doi:10.1246/cl.2012.173
Published on the web February 4, 2012

Synthesis of Echinoid-like TiO_2 Particles through Modified Sol–Gel Method Using PVA as a Surface-directing Agent and Their Photocatalytic Activity

Inseok Jang, Kyungho Song, and Seong-Geun Oh*
Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

(Received October 28, 2011; CL-111057; E-mail: seongoh@hanyang.ac.kr)

Echinoid-like TiO_2 particles were prepared via modified sol–gel process using PVA as a surface-directing agent in acetic acid solution. The surface of echinoid-like TiO_2 particle is significantly rough, and the size of the particles is 800–1100 nm. The specific surface area and average pore size of echinoid-like TiO_2 particles are 82.81 $m^2 g^{-1}$ and 11.79 nm, respectively. The photocatalytic activity of echinoid-like TiO_2 particles was very high compared with P25 due to larger surface area.

Since its commercial production in the early twentieth century, titanium dioxide (TiO_2) has been widely used as a pigment and in sunscreens, paints, ointments, toothpaste, etc.[1] In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO_2 material, which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo- and electrochromics and sensors.[2–5] TiO_2 exists in two main crystallographic forms, anatase and rutile. The energy band gaps of anatase (3.23 eV, 384 nm) and rutile (3.02 eV, 411 nm)[6] combine with the valence band positions to generate highly energetic holes at the interface, giving rise to easy oxidation reactions. Anatase has been found, in most cases, to be photocatalytically more active than rutile. The most popular commercial form of TiO_2 is produced by the German company Degussa under the name P25 containing around 80% anatase and 20% rutile phases. The performances of particles are closely related to their structures, particle sizes, and morphologies; thus, it would be a promising approach to prepare TiO_2 particles of novel morphology for improving their photocatalytic properties.[7] In this study, we prepare the echinoid-like TiO_2 particles which have larger surface area than spherical particles.

The echinoid-like TiO_2 particles were synthesized with poly(vinyl alcohol) (PVA) as a surface-directing agent in acetic acid via modified sol–gel process. 0.6 g of PVA was dissolved in 18 mL of dimethyl sulfoxide (DMSO) under stirring at 100 °C for 1 h. 9 mL of titanium tetraisopropoxide (TTIP) was added to 30 mL of 2-propanol under stirring at room temperature for 1 h. The PVA/DMSO solution and TTIP/2-propanol solution were added dropwise to 600 mL of acetic acid under vigorous stirring at 100 °C. The resultant solution was refluxed with vigorous stirring at 100 °C for 4 days. After the reaction, the synthesized particles were centrifuged and washed with acetone several times. The washed particles were oven-dried at 70 °C for 24 h and calcined at 450 °C for 2 h. Then the powders were refluxed in 0.5 M NH_4OH solution for the hydroxylation. To evaluate the photocatalytic activity of the echinoid-like TiO_2 particles, Methylene Blue (MB) was used at room temperature, and P25 was employed as a reference. In each sample, 0.1 g of the TiO_2 particles was added into 100 mL of aqueous MB solution (10 ppm). The suspensions were stirred in the dark for 30 min before UV irradiation, and then the reaction started with UV irradiation.

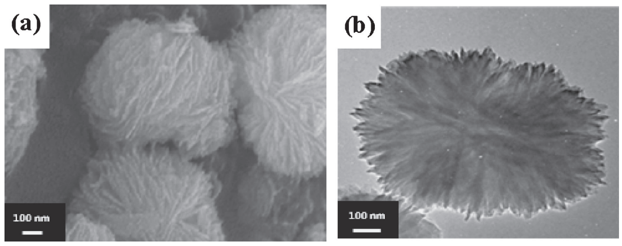

Figure 1. FE-SEM (a) and HR-TEM (b) images of the synthesized echinoid-like TiO_2 particles.

