Preparation and Photocatalytic Activity of Hexagonal Plate-like ZnO Particles Using Anionic Surfactants
Masato Amano, Kazuaki Hashimoto, and Hirobumi Shibata

Faculty of engineering, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, JAPAN

Abstract: Hexagonal plate-like ZnO particles with a high degree of c-face orientation have been synthesized using hydrothermal method in the presence of various anionic surfactants bearing different hydrocarbon chains. The c-face of the ZnO particles increased upon increasing the surfactant alkyl chain length. The photocatalytic activity of the as-obtained hexagonal plate-like ZnO particles was evaluated using the degradation of methylene blue (MB). Although the specific surface area of hexagonal rod-like particles is higher than that of hexagonal plate-like particles, the amount of MB adsorption on the ZnO particle surface was different for the hexagonal plate-like and rod-like particles. In addition, the hexagonal plate-like ZnO particles showed a significantly higher decrease in the MB concentration with the duration of ultraviolet light irradiation when compared to the hexagonal rod-like ZnO particles obtained in the absence of a surfactant. These results indicate that crystal-face-controlled ZnO with a high degree of c-face orientation exhibits high photocatalytic activity.

Key words: zinc oxide, photocatalysis, anionic surfactant, crystal growth

1 Introduction
ZnO is a functional inorganic material applicable to pigments, cosmetics, photocatalysts, self-cleaning glass, and electronic devices. Controlling the ZnO particle shape is important because the various functions of ZnO are dependent on the particle shape. ZnO synthesis methods include sol-gel¹⁴, precipitation⁰, hydrothermal⁷, and chemical vapor deposition⁰⁹ methods. Changing the reaction conditions such as the pH, temperature, time and additives during the hydrothermal synthesis has yielded various shapes of ZnO particles including spherical¹³, whisker-like⁴, and tube-like materials¹⁰. However, controlling the morphology of ZnO particles is difficult. Controlling the shape, size, and homogeneity of ZnO particles would expand their applications as functional inorganic materials.

ZnO has a band gap of 3.37 eV and exhibits photocatalytic activity under ultraviolet (UV) irradiation. When the particles are irradiated with light corresponding to the band gap, the electrons of oxygen and zinc atoms are excited, and holes and electrons are generated in the valence and conduction bands, respectively. The generated electrons and holes react with oxygen and absorb water on the surface of the ZnO particles, generating active oxygen species, such as hydroxyl radicals and superoxide anions. Active oxygen species can easily decompose organic compounds containing carbon and nitrogen atoms. Therefore, ZnO has been applied in environmental fields, such as air purification and soil treatment processes used to decompose environmental pollutants. During the photocatalytic reaction, the reaction is limited to the particle surface; therefore, the smaller the particle size, the higher the specific surface area and the better the photocatalytic activity. However, agglomeration accompanied by a decrease in the particle size reduces the dispersion stability, which results in a decrease in the photocatalytic activity. Furthermore, it is important to control the shape and size of the particles because it is necessary to consider the adsorbability of the reactants. Maclaren et al. reported the synthesis of ZnO particles with a hexagonal plate-like shape, which was controlled using a hydrothermal method in the presence of oleic acid. Oleic acid is adsorbed specifically on the c-face of the ZnO particles, which changes the interfacial free energy of the particle surface, thereby changing both the crystal growth rate and particle shape. The presence of additives interacting with the particle surface significantly affect the particle shape. Therefore, we focused on surfactants that exhibit specific adsorption behavior at the interface. In this study, we prepared ZnO particles with various shapes using anionic surfactants bearing different alkyl chain lengths.
and investigated the effect of their shape on the photocatalytic activity.

2 Experimental Section

2.1 Materials

Zinc sulfate heptahydrate (Wako Pure Chemical Co., Ltd.) was used as the precursor for ZnO particles. Sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium hexadecyl sulfate (SHS) were used as anionic surfactants (ASs) and purchased from Wako Pure Chemical Co., Ltd. Methylene blue (MB; Kishida Chemical Co., Ltd.) was used as the reaction substrate to investigate the photocatalytic activity.

