

Photocatalytic Reactivities of Nafion-Coated TiO₂ for the Degradation of Charged Organic Compounds under UV or Visible Light

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Nafion (perfluorinated polymer with sulfonate groups)-coated TiO₂ particles (Nf/TiO₂) were prepared and their reactivities for the photocatalytic degradation (PCD) of charged organic substrates were investigated. The presence of Nafion adlayers drastically changed the positive TiO₂ surface charge to a negative one over the entire pH range and significantly influenced the PCD kinetics and mechanisms. The UV-induced PCD of tetramethylammonium (TMA; cationic substrate) was greatly enhanced in the presence of Nafion adlayers on TiO₂ because the ion-exchange sites within the Nafion can hold cationic substrates. On the other hand, despite the unfavorable electrostatic interaction between the Nf/TiO₂ and anionic substrates, the PCD of dichloroacetate (DCA) and acid orange 7 (AO7) with Nf/TiO₂ was not significantly inhibited. The visible-light-sensitized degradation of dyes was enhanced with Nf/TiO₂ not only for cationic dyes (methylene blue (MB) and rhodamine B (RhB)) whose uptake on Nf/TiO₂ is enhanced, but also for an anionic dye (AO7) that is less adsorbed on Nf/TiO₂. The unexpected behavior in AO7 degradation seems to be related to the role of the Nafion layer in retarding the charge recombination. These observations indicate that Nf/TiO₂ can enhance the PCD reactivity for cationic substrates without sacrificing the PCD reactivity for anionic substrates. In addition, it was found that the sensitized degradation of RhB followed a different path when the surface of TiO₂ was coated with Nafion. The N-de-ethylation of RhB that leads to the generation of rhodamine-110 was a prevailing path with Nf/TiO₂, whereas the cleavage of the chromophoric ring structure was dominant with pure TiO₂. The effects of Nafion adlayers on the photoinduced electron transfer and PCD kinetics and mechanisms are discussed.

Introduction

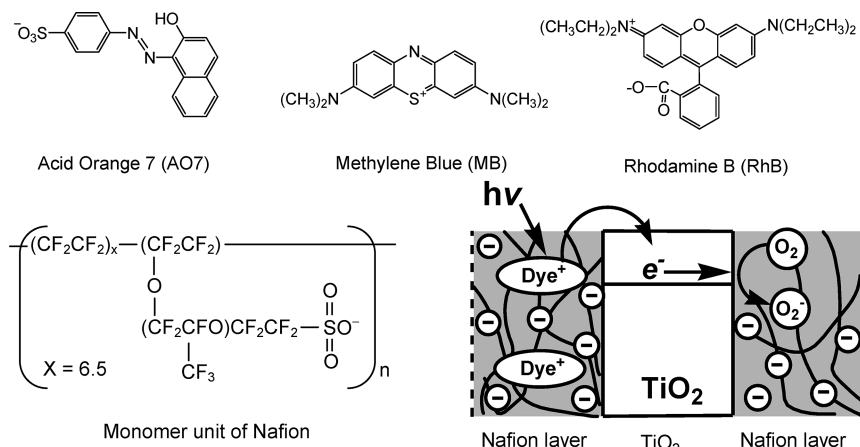
TiO₂-based photocatalysis has been extensively studied for the destruction of environmental pollutants.^{1–5} Because the photocatalytic reactions mostly take place on the surface, the surface property of TiO₂ is regarded as one of the most important factors in determining the photocatalytic reaction kinetics and mechanisms.^{6,7} The surface properties of TiO₂ are closely related to a variety of parameters such as pH, surface hydroxyl groups, particle size, crystalline phase, surface defects, surface metal deposits, and surface complexes or adsorbates.

It is well recognized that the surface of TiO₂ in an aqueous environment takes electric charges that are dependent on pH. The surface charge is positive at acidic conditions (pH ≤ 5) due to the presence of ≡TiOH₂⁺ groups, near neutral at pH 5–7, and negative at basic conditions (pH ≥ 7) owing to ≡TiO[−] groups.^{3,8} This pH-dependent surface charge should affect the adsorption of substrates and consequently photocatalytic reactions. For instance, the photocatalytic degradation (PCD) of dichloroacetate is significantly retarded at basic pH because of the electrostatic repulsion between the anions and the negative surface charge.⁹ The sensitized degradation of charged dyes on visible-light-illuminated TiO₂ is also highly influenced by the surface charge since this process requires that dye molecules be in direct contact with the TiO₂ surface for efficient electron injection.¹⁰ Anionic dyes such as acid orange 7 (AO7) are readily degraded in visible-light-illuminated TiO₂

suspension,¹¹ whereas cationic dyes such as methylene blue (MB) are little degraded under the same conditions in the acidic pH range (i.e., where the surface charge is positive).¹² The surface charge of TiO₂ can be modified by adsorbing charged organic molecules. For example, ionic surfactant molecules adsorbed on the TiO₂ surface drastically modify the surface charge.^{13,14} Although surfactant is a good surface charge modifier, the surfactant/TiO₂ system should be applied only to visible-light-utilizing systems (e.g., sensitized degradation of dyes) because surfactant itself is decomposed by TiO₂ under UV illumination.¹⁵ In addition, surfactant solutions easily foam, which makes them difficult to manipulate.

