Synthesis of $AgBiS_2$ microspheres by a templating method and their catalytic polymerization of alkylsilanes†

Jiaqiang Wang,*[a] Xikung Yang,[b] Wenbing Hu,[a] Bin Li,[a] Jiangmei Yan[a] and Jinjin Hu[a]

Received (in Cambridge, UK) 16th July 2007, Accepted 3rd September 2007
First published as an Advance Article on the web 19th September 2007
DOI: 10.1039/b710832j

$AgBiS_2$ microspheres synthesized by using PEG as a template serve as active catalysts for the polymerization of an alkylsilane, $C_{18}H_{37}SiH_3$ with water to form silanols.

In recent years, I–V–VI ternary chalcogenide semiconducting compounds have been found to have special physical characteristics which can be applied in linear, nonlinear, optoelectronic, and thermoelectric devices as well as optical recording media.[1] Among these compounds, there has been much interest in $AgBiS_2$ due to its unusual electronic and magnetic properties. Traditionally, $AgBiS_2$ has been prepared through a solid-state reaction, a solid solution technique and a flux technique.[2] By contrast, the Tang and Xie groups have synthesized cubic phase $AgBiS_2$ nanorods by a direct low temperature polyol route[1b] and a solvothermal route.[1c] They also synthesized dendritic crystals of $AgBiS_2$ under microwave irradiation.[1d]

The development of a rational route to the multidimensional assembly of nano building blocks into desired structures is a significant challenge in the design of advanced nanodevices.[3] A variety of chalcogenide compounds with desired shape, morphology, and crystal phase were achieved by applying solution chemistry approaches.[4] More recently, the sphere organization of Bi_2S_3 nanorods directed by poly(ethyleneglycol) (PEG) linear polymer has been demonstrated.[5] One-dimensional $ZnIn_2S_4$ nanotubes and nanoribbons were also synthesized by a solvothermal method with pyridine as the solvent, while $ZnIn_2S_4$ solid or hollow microspheres were hydrothermally prepared in the presence of a surfactant such as cetyltrimethylammonium bromide (CTAB) or PEG.[6] However, the development of chemical methods suitable for the synthesis of a ternary chalcogenide with controlled shape and size still remains a major challenge. In particular, to the best of our knowledge, there has been no report on the synthesis and possible catalytic properties of $AgBiS_2$ microspheres.

On the other hand, there have been a few reports on the syntheses of siloxane polymers catalyzed by noble metal nanoparticles.[7] For instance, Klabunde and co-workers have demonstrated that uncapped gold nanoparticles can be employed as catalysts for the polymerization of alkylsilanes to one-dimensional siloxane nanowires, filaments, and tubes from $RSiH_3$ and water.[7a] More recently, we have demonstrated that poly(vinylpyrrolidone) (PVP)-capped silver spherical nanoparticles and nanorods can be used as catalysts for the polymerization of alkylsilanes to fabricate siloxane microspheres.[7b] In addition, Chauhan and Rathore have reported the regioselective synthesis of hybrid polysiloxanes achieved by Pt-nanocluster catalysis.[7c] Obviously, all these reports about the siloxane polymers were limited to noble metal nanoparticles catalysis. To the best of our knowledge, the polymerization of alkylsilanes by using ternary chalcogenide semiconducting compounds instead of noble metal nanoparticles as catalysts has not been exploited so far.

Herein, we report the synthesis of $AgBiS_2$ microspheres by using PEG as a template. More importantly, we found that $AgBiS_2$ can also catalyze the polymerization of alkylsilanes.‡

Fig. 1a shows XRD patterns of a $AgBiS_2$ sample prepared by using PEG as a template. In contrast to ref. 1*b* in which only a cubic phase of $AgBiS_2$ was obtained, in our system both the cubic Schapbachite (51.7%) and hexagonal phase Matildite (48.3%) $AgBiS_2$ were obtained. No characteristic peaks corresponding to Ag_2S or Bi_2S_3 were observed. The morphology of the prepared $AgBiS_2$ was further studied by scanning electron microscopy (SEM) (Fig. 1b). It reveals that the diameters of $AgBiS_2$ fibrous microspheres ranged from 1.5 to 4.0 µm (ESI,† Fig. SI-1). It has been reported that Bi_2S_3 microspheres prepared also with PEG are the secondary structures made from an aggregate of nanorods and discrete individual Bi_2S_3 nanorods can be clearly observed.[5] In contrast, a $AgBiS_2$ microsphere looks like a few stars intertwisted with very tiny fibers to form a fibrous spheroid. Moreover, it is hard to observe discrete individual $AgBiS_2$ nanorods; only significant aggregates of nanorods were observed by TEM (Fig. SI-2) even after the products were subjected to 30 min of

