

## A Facile Method to Prepare Ag<sub>2</sub>S/SiO<sub>2</sub> Nanocomposite with Predictable Morphologies

M. Sadjadi, H. Mossalayi and K. Zare

Department of Chem., Faculty of Science, Science and Research Campus,  
Islamic Azad University Tehran, Tehran, Iran

**Abstract:** In this study, Silver sulfide (Ag<sub>2</sub>S) nanoparticles embedded in SiO<sub>2</sub> matrix were obtained by the sol-gel method with different concentration of precursors and were calcined at 550°C. This method has been used to achieve good control over composition and morphology of the products. The calcined Ag<sub>2</sub>S/SiO<sub>2</sub> powders were characterized by Transmission electron microscopic (TEM) analysis, X-ray powder diffraction (XRD) and Scanning electron microscopy (SEM) respectively. The XRD results indicated that the synthesized Ag<sub>2</sub>S nanoparticles had a pure monoclinic acanthite structure. And a fraction of nano-sized Ag<sub>2</sub>S powders were in the form of aggregates, which was also verified by SEM and TEM image. In addition, both the SEM image and the TEM photograph demonstrated that the nano-sized Ag<sub>2</sub>S particles were of a pseudo-hexagonal shape.

**Key words:** Ag<sub>2</sub>S /SiO<sub>2</sub> • Nanocomposite • Thioacetamide • Silver sulfides crystallites • Semiconductor materials • Morphology

### 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 [1-4]. Among the nano-composite processing techniques, sol-gel process is one of the most used technologies for the development of nanostructure materials, thin layer coating, nanopowders, fibers and thin films [5-7].

There are 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, includes electrically conductive materials, holographic memory and protective coatings [4-9].

The control of crystal shapes, in addition to their sizes and the higher surface-to volume ratio, provides more key factor to manipulate the properties of nanocrystals.

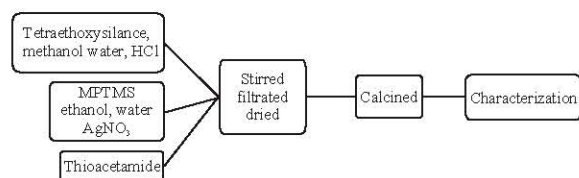
The sol-gel method has revealed the formation of the Ag<sub>2</sub>S nanoparticles in organic polymers or in silica matrixes [10-12]. Such inorganic-inorganic hybrids prepared by sol-gel process show unique mechanical properties such as high ductility, low elastic modulus and high mechanical strength [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 silver 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].

In the present work, a sol-gel method was employed to synthesize nano-sized Ag<sub>2</sub>S particles using different concentration of precursors which were different from those used in literatures. The structural characteristics of these nano-sized Ag<sub>2</sub>S particles such as the morphology, crystal type, crystal size, particle shape, degree of agglomeration were determined by XRD, SEM and TEM analysis, respectively.

### Experimental Procedure and Details

**Chemicals:** All chemicals were of analytical grade and used as received without further silver nitrate (Aldrich, 99%), Tetraethoxysilan (TEOS) (Fluka, 98%), mercaptopropyl trimethoxysilane (MPTMS) (Fluka, 97%), thioacetamide (TA) (BDH, 98%) and methanol (BDH, 99%) were used as the starting ingredients.



Scheme 1:

**Synthesis:** The synthetic procedures for the  $\text{Ag}_2\text{S}/\text{SiO}_2$  nanocomposite are briefly summarized in Scheme 1. Synthesis of  $\text{Ag}_2\text{S}/\text{SiO}_2$  nanocomposite was carried out by sol-gel technique through the following steps:

- In a dry nitrogen atmosphere, a mixture of 9.6 mMol of Tetraethoxysilane (TEOS), 2ml of methanol, 26.4mmol of water and 3 drops HCl (0.1M) was prepared.
- After stirring the solution for 30 min at  $30^\circ\text{C}$ , a mixture of 12 mMol of MPTMS with 13.9 mmol ethanol, 28.8 mmol water and 1.5 mmol of  $\text{AgNO}_3$  were added and stirred for 10 min .
- In order to obtain  $\text{Ag}_2\text{S}/\text{SiO}_2$  nanocomposite, 1.5 mmol of thioacetamide was added dropwise to the above cited solution and the mixture was vigorously stirred for 30 min at  $60^\circ\text{C}$ .
- The filtrate was dried and heated at  $80^\circ\text{C}$  for 24 h. The precursors were calcined at a temperature of  $550^\circ\text{C}$  for 6 h.
- with the same procedure 6/1, 4/1 and 2/1 portions of mercapto/silver nitrate were made too.

