Materials Science & Engineering B 225 (2017) 68–74

Contents lists available at ScienceDirect

Materials Science & Engineering B

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

3D mace-like hierarchical ZnO nanoarchitecture constructed with microrod bundles and porous single-crystalline nanosheets for acetone sensors with enhanced performances

Jun Zhou[a], Feilong Gong[b], Huanxin Wang[b], Yuanhua Xiao[b,*], Feng Li[b,*], Wenning Mai[a,*]

[a] College of Public Health, Zhengzhou University, Zhengzhou 450001, PR China
[b] Key Laboratory of Surface and Interface Science and Technology, Zhengzhou University of Light Industry, Zhengzhou 450002, PR China

ARTICLE INFO

Keywords:
ZnO
Hierarchical nanoarchitectures
Core-shell
Acetone
Gas sensor

ABSTRACT

3D mace-like hierarchical ZnO nanoarchitectures consisting of porous single-crystalline nanosheets as well as microrod bundles were synthesized by growing $Zn_4CO_3(OH)_6{\cdot}H_2O$ nanosheets on the surfaces of ZnO microrod bundles on the basis of a facile one-step solution method combined with a successive annealing treatment at 400 °C. The investigation for the evolution mechanism of hierarchical ZnO nanoarchitectures shows that the reaction time, concentrations of reactants together with the surfactant can radically influence the compositions and morphologies of materials generated during the reactions. A potential mechanism is suggested to help in understanding the formation of the hierarchical nanoarchitectures based on the reaction time and the concentrations of reactants effect on the morphologies of the products. The chemical sensors made with 3D mace-like hierarchical ZnO nanoarchitectures reveals enhanced sensing performances with high responses, selectivity as well as stability to acetone vapor.

1. Introduction

Three-dimensional (3D) hierarchical nanoarchitectures have been studied broadly in the recent years due to their high surface/body ratios, large surface areas, better permeability as well as more surface active sites in comparison with the low dimensional materials [1–3]. Due to this, the 3D hierarchical materials have been applied in the design of chemical sensors, catalysts and energy storage devices [3–7]. However, most of the reported 3D hierarchical nanoarchitectures have been constructed with one-dimensional (1D) and two-dimensional (2D) building blocks in nanoscale to form spherical, flower and urchin-like structures [6,8–10]. In the recent past, a relatively little amount of 3D nanoarchitectures that consist of 2D nanosheets or 1D nanowire (nanotubes) grown on 1D nanostructures have been synthesized successfully and applied in catalyst, Li-ion battery, supercapacitor, biosensor as well as gas sensor for enhancing performance [11–18]. Thus, it is of great importance to control the nucleation and growth of shell materials on the 1D nanostructure.

As one of significant semiconductor materials with a wide band gap of 3.37 eV [19], ZnO has been widely studied in the past decade owing to its applications in photodetectors, solar cells and biosensors [20–23]. The ZnO nanocrystals including nanowires, nanorods and nanoparticles have also been utilized as building blocks to construct chemical sensors [24–27]. Lately, it was realized that 3D ZnO nanoarchitectures exhibit interesting gas sensing properties with enhanced sensing performances [3,28–30]. Nonetheless, to the best of our knowledge, there is little report in literature regarding constructing hierarchical ZnO nanoarchitectures by growth 2D nanosheets on the surfaces of 1D nanostructure so far.In this present study, we report a simple one-step solution reaction to first obtain a 3D mace-like ZnO nanoarchitecture constructed with $Zn_4CO_3(OH)_6{\cdot}H_2O$ nanosheets and ZnO microrod bundles. In this process, the $Zn_4CO_3(OH)_6{\cdot}H_2O$ nanosheets and ZnO microrod bundles can be produced in turn to form $Zn_4CO_3(OH)_6{\cdot}H_2O$ nanosheets @ ZnO microrod bundles in the solution. Subsequently, the $Zn_4CO_3(OH)_6{\cdot}H_2O$ nanosheets were transformed into single-crystalline ZnO nanosheets with porous structures after being annealed at 400 °C to acquire porous single-crystalline ZnO nanosheet @ ZnO microrod bundle 3D core-shell mace-like hierarchical nanoarchitectures. A potential growth mechanism is suggested to comprehend the formation of the ZnO nanoarchitectures. In addition, a comparative study of gas sensing performances between ZnO microrod bundles and 3D nanoarchitectures has revealed that the hierarchical materials exhibit highly improved gas sensing responses to acetone vapor. The novel 3D structures with high surface area and 2D porous ZnO nanosheets on the microrod bundles

