

Preparation of the TiO₂ – SiO₂ nano-hybrid particles by Nano-coating of TiO₂ layer on Monodispersed SiO₂ Nano-particles

Tomoya Ohno, Takeshi Matsuda, Naoki Wakiya* and Hisao Suzuki*

Department of Materials Science, Kitami Institute of Technology
165 Kouen-cho Kitami, 090-8507, Japan

Fax: 81-157-26-9456, e-mail: ohno@mail.kitami-it.ac.jp

* Graduate School of Science and Technology, Shizuoka University

3-5-1 Johuku, Hamamatsu, Shizuoka 432-8561, Japan

Fax: 81-53-471-1157, e-mail: tchsuzu@ipc.shizuoka.ac.jp

TiO₂-SiO₂ nano-hybrid particles were prepared by the sol-gel method. TiO₂ nano-layer was nano-coated on the surface of SiO₂ monodispersed nano-particles. In this study, we changed the [CH₃COOH]/[Ti] (R_A) and [H₂O]/[Ti] (R_W) to control the hydrolysis and following condensation rate of titanium alkoxide to coat the SiO₂ nano-particles uniformly. In addition, the different hydrolysis conditions were applied to deposit the TiO₂ nano-layer on the SiO₂ nano-particles (Step wise hydrolysis method and One step hydrolysis method). The resultant TiO₂-SiO₂ hybrid sol was evaluated by measuring the particle size distribution using the dynamic light scattering method to determine the thickness of TiO₂ layer on the SiO₂ surface. The surface morphology and the crystal structure of the calcined nano-hybrid particles were observed by high resolution transmission electron microscope (HR-TEM) and X-ray Diffraction (XRD).

Key words: Hybrid Particles, Chemical Solution Deposition, Nano-coating, TiO₂-SiO₂

1. INTRODUCTION

Nano-materials science is expected to create a new dimension in technology, which is promising for micro- and nano- sized devices with novel properties. A number of reviews and research articles on nano-crystalline materials have been published in various journals [1-3]. In addition, the quantum size effect has been focused on the nano-materials science. Many studies reported that the size effect has led to novel properties [4-8]. For example, M. Anpo *et. al.* reported that the size effect led to the blue shift of the band gap energy in titania [6]. On the other hand, our previous reports indicated that the size effect has led to the increased intrinsic dielectric constants for lead based ferroelectric materials [7] and barium titanate [8]. However, it is difficult to use the quantum size effect for electrical and optical devices in practice, due to the coagulation between the nano-particles during preparation and drying process. Therefore, development of the smart methods to handle the nano-particles without aggregation is expected in many fields such as in electric, optic and catalytic materials, and so on.

In this study, we propose the method of nano-coating on the monodispersed nano-sphere as the smart processing to answer the above demands. In this method, the size effect of the nano-crystalline materials can be effectively controlled by changing the coating thickness and the particle diameter as well as the ease of the handling. However, only a few study reports this kind of materials because of the difficulty in the control of the chemical reaction to prepare the nano-hybrid materials. It is well known that the metal alkoxide including titanium iso-propoxide are hydrolyzed very easily except

for silicon alkoxide. Recently, there were many attempts to design the precursors on molecular level by controlling the hydrolysis rate and following condensation reaction among the metal alkoxide [9-11]. To suppress the hydrolysis reaction among the metal alkoxide, many attempts to design the precursors have been proposed from now on. For example, Suzuki *et. al.* reported that the acetic acid was very effective to control the hydrolysis and condensation rates of zirconium alkoxide [9,10]. On the other hand, Mine *et. al.* prepared the monodispersed titania nano-particles from the hydrolysis reaction of titanium alkoxide with dimethylamine [2]. In this study, we attempt to control the hydrolysis rate of titanium iso-propoxide by adding the appropriate amounts of acetic acid and water to the precursor solutions to control the steric hindrance of the titanium alkoxide for the TiO₂-SiO₂ nano-hybrid sol. The chelation of the acetoxy group to titanium iso-propoxide could suppress the polycondensation to continue the partial hydrolysis of the titanium iso-propoxide. Therefore, we changed the [CH₃COOH]/[Ti] (R_A) to control the hydrolysis rate of metal alkoxide. In addition, the different amount of water, [H₂O]/[Ti] (R_W), was added to control the polycondensation reaction of the partially hydrolyzed titanium alkoxide on the surface of SiO₂ nano-particles.