In this study, we prepared Nafion-coated TiO₂ (Nf/TiO₂) particles to modify the surface charge. Because Nafion, an anionic perfluorinated polymer with sulfonate groups,¹⁶ is chemically and photochemically inert, Nf/TiO₂ should be stable even under UV illumination. Some previous studies have tried to incorporate TiO₂ nanoparticles within the Nafion matrix to obtain better photochemical efficiencies.^{17,18} However, only one study reported the photocatalytic use of TiO₂ particles whose surface was coated with Nafion: Vohra and Tanaka demonstrated that the PCD of a cationic herbicide, paraquat, was accelerated with Nf/TiO₂ owing to the surface charge modification.¹⁹ However, no further studies on Nf/TiO₂ as an efficient photocatalyst have been reported. In this study, several charged organic compounds were chosen as probe molecules to investigate the effects of the Nafion coating on the PCD reactions under UV or visible light illumination. The PCD reactions taking

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SCHEME 1: Structures of the Charged Organic Dyes and Nafion Used in This Study^a

^a Visible-light-sensitized degradation of cationic dyes on Nf/TiO₂ is schematically illustrated.

place on Nf/TiO₂ were very different from those on naked TiO₂ in both kinetics and mechanisms and were influenced by the molecular charge and structure of the substrates.

Experimental Section

Materials and Reagents. TiO₂ powder (Degussa P25), a mixture of anatase and rutile (8:2), was used as received as a base photocatalyst. Nafion (perfluorinated ion-exchange resin) was purchased from Aldrich as a 5 wt % solution in a mixture of alcohol and water. Sodium dichloroacetate (DCA) (Aldrich, 98%), tetramethylammonium (TMA) hydroxide (Aldrich), acid orange 7 (AO7) (Aldrich, 85%), rhodamine B (RhB) (Aldrich, 80%), rhodamine 110 (Rh-110) (Aldrich, 90%) [a fully de-ethylated form of RhB], and methylene blue (MB) (Aldrich, 85%) were all used as received. The structures of Nafion and dyes used in this study are shown in Scheme 1. Nf/TiO₂ was prepared by adding an aliquot of Nafion solution to TiO₂ powder, through mixing, and subsequent drying overnight at room temperature. A typical amount of Nafion loading was 45 mg/g of TiO₂. Although the resulting Nf/TiO₂ powder was not initially well suspended in water because of the hydrophobic nature of the Nafion coating, vigorous stirring for 30 min mixed Nf/TiO₂ well.

ζ Potential Measurement. The electrophoretic mobilities of TiO₂ and Nf/TiO₂ particles in aqueous suspensions were measured to determine their ζ potentials as a function of pH and Nafion concentration. Various amounts of Nafion were added to the TiO₂ suspension, and the resulting mixture was mixed well. ζ potentials were measured using an electrophoretic light scattering spectrophotometer (ELS 8000, Otsuka) equipped with a He–Ne laser and a thermostated flat board cell.²⁰

Photocatalytic Reactivity Test. A 40 mL glass reactor with a quartz window was used for photocatalytic reactivity measurements. Substrate (DCA, TMA, AO7, RhB, Rh-110, or MB) and other necessary reagents were added to an aqueous TiO₂ (or Nf/TiO₂) suspension (0.5–1.0 g of TiO₂/L) in the reactor, and the resulting mixture was equilibrated for 30 min with vigorous agitation prior to illumination. The initial pH of the suspension was adjusted to different values depending on the kind of substrate because each substrate differs in its pH-dependent adsorption on TiO₂. A 450 W Xe arc lamp (Oriel) was used as a light source. Light passed through a 10 cm IR water filter and a cutoff filter ($\lambda > 300$ nm for UV or $\lambda > 420$ nm for visible light illumination), and then the filtered light was focused onto the reactor. Sample aliquots were withdrawn by a syringe

intermittently during the illumination and filtered through a 0.45 μm PTFE filter (Millipore). Nf/TiO₂ was stable, and a prolonged irradiation of UV and visible light did not produce any detectable amount of sulfites and sulfates in its aqueous suspension, which confirms the previous claim.

For the analysis of DCA and TMA, an ion chromatograph (IC, Dionex DX-120) which was equipped with a Dionex IonPac AS 14 (4 mm × 250 mm) for anions, a Dionex IonPac CS 12A (4 mm × 250 mm) for cations, and a conductivity detector was used. The eluent solution was 3.5 mM Na₂CO₃/1 mM NaHCO₃ for anion or 20 mM methansulfonic acid for cation analysis. The degradation of AO7, RhB, Rh-110, and MB was monitored by measuring the absorbance with a UV–vis spectrophotometer (Shimadzu UVPC-2401) at $\lambda = 485, 556, 499,$ and 663 nm, respectively, as a function of irradiation time. The photodegradation of RhB and Rh-110 was also analyzed for their fluorescence spectra using a spectrofluorometer (Shimadzu RFPC-5301). Total organic carbon (TOC) variation as a result of the photodegradation of AO7, RhB, and MB was monitored using a TOC analyzer (Shimadzu).

Photoelectrochemical Test. The UV- or visible-light-induced current generation in a short-circuited electrochemical cell was compared between TiO₂ and Nf/TiO₂ electrode systems to investigate the effect of the Nafion coating on the interfacial electron transfer. The photocurrent was measured with a potentiostat (EG&G 263A2). To prepare the TiO₂ electrode, a SnO₂-coated conducting glass (Samsung) was dipped into a TiO₂ suspension and dried. To obtain the Nf/TiO₂ electrode, 0.3 mL of Nafion solution (0.25 wt % in ethanol) was added onto the TiO₂ electrode and dried. A graphite rod was used as a counter electrode. For the measurement of UV-induced current generation, the electrode was immersed into an aqueous electrolyte (10 mM NaCl) solution that contained 4.5 mM methanol as a hole scavenger. On the other hand, the dye-sensitized current generation on TiO₂ or Nf/TiO₂ under visible light illumination was measured in the presence of 40 μM RhB or 50 μM AO7 instead of methanol. Prior to the photoelectrochemical test, the dyes were sufficiently adsorbed on the TiO₂ (and Nf/TiO₂) electrode overnight. The electrodes were held at +0.3 V vs SCE during the photocurrent measurement. The 450 W Xe arc lamp was used as a light source.

