Photoinduced Reduction of Methylviologen with TiO_2/Polymer Films

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TiO_2/polymer films on quartz substrate were fabricated by layer-by-layer method and the ultrathin films showed photocatalytic activity for reduction of 1,1′-dimethyl-4,4′-bipyridinium dichloride on the irradiation of UV light.

Despite the recent progress in fabrication and photophysical characterization of layer-by-layer assembly of TiO_2 ultrathin films embedded on solid substrate such as quartz slide reported by several groups,[1–8] little is known concerning the photocatalytic activity of these materials systematically although TiO_2 has been known as a good photocatalyst.[9] In this paper, we report the photocatalytic activities of TiO_2-immobilized quartz plates for photoinduced reduction of 1,1′-dimethyl-4,4′-bipyridinium dichloride, namely methylviologen on the irradiation of UV light.

Nanoparticles of TiO_2 were purchased from Shokubai Kasei Kogyo Co. Ltd.[10] X-ray diffraction patterns of the TiO_2 powders at room temperature indicate the dominant peaks for anatase. The crystallite sizes were 6 nm, 10 nm, 59 nm, and 114 nm calculated from their half-height widths of the (101) diffraction peak of anatase by the Scherrer equation with a value of the shape factor K set at 0.9. Negatively charged ζ potentials of the TiO_2 nanoparticles were observed as −29.3 mV (ϕ 6 nm), −33.4 mV (10 nm), −72.3 mV (59 nm), and −41.4 mV (114 nm), respectively at pH 7.0 by using an electrophoretic light scattering spectrophotometer (Photal, Otsuka Electronics Co., Ltd. ELS-8000KO). In order to immobilize the TiO_2 nanoparticles onto the quartz plate, we adopted layer-by-layer method because of the simplicity for preparation and the precise control of a thickness on a micro- or meso-scale without high-cost equipments and conditions.[11–13] We chose poly(diallyldimethylammonium chloride) (PDDA, purchased from Aldrich Co., Mw 200000–300000) as positively charged polymer of 6 mg cm^{-3} in 10 mmol dm^{-3} HEPES buffer (pH 7.0) and potassium poly(vinyl sulfate) (PVS, purchased from Wako Co., Mw 240000) as polyanion of 4 mg cm^{-3} in 10 mmol dm^{-3} HEPES buffer (pH 7.0). Alternate assembly based on spontaneous ionic adsorption of oppositely charged materials from their stock solution was performed as follows. In the first stage a well-defined precursor film with the thickness of ca. 2 nm was assembled from PDDA and PVS onto quartz crystal microbalance (QCM) resonators or onto quartz slides. The precursor films contained four-polyion layers in the alternate mode $(PDDA/PVS)_2$, and the terminal (upper) layer was "positive" PDDA. The resonator or quartz slide was alternately immersed for 20 min in dispersed solutions of TiO_2 (5 mg cm^{-3}) and PDDA with intermediate water washing and periodical interruption of the process for measuring the resonance frequency {by using QCM device (USI System)} or the UV spectra (by using Pharmacia Biotech, Ultrospec 4000). The QCM frequency shifts on the cycles of alternate TiO_2/PDDA adsorption are proportional to the adsorbed mass. The frequency shift of 1 Hz corresponds to 0.576 ng of adsorption increase. For example, when the crystallite size was 10 nm, the adsorbed mass of TiO_2 for one cycle of alternate TiO_2/PDDA adsorption corresponds to 1.11 μg cm^{-2} ($\Delta f =$ 640 Hz). The linear growth of the film adsorption was observed during at least 15 steps of the alternate assembly. Absorption spectra of TiO_2/PDDA films on quartz slides also show linear absorbance increase at 240 and at 280 nm with the number of the adsorption cycle. Figure 1 shows absorption spectra of 5-layered TiO_2 of various nanoparticles. Although we could not clearly distinguish the blue-shift of absorption edge of smaller nanoparticle, linear relationships between the adsorbed mass of TiO_2 and the ζ potential were confirmed. Negatively charged particle was much adsorbed onto the substrate as shown in Figure 2.

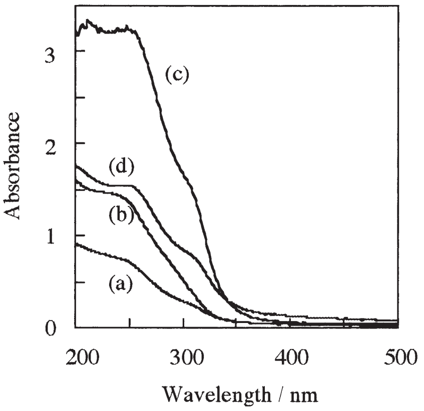

Figure 1. Absorption spectra of 5-layered TiO_2 of various nanoparticles. The crystallite sizes were (a) 6 nm, (b) 10 nm, (c) 59 nm, and (d) 114 nm, respectively.

