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Highly sensitive gas sensors based on hollow SnO_2 spheres prepared by carbon sphere template method

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Abstract

Hollow SnO_2 spheres were prepared in dimethylfomamide (DMF) by controlled hydrolysis of $SnCl_2$ using newly made carbon microspheres as templates. The phase composition and morphology of the material particles were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The gas sensing properties of sensors based on the hollow SnO_2 spheres were investigated. It was found that the sensor exhibited good performances, characterized by high response, good selectivity and very short response time to dilute $(C_2H_5)_3N$ operating at 150 °C, especially, the response to 1 ppb $(C_2H_5)_3N$ attained 7.1 at 150 °C. It was noteworthy that the response to 0.1 ppm C_2H_5OH of the sensor was 2.7 at 250 °C.

Keywords: SnO_2; Hollow sphere; Gas sensor

1. Introduction

There is a great demand in enhancing the sensitivity of chemical sensors for applications such as monitoring and control of air quality, detection of flammable or toxic gases, medical diagnosis, detection of chemical-warfare agents, and optimization of combustion efficiency in automobile engines. Metal oxides are extensively used as gas-sensing materials because of their low cost, high sensitivity and simplicity in fabrication. The sensing mechanism of metal oxide gas-sensing materials is based on the reaction between the adsorbed oxygen on the surface of materials and the gas molecules to be detected. The decrease in resistance of n-type metal oxide sensors upon exposure to reducing gases was typically explained by a decrease in concentration of adsorbed oxygen ($O_2^-{}_{(ad)}$, $O^-{}_{(ad)}$) and a consequent increase in electron concentration. The sensitivity was related to the amount of active sites on the surface of materials that could adsorb oxygen and reducing gases. Hence, to increase the surface area and change the microstructure of materials are effectual methods to enhance the sensitivity.

Tin dioxide, an important wide bandgap semiconductor, plays a key role in potential technological applications such as gas sensors [1], dye-based solar cells [2], and solar cells [3]. As an n-type semiconductor gas sensing material, tin dioxide has attracted great attention for a long time due to its excellent gas sensitivity [4,5].

Hollow spheres with nanometer to micrometer diameter are known to have potential applications in various fields; for example, they could be used as controlled-release capsules of various substances (drugs, cosmetics, and dyes), catalysts, chemical sensors, photonic crystals, low-density structural materials, and in biotechnology [6,7]. Various methods have been developed for preparing hollow spheres. The general approach is based on the use of various removable templates, including polystyrene latex spheres [8–10], liquid crystals [11], surfactant vesicles [12,13], polymer micelles [14] and microemulsion droplets [15]. Recently, the preparation of some metal oxides hollow spheres with nanometer to micrometer diameter such as SiO_2 [16], TiO_2 and SnO_2 [17,18] was reported.

Li et al. [19] prepared hollow WO_3 microspheres by using newly made carbon spheres as templates and found that the sensors based on the hollow microspheres showed high sensitivity to alcohol and acetone. Martinez et al. [20] also investigated the gas-sensing properties of hollow Sb:SnO_2 nanoparticle microspheres prepared by using latex as templates, and the sensitivity

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of the hollow nanoparticle microspheres was higher than those of the sensors based on SnO_2 films prepared by CVD and Sb:SnO_2 microporous nanoparticles. Hyodo et al. [21] prepared hollow SnO_2 spheres by using polymethylmethacrylate (PMMA) as templates. The microporous structure provided an enhancement in both active surface area and analyte diffusion throughout the film, and these films exhibited good sensitivity to H_2 and NO.

Herein, we prepared hollow SnO_2 spheres by employing newly made carbon microspheres as templates and fabricated thick film sensors based on the hollow spheres. We found these sensors showed high responses to C_2H_5OH, $(C_2H_5)_3N$, and H_2S when operated at different temperatures. Especially, the response to 1 ppb $(C_2H_5)_3N$ attained 7.1 at 150 °C and the response to 0.1 ppm C_2H_5OH was 2.7 at 250 °C.

2. Experimental

Carbon microspheres were synthesized through the polycondensation reaction of glucose under hydrothermal conditions according to the method reported in Ref. [22]. All chemicals used in this work were analytical-grade reagents. Three gram of glucose was dissolved in 30 mL water to form a clear solution. The solution was placed in a 40 mL teflon-sealed autoclave and maintained at 160–180 °C for 3–6 h. The products were filtered, washed with water and alcohol for five times, respectively, and dried at 70 °C in air for 12 h.

