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Synthesis of mesostructured indium oxide doped with rare earth metals for gas detection

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ABSTRACT

Utilizing an improved one-step nanocasting method, ordered mesostructured In_2O_3 doped with different rare earth metals was synthesized. The obtained materials showed tunable doping ratios and ordered pore structure with high surface area, which led to remarkable sensitivity and selectivity for NH_3 gas.

1. Introduction

Nowadays, with the serious situation for the ecological pollutions, harmful or inflammable gases have caused problems of explosion, fire disaster and gas poisoning as well as greenhouse effect, acid rain and ozonosphere destroy [1]. One of the most important steps to solve this problem is to detect these dangerous gases rapidly and accurately [2,3].

In the field of gas detection, semiconductor gas sensors have been well studied for the advantages of high sensitivity, low cost and easy process of fabrication [4,5]. Metal oxides are the major part of the semiconductive materials and the electrical conductivities vary for those oxides in different atmospheres, which can be measured to determine the types of the gases [6]. Nanoscale materials provide more advantages to fabricate this kind of sensors for higher sensitivity and lower working temperature with the enhanced surface areas and quantum sized effect. As a result, the sizes of the sensors are remarkably minimized, which attracted much attention for extensive research [7,8].

In_2O_3 is a kind of III–VI n-type compound with the cubic bixbyite-type structure. Compared with SnO_2, ZnO, Fe_2O_3 and other gas-sensible oxides, the band gap of In_2O_3 (3.55–3.75 eV) is wider and the electric conductivity is lower, which is especially benefit for using as the material of gas sensors [9]. Moreover, the sensitivity and selectivity of In_2O_3-based sensors can be tuned by doping different metals in traced quantity. We have reported a one-step nanocasting method for creating a unique In_2O_3 mesostructured material which could be considered as ordered In_2O_3 nanowire bundles with high surface area and regular open channels [10]. Several groups reported the gas sensing properties of similar materials; however, few doping effect has been studied for the kind of materials till now [11–14].

In this paper, we firstly reported an improved one-step nanocasting synthesis method to obtain ordered mesostructured In_2O_3 doped with a serial of rare earth metals (RE) with tunable ratios (denominated as RE:In_2O_3 in the following part of the paper). The ordered structures were well maintained with high surface area and large pore size. Those materials have proved to be highly sensitive and selective to NH_3 gas, which showed potential application for harmful gas detection.

2. Material and methods

For synthesizing the doped In_2O_3 mesostructure, a silica/surfactant sol was obtained doped with In^{3+} and RE^{3+} (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Yb, respectively), which was treated by a liquid paraffin protected fast evaporation to form mesostructured monoliths [15]. After the calcinations and NaOH treatment, ordered In_2O_3 mesostructured doped with different RE ions were derived. The details for synthesis, characterization and property investigation are specified as follows.

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2.1. Synthesis

For a typical synthesis, 1 g of Pluronic 123 (P123, $EO_{20}PO_{70}EO_{20}$, MW = 5800, Aldrich) was dissolved in 5 g ethanol and stirred for 0.5 h. Various amount of hydrate rare earth metal nitrite was added and stirred for 0.5 h. Then hydrate indium nitrite was added and stirred for another 0.5 h. While still stirring, 2.08 g TEOS and 0.2 g of aqueous HCl (1 mol/L) was added to the solution and stirred for 0.5 h. The derived homogenous solution was then transferred into a ceramic vessel and aged for 18 h at 25 °C in air to for rigid gel. The gel was covered with a layer of liquid paraffin in 2–3 mm thickness and heated at 60 °C for 18 h to remove ethanol completely. After the heating treatment, liquid paraffin on the surface of the products was collected and cleared by using filter paper. Finally, the sample was calcined at 550 °C in air for 6 h to make metal nitrite pyrolyze and surfactant remove. The derived metal oxide/silica mesostructured composites were grinded into fine powders and stirred in 2 M NaOH solution for 12 h. After collecting the samples by centrifugation, the dissolving process was repeated twice. For the finally products, the sample were rinsed by the mixture of distill water and ethanol (volume ratio of 1:1) and dried at ambient condition.

2.2. Atmosphere-response testing

Traditional gas-sensing workstation (Fig. 1) was used for the test. The powder of the doped In_2O_3 mesostructured materials was mixed with ethanol to form a kind of slurry. The slurry was coated onto an alumina ceramic tube printed with gold electrodes, which was calcined at 600 °C for 1 h after drying in ambient condition. NiCr heater strips were used to connect the as-made testing electrodes, heating electrodes and gas-sensing devices (Fig. 2). Before the experiment, all the devices should be aging for 5 d with the heating voltage of 5 V. All the data used here were recorded under the ambient condition, namely room temperature (20 °C) and humidity around 20–30%. The working temperature of the testing electrodes was around 40 °C.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded with Bruker D8 Focus powder X-ray diffractometer using Cu-Kα radiation. Transmission electron microscopy (TEM) images were taken with a JEOL JEM2011 electron microscope operating at 200 kV. For TEM measurements, the samples were prepared by dispersing the powdered products as slurry in ethanol, after which they were dispersed and dried on a holey carbon film on a Cu grid. Nitrogen adsorption–desorption isotherm were measured with a Tristar 3300 analyzer at 77 K. Barrett–Emmett–Teller (BET) method was utilized to calculate the surface areas. The pore volume and pore size distributions were derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. Elements analytic data were measured with Varian 725-ES ICP-AES apparatus, and all the samples were dissolved in 10% HNO_3 before the measurements.

Fig. 1. A typical photograph of the gas-sensing workstation.

Fig. 2. A typical photograph of the gas-sensing device.

3. Results and discussion

Ordered RE:In_2O_3 mesostructured materials can be obtained by our one-step nanocasting method when the mass ratio of In to Si is less than 1:3 and RE to In is less than 1:15. For the convenience of discussion, Dy:In_2O_3 material with the doping mass ratio of In:Si = 1:8 and Dy:In = 1:30 was used as representative in the following part of the paper.

Represented by Dy:In_2O_3, after calcinations and dissolution, small-angle XRD pattern for both samples before (see Supplemental Materials) and after (inset of Fig. 3) the silica-dissolution treatment showed that the (100) peak with low intensity could be still assigned at 2 theta of 1.17° for 2D-hexagnol mesostructure the corresponding *d* spacing value was 7.54 nm [10], which implied that the long-range order of the sample was partially retained. The reason for the weak reflection in XRD may be due to the small domains for the ordered framework as we reported before [10]. The high angle XRD pattern showed well-resolved peaks for high crystallinity of Dy:In_2O_3, which could be indexed to a body-centered cubic (bcc) structure for In_2O_3 with a lattice constant of a = 1.01 nm and no amorphous silica species (with a characteristic peak around 2 theta of 22°) was detected, which implied the effectiveness of dissolution and also proved by EDX characterization (see Supplemental Materials, and no Si signals were found). Moreover, the RE species were not recorded by XRD either, implying a wide and even dispersancy of the doping elements and no phase separation during the synthesis, which was also proved by SEM observation combined with element mapping analysis (see Supplemental Materials).

The ordered mesostructure of the material was also observed by TEM. Fig. 4 clearly showed that the framework for the obtained