**Characterization:** The Powder X-ray diffraction (XRD) pattern was recorded on a Seisert Argon 3003 PTC using nickel-filtered XD-3a  $\text{CuK}\alpha$  radiations ( $\lambda=0.1542\text{ nm}$ ). The morphology and particle size of the nano-sized  $\text{Ag}_2\text{S}$  particles were also analyzed by a scanning electron microscope (SEM, JXA840). SEM photographs for the nano-sized  $\text{Ag}_2\text{S}$  particles were recorded (LEO 435) at 30 kV from samples covered with a gold thin film. The morphology and structure of the  $\text{Ag}_2\text{S}$  nano-sized powders were further investigated by transmission electron microscope (TEM). TEM (Philips EM208) were operated at 100 kV.

## DISCUSSION

The X-ray phase analysis of the samples prepared is given in Fig. 1 All peaks can be indexed to monoclinic acanthite  $\text{Ag}_2\text{S}$  and no impurities can be detected in those patterns, indicating that crystalline  $\text{Ag}_2\text{S}$  is formed from solution at room temperature. From the patterns of sample (a-d), no peak of  $\text{SiO}_2$  was detected, suggesting that  $\text{SiO}_2$  was amorphous. And the peak of  $\text{Ag}_2\text{S}$  intensified with the concentration of the MPTMS used.

The broadening of these diffraction peaks indicates that the sample is nanosized. some peaks in the XRD patterns show different intensity ratios because of the diverse morphologies of samples. The crystalline size of  $\text{Ag}_2\text{S}/\text{SiO}_2$  nanoparticles determined by the Scherrer equation is mentioned in Table 1. the results shows that as the capping agent concentration (MPTMS) decreases the size of the nanoparticles increases with different degrees.

Table 1 size of  $\text{Ag}_2\text{S} / \text{SiO}_2$  nanoparticles prepared with MPTMS/ $\text{AgNO}_3$  molar ratio of (a) 8/1, (b) 6/1, (c) 4/1 and (d) 2/1

| Particle size (nm)<br>MPTMS/ $\text{AgNO}_3$ 2/1 | Particle size (nm)<br>MPTMS/ $\text{AgNO}_3$ 4/1 | Particle size (nm)<br>MPTMS/ $\text{AgNO}_3$ 6/1 | Particle size (nm)<br>MPTMS/ $\text{AgNO}_3$ 8/1 | hkl planes |
|--|--|--|--|------------|
| 32   | 26   | 26   | 23   | 101        |
| 27   | 23   | 22   | 20   | 110        |
| 26   | 26   | 21   | 21   | 111        |
| 28   | 28   | 22   | 20   | 012        |
| 27   | 27   | 22   | 19   | 112        |
| 26   | 21   | 21   | 21   | 120        |
| 30   | 24   | 24   | 21   | 121        |
| 30   | 22   | 24   | 21   | 103        |
| 28   | 25   | 22   | 20   | 031        |
| 29   | 23   | 23   | 19   | 200        |
| 26   | 23   | 21   | 19   | 202        |
| 27   | 27   | 22   | 18   | 014        |
| 28   | 26   | 22   | 19   | 213        |
| 25   | 25   | 20   | 18   | 141        |

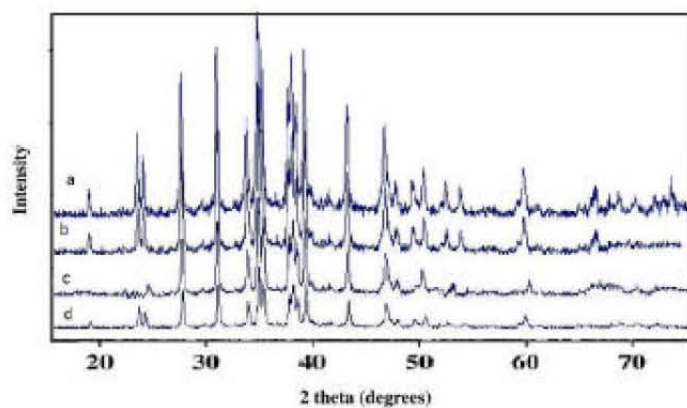


Fig. 1: XRD powder patterns of Ag<sub>2</sub>S /SiO<sub>2</sub> nanoparticles prepared with MPTMS/AgNO<sub>3</sub> molar ratio of (a) 8/1, (b) 6/1, (c) 4/1 and (d) 2/1

