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Photocurrent-Boosting by Intramembrane Electron Mediation between Titania Nanoparticles Dispersed into Nafion−Porphyrin Composites

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We have used titania nanoparticles (TiO_2) to establish a facile preparation of a highly photoresponsible membrane. An improved photocurrent generator was prepared easily using spin coating of a Nafion/porphyrin/TiO_2 mixture on an indium−tin−oxide substrate. Generated photocurrent density was about 10 times higher than that in the absence of TiO_2. The resultant electrode shows distinct photocurrent generation despite impediments derived from high dye-concentration (i.e., self-quenching of photoexcited states) and membrane thickness (i.e., losses of electron flow passing through membrane into electrode). Photocurrent densities increased linearly concomitant with high surface concentrations of porphyrin and high membrane thickness. It became evident that TiO_2 contributes to more efficient photocurrent generation by intramembrane electron mediation.

Introduction

Organic photocurrent generators consisting of electron-donor or electron-acceptor molecules have provoked a great deal of interest in the development of photovoltaics.[1−26] An important present concern is how to collect numerous photons in the limited surface area of the device: the surface area is determined by the electrode size. Consequently, light-harvesting molecules with a high molecular absorption coefficient (e.g., dyes) and electrochemically active materials must be arranged on an electrode with high density (concentration) and a long optical path (membrane thickness). Numerous studies have reported development of photocurrent generators comprising mono/multilayers with high packing density such as Langmuir−Blodgett (LB) membranes[13−16] and self-assembled monolayers (SAMs).[17−26] Especially, monolayer systems comprising covalently linked donor−acceptor molecules show excellent light-to-current conversion yields.[10−12,18−26] However, difficulties in synthesis arise in covalent linkage of all thin-layer-forming substituents (donor units or acceptor units) together in one molecular system. We investigated two methods using an electroconductive polymer[27,28] and a polyelectrolyte[29] as a supporting matrix

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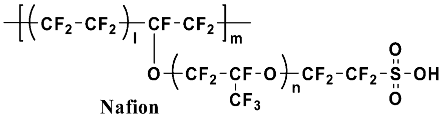
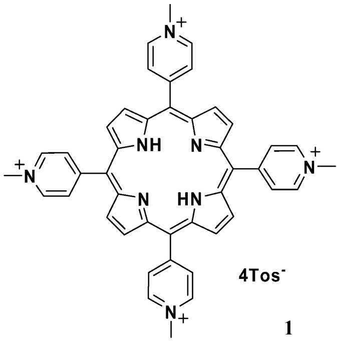
to deposit small molecules on electrodes without chemical modification of donor−acceptor molecules to achieve facile deposition of donor−acceptor molecules on the electrode. In particular, we have clarified that Nafion membranes can be used as stationary phases to deposit porphyrins on an indium−tin−oxide (ITO) electrode.[29] The resultant Nafion−porphyrin (**1**) membrane is stable and does not peel from the ITO electrode. Generation of photocurrent waves was observed in response to visible light. However, we found that this approach presents a serious problem in actualizing high photocurrent density for two reasons: (i) in a thick membrane, porphyrins (**1**) in distant positions from the electrode cannot transmit electrons with ITO electrodes; (ii) in a high surface concentration of **1**, inactive self-aggregates of **1** form. Subsequently, quantum yields for photoinduced electron transfer are suppressed considerably by fast self-quenching of photoexcited states.



Nafion



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In this study, we attempted to resolve these major obstacles (i and ii) and construct an advanced method using Nafion to deposit photofunctional molecules while sustaining its intrinsic photochemical activation and coverage density on electrodes with great facility and efficiency. We added titania nanoparticles (TiO_2) as an electronic conductor into the Nafion−**1** membrane. Consequently, it is expected that the efficient photoinduced electron transfer from porphyrin **1** to the ITO electrode occurs through electroconductive TiO_2 because **1** should be in close proximity to TiO_2. Furthermore, it is expected that Nafion−TiO_2−**1** membrane is also robust against peeling from the ITO electrode without sintering at high temperatures. Additive effects of TiO_2 into Nafion−**1** membrane were verified mainly by measurements of photocurrent density and TEM.

