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Review

In_2O_3-SnO_2 hybrid porous nanostructures delivering enhanced formaldehyde sensing performance

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Novel In_2O_3-SnO_2 hybrid sensing nanostructures with porous nature were successfully prepared and characterized by various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM). Gas sensing properties of the fabricated sensor based on the as-prepared In_2O_3-SnO_2 hybrid nanostructures were systematically investigated and compared with those of pure SnO_2. The hybrid nanostructures containing 3% In_2O_3 exhibit the highest response value of 30.7–100 ppm formaldehyde at 100 °C, which was 14 times higher than that of pure SnO_2. Moreover, gas sensors based on the as-prepared In_2O_3-SnO_2 hybrid nanostructures also exhibit high stability and good selectivity for formaldehyde. The enhanced sensing performances of formaldehyde were mainly attributed to the formation of n-n heterojunctions and the synergistic interaction between In_2O_3 and SnO_2.

Contents

1. Introduction

Formaldehyde is one of the most toxic indoor air pollutants, which is mainly released from building materials, furniture, varnishes, and household cleaning products. Many reports have shown that a long-term exposure to formaldehyde affects the human

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immune system and may cause respiratory diseases, skin sensitization, and even cancer [1–4]. Traditional formaldehyde detection technologies, such as gas chromatography, polarography, fluorimeter, and spectrophotometry are expensive, time-consuming and difficult to operate, which limit their wide applications [5–9].

Semiconducting metal oxide gas sensors are attractive for solid-state gas detecting devices because of their high sensitivity, low-cost, simplicity, and compatibility with modern microelectronic processing devices [10–15]. SnO_2 is a chemically and thermally stable n-type wide band gap semiconductor ($Eg = 3.6$ eV at room temperature) and has been widely utilized as a gas-sensing material [16–22]. Its sensing process can be attributed to the resistivity changes with gas adsorption and desorption at the surface [23,24].

Although SnO_2 is one of the most promising metal oxides for gas sensors, many problems concerning its sensing performances, such as working temperature, sensitivity and selectivity remain to be solved [25,26]. Hierarchical SnO_2 architectures are always attractive for sensing applications due to their large specific surface area and porous nature [27–29]. Many recent studies have also shown that the selectivity and other important sensing characteristics can be enhanced by using hybrid nanostructures [30–34]. Hybrid nanostructures integrate different physicochemical properties of two or more components and usually exhibit superior sensing performance over their single component counterparts due to their synergistic interactions and the formation of heterojunctions.

To date, various hybrid nanostructures have been reported by many groups. For example, Zeng et al. synthesized SnO_2 functionalized TiO_2 nanobelts with high response to volatile compounds (VOCs) [35]. Li et al. reported In_2O_3/SnO_2 heterojunction microstructures with a high response to Cl_2 [36]. In addition, ZnO-doped porous SnO_2 hollow nanospheres and NiO-SnO_2 hybrid nanostructures have been successfully prepared by our group with superior sensing properties to ethanol and formaldehyde respectively [37,38].

As an n-type semiconductor, indium oxide (In_2O_3) has also been intensively investigated as gas sensor materials. The electrical conductivity of In_2O_3 is very sensitive to the external environment, which makes it very suitable to act as dopants in the design of gas sensors with high sensitivity. Therefore, it will be of great importance to explore the possibility of obtaining new In_2O_3-SnO_2 hybrid hierarchical nanostructures with controlled contents and tailored performances. In this work, In_2O_3-SnO_2 hybrid porous nanospheres were prepared using a facile hydrothermal method followed by calcination. Compared with pure SnO_2, markedly decreased optimum working temperature, significantly improved gas sensitivity and selectivity have been achieved by the as-prepared In_2O_3-SnO_2 hybrid nanostructure towards formaldehyde. The optimum amount of In_2O_3 and the possible enhancement mechanism were also discussed.