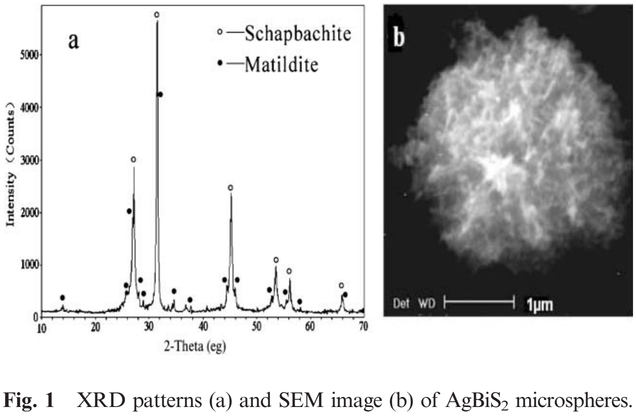

Fig. 1 XRD patterns (a) and SEM image (b) of $AgBiS_2$ microspheres.

---

[a] *Department of Applied Chemistry, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan University, Kunming 650091, P. R. China. E-mail: jqwang@ynu.edu.cn; Fax: +86-871-5031567; Tel: +86-871-5031567*
[b] *Research Center for Analysis and Measurement, Kunming University of Science and Technology, Kunming 650093, P. R. China*

† Electronic supplementary information (ESI) available: Detailed preparation of $AgBiS_2$ microspheres; characterizations; TEM of $AgBiS_2$ microspheres and SEM images of the products of Bi_2S_3 microspheres incorporated with and without silver nanorods, and the mixture of $AgBiS_2$–Bi_2S_3 microspheres with $C_{18}H_{37}SiH_3$; O1s XPS spectra of as-synthesized products. See DOI: 10.1039/b710832j

ultrasonic agitation in ethanol. Therefore, $AgBiS_2$ microspheres are robust enough to withstand vigorous ultrasonic treatment.

Very interestingly, similar to ref. 7*a*,*b*, refluxing $AgBiS_2$ with $C_{18}H_{37}SiH_3$ in the presence of small amounts of water resulted in a distinct difference in the morphologies of the products (Fig. 2) and smelly H_2S gas was also detected. It seems that those fibers twisting $AgBiS_2$ microspheres were untwisted and yielded microspheres consisting of some spindles radiating from a common origin (Fig. 2a) or these spindles were aggregated to form a big hole with a diameter of ~ 5 µm (Fig. 2b). Moreover, a few products looked like sisal hemps in lengths of ~ 16.8 µm (Fig. 2c).

To gain insight into the morphology change of the products, XRD, FTIR, and XPS were employed. Characterizations of the as-synthesized samples by XRD indicate that only $AgBiS_2$ and no crystalline SiO_2 was observed. This is in sharp contrast to ref. 7*a*,*b* in which gold nanoparticles and PVP-capped silver nanoparticles were used, respectively. In ref. 7*b* trace amounts of silver and silver oxide in addition to SiO_2 were observed by XRD when using only capped-silver nanoparticles as catalysts,[7b] while no peak other than that corresponding to SiO_2 was observed on using uncapped gold nanoparticles.[7a] It was only found that the intensity of XRD patterns of $AgBiS_2$ became weaker after the refluxing. This indicates the bulk crystalline $AgBiS_2$ was covered by the polymer film. Similar observations have been reported for silica-coated Bi_2S_3 nanorods.[8] Moreover, similar to those pure $AgBiS_2$ microspheres without adding $C_{18}H_{37}SiH_3$, even though the products experienced 30 min of ultrasonic agitation in ethanol, few discrete individual $AgBiS_2$ nanorods were observed by TEM (Fig. SI-3).

