Shape tuning of ZnO with ammonium molybdate and their morphology-dependent photoluminescence properties

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Abstract. In this work, several nano/microscale structures of ZnO including nanospindles, microbundles, microrods, and nanoflowers have been prepared via a facile template and surfactant-free hydrothermal method mediated with ammonium molybdate. It is found that the morphology of ZnO could be readily tailored by simple variation of the concentration of ammonium molybdate. The effects of the concentration of ammonium molybdate and reaction temperature on the synthesis were investigated. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and spectrofluorometer (FL) were used to characterize the products. Results reveal that the photoluminescence (PL) properties of the as-prepared ZnO are strongly dependent on their morphologies.

1. Introduction

As a typical II-VI wide bandgap semiconductor, zinc oxide (ZnO) have been used as transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics due to its larger excitonic binding energy (60 meV) and high mechanic and thermal stabilities[1-3]. It is well known, the properties of nano/microscale materials depend greatly on their shape, size, and crystallinity. In recent years, morphology control of ZnO received intensive attention. Various morphologies of ZnO such as nanorods[4-6], nanotubes[7,8], nanowires[9], porous nanobelts[10], nanosheets[11,12], flowerlike structures[13], and bundles[14-16] have been synthesized successfully. It turns out that the use of organic molecules such as surfactants, polymers, and capping ligands is an effective method to control the size, morphology, and crystal structure of ZnO[15,17-19].

In recent years, the controlled synthesis of nanomaterials by the addition of inorganic species received increasing research and many interesting results were obtained. Various morphologies of Ag nanoparticles have been prepared by Xia and co-workers[20] using inorganic ions as capping agent. Silver nanowires have been synthesized by controlling the amount of NaOH in the reaction without the use of a polymer or a surfactant[21]. Controlled synthesis of copper nanostructures has been prepared in a micelle system in the present of inorganic salts[22]. Crystalline 3C−SiC nanobelts have been synthesized by a lithium-assisted synthesis method[23]. EuF3 with different crystalline phases and morphologies have been prepared by reactions between Eu(NO3)3−6H2O and fluoride sources XF (X = K+, H+, NH4+, Na+, Rb+, and Cs+) under ambient conditions[24]. To the best of our knowledge, the morphology control of ZnO mediated by the addition of inorganic species has been rarely concerned.

In this work, ZnO with different morphologies was obtained by a facile hydrothermal process with the assistance of ammonium molybdate. It turns out that several morphologies of ZnO can be readily obtained by only tuning the ammonium molybdate concentration in the synthesis system. Furthermore, their morphology-dependent photoluminescence properties were investigated. To whom any correspondence should be addressed.
2. Experimental section

2.1. Synthesis. All the reagents were of analytical grade and used without further purification. In a typical synthesis, 1 mmol Zn(NO$_3$)$_2$·6H$_2$O and 0.00166 mmol (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O were dissolved in 32 mL deionized water, then 1 mL diethanolamine (DEA) was introduced into above mixture under stirring and a white colloidal precipitate was obtained. After additional 30 min of stirring, the white colloid was transferred into a 45 mL Teflon-lined autoclave, sealed and heated at 160 °C for 24 h. After being cooled to room temperature naturally, the white precipitates were centrifuged and washed with alcohol and deionized water in sequence, and then dried at 80 °C for 6 h.

2.2. Characterization. The crystalline phase of the as-prepared products were measured on a Philips X’ Pert Pro Super powder X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.541 78 Å). The morphologies and sizes of the samples were obtained using an environmental scanning electron microscope (QUANTA 200). EDS analysis was obtained with an Oxford EDS detector installed on an environmental scanning electron microanalyzer (QUANTA 200). The PL spectra were recorded with a Fluorolog3-TAU-P spectrofluorometer at room temperature.

3. Results and discussion

Figure 1: Typical SEM photos of the products prepared at 160 °C for 24 h with the concentration of ammonium molybdate is 0.005 mol/L.