Experimental Section

Materials. Nafion and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphine, tetra-*p*-tosylate salt (TMPyP, **1**) were purchased from Aldrich Chemical Co. and Tokyo Chemical Ltd., Japan, respectively. Titania (anatase) sol (20.5 wt % in aqueous solution, 6 nm diameter, TKS-203) was obtained from Tayca Corp., Osaka, Japan. The titania has an anionic surface because the titania was coated by phosphoric acid. 2,2′,2″-Nitrilotriethanol (TEOA) was purchased from Kanto Chemical Co., Inc, Japan.

Preparation of ITO Electrodes with Modified Nafion−TiO_2−Porphyrin Membrane. Nafion ethanol solution (17.0 g/L, 5 mL) and TiO_2 aqueous solution (242 g/L, 2 mL) were dispersed by ultrasonic agitation for 30 min to mix well. Nafion (12.1 g/L) and Nafion−TiO_2 (12.1 and 69.1 g/L, respectively) aqueous−ethanol (2:5 (v/v)) solutions were dropped onto SAM-coated ITO electrodes with a cationic surface by 2-aminoethantiol hydrochloride. Then the electrodes were spun at 3000 revolutions per minute (rpm) for 30 s. The solvent evaporated readily, leaving thin homogeneous films on the ITO electrode. The modified ITO electrodes were immersed into an aqueous solution containing **1** (0.25 mM). After 6 h, the electrodes were washed with ultrapure water and 0.1 M Na_2SO_4 aqueous solution and dried with a nitrogen stream.

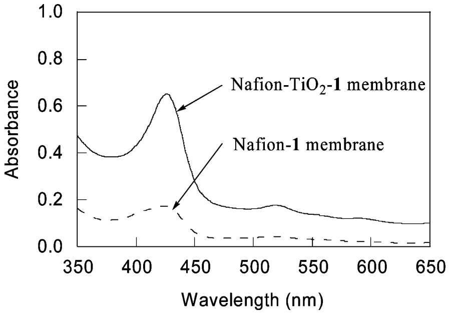

Figure 1. Absorption spectra of the Nafion−TiO_2−**1** (solid line) and the Nafion−**1** (dashed line) membranes with a saturated adsorption of **1** on ITO electrode. TiO_2:Nafion = 69.1:12.1 (wt/wt).

Characterization of Membrane. UV−vis spectroscopic measurements were carried out with a Shimadzu UV-2550PC spectrometer. The ITO electrodes coated with Nafion−**1** and Nafion−TiO_2−**1** membranes were measured in an aqueous Na_2SO_4 (0.1 M) solution. Transmission electron microscopy (TEM) investigations were carried out with a JEOL JEM-3100FEF-3500N instrument. The Nafion (12.1 g/L) and the Nafion−TiO_2 (12.1 g/L and 69.1 g/L, respectively) aqueous ethanol (2:5 (v/v)) solutions were dropped onto a collodionized carbon-deposited 200-mesh copper grid (Nissin EM Co., Ltd.) and a 150-mesh copper microgrid (Ohkenshoji Co., Ltd.), respectively, and the solvent was then evaporated at room temperature.

Photoelectrochemical Measurements. A 500-W Xe-arc lamp (UI-502Q; Ushio, Inc.) was used as the light source in the photoelectrochemical studies, and a monochromator (SPG 120S; Shimadzu Corp.) was used to obtain different wavelengths. The light intensity was measured with an energy and power meter (TQ8210, Advantest Corp.). Photocurrent measurements were carried out in an aqueous Na_2SO_4 (0.1 M) solution by using a three-electrode photoelectrochemical cell, consisting of the modified ITO electrode. All measurements were carried out in the presence of TEOA (0.05 M) as a sacrificial reagent under argon atmosphere.

Results and Discussion

We measured UV−vis absorption spectra of the ITO electrodes coated with Nafion−**1** and Nafion−TiO_2−**1** membranes to determine the surface concentration of **1** (Figure 1).[30] Spectra of **1** in the absence and presence of TiO_2 show absorption maxima (λ_{max}) at 427 and 431 nm, respectively, which correspond respectively to the Soret

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(30) We also used a cyclic voltammogram of the deposited ITO electrode to obtain further evidence of **1** deposition. However, because the electron transfer between the ITO electrode and **1** occurs at only a part of the membrane close to the electrode surface, the surface concentration of **1** was not computed accurately by the oxidation peak area of **1**.[29] Moreover, Uosaki et al. have also determined the concentration of porphyrin by the absorption of porphyrin. See: Shimazu, K.; Takechi, M.; Fujii, H.; Suzuki, M.; Saiki, H.; Yoshimura, T.; Uosaki, K. *Thin Solid Film* **1996**, *273*, 250.

