Synthesis of Photofunctional Titania Nanosheets by Electrophoretic Deposition

Tatsuto Yui,[†,§] Yumiko Mori,[†] Takako Tsuchino,[†] Toshio Itoh,[†] Takeshi Hattori,[†] Yoshiaki Fukushima,[‡,§] and Katsuhiko Takagi*,[†,§]

Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, 464-8603, Japan, Toyota Central R & D Labs Inc., Yokomichi, Nagakute, Aichi 480-1192, Japan, and Japan Science and Technology (JST)

This work presents the first investigation of an effective methodology for the synthesis of transparent and durable thin films with a high regularity along the *c*-axis using titania nanosheets (TN) on electrodes. This technique, an electrophoretic deposition method (EPD), was found to be applicable for the preparation of TN thin films deposited on ITO electrodes, a promising nanomaterial for the design of UV−visible light-sensitive energy conversion systems. The deposition of TN was found to be significantly affected by the concentrations, viscosity, and pH values of the aqueous TN solutions. Using quartz crystal analysis (QCA), the optimal deposition conditions for the most adhesive amounts of TN were established, and the delicate balance between the TN solution viscosity and surface charges of the TN layers that govern the amount of TN deposited on the substrate was discerned. Moreover, the deposited thin films were greatly improved by the addition of poly(vinyl alcohol) (PVA) into the solutions, initiating an increase in the deposition weight and optical transmittance, thus leading to firm adhesion onto the substrate. Methyl viologen (MV^{2+}) was intercalated into the TN layers and irradiated with UV light shorter than the end absorption of TN, leading to a blue coloring for the TN/MV^{2+} thin films attributed to the formation of reduction products from MV^{2+} and clearly indicating photocatalytic reactivity.

Introduction

In recent years, nanostructured organic−inorganic materials have been actively investigated for the preparation of photofunctional compounds.[1,2] The hybridization of photofunctional organic molecules with layered metal oxide semiconductors (LMOS) is especially attractive due to their intercalation properties, large surface area, and photocatalytic reactivity.[3−5] Studies have also focused on the delamination of a number of layered host compounds as well as exfoliated single sheets, i.e., new classes of nanoscale materials exhibiting novel physical and chemical properties associated with a thinness of a nanometer order.[6−9] Titania nanosheets (TN) were first synthesized and characterized by Sasaki et al and these were reported to be two-dimensional semiconductors with diameters and thicknesses of several micro-

meters and sub-nanometers, respectively, and thus can be considered the building blocks for the development of efficient TiO_2 photocatalysts.[10−13] Along these lines, laminated composites of TN alternatively stacked with poly-cations and poly-anions have been reported to have unique physical and chemical properties.[13] Thus far, various techniques such as the alternate stacking of ionic polymer nanosheets have been reported; however, not all of these methods are able to produce smooth, well-organized films.

* To whom correspondence should be addressed. Tel: +81-52-789-4501. Fax: +81-52-789-3338. E-mail: ktakagi@apchem.nagoya-u.ac.jp.
† Nagoya University.
‡ Toyota Central R & D Labs Inc.
§ Japan Science and Technology.

