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Combining Light Harvesting and Electron Transfer in Silica–Titania-Based Organic–Inorganic Hybrid Materials

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In memory of Yoshihiro Matsumara

Abstract: A convenient protocol to fabricate an organic–inorganic hybrid system with covalently bound light-harvesting chromophores (stilbene and terphenylene–divinylene) and an electron acceptor (titanium oxide) is described. Efficient energy- and electron-transfer processes may take place in these systems. Covalent bonding between the acceptor chromophores and the titania/ silica matrix would be important for electron transfer, whereas fluorescence resonant energy transfer (FRET) would strongly depend on the ratio of donor to acceptor chromophores. Time-resolved spectroscopy was employed to elucidate the detailed photophysical processes. The coupling of FRET and electron transfer was shown to work coherently to lead to photocurrent enhancement. The photocurrent responses reached a maximum when the hybrid-material thin film contained 60% acceptor and 40% donor.

Keywords: electron transfer · FRET (fluorescence resonant energy transfer) · hybrid materials · silica · titania

Introduction

The natural photosynthetic process involves the extremely efficient capture of solar energy, energy transfer, and electron transfer, which ultimately reaches the reaction center where the reduction of various substrates takes place.[1] The process occurs in a nanometric assembly of chromophores that serves as an antenna to induce energy/electron transfer and initiate charge separation. There has been an ever-burgeoning interest in artificial systems to mimic this process, and a range of organic or organometallic systems, such as dendrimers,[2] porphyrins,[3] functionalized polymers,[4,5] Langmuir–Blodgett films,[6] thin films,[7] microspheres,[8] monolayers,[9] hydrogen-bound organic gels,[10] and organic–inorganic hybrid materials,[11] has been employed for this purpose. However, the integration of light-harvesting and electron-transfer components into one system has only been sporadically explored.[12] To illustrate, supramolecular systems involving covalently bound metal prophyrins, metal-free porphyrins, and fullerene and related approaches have been designed as models for photosynthetic processes.[12] We recently reported that highly efficient fluorescence resonant energy transfer (FRET) was found in covalently bound silica-based organic–inorganic hybrid systems that contain two or more types of homogeneously distributed chromophores.[11] For example, the FRET efficiencies for hybrid materials containing different ratios of stilbene (as donor-derived form **1**) and terphenylene–divinylene (as acceptor-derived form **2**) chromophores were 88–97%. We also found that silica-based organic–inorganic hybrid materials can also bind covalently to the surface of titanium oxide so that a prototype photovoltaic cell can be fabricated.[13] The efficiency was further improved by incorporating titanium tetraisopropoxide (TTIP) during the course of the preparation of the hybrid materials.[13] It seems likely that titanium oxide species may have penetrated the silicon oxide network in these hybrid films so that the electron–hole separation may be facilitated. It is envisaged that these organic–inorganic hybrid materials could provide a nanometric assembly of multiple chromophores, including electron-acceptor moieties, to couple FRET and electron transfer (ET). This strategy has been briefly explored in zeolite systems[14] as well as
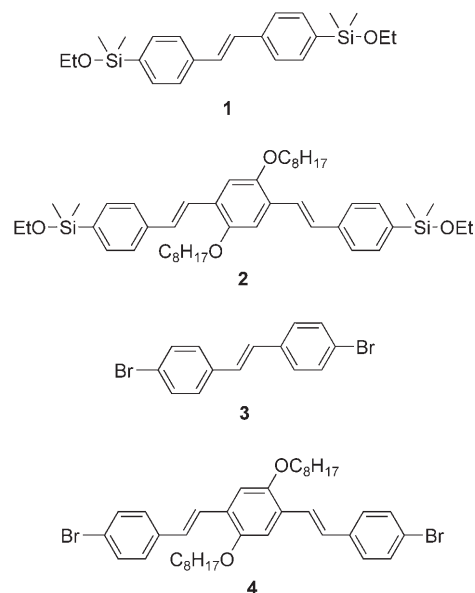
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in self-assembled monolayers.[15] We now report a fascinating example of the integration of light-harvesting chromophores and electron acceptors into silica–titania-based organic–inorganic hybrid systems and the enhancement of photocurrent due to coherent coupling of FRET and ET processes in these hybrid materials (Scheme 1).

