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Enhanced acetone sensing performance of an α-Fe_2O_3-In_2O_3 heterostructure nanocomposite sensor

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ABSTRACT

The reasonable design of heterojunction nanostructures is a useful method for enhancing the properties of gas sensors based on metal oxide semiconductors. In this study, α-Fe_2O_3-In_2O_3 heterostructure nanocomposites were synthesized via a low-cost and simple hydrothermal route. The structure and morphology of α-Fe_2O_3-In_2O_3 heterostructure nanocomposites were investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, the Brunauer–Emmett–Teller (BET) approach, and X-ray photoelectron spectroscopy. The results showed that the diameter of the α-Fe_2O_3-In_2O_3 heterostructure nanocomposites was about 2–3 μm, and the length and diameter of the Fe_2O_3 nanorods were about 1 μm and 10–15 nm, respectively. The BET surface area was calculated as 67.23 m^2/g and the pore size was mainly distributed around 11 nm. Gas-sensing tests showed that the optimum operating temperature for the as-obtained α-Fe_2O_3-In_2O_3 heterostructure nanocomposite-based sensor was 300 °C. When the acetone concentration was 20 ppm, the response of the α-Fe_2O_3-In_2O_3 heterostructure nanocomposite-based sensor was about 37, which was about seven times higher than that of the pure material. Therefore, this α-Fe_2O_3-In_2O_3 heterostructure nanocomposite system merits further systematic investigation.

1. Introduction

Metal oxide semiconductors with outstanding advantages in terms of their low cost, non-toxicity, non-polluting properties, and stable performance have been studied widely, and they have a wide range of practical applications [1]. Among these metal oxides, indium oxide (In_2O_3) is a new n-type semiconductor material with a large band gap (between 3.55 and 3.75eV) and low resistivity, and it has been used widely in fields such as optoelectronics, gas sensing, and catalysis [2]. To obtain high gas-sensing performance with In_2O_3, pure or different types of metal-doped In_2O_3 have been prepared with different morphologies and structures. At present, nanostructure In_2O_3 products are mainly zero-dimensional, one-dimensional, two-dimensional, and three-dimensional, such as nanospheres [3], nanowires [4], nanotower [5], nanocubes [6], and nanosheets [7], and the different structures of In_2O_3 comprise hierarchical structures [8], hollow structures [9], and porous structures [10]. However, greatly improving the sensing properties of these materials is still a challenge. Several methods have been employed to improve the sensing properties, such as loading with noble metals [11], heterostructure formation [12], and metal cationic doping [13].

Heterostructure formation is a commonly used method for improving the sensing properties of materials. Synthesizing a heterojunction structure between In_2O_3 nanospheres and other metal oxide semiconductors is a suitable method for enhancing their sensing performance. For instance, Liu et al. reported a method for preparing In_2O_3-ZnO hollow microtubules by using cotton as the template and subjecting to calcination, which significantly improved the gas sensing performance with acetone [14]. Ma et al. reported the synthesis of a ZnO-modified In_2O_3 heterojunction via a simple two-stage route, which exhibited enhanced HCHO sensing performance [15]. Lee et al. reported the synthesis of In_2O_3 nanowires decorated with TeO_2 nanobeads via a facile single-step thermal evaporation process, which enhanced the sensing properties with acetone [16]. According to these previous studies, designing the morphology and constructing a heterojunction structure at the same time would be beneficial for improving the gas-sensing properties, but this important issue has not been addressed adequately.

Iron oxide (Fe_2O_3) is another typical n-type metal oxide semiconductor, which has a band gap of ~2.2 eV. Nanoscale Fe_2O_3 is a traditional type of sensing material and it has been investigated widely due to its high sensitivity, rapid response, long-term stability, and other

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advantages [17]. Recently, Fu et al. reported a facile two-step synthesis route for preparing flower-like ZnO/α-Fe_2O_3 nanosheets, where the as-obtained samples exhibited excellent properties, such as a high response and recovery capacity, and they have potential applications in detecting ethanol at low concentrations [18]. Similarly, Choi et al. found that the response of a sensor based on SnO_2 nanowires coated with Fe_2O_3 nanoparticles was 1.48–7.54 times higher than that of a sensor based on pure SnO_2 nanowires [19]. Thus, the design and synthesis of In_2O_3/Fe_2O_3 heterostructure nanocomposites could be highly beneficial. However, few studies have considered the construction of heterojunction nanocomposite systems based on In_2O_3 and Fe_2O_3. In this study, we synthesized In_2O_3 nanospheres with regular size and distribution properties using a facile and green hydrothermal route. Fe_2O_3 nanorods were subsequently grown on the In_2O_3 nanospheres to form a heterojunction structure. The microstructure and sensing properties of the Fe_2O_3-In_2O_3 heterostructure nanocomposites were also investigated.

2. Experimental

2.1. Synthesis of mesoporous In_2O_3 nanospheres

All of the reagents used in this study were analytical grade and no further purification was performed. Mesoporous In_2O_3 nanospheres were prepared via a facile and pollution-free hydrothermal method, with subsequent calcination. In a typical process, 1 mmol $InCl_3{\cdot}4H_2O$ and 1 mmol $C_{12}H_{27}N$ (dodecylamine) were dissolved in 35 mL of absolute ethanol under continuous stirring to obtain a homogeneous solution. The mixed solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave. The reaction temperature was maintained at 180 °C for 12 h. After completing the reaction, the autoclave was allowed to cool to room temperature, the supernatant was decanted, and the precipitates were collected by centrifugation. The precipitates were dried at 60 °C. Finally, the as-obtained $In(OH)_3$ precursors were calcined at 500 °C for 3 h to obtain mesoporous In_2O_3 conversions.

