

## Preparation and Optical Property of Hierarchical Structured Porous ZnO Microplates†

GUOQUAN SHAO\*, XIUMIN FANG, CHANG XU and LIANGQIN WEI

Department of Chemical and Materials Engineering, Hefei University, Hefei, P.R. China

\*Corresponding author: Tel: +86 551 2158436; E-mail: [sgq@hfu.edu.cn](mailto:sgq@hfu.edu.cn)

Published online: 10 March 2014;

AJC-14850

Hierarchical structured porous ZnO microplates have been prepared by thermal decomposition of  $Zn_5(CO_3)_2(OH)_6$  precursor. The products are characterized by X-ray diffraction, field-emission scanning electron microscopy, high resolution transmission electron microscopy, transmission electron microscopy, UV-visible absorption spectrum and photoluminescence spectra. Each ZnO microplate is made up of nanoparticle-based nanowires with diameters of 40-80 nm and lengths of 2-3  $\mu\text{m}$  and the diameter of constituent nanoparticles ranges from 10 to 20 nm. Due to their porous hierarchical microstructures, the prepared ZnO products exhibit excellent optical properties.

**Keywords:** Porous microstructure, Zinc oxide, Optical property, Nanomaterials.

### INTRODUCTION

In recent years, self-assembly of nanoscaled building blocks (nanoparticles, nanorods, nanosheets) into two- and three-dimensional (2D/3D) ordered superstructures or complex functional architectures has been a research hotspot<sup>1</sup>. Various ZnO hierarchical architectures have been reported, such as flower-like hierarchical microstructures<sup>2</sup>, hierarchical mesocrystal microtubules<sup>3</sup>, hexagonal disks based nanowire bundled structures<sup>4</sup>, hierarchical nanowires<sup>5</sup>, rod-in-tube nano-architecture arrays<sup>6</sup>, hierarchical micro/nanorods<sup>7</sup>, double-caged peanut-like ZnO hierarchical superstructures<sup>8</sup>. Herein, we developed a facile environmental friendly two-step process to prepare two dimensional (2D) hierarchical structured porous ZnO microplates, which is assembled by nanoparticle-based nanowires with diameters of 40-80 nm and lengths of 2-3  $\mu\text{m}$ . The optical properties were investigated using optical absorption and photoluminescence spectra.

### EXPERIMENTAL

All chemicals (analytical grade reagents) were purchased from Shanghai Chemical Reagents Co. and used without further purification. Microwave-heating was performed on a MAS-II microwave synthesis/extraction reaction workstation (work frequency 2.45 GHz, power adjustable range 0-1000W, Shanghai Sineo Microwave Chemistry Technology Co., China).

**General procedure:** 1 mmol of  $Zn(CH_3COO)_2 \cdot 2H_2O$  and 20 mmol urea were added into a 100 mL conical flask containing 60 mL deionized water under stirring. The obtained reaction solution was transferred into a MAS-II apparatus, irradiated with microwave irradiation (power 500 w) under stirring with 1000 rpm at 80 °C for 0.5 h. After cooling down to room temperature, the precursor was washed with anhydrous ethanol and deionized water for several times and then finally dried in a vacuum at 60 °C for 6 h. The precursor was finally calcined at 400 °C for 2 h and collected for further characterization.

**Detection method:** The phase purity of the as-synthesized products was examined by X-ray diffraction (XRD) using a Philips X'Pert PRO X-ray diffractometer equipped with graphite monochromatized  $CuK_{\alpha}$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Field-emission scanning electron microscope (FESEM) images of the sample were taken on a field-emission microscope (FEI Sirion 200, 15 kV). The transmission electron microscope (TEM) images of the samples were performed on a JEOL-2010 transmission electron microscope with an accelerating voltage of 200 kV. UV-visible spectrum was studied using a UV-VIS spectrophotometer (TU-1800PC). Photoluminescence (PL) spectrum was recorded on a Laser MicroRaman Spectrometer (JYLABRAM-HR) using the 325 nm exciton of the He-Cd laser at room temperature.

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

## RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of precursor (sample A) and calcined product (sample B). The diffraction peaks of the precursor A can be indexed to monoclinic  $Zn_5(CO_3)_2(OH)_6$  (JCPDS card No. 19-1458). All the diffraction peaks of the calcined product B are well indicated to Wurtzite structure of ZnO with lattice parameters  $a = 3.247 \text{ \AA}$  and  $c = 5.202 \text{ \AA}$ , consistent with the reported data for ZnO (JCPDS card No. 5-664,  $a = 3.249 \text{ \AA}$ ,  $c = 5.205 \text{ \AA}$ ). No characteristic peaks belonging to other impurities were detected. The sharp diffraction peaks indicate the good crystallinity of the as-prepared ZnO products.