Hollow SnO_2 spheres were obtained by controlled hydrolysis of $SnCl_2$ and subsequent removal of the templates by calcination in air. The typical synthesis process was as follows: tin bichloride ($SnCl_2$, 0.25 mmol) was dissolved in 5 mL of DMF, forming a 0.05 M solution. The core templates, carbon microspheres (about 0.12 g), were uniformly dispersed in 25 mL of DMF by ultrasonication, and then the $SnCl_2$ solution was added slowly to the 25 mL of DMF at a speed of 20 s per drop while being ultrasonicated. After ultrasonicating for about 30 min, a small amount of distilled H_2O (e.g. 2 mL) was added to the solution dropwise to ensure hydrolysis. After continuous ultrasonication for 1 h, the mixed solution was aged at room temperature for 1 day. The precipitate was filtered, washed with alcohol and distilled water, and dried in air. The as-prepared precursor was loaded into a quartz boat and put in a hot zone of a furnace. After calcination at 500 °C for 2 h in air, the product was cooled to room temperature, and hollow SnO_2 spheres were finally obtained. The phase composition and morphology of the material particles were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

The paste prepared from a mixture of hollow SnO_2 spheres with a poly vinyl alcohol (PVA) solution was coated onto an Al_2O_3 tube on which two gold leads had been installed at each end. The Al_2O_3 tube was about 8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter. A heater of Ni–Cr wire was inserted into the Al_2O_3 tube to supply the operating temperature which could be controlled in the range of 80–500 °C. The electrical resistance of a sensor was measured in air and in sample gases. The response was defined as the ratio of the electrical resistance in air (R_a) to that in a sample gas (R_g).

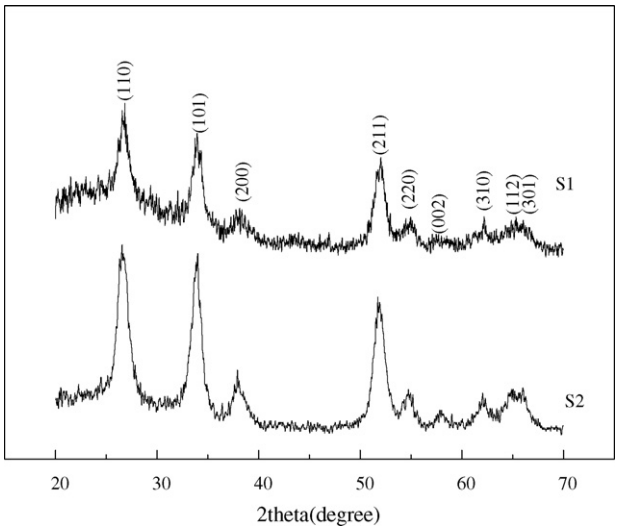

Fig. 1. The XRD pattern of samples prepared under different conditions.

3. Results and discussion

Hydrothermal reaction conditions of carbon microspheres, the composition of starting materials, and the typical XRD patterns of the products are shown in Table 1 and Fig. 1, respectively. The intensities and locations of all peaks match with those on JCPDS#71-0652, confirming that the SnO_2 shell has a tetragonal structure with $a = 4.738$ Å and $c = 3.187$ Å. According to Scherrer's equation, the crystallite size of S1 and S2 samples was 23 and 25.8 nm, respectively. There were no peaks of carbon in XRD patterns that manifested that carbon had been removed during calcination process.

Fig. 2 shows SEM images of carbon microspheres and carbon/$Sn(OH)_2$ microsphere composites. The diameters of carbon microspheres increased with increasing the hydrothermal reaction time. Aggregated carbon microspheres were found (Fig. 2a) when hydrothermal reaction time was 3 h and the corresponding carbon/$Sn(OH)_2$ microspheres with diameter 0.5–1.3 μm (Fig. 2c) were regular. When hydrothermal reaction time was 6 h, carbon microspheres were regular and the

Table 1
Hydrothermal reaction conditions of carbon microspheres and the composition of starting materials

Sample number	Hydrothermal reaction conditions of carbon microspheres			$SnCl_2·2H_2O$ (mmol)	Carbon microspheres (g)	H_2O (mL)
	Glucose concentration (mol L^{-1})	Temperature (°C)	Time (h)			
S1	0.5	160	3	0.25	0.12	1
S2	0.5	160	6	0.25	0.12	1