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Synthesis of SnO_2 hollow microspheres with core-shell structures through a facile template-free hydrothermal method

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ABSTRACT

SnO_2 hollow microspheres with core-shell structures were fabricated by a template-free hydrothermal reaction of a simple aqueous solution containing $SnCl_4$ and NaOH. This process was carried out under mild conditions and required no high-temperature heat treatment. By simply adjusting the molar ratio of $SnCl_4$ to NaOH, hollow microspheres, hollow core-shell microspheres and nanoparticles can be selectively synthesized. The products were characterized by powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and nitrogen BET measurements. The as-prepared SnO_2 hollow core-shell microspheres present a high Brunauer-Emmett-Teller surface area of 122.4 m^2/g and a mesoporous structure. A possible formation mechanism for this kind of core-shell structure was proposed.

1. Introduction

As an important n-type semiconductor with a wide band gap, SnO_2 has attracted extensive attention due to its broad applications such as gas sensors, transparent conducting films, and catalytic materials, etc. It is believed the properties of this material strongly depend on the size and morphology. Recently, hollow spheres, including those with core-shell structures, have attracted considerable interest because of their novel properties different to their solid counterparts and their promising applications such as nanocatalysts, gas sensors, drug delivery and controlled release, etc. [1–5]. To date, various template-assisted processes have been developed to synthesize SnO_2 hollow spheres [6–11]. However, only a few papers have reported the fabrication of hollow core-shell SnO_2 spheres. For instance, hollow core-shell SnO_2 mesospheres have been prepared by a template-assisted solvothermal procedure, where a subsequent calcination at 550 ° C is needed [12]. Hollow core/shell-type SnO_2 nanostructures with sizes in the range of 200-500 nm were synthesized by hydrothermal treatment of stannate in a mixed ethanol-water solvent [13]. Multilayered SnO_2 hollow microspheres were fabricated by a hydrothermal method in aqueous sucrose/$SnCl_4$ solution and postsynthesis high-temperature calcination [14]. For the template-assisted methods, relatively high temperatures and tedious synthetic procedures are generally involved, and the removal of the templates may damage the desired configurations. Thus, it is highly desirable to synthesize hollow core-shell SnO_2 microspheres through a templateless route under mild conditions.

In this report, we demonstrate a facile template-free hydrothermal method for the preparation of hollow core-shell SnO_2 microspheres in a solvent of water. The effect of molar ratio of $SnCl_4$ to NaOH on the products was investigated. A possible growth mechanism of such core-shell structures was proposed based on time-dependent experiments.

2. Experimental

The synthesis was performed in a solvent of water starting from $SnCl_4.5H_2O$ and NaOH. Typically, 40 mL of NaOH solution (0.5 M) was added to 5-25 mL of $SnCl_4$ solution (0.3 M) with vigorous stirring to obtain a clear or milky solution. The obtained solution was then transferred into a 100 mL Teflon-lined autoclave and maintained at 160 ° C for about 12 h. After cooled down to room temperature naturally, the resulting white precipitation was centrifuged and thoroughly washed with deionized water and absolute ethanol before drying at 60 ° C in vacuum. The structure and morphology of the products were characterized by XRD (Bruker AXS, D8 Advance), FESEM (Hitachi, S-4800) and TEM (FEI, Tecnai F20), respectively. The specific surface area was determined by nitrogen BET measurement (Micromeritics ASAP 2020) and the pore-size distribution was calculated from the desorption branch of the isotherm using BJH formula.

3. Results and discussion

XRD measurements reveal that all the products are pure SnO_2 with tetragonal rutile structure as illustrated by typical XRD pat-

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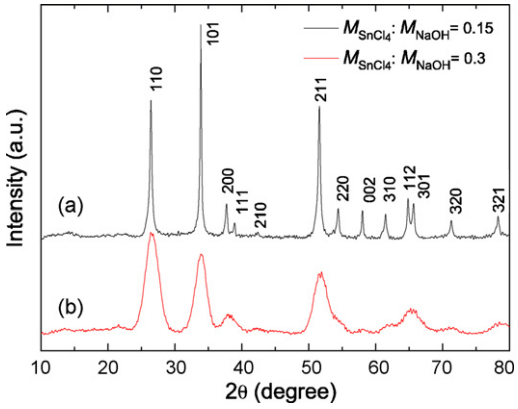

Fig. 1. Representative XRD patterns of the products prepared at 160 ° C for 12 h with different molar ratios: (a) $M_{SnCl4} : M_{NaOH} = 0.15$ and (b) $M_{SnCl4} : M_{NaOH} = 0.3$.

terns in Fig. 1. As a case with a low molar ratio, the diffraction peaks of pattern (a) can be well indexed to tetragonal rutile SnO_2 with lattice constants of $a = 4.766$ Å and $c = 3.177$ Å, in accordance with the standard XRD pattern of SnO_2 (JCPDS card, No. 41-1445). The diffraction peaks are sharp, indicating the product is well crystallized. However, for a high molar ratio such as 0.3, the diffraction peaks are significantly broadened along with decreasing of intensity as shown in pattern (b), suggesting very small crystallite size (~3 nm) and poor crystallinity. This is likely due to faster SnO_2 nucleation without enough time to grow, as the faster nucleation rate, the smaller particle size and the poorer crystallization.

