Nanoscale morphological design of ZnO crystals grown in aqueous solutions

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In the past decade, a wide variety of ZnO crystals were prepared through wet chemical processing. However, the fundamentals of the nanoscale morphological variation of ZnO crystals on the crystal growth in aqueous solution systems have not been sufficiently studied. This paper is a review of the various morphologies of ZnO crystals in relation to the preparation conditions, including the source chemicals, the role of seeds or substrates, and the presence of organic molecules as a shape modifier. Versatile guidelines for controlling the nanoscaled morphologies of ZnO crystals in the forms of individual particles and films as assembly of nanocrystals are proposed on the basis of the classification of typical phenomena. The essential parameters, such as the growth rate, growth site, and growth direction of ZnO crystals, are successfully tuned by varying the degree of supersaturation, the presence of seeds or substrates, and the addition of specific organic molecules, respectively.

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Key-words : Zinc oxide, Nanocrystal, Particle, Film, Nucleation, Crystal growth, Crystallization, Supersaturation, Morphology, Epitaxial growth, Soft solution process, Wet chemical processing, Chemical bath deposition (CBD), Liquid phase deposition (LPD)

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1. Introduction

Wurtzite-type ZnO, a wide band-gap 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.1–6 Because the properties determining the performance of ZnO-derived devices strongly depend on the size and the shape, precision control of the morphology of ZnO crystals is a matter of considerable importance for exploring the potential oxide material. In consequence, many approaches, including chemical vapor deposition,7–9 sputtering,7,8 molecular beam epitaxy,9 sol–gel routes,10,11 electrodeposition,12–14 and various kinds of solution-based methods,15–67 have been investigated for the size- and morphology-controlled synthesis of ZnO crystals.

In recent years, aqueous solution-based processing has been utilized for the fabrication of crystalline ZnO particles and the deposition of ZnO films on a substrate because of the advantages of the methods, such as low cost, low energy consumption, ease of large-scale production, and controllability of the morphology. Table 1 is a summary of the typical morphologies of ZnO crystals in particles and films grown in aqueous solutions.15,16,38–38 A wide variety of ZnO nanocrystals were prepared using various solution systems containing different chemicals, additives, and seeds or substrates. Unfortunately, the fundamentals of the morphological variation have not been discussed because the chemical reactions and the growth conditions were quite different in previous works. However, guidelines for the morphology-controlled synthesis of ZnO particles and films are generally required for the development of highly functional nanoscale devices.

This paper is a review of the various morphologies of ZnO crystals in relation to the preparation conditions, including the source chemicals, the role of seeds or substrates, and the presence of organic molecules as a shape modifier. Based on the classification of typical phenomena observed in previous works, parameters such as the growth rate, growth site, and growth direction of ZnO crystals are inferred to be essential for the control of the morphology. Here, a principle for guiding the essential parameters is discussed on the basis of the review of our previous studies and representative articles reported by many researchers on the morphological variation of ZnO particles precipitated in bulk solution and ZnO films grown on a substrate.

2. Classification of the essential parameters affecting ZnO morphologies

As listed in Table 1, nanoscale grains, rods, and plates were selectively produced as precipitates in aqueous solution systems. Fundamentally, solution systems containing Zn2+ ions as a zinc source are categorized into two main cases: a hexamethylenetetramine (HMT) solution and an alkaline solution with NH3 or NaOH. The degree of the supersaturation, which is associated with the driving force of crystallization, is tuned by varying the pH of the chemical systems as shown in Fig. 1. In the presence of substrates, the nanorods and nanoplates were arranged on the surface. The orientation of the ZnO rods and plates could be controlled under specific conditions. The addition of particular organic molecules influenced the morphology of the grown crystals.

The overall architecture of crystals is basically controlled by tuning the crystal growth, including the growth rate, growth site, and growth direction. Here, the degree of the supersaturation, the

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Table 1. A list of representative reports on the solution-based fabrication of ZnO particles and films with the classification from A to I shown in Fig. 2

