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Facile synthesis of In_2O_3 nanoparticles for sensing properties at low detection temperature

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ABSTRACT

In_2O_3 nanoparticles are successfully prepared via a facile solvothermal method without any templates or surfactants at a rather low temperature (100 °C). The results of various physical characterizations revealed that the solvothermal precursor is irregular-shaped and the as-prepared In_2O_3 samples are constructed from uniform nanoparticles with unique diameter (20–30 nm) after calcining. Time-dependent experiment was carried out to understand morphology evolution during the calcining process. The In_2O_3 nanoparticles as novel gas sensors exhibit fast and high response as well as good selectivity toward NO_2 gas at ppb level at a rather low operating temperature (60 °C). The sensing process is tentatively explained in terms of the adsorption-desorption mechanism and chemical kinetics theories.

1. Introduction

With the rapid development of economic, a series of problems on environment and energy have become more and more serious. Nitrogen dioxide (NO_2), constantly discharged from exhaust of factories and vehicles, has been the main pollutants in the ambient atmosphere [1]. As the toxic and corrosive gas with a pungent odour, NO_2 can irritate to the respiratory tract, even cause the lung lesion and pulmonary edema [2]. As the results, human being is suffering from threat of health over the past decades, for which it is urgent to find the desired solution [3]. Thus, it is urgent to develop gas sensors to detect the poisonous, hazardous and inflammable gases, which is benefit for assessing and controlling air pollution. Consequently, the sensors have recently attracted substantial research attention in many potential fields in mining, pharmaceutical, environmental monitoring and air quality control, etc [4]. Up to now, a diversity of functional materials have been employed in sensors for this reason [5–11]. Among the several attempts, in light of the fascinating merits of simplicity of synthesis, low cost and strong response to target gases, metal-oxide semiconductors with the most potential have been extensively studied as sensitive materials [1]. As far as we know, the morphology is a key parameter while performing as the sensors, for the reason that the response characteristic of sensors depends on the reaction occurring on the surface of sensors between the sensing materials and gases [12]. In addition, the surface area could directly influence the amount of adsorbed gases. The zero-dimension semiconductor nanoparticles are an important kind of the sensing materials, which generally possesses higher special surface area to absorb more tested gases, results the higher sensitivity and the shorter response time. In briefly, the improved response could be obtained through the smaller crystallite sizes [13]. In previous works, Xu et al. have studied SnO_2 based sensors with various diameters in range of 5–32 nm, and reported that the sensitivity is decreasing with the increasing diameter [14]. Lu et al. have pointed out that the sensitivity values of WO_3 nanoparticles with 25 nm in diameter reveal the best sensitivity in gases sensing [15].

Indium oxide (In_2O_3), n-type semiconductor materials with a wide band gap of 3.55–3.75 eV, has been widely investigated to be promising candidate materials for gas-sensing applications [16]. Therefore, various In_2O_3 nanostructures including nanocrystals, nanowires, hollow microspheres, thin films and many hierarchical nanostructures have been developed for sensors [2] [17–19]. However, it still remains a significant challenge to develop a facile method to prepare In_2O_3 sensors with excellent 4S properties-sensitivity, speed, selectivity and stability as well as the low detection temperature and limit [20]. On basis of the above considerations, the In_2O_3 nanoparticles sensor with a rather low detection temperature and limit has been successfully synthesized in this work via a facile and economical solvothermal synthetic method without any templates or surfactants at a relatively low temperature (100 °C). The sensing performance of which also reveals a

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rather fast and high response as well as good stability toward NO_2 gas at ppb level at a rather low operating temperature (60 °C).

2. Experimental

2.1. Synthesis of In_2O_3 nanoparticles

All the reagents (analytical-grade) were used without further purification. Deionizer water was used throughout the experiments. In a typical procedure, 0.50 mmol of indium nitrate In $(NO_3)_3{\cdot}4.5H_2O$ were dissolved in 20 mL DMF to form a transparent solution under stirring. After that, 0.01 mol urea was added in the solution and followed by stirring for 1 h to form a transparent solution. Then the solution was transferred to a 20 mL vial, sealed, and subsequently heated at 100 °C for 24 h. The resulting white precipitates were centrifuged, washed with distilled water and ethanol, dried at 60 °C for 2 h in air and calcined at 500 °C for 2 h to measure the gas response.

2.2. Characterization

The In_2O_3 samples were characterized by the X-ray diffraction (Rigaku D/max-Ra), transmission electron microscope (JEOL JEM-2200FS) and the Scanning electron microscopy using a Magellan 400, FEI microscope operating at 200 kV. The TGA was carried out on a TG 209 F1 Netzsch apparatus under nitrogen with a 10 °C min^{-1} heating rate. The specific surface area was estimated using the Brunauer-Emmett-Teller (BET) equation based on the nitrogen adsorption isotherm. Pore diameter distribution was calculated by Barrett–Joyner–Halenda (BJH) method using the adsorption branch of the isotherms. Photoluminescence spectra was recorded on a FluoroMax-4 fluorescence spectrophotometer (Horiba Scientific) equipped with a 450 W xenon arc lamp.