We examined the photocatalytic activities of the above TiO_2-containing ultrathin films for photoinduced reduction of methylviologen (MV^{2+}) on the irradiation of UV light. Buffered solution (3 cm^3) of 200 mmol dm^{-3} tris-HCl (pH 7.0) including 15 mmol dm^{-3} of MV^{2+} was irradiated by 500 W xenon lamp light with stirring in a quartz cell ($10 \times 10 \times 40$ mm^3) under an atmospheric Ar with or without the TiO_2-containing quartz plate ($30 \times 9.0 \times 1.0$ mm^3) under the conditions of $\lambda >$ 325 nm at 25 °C. The formation of $MV^{\bullet+}$ whose color is blue (viz. ε_{605} of $MV^{\bullet+}$ is 12400 M^{-1}cm^{-1})[14] was easily recognized only in the reaction with the TiO_2-containing ultrathin film. Using the various TiO_2-containing ultrathin films shows time courses of the formation of $MV^{\bullet+}$. The amount of $MV^{\bullet+}$ formed from MV^{2+} increased remarkably with the number of the at-

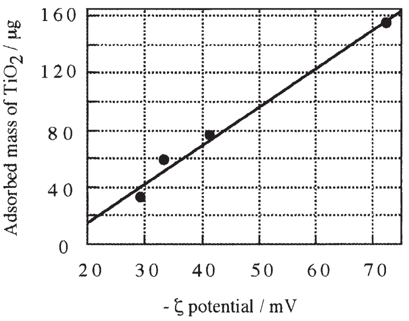

Figure 2. Relationship between the adsorbed mass of 5-layered TiO_2 and the ζ potential of the TiO_2 nanoparticle.

tached layers of TiO_2/PDDA from 1 to 5. On the other hand, the small extent of $MV^{\bullet+}$-generation-increase was observed when the number of the attached layers of TiO_2/PDDA increased from 5 to 10, 15, or 20. This result implies that the rate of diffusion of viologens in the 10, 15, or 20-layered film is the similar extent of that in the 5-layered one. It is also notable that the magnitude of $MV^{\bullet+}$-generation by using the 2, 3 or, 4-plates of 5-layered TiO_2/PDDA film is larger than that by using the 1-plate of 10, 15, or 20-layered one as shown in Figure 3. This result suggests that the effective contact area of the 2, 3, or 4-plates of 5-layered TiO_2/PDDA film for the photoreduction of MV^{2+} is larger than that of the 1-plate of 10, 15, or 20-layered one. Using the 5-layered TiO_2/PDDA film does not decrease the amounts of the produced $MV^{\bullet+}$ through the 10 times-iterative uses with 15 minutes-illumination. This result indicates that removal of the attached layers of TiO_2/PDDA from the quartz plate does not occur during the photoreduction. Using the various sizes of the crystallite of TiO_2 immobilized films summarizes quantum yields of the produced $MV^{\bullet+}$ in Table 1. The smallest particle of 6 nm TiO_2 enhances the quantum yield as 2 times larger compared to the largest one of 114 nm TiO_2.

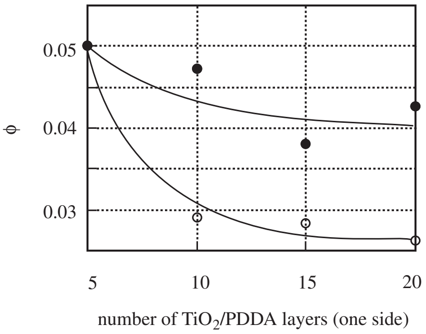

Figure 3. Quantum yield (Φ) of $MV^{\bullet+}$-formation by using 2, 3, or 4-plates of 5-layered TiO_2/PDDA film (●) or by using 1-plate of 5, 10, 15, or 20-layered one (○).

Table 1. Particle size effects upon the quantum yield (Φ) of $MV^{\bullet+}$-generation by using the 5-layered TiO_2/PDDA film[a]

particle size nm	$[MV^{\bullet+}]$ μmol $dm^{-3} min^{-1}$	Φ
6	3.29	0.050
10	5.11	0.032
59	12.33	0.037
114	9.20	0.022

[a] The photoreaction was done as described in the text.

Consequently, increasing the number of the quartz plates of TiO_2 immobilized film is more effective for the photoinduced reduction of viologen than increasing the number of the attached layers of the film and the small extent of the effect of the small size on the photocatalytic reaction such as size quantization effect[15] was observed.

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