Effect of Anionic Amphiphiles on the Morphology of Hexagonal Plate-like ZnO Particles

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Abstract: Zinc oxide (ZnO) particles were synthesized in the presence of anionic surfactants (ASs). The effect of ASs on the morphology of the ZnO particles was investigated by using ASs with various alkyl chain lengths and changing the molar ratio of AS/ZnSO₄. Hexagonal plate-like ZnO particles were formed in the presence of ASs. Adsorption of the AS on the c face of the ZnO crystals inhibited (promoted) crystal growth along the c-axis (ab-axis) direction. Increasing the molar ratio of AS/ZnSO₄ decreased the particle thickness, owing to the resulting increase in the coverage of the c face with AS. The particle diameter of the hexagonal plate-like ZnO particles (the diagonal length of the hexagonal plate) increased with increasing alkyl chain length of AS as a result of the van der Waals interactions between the alkyl chains. The data indicate that the particle diameter and thickness can be controlled by fine-tuning the van der Waals interactions between the alkyl chains and the coverage of the c face of the ZnO particles with AS.

Key words: crystal-growth-directing agent, zinc oxide, van der Waals interaction, anionic amphiphiles

1 Introduction

Zinc oxide (ZnO) is a well-known semiconductor used in photocatalysis to decompose organic compounds in electronic devices, as it generates holes and electrons under UV irradiation. The crystallinity and particle size of ZnO significantly influence its properties. Thus, methods of controlling the crystal growth and morphology of ZnO have been investigated. One of the most favorable morphologies is the one-dimensional morphology, including the rod-like shape, which is the most favorable morphology controlling the crystal growth and morphology of ZnO particles free of mesopores via hydrothermal treatment in the presence of an anionic surfactant (AS). Therein, the surfactant determined the crystal growth direction. However, the mechanism by which the surfactant acts as a crystal growth-directing agent is unclear. In this study, the fabrication of ZnO particles using ASs as a crystal-growth-directing agent is discussed based on the above results.
2 Experimental

2.1 Materials

Zinc sulfate heptahydrate (ZnSO₄·7H₂O; Wako Pure Chemical Industries, Ltd.) was used as the ZnO precursor. Sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium hexadecyl sulfate (SHS), used as ASs, were purchased from Wako Pure Chemical Industries, Ltd. An aqueous ammonia solution (Kanto Chemical Co., Inc.) was used for pH adjustment. 1,3,5-Trimethylbenzene (Kanto Pure Chemical Industries, Ltd.) was used to determine the dispersion properties.

2.2 Preparation of zinc oxide particles

Each AS was added to 45 mL of ion-exchanged water and stirred at 343 K for 2 h. Five milliliters of an aqueous ammonia solution and 10 mL of a 1 M aqueous ZnSO₄ solution were mixed with 45 mL of the aqueous AS solution and stirred at 343 K for 24 h. The ZnSO₄ concentration was fixed. The molar ratio of AS/ZnSO₄ ([AS]/[ZnSO₄]) was varied from 0 to 0.50. After stirring at 343 K for 24 h, hydrothermal treatment was carried out at 423 K for 24 h. A certain portion of the obtained particles was centrifuged and washed with ion-exchanged water. The morphology of the particles was observed by scanning electron microscopy (SEM; Keyence, VE-7800). The remainder was filtered, washed with ion-exchanged water, and dried at 333 K for 24 h. The samples were characterized by X-ray diffraction (XRD; Rigaku, MiniFlex600 Cu-Kα radiation) and Fourier-transform infrared spectroscopy (FT-IR; JASCO, FT/IR-4200).

3 Results and Discussion

3.1 Preparation of zinc oxide particles using various anionic surfactants

First, ZnO particles were synthesized using various ASs and the morphology of the resulting particles was examined. The molar ratio of AS to ZnSO₄ was 0.50. For comparison, ZnO particles were synthesized without the addition of ASs. Figure 1 shows the XRD patterns of the particles synthesized in the presence and absence of the ASs. All XRD patterns have five diffraction peaks at approximately 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 [10, 15]. The intensity of the (002) peak for the particles synthesized with ASs was much higher than that of the particles obtained in the absence of ASs. The I_{002}/I_{101} intensity ratio was calculated to normalize the (002) peak intensity with respect to the (101) peak intensity. The I_{002}/I_{101} ratio for the particles fabricated in the absence of AS was 0.21, compared to an I_{002}/I_{101} ratio of ~24 for all samples synthesized in the presence of ASs. These results suggest that the particles synthesized with ASs are zinc oxide particles with a high c face orientation.