2.3. Gas response test

The detailed fabrication and measurement of gas sensor were similar to the methods reported in our previous works [21]. Briefly, 0.05 g In_2O_3 powder was uniformly dispersed in the deionized water to form a paste, coated on an alumina tube-like substrate with a pair of gold electrodes, dried in air at room temperature and followed by aging at 120 °C for one day in air to improve their stability and repeatability. Subsequently, a Ni—Cr heating coil was inserted. The electrical properties of the sensor were measured by a static process: the sensor was firstly placed in a test chamber full of fresh air, and then the test gas was injected into the chamber by an injector. The sensor was transferred into another chamber also full of air while the response reached a steady value. According to the chemical properties of different test gases, the response (S) of sensor was defined as S = Rg/Ra (for oxidizing test gases) and S = Ra/Rg (for reducing test gases), respectively. Here, Ra and Rg were the resistances of the sensor when exposed in the air and test gas atmosphere. The time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption were designated as the response time and recovery time, respectively.

3. Results and discussion

3.1. Characterization of In_2O_3 nanoparticles

Fig. 1a shows the powder X-ray diffraction (XRD) patterns of the InOOH precursor and the annealed In_2O_3 products. The detectable peaks can be indexed to pure InOOH with the orthorhombic phase (JCPDS card, No. 71-2283) and pure rhombohedral In_2O_3 phase

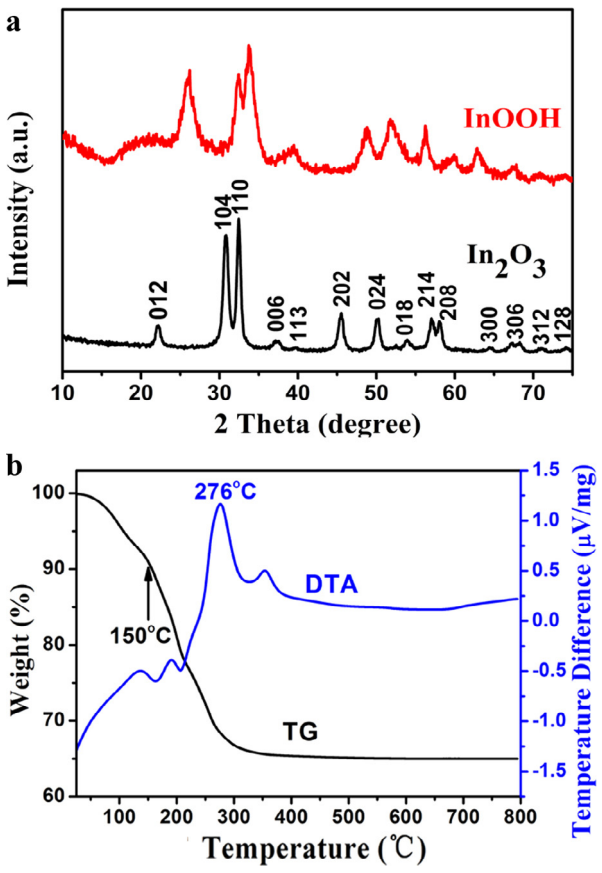

Fig. 1. (a) X-ray diffraction patterns of the InOOH and In_2O_3 (b) TG and DTA curves of the acid-treated products.

(JCPDS Card, No. 22-336). Besides, no other crystalline phase was detected, indicating that the products had a high purity. It is well known that the conversion from InOOH to In_2O_3 is realized by release of H_2O in the annealing process. The thermo-gravimetric (TG) and differential thermal analysis (DTA) curves for the as-synthesized sample were obtained, as depicted in Fig. 1b. From the TG curve, the first weight-loss of 9.05% occurs between 25 °C and 150 °C is assigned to the removal of absorbed water and structural water. The second mass-loss of 24.18% between 150 °C and 300 °C might be assigned to the release of the water from the thermal decomposition of InOOH. The third stage of weight loss, about 1.61%, can be assigned to the combustion of the organics adsorbed on the surface of the sample. There is also a strong endothermic peak near 276 °C. After 500 °C, the weight loss does not change significantly, which indicates that the InOOH is almost entirely converted into In_2O_3, and the weight tends to be stable.

The nanostructure was further investigated by TEM analysis. The general morphologies of the In_2O_3 nanoparticles sample at different magnification are shown in Fig. 2a and b. It can be clearly observed that In_2O_3 nanoparticles are dispersed uniformly and are a little agglomerate. A majority of particles are elliptical and in size of 20–30 nm. Fig. 2c is the selected area electron diffraction (SAED) pattern of the nanoparticles shown in Fig. 2a, which confirms the multi-crystals constitutes by lots of single crystallines in nature and with continuous clear diffraction ring at surface as (012), (104), (202), (024), (116), (214) and (220) in conformance with XRD analysis results. Fig. 2d presents a high-resolution TEM (HRTEM) image of one of the nanoparticles. In this image the clear lattices fringes can be obviously observed at the particle-located position, suggesting a highly-crystallized single crystalline nature of the In_2O_3 nanoparticles. The interplanar spacing of both the direction indicated in the