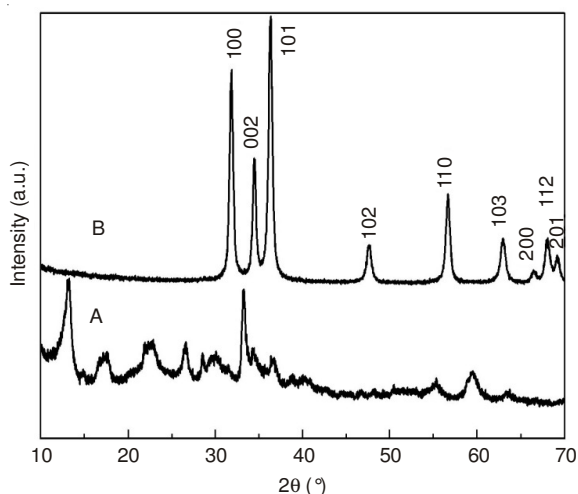


Fig. 1. XRD patterns of precursor A and calcined product B

The morphologies of  $Zn_5(CO_3)_2(OH)_6$  precursor and ZnO products were detected by FESEM. Fig. 2(a) and (b) are FESEM images of  $Zn_5(CO_3)_2(OH)_6$  precursors prepared through microwave heating technique using  $Zn(CH_3COO)_2 \cdot 2H_2O$  and urea as starting materials. Abundant thin nanosheets are observed and their surfaces are very smooth. Because of very thin, these nanosheets stacked on top of each other through van der Waals force. In addition, one can see some nanosheets crack and even producing thin strips (marked by white dashed circles in Fig. 2(b)). Fig. 2(c) and (d) show the morphology of ZnO products obtained by calcinating  $Zn_5(CO_3)_2(OH)_6$  precursor at  $400 \text{ }^\circ\text{C}$  for 2 h in air. It can be seen that the morphology of ZnO products change a lot comparing with precursor. Hierarchical plate-like porous microstructures with considerable rough surfaces are found in the prepared ZnO products and the size and thickness are increased. Each ZnO microplate is made up of nanoparticle-based nanowires with diameters of 40-80 nm and lengths of 2-3  $\mu\text{m}$ . Due to the stacking of sheet-like precursors, the obtained ZnO nanoproducs are fused together in the process of calcination, thus, the size and thickness of the obtained ZnO microplates are accordingly increased.

Fig. 3(a) and (b) show typical TEM images of the porous ZnO microplates with pore diameters of 5-30 nm, which indicate the morphology is basically accordance with FESEM results, the diameter of constituent nanoparticles ranges from 10 to 20 nm. Some 1D nanoparticle-based nanowires were

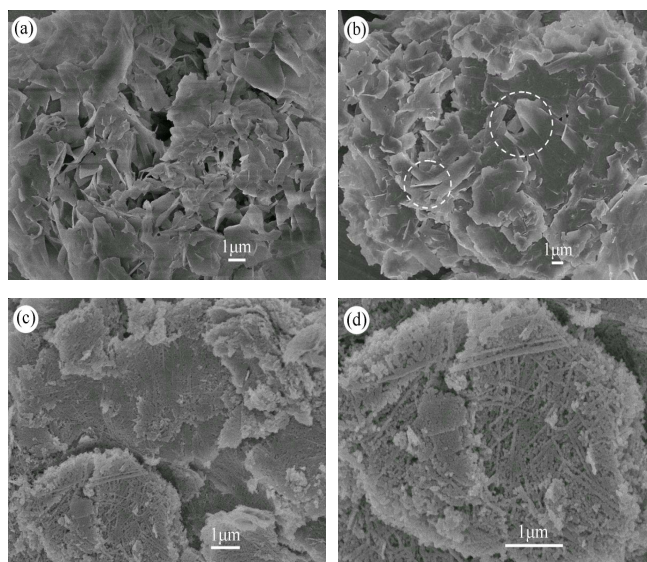


Fig. 2. (a,b) FESEM images of  $Zn_5(CO_3)_2(OH)_6$  precursor, (c,d) FESEM images of ZnO products obtained by calcinating precursor at  $400 \text{ }^\circ\text{C}$  for 2 h

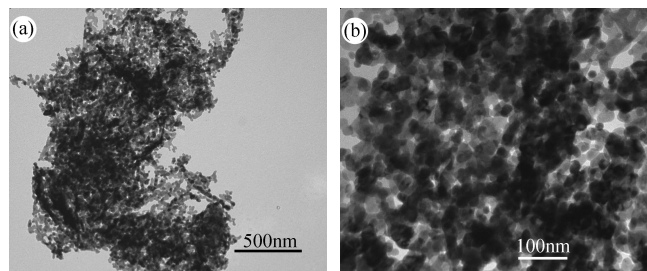
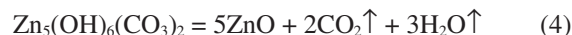
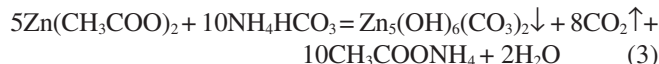


Fig. 3. TEM images of ZnO porous microplate

destroyed during the ultrasonic treatment possibly because of weak interacting forces between the adjacent nanoparticles.