* Corresponding authors.
E-mail addresses: yuanhua_xiao@163.com (Y. Xiao), fengli696@126.com (F. Li), wen1991@zzu.edu.cn (W. Mai).

http://dx.doi.org/10.1016/j.mseb.2017.08.009
Received 19 May 2017; Received in revised form 17 July 2017; Accepted 7 August 2017

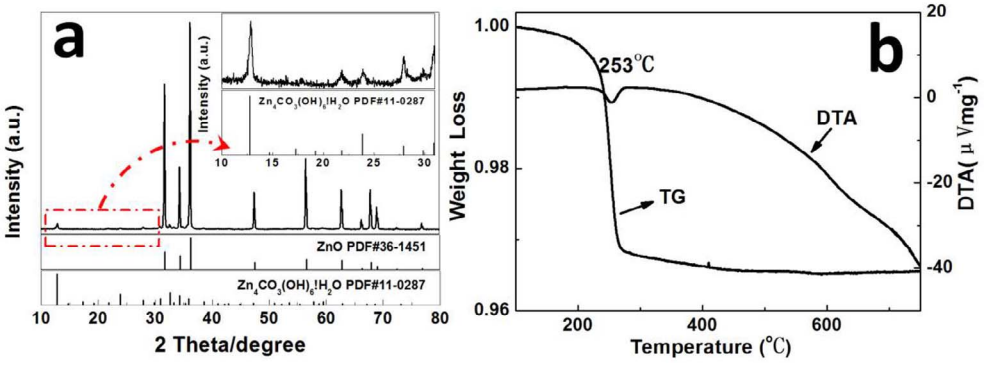

Fig. 1. (a) XRD patterns of the synthetic samples. (b) TG and DTA curves of the synthetic precursor. Inset in 2a is partially amplified pattern highlighted with red frame. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

exposed in (1$\bar{1}$ 0) facets at high percentage nanocrystals could attribute to their excellent gas sensing performances.

2. Experimental section

2.1. Reagents and materials

All chemicals that were used all through this study were of analytical (AR) grade. They were obtained from Shanghai Analytical Chemicals Company.

2.2. Synthesis of Mac-like ZnO nanoarchitectures

In a distinctive synthesis, zinc chloride (1 mmol, 0.136 g), urea (1 mmol, 0.060 g) together with polyvinyl pyrrolidones (PVP, K30, 0.2 g) were added to a solvent prepared by means of mixing water (35 mL) and ethanol (5 mL) in a beaker. The suspension was then stirred with a magnetic stirrer for about 30 min at room temperature. It was then transferred into a Teflon-line autoclave (50 mL) and heated at 180 °C for 16 h. After being cooled to room temperature, the white products formed were collected through centrifugation process and then washed 5 times with deionized water so as to eliminate impurities. The products were then dried at 70 °C and calcined at 400 °C for about 2 h to obtain white powder.

2.3. Material characterization

X-ray diffraction (XRD) analysis was performed on a D/max 2550 V diffractometer with Cu Kα radiation (λ = 1.5406 Å). Thermal analysis was also performed on a SDTQ600 thermal analyzer at a constant heating rate of 5 °C per minute. The microstructures of the materials were characterized by use of field emission scanning electron microscopy (FESEM, JSM-7001F, accelerating voltage: 10 kV) as well as transmission electron microscopy (TEM, JEM-2100, accelerating voltage: 200 kV). The specific surface areas of the materials were computed by use of a Belsorp-Mini adsorption apparatus (Bel Japan Inc), while the pore sizes distribution curves were established by use of BJH method applied to the desorption isotherms.

