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Synthesis of hexagonal ZnO microtubes by a simple soft aqueous solution method

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A facile novel approach to synthesize the hexagonal zinc oxide microtubes is demonstrated at low temperature and normal pressure under a kind of soft aqueous solution method. Hexagonal-faceted ZnO tubes with length of 1 μm, diameter of 300 nm and shells thickness of 30 nm on average were synthesized by this new simple method. The SEM results indicate that the drying temperature played an important role on the formation of hexagonal ZnO microtubes. It was interesting to find that ZnO particles exhibited different morphologies on changing the reaction temperature. The growth mechanism is briefly discussed in this paper.

Key-words : Microtubes, Aqueous solution method, Synthesis, Zinc oxide, Morphology, Mechanism

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1. Introduction

As a well-known photocatalyst, ZnO has been paid much attention in the degradation and complete mineralization of environmental pollutants due to their applications in antibacterials, water treatment, deodorants, self-cleaning and so on.[1)-4)] Since the high surface area and the special structure of ZnO hexagonal tubes, they have special magnetic, dielectric, optical, and thermal properties. In order to increase the surface area and further increase the effective reaction area of a photocatalyst, many groups make considerable efforts to synthesize ZnO tube-like particles.[5),6)]

Various chemical, electronic and physical deposition techniques have been reported for synthesis of zinc oxide particles with various morphologies.[7),8)] Among them, the wet chemical method[9),10)] attracts intensive interests due to its unique advantages of simple equipments, low temperature, low cost and high efficiency. To the best of our knowledge, there are few reports on synthesis of ZnO microtubes using the simple aqueous solution method. In our group, we proposed a new and facile method to synthesize the hexagonal ZnO microtubes in a large scale by a low cost aqueous solution method.[11)] In comparison with other previous studies, we did not introduce any other chemicals except reactants in the reaction solution. Besides this, the advantages of our utilizing-aqueous solution-based method are template-free, surfactant-free, low temperature and normal pressure. The effect of drying temperature on the evolution of ZnO particles was mainly investigated through a series of temperature-dependent experiments.

2. Experiments

All of the reagents were of analytical grade and were used as received. The typical experiment procedure was as follows: The conical flask with the aqueous solution (400 ml) of zinc chloride (purity of 98% from Wako, Japan) of which zinc ionic concentration was 0.5 M was heated in the water bath under stirring. The synthesis temperature controlled by the water bath is kept at 90°C. The ammonia bubbles were introduced into the bottom of the solution through a bubble generator (Tekeno, Japan). As introducing ammonia bubbles into solution, the precipitation reaction immediately started with an increase of pH. When the pH arose about 7.5, the ammonia gas was stopped and the white precipitates were filtered and then dried at different temperatures, and used for the following characterizations.

The composition of as-synthesized samples were characterized by X-ray diffraction (XRD, RINT1100, Rigaku, Japan) by employing a scanning rate of 0.02°/s in the 2θ range from 3° to 90° with CuKα_1 (40 kV, 30 mA) radiation. Morphologies of products were examined by field emission scanning electron microscope (SEM, JEOL JSM-7000F, Japan). Transmission electron microscopy was performed using the JEM2000 EXII TEM equipment (JEOL, Japan) with an accelerating voltage of 160 kV.

3. Results and discussions

Figure 1 shows typical XRD patterns of as-synthesized ZnO crystal. All of the diffraction peaks can be indexed to the hexagonal phase of zinc oxide (wurtzite structure, space group P63mc). The lattice parameters were calculated to be $a=3.25$ Å, $c=5.21$ Å, which agreed well with the reported value (JCPDS card NO 36-1451) and there was no characteristic peaks of impurities observed. The sharp shape of the diffraction peaks suggests that the as-synthesized ZnO samples should be well crystallized.

The morphologies of ZnO microtubes are revealed through SEM observations. From the magnified view of the tubes (**Fig. 2a**), it can be clearly found that the tubes show smooth surface and one end is broken with hollow inside. The bottom-view and the top-view of ZnO microtubes are shown in Fig. 2b and c, respectively. The individual ZnO microtube exhibits an obvious hexagonal structure with the diameter of 300 nm and the 30 nm thickness of wall. Fig. 2d is the TEM image of a horizontally-cut tube. The dark center and bright edge indicated the presence of hollow structure inside.

The key result presented in this paper is the high-yield synthesis of ZnO microtubes using a simple aqueous solution method. To investigate the growth mechanism of ZnO microtubes by a soft aqueous solution synthesis, a series of

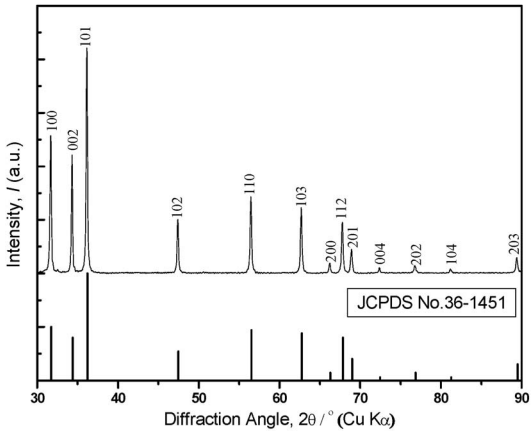

Fig. 1. XRD patterns of as-synthesized ZnO samples and standard XRD pattern of wurtzite ZnO (JCPDS card NO 36–1451).

