Fabrication and Gas-sensing Properties of Hollow SnO_2 Microspheres

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Hollow SnO_2 microspheres with diameters ranging from 300–500 nm have been prepared via a simple template-free hydrothermal method in ethanol–water mixed solution. X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to characterize the hollow microspheres. The gas-sensing properties of the hollow SnO_2 microspheres have been investigated. The satisfactory gas response indicated that the hollow SnO_2 microspheres have excellent potential application for ethanol sensors.

Tin dioxide (SnO_2), an important n-type semiconductor with a wide band gap of 3.6 eV, has attracted great interests in recent years owing to its wide applications in gas sensors,[1] lithium rechargeable batteries,[2] catalysts, and dye-sensitized solar cells.[3,4] Up to now, to meet the requirements of these applications, various structures of SnO_2 nano- and micromaterials have been prepared, such as nanoparticles,[5] nanowires,[6] nanobelts,[7] nanoflowers,[8] hollow nano- and microspheres.[9] Compared with other morphologies, hollow structures with relatively lower densities and larger specific surface areas may provide some favorable applications as gas sensors. Several template methods have been developed for the fabrication of hollow SnO_2 spheres, such as polystyrene beads,[10] carbonaceous polysaccharide microspheres or surfactant micellar templates.[8,11] Generally, the above methods need to remove template materials later, which prevent them from being used in large-scale applications.[12] Apart from templating synthesis, recently, a novel inside-out Ostwald ripening route was used to prepare hollow nanomaterials, which were created in the process of dissolving smaller, less crystalline or less dense particles in a colloidal aggregate gradually, while larger, better crystallized, or denser particles in the same aggregate are growing.[13] A variety of hollow materials, such as CuO,[14] ZnO,[15] TiO_2, and SnO_2,[12,13] have been successfully prepared through this route.

Herein we report a facile hydrothermal method to prepare hollow SnO_2 micropheres via Ostwald ripening.[18] The results of gas sensitivity test indicated that the hollow SnO_2 micropheres might be a good choice for gas-sensing materials.

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, $Na_2SnO_3 \cdot 4H_2O$ (1.0 mmol) was added to 20 mL of distilled water under continuous magnetic stirring to form a clear solution. Twenty min later, absolute ethanol (20 mL) was added to the reaction system to obtain a white translucent suspended solution, which was then transferred into a stainless steel autoclave (50 mL). The autoclave was sealed and maintained at 200 °C for 24 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 5 h.

The microstructures of the samples were characterized with field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL JEM-200CX working at 160 kV; JEOL JEM 2010F operated at 200 kV). The crystal structure of the materials was examined via the X-ray diffraction (XRD) pattern using a Rigaku D/max-2550 V diffractometer employing Cu Kα radiation (λ = 1.54056 Å; scanning rate: 0.02° s^{-1}). Meanwhile, the specific surface area (SSA) was examined using the single point Brunauer–Emmett–Teller (BET) method by the 3H-2000 nitrogen adsorption apparatus. The gas-sensing properties of the materials were measured with an HW-30 gas-sensing testing instrument (Henan Hanwei Electronics Co., Ltd). The gas sensitivity was defined as the ratio of the sensor resistance in air (R_a) to that in test gas (R_g), $S = R_a/R_g$.[6]

The crystal structure of the hollow SnO_2 microspheres was determined by XRD, the result is shown in Figure 1. All of the peaks can be indexed to tetragonal SnO_2 (JCPDS card No. 41-1445, $a = b = 4.738$ Å, $c = 3.187$ Å) with high crystallinity. There was no other crystallilline phase detected, indicating the high purity of the final products. The mean grain size of the SnO_2 nanoparticles is calculated to be about 9 nm according to the Debye–Scherrer formula.

The morphology and size of the hollow SnO_2 microspheres were investigated by TEM and SEM. Figure 2a illustrates a representative TEM image of the product prepared at 200 °C, which shows that a bright contrast (dark/bright) between the outer part and the center of the sphere-like structures, confirming their hollow nature. The external diameter of the hollow spheres is 300–400 nm, and the thickness of the shell is about 100 nm. SEM image of the hollow spheres are shown in Figure 2b. The typical SEM image also reveals that the SnO_2 microspheres are hollow, as revealed by the broken regions of spheres. The TEM and SEM images show that the shells of hollow SnO_2 microspheres seem to be rough and consist of short nanoparticles with a size of

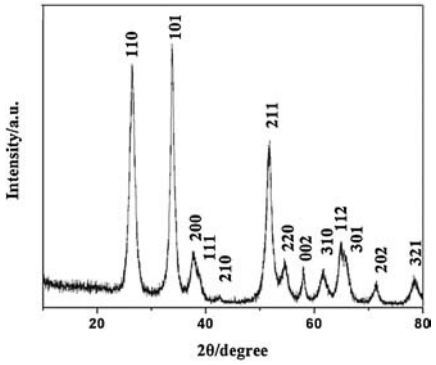


Figure 1. The representative XRD pattern of as-prepared SnO_2.

