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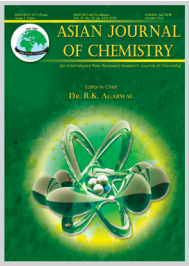

Novel Handbell-Like ZnO Architectures Fabricated by One-Pot Sonochemical Method†

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A facile green ultrasonic-assisted chemical reaction has been employed to controllably fabricate handbell-like ZnO architectures without using any templates, surfactants and organic additives. The products were characterized by X-ray diffraction, energy dispersive X-ray spectrometry and field-emission scanning electron microscopy. Field-emission scanning electron microscopy observation indictates that most of the ZnO handbell-like structures are built by hexagonal trumpet-shaped shell (called as bell hood) and hexagonal rod-shaped core (called as bell tongue), which have the nature of hexagonal symmetry. The growth mechanism and its succedent evolution of handbell-like ZnO architectures contolled by dynamical process with the change of ultrasonic irradiating time are investigated.

Key Words: Zinc oxide, Handbell-like, Ultrasonic technique, Nanomaterials.

INTRODUCTION

Zinc oxide (ZnO), a most widely studied metal oxide semiconductor with a direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature, has considerable interests due to potential applications in photodetectors[1], transistors[2], opt-electronics[3], solar cells[4], sensors[5], catalysts[6], *etc*. The wide variety of applications requires the fabrication of morphologically and functionally distinct ZnO nanostructures. Up to date, varoius methods including physical and chemical techniques have been used to synthesize ZnO micro/nanostructures with particular morphologies, such as nanorings[7], nanotube arrays[8], hollow dumbbell-like architectures[9], hollow microspheres[10,11], nanocombs[12], hollow star-shaped architectures[13], hollow nanofibers[14], nanonecklace[15], porous polygonal nanoflakes[16] and so forth.

The sonochemical method has been proved to be a useful method to obtain novel and unique structures[10]. The chemical effects of ultrasonic irradiation arise from acoustic cavitation, which result in an instantaneously high temperature and pressure. These special conditions attained during acoustic cavitation may lead to many unique structures and properties. Herein, we demonstrate that a new type of handbell-like ZnO architectures can be fabricated by a green and facile sono-chemical process that only involves the reaction of zinc acetate in the presence of aqueous solution of hexamethylenetetramine.

EXPERIMENTAL

All chemicals (analytical grade reagents) were purchased from Shanghai Chemical Reagents Co. and used without further purification.

General procedure: In a typical procedure, 1 mmol $Zn(CH_3COO)_2{\cdot}2H_2O$ and 5 mmol hexamethylenetetramine (HMT, $C_6H_{12}N_4$) were dissolved in 60 mL deionized water under stirring. After continuous stirring for 20 min, the reaction mixture was transferred into a 100 mL autoclavable bottle, which was sealed with attached screw cap to form a closed system. The bottle containing reaction mixture was then put into a sonication bath with the water bath temperature of 90 ºC and irradiated for 10 min by ultrasound wave. After cooling down to room temperature, the ivory white precipitation was filtered out, washed several times with anhydrous ethanol and deionized water and then dried in a vacuum at 60 ºC for 6 h.

Detection method: Sonication was performed using a locally supplied ultrasonicator (KQ-50, 40 kHz, 50 W). The phase purity of the as-synthesized products was examined by X-ray diffraction (XRD) using a Dandong Y-2000 X-ray diffractometer equipped with graphite monochromatized CuK_α radiation (λ = 1.54178 Å). Field-emission scanning electron microscope (FESEM) images of the samples were taken on a field-emission microscope (Sirion 200, 15 kV) attached with the energy dispersive X-ray spectrometry (EDX).