Results and Discussion

Effect of Nafion Coating on Surface Charge and Photocatalytic Reactivity under UV Illumination. Figure 1 shows

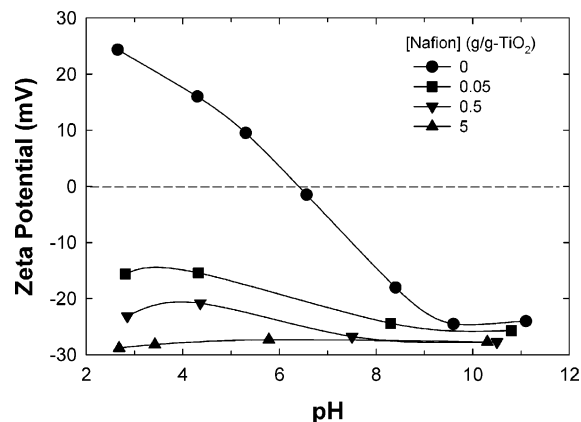


Figure 1. ζ potentials of suspended TiO₂ particles in the presence or absence of Nafion as a function of pH. [TiO₂] = 2 mg/L.

the variation of ζ potentials of suspended TiO₂ particles as a function of pH and Nafion concentration. The point of the ζ zeta potential (PZZP) of TiO₂ was measured to be ca. 6.2, which is in agreement with the literature value.^{20,21} However, upon adding Nafion to the aqueous suspension, ζ potentials became negative over the entire pH range. The negative shift of ζ potentials was larger with higher Nafion concentration. This should be ascribed to the fact that the anionic sulfonate groups ($-\text{SO}_3^-$) in the Nafion layer outnumber the positively charged surface functional groups on TiO₂ ($\equiv\text{TiOH}_2^+$). The surface charge modified by Nafion adlayers directly influences the electrostatic interaction between charged substrates and the catalyst surface. Negatively charged molecules should be repelled from the surface of Nf/TiO₂, whereas positively charged ones should be attracted.

Figure 2 compares the photocatalytic reactivities of pure TiO₂ and Nf/TiO₂ for the degradation of anionic molecules (DCA and AO7) and a cationic molecule (TMA) under UV illumination. The initial concentrations at time zero represent the equilibrated ones in the presence of TiO₂ or Nf/TiO₂. Dark control experiments with Nf/TiO₂ showed that the concentration of the substrates changed little with time, which indicates that the substrate removal was due to degradation, not to slow uptake by the Nafion layer. The adsorption of DCA anions on pure TiO₂ was insignificant and was changed little by the presence of Nafion adlayers. Although DCA is an anion and should be repelled from the surface of Nf/TiO₂, the PCD of DCA with Nf/TiO₂ was only slightly retarded. As for AO7, the adsorption of the anionic dye molecule on Nf/TiO₂ was almost completely inhibited as expected. However, the PCD rate of AO7 does not seem to be affected by the presence of the Nafion layer on TiO₂. The above results (both DCA and AO7) indicate that the Nafion coating on TiO₂ does not significantly sacrifice the PCD reactivity for anionic substrates despite the unfavorable electrostatic interaction between anions and Nf/TiO₂. Considering that both DCA and AO7 can be degraded through a direct hole transfer path,²⁰ the electrostatic repulsive force does not seem to be strong enough to prevent the electron transfer from the substrate to Nf/TiO₂. An alternative explanation is that the surface of TiO₂ is only partially covered by Nafion and the PCD of anionic substrates takes place on the uncovered TiO₂ surface. On the other hand, the effect of the Nafion coating on the PCD of cationic TMA is outstanding (Figure 2c). Tetraalkylammoniums such as TMA are very stable and hard to oxidize by a direct electron transfer. For this reason, tetraalkylammoniums have been widely used as supporting electrolytes in electrochemical studies. Therefore, PCD of TMA can be initiated only by OH radical attack, not by direct hole transfer.²² The TMA

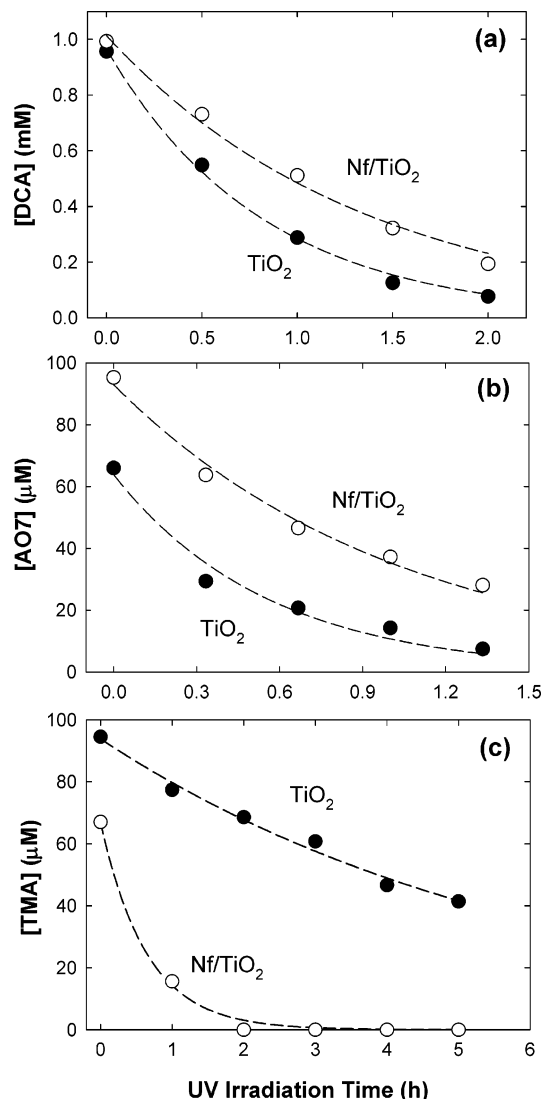


Figure 2. Photocatalytic degradation of charged organic compounds under UV illumination: (a) DCA, (b) AO7, (c) TMA. [TiO₂] = 0.5 g/L, [Nafion] = 45 mg/g of TiO₂, [DCA]₀ = 1 mM at pH_i 5, [AO7]₀ = 0.1 mM at pH_i 3.0, and [TMA]₀ = 0.1 mM at pH_i 6.5.

