

Synthesis of Highly Soluble TiO₂ Nanoparticle with Narrow Size Distribution

Seong Yong Baek, Seung Yong Chai, Kap Soo Hur, and Wan In Lee*

Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: wanin@inha.ac.kr

Received March 25, 2005

Key Words : TiO₂, Nanoparticle, Reverse micelle, Quantum size effect

With unique characteristics in band position and surface structure, TiO₂ provides a variety of potential applications. It has typical applications as a photocatalyst decomposing organic pollutants¹ and/or producing hydrogen by water-splitting,² and as a smart material with self-cleaning and/or super-hydrophilic properties.³ It also draws great attention as an electrode material for light-sensitizers or electrochromophores, consisting of dye-sensitized solar cells⁴⁻⁷ or electrochromic devices,⁸ respectively.

Recently, the reverse micelle process has widely been applied to the syntheses of size-controlled nanoparticles for various metals^{9,10} and semiconductors.^{11,12} The carboxylic acids or amines with long hydrocarbon chains form a stable reverse micelle array in nonpolar ethers, and the cavities inside these arrays possibly be used as nanoreactors for the synthesis of nanoparticles.^{13,14} Moreover, it has been well-known that the carboxylic acids have strong binding affinity toward TiO₂.^{4,5} Thus, the carboxylic acids with long hydrocarbon chain would be an appropriate surfactant for the synthesis of titania nanoparticles. Nonetheless, the synthesis of TiO₂ nanoparticle is still very complicated, and only a limited success has been achieved so far in controlling its shape and size.¹⁵⁻¹⁹ Under a typical synthetic condition, such as reflux of reactants in flask, the obtained titania nanoparticles are heavily aggregated and their crystallinities are not so high in most case. So far, the hydrothermal or solvothermal reaction has usually been applied for the syntheses of various metal oxides at relatively low temperatures.²⁰ Since the reaction is performed at an elevated pressure, more crystallized and denser structures have been obtained at a given temperature. Thus, in this work, we combined the solvothermal technique and reverse micelle method to obtain more crystallized and monodispersed titania nanoparticles without aggregation.

A 0.45 g of titanium isopropoxide (Ti(OPrⁱ)₄) was added to a solution containing 0.50 ml of oleic acid and 10 mL of octyl ether (molar ratio of Ti(OPrⁱ)₄ to oleic acid = 1 : 1). All the chemicals were purchased from Aldrich Chemical Co. The mixture was stirred a few hours, and the clear solution was transferred to a glass-lined autoclave. The temperature of autoclave was raised to 240-300 °C with a rate of 5 °C/min, and held for 6 hr. During this anhydrous solvothermal reaction the Ti(OPrⁱ)₄ was thermally decomposed to form TiO₂, and the TiO₂ nanoparticles were finally obtained as a form of colloidal suspension. The optimum reaction temperature for the formation of anatase TiO₂ nanoparticle has been determined to 260 °C, which is relatively high

compared with that from other synthetic methods.¹⁵⁻¹⁹ Here, we believe that the absence of water during the solvothermal reaction retards the crystallization and grain growth of titania nanoparticle. The crystallite size of TiO₂ nanoparticle, calculated from the XRD peak of anatase (101) by applying the Scherrer equation, was 4.4 nm.

TEM image in Figure 1a shows that the prepared TiO₂ nanoparticles are monodispersed primary particles basically free from mutual aggregation, and they are mainly spherical shape with a diameter of 4.5 ± 0.5 nm, which corresponds to the crystallite size calculated from XRD patterns. Figure 1b shows the high resolution TEM image for an individual titania nanoparticle. The uniform fringes with an interval of 0.35 nm, corresponding to (101) lattice spacing of anatase phase, were observed over the entire particle. This indicates the synthesized each nanoparticle consists of single anatase grain.