2.2 Preparation of ZnO particles

The various ASs were dissolved in 45 mL of ion-exchanged water and stirred at 70°C for 2 h to obtain a 300 mM AS solution. Next, 5 mL of an aqueous ammonia solution was added to the AS solution to adjust the pH to 13–14, and 10 mL of 2 M aqueous zinc sulfate solution was added to obtain the precursor solution. After stirring this precursor solution at 70°C for 24 h, the hydrothermal synthesis was performed at 150°C for 24 h. The obtained particles were then washed with ion-exchanged water. For comparison, ZnO particles were synthesized in the absence of the ASs. The samples were characterized using X-ray diffraction (XRD; Rigaku, MiniFlex600 Vu-Kα radiation) and Fourier-transform infrared (FT-IR) spectroscopy (JASCO, FT/IR4200). The morphology of the particles was observed using scanning electron microscopy (SEM; Keyence VE-7800).

2.3 Evaluation of the photocatalytic activity of ZnO particles

ZnO particles (0.2 g) calcined at 450°C for 1 h were added to 50 mL of a 0.01 mM MB aqueous solution. The mixed solution was stirred for 90 min under irradiation with UV light at 240 mW/m² from a xenon lamp (XF-152S Tokina Co., Ltd.). The discoloration of MB under light irradiation was monitored every 15 min using UV-visible (vis) spectroscopy (JASCO, V-750).

3 Results and Discussion

3.1 Preparation of ZnO particles using ASs

ZnO particles were synthesized with and without ASs bearing different alkyl chain lengths. Figure 1 shows the XRD patterns obtained for the particles synthesized in the presence of the various ASs. SDS/ZnO, STS/ZnO, and SHS/ZnO were synthesized using SDS, STS, and SHS, respectively. All the XRD patterns obtained for the as-prepared particles show five diffraction peaks at 31.8°, 34.4°, 36.2°, 47.5°, and 56.6° corresponding to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), and (1 1 0) reflections, respectively, indicating the formation of ZnO. The intensity of the peak assigned to the (0 0 2) plane of the ZnO particles obtained in the absence of the ASs was lower than that of the (1 0 0) plane. In contrast, the intensity of the (0 0 2) peak observed for ZnO synthesized in the presence of the ASs was higher than that of the (1 0 0) plane. The I_{002}/I_{100} intensity ratio was calculated to normalize the intensity of the (0 0 2) plane with respect to the (1 0 0) plane. Although the I_{002}/I_{100} ratio for the particles fabricated in the absence of AS was 0.44, the I_{002}/I_{100} ratios for SDS/ZnO, STS/ZnO, and SHS/ZnO were 0.78, 5.55, and 11.4, respectively. These results suggest that the particles synthesized using ASs bearing longer alkyl chains are ZnO particles with a higher degree of c-face orientation.

Figure 2 shows the SEM images of the ZnO particles obtained in the absence and presence of ASs. The particles synthesized without ASs exhibit rod-like shapes (Fig. 2a), whereas hexagonal plate-like particles were formed in the presence of the ASs (Figs. 2b-2d). The thermodynamically stable crystal structure of ZnO is wurtzite. This indicates that the ZnO particles synthesized in the presence of the ASs have a high degree of c-face orientation. These results were in good agreement with the XRD measurements obtained for the particles prepared in the presence of the ASs.
The particle diameter of the $c$-face and thickness of the ZnO particles were estimated using SEM images; the particle diameter was defined as the diagonal length of the hexagonal plate, as shown in Fig. 3. The diameter and thickness of the hexagonal rod-like particles were 0.9 and 3.5 µm, respectively. The aspect ratio was 0.3. In contrast, the diameters of SDS/ZnO, STS/ZnO, and SHS/ZnO were 2.9, 5.2, and 6.7 µm, respectively, while the thickness of the particles synthesized using ASs bearing longer alkyl chain lengths increased. The ASs adsorbed on the $c$-face of the ZnO particles experience van der Waals forces between the alkyl chains in the ASs, which change depending on the alkyl chain length\textsuperscript{27}. The longer the alkyl chain, the larger the van der Waals force acting between the alkyl chains in the AS and larger particles are formed\textsuperscript{28, 29}. In contrast, the adsorption of ASs on the $c$-face inhibits crystal growth along the $c$-axis. The hydrophilic groups in the ASs are identical, and the attractive forces formed between the Zn atoms of the $c$-face and the hydrophilic groups in the ASs are constant. This means that the force to inhibit crystal growth against the $c$-axis does not vary with the type of AS used. Consequently, the particle thicknesses obtained using the various ASs were the same. Therefore, we successfully prepared hexagonal plate-like ZnO particles with control of their diameters using ASs bearing various alkyl chain lengths.