cations are expected to be located at cation-exchange sites within the Nafion layer. TMA molecules localized within the Nafion layer have a higher chance to react with OH radicals generated on the TiO₂ surface and can be degraded at a faster rate. This observation is very similar to the previous one that reported the enhanced PCD of paraquat (a cationic substrate) on Nf/TiO₂.¹⁹ According to the manufacturer, the ion-exchange capacity of Nafion is ca. 0.9 mequiv/g of Nafion. With the Nafion loading of 45 mg of Nf/g of TiO₂, the total ion-exchange capacity of 30 mg of Nf/TiO₂ suspended in the reactor is about 1.2 μequiv . The number of TMA molecules adsorbed onto the suspended Nf/TiO₂ was estimated to be 0.75 μmol (at pH 6.7): the difference in the initial TMA concentration in Figure 2c represents the fraction of adsorbed TMA molecules. This implies that ca. 60% of the sulfonate groups in the Nafion layer on TiO₂ are associated with TMA through electrostatic attraction.

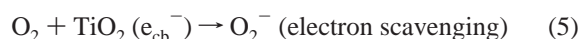
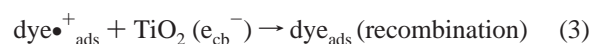
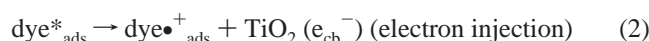
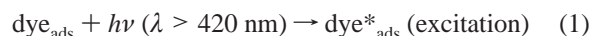
Visible-Light-Sensitized Degradation of Dyes on Nf/TiO₂. Unlike most organic compounds whose PCD on TiO₂ can proceed only under UV illumination, dyes can be degraded on visible-light-illuminated TiO₂ through a sensitized path.^{6,11,23} Excited dye molecules are generated upon absorption of visible photons and subsequently inject electrons into TiO₂ CB. Primary

TABLE 1: Physicochemical Properties of AO7, RhB, and MB

	AO7 ²⁵	RhB ²⁶	MB ^{24,26}
molecular charge	anion	zwitterion (or cation)	cation
λ_{\max} (nm) in water	485	556 (cation) 553 (neutral)	663
pK_a	—OH: ~ 11	—COOH: 3.2 —N(CH ₂ CH ₃) ₂ : 0	—N(CH ₃) ₂ : 0
$E(D/D^+)$ (V_{NHE})	+0.76	+1.04	+1.08
$E(D^*/D^{*+})$ (V_{NHE})	−1.24	−1.09 (s) ^a −0.82 (t) ^a	−0.78 (s) ^a −0.47 (t) ^a

^a Key: s, singlet; t, triplet.

reaction steps in this process can be represented by reactions 1–5.



The adsorption of dyes on the TiO₂ surface is a prerequisite for the sensitization. The presence of the Nafion layer on TiO₂ changes the surface charge and hence modifies the dye–surface interaction. Therefore, the visible-light-sensitized degradation of dyes on Nf/TiO₂ is expected to be quite different from that on pure TiO₂. Three dyes (AO7, RhB, and MB) were tested for their visible-light-sensitized degradation on Nf/TiO₂ to investigate how the Nafion layer influences the kinetics and mechanism of the dye degradation. The properties of the three dyes are compared in Table 1.

AO7 is an anionic dye molecule, and its adsorption on Nf/TiO₂ should be hindered because of the electrostatic repulsion between the negative molecular charge and the negative sulfonate group in Nafion. Therefore, the adsorption of AO7 on TiO₂ decreased with increasing Nafion loading as shown in Figure 3. Contrary to the expectation, however, the rate of AO7 degradation under visible light increased with the Nafion loading and was maximal around [Nafion] = 67.5 mg/g of TiO₂. This is also supported by the TOC removal data shown in Table 2. The initial TOC was measured to be higher in Nf/TiO₂ than that in pure TiO₂ suspension because of the hindered adsorption of AO7 on Nf/TiO₂. Nevertheless, TOC removal was higher by ca. 70% with Nf/TiO₂ compared to the case of pure TiO₂. The apparent anticorrelation between the adsorption of AO7 and the degradation rate appears abnormal. The most plausible explanation seems to be related to the effect of the Nafion layer on the rate of reaction 3 (charge recombination). The overall rate of the dye degradation should be determined by the competition between the forward electron injection (reaction 2) and the backward recombination (reaction 3). Therefore, the apparent dye degradation rate can be enhanced either by accelerating reaction 2 or by retarding reaction 3. Because the presence of the Nafion layer on TiO₂ reduces the adsorption of AO7, both reactions 2 and 3 should be retarded on Nf/TiO₂ but by different extents. In most dye-sensitized TiO₂ systems, reaction 2 is faster than reaction 3 by several orders of magnitude. Under such conditions, retarding reaction 2 cannot decelerate the overall rate efficiently and reaction 3 should be the rate-determining step. Therefore, in case the net effect of

