A simple preparation technique for shape-controlled zinc oxide nanoparticles: Formation of narrow size-distributed nanorods using seeds in aqueous solutions

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Abstract

Various shapes of wurtzite-type ZnO nanoparticles were selectively produced in a simple aqueous system prepared by mixing ZnSO₄ and NaOH solutions. Ellipsoidal nanoparticles were obtained by the addition of an alkaline agent into an acidic zinc solution (acidic route), while nanorods were grown by mixing a zinc precursor into an alkaline solution (basic route). The aspect ratio and size distribution of the nanorods grown through the basic routes were controlled by the addition of nanoparticles prepared by the acidic route as seeds. On the other hand, micrometric branching rods were obtained by dilution of the reaction solution in the basic routes. The morphological variation of ZnO particles is ascribed to the balance of the nucleation and crystal growth depending on the degree of the supersaturation. We successfully prepared narrow size-distributed rods with a nanometric width and a submicrometric length using the seed particles, because the presence of the seeds suppressed additional nucleation and then controlled the degree of the supersaturation for steady growth of the crystalline particles.

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1. Introduction

Wurtzite-type zinc oxide (ZnO), a wide band-gap (3.37 eV) semiconductor with a large exciton-binding energy, is an attractive material because of its unique properties, such as optical transparency, electric conductivity, piezoelectricity and near-UV emission [1–4]. The size and morphology are important parameters to determine the physical and physicochemical properties of ZnO crystals. Various kinds of nanoscale morphologies, such as spherical particles [5], rods [6–9], whiskers [10], columns [11–13], wires [14], tubes [15], rings [16], disks [17] and other characteristic shapes [18–20], were fabricated. Wet chemical methods using aqueous solution-based systems have been widely applied for the preparation of the ZnO crystals with various morphologies. The size and shape of ZnO crystals grown in the solutions were controlled by the reaction conditions [21], selection of precursors [22] and addition of organic molecules including surfactants [21,22], amine [23], solvents [24,25] and polymers [26,27].

One-dimensional (1D) ZnO materials were prepared using various methods [6–10,14,15,28–33]. In particular, nanorods have been produced in basic solution systems at low temperatures [6–9,33] and under hydrothermal conditions [7]. The submicrometric control of the length of the nanorods in a range smaller than the wavelength of visible light is essential for applications to optically transparent materials, such as ZnO–polymer composite films for a component of recording media [4]. Although the aspect ratio varied in the range of 50–100 with a width of 10–30 nm by changing [OH⁻]/[Zn²⁺] [6], preparation techniques for nanorods with submicrometric lengths have not been established.

We selectively produced nanoparticles and nanorods of ZnO crystals using a simple mixing technique of ZnSO₄ and NaOH solutions without any organic additives [9]. However, the size distribution of the nanorods broadened because the nucleation was not controlled in the mixtures. In the present study, we performed further control of nanometric shapes and size distribution of ZnO particles by addition of seeds into the simple system. The
mechanism of morphological variation is discussed on the basis of the balance of the nucleation and crystal growth at a certain degree of supersaturation. This work would provide not only a simple method for selected fabrication of 1D ZnO particles with a nanometric width and a submicrometric length, but also fundamental information for shape control of nanoparticles prepared through the crystal growth in aqueous solutions.

2. Experimental

A stock solution (pH 5.3) of 0.2 M zinc sulfate (ZnSO$_4$) and an alkali solution (pH 13.8) of 4.0 M sodium hydroxide (NaOH) were prepared by dissolution of zinc sulfate heptahydrate (ZnSO$_4$·7H$_2$O, 99.5%; Kanto Chemical) and NaOH (Junsei Chemical) into purified water, respectively. The reactions were fundamentally performed with stirring by mixing the stock solution of ZnSO$_4$, the alkali solution of NaOH and a certain amount of purified water. The final pH of the mixture was fixed to ca. 13 because a highly basic condition is suitable for the direct preparation of wurtzite-type ZnO crystals [12]. Precipitation occurred at 60 °C for 2 h after the mixing of the solutions. The products obtained by centrifugation were washed with purified water and then dried at 60 °C in air. However, the shape and size of resultant particles depended on the mixing procedure of the solutions.