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RESULTS AND DISCUSSION

Fig. 1(a) shows the XRD pattern of the as-prepared sample. Nine prominent XRD peaks can be indexed to the ZnO crystal planes of (100), (002), (101), (102), (110), (103), (200), (112) and (201), which give a hexagonal structure with the measured lattice constants of a and c of 3.25 and 5.22 Å, respectively, consistent with the standard values of the reported ZnO data (JCPDS File, 5-664). No characteristic peaks belonging to other impurities were detected. The sharp diffraction peaks indicate the good crystallinity of the as-prepared ZnO crystals. Fig. 1(b) is the EDX spectrum of the obtained ZnO products, which indicates that only the Zn and O elements exists in the products. The molar ratio of Zn:O obtained from the peak areas is 0.97:1.02, which is in agreement with stoichiometry of ZnO.

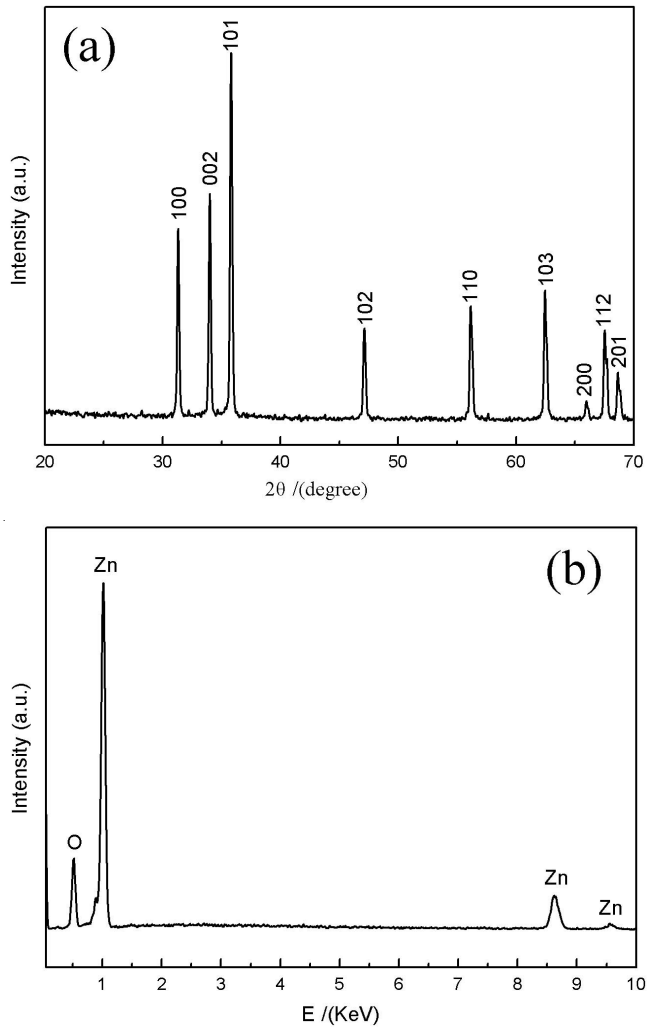

Fig. 1. XRD pattern (a) and EDX result (b) of the as-prepared sample

Fig. 2 shows the FESEM images of ZnO products obtained by ultrasound irradiation for 10 min, which indicates that the prepared ZnO products are mainly consisted of uniform handbell-like architectures. By careful observation, we found that most of the ZnO handbell-like structures are built by hexagonal trumpet-shaped shell (called as bell hood) and hexagonal rod-shaped core (called as bell tongue), which have the nature of hexagonal symmetry. The mouth diameter and depth of the bell hoods are estimated to be 200-300 nm and 300-400 nm, respectively. The diameter and length of the bell tongue are calculated to be 120-180 nm and 350-450 nm, respectively. Surely, some irregullar hexagonal and trigonal handbell-like ZnO are also existed in the products. Interestingly, dumbbell-shaped ZnO nanohandbells are also ocassionally observed in the products (inserted at the lower right corner of Fig. 2(b)). The inset image inserted at the upper right corner of Fig. 2(b) is the full-face image of a single handbell-like ZnO, which clearly reveals that the bell tongue grows out from the bottom of trumpet-shaped bell hood. In addition to handbell-like architectures, very few ZnO hollow bell hoods and nanosheets are also found in the products, which may be related with the formation of handbell-like ZnO [marked by white dashed circles in Fig. 2(a)].