Furthermore, a pronounced change in intensity was noticed for the FTIR spectra in the Si–H stretching peak at 2150 cm^{-1}.[9] Fig. 3 shows that this band of Si–H bonds of $C_{18}H_{37}SiH_3$ at 2150 cm^{-1} almost disappeared after the polymerization. In addition, two bands at 2925 and 2854 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of CH_2 in alkyl chains, as well as a band at 1462 cm^{-1} assigned to CH_2 bending vibrations, are evident.[10] In correspondence with the XRD results, the peaks which represent the antisymmetric stretching vibration of Si–O–Si bonds are hardly observed. Importantly, the 928 cm^{-1} is clearly seen which corresponds to Si–O stretching of the silanol group. The very weak band which is observed at 3740 cm^{-1} is also regarded as characteristic of the silanol group.[11] This indicates that the surface binding of the polymer was not by siloxane but by silanol bonds. This is different from those reaction products of polymerizations catalyzed by noble metal nanoparticles which produced siloxane instead of silanol. Moreover, it is believed that the broad peaks at 3430 and 1716 cm^{-1} correspond to the surface-adsorbed water and hydroxyl groups.[12] The peaks observed at about 530 and 465 cm^{-1} are associated with the $AgBiS_2$ lattice vibrations.

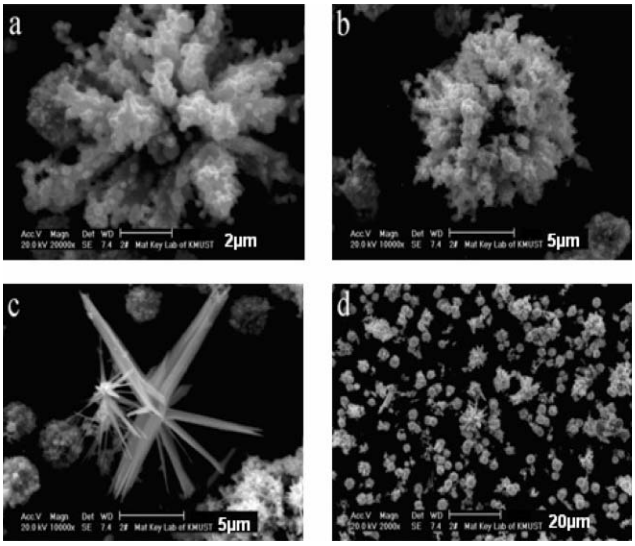

Fig. 2 SEM images of as-prepared samples by refluxing $AgBiS_2$ with $C_{18}H_{37}SiH_3$ in the presence of small amounts of water.

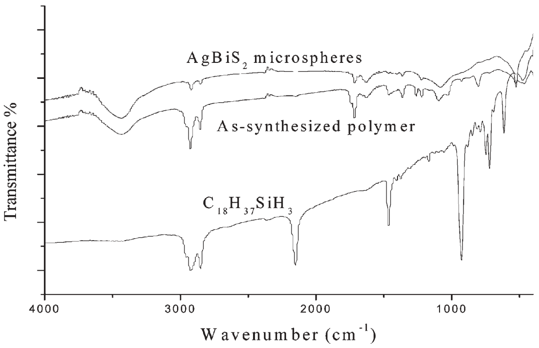

Fig. 3 FTIR spectra of $AgBiS_2$ microspheres, as-synthesized polymer, and $C_{18}H_{37}SiH_3$.

To study the surface nature of the as-prepared polymer sample, the sample was also characterized by an XPS procedure. The XPS results showed the presence of Ag, Bi, and S, as well as C and O. In spite of the overlap between the peaks of Bi $4f_{7/2}$ and S 2p, investigation of the surface of the polymer to a depth of 2–5 nm by XPS revealed that the concentration of S on the surface of the as-synthesized polymer is much lower than that of unreacted $AgBiS_2$ microspheres since the atomic ratio of Ag : Bi and Bi : S, calculated by using the integrated peak area and sensitivity factors, is about 1 : 1.2 and 1 : 1.5, respectively, close to the stoichiometric composition of Bi_2S_3, but smaller than the stoichiometric composition of $AgBiS_2$ which is in agreement with the observations of the formation of H_2S and the desolvation of fibrous microspheres to form sisal hemps. However, it is obvious that both Ag $3d_{5/2}$ (367.44 eV) and Bi $4f_{7/2}$ (157.97 eV) match exactly values reported in the National Institutes of Standards and Technology XPS database for only $AgBiS_2$ other than Ag_2S, Bi_2S_3, Ag, and Bi,[13] which is in accordance with XRD results. This was further proved by the following investigations: Refluxing Bi_2S_3 microspheres, Bi_2S_3 microspheres incorporating PVP-capped silver nanorods, and the mixture of $AgBiS_2$–Bi_2S_3 microspheres, respectively, with $C_{18}H_{37}SiH_3$ was also carried out in the presence of small amounts of water. Different morphologies from the products by reaction of $AgBiS_2$ were obtained (Fig. SI-4–7). Therefore, all these observations imply that only the defective $AgBiS_2$ with decreased surface sulfur did work as a catalyst for the polymerization.