As an acidic route, 25.0 cm$^3$ of the alkali solution (4.0 M NaOH) was dropped at an approximate rate of 5 cm$^3$/min into an acidic mother solution (pH 5.6) prepared from 25.0 cm$^3$ of the stock solution (0.2 M ZnSO$_4$) and 50.0 cm$^3$ of purified water. As a basic route, 25.0 cm$^3$ of the stock solution (0.2 M ZnSO$_4$) was dropped at an approximate rate of 5 cm$^3$/min into a basic mother solution (pH 13.6) obtained by mixing the alkali solution (4.0 M NaOH) and purified water. Typically, 25.0 cm$^3$ of the stock solution was added into a mixture of 25.0 cm$^3$ of the alkali solution and 50.0 cm$^3$ of purified water (basic route 1). The final concentrations of ZnSO$_4$ and NaOH for the acidic route and basic route 1 were 0.050 and 1.0 M, respectively.

Seed-mediated crystal growth was performed using the basic route to modify the morphology of resultant ZnO crystals. Initially, seed particles of ZnO crystals were prepared via the above-mentioned acidic route and washed with abundant purified water. Then, 12.5 cm$^3$ of the stock solution (0.2 M ZnSO$_4$) was dropped at an approximate rate of 5 cm$^3$/min into a seeded mother solution produced from 12.5 cm$^3$ of the alkali solution (4.0 M NaOH), 25.0 cm$^3$ of purified water and 50.0 cm$^3$ of a seed suspension (basic route 2). The amount of seeds varied from 0 to 0.077 g in 100 cm$^3$ of the final solution by changing the concentration of the seed suspension. The degree of supersaturation was lowered during the formation of ZnO crystals by subsequent dilution (basic route 3). A mother solution for basic route 1 was initially prepared by mixing 12.5 cm$^3$ of the stock solution, 12.5 cm$^3$ of the alkali solution and 25.0 cm$^3$ of purified water. After being stirred for 5 min, the reaction solution was diluted by addition of an excessive amount of water with a volume of 50.0 cm$^3$. The concentrations of ZnSO$_4$ and NaOH in the resultant solution for basic routes 2 and 3 were 0.025 and 0.5 M, respectively. The preparation conditions are listed in Table 1.

The precipitated particles were characterized by θ/2θ X-ray diffractometry (XRD; Rigaku RAD-C and Bruker D8 Advance) using Cu Kα radiation. The morphologies of the particles were observed with a field-emission scanning electron microscope (FESEM, Hitachi S-4700) at 5 kV accelerating voltage and a field-emission transmission electron microscope (FETEM, Philips TECNAI F20). The size of the ZnO particles was estimated from the FESEM images.

3. Results

According to the XRD patterns (Fig. 1), the precipitates were assigned to wurtzite-type ZnO regardless of the preparation routes. However, the shape of the products was obviously influenced by the preparation route as shown in Figs. 2 and 3, and listed in Table 2. Ellipsoidal nanoparticles with an average width of 32 nm and a length of 44 nm were grown at pH 12.8 through the acidic route (Fig. 2(a) and (b)). On the other hand, ZnO nanorods with a high aspect ratio were obtained at pH 12.8 through basic route 1 (Fig. 2(c) and (d)). The lattice image indicates that the ZnO rods were single-crystalline and were elongated along c axis (Fig. 4). Fig. 5 shows cumulative undersize distribution of ZnO particles estimated from FESEM images. The median width and length of the rods pre-