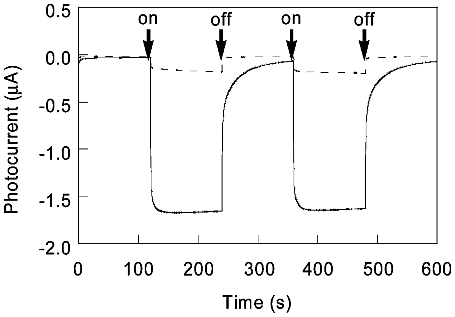

Figure 2. Photoelectrochemical responses of the Nafion−TiO$_2$−**1** (solid line) and the Nafion−**1** (dashed line) membranes with a saturated adsorption of **1** on the ITO electrode. Illumination wavelength = 420 nm. Solution: Ar-saturated, [Na$_2$SO$_4$] = 0.1 M (supporting electrolyte), [TEOA] = 0.05 M (sacrificial electron donor). Input power = 2.2 mW/cm^2. Electrode radius = 3 mm, applied potential = 0.4 V vs Ag/AgCl.

bands of porphyrin in Nafion membrane ($A_{427} = 0.087$ and $A_{431} = 0.221$). The Soret band shifted to a longer wavelength than that of aqueous solution of **1** ($\lambda_{\max} = 422$ nm, $\epsilon_{422} = 2.3 \times 10^5$ M^{-1} cm^{-1}). Presumably, these longer wavelength shifts are related to aggregation of **1** in the Nafion membrane. From the observed absorption, surface concentration of **1** on the ITO electrodes coated with Nafion−**1** and Nafion−TiO$_2$−**1** membranes can be estimated as 3.8×10^{-10} and 9.6×10^{-10} mol/cm^2, respectively. The value of the Nafion−TiO$_2$−**1** membrane is about 2.5 times greater than that of the Nafion−**1** membrane. Results indicate that, in Nafion−TiO$_2$−**1** membrane, **1** (0.25 mM) was adsorbed not only by Nafion polymer but also by TiO$_2$ surface by electrostatic interaction. In fact, when TiO$_2$ particle (69.1 g/L) was mixed with **1** (4.29 mM) in an aqueous solution, 94% of **1** was adsorbed by TiO$_2$ particle.

Photocurrent measurements were carried out for the Nafion−**1** and the Nafion−TiO$_2$−**1** membranes deposited on the ITO electrode (experimental conditions: working electrode = the Nafion-modified ITO, counter electrode = Pt wire, reference electrode = Ag/AgCl (3 M NaCl). These electrodes were immersed in a 0.10 M Na$_2$SO$_4$ aqueous solution containing 0.05 M 2,2′,2″-nitrilotriethanol (TEOA) as an electron sacrificial compound). Photocurrent waves were observed (1.6 μA, Figure 2) when the Nafion−**1**−TiO$_2$ membrane-deposited ITO electrode was irradiated with 420 nm light at 0.4 V bias voltage by use of TEOA as an electron sacrificial compound.[31] This photoresponsive phenomenon was repeated reversibly. The photocurrent density of the Nafion−TiO$_2$−**1** system was about 10 times higher than that of the Nafion−**1** system (Figure 2). The result is attributable not only to the increase of surface concentration of **1** on the ITO electrode but also to the effect by the addition of TiO$_2$ because the surface concentration of **1** in the Nafion−TiO$_2$−**1** system was only 2.5 times greater than that in the Nafion−**1** system.

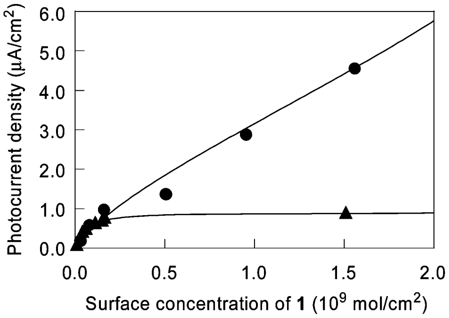

Figure 3. Plots of photocurrent density vs surface concentration of **1** for the Nafion−TiO$_2$−**1** (circle) and the Nafion−**1** (triangle) membranes on ITO electrodes. Illumination wavelength = 420 nm, input power = 1.0 mW/cm^2, applied potential = 0.4 V (vs Ag/AgCl).

