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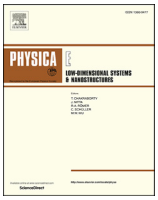

Template-free fabrication of hierarchical In_2O_3 hollow microspheres with superior HCHO-sensing properties

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ABSTRACT

Hierarchical In_2O_3 hollow microspheres were successfully prepared via a facile and low-cost hydrothermal method. Their morphology and structure were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and the Brunauer-Emmett-Teller (BET) approach. The SEM and TEM results revealed that the as-obtained hollow In_2O_3 microspheres is composed of In_2O_3 nanospheres with 200–400 nm in diameter, and the size of In_2O_3 microspheres is about 2–4 μm. The specific surface area of the as-prepared In_2O_3 is about 40.94 m^2/g. The sensor based on hierarchical In_2O_3 hollow microspheres displays excellent sensing properties to 10 ppm HCHO, and the optimum operating temperature is relatively low (200 °C). The response value of the as-fabricated sensor to 10 ppm HCHO is about 20. Due to the sensor based on hierarchical In_2O_3 hollow microspheres has many advantages, such as facile preparation and excellent gas-sensing properties, it has a wide range of prospects in practical applications.

1. Introduction

In recent years, the impact of gas pollution on the environment and the adverse effects on human health has aroused great concern, therefore, it is necessary to detect and control the harmful gases in the environment to protect human health and personal safety [1–6]. The structure of the metal oxide semiconductor is easy to change according to the change of the external environment, and the change of the electronic structure affects the resistance. When the resistance of the metal oxide semiconductor changes, it is relatively easy to be detected, so it can be used as gas-sensing material. Semiconductor based sensors with low cost, high response, fast response time, has been widely applied to various fields [7–10].

Metal oxide semiconductor materials include n-type and p-type semiconductors, among them, In_2O_3 as a typical n-type semiconductor, has a wide band gap, a smaller resistivity and a higher catalytic activity, its excellent performance has attracted widespread attention [11–15]. The structure and morphology of In_2O_3 nanomaterials affect its gas-sensing properties. In recent decades, many researchers have been working to control the structure and morphology of In_2O_3 nanomaterials to enhance its performance. In_2O_3 nanomaterials with different morphology have been reported, include nanoparticles [16], nanocubes [17], nanotubes [18], nanofibers [19], nanospheres [20], etc. Among the various nanostructure, the hierarchical structure or hollow structures with plenty pores are very beneficial for use in gas sensors. The hierarchical structure exhibits the ordered porous structure and increases the specific surface area, while low-dimension of metal oxide semiconductor does not possess this advantage [21].

In recent years, the three-dimensional hierarchical structure composed of low dimension has been widely concerned, and it has numerous advantages including easy to control shape, size and structure, so the kind of structure is expected to promote the improvement of sensing properties [22–24]. Based on this point, it is becoming more and more important to design a hierarchical structure sensing material with novel structure of high properties gas sensor. Metal oxide semiconductors with hollow structure have the advantages of high specific surface area, low density, good surface permeability and high efficiency, it has great potential in the practical application [25]. As we know, the methods of prepare hollow structures can be approximately summarized as four categories, which involve soft-templating [26], hard-templating [27], template-free [28] and sacrificial-templating [29]. Except template-free method, the other three methods need to calcine at a high temperature or by acid (alkali) washing to remove the template [30,31]. That may easily destroy the hollow structure and decrease the activity of the materials. On the contrary, the template-free method does not require to remove the template, it has no effect on the integrity of the hollow

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structures. So as to avoid damaging the structure and performances of the material, many routes have been reported the synthesis of metal oxide semiconductors with hollow structural, such as M. Z. An and co-partners have reported the ZnO nanowire film prepared by a template-free route, and tested the gas-sensing properties at room temperature. The as-obtained ZnO nanowire film by the facile method is promise for large-scale production [32]. Similarly, H. J. Zhang and co-workers have reported the preparation of ZnO hierarchical nanostructures by a low-cost and template-free method, and shows good recycling stabilities over several separation cycles in photodegradation [33]. Despite the tremendous efforts already made, the synthesis of hollow metal-oxide semiconductors without the template is still a great challenge. And In_2O_3 as a newly developed high-performance gas-sensing material in recent years is very lacking in this research. In this work, a simple and green hydrothermal route without templates was designed for the hierarchical In_2O_3 hollow microspheres, the as-obtained In_2O_3 microspheres were composed of plenty nanoparticles, and the size of these constituent units is 200–400 nm. Further testing the gas-sensing performances of the hierarchical In_2O_3 hollow microspheres based sensor. From the results, the hierarchical In_2O_3 hollow microspheres based sensor shown high response, short response time, excellent selectivity and long-term stability to HCHO at a relatively low of 200 °C.

