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Facile hydrothermal synthesis of mesoporous In_2O_3 nanoparticles with superior formaldehyde-sensing properties

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ABSTRACT

Mesoporous In_2O_3 nanoparticles were successfully synthesized via a facile, template free, and low-cost hydrothermal method. Their morphology and structure were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential thermal and thermogravimetry analysis (DSC-TG), and N_2 adsorption-desorption analyses. The results reveal that mesoporous In_2O_3 nanoparticles with a size range of 40–60 nm, possess plenty of pores, and average pore size is about 5 nm. Importantly, the mesoporous structure, large specific surface area, and small size endow the mesoporous In_2O_3 nanoparticles with highly sensing performance for formaldehyde detection. The response value to 10 ppm HCHO is 20 at an operating temperature of 280 °C, and the response and recovery time are 4 and 8 s, respectively. It is expected that the mesoporous In_2O_3 nanoparticles with large specific surface area and excellent sensing properties will become a promising functional material in monitoring and detecting formaldehyde.

1. Introduction

In recent years, with the rapid development of industrialization, pollution and atmospheric environment issues have become more and more serious, the atmospheric where people lives contains large amounts of imperceptible nanoparticles, dust and toxic gases, high-performance gas sensors for detecting toxic gases is needed for supervising air quality and protecting human health [1,2]. Metal oxide semiconductors (MOSs) with high response, fast response and recovery time, simple circuits and operation, low cost, has been widely applied to various fields, such as photocatalytic degradation, lithium storage, electrode materials, gas sensors [3–7]. Among these metal oxides, indium oxide (In_2O_3), as an important n-type and wide direct band-gap semiconductor (3.55–3.75 eV), has received extensive attention because of its unique physical and chemical properties, which is widely used in many fields, especially in resistive gas-sensing, including toxic/dangerous reducing gases and oxidizing gases [8–11]. Many people committed to improve the performances of In_2O_3 based gas sensors. Morphology of In_2O_3 surface and nanostructure are the main factor, which strongly influence the application performance, many studies have committed to control its shape and nanostructure, or the development of new structures in the production process to achieve high performance [12]. Various morphologies and sizes of In_2O_3 were prepared by many different method, such as nanoparticles [13], nanowires [14], nanoflower [15], nanosheets [16], nanocubes [17], hollow [18], mesoporous [19] and hierarchical [20] structures, etc.

Among these various structures, sensing materials with mesoporous has been reported to exhibit better gas-sensing, the interconnected pores are benefit for gas diffusion and mass transport in the materials, the plenty of pores also provides more active sites for reaction between chemisorbed oxygen ions and test gases [21]. Based on above traits, various methods have been developed to synthesize mesoporous structure. Using supramolecular aggregates of amphiphilic species, such as surfactants or blockcopolymers can synthesize mesoporous silica or aluminosilicate phases, which is often referred to as 'soft templating'. For instance, D. Y. Zhao et al. summarized the recent developments in the syntheses of ordered mesoporous materials by the surfactant assembly, especially for mesoporous silicates [22]. Another method to synthesize mesoporous structure is by nanocasting, also referred to as 'hard templating' [23]. The desired product is created inside the pores of the matrix which is selectively removed afterwards. Many literature have reported this method, for example, J. L. Wang et al. reported a mesoporous In_2O_3 materials was prepared by solid-state thermolysis of indium-organic frameworks, and obtained high HCHO-sensing performance [24]. However, the 'soft templating' method is not universally applicable to every mesoporous material. When the semiconductors are

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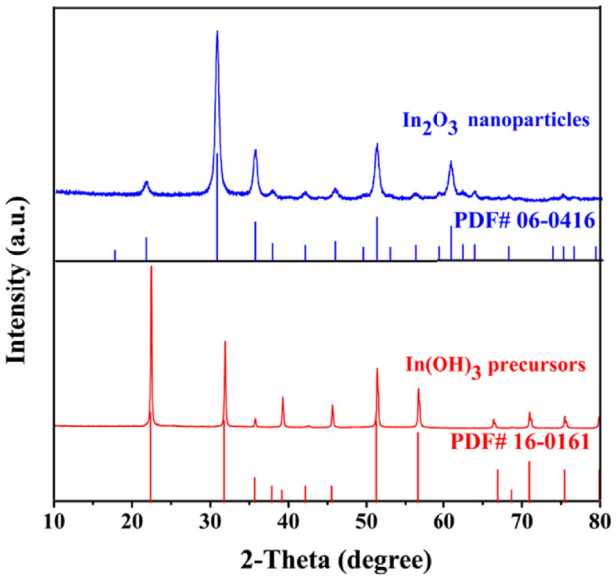

Fig. 1. XRD patterns of $In(OH)_3$ precursors and In_2O_3 samples.

