RAPID PAPER

Preparation of Hexagonal Plate-like ZnO Single-crystal Particles in the Presence of Anionic Amphiphiles

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Abstract: In this study, we synthesized ZnO particles using anionic amphiphiles as an additive. While the single-crystal particles prepared in the absence of such amphiphiles had a hexagonal rod-like shape, those fabricated using anionic amphiphilic molecules had a hexagonal plate-like shape. The anionic amphiphiles inhibited crystal growth in the *c*-axis direction of ZnO. This demonstrated that the anionic surfactants served as crystal-growth-directing agents, controlling the shape of the ZnO particles.

Key words: zinc oxide, single crystal, anionic amphiphiles, crystal-growth-directing agents

Zinc oxide (ZnO) is one of the most important materials used in photocatalysts¹⁻⁹ and electronic devices¹⁰⁻²⁰. The particle size, particle shape, and crystallinity strongly affect the physical and chemical properties of ZnO. By varying reaction conditions such as the species used as the zinc oxide precursor, the pH value, the reaction temperature, the reaction time, and the additives used, the particle size, particle shape, crystallinity, and orientation can be easily controlled²¹. The present investigation aimed to achieve control of the shape and properties of ZnO by changing the reaction conditions. Various ZnO shapes, such as rods, tetrapods²²⁻²⁴ and flower-like particles²⁵⁻²⁸, were clearly identified. These structures were assumed to be the polar surfaces of *c*-faces. Here, two-dimensional materials, such as sheet-like structure, have gathered increasing attention due to their possible applications to heterogeneous catalysts and energy-related materials²⁹⁻³¹. However, two-dimensional ZnO has not been reported.

Amphiphilic molecules often form self-assemblies and are adsorbed on inorganic materials in specific ways. These properties have been exploited in the synthesis of inorganic materials. Much effort has been devoted to the fabrication of mesoporous inorganic materials using self-assemblies of

amphiphiles as templates³²⁻³⁹. Mesoporous materials are typically synthesized using cationic surfactants as amphiphilic molecules. On the other hand, specific adsorption of amphiphiles often occurs on inorganic materials⁴⁰⁻⁴². This property promises that the synthesis of ZnO particles with amphiphiles as additives will provide a novel technique for controlling the particle shape, particle size, crystallinity, and orientation of ZnO due to their specific adsorption. However, few studies have addressed the synthesis of ZnO using amphiphilic molecules as additives. Here, we report a novel technique for preparing ZnO single-crystal particles using anionic amphiphiles. We also demonstrate the role of anionic amphiphilic molecules in the formation of ZnO.

Zinc sulfate heptahydrate (ZnSO₄·7H₂O; Wako Pure Chemical Industries, Ltd.) and sodium hexadecyl sulfate (SHS; Wako Pure Chemical Industries, Ltd.) were used as the zinc oxide precursor and anionic surfactant, respectively. An aqueous ammonia solution (Kanto Chemical Co., Inc.) was used for pH adjustment.

6.20 g of SHS was added to 45 ml of ion-exchanged water and stirred at 343 K for 2 h. The resulting SHS solution, which was adjusted to pH 12 using the ammonia solution, was mixed with 10 ml of 2 M aqueous ZnSO₄ solution

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Fig. 1 XRD patterns for particles synthesized in the (a) presence and (b) absence of SHS.

and stirred at 343 K for 24 h. After stirring, a hydrothermal treatment was carried out at 423 K for 24 h. For comparison, the particles were synthesized through the same procedure without the addition of SHS. A part of the mixture was centrifuged and washed with ion-exchanged water. The samples obtained were characterized using scanning electron microscopy (SEM; Keyence, VE-7800). The rest of the mixture was filtered, washed with ion-exchanged water and dried at 333 K for 24 h. The crystal structure of these particles was investigated using X-ray diffraction (XRD; Rigaku, MiniFlex600 CuK α radiation) and high-resolution transmission electron microscopy (TEM; H-9000UHR).

Figure 1 shows XRD patterns of the particles obtained in the (a) presence and (b) absence of SHS. Both XRD patterns showed five diffraction peaks at around 31.8, 34.4, 36.2, 47.5 and 56.6° due to the (100), (002), (101), (102), and (110) reflections, respectively, indicating the formation of zinc oxide. The intensity of the peak assigned to the (002) reflection of the particles obtained with SHS was higher than that for the particles synthesized without SHS. The intensity ratio $I_{(002)}/I_{(101)}$ was calculated to normalize the intensity of the peak assigned to the (002) reflection with respect to that of the (101) reflection. The $I_{(002)}/I_{(101)}$ ratios

for the particles fabricated in the presence and absence of SHS were 4.6 and 2.6×10^{-1} , respectively. These results suggested that the particles synthesized with SHS were zinc oxide particles with a strong (002) orientation.

Next, we conducted SEM to investigate the morphologies of the synthesized particles. Figure 2(a) shows an SEM image of hexagonal plate-like particles (size: 10 μm) fabricated in the presence of SHS. The particles fabricated in the absence of SHS had rod-like shapes with a size of around 1.0 μm (Fig. 2(b)). Wurtzite (hexagonal crystal system) is known to be the thermodynamically stable crystal structure of ZnO. This means that the *c*-face of ZnO has a hexagonal structure. The SEM image of ZnO particles synthesized in the presence of SHS strongly suggested that preferential crystal growth of the *c*-face occurred. This is in good agreement with the XRD patterns obtained.

Figure 3 shows electron diffraction (ED) patterns for the samples obtained using a focused ion beam (FIB). Figures 3(a) and 3(b) clearly show ED patterns for the hexagonal face of ZnO and for a face perpendicular to this hexagonal face. Figures 3(a) and 3(b) indicate that the hexagonal face and perpendicular face are the *c* and *a-c* faces, respectively, indicating the formation of ZnO single-crystal particles. These results clearly showed that the particles obtained in the presence and absence of SHS were hexagonal plate-like and hexagonal rod-like ZnO single-crystal particles, respectively.

Finally, we consider the role of SHS. Figure 4 shows a schematic illustration of the formation mechanism of ZnO particles in the absence and presence of SHS, respectively. Hexagonal plate-like ZnO single-crystal particles were formed in the presence of SHS. This suggests that SHS was adsorbed on the *c*-faces of ZnO particles during ZnO crystal growth and that SHS inhibits crystal growth along the *c*-axis direction. These results indicate that SHS acts as a crystal-growth-directing agent.

In this study, ZnO particles were synthesized in the presence and absence of SHS, and the morphology and crystal structure of the resulting particles were investigated. The particles obtained in the presence and absence of SHS were hexagonal plate-like and hexagonal rod-like single-

Fig. 2 SEM images of particles synthesized (a) with and (b) without SHS.

Fig. 3 ED patterns for (a) the hexagonal face and (b) the face perpendicular to the hexagonal face of particles synthesized in the presence of SHS.

crystal ZnO particles, respectively. Clearly, SHS acted as a crystal-growth-directing agent. This represents the first study to use amphiphilic molecules to govern the crystal growth direction. This novel function is expected to play an important role in the fabrication of crystal-growth-controlled inorganic materials.

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Fig. 4 Schematic illustration of ZnO particles formation in the absence and presence of SHS, respectively.

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