(1) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995**, *95*, 399.
(2) (a) Takagi, K.; Shichi, T. In *Solid State and Surface Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 2000; Vol. 5, p 31. (b) Shichi T.; Takagi K. *J. Photochem. Photobiol., C* **2000**, *1*, 113.
(3) (a) Yamaguch, Y.; Yui, T.; Takagi, S.; Shimada, T.; Inoue, H. *Chem. Lett.* **2001**, 644. (b) Tong, Z.; Shichi, T.; Kasuga, Y.; Takagi, K. *Chem. Lett.* **2002**, 1206.
(4) (a) Tong, Z.; Shichi, T.; Oshika, K.; Takagi, K. *Chem. Lett.* **2002**, 876. (b) Tong, Z.; Shichi, T.; Takagi, K. *J. Phys. Chem. B* **2002**, *106*, 13306.
(5) (a) Furube, A.; Shiozawa, T.; Ishikawa, A.; Wada, A.; Domen, K.; Hirose, C. *J. Phys. Chem. B* **2002**, *106*, 3065. (b) Takahara, Y.; Konodo, J. N.; Takada, T.; Lu, D.; Doumen, K. *Chem. Mater.* **2001**, *13*, 1194.
(6) (a) Kellar, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817. (b) Fang, M.; Kim, C. H.; Saupe, G. B.; Kim, H.-N.; Waraksa, C. C.; Miwa, T.; Fujishima, A.; Mallouk, T. E. *Chem. Mater.* **1999**, *11*, 1526. (c) Kaschak, D. M.; Lean, J. T.; Waraksa, C. C.; Saupe, G. B.; Usami, H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 3435.
(7) Kotov, N. A.; Dekany, I.; Fender, J. H. *Adv. Mater. (Weinheim, Ger)* **1996**, *8*, 637.
(8) (a) Wang, L.; Omomo, Y.; Sakai, N.; Fukuda, K.; Nakail, I.; Ebina, Y.; Takada, K.; Watanabe, M.; Sasaki, T. *Chem. Mater.* **2003**, *15*, 2873. (b) Wang, L.; Takada, K.; Kajiyama, A.; Onoda, M.; Michiue, Y.; Zhang, L.; Watanabe, M.; Sasaki, T. *Chem. Mater.* **2003**, *15*, 4508. (c) Xu, F. F.; Ebina, Y.; Bando, Y.; Sasaki, T. *J. Phys. Chem. B* **2003**, *107*, 9638. (d) Xu, F. F.; Ebina, Y.; Bando, Y.; Sasaki, T. *J. Phys. Chem. B* **2003**, *107*, 6698.
(9) (a) Takagi, A.; Sugisawa, M.; Lu, D.; Kondo, J. N.; Hara, M.; Domen, K.; Hayashi, S. *J. Am. Chem. Soc.* **2003**, *125*, 5479. (b) Nakato, T.; Miyamoto, N.; Harada, A. *Chem. Commun.* **2004**, 7 8.
(10) Sasaki, T.; Ebina, Y.; Tanaka, T.; Watanabe, M.; Decher, G. *Chem. Commun.* **2000**, 2163.
(11) Sasaki, T.; Watanabe, M.; Hashizumi, H.; Yamada, H.; Nakazawa, H.; *Chem. Commun.* **1996**, 229. (b) Sasaki, T.; Watanabe, M. *J. Am. Chem. Soc.* **1998**, *120*, 4682.
(12) Sasaki, T.; Watanabe, M.; Hashizume, H.; Yamada, H.; Nakazawa, H. *J. Am. Chem. Soc.* **1996**, *118*, 8329.
(13) (a) Sasaki, T.; Ebina, Y.; Tanaka, T.; Harada, M.; Watanabe M. *Chem. Mater.* **2001**, *13*, 4661. (b) Wang, L. Z.; Sasaki, T.; Ebina, Y.; Kurashima, K.; Watanabe, M. *Chem. Mater.* **2002**, *14*, 4827. (c) Sasaki, T.; Ebina, Y.; Fukuda, K.; Tanaka, T.; Harada, M.; Watanabe, M. *Chem. Mater.* **2002**, *14*, 3524.

Electrophoretic Deposition of Titania Nanosheets

Chem. Mater., Vol. 17, No. 1, 2005 207

Moreover, although the LB method can produce films of good quality, its disadvantage is the long preparation time necessary for the synthesis of the composites. For example, the procedure for applying each layer is so time-consuming and tedious that 10 layers (or less) is the upper limit for TN stacking. In principle, with unlimited time, more may be stacked, however this is not realistic or practical. In contrast, the electrophoretic deposition method (EPD) used here has the advantage of relatively easy synthesis and handling of materials while many layers can also be quickly applied in a single process. Moreover, the direct control of the structure and thickness by changing the concentrations of nanosheets and the electric currents is also possible.[14-18] The thin films prepared, i.e., transparent and uniform TN films of only few micrometers thickness on an ITO electrode, were also found to exhibit photocatalytic reactivity. The preparation of these TN thin films by an electrophoretic deposition method (EPD) and investigations of their chemical characteristics and photofunctional properties are presented here.

Experimental Section

Materials. Tetrabutylammonium hydroxide (TBA$^+$OH$^-$; Aldrich), poly(vinyl alcohol) (PVA; Wako Co. Ltd., $M_w = 900-1100$), poly(vinylpyrrolidone) (PVP; TCI, $M_w = 1000$), and methyl viologen diiodide (MV^{2+} 2I$^-$; TCI) of extra pure grade (>99.9%) were used without further purification. The other reagents were of analytical grade and used as received. Milli-Q filtered water (Millipore Co.) was used as the pure water source throughout the experiments.