### 3.2 Evaluation of the photocatalytic activity

The photocatalytic activities of the as-obtained hexagonal rod-like and calcined hexagonal plate-like ZnO particles were evaluated. Figure 4 shows the UV-vis spectra obtained for the MB solutions containing ZnO particles under UV light irradiation from a xenon lamp. The absorbance of the solutions was measured every 15 min. The absorbance attributed to MB decreases over time for all the samples studied. There was a difference in the decrease in the absorbance between the hexagonal rod-like ZnO particles and various hexagonal plate-like ZnO particles. Furthermore, the specific surface areas estimated using the Brunauer–Emmett–Teller (BET) method from the nitrogen adsorption-desorption isotherms of various hexagonal plate-like ZnO particles were 0.45, 0.39, 0.29, and 0.82 m$^2$/g for SDS/ZnO, STS/ZnO, SHS/ZnO, and rod-like ZnO, respectively. Although the specific surface areas of all the particles were approximately the same, the MB degradation rates of the plate-like ZnO particles were clearly higher than those of the rod-like ZnO particles. These results suggest that hexagonal plate-like ZnO particles have a higher photocatalytic activity than rod-like ZnO particles.

---

**Fig. 2** SEM images of ZnO particles synthesized in the presence of various ASs (a: ZnO without AS; b: SDS/ZnO; c: STS/ZnO; d: SHS/ZnO).

**Fig. 3** Average particle size ($c$ face diameter) and thickness measurements of various shaped ZnO particles.
The concentration of MB was calculated utilizing the Lambert–Beer equation using the absorbance observed at 664 nm, which is the maximum absorption wavelength of MB. The change in the concentration of the MB solution with the UV irradiation time was plotted, as shown in Fig. 5. The samples were placed in the dark from –45 to 0 min and irradiated with UV light from 0 min. When the hexagonal rod-like ZnO particles prepared in the absence of the ASs were dispersed, the concentration of the MB solution was almost constant in the dark and gradually decreased under UV light irradiation. This indicates that the decrease in the MB concentration in the dark and under UV light irradiation originates from its adsorption on the rod-like ZnO particles and photocatalytic decomposition, respectively. Conversely, the concentration of the MB solution significantly decreases from –45 to –30 min for all the hexagonal plate-like ZnO particles. This means that the concentration decreases owing to adsorption on the ZnO surface. In addition, the MB concentration observed for the hexagonal plate-like ZnO particles gradually decreases under UV irradiation from 0 to 90 min, indicating that the hexagonal plate-like ZnO particles exhibit photocatalytic activity.

The surface hydroxyl groups on the ZnO particles are involved in the adsorption of MB. MB was adsorbed via electrostatic interactions between S” in the molecular structure of MB and the surface hydroxyl groups of the ZnO particles. The ratio of the surface area occupied by the c-face was significantly different between the hexagonal rod-like ZnO particles and hexagonal plate-like AS/ZnO particles. The number of surface hydroxyl groups in the hexagonal plate-like AS/ZnO particles is expected to be higher than that of hexagonal rod-like ZnO particles. Therefore, the amount of MB adsorbed on the hexagonal plate-like ZnO particles gradually decreases under UV irradiation from 0 to 90 min, indicating that the hexagonal plate-like ZnO particles exhibit photocatalytic activity.
plate-like ZnO particles in the dark was higher than that adsorbed on the hexagonal rod-like ZnO particles. These results clearly show that we have successfully prepared novel ZnO photocatalysts with specific adsorption abilities for MB in the dark.

4 Conclusions
In this study, we synthesized hexagonal plate-like ZnO particles using a hydrothermal process in the presence of ASs bearing various alkyl chain lengths. When ZnO particles were prepared without the ASs, the as-obtained particles possessed a hexagonal rod-like morphology. These results demonstrated that the ASs adsorbed on the c-face of ZnO inhibit crystal growth in the c-axis direction. Furthermore, the particle size increased upon increasing the alkyl chain length of the AS used.