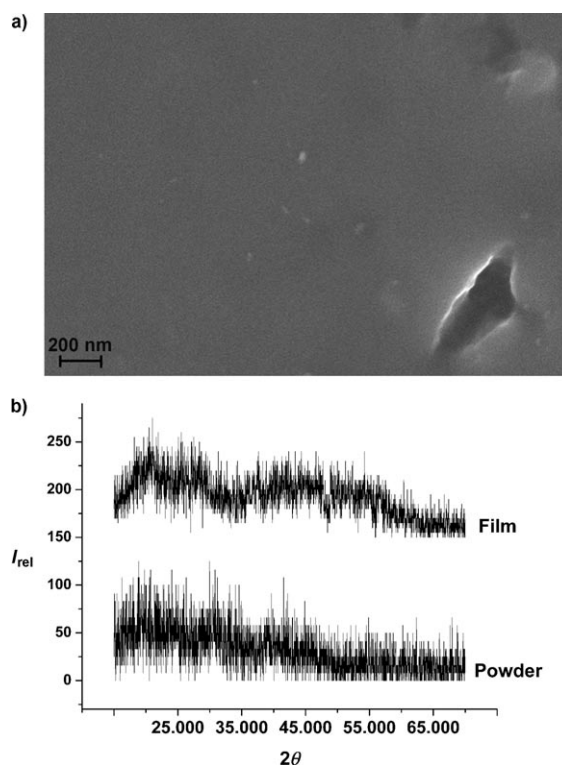Scheme 1. Chromophores **1**, **2**, **3**, and **4**.

Figure 1. a) Typical SEM images of the organic–inorganic hybrid-material thin films on ITO glass prepared from **1**, **2**, TEOS, and TTIP. b) Typical XRD patterns of the hybrid-material thin films on quartz substrate and grind powder.

Results and Discussion

Fabrication of Silica–Titania-Based Organic–Inorganic Hybrid Materials

A pair of stilbene and terphenylene–divinylene chromophores was chosen for the preparation of organic–inorganic hybrid materials because, as mentioned, efficient FRET was observed between these chromophores in such a hybrid network.[11] Thus, **1** and **2**, which have ethoxysilyl substituents,[11,13] were employed as precursors for the preparation of titania–silica hybrid materials by using a sol–gel technique. Hybrid materials A_i with different Ti/Si ratios (i (=1–6) denotes the molar ratio of **2** to **1** as shown in Table 1) were prepared by employing different ratios of the starting TTIP and tetraethoxysilane (TEOS), while the sum of the molar quantities of the donor and acceptor chromophores remained constant in the sol solutions for the fabrication of the hybrid films.

Transparent thin films of the hybrid material were obtained by spin-coating of the sol solutions onto indium tin oxide (ITO) glasses. The evidence for Ti–O–Si bonding in such Ti/Si hybrid materials by FTIR spectra has been documented.[13] The average thickness of these thin films was (170 ± 10) nm, as examined by a surface profilometer. A typical scanning electron microscopy (SEM) image is shown in Figure 1a, and the Brunauer–Emmett–Teller (BET) method for porosity measurements suggests that these hybrid materials A_i are nonporous. X-ray diffraction (XRD) of both thin-film and powder (the ground powder of aerogel bulk) materials were examined, and no characteristic peaks of anatase- or rutile-phase titania were observed (Figure 1b).

