Large-scale Growth of Hollow Sb Microspheres

Wanqun Zhang, Liqiang Xu, Guangchen Xi, Weichao Yu, and Yitai Qian*
Department of Chemistry, University Science and Technology of China, Hefei, Anhui, 230026, P. R. China

(Received August 9, 2004; CL-040938)

Uniform hollow antimony micron spheres were synthesized on a large scale using $SbCl_3$ and dithizone as starting reagents in ethylenediamine at 140 °C for 72 h. XRD and Raman results reveal that the as-obtained final product is pure Sb. FE-SEM and TEM observation reveals that the prepared hollow microspheres are composed of nanoparticles. The possible formation mechanism was briefly discussed.

Recently, fabrication of uniform hollow spheres with dimensions from nanometer to micrometer has become a focus in nanoscience and nanotechnology because of their broad range of applications. For example, they can serve as photonic crystals, catalysts, coatings, composites, fillers, and the protection of the light-sensitive components, especially as delivery vehicle systems for the controlled release of drugs, cosmetics, inks, and dyes.[1–5] Several methods have been developed for the fabrication of micrometer hollow sphere of inorganic materials, such as liquid droplets,[6] latex templates,[7] polymer beads,[8] or inorganic nanoparticles.[9] Generally, the above methods require additional template materials to build sphere architectures and the template needs to be removed later. It is obvious that the procedure to obtain hollow-sphere structures of inorganic materials will be greatly simplified if only the essential reactants are used in the reaction process, with no need for supporting templates.

Antimony is an important element in both fundamental research and practical application. For example, Sb is an important component in forming III–V antimony-based semiconductor materials that are valuable in electronics and optoelectronics as well as in forming thermoelectric materials.[10] Amorphous or polycrystalline antimony nanowires have been prepared in porous anodic alumina templates using the vapor-phase deposition technique and their particular transport properties have been also studied.[11] Single-crystalline antimony nanowires arrays have been prepared by pulsed electropodeposition in anodic alumina membranes.[12] Recently, our group have reported the synthesis of Sb nanotubes by solvothermal route.[13] However, no hollow antimony spheres are reported in the literature. Herein, we reported a novel template-free route to fabricate hollow antimony micron spheres via a simple low-temperature solvothermal complexing–reduction approach. In the system, dithizone (H_2Dz) acted as both ligand and reducing agent.

All the reagents are of analytical grade and purchased from Shanghai Chemical. In a typical synthesis, $SbCl_3$ (0.7 mmol) and H_2Dz (2.1 mmol) were put into 50 mL of ethylenediamine and the mixture was stirred vigorously for about 1 h to form a homogeneous solution. The resulting solution was transferred into a 60-mL Teflon-lined autoclave, then, the autoclave was sealed and maintained at 140 °C for 72 h, and then was cooled to room temperature on standing. The precipitate was filtered off and washed with distilled water and absolute ethanol several times and dried in vacuum at 60 °C for 7 h.

SEM images were obtained by a JSM-6700F field emission scanning electron microscope. XRD patterns of the products were recorded by employing a Philips X'pert X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54187$ Å). The Raman spectra were produced at room temperature with a LABRAM-HR Confocal Laser MicroRaman spectrometer. TEM images were collected on a Hitachi Model H-800 instrument using an accelerating voltage of 200 kV.

The XRD pattern of sample was shown in Figure 1. All of the peaks can be indexed as the rhombohedral structure of antimony with calculated lattice parameter $a = 4.290$ Å and $c = 11.267$ Å, which is consistent with the reported data ($a = 4.307$ Å, $c = 11.273$ Å, JCPDS NO. 71-1173). The crystal size calculated by the Scherrer formula from antimony (012) peak is about 53.9 nm. No characteristic peak for impurities was detected.

The Raman spectrum of the as-prepared antimony hollow spheres is shown in Figure 2. The bulk trigonal Sb has two first-order Raman modes, E_g mode at 117 cm^{-1} and A_{1g} at 152 cm^{-1}.[14] Comparing the Raman spectrum of hollow spheres with that of Sb, it is clear that Raman lines of the hollow spheres (especially E_g mode) are blue-shifted. The blue-shift in Raman line shape probably results from the nanosize effect according to analysis of Anushree et al.[15] Obviously, the Raman spectrum reveals that the as-obtained antimony hollow spheres are composed of Sb nanoparticles with a rhombohedral structure.

