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# Synthesis and photoluminescence properties of single-crystal ZnO hexagonal pyramids by PEG400-assisted thermal decomposition route

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Abstract: Large-scale synthesis of ZnO hexagonal pyramids was achieved by a simple thermal decomposition route of precursor at 240  $^{\circ}$ C in the presence of PEG400. The precursor was obtained by room-temperature solid-state grinding reaction between Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub>. Crystal structure and morphology of the products were analyzed and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The results of further experiments show that PEG400 has an important role in the formation of ZnO hexagonal pyramids. Difference between the single and double hexagonal pyramid structure may come from the special thermal decomposition reaction. The photoluminescence (PL) spectra of ZnO hexagonal pyramids exhibit strong near-band-edge emission at about 386 nm and weak green emission at about 550 nm. The Raman-active vibration at about 435 cm<sup>-1</sup> suggests that the ZnO hexagonal pyramids have high crystallinity.

Key words: ZnO hexagonal pyramids; thermal decomposition route; formation mechanism; photoluminescence property

# **1** Introduction

As known, the shape and size of nanomaterials tremendously affect their physical and chemical properties. Zinc oxide is an important wide-band-gap semiconductor, and has a variety of applications including varistors, transparent conductors, transparent UV-protection films and chemical sensors [1,2]. To date, well-defined ZnO with different morphologies have been successfully synthesized by various methods [3–8]. However, it seems that either complex process control or long synthesis time might be required for these routes.

Solid-state synthesis is an effective approach to obtain nanoparticles, and it exhibits many advantages such as solvent-free, simplicity and low cost, which has been extensively used in the synthesis of many nanomaterials [9]. To obtain other nanomaterials with different morphologies, surfactant-assisting or microwave-assisting solid-state method has been developed [10–12], which extends its application in the field of synthesizing nanomaterials. ZnO hexagonal pyramids are special structures with different shapes and exposed surfaces, and it is not reported to synthesize through solid state thermal decomposition reactions.

In this work, a novel synthetic method of hexagonal pyramid ZnO nanostructures was developed and the surfactant was introduced into solid-state thermal decomposition route. Hexagonal pyramid ZnO was synthesized by simple thermal decomposition route at about 240 °C in the presence of PEG400. The synthesized products were single-crystalline ZnO

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hexagonal pyramid. The effect of various factors on the products was studied, and the photoluminescence properties of the products were investigated.

## 2 Experimental

All the chemical reagents used in the experiment were of analytical grade. The detailed synthetic process was as follows. In a typical synthesis, 0.005 mol hydrated zinc acetate  $[Zn(CH_3COO)_2 \cdot 2H_2O]$  was ground for 5 min before mixing with 2.0 mL polyethylene glycol (PEG400). Afterward, 0.005 mol sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) was added to the mixture. After 20 min of grinding, the mixture was washed with distilled water to remove any by-product, and then filtrated. It was transferred to a 100 mL Teflon container with 40 mL PEG400. The mixture was then heated at 240 °C for 1 h. The product was washed and dried in air.

The X-ray diffraction (XRD) analysis was carried out on a Bruker D8-Advance X-ray diffractometer with Cu K<sub>a</sub> radiation. The transmission electron microscopy (TEM) images were taken using an FEI Tecnai-20 transmission electron microscope. The scanning electron microscopy (SEM) images were taken with an LEO1530VP field emission scanning electron microscope. The Raman spectra were recorded on an HR-800 spectrometer. The photoluminescence (PL) spectra were recorded on a Varian Cary-Eclipse spectrometer.

### **3** Results and discussion

#### 3.1 XRD pattern analysis

The crystallinity and phases of the product were confirmed by X-ray diffraction. Figure 1 shows the XRD pattern of the final product obtained by the thermal decomposition route at 240 °C for 1 h in the presence of PEG400. In contrast to the standard diffraction peaks (JCPDS card No. 36–1451, a=0.3249 nm, c=0.5206 nm), the pronounced ZnO peaks for (100), (002), (101), (102),



Fig. 1 XRD pattern of ZnO nanostructure

(110), (103), (200), (112), (201), (004) and (202) appear at  $2\theta$ =31.8, 34.5, 36.3, 47.6, 56.6, 62.9, 66.3, 68.0, 69.2, 72.5 and 76.9°, respectively. These results indicate that the ZnO obtained has a hexagonal wurtzite structure with high crystallinity. In addition, it can be seen that only ZnO diffraction peaks are found, and the characteristic peaks of other impurities such as Zn(OH)<sub>2</sub> are not observed in the figure.

