Sensors and Actuators B 262 (2018) 655–663

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Highly sensitive NO_2 gas sensor of ppb-level detection based on In_2O_3 nanobricks at low temperature

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ARTICLE INFO

Article history:
Received 26 November 2017
Received in revised form 26 January 2018
Accepted 6 February 2018
Available online 7 February 2018

Keywords:
In_2O_3
NO_2
Gas sensor
Low operating temperature

ABSTRACT

The brick-like In_2O_3 nanomaterials were synthesized by oil bath precipitation and subsequent calcination method without any templates or surfactants. Technologies of X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were carried out to characterize the morphological and structural of the In_2O_3 samples. Photoluminescence spectra (PL) and X-ray photoelectron spectroscopy (XPS) were used to illustrate the influence of material surface states and internal defects on gas-sensing properties. The In_2O_3 nanomaterials annealed at 400 °C exhibited a high response (402) toward 500 ppb NO_2 with the fast response/recovery time (114 s/49 s) at rather low operating temperature of 50 °C. Besides, it had a good linear relationship in the range of 100–500 ppb. Such excellent gas sensing properties could be on account of the relative large surface area, abundant adsorbed oxygen and good electrical properties.

1. Introduction

As one of the most dangerous air pollutants, Nitrogen dioxide (NO_2) plays a major role in formation of acid rain [1]. However, with the development of industry large amount of NO_2 gas has been discharged into the environment. A low concentration of 3 ppm NO_2 can cause irritation to the throat and respiratory system [2,3], and if the concentration is higher, it can impair lung function and even death [4]. Thus, it is urgent to develop gas sensing devices of high response and excellent selectivity for detecting the poisonous NO_2 gas at low concentration, which is benefit for the environmental monitoring and human health.

Nanostructured resistive type metal oxide semiconductors are well suited for the toxic gas detection because of facile synthesis, low cost and strong response to target gas. Indium oxide (In_2O_3) is one of the typical n-type metal oxide semiconductors with a wide band gap (3.55–3.75 eV), and various In_2O_3 nanostructures have been developed for sensors including nanowires [5], nanorods [6], nanoplates [7], nanofibers [8], hollow microspheres [9] and many hierarchical nanostructures [10,11].

For the n-type semiconductor a surface adsorption oxygen ion model is generally accepted to explain the gas sensing mechanism [12–14]. Thus, many studies focus on controlling the morphology for gaining more active sites to adsorb oxygen. Feng Huang et al. [15] synthesized three kind of different microstructures In_2O_3, where the flower-like In_2O_3 microrods had a good performance to ethanol because that products could provide more available active surface areas. Arunkumar et al. [16] explored the different nanostructures to hydrogen gas sensing properties, and the results showed that In_2O_3 nanocubes exhibited superior response to low concentration hydrogen with the help of the porous structures and larger surface area. On the other side, calcination temperature has a great influence on the state of the nanostructure surface. Y. Lü et al. [17] found that an appropriate calcination temperature was vital for acquiring large specific surface area and the ability to gain more oxygen species. C. Mei et al. [18] investigated the calcination temperatures could result in the differences in crystal defect structure. Combined with the above analysis, a specific morphology is significant for the prepared nanoparticles by a simple synthesis route. Controlling the surface state by calcination temperature is also the key to the gas sensing performance.

Herein, we successfully prepared indium oxide nanobricks in a simple oil bath heating method under lower heating temperature (96–98 °C) within only 2 h. Besides, HMTA was used as alkali source and morphology control reagent without any surfactants. Moreover, we found that the gas sensing performances of the samples obtained by calcination at different temperatures were significantly different. The optical sensing performance revealed a fast and high response to ppb level NO_2 gas at a very low operating temperature of 50 °C. A possible gas sensing mechanism through the

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https://doi.org/10.1016/j.snb.2018.02.052
0925-4005/

depletion layer theory was proposed to clarify the synergistic effects of surface adsorbed oxygen, specific surface area and electronic properties on the gas sensing performances.

2. Experimental

2.1. Material synthesis

All of the chemicals were used as received without further purifications. In_2O_3 nanobricks were synthesized at low-temperature by improving the method of previous research [19], 5 mL 1 mmol $In(NO_3)_3{\cdot}4.5H_2O$ (Sinopharm Chemical Reagent Co., Ltd. Shanghai China) was added into 40 mL deionized water at 96 °C in a three-necked flask under stirring. After a few minutes, 5 mL 0.5 mmol HMTA ($C_6H_{12}N_4$, Xilong Chemical Co., Ltd. Guangdong China) was added in the flask. The mixed solution was then heated and refluxed with continuous stirring for 2 h. Temperature of the solution was controlled by a thermometer, keeping the heating process in the range of 96–98 °C. After reflux reaction, white precipitates were obtained and washed with deionized water for several times and dried at 60 °C in a vacuum oven overnight. Then, the precipitates were loaded into an alumina boat and calcined at 300, 400, 500 °C for 2 h with a heating rate of 5 °C/min. The calcined products were collected for further analyses.