Photophysics of Thin Films of Hybrid Material

The absorption and emission spectra of A_i are shown in Figure 2. As expected, the intensity of the absorption at around 390 nm (λ_{max} of the chromophore from **2**) increased with increasing molar fraction of **2** in the preparation of films of the hybrid material. It is known that efficient FRET between stilbene and terphenylene–divinylene chromophores in silicon-based hybrid materials occurs readily.[11] The fluorescence quantum yields of **1** and **2** in EtOAc were 0.13 and 0.65, respectively. Emission spectra ($\lambda_{ex} = 300$ nm) of the hybrid material thin films are shown in Figure 2b. The donor emission was observed at around 400 nm in A_6, whereas only the emissions from the acceptor chromophore at 450 and 470 nm were observed in the hybrid thin films A_1–A_5. Notably, the emission intensities of the acceptor increased with increasing donor molar fractions in these hybrid systems. Although the acceptor chromophores in these hybrid films may also absorb at 300 nm, the complete absence of emission from the donor chromophore, even with relatively high donor molar fractions (e.g., A_4 or A_5),
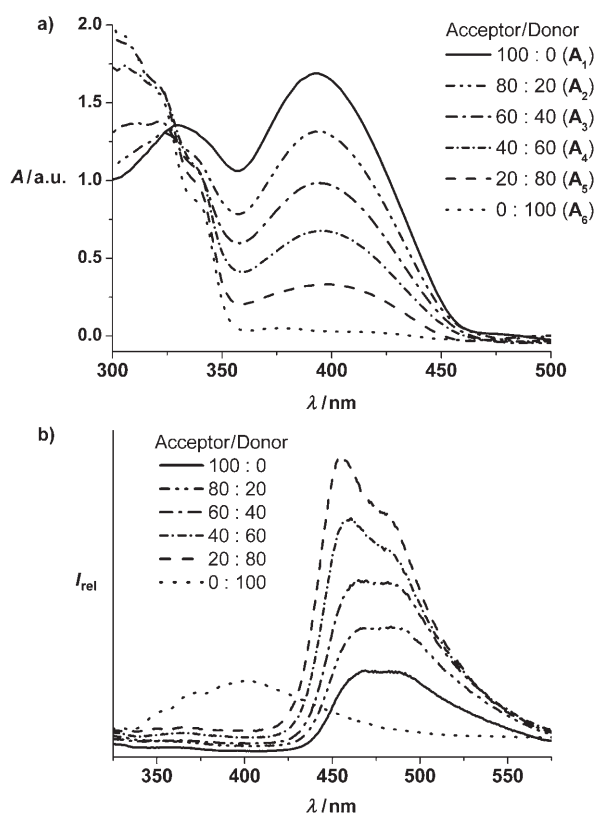
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Figure 2. a) Absorption and b) fluorescence ($\lambda_{ex} = 300$ nm) spectra of films A_i. The ratios of 2 (acceptor) to 1 (donor) are shown in the figure.

Figure 3. a) Time-resolved fluorescence spectra of films A_i monitored over a period of 0–20 ps after irradiation at 300 nm. b) Corresponding fluorescence-decay profiles of the acceptor moiety monitored at 460–480 nm. The dashed line represents the instrument response.

indicates that FRET may take place readily and an antenna effect may be exhibited.[16]

Time-Resolved Fluorescence Spectroscopy

Time-resolved fluorescence spectroscopy was utilized to elucidate the mode of interactions among relevant species in these hybrid films. Representative decay profiles are shown in Figure 3, and the results are also tabulated in Table 1. As shown in Figure 3a, the time-resolved fluorescence spectra of A_2–A_5 monitored over a period of 0–20 ps after irradiation exhibited only the emission for the acceptor chromophore derived from 2. These results suggest that the excited state of the donor chromophore derived from 1 was completely quenched, which is consistent with the results obtained in the steady-state fluorescence spectra (Figure 2b).

Silica-based hybrid films **B** (containing only acceptor) and **C** (containing only donor) were prepared from 2 and 1, respectively, and the fluorescence lifetimes of **B** (200 ps) and **C** (30 ps) are compared in Table 1. The fluorescence-decay profiles of the acceptor moiety in A_2–A_5 are shown in Figure 3b. Biexponential fittings gave two components of lifetimes. The longer lifetimes in A_1–A_5 (130–215 ps) were comparable with that of **B**. Similarly, the longer lifetime in A_6 (33 ps) was similar to that of **C**. Titanium oxide is known to quench efficiently the fluorescence from the organic chromophores by electron transfer.[17] It seems reasonable that
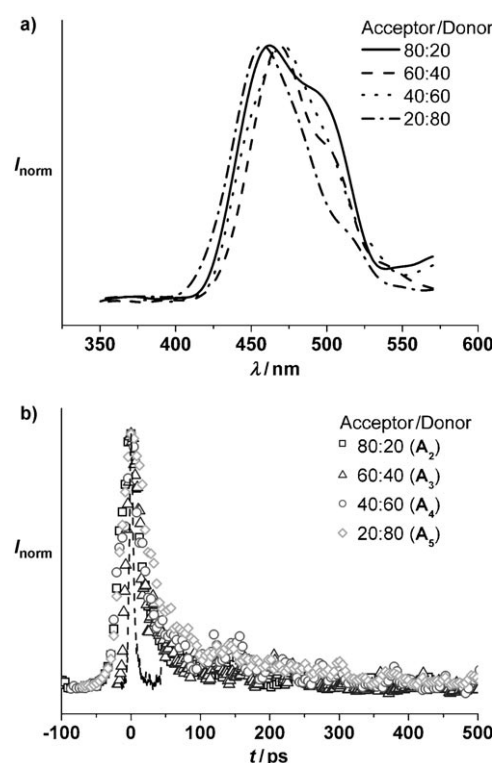
Table 1. Fluorescence-decay lifetimes of hybrid thin films A_i.