#### 3.2 SEM and TEM analysis

The typical SEM images of as-obtained wurtzite ZnO nanostructure are shown in Fig. 2, as well as the TEM images and SAED pattern for detail illustration. Figure 2(a) is a low-magnification SEM image that shows the high yield of the hexagonal pyramid ZnO. The product consists of different morphologies with single and double hexagonal pyramids. The high-magnification SEM image (Fig. 2(b)) shows the hexagonal bottom and pyramid-like surface of the ZnO. The bottom has a hexagonal structure and the side length is about 500 nm. Figures 2(c) and (e) present the typical TEM images of the ZnO nanostructure. The product has a hexagonal pyramid shape which is in good agreement with the SEM results. The electron diffraction patterns shown in Figs. 2(d) and (f) indicate that the product has a singlecrystal structure.

High-resolution TEM (HRTEM) could provide the structural details of the products. Figure 3 reveals the HRTEM image of the ZnO nanostructure. An interplanar spacing of the crystalline stripes is about 0.261 nm, corresponding to the separation between the (002) planes of ZnO. It indicates that the growing plane and the growing direction of the ZnO are along the (002) plane and the [002] direction, respectively.

#### 3.3 Further experiments and analysis

To explore the formation mechanism of the ZnO hexagonal pyramid, further experiments were designed and more information was obtained. Figure 4(a) shows the XRD pattern of the precursor. Based on the comparison with the JCPDS cards, the diffraction peaks of the precursor are consistent with  $Zn_4CO_3(OH)_6$ ·H<sub>2</sub>O. The product obtained is not ZnO but Zn<sub>4</sub>CO<sub>3</sub>(OH)<sub>6</sub>·H<sub>2</sub>O when the reaction temperature is 200 °C in the presence of PEG400 (Fig. 4(b)). This shows that the precursor does not decompose to ZnO at 200 °C. Only ZnO nanoparticles are required by heating the precursor at 240 °C in the absence of PEG400 (Fig. 4(c)). The broadness of the diffraction peaks indicates that the dimensions of the ZnO nanoparticles are very small. The hexagonal pyramid ZnO products can be obtained at 240 °C in the presence of PEG400 for different durations, namely, 0.5, 2 and 4 h, respectively (Figs. 4(d)-(f)).



Fig. 2 SEM images (a, b), TEM images (c, e) and corresponding SAED patterns(d, f) of ZnO nanostructure



Fig. 3 HRTEM image of ZnO nanostructure



**Fig. 4** XRD patterns of precursor (a), products obtained at 200 °C in the presence of PEG400 (b), at 240 °C in the absence of PEG400 (c), at 240 °C in presence of PEG400 for 0.5 h (d), 2 h (e) and 4 h (f)

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The SEM image of the product obtained at 240 °C without PEG400 for 4 h (Fig. 5(a)) shows that the typical morphology of the products consists of small spheres. The SEM images of the ZnO products (Figs. 5(b)–(d)) obtained by heating for 0.5, 2 and 4 h in the presence of PEG400 show hexagonal pyramid ZnO nanostructures instead of spherical particles typical of the common thermal decomposition reaction [13].

#### 3.4 Growth mechanism

Based on the above experiments, a possible growth

mechanism was proposed. Two steps in the formation process of ZnO hexagonal pyramid nanostructure were employed, as shown in Fig. 6. First, the solid-state reaction between  $Zn(CH_3COO)_2 \cdot 2H_2O$  and  $Na_2CO_3$  can occur in the process of grinding, and then the precursor nanoparticles  $(Zn_4CO_3(OH)_6 \cdot H_2O)$  form. PEG400 is a uniform and ordered chain structure and it is easily adsorbed on the surface of reactant, and it will modify the growth kinetics of the growing colloids, which finally leads to anisotropic growth of the crystals. When the precursor is combined with PEG400, the surface of the



