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SHORT COMMUNICATION

Synthesis and evolution of novel double tower-like ZnO by a simple method

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Abstract Delicate double tower-like ZnO have been fabricated through the decomposition of the zinc nitrate hexahydrate ($Zn(NO_3)_26H_2O$). The phase transformation and morphology evolution of the products were carefully studied and investigated with X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and Raman spectra. The resultant results indicated that the obtained double tower-like ZnO materials possess pure wurtzite hexagonal phase, growing along the [100] direction. A reasonable formation mechanism was also presented in this paper.

Keywords Nanostructures · Zinc oxide · Tower-like

Introduction

In recent years, synthesis of inorganic materials with specific size and morphology has attracted significant attention due to their possible use in different fields [1–7]. For example, one-dimensional ZnO nanostructures are especially attractive for their promising applications in electronic or optoelectronic devices [8–10]. Qian et al. [11] reported the synthesis of urchin-, flower-like, and hierarchical ZnO 3D architectures and the photoluminescence spectra of the resultant ZnO 3D architectures presented an intensive ultraviolet emission at about 385 nm and weak green emission, which indicated their high structural and optical quality. Because the size, morphology, and dimensionality of ZnO have great effects on its properties and applications, researchers have prepared many different-shaped ZnO structures in order to fit different applications [12]. Until now, many different synthetic strategies have been developed to synthesize flower-like, funnel-like, propeller-like, and one-dimensional nanowires, nanoneedles, nanorods, nanotubes, and nanobelts ZnO based on the chemical vapor deposition, vapor–solid process, aqueous method, and other physical and chemical techniques [13–17].

ZnO is a valuable electronic and photonic material [18, 19] because of its wide direct band gap energy of 3.67 eV and large exciton binding energy of 60 meV [20, 21]. Owing to the unique physical and chemical properties of nanocrystalline ZnO, it has attracted more and more attention and exhibited potential applications in many different fields, such as acoustic wave filters [22], photonic crystals [23], UV photo detectors, field effect transistors, intramolecular p–n junction diodes, Schottky diodes, photodiodes [24], light-emitting diodes [25], optical modulator wave guides [26], and gas sensors [27]. ZnO is also an exceptionally important material having applications in pigments, rubber additives, varistors, and optical devices and thus interesting for both application and fundamental studies. Furthermore, ZnO is known to have antibacterial properties and along with its arsenic-scavenging ability finds use in water treatment and purification.

Although tower-like ZnO has been prepared through different techniques [12, 13, 28–30], to the best of our knowledge, there is no report on the synthesis of double tower-like ZnO. In this paper, we report a very simple method to grow novel double tower-like ZnO without use

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of additive, high-temperature, or intricate processing. The structure and morphology of the resultant ZnO materials were characterized in detail by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Raman spectra. This novel double tower-like ZnO may be extended the potential applications of ZnO in electronic or optoelectronic fields.

Experimental section

Synthesis was carried out by solution process at 180 °C using zinc nitrate hexahydrate and ethanol as source materials. For synthesis, 10 mmol $Zn(NO_3)_2 6H_2O$ was dissolved in 25 mL of ethanol, then all the above solution was loaded into Teflon tube, which was then heated at 180 °C for 10 h in an electric oven. Finally, the ZnO product was filtered off, washed thoroughly with deionized water, and dried in a container at 25 °C for 24 h.

General morphologies and detailed structure characterizations were obtained using a JSM-6480 SEM and a FEI Tecnai G2 S-TWIN electron microscope with an acceleration voltage of 200 kV. TEM experiments were performed on a Philips CM 200 FEG electron microscope with an acceleration voltage of 200 kV. The structure and crystal phases were determined by XRD (Rigaku D) with Cu Kα radiation (λ=1.54178 Å) with Bragg angle ranging from 20° to 80°. The surface states were analyzed by XPS (AXIS-NOVA, Kratos Inc.). Raman measurement was performed using a Renishaw 1000 model confocal microscopy Raman spectrometer.