SEM images of the particles synthesized in the (a) absence and (b–d) presence of ASs having different alkyl chain lengths. (b), (c), and (d) are for SDS, STS, and SHS, respectively.

Fig. 1 XRD patterns of particles synthesized in the (a) absence and (b–d) presence of ASs having different alkyl chain lengths. Panels (b)–(d) correspond to SDS, STS, and SHS, respectively.

Fig. 2 SEM images of particles prepared in the (a) absence and (b–d) presence of ASs having different alkyl chain lengths. (b), (c), and (d) are for SDS, STS, and SHS, respectively.
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The mechanism of formation of the hexagonal plate-like ZnO particles was evaluated. A Zn atomic layer was present along the c face of the ZnO crystal structure. ASs can be easily adsorbed on the c faces of the ZnO particles owing to the electrostatic interaction between the Zn atoms and the hydrophilic groups of the ASs during growth of the ZnO crystals. Adsorption of the AS inhibits crystal growth along the c-axis (ab-axis) direction. As a result, hexagonal plate-like ZnO particles are formed when ASs are present in the solution. These results indicate that ASs can serve as crystal-growth-directing agents.

3.2 Effects of AS alkyl chain length and AS/ZnSO₄ molar ratio on ZnO particles

The effect of the AS/ZnSO₄ molar ratio on the morphology of the ZnO particles was investigated. [AS]/[ZnSO₄] varied from 0 to 0.50. Figure 4 shows the XRD patterns of the ZnO particles synthesized using SDS. The XRD patterns of the particles fabricated using STS and SHS are shown in Figs. S2 and S3, respectively. The diffraction peaks assigned to ZnO were observed at all molar ratios, regardless of the type of AS. The intensity of the (002) peak increased with increasing [AS]/[ZnSO₄]. The I₀₀₂/I₁₀₀ intensity ratio was then calculated. Figure 5 shows the plot of I₀₀₂/I₁₀₀ versus [AS]/[ZnSO₄]. I₀₀₂/I₁₀₀ gradually increased for [SDS]/[ZnSO₄] = 0–0.15. At [SDS]/[ZnSO₄] > 0.20, I₀₀₂/I₁₀₀ was constant. The same trends were observed when ZnO particles were prepared using STS and SHS. These results suggest that hexagonal plate-like ZnO particles are formed when [AS]/[ZnSO₄] is 0.20 or higher.

SEM was used to observe the effects of changing the AS species and [AS]/[ZnSO₄] on the particle shape. Figure 6 shows the SEM images of the ZnO particles synthesized using SDS. When [SDS]/[ZnSO₄] was changed from 0 to 0.15, ZnO particles with hexagonal rod-like shapes were formed. The average particle diameter (diameter means the diagonal length of the hexagonal plate) and thickness were 0.8 and 2.9 μm, respectively. When [SDS]/[ZnSO₄] was 0.20 or higher, hexagonal plate-like particles were formed.

**Fig. 3** Photographs of solutions having two phases after the addition of ZnO particles synthesized in the (a) absence and (b) presence of SHS. The upper and lower phases were 1,3,5-trimethylbenzene and water, respectively.

**Fig. 4** XRD patterns of particles synthesized in the (a) absence and (b-k) presence of SDS. Curves (b)-(k) show diffraction patterns for ZnO particles fabricated with SDS/ZnSO₄ molar ratios of 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, and 0.50, respectively.
where the particle diameter was \( \sim 1.8 \, \mu m \), with a particle thickness of \( \sim 0.8 \, \mu m \). SEM images of the particles prepared using STS and SHS are shown in Figs. S4 and S5, respectively. Regardless of the AS species, the particle shape showed the same trends as in the case of SDS. These results indicate that the morphology of the ZnO particles can be controlled by varying the ASs/ZnSO\(_4\) molar ratio.