Fig. 5 SEM images of products obtained at 240 °C without PEG400 for 4 h (a), in the presence of PEG400 heated for 0.5 h (b), 2 h (c) and 4 h (d)



Fig. 6 Schematic illustration of formation mechanism of ZnO hexagonal pyramid

precursor colloid adsorbs PEG400, which greatly decreases the activities of the colloid [14]. This confines the growth rate to some directions [15]. Therefore, in the presence of PEG400, the precursor is decomposed and ZnO hexagonal pyramids form. Difference between the single and double hexagonal pyramids may come from the special thermal decomposition reaction in the presence of PEG400. When the suitable lattice plane between the particles is close enough to each other [16], the simultaneous growth starts during thermal decomposition, which is responsible for the formation of the double hexagonal pyramid.

#### 3.5 PL spectra analysis

The corresponding PL spectra of the products are shown in Fig. 7(a). All the spectra have a relatively sharp ultraviolet emission centered at about 386 nm. The strong near-band-edge emission at 386 nm is similar to the ZnO bulk band gap at 380 nm which originates from the recombination of free excitons [17,18]. The weak green emission band at about 550 nm is attributed to a singly charged oxygen vacancy, which results from the recombination of a photo-generated hole with a charge state of the specific defect, or from the surface deep traps [19,20]. The results illustrate that ZnO hexagonal pyramids possess high crystallinity and few oxygen



Fig. 7 PL (a) and Raman spectra (b) of product obtained at 240  $^\circ$ C for 1 h in the presence of PEG400

vacancies. The PL emission intensities of the products increase with increasing reaction time at 240 °C, which suggests that the optical property of the products could be tuned by the reaction parameter. LI et al [15] reported the similar results of PL emission coming from different morphologies of ZnO. To further understand the crystalline structure, the product obtained at 240 °C heated for 1 h in the presence of PEG400 was characterized by Raman spectroscopy (Fig. 6(b)). The Raman-active vibration of the product was detected at about 435 cm<sup>-1</sup>, which is characteristic of the high-frequency E2 mode of the wurtzite structure [21]. The strong E2 peak centered at about 435 cm<sup>-1</sup> suggests that the ZnO nanostructures are of good crystalline, which is consistent with the PL observation.

#### **4** Conclusions

1) A simple PEG400-assisted thermal decomposition route of the precursor to synthesize ZnO hexagonal pyramids is successfully developed. The precursor  $Zn_4CO_3(OH)_6 \cdot H_2O$  nanoparticle is obtained by room-temperature solid-state grinding reaction between  $Zn(CH_3COO)_2 \cdot 2H_2O$  and  $Na_2CO_3$ .

2) The results of XRD, SEM, TEM, SAED and HRTEM characterizations indicate that the product is hexagonal wurtzite ZnO with hexagonal pyramid morphology.

3) Further experiments show that PEG400 has an important role in the formation of ZnO hexagonal pyramids. Difference between the single and double hexagonal pyramids comes from the special thermal decomposition reaction.

4) The PL spectra exhibit strong near-band-edge emission at about 386 nm and weak green emission at about 550 nm, and their intensities could be tuned by the reaction time. The Raman-active vibration at about 435 cm<sup>-1</sup> suggests that the ZnO hexagonal pyramid has high crystallinity.

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# 单晶 ZnO 六棱锥的 PEG400 辅助热分解合成及其 光致发光性能

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摘 要:将由Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O和Na<sub>2</sub>CO<sub>3</sub>通过室温研磨反应获得的前驱体在PEG400存在下于240°C热分解 获得大量的ZnO六棱锥产物。用X射线衍射仪(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和高分辨 透射电子显微镜(HRTEM)表征产物的晶体结构和形貌。进一步的实验结果表明:PEG400在ZnO六棱锥形成过程 中发挥着重要作用,单六棱锥和双六棱锥的结构差异来自于热分解反应。光致发光谱(PL)测试表明:ZnO六棱锥 在386 nm处展示强的近带隙发射,在550 nm处展示较弱的绿光发射。435 cm<sup>-1</sup>处的拉曼振动表明ZnO六棱锥具 有良好的晶体质量。

关键词: ZnO 六棱锥; 热分解路线; 形成机理; 光致发光性能

(Edited by FANG Jing-hua)