Fabrication of Hollow Sb_2O_3 Microspheres by PEG Coil Template

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PEG coils have been exploited as chemical template to fabricate hollow Sb_2O_3 microspheres in water–ethanol solution at room temperature. The obtained hollow Sb_2O_3 microspheres were in the range of about 50–200 nm in diameter, and the shell were in the range of obout 10–20 nm in thickness. In the method, the formation of a certain sized hydrating PEG coil is crucial step, which is related with the process orders.

Hollow spheres exhibit special properties such as low density, large surface area, mechanical, thermal stability, and so on,[1–4] which make them have wide potential applications including capsule agent,[5] light-weight structure materials,[6] and catalysis.[7] Recently, a variety of methods have been employed to produce hollow spheres by nozzle reactor approaches, emulsion/phase separation techniques, self-assembly process,[8] and hydrothermal method.[9] The methods have been focused on inorganic precipitation against a variety of sacrificial templates, including polymeric or inorganic latex spheres,[10] in which the core had to be subsequently removed by heating or by dissolving. In addition, liquid droplets,[11] bioscafflid,[12] aggregation of surfactant,[13] and block polymer[14] used as "soft" template to produce hollow spheres.

Polymer coil is a common phenomenon when the polymer is dissolved in solvent, which was insensitive to pH value, ionic strength, and solvent in reaction; therefore, the surface of coil may be used as a novel template for fabrication of hollow spheres. In order to obtain a certain sized coil, the polymer molecules should have below features. First, polymer molecules could be dispersed in at least two solvents but have different affinity. Secondly, appropriate length and strength of polymeric chain are claimed and then ensure a number of molecule chains to entangle together to a certain sized coil template in the medium. Thirdly, water molecule could bind with single polymer chain to form hydrate layer and act as "bridge" molecule to combine two or more polymer chains together through hydrogen bond, through which the shaped coils could be stabilized under certain reaction process. Polyethylene glycol (PEG) with uniform and ordered chain structure is easily adsorbed at the surface of metal oxide colloid mainly through hydrogen bond;[15] therefore, PEG coils may be as template to produce metal oxide hollow spheres.

Antimony oxide (Sb_2O_3) is very useful as a high-efficiency flame retardant synergist in polymers and also has wide applications in other field, such as PET-catalyst and gas-sensor.[16] Currently, Sb_2O_3 nanoparticles have been synthesized using microemulsion,[17] templating carbon nanotubes,[18] vapor phase,[19] and hydrothermal method.[20] For the special properties of hollow structure, the hollow Sb_2O_3 microsphere is promising to behave uncommonly in the applications. In our work, we first fabricated hollow Sb_2O_3 microspheres by PEG coils template in water–ethanol system, which is novel, facile, and cost-effective.

The procedure for preparation is as follows: 1 g of PEG (MW ca. 4000) was first dissolved in 5 mL of diluted ammonia about 15 °C. Then, abundant of absolute ethanol was introduced, and the obtained solution continued vigorously stirring for 1 h to ensure its equilibration of the systems. Finally, ethanol solution containing antimony trichloride ($SbCl_3$) was added dropwise into above solution and the mixture was kept for 1 h at the same condition. The suspension was then filtered, thoroughly washed with water and ethanol, and dried at 60 °C in vacuum drier for 5 h to get powder sample.

Transmission electron microscopy (TEM) was used to characterize the products of the reaction, which resulted in hollow spheres as shown in Figure 1a. From the TEM image, it can be seen that there is a very strong contrast between the dark edge and pale center of the spheres, which revealing the sphere is hollow.[21] The structure could be further confirmed by broken sphere image inserted. The hollow spheres were in the range of about 50–200 nm in diameter, and the shell was in the range of about 10–20 nm in thickness. The magnified image of single sphere inset showed that the wall of microsphere was covered with nanoparticles with the diameter of about 10 nm.

To study the formation mechanism of hollow microspheres, a drop of liquid sample without drying was observed by TEM in Figure 1b. It can be seen that isolated nanoparticles with rough surface appear to be sphere in shape, and the smaller nanoparticles covered on the larger microspheres (inset). The observation should be explaind by the primary Sb_2O_3 particles with 10 nm in diameter absorbed on the surface of the hydrating PEG coils. To understand better the role of PEG in the system and to discuss the possible mechanism, we directly put PEG into water–ethanol solution, instead of dissolving PEG in water and ethanol in turn, the obtained morphology is solid particles rather than hollow microspheres, which can be seen in Supporting Information

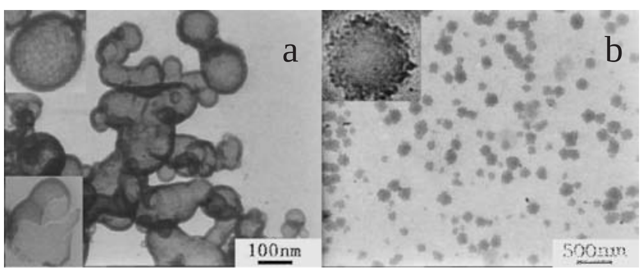

Figure 1. TEM images showing: **a**. hollow Sb_2O_3 microspheres and images of a magnified single hollow sphere and a broken sphere inserted the top and the bottom of image, respectively; **b**. particles before dried and magnified image of the particle inset.