Interestingly, the peaks in the Si 2p spectra of both unreacted $C_{18}H_{37}SiH_3$ and the as-synthesized polymer (Fig. 4) have been fitted to two components: one is Si–H (101.45 eV), the other is Si–OH (102.49 eV). The presence of Si–OH in unreacted $C_{18}H_{37}SiH_3$ is caused by the adsorbed water in the air which easily attacked the

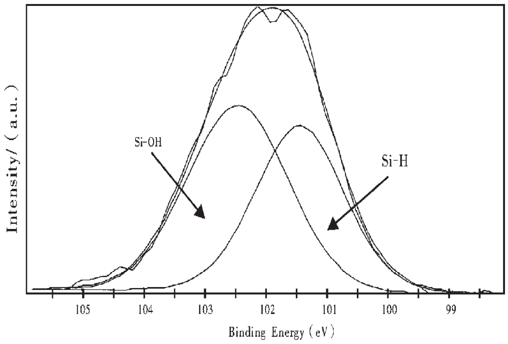

Fig. 4 Si 2p XPS spectrum of the as-prepared products.

Si–H to form Si–OH.[7a] However, in good agreement with observations by FTIR, the contribution of Si–H significantly decreased from 45% for unreacted $C_{18}H_{37}SiH_3$ to 26.4% for the as-synthesized polymer whereas the contribution of Si–OH significantly increased from 55% for unreacted $C_{18}H_{37}SiH_3$ to 73.6% for the as-synthesized polymer. Moreover, the O 1s spectra showed the as-synthesized contributions of three components (Fig. SI-8): the first one with 42.1% in contribution is Si–O (532.7 eV) or adsorbed water; the second one with 42.3% in contribution is hydroxyl groups (O–H) (531.7 eV); the third one with 15.6% in contribution may be caused by adsorbed O_2 (530.6 eV) due to the exposure to the atmosphere.

On the basis of characterizations and the observed structures, although the exact growth process of the products with different morphologies is not very clear, we may suggest that the formation of these products can be attributed to the $AgBiS_2$ microspheres catalyzing and orienting the growth of silanol polymers. This is because the control experiments were carried out when no $AgBiS_2$ microspheres were added to the solution and no formation of sisal hemps or any other well-defined structures was observed. Clearly, $AgBiS_2$ microspheres are crucial and work as catalysts for the polymerization. In support of the catalysis of $AgBiS_2$ are the reports that metal chalcogenide may be implied in the catalytic field, particularly in hydrodesulfurization reaction.[14] $AgBiS_2$ microspheres may have better catalytic performance due to their morphology of fibrous microspheres. When the alkylsilane is attached to the surface of $AgBiS_2$ microspheres, because the surface of the microspheres is more active than the bulk ones, alkylsilane loses hydrogen and $AgBiS_2$ microspheres lose sulfur, forming H_2S and weak Ag–Si and/or Si–Bi bonds.[15] These weak bonds and defective $AgBiS_2$ are easily attacked by water molecules, leading to the formation of $Si(OH)_x$.[7a] The $RSi(OH)_x$ molecules then react with themselves. Unlike those catalyzed by noble metal nanoparticles, the reaction catalyzed by $AgBiS_2$ produced silanol instead of siloxane, even SiO_2. Since the presence of surface silanols favors the coating on the surface of $AgBiS_2$, the silanol works as a "glue" which causes $AgBiS_2$ nanorods to stick at one point, leading to the observed structures. Similar morphology of hollow silica tubes synthesized by silica-coated Bi_2S_3 nanorods has been reported.[8]

In summary, $AgBiS_2$ microspheres were synthesized by using PEG as a template and their catalytic polymerization reaction involving alkylsilanes and water is reported. Products with novel morphologies are readily prepared through a simple reflux reaction. These findings further expand our knowledge on the catalytic polymerization of alkylsilanes.

This work was supported by the National Natural Science Foundation of China (Project 20463003) and the Natural Science Foundation of Yunnan Province (Project 2004E0003Z).

Notes and references

‡ Synthesis of $AgBiS_2$ microspheres: A modified process based on Ref. 5 and Ref. 1 is described in detail in the ESI. Polymerization of alkylsilanes: $AgBiS_2$ microspheres were used as catalysts in the polymerization of alkylsilanes. In a typical reaction, 165 mg microsphere catalyst and 10 μL water were put into 10 mL butanone, and 300 mg of $C_{18}H_{37}SiH_3$ were added to the above mixture, followed by refluxing at 90 °C for 4 h. After that, the reaction mixture was filtered under reduced pressure, and the acquired solid was washed with butanone and then dried at 40 °C. Characterizations are described in the ESI.