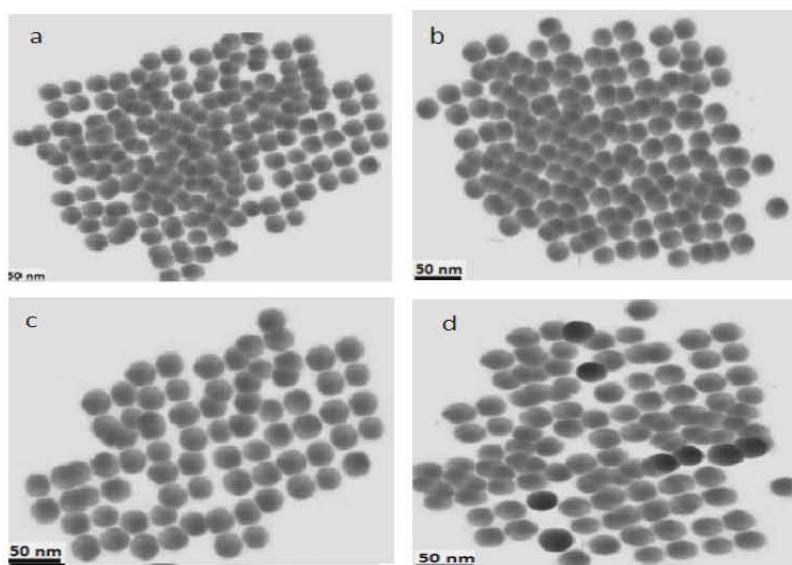


Fig. 2: TEM images of Ag<sub>2</sub>S /SiO<sub>2</sub> nanoparticles prepared with MPTMS/AgNO<sub>3</sub> molar ratio of (a) 8/1, (b) 6/1, (c) 4/1 and (d) 2/1

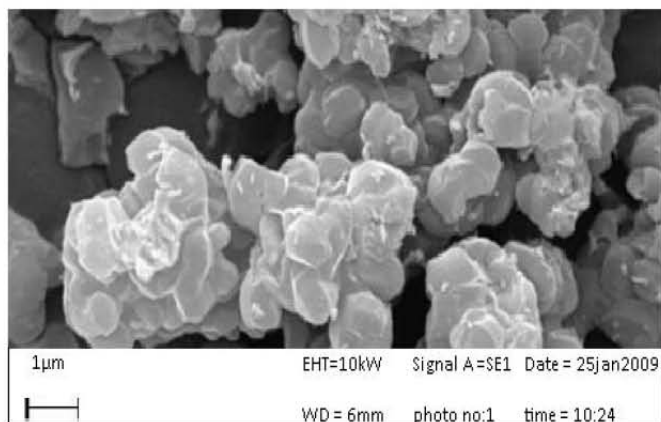


Fig. 3: SEM pattern Ag<sub>2</sub>S /SiO<sub>2</sub> nanoparticles prepared with MPTMS/AgNO<sub>3</sub> molar ratio of 8/1

TEM images (Fig 2) show that the products were successfully produced in a variety of shapes and sizes which are summarized in Table 1.

Nucleation and growth of the particles can play roles in the morphology. The crystal growth of some preferred structures or planes relates to the surface energy of the planes in the specified condition. It is described as the shape selective surface absorption process [18].

The amount of starting agents in the solution also has the influence on different orientation of the particles which reflects the nucleation and the growth of the crystals. The particle orientations were increased with the increase in the amount of starting agents [19].

Phase with the lowest free energy is thermodynamically stable and has more chance to exist in the process [20]. This reflects the product morphologies. Apart from the above, crystal growth is influenced by the solubility of the precursors in the particular solvent and synthesized temperature which reflects the morphologies.

The size of the nanocrystals generated appears to be dependent on a delicate balance between the surface-capping role, the size controlling role of MPTMS dominates. As such, smaller crystals are obtained when more capping agent is present (Fig. 3).