The photocatalytic activity of the as-obtained particles under UV light irradiation was also investigated. The photocatalytic activities of the hexagonal plate-like and rod-like particles were almost identical. However, the amount of MB degradation exhibited by the hexagonal plate-like ZnO particles in the dark was much higher than that of the hexagonal rod-like ZnO particles. Although the specific surface area was lower, the amount of MB degradation observed for the ZnO particles with larger size was higher. The MB degradation observed in the dark is attributed to its adsorption on the ZnO particles. This observation showed that the hexagonal plate-like ZnO particles exhibit a specific adsorption ability toward MB. Considering these results, we have successfully synthesized a novel ZnO photocatalyst with specific absorption ability. The present technique is important for the fabrication and control of the shape of novel ZnO photocatalysts.

Conflicts of Interest
The authors declare that there are no conflicts of interest.

Author Contributions
M. Amano: Conception and design of study, Acquisition of data, Analysis of data, Drafting manuscript. K. Hashimoto: Conception and design of study, Analysis of data, Drafting manuscript. H. Shibata: Conception and design of study, Analysis of data, Drafting manuscript.

References
1) Clausen, C.A.; Green, F. III; Kartal, S.N. Weatherability and leach resistance of wood impregnated with nano-zinc oxide. *Nanoscale Res. Lett.* 5, 1464-1467 (2010).
2) Saito, N.; Goto, K. Development of a novel ZnO-cellulose complex with an excellent deodorant performance. *Flavour Frag. J.* 34, 31-37 (2006).
3) Wang, R.H.; Xin, J.H.; Tao, X.M. UV-blocking property of dumbbell-shaped ZnO crystallites on cotton fabrics. *Inorg. Chem.* 44, 3926-3930 (2005).
4) Look, D.C. Recent advances in ZnO materials and devices. *Mater. Sci. Eng. B* 80, 383-387 (2001).
5) Ohyama, M.; Kozuka, H.; Yoko, T. Sol-gel preparation of ZnO films with extremely preferred orientation along (002) plane from zinc acetate solution. *Thin Solid Films* 306, 78-85 (1997).
6) Chen, C.C.; Liu, P.; Lu, C.H. Synthesis and characterization of nano-sized ZnO powders by direct precipitation method. *Chem. Eng. J.* 144, 509-513 (2008).
7) Baruah, S.; Dutta, J. Hydrothermal growth of ZnO nanostructures. *Sci. Technol. Adv. Mater.* 10, 1-18 (2009).
8) Razail, R.; Zak, A.K.; Abd. Majid W.H.; Darroudi, M. Solvothermal synthesis of microsphere ZnO nanostructures in DEA media. *Ceram. Int.* 37, 3657-3663 (2011).
9) Lu, C.H.; Yeh, C.H. Influence of hydrothermal conditions on the morphology and particle size of zinc oxide powder. *Ceram. Int.* 26, 351-357 (2000).
10) Leelavathi, A.; Madras, G.; Ravishankar, N. Origin of enhanced photocatalytic activity and photoconduction in high aspect ratio ZnO nanorods. *Phys. Chem. Chem. Phys.* 15, 10795-10802 (2013).
11) Vernardou, D.; Kenanakis, G.; Couris, S.; Koudoumas, E.; Kymakis, E. *et al.* pH Effect on the morphology of ZnO nanostructures grown with aqueous chemical growth. *Thin Solid Films* 515, 8764-8767 (2007).
12) Zhao, X.; Li, M.; Lou, X. Sol-gel assisted hydrothermal synthesis of ZnO microstructures: Morphology control and photocatalytic activity. *Adv. Powder Technol.* 25, 372-378 (2014).
13) Zhou, J.; Zhao, F.; Wang, Y.; Zhang, Y.; Yang, L. Size-controlled synthesis of ZnO nanoparticles and their photoluminescence properties. *J. Lumin.* 122-123, 195-197 (2007).
14) Hu, J.Q.; Li, Q.; Wong, N.B.; Lee, C.S.; Lee, S.T. Synthesis of uniform hexagonal prismatic ZnO whiskers. *Chem. Mater.* 14, 1216-1219 (2002).
