Low-temperature synthesis of ultrathin Sb_2S_5 nanofibers and their application as highly selective Pb-adsorbents in water†

Kang Hyun Park,[a] Jaewon Choi,[a] Jiseul Chun,[a] Hae Jin Kim[b] and Seung Uk Son*[a]

Received (in Cambridge, UK) 24th October 2007, Accepted 15th January 2008
First published as an Advance Article on the web 1st February 2008
DOI: 10.1039/b716378a

Ultrathin Sb_2S_5 nanofibers were prepared using a wet chemical method at 50 °C and applied as selective adsorbents of Pb ions in water.

The development of nanosized and nanoporous materials has resulted in a range of products with enhanced surface areas and diverse properties. For example, industrial heterogeneous nanocatalysts and efficient gas-storage materials have been actively developed.[1] Another important application area of nanomaterials is as adsorbent materials.[2] It is well recognized that adsorption phenomena are highly dependent on the surface physical and chemical properties of adsorbents.[2] Currently, diverse industrial nanofilters based on organic polymer nanofibers have been developed,[3] and a number of reports have been published on the use of sulfur-based inorganic porous adsorbents.[4] For example, mesoporous silica containing layers of thiol-terminated organic molecules on pore walls has been used to remove lead and mercury from water.[4a]

Metal chalcogenide nanomaterials are very important solid materials in the nanoscience area.[5] For the last two decades, diverse metal sulfide nanomaterials have been prepared, and studies performed on these have focused on their size- or shape-dependent physical properties. However, few reports are available on the applications of these materials as adsorbents.[6] It is well known that the surfaces of nanomaterials are thermodynamically unstable, because surface atoms are believed to have unsaturated dangling bonds. It might be expected that metal chalcogenide nanomaterials have applications as adsorbents due to their coordination abilities to transition metals using unsaturated surface sulfur atoms.

It has been reported that antimony sulfide can be used as a carrier of radioactive metals, like technetium, for radiopharmaceutical or assay purposes.[6] Our group has studied the shape controlled synthesis of semiconductor nanomaterials including the preparation of Sb_2S_3 nanotubes using antimony (III) chloride *via* aspect ratio control of nanoribbons at 175 °C.[7] We have turned our attention to another precursor, antimony (V) pentachloride, which is commercially available and a liquid at room temperature. This liquid precursor is highly reactive, and thus, allowed antimony sulfide formation at lower temperatures. It might be expected that antimony sulfide prepared using $SbCl_5$ would be more sulfur-rich than that prepared using $SbCl_3$. In this communication, we present the synthesis of ultrathin Sb_2S_5 nanofibers at low temperature (50 °C), and describe the application of these materials as selective adsorbents for the removal of Pb ions from water.

To prepare Sb_2S_5 nanofibers, $SbCl_5$ (0.10 mL, 0.79 mmol) was carefully added to well-dried oleylamine (7 mL) (*note*: $SbCl_5$ is highly hygroscopic and reacts vigorously with water to generate hydrogen chloride gas and antimony oxides). For successful preparation, water should be strictly excluded during the synthesis. The addition of $SbCl_5$ to oleylamine is exothermic and forms a black precipitate. After sonication for 2 hours, this precipitate completely dissolves in oleylamine to form a reddish brown colored solution, which was then slowly added to sulfur solution (0.126 g (3.94 mmol) of sulfur in 2 mL of oleylamine) at room temperature. The temperature of this mixture was then raised gradually to 50 °C over an hour. Interestingly, any rapid increase in reaction temperature resulted in gelation of the solution, which blocked further reaction. The reaction solution was then stirred at 50 °C overnight, during which the mixture became more viscous. The resulting solution was poured into methanol and the resultant precipitates were retrieved by centrifugation.