Film	2/1[a] (Acceptor/ donor)	TTIP [10^{-1} M]	TEOS [10^{-1} M]	Monitoring λ [nm]	Lifetime[b] [ps]
A_1	100:0	2	4	460–480	11 (0.9), 132 (0.1)
A_2	80:20	2	4	460–480	18 (0.9), 211 (0.1)
A_3	60:40	2	4	460–480	17 (0.86), 181 (0.14)
A_4	40:60	2	4	460–480	16 (0.77), 147 (0.23)
A_5	20:80	2	4	460–480	29 (0.81), 215 (0.19)
A_6	0:100	2	4	390–410	< 3[c] (0.88), 33 (0.12)
B	100:0	0	6	460–480	200
C	0:100	0	6	390–410	30

[a] Total chromophore concentration in films **A**–**C** is 0.04 M. [b] The relative weights of the different time constants are included in parentheses. [c] Beyond the limits of the instrument.

the shorter lifetimes in A_1–A_5 (11–29 ps) may be due to ET from the acceptor chromophore to titania.

These results indicate that several competitive pathways may be involved. They are electron transfer from chromophores to titania matrix and FRET between donor and acceptor chromophores. We previously showed that the FRET rate between chromophores derived from 1 and 2 is faster than 1 ps^{-1} in silica-based hybrid films.[11] The fast FRET in these systems may imply that interaction between donor and acceptor chromophores might play a pivotal role in the photoinduced processes in these hybrid systems.

It has been established that covalent bonding of chromophores with the silica–titania-based matrix was essential for enhancing photovoltaic performance,[13] and a similar strategy was also found in the Grätzel-type solar cell between chromophore and titania surface.[18] In other words, when a chromophore is blended with the silica–titania hybrid material, the photocurrent response is much lower than those of the covalent analogues.[13] Apparently, the photophysical behavior of this blended system would be distinctly different from those of the covalent ones. Accordingly, blended thin films D_i were prepared from a 2:4:0.4 molar ratio mixture of TTIP, TOES, and chromophores **3** and **4** of different ratios (i (1–6) denotes the different molar ratios of donor and acceptor chromophores in these hybrid films; Table 2).

Table 2. Fluorescence-decay lifetimes of hybrid thin films D_i fabricated by **3** and **4**, and E_i fabricated by **3** and **2**.

Film	Acceptor/donor[a]	Lifetime[b] [ps]	
		Monitoring at 390–410 nm	Monitoring at 460–480 nm
D_1	100:0	–	28 (0.26), 133 (0.74)
D_2	80:20	–	24 (0.26), 148 (0.74)
D_3	60:40	–	24 (0.35), 161 (0.65)
D_4	40:60	43 (0.69), 612 (0.31)	27 (0.38), 177 (0.62)
D_5	20:80	125 (0.8), 621 (0.2)	57 (0.34), 308 (0.66)
D_6	0:100	720	–
E_1	100:0	–	17 (0.84), 208 (0.16)
E_2	80:20	–	30 (0.81), 217 (0.19)
E_3	60:40	–	16 (0.85), 190 (0.15)
E_4	40:60	42 (0.6), 750 (0.4)	15 (0.89), 150 (0.11)
E_5	20:80	110 (0.7), 770 (0.3)	20 (0.8), 192 (0.2)
E_6	0:100	700	–

[a] The composition of the films D_i and E_i is chromophore/TTIP/TEOS = 0.4:2:4. [b] The relative weights of different time constants are included in parentheses.