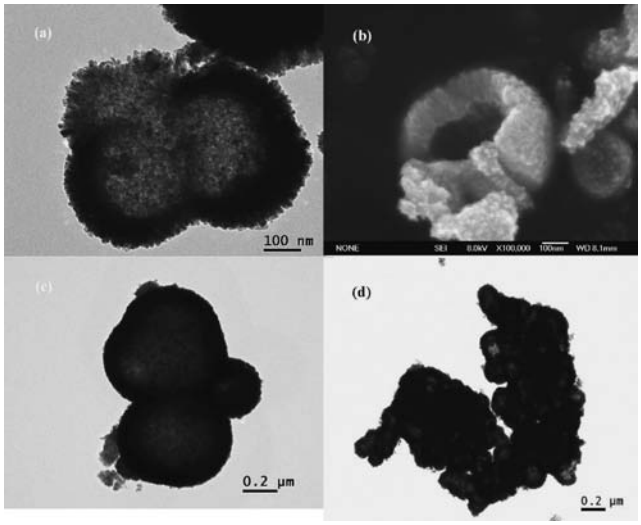
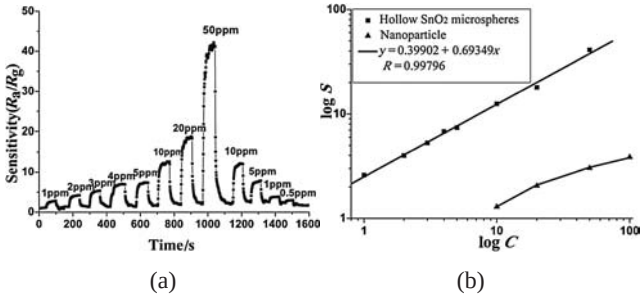


Figure 2. TEM (a, c, d) and SEM (b) image of hollow SnO_2 microspheres at different hydrothermal temperature. (a, b) 200, (c) 180, and (d) 220 °C.

≈10 nm in diameter, which corresponds to the particle size observed by the Debye–Scherrer formula. As the reaction temperature was decreased to 180 °C, the hollow structures were also obtained, but the contrast between the outer part and the center part was less obvious than the product obtained at 200 °C, as shown in Figure 2c. As the reaction temperature was increased to 220 °C (Figure 2d), the hollow structures became more obvious but they were connected to each other. This suggests that the temperature plays an important role in the formation of hollow structure.

The gas-sensing mechanism of SnO_2 is based on the change in resistance of the gas sensors when exposed to different atmospheres, which is due to the charge-carrier exchange of adsorbed gas with the oxide surface.[6] The gas concentration dependent response of SnO_2 sensors to ethanol under heating voltage of 4.5 V (working temperature about 290 °C) are shown in Figure 3a. SnO_2 sensors show considerable responses to ethanol even at concentrations as low as 1 ppm. The response time and recovery times are 10 and 30 s, respectively. In addition, the reversibility and repeatability of the gas sensors are very good. A log–log plot of the sensitivity versus concentration (C) is shown in Figure 3b. The fit curve shows the linear relationship $\log S = 0.39902 + 0.69349 \log C$. The correlation coefficient R of the sensor fit curve is 0.99796. The linear behavior shows a power law dependence of the response on the concentration, i.e., $S = AC^{\alpha}$, as also reported in earlier studies.[6,16] In order to explain the good sensitivity of the hollow SnO_2 microsphere sensors, we fabricated nanoparticle SnO_2 sensors. The preparation of SnO_2 nanoparticles are described elsewhere.[17] From Figure 3b, it can be clearly seen that the hollow microsphere sensors show higher sensitivity than the nanoparticles at 290 °C. Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption measurements showed that the surface area of the hollow SnO_2 microspheres is 32.17 $m^2 g^{-1}$, bigger than that of SnO_2 nanoparticles (10.32 $m^2 g^{-1}$), which make the gas molecules have more chances to adsorb or desorb and may lead to a higher sensitivity and quick response when used as gas sensors.[8]

In a summary, a simple hydrothermal route was developed to fabricate hollow SnO_2 microspheres, which is feasible for large-scale production. The gas sensing properties of the materials indicated that the hollow SnO_2 microspheres have excellent potential application for ethanol sensors.



(a) (b)

Figure 3. The gas-sensing properties: (a) typical response curve of the sensor to different concentration (0.5–50 ppm) of ethanol at 290 °C, (b) di-logarithm fit curve of the sensitivity with the concentration of ethanol.

This work were supported by the Science & Research Fund of Education Commission of Shanghai (No. 07ZZ12), and Supported by Leading Academic Discipline Project of Shanghai Municipal Education Commission (J50102).

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18 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) September 25, 2008; doi:10.1246/cl.2008.1086