

TiO₂-SiO₂ nanoparticles for suppressing photocatalytic activities and improving hydrophilicity

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Titanium dioxide (TiO₂) has attracted significant attention because of its photocatalytic and UV absorbance properties. However, despite the good UV-shielding property of TiO₂, it is not suitable for use in outdoor UV-shielding protective films because of its strong photocatalytic behavior when absorbing UV radiation. Here, we describe a TiO₂@SiO₂ core shell structure with uniform and thin SiO₂ layer; the SiO₂ shell suppresses TiO₂ photocatalytic activity and improves the wettability of the TiO₂. TiO₂@SiO₂ nanoparticles were characterized by TEM, FT-IR, XPS, and VB-XPS. A uniform, thin SiO₂ shell suppressed the photocatalytic activity of the TiO₂ core by broadening the band gap because of the existence of Ti-O-Si chemical bonds at the interface of TiO₂ and SiO₂. Moreover, the increase in wettability of the TiO₂@SiO₂-coated films observed was a permanent property and did not require UV activation.

Key words: Titanium dioxide, SiO₂ shell, Photocatalytic activity, Hydrophilicity.

Introduction

Ultraviolet (UV) radiation degrades plastics, resins, and polymer substrates such as outdoor color banners and signboards that are exposed to sunlight. In a recent study, this problem was solved by embedding UV-shielding materials, such as titanium dioxide (TiO₂), into inorganic-coated protective films to enhance the stability of the films and to maintain their highly efficient UV-absorption [1]. Titanium dioxide has attracted significant attention in past decades because of its excellent physicochemical properties and many potential applications in industry. Current research on TiO₂ is focused on its photocatalytic properties to develop photocatalysts [2], and UV absorbance properties to develop materials that can protect against UV damage [3-5]. However, despite the good UV-shielding property of TiO₂, it also exhibits strong photocatalytic behavior upon absorption of UV radiation when the TiO₂ nanoparticles are coated directly onto polymer protective substrates [3]. This main drawback to the use of TiO₂ as a UV-shielding material is its strong, yellowish coloration due to its photocatalytic properties, which limits its usage in color-sensitive applications, such as outdoor protective films.

To suppress the photocatalytic property of TiO₂ while ensuring that it retains its UV-protective property, inert shells composed of stable oxide [6-7] have been coated onto TiO₂ cores. For example, Atou *et al.* reported that

the photocatalytic activity of titania nanoparticles could be reduced by spray coating the surfaces of the nanoparticles with different stable oxide layers, such as silica or alumina [7]. Toni *et al.* coated dense SiO₂ shell onto TiO₂ particles by a seeded sol-gel process using tetraethyl orthosilicate (TEOS) in ethanol [6]. Several researchers had reported producing silica-coated TiO₂ nanoparticles with hydrophilic and insulating properties. In particular, the TiO₂-SiO₂ core-shell structure is low cost and the fabrication conditions are mild [8]. Furthermore, a SiO₂ ultrathin layer improves the hydrophilicity of TiO₂ particles, thereby improving the clarity of TiO₂-coated films by preventing distortion by water drops [9-15]. However, the active sites of TiO₂ nanoparticles may be incompletely shielded by the SiO₂ shell, resulting in residual photocatalytic activity. Furthermore, the direct suppressive effect of the SiO₂ shell on the photocatalytic activity of TiO₂ nanoparticles has not been explicitly evaluated.

In this study, we coated commercial TiO₂ nanoparticles with uniform and thin SiO₂ shells using the simple wetting method in order to suppress the photocatalytic activity of TiO₂ and improve the hydrophilicity of the resulting nanoparticles. TiO₂@SiO₂ nanoparticles were characterized by TEM, FT-IR, XPS, and valence band XPS, which show uniform SiO₂ coating layer and explain why the coated TiO₂ particle shows low photocatalytic activity and enhances hydrophilicity.

