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ZnO microrods with etched surface prepared by two-step hydrothermal reaction

Ying Hou · Ming Yang · Guangsheng Pang · Shouhua Feng

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Abstract In this work, ZnO microrods with etched surface are prepared by two-step hydrothermal reaction. ZnO microrods are prepared firstly by decomposing LHS-Zn under hydrothermal conditions. It is found that the (0001)-Zn face of ZnO microrods will dissolve partly due to the existence of LHS-Zn during further hydrothermal treatment, and ZnO microrods with etched surface are obtained. X-ray powder diffraction is used to determine the crystal structure, and scanning electron microscopy is used to observe the morphology of products. The photoluminescence spectra are investigated.

Introduction

ZnO is an exceptionally important material and has been used considerably for its catalytic [1], electrical [2], optoelectronic [3–8] and photochemical properties [9]. ZnO exhibits a hexagonal structure with a direct band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. The strong exciton binding energy, which is much larger than the thermal energy at room temperature (ca. 25 meV) can ensure an efficient exciton emission at room temperature under low excitation energy. Therefore, ZnO is recognized as a promising photonic material in the blue-UV region [10].

During the past few years, much effort has been invested in controlling the sizes and shapes of inorganic nanocrystals, because these parameters represent key elements that determine their electrical and optical properties [11, 12]. Among various nanocrystals, ZnO nanostructures have been of great interest due to numerous morphologies, including ZnO films, disordered nanoparticles [13], nanobelts [14], nanotubes [15], nanowires [16], and so on. Some interesting ZnO nanostructures such as helical ZnO columns [17], rotor-like ZnO [18], nanohelixs [19], nanorings [20], nanonails [21] and tetrapods [22] are also prepared. In this work, two-step hydrothermal reaction is used to prepare surface etched ZnO microrods and the optical properties are investigated.

Experimental

Preparation of LHS-Zn [$Zn_5(OH)_8(CH_3COO)_2H_2O$]

LHS-Zn was prepared according to the method described in [23]. A typical method is described as follows: 250 mL zinc acetate ethanol solution (0.025 mol L^{-1}) was prepared by dissolving 5.49 g zinc acetate dehydrate in ethanol at 80 °C. After cooling the above solution to room temperature, 110 mL distilled water was added and white precipitates appeared immediately. The as-prepared precipitates were filtered and washed with distilled water, and then dried at room temperature.

Preparation of ZnO microrods

ZnO microrods were prepared as follows: LHS-Zn (0.1 g) was dispersed in 50 mL distilled water under sonication and then was transferred into an 80-mL Teflon-lined stainless steel autoclave and sealed tightly. Thermal

Y. Hou · M. Yang · G. Pang (✉) · S. Feng (✉)
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China
e-mail: panggs@jlu.edu.cn

treatments were carried out at 160 °C for 2 days. Then the autoclave was allowed to cool to room temperature. A white precipitate was collected, washed with distilled water and ethanol several times, and dried at 50 °C for 6 h.

Surface etching

The surface etched ZnO microrods were prepared by further hydrothermal treatment of ZnO microrods in the presence of LHS-Zn. A typical procedure is described as follows: ZnO microrods (0.08 g) were first dispersed in 50 mL distilled water and then LHS-Zn (0.0122 g) was added and dispersed. The obtained suspension was transferred into an 80-mL Teflon-lined stainless steel autoclave and sealed tightly. Thermal treatments were carried out at 160 °C for 1 day. After the autoclave was cooled to room temperature, the white precipitate was collected and washed with distilled water and ethanol several times. The products were dried at room temperature.

Characterization

The products were characterized by X-ray powder diffraction (XRD) on a Siemens D5005 diffractometer with graphite-filtered Cu Kα radiation. The morphologies of the products were observed by scanning electron microscopy (SEM) (JSM-6700F). The photoluminescence (PL) spectra measurements were performed at room temperature using a He–Cd laser with an excitation wavelength of 325 nm.

Results and discussions

The surface etched ZnO microrods are structurally characterized by XRD (Fig. 1) which indicate a Wurtzite-type structure (hexagonal phase, space group $P6_3mc$) with high crystallinity. All diffraction peaks are well indexed to hexagonal phase ZnO (JCPDC card No. 36-1451).