The titania nanosheets (TN) were prepared by procedures previously reported by Sasaki et al., as follows. A stoichiometric mixture of Cs$_2$CO$_3$ and TiO$_2$ was calcined at 800 °C for 20 h to form a cesium titanate as the precursor (Cs$_{0.7}$Ti$_{1.825}$□$_{0.175}$O$_4$; □ = a vacancy). Approximately nine grams of cesium titanate was treated with 900 mL of a 1 M HCl solution and this treatment was repeated 4× at room temperature, each time for 24 h, while the resulting products were filtered, washed well with water, and air-dried in vacuo.[10-12] The obtained protonated titanate (H$_{0.7}$Ti$_{1.825}$□$_{0.175}$ O$_4$·H$_2$O, 1.2 g) was shaken vigorously with 100 mL of a 33 mM tetrabutylammonium hydroxide (TBA$^+$) aqueous solution, corresponding to 0.7 of the anionic sites of the TN, for 2 weeks at ambient temperature and leading to exfoliated titania nanosheets (TN) in a colorless turbid solution.

Electrophoretic Deposition (EPD). Electrophoretic deposition (EPD) was carried out at a constant current of 0.04-2.5 mA/cm^2 employing both ITO anodic and cathodic electrodes with a working area of 2 cm × 2 cm.[14-18] The distance between the anodic and cathodic plates was fixed at 1.0 cm and the TN sheets were observed to be deposited only on the anodic electrode. The electrophoretic substrates were then dried under aerated conditions at room temperature.

Quartz Crystal Analysis (QCA). The amounts of TN sheets deposited on the electrodes were measured by a piezoelectric quartz crystal analyzer (QCA; Seiko EG & G Co. Ltd.) and the changes in the mass were monitored by the changes in the frequency

responses for the composite samples. Deposition of the ITO electrode was carried out using a quartz crystal (Seiko) as the receiving electrode at a frequency of 9 MHz, along with a counter-electrode of the ITO substrate which was placed at a distance of ca. 1 cm from the anodic electrode. The frequency changes were monitored directly using the QCA instrument. The increase in the amount of TN deposited on the ITO substrate could be estimated by the decrease in the quartz frequency in a linear relationship, as shown in eq 1.

$$\Delta m = \frac{-\Delta F \times A \times \sqrt{\mu \times \rho}}{2 \times (F_q)^2} \tag{1}$$

Here, Δm, ΔF, F_q, A, ρ, and μ represent the changes in the mass on the quartz crystal electrode, the observed frequency changes, the resonant frequency of the crystal (in this case, 9.00 MHz), the surface area of the quartz (0.196 cm^2), the density of the quartz crystal (2.648 g/cm^3), and the share modulus of the quartz (2.947 × 10^{11} g/cm/sec^2), respectively. Analysis showed that $\Delta F = 1$ Hz corresponded to 1.068 ng of the weight change of TN, indicating a detection limit up to 1.0 ng.

Photocatalytic Reactivity of the TN Film. The intercalation of MV^{2+} ions into the PVA coadsorbed TN thin film was carried out according to the following procedures. The TN thin films deposited on the ITO electrode by EPD, at 10 mA/cm^2 for the current density, 5 min for the electrophoretic time, and at [TN] = 0.4 wt % and [PVA] = 0.2 wt %, were soaked in an aqueous solution of [MV^{2+}] = 4.1 × 10^{-5} M at room temperature. The intercalated amounts of MV^{2+} were estimated by the absorbance intensities of the MV^{2+} desorbed in the solutions in proportion to the soaking time. However, after ca. 3 h, saturation was observed and the intercalation of MV^{2+} ceased, so that the amount remained constant even after soaking for up to 16 h in the MV^{2+} aqueous solution. Furthermore, MV^{2+} was deposited in amounts corresponding to 30% CEC based on the surface charge of the TN.[11] MV^{2+} intercalated into the interlayers of the TN thin films were irradiated with a 300 W Xe lamp (XDS-301S, WACOM Co.) combined with a cutoff filter, UTVAF-50S and −43U (HOYA), eliminating wavelengths longer than 300 nm. Under these conditions, only the TN sheets (not the MV^{2+} or reduction products) could absorb the incident light. The samples were placed 10 cm from the light source and irradiated under aerated atmosphere.

Poly(vinylpyrrolidone) (PVP) was used as the electron donor, and a control experiment was separately carried out with light irradiation of the PVP/MV^{2+} films, i.e., a PVP/MV^{2+} aqueous mixture was cast on a glass substrate and dried by air flushing. The cast samples were then irradiated with 235 nm light to form cation radicals (MV$^{+•}$) of MV^{2+}. Both the TN/MV$^{+•}$ film and control PVP/MV$^{+•}$ cast film were kept under aerated conditions and their absorptions of MV$^{+•}$ (605 nm) were measured as a function of time after irradiation.

