The average primary particle size was also estimated from the XRD pattern using the X-ray line broadening analysis[18].

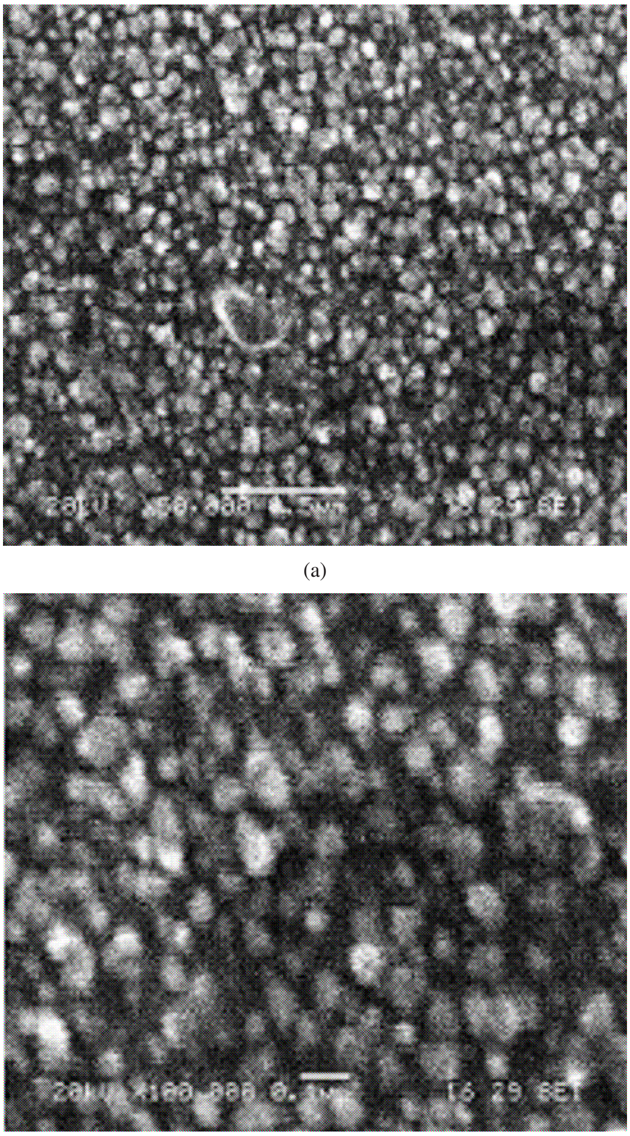
RESULTS AND DISCUSSION

The influence of the salts source on the properties of the prepared nanocomposites is also evidenced in Fig. 1a and 1b, which presents the TEM micrographs of the samples. It is observed that the samples were both made up of particles with sizes in nanometer range.

The growth of HgS particles may occur into hexagonal or cubic cells, which might lead to grown particles of different shapes. The experimental results obtained strongly indicate that the methodology employed favoured the formation of particles with cubic lattices.

HgS grown from their respective acetate salt (Fig. 1b) are larger than when grown from their nitrate salt (Fig. 1a) This size difference can be clearly observed in low magnification electron micrographs. As controls, HgS was also grown in aqueous environments from both the nitrate and acetate precursors. The reason may be that the by product of the synthesis from the nitrate salt is nitric acid, whereas the byproduct of the synthesis from the acetate salt is acetic acid. Nitric acid is a much stronger acid and apparently enables the siloxane phase to reform faster around the template during growth so as to remove any structural defects.

Fig. 2 shows XRD patterns of the HgS/SiO_2 nanocomposite particles. The broad reflections in the XRD pattern, confirm the formation of cubic HgS nanoparticles. While several other peaks are observed at these peaks are associated to the presence of HgS nanocrystals.


(a)

(b)

Fig. 1. Transmission electron micrographs of HgS from their respective (a) nitrate (b) acetate salts and H_2S

Development of the HgS cubic phase which was thermodynamically more stable was hindered by co-existence of SiO_2 component, indicating some kind of interaction being between both components. The average grain size of HgS/TiO_2 primary particles estimated from the X-ray line broadening analysis by the Sherrer equation.

The size of the nanocrystals (diameter D) was determined from the full-width-at-half-maximum (B) of the (111), (220) and (311) peaks by using the Debye-Scherrer formula

$$D = \frac{k\lambda}{(B\cos\theta)}$$

where D is the crystallite size that has been calculated for mercury nitrate precursor for nano-structured HgS. was between 18 and 24 nm. The sizes of the evolving nanocrystals depend mainly on the concentration ratios of the chemicals involved and on the duration of the heat treatment.

Fig. 2 showed that the powder X-ray diffraction patterns (XRD) HgS nanocrystals. To confirm the structure, a XRD pattern was simulated for the cubic HgS crystal structure (broken curve in Fig. 2) which compares well with the observed patterns.