Experimental

Preparation of SiO₂-coated TiO₂ (TiO₂@SiO₂)

The modification was carried out on a commercial

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TiO₂ (ST-21) purchased from Ishihara Sangyo Kaisha Ltd., Japan. The uniform SiO₂ shells were coated by typical Stöber method which has attracted much interest for fabrication of silica shells on nanoparticles via the facile hydrolysis of tetraethyl orthosilicate (TEOS) [10]. TiO₂ particles (1.0 g) was dispersed into 20 mL of EtOH, and the solution was sonication for 10 min. the suspension of TiO₂ was added to a given concentration of TEOS (1.0 ml), NH₄OH (0.8 ml). And then, the solution was heated at 40 °C for 24 h, stirring of 300 rpm. The TiO₂@SiO₂ particles were filtered and washed to remove the residual TEOS and NH₄OH with water and ethanol. The sample was dried at 80 °C for 12 h.

Photocatalytic activity measurements

Methylene blue dye (10⁻⁴ M) in DI water was used for the photocatalytic activity. Known amounts of each TiO₂ and TiO₂@SiO₂ nanoparticles were taken and dispersed in given aqueous methylene blue solution. The mixtures were sonicated for 10 min before the photocatalytic activity measurements. Solutions containing the particles were placed in Petri dishes in equal amounts and placed below a UV lamp (160 W) so that fluxes of the UV radiations were uniform on all samples. During the experiments, the Petri dishes were taken out after specific time intervals to monitor the degradation of methylene blue dye. A UV-vis spectrophotometer was used to monitor changes in the spectral intensity distribution of the dye.

Characterizations

The size and morphology of TiO₂ and TiO₂@SiO₂ nanoparticles was characterized using a transmission electron microscope (Jeol 2000-EX). Fourier transform infrared (FT-IR) studies were carried out on a Nexus 470 FTIR spectrometer (Nicolet Instruments, Madison, WI). X-ray photoelectron spectroscopy (XPS) analysis

of the samples was performed by means of a VG ESCALAB MKII spectrometer. The UV-vis spectrophotometer (Jasco V-570) was used to monitor changes in the spectral intensity distribution of the methylene blue. Surface morphology of optical protective films was examined by field emission scanning electron microscopy (FE-SEM, JEOL 6700). The hydrophilicity of the optical protective films was evaluated via a sessile drop method using a goniometer (Phoenix).

Results and Discussion

The morphologies of pure TiO₂ and TiO₂@SiO₂ nanoparticles were directly observed by high-resolution TEM (HRTEM) measurements. The morphologies of the pure TiO₂ nanoparticles with diameters of 20 to 30 nm are shown in Fig. 1(a). Fig. 1(b, c) also shows HRTEM image of TiO₂@SiO₂ nanoparticles. TiO₂@SiO₂ nanoparticles are exhibited to have SiO₂ shell thickness with ca. 4 nm around TiO₂ core uniformly in Fig. 1(b). Under higher magnification (Fig. 1 (c)), crystalline lattice fringes of TiO₂ core and amorphous SiO₂ shell are clearly observed.

FT-IR spectra of pure TiO₂ and TiO₂@SiO₂ nanoparticles are shown in Fig. 2. All spectra indicated the presence of water and hydroxyl groups in all samples because of the presence of a bending vibration of H-O-H at 1630 cm⁻¹ and a strong stretching vibration of O-H at 3200-3400 cm⁻¹, respectively [5]. The band at 400-800 cm⁻¹, which we assigned to Ti-O-Ti, was observed in all samples. For the TiO₂@SiO₂ nanoparticles, the band at 1040 cm⁻¹ was assigned to the asymmetric stretching vibration modes of the Si-O-Si bridge [2, 6], while the band at 965 cm⁻¹ was assigned to Ti-O-Si [2, 6, 12]. From this observation, SiO₂ chemically binds on the surface of TiO₂ nanoparticles and grows the layers.

The pure TiO₂ and TiO₂@SiO₂ nanoparticles were examined by XPS analysis in Fig. 3. Wide-scan XPS spectra give information of chemical analysis of both the pure TiO₂ and TiO₂@SiO₂ nanoparticles indicated