Apparatus. Powder X-ray diffraction analysis (XRD) was carried out with a Rigaku RINT-2100 XRD apparatus operating at 40 kV and 40 mA and set at a Ni-filtered Cu Kα radiation wavelength of 1.54 Å. The UV−visible absorption spectra were directly measured on the ITO substrate in the transmittance mode with a JASCO spectrometer, type V-550. Scanning electron micrograph (SEM) images were recorded on a JSM-5600 apparatus (JEOL) operating at 20 kV for the Au-coated samples.

Results and Discussion

Preparation of TN Thin Films by the EPD Method. The titania nanosheets (TN) deposited on the ITO electrode

(14) Zhitomirsky, I. *Adv. Colloid Interface Sci.* **2002**, 279.
(15) Sarkar, P.; Haung, X.; Nicholson, P. *J. Am. Ceram. Soc.* **1992** *75*, 2907.
(16) Hatton, B.; Nicholson, P. *J. Am. Ceram. Soc.* **2001** *84*, 571.
(17) Zitomirsky I. *Mater. Lett.* **1998** *37*, 72.
(18) Graham, J.; Rosseinsky, D.; Slocombe, J.; Barrett, S. Francis, S. *Colloids Surf.* **1995**, *94*, 177.
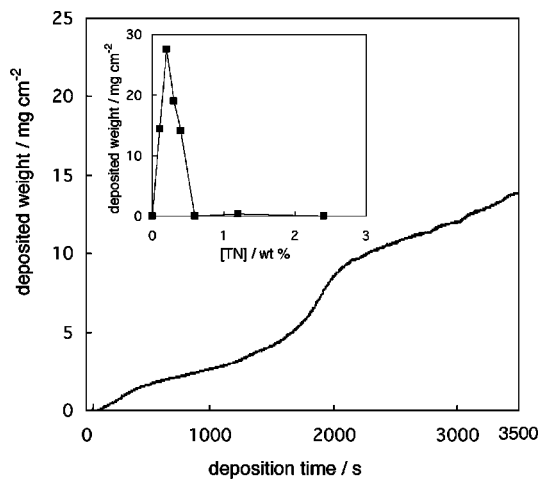
Figure 1. QCA profile of TN by an EPD method onto the ITO electrode: [TN] = 0.2 wt %, current = 10 mA/cm². Inset shows the relationship between the deposited weight of TN on the ITO electrode and the concentration of TN, at 5 min deposition.
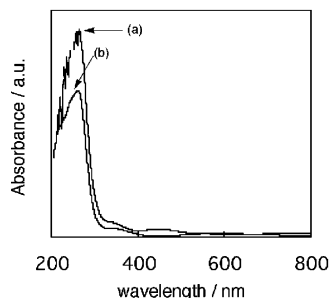

Figure 2. Absorption spectra of (a) the TN thin films prepared by the EPD method, [TN] = 0.2 wt %; electric current = 10 mA/cm² for 5 min and; (b) the [TN] = 0.2 wt % aqueous dispersion.

were weighed by quartz crystal analysis (QCA) as a function of the EPD time at a constant current of 0.2 mA/cm². A profile of the adsorbed weight of TN against the electrophoretic time at [TN] = 0.4 wt % including TBA⁺ is shown in Figure 1. The deposition weight continuously increased monotonically and was not saturated under these experimental conditions (deposition time < 3600 s) so that smooth and transparent thin films could be obtained by EPD with a transmittance above 70% at visible light regions of 350– 800 nm, as shown in Figure 2. The transmittance absorption spectrum of TN on the ITO electrode by EPD (Figure 2a; at [TN] = 0.2 wt %, current = 10 mA/cm²) indicated that the absorption maximum at around 265 nm and its end absorption correspond to those for the aqueous dispersion of TN, as shown in Figure 2b.[10−13]

The XRD profiles of the protonated TN powdered samples prior to TBA⁺ intercalation and the TN thin films incorporated with TBA⁺ by EPD are shown in Figure 3a and b, respectively. The protonated precursor showed a relatively weak diffraction *d(001)* peak with a layer distance of *d* = 9.2 Å, while the TBA⁺ incorporated EPD thin films exhibited a series of *d(001)* to *(004)* diffraction peaks, by which the layer distance was estimated at 15.8 Å, due to their regularly layered structure, resulting in a large expansion of the layer distances. The estimated clearance space (CLS) of 11.3 Å for the TN layers incorporated with TBA⁺ suggests a monolayer packing of these TBA⁺ molecules in the TN
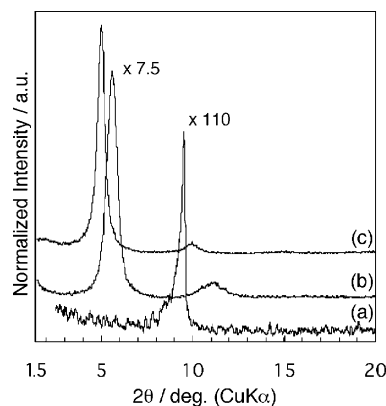

