DOI 10.5162/IMCS2012/P1.7.1

Synthesis and Gas-sensing Properties of Flower-like SnO_2 Architectures

Shouli Bai[1], Dianqing Li[1], Ruixian Luo[1], Kewei Zhang[1], Aifan Chen[1], Chung Chiun Liu[2]**
[1] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing100029, China*
luorx@mail.buct.edu.cn
[2] *Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA*
cxl9@case.edu

Abstract:
Flower-like SnO_2 architectures constructed of one-dimensional tetragonal prism nanorods were synthesized by a simple hydrothermal method using ethanol as dispersant agent. The morphology and structure of crystals were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The results revealed that the SnO_2 nanorods exhibited a single crystalline rutile structure with aspect ratio of nearly 20, and lattice fringes of (1 0 1) plane was 0.263 nm. The heat treatment experiments confirmed the appropriate calcination condition for as-synthesized SnO_2 precursors was 400^{o}C for 1 h. Sensor based on the flower-like SnO_2 architectures exhibited the highest sensitivity of 205 to 40 ppm of CO at optimal operating temperature of 200^{o}C, which makes it a satisfactory candidate for application in practical detecting of CO.

Key words: SnO_2, nanorod, hydrothermal synthesis, gas-sensing properties.

1. Introduction

With increasing concerns of air pollution on human health and safety, significant efforts have been focused on developing of gas sensors with excellent sensing performance. Tin oxide (SnO_2), as one of the most important wide bandgap semiconductors, has been reported to be a promising gas-sensing material of sensors due to its excellent chemical and thermal stability [1, 2]. It is well known that the gas-sensing properties of materials are greatly affected by their size, morphology and defect structures [3-5]. Various morphological and structural forms of SnO_2 nanocrystals have been synthesized over the past several years, including nanoparticles, nanodisks, nanowires, nanorods, nanotubes, and thin films. One-dimensional (1-D) SnO_2 nanostructures have attracted considerable attentions owing to their large surface-to-volume ratio, well-controlled dimensionality and excellent electronic radial transport. Thus, designing 1D SnO_2 building blocks and their well-defined architectures with high surface-to-volume ratio is of importance for the application in effectively detecting toxic gases.

In this work, we demonstrate a facile route for the synthesis of flower-like SnO_2 nanorods bundles without using poisonous structure directing agents. The as-synthesized products have uniform three-dimensional architectures, which are built by numerous 1D tetragonal prism nanorods. The flower-like SnO_2 architectures exhibited high response to CO, which makes it a competitive candidate for application in CO detecting.

2. Experimental

All of the reagents were of analytical grade and used as received without further purification. In a typical procedure, 25 mL of $SnCl_4{\cdot}5H_2O$ (0.06 M) and 25 mL of NaOH (0.36 M) were mixed under mild stirring, then 100 mL H_2O-C_2H_5OH solution (1:1) was added. This solution was transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 240^{o}C for 24 h. After cooling to room temperature, the white precipitates were collected by centrifuging, washed sequentially with water and ethanol, and then dried at 60°C overnight.

Field emission scanning electron microscopy (FE-SEM) was performed on a Hitachi S-4700 electron microscope operated at 20.0 kV. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were recorded with a JEOL JEM-2100F instrument,

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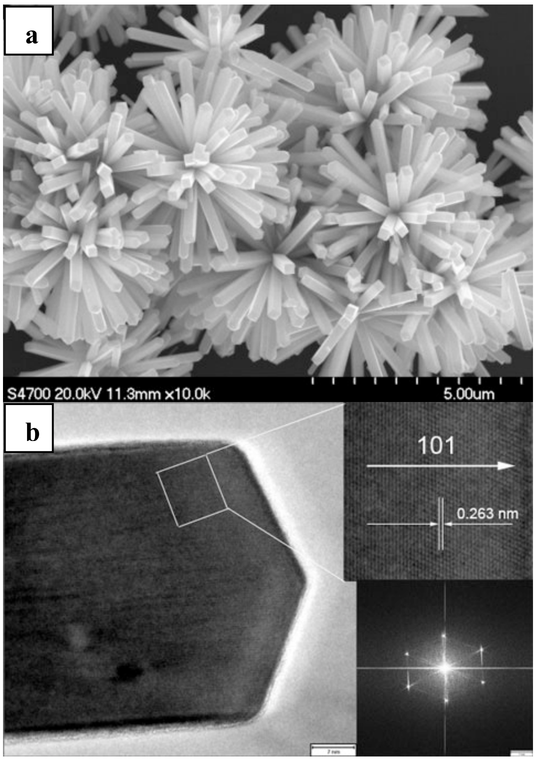

Fig. 1. (a) FESEM image and (b) HRTEM image of the products.

operating at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 diffractometer with copper Kα radiation (λ = 0.154 nm). A scanning rate of $10^{\circ}\cdot min^{-1}$ was applied to record the pattern in the range of 3-60° (2θ).

3. Results and Discussion

3.1. Morphology and Structure

Fig. 1 showed the morphology and size of as-synthesized products, it revealed the products were constructed of high crystalline SnO_2 nanorods with diameter of about 100 nm, and the aspect ratio was estimated to be about 20. The electron microscopy taken from one nanorod of the flower-like architectures indicated the as-synthesized SnO_2 nanorods were single crystalline, and the spacing between two adjacent lattice fringes was 0.263 nm, coincident with the d-spacing of (1 0 1) plane of tetragonal SnO_2 (JCPDS No. 21-1250). The ethanol, as a dispersant, was of great importance to synthesize the uniform SnO_2 nanorods in the hydrothermal reaction.