2. EXPERIMENTAL PROCEDURE

At first, monodispersed silica nano-particles less than 100 nm were prepared by the modified Stöber process as core particles for nano-hybrid particles [12]. The particle diameter was

controlled by changing R_{NH_3} ($[\text{NH}_3]/[\text{TEOS}]$) and R_{W} ($[\text{H}_2\text{O}]/[\text{TEOS}]$). As a result, we successfully prepared monodispersed silica particles with the diameter of 66 nm at $R_{\text{NH}_3} = 0.45$ and $R_{\text{W}} = 4.5$. The solvent of the obtained silica sol was replaced with 1-butanol to remove the residual water in silica sol.

The partially hydrolyzed titanium alkoxide precursor solution was prepared by the controlled chemical modification method of alkoxide. The starting reagents were titanium iso-propoxide, 1-butanol and acetic acid. Titanium iso-propoxide was refluxed in 1-butanol at 125 °C for 24 hour to exchange the sidechain group of a titanium alkoxide from iso-propoxide group to n-butoxide group. The acetic acid was mixed into the obtained Ti alkoxide solution at room temperature for 1 hour to induce the chelation. The chelation reaction was checked by Fourier Transform Infrared Spectroscopy (FT-IR) of the precursor solution. The ratio of acetic acid to titanium alkoxide (R_{A}) was varied to attain the partial hydrolysis of titanium alkoxide with the different extent of chelation.

Finally, silica monodispersed sol and the partially hydrolyzed titania precursor solution was mixed and react at room temperature for 1 hour, followed by the stepwise addition of water into the mixed solution. The ratio of water to titanium alkoxide (R_{W}) varied in the range of 1.0 to 2.0. The particle size distribution was measured by the dynamic light scattering method using He-Ne Laser.

The resultant TiO_2 - SiO_2 nano-hybrid sols were suction filtrated and dried at 150 °C for 10 min, and calcined at 600 °C for 2 hours to prepare the TiO_2 - SiO_2 hybrid nano-particles. The resulting nano-hybrid particles were analyzed by X-ray diffraction to identify the crystalline phase. The surface morphology was observed by high-resolution transmission electron microscope (HR-TEM).

3. RESULTS AND DISCUSSION

3.1 Controlled Chemical Modification

Figure 1 shows the IR spectra for titanium iso-propoxide refluxed in 1-butanol, acetic acid, and titanium alkoxide precursor solution with $R_{\text{A}}=1.5$, respectively. The obtained IR spectra were separated by simply the sum of Lorentz function to decide the peak position. Figure 1(a) exhibited 3 sharp peaks around 3000 cm^{-1} corresponding to the stretching vibration of the aliphatic CH_2 and CH_3 groups. In addition, 2 peaks around 1500-1400 cm^{-1} corresponding to the bending vibrations of the aliphatic CH_2 and CH_3 groups. The characteristic bands of C=O stretching (monomer) around 1770 cm^{-1} , C=O stretching (dimer) around 1720 cm^{-1} , CH_3 asymmetric deformation around 1415 cm^{-1} , CH_3 symmetric deformation and COH bending around 1295 cm^{-1} appeared in Fig. 1(b). Figure 1(c) exhibited the characteristic bands mentioned above, together with new bands at 1560 cm^{-1} and

1459 cm^{-1} . These new bands were assigned to the antisymmetric stretching of COO^- vibration (ν_{asym}) and symmetric stretching of COO^- vibration (ν_{sym}) of the bidentate acetate ligand linked to titanium. Alcock *et. al.* reported that the smaller frequency separation between the ν_{sym} and ν_{asym} ($\Delta\nu_{\text{COOH}}$ is about 100 cm^{-1}) was related to a bidentate chelating coordination mode rather than a bidentate bridging coordination mode, because the O-C-O angle in chelating acetate is smaller than that in bridging acetates [13]. From this result, it was found that the added acetic acid was reacted with titanium alkoxide as chelating reagent. However, the one weak band around 1720 cm^{-1} due to free acetic acid was identified in Fig. 1(c), indicating that some acetic acid remained without chelating.

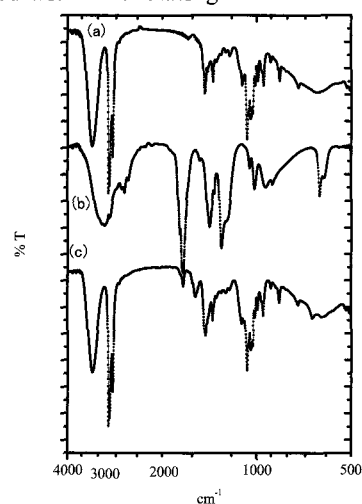


Fig.1 Infrared spectra for (a) titanium iso-propoxide in 1-butanol, (b) acetic acid and (c) titania precursor solution with $R_{\text{A}}=1.5$

