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Interfacial oxidation–dehydration induced formation of porous SnO_2 hollow nanospheres and their gas sensing properties

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ABSTRACT

Uniform porous SnO_2 hollow nanospheres with average diameters of about 100–200 nm have been reproducibly synthesized via a facile template- and surfactant-free hydrothermal method, using hydrogen peroxide 30% and stannous sulfate as precursors. The morphology, composition and structure of the resultant products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy and nitrogen adsorption–desorption technique. Experimental results demonstrated that the formation of these porous SnO_2 nanostructures is ascribed to an interfacial oxidation–dehydration mechanism. H_2O_2 usage has an important effect on both the morphology and purity of the final products. The gas sensing properties of the as-prepared porous SnO_2 hollow nanospheres were investigated. By comparative gas sensing tests, the porous SnO_2 hollow nanospheres exhibited superior gas sensing performances over commercial SnO_2 nanopowders toward some typical volatile organic compounds (VOCs), implying their promising applications in gas sensors.

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1. Introduction

Design and synthesis of nanoscale materials with controlled size and morphology have been intensively pursued and well developed in the past decade for their size and shape-dependent properties [1–5]. As a wide band gap n-type semiconductor, SnO_2 is of great importance in a wide range of technological applications, such as gas sensing [6–8], Li-ion battery anode [9–11], photocatalyst [12–15] and solar cells [16–18]. To date, diverse SnO_2 nanostructures such as quantum dots [19], nanowires [20], nanorods [21], nanobelts [22], nanosheets [23], nanotubes [24,25], and hollow spheres [26,27] have been successfully fabricated by a variety of methods. Among various kinds of morphologies, porous hollow nanostructures have gained special attention to be used as excellent gas sensing materials because of their low density, large surface area, stability, and surface permeability [28,8,29,30]. Currently, an effective synthetic strategy for the preparation of hollow nanostructures is the utilization of various removable or sacrificial templates, which should be prepared beforehand and removed by calcinations or dissolution afterwards [31–35]. However, the difficulty in preparation of suitable templates and the complicated multistep preparation processes restrict the general application of this technique. Therefore, simple, one-step and template-free approaches by using ordinary inorganic salts are strongly desirable for the fabrication of hollow nanostructures because of their simplicity, low cost, flexibility and relatively environment-friendly process. Previously, Guo and Ji [36,37] have successfully prepared intestine-like SnO_2 nanostructures by using $SnSO_4$ as precursor via a one-step H_2O_2-assisted method at room temperature. However, this method is only suitable for low $SnSO_4$ concentration range. According to the authors' report, solid aggregates rather than hollow nanostructures were generated if the $SnSO_4$ concentration was increased to 18.4 mM. In addition, this method needs longer reaction time. Therefore, developing a facile effective template-free route to synthesize porous hollow nanostructures with mass production to meet the growing demands required in gas sensor technology is still a challenge.

Herein, we report a facile template- and surfactant-free hydrothermal method to synthesize SnO_2 porous hollow nanospheres with nearly 100% morphological yield. This method was similar to the previous Guo and Ji's report but with some modifications as follows: Firstly, we reversed the adding sequence of $SnSO_4$ and H_2O_2 to solution, thus, a completely different mechanism may be followed by the reaction. Secondly, we performed the reaction in autoclave at a higher temperature. And thirdly, we increased the amount of hydrogen peroxide. As a result, the crystallinity, purity and yield of the products were totally enhanced. Significantly, the as-prepared SnO_2 porous hollow nanospheres exhibit superior gas sensing performances over commercial SnO_2 nanopowders, implying their promising applications in gas sensors. This simple synthesis method allows the obtainment of mass production of high-purified products. It has the ability

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to control the morphologies and meet the growing demands for porous hollow nanospheres required in gas sensor technology. In this paper, a novel interfacial oxidation–dehydration mechanism was also proposed to the formation of these porous SnO_2 hollow nanospheres.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used as received without further purification. Stannous sulfate ($SnSO_4$) and hydrogen peroxide (H_2O_2) 30% were purchased from Guangcheng Chemical Reagent Co. (Tianjin, China). Distilled water was used throughout the experiments.

2.2. Synthesis process

In a typical experiment, first, 2 mmol $SnSO_4$ was dispersed into 20 mL distilled water under continuous magnetic stirring to form yellowish slurry. The concentration of $SnSO_4$ was about 100 mM. Then 5 mL of 30% H_2O_2 was introduced by dropping to the well-stirred mixture at room temperature with simultaneous vigorous agitation. After several minutes of stirring, the obtained solution was transferred into a 30 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 180 °C for 12 h and afterwards allowed to cool to room temperature naturally. The white precipitate was collected by centrifugation, washed several times with distilled water and absolute ethanol. Subsequently, the products were dried in vacuum at 60 °C for 5 h for further characterization.

