Ultrasonics Sonochemistry 21 (2014) 1335–1342

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

# Synthesis of morphology-controlled ZnO microstructures via a microwave-assisted hydrothermal method and their gas-sensing property

Sa Liang [a,1], Lianfeng Zhu [b,1], Guosheng Gai [b], Youwei Yao [c], Jue Huang [c], Xuewen Ji [d], Xiaoming Zhou [a], Dongyun Zhang [a], Peixin Zhang [a,*]

[a] School of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, PR China
[b] Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China
[c] Graduated School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China
[d] Shenzhen Dovelet Sensors Technology Co., Ltd., Shenzhen 518057, PR China

ARTICLE INFO

*Article history:*
Received 25 June 2013
Received in revised form 20 November 2013
Accepted 7 February 2014
Available online 18 February 2014

*Keywords:*
ZnO
Microwave
Hydrothermal
Ethanol
Gas sensors

ABSTRACT

Controllable ZnO architectures with flower-like and rod-like morphologies were synthesized via a microwave-assisted hydrothermal method. By adjusting the concentration of $Zn^{2+}$ in the aqueous precursors, different morphologies of ZnO microstructures were obtained. The size of ZnO was uniform after ultrasonic treatment. The growth process of ZnO in solution was studied by monitoring the intermediate products, which were extracted at different stages of the reactions: (i) precursor preparation, (ii) microwave irradiation heating, (iii) natural cooling. Studies of the SEM images and XRD data revealed that the formation of ZnO occurred via in situ assembly or dissolution–reprecipitation of zinc hydroxide complexes. The morphology-dependent ethanol sensing performance was observed; the seven-spine ZnO structures exhibit the highest activity.



## 1. Introduction

ZnO is an important crystalline functional semiconductor with a large binding energy ($E_g$ = 60 meV) and a wide band gap (3.37 eV). It has attracted research attention because it is non-toxic, inexpensive and suitable for applications in solar cells [1], luminescent materials [2], optical devices [3], gas sensors [4,5] and others. Controlling the size, shape and orientation of ZnO crystallites is a prerequisite for high device performances. To date, considerable efforts have been devoted to develop syntheses of ZnO with tunable size and morphology; synthetic methods have included zinc oxidation [6], vapor phase deposition [7], metal-organic chemical vapor deposition (MOCVD) [8], sol–gel [9] and hydrothermal syntheses [10], as well as others. Of these methods, hydrothermal syntheses is particular interesting because ZnO microstructures can be fabricated under mild conditions (aqueous solution, <100 °C) and are highly reproducible.

A number of previous studies have investigated hydrothermal syntheses of zinc oxide microstructures and the principles are now broadly understood [11–15]. Briefly, the $Zn(OH)_4^{2-}$ species, which make up the majority of the solution species in alkaline solution (i.e. pH 11.5) [16], decompose into $Zn(OH)_2$ at moderate temperature; this decompositions is followed by further condensation and dehydration to form ZnO. The growing units, which are the $Zn(OH)_4^{2-}$ species, are stored in the solution [17,18] or generated from the dissolution of $Zn(OH)_2$, which may precipitate from the aqueous precursor [15]. The shapes and sizes of the zinc oxide crystals are variable and depend upon the decomposition kinetics of the $Zn(OH)_4^{2-}$ species [18], as well as the morphologies of nucleation sites [19]. Slow decomposition of the $Zn(OH)_4^{2-}$ species facilitates the self-assembly of $Zn(OH)_2$ conforming to the crystal nature of ZnO on the nucleation sites. Due to the different face-polarities of hexagonal ZnO [18], small molecules (or unreactive complexes) can selectively adsorb to different crystal faces during growth; these "capping agents" prevent the self-assembly of $Zn(OH)_4^{2-}$ ions and lead to slower growth of ZnO normal to the capped crystalline face. Therefore, organic additives or auxiliaries are usually introduced to tune the shapes of the products effectively: metal sulfate hydrates for the synthesis of ZnO nanoplates or nanowires [18], citrate generates oriented ZnO columns and plates [20], ascorbate triggers the formation flower-like ZnO microstructures [21], and ethanolamine facilitates the growth of nano-rods [22].

* Corresponding author. Tel./fax: +86 755 26558134.
*E-mail address:* pxzhang@szu.edu.cn (P. Zhang).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.ultsonch.2014.02.007
1350-4177/

Previous works concerning hydrothermal synthesis methods provide an array of phenomenology and understanding of the mechanisms for the formation of ZnO. However, the batch processing techniques utilized in hydrothermal synthesis are rather inefficient; some of them involve tens of hours of thermal treatment at a constant temperature. It is a challenge to fabricate ZnO microstructures with superior control of shape and size efficiently when considering the cost of manufacture. Alternatively, the microwave-assisted hydrothermal method has a number of advantages, such as higher reaction rate, rapid volumetric heating, higher yields of products and energy savings [23–25]. In this paper, we rapidly synthesize ZnO with varied morphologies through a microwave-assisted hydrothermal method. Flower-like or rod-like microstructures can be fabricated by simply changing the concentration of the zinc ions in the aqueous precursors instead of using any auxiliaries. This process is rapid and reproducible compared to the conventional heating and hydrothermal routes. Additionally, the gas sensing properties of morphologically different ZnO materials are compared.