From FE-SEM image (Figure 3a), one can see that the pan-

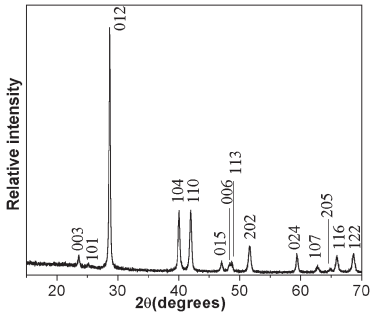


Figure 1. XRD pattern of the as-prepared antimony.

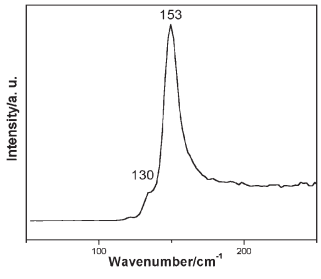


Figure 2. Raman spectrum of the sample.

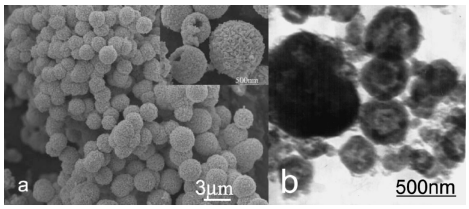


Figure 3. Morphology of the as-prepared product. (a) FE-SEM image of the sample obtained at 140 °C for 72 h. (inset is the magnified FE-SEM image of the "open" structure of the hollow spheres) (b) TEM image of the sample obtained at 140 °C for 28 h.

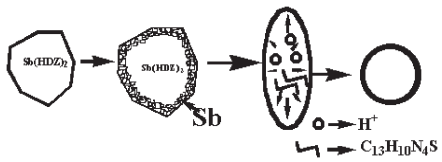
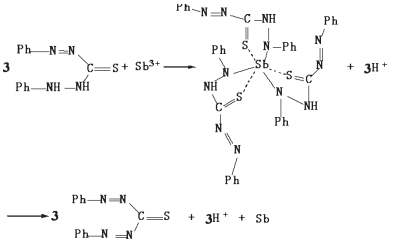


Figure 4. Schematic illustration of the possible mechanism for Sb hollow spheres.

oramic morphology of the as-prepared Sb is spherical with diameters ranging from 2.0 to 3.0 μm. The hollow nature of the spheres is confirmed by another typical FE-SEM (inset in Figure 3a), which provided an opportunity to see the "open" structure. Careful observation shows that the surfaces of these hollow spheres are constructed by many nanoparticles with diameters ranging from 50 to 90 nm, as seen in a magnified FE-SEM image (inset in Figure 3a). When reaction time was shortened to 28 h, the TEM image of as-prepared product shown in Figure 3b further reveals the hollow nature of spheres.

It is well known that H_2Dz is a good linker ligand, which can form $Sb(HDz)_3$ with Sb^{3+} in alkaline condition.[16] At a certain temperature and pressure, the preformed complexes decomposed to release Sb^{3+}. At the same time, as a reducing reagent, dithizone can reduce Sb^{3+} to Sb at certain conditions. A possible growth mechanism for the Sb hollow spheres will now be proposed, a schematic illustration of which is shown in Figure 4. First, $Sb(HDz)_3$ developed into aggregated particles in the initial solvothermal process. Then, a little amount of Sb is formed via the decomposition and reduction processes and attached on the outer surface of aggregated particles. At the same time, the inner aggregated $Sb(HDz)_3$ particles gradually decomposed to form Sb particles, H^+, and $C_{13}H_{10}N_4S$. The as-formed Sb nanoparticles will attach on the inner surface while the H^+, and $C_{13}H_{10}N_4S$ will diffuse to the outside to retain the equilibrium between the surface energy and the interface energy. With the prolonged reaction time and continued growth, Sb tends to form microspheres with hollow core structure in order to reduce surface areas (Figure 3b). More in-depth studies are still needed to explore the formation mechanism.

