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LETTER

Self-assembly of ZnO nanoplates into microspheres

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The chemical fabrication of materials with a controllable size and shape has attracted considerable interest due to the obvious importance of size and shape of materials in determining their properties [1–5]. Recently, the research on the structures of materials is expanding rapidly to the assembly of nanoparticles into two-dimensional (2-D) or three-dimensional (3-D) ordered superstructures [6–8]. However, few reports on the self-assembly nanoplates into microspheres have been made to date.

As a wide bandgap semiconductor material with a large excitation binding energy, ZnO has promising applications in catalytic, electrical, optoelectronic and photochemical fields [9–11]. It is known that the properties of ZnO depend closely on its microstructures, thus its surface area and morphology (how the crystals are stacked) have a crucial role in many applications of ZnO [12]. Therefore, the development of morphologically controllable synthesis of ZnO with different structures is important to meet the demand for exploring its potential utilities. Recently, there are numerous efforts afforded to synthesize ZnO with different morphologies and different crystallographic forms [8, 13–20]. However, it is still considerably difficult for these ZnO structures to self-assemble into 2-D and 3-D superstructures [8]. Herein, we have successfully fabricated ZnO microspheres self-assembled by single-crystal nanoplates using $ZnC_2O_4 \cdot 2H_2O$ as a precursor. Photoluminescence (PL) spectrum of the ZnO microspheres exhibits an intensive UV emission at 389 nm at room temperature, which suggests a new candidate for fabricating optoelectronic devices. The method is simple, and may be extended to synthesize other inorganic materials with complex structures.

In a typical procedure, the precursors of hydrous zinc oxalate were obtained through dissolving 3 mmol of $ZnCl_2$ and 3 mmol of $Na_2C_2O_4$ in 30 mL distilled water under constant magnetic stirring for 10 min. The precipitates obtained were filtered, washed with distilled water and dried. All the precipitates and 8.5 mmol of NaOH were loaded into a 50 mL Teflon-lined stainless steel autoclave, which was then filled with distilled water up to 90% of the total volume. Then the autoclave was sealed and maintained at 180 °C for 8–10 h. After being cooled to room temperature naturally, the powders were washed with distilled water and absolute ethanol several times. White products could be obtained after being dried in air at 60 °C for 10 h.

The X-ray powder diffraction (XRD) patterns of the products were recorded on a Philips X′ pert X-ray diffractometer with CuK_α radiation ($\lambda = 1.54187$ Å) employing a scanning rate of $0.02° S^{-1}$ in the 2θ ranges from 10 to 70°. Scanning electron microscope (SEM) images were performed on a Philips XL30 ESEM. The transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were collected on a Hitachi Model H-800 instrument with a tungsten filament. The Raman spectrum was acquired at room temperature with a LABRAM-HR Confocal Laser MicroRaman Spectrometer. The room temperature photoluminescence

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(PL) spectrum was performed on a Jobin Yvon-Labram spectrometer with a He–Cd laser.

The XRD pattern of the precursors obtained (data not shown) shows that they were $ZnC_2O_4 \cdot 2H_2O$ (ICSD card NO. 6466). The morphology of those precursors was also investigated and their SEM microscopy in Fig. 1 exhibits that they was composed of many micro-polyhedra.

Figure 2 shows a typical XRD pattern of the as-prepared ZnO products. All the diffraction peaks of the XRD pattern could be indexed to a pure hexagonal phase of ZnO with lattice constants (a = 0.325 nm, c = 0.521 nm), which are in good agreement with the reported data (JCPDS card No. 89-0510). The strong and clear peaks reveal good crystallinity of the as-obtained product. No characteristic peaks could be observed for other impurities such as $ZnC_2O_4 \cdot 2H_2O$ and $Zn(OH)_2$.

A representative TEM image shown in Fig. 3a indicated that there are a large quantity of microspheres with diameters ranging from 1.3 to 2 μm distributed in the products. These microspheres are self-assembled by many nanoplates with a size of about 0.5–1 μm, which can be seen in the insert of Fig. 3a. TEM images in Fig. 3b,c shows that the thickness of about 50 nm is estimated from these nanoplates standing on the copper grid. It is worthy noting that the microspheres preserve their shapes after the ultrasonic treatment thus displaying good structural stability. The size and shape of these microspheres enables them to possess high specific surface reactivity due to the gaps between the nanoplates. The ED pattern (shown as an inset in Fig. 3c) obtained from a thin plate of the microsphere reveals the ZnO nanoplates have a single-crystalline nature.

Figure 4 shows the Raman spectrum of ZnO microspheres. The Raman bands at 330, 383, 436, 571 and 581 cm^{-1} are assigned as the E_2, $A_1(TO)$, E_2, $A_1(LO)$ and $E_1(LO)$ modes, respectively [21]. And, one phonon of unspecified symmetry at 543 cm^{-1} [21] can also be found.

The room temperature PL spectrum of the ZnO products was measured using a He–Cd laser (325 nm) as the excitation source and no filter was used. The PL spectrum (Fig. 5) of ZnO microspheres reveals an intensive UV emission at around 389 nm, which should correspond to the near band edge emission of the wide band gap of ZnO due to the annihilation of excitons [22] and as a result of the quantum confinement effect [23].