## 2. Experimental

### 2.1. Preparation of ZnO microstructures

All chemicals used were analytical-grade and used without further purification. Different morphologies of ZnO were prepared with a microwave-assisted hydrothermal method. Flow charts containing the experiment procedure are illustrated in Fig. 1. Typically, 6 ml of ammonia (95%) were dissolved in deionized water to form a 100 ml solution. The diluted ammonia solution was added dropwise to 100 ml of aqueous zinc nitrate hexahydrate, $[Zn^{2+}] = 0.02$ or 0.06 M, with magnetic stirring. $[Zn^{2+}]$ represents the concentration of zinc ion in solution. Subsequently, the solutions were irradiated with a power-controlled microwave synthesis system (GALANZ WD800 (B123)) for 8 min at 800 W ultrasonic treated for 30 min, then cooled naturally to room temperature. Finally, the white products were collected by filtration before being washed with deionized water three times and anhydrous ethanol one time; the resultant solids were dried under vacuum at 130 °C for 5 h. Hereafter, the mixture of aqueous precursor of $NH_3 \cdot H_2O$ mixed and the initial solution of $Zn(NO_3)_2$ with $[Zn^{2+}] = 0.02$ M will be called *precursor A*, while the mixture with $[Zn^{2+}] = 0.06$ M will be called *precursor B*.

### 2.2. Gas sensing measurement

The ZnO microstructures were coated directly onto the surface of an alumina substrate ($2 \times 2\ mm^2$) with a pair of printed gold electrodes already installed; the system was dried at 60 °C for approximately 2 h. A ceramic heater was printed onto the backside of the alumina substrate to provide the working temperature of the gas sensor. The working temperature of the sensor was adjusted by changing the heating voltage and the substrate temperature was measured with a thermocouple. To improve the long-term stability, the sensors were maintained at the working temperature for 2 days. A stationary-state gas distribution method was used while testing gas responses in dry air. The gases for detection, which included $C_2H_5OH$, were injected into a test chamber and mixed with air. The volume of the chamber was 16 L and vaporizing 1 M of $C_2H_5OH$ generates 22.4 L of pure ethanol gas. The gas concentration was determined via the volume ratio of ethanol and the chamber dimensions. The electrical current of the sensors was monitored with a picoammeter (Keithley 6487) and an applied voltage of 5.0 V. The current values were recorded twice per second by computer. The gas response of the sensor in this paper was defined as $S = R_a/R_g$, where $R_a$ and $R_g$ were the resistance of the gas sensor in air and the test gas [4], respectively.

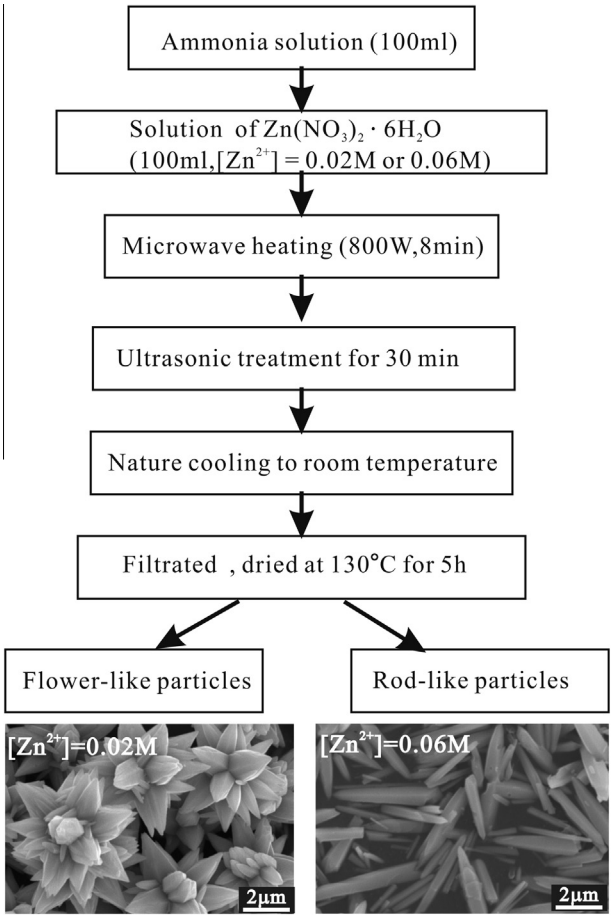


**Fig. 1.** Flow-charts representing the experiment procedure for the fabrication of ZnO particles with flower- and rod-like morphologies. $[Zn^{2+}]$ represents the concentration of zinc ion in solution.

### 2.3. Characterization

Phase identification for the powders obtained was performed with a D8ADVANCE X-ray diffraction (XRD) instrument. The microstructures and morphologies of the particles were determined via scanning electron microscopy (SEM) on a Hitachi S-3400N (II) instrument. The change in the zinc ion concentrations over time was recorded by inductively coupled plasma emission spectrometry (ICP – OPTIMA2100DV).

## 3. Results and discussion

### 3.1. Formation process for the flower-like and rod-like ZnO

The zinc oxide was produced by microwave irradiating the aqueous precursors. The flow chart was shown in Fig. 1, the use of different aqueous precursors resulted in products with two distinct morphologies. Using *precursor A* yielded flower-like materials, whereas using *precursor B* yielded rod-like microcrystalline. To study the growth process of these ZnO products, we carried out the following experiments. The growing process was divided into three steps for study: (i) preparing the aqueous precursor; (ii) heating through microwave irradiation; (iii) cooling naturally.