2.3. Characterization

The as-prepared products were characterized by X-ray diffraction (XRD) using a Bruker D8 advanced X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.5418 Å) at a scanning rate of 10° min^{-1}. Field emission scanning electron microscope (FSEM: Japan, JSM-6700F) was also taken. TEM and HRTEM images were recorded with a JEOL JEM-2100 transmission electron microscope operating at an accelerating voltage of 200 kV. The elemental analyses were investigated by energy-dispersive X-ray spectroscopy (EDS) using an X-ray microanalyzer embedded in the JEM-2100 microscope. The Brunauer–Emmett–Teller (BET) specific surface areas were calculated using the BET equation. Desorption isotherm was used to determine the pore size distribution using the Barret–Joyner–Halender (BJH) method.

2.4. Measurement of gas sensoring

Gas sensing properties of the samples were measured using a China HW-30A gas sensitivity instrument. The details of the sensor fabrication are similar to the reported in the literature [38,39], as follows: SnO_2 powders were mixed with deionized water at a weight ratio of 4:1 to form a paste, and then coated onto an Al_2O_3 tube on which two platinum wires had been connected at each end. A Ni–Cr heating wire was inserted into the tube to form an indirect-heated gas sensor. The sensor was aged at 300 °C for 3 days before measurements in order to improve its stability and repeatability. The measurement followed a static process: a given amount of tested gas was injected into a gas chamber and mixed with air. The response ($S = R_a/R_g$) of the sensor was defined as the ratio of sensor resistance in dry air (R_a) to that in a tested gas atmosphere (R_g).

3. Results and discussion

3.1. Morphology and structure

The phase and purity of the as-prepared porous SnO_2 hollow nanospheres were determined by XRD. Fig. 1 illustrates the typical diffraction pattern. The diffraction peaks reveals that these SnO_2 nanospheres have a tetragonal crystal structure with lattice parameters $a = b = 4.74$ Å and $c = 3.19$ Å, which are well matched with those of the corresponding bulk rutile SnO_2 (JCPDS No. 41-1445). The broadened diffraction peaks indicate that the nanostructures are composed of nano-sized SnO_2 crystallites. The average crystallite size of the as-obtained SnO_2 products were calculated to be about 8 nm by Scherer's equation: $D = 0.89\lambda/(\beta \cos\theta)$, where D is the mean size of the particle, λ is the X-ray wave length (Cu-0.15418 nm), β is the full-width at half- maximum of pattern peaks and θ is the Braggs angle. No characterized peaks were observed for other impurities, revealing the high purity of the prepared SnO_2 nanospheres.

The morphology and structure of the as-prepared SnO_2 nanospheres were investigated by FSEM and TEM. Fig. 2a shows the typical FSEM image of the as-prepared SnO_2 nanospheres. It clearly shows that the products consist of interconnected hollow spheres. Some small openings in the spherical shells can also be seen, indicating the hollow structure of these spheres. Fig. 2b displays a representative TEM image of the as-prepared SnO_2 nanospheres. The average diameters of the hollow nanospheres are about 100–200 nm. The contrast between the boundary and the center of the spheres confirms their hollow nature. From this figure, it can also be observed that these spheres are composed of numerous nanoparticles and there are abundant small pores between these interconnected nanoparticles, confirming the porous nature of these SnO_2 spheres. The inset in Fig. 2b displays the corresponding SAED pattern, which shows a ring-like diffraction, suggesting that these porous SnO_2 hollow spheres are polycrystalline, due to the numerous SnO_2 nanoparticles.

To further study the fine structure and composition of these SnO_2 nanospheres, HRTEM combined with EDS has been performed. Fig. 2c shows a typical HRTEM image taken at the edge area of a single nanosphere. This image clearly reveals that the surface of SnO_2 nanosphere is rough and the sphere is composed of numerous primary nanocrystallites with an average size of about 7–9 nm, which agrees well with the XRD calculated results. Two groups of lattice fringes can be readily resolved in this image, and the distances of 0.334 and 0.264 nm between adjacent lattice planes in

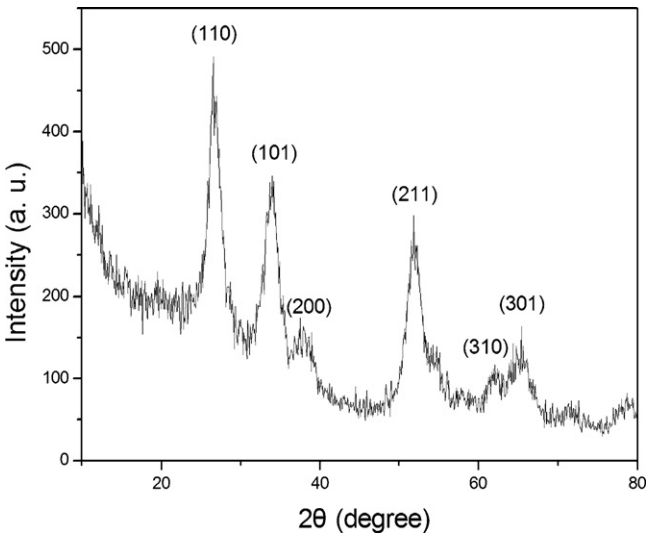

Fig. 1. XRD pattern of the as-prepared SnO_2 nanospheres.

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