3.2 Preparation of Hybrid Nano-particles

In our previous study, water was added into the mixing sol at once (abbreviated as procedure A) in hydrolysis reaction [14, 15]. However, the non-uniform particle distribution was obtained in this case, because of the nano coating was not attained perfectly. Therefore, the stepwise addition of hydrolysis water (procedure B) was tried to coat the surface of the core particles uniformly. In procedure B, water was dropped into the precursor solutions slowly to attain R_{W} of 0.5, followed by mixing for 30 min, and then, this procedure was repeated until R_{W} reached an intended value. Figure 2 shows the gelation condition with R_{A} and R_{W} in the case of $[\text{Ti}]/[\text{Si}]=10.0$. The dotted and solid lines indicate the boundary conditions of sol to gel for hybrid sol in procedure A and B, respectively. When compared at $R_{\text{A}}=1.5$, the hybrid sol did not gel at $R_{\text{W}}=1.5$ in the procedure B while the hybrid sol gelled at the same condition in the procedure A. These results clearly shows that the gelation of the hybrid sol can be controlled by changing the way of water adding process.

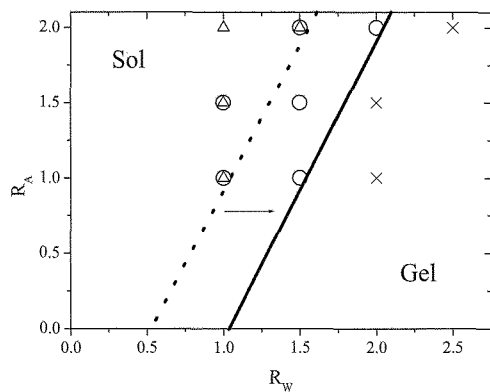


Fig. 2 Gelation condition with R_A and R_W ; \triangle : hybrid sol (procedure A), \circ : hybrid sol (procedure B) and \times : gel (procedure B), dot line: boundary from sol to gel in procedure A, solid line: boundary from sol to gel in procedure B.

3.3 Particle Size Distribution of Hybrid Nano-particles

Figure 3 shows the particle size distribution for the resultant hybrid sols at $R_A=1.0$. All hybrid sol was adjusted at the ratio of Ti to Si as 2.0 to form the thinner nano-coating layer. Theoretical value was calculated from the mixing ratio of titanium to silicon under the assumption that all titanium alkoxide was reacted on the SiO_2 particles to form the coating layer. In the case of $R_W=1.0$, the particle diameter of the resulting hybrid sol was smaller than that of the theoretical value. The particle size distribution was almost same as that of the core particles but just shifted to the larger particle size, showing the uniform nano-coating on the core particles. However, it was also confirmed that all of the titanium alkoxide did not react completely as a nano-coating layer at $R_W=1.0$. On the other hand, the resultant hybrid sol at $R_W=1.5$ included the precipitation in the sol. Therefore, this hydrolysis condition was not suitable to suppress the hydrolysis rate appropriately, and the $R_W=1.0$ was not enough for the complete hydrolysis reaction to form the nano-coating.

From the above results, the R_A value was increased to 1.5 to find the appropriate condition for partial hydrolysis. Figure 4 shows change in the particle size distribution of the hybrid sols with R_W at $R_A=1.5$. The figure showed that the $R_W=1.5$ was the appropriate amount of water to form the nano-coating under this condition, since the particle distribution of this condition and the theoretical value was much the same. On the other hand, the average particle diameter became larger than that of the theoretical value at R_W of 3.0 and 3.5, indicating the existence of the coagulated particles and/or the hybrid particles with non-uniform coating. Finally, the suitable amount of acetic acid for the partial hydrolysis reaction was investigated. Fig. 5 shows the change in the particle size distribution of the hybrid sols at $R_W=1.5$ with R_A . In the case of $R_A=2.0$, the hydrolysis was too suppress to form

the nano-coating, since the average particle size at $R_A=2.0$ was smaller than that of the theoretical value. On the other hand, in the case of $R_A=1.0$, the amount of acetic acid was not enough to suppress the hydrolysis reaction at $R_W=1.5$. Particle size distribution of the hybrid sol at $R_A=1.5$ was almost same as that of the theoretical value, showing the deposition of the uniform nano-coating by the successive reaction of the partially hydrolyzed titanium alkoxide precursors on the SiO_2 nano-particles.