Figure 3. XRD profiles of (a) the powdered samples of the protonated precursor material of TN (without TBA⁺); (b) the TN EPD films with TBA⁺; and (c) the TN EPD films with TBA⁺ and PVA. The intensities were multiplied 110 times for (a) and 7.5 times for (b).

interlayers.[19] The CLS was, thus, shown to exhibit a good correspondence with the TBA⁺ molecular length of 12 Å. Moreover, analyses of the QCA, absorption spectra, and XRD clearly indicated that the TN thin films formed on the ITO electrode by EPD were transparent and laminated.

Effect of [TN] on EPD. The amount of TN deposited on the ITO was strongly affected by the initial TN concentration, [TN], as shown in Figure 1. At less than 0.2 wt % [TN], the deposited weights increased with an increase in the concentration, as can be seen in the inset of Figure 1. This was in stark contrast to the case of higher concentrations (>0.2 wt %) where the deposited weights decreased with an increase in the [TN]. The deposition rate (*v*) could be determined by the following eq 2:

$$v = \frac{2\,\epsilon_0\,\epsilon}{3\,\eta}\frac{E}{l}\zeta \tag{2}$$

where ϵ_0, ϵ, η, E/l, and ζ denote the dielectric constant under vacuum, the relative dielectric constant, the solution viscosity, strength of the electric field, and the ζ-potential, respectively.[20] On the basis of eq 2, the viscosity (η) of the TN solution was seen to be one of the most important factors for effective electrophoretic deposition. The η-values of the TN solution were estimated at various TN concentrations using eq 3:

$$-\Delta F = (F_q)^{3/2} \times \left(\frac{\rho_l \times \eta}{\pi \times \rho_q \times \mu}\right)^{1/2} \tag{3}$$

where ρ_l, ρ_q, and μ denote the density of the TN solution (0.9996 g/cm³), the density of the quartz crystal (2.648 g/cm³), and the elastic rate for the quartz crystal (7.31 × 10¹⁰ Pa), respectively. The viscosity of the solution (η) was estimated from the changes in frequency (ΔF) as measured by a QCA instrument. The viscosity (η) and pH values of the solutions having various TN concentrations are shown in Figure 4 a and b, respectively. It can be seen that the η and pH values monotonically increased with an increase in the TN concentrations. Under these experimental conditions,

(19) Estimation from subtraction of the layer thickness of TN (4.5 Å)[15] from the *d(001)* values obtained from XRD.
(20) Matsuda, Y.; Iwakura, C. *Introduction to Electro Chemistry*; Maruzen: Tokyo, 2000.

Electrophoretic Deposition of Titania Nanosheets

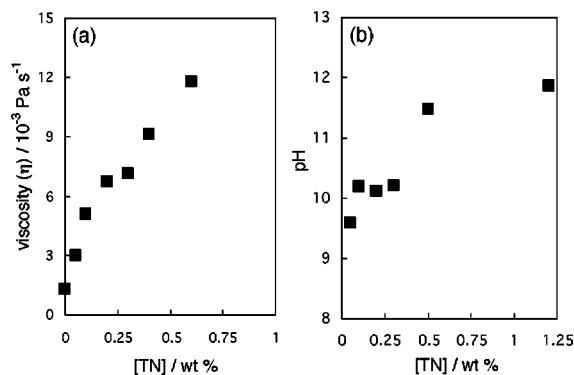*Chem. Mater., Vol. 17, No. 1, 2005* **209**

Figure 4. Effect of the concentration of TN on (a) the solution viscosity; and (b) the pH values.

Table 1. Relations between EPD Current (mA/cm²) and Deposition Rate (ng cm⁻²s⁻¹)[a]

current	0.04	0.12	0.49
deposition rate	3.2	44.2	624.0

[a] [TN] = 0.4 wt %.

the ϵ_0, ϵ, and E/l values in eq 3 were assumed to be constant. The deposition rate (v), thus decreased with an increase in the viscosity (η) of the solution. Also, an increase in the pH values enhanced the negative charges on the surface of the TN layers, thus inducing an increase in the deposition rate. These results indicate the delicate balance between the viscosity of the TN solution and the surface charge of the TN layered surface that governs the deposition weights.