In these cases, neither **3** nor **4** formed covalent bonds with the silica–titania matrix. On the other hand, films E_i were obtained similarly by mixing TTIP, TEOS, and chromophores **2** and **3** in same molar ratios as those for D_i. The difference between films D_i and E_i is that the latter has the acceptor chromophore covalently bound to the silicon–titanium matrix.

Time-resolved fluorescence spectroscopy was employed to investigate the photophysical behavior of these blended films. The results are summarized in Table 2. When the fluorescence decay was monitored at 390–410 nm, the emission wavelength of the donor moiety, only those films with a molar ratio of the acceptor chromophore lower than 40% (D_4–D_6 and E_4–E_6) were detected. Biexponential fitting gave two lifetimes. As seen in Table 2, the shorter lifetimes (42–125 ps) decreased with increasing molar fraction of the acceptor chromophore, presumably due to FRET between donor and acceptor chromophores in these blended systems.

When the fluoresence decay was monitored at 460–480 nm (due to the emission of the acceptor chromophore), two decay lifetimes were obtained from the fittings for these blended films D_i and E_i. Interestingly, both shorter (24–

57 ps) and longer lifetimes (133–308 ps) were comparable to those observed for films A_i. However, the relative weight distributions of D_i and E_i were quite different. The weights for short lifetimes owing to ET from the acceptor chromophore to titania were smaller for D_i (26–38%) than for E_i (80–89%). These results suggest that the electron-transfer process is more efficient in E_i than in D_i. Apparently, covalent bonding between the acceptor chromophores and the titania matrix would make the ET process more facile. This photophysical behavior is also consistent with our earlier findings that covalent bonding between chromophores and the silica–titania lattice is essential for improving photovoltaic performance.[13] Moreover, as seen in Tables 1 and 2, the lifetimes and relative weight distributions of A_i and E_i are comparable. It seems likely that, as long as the molar ratio of donor and acceptor chromophores remains similar, the environment between these two chromophores in the blended system and the covalently bound hybrid materials may be alike for FRET.

Photocurrent Response of Thin Films

To investigate the photoinduced electron transfer between the hybrid materials described above and the amorphous titanium oxide film, the electrochemical properties of **1** and **2** were examined (Table 3). The frontier orbital energies of the chromophores in the hybrid system are compared with the work function of titanium oxide in Figure 4. The HOMO–LUMO energy levels of the donor and acceptor were estimated on the basis of the cyclic voltammetric and photophysical properties of **1** and **2**. Notably, the lower edge

Table 3. Electrochemical parameters of **1** and **2** in solution.

	E_{0-0}[a] [eV]	$E_p^{1/2}$[b] [V]	HOMO [eV]	LOMO [eV]
1	3.61	1.05	−5.85	−2.24
2	2.81	0.52	−5.32	−2.51

[a] The band-gap energy was determined by the absorption edge of the chromophore in EtOAc. [b] The potentials are relative to Fc/Fc+ (Fc = ferrocenyl).
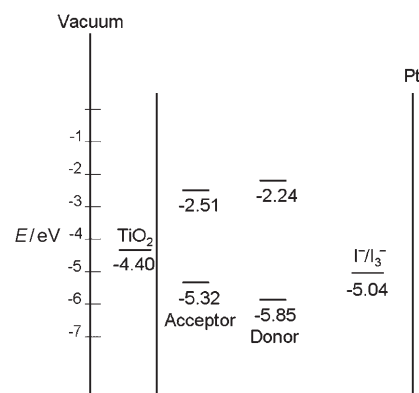

Figure 4. Energy diagram of the chromophores used in the hybrid-material thin films.

of the conduction band of anatase-phase titania may be changed by silica incorporation, and the shift in the band edge was shown to be less than 0.2 eV.[19] It seems likely that the conduction band of the titania/silica network would fit into the energy diagram of the frontier orbitals of chromophores used in these hybrid thin films.