2. Experimental

2.1. Synthesis of hierarchical In_2O_3 hollow microspheres

All of the reagents used in this experiment are of analytical grade and are not further purified. Hierarchical In_2O_3 hollow microspheres were synthesized via hydrothermal method. In a typical process, 1 mmol $InCl_3 \cdot 4H_2O$ and 2 mmol 1,4-butanediamine were dispersed into 40 mL deionized water to form a mixed solution. Then, 1 mmol citric acid was added into above solution under stirring for 10 min to mix the solution evenly. Then, transferred the above solution into a 50 mL Teflon-lined stainless steel autoclave, set the reaction temperature was 180 °C and maintained at this temperature for 20 h. After the reaction is over, the as-obtained precipitates were washed by centrifugation to remove impurities and unreacted raw materials. Finally, the pre-synthesized $In(OH)_3$ precursors were calcined at 500 °C for 3 h at air atmosphere. After calcined, the hierarchical In_2O_3 hollow microspheres were obtained.

2.2. Characterization

The as-prepared hierarchical In_2O_3 hollow microspheres sample was characterized by X-ray diffractometer (XRD, Bruker D8 Advance, $\lambda = 0.15406$ nm) with CuKα radiation. The morphology of the surface of the sample was recorded with the field-emission scanning electronic microscope (FESEM, FEI Company, QUANTA FEG 250). The internal structure of the sample was observed by transmission electron microscope (TEM, Hitachi H-800). The pore-size distribution and specific surface area of the sample were obtained by Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) methods using N_2 adsorption-desorption isotherms (Micromeritics Instrument Corp., ASAP2460), respectively.

2.3. Fabrication and measurement of the gas sensors

The sensors were fabricated by a common method, as Fig. 1 shows, the Al_2O_3 ceramic tubes were welded to the base, a Ni-Cr resistor was put into the ceramic tube, which is used as a heater. Then, 50 mg as-obtained hierarchical In_2O_3 hollow microspheres sample were dispersed uniformly into anhydrous ethanol to obtain homogeneous slurry. The slurry with moderate viscosity was uniformly coated on the Al_2O_3 ceramic tube by a small brush to form a thin sensing layer. The as-fabricated sensor was aged in air surroundings at 200 °C for at least 24 h before test. Therefore, an indirectly-heated gas sensor has been fabricated. Gas sensing tests were carried out on an indigenously built computer controlled WS-30A system (Weisheng Instruments Co., Zhengzhou, China). The measurement was carried out as follows: the as-fabricated sensor was put into the test chamber (18 L in volume) to measure of the gas-sensing performances and then a certain amount of target gas was injected into the chamber with a small injector. The response is defined as R_a/R_g for n-type sensor and R_g/R_a for p-type sensor (R_a and R_g are the resistances of the sensors in air and in the target gas, respectively). The response and recovery times are defined as the time required to reach 90% of the final equilibrium value.

3. Results and discussion

3.1. Morphologies and structure properties of sample

The XRD patterns of the $In(OH)_3$ precursors and hierarchical In_2O_3 hollow microspheres samples are shown in Fig. 2. From Fig. 2(a) we can see that the detectable peaks can be indexed to $In(OH)_3$ with the cubic phase, all the main peaks can be correspond to PDF standard card (No. 16-0161) and no other peaks from other materials are detected. As it can be seen in Fig. 2(b), all the diffraction peaks could be indexed to the cubic structure of In_2O_3, which were in good consistent with the JCPDS No. 06-0416. According to the XRD patterns, there are no diffraction peaks from any other impurities were detected, which indicating that the as-obtained samples possess high purity. The average crystallite size of as-prepared hierarchical In_2O_3 hollow microspheres was calculated by Scherrer formula,

$$D = K\lambda/\beta\cos\theta \tag{1}$$

where D is the grain size, K is the Scherrer constant, usually is 0.89, λ is the incident X-ray wavelengths, and β is the wide of the half of the diffraction peak, θ is the Bragg diffraction Angle. By calculating, we can know the crystallite size of as-prepared In_2O_3 sample is 15.8 nm.

The surface morphology of the hierarchical In_2O_3 hollow microspheres was observed by field emission scanning electron microscopy (FESEM). Fig. 3 exhibits the FESEM images and EDS pattern of the as-synthesized hierarchical In_2O_3 hollow microspheres sample. Fig. 3(a) shows the low magnification SEM image, it can clearly display that the

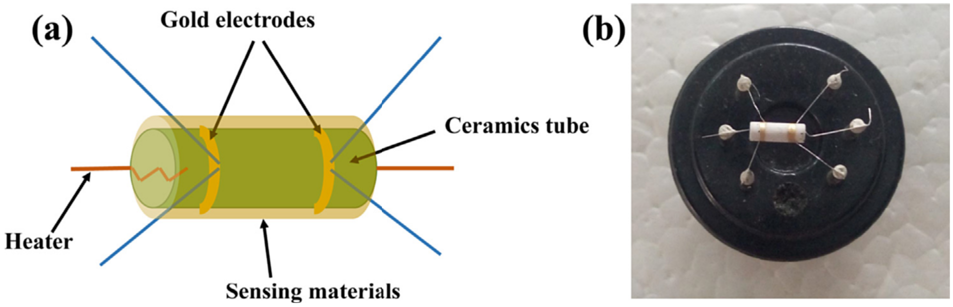

Fig. 1. (a) Schematic and (b) photograph images of the as-fabricated gas sensor.