We have found that by increasing the MPTMS hexagonal Ag<sub>2</sub>S nanocrystals were obtained Exclusively (Figure-3 a, b and c). The diameter of these nanocrystals is mentioned in Table 1. While exclusive formation of hexagonal nanocrystals is obtained at molar ratio 8/1, 6/1 and 4.1, respectively, mixtures of Nanospheres and hexagonal nanocrystals is obtained in low mercapto Concentration at ratio 2/1.

SEM image (Fig. 3) shows that the product morphology for mercapto to silver nitrate ratio 8/1 nanoparticles are in the shapes of hexagonal.

## CONCLUSION

Controlling the shape of nanoparticles has been achieved employing appropriate capping agents in solutions. This method is more attractive owing to higher yield and simplicity. The above discussion should demonstrate the success of latter process in preparing Ag<sub>2</sub>S/SiO<sub>2</sub> nanocomposites and the related structures of semi-conducting metal sulfides. In particular, the use of new reagents and precursors can yielded excellent results. What was interesting is the simplicity of the synthesis method and good quality of the nanocrystals in the soft-chemical method.

We have described an unprecedented mercaptopropyl trimethoxy silane mediated reaction for preparing Ag<sub>2</sub>S/SiO<sub>2</sub> nanocomposites under mild conditions. By controlling the concentration ratio, a simple route that provides Ag<sub>2</sub>S nanocrystals of predictable size and shape is presented. Our preliminary investigations show that this general route can also be applied to the preparation of other chalcogenide nanocrystals.

it was conceivable that SiO<sub>2</sub> operated as a very effective protective matrice for the preparation of Ag<sub>2</sub>S nanoparticles. The sol-gel method has been shown to be a suitable procedure for controlling the size of the metal sulfide particles.

## REFERENCES

1. Goldstein, A.N., C.M. Echer and A.P. Alivisatos, 1992. *Science*, 256: 1425.
2. Mitchell, K. And J.A. Ibers, 2002. *Chem. Rev.*, 102: 1929.
3. Heron, N., J.C. Calabrege, W.E. Garnet and U. Wang, 1993. *Science*, 259: 1426.
4. Yu, D. And Z. Bai, 1998. *Appl. Phys. Lett.*, 72: 3458.
5. Tans, S.J., M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs and C. Dekker, 1997. *Nature*, 386: 474.
6. Frank, S., P. Poncharal, Z.L. Wang and W.A. de Heer, 1998. *Science*, 280: 1744.
7. Alivisatos, A.P., 1996. *Science*, 271: 933.
8. Henglein, A., 1989. *Chem. Rev.*, 89: 1861.
9. Wang, Y. and N. Herron, 1991. *J. Phys. Chem.*, 95: 525.
10. Weller, H., 1993. *Adv. Mater.*, 5: 88.
11. Michael, H.H., M. Samuel, F. Henning, Q.Y. Hao, Y.W. Yi, K. Hannes, W. Eicke, R. Richard and D.Y. Pei, 2001. *Science*, 292: 1897.
12. Munoz, J.A., C. Gomez, A. Ballester, M.L. Blazquez, F. plex Gonzalez and M. Figueroa, 1998. *J. Appl. Electrochem.*, 28: 49.
13. Brelle, M.C. and J.Z. Zhang, 1998. *J. Chem. Phys.*, 108: 3119.
14. Kitaev, G.A., T.P. Bol'shchikova and T.A. Ust'yantseva, 1967. *Izv. Akad. SSSR. Neorg. Mater.*, 3: 1080.
15. Dhumure, S.S. and C.D. Lokhande, 1991. *Mater. Chem. Phys.*, 27: 321.
16. Dlala, H., M. Amlouk, S. Belgacem, P. Girard and D. Barjon, 1998. *Eur. Phys. J. Appl. Phys.*, 2: 13.

17. Liz, L.M., M. Giersig and P. Mulvaney, 1996. Langmuir, 12.
18. Biswas, S., S. Kar and S. Chaudhuri, 2007. J. Cryst. Growth, 299: 94.
19. Zhang, Y.C., X.Y. Hu and T. Qiao, 2004. Solid State Commun., 132: 779.
20. Sopunna, K., T. Thongtem, M. McNallan, S. Thongtem, 2004. Surf. Sci., 810: 566-568.