The average particle diameter and thickness were estimated from the SEM images. Figure 7 shows the relationship between the average particle diameter, thickness, and [AS]/[ZnSO\(_4\)]. With increasing [AS]/[ZnSO\(_4\)], the average particle diameter (thickness) gradually increased (decreased) and became saturated at [AS]/[ZnSO\(_4\)] \( \geq 0.20 \). These results demonstrate successful control of the particle diameter and thickness by changing the amount of AS within the range of [AS]/[ZnSO\(_4\)] \( = 0 \rightarrow 0.20 \). In this study, we focused on the average particle diameter obtained at [AS]/[ZnSO\(_4\)] \( \geq 0.20 \). The diameters of the particles synthesized with SDS, STS, and SHS were 1.8, 3.4, and 5.2 \( \mu m \), respectively. The particles prepared with STS and SHS are approximately two and three times larger than those fabricated with SDS. This confirms successful control of the particle diameter by varying the AS species.

Finally, the effects of the ASs on the particle diameter and thickness were evaluated. First, the effect of the ASs on the particle thickness was considered. AS is adsorbed on the \( c \) face of ZnO and results in the formation of hexagonal plate-like particles. When [AS]/[ZnSO\(_4\)] was below 0.20, only a small amount of AS was adsorbed onto the \( c \) face. This enhances crystal growth along the \( c \)-axis direction, and thus the formation of thick ZnO particles. The thickness decreased with increasing [AS]/[ZnSO\(_4\)]. This is because adsorbed ASs inhibit crystal growth along the \( c \)-axis direction given that the AS coverage increases as the amount of AS adsorbed on the \( c \) face of ZnO increases. The thickness was constant for [AS]/[ZnSO\(_4\)] \( \geq 0.20 \), presumably because the coverage of the \( c \) face was saturated. There was no significant variation in the average particle thickness with the AS type. The ASs with different alkyl
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The effect of the ASs on the particle diameter was also considered. When $[\text{AS}] / [\text{ZnSO}_4]$ was below 0.20, the particle diameter increased as the amount of AS increased. The particle diameter was constant for $[\text{AS}] / [\text{ZnSO}_4] \geq 0.20$. As with the particle thickness, this is assumed to be because increasing the coverage of the $c$ face inhibits (promotes) crystal growth along the $c$-axis ($ab$-axis) direction. Meanwhile, increasing the alkyl chain length resulted in the formation of larger particles. The van der Waals interaction between the alkyl chains of the ASs increases with increasing number of carbon atoms in the alkyl chain. Thus, the interaction between ASs having longer alkyl chains is stronger. The stronger hydrophobic interaction due to ASs with longer alkyl chains adsorbed on the $c$ faces promotes crystal growth along the $ab$-axis (parallel to the $c$ face). As a result, the diameters of the particles prepared using an AS with a longer alkyl chain are larger. ASs can act as crystal-growth-directing agents owing to interactions such as van der Waals and electrostatic attraction.

4 Conclusions

In this study, hexagonal plate-like ZnO particles were synthesized through a hydrothermal process in the presence of ASs with different alkyl chain lengths. The effect of the ASs on the morphology of the ZnO particles was investigated. AS adsorption on the $c$ face of ZnO inhibited crystal growth along the $c$-axis direction, resulting in the formation of hexagonal plate-like particles. The diameter and thickness of the ZnO particles were determined by the coverage of the $c$ face, that is, the amount of adsorbed AS. It was also demonstrated that the alkyl chain length of the AS affected the particle diameter. When ZnO particles were synthesized with an AS having a long alkyl chain length, large ZnO particles were formed. The van der Waals interactions between the alkyl chains of the AS determined the particle diameter. These findings suggest that the particle diameter and thickness can be controlled by fine-tuning the van der Waals interactions and the coverage of the $c$ face. To the best of our knowledge, this is the first report on the control of the shape, diameter, and thickness of metal oxide particles using surfactants. The present technique is expected to play an important role in the fabrication of inorganic particles that require precise control of the shape, diameter, and thickness.

Supporting Information

This material is available free of charge via the Internet at https://dx.doi.org/ios.70.10.5650/jos.ess21062

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