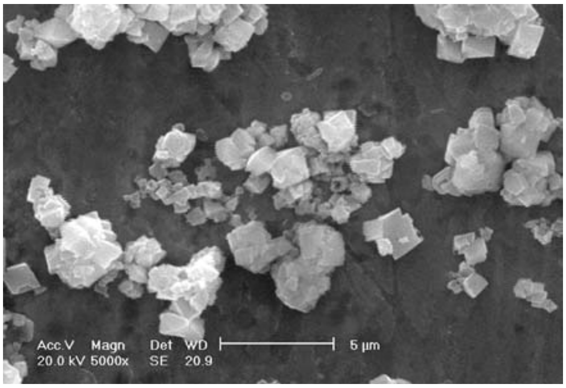

Fig. 1 SEM image of the as-prepared $ZnC_2O_4 \cdot 2H_2O$ precursors

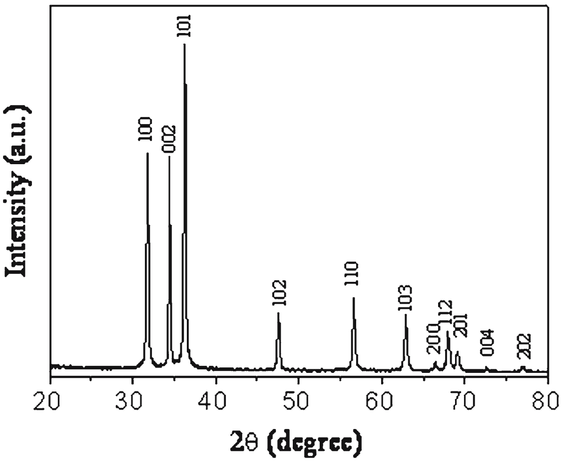

Fig. 2 A typical XRD pattern of the synthesized ZnO microsphere

On the basis of the experimental results, a possible mechanism for the formation of ZnO microspheres is proposed, and the reaction process can be described as follows:

$$Zn^{2+} + C_2O_4^{2-} + 2H_2O \rightarrow ZnC_2O_4 \cdot 2H_2O, \qquad (1)$$

$$ZnC_2O_4 \cdot 2H_2O + 2OH^- \rightarrow ZnO + CO_4^{2-} + 3H_2O. \qquad (2)$$

It is supposed that the precursors $ZnC_2O_4 \cdot 2H_2O$ obtained in Eq. (1) played an important role in the formation of ZnO microspheres and served as a template in the formation of ZnO microspheres. The $C_2O_4^{2-}$ might act as a bidentate ligand in aqueous solution forming the stable complexes, which is shown in Fig. 6. In the complex, the central metal atom is bonded by two $C_2O_4^{2-}$ ions forming a planar molecular and there are two coordinated H_2O molecules perpendicular to the molecular plane [24]. When the conversion in Eq. (2) proceeded in NaOH solution under hydrothermal conditions, the H_2O molecules of the complexes (Fig. 6) were quickly replaced by OH^- and formed ZnO while losing water molecules. At some relatively high temperature, oxygen atoms could coordinate to the neighboring complexes, causing the 3-D ZnO structure to condense; at the same time the $C_2O_4^{2-}$ ions were gradually substituted by OH^-. Then the polyhedral $ZnC_2O_4 \cdot 2H_2O$ precursors converted to the ZnO nanopaltes, which self-assembled into microspheres to decrease the overall surface energy.

