Controlled Synthesis of SnO_2 Hollow Microspheres via a Facile Template-free Hydrothermal Route

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Hollow rutile-like SnO_2 microspheres were synthesized via a facile template-free hydrothermal method at 160 °C for 5–28 h. The as-prepared samples were characterized with XRD, SEM, and PL. A possible formation mechanism of the hollow spheres is briefly discussed.

Tin dioxide (SnO_2), an n-type semiconductor with a wide band gap (Eg = 3.62 eV, at room temperature), is considered as one of the most important strategic materials used in a wide range of technological application, such as optoelectronics,[1,2] gas sensing,[3] energy storage (lithium batteries),[4] and energy conversion.[5] The promise that the different structures may dramatically improve the desired properties of materials for many potential applications has stimulated great enthusiasm in synthesizing structures of all shapes. Over the past several years, various structural and morphological forms of SnO_2 nano- and micromaterials have been fabricated, including nanoparticles, nanowires, nanoribbons, nanorods, nanodiskettes, nanocomposites, mesoporous powders, thin films, nanotubules, hollow microspheres, hollow octahedras, and so on.[6–13] Methods to synthesize hollow microspheres are mainly using various templates. However, to the best of our knowledge, there has no report of SnO_2 hollow microspheres formed through the self-aggregation, via a simple hydrothermal method, without using any additional template. And it is thought that a simple template-free method to prepare semiconductor microspheres with intrinsic optical properties is much needed.

Herein, we report a simple template-free hydrothermal method to prepare SnO_2 hollow microspheres at low temperature by hydrolysis of $SnCl_4$ in alkaline media. Compared with template methods, this method is convenient because it avoided the complicated procedure of removing templates. This method may be helpful for preparing other materials with hollow morphology.

All of the chemical reagents used in these experiments were of analytical grade, and were purchased from Shanghai Chemical Reagents Company. In a typical procedure, $SnCl_4 \cdot 5H_2O$ (10 mmol) was dissolved in 60 mL of distilled water in a beaker, and then the solution was transferred to a 75-mL Teflon-lined stainless steel autoclave. Following that, the pH value of the resulting solution at room temperature was adjusted to 13 by the addition of NaOH. The autoclave was sealed and kept at 160 °C for 5–28 h, and then was cooled to room temperature on standing. After that, the precipitate was collected, washed several times with distilled water, and then was dried at 60 °C for 2 h.

X-ray powder diffraction (XRD) patterns were recorded on a Philips X' pert diffractometer with Cu Kα radiation (λ = 0.154187 nm). Scanning electron microscopy (SEM) images and field emission scanning electron microscopy (FESEM) images were taken on an X-650 scanning electron microanalyzer and a JEOL 6700F field emission scanning electron microscope. Photoluminescence (PL) spectrum of the sample was measured on a Shimadzu PLRF-5301 PC spectrometer with a Xe lamp as exciting source at room temperature.

Figure 1 shows a typical XRD pattern of the as-prepared sample. All the reflection peaks of this pattern can be indexed to tetragonal rutile structure of SnO_2 with lattice constants of a = 4.751 and c = 3.183 Å, which are in good agreement with the reported data of a = 4.738 and c = 3.187 Å (JCPDS 41-1445).

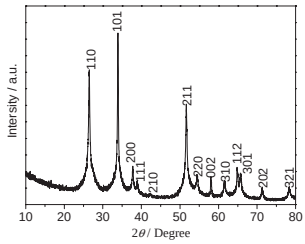


Figure 1. The representative XRD pattern of as-prepared SnO_2.

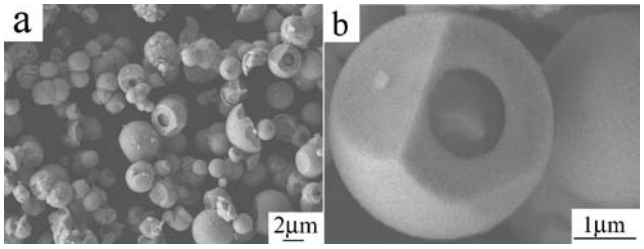


Figure 2. FESEM images of the as-prepared SnO_2 hollow microspheres (160 °C, 10 h), (a) overall product morphology, (b) a hollow microsphere with cross-sections.