Effect of the Electric Currents on EPD. EPD was carried out under various electric currents to study their effect on the formation of the TN thin films. An increase in the EPD currents was observed to increase the deposition rates, as summarized in Table 1, and thus, the deposition time could be shortened so that the amount of TN deposited on the ITO electrode could be controlled by variations in the EPD current. However, the deposition efficiency was seen to drop after 100 and 500 s at currents of 0.6 and 2.5 mA/cm², respectively, due to bubble formation on the electrode. As the deposition weights increased on the ITO electrode, the electric current began to decrease, while the voltage began to rise and, at the same time, induce the splitting of water into H_2 and O_2.

Effect of the Added PVA on EPD. A nonionic but hydrophilic coadhesive agent was investigated in order to improve the physical strength of the films prepared by EPD; i.e., poly(vinyl alcohol) (PVA), was added to the TN solutions to improve the optical transparency, the adhesive properties, and the photocatalytic efficiency of the TN films.[21,22] The TN deposition profiles in the presence and absence of 0.2 wt % PVA by QCA analysis are shown in Figure 5. Without the PVA, the deposition weights gradually increased and did not saturate, even after an EPD time of up to 3600 s. This was in stark contrast to the results in the presence of PVA where the deposited weights were saturated within 1800 s. As the deposition weight increased, the nonionic PVA film was seen to cover the entire electrode
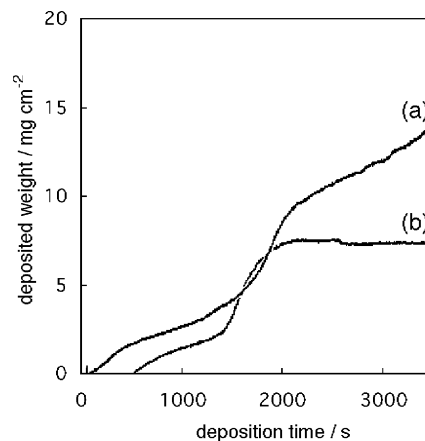
(21) Zhitomirsky, I. *Adv. Colloid Interface Sci.* **2002**, *97*, 277.
(22) Mizuguchi, J.; Sumi, K.; Muchi, T. *J. Electrochem. Soc.* **1983**, *130*, 1819.


Figure 5. QCA profiles of the deposition of TN by EPD onto the ITO electrode at [TN] = 0.4 wt %: (a) without PVA; and (b) with PVA, i.e., [PVA] = 0.2 wt %.

surface. At the same time, the surface conductivity decreased due to the PVA coverage of the surface, ultimately inducing saturation of the deposition weight.

The XRD profiles of the TN thin films with and without PVA are shown in Figure 3c and b, respectively. The profiles of the films with PVA (Figure 3c) exhibit relatively strong *d(001)* to *d(004)* diffraction peaks, indicating films of a characteristic layered structure even after EPD treatment with PVA. The layer distances of the TN thin films were estimated to be 15.8 and 17.6 Å in the absence and presence of PVA, respectively. The expansion of the layer distance indicated that the PVA molecules were co-intercalated into the TN layer with TBA^+ molecules. Similarly to the TN films without PVA (Figure 2a), a clear absorption maximum characteristic of TN particles with PVA could be observed at around 265 nm. Moreover, the resulting PVA-modified TN films showed more transparency than the films without PVA, i.e., the transmittances of the films were >70% for [TN] = 0.2 wt % without PVA; >80% for [TN] = 0.2 wt % with PVA; >50% for [TN] = 0.4 wt % without PVA; and >70% for [TN] = 0.4 with PVA at visible light regions (400−800 nm). The PVA additive was, thus, seen to play a major role in the improvement of not only the transparency but also the adhesive properties of the films. Scanning electron micrograph (SEM) images show the TN thin films prepared on the ITO electrode by EPD under deposition conditions of 0.4 wt % TN, 0.2 wt % PVA, and with current densities of 1.6 mA/cm² for a deposition period of 5 min to be uniform and smooth, as shown in Figure 6.

The durability of the PVA-modified TN thin films was compared with samples without PVA. The TN films prepared were deposited electrophoretically or cast on the electrode and then dried under air at room temperature, followed by soaking in water for 1 h. The weight changes in the films on the electrode before and after the soaking procedures were monitored by QCA analysis and the results are summarized in Table 2. For the thin films without PVA as an additive, desorption of the films from the ITO electrode surface during the soaking procedure could be seen for both the EPD and casting methods. In contrast to these results, for the 80% PVA-modified TN films, the adsorbed TN particles were hardly seen to change and remained securely attached onto
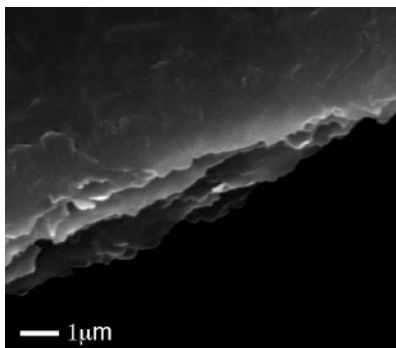
Figure 6. SEM images of the TN thin films at [TN] = 0.4 wt %, [PVA] = 0.2 wt %, and electric current = 1.6 mA/cm^2 for 5 min.