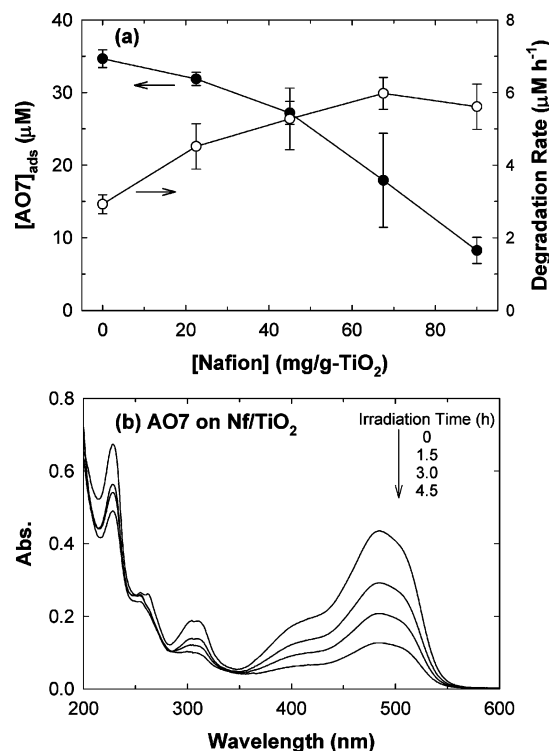


Figure 3. (a) Adsorption and visible-light-sensitized ($\lambda > 420$ nm) degradation of AO7 in Nf/TiO₂ suspension as a function of Nafion concentration. (b) UV–vis absorption spectral changes of AO7 with visible light irradiation time in the Nf/TiO₂ suspension. [TiO₂] = 0.5 g/L, [AO7]₀ = 50 μM, pH_i 3.0, and [Nafion] = 45 mg/g of TiO₂ for (b).

TABLE 2: Dye TOC Removal in Naked and Nafion-Coated TiO₂ Suspension under Visible Light Illumination

conditions ^a	TOC _i (ppm)	TOC _f (ppm)	ΔTOC (ppm)
AO7 + TiO ₂	12.9	9.5	3.4
AO7 + Nf/TiO ₂	15.2	9.3	5.9
MB + TiO ₂	13.6	12.6	1.0
MB + Nf/TiO ₂	6.5	2.6	3.9
RhB + TiO ₂	14.3	9.4	5.9
RhB + Nf/TiO ₂	9.8	3.5	6.3

^a [AO7]₀ = 50 μM, [MB]₀ = 40 μM, [RhB]₀ = 40 μM, [TiO₂] = 0.5 g/L, [Nafion] = 45 mg/g of TiO₂, and pH_i 3. TOC_f was taken after 4, 11, and 2 h of illumination for AO7, MB, and RhB, respectively.

the Nafion coating is retarding the recombination (reaction 3) more preferentially than the electron injection (reaction 2), the apparent dye degradation rate could be enhanced, as shown in Figure 3.

As another example, MB that is a cationic dye molecule was tested. MB has been known to be unreactive in the TiO₂/visible light system.¹² In agreement with the previous reports, MB was hardly degraded in the naked TiO₂ suspension under visible light as shown in Figure 4a. This is attributable not only to the weaker thermodynamic driving force for the electron injection from MB* to TiO₂ CB (Table 1), but also to the electrostatic repulsion between MB cation and the positively charged TiO₂ surface ($\equiv\text{TiOH}_2^+$) at pH 3. The dark adsorption of MB on the naked TiO₂ surface was negligible. On the other hand, in the presence of Nafion, a large fraction of MB was initially adsorbed (about 50% of the initial MB concentration) on the Nf/TiO₂ surface and gradually degraded (*discolored*) under visible light. The discoloration of MB can be induced by two different mechanisms: one is the oxidative degradation of MB, and the other is the two-electron reduction to its colorless form, *leuco*-MB,

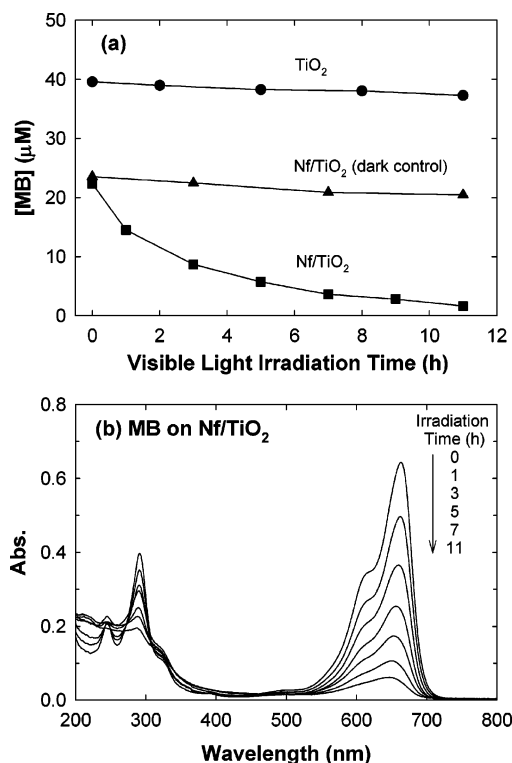


Figure 4. (a) Comparison of visible-light-sensitized degradation of MB in the naked TiO₂ and Nf/TiO₂ suspension. (b) UV-vis absorption spectral changes of MB with visible light irradiation time in the Nf/TiO₂ suspension. [TiO₂] = 1 g/L, [Nafion] = 45 mg/g of TiO₂, [MB]₀ = 40 μM, and pH_i 3.0. Absorption spectra were recorded after 2-fold dilution.

whose production should be accompanied by the absorbance at 256 nm.²⁴ The absorbance peaks at 246, 291, and 663 nm that are all associated with MB decreased with irradiation time, but the absorbance band at 256 nm (contributed by *leuco*-MB) did not appear at all. This indicates that the MB discoloration observed in this study should be due to the oxidative degradation (i.e., destruction of the chromophoric aromatic rings (phenothiazine moiety)), not to the reductive conversion to *leuco*-MB.²⁴ Like TMA cations, cationic MB molecules are expected to be ion-exchanged into the Nafion layer, and hence, their sensitized degradation rate is highly accelerated. In this case, the effect of the Nafion layer on enhancing the rate of reaction 2 should outweigh that on accelerating the rate of reaction 3. As in the case of AO7, the TOC removal with Nf/TiO₂ was higher than with naked TiO₂ (Table 2).

