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Synthesis and characterization of mesoporous indium oxide for humidity-sensing applications

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ABSTRACT

An ordered mesoporous In_2O_3 material with crystalline walls has been synthesized through the nanocasting method. It was investigated as an impedance-type humidity sensor for the detection of water vapor. A nanostructured In_2O_3 matrix has been obtained by the hard template route from the KIT-6 silica template. The crystalline In_2O_3 belonged to the Ia3d space group, and its structure was characterized by X-ray diffraction (XRD), N_2 adsorption–adsorption, and transmission electron microscopy (TEM). The sensor based on mesoporous In_2O_3 showed excellent performance in terms of humidity changes and favorable stability. Through the analysis of its semiconductor characteristics, Kelvin equation, and complex impedance, we found that the 3D mesoporous structure contributes greatly to the improvement of humidity-sensitive properties. A possible mechanism was established to explain the excellent performance of the mesoporous In_2O_3-made humidity-sensing device. The evaluation of its electrical characterization and the establishment of its sensing mechanism shows that mesoporous In_2O_3 is a good candidate for developing humidity sensors. It has potential applications in the chemical-sensing field.

1. Introduction

It has been established half a century ago that metal oxide semiconductors have great potential as gas-sensing materials. Several reports devoted to semiconductor sensors have shown the importance of enhancing the oxide surface area [1–3]. Within this context, the synthesis of a metal oxide semiconductor with a mesoporous structure has become an important issue. Since the ordered mesoporous silicas, KSW-1 [4] and MCM-41 [5,6], were first reported in the 1990s, many other mesoporous silicas such as SBA-15 [7,8], KIT-6 [9], FDU-12 [10,11], and SBA-16 [12,13] have been synthesized and characterized chiefly by low-angle XRD, TEM, and N_2 adsorption–desorption. Aside from the conventional "soft template" method, the "hard template" method employing an ordered mesoporous solid as a structural matrix, which is called "nanocasting," has also been employed to prepare various mesoporous materials. A great number of porous crystalline transition-metal oxides which present small uniform-sized stabilized crystals and large active surface areas (WO_3 [14–16], Cr_2O_3 [17–19], Co_3O_4 [20–22], NiO [20,23], CeO_2 [24–26], MnO_2 [27,28], Fe_2O_3 [29], and In_2O_3 [30]), have been synthesized using mesoporous silica as the hard template. The successful synthesis of various mesoporous metal oxides established a good foundation for mesoporous materials' application in different fields.

Soft template method, which the utilization of simple and direct sol–gel method, was implied in the traditional synthesis of the ordered mesoporous materials. However, it has some difficulties when concern to the synthesizing of transition-metal oxide, and the collapsing of mesostructure could be expected during the crystallization process. Therefore, an attractive alternative, which was widely used in synthesizing of CMK-3, was developed. Such methods employed mesoporous silica as rigid framework (hard template method, or nanocasting method), thus the subsequent crystallization can be reasonable. After removing of the template by NaOH or HF solution, the object mesoporous metal oxide can be obtained.

Indium oxide (In_2O_3), an n-type semiconductor, has high electrical conductivity and optical transparency in the visible range [31]. Hence, it is useful as a material for low-emissivity widows [32], solar cells [33], flat-panel liquid-crystal displays [34], and so on. Furthermore, In_2O_3 is also a kind of promising semiconductor gas-sensing material that possesses high sensitivity to certain gases [35,36]. For most of these applications, mesoporous indium oxide with a large specific surface area is desirable. In principle, increasing its specific surface area could generate more active sites on its surfaces and lead to a change in the semiconductor's surface states. Although many In_2O_3 applications have been reported, the humidity-sensitive properties of mesoporous In_2O_3 have been rarely examined to date. Humidity sensors are receiving increasing attention due to their applications in many fields. For example,

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humidity sensor is widely used for industrial, agriculture, foodstuff storage, environmental, meteorology and many other fields. It is a very important member in the chemical sensor family.

In this report, we used the nanocasting method to synthesize crystalline mesoporous In_2O_3 material and explored it as a kind of humidity-sensing material for the first time. We chose a kind of mesoporous silica, which is 3D cubic (space group Ia3d) named KIT-6, as a hard template and impregnated into it an ethanol solution of $In(NO_3)_3{\cdot}4.5H_2O$. The obtained mesoporous material was characterized by low-angle XRD, TEM, and N_2 adsorption–desorption. We then fabricated impedance-type humidity sensors based on the mesoporous In_2O_3 and assessed the electrical characterizations (humidity hysteresis, response-recovery property and stability) of the resulting humidity-sensing devices. Moreover, the characteristics of the semiconductor were engaged to investigate the sensing mechanism. Complex impedance was also employed in assessing the sensing mechanism. A possible process was established to explain the excellent performance of the mesoporous In_2O_3-made humidity-sensing devices.