Results and discussions

Figure 1 shows the typical SEM images of the resultant double tower-like ZnO at different magnifications. Figure 1a,b show the low-magnification SEM images and Fig. 1c presents the high-magnification images of the grown products of ZnO. The images clearly revealed the double tower-shaped structures that are constituted by the accumulation of several hundreds of ZnO nanosheets. The longest diameter of the crystals is about 8–10 μm; the topmost diameter of the

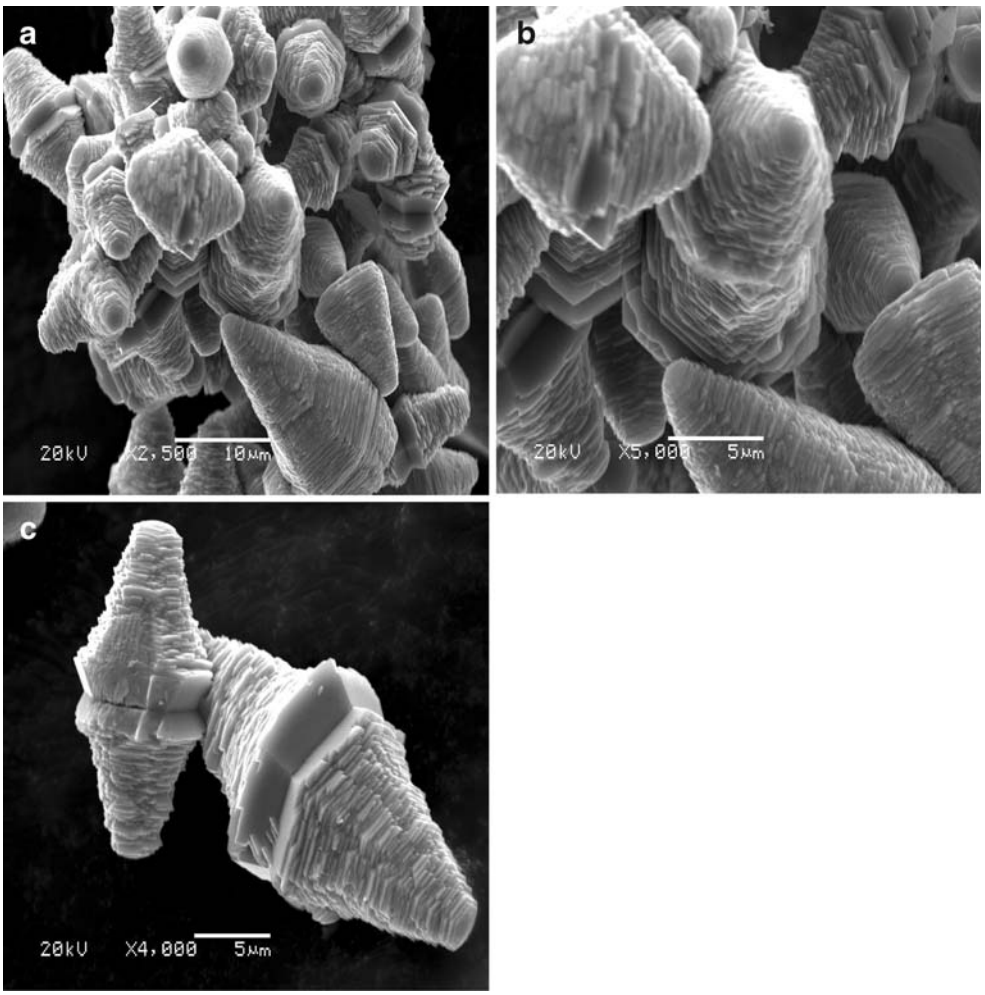

Fig. 1 SEM images of the resultant double tower-like ZnO at different magnifications

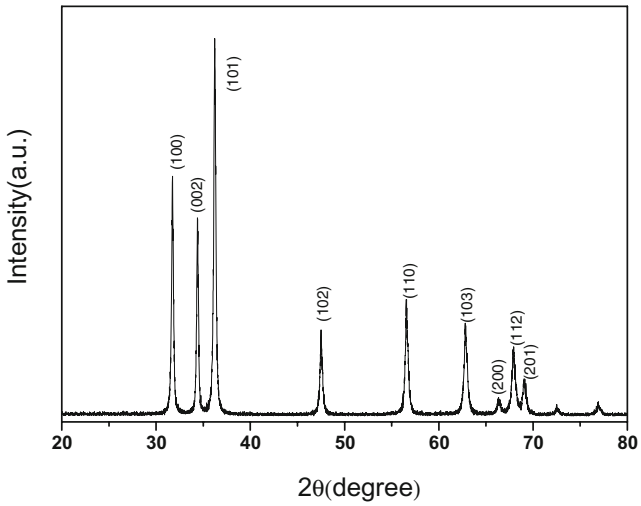

Fig. 2 Typical XRD pattern of the obtained ZnO materials

crystals is about 2–3 μm, and the length of double tower-shaped ZnO is about 20–25 μm.