The hybrid-material-coated ITO glass thin film was used as the working electrode in combination with a platinum counter electrode in a quartz cell containing a solution of I^-/I_3^- for photoelectrochemical measurements. In AC impedance experiments, the resistance of films A_i was about 80 000 Ω in the dark and 130 Ω upon irradiation with AM 1.5 radiation. In the absence of chromophore(s), the resistance was 220 000 Ω both in the dark and under irradiation. This observation indicates that the chromophores play a pivotal role in inducing ET upon illumination in organic–inorganic hybrid thin films A_i.

In general, photovoltages of around 400 mV at open circuit (zero current) were observed for these hybrid-material thin films. Hence, external bias potentials were applied to induce oxidative or reductive photocurrents. The molar ratio of chromophore(s) to TTIP/TEOS in the hybrid thin films was crucial to photocurrent response. For example, the plot of photocurrent against the concentration of **2** used in the preparation of the hybrid materials (Figure 5) suggests that

Table 4. Photocurrent responses of the hybrid-material thin films A_i with different total chromophore concentrations and acceptor-to-donor ratios.

Molar ratio[b]	Acceptor-to-donor ratio in sol solution					
	100:0 (A_1)	80:20 (A_2)	60:40 (A_3)	40:60 (A_4)	20:80 (A_5)	0:100 (A_6)
j_{oxi}[a] 0.1:2:4	0.92	1.02	2.05	1.17	0.85	0.61
0.4:2:4	0.89	1.21	1.52	1.15	1.03	0.36
1:2:4	0.29	0.35	0.43	0.57	0.49	0.35
j_{red}[a] 0.1:2:4	−1.07	−1.47	−1.55	−1.05	−0.96	−0.76
0.4:2:4	−1.05	−1.15	−1.41	−1.03	−0.92	−0.82
1:2:4	−0.27	−0.33	−0.34	−0.45	−0.36	−0.36

[a] Oxidative and reductive photocurrent densities ($\mu A\,cm^{-2}$) of the hybrid-material thin films. The applied bias was 500 and 300 mV for oxidative and reductive photocurrents, respectively. [b] Chromophore/TTIP/TEOS ratios in sol solution.
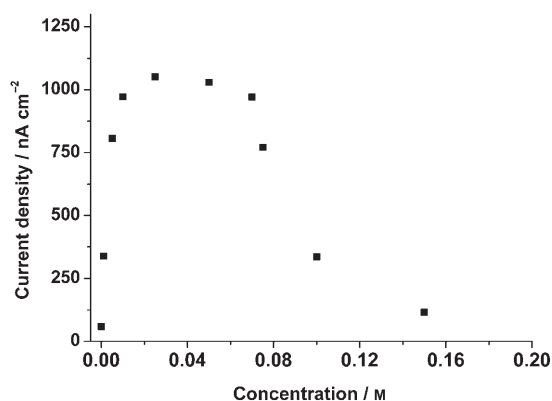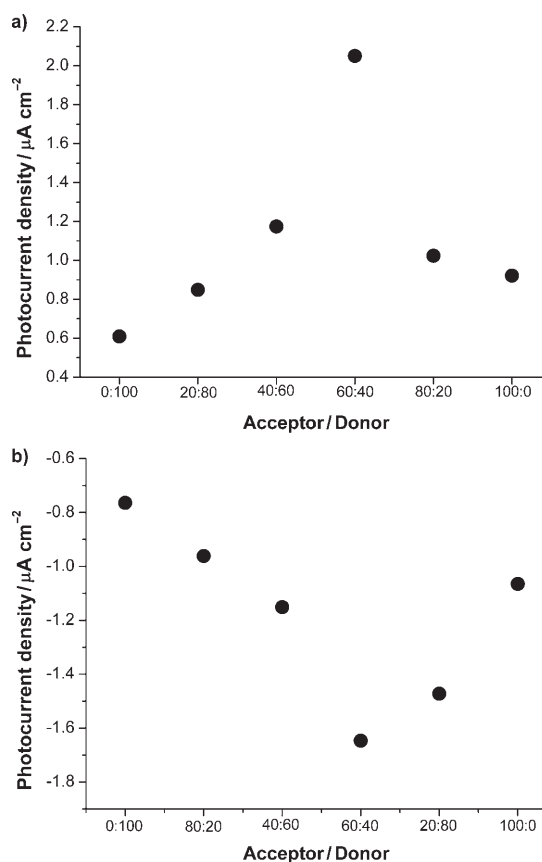

Figure 5. Photocurrent responses of the hybrid thin films derived from sol solutions with different concentrations of **2**. 0.2 M of TTIP and 0.4 M of TEOS were used for the preparation of the sol solutions. The applied bias was 500 mV.