As the final example of sensitized degradation of dyes, RhB was tested. RhB is a cationic or neutral dye molecule depending on whether the carboxyl acid group is dissociated or not (see Scheme 1). Figure 5 shows that RhB was degraded on naked TiO₂ under visible light and its degradation rate was enhanced on Nf/TiO₂. However, the spectral change with the irradiation time indicates that RhB degradation on Nf/TiO₂ is quite different from that on naked TiO₂. The position of the visible absorption band of RhB with Nf/TiO₂ gradually shifted to the shorter wavelength region with irradiation time, whereas that with naked TiO₂ remained relatively unchanged throughout the degradation. The peak shifted by 18 nm for 4 h with naked TiO₂ and by 60 nm for 2 h with Nf/TiO₂. Figure 6 shows the effect of Nafion loading on the RhB degradation rate and on the spectral shift of λ_{\max} ($\Delta\lambda_{\max}$). The photodegradation rate of RhB increased with increasing Nafion loading up to 45 mg/g of TiO₂, above which the rate decreased (Figure 6a). The variation of $\Delta\lambda_{\max}$ with the Nafion loading (Figure 6b) showed a similar trend.

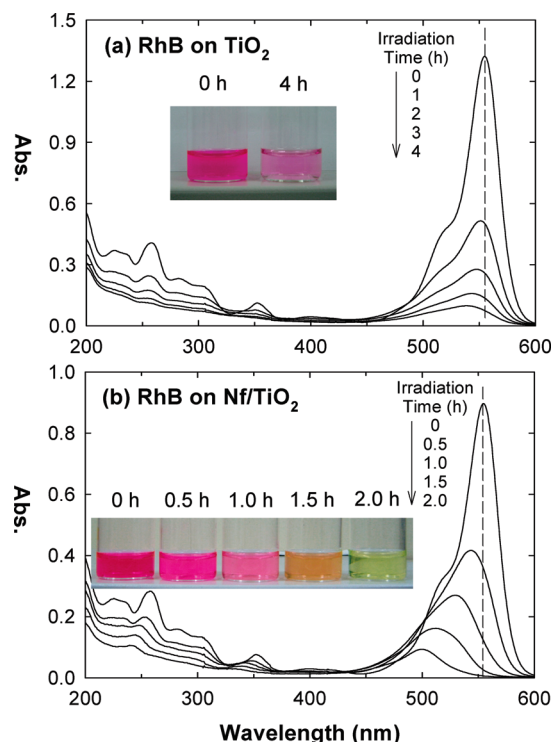


Figure 5. UV-vis absorption spectra of RhB in (a) TiO₂ and (b) Nf/TiO₂ suspension under visible light illumination. The insets show the color changes of the irradiated RhB solution, which are very different between the two systems. Absorption spectra were recorded after 3-fold dilution. [TiO₂] = 1 g/L, [Nafion] = 45 mg/g of TiO₂, [RhB]₀ = 40 μM, and pH_i 3.0.

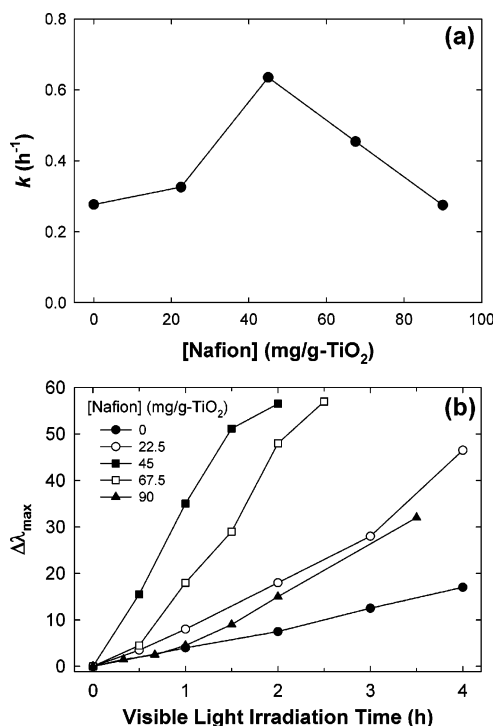


Figure 6. Effect of Nafion concentration on (a) the visible-light-sensitized degradation rate (k) of RhB and (b) the spectral shift ($\Delta\lambda_{\max}$). [TiO₂] = 1 g/L, [RhB]₀ = 40 μM, and pH_i 3.0.

The rate of $\Delta\lambda_{\max}$ showed a maximal value (~ 36 nm/h) at [Nafion] = 45 mg/g of TiO₂ but decreased with further increasing Nafion loading. With naked TiO₂, the rate of $\Delta\lambda_{\max}$ was as low as 5 nm/h. The TOC removal also increased by ca. 30% in the presence of the Nafion layer (Table 2). The fact

that there was an optimal Nafion loading for the degradation of RhB indicates that excessive Nafion loading on TiO_2 inhibits the overall sensitized process. Higher Nafion loading should uptake more RhB molecules that should inject more electrons into TiO_2 (reaction 2), which cannot account for the reduced activity at higher Nafion loading. It seems that higher Nafion coverage on TiO_2 blocks the active sites for the electron transfer to O_2 (reaction 5). Without the efficient electron scavenging, the overall sensitized process cannot proceed (see Scheme 1).