Figure 2 presents the XRD pattern of the obtained ZnO powder. All of the indexed peaks in the obtained spectrum are well consistent with the bulk ZnO (JCPDC Card No.36-1451), which confirmed that the as-synthesized powder is a wurtzite hexagonal structure. No other peak related to impurities was detected in the spectrum within the detection limit of the X-ray diffraction, which further confirms that the synthesized powders are pure ZnO.

Further structure characterization was carried out by the TEM equipped with the Fast Fourier transform (FFT) setup. Figure 3(a) shows the low-magnification TEM image of the ZnO nanosheets grown in the tower-shaped structures. ZnO nanosheets are clearly evident from this image. The corresponding FFT pattern shown in the inset of Fig. 3b confirmed that the obtained products grow along the [100] direction. Figure 3b shows the high-resolution transmission electron microscopy (HRTEM) image of a nanosheet. The lattice fringes between two adjacent planes is about 0.28 nm, which is equal to the lattice constant of the ZnO. This further indicated that the obtained double tower-like ZnO has a wurtzite hexagonal phase and are preferentially grown along the a-axis [100] direction. The corresponding FFT pattern (inset in Fig. 3b) is consistent with the HRTEM observation.

The surface element composition of the as-prepared sample was also studied by XPS analysis. Figure 4a shows the survey spectrum of the sample. No peaks of other elements except Zn, O, and C were observed. The presence of C comes mainly from atmospheric contamination due to the exposure of the sample to air. The binding energies in all the XPS spectra were calibrated using that of C 1 s (292.9 eV). Figure 4b,c also displays high-resolution spectra for Zn and O regions, respectively. The binding energies of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ are 1,030 and 1,053 eV, respectively. And the O 1-s peak is centered at 539.4 eV. These binding energies are very close to the standard values of bulk ZnO [31]. Both XRD and XPS analysis indicate that the as-prepared products are pure ZnO.

The optical properties of the synthesized ZnO nanostructure were observed by the Raman scattering measurement. The Raman spectra are sensitive to the crystal quality, structural defects, and disorders of the grown products. With a wurtzite hexagonal, ZnO belongs to theC_{6V}^4 with two formula units per primitive cell. The primitive cell includes two formula units in which all the atoms are occupying the 2b sites of the C_{3V} symmetry. Group theory predicts that, at the Γ point of the Brillouin zone, there is an existence of following optic modes: $\Gamma = A_1 + 2B_1 + E_1 + 2E_2$. The A_1, E_1 and E_2 modes are Raman active. Furthermore, the A_1 and E_1 are infrared active and splits into longitudinal optical components and transverse optical components [32]. Figure 5 shows the Raman spectrum of the synthesized powder. A sharp and strong peak at 441 cm^{-1} is observed which is attributed to the optical phonon E_2 mode of the ZnO and a characteristic Raman

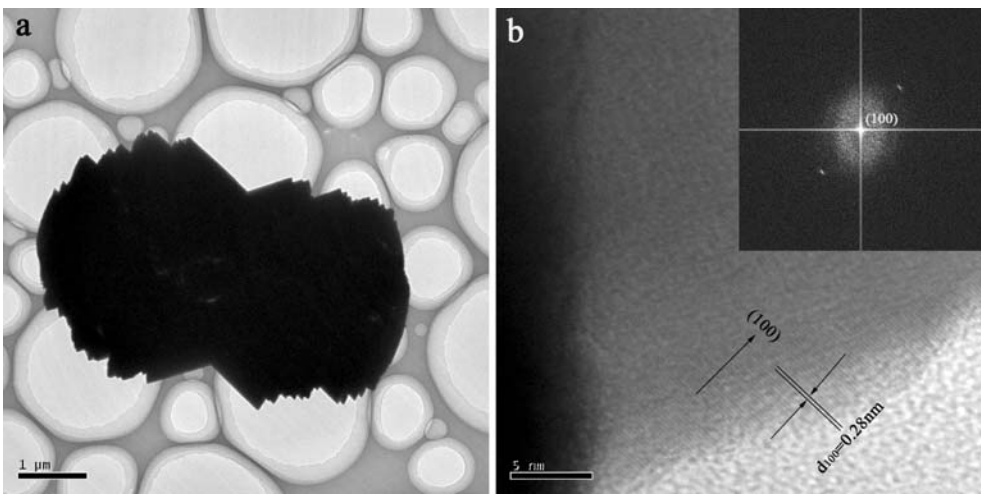

Fig. 3 **a** Low-magnification TEM image of the grown ZnO. **b** HRTEM image showing the difference between two lattice fringes, which is about 0.28 nm. Corresponding FFT pattern (*inset*) is consistent with the HRTEM observation