<table>
<thead>
<tr>
<th>Type</th>
<th>Morphology</th>
<th>Seed</th>
<th>Substrate</th>
<th>Chemical system</th>
<th>Additive</th>
<th>Condition</th>
<th>Ref.</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle</td>
<td>nanograin</td>
<td>—</td>
<td>—</td>
<td>ZnSO$_4$·NaOH</td>
<td>—</td>
<td>60°C/2h</td>
<td>15, 16</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>spherical</td>
<td>—</td>
<td>—</td>
<td>(in alcohol)</td>
<td>—</td>
<td>35°C/2--120 min</td>
<td>17</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>nanorod</td>
<td>—</td>
<td>—</td>
<td>Zn(NO$_3$)$_2$·HMT</td>
<td>—</td>
<td>55--85°C/3 h--</td>
<td>18</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>nanorod</td>
<td>yes</td>
<td>—</td>
<td>Zn(NO$_3$)$_2$·HMT</td>
<td>/trisodium citrate</td>
<td>75°C/2.5 h</td>
<td>20</td>
<td>C, G</td>
</tr>
<tr>
<td></td>
<td>nanorod</td>
<td>yes</td>
<td>—</td>
<td>Zn(NO$_3$)$_2$·HMT</td>
<td>/trisodium citrate</td>
<td>75°C/2.5 h</td>
<td>20</td>
<td>C, G</td>
</tr>
<tr>
<td></td>
<td>hexagonal plate</td>
<td>—</td>
<td>—</td>
<td>Zn(NO$_3$)$_2$·TRIZMA</td>
<td>gelatin</td>
<td>37°C/4h</td>
<td>21</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td>disk</td>
<td>—</td>
<td>—</td>
<td>Zn(NO$_3$)$_2$·KOH</td>
<td>trisodium citrate</td>
<td>50°C/1h</td>
<td>22</td>
<td>F</td>
</tr>
</tbody>
</table>

Fig. 1. Phase stability diagram for crystalline ZnO--H$_2$O$_3(t)$ in a wide-pH region.

Fig. 2 shows a schematic illustration of the effects of the guiding parameters. Regarding the crystallization in bulk solution, the size and shape are influenced by the balance of the nucleation rate and the growth rate depending on the degree of the supersaturation. Under a high degree of supersaturation, fine grains are produced through a high rate of nucleation. On the other hand, nanorods elongated in the c direction (Fig. 3) are obtained through gradual crystal growth with a low rate of the nucleation under a low degree of supersaturation. In this case, however, the size distribution of the resultant particles is broadened due to the variation of the nucleation time. The presence of seeds could control the size distribution and the orientation of the resultant crystals. Overgrowth on nanograins as a seed leads to the preparation of monodispersed nanorods. The nanograins covered on a substrate achieve the formation of films presence of seeds, and the adsorption of additives are regarded as essential parameters for the control of the growth modes.
consisting of oriented nanorods. Highly oriented nanorods are obtained through epitaxial growth on a single-crystalline substrate. Adsorption on specific faces, such as (001) (Fig. 3), limits the growth direction of ZnO crystals, resulting in the formation of platy morphologies, such as discs and sheets, regardless of the presence of the seeds. In the main text, the guiding principle for the morphological design of ZnO crystals in solutions is systematically discussed with an interpretation of the typical results from our previous works and representative articles reported by many researchers.

Fig. 2. Schematic illustration of the effects of the guiding parameters for the morphological design of ZnO crystals in solutions. The degree of supersaturation, the growing sites, such as the seed particles and substrates, and the addition of organic molecules as shape modifiers of ZnO crystals mainly determined the final morphologies of ZnO crystals. Therefore, the classifications, such as A to I, were given on the basis of the corresponding essential parameters through the wet chemical processing routes.

Fig. 3. Schematic illustration of (a) a unit cell of the wurtzite structure of ZnO and (b) (c) examples of modeling morphologies.

3. Effect of the degree of supersaturation: From nanograins to nanorods

3.1 Variation of the degree of supersaturation

As shown in Fig. 1, the solubility of ionic zinc species depends on the pH of the solution. Thus, the degree of supersaturation can be controlled by the change in pH. Crystalline ZnO was found to be directly deposited at pH in the range from 9 to 13.33) In our previous work using alkali solutions of Zn\(^{2+}\) ions, the degree of supersaturation was simply increased with the addition of an NaOH solution.15,16) The concentrations of alkali species, Zn\(^{2+}\) ions, and chelating agents should be delicately tuned in this procedure. As another approach for the production of crystalline ZnO, aqueous solutions containing HMT have been widely reported.18)-20,23)-26,28)-30) The decomposition of HMT serves OH\(^{-}\) ions besides NH\(_4\)\(^{+}\) as a buffer and gradually increases the pH. In this case, the degree of the supersaturation of mild basic solutions was easily kept at a low level.