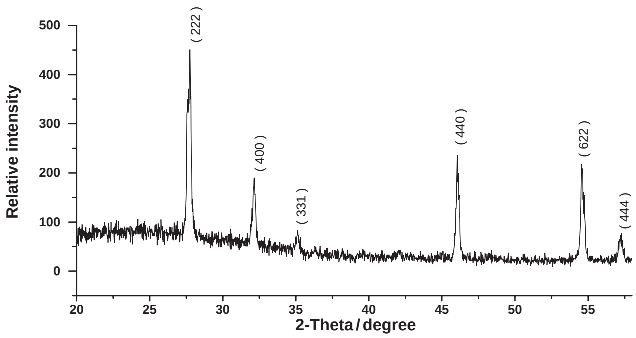

Figure 2. X-ray diffractogram showing the fcc crystal structure of the hollow Sb_2O_3 microsphere.

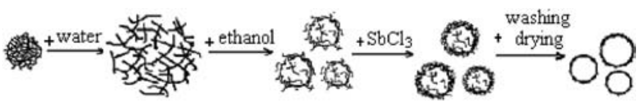

Figure 3. Schematic illustration of the key stages in the formation of hollow Sb_2O_3 microsphere.

(SI 1). Therefore, the step of forming hydrating PEG chains is crucial in the present method.

Figure 2 displays the typical X-ray diffraction (XRD) pattern of hollow Sb_2O_3 spheres prepared by the route. It is clear that XRD pattern exhibits prominent peaks at scattering angle (2θ) of 27.72, 32.11, 35.08, 46.05, 54.60, and 57.25, which are assigned to scattering from 222, 400, 331, 440, 622, and 444 crystal planes, respectively, of the face-centered cubic structure of Sb_2O_3 with the lattice constants comparable to the values of JCPDS 75-1565. From which one can see that addition of PEG in the reaction did not affect native crystal structure of Sb_2O_3.

On the basis of the results obtained in study, the possible formation mechanism of the hollow Sb_2O_3 microspheres was shown in Figure 3. When PEG was dispersed in water, water molecule could bind with single PEG chains to form hydrate layer and act as "bridge" molecule to combine PEG chains together through hydrogen bonding (between the isolated hydroxy groups of water and the ether oxygen in PEG) to form physical linked coils. Because of stronger affinities between PEG and water, the subsequent ethanol did not effectively replace "binding water" of PEG chains. So, under the shear force of stirring, the physically linked coils would be destroyed and dispersed into certain sized PEG coil microspheres, which can be seen in Figure 4. While $SbCl_3$ was added, the surface of hydrating PEG coils supplied H_2O to react with $SbCl_3$ in ethanol and acted

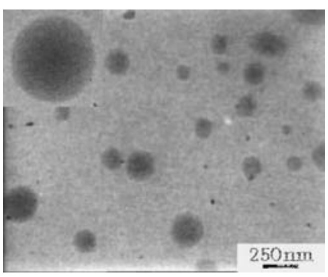

Figure 4. TEM image of PEG coil microspheres template (magnified image inset) from the system before addition of $SbCl_3$.

as the template to be covered with Sb_2O_3 nanocrystallines. So, the "core–shell" structure was formed in the reacting system. When Sb_2O_3 nanoparticle-coated PEG sphere-shaped coils were dried at 60 °C, the volatilization of water in the PEG coils led to the deposition of PEG chains on the inner layer of Sb_2O_3 shell. Therefore, the hollow Sb_2O_3 microspheres were formed in the end. If PEG was directly dispersed into the water–ethanol solution, the PEG chains reacted with molecules of water and ethanol simultaneously, which formed smaller coils with several PEG molecules (SI 2), and the obtained Sb_2O_3 was solid particles instead of hollow microspheres.

In summary, the fabrication of hollow Sb_2O_3 microspheres is successfully demonstrated by template definitely sized net-like PEG coils in water–ethanol solution at room temperature. The corresponding formation mechanism indicates that forming hydrating PEG coils in the system is crucial step in fabrication. What is more, PEG is a nontoxic substance and widely applied in materials science,[22] and the water–ethanol solution is a familiar system for preparation of nanoparticles. Ultilization of PEG coils in water–ethanol as template to fabricate hollow microsphere is a novel, promising method and would be potentially widely applied in materials science.

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