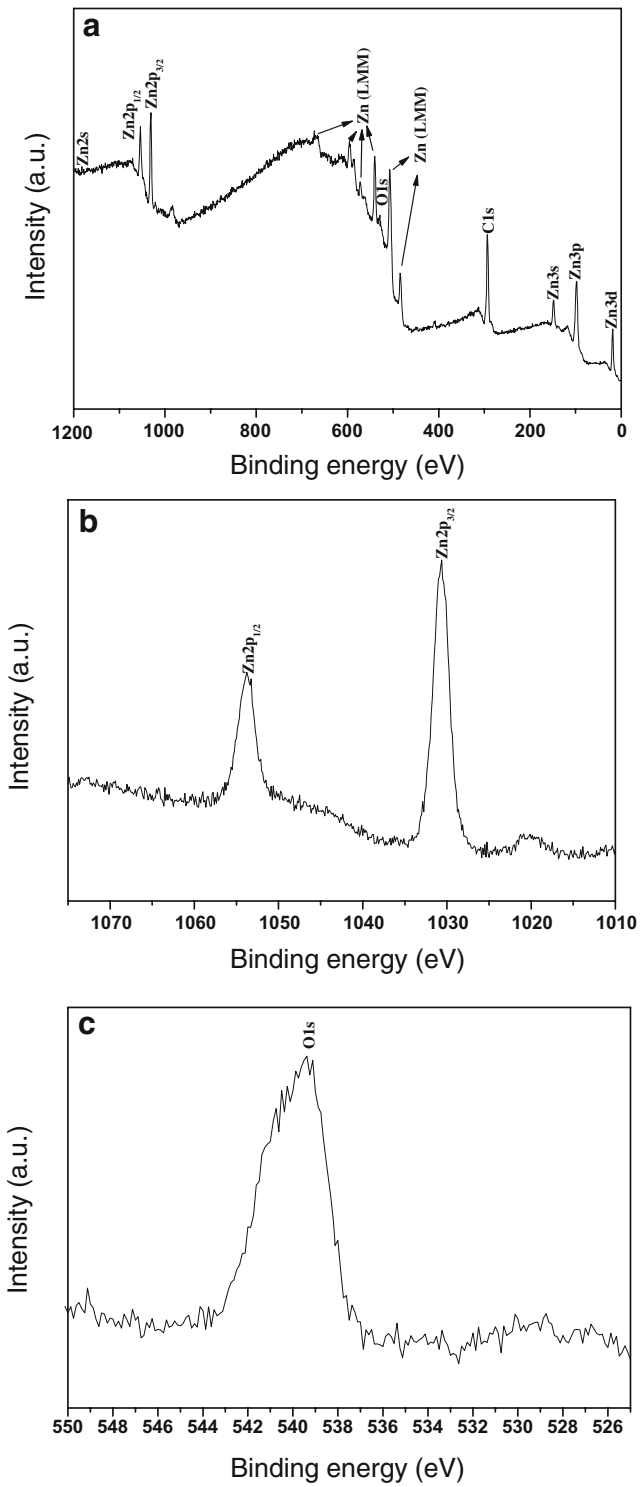

Fig. 4 XPS spectra of the obtained ZnO sample: **a** survey spectrum of the sample, **b** Zn 2p spectrum, and **c** O 1 s spectrum

active peak for the wurtzite hexagonal phase of ZnO [33]. Furthermore, two very small peaks at 335 and 383 cm^{-1} are also observed in the spectrum which are assigned to be as E_{2H}–E_{2L} (multiphonon process) and A_{1T} modes, respectively. Additionally, a very suppressed and short peak at