The reaction may be expressed as follows:



In the route, solvent has great influence on the final product. When ammonia or sodium hydroxide solution was used, with other conditions kept constant, only Sb_2O_3 was obtained. Besides the influence of solvent, it was found that the reaction time also has an important effect on the morphology of Sb crystals. When the reaction time was shorter than 24 h, only Sb aggregated nanoparticles were obtained, prolonging the reaction time to 48 h, hollow antimony micron spheres will be obtained. The optimum reaction time for hollow sphere structure of Sb is no shorter than 72 h.

In conclusion, hollow antimony micron spheres have been successfully prepared in a simple system containing $SbCl_3$, H_2Dz and ethylenediamine without assistant of any template. The hollow Sb antimony spheres were formed via self-assembly of small nanoparticles. Compared with those methods assisted by templates, the template-free route is very simple and facile.

This work was supported by the National Natural Science Foundation of China and the 973 Project of China.

References

1 F. Caruso, *Adv. Mater.*, **13**, 11 (2001).
2 F. Caruso, R. A. Caruso, and H. Möhwald, *Chem. Mater.*, **11**, 3309 (1999).
3 E. Mathlowitz, J. S. Jacob, Y. S. Jong, G. P. Carino, D. E. Chickering, P. Chaturvedl, C. A. Santos, K. Vijayaraghavan, S. Mantgomery, M. Bassett, and C. Morrell, *Nature*, **386**, 410 (1997).
4 H. Huang and E. E. Remsen, *J. Am. Chem. Soc.*, **121**, 3805 (1999).
5 M. Ohmori and E. Matijevic, *J. Colloid Interface Sci.*, **150**, 594 (1992).
6 D. Walsh and S. Mann, *Nature*, **377**, 320 (1995).
7 F. Caruso, R. A. Caruso, and H. Möhwald, *Science*, **282**, 1111 (1998).
8 Z. Y. Zhong, Y. D. Yin, B. Gates, and Y. N. Xia, *Adv. Mater.*, **12**, 206 (2000).
9 S. Y. Chang, L. Liu, and S. A. Asher, *J. Am. Chem. Soc.*, **116**, 6745 (1994).
10 R. M. Biefeld, *Mater. Sci. Eng.*, **36**, 105 (2002); A. L. Prieto, M. Martin-Gonzalez, J. Keyani, R. Gronsky, T. Sands, and A. M. Stacy, *J. Am. Chem. Soc.*, **125**, 2388 (2003).
11 J. Heremans, C. M. Thrush, Y. M. Liu, S. Cronin, Z. Zhang, M. S. Dresselhaus, and J. F. Mansfield, *Phys. Rev. B*, **61**, 2921 (2000); J. Heremans, C. M. Thrush, Y. M. Liu, S. B. Cronin, and M. S. Dresselhaus, *Phys. Rev. B*, **63**, 85406 (2001); M. Barati, J. C. L. Chow, P. K. Ummat, and W. R. Datars, *J. Phys.: Condens. Matter*, **13**, 2955 (2001).
12 Y. Zhang, G. H. Li, Y. Ch. Wu, B. Zhang, W. H. Song, and L. D. Zhang, *Adv. Mater.*, **14**, 1227 (2002).
13 H. M. Hu, M. S. Mo, B. J. Yang, M. W. Shao, Sh. Y. Zhang, Q. W. Li, and Y. T. Qian, *New J. Chem.*, **27**, 1161 (2003).
14 R. I. Sharp and E. Warming, *J. Phys. F: Met. Phys.*, **1**, 570 (1971).
15 R. Anushree, M. Komastu, K. Matsuishi, and S. Onari, *J. Phys. Chem. Solids*, **58**, 741 (1997).
16 Z. Holzbecher, "Hand Book of Organic Reagents in Inorganic Analysis," trans. by Zhongshan University, Higher Education Press, Beijing (1983), Chap. 5, p 280.

Published on the web (Advance View) October 16, 2004; DOI 10.1246/cl.2004.1476