Figure 2 shows SEM image of products obtained by hydrothermal treatment of LHS-Zn. ZnO microrods with a small aspect ratio are obtained. The diameter of ZnO microrods ranges from ca. 1 to 2 μm. The length of ZnO microrods ranges from ca. 3 to 5 μm. The ZnO microrods exhibit a hexagonal characteristic. Vayssieres et al. reported that the aligned zinc oxide micro-size rod arrays can be prepared on conducting tin oxide glass by hydrothermal procedure at 95 °C using aqueous solution containing methenamine and zinc nitrate [24]. Such hexagonal-shaped micro-size rods can be further dissolved and arrays of ZnO microtubes will form [25]. Vayssieres et al. attribute this transformation drive to the thermodynamic unstable crystal

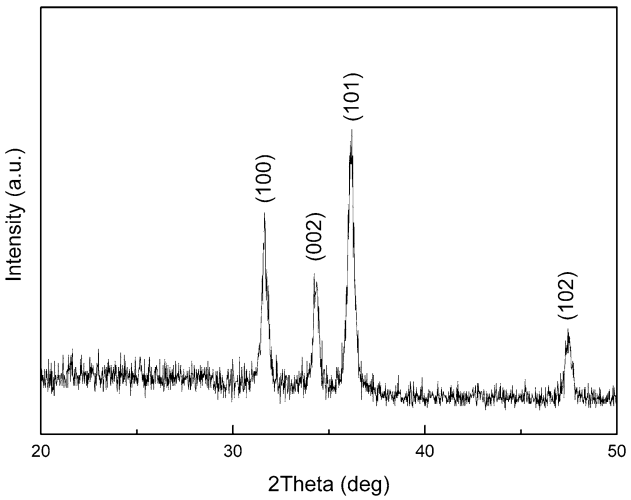

Fig. 1 X-ray powder diffraction (XRD) pattern of surface etched ZnO microrods

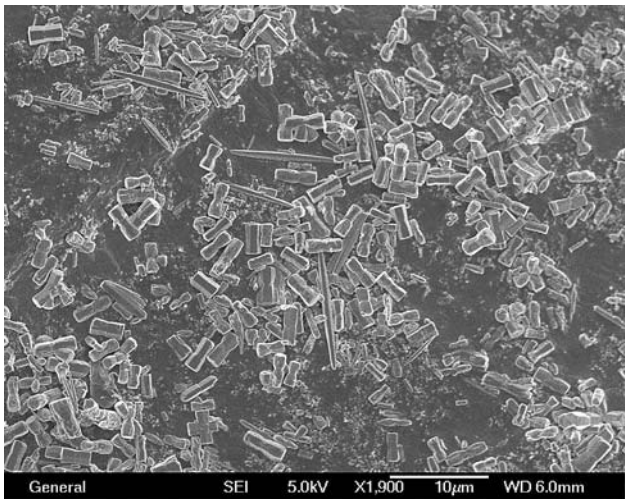

Fig. 2 Scanning electron microscopy (SEM) image of ZnO microrods

faces in ZnO anisotropic crystallites. Such dissolution phenomena can provide a good opportunity for morphology control.

Figure 3 shows SEM images of surface etched ZnO microrods. We could see clearly that ZnO microrods hold their hexagonal characteristic after the hydrothermal treatment, whereas, the ends have been dissolved partly (Fig. 3a). The thickness of the sunken prisms' wall is uniformly ca. 30 nm as shown in Fig. 3b. The bare planes have been interspersed with nano-scale ZnO crystals. The size of ZnO nanocrystals is in the range from 30 to 80 nm. To investigate the formation process of surface etched ZnO microrods, we examine the morphology of products obtained at initial reaction stage. Figure 4 shows the SEM images of typical morphology of products obtained after

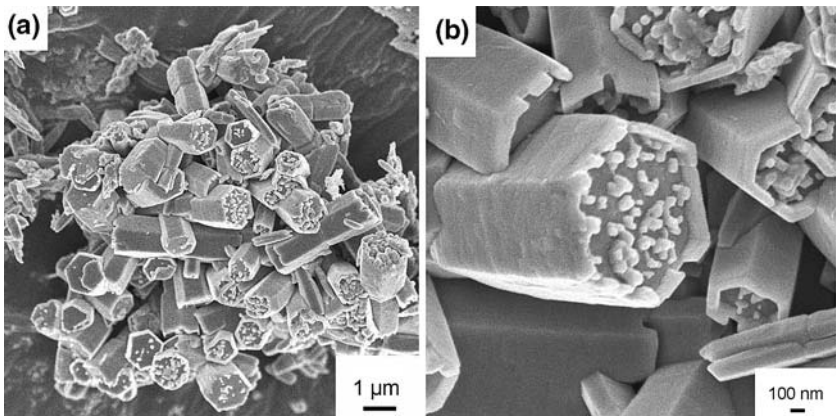

Fig. 3 Scanning electron microscopy (SEM) image of surface etched ZnO microrods (**a**) with low- and (**b**) high-magnification