### Table 1

<table>
<thead>
<tr>
<th>Route</th>
<th>Mother solution</th>
<th>Additional solution</th>
<th>Final concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnSO$_4$ (M)</td>
<td>NaOH (M)</td>
<td>Seed (g/100 cm$^3$)</td>
</tr>
<tr>
<td>Acidic 0.2 M ZnSO$_4$ 25.0 cm$^3$; H$_2$O 50.0 cm$^3$</td>
<td>4.0 M NaOH 25.0 cm$^3$</td>
<td>0.050</td>
<td>1.0</td>
</tr>
<tr>
<td>Basic 1 4.0 M NaOH 25.0 cm$^3$; H$_2$O 50.0 cm$^3$</td>
<td>0.2 M ZnSO$_4$ 25.0 cm$^3$</td>
<td>0.050</td>
<td>1.0</td>
</tr>
<tr>
<td>Basic 2–1 4.0 M NaOH 12.5 cm$^3$; H$_2$O 75.0 cm$^3$</td>
<td>0.2 M ZnSO$_4$ 12.5 cm$^3$</td>
<td>0.025</td>
<td>0.5</td>
</tr>
<tr>
<td>Basic 2–2 4.0 M NaOH 12.5 cm$^3$; H$_2$O with seeds 75.0 cm$^3$</td>
<td>0.2 M ZnSO$_4$ 12.5 cm$^3$</td>
<td>0.025</td>
<td>0.5</td>
</tr>
<tr>
<td>Basic 2–3 4.0 M NaOH 12.5 cm$^3$; H$_2$O with seeds 75.0 cm$^3$</td>
<td>0.2 M ZnSO$_4$ 12.5 cm$^3$</td>
<td>0.025</td>
<td>0.5</td>
</tr>
<tr>
<td>Basic 3 4.0 M NaOH 12.5 cm$^3$; H$_2$O 25.0 cm$^3$</td>
<td>First 0.2 M ZnSO$_4$ 12.5 cm$^3$; second H$_2$O 50.0 cm$^3$</td>
<td>0.025</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Stock solution: 0.2 M ZnSO$_4$, Alkali solution: 4.0 M NaOH.
In order to control the morphology, ellipsoidal nanoparticles were added as seeds into a diluted mother solution (0.025 M ZnSO$_4$ and 0.5 M NaOH) for the basic route. No precipitation was observed without the seed particles (basic route 2–1), because the final concentration of Zn$^{2+}$ was lower than the typical condition of basic route 1 (0.050 M). In this case, the final pH of the resultant solution was slightly changed by the dilution (pH 12.9). This fact indicates that the nucleation did not occur practically at a relatively low concentration whereas the basic solution was supersaturated. Here, the addition of seed particles could mediate the precipitation accompanied with the growth of ZnO crystals. As shown in Fig. 3, nanorods were obtained by seed-mediated crystal growth (basic routes 2–2 and 2–3). Since the aspect ratio of the seed-mediated products was higher than that of the original seed (Table 2), the ZnO particles were preferentially grown in c axis. The aspect ratio increased through promotion of the axial growth by decreasing the amount of the seeds in the mother solution. Moreover, these nanorods exhibited a narrow size-distribution in comparison with those prepared without the seeds (Fig. 5). Regarding to the product yield, it was not sufficient without using seed particles (acidic route: 11.4%; basic 1: 7.0%). However, the yield was found to be drastically increased to 73.0% by introduction of the seed particles (basic 2–3).

A typical reaction solution was diluted with an excessive amount of water to lower the degree of supersaturation during the precipitation (basic route 3). As shown in Fig. 2(e) and (f), micrometeric branching rods with hexagonal habits were obtained in the solution. The definite hexagonal features were not observed on the nanoparticles (Fig. 2(b)) and nanorods (Fig. 2(d)). In the diluted solution, considerably large ZnO crystals were gradually grown at a relatively low degree of supersaturation. Interestingly, the tilted angle of most branches on a basal rod was observed to be around 90°. Similar structures of wurtzite ZnO rods having oriented branches with a tilted angle of 80 ± 3° were reported as a secondary branch crystal [34]. Therefore, the branching rods are suggested to be twinned crystals rather than random aggregates of independently grown rods.

4. Discussion

Wurtzite-type ZnO crystals were directly grown in a basic solution containing Zn$^{2+}$ ions at pH ~13 [9]. Crystalline particles were gradually formed in a suitable degree of supersaturation for crystal growth at pH ~13 as shown in Fig. 6. However, the morphology of the resultant ZnO particles depended on the condition during the precipitation. A large amount of nuclei of ZnO were generated through the acidic route, because the degree of supersaturation on the initial stage was extremely high due to the low solubility of ZnO under the acidic condition (acidic route in Fig. 6). Further crystal growth was then suppressed because most of the Zn$^{2+}$ ions were consumed for the initial nucleation. Finally, the resultant particles were nanometric grains with an ellipsoidal shape. On the other hand, the nucleation was limited on the initial stage of the basic route because of the low degree of supersaturation in the mother solution at pH 13.6 (basic route 1 in Fig. 6). Thus, subsequent crystal growth was

![Fig. 1. Typical X-ray diffraction patterns of the precipitates obtained through (a) acidic route, (b) basic route 1, and (c) basic route 3.](image)