Under microwave heating condition, urea may gradually hydrolyze to produce  $NH_4HCO_3$  (eqns. 1-2). Then,  $Zn(CH_3COO)_2$  rapidly react with new-produced  $NH_4HCO_3$  to form  $Zn_5(OH)_6(CO_3)_2$  precipitation (eqn. 3). Finally, ZnO product was obtained through the thermal decomposition of  $Zn_5(OH)_6(CO_3)_2$  precursor at proper temperature (eqn. 4). The whole reaction process for preparing porous ZnO microplates are possibly as follows:



The optical properties of plate-like ZnO porous microstructures were investigated using optical absorption and photoluminescence technology. Fig. 4a shows the UV-visible absorption spectrum of the ZnO products dispersed in deionized water at room temperature. The blue shifted absorption at 366 nm is observed compared with the band gap of bulk ZnO (375 nm), which may be ascribed to an enhanced surface effect due to a large surface-to-volume ratio of the synthesized porous ZnO hierarchical microstructures<sup>9</sup>. Fig. 4b presents the room temperature photoluminescence spectrum

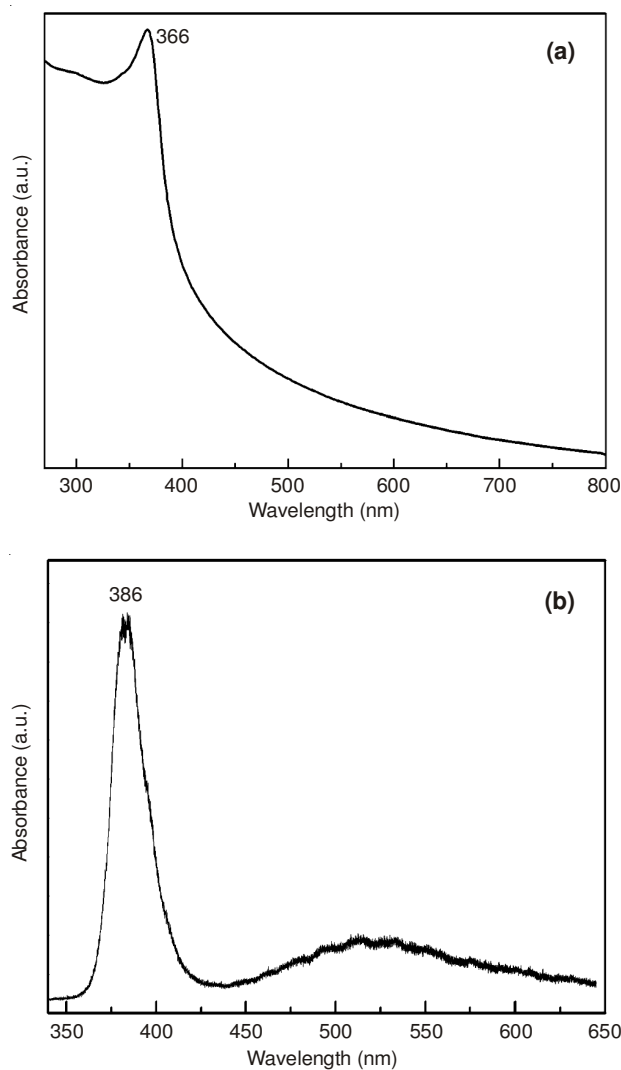


Fig. 4. UV-VIS absorption spectrum (a) and photoluminescence spectrum (b) of the plate-like ZnO porous microstructures

of the ZnO products. Two luminescence bands, including a strong UV emission peak located at 384 nm and a weak defect-related broad emission band centered at 520 nm (from blue to red), were observed. The UV emission band was attributed to the near-band emission of the ZnO products, which arises from

the recombination of photogenerated charge carriers across the band gap<sup>10</sup>. The defect-related emission of ZnO can be ascribed to the luminescence of oxygen vacancies and zinc interstitials<sup>11</sup>.

### Conclusion

Hierarchical structured porous ZnO microplates were prepared through thermal decomposition of sheet-like  $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$  precursor. The precursor was pre-synthesized via a convenient microwave heating reaction of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and urea in the aqueous solution. Each hierarchical structured ZnO microplate is made up of nanoparticle-based nanowires with diameters of 40-80 nm and lengths of 2-3  $\mu\text{m}$ . Based on UV-visible absorption and room-temperature photoluminescence spectra, the as-obtained porous ZnO products exhibit excellent optical properties, which may be used as optical materials and catalysts.

### ACKNOWLEDGEMENTS

This work was supported by the Science and Research Foundation for Development of Hefei University (Grant No. 11KY01ZD).

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