A Novel One-step Solution Approach to Synthesize Tubular ZnO Nanostructures

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Tubular ZnO nanostructures were synthesized by a new and one-step method which involved the introduction of ammonia bubbles into a zinc chloride aqueous solution, and the formation mechanism was briefly discussed in this paper.

Zinc oxide (ZnO) is an important semiconductor and piezoelectric materials with a broad range of high-technology applications[1–3] ranging from surface acoustic wave filters, photonic crystals, varistors, and gas sensor to solar cells, owing to its wide band gap, excellent chemical and thermal stability, and its specific electronic and optoelectronic property. Various chemical, electrochemical and physical deposition techniques[4,5] have been reported to prepare a diversity group of ZnO nanostructures[6,7] including nanobelts, nanocombs, nanosprings, nanorings, nanobows, nanojunction arrays, and nanopropeller arrays. As for ZnO nanotube or microtube, even though the tubular ZnO nanostructures promise some interesting physical and chemical properties unattainable by other nanostructures, the preparation reports were limited and most of them were published recently.[8–12] In these limited reports, rigid experimental conditions (such as high temperature), sophisticated equipments (such as autocalve), and complex procedure were usually employed in order to obtain single-crystalline ZnO tubes. Furthermore, most of the reported approaches produced ZnO tubes in small quantities and high cost, restricting their commercial applications. In this paper, we proposed a new and facile method to synthesize tubular ZnO nanostructures in a large quantity with the characteristics of low cost and high production.

The preparation of ZnO tubes were started from introducing an aqueous solution of zinc chloride (purity of 98% from Wako, Japan) with zinc ionic concentration of 0.5 M into a conical flask which was heated in a water bath at 90 °C. Then, ammonia gas was introduced into the bottom of the solution through a bubble generator (Tekeno, Japan). The bubbles were quite uniform and in the size of approximately 100 µm. The introduction of ammonia bubble immediately resulted in the change of solution from transparent to turbid, following with the formation of white precipitates. After several minutes reaction, the ammonia bubbles were stopped, and the resultant white precipitates were collected by filtering through membrane filter, and dried at 110 °C for 24 h. X-ray Diffraction (XRD) (RINT 1100, Rigaku, Japan) measurements were conducted using Cu $K\alpha_1$ radiation to identify the composition of the samples. A JSM-7100F (JEOL, Japan) scanning electron microscope (SEM) was used to observe the morphology of samples. Transmission electron microscopy (TEM) was performed using a JSM2000 EXII TEM equipment (JEOL, Japan) with an accelerating voltage of 160 kV. The TEM samples were prepared by solidifying the precipitates in polymer firstly following with cutting the solidified samples in a thickness of 200 nm. The cutting of samples was carried out using a LEICA EM U6 ultramicrotome (Leica, U.S.A.).

The morphologies of synthesized samples were firstly characterized by SEM. It was interesting to find that the products are rod-like particles with the length of 1–2 µm. Some rods are broken and show hollow structure inside, as shown in Figure 1A. To further examine whether other rods are hollow or not, the samples were solidified, cut, and observed by SEM, as shown in Figure 1B. It is found that almost all rod-like particles have hollow structures inside. Figure 1C is another view of the sample. It is lucky to find that some tubes assemble together with their open ends extending to readers, which clearly reveal the tubular structure. Figure 1D is a magnified view of the tubes. The tubes show clean and smooth surface and one end open. The diameter of tubes is approximately 200–300 nm, and their thickness is about 20–30 nm. Some broken or imperfect tubes are also observed and mixed in the sample. The inset of Figure 1D presents the magnified front view of a tube, which revealed that the opening of tube presents a hexagonal shape.

X-ray Diffraction (XRD) pattern shown in Figure 2 confirms that the prepared sample is pure ZnO crystal. All diffraction peaks can be indexed to the typical wurtzite structure of ZnO (JCPDF 36-1451).

Figure 3 shows the further characterization of the prepared tubes using TEM and SEM. Figure 3A is the TEM images of a horizontally cut tube. The dark center and bright edge indicates the presence of hollow structure inside of the tube.

The small particles observed inside of the tube are believed to be the result of cutting. The inset of Figure 3A is an electron diffraction (ED) pattern selected from the wall of tube, which reveals that the tube was single crystalline. Figure 3B is a front view of a tube, which clearly shows that the tube has an hexagonal-faceted surface. Figure 3C shows a TEM image of vertically cut tube and also displays a hexagonal opening.