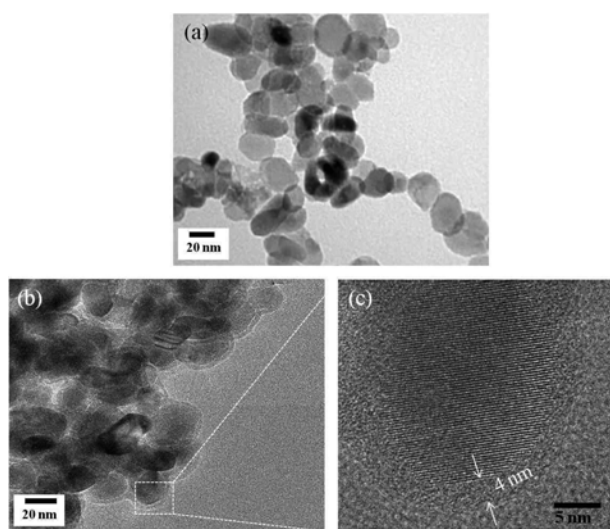


Fig. 1. TEM images of (a) pure TiO₂, (b) TiO₂@SiO₂ nanoparticles, and (c) high magnification HRTEM image of Fig. 1(b).

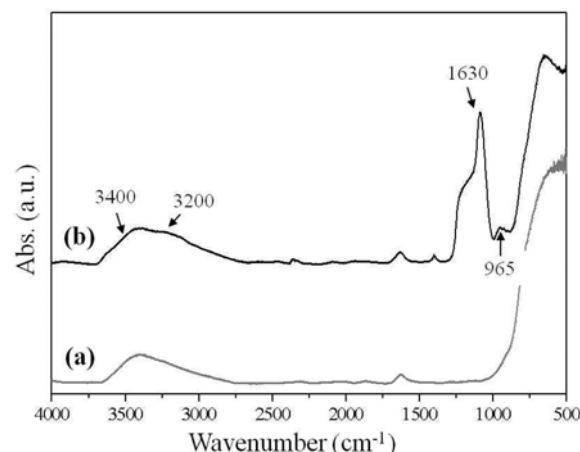


Fig. 2. FT-IR spectra of (a) pure TiO₂ (gray line) and (b) TiO₂@SiO₂ (black line) nanoparticles.

in Fig. 3(a). The both spectra contain elements of Ti, O, and C, together. The C 1s peaks come from carbon tape. Only the $\text{TiO}_2@/\text{SiO}_2$ nanoparticles show Si 1s and Si 2p peaks, which indicate that the TiO_2 particle was covered with silica. O 1s XPS spectra of pure TiO_2 and $\text{TiO}_2@/\text{SiO}_2$ nanoparticles are shown in Fig. 3(b). The binding energies of the O 1s peaks are 529.3 eV for pure TiO_2 , and weak 529.8 eV, strong 532.6 eV for $\text{TiO}_2@/\text{SiO}_2$ nanoparticles. Strong 532.6 eV peak might be attributed to the SiO_2 shells surrounding the TiO_2 cores, because the electronegativity of Si is greater than that of Ti. The O 1s peak of TiO_2 for $\text{TiO}_2@/\text{SiO}_2$ showed a chemical shift of 0.5 eV to higher binding energy than that of pure TiO_2 [13]. The Ti 2p spectra of pure TiO_2 and $\text{TiO}_2@/\text{SiO}_2$ nanoparticles are exhibited in Fig. 3(c). The binding energy of the Ti 2p peak for pure TiO_2 is 458.3 eV. The Ti 2p peak for $\text{TiO}_2@/\text{SiO}_2$ nanoparticles shifted to 458.5 eV (+ 0.2 eV) compared to the Ti 2p peak of pure TiO_2 . The chemical shifts of the Ti 2p and O 1s peaks indicated that the surface of TiO_2 particles was coated with a SiO_2 shell due to Ti-O-Si chemical bonds at the interface of the core-shell.

To investigate the band gap of pure TiO_2 and $\text{TiO}_2@/\text{SiO}_2$ nanoparticles, we performed valence band XPS (VB XPS) analysis indicated in Fig. 4. The pure TiO_2 nanoparticles displayed typical valence band characteristics of TiO_2 , with the edge of the maximum energy at about 1.6 eV below the Fermi level (E_F) [14]. For the $\text{TiO}_2@/\text{SiO}_2$ nanoparticles, the valence band maximum shifted toward 2.2 eV. This observation explains band gap broadening after SiO_2 coating on TiO_2 nanoparticles and increase in the band gap energy of $\text{TiO}_2@/\text{SiO}_2$ nanoparticles caused by a shift of the valence band edges through the formation of interface Ti-O-Si bonds. Band gap broadening can be caused by a quantum size effect, as well as the formation of a titania-silica interface, as hypothesized by Lassaletta and colleagues [16-17]. When we physically mixed different amounts of TiO_2 and SiO_2 by grinding, no