Fig. 1 shows a typical TEM image of the resultant nanofibers. Thicknesses were between 1–2 nm and lengths reached a few tens of micrometres. The described preparation was highly reproducible. After optimizing the above procedure, nanofibers were prepared reproducibly at least ten times in our lab. One interesting observation is shown in the inset in Fig. 1. The volume of the brown precipitates obtained by centrifugation

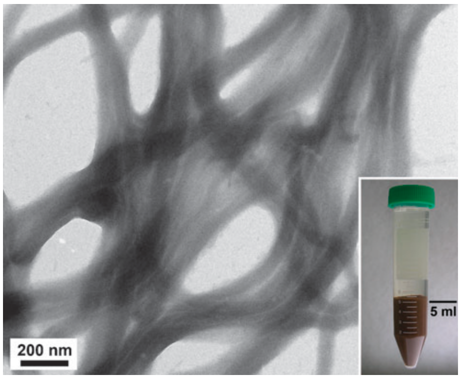

Fig. 1 Representative TEM image and picture (inset) of ultrathin antimony sulfide nanofibers.

---

[a] *Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: sson@skku.edu; Fax: +82-031-290-4572; Tel: +82-031-299-5932*
[b] *Korea Basic Science Institute, Daejeon 350-333, Korea*

† Electronic supplementary information (ESI) available: Additional TEM and SEM images, time-dependent adsorption behavior of nanofibers. See DOI: 10.1039/b716378a

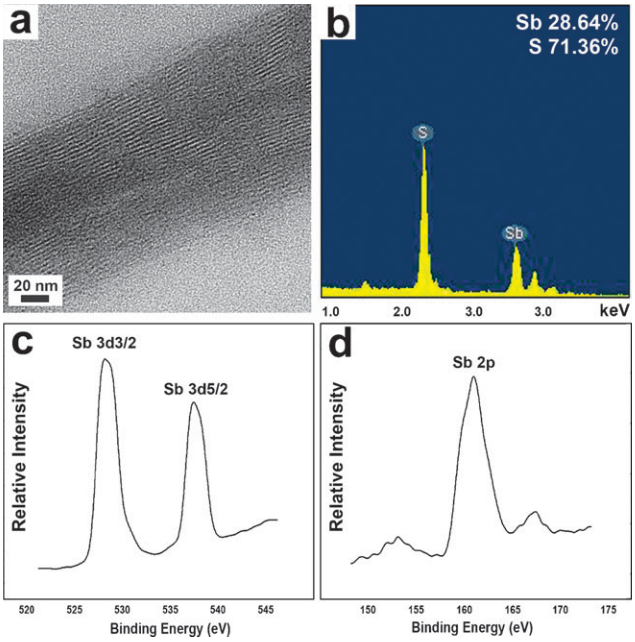

Fig. 2 HR-TEM image (a), EDS spectrum (b), Sb 3d orbital peaks (c), and S 2p orbital peak (d) in the XPS spectrum of Sb_2S_5 nanofibers.

was *ca.* 5 mL. Actually, this observation raised the issue of the use of these materials as adsorbents, because recently described superadsorbents like aerogel or hydrogels[8] have huge volume to weight ratios.

High-resolution TEM studies showed very thin lines along the length direction (Fig. 2a). However, powder X-ray diffraction studies showed no detectable peaks due to the diminutive thickness of the fibers. Energy dispersive X-ray spectroscopy (EDS) using FE-SEM showed a 1 : 2.49 ratio of antimony to sulfur as shown in Fig. 2b. The Sb 3d orbital peaks observed at 529.6 and 538.3 eV by X-ray photoelectron spectroscopy (XPS) were very close to reported values (529.4 and 538.7 eV for Sb_2S_5).[9]‡

During the optimization of the synthetic procedure, we observed the influences of the experimental conditions on the material obtained. Changing the molar ratio of sulfur to antimony changed fiber lengths. Nanofibers were formed when the molar ratio of sulfur to antimony was close to 2.5 (Fig. 3d and 3e), and when this was increased to 5, similar nanofibers were obtained (Fig. 3f). At a molar ratio of 1 short and irregular rod like materials were observed, as shown in Fig. 3a and S3 in ESI.† The thickness of these rods was about 3.5 nm. When the absolute concentration of antimony and sulfur was increased to double with a 1 : 1 ratio of sulfur to antimony, thinner (2.5 nm thickness) and longer (500–800 nm) sized wires were obtained as shown in Fig. 3b and 3c. Thus, the molar ratios and concentrations of these precursors critically determine the nature of the materials obtained. In addition, we found that reaction temperature is another important experimental factor, and that it should be kept low. At elevated reaction temperatures, *e.g.* 100 °C, large broom-like materials were formed.