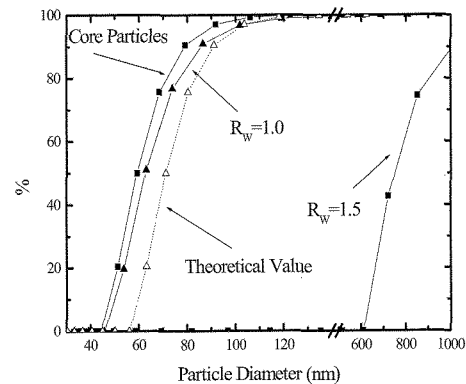


Fig. 3 Change in the particle distribution with R_W at $R_A=1.0$

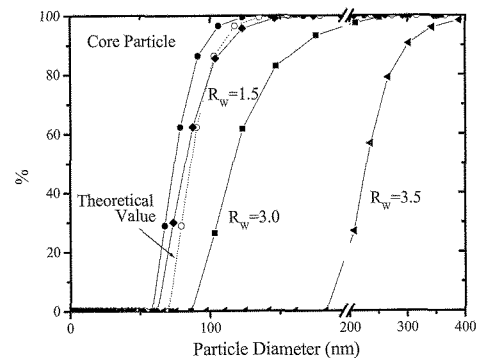


Fig. 4 Change in the particle distribution with R_W at $R_A=1.5$

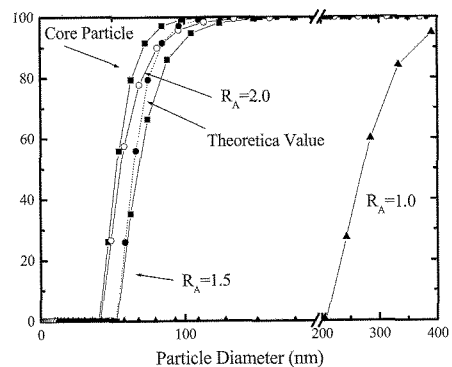


Fig. 5 Change in the particle distribution with R_A at $R_W=1.5$

3.4 TEM Observation

Crystallization into the TiO_2 anatase phase was confirmed from the XRD analysis (Fig. 6) after calcination. The surface morphology of the

resultant nano-hybrid particles was observed by high-resolution transmission electron microscope (HR-TEM). Figure 7(a) shows the surface morphology of the resultant nano-hybrid particles at $R_A=1.5$ and $R_W=1.5$. The rough surface is derived from the nano-sized crystal grown on the silica particles. All of these nano-crystals were identified as the anatase phase from the diffraction patterns from the selected areas. Fig. 7(b) shows the TEM image of the nano-hybrid particles. Some large anatase crystals were identified on the surface of the silica nano-particles, from this TEM image.

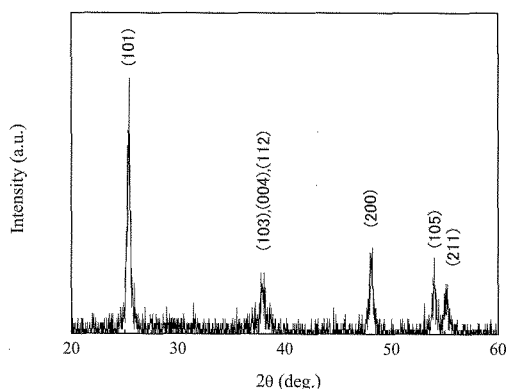


Fig.6 XRD pattern for TiO_2 - SiO_2 Hybrid nano-particles Number in the pattern indicate the Miller indices of anatase phase

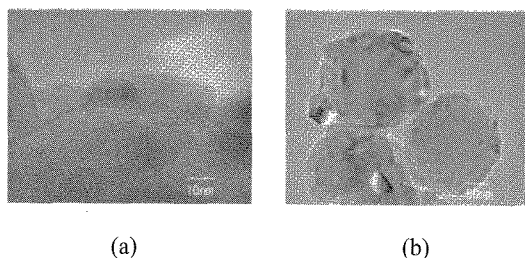


Fig.7 TEM images of TiO_2 coated SiO_2 particles (a) surface morphology, (b) nano-hybrid particles

4. CONCLUSION

TiO_2 - SiO_2 nano-hybrid particles were prepared by the sol-gel technique with controlled chemical modification of titanium alkoxide. It was confirmed that the acetic acid has been reacted with titanium alkoxide as a chelating reagent and it was confirmed by IR spectrum analysis. In our previous study, the water was added into the mixed sol at once, resulting in the non-uniform nano-coating. In contrast, the stepwise addition of water was into the mixed sol resulted in the uniform nano-coating. It was concluded that there existed the suitable R_A and R_W for the controlled hydrolysis and following condensation reaction on the surface of the monodispersed SiO_2 nano-particles. As a result, the nano-hybrid particles with almost the same particle size distribution as the theoretical value at $R_A=1.5$ and $R_W=1.5$ in our new process. The crystalline phase

of the titania on the surface of silica nano-particles were identified as anatase phase by XRD and HR-TEM.

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