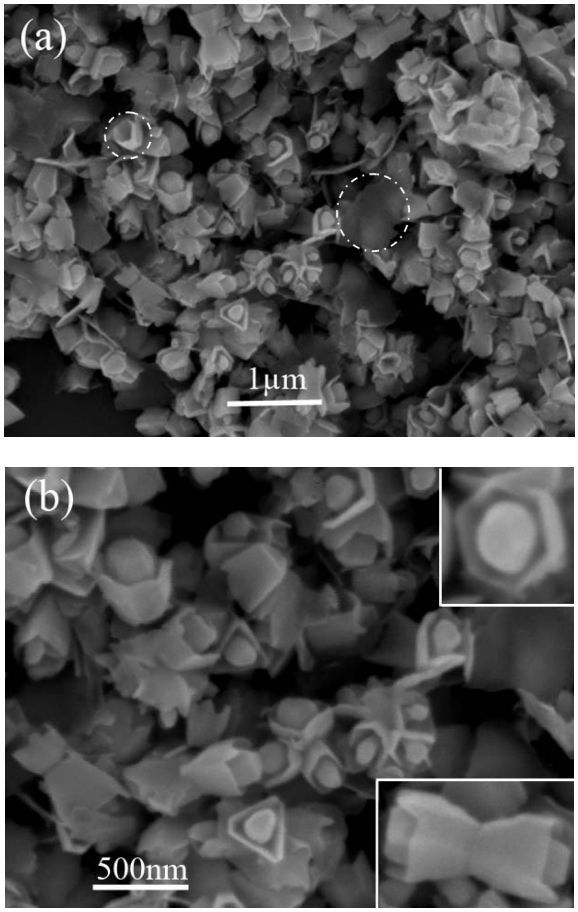

Fig. 2. FESEM images of handbell-like ZnO products recorded at different magnification

To investigate the growth process of the handbell-like ZnO architectures, time-dependent experiments were carried out by tuning the ultrasonic irradiating time from 5 to 20 min while keeping other parameters constant. FESEM images of the products obtained at different growth stages were shown in Fig. 3, which reveal the growth and evolution of handbell-like ZnO architectures. When the ultrasonic irradiating time is reduced to 5 min, a good deal of thin nanosheets were found in the obtained products [Fig. 3(a)]. When the ultrasonic irradiating time is 7.5 min, hollow bell hoods are main products

and coexiting with some nanosheets [Fig. 3(b)]. Hollow bell hoods and some nanosheets are also obtained when ultrasonic irradiating time is increased to 15 min [Fig. 3(c)]. While ultrasonic irradiating time is prolonged to 20 min, the handbell-like ZnO architectures are corroded seriously in the alkaline solution. The major products are cracked nanosheets and few hollow bell hoods are found [Fig. 3(d)].