Several types of polymer nanofibers have found applications as industrial air or water filters.[3,10] We hope that antimony sulfide nanofibers can also be used as transition metal adsorbents. In the literature, 3–30 nm spherical antimony sulfide particles have also been used as metal ion adsorbents.[11] To test the performances of nanofibers as adsorbents for metal ions in water, we prepared a model solution containing eight metal ions, *i.e.*, Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} or Pb^{2+}. Known amounts of metal nitrates were added to distilled water to prepare 1 L quantity of 100 ppm solution; by ionic coupled plasma-atomic emission spectroscopy (ICP-AES), the actual amounts of Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} in this model solution were 109, 106, 106, 101, 90, 99, 101, and 100 ppm, respectively. Sb_2S_5 nanofibers are hydrophobic due to the presence of organic surfactants on surface, and are insoluble though dispersible in water. In typical adsorption experiments, Sb_2S_5 nanofibers (0.5 g) were added to model solution (50 mL), and after stirring for 24 hours at room temperature, nanofibers were retrieved by centrifugation. The remaining aqueous solutions were directly analyzed by ICP-AES. Fig. 4 and S4† present the results of these adsorption experiments.

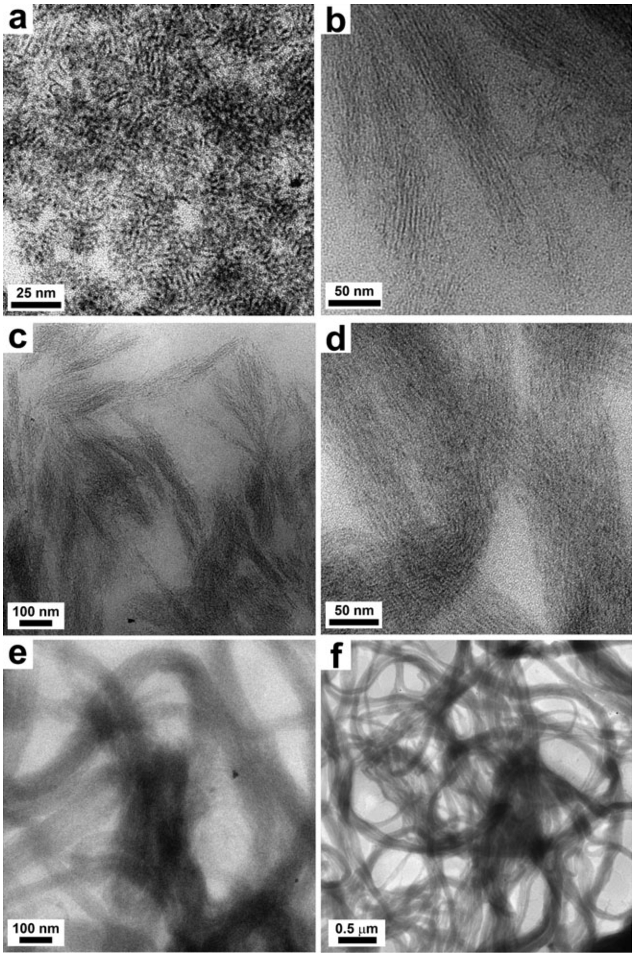

Fig. 3 TEM images of nanofibers obtained using 0.79 mmol $SbCl_5$ and 0.79 mmol sulfur (a), 1.58 mmol $SbCl_5$ and 1.58 mmol sulfur (b, c), 0.79 mmol $SbCl_5$ and 1.97 mmol sulfur (d, e), 0.79 mmol $SbCl_5$ and 3.94 mmol sulfur (f), respectively.