To control the hydrolysis of Ti(OPrⁱ)₄, two equivalents of water relative to Ti(OPrⁱ)₄ were added to the precursor solution before the solvothermal reaction. Then, it was

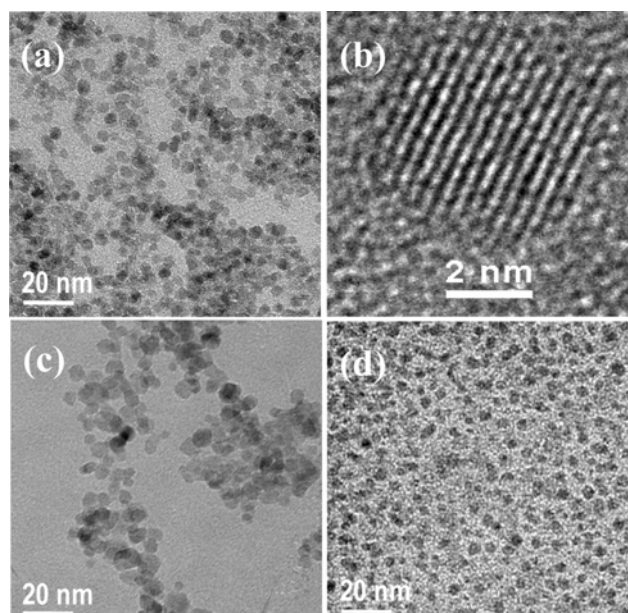


Figure 1. TEM images of TiO₂ nanoparticles synthesized at 260 °C: (a) TiO₂ nanoparticle synthesized in anhydrous condition. (b) High resolution TEM image for a nanoparticle in (a). (c) TiO₂ nanoparticle synthesized in a hydrous condition (Two equivalents of water relative to Ti(OPrⁱ)₄ were added to the precursor solution prior to solvothermal reaction.). (d) Citrate-capped TiO₂ nanoparticle suspended in aqueous solution.

found that the average particle size of TiO₂ synthesized at 260 °C was increased to 6-7 nm, as shown in Figure 1c. Also, the sizes and shapes of nanoparticles were considerably more deviated than those of TiO₂ prepared at the anhydrous condition. This clearly indicates the particle size of TiO₂ is strongly dependent on the rate of hydrolysis for Ti(OPrⁱ)₄ at early stage. That is, the slow formation of TiO₂ by the thermal decomposition of alkoxide under an anhydrous condition induces smaller and more monodispersed nanoparticles without agglomeration.

To obtain powdered TiO₂ from the suspension in octyl ether, 10 mL of ethanol was added to the 10 mL of prepared suspension. The suspended oleate-capped TiO₂ nanoparticles were then slowly precipitated. The precipitate was collected by centrifugation, rinsed with ethanol several times, and dried in a vacuum oven at room temperature. The dried TiO₂ nanoparticles capped with oleate group were readily soluble in nonpolar solvents, such as toluene. That is, a 10 mL of toluene suspension containing 0.3 g of powdered TiO₂ looks optically transparent. It has been found from the light scattering measurement that the diameter of colloids suspended in toluene is only 10.9 nm in volume average, which indicates only 14 of TiO₂ nanoparticles are agglomerated to form an individual colloid in solution.

The absorption band edge of 4.5 nm-sized TiO₂ nanoparticles has been measured by UV-visible spectroscopy. For the comparison, the absorption spectra of 15 and 25 nm-sized anatase nanoparticles¹⁹ were also included in Figure 2. Each 3 mg of oleate-capped 4.5 nm-sized TiO₂, and naked 15 and 25 nm-sized TiO₂ was suspended to 100 mL of toluene and water, respectively. We observed a noticeable quantum size effect for the 4.5 nm-sized TiO₂ nanoparticles. That is, the absorption edge of the 4.5 nm-sized TiO₂ suspended in toluene was blue-shifted about 30-40 nm, compared with that of 15 or 25 nm-sized nanoparticles. Our observation is appreciably different from the previous report by Sanchez et al. that the size of TiO₂ nanoparticle should be 1.5 nm or less in order to show quantum size effect.²¹ This