Nucleation and crystal growth occur in bulk solution and on the surface of solid phases.87) Here, the degree of supersaturation in the system determines the crystal formation via homogeneous or heterogeneous nucleation. Relatively high supersaturation, which determines the final pH and the changing pathways of pH in the corresponding systems, promotes homogeneous precipitation in solution. Ammonium compounds, including NH\(_3\), NH\(_4\)Cl, and NH\(_2\)NO\(_3\), and their precursors, such as HMT, have often been used as complexing agents (chelating agents) because they suppress the degree of supersaturation in the system.24)-31,33)-35) The shape of the resultant ZnO crystals is governed by the balance of the nucleation rate and the growth rate (Fig. 2).
3.2 Formation of ZnO nanosized grains

Nanograins of ZnO with a diameter of ca. 40 nm (Fig. 4(a)) were synthesized in a solution of 0.2 M ZnSO₄ around pH 12.8 at 60°C.¹⁵,¹⁶ Under a highly basic condition, a large number of fine grains are produced because nucleation, rather than crystal growth, is predominant at a high degree of supersaturation. The introduction of alcohols into the solvent is useful for downsizing of the grains with an increase in the degree of supersaturation. Single nanometer-sized ZnO grains were prepared in a series of alkanols (from ethanol to 1-hexanol) containing Zn(CH₂COO)₂ and NaOH.¹⁷ The solubility of ZnO decreases with an increase of alkanols in the content of the mixed solution. A great difference in grain size is ascribed to a higher number of nuclei of ZnO formed in alkanols due to low solubility.

3.3 Formation of ZnO nanorods

The ZnO grains have a tendency to grow to rods elongated in the c direction due to the anisotropic nature of the unit cell (Fig. 3). For example, fine nanorods of ZnO ranging from ca. 100 to ca. 600 nm in length were prepared in the ZnSO₄–NaOH aqueous system.¹⁵ The addition of a zinc ion solution into an alkali solution at pH 13.6 resulted in the formation of nanorods of ca. 50 nm in width and ca. 600 nm in length (Fig. 4(b)).¹⁵ The number of nuclei was limited in the initial stage, and the particle size increased through subsequent growth in the progressive stage. The aspect ratio within ~12 was controlled through this route by changing the pH value at the end of the reaction performed at 60°C for 2 h, although the length of nanorods exhibited a wide distribution, which is attributable to the time variance of the nucleation during the precipitation reaction.

The Zn(NO₃)₂–HMT system has been widely used to synthesize ZnO nanorods.¹⁸–⁲⁰ The decomposition of HMT serves OH⁻ ions besides NH₄⁺ as a buffer and gradually increases the pH. Therefore, the degree of the supersaturation of mild basic solutions was easily kept at a low level. The controlled degree of supersaturation under basic conditions causes the ZnO nanorods to elongate along the c-axis direction. The length of the rods is usually on the micrometer scale because of the long-term growth at a low degree of supersaturation (Fig. 4(c)).

4. Control of crystal growth with seeds

4.1 Variation of the growth site with seeds

The presence of seeds, such as dispersed nanocrystals and nanocrystalline coatings of ZnO, mediates the crystal growth in solution systems at a low degree of supersaturation. The separation of the nucleation and the crystal growth is essential for morphological control with the seeds. The growth site, size, and orientation of ZnO nanocrystals can be controlled by varying the seeds, including nanograins,¹⁰ nanocrystalline coatings,³³ and single-crystalline substrates (Fig. 2).³⁴

4.2 Narrowing the size distribution of ZnO nanorods

The presence of seeds, such as dispersed nanocrystals and nanocrystalline coatings of ZnO, mediates the crystal growth in solution systems at a low degree of supersaturation. The separation of the nucleation and the crystal growth is essential for morphological control with the seeds. Nanograins of ca. 40 nm in diameter were added as a seed into a ZnSO₄–NaOH aqueous solution system at a relatively low degree of supersaturation in which no precipitation was observed.¹⁶ Nanorods having a narrow size-distribution were obtained because of the preferential growth of the seed grains in the c direction without homogeneous nucleation.

4.3 Arrangement of ZnO nanorods on a substrate: Formation of a film consisting of ZnO nanorods

A seed layer of nanocrystalline ZnO prepared through a sol–gel route was utilized to promote the formation of nanorods arranged on the surface.³²,³³ As shown in Fig. 5(a) and (b), films comprising ZnO nanorods were successfully grown on glass slides covered with ZnO seed particles in a ZnSO₄–NH₄Cl–NaOH aqueous solution system.³⁴ In this system, precipitates of ZnO crystals were rapidly formed through homogeneous nucleation at a low concentration of [NH₄⁺]. A limited range of [NH₄⁺] is suitable for the crystal growth of ZnO through heterogeneous nucleation and growth on the substrate. Highly oriented ZnO nanorods were formed by seeded growth in a solution system of Zn(NO₃)₂–HMT.⁶ In addition to controlling the degree of supersaturation in the system, a seed layer on the surface of the substrate is required for the fabrication of densely packed ZnO nanorods on the substrate. The degree of orientation of the nanorods grown in a Zn(NO₃)₂–HMT system was reported to be dominated by the seed density.²⁵ The diameter of ZnO nanorods decreased, and the arrangement changed from a random to a high orientation with the increase in the seed density. This indicates that the direction of ZnO nanorods was oriented through geometrical selection.⁶ The introduction of seed particles with various densities on a substrate to a solution having a controlled degree of supersaturation is an effective way to obtain ZnO-arranged nanorods with controlled diameters.