The different spectral change behaviors between TiO_2/RhB and $\text{Nf}/\text{TiO}_2/\text{RhB}$ systems imply that the degradation mechanisms are different. Liu et al.¹⁴ observed a similar behavior from the visible-light-sensitized degradation of sulforhodamine B in TiO_2 suspension. Two degradation pathways of sulforhodamine B were found to be present: the cleavage of the chromophoric ring structure versus the N-de-ethylation. The former path accompanied the disappearance of the visible absorption band with the peak position unchanged, but the latter path gradually shifted the position to the blue region as the ethyl groups were removed one by one. In the presence of anionic dodecylbenzenesulfonate surfactant, sulforhodamine B preferentially favored the N-de-ethylation path because the dye is adsorbed on the negatively charged surfactant/ TiO_2 surface through the positively charged diethylamine group. Considering that this work used Nafion instead of anionic surfactant and RhB, which has the same structure as sulforhodamine B except that the sulfonate group is replaced by a carboxylate group, the two paths of the cleavage of the chromophoric ring and the N-de-ethylation are likely to exist in the degradation of RhB. The presence of the Nafion layer seems to favor the N-de-ethylation path with an accompanying blue shift of the visible band because the adsorption mode of RhB on the TiO_2 surface should be changed with reversal of the surface charge to highly negative values. The fact that $\Delta\lambda_{\text{max}}$ increased with increasing Nafion loading up to 45 mg/g of TiO_2 supports the rate of N-de-ethylation accelerating on Nf/TiO_2 .

To verify the existence of the N-de-ethylation path, it was investigated whether Rh-110, a fully N-de-ethylated form of RhB, was produced from the visible-light-sensitized degradation of RhB in the naked TiO_2 and Nf/TiO_2 suspensions. The degradation of RhB was followed by monitoring its fluorescence spectra. RhB and Rh-110 generate strong fluorescence bands centered at 573 and 520 nm, respectively. The evolution of the emission spectrum with illumination is shown in Figure 7. As visible light was illuminated onto the naked TiO_2 suspension, the intensity of the fluorescence band of RhB gradually decreased without the appearance of the Rh-110 band. The UV-vis absorption spectrum of the illuminated RhB solution (inset in Figure 7a) was completely different from that of Rh-110, which also confirms that the formation of Rh-110, and hence the N-de-ethylation path, is insignificant in this case. On the other hand, in the Nf/TiO_2 suspension, the gradual change of the RhB spectrum led to that of Rh-110 in 100 min of illumination (Figure 7b). The comparison between the UV-vis spectrum of the 2 h illuminated RhB and that of pure Rh-110 solution (inset in Figure 7b) further verifies that the two are nearly identical. Therefore, it is concluded that the ionic interaction between the sulfonate groups in Nafion and the positively charged diethylamine groups in RhB changes the sensitized degradation pathway to favor the N-de-ethylation that leads to the production of Rh-110. On the other hand, Rh-110 generated in the $\text{Nf}/\text{TiO}_2/\text{RhB}$ system was further degraded under visible light with production of an intermediate whose fluorescence emission is centered at 464 nm (Figure 7b). As a

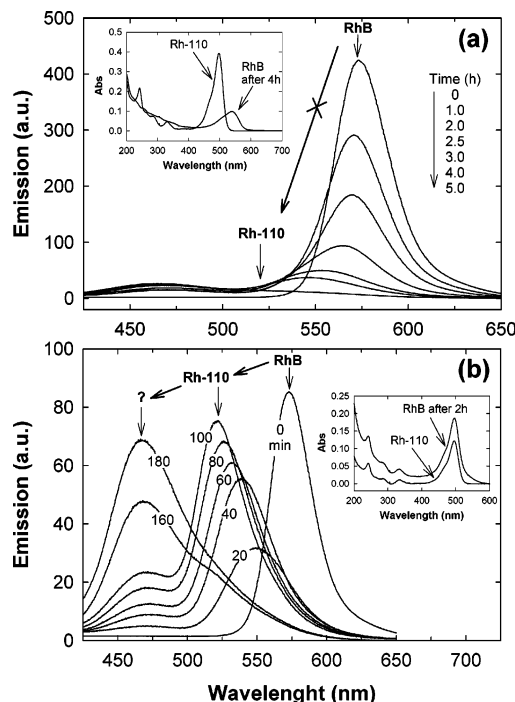


Figure 7. Evolution of the fluorescence spectra of RhB (excited at 355 nm) in (a) naked TiO_2 and (b) Nf/TiO_2 suspension under visible light illumination. The insets compare the UV-vis absorption spectrum of authentic Rh-110 and photodegraded RhB. $[\text{TiO}_2] = 1 \text{ g/L}$, $[\text{RhB}]_0 = 40 \text{ }\mu\text{M}$, and $\text{pH} = 3.0$.

control experiment, the visible-light-sensitized degradation of Rh-110 in pure TiO_2 suspension was carried out. In this case, the fluorescence emission at 464 nm was not observed at all throughout the degradation process. However, the degradation of Rh-110 under visible light in the Nf/TiO_2 suspension showed the appearance of the emission band at 464 nm as in the case of Figure 7b. This indicates that the degradation mechanism of Rh-110 is also dependent on whether the surface of TiO_2 is coated with Nafion or not. The Nafion layer on the TiO_2 surface certainly plays dual roles of enhancing the photodegradation rate and changing the photodegradation pathway.