2.4. Sensor fabrication and test

The sensors were made by use of the ZnO nanocrystal powder. The comprehensive fabrication can be illustrated in the ensuing method reported by our group [20]: First, ZnO powder was mixed with terpineol and ground in an agate mortar so as to form a paste. After that, the paste was coated on an alumina ceramic tube with a pair of Au wire electrodes (Fig. S1a). Then, the device with paste was dried at 80 °C for about 20 min and subsequently annealed at 600 °C for about 1 h. The thickness of the ZnO film on the alumina ceramic tube is 10–30 μm (Fig. S1b). Lastly, a small Ni-Cr alloy coil was inserted into the tube as a heater to obtain the working temperature. Prior to the testing, the sensors were kept at the working temperature for some days to enhance their stabilities. A stationary state gases distribution method was performed in a measuring system of HW-30A (Hanwei Electronics Co. Ltd., P.R. China) to test the gas responses (the working principle of gas sensor test as shown in Fig. S1c). The working temperature of a sensor was adjusted by varying the heating voltage. Detecting gases were also injected into a test chamber and mixed with air. The gas response of the sensor was defined as $Response = R_a/R_g$ (reducing gases) or $Response = R_g/R_a$ (oxidizing gases), where R_a and R_g are the resistance in air and test gas, respectively. The response or recovery time was identified as the time needed for the sensor output to reach 90% of its saturation after application or switching off of the gas in a step function.

3. Results and discussions

Before annealing of the white powders at 400 °C, they were first characterized with XRD (Fig. 1a) to establish their compositions of materials obtained in the solvothermal reactions. The strong and sharp diffraction peaks of the products may be assigned to ZnO (JCPDS Card No. 36-1451) [31,32]. Additionally, the broad and weak diffraction peaks magnified in the inset of Fig. 1a can be indexed to zinc carbonate hydroxide hydrate, $Zn_4CO_3(OH)_6{\cdot}H_2O$, (JCPDS Card No. 11-0287) [33]. The results show that the as-prepared materials comprise of two components – ZnO and $Zn_4CO_3(OH)_6{\cdot}H_2O$. Fig. 1b illustrates the TG-DTA curves of the precursors. Two weight losses were observed and in the TG curve, respectively. After first losing weight of 0.3% between 100 and 200 °C for the removal of surface water, the products decomposed endothermically at 253 °C and lost 3.3% of their weight for the release of CO_2 and H_2O (Eq. (1)) from the system. This total weight loss is much lower as compared with the theoretical mass loss of 26.3% calculated for the decomposition of pure $Zn_4CO_3(OH)_6{\cdot}H_2O$. We can approximate the content of 14.3% $Zn_4CO_3(OH)_6{\cdot}H_2O$ in as-prepared products on the basis of the results from the thermal analysis.

$$Zn_4CO_3(OH)_6H_2O(s) \rightarrow 4ZnO(s) + CO_2(g) + 4H_2O(g) \quad (1)$$

After calcined at 400 °C for about 2 h, the as-synthesized mace-like $Zn_4CO_3(OH)_6{\cdot}H_2O$@ZnO nanoarchitectures converted entirely into phase-pure ZnO. The XRD pattern porous ZnO nanosheets @ ZnO microrod bundles correspond well with the pure ZnO (Fig. S2, Supplementary Information). To investigate the surface areas and porous features of the porous ZnO mace-like nanoarchitectures, nitrogen adsorption and desorption measurements were carried out. ZnO microrod bundles with smooth surfaces were selected as control for comparing the differences.

Fig. 2 illustrates the adsorption-desorption isotherm and the matching BJH pore size distribution plot (inset in Fig. 2) of the materials. The mace-like ZnO nanoarchitectures depict a loop with type H3, as per the IUPAC classification [34]. Accordingly, there are plentiful pores of 2–50 nm in diameter existing in the materials. The pore volume and average pore diameter are 0.09 cm^3/g and 32 nm, respectively. It is