

The Effect of Ultrasonic Waves on the Fabrication of TiO₂ Nanoparticles on a Substrate Using a Self-assembly Method

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Abstract—A method for enhancing surface uniformity was investigated during the formation of titania film. A self-assembling technique with ultrasonic applications was effectively used to fabricate titania nanoparticles on the solid substrate after surface functionalization by APTES (3-amino-propyl-tri-ethoxy-silane). Morphological changes associated with structural evolution were observed by using AFM (atomic force microscopy). Results showed that ultrasonic waves were very effective in both enhancing the surface uniformity and narrowing the particle size distribution of the titania nanoparticles.

Key words: TiO₂, Titania, Ultrasonic Wave, SAM, Fabrication

INTRODUCTION

Nanostructured titania materials are of interest due to their technical applications in photocatalysis and photoelectric conversion [Aguado et al., 2002; Nakashima et al., 2002; Zakeeruddin et al., 2002]. In particular, the fabrication technique of these nanoparticles is important in terms of their effective utilizations. A variety of methods have been developed for fabricating titania nanoparticles including a sol-gel process, gas condensation technique and hydrolysis technique [Lin et al., 1997; Xianyu et al., 2001; Xie et al., 2002; Xiaoli et al., 2003]. Among the thin film formation strategies, self-assembled monolayer (SAM) is the most feasible and widely used technique for producing materials in the nanosize scale range [Ulman, 1996; Burnside et al., 1999; Chen et al., 2001]. SAM has the advantage that it is possible to fabricate materials layer-by-layer. The surface uniformity, however, becomes worse with the increase in the number of deposited layers. In this study, we propose a method for enhancing surface uniformity during the self-assembly process using ultrasonic waves.

EXPERIMENTAL

The film formation procedure consists of three steps. The first step is the preparation of colloidal titania particles. Colloidal titania particles were synthesized as described in the literature [Wang et al., 1998]. Two ml of 0.2 mol l⁻¹ HCl was added to 88 ml ethanol (A). Titanium-tetraisopropoxide, 0.5 ml, was dissolved in 9.5 ml of ethanol (B). Solution A was slowly added dropwise to solution B with vigorous stirring at 0 °C. The resulting solution was peptized by further stirring for 3-5 h to give a transparent titania sol which contained 1.8×10⁻² mol l⁻¹ titania. Using this method, 2-3 nm size colloidal titania particles were prepared.

The second step involves the self-assembling of APTES on substrate (Quartz). After the substrate was cleaned, it was immersed in piranha solution (H₂SO₄:H₂O₂=7:3 vol%) at 110 °C for 30 min

to convert siloxane bonds to hydroxyl groups on the substrate. The resulting quartz surface was considered to have ca. five hydroxyl groups per nm² [Zhuravlev et al., 1987; Hu et al., 2001]. After the number of hydroxyl groups was maximized, the substrate was dried under a stream of nitrogen. The substrate was immersed in a 4.0 mmol l⁻¹ APTES solution (H₂O concentration was less than 300 ppm) for alcohol condensation between the ethoxy-silane groups and the hydroxyl groups for 6 hr. As a result, the silanol groups produced siloxane bonds and ethyl alcohol was formed as a by-product.

The third step is the fabrication of the thin solid film of titania nanoparticles on the substrate. At this stage, the substrate was immersed into the titania sol for 1 hr with or without the ultrasonic application to the solution. As a result, titania particles were attached onto the amine groups of APTES. Fig. 1 shows a schematic diagram of a titania thin film formed by SAM on the solid substrate.

