Fabrication of ZnO Microtubes by Using Electrospun Polymer Fiber Templates

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ZnO microtubes were prepared by an electrospun polymer fiber template method. The product was well-crystallized hexagonal ZnO with high purity and had a tubular structure with length above 15 μm, diameter of ≈ 1.0 μm and wall thickness of ≈ 120 nm. A weak UV emission at ≈ 394 nm and strong green emission at ≈ 545 nm were detected.

Zinc oxide (ZnO) is a very important semiconducting metal oxide material with a wide band gap of 3.37 eV and large excitation binding energy of 60 meV and has received great interest in field-emission displays, optical electric devices, solar cells, gas sensors, and catalysts.[1–3]

Since the first report of ultraviolet lasing from ZnO nanorods,[4] substantial efforts have been devoted to fabricating ZnO nanomaterials with 1D structure. Many approaches, including low-temperature solution routes,[5] thermal evaporation methods,[6] gas-phase methods,[1] thermal reduction and oxidation of ZnS,[7] and biotemplate methods[8] have been developed to produce different kinds of 1D ZnO entities. Among them, template method is one of the most commonly used approaches to fabricate inorganic micro- and nanotubes because of the simple and easy procedure.[9] Recently, electrospun polymer fibers have been proven to be a promising template to fabricate 1D micro- and nanomaterials because of some advantages, such as high fidelity, low-cost, and easy control of the tube size.[10] Up to now, some metal and metal oxide micro- and nanotubes have been made through electrospun polymer fiber template method.[10] However, to our knowledge, electrospun polymer fibers have not been used as templates for producing ZnO tubes yet. In this communication, ZnO microtubes were prepared by using electrospun polyacrylonitrile (PAN) fibers as templates. The obtained ZnO microtubes show high promise in field-emission displays, solar cells, gas sensors, and catalysts.

Details of the fabrication of ZnO microtubes are as follows: Polyacrylonitrile (PAN, Mw 150000) was dissolved in dimethylformamide (DMF) solvent at a concentration of 14 wt %. The electrospinning process was carried out at 20 kV, and an aluminum foil was used as the collector. The electrospun PAN fibers were pretreated at 250 °C for 2 h in air for stabilization. Thereafter, 500 mg of treated PAN fibers was impregnated with 5 mL of aqueous $Zn(NO_3)_2$ solution at a concentration of 3.0 wt % and then 5 mL of 0.1 M ammonia solution, After air-drying for about 12 h, the sample was heated from room temperature to 650 °C at a heating rate of 0.5 K/min and maintained at 650 °C for 2 h in air and finally cooled down to room temperature. The morphology of the sample was characterized by scanning electron microscopy (SEM, HITACHI S-4700). X-ray diffraction (XRD) pattern of the sample was recorded with a Rigaku D/Max 2500 PC diffractometer equipped with a source of Cu Kα radiation ($\lambda = 1.54178$ Å) at a step width of 0.02°.

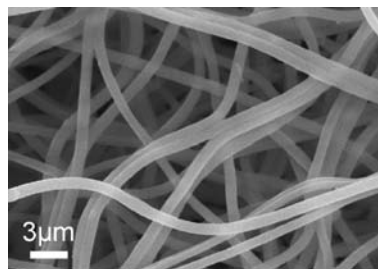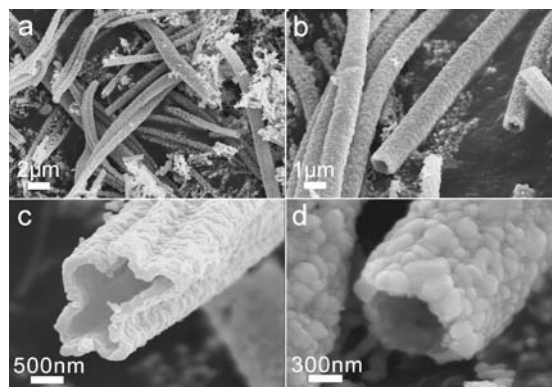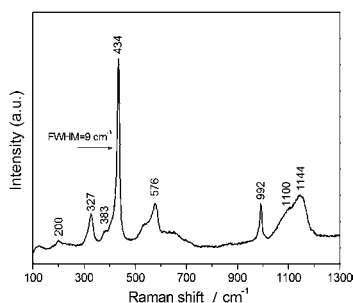**Figure 1.** SEM image of the PAN fibers.

Figure 2. SEM images of the ZnO microtubes at different magnifications.