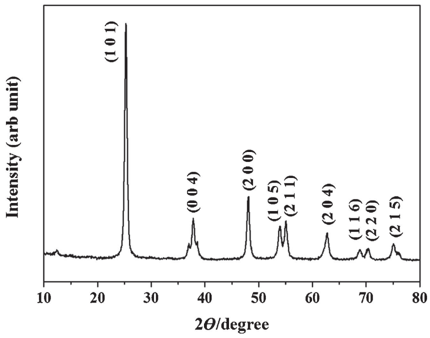

Figure 2. XRD patterns of the echinoid-like TiO_2 particles after calcination at 450 °C for 2 h.

FE-SEM and HR-TEM images of the synthesized particles are presented in Figure 1, which show the morphological properties of the particles. As shown in Figure 1a, the surface of TiO_2 particle is significantly rough, and the size of the particles is 800–1100 nm. Figure 1b shows that the echinoid-like TiO_2 particle is the aggregation of many plate-shaped particles.

Figure 2 shows the XRD patterns of the synthesized echinoid-like TiO_2 particles in this study. The main peaks are clearly observed at $2\theta = 25.28$, 37.80, and 48.04°, and they are assigned as the (101), (004), and (200), respectively (JCPDS No. 21-1272). It means that the particles are completely crystallized as anatase phase after calcination.

Figure 3 represents the nitrogen adsorption–desorption isotherm and pore size distribution of the echinoid-like TiO_2 particles. The isotherm pattern exhibits typical type IV, and it indicates the characteristics of mesoporous materials based on the IUPAC classification.[8] The specific surface area and average pore size of the echinoid-like TiO_2 are 82.81 $m^2 g^{-1}$ and 11.79 nm, respectively. The specific surface area of the echinoid-like TiO_2 particles is higher than P25 powder of which the specific surface area and average particle size are 56 $m^2 g^{-1}$ and 26 nm,

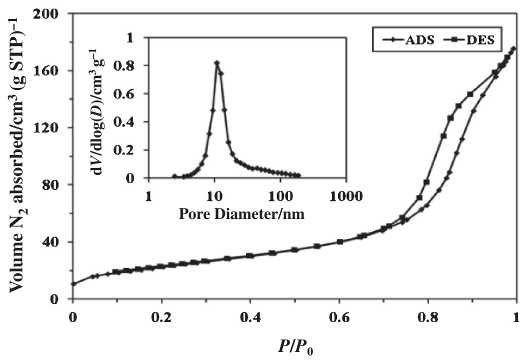

Figure 3. Nitrogen adsorption–desorption isotherm curve and the inset shows their BJH pore size distribution of the echinoid-like TiO_2 particles.

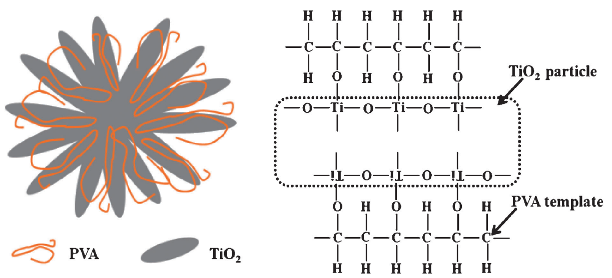

Figure 4. Schematic illustration of the formation for the echinoid-like TiO_2 particles.

respectively.[9] Although the average particle size of echinoid-like TiO_2 is bigger than the average particle size of P25, the specific surface area is larger. By assuming all the particles have the same spherical shape and size, the theoretical average particle size can be estimated by using the specific surface area. The average particle diameter, D, is calculated by the formula: $D = 6/\rho A$,[10] where ρ is the density and A is the specific surface area of the particles. The calculated particle size is 18.6 nm. This result indicates that the echinoid-like TiO_2 particles have the specific surface area of nanoscale particles although the size of them is microscale.