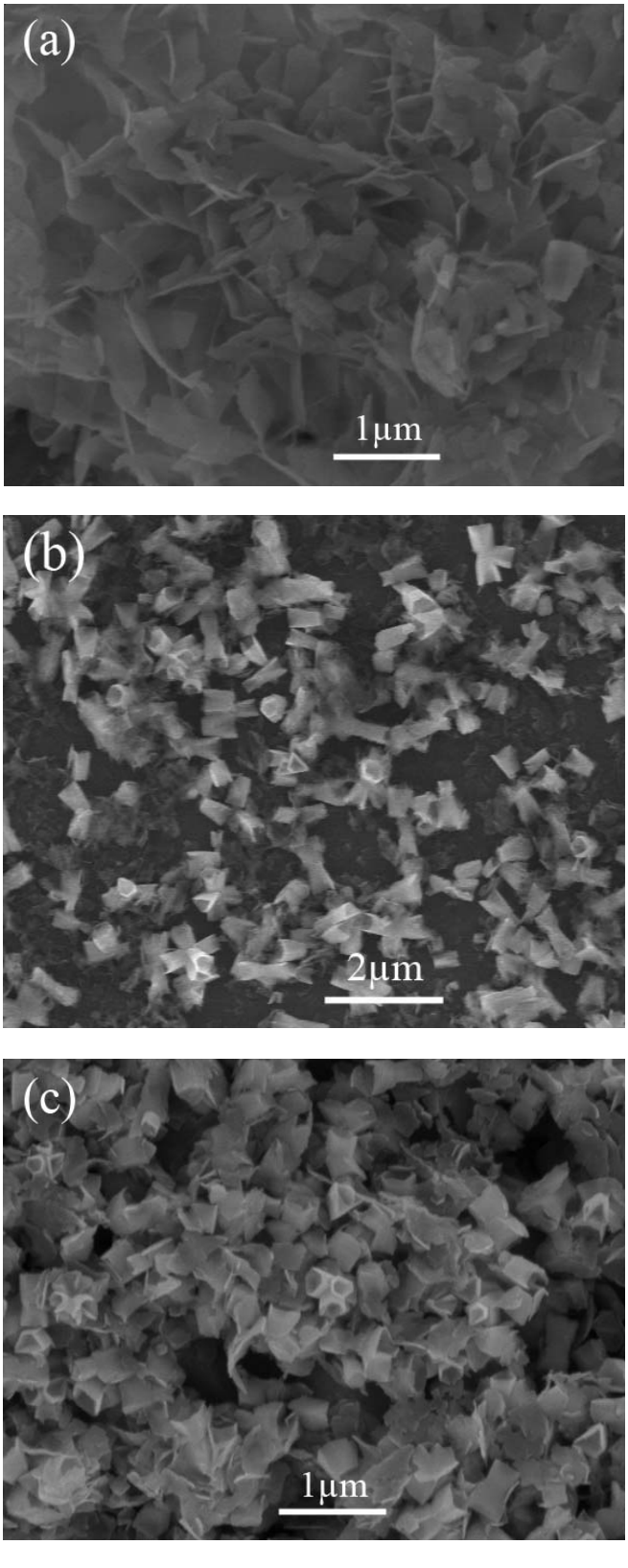

Fig. 3. FESEM images of ZnO products obtained by ultrasonic irradiating for (a) 5 min, (b) 7.5 min, (c) 15 min, (d) 20 min

Based on the above experimental results, the growth mechanism and its succedent evolution of handbell-like ZnO architectures contolled by dynamical process with the change of ultrasonic irradiating time are described as follows: First, Zn^{2+} in the aqueous solution combine with OH^- coming from the hydrolyzation of hexamethylenetetramine to form the growth units of $Zn(OH)_4^{2-}$ complexes. The newly-produced $Zn(OH)_4^{2-}$ complexes dehydrolyze to generate ZnO nucleus and further growth into thin nanosheets under ultrasonic irradiation. Second, under the role of ultrasonic wave, thin nanosheets can roll up into hexagonal trumpet-shaped shells in accordance with the growth habit of ZnO crystal. Third, with the process of reaction, second nucleation and growth take place at the bottom of hexagonal trumpet-shaped ZnO shells. So, the strong oriented growth of ZnO crystal along the c-axis make hexagonal rod-shaped tongues grow out from the bottom of the bell hoods to form handbell-like ZnO architectures. It is deserved to be mentioned that overlong ultrasonic irradiating time (above 15 min) will corrode and destroy the beautiful handbell-like ZnO architectures in the alkaline solution.