Table 2. Weight Loss (%) of TN on ITO- and Ni-Electrode by Soaking Procedures

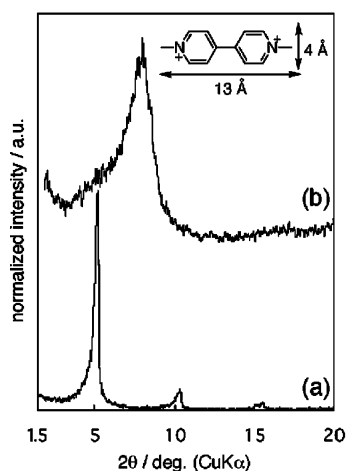|	cast film	cast film with PVA	EPD	EPD film with PVA
ITO	100	83	17	14
Ni		73	69	0

Figure 7. XRD profiles of the TN EPD thin films: (a) before soaking in MV^{2+} aqueous solution; and (b) after soaking in MV^{2+} aqueous solution. Inset shows the molecular structure of MV^{2+} together with its molecular size.

the ITO electrode. Moreover, by using a Ni-electrode in place of the ITO electrode, ca. 100% of the PVA-modified TN stayed tightly adsorbed onto the electrode. The viscous liquid PVA was, thus, observed to act as a sort of glue to improve the adhesive properties, i.e., the affinity between the TN particles and electrode surface could be improved by the penetration of poly-hydroxylic PVA into the TN particles by H-bonding with the TBA$^+$ ammonium nitrogen adsorbed on the TN surface. It can, therefore, be concluded that PVA coadsorption was very effective in improving the durability of the TN films on the ITO electrode in addition to improving the transparency and smoothness.

Intercalation of MV^{2+} into the TN Thin Films. To clarify the photocatalytic activity of the EPD thin films, methyl viologen (MV^{2+}) was introduced into the layer surface of the films and was subject to a one-electron reduction by the excited TN thin film to form MV cation radicals (MV$^{+\bullet}$). The XRD profiles of TN before and after soaking in the MV^{2+} aqueous solution are shown in Figure 7. The TN layer distances decreased from 17.4 to 11.0 Å by the substitution of both TBA$^+$ and PVA with MV^{2+}. The
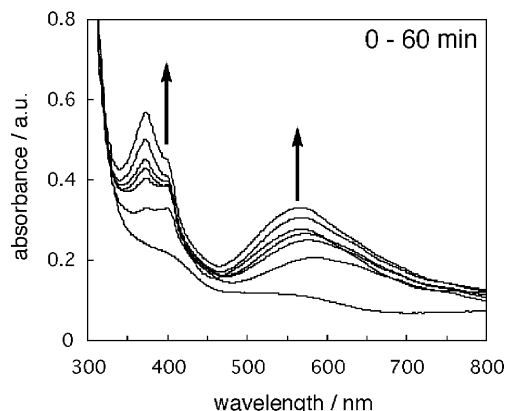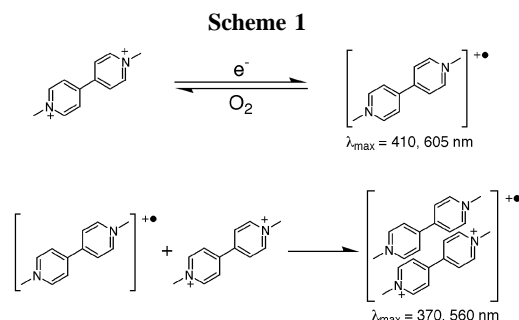

Figure 8. Changes in the absorption spectra of the TN/MV^{2+} thin films by irradiation at 300 nm for 0−60 min.

Scheme 1

incorporated MV^{2+} molecules were assumed to be arranged in a parallel orientation within the layers of TN in a monolayer structure, based on the molecular length of MV^{2+} (long axis ca. 13 Å; short axis ca. 5 Å; Figure 7 inset) and the clearance space of the TN (4.5 Å) for these MV^{2+}/TN films.

