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Novel lotus root slice-like self-assembled In_2O_3 microspheres: Synthesis and NO_2-sensing properties

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ABSTRACT

Novel lotus root slice-like self-assembled hierarchical In_2O_3 microspheres with porous structure are fabricated successfully by a facile, template-free solvent-thermal method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) are employed to characterize their structures and morphologies. The results reveal that the as-synthesized microspheres after calcination are cubic phase In_2O_3 and subunits are lotus root slice-like nanosheets with porous structure benefiting enhancement of gas sensing. The sensing properties of the sensors based on the In_2O_3 microspheres are investigated. The sensors show fast and excellent response to NO_2. We think this higher response more than that of In_2O_3 nanoparticles is attributed to unique hierarchical and porous structures. Furthermore, the obtained NO_2 sensor has a prominent long-term stability.

1. Introduction

Resistance changes in oxide-based semiconductor gas sensors have been used extensively to monitor toxic gas species due to their simple working principle, high sensitivity, portability and low cost [1–3]. And long-term stability of the sensor is also required in application of detection [4]. Nanocrystalline particles of semiconducting metal oxides show high sensitivity performance, but lack of long-term stability of nanoparticles caused by particles agglomeration and grain growth limited their application in gas sensors [5,6]. Previous works revealed hierarchical microstructures materials possess excellent stability and reversibility compared with single nanoparticles, although they do not always show high sensitivity [7]. However, the sensitivity of hierarchical microstructures gas sensor can be enhanced by porous structures, because the amount of pores in the materials exhibit large effective surface areas and facilitate high accessibility for gas molecules [8,9]. Therefore, we develop a kind of self-assembled hierarchical microspheres with porous structure expected to achieve high sensitivity and long-term stability.

Indium oxide (In_2O_3), an important *n*-type (III–VI) semiconductor functional material with a wide band gap of ca. 3.6 eV, exhibits excellent optical, chemical, and electronic properties, thus drawn a worldwide attention in optoelectronic devices, such as solar cells [10], flat-panel display materials [11], and gas sensors [12]. As the morphology and structure of In_2O_3 materials are key factors affected their performances, many efforts have been devoted to control the morphology and structure so as to enhance their properties [13]. Numerous In_2O_3 nanostructures of different morphologies, such as quantum dots [14], nanorods [15], nanofibers [16], nanotubes [17], nanobelts [18], nanocrystal chains [19], and nanosheets [20] have been successfully fabricated by a variety of methods. Whereas controlled synthesis of three-dimensional (3D) In_2O_3 hierarchical micro-/nanostructures are highly desirable for a vast range of applications due to their peculiar structures. Especially, In_2O_3-based gas sensor with hierarchical and porous structure which is especially suitable for gas adsorption and diffusion, possess excellent gas-sensing performance, making it to be a promising material for detection of low concentrations of target gases.

Nitrogen dioxide (NO_2) is a typical air pollutant, furthermore, is a main source of acid rain and photochemical smog which are harmful to people, animals and plants [21]. Aiming to detect such hazardous NO_2 gas, lots of efforts have been developed to a variety of NO_2 gas sensors such as electrochemical sensors [22], SAW sensors [23], and polymer sensors [24]. Among these gas detection methods, semiconductor gas sensors played an important role, because of its inexpensive and high sensitivity in the low concentration range for NO_2 monitoring. Meanwhile semiconductor gas sensors make it possible to detect NO_2 in real time [25]. Herein, we report a facile way for preparing novel lotus root slice-like

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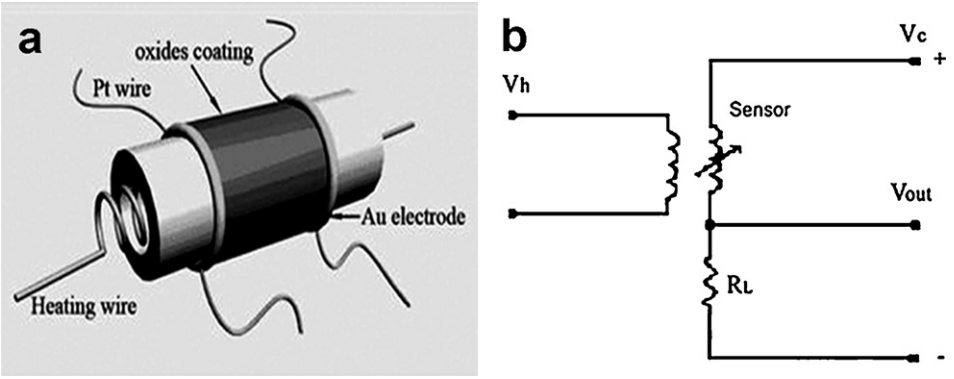

Fig. 1. (a) The sketch of the gas-sensor element and (b) the measuring electric circuit for the gas sensor.

self-assembled In_2O_3 microspheres by a template-free solvent-thermal method. The as-prepared hierarchical and porous structures of In_2O_3 microspheres show excellent gas-sensing properties toward NO_2 gas, even its concentration low down to 5 ppm, and no obvious interference from other common gases could be seen.