The characteristic property of adsorption behavior of Sb_2S_5 nanofibers is their excellent selectivity (Fig. 4 and Table 1).

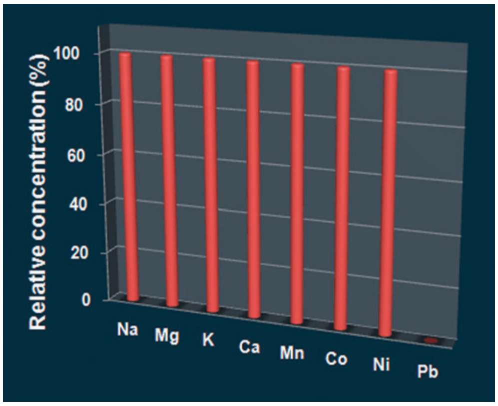

Fig. 4 Selective adsorption behavior of Sb_2S_5 nanofibers. Relative concentration on *y*-axis reveals the remaining portion compared to original amount. The data are the average values from five experimental sets.

Table 1 Adsorption experiments of nanofibers (concentration in ppm)[a]

Entry	Na	Mg	K	Ca	Mn	Co	Ni	Pb
1[b]	109	106	101	105	90	99	101	100
2	108	109	103	108	89	97	102	5
3	107	108	101	107	89	96	101	4
4	109	109	98	111	90	97	103	4
5	109	110	99	109	90	97	103	N.D.
6	109	106	106	101	90	99	101	N.D.

[a] Measurements performed with five independent sets (entries 2–6): 50 mL of model solution was treated with 0.50 g of nanofibers for 24 h. [b] The model solution.

Developments of adsorbents have resulted in large increases in adsorption capacity.[4] However, we believe that adsorption selectivity is equally important, because certain minerals found in water are important for animals and plants. Usually, adsorbents based on thiol-modified mesoporous silica adsorb toxic metals from water well.[4] However, they also adsorb other transition metals like cobalt and copper. In our experiments, the lead ion was removed selectively.[12] As shown in Fig. 4, alkali metals, manganese, cobalt, and nickel were not absorbed. We believe that this resulted from the relatively weaker coordination ability of surface sulfide for these metals, as compared to thiol-based adsorbents. Also, the relatively softer lead may have better coordination ability to sulfur in nanofibers than the other transition metals and alkali metals used.

In conclusion, ultrathin (1–2 nm) Sb_2S_5 nanofibers were prepared at 50 °C from $SbCl_5$ and sulfur in a highly reproducible manner during this study. The thickness and length of the nanofibers could be controlled by changing S : Sb molar ratios. The nanofibers produced showed excellent selectivity for lead adsorption. We believe that the described nanofibers can be used to produce industrial adsorbent materials for water or air purification.

This work was supported by a 21st Century Frontier R&D Program funded by the Ministry of Science and Technology of Korea. KHP thanks the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-005-J11901).

Notes and references

‡ TEM and HRTEM images were recorded with a JEOL 2100F unit operated at 200 kV. The samples for TEM study were prepared by drop casting nanomaterials dispersed in hexane on carbon-coated copper grids. The TEM studies were performed on as-prepared samples without employing a size-selection process. EDS was performed on a FE-SEM (JSM6700F). X-Ray photoelectron spectroscopy (XPS) was obtained using a Thermo VG and monochromatic Al-Kα radiation.