Photoinduced Electron Transfer from TN to MV^{2+}. The absorption edge of TN lies at a wavelength of ca. 300 nm irradiated on the MV^{2+}/TN thin films, and thus, was selectively absorbed by TN. During steady irradiation at 300 nm, the color of the MV^{2+}/TN film changed to blue, indicating the formation of MV$^{+\bullet}$; i.e., the TN stacked films were observed to exhibit photocatalytic activity even upon deposition by EPD. Moreover, changes in the absorption spectra of MV^{2+}/TN could be observed upon UV irradiation at 300 nm, as shown in Figure 8. Within 1 min irradiation, new absorption bands could be seen at around 410 and 605 nm, both of which corresponded to those for the MV$^{+\bullet}$ monomers observed at λ_{max} = 410 and 600 nm in aqueous solution.[4,23−25] With an increase in the irradiation time, the absorption intensities of MV$^{+\bullet}$ shifted to blue, i.e., 371 and 571 nm after 5 min irradiation, and these could be assigned to MV$^{+\bullet}$ dimers of λ_{max} = 370 and 530 nm in aqueous solution.[23−25] The formation of the MV$^{+\bullet}$ monomers and their dimers could be understood as shown in Scheme 1.

The TN/MV^{2+} films thus prepared by EPD and dried under air at room temperature were shown to exhibit photocatalytic

(23) Kamogawa, H.; Mizuno, H.; Todo, Y.; Nanasawa, M. *J. Polym. Sci.* **1979**, *17*, 3149.
(24) Lee, C.; Lee, Y. M.; Moon, M. S.; Park, S. H.; Park, J. W.; Kim, K. G.; Jeon, S.-J. *J. Electroanal. Chem.* **1996**, *416*, 139.
(25) Monk, P. M. S.; Fairweather, R. D.; Ingram, M. D.; Duffy, J. A. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2039.

reactivity. However, interestingly, when the TN aqueous solution was cast to form a film on the silica slide followed by vapor evaporation and the photochemical reduction of MV2+ in the interlayers of the TN films was investigated, no photochemically reductive products could be observed even after 3 h irradiation. Also, $MV^{+\bullet}$ is known to be efficiently oxidized by molecular oxygen and to recover the original colorless MV^{2+}. The cast TN films may include molecular oxygen within its interlayers since the photoreaction products from MV^{2+} could be observed when the films were dried under vacuo overnight.

The obtained TN particles were characteristic of the closely packed structure of titania sheets, as evidenced by XRD analysis. Oxygen gas permeation was also investigated by measuring the decay rate of the $MV^{+\bullet}$ ions. Here, the EPD films incorporating MV^{2+} were compared with the cast films of a mixed solution of MV^{2+} and poly(vinylpyrrolidone) (PVP). These two kinds of films, after being kept in air under dark conditions and then irradiated for 30 min, were analyzed to monitor the decomposition rates of $MV^{+\bullet}$ at 605 nm. Both the TN/MV^{2+} and PVP/MV^{2+} films could be seen to undergo oxidation of $MV^{+\bullet}$ to MV^{2+}, however, a large difference in the lifetimes of $MV^{+\bullet}$ could be seen between these films. The lifetimes were strongly dependent on the O_2-permeation resistant environment surrounding $MV^{+\bullet}$ and the half-lifetimes ($\tau_{1/2}$), i.e., 9 h for the TN/MV^{2+} and 0.5 h for the PVP/MV^{2+} films. Moreover, the $MV^{+\bullet}$ in the TN/MV^{2+} film was found to be 18 times more stable than that in the PVP/MV^{2+} film, suggesting the close packing arrangement of the TN films was effective in suppressing gas permeation.

Conclusions

Titania nanosheet (TN) thin films were prepared on an ITO-electrode substrate by an electrophoretic deposition (EPD) method and these photocatalysts exhibited high transmittance in visible light regions. Quartz crystal analysis (QCA) showed that the TN deposition amounts were strongly affected by the concentrations of the TN aqueous solutions. The deposition weights were shown to be governed by a delicate balance between the viscosity and pH values of the TN solution. Moreover, the durability of the deposition films could be significantly improved by the addition of polyvinylacohol (PVA) without any changes in their chemical and physical properties. When methyl viologen (MV^{2+}) molecules were intercalated into the TN layers, they were confirmed to be photochemically active under irradiation at the absorption band of TN for the TN/MV^{2+} thin films. Moreover, the reduction products of MV^{2+} were stable in the films and their lifetimes were 18 times longer than those in the absence of a TN system. These results showed that durable and photofunctional hybrid thin films of a closely packed orientation could be developed for use in energy conversion systems by the present EPD technique together with PVA.

CM0491882