2. Experiments

2.1. Synthesis

In a typical synthesis, 2 mmol $In(NO_3)_3$ is dissolved into 40 mL EtOH–H_2O mixture solution with r (EtOH vol.% in the solvent of EtOH–H_2O) value of 75%, under continuously and strong stirring, and then 0.5 mmol sodium citrate is added into the solution. After vigorous stirring for 30 min, the slurry-like solution is transferred into a Teflon-lined stainless steel autoclave of 50 mL capacity. The autoclave is sealed and maintained at 200 °C for 4 h, and then naturally cooled down to room-temperature, after which white precipitates are collected, centrifuged, washed with distilled water and ethanol for several times before drying at 70 °C overnight. Ultimately, the precipitates are annealed in a muffle furnace at 600 °C for 3 h by putting them in a quartz crucible.

2.2. Characterization

The crystal phase and crystallinity of the powders are analyzed by X-ray diffraction (XRD), using a *D*/max 2550 V diffractometer with Cu Kα1 radiation (λ = 1.54056 Å) (Rigaku, Tokyo, Japan), and the XRD data are collected at a scanning rate of 0.02° s^{-1} for 2θ in a range of 10–70°. The morphology of the powders is investigated with the help of field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Co. Ltd., Japan). The decomposition process of the InOOH precursor is investigated on a STA499C thermal analyzer (Netzsch, Germany) with a heating rate of 10 °C min^{-1} under an air atmosphere. Meanwhile quadrupole mass spectrometer (QMS) connected in series after thermal analyzer is planned to characterize the evolved gases during reactions.

2.3. Gas response test

A side-heated structure is accepted to fabricate gas sensors. At first, the powder product is mixed and ground with an adhesive in an agate mortar to form a gas-sensing paste. Then the paste is coated onto an alumina tube on which a pair of Au electrodes is previously printed and dried under IR radiation for several minutes in air, subsequently sintered at 500 °C for 2 h. The gas sensors are aged at 300 °C for 7 days in order to improve their stability. Fig. 1a shows the sketch of the gas-sensor element. Measurements on gas response are performed with a static test system made by Henan Hanwei Electronics Co. Ltd., Henan Province, China. The measuring electric circuit for the gas sensor is shown in Fig. 1b. The working temperature of the sensors is adjusted by varying the heating voltage (V_h). Output voltage (V_{out}) is the terminal voltage of the load resistor. By monitoring output voltage (V_{out}), the resistance of the sensor in air or test gas can be measured. In the tests, we operate electric circuit at constant working voltage (V_c), as detected gas is injected into a test chamber and mixed with air, the change of the resistance of the sensor, therefore the change of output voltage (V_{out}) can be obtained. The gas response of the sensor in this paper is defined as $S = R_g/R_a$ (oxidizing gases) where R_a and R_g are the resistance in air and test gas, respectively. The response or recovery time was expressed as the time taken for the sensor output to reach 90% of its saturation after applying or switching off the gas in a step function. In the measurements the humidity is controlled condition with 40–50% RH.

3. Results and discussion

3.1. Characterization of the samples

Crystal structure of the precursor and the calcinated product of In_2O_3 samples are characterized by X-ray diffraction (XRD). Fig. 2a displays a XRD pattern of the precursor, all the detectable peaks could be easily indexed to orthorhombic InOOH (JCPDS card No. 17-0549, *a* = 5.26 Å), space group *Pnnm* (58), and without other impurity peaks. The product after sintering is also shown in Fig. 2b. It reveals that all the diffraction peaks completely agree with those of JCPDS card No. 06-0416, space group *Ia*3 (206), *a* = 10.14 Å,

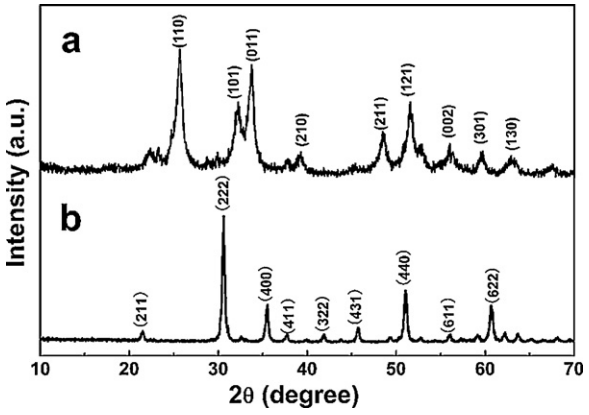

Fig. 2. (a) XRD patterns of the precursor InOOH and (b) the final product of In_2O_3 microspheres.