Table 1. Surface Concentration, Photocurrent Density, Quantum Yield, and IPCE of Nafion−TiO$_2$−1 and Nafion−1 Membranes

membrane	surface concentration (mol/cm^2)	photocurrent density (μA/cm2)	quantum yield (%)	ICPE (%)
Nafion−TiO$_2$−**1**	1.56×10^{-9}	4.54	2.4	1.3
Nafion−**1**	1.51×10^{-9}	0.90	0.5	0.3

We examined the influence of surface concentration of **1** on photocurrent values (Figure 3). The stoichiometry between Nafion and **1** was maintained at 48:1 (wt/wt) because no effects of varying the **1** concentrations were shown in the Nafion membrane on either the photocurrent or the quantum yields. On the other hand, Nafion−TiO$_2$-deposited electrodes were immersed into an aqueous solution containing **1** with identical concentration (0.25 mM) for 6 h, and Nafion−**1**−TiO$_2$ membranes with saturated adsorption of **1** were prepared because of the same reason mentioned above. Absorbance of **1** on the ITO electrode increases linearly with the membrane thickness regardless of the presence or absence of TiO$_2$, but much correlation does not exist between the membrane thickness of the Nafion−TiO$_2$−**1** and that of the Nafion−**1** membrane because of an occupied volume of TiO$_2$. In the Nafion−TiO$_2$−**1** system, the photocurrent increases linearly with the absorbance of **1**, indicating that electron transfer occurs efficiently from **1** to the ITO electrode even when **1** is placed far from the ITO electrode. On the other hand, in the Nafion−**1** membrane, a plot of absorbance of **1** on the ITO electrode vs photocurrent showed a saturation curve, indicating that electron transfer could not occur from **1** to the ITO electrode when **1** is placed far from the ITO electrode. In the Nafion−TiO$_2$−**1** membrane, the quantum yield and the incident-photon-to-current efficiency (IPCE) was estimated at about five times larger than that in the Nafion−**1** membrane (the quantum yield, 2.4 and 0.5%, respectively; IPCE, 1.3 and 0.3%, respectively; each surface concentration of **1** is 1.5×10^{-9} mol/cm^2, irradiated at 420 nm and −0.4 V bias voltage) (Table 1).

We examined the influence of TiO$_2$ upon surface concentration of **1**, photocurrent values, and quantum yields (Figure 4). ITO electrodes were spin coated with aqueous−ethanol (2:5 v/v) solutions containing [Nafion] = 12.1 g/L and [TiO$_2$] = 0−69.1 g/L. The adsorption of **1** onto each modified electrode was carried out in the foregoing manner. In a low concentration range of TiO$_2$ ([TiO$_2$] < 11.7 g/L), the absorbance of **1** remained nearly constant irrespective of the presence of TiO$_2$, suggesting that **1** is scarcely adsorbed on the surface of TiO$_2$ because the surface of TiO$_2$ was entirely covered by Nafion. On the other hand, in a higher concentra-

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(31) In contrast, by the use of ascorbic acid as an electron sacrificial compound, the photocurrent in the Nafion−TiO$_2$−**1** system decreased, indicating that anionic ascorbic acid cannot penetrate into the Nafion membrane. To the contrary, the result which generated a photocurrent constantly by use of TEOA in the Nafion−TiO$_2$−**1** system, indicates that TEOA can penetrate continuously into the Nafion membrane.

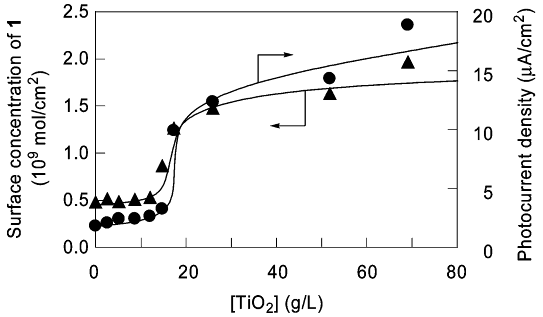

Figure 4. Plots of the surface concentration of **1** (triangle) and photocurrent density (circle) vs concentration of TiO_2 in the Nafion (12.1 g/L) aqueous−ethanol (2:5 (v/v)) solution for the spin coated method on ITO electrodes. Illumination wavelength = 420 nm, input power = 1.0 mW/cm^2, applied potential = 0.4 V (vs Ag/AgCl).

