Synthesis of TiO₂ Nanoparticles Coated with SiO₂ for Suppression of Photocatalytic Activity and Increased Dispersion Stability

Ok Kyung Park, Young Soo Kang†, and Beong Gi Jo*

Department of Chemistry, Pukyong National University, Busan 608-737, Korea
*R & D Center, Coreana Cosmetics Co., Ltd., Cheoan-si, 330-830, Korea

Received April 16, 2004; Accepted July 21, 2004

Abstract: For its use as an absorber of UV light in cosmetic products, TiO₂ was coated with a SiO₂ layer to suppress its photocatalytic activity and to increase its dispersion ability. Silica-coated TiO₂ nanoparticles were prepared by a sol-gel process. High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analyses showed that hydrous silica was coated evenly on the surface of the TiO₂ particles. The effect of heat-treatment on the products, i.e., increasing annealing time and temperature, was followed by X-ray powder diffraction (XRD) spectroscopy. To study the suppression of the photocatalytic effect, an organic compound was added to the silica-coated TiO₂ sol and the solution was irradiated with UV light. The decrease in the photocatalytic activity and the UV shielding effect of the silica-coated TiO₂ nanoparticles were confirmed by recording UV-vis spectra, which showed more than an 80% decrease in the photocatalytic effect. Improved dispersion of the silica-coated TiO₂ nanoparticles, as compared with that of pure TiO₂, was verified by the increased Zeta potential value, from -22 ζ/mV for pure TiO₂ to -47 ζ/mV for the silica-coated TiO₂, at pH 7 as measured using a Zeta potential analyzer.

Keywords: Sol-gel process, TiO₂ particles, silica coating layer

Introduction

Fine TiO₂ particles are used widely as a white pigment in the paint, plastic, and paper industries, and as an absorber of UV rays in the cosmetics industry. Organic molecules are readily photodegraded by photocatalytic TiO₂ particles, especially when they are exposed to ultraviolet radiation, or sunlight [1]. Generally, TiO₂ particles having 100 ~ 200 nm diameters generate their whitening effect because of scattering. On the other hand, smaller TiO₂ particles, with diameters of less than 100 nm, are transparent and exhibit maximum interception of UV light. Therefore, the crystal size of TiO₂ must be reduced to less than 20 ~ 50 nm to decrease the whitening effect and to increase transparency for its use as a fundamental additive material of cosmetics. In addition, because TiO₂ particles have photocatalytic properties, to prevent their reactions with organic compounds, the TiO₂ surface should be covered with a stable oxide layer [2].

A coating layer thicker than 10 nm captures electrons and prevents further oxidization of organic molecules. The hydrated oxide groups of the coating components are able to capture the electrons produced by photoinduced electron transfer into the coating layer, which thereby stabilizes the TiO₂ crystal [3]. Hydrous silica and hydrous alumina are the coating materials most commonly used as inorganic coatings of TiO₂ particle surfaces [4,5]. Hydrous silica coatings can improve both the pigment weather durability and the dispersion properties. TiO₂ particles covered with zinc oxide have UV-B-ray protection properties through absorbance. The coating of stable oxide layers has been performed mainly by spraying a metal oxide precursor solution onto the surface of solid particles. Unfortunately, this process results in many defects on the surfaces of the TiO₂ particles [2].

In this paper, we introduce a new method for coating SiO₂ onto the TiO₂ surface using a phase transfer reaction between organic chloroform and aqueous water phases. The evenly SiO₂-coated TiO₂ nanoparticles were characterized for their structure and morphology by using X-ray powder diffraction (XRD), TEM, energy dispersion
Experimental

Materials and Methods
Tetraethylorthosilicate (TEOS: Si(OC₂H₅)₄, 98%) was obtained from Aldrich. TiO₂ particles were obtained from Degussa (P-25). 3.2 g of TiO₂, 0.9 mL of water and 200 mL of chloroform (CHCl₃) were mixed at room temperature and this solution was sonicated for dispersion for 0.5~1 h. 12.499 g of TEOS and 5.83 mL of ethanol (C₂H₅OH) were mixed at room temperature. 7.34 mL of acetone (CH₃OCH₃) was dissolved in the mixture. The molar ratio of acetone (CH₃OCH₃) to ethanol (C₂H₅OH) in the solution was 1:1 and chloroform was used in excess as the solvent; the amount of chloroform critically affected the coating time. The TiO₂-to-TEOS molar ratio was 4:6. The mixtures were stirred at room temperature for 2 h and then filtered. The product was dried under reduced pressure in a vacuum oven and sintered at 800°C for 1 h. This synthetic route was used to prepare silica-coated TiO₂ nanoparticles.