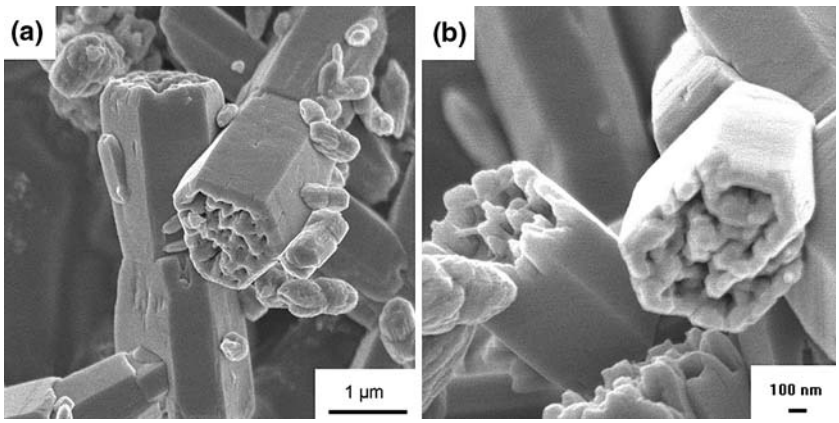

Fig. 4 Typical scanning electron microscopy (SEM) images of products obtained after 2 h reaction

2 h reaction. Some ZnO microrods with partly etched ends can be observed as shown in Fig. 4a and b. The dissolution of the center of hexagonal ends is responsible for the formation of such unique morphology. Compared with the basic environment [25], our conditions are rather "soft". Higher reaction temperature may promote such dissolution process, which can achieve partly dissolved, bare and hexagonal crystal faces. During the hydrothermal process, hydroxyl and acetate ions of LHS-Zn have tendency to adsorb on the (0001)-Zn face of ZnO microrods which resulting in the dissolution of (0001)-Zn face. The hydroxyl and acetate ions are not enough to dissolve totally (0001)-Zn face under hydrothermal conditions and the bare (0001)-Zn face covered with residual ZnO nanocrystals can be formed. Such unique morphologies cannot be obtained if further hydrothermal treatment process is not applied.

The optical properties of ZnO microrods and surface etched ZnO microrods are investigated. The PL spectra are shown in Fig. 5. The narrow UV peak before 400 nm (ca. 399 nm for ZnO microrods and ca. 393 nm for surface etched ZnO microrods, respectively) came from the recombination of excitation centers in the ZnO crystal [26]. The slight blue-shift of UV peak after surface etching may be related to the presence of small ZnO particles. The

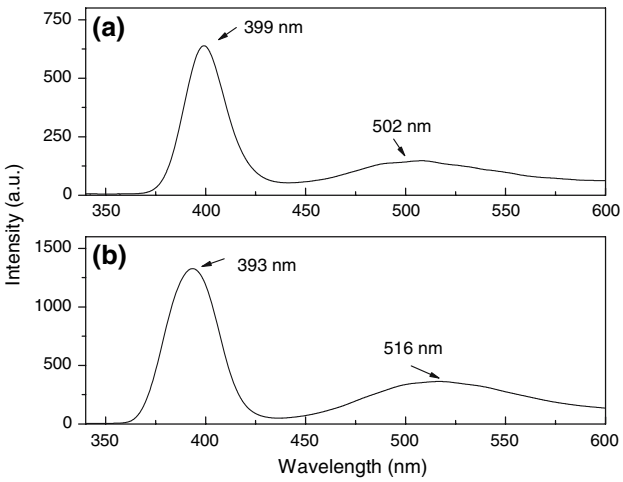

Fig. 5 Photoluminescence (PL) spectra of (**a**) ZnO microrods and (**b**) surface etched ZnO microrods

broad visible emission peak (ca. 502 nm for ZnO microrods and ca. 516 nm for surface etched ZnO microrods, respectively) was generally attributed to the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes [26].

Conclusion

Surface etched ZnO microrods are prepared by two-step hydrothermal reaction. ZnO microrods are added during the decomposition of LHS-Zn under hydrothermal conditions. The (0001)-Zn face of ZnO microrods are dissolved partly and some nano-scale ZnO crystals disperse on the bare (0001)-Zn face. The optical properties are investigated primarily. The unique morphology obtained in our system may find some applications in nanodevices.

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