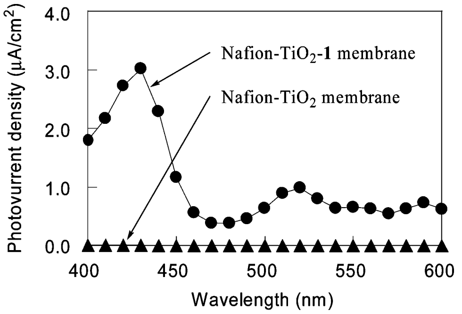

Figure 5. Action spectra of Nafion−TiO_2−**1** (circle) and Nafion−TiO_2 (triangle) membranes with and without a saturated adsorption of **1** on ITO electrodes. Solution: Ar-saturated, [Na_2SO_4] = 0.1 M, [TEOA] = 0.05 M. Illumination wavelength = 420 nm, input power = 1.0 mW/cm^2, applied potential = 0.4 V (vs Ag/AgCl), TiO_2:Nafion = 69.1:12.1 (wt/wt), surface concentrations of **1** = 9.6 × 10^{-10} and 0 mol/cm^2, respectively.

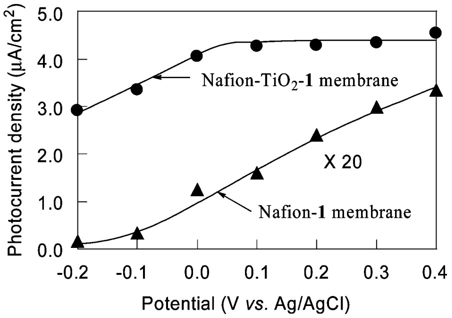

Figure 6. Plots of photocurrent vs bias voltage for the Nafion−TiO_2−**1** (circle) and the Nafion−**1** (triangle) membranes with a saturated adsorption of **1** on ITO electrode. Illumination wavelength = 420 nm, input power = 1.0 mW/cm^2, TiO_2:Nafion = 69.1:12.1 (wt/wt), surface concentrations of **1** = 1.5 × 10^{-9} and 3.8 × 10^{-10} mol/cm^2, respectively.

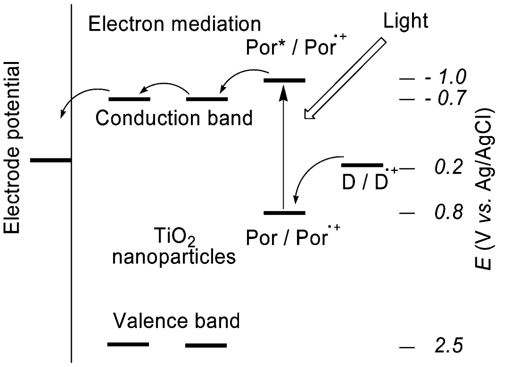

Figure 7. An energy-level diagram for the Nafion−TiO_2−**1** membrane on an ITO electrode. Arrows indicate possible directions of electron propagation.

tion range ([TiO_2] > 18.8 g/L), absorbance of **1** increased concomitant with the TiO_2 concentration, indicating that the adsorption of **1** occurred not only by Nafion but also by the TiO_2 surface because a portion of the TiO_2 surface cannot be covered with Nafion.[32] Furthermore, the increased surface concentration of TiO_2 brought about increases of photocurrent and quantum yields. Actually, the quantum yields with high surface concentration of TiO_2 (1.2% for [TiO_2] = 69.1 g/L) were higher than that with a low one (0.4% for [TiO_2] = 9.4 g/L).

These results are derived from two inherent functions of TiO_2: (i) an electron transfer between TiO_2 and **1** occurs efficiently at higher concentration ranges of TiO_2 and (ii) a generated electron can migrate efficiently among the membranes using dispersed TiO_2. Finally, the electron reaches the ITO electrode.