Samples for photocatalytic activity tests were prepared by adding 0.01 g of silica-coated TiO₂ or pure TiO₂ to 100 mL of 1.0 × 10⁻⁵ M aqueous Rhodamine B solution. This aqueous Rhodamine B solution was prepared by dissolving 0.0048 g of Rhodamine B in 1 L of distilled water.

To check the dispersion of the coated TiO₂ particle, samples for testing were prepared by adding 0.01 g each of silica-coated TiO₂, pure SiO₂, or pure TiO₂ to 100 mL of distilled water. The mixtures were sonicated for 30 min. These three solutions were adjusted to values of pH of 2~11 by adding 0.1 M NH₄OH and 0.1 M HCl.

Sample Characterization
The products were characterized by using HR-TEM and EDS to determine their morphology and composition. The HR-TEM images were obtained using a Hitachi Model S-2400 and a Jeol Model JEM-2010. EDS was obtained using a HITACHI model, H-7500. The interfacial chemical bonding structure was checked by analyzing FT-IR spectra recorded on a PERKIN-ELMER SPECTRUM 2000. The heat-treatment effect and crystal structure of the products were measured by analyzing XRD spectra collected using a Philips X'Pert-MPD system. The chemical bonding between the coating layer and the TiO₂ particle surface was studied with XPS, using a VG-Scientific ESCALAB 250 spectrometer equipped with a monochromated Al Kα X-ray source. The photocatalytic activity and UV shielding effect of the silica-coated TiO₂ nanoparticles were confirmed by using a UV-vis spectrophotometer (Varian, Cary 1C). The UV-irradiation source was a Cermag LX125UV 300-Watt xenon lamp. Finally, the dispersion of the silica-coated TiO₂ nanoparticles is confirmed by using a Zeta plus potential analyzer (Brookhaven Instrument, USA). The pH of the solution was adjusted using a METTLER TOLEDO 320 pH meter.

Results and Discussion
Sintered silica-coated TiO₂ nanoparticles were investigated by HR-TEM and EDS to determine their morphology and composition. Figure 1 shows an HR-TEM image of the silica-coated TiO₂ nanoparticles. A comparison of the two pictures shows that the TiO₂ particles’ surfaces were evenly surrounded with an amorphous layer. The average diameter of the coated TiO₂ particles was determined to be 40~50 nm. The thickness of the amorphous layer was estimated to be about 10~15 nm.
The atomic weight composition of TiO$_2$ particles can be determined qualitatively by EDS data (Figure 2). A Si peak appeared in Figure 2(b). By comparing the EDS analysis and the TEM image, the presence of silicon in the coated SiO$_2$ layer on the surface of TiO$_2$ particles was identified. We conclude that the amorphous layer is silicon oxide coated on the surface of TiO$_2$ particles.