1 Selected recent examples: (*a*) W. Yan, S. M. Mahurin, Z. Pan, S. H. Overbury and S. Dai, *J. Am. Chem. Soc.*, 2005, **127**, 10480; (*b*) Y. Gogotsi, R. K. Dash, G. Yushin, T. Yildirim, G. Laudisio and J. E. Fisher, *J. Am. Chem. Soc.*, 2005, **127**, 16006; (*c*) R. Bacsa, C. Laurent, R. Morishima, H. Suzuki and M. Le Lay, *J. Phys. Chem. B*, 2004, **108**, 12718.
2 J. Wang, Z. Yue, J. S. Ince and J. Economy, *J. Membr. Sci.*, 2006, **286**, 333.
3 A. Greiner and J. H. Wendorff, *Angew. Chem., Int. Ed.*, 2007, **46**, 5670.
4 (*a*) X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923; (*b*) L. Mercier and T. J. Pinnavaia, *Environ. Sci. Technol.*, 1998, **32**, 2749; (*c*) R. I. Nooney, M. Kalyanaraman, G. Kennedy and E. J. Maginn, *Langmuir*, 2001, **17**, 528; (*d*) A. M. Liu, K. Hidajat, S. Kawi and D. Y. Zhao, *Chem. Commun.*, 2000, 1145; (*e*) J. Brown, R. Richer and L. Mercier, *Microporous Mesoporous Mater.*, 2000, **37**, 41; (*f*) L. Bois, A. Bonhomme, A. Ribes, B. Pais, G. Raffin and F. Tessier, *Colloids Surf., A*, 2003, **221**, 221; (*g*) A. Sayari, S. Hamoudi and Y. Yang, *Chem. Mater.*, 2005, **17**, 212; (*h*) W. Han, M. Lu, H. Wang, S. Mu and G. Liu, *Nanoscience*, 2006, **11**, 195.
5 (*a*) C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706; (*b*) T. Vossmeyer, L. Katsikas, M. Giersig, I. G. Popvic, K. Diesner, A. Chemseddine, A. Eychmuller and H. Weller, *J. Phys. Chem.*, 1994, **98**, 7665; (*c*) X. Peng, J. Wickham and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1998, **120**, 5343; (*d*) C. J. Barrelet, Y. Wu, D. C. Bell and C. M. Lieber, *J. Am. Chem. Soc.*, 2003, **125**, 11498; (*e*) C. H. An, K. B. Tang, Q. Yang and Y. T. Qian, *Inorg. Chem.*, 2003, **42**, 8081; (*f*) Y. C. Cao and J. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 14336.
6 (*a*) C. Tsopelas, *J. Nucl. Med.*, 2001, **42**, 46; (*b*) S. N. Reske, *Eur. J. Nucl. Med.*, 1991, **18**, 203; (*c*) L. Gang, W.-J. Shih and C. Chou, *Clin. Nucl. Med.*, 1995, **20**, 706.
7 (*a*) K. H. Park, J. Choi, H. J. Kim, J. B. Lee and S. U. Son, *Chem. Mater.*, 2007, **19**, 3861; (*b*) K. H. Park, K. Jang, S. Kim, H. J. Kim and S. U. Son, *J. Am. Chem. Soc.*, 2006, **128**, 14780; (*c*) K. H. Park, K. Jang and S. U. Son, *Angew. Chem., Int. Ed.*, 2006, **45**, 4608.
8 Selected examples: (*a*) Y. Hanzawa, K. Kaneko, R. W. Pekala and M. S. Dresselhaus, *Langmuir*, 1996, **12**, 6167; (*b*) Z. Knez and Z. Novak, *J. Chem. Eng. Data*, 2001, **46**, 858; (*c*) M. L. Anderson, C. A. Morris, R. M. Stroud, C. I. Merzbacher and D. R. Rolison, *Langmuir*, 1999, **15**, 674.
9 W. E. Morgan, W. J. Stec and J. R. V. Wazer, *Inorg. Chem.*, 1973, **12**, 953.
10 (*a*) E. H. Jeong, J. Yang and J. H. Youk, *Mater. Lett.*, 2007, **61**, 3991; (*b*) K. Jayaraman, M. Kotaki, Y. Zhang, X. Mo and S. Ramakrishna, *J. Nanosci. Nanotechnol.*, 2004, **4**, 52.
11 B. Pedersen and K. Kristensen, *Eur. J. Nucl. Med.*, 1981, **6**, 521.
12 This does not mean that our material was optimized for adsorption of Pb^{2+} among all metal ions.