RESULTS AND DISCUSSION

Results show that the titania absorption spectrum (dash-dot line in Fig. 2) clearly appeared in the UV region after the titania particles were self-assembled onto the solid substrate. This titania absorption spectrum did not appear when the second step described in the experimental section was omitted. This result provides evi-

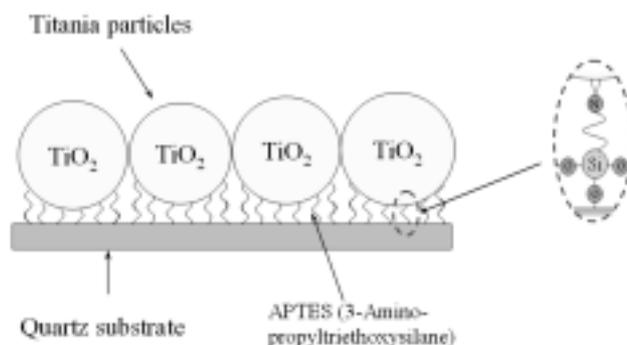


Fig. 1. Schematic diagram of titania thin film.

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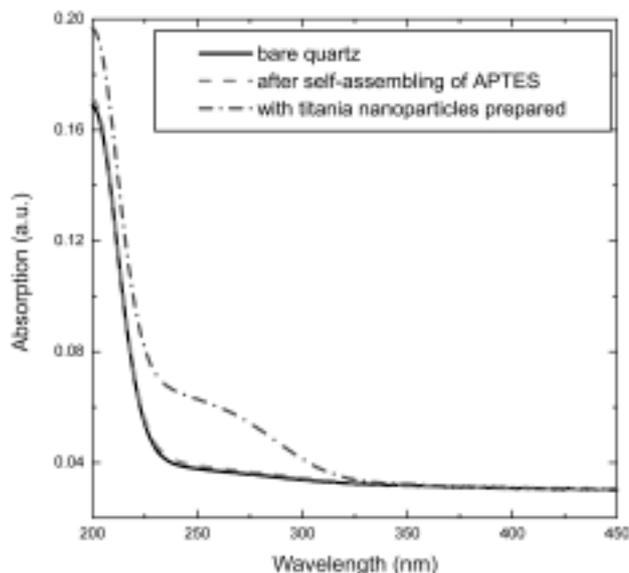


Fig. 2. UV-Vis. absorption spectra of a titania thin film at each step.

dence that the titania particles are attached on the substrate as depicted in Fig. 1.

Morphological changes associated with structural evolution were observed by using an AFM with the tapping mode. Application of ultrasonic waves to the solution was very effective in enhancing surface uniformity of the thin film of titania nanoparticles on the solid substrate. Fig. 3 shows AFM images of the assembled titania nanoparticles and cross-sectional views of the film. Without application of ultrasonic wave, titania particles with an average diameter of ca. 20 nm were fabricated on the substrate but the morphology

was quite rough (Fig. 3(a)). However, the surface uniformity was considerably increased after the application of ultrasonic waves (frequency=40 kHz, power=154 W), as seen in Fig. 3(b).

The results show that the particles grew to a size of ca. 20 nm on the substrate in both cases, while the uniformity was changed. Two types of particle growth mechanisms are reported elsewhere [Lu et al., 1999]. The first one is that primary particles are coalesced into one another. This type of particle growth occurs when the coalescence time is shorter than the collision time among primary particles. In case of the small particles, they have a greater chance to coalesce because small particles have larger surface activity than large ones. The second possible growth mechanism is that primary particles are aggregated with each other. This type of particle growth occurs when the coalescence time is longer than the collision time. When the particles are relatively large, they have a greater chance to aggregate because large particles have continuous collisions before complete coalescence. These particle growth mechanisms simultaneously occur during the fabrication of titania particles. It is well known that coalescence is dominant at the beginning of the process, while aggregation is effective during the particle growth. Consequently, the particle sizes become non-uniform.