2. Experimental

2.1. Synthesis

KIT-6 was synthesized according to the literature, with a little difference in aging time [9]. Hydrochloric acid (HCl), ethanol, and tetraethyl orthosilicate (TEOS) of analytical grade were purchased from Tianjin Chemical Co. (China). Indium nitrate hydrate $In(NO_3)_3{\cdot}4.5H_2O$ of analytical was purchased from Sinopharm Chemical Reagent Co. (China). $EO_{20}PO_{70}EO_{20}$ (Pluronic P_{123}) was purchased from Aldrich. The deionized water with a resistivity of 18.0 MΩ cm^{-1} was used in all experiments. The detailed procedure was as follow: 2.0 g of P_{123} triblock copolymer were dissolved in a mixture of 60 g deionized water and 7.0 g hydrochloric acid (36%), then 2.0 g n-butanol was added and the solution was stirred for 1 h. 4.0 g of tetraethyl orthosilicate (TEOS) was added to the mixture and stirred for 24 h at 35 °C. The resulting gel was transferred to a Teflon-lined autoclave and kept for 24 h at 140 °C. The resulting solid product was filtered and washed with ethanol. The as-synthesized white powder was first slurried in an ethanol/HCl mixture overnight, filtered, dried, and subsequently calcined at 550 °C for 2 h (heating rate 2 °C/min) for the removal of the P_{123} block copolymer. Mesoporous silica KIT-6 was impregnated by the incipient wetness technique with ethanol solution of $In(NO_3)_3{\cdot}4.5H_2O$. It was synthesized in modifications of the literature [22] procedures: 0.15 g of silica KIT-6 was dispersed in 8 ml of ethanol, then 0.6 g of $In(NO_3)_3{\cdot}4.5H_2O$ was added. This mixture was left for 2 h under stirring at room temperature. Then the mixture was carefully transferred to a dish and dried overnight at 40 °C to evaporate the solvent. The resulting powder was subsequently calcined at 250 °C for 5 h (with an intermediate plateau at 130 °C for 2 h to decompose the nitrate). In the second impregnation step, the same impregnation step was repeated. 0.3 g of $In(NO_3)_3{\cdot}4.5H_2O$ was added to the powder and dispersed in 8 ml of ethanol. After overnight evaporation of the solvent, the second calcination was performed at 550 °C for 5 h, with the same intermediate step of 2 h at 130 °C. The silica template was removed at room temperature using 30 ml of NaOH aqueous solution (2 M) at 70 °C for 6 h. Above etching process was repeated twice. The indium oxide material was recovered by centrifugation, washed with deionized water and finally dried at room temperature.

2.2. Characterization

Mesoporous In_2O_3 powder was characterized by Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA. The nitrogen adsorption–desorption isotherm measurement was performed on a Quantochrome Autosorb1 sorption analyzer at the temperature of liquid nitrogen. Transmission electron microscopy (TEM) images were performed on Hitachi H8100IV operating at 200 kV. Humidity sensors were prepared on the alumina substrates on which screen-printed with In–Pd interdigitated electrodes. The photograph of the devices was obtained by a MEIJI three-dimensional microscope (made in Japan). The electronic test results were obtained by a ZL-5 model LCR analyzer (made in Shanghai, China) at room temperature. The controlled humidity environments were achieved using supersaturated aqueous solutions of different salts of LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, and KNO_3 in a closed glass vessel, which yielded 11, 33, 54, 75, 85 and 95% relative humidity, respectively.

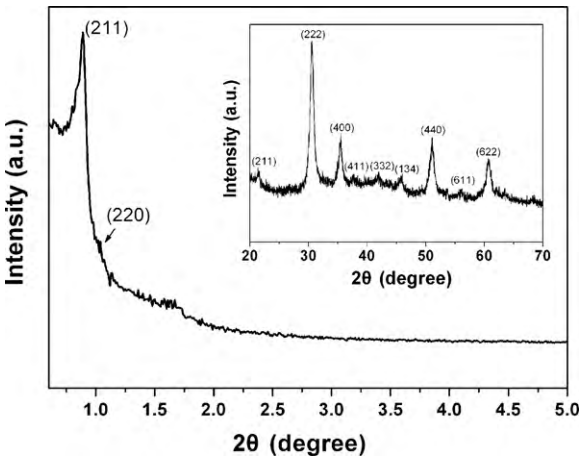

Fig. 1. Low-angle XRD pattern of In_2O_3 powder. The inset shows its wide-angle XRD pattern.

3. Results and discussion

3.1. Characterization of mesoporous In_2O_3 powder

The power In_2O_3 sample was investigated by small-angle X-ray diffraction (SXRD) pattern (Fig. 1). The XRD trace features one high-intensity Bragg peak, a shoulder peak, and a broad diffraction peak, indicating that the gained indium oxide is a highly ordered mesoporous material. The $1/d_{(hkl)}$ value ratios of the first two peaks are exactly 1.167, which implies that these two peaks can be indexed as (2 1 1) and (2 2 0) diffraction peaks of the mesoporous bicontinuous cubic space group Ia3d. The additional broad diffraction peak in the range of $2\theta = 1.5–1.8°$ may arise from the overlapping of the (3 2 1), (4 0 0), (4 2 0), and (3 3 2) diffraction peaks of the Ia3d space group. Moreover, the unit cell parameter of the sample, calculated from $d_{(2\,1\,1)}$, is as large as 20.0 nm. Combined with the following nitrogen adsorption–desorption data, the sizes of the indium oxide pore wall can be calculated by theory, which is 8.4 nm.

The wide-angle X-ray diffraction (WXRD) pattern of the mesoporous indium oxide is shown in the inset of Fig. 1. This WXRD pattern shows clearly several well-resolved peaks which can be indexed as (2 1 1), (2 2 2), (4 0 0), (4 1 1), (3 3 2), (1 3 4), (4 4 0), (6 1 1), and (6 2 2), and so on. These peaks were in agreement with the cubic phase of In_2O_3 (JCPDF 65-3170), indicating that mesoporous indium oxide has highly crystalline walls.

To further investigate the mesoporous structure of In_2O_3, the N_2 adsorption–desorption isotherm of In_2O_3 is shown in Fig. 2. A type IV isotherm, which is the typical isotherm of mesoporous metal oxide material, had been observed. However, the capillary condensation was not very pronounced, indicating the relatively small sizes of the ordered domains. For a better under-