15) Yu, L.; Zhang, G.; Li, S.; Xi, Z.; Guo, D. Fabrication of arrays of zinc oxide nanorods and nanotubes in aqueous solution under an external voltage. *J. Cryst. Growth* 299, 184-188 (2007).
16) Li, Y.; Zhang, W.; Niu, J.; Chen, Y. Mechanism of photo-
generated reactive oxygen species and correlation with the antibacterial properties of engineered metaloxide nanoparticle. ACS Nano. 6, 5164-5173 (2012).
17) Ong, C.B.; Ng, L.Y.; Mohammad, A.W. A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications. Renew. Sustain. Energy Rev. 81, 536-551 (2018).
18) He, W.; Jia, H.; Cai, J.; Han, X.; Zheng, Z. et al. Production of reactive oxygen species and electrons from photoexcited ZnO and ZnS nanoparticles: A comparative study for unraveling their distinct photocatalytic activities. J. Phys. Chem. C 120, 3187-3195 (2016).
19) Klubnuan, S.; Amornptioksuk, P.; Suwanboon, S. Structural, optical and photocatalytic properties of MgO/ZnO prepared by a hydrothermal method. Mater. Sci. Semicond. Process 39, 515-520 (2015).
20) Parea, B.; Jonahalagaddab, S.B.; Tomara, H.; Singha, P.; Bhagwata, V.W. ZnO assisted photocatalytic degradation of acridine orange in aqueous solution using visible irradiation. Desalination 232, 80-90 (2008).
21) Richard, C.; Bosquet, F.; Pilichowski, J.F. Photocatalytic transformation of aromatic compounds in aqueous zinc oxide suspensions: effect of substrate concentration on the distribution of products. J. Photochem. Photobiol. A: Chem. 108, 45-49 (1997).
22) Driessen, M.D.; Miller, T.M.; Grassian, V.H. Photocatalytic oxidation of trichloroethylene on zinc oxide: characterization of surface-bound and gas-phase products and intermediates with FT-IR spectroscopy. J. Mol. Catal. A: Chem. 131, 149-156 (1998).
23) Dodd, A.C.; Mckinley, A.J.; Saundres, M.; Tsuzuki, T. Effect of particle size on the photocatalytic activity of nanoparticulate zinc oxide. J. Nanoparticle Res. 8, 43-51 (2006).
24) Hariharan, C. Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: Revisited. Appl. Catal. A: Gen. 304, 55-61 (2006).
25) Maclaren, A.; Valdes-Soil, T.; Li, G.; Tsang, S.C. Shape and size effects of ZnO nanocrystals on photocatalytic activity. J. Am. Chem. Soc. 131, 12540-12541 (2009).
26) Li, W.J.; Shi, E.W.; Zhong, W.Z.; Yin, Z.W. Growth mechanism and growth habit of oxide crystals. J. Cryst. Growth 203, 186-196 (1996).
27) Spori, D.M.; Venkataraman, N.V.; Tosatti, S.G.P.; Durmaz, F.; Spencer, N.D. et al. Influence of alkyl chain length on phosphate self-assembled monolayer. Langmuir 23, 8053-8060 (2007).
28) Shibata, H.; Iizuka, Y.; Kawai, T.; Watai, Y.; Amano, M. et al. Preparation of hexagonal plate-like ZnO single-crystal particles in the presence of anionic amphiphiles. J. Oleo Sci. 69, 783-787 (2020).
29) Shibata, H.; Iizuka, Y.; Amano, M.; Takayanagi, E.; Ogura, T. et al. The effect of anionic amphiphiles on the morphologies of hexagonal plate-like ZnO particles. J. Oleo Sci. 69, 783-787 (2020).
30) Kong, J.Z.; Li, A.D.; Li, X.Y.; Zhai, H.F.; Zhang, W.Q. et al. Photo-degradation of methylene blue using Ta-doped ZnO nanoparticle. J. Solid State Chem. 183, 1359-1364 (2010).
31) Meyer, B.; Marx, D.; Duhu, O.; Diebold, U.; Kunat, M. et al. Partial dissociation of water leads to stable superstructures on the surface of zinc oxide. Angew. Chem. Int. Ed. 43, 6642-6645 (2004).
32) Liu, Y.; Xu, W.; Shan, Y.; Xu, H. High reactivity of the ZnO(0001) polar surface: The role of oxygen adatoms. J. Phys. Chem. C 121, 15711-15718 (2017).