Sonochemical synthesis of ZnO nanotubes and their optical emissions

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Hexagonal zinc oxide (ZnO) nanotubes were synthesized from 0.05 M zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) by a sonochemical method under ambient conditions. White precipitates, obtained after ultrasonic irradiation for 60 min, were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectroscopy (PL). The ZnO crystals had a tubular structure ~ 500 nm in length with a hexagonal cross section for both the inner and outer walls. The room temperature PL spectrum of ZnO nanotubes exhibited an ultraviolet (UV) emission peak, a sharp violet peak and a further broad visible band centered at 650 nm.

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Micro- and nano-scale tubular structures have attracted extensive interest due to their unique hollow morphology with space confined transport properties, large surface area and potential applications in nanotechnology. Since the discovery of carbon nanotubes,¹⁾ such structures have been fabricated using many different compounds including zinc oxide (ZnO). ZnO microtubes with well faceted surfaces have been successfully synthesized by chemical solution techniques,²⁾ thermal evaporation,³⁾ hydrothermal methods,⁴⁾ and direct microwave heating.⁵⁾

With the rapid development in ultrasonic sonochemistry, a variety of chemical reactions can acquire energy from the process of acoustic cavitations driven by ultrasound waves involving the formation, growth and implosive collapse of bubbles in the liquid.⁶⁾ The process is generally simple and requires low-cost setups with moderate energy demand. The sonochemical method is therefore a real alternative for producing ZnO of varying morphologies. Ultrasound pretreatments prior to solution synthesis and an ultrasonically assisted 2-step polyol process have previously been shown to enable the formation of ZnO tubes.^{2,7)} In this work, ZnO hexagonal nanotubes were prepared by a sonochemical method. Their morphological and optical properties were then examined.

Reagent grade zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) powders ($\geq 99.0\%$ in purity) were used as starting materials without any pretreatment. The solution, 0.05 M in $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ in 50 ml deionized water, was prepared and stirred for 10 min with heating up to 50°C until a stable viscous white colloid formed. The colloid was then transferred to a vertical cylindrical glass vessel and placed in a 30 W ultrasonic reactor. It was sonicated at 35 kHz for 1 h under ambient conditions. During the ultrasonic irradiation, the temperature of the colloid rose to approximately 70°C . After the reaction was complete, the white precipitate was collected by filtration and thoroughly rinsed with distilled water and ethanol. Finally, the precipitate was dried in an oven at 60°C

Fig. 1. XRD pattern of the product synthesized by sonochemical method.

in an air atmosphere. The crystallographic structure and morphology of the product were respectively examined by X-ray diffraction (XRD, Philips X'Pert MPD) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and scanning electron microscopy (SEM, FEI Quanta 400) operating at 25 kV. The room temperature photoluminescence (PL) spectrum was measured using a luminescence spectrometer (LS/55, PerkinElmer). The results were compared with those from samples prepared without ultrasonic irradiation.

The XRD pattern of the product from the sonochemical synthesis in Fig. 1 is identified as the hexagonal wurtzite ZnO structure. An SEM micrograph in Fig. 2(a) shows the morphology of the ZnO. The inset is a magnified image of the tubular clusters. Each tube is symmetrically formed with hexagonal cross sections for both the inner and outer walls. The diameter of the tubes is on average around 260 nm and the length is ca. 500 nm making these amongst the smallest ZnO nanotubes currently reported in the literature.^{2)–5),7)} It has been proposed that ZnO tubular structures are formed from ZnO nuclei. Subsequent growth results in hexagonal nanorods around which an outer

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Fig. 2. SEM micrographs of ZnO products from 0.05 M $\text{Zn}(\text{NO}_3)_2\text{-C}_6\text{H}_{12}\text{N}_4$ aqueous solution after 60 min; (a) with sonication at 70°C, (b) without sonication at 70°C and (c) without sonication at 90°C.

layer grows causing decomposition of the inner nanorod. Continued growth eventually results in complete loss of the ZnO nuclei and hollow nanotubes. ZnO is known to grow fastest in the [0001] direction and thus the ZnO nanotubes tend to grow along the *c*-axis.^{3),5)} This model is supported by Fig. 2(a) in which different morphologies from each growth step co-exist in our products. The series of circles indicate the growth step including the decomposition of the inner layers at the center of the hexagonal nanorods. Interestingly, with the same starting materials Hu et al. observed linked ZnO nanorods using a 20 kHz sonicator for 30 min, although the concentration of $\text{Zn}(\text{NO}_3)_2$ was 0.005 M.⁶⁾ It is clear that both the time and the frequency of sonication play a critical role in determining the morphology of the ZnO obtained. For the ZnO prepared from 0.05 M $\text{Zn}(\text{NO}_3)_2\text{-C}_6\text{H}_{12}\text{N}_4$ aqueous solution at 70°C in the absence of sonication, hexagonal prisms without hollow cores were obtained as shown in Fig. 2(b). By increasing the temperature up to 90°C, prismatic ZnO in Fig. 2(c) grows larger during the same 60 min period but its morphology remains different from that obtained by the sonochemical method indicating that sonication is vital in the preparation of ZnO nanotubes.

The room temperature PL spectrum of the hexagonal ZnO nanotubes is shown in Fig. 3. A UV emission peak and 2 peaks at both ends of the visible region are observed. The UV emission at 398 nm corresponds to the well-known near band-edge recombination of excitons.^{5),6),8)-10)} Visible emissions from ZnO are universally regarded as defect emissions from interstitial atoms and vacancies.⁹⁾ Different defect levels of oxygen vacancies were positioned beneath the conduction band. The narrow violet emission peak at 412 nm appears to originate from the transition between a shallow defect level and the valence band. Instead of the green emission often reported in literature,⁸⁾⁻¹¹⁾ a broad visible peak centered around 650 nm (red) is observed in our ZnO product. It is of note that similar broad emission is also observed in ZnO microtubes, although the peak is centred at 485 nm.⁵⁾ This can be explained in terms of the difference in the growth conditions. It has been shown that different growth conditions affect the visible emissions via different morphologies and defects.¹⁰⁾ The broad visible peak in Fig. 3 is related to nanostructured ZnO with different morphologies from each growth step. The peak is shifted to the red emission because of deep defect levels well below the conduction band. Compared to a previous report on ZnO nanoparticles, the infrared and orange emissions were enhanced by annealing in an air atmosphere.¹²⁾ The intensity of this visible peak is stronger than that of the near band-edge UV emission peak, which suggests a high density of interstitial atoms and vacancies. Figure 3 also shows the PL

Fig. 3. Comparison of room temperature PL spectra of the sonochemical synthesized ZnO and ZnO products prepared without sonication.

spectra of ZnO from aqueous solution at 70 and 90°C. Their optical emissions resemble that of sonochemical synthesized ZnO microtubes with peak shifts within 5 nm. The intensity is, however, significantly reduced in the ZnO prepared at 90°C corresponding to the smaller surface-to-volume ratio of the larger prisms.

In summary, hexagonal ZnO nanotubes were obtained from the reaction between $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ under an ultrasonic irradiation at 35 kHz for 1 h. Compared to the control experiments without sonication, the ultrasonic treatment proved to be effective in promoting active ZnO nuclei and growth of hexagonal tubes from active nanorods. The proposed growth mechanism was supported by SEM. In addition to a UV emission peak, an intense broad red emission band centered at 650 nm was identified in the PL spectrum.

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