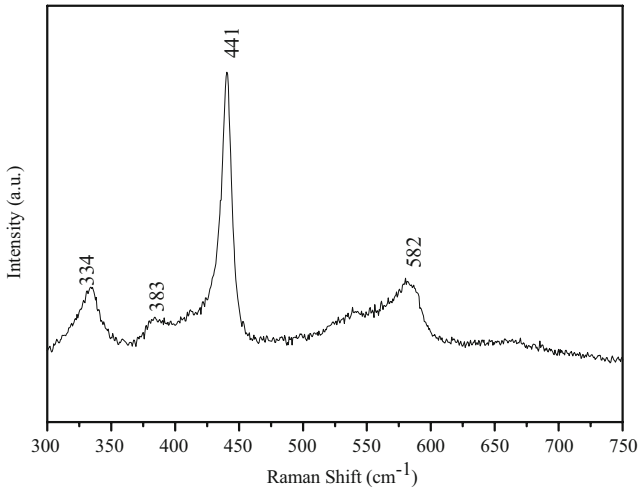

Fig. 5 Typical Raman spectrum of the synthesized nanostructure

582 cm^{-1} is seen in the spectrum and attributed as E_{1L} mode [34, 35]. The origination of E_{1L} mode in the Raman scattering is because of the impurities and structural defects (oxygen vacancies and Zn interstitials) of the synthesized products. Therefore, the presence of high-intensity E_2 mode with the suppressed and very short E_{1L} peak in the Raman scattering indicate that the synthesized sphere-shaped ZnO nanostructures are good in crystal quality and possess the wurtzite hexagonal crystal structure.

On the basis of the obtained experimental results and the published references [12, 13, 28–30], a possible growth mechanism of the double tower-like ZnO was proposed as illustrated in Fig. 6. Owing to the reaction of zinc nitrate hexahydrate, a small piece of ZnO nanocrystal was first deposited. Due to the very high temperature, the lateral growth became more faster. Moreover, the edge areas were much more active than the center. After a period of time, a diametric sheet was formed with an increasing thickness from edges to center. Finally, ideal ZnO nanosheets were finished. This can be confirmed by our SEM and TEM observations, where layered nanosheet structures can be clearly observed in the double tower-like ZnO. This indicated that, under this condition, tower-like ZnO crystals form from stacking structure layer by layer. The diameter of middle structure became thicker than the two poles due to the centripetal force. The growth of these nanosheets produces the perfect helical nanostructure reported in this work.

Conclusion

Double tower-like structures of ZnO were fabricated through a simple solution using zinc nitrate hexahydrate and ethanol as source materials. XRD, SEM, TEM, XPS, and Raman were used for the characterization of the novel

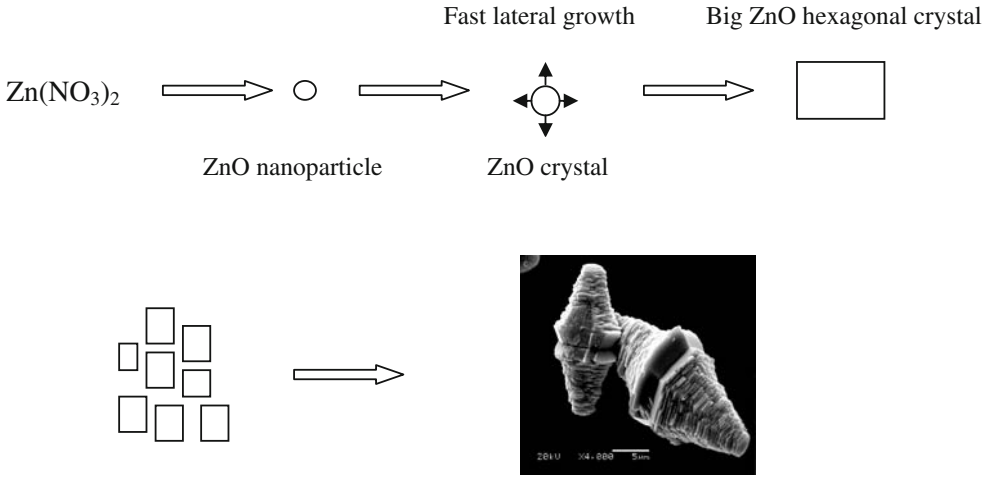

Fig. 6 Illustration of the formation mechanism of double tower-shaped ZnO

structures. The method is advantageous as it is cheap, easily controlled, and environmentally safe. Double tower-like microstructures of ZnO are quite interesting because of its unique morphology. We hope that this simple synthetic route can be extended to other systems involving metal complexes with suitable combination of metals and ligands. Such delicate double tower-like ZnO nanomaterials would be expected to have some potential applications in optical electronic devices.

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