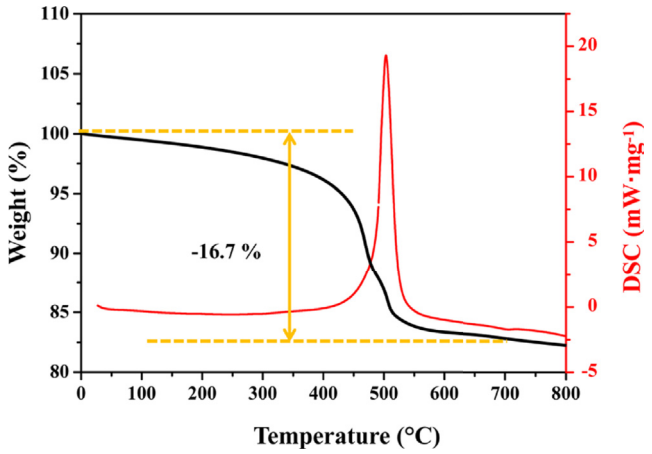

Fig. 2. TG-DSC curves of conversion process of $In(OH)_3$ precursors.

fabricated as resistive gas sensors, it cannot obtain sufficient structural quality by this procedure [14]. The 'hard templating' method need calcined at a high temperature or by acid (alkali) washing to remove the template. That may easily destroy the as-obtained mesoporous structure of the materials. Therefore, a facile, template free, and low-cost method is needed for synthesizing mesoporous structure. This paper provides a facile way to prepare mesoporous sensing materials, do not need to remove the templates, and do not worry about the destruction of the structure of the material, it also do not use any of the surfactants, which greatly reduces the cost and simplifies the experiment. With this simple method, the desired mesoporous material can be prepared.

Another way to increase the surface area of sensing materials is to reduce the size. The surface area could directly influence the amount of adsorbed oxygen molecules and target gases. Namely, through declining the size, the sensing properties can be improved [25]. Many literature have been reported the relationship between the size and gas-sensing properties of materials, for example, Xu et al. have reported sensors based SnO_2 nanoparticles with various diameters in range of 5–32 nm, and proposed that with the increase of the size of SnO_2 nanoparticles, the response is decreasing [26]. In this work, we prepared mesoporous In_2O_3 nanoparticles with 40–60 nm, and did not use any surfactants and templates, only use $InCl_3$ as a source of indium and $C_{12}H_{27}N$ as the alkali source, simplifying the synthesis step and reducing the cost. The mesoporous In_2O_3 nanoparticles exhibited high gas-sensing performance to HCHO, including high response, good selective and short response and recovery times.

2. Experimental

All the reagents we used in this experiment are of analysis grade and used without further purification. Mesoporous In_2O_3 nanoparticles were prepared by an environmentally friendly and simple hydrothermal route. In a typical process, 1 mmol $InCl_3$ and 1 mmol $C_{12}H_{27}N$ were dissolved in 35 mL absolute ethanol under stirring until completely dissolved to form a uniform solution. The solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, and the temperature was raised to 180 °C at a heating rate of 10 °C/min and maintain at constant temperature for 12 h. After the completion of reaction, the resultant precipitates were collected by centrifugation, washed several times with deionized water and absolute ethanol, respectively. Then the as-obtained precipitates were dried at 60 °C for 6 h. Finally, the presynthesized $In(OH)_3$ precursors were put into a quartz crucible and calcined at 500 °C for 3 h in a conventional muffle furnace at air atmosphere. After calcined, the pale yellow In_2O_3 sample was obtained.

3. Results and discussion

3.1. Structural and morphological characteristics

To obtain the phase and crystal structure of the as-prepared sample of, X-ray diffraction was performed immediately after the sample preparation. Fig. 1 shows the XRD patterns of $In(OH)_3$ precursors and mesoporous In_2O_3 nanoparticles samples. From the XRD pattern of $In(OH)_3$ precursors we can see that all the main and sharp diffraction peaks can be indexed to the cubic lattice of pure $In(OH)_3$ according to the JCPDS data card No. 16–0161. And sharp peaks indicates the well crystalline nature of $In(OH)_3$ precursors. From XRD pattern of mesoporous In_2O_3 nanoparticles we can clearly observed that all the strong diffraction peaks can be indexed to the body-centered cubic crystalline phase In_2O_3 (JCPDS No. 06–0416), and no other impure diffraction peaks of other compounds are detected, which indicates the powder we obtained is a pure In_2O_3 phase product.

To determine the conversion temperature of $In(OH)_3$ precursors, the TG-DSC analysis was characterized at heating rate of 10 °C·min^{-1} in air surrounding, which controlled by program. Fig. 2 shows the TG-DSC curves of conversion process of $In(OH)_3$ precursors. As it can be observed from the TG curve, there is an obviously weight loss at 450–550 °C, accompanied with a sharp peak in the DSC curve. After 550 °C, the TG and DSC curves are both become flat. This phenomenon can be interpreted as rapidly conversion of $In(OH)_3$ precursors in this temperature range. The equation of this dehydration reaction of $In(OH)_3$ is shown in eq. (3):

$$2\ In(OH)_3 \rightarrow In_2O_3 + 3H_2O\ (\text{loss } 16.28\ \text{wt } \%) \quad (3)$$

According to the result of TG analysis, the actual mass loss of this reaction is about 16.7%, which is approached to the theoretical value (16.28 wt%). From the DSC curve, we know that this dehydration reaction is a typical exothermic reaction. Based on the result of TG-DSC analysis, we choose 500 °C as the calcination temperature of $In(OH)_3$ precursors.

The morphology and distribution of the mesoporous In_2O_3 sample were investigated by SEM. The SEM images of $In(OH)_3$ precursors and mesoporous In_2O_3 nanoparticles are shown in Fig. 3. From Fig. 3 (a), we can see that the as-synthesized $In(OH)_3$ nanoparticles have good dispersibility and the shape and size of $In(OH)_3$ precursors are very uniform. High-resolution SEM image of $In(OH)_3$ nanoparticles is showed in Fig. 3(b), from this image we can find that the shape of $In(OH)_3$ nanoparticles is not spherical but irregular nanoparticles and the size of these