4.4 Epitaxial growth of ZnO nanocrystals on a single-crystalline substrate

Although the nanorods of ZnO grown on a substrate covered with a low density of seed particles were roughly arranged on a
substrate, a deficient crystallographic arrangement was achieved through the geometrical selection. When a single-crystalline ZnO(001) substrate rather than a polycrystalline layer was utilized as a substrate for crystal growth, vertical and in-plane crystallographic orientation of ZnO rods was preferentially achieved through epitaxial growth on a Zn-face single-crystalline ZnO(001) substrate, as shown in Fig. 5(c) and (d).51) Homoeptaxial growth of upright ZnO rods was successfully achieved on a mirror-polished Zn face on a single-crystalline ZnO(001) substrate. Needle-shaped ZnO crystals with a pointed top (Fig. 5(e)) and hexagonal ZnO prisms with a flat end (Fig. 5(f)) were epitaxially grown on GaN-buffered Al2O3(001) substrates in a solution system of Zn(NO3)2–NH4NO3–NH4OH and Zn(NO3)2–sodium citrate–NH4OH, respectively.53) The needle-shape with a pointed top was frequently observed when the growth rate was relatively high not only on a substrate but also in precipitates. Metastable high index faces would appear in the acicular forms rather than the stable facets when relatively fast growth in c direction occurred.59) On the other hand, the c face of hexagonal prisms was stabilized with the adsorption of citrate ions as mentioned in the following section. The epitaxial growth was not restricted to the perpendicular direction to the substrate surface. By combining the saturated solution of Zn(NO3)2 and NaOH and the degenerate p-type Si(001), tilted epitaxial deposition of ZnO nanospears was reported (Fig. 5(g, h)).56) On the basis of the data of X-ray pole figure analysis, 51°-tilting nanospears relative to the surface normal were reported. From these examples, it is clear that the surfaces of single-crystalline films and substrates strictly govern the orientation of ZnO crystals through homo- and hetero-epitaxial growth.

4.5 Complex structures developing on the initially grown crystal through secondary nucleation and growth

We described the secondary crystal growth of ZnO by introducing seed particles and seed-coated and single-crystalline substrates into the aqueous system. However, similar progressive growth is also promoted through secondary nucleation and growth under a controlled degree of supersaturation, and complex shapes are then formed even without seeding. Complex structures with oriented branches on the side planes of core crystals have been reported.48)−51) In Fig. 6, several kinds of ZnO branched crystals precipitated in an agar gel and grown on a glass microslide in solutions are shown. A star shape (Fig. 6(b)) was formed through the projections attributed to the six-fold symmetry of the wurtzite structure in the upper layer of the gel from the side of NaOH diffusion. We also observed an embryo of the projection at the center of an ellipsoidal particle (Fig. 6(a)). Therefore, the star shape is presumed to be produced by branching growth on the ellipsoid through the twin formation.
Furthermore, some of the typical star-shaped particles were changed to the characteristic morphologies shown in Fig. 6(c). Thus, the characteristic shapes are deduced to be formed through a process including nucleation and subsequent crystal growth.

Furthermore, as shown in Fig. 6(e), branched structures were observed on substrates in a Zn(NO$_3$)$_2$-HMT system with diaminobutane.$^{40}$ Here, after the core rods (Fig. 6(d)) were prepared on substrates in solutions, the branches were oriented on the side planes of core crystals through the site-specific nucleation and growth.$^{40,41}$ As a result, we assume that the core crystals can be regarded as a kind of seed regardless of the existence of substrates.

5. Effect of the organic additives as shape modifiers of ZnO crystals

5.1 The principle of morphological variation with adsorption

Generally, isotropic small grains are formed in the initial stage of crystal growth through homogeneous nucleation. In the case of ZnO, hexagonal rods are naturally produced in the successive stage due to the shape of the unit cell. The adsorption of organic species on specific surfaces, such as (001), changes the morphology from the rods to plates (Fig. 2). The balance of the growth rates in the crystallographic directions determines the final shape of the ZnO crystals.