Figure 2: (a) Typical XRD pattern of the as-synthesized bundle-like ZnO; (b) typical EDS spectrum of the as-synthesized bundle-like ZnO.

Figure 1 shows the typical SEM images of as-obtained product prepared at 160 °C for 24 h when the concentration of ammonium molybdate is 0.005 mol/L. Low-magnification SEM image of as-prepared product is shown in the figure 1a, which clearly reveals that the as-synthesized ZnO with average length of ca. 60 µm is obtained in large scale. From the enlarged image shown in figure 1b, it is
interesting that an individual bundle-like structure is composed of many hexagonal microwires with a diameter of about 800-1000 nm and length of around 30 µm, and the microwires align in a radial way from a center. Furthermore, every microwire is with a sharp top and has a hexagonal cross section, which is different from the previously reported ZnO bundle-like structures [14-16].

The crystal phase and chemical composition of the as-prepared product were determined by XRD and EDS. A typical XRD pattern of the as-obtained bundle-like ZnO is shown in figure 2a. The position of all diffraction peaks for the as-prepared products can be indexed to pure hexagonal wurzite ZnO structure, which agrees well with the standards JCPDS file (No.36-1451). No additional peaks have been found in the XRD pattern, indicating high purity of the sample. It is worth noting that compared to the standard file of hexagonal wurzite ZnO, the relative intensity of (100) is much stronger that of (002), which may be attributed to the preferential growth of the microwires. The composition of the ZnO bundles was further confirmed by EDS. Figure 2b shows the corresponding EDS spectrum of the as-synthesized bundle-like ZnO. From it can be seen, no other elements other than Zn and O are found, and the Zn: O molar ratio is around 1.09:1, which agrees well with the theoretical composition of ZnO. It also reveals that the molybdate anions can be completely eliminated away from the product after washing with deionized water and ethanol.

![Figure 3](image)

**Figure 3:** SEM images of the as-synthesized ZnO prepared at different concentration of ammonium molybdate. (a) 0 mol/L; (b) 0.0025 mol/L; (c) 0.01mol/L. All the sample were hydrothermally treated at 160 °C for 24 h.

![Figure 4](image)

**Figure 4:** SEM images of ZnO prepared at different temperature for 24 h when the concentration of ammonium molybdate is 0.005 mol/L. (a) 100 °C; (b) 120 °C; (c) 180 °C.

To investigate the effect of the addition of ammonium molybdate on the morphology of the products, experiments were carried out at different concentration of ammonium molybdate with other experimental conditions unchanged. In the absence of ammonium molybdate, ZnO nanospindles with average diameter about 150 nm and length around 400 nm were obtained in large scale (figure 3a). Figure 3b show the SEM image of as-prepared ZnO when the concentration of ammonium molybdate is 0.0025 mol/L, which clearly exhibits that the as-prepared ZnO is microwires with lengths of ca. 15
µm and diameters of around 600-700 nm. Increasing the concentration of ammonium molybdate to 0.01 mol/L, flower-like ZnO is formed (figure 3c). The ZnO flowers are in the diameter of ca. 20 µm. And the flowers are constructed by a large quantity of nanopetals with a thickness about 70-100 nm. Based on above results, it is clear that the concentration of ammonium molybdate has great effect on the morphology of the final products. With the increasing of concentration ammonium molybdate, the final morphologies of ZnO transform from nanospindle to nanoflower. However, the exact role of ammonium molybdate plays on the synthesis is still not clear, further work is needed.