2.2. Characterization

The crystal phase of the synthesized samples were recorded via X-ray diffraction (XRD, Bruker-D8 Advance) by using Cu Kα radiation (λ = 0.15406 nm) at a scanning rate of 10°/min in the range 10–80°. The specific surface areas were studied by the Brunauer-Emmett-Teller (BET) method. The morphology of the samples was observed by scanning electron microscopy (SEM, S-4700) and transmission electron microscopy (TEM, HT-7700). The thermogravimetric analysis (TGA, NETZSCH STA 449 F3) was carried out under air atmosphere with a heating rate of 5 °C/min. X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250X) was used to characterize the indium and oxygen species and surface properties. Photoluminescence measurement (PL, Hitachi Model F-7000 spectrophotometer) was operated with an excitation wave-length of 325 nm at room temperature. The electrical properties were measured through a Hall effect measurement system (RH2030, Phys Tech).

2.3. Gas sensing measurement

Gas sensors were fabricated as follows. The as-obtained powder was mixed with ethanol to make a paste, which was coated onto commercial ceramic substrates with Ag-Pd interdigital electrode (13.4 mm in length, 7 mm in width) by a small brush to form a homogeneous film. After drying at room temperature, the prepared sensors were aged at 130 °C for 24 h. Then the gas sensing properties of In_2O_3 samples were characterized on a CGS-4TPs intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China). Each substrate covered with In_2O_3 nanomaterials was fixed by two metal probes and then preheated at the operating temperature till its resistance value reached a steady state. After that, the test chamber (1.8 L) was closed and the target gas was quickly injected into this chamber. When the resistance value reached a new steady state, the test chamber could be opened to expose the sensor in the air again. The resistances were recorded in the whole process. The gas sensing properties were measured under laboratory conditions with the humidity range of 25 ± 5%. The schematic illustration of the experimental procedure is shown in Fig. 1.

The response is defined as R_g/R_a for testing oxidizing gas or R_a/R_g for testing reducing gas, where R_g and R_a are the resistance values of a sensor in target gas and air, respectively. The response time is defined as the time to reach 90% of maximum response during the process of adsorption and the recovery time is defined as the time to recover 90% of the maximum response in the case of desorption.

3. Results and discussion

3.1. Characterization of precursors

In order to get good morphology of precursor samples, the effect of concentration of HMTA had been examined. The SEM images exhibit that the different nanostructures grown in different concentration of HMTA (Fig. S1). Fig. S1a reveals that the precursor $In(OH)_3$ nanoparticles are brick-like and dispersion uniformly in length of 100–200 nm and in width of 50–100 nm by using 0.05 M HMTA. However, when increasing the amount of HMTA to 0.1 M or 0.2 M (shown in Fig. S1b, c), the morphologies of $In(OH)_3$ nanoparticles are irregular and exhibit serious agglomerations. This may be related with the concentration of OH^- ions induced by the decomposition of HMTA at a hot water. This hydrolysis reaction occurs as follows.

$$(CH_2)_6N_4 + 10H_2O \rightarrow 6HCHO + 4NH_4OH \quad (1)$$

$$NH_4OH \rightarrow NH_4^+ + OH^- \quad (2)$$

OH^- ions can be released quickly forming a relative high concentration at higher concentrations of HMTA (0.1 or 0.2 M), which results in the precursor nucleation and fast growth and forming an irregular shape. Therefore, the HMTA concentration has an important influence on the forming a brick-like morphology. Fig. S1d is the X-ray diffraction (XRD) pattern of the as-prepared precursor with 0.1 M $In(NO_3)_3$ and 0.05 M HMTA. The diffraction peaks are indexed to the cubic crystal phase of $In(OH)_3$ (JCPDS 16-0161) and no other impurity peaks appear.

In order to investigate the growth mechanism of the $In(OH)_3$ nanobricks, the synthesis process was terminated at different reaction times of 10, 30, 60 and 120 min to examine the evolution of the morphologies and microstructures of the resultant products as shown in Fig. S2. In the initial stages within 10 min (Fig. S2a), the sample displays rod-like morphology with the length of 40 nm. When the reaction time is extended to 30 and 60 min (Fig. S2b, c), small cubic-like paticles appear among the small nanorods. As the reaction time is up to 120 min, the $In(OH)_3$ nanobricks are totally formed. The growth progress can be inferred as a result of the self-assembly attachment of simple small nanorods. The size of $In(OH)_3$ nanobricks depends on the agglomeration of the small nanorods during the reaction period. Fig. S2e shows the schematic diagram of the growth process.

The decomposition process of the $In(OH)_3$ precursor was investigated on the thermal analyzer as depicted in Fig. S3. There is only one endothermic peak nearby 250 °C in the DSC curve. Correspondingly, the TG curve shows an obvious weight loss about 16.4%, which is close to the theoretical calculating value 16.2%. Thus the mass-loss of between 150 and 500 °C might be assigned to the release of the water from the thermal decomposition of $In(OH)_3$ to In_2O_3. Above 500 °C, the weight loss does not change significantly and tend to be stable, which indicates that $In(OH)_3$ is totally converted into In_2O_3.

3.2. Effects of calcination temperatures

For convenience, the In_2O_3 nanobricks prepared by calcining the precursors at 300, 400, 500 °C are denoted as In-300, In-400, In-500, respectively. NO_2 that may damage human's health with a low tolerance limit is used for evaluating the gas sensing properties of In_2O_3 nanobricks. The temperature dependent experiment