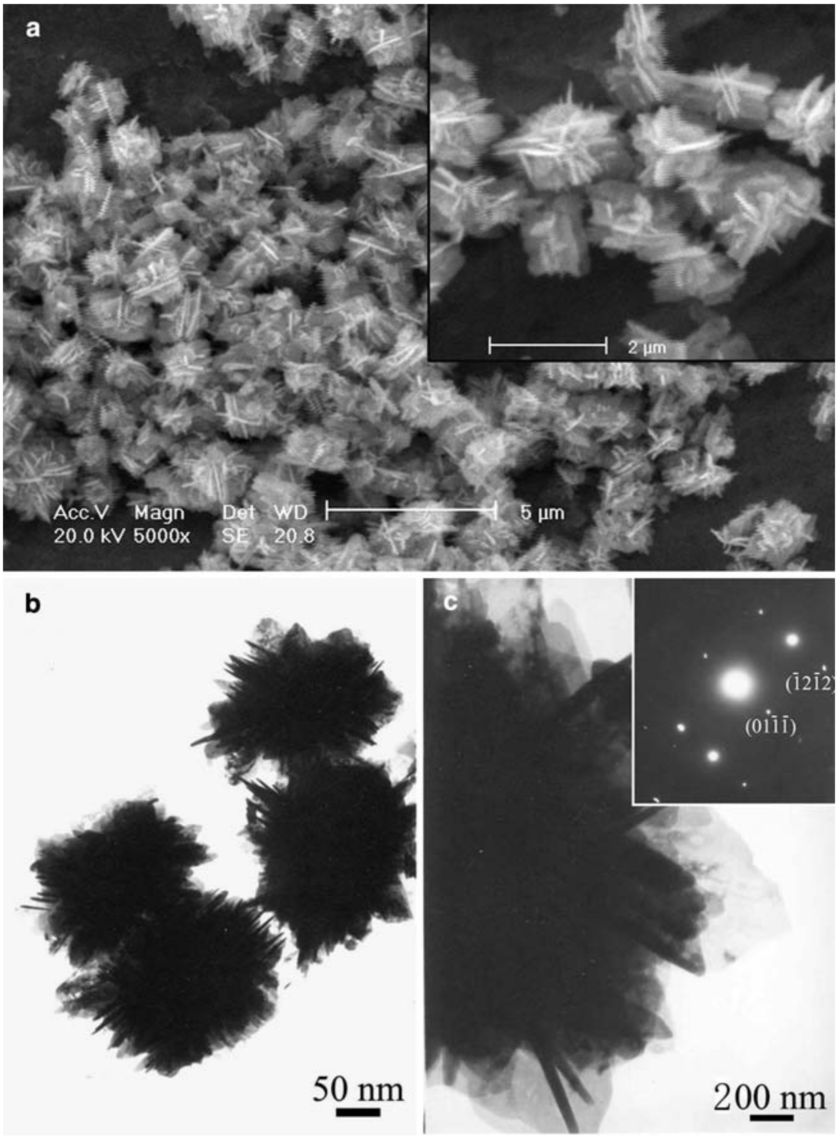

Fig. 3 (**a**) SEM image of the ZnO products, the inset is a magnified SEM image; (**b**) TEM image of the sample; (**c**) TEM image of a part of a microsphere, inset is the corresponding ED pattern

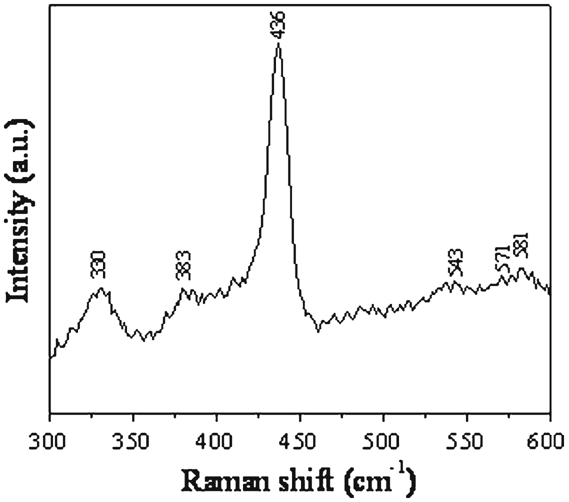

Fig. 4 Raman spectrum of the ZnO products

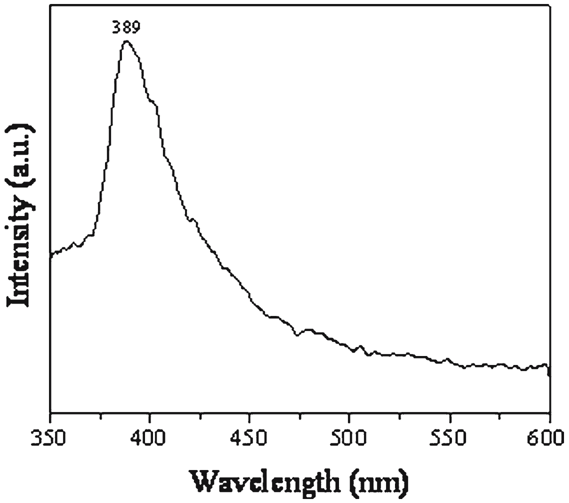

Fig. 5 Room-temperature PL spectrum of the ZnO products

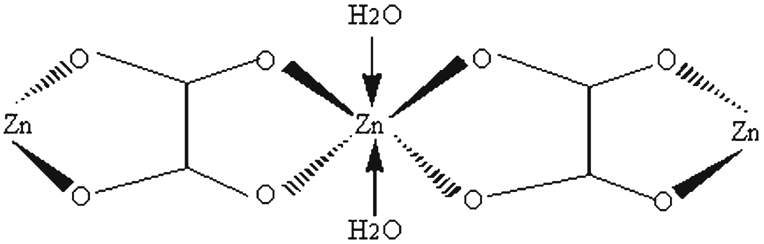

Fig. 6 Schematic image of $ZnC_2O_4 \cdot 2H_2O$

In summary, we have demonstrated a facile precursors route for the preparation of 3-D ZnO microspheres constructed from 2-D nanoplates. Due to their good crystallinity, PL properties and high specific surface area, the products can be used in studies considering the effects of spatial orientation and arrangement of 2-D nanoscale building blocks on their collective sensing, catalytic, optical, electronic, optoelectronic, and piezoelectric properties. The as-created $ZnC_2O_4 \cdot 2H_2O$ precursors played an important role in the formation of this structure. Further investigations may lead to an extension of this technique to the preparation of assemblies of other materials based on the precursors method.

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