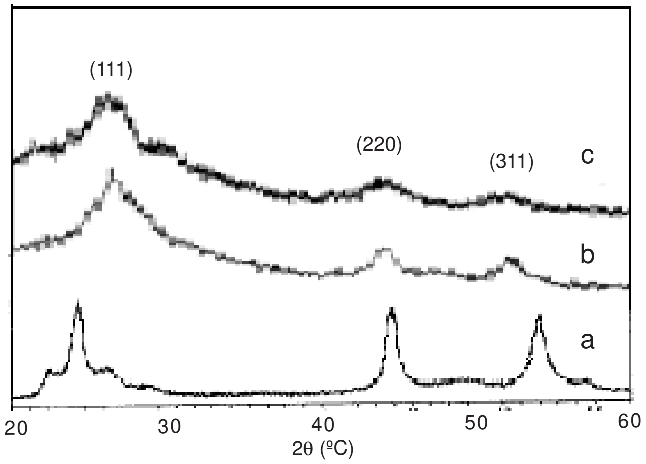


Fig. 2. X-ray diffraction patterns for (a) pure HgS (b) HgS/SiO_2 with acetate precursor c: HgS/SiO_2 with nitrate precursor

Conclusion

The above discussion should demonstrate the success of some of the soft-chemical routes in preparing nanocomposites and related structures of semi-conducting metal sulfides. In particular, the use of new reagents and precursors has yielded excellent results. What is interesting is the simplicity of the synthesis and good quality of the nanocrystals in the soft-chemical methods.

The ability to define the structure of hard minerals such as a semiconductor with soft organic structures at room temperature provides a new methodology for the formation of interesting nanostructures. This strategy is a potential source of new properties using controlled syntheses.

The results obtained with XRD and TEM of HgS nanoparticles grown in aqueous suspension show that our experimental methodology produces nanoparticles predominantly grown in a hexagonal lattice. Also the nature of the acetate and nitrate precursors in determination and controling the size of the nanocomposites was shown.

REFERENCES

1. B.R. Mattes, E.T. Knobbe, P.D. Fuqua, F. Nishida, E.W. Chang, B.M. Pierce, B. Dunn and R.B. Kaner, *Synth. Metals*, **43**, 3183 (1991).
2. H. Krug and H. Schmidt, *New J. Chem.*, **18**, 1125 (1994).
3. V. Mehrotra and E.P. Giannelis, *Solid State Ion.*, **51**, 115 (1992).
4. J.D. Mackenzie, Hybrid Organic-Inorganic Materials: The Sol-Gel Approach, In Hybrid Organic-Inorganic Composites, American Chemical Society, Washington D.C., Vol. 585, p. 226 (1995).
5. J.E. Mark, *Polym. Eng. Sci.*, **36**, 2905 (1996).
6. E.J.A. Pope, M. Asami and J.D. Mackenzie, *J. Mater. Res.*, **4**, 1018 (1989).
7. V. Mehrotra, J.L. Keddie, J.M. Miller and E.P. Giannelis, *J. Non-Cryst. Solids*, **136**, 97 (1991).
8. P. Cheben and M.L. Calvo, *Appl. Phys. Lett.*, **78**, 1490 (2001).
9. A.E. Stiegman, H. Eckert, G. Plett, S.S. Kim, M. Anderson and A. Yavrouian, *Chem. Mater.*, **5**, 1591 (1993).
10. S. Onodera, H. Kondo and T. Hawana, *MRS Bull.*, **21**, 35 (1996).
11. C.R.F. Lund and J.A. Dumesic, *J. Phys. Chem.*, **86**, 130 (1982).
12. L. Nixon, C.A. Koval, R.D. Nobl and G.S. Staff, *Chem. Mater.*, **4**, 117 (1992).
13. Q. Chen, F. Miyaji, T. Kokubo and T. Nakamura, *Biomaterials*, **20**, 1127 (1999).
14. C. Cannas, D. Gatteschi, A. Musinu, G. Piccaluga and C. Sangregorio, *J. Phys. Chem. B*, **102**, 7721 (1998).
15. G. Ennas, A. Musinu, G. Piccaluga, D. Zedda, D. Gatteschi, C. Sangregorio, J.L. Stanger, G. Concas and G. Spano, *Chem. Mater.*, **10**, 495 (1998).
16. S.-T. Hwang and Y.-B. Hahn, *Colloids Surf. A*, **259**, 63 (2005).
17. I. Fortunati, R. Signorini, R. Bozio, G. Brusatin and M. Guglielmi, *J. Non-Cryst. Solids*, **354**, 3317 (2008).
18. D.C. Bradley, R.C. Mehrotra and D.P. Gaur, Metal Alkoxides, Academic Press, New York, p. 150 (1978).