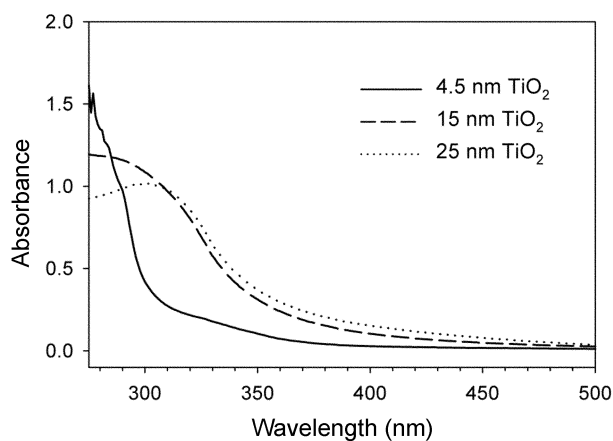


Figure 2. UV-visible absorption spectra for the oleate-capped 4.5 nm-sized TiO₂, and the naked 15 and 25 nm-sized particles suspended in toluene and water, respectively.

discrepancy may be explained by the fact that in our case the individual TiO₂ nanoparticles are mostly separated in toluene suspension without agglomeration.

Differently from other surfactants, such as phosphates, removal of oleate group or replacement to other capping agent on the surface of TiO₂ nanoparticle is quite straight forward. For example, several drops of 0.3 M HCl were added to the oleate-capped TiO₂ suspensions in octyl ether (0.15 g of TiO₂ in 10 mL of octyl ether). The TiO₂ nanoparticles were then slowly precipitated. We guess that the capped oleate groups on the surface of TiO₂ nanoparticle were gradually removed during this acidic treatment. The precipitated TiO₂ nanoparticles were collected by centrifugation, washed several times with ethanol/water (50/50 in volume ratio), and again suspended in aqueous solution. The 10 mmol of citric acid was then added, and the suspension was stirred 2 hr at 55 °C, after adjusting the pH to 10. With this procedure, the surfaces of TiO₂ nanoparticles were replaced with hydrophilic citrate groups, and the resultant TiO₂ nanoparticles could be stably dispersed in aqueous solution, as demonstrated in the TEM image of Figure 1d.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF 2002-1-12200-002-3).

References

- Turchi, C. S.; Ollis, D. F. *J. Catal.* **1990**, *122*, 178.
- Honda, K.; Hujishima, A. *Nature* **1972**, *238*, 38.
- Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431.
- O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
- Grätzel, M. *Nature* **2001**, *414*, 338.
- Cheon, I. C.; Lee, S. L.; Shim, H. K.; Kim, Y. I. *Bull. Korean Chem. Soc.* **2003**, *24*, 1535.
- Kang, M. G.; Ryu, K. S.; Chang, S. H.; Park, N. G.; Hong, J. S.; Kim, K.-J. *Bull. Korean Chem. Soc.* **2004**, *25*, 742.
- Grätzel, M. *Nature* **2001**, *409*, 575.
- Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
- Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 882.
- Puntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.
- Jun, Y.; Jung, Y.; Cheon, J. *J. Am. Chem. Soc.* **2002**, *124*, 615.
- Hyeon, T.; Lee, S. S.; Park, J.; Chung, Y.; Na, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 12798.
- Seo, W. S.; Jo, H. H.; Lee, K.; Park, J. T. *Adv. Mater.* **2003**, *15*, 795.
- Martin, S. T.; Herrmann, H.; Choi, W.; Hoffmann, M. R. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 3315.
- Stathatos, E.; Lianos, P.; Del Monte, F.; Levy, D.; Tsiourvas, D. *Langmuir* **1997**, *13*, 4295.
- Trentler, T. J.; Denler, T. E.; Bertone, J. F.; Agrawal, A.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 1613.
- Scolan, E.; Sanchez, C. *Chem. Mater.* **1998**, *10*, 3217.
- Chae, S. Y.; Park, M. K.; Lee, S. K.; Kim, T. Y.; Kim, S. K.; Lee, W. I. *Chem. Mater.* **2003**, *15*, 3326.
- Byrappa, K.; Yoshimura, M. *Handbook of Hydrothermal Technology*; Williams Andrew Publishing: New York, 2001.
- Monticone, S.; Tufel, R.; Kanaev, A. V.; Scolan, E.; Sanchez, C. *Appl. Surf. Sci.* **2000**, *162-163*, 565.