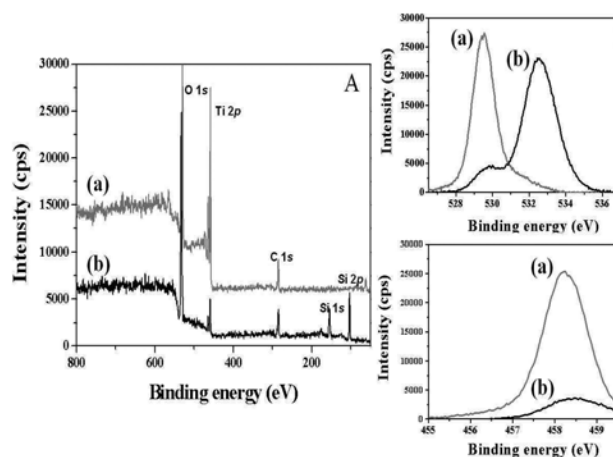


Fig. 3. XPS spectra of (A) wide scan XPS spectra, (B) O1s XPS spectra, and (C) Ti 2p XPS spectra; (a) pure TiO_2 (gray line) and (b) $\text{TiO}_2@/\text{SiO}_2$ (black line) nanoparticles.

significant changes in the optical band gap of TiO_2 were observed. As pointed out above, the crystal size of the pure TiO_2 and $\text{TiO}_2@/\text{SiO}_2$ nanoparticles did not change (see the TEM images in Fig. 1). These results indicate that a quantum size effect did not contribute to the observed band gap broadening of the $\text{TiO}_2@/\text{SiO}_2$ nanoparticles. We therefore attributed the shift and broadening of the band gap edge of $\text{TiO}_2@/\text{SiO}_2$ nanoparticles to the formation of Ti-O-Si bonds at the core-shell interface and not to a quantum size effect [18].

We measured the photocatalytic activities of pure TiO_2 and $\text{TiO}_2@/\text{SiO}_2$ nanoparticles by monitoring the photodegradation of the organic dye methylene blue (MB) in water. The kinetics of this reaction can be monitored by UV-vis spectroscopy, because MB shows a strong absorption band at 660 nm. The relative extinction A/A_0 was measured at 660 nm. Pure TiO_2 nanoparticles showed very high photocatalytic activity; 94% decomposition after 180 min (Fig. 5 (a)). The data for the pure TiO_2 clearly show a significant decrease in the spectral intensity of MB, indicating substantial

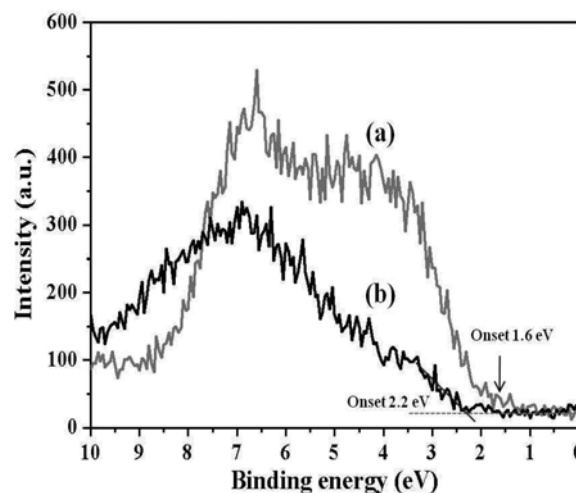


Fig. 4. Valence-band XPS spectra of (a) pure TiO_2 (gray line) and (b) $\text{TiO}_2@/\text{SiO}_2$ (black line) nanoparticles.