In this study, sonochemistry was successfully applied to prepare titania thin films with uniform particle size. During the fabrication of titania nanoparticles, the application of ultrasonic waves has two main advantages for increasing surface uniformity. The first one is that ultrasonic waves play a role in reducing the size of coalesced particles. When titania particles are placed under the ultrasonic waves, the collision time among the particles is reduced. As a result, the size of the primary particles is decreased. The second advantage is that ultrasonic waves play a role in reducing the tendency of particle aggregation. Since the ultrasonic waves force the particles to

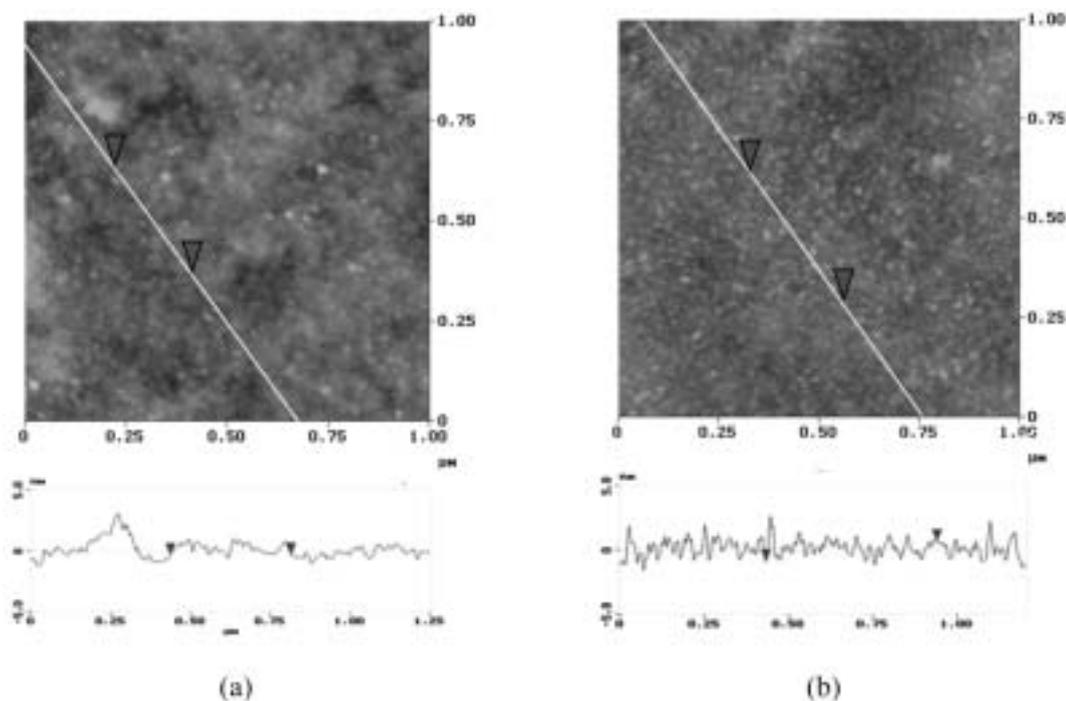


Fig. 3. Atomic force microscopy images of self-assembled titania nanoparticles and a cross-sectional views: (a) without ultrasonic wave (b) with ultrasonic wave.

Table 1. Summary of the atomic force microscopy data of self-assembled titania nanoparticles

Items	Temp.			
	5 °C	30 °C	60 °C	90 °C
RMS roughness (nm)	0.89	0.91	1.26	1.39
Mean roughness (nm)	0.70	0.71	1.00	1.13
Average particle size (nm)	18.1	18.9	23.3	28.8
Peak-Valley height (nm)	9.12	9.24	10.08	10.28

form relatively large shear gradient in the titania sol, the particles do not have the much chance to agglomerate to form a bunch of particles. Because of these advantages, the size distribution of the titania particles tends to be uniform as shown in Fig. 3(b).

Additional experiments were performed to investigate the effect of the temperature and power of ultrasonic waves on the particle size. The average particles size was changed from 18 nm to 30 nm by changing the reaction temperatures from 5 °C to 90 °C (Table 1). When the reaction temperature was increased, the coagulation time was decreased. As a result, the secondary particles size was increased. This suggests that the average particle size can be controlled by changing the reaction temperature. In case of the power effect, the results showed that titania surface uniformity in terms of particle size distribution was gradually increased with increasing ultra sonic power

from 57 W to 154 W.