Raman spectrum was examined using an argon ion laser with $\lambda = 514.5$ nm, and photoluminescence (PL) spectrum was measured using a He-Cd laser with $\lambda = 325$ nm (KIMMON, IK3301R-G) as the excitation source at room temperature.

Figure 1 shows the SEM image of the PAN fibers used as the templates. The PAN fibers are very smooth in surface and uniform in diameter, which was measured to be about 1.0 μm on the average. Figure 2 shows the SEM images of the product with orderly increased magnification. Clearly, the product shows fibrous and hollow structure. Most of the ZnO tubes are longer than 15 μm, and they have an average outer diameter of about 1.0 μm. The SEM images with high magnification show that the average wall thickness of the ZnO microtubes is about 120 nm and that the tube walls are composed of many particles bigger than 100 nm (Figures 2c and 2d). The average inner diameter of the ZnO microtubes is about 760 nm. In the present work, the outer diameter of the ZnO tubes is close to that of the template fibers while the inner diameter is smaller than that of the template fibers because both the template polymer fibers and the encapsulating precursor layers shrank during heat treatment.[11] Additionally, although most of the ZnO microtubes have circular cross sections (Figures 2b and 2d), small quantities of the cross sections are petal-like (Figure 2c), possibly resulting
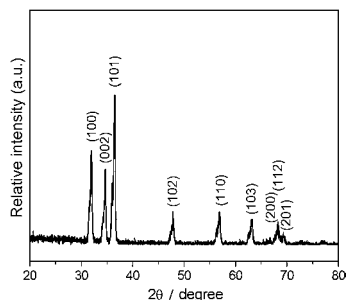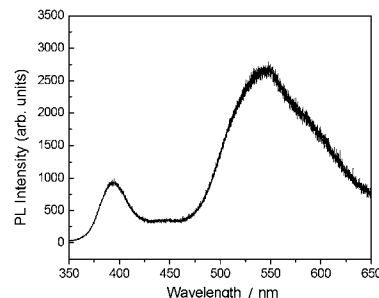
Figure 3. XRD pattern of the ZnO microtubes.

Figure 4. Raman spectrum of the ZnO microtubes.

Figure 5. Photoluminescence spectrum of the ZnO microtubes.

cies.[16] Generally, the PL spectrum is strongly dependent on the crystallinity and defect density of materials. Considering the large size of the ZnO crystals composing the microtubes, the present PL spectrum should be mainly determined by the crystallinity and lattice perfection rather than size effect. The green emission dominates over the near band-edge emission, indicating a high concentration of oxygen vacancies in the ZnO microtubes, which is basically consistent with the above Raman result. The strong green emission in the ZnO microtubes will attract great attention for typical applications of ZnO phosphors, such as field emissive display technology, etc.

from the deformation of the encapsulating layers when removing the templates during heat treatment.

Figure 3 presents the XRD pattern of the ZnO product. The peak positions exhibit good agreement with those of the hexagonal ZnO with lattice constants $a = 0.3250$ nm and $c = 0.5207$ nm.[12]

Optical properties of the ZnO microtubes were characterized by Raman and photoluminescence (PL) spectrum. Figure 4 shows the Raman spectrum of the ZnO microtubes ranging from 100 to 1300 cm^{-1}. Among the Raman peaks of the ZnO microtubes (Figure 4), the E$_2$(high) mode at 434 cm^{-1} has the strongest intensity and a full width at half maximum (FWHM) of about 9 cm^{-1}, suggesting that the ZnO microtubes have hexagonal wurtzite structure and good crystallinity.[13] The blue shift about 5 cm^{-1} of the E$_2$(high) mode originates from the intrinsic defects in the ZnO crystallites. The two peaks at 383 and 576 cm^{-1} are observed corresponding to A$_1$(TO) and A$_1$(LO) phonon modes, respectively, further indicating that there are some defects of O vacancy and/or Zn interstitial in the ZnO crystallites.[14] The peaks located at 200, 327, and 1050–1200 cm^{-1} belong to the second-order vibrations arising from zone boundary phonons.[14] Additionally, the peak at 992 cm^{-1} is the vibration modes due to multiple-phonon scattering.[13]

Figure 5 provides the room-temperature photoluminescence (PL) spectrum of the ZnO microtubes. The PL spectrum exhibits two broad peaks. One is a weak ultraviolet (UV) emission centered at about 394 nm, and the other is a broader and stronger green band centered at about 545 nm. The UV emission could be assigned to the near band-edge emission of the intrinsic wide band gap of ZnO.[15] The green emission is also called defect-related peak, mainly originated from the oxygen vacan-

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