1 (*a*) L. K. Snmanta and S. Chatterjee, *Phys. Status Solidi B*, 1994, **182**, 85; (*b*) G. Shen, D. Chen, K. Tang and Y. Qian, *J. Cryst. Growth*, 2003, **252**, 199; (*c*) B. Li, Y. Xie, S. Yuan, Y. Jiang, J. Lu, Q. Li, Y. Wu, W. Yu, H. Zhang and Y. Qian, *Chem. Lett.*, 2002, **31**, 612; (*d*) D. Chen, G. Shen, K. Tang, X. Jiang, L. Huang, Y. Jin and Y. Qian, *Inorg. Chem. Commun.*, 2003, **6**, 710; (*e*) F. J. Disalvo, *Science*, 1991, **247**, 649; (*f*) W. S. Sheldrick and M. Wachhold, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 206.
2 (*a*) N. Wang, *Mineral. Mag.*, 1994, **58**, 201; (*b*) H. S. G. Kullerud, *Econ. Geol.*, 1959, **54**, 533; (*c*) G. H. Moh and L. A. Taylor, *Neues Jahrb. Mineral.*, 1971, **H9**, 405.
3 Y. Huang, X. F. Duan, Q. Q. Wei and C. M. Lieber, *Science*, 2001, **291**, 630.
4 (*a*) I. Gur, N. A. Fromer, M. L. Geier and A. P. Alivisatos, *Science*, 2005, **310**, 462; (*b*) L. Zhang, J. C. Yu, M. Mo, L. Wu, Q. Li and K. W. Kwong, *J. Am. Chem. Soc.*, 2004, **126**, 8116; (*c*) N. Duxin, F. Liu, H. Vali and A. Eisenberg, *J. Am. Chem. Soc.*, 2005, **127**, 10063; (*d*) Q. Peng, Y. Dong and Y. Li, *Angew. Chem., Int. Ed.*, 2003, **42**, 3027.
5 X. Zhou, S. Chen, D. Zhang, X. Guo, W. Ding and Y. Chen, *Langmuir*, 2006, **22**, 1383.
6 X. Gou, F. Cheng, Y. Shi, L. Zhang, S. Peng, J. Chen and P. Shen, *J. Am. Chem. Soc.*, 2006, **128**, 7222.
7 (*a*) B. L. V. Prasad, S. I. Savka, C. M. Sorensen, V. Zaikovski and K. J. Klabunde, *J. Am. Chem. Soc.*, 2003, **125**, 10488; (*b*) Q. Wei, B. Li, C. Li, J. Wang, W. Wang and X. Yang, *J. Mater. Chem.*, 2006, **16**, 3606; (*c*) B. P. S. Chauhan and J. S. Rathore, *J. Am. Chem. Soc.*, 2005, **127**, 5790.
8 S. F. Wang, F. Gu, Z. S. Yang, M. K. Lü, G. J. Zhou and W. G. Zou, *J. Cryst. Growth*, 2005, **282**, 79.
9 Y. Li and J. M. Buriak, *Inorg. Chem.*, 2006, **45**, 1096.
10 P. Wu and Z. Xu, *Ind. Eng. Chem. Res.*, 2005, **44**, 816.
11 K. A. Andrianov and B. A. Izmaylov, *J. Organomet. Chem.*, 1967, **8**, 435.
12 (*a*) T. Peng, D. Zhao, H. Song and C. Yan, *J. Mol. Catal. A: Chem.*, 2005, **238**, 119; (*b*) G. Soler-Illia, A. Louis and C. Sanchez, *Chem. Mater.*, 2002, **14**, 750; (*c*) J. C. Yu, L. Z. Zhang, Z. Zheng and J. C. Zhao, *Chem. Mater.*, 2003, **15**, 2280; (*d*) K. E. Karakitsou and X. E. Verykios, *J. Phys. Chem.*, 1993, **97**, 1184.
13 NIST X-ray photoelectron spectroscopy database http://srdata.nist.gov/xps/, last accessed 10th May 2007.
14 *Heterogeneous Catalysis in Practice*, ed. C. N. Satterfield, McGraw-Hill, Inc., New York, 1980, ch. 6, p. 180.
15 A. Marchenko, N. Katsonis, D. Fichou, C. Aubert and M. Malacria, *J. Am. Chem. Soc.*, 2002, **124**, 9998.