2. Experimental

2.1. Materials

All the reagents were of analytical grade and used without any further purification. Tin dichloride ($SnCl_2$ $2H_2O$), sodium hypochlorite (NaClO), were purchased from Aladdin Reagent Co. Ltd. Hydrochloric (HCl, 36%) was obtained from Shanghai Chemical Reagent Company. Indium (III) acetate ($C_6H_9InO_6$) was procured from Alfa Aesar Chemical Co. Ltd (China). Distilled water was used throughout the experiments (18.2 MΩ cm).

2.2. Preparation of porous SnO_2 nanostructures

The SnO_2 porous nanostructures were synthesized similar to our previous work [22]. In a typical procedure, 0.6 mL of HCl and 2.0 mmol of $SnCl_2$ $2H_2O$ was dissolved in 30 mL ethanol under continuous stirring condition. Then, 1.5 mL of NaClO was added into the ethanol solution. After several minutes of stirring, the obtained white slurry was sealed into a Teflon-lined stainless-steel autoclave with a capacity of about 50 mL and heated at 180 °C for 24 h. After the autoclave was cooled to room temperature naturally, the products were collected and thoroughly washed with distilled water and absolute ethanol.

2.3. Preparation of In_2O_3-SnO_2 hybrid porous nanostructures

In_2O_3-SnO_2 hybrid porous nanostructures were prepared by ultrasonic deposition, followed by calcination. Typically, 0.2 g SnO_2 was suspended in 30 mL of ethanol solution respectively containing 0.0265, 0.0796, 0.132 and 0.265 mmol $In(CH_3COO)_3$ and then ultrasonicated for 30 min to obtain hybrid nanostructures with different content of In^{3+}. The products were centrifuged and dried at 60 °C for 12 h and then calcined at 500 °C for 3 h in air atmosphere. Finally, In_2O_3-SnO_2 hybrid porous nanostructures were obtained for gas sensor fabrication.

2.4. Characterization

The as-prepared products were characterized by X-ray diffraction (XRD) using a Bruker D8 advanced X-ray diffractometer equipped with a graphite monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å). The morphology of the products was taken using Emission scanning electron microscope (SEM: Japan, JSM-6700F). HRTEM images were recorded with a JEM-2100 transmission electron microscope operating at an accelerating voltage of 200 kV. The surface state analysis was carried out by using X-ray photoelectron spectroscopy (XPS), which was conducted on an ESCALAB 250 photoelectron spectrometer with Al Kα radiation as the X-ray source for excitation. The Brunauer–Emmett–Teller (BET) specific surface area measurements were performed using ASAP2020 HD88.

2.5. Gas sensing measurements

The gas sensing test was operated on a HW-30A system (Hanwei Electronics Co. Ltd.). The pure SnO_2 and In_2O_3-SnO_2 hybrid powders were mixed in ethanol to obtain a paste, followed by printed onto alumina tubes with a Ni–Cr heating wire placed inside. And then, the tubes were aged at 450 °C for 120 h to improve the stability and repeatability. The measurements followed a static process: a given amount of tested gas was injected into a gas chamber and mixed with air. Sensor response (S) is defined as $S = R_a/R_g$, where R_a and R_g represent the resistance in air and target gas, respectively. In the measuring electric circuit for gas sensors (as shown in Fig. 1), a load resistor was connected in series with a gas sensor.

3. Results and discussion

3.1. Possible mechanism of formation

In order to understand the formation mechanism of the In_2O_3-SnO_2 hybrid porous nanostructures, the thermal behavior of the indium acetate was investigated first, as shown in Fig. 2. The TGA curve of indium acetate shows two distinct steps: the first weight loss was due to the evaporation of water (ca. 13.8%), and the weight loss (ca. 32.8%) from 243.6 °C to 348.7 °C was caused due to the decomposition of labile oxygen groups. After 500 °C, a simple linear dependence was displayed, indicating the weight loss of carboxyl. The weight loss results observed from Fig. 2 were in good