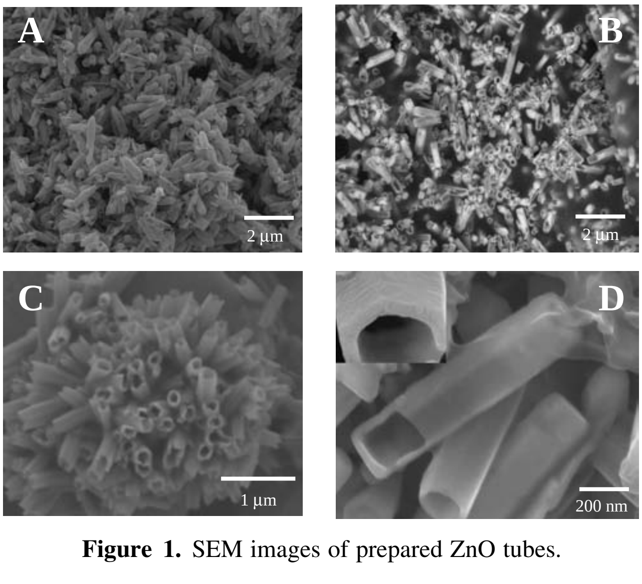

Figure 1. SEM images of prepared ZnO tubes.

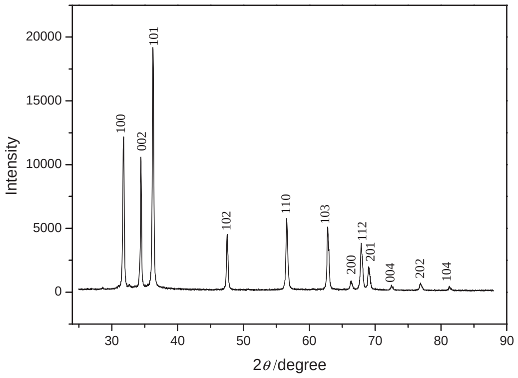

Figure 2. XRD pattern of prepared ZnO tubes.

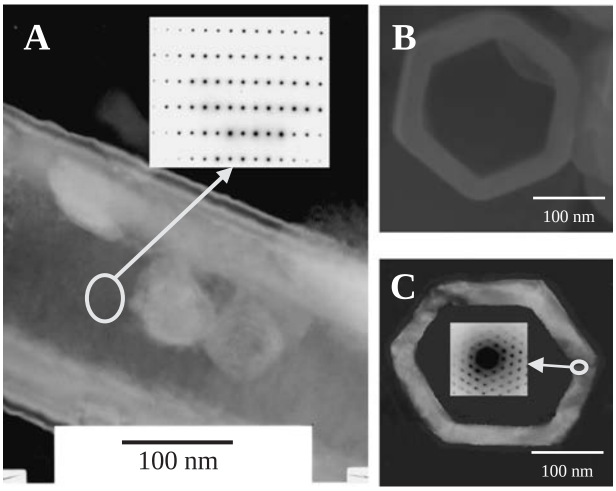

Figure 3. Further characterization of the prepared ZnO tubes.

The inset of Figure 3C is an ED pattern selected from the hexagonal opening, which indicates that the tube is single crystalline and grew along [001] direction (*c* axis). Regarding the ZnO crystal having a single crystallographic direction of [001], it can be simply explained by the "lowest energy" argument, i.e., the hexagonal (001) plane of ZnO with wurtzite structure is the closest packed plane in the crystal, and stacking along the [001] direction, therefore, becomes energetically favorable.[10]

It was found that the formation of tubes was closely relative to the pH of solution. When ammonia bubbles were passed into solution, the pH of solution increased as the result of ammonia dissolution. The initial pH of solution was about 5, while the final pH depended on the time of ammonia passing. We stopped the ammonia passing at pH 6, 7, and 8. It was found that tubes were only formed at the pH 8 while lower pH leaded to the formation of rod-like particles. XRD results showed that the rod-like particles were mainly zinc chloride hydroxide. Therefore, the rod-like zinc chloride hydroxide was firstly precipitated at lower pH. With the increase of pH, zinc hydroxide was preferentially precipitated because the zinc chloride hydroxide is not so stable at neutral condition.[13] So the late precipitation was mainly zinc hydroxide which favorably nucleated at the surface of rods, coving the rods and forming core/shell structure. With the further increase of pH, the initially formed zinc chloride hydroxide started to dissolve at basic condition. Because of the preferential chemical dissolution of the metastable (001)-Zn faces,[14] tubes were formed with the composition of zinc hydroxide which was transformed into zinc oxide at drying process.

In summary, a new and facile method to synthesize ZnO tubes was proposed in this paper, which involved the introduction of ammonia bubbles into zinc chloride solution at 90 °C in atmospheric condition. A large quantity of pure single-crystalline ZnO tubes was produced in several minutes with a tube diamter of 200–300 nm and wall thickness of 20–30 nm. As far as our knowledge is concerned, it is the first time to report the fabrication of ZnO tube efficiently in one step, in short time and without additional templates. A deep understanding of the formation mechanism and the controllable fabrication of tube need more investigations.

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