In conclusion, films of uniform titania nanoparticles were effectively fabricated onto a solid substrate by using SAM under the application of ultrasonic waves. During the fabrication process, ultrasonic waves play a role in preventing the irregular growth of the secondary titania particles because of the large shear gradients. The high sonic power results in a narrow particle size distribution. As a result, surface uniformity was highly increased when ultrasonic waves were applied. In addition, the size of the titania particles was controllable from 18 nm to 30 nm by changing reaction temperature. This study provides a method for the preparation of nanoparticles with a better surface uniformity on a self-assembly, and layer-by-layer film fabrication of nanoparticles with a narrow size distribution.

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REFERENCES

Aguado, J., van Grieken, R., Lopez-Munoz, M. J. and Marugan, J., "Removal of Cyanides in Wastewater by Supported TiO₂-Based Photo-

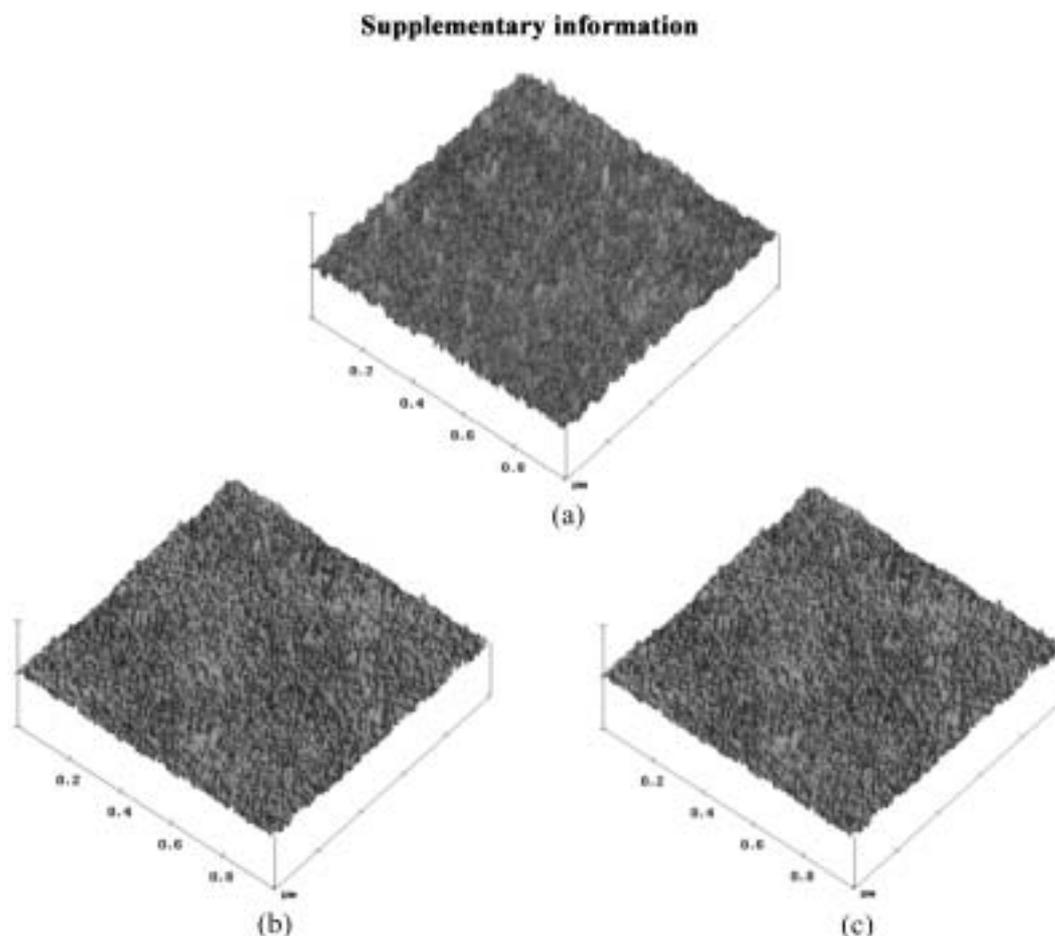


Fig. A. Atomic force microscopy image of self-assembled titania nanoparticles by changing the ultrasonic power from 57 W to 154 W: (a) 57 W, (b) 88 W, (c) 154 W.