2.2. Synthesis of α-Fe_2O_3-In_2O_3 heterostructure nanocomposites

First, 50 mg of the as-obtained In_2O_3 nanospheres were dissolved in 40 mL of deionized water. Next, 0.108 g $FeCl_3{\cdot}6H_2O$ and 0.129 g $Na_2SO_4{\cdot}10H_2O$ were added to the solution under stirring. This mixed solution was then transferred to a 50 mL Teflon-lined stainless steel autoclave and hydrothermally treated at 120 °C for 10 h. The as-prepared precipitates were washed three times with deionized water and absolute ethanol, and then dried at 60 °C in the air. Finally the as-obtained products were annealed at 500 °C for 2 h in a muffle furnace. Pristine Fe_2O_3 samples were also obtained by adding In_2O_3 nanospheres according to the same procedure.

2.3. Characterization

The phase composition, crystal structure, and purity of the as-obtained pure mesoporous In_2O_3 nanospheres and α-Fe_2O_3-In_2O_3 heterostructure nanocomposite samples were estimated by powder X-ray diffraction (XRD; Bruker D8 Advance; λ = 0.15406 nm) using Cu-Kα1 radiation. The surface morphology of the samples was observed by field emission scanning electronic microscopy (FESEM, FEI Company, QUANTA FEG 250) and energy-dispersive X-ray spectroscopy (EDS) analysis was conducted using the FESEM attachment. Further analyses of the samples were performed by transmission electron microscopy (TEM, Hitachi H-800). X-ray photoelectron spectroscopy (XPS) data were acquired with a Thermo Scientific Escalab 250Xi in order to determine the elemental composition and the valences in the samples. The specific surface area was estimated according to the Brunauer–Emmett–Teller (BET) equation based on the nitrogen adsorption isotherm.

2.4. Fabrication and measurement of the gas sensors

The sensors were fabricated using a standard method [20,21]. Al_2O_3 ceramic tubes (7 mm in length and 1.5 mm in diameter, with a pair of gold electrodes and four Pt wires) were welded to a base with six terminals, and a Ni-Cr resistor was placed in the ceramic tube and fixed to the base to provide the operating temperature as a heater. Next, 50 mg of the as-prepared pure mesoporous In_2O_3 nanospheres and 50 mg of the α-Fe_2O_3-In_2O_3 heterostructure nanocomposites were dispersed uniformly in deionized water to form separate pastes. The pastes were uniformly coated on the ceramic tube with a small brush to form a thin sensing layer. The as-fabricated sensors were aged in the air at 280 °C for at least 1 day before testing, which made them more stable. Therefore, indirectly heated gas sensors were produced. The as-fabricated sensors were placed in the test chamber of a WS-30 A measuring system in a static process. In a typical test procedure, after the resistances of all the sensors stabilized, a specific amount of the target gas or liquid was injected into the chamber using a micro-injector. If the test gas was an aqueous solution, the concentration of the test gas was calculated using the following formula:

$$C = (22.4{*}\rho{*}d{*}V_1)/(M{*}V_2), \quad (1)$$

where C (ppm) is the required concentration of the target gas, ρ (g/mL) is the density of the liquid, d is the purity of the liquid, V_1(L) is the volume of the liquid, V_2(L) is the volume of the test chamber, and M (g/mol) is the molecular weight of the liquid. The response of the sensor in the air or in the target gas could be measured by monitoring the voltage across the reference resistor. The sensor response was defined as:

$$\mathrm{Re}\,sponse = R_{gas}/R_{air}, \quad (2)$$

where R_{air} and R_{gas} are the resistances of the sensor in the air and in the presence of the test gas, respectively.

3. Results and discussion

3.1. Structural and morphological characteristics

Fig. 1 shows the XRD patterns obtained for the pure In_2O_3 samples, pure α-Fe_2O_3, and α-Fe_2O_3-In_2O_3 heterostructure nanocomposites. Fig. 1(a) shows the XRD patterns for the In_2O_3 obtained by calcining the $In(OH)_3$ precursors. The main diffraction peaks obtained for the product are consistent with the standard card for In_2O_3 (JCPDS No.06–0416), which has a typical cubic structure (space group Ia-3), thereby confirming that the pure phase In_2O_3 was synthesized. Fig. 1(b) shows the XRD pattern obtained for the α-Fe_2O_3 samples, where all of the main diffraction peaks correspond to orthorhombic α-Fe_2O_3 (JCPDS No.33–0664). Fig. 1(c) shows the XRD pattern for the α-Fe_2O_3-In_2O_3 heterostructure nanocomposite product obtained by heat treatment of the α-FeOOH-In_2O_3 nanocomposite powder at 500 °C for 2 h, where the main diffraction peaks correspond to orthorhombic α-Fe_2O_3 (JCPDS No. 33–0664) and cubic In_2O_3 (JCPDS NO.06–0416). No other impurity peaks were observed, thereby indicating that no chemical reaction occurred between the different types of metal oxides at the calcination temperature of 500 °C.

The surface morphologies of the samples were determined by scanning electronic microscopy (SEM). Fig. 2 shows SEM images of the $In(OH)_3$ precursors, pure In_2O_3 nanospheres, α-FeOOH-In_2O_3 nanocomposites, and α-Fe_2O_3-In_2O_3 heterostructure nanocomposites, as well as the mapping patterns of the α-Fe_2O_3-In_2O_3 heterostructure nanocomposites. Fig. 2(a) shows an SEM image of the $In(OH)_3$ precursors. The $In(OH)_3$ particles appeared to have a spherical morphology, where the nanospheres measured 200–300 nm with relatively smooth surfaces, while the size distribution of $In(OH)_3$ nanospheres was uniform and they were well dispersed. Fig. 2(b) shows an SEM image of In_2O_3,