The silica-coated TiO$_2$ nanoparticles were studied using FT-IR spectra and XPS to confirm the interfacial chemical bonding structure. Figure 3 shows the FT-IR spectra of the pure and silica-coated TiO$_2$ particles. It shows that the comparison between the two spectra, absorption peaks of Ti-O, Si-O, and Ti-O-Si are observed at 600-900 cm$^{-1}$, 1000–1200 cm$^{-1}$, and 950 cm$^{-1}$, respectively [6,7]. The O1s spectra of the pure and silica-coated TiO$_2$ particles are shown in Figure 4. The binding energies of the O1s peaks for pure TiO$_2$ particles are 527.6 and 529.9 eV. The intensity of peak at 527.6 eV is much higher than that at 529.9 eV. For the silica-coated TiO$_2$ particles, the intensity of the peak at 530.3 eV is higher than that at 528.1 eV for the O1s binding energy. The higher peak intensity at 530.3 eV is attributable to the silicon oxide coating on the particle surface. It indicates that the peak at 528.1 eV of the O1s of the silica-coated TiO$_2$ particles resulted from a chemical shift of the peak at 527.6 eV of the O1s of the pure TiO$_2$ particles. In the SiO$_2$-coated TiO$_2$ particles we conclude that Si is bonded on the surface of the TiO$_2$ particles, and it forms Ti-O-Si bonds. Since the electronegativity of Si is greater than that of Ti, the O1s peak of the SiO$_2$-coated TiO$_2$ particles has a chemical shift of about +0.5 eV when compared to the TiO$_2$ particles. The Ti2p spectra of the pure and SiO$_2$-coated TiO$_2$ particles are shown in Figure 5. The binding energy of the Ti2p peak of the pure TiO$_2$ particles was determined as 456.2 eV. The Ti2p peak for the SiO$_2$-coated TiO$_2$ is 456.6 eV, +0.4 eV larger than the Ti2p peak of the pure TiO$_2$ particles. This finding also indicates Ti-O-Si bond formation [8]. The decrease of the electron density around the Ti atom results from the greater electronegativity of Si, via O, acting on the Ti atom. The shielding effect is, therefore, lessened, and the binding energy is increased. From the chemical shift of the Ti2p and O1s peaks of the XPS and FT-IR spectra, we conclude that silicon oxide is coated on the surface of the
The effect of heat-treatment and the crystal structure of the products were measured using XRD and ED. To confirm the coating of the silica layer on the TiO₂ particles, the produced particles were annealed by increasing the temperature. Figure 6 shows the XRD patterns of silica-coated TiO₂ sintered at (a) 500°C and (b) 1100°C. The XRD results show that the sintered products contain a mixture of rutile and anatase phases and that the seed particles of TiO₂ had a phase transition from the anatase to rutile phase at above 900°C. However, the coated SiO₂ layer did not show a phase transition upon heating, even at 1100°C. Figure 7 shows the XRD patterns of sintered SiO₂-coated TiO₂ particles at 800°C as a function of the sintering time (1-24 h). This study was performed to determine the change in the phase structure of the amorphous SiO₂ layer at the same temperature with respect to the sintered time. There was no phase transition of the SiO₂ layer and the TiO₂ nanoparticles upon increasing the sintering time. Amorphous silica layers act as a barrier that prevents the phase transition of the TiO₂ particles upon heating [9]. Consequently, this result shows that the surface of the TiO₂ is covered uniformly by the SiO₂ layer and that the phase transition temperature of the silica-coated TiO₂ particle is higher than the phase transition temperature of pure TiO₂ particles [10-12]. The increased phase transition temperature of SiO₂-coated TiO₂ is also attributed to possible dissolution of SiO₂ in the TiO₂ particles and to compact SiO₂ layer formation. However, when heating above 1300°C, breakage of Ti-O-Si bonds results in the crystallization of SiO₂ [13]. Therefore, SiO₂ cannot dissolve into the TiO₂ particles. Thus, SiO₂-coated TiO₂ particles are well sintered at 800°C to stabilize the amorphous silica layer on the TiO₂ surface. Figure 8 shows the ED pattern of silica-coated TiO₂. Diffraction data of the cubic silica-coated TiO₂ was obtained from JCPDS card files 83-2243 (anatase) and

---

TiO₂ particles through chemical bonding. The Ti-O-Si bond forms at the interface of the silica coating layer and the TiO₂ particle surface.
Figure 8. ED image of silica-coated TiO$_2$ sintered at 800°C for 1 h.

Figure 9. UV-vis absorption spectra of pure TiO$_2$ and sintered silica-coated TiO$_2$.

Figure 10. Molecular structure of Rhodamine B.

78-1510 (rutile).