The images in Fig. 2 show the morphological evolution of the products prepared with different molar ratios of $SnCl_4$ to NaOH. It is found that the molar ratio affects the morphology dramatically. As shown by the FESEM and TEM images (Fig. 2a and the inset), very tiny nanoparticles were produced for $M_{SnCl4} : M_{NaOH}$ =0.3, in agreement with the XRD result. These nanoparticles connect to each other into a random network with many nano-sized holes. A large BET surface area of 178.7 m^2/g with a BJH adsorption average pore diameter of 3.5 nm is obtained for this microstructure. When the molar ratio decreased to 7/40, hollow core-shell microspheres can be obtained (Fig. 2b and c). Fig. 2b shows a typical low-magnification FESEM image of the hollow core-shell structures. It can be seen that the product consists of spherical particles with a size in the range of around 0.7 μm to 2 μm, and some of them aggregate together. The core-shell nature with hollow interior was presented vividly by a high-magnification FESEM examination of broken microspheres (Fig. 2c), and further confirmed by the TEM image (the inset of Fig. 2c), where the dark solid core and the shell are well separated. It is found that the shell is well-defined and the core is composed of aggregated nanoparticles. The shell thickness is in the range of about 30–80 nm. For $M_{SnCl4} : M_{NaOH} = 0.15$, microspheres with diameters of around 1–2 μm were obtained (Fig. 2d). The inset of Fig. 2d shows a broken microsphere, exhibiting a hollow interior. It is noted that arc sheets are observed on the surface of the hollow microspheres. Upon further decreasing the molar ratio, no product but a clear solution can be obtained. These results clearly suggest that a proper molar ratio of $SnCl_4$ to NaOH plays an important role in the synthesis of homogeneous core-shell structure, and the morphology of the products can be tuned by simply adjusting the molar ratio.

The reaction process in the $SnCl_4$-NaOH-H_2O system was investigated in details. The pH value of the initial $SnCl_4$ solution(0.3 M) was about 0.44 due to the hydrolyzation process. It increased from 0.44 to 12 with the addition of NaOH solution for the case of $M_{SnCl4} : M_{NaOH} = 7/40$. A white precipitate was observed in the solution immediately with the addition of NaOH solution, and then the solution turned clear with vigorous stirring. Similarly, a clear solution with a pH value of about 12.7 was finally obtained for $M_{SnCl4} : M_{NaOH} = 0.15$. However, a milky solution with a pH value

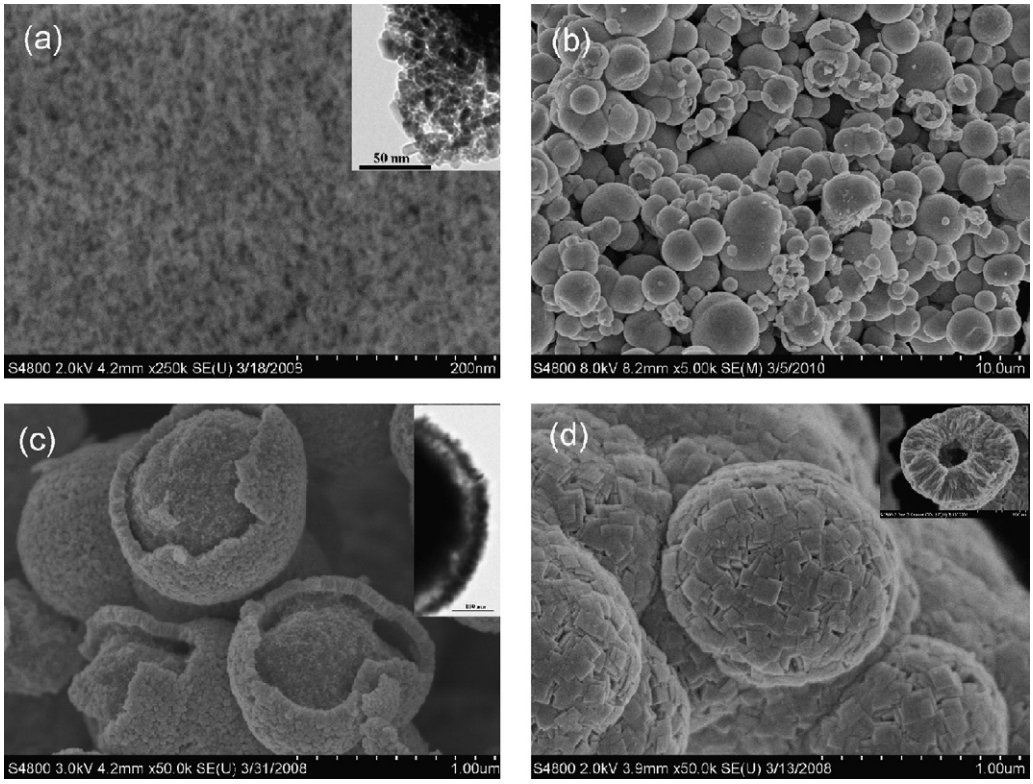

Fig. 2. FESEM and TEM images of the products prepared at 160 ° C for 12 h with different molar ratios: (a) $M_{SnCl4} : M_{NaOH} = 0.3$, (b) low magnification and (c) high magnification for $M_{SnCl4} : M_{NaOH} = 7/40$, (d) $M_{SnCl4} : M_{NaOH} = 0.15$.