It was found that the morphology of the as-prepared ZnO was dependent on the reaction temperature. Temperature-dependent experiments were carried out when the concentration of ammonium molybdate was 0.005 mol/L, as shown in figure 4. ZnO hexagonal plates are obtained when the reaction temperature is 100 °C (figure 4a). The individual hexagonal plate is in the size varying from 1 µm to 2.5 µm. Bundle-like ZnO architectures also can be obtained at 120 °C and 180 °C. A detail morphological observation of bundle-like ZnO architectures obtained at 120 °C is shown in figure 4b, which clearly reveals the ZnO bundles is majorly composed of microbelts with a width of ca. 1 µm. Increasing the reaction temperature to 180 °C, bundles still can be obtained, as shown in figure 4c. However, the microwires are not as the microwires prepared at 120 °C, and some nanobelts are found in the product.

On the basis of above results, a possible for the formation mechanism for the crystal growth of ZnO was proposed. The possible involved reaction during the synthesis is as below:

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\begin{align*}
HN (CH_2CH_2OH)_2 + H_2O & \rightarrow H_2N (CH_2CH_2OH)_2^+ + OH^- \quad (1) \\
Zn^{2+} + 2 OH^- & \rightarrow Zn(OH)_2 \quad (2) \\
Zn(OH)^{2+} + 2OH^- & \rightarrow Zn(OH)_4^{2-} \quad (3) \\
Zn(OH)_4^{2-} & \rightarrow ZnO + 2OH^- + H_2O \quad (4)
\end{align*}
\]

Firstly, with the addition of DEA into the reaction system, it hydrolyze to produce OH⁻, and the Zn²⁺ reacts with OH⁻ to form white Zn(OH)_2 colloid precipitate. With the prolonging of reaction time, more DEA hydrolyze and provide more OH⁻. Secondly, the newly formed Zn(OH)_2 colloids gradually dissolves to form Zn(OH)_4^{2-}. Thirdly, the ZnO seeds are formed through reaction (4) [25]. Pileni et al. find anions Cl⁻ and Br⁻ in the added salts can control the morphology of the products by selectively adsorbing on the different crystal faces of copper particles [22]. Wang et al have suggested the action of different cations absorbed on the EuF₃ crystal faces of the initial particles is probably different on the morphology of EuF₃ [24]. So the adsorption of molybdate on the surface of ZnO seeds also affects the crystal growth of ZnO. With different concentration of the ammonium molybdate, the selective adsorption of molybdate on certain crystallographic planes results in the morphology variations.

The photoluminescence properties of the four samples with different morphologies prepared at different concentration of ammonium molybdate were investigated, as shown in figure 5. From it can
be seen, the ZnO nanospindles, microbundles, microwires, and nanoflowers exhibit the typical characteristic peaks of ZnO under 325 nm excitation [17, 28]. There are two emission peaks in the spectrum: one is in the ultraviolet region; the other is in the visible region. The emission in the ultraviolet comes from the recombination of free excitons of ZnO [26, 27], while the visible emission is attributed to the presence of singly ionized oxygen vacancies [28]. The emission in the ultraviolet region for the ZnO nanospindles, microbundles, microwires and nanoflowers is centered at 375 nm, 385 nm, 387 nm and 379 nm, respectively. And the visible emission for the ZnO nanospindles, microbundles, microwires and nanoflowers is centered at 507 nm, 563 nm, 562 nm and 507 nm, respectively. From it can be seen, obvious shift was realized in these products, especially at in the visible emission region. And the emission intensity of the four samples increases in the order of nanospindles, microbundles, microwires, and nanoflowers. It is also found that the emission intensity for the ZnO nanospindles, microbundles, and microrods in the visible region is stronger than that of the ultraviolet region. However, for the ZnO nanoflowers, the emission intensity in the ultraviolet region is much stronger than that of the visible region. From above it can be drawn a conclusion that the photoluminescence properties of the as-prepared ZnO depend greatly on their morphologies.

4. Conclusion

In summary, a variety of morphologies of ZnO have been prepared though a facile hydrothermal method in the presence of ammonium molybdate. It turns out that the addition of ammonium molybdate has great effects on the final morphologies of the products. The photoluminescence properties of the as-prepared ZnO are strongly dependent on their morphologies.

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