We measured action spectra in the absence and presence of **1** (Figure 5) and current−potential curves in the absence and presence of TiO_2 under photoirradiation of 420 nm light to elucidate the explanation (i) mentioned above (Figures 6). Action spectra for the Nafion−TiO_2−**1** membrane between 400 and 600 nm are comparable with the UV−vis absorption spectrum of **1**. In the Nafion−TiO_2 membrane, no photocurrent was observed (Figure 5). These findings show that **1** acts efficiently as the photoactive species. Figure 6 shows that the Nafion−**1** system gives a rising curve of photocurrent density that increases in positive bias, indicating that the photocurrent flows directly from **1** to the ITO electrode. On the other hand, in the Nafion−TiO_2−**1** system, the photocurrent remained nearly constant at more over 0.1 V bias voltage, probably because the electronic pathway between **1** and TiO_2 determines the photocurrent.[33,34,35] These findings indicate that almost all photocurrent flows from **1** to the ITO electrode through the intermediary of TiO_2. Therefore, photocurrent flow can be expressed as: **1** → TiO_2 → ITO electrode (Figure 7).

We took TEM images of the TiO_2 and the Nafion−TiO_2 membranes on a grid to elucidate the explanation (ii). Figure 8a shows a TEM image of TiO_2 on a grid cast from an aqueous solution of TiO_2 (11.3 g/L) without Nafion. The TiO_2 aggregates in itself, and no space exists between TiO_2. On the other hand, Figure 8b shows a TEM image of Nafion−TiO_2 mixture on a grid cast from a water−ethanol (2:5 v/v) solution of Nafion (0.12 g/L) and TiO_2 (0.69 g/L).

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(32) In Figure 4, the reason for the sudden increase in the surface concentration and photocurrent at about 15 g/L TiO_2 is not clear at this time. The quantum yields over [TiO_2] = 15 g/L (1.0%) also were about two times higher than that under [TiO_2] = 15 g/L (0.5%), suggesting that the higher quantum yields over [TiO_2] = 15 g/L arose from efficient electron migration among TiO_2 because of self-aggregation of TiO_2. The increase of the TiO_2 surface uncovered by Nafion gave rise to the increase of surface concentrations of **1** and the photocurrent at the same time.

(33) The result of the Nafion−TiO_2−**1** membrane in Figure 6 is similar to the result of the Grätzel cell in ref 34. The reason the photocurrent is effectively observed in not only positive but negative bias voltages in the Nafion−TiO_2−**1** membrane was explained by the fact that a negative displacement of the Felmi level of TiO_2 is under −0.8 V as mentioned in ref 34.

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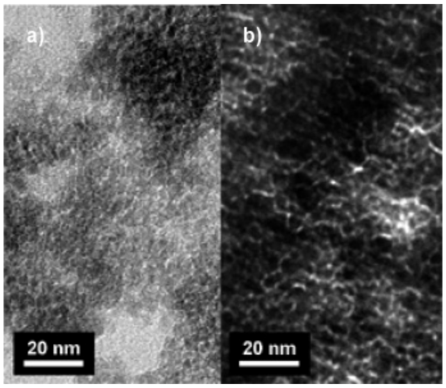

Figure 8. TEM images of the surface of (a) the TiO_2 particles deposited film and (b) the Nafion−TiO_2 deposited film.

TiO_2 of 6-nm diameter was dispersed (black), and almost all TiO_2 was coated by Nafion (white). Figure 8b shows that the distance between TiO_2, i.e., thickness of the Nafion phase, was less than 2 nm, indicating that the distance between TiO_2 and **1** was less than 1 nm, which is sufficiently short to attain electron transfer because all of **1** exists among or on the surface of their TiO_2. These results suggest that electron transfer from photoactivated **1** to TiO_2 takes place efficiently in Nafion membrane.

Conclusions

This study demonstrated a new method to construct an efficient organic photocurrent generators without lowering the quantum yield even in high optical dense compositions. Photocurrent density and IPCE in the Nafion−**1** system is improved remarkably by the addition of TiO_2. Achievement of high photocurrent density arose from efficient electron transfer from **1** to TiO_2 and then to electron migration among TiO_2 in the system. In brief, we succeeded in developing an electron-transfer system using TiO_2 particles as a membrane-penetrated mediator. This system needs not be sintered at high temperature. Therefore, we anticipate that this system provides a new material by deposition on various thermally unstable substrates or electrodes. Further applications of this system are currently being investigated in this laboratory.

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