- catalysts," *Catalysis Today*, **75**, 95 (2002).
- Burnside, S. D., Shklover, V., Barbe, C., Comte, P., Arend, F., Brooks, K. and Gratzel, M., "Self-Organization of TiO₂ Nanoparticles in Thin Films," *Chem. Mater.*, **10**(9), 2419 (1998).
- Chen, Y., Liu, W., Ye, C., Yu, L. and Qi, S., "Preparation and Characterization of Self-assembled Alkanephosphate Monolayers on Glass Substrate Coated with Nano-TiO₂ Thin Film," *Materials Research Bulletin*, **36**, 2605 (2001).
- Hu, M., Noda, S., Okubo, T., Yamaguchi, Y. and Komiyama, H., "Structure and Morphology of Self-assembled 3-mercaptopropyltrimethoxysilane Layers on Silicon Oxide," *Applied Surface Science*, **181**, 307 (2001).
- Lin, H., Keng, C. and Tung, C., "Gas-sensing Properties of Nanocrystalline TiO₂," *NanoStructured Materials*, **9**, 747 (1997).
- Lu, S., Lin, H. and Lin, C., "Modeling Particle Growth and Deposition in a Tubular CVD Reactor," *J. of Crystal Growth*, **200**, 527 (1999).
- Nakashima, T., Ohko, Y., Tryk, D. A. and Fujishima, A., "Decomposition of Endocrine-disrupting Chemicals in Water by Use of TiO₂ Photocatalysts Immobilized on Polytetrafluoroethylene Mesh Sheets," *J. of Photochemistry and Photobiology A: Chemistry*, **6051**, 1 (2002).
- Ulman, A., "Formation and Structure of Self-Assembled Monolayers," *Chem. Rev.*, **96**, 1533 (1996).
- Wang, C., Liu, C., Zheng, X., Chen, J. and Shen, T., "The Surface Chemistry of Hybrid Nanometer-sized Particles I. Photochemical Deposition of Gold on Ultrafine TiO₂ Particles," *Colloids and surfaces A*, **131**, 271 (1998).
- Xianyu, W. X., Park, M. K. and Lee, W. I., "Thickness Effect in the Photocatalytic Activity of TiO₂ Thin Films Derived from Sol-Gel Process," *Korean J. Chem. Eng.*, **18**, 903 (2001).
- Xiaoli, Y., Huixiang, S. and Dahui, W., "Photoelectrocatalytic Degradation of Phenol Using a TiO₂/Ni Thin-film Electrode," *Korean J. Chem. Eng.*, **20**, 679 (2003).
- Xie, H., Zhang, Q., Xi, T., Wang, J. and Liu, Y., "Thermal Analysis on Nanosized TiO₂ Prepared by Hydrolysis," *Thermochimica Acta*, **381**, 45 (2002).
- Zakeeruddin, S. M., Nazeeruddin, Md. K., Humphry-Baker, R., Pechy, P., Quagliotto, P., Barolo, C., Viscardi, G. and Gratzel, M., "Design, Synthesis, and Application of Amphiphilic Ruthenium Polypyridyl Photosensitizers in Solar Cells Based on Nanocrystalline TiO₂ Films," *Langmuir*, **18**, 952 (2002).
- Zhuravlev, L. T., "Concentration of Hydroxyl Groups on the Surface of Amorphous Silicas," *Langmuir*, **3**, 316 (1987).