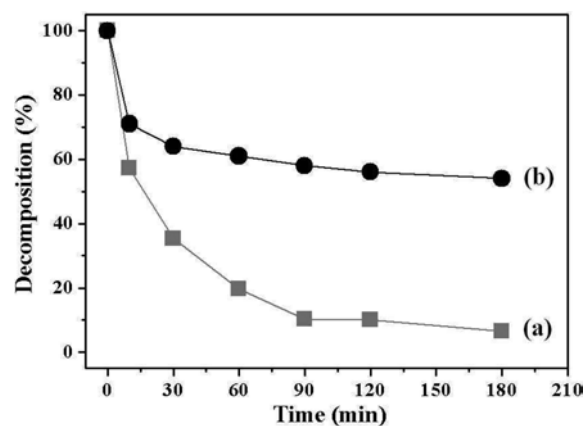


Fig. 5. Photocatalytic degradation of methylene blue solution as a function of UV irradiation time in the presence of (a) pure TiO_2 and (b) $\text{TiO}_2@/\text{SiO}_2$ nanoparticles.

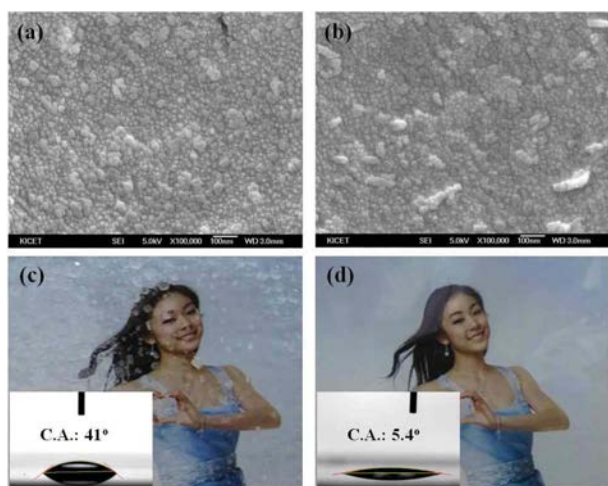


Fig. 6. SEM images of the surface morphology coated with (a) pure TiO₂ and (b) TiO₂@SiO₂ nanoparticles on the PET substrates. Color photographs (inset water contact angles) underneath transparency PET films coated pure (c) pure TiO₂ and (d) TiO₂@SiO₂ nanoparticles.

degradation of the dye under UV light-dominated illumination. In contrast, the TiO₂@SiO₂ nanoparticles had much lower photocatalytic activity; only 46% decomposition after 180 min. This result was anticipated for several reasons. Photogenerated electrons in TiO₂@SiO₂ nanoparticles should have a lower reducing power than those in TiO₂ nanoparticles due to band gap broadening, which would decrease the driving force for oxygen reduction [14]. Furthermore, the TiO₂ nanoparticles were enclosed by inactive, insulating silica shells uniformly.

SEM images and color photographs (inset water contact angles) of PET substrates coated with pure TiO₂ nanoparticles and TiO₂@SiO₂ nanoparticles are shown in Fig. 6. Based on the SEM images shown in Fig. 6(a) and (b), both coated surfaces exhibited nearly identical surface morphologies. Photographs and water contact angles of the surfaces of coated pure TiO₂ and TiO₂@SiO₂ nanoparticles are shown in Fig. 6 (c) and (d), respectively. The water contact angle of TiO₂@SiO₂-coated film was lower than that of pure TiO₂-coated film (41° and 5.4° in case of pure TiO₂ and TiO₂@SiO₂ nanoparticles, respectively), and we were able to exclude the effect of surface roughness based on the SEM images. From a practical point of view, it is desirable that the hydrophilic state of TiO₂@SiO₂-coated films be a permanent property without the need for UV activation. As seen in Fig. 6 (c) and (d), when PET substrates were coated with the either type of nanoparticle, the color pictures underneath the films were clearly visible. However, a clearer image was obtained when using TiO₂@SiO₂-coated film due to the improved wettability of the film without any distortion by water drops.

Conclusions

We prepared TiO₂ cores surrounded by SiO₂ shell

structures to suppress the photocatalytic activity of the TiO₂ cores and to improve the wettability of the resultant UV-shielding protective film. We characterized the TiO₂@SiO₂ nanoparticles by TEM, FT-IR, XPS, and VB-XPS. The photocatalytic activity of the TiO₂ cores was suppressed by the SiO₂ coating because of the broadening of the band gap due to the formation of Ti-O-Si chemical bonds at the core-shell interface. Moreover, the wettability of the TiO₂@SiO₂-coated films due to the formation of a hydrous SiO₂ shell around the TiO₂ core was a permanent property that did not require UV activation.

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