Based on the observation of morphological analysis, the schematic formation of the echinoid-like TiO_2 particles is illustrated in Figure 4. The hydroxy groups of PVA react with the Ti–OH which is on the surface of TiO_2 particles, and the TiO_2 particles are grown one-dimensionally.[11] After 4 days, the particles one-dimensionally grown aggregated because of PVA which acts as templates, and it takes a relatively long time for the activation of PVA as polymer micelles.[12,13]

As shown in Figure 5, the photodegradation of MB by using echinoid-like TiO_2 particles was lower than that by using P25 before hydroxylation. This result can be explained in that the echinoid-like TiO_2 particles are hard to disperse in the solution completely because the particle size is microscale and the hydroxy groups on the surface of particles are eliminated during calcination.[14] After the hydroxylation process, the photocatalytic performances were enhanced, and this result can be elucidated by two reasons. First, the modification of the TiO_2 surface with hydroxy groups improves the dispersion of the TiO_2 particles because of hydrogen bonding with water molecules. Second,

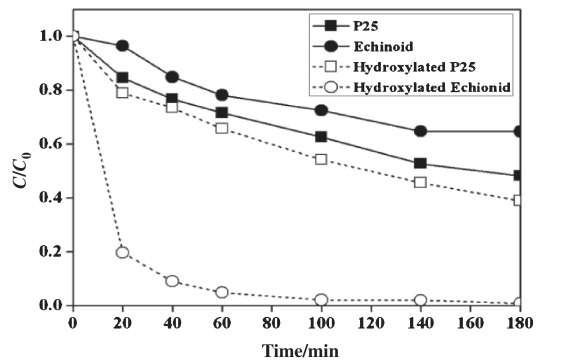

Figure 5. Photocatalytic activity of P25 and echinoid-like TiO_2 particles.

hydroxy groups on the TiO_2 surface also enhance the photocatalytic performance of the TiO_2 particles by producing hydroxyl radicals.[15] The photocatalytic activity of the TiO_2 particles was significantly enhanced after hydroxylation. This is because the particles are well dispersed in the solution by hydroxylation and the surface area is very large.

In summary, we report the synthesis of the echinoid-like TiO_2 particles through modified sol–gel process with PVA. The crystal phase of the particles is pure anatase phase after calcination. The surface of echinoid-like TiO_2 particles is significantly rough, and the size of the particles is 800–1100 nm. The specific surface area of the echinoid-like TiO_2 particles is confirmed to correspond with specific surface area of the spherical particles of which average size is 18.6 nm. The echinoid-like TiO_2 particles show very high photocatalytic activity after hydroxylation compared with P25 because of larger surface area.

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) grant funded from the Ministry of Education, Science and Technology (MEST) of Korea for the Center for Next Generation Dye-sensitized Solar Cells (No. 2011-0001055).

References

1 X. Chen, S. S. Mao, *Chem. Rev.* **2007**, *107*, 2891.
2 M. Grätzel, *Nature* **2001**, *414*, 338.
3 A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49.
4 A. L. Linsebigler, G. Lu, J. T. Yates, Jr., *Chem. Rev.* **1995**, *95*, 735.
5 A. Mills, S. Le Hunte, *J. Photochem. Photobiol., A* **1997**, *108*, 1.
6 M. D. Ward, J. R. White, A. J. Bard, *J. Am. Chem. Soc.* **1983**, *105*, 27.
7 M. Yan, Y. Shen, L. Zhao, Z. Li, *Mater. Res. Bull.* **2011**, *46*, 1648.
8 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, *57*, 603.
9 K. J. A. Raj, B. Viswanathan, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.* **2009**, *48A*, 1378.
10 J. K. Burdett, T. Hughbanks, G. J. Miller, J. W. Richardson, Jr., J. V. Smith, *J. Am. Chem. Soc.* **1987**, *109*, 3639.
11 X. Chen, *J. Mater. Sci. Lett.* **2002**, *21*, 1637.
12 S. Matsuzawa, K. Ueberreiter, *Colloid Polym. Sci.* **1978**, *256*, 490.
13 G. Wu, B. Su, W. Zhang, C. Wang, *Mater. Chem. Phys.* **2008**, *107*, 364.
14 W. Gao, L. Reven, *Langmuir* **1995**, *11*, 1860.
15 P. G. Belelli, R. M. Ferullo, M. M. Branda, N. J. Castellani, *Appl. Surf. Sci.* **2007**, *254*, 32.