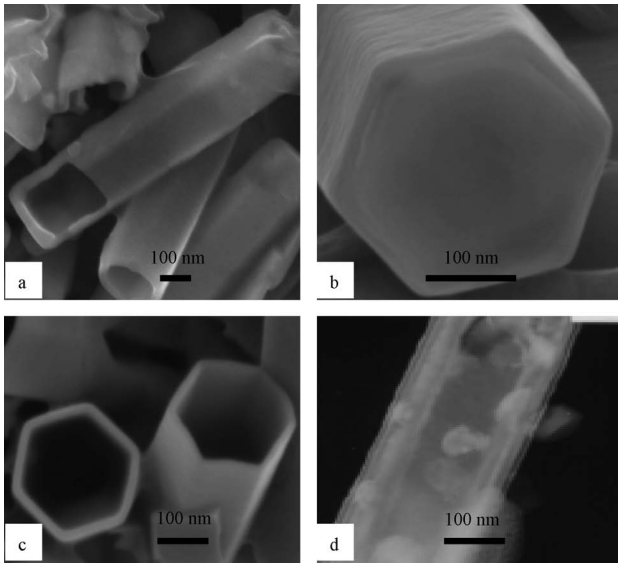

Fig. 2. SEM and TEM images of ZnO microtubes.

controlled experiments were carried out with changing drying temperature during the heat treatment. And their shapes and morphologies at the drying process were investigated by SEM images. The morphology in the initial stage of precipitate is given in **Fig. 3a**. It can be clearly seen that the particles were in the form of the regular hexagonal layer-like structure. The length of the hexagonal side was about 5–10 μm. After being dried at 50°C for 12 h, as shown in Fig. 3b, layer-like particles begin to decompose into crystal grains. Figure 3c and d show the SEM images of the sample obtained when dried at 70°C and 110°C, respectively. Figure 3c clearly reveals that ZnO rod-like growing at this temperature: some of particles still kept the layer-like, while others already have the rod-like particles with the length of more than 500 nm. In another image (Fig. 3d) of the sample dried at 110°C, ZnO microtubes grow both in size and morphology. And ZnO microtubes have the length of about 1 μm. Finally, ZnO microtubes with hexagonal structure were obtained. The above experiments and results manifested that

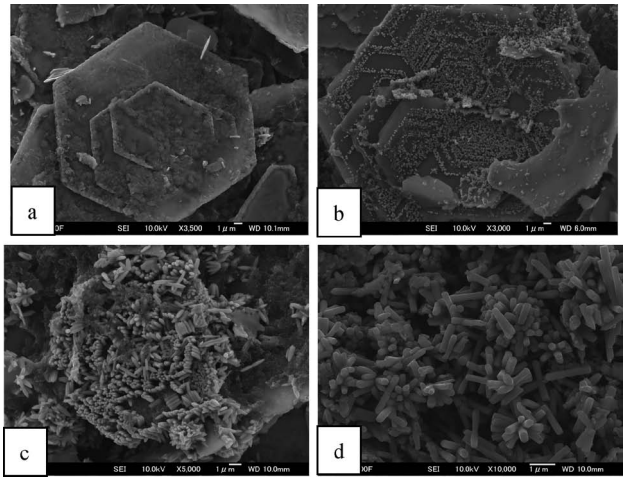

Fig. 3. SEM images of products dried at different temperatures (a-room temperature; b-50°C, c-70°C, d-110°C).

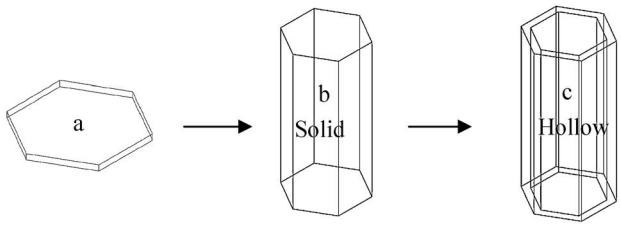

Fig. 4. Schematic illustration of possible growth mechanism for ZnO microtubes.

the drying temperature plays an important role on the formation of ZnO microtubes.

On the basis of the drying temperature-dependent experimental details, we found that the morphological evolution of ZnO by increasing the heating temperature, as shown in **Fig. 4**. Under the lower drying temperature, owing to the large lattice energy of ZnO, rearrangement and diffusion of growth nucleus has been limited to a certain extent. At this stage, the morphology of samples was the hexagonal layer-like (Fig. 4a). With the heat temperature increasing, layer-like evolved into rod-like particles (Fig. 4b). The orientation was improved, which meant that the crystals grow along the c-axis with the increase of the heating temperature. When the temperature further increasing, the morphology of ZnO will be directed to lower the system energy and form ZnO microtube (Fig. 4c). The hollow structure may have a lower energy than that of the solid structure due to the higher energy at the polar surface. This may facilitate the formation of ZnO microtubes.

4. Conclusion

In summary, it has been shown that ZnO microtubes could be easily synthesized at low temperature in high yield by a very simple soft aqueous solution process. The tubes presented the diameter in the range of 300 nm, and the thickness of wall 30 nm, the length of the tubes 1 μm on average. The possible growth mechanism of zinc oxide microtubes has been elaborated based on the SEM observation of the sam-

ples obtained from a series of successful controlled growth experiments, which were carried out through changing reaction temperature.

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