Figure 6. a) Oxidative and b) reductive photocurrents of films A_i on ITO upon irradiation with AM 1.5. The applied bias was 500 and 300 mV for oxidative and reductive photocurrents, respectively.

the optimal concentration of **2** for the preparation of the sol solution was 0.01–0.05 M, which corresponds to a chromophore/TTIP/TEOS molar ratio of 0.1–0.5:2:4. Under these conditions, a higher photocurrent was generated. Interestingly, a higher ratio of **2** to the titania moiety gave a poorer performance in photocurrent. Presumably, a critical ratio between the excited chromophore and the electron acceptor would be essential to facilitate the electron-injection process.

The photocurrents of films A_i were responsive to the molar ratios of donor and acceptor (Table 4 and Figure 6). As seen in Figure 6, both reductive and oxidative photocurrent responses reached a maximum when the thin film contained 60% acceptor and 40% donor. The trends appear to be independent of the total concentration of the two chromophores. Interestingly, as with the photocurrent responses shown in Figure 5, the photocurrents were smaller when a higher total concentration of the donor and acceptor chromophores was used.

Wavelength-dependent photocurrent-response investigations were employed to scrutinize the effect of energy trans-

fer between chromophores on photocurrent generation. The photoaction spectra are shown in Figure 7; films A_3, D_3, and E_3 were chosen because, as shown in Figure 6, the 6:4 molar ratio of acceptor to donor chromophores exhibited a stron-
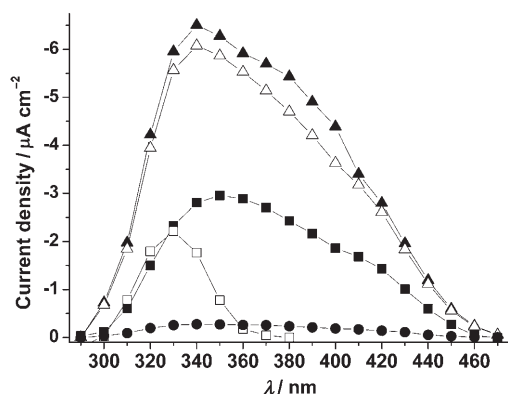

Figure 7. Photoaction spectra of hybrid-material thin films containing different chromophores on ITO. ▲ = A_3, △ = E_3, ■ = A_1, □ = A_6, ● = D_3. The chromophores/TTIP/TEOS molar ratio is 0.1:2:4. The external applied bias was 0 V.

ger photocurrent response. Thus, at 340 nm, the photocurrents of films A_3 and E_3 were 6–6.5 $\mu A\,cm^{-2}$, whereas that of D_3 was 0.3 $\mu A\,cm^{-2}$. These results reveal that a lack of covalent bonding between acceptor chromophore and silica–titania matrix may cause a significant decrease in photocurrent, as in the case of D_3. On the other hand, covalent bonding between the donor chromophore and the lattice of hybrid materials may not be essential for photocurrent response (e.g., E_3 vs. A_3). It seems likely that, as long as the molar amounts of donor and acceptor remain similar, the environment between these two chromophores in the blended system and in the covalently bound hybrid materials might be similar. In other words, the photocurrent enhancement due to FRET would depend mainly on the ratio of donor to acceptor in these hybrid systems. On the other hand, ET would rely strongly on the covalent bridge between chromophore and titania matrix.

The photoaction spectra of A_1 (containing acceptor chromophore only) and A_6 (containing donor chromophore only) were also examined. As shown in Figure 7, the photoaction spectrum of A_6 exhibited a much lower photocurrent than that of A_3. At this stage, direct electron transfer from the excited donor chromophore to the titania species in the hybrid materials cannot be ruled out. However, the relatively low photocurrent by A_6 indicates that direct electron transfer from the excited donor chromophore to titania may not be a major pathway contributing to the overall enhancement of the photocurrent in A_3.