Figure 9 shows UV-vis spectra of pure TiO$_2$ and silica-coated TiO$_2$. The absorbance range is 260 ~ 340 nm. Although TiO$_2$ was coated with silica, the UV absorption of TiO$_2$ was maintained. Silica-coated TiO$_2$ and pure TiO$_2$ (0.01 g each) were dissolved in individual 100 mL samples of $1.0 \times 10^{-3}$ M aqueous Rhodamine B solution. Figure 10 shows the molecular structure of Rhodamine B, which is reddish-violet in color and has its $\lambda_{\text{max}}$ in the UV-vis spectrum at 543 nm. The mixture was sonicated for 30 min and irradiated using a weak Xe lamp for 1 ~ 30 min to determine the SiO$_2$ coating effect [14]. Figure 11 shows the UV-vis absorption intensity at 543 nm of pure TiO$_2$ and sintered silica-coated TiO$_2$ nanoparticles containing Rhodamine B as a function of time. It shows that Rhodamine B was not photodegraded by the silica-coated TiO$_2$, in contrast to the result obtained with pure TiO$_2$. It shows that the photocatalytic activity of TiO$_2$ particles is suppressed by the amorphous SiO$_2$ layer.

The Zeta potential-pH curves to silica-coated TiO$_2$, pure SiO$_2$, and pure TiO$_2$ were measured to determine the surface coating effect of the dispersion. Samples for testing were prepared by adding 0.01 g of silica-coated TiO$_2$, pure SiO$_2$, or pure TiO$_2$ to 100 mL of distilled water. The mixtures were sonicated for 30 min. The three solutions were adjusted to values of pH of 2 ~ 11 by adding NH$_4$OH and HCl. Figure 13 shows the Zeta potential-pH...
curves of silica-coated TiO₂, pure SiO₂, and pure TiO₂. We see that the Zeta potential value of the silica-coated TiO₂ is similar to that of pure SiO₂. The zeta potential value of the silica-coated TiO₂ nanoparticles at pH 7 is -47 ζ/mV while that of pure TiO₂ particle is -22 ζ/mV. This finding shows that surface of the TiO₂ particle is modified with the amorphous SiO₂ layer. The Zeta potential is directly dependent on the pH. When oxide powders are dispersed in water, there is a surface reaction that leads to the formation of M-OH- type hydroxide groups that can be dissociated as weak acids or bases. Therefore, the surface of the silica-coated TiO₂ is composed of -Si-OH groups. When the pH in the aqueous solution is lower than the IEP (isoelectric point), -Si-OH₂⁻ forms and the surface possesses positive charge. When the pH is higher than the IEP, -Si-O⁻ forms and the surface possesses negative charge. Figure 12 shows that the dispersion of the solution is good when the absolute value of the zeta potential is over 30 mV [15]. The absolute value of the zeta potential is over 40 mV at pH 7, and so the coated particles can disperse readily when compared with the non-coated particle.

**Conclusion**

HR-TEM images of the TiO₂ particles show that TiO₂ is evenly coated with an amorphous SiO₂ layer. The average diameter of silica-coated TiO₂ was determined to be 40 ~ 50 nm and the thickness of the SiO₂-coated layer was about 10 ~ 15 nm. As a result of the EDS analysis, the amorphous layer was determined to be silica. The XRD result shows that there was no phase transition of the SiO₂ layer upon increasing the annealing temperature and time. Therefore, HR-TEM, FTIR, XPS, and EDS results all show that SiO₂ is coated even on the surface of TiO₂ particles through Ti-O-Si chemical bonding. The decrease in the photocatalytic activity and the UV shielding effect of silica-coated TiO₂ nanoparticles were confirmed by recording UV-vis spectra. Rhodamine B was not photo-degraded by the silica-coated TiO₂. This finding shows that the photocatalytic activity of TiO₂ particles is suppressed well by the amorphous SiO₂ layer. Dispersion of the silica-coated TiO₂ nanoparticles was confirmed by Zeta potential analysis. The value of the Zeta potential of silica-coated TiO₂ is similar to that of pure SiO₂. Thus, the SiO₂-coated particles can be dispersed more readily when compared with the non-coated particle.

**Acknowledgments**

This work was supported by the Functional Chemical Development Program in 2003-2004, the Brain Busan 21 Project in 2003, and Coreana Cosmetics Co., Ltd.

**References**