<table>
<thead>
<tr>
<th>Shapes of wurtzite-type ZnO particles</th>
<th>Route</th>
<th>Shape</th>
<th>Sizes (nm)</th>
<th>Aspect ratio (length/width)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Length</td>
<td>Width</td>
</tr>
<tr>
<td>Acidic</td>
<td>Ellipsoid</td>
<td>44</td>
<td>32</td>
<td>1.4</td>
</tr>
<tr>
<td>Basic 1</td>
<td>Rod</td>
<td>624</td>
<td>53</td>
<td>12</td>
</tr>
<tr>
<td>Basic 2–1</td>
<td>No precipitation</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Basic 2–2</td>
<td>Rod</td>
<td>539</td>
<td>98</td>
<td>5.5</td>
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<tr>
<td>Basic 2–3</td>
<td>Rod</td>
<td>208</td>
<td>49</td>
<td>4.2</td>
</tr>
<tr>
<td>Basic 3</td>
<td>Flower-like</td>
<td>4200</td>
<td>320</td>
<td>13</td>
</tr>
</tbody>
</table>

* The length and width of ZnO nanoparticles were fundamentally obtained from the median values of the cumulative undersize distributions of the particles. The values for basic route 3 were estimated from typical several products shown in Fig. 2(e).
promoted on the next stage in the solution containing abundant Zn\(^{2+}\) ions. The formation of nanorods elongated along \(c\) axis indicated that preferential growth occurred in the \(c\) direction of the wurtzite structure in the basic route. Since anionic zinc species, Zn(OH)\(_4\)\(^{2-}\), dominantly exist under a highly basic condition, the growth in the \(c\) direction could be initiated with preferential adsorption of the anionic precursor on the positively charged (0 0 1) face.

The length of nanorods prepared through basic route 1 exhibited a wide distribution (Fig. 5). However, monodispersion is generally required for homogeneous functionality of colloidal and composite materials. The wide distribution of the nanorods is attributable to the time variance of the nucleation during the precipitation reaction. In the present study, seed-mediated crystal growth was found to be effective for the control of the shape of the nanoparticles. In a mother solution at relatively low degree of supersaturation (0.025 M ZnSO\(_4\) and 0.5 M NaOH), the nucleation of ZnO crystal could not occur, but the crystal growth could be induced around the seed particles added into a mother solution (basic route 2 in Fig. 6). Then, narrow size-distribution of the ZnO rods was achieved by homogeneous crystal growth of the seed particles. The length of the rods increased primarily by decreasing the number of seeds. Here, the separation of the nucleation and the crystal growth is essential for the morphological control.

As shown in Fig. 2(e) and (f), micrometric ZnO rods having a branching morphology were obtained by dilution of the reaction solution (basic route 3). In this case, a small number of nanoparticles could be generated on the initial stage before the dilution (basic route 3 in Fig. 6). The considerably large rods having hexagonal habits would be grown from the nanoparticles at a low degree of supersaturation. Since the rod size obtained in the diluted solution was larger than that using seed particles, the amount of the nanoparticles prepared on the initial stage was smaller than that of the seeds. Interestingly, branching, thick rods were obtained through basic route 3, although longer nanofibers would be formed with a smaller amount of seeds with basic route 2. These facts suggest that the growth condition on the later stage in basic route 3 was slight different from that in basic route 2 using seeds. Similar branching morphologies were obtained by hydrothermal treatment at 150 °C in systems containing Zn(NO\(_3\))\(_2\)-NaOH (or KOH) [28] or zinc.
A certain angle of branching indicates the formation of twinned crystals under a relatively high degree of supersaturation. Thus, the degree of supersaturation on the later stage in basic route 3 is tentatively estimated to be larger than that in basic route 2, whereas the final concentrations of ZnSO$_4$ and NaOH were the same for both routes. The concentration of zinc ions and the degree of supersaturation were lowered with the crystal growth of the seeds. On the other hand, a decrease in the concentration of zinc ions is assumed to be very slow due to a small amount of

Fig. 5. Cumulative undersize distribution (width and length) of ZnO particles prepared through the basic routes. The plots were shown with the following symbols: (○) basic 1; (▲) basic 2–2; (□) basic 2–3.

Fig. 6. Phase stability diagrams for crystalline ZnO–H$_2$O [9,12,35]. Arrows demonstrate variations of pH and zinc concentration through acidic, basic 1, basic 2, and basic 3 routes, respectively.
nanoparticles as seeds in basic route 3. Therefore, the branching would occur on the basal rods. However, further investigation is required to clarify the details of the formation mechanism for the complicated morphologies.

5. Conclusions

Various shapes of wurtzite-type ZnO crystals including nanometric ellipsoids, nanorods and micrometric branching rods were prepared by a simple aqueous system using ZnSO₄ and NaOH solutions. The morphology of ZnO particles would be governed by the balance of the nucleation and crystal growth determined by the reaction route. The aspect ratio and size distribution of the nanorods were successfully controlled by seed-mediated crystal growth in basic solutions.

References