As shown in Figure 7, the photocurrent response of A_1 was only about 50% that of A_3. Hence, the presence of both donor and acceptor chromophores in these hybrid systems would enhance the photocurrent response. As discussed in the previous sections, FRET between the donor and acceptor chromophores would occur readily. Because of the effi-

cient energy transfer between the donor and acceptor chromophores in these films, a significant increase in photocurrent generation was observed.

Conclusions

We have demonstrated the first silica–titania-based organic–inorganic hybrid systems that contain both light-harvesting organic chromophores and electron-acceptor titanium oxide. Efficient energy- and electron-transfer processes may take place in these systems. FRET and ET may couple coherently to lead to enhancement of photocurrent generation. Our observations of these systems suggest that covalent bonding between the acceptor chromophores and the titania/silica matrix would be important for ET. Relatively speaking, FRET would strongly depend on the ratio of donor to acceptor chromophores. Although the present system is far from practical application because the photocurrent generation was relatively low, with the relatively simple strategy developed in this study, our approach may provide room for further extension to carry out photocatalytic reactions as well as to mimic natural photosynthetic processes.

Experimental Section

General

Hitachi U-3310 UV/Vis and Hitachi F-4500 fluorescence spectrophotometers were used to acquire the absorption and emission spectra of the hybrid-material films on ITO. The crystalline phase was identified by X-ray diffraction on an MAC diffractometer (model M03XHF, Material Analysis and Characterization, Japan). An ECO Chemie µAutolab III potentiostat/galvanostat was used for photoelectrochemical experiments. An Hg(Xe) arc lamp (Oriel, model 66984) equipped with an AM 1.5 Global filter or a monochromator (Thermo Oriel cornerstone 260) was employed as the light source. The thickness of the hybrid-material thin films was measured by a surface profilometer (Dektak3, Veeco/Sloan Instruments, Inc.). BET surface-area measurements were obtained at 77 K on a Micromeritics ASAP 2010 apparatus.

Preparation of the Hybrid-Material Thin Films

The silica–titania-based hybrid-material thin films were prepared by using a sol-gel protocol. TTIP (0.2 M) and TEOS (0.4 M) were added to a dry solution of **1** and **2** of different ratios and concentrations in THF. A solution of tetrabutylammonium fluoride (1 mol% relative to the total amount of alkoxy moieties on silicon) in THF was then added, and the mixture was kept at room temperature for 30 min. A mixture of water (50 mol% relative to the total amount of alkoxy moieties on silicon and titanium) and THF was then introduced under ultrasonic conditions at 0 °C to afford the sol solution. The sol solution was spin-coated (5000 rpm for 30 s) on ITO glass. A transparent thin film with homogeneous surface morphology was obtained[11] and subject to spectroscopic or photoelectrochemical measurements.

Blending of 3 with Hybrid-Material Thin Films Containing Covalently Bound 2

TTIP (0.2 M) and TEOS (0.4 M) were added to a dry solution of **3** and **2** of different ratios and concentrations in THF. A solution of tetrabutylammonium fluoride (1 mol% relative to the total amount of alkoxy moieties on silicon) in THF was then added, and the mixture was kept at room temperature for 30 min. A mixture of water (50 mol% relative to the total amount of alkoxy moieties on silicon and titanium) and THF was

then introduced under ultrasonic conditions at 0 °C to afford the sol solution. The sol solution was spin-coated on ITO by following the same procedure described above.

Photoelectrochemical Measurements

A two-electrode system with a quartz electrochemical cell was used for measurement of photocurrent generation. The working electrode was an ITO glass coated with hybrid-material thin film as described above, and a Pt foil was used as the counter electrode in a aqueous KI (0.5 M) as the electrolyte. The electrochemical cell was purged with Ar for at least 15 min before measurement. The incident light intensity was 100 mW cm^{-2} at AM 1.5.

Photoaction Spectra

Monochromatic wavelengths were generated by using an Hg(Xe) arc lamp (Oriel, model 66984) equipped with a monochromator (Thermo Oriel cornerstone 260). The photocurrent responses at different wavelengths were recorded by using the same procedure described above.

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