The morphology of ZnO products are greatly affected by the dosage of hexamethylenetetramine. Fig. 4a give the picture of ZnO products obtained in 2.5 mmol hexamethylenetetramine reaction solution, which indicates the products are mainly nanosheets as well as a few hollow bell hoods. While the amount of hexamethylenetetramine is increased to 7.5 mmol, the products are also the mixture of nanosheets and hollow bell hoods. The comparative experimental results suggest that only at proper concentration of organic base (5 mmol hexamethylenetetramine), perfect handbell-like ZnO architectures are formed. Lower concentration of organic base (2.5 mmol hexamethylenetetramine) is not enough for the rolling-up of nanosheets and the second nucleation and growth of rod-shaped bell tongue. Higher concentration of organic base (7.5 mmol hexamethylenetetramine) will corrode and destroy preformed handbell-like ZnO.

Conclusion

In conclusion, novel and beautiful handbell-like ZnO architectures have been successfully prepared *via* a one-pot

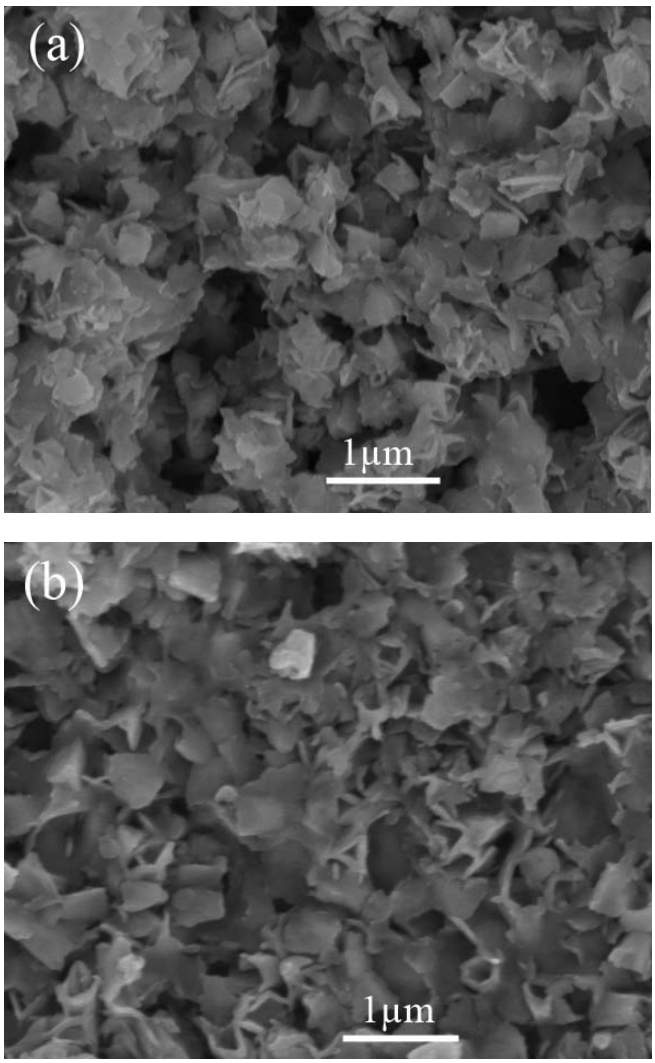

Fig. 4. FESEM images of ZnO products obtained using different amount of hexamethylenetetramine: (a) 2.5 mmol, (b) 7.5 mmol

sonochemical method. The prepared ZnO handbell-like structures are built by hexagonal trumpet-shaped shell (called as bell hood) and hexagonal rod-shaped core (called as bell tongue). The mouth diameter and depth of the bell hoods are estimated to be 200-300 nm and 300-400 nm, respectively. The diameter and length of the bell tongue are calculated to be 120-180 nm and 350-450 nm, respectively. This configuration is a new member in the family of ZnO nanostructures, which may bring novel physical and chemical properties in the field of microscale electronics and photonics.

ACKNOWLEDGEMENTS

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