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Controllable biomolecule-assisted synthesis and gas sensing properties of In_2O_3 micro/nanostructures with double phases

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ABSTRACT

In_2O_3 micro/nanostructures including nanosheet-based microflowers, nanoparticle-based nanorods and nanoparticles with mixed hexagonal and cubic phases were fabricated by one-pot hydrothermal/solvothermal treatment of D-glucose/$In(NO_3)_3 \cdot xH_2O$ mixture using urea as a precipitating agent in water-ethanol mixed solution followed by calcination. The effect of solution on the fabrication of In_2O_3 micro/nanostructures was investigated and a possible mechanism was proposed to explain the formation of In_2O_3 micro/nanostructures. The mixed hexagonal and cubic phases of In_2O_3 micro/nanostructures were further proved in Raman spectra. The gas sensor based on the nanosheet-based In_2O_3 microflowers exhibited excellent sensing properties for the detection of formaldehyde.

1. Introduction

Formaldehyde, an important chemical used widely by industry to manufacture building materials and numerous household products, is colorless and pungent-smelling, which can cause burning sensations in the eyes and throat, nausea, and difficult in breathing in some human exposed at elevated levels. Formaldehyde is considered as a major cause of sick building syndrome (SBS) [1]. Thus, it is significant to detect formaldehyde quickly and accurately. Till now, metal oxide semiconductors such as ZnO, SnO_2 and WO_3 have been successfully synthesized for the formaldehyde detection.

In_2O_3 is an important n-type semiconductor with a wide bandgap of 3.55–3.75 eV, which holds potential applications in electronic and optoelectronic devices such as transparent electronics, flat panel displays, light-emitting diodes, solar cells, and gas sensors because of its high optical transparency and electrical conductivity [2]. In_2O_3 typically exists in cubic bixbyite (c-In_2O_3) and hexagonal corundum (rh-In_2O_3) forms. To date, various In_2O_3 nano/microstructures such as 0D nanocrystals [3], 1D nanowires/nanorods/nanobelts/nanotubes [4–7], 2D thin films [8] and nanosheets [9] and 3D hierarchical nano/microstructures [10–13] have been synthesized by different methods. Among them, 3D hierarchical nano/microstructures, assembled with nanoparticles, nanocubes, nanorods, nanowires or nanosheets, are considered to be the promising candidate of electronic and optoelectronic devices due to their unique structure with low density and high specific surface area. In_2O_3 was a promising candidate for the effective detection of NO_2 [14], C_2H_5OH [15], formaldehyde [16–25] and so on. However, much research attention focuses on the gas sensing properties of c-In_2O_3. There are only few reports on the gas sensing properties of rh-In_2O_3 [26–29] and In_2O_3 with mixed hexagonal and cubic phases [30]. P.Y. Song and W.D. Zhang reported that the response of In_2O_3 with mixed hexagonal and cubic phases was higher than that of pure c-In_2O_3 and rh-In_2O_3 [30].

Biomolecules such as sugars and amino acids are often used as the template to prepare metal oxide hollow spheres [31–34]. In our previous study, nanosheet-based rh-In_2O_3 microflowers [35] and single In_2O_3 nanosheets mixed hexagonal and cubic phase [36] were obtained by D-fructose-assisted hydrothermal/solvothermal process. In this study, In_2O_3 micro/nanostructures including nanosheet-based microflowers, nanorods and nanoparticles were accomplished by D-glucose-assisted hydrothermal/solvothermal process. This approach involves none of the toxic organic solvents or surfactants and is simple, inexpensive and productive.

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Table 1
Experimental conditions, phase and morphology of the samples.

Experimental conditions		Phase	Morphology
Water (mL)	Ethanol (mL)		
16	0	rh-In_2O_3 and c-In_2O_3	nanosheet-based microflowers
14	2	rh-In_2O_3 and c-In_2O_3	nanosheet-based microflowers
10	6	rh-In_2O_3 and c-In_2O_3	nanoparticle-based nanorods
2	14	rh-In_2O_3 and c-In_2O_3	nanoparticles
0	16	c-In_2O_3	microspheres

2. Experimental section

All reagents were of analytical grade without further purification. The preparation method is similar to our reported literature [36]. 0.1058 g $In(NO_3)_3{\cdot}xH_2O$, 0.432 g D-glucose and 0.064 g urea were added to 16 ml deionized (DI) water and absolute ethanol mixed solution in a 50 ml Teflon-lined stainless steel autoclave, and the mixture was stirred magnetically for 5 min at room temperature, the autoclave was sealed and maintained at 160 °C for 16 h in an oven. Subsequently, the obtained product was filtered, washed several times with DI water and then dried in air at 60 °C overnight. Finally, the precursor was calcined at 450 °C for 6 h to obtain In_2O_3. The experimental conditions were shown in Table 1.

X-ray diffraction (XRD) analysis was carried out on a Siemens D5005 X-ray diffractometer with Cu Kα1 radiation ($\lambda = 1.5406$ Å). The morphology of the samples was observed by a scanning electron microscope (SEM; Hitachi S-4800, Japan) and transmission electron microscope (TEM; JEOL JEM 2100F, Japan). The Raman spectroscopy was recorded on a LabRam HR spectrometer (JY-Horiba) with He–Cd laser as the excitation source ($\lambda_{ex} = 325$ nm). The XPS data were recorded at different temperatures on an ESCALAB 250 Xi XPS system from Thermo Fisher Scientific, England and excited by monochromatic Al Kα radiation. The peak at 284.6 eV attributed to the C—C band in the C1s spectrum was used as a binding energy reference.