Effect of Nafion on the Photoinduced Electron Transfer on TiO_2 . The results presented above imply that the charge transfer from dye to TiO_2 should be markedly affected by the Nafion coating. To investigate the effect of the Nafion layer on the visible-light-induced electron transfer, the dye-sensitized photocurrents were compared between the naked TiO_2 and Nf/TiO_2 electrode systems. Figure 8 shows how the sensitized photocurrent generation in the presence of RhB or AO7 is influenced by the Nafion coating. It is noted that the effects of the Nafion coating were opposite between the RhB and AO7 cases. The RhB-sensitized currents were greatly enhanced with Nf/TiO_2 , whereas the AO7-sensitized currents were markedly suppressed with the Nf/TiO_2 electrode. This behavior is in accord with the electrostatic consideration. It is estimated that RhB adsorbed on the Nf/TiO_2 electrode is ca. $38 \text{ }\mu\text{mol}/\text{cm}^2$, which is 4 times as large as that ($9 \text{ }\mu\text{mol}/\text{cm}^2$) obtained on the naked TiO_2 electrode. The higher photocurrent obtained with Nf/TiO_2 should be ascribed to the enhanced adsorption of RhB. This case is very similar to a previous report that $\text{Ru}(\text{bpy})_3^{2+}$ -sensitized photocurrent generation under visible light increased by a factor of 4 when the surface of the TiO_2 electrode was coated with Nafion.²⁷ On the other hand, being an anionic molecule, AO7 was not adsorbed on the Nf/TiO_2 electrode at all and consequently was very inefficient in generating sensitized currents. However, such a drastic difference in photocurrents

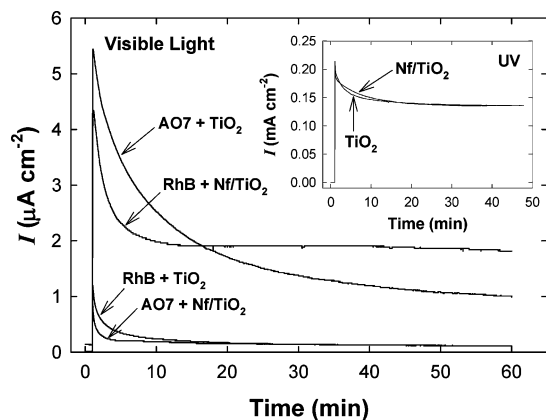


Figure 8. Dye (RhB or AO7)-sensitized photocurrent profiles generated on the visible-light-illuminated TiO₂ electrode in the absence or presence of a Nafion coating. The inset compares the UV-induced photocurrent profiles obtained with TiO₂ and Nf/TiO₂ electrodes in the presence of methanol as an electron donor.

between the AO7/TiO₂ and AO7/Nf/TiO₂ systems is apparently inconsistent with the sensitized degradation of AO7 shown in Figure 3a. Although the AO7-sensitized currents were extinguished when the Nf/TiO₂ electrode was used, the sensitized degradation of AO7 was enhanced in the Nf/TiO₂ suspension on the contrary. To understand the discrepancy, it should be recognized that the electron-transfer kinetics on a suspended particle is different from that on a thin film electrode. TiO₂ particles in a thin film are interconnected, and electrons injected from the dye rapidly migrate from particle to particle to reach the underlying electrode, and therefore, the chance of recombination (reaction 3) in particles in a thin film should be much lower than that on a suspended particle.²⁸ In a suspended TiO₂ particle, most of the injected electrons recombine and only a small fraction of them are transferred at the interface. Therefore, a higher sensitized photocurrent obtained with a thin film electrode does not necessarily mean a faster rate of sensitized degradation in a suspension. As mentioned earlier, not only the electron injection (reaction 2) but also the recombination (reaction 3) is influenced by the Nafion layer. Whether the net effect of the Nafion coating is positive or negative depends on the balance between the two competing factors.

On the other hand, the UV-induced photocurrents generated in the presence of methanol (instead of dye) were little affected by Nafion (see the inset of Figure 8). This indicates that the photoinduced electron transfer from methanol (a neutral molecule) to TiO₂ should not be much influenced by the presence of Nafion. We also carried out the PCD of phenol under UV irradiation and found that the presence of the Nafion layer on TiO₂ did not much change the kinetics of phenol degradation. The photoinduced electron transfers with neutral substrate molecules on Nf/TiO₂ appear to be little different from those on naked TiO₂. The present study confirms the previous claim that Nf/TiO₂ does not significantly reduce the rate of PCD of neutral and anionic compounds.¹⁹

Conclusions

Various methods for the modification of the TiO₂ surface have been developed to enhance and control photocatalytic reactivities. This study investigated the Nafion coating on TiO₂ as a simple method of surface charge modification. The presence of Nafion adlayers on TiO₂ particles made the surface charge highly negative in the whole pH range and significantly changed the PCD kinetics and mechanisms of charged organic substrates.

It is expected that the ion-exchange sites within the Nafion layer can hold cationic substrates. In terms of the simple electrostatic interaction, PCD reactions with Nf/TiO₂ should be enhanced for cationic substrates and inhibited for anionic substrates. However, the observed PCD behaviors of Nf/TiO₂ were more complex. The UV-induced PCD was markedly improved for the cationic substrate (TMA) but not significantly retarded for the anionic substrate (DCA and AO7). Similar behaviors were also observed in the visible-light-sensitized degradation of dyes. The dye degradation in the Nf/TiO₂ suspension was enhanced not only for cationic dyes (MB and RhB) that should be attracted onto Nf/TiO₂ but also for an anionic dye (AO7) that should be repelled from Nf/TiO₂. This is advantageous for practical applications because Nf/TiO₂ can enhance the PCD reactivity for cationic substrates without sacrificing the PCD reactivity for anionic substrates. In addition, as for RhB, the presence of Nafion adlayers on TiO₂ not only accelerated its degradation rate but also changed its degradation path with generation of different products. The PCD reactivities for neutral substrates seem to be less affected by the Nafion layer. The unique characteristics of Nf/TiO₂ as a novel photocatalyst can be utilized when the PCD reactivity for charged organic compounds needs to be enhanced and controlled.

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