The morphology and size of the as-prepared SnO_2 were characterized with FESEM shown in Figure 2. Figure 2a shows the overall morphology of the SnO_2, which indicates that the sample is composed of microspheres. From some incompletely developed microspheres, it can be seen that they are hollow interior. The diameters of these hollow spheres are as large as several micrometers and the thickness of the shell walls is about several hundred nanometers. Interestingly, it can be seen form Figure 2b that there is always a distinct block region in the middle of each microsphere and the as-prepared microspheres have smooth surfaces and cross sections. The hollow microspheres with cross sections could be intermediate and the final product could be the integrated hollow microspheres.

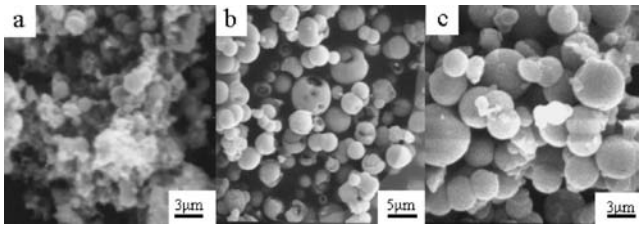
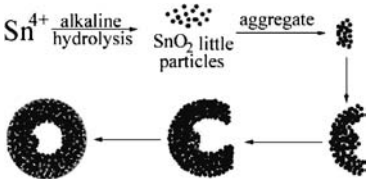


Figure 3. SEM images showing the representative morphology of the as-grown SnO_2 at different time, (a) 2, (b) 17, and (c) 28 h.

For comparison, a series of similar experiments were also done to determine the possible influencing factors on the preparation of SnO_2 hollow spheres. In our experiments, we find that moderate pH value and reaction temperature will facilitate the formation of hollow microspheres. When the pH value is more than 13 or less than 12, the yield of hollow spheres is dramatically decreased. The optimal reacting temperature is in the range of 140–160 °C. Higher or lower temperature is not favorable for the formation of hollow spheres. We have also studied the growth process of the hollow spheres. Figure 3 shows SEM images of the products prepared at 2, 17, or 28 h. The products obtaind after reaction for 2 h is mainly composed of amorphous particles. When the reaction has proceeded for 17 h, more spheres are present in the products, some of spheres are hollow. After reacted for 28 h, the average sizes of the microspheres are larger and more integrated.



Scheme 1. Formation process of the SnO_2 hollow spheres.

On the basis of the results of our experiments, we speculate the growth of the SnO_2 microspheres is through a self-assembly process, as shown in Scheme 1. The initial product of the reaction was amorphous SnO_2 colloids. When the reaction was processed in the alkaline solution at 160 °C, amorphous SnO_2 will slowly turn into little SnO_2 nanoparticle. These particles would rapidly self-assembly into sphere-like polycrystals. Since the hydrolysis reaction in alkaline media processed very slowly, it could not provide enough SnO_2 nanoparticles for the self-assemble of the growing spheres. This would lead to undersaturation in the central part of the growing faces of each seed (spherical polycrystals), and the continuous addition of SnO_2 nanoparticles to the seed surface would preferentially occur at the circinal edges of each regular-shaped seed because these sites had relatively higher free energies than other sites on the surface. Thus, the hollow sphere structures would be formed because of no mass transportation to the inner region until all SnO_2 had been completely consumed, eventually resulting in the formation of spherical polycrystals having well-defined hollow interiors. This growth process is similar to the gowth of Te nanotubes reported previously.[14,15] The average sizes and morphologies of the hollow microspheres could be varied by controlling the growth time (Figure 3).

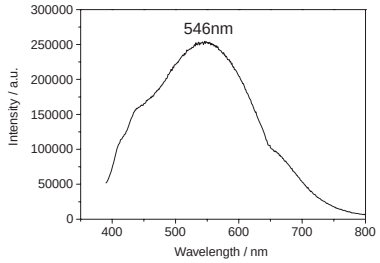


Figure 4. Room-temperature photoluminescence spectrum of the as-prepared SnO_2 hollow microspheres.

Figure 4 shows the room-temperature photoluminescence spectrum (≈310 nm as the excitation source) of the as-prepared SnO_2 hollow microspheres. It is can be seen that a very broad PL peak (from 400 to 700 nm) is dominant centering at ≈546 nm. Compared to the bulk SnO_2,[16] there has a blue shift of approximately 30 nm.

In summary, we have successfully synthesized hollow microsphere structures of rutile-like SnO_2 via a template-free hydrothermal route under a low temperature. In this approach, no additional template materials are needed to obtain micrometer spheres. The microsphere of SnO_2 ceramic material achieved from the reaction may be of interest for potential applications.

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