5.2 Variation of ZnO particles through homogeneous nucleation

The presence of various organic molecules obviously resulted in the formation of the characteristic structure. Sophisticated nanorods with controlled aspect ratios were formed by the addition of poly (diallyldimethylammonium chloride) (PDADMAC) with tertiary amine groups, sodium poly (styrene sulfonate) (PSS) with sulfonate groups, and trisodium citrate with three carboxylic groups as crystal growth modifiers into the seed-containing aqueous system comprising Zn(NO$_3$)$_2$ and HMT.$^{39}$ As typically shown in Fig. 7(a)–(d), the morphological change was observed using sodium citrate. The aspect ratio was reduced in the presence of sodium citrate. Thus, the specific adsorption on the basal planes of ZnO crystals suppresses the growth along the c direction. These organic additives could alter the relative growth rates of each crystal face and influence the crystal shape during the growth stage of the seed particles.

5.3 Morphological variation of oriented ZnO crystals on substrates

The effects of various organic molecules as crystal growth modifiers were investigated for the growing process of ZnO crystals under the proper supersaturation on ZnO seed layers in aqueous systems. The morphological variation of wurtzite-type ZnO crystals grown on a substrate in basic aqueous solutions was investigated using a wide variety of organic molecules with carboxy and sulfonic groups.$^{37}$ The effect of the organic molecules on the nanometric morphology was classified into several categories, such as rods, plates, grains, mosaics, and fibrils, as shown in Fig. 8.
Hexagonal plates exhibiting the (001) planes (Fig. 8(a)–(d)) were obtained by a planarizing effect with the addition of sodium citrate, tartaric and maleic acids as shown in Fig. 3. On the other hand, sodium acetate, salicylic, fumaric, and succinic acids exhibited no effects on the morphology. The production of nanograins (Fig. 8(e) and (i)) was observed by a miniaturizing effect with the addition of a polymeric molecule with carboxy groups and an anionic surfactant with a sulfonic group. Mosaic structures composed of granular crystals (Fig. 8(g) and (h)) and bundles consisting of fibrils (Fig. 8(i) and (j)) elongated in a direction toward the c axis were produced by the addition of bulky dye molecules having benzene rings and carboxy or sulfonic groups. Similar mosaic structures were also obtained by electrodeposition with dye molecules.  

Interestingly, nanograins in the structure were oriented in the same crystallographic orientation. Moreover, nanowires consisting of oriented ZnO nanograins were prepared in the presence of pyranine. These are regarded as a new type of assembled crystals named mesocrystal. The influence of the organic molecules was related to the number of functional groups and the stereochemical structure. The adsorbability of the organic molecules depending on the chemical structure to the specific crystal faces is found to be essential for the variation of the nanometric morphology. These results are associated with the nanoscale morphological design of wurtzite ZnO crystals grown in aqueous systems. In the end, it seemed better to introduce the organic crystal growth modifiers in the system during the growth stage without or after the nucleation process in order to obtain ZnO crystals with controlled sizes, morphologies, and high crystallinity.

5.4 Morphological variation of epitaxial ZnO crystals on substrates

The combination of epitaxial growth and morphological variation with an organic molecule was utilized for the production of crystallographically oriented nanoscale architectures. A unique ZnO nanostructure with a crystallographic symmetry yet a nanoscopically winding complex morphology was formed in a solution system including a single-crystalline ZnO substrate and a pyramidal molecule with sulfonic groups, as shown in Fig. 5(i) and (j). Although nanowires exhibited a winding and bending morphology, the six-fold symmetry of the crystal lattice suggests that the nanowires were crystallographically connected in the nanoarchitectures, from the GI-XRD measurement which was previously described in detail. This regularity was due to the introduction of a single-crystalline substrate instead of the polycrystalline substrate, while the orientation of each wire was random in our previous work.

6. Summary

In this review, we showed a wide variety of effective approaches to control the nanoscaled morphologies of ZnO crystals through wet chemical processing routes. The morphologies of ZnO crystals are classified into several categories. The morphological variation of ZnO crystals was achieved by controlling the degree of supersaturation, introducing seed particles and seed-coated or single-crystalline substrates, and adding organic molecules with specific groups. These actions brought control of the following: (i) the degree of supersaturation (balance of the nucleation and the growth), (ii) the growth sites (growth on seed particles and on several substrates), and (iii) the growth direction (growth rate) using organic additives. Therefore, various targeted morphologies could be obtained by the selection of the strategy on the basis of the guiding principle for the morphological design of ZnO crystals in solutions. The concept would be useful in the design of functional ceramic materials produced in solution systems for industrial process.

References
Kawano et al.: Nanoscale morphological design of ZnO crystals grown in aqueous solutions