The structure of a sensor element is illustrated in Fig. 1(A). Details of gas sensing measurement were reported in our previous paper [37]. The sample was mixed with an organic binder (terpilenol) to form a paste. The paste was coated onto an Al_2O_3 tube with two gold leads at each end. After being dried in air, it was sintered at 300 °C for 2 h. Finally, the electrodes were fixed on the circuit for measurement. A heater using Ni-Cr wire was inserted into the Al_2O_3 tube to provide the necessary operation temperature. The measuring electric circuit is shown in Fig. 1(B). Through varying heating voltage (V_h), different operating temperatures of a sensor could be obtained. In the measurement of electric circuit for gas sensors, a load resistor (R_L) was connected in series with a gas sensor. The circuit voltage (V_c) was set at 5 V, and the output voltage (V_{out}) was the terminal voltage of the load resistor. The response (S) was defined as the ratio (R_a/R_g) of the resistance in air (R_a) and in a sample gas or vapor (R_g). The response/recovery time is defined as the time to reach 90% of the final change in resistance, when the gas is turned on or off, respectively. Fig. 1(C) shows the gas sensing test device. The test was operated in a measuring system of HW-30A (Hanwei Electronics Co. Ltd., Henan, China). A stationary state gas distribution method was used for testing gas response. The gas concentration in the chamber was calculated according to the amount of gas or liquid injected and the chamber volume. When the gas (CO, H_2, CH_4, liquefied petroleum gas (LPG)) was injected into the test chamber, it could mix with air and then adsorb on the surface of the sensor. For the liquid (formaldehyde (37 wt%), ammonia, benzene, toluene, ethanol, methanol, and acetone), it should be injected on an evaporator through the hole at the back of the chamber. Through the heating evaporator, the liquid sample was converted to its vapor phase, and then mixed with air. The resistance of the sensor changed and reached a stable value several seconds later through contacting and reacting with the gas. In the meantime, the resistance of the sensor in the test gas (R_g) can be recorded. Finally open the test chamber, the sensor contacted with air again, and then the resistance of the sensor returned to the level before the gas injection. The relative humidity of background air was controlled by a humidifier.

3. Results and discussion

3.1. Crystal structure and morphology of the samples

The XRD patterns of the samples are shown in Fig. 2. In can be seen from Fig. 2(a–d) that the samples prepared with 0–14 ml ethanol were the mixed crystal structure of rh-In_2O_3 (JCPDS 22-0336) and c-In_2O_3 (JCPDS 06-0416), and the diffraction peak intensity of rh-In_2O_3 decreased with the increase of the ethanol volume. As shown in Fig. 2(e), the peaks of the sample prepared with 16 ml ethanol were well index to the standard c-In_2O_3 (JCPDS 06-0416).

Fig. 3 shows SEM images of the samples before sintering process. The morphology of sample prepared without ethanol (Fig. 3(a)) was the mixture of carbon spheres and microflowers. When 6 ml and 14 ml ethanol were used, the sample was changed into the mixture of carbon spheres with nanorods (Fig. 3(b)), and nanoparticals (Fig. 3(c)), respectively. When ethanol was increased to 16 ml, microspheres were formed, as shown in Fig. 3(d). Figs. 4 and 5 show SEM, TEM and HRTEM images of the samples after sintering process. As shown in Figs. 4 (a and b) and 5 (a and b), without adding ethanol, upon calcination in air, the carbon in the sample was oxidized to CO_2, only nanosheet-based microflowers were leaved. The product consisted of many microflowers with diameter about 1.7 μm and these microflowers were built up by many interlaced nanosheets with thickness of about 20 nm and length of several hundred nanometers. Careful observation from the SEM and TEM images revealed that the nanosheets were composed of many small nanoparticles. There were many nanopores with different sizes among nanosheets, and their diameter ranged from 10 to 200 nm. The carbon among nanosheets disappeared after being calcined, resulting in the formation of nanopores. The corresponding HRTEM image (Fig. 5(b)) of a typical microflower exhibited well defined lattice fringes. The interplanar spacing of 0.397 nm and 0.292 nm corresponded to the lattice distance of the (012) planes of rh-In_2O_3 and (222) planes of c-In_2O_3, respectively. The HRTEM image further confirmed that this sample was the mixed phase of rh-In_2O_3 and c-In_2O_3. By increasing the amount of ethanol to 2 ml (Figs. 4 (c and d) and 5 (c and d)), the product was still nanosheet-based microspheres, and the diameter of microflowers increased to about 3.1 μm. When the amount of ethanol was further increased to 6 ml (Figs. 4 (e and f) and 5 (e–g)), the nanorods appeared, and the average diameter and length of nanorods were 20 nm and 160 nm, respectively. Careful observation from the TEM images revealed that the nanorods were assembled with nanoparticles and the average diameter of nanoparticles was 16 nm. However, more ethanol (14 ml and 16 ml) resulted in the formation of nanoparticles (Figs.