In the synthesis process, the base concentration greatly affected the size and shape of precursor, resulting in different morphologies of the products [6]. Fig.2A showed the morphologies of SnO_2 architectures synthesized at 240°C under different base ratio. The corresponding XRD patterns were shown in Fig. 2B. All the samples showed well-defined peaks at 2θ = 26.58, 33.88 and 51.75 correspond to the planes of (1 1 0), (1 0 1) and (2 1 1), respectively, which confirmed that a tetragonal rutile structure of SnO_2 (JCPDS No. 21-1250) was produced.

3.2. Gas-sensing Properties

The gas sensing property of the flower-like SnO_2 architectures was measured by monitoring the resistance change of the calcined SnO_2 powders during exposure to ppm level target gas in a flow test apparatus. The SnO_2 architectures calcined at different temperatures were pressed into pellet of 8 mm in diameter and 1 mm in thickness on which a pair of Au electrodes was set on surface of the pellet to form the sensor. Then the sensor was placed in the gas-sensing apparatus and aged at 320°C for several hours to remove the adsorbates on surface of the element. The sensor response of CO is defined as the ratio of R_{air}/R_{CO}, where R_{air} is the steady-state resistance of the sensor in air and R_{CO} is the steady-state resistance in the air-CO mixture.

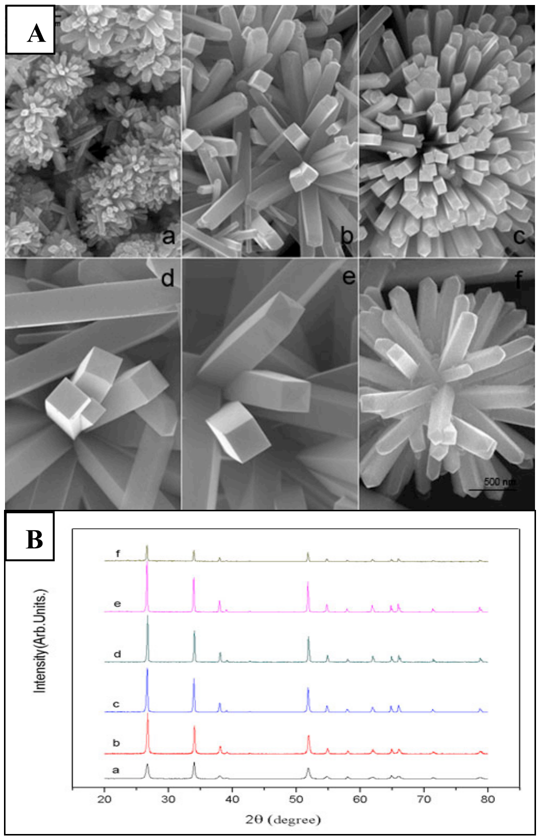

Fig. 2. (A) FESEM images of the SnO_2 nanorods bundles synthesized under different base ratio: (a) 1:7, (b) 1:8, (c) 1:9, (d) 1:10, (e)1:11, (f)1:12; and (B) corresponding XRD patterns.

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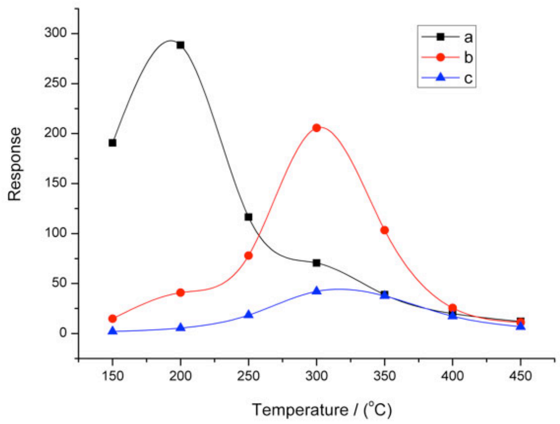

Fig. 3. Responses of SnO_2 nanorods bundles calcined at different temperatures for 1 h: (a) 400°C, (b) 600°C, (c) 800°C.

Fig. 3 showed the sensor responses of the flower-like SnO_2 architectures calcined at 400°C, 600°C, and 800°C for 1 hour, respectively. Results indicated that the sensor based on the sample calcined at 400ºC exhibited the maximum response. Calcination temperature of 400°C ensured sufficient crystallinity of SnO_2 nanorods without destroying the compact structure and reducing active surface sites. Besides, the dependent behavior of the sensors on operating temperature can also be clearly demonstrated. There was an optimal operating temperature for each curve in Fig. 3. For the sensor based on SnO_2 calcined at 400°C, the maximum response appeared at operating temperature of 200°C. Before the optimal operating temperature, the sensor response increased with increasing operating temperature, which can be attributed to the fact that abundant of thermal energy is essential to overcome the activation energy barrier for completing chemisorption and reaction on the sensing material surface. If the temperature was further enhanced above the optimal operating temperature, the amount of adsorbed gas on sensing material surface will decrease with operating temperature, leading to the decrease of sensor response.

4. Conclusions

In summary, a simple hydrothermal route using ethanol as dispersant agent has been demonstrated for the synthesis of flower-like SnO_2 architectures. The SnO_2 architectures are constructed of one-dimensional tetragonal prism nanorods, which exhibit a single crystalline rutile structure with aspect ratio of nearly 20. The appropriate calcination conditions of the flower-like SnO_2 architectures are defined to be 600°C and 4 h for gas-sensing applications. Gas-sensing tests reveal that the flower-like SnO_2 architectures exhibited high response to CO, which makes it a competitive candidate for application in CO detecting.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51072014 and 21177007) and Beijing Natural Science Foundation (Grant Nos. 8102028 and 8112022).

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