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Fast cascade neutralization of an oxidized sensitizer by an in situ-generated ionic layer of I⁻ species on a nanocrystalline TiO₂ electrode

Jongchul Lim, Taewan Kim and Taiho Park∗

We report a novel way to accelerate the rate of oxidized sensitizer neutralization on nanocrystalline TiO₂ electrode surfaces using a novel coadsorbent, 3,4,5-tris-butenyloxy benzoic acid (TD), having three terminal double bonds. ¹H NMR and contact angle measurements revealed that the terminal double bonds reacted with I₂ to form an in situ-generated ionic layer of I⁻ species. Transient absorption spectroscopy (TAS) and electrochemical impedance spectroscopy (EIS) studies demonstrated that I⁻ species neighbouring the cationic dye molecules (D⁺) accelerate the neutralization (or regeneration) rate (kD⁺), as well as decrease the recombination reactions of photoinduced electrons with D⁺ (k₁) and I₃⁻ (k₂). Dye-sensitized solar cells treated with TD exhibit 10.2 % of power conversion efficiency, 22% higher due to the simultaneous improvements in JSC and VOC, even at 15% low dye loading levels, compared to the values obtained from a conventional device.

Broader context

The rate of oxidized sensitizer neutralization is considered as a rate-determining step among the many electrochemical reactions at the interfaces of TiO₂ / sensitizers (D) / electrolytes (redox species) in dye-sensitized solar cells. Therefore, the faster rate of oxidized sensitizer neutralization might lead an improved light harvesting, resulting in a highly efficient dye-sensitized solar cell. Here, a new concept to accelerate the rate of oxidized sensitizer neutralization is constructed using in situ-generated ionic layer of I⁻ species on a nanocrystalline TiO₂ electrode. The estimated regeneration time of the our device is one order of magnitude shorter than the control device, demonstrating that in situ-generated I⁻ participated in the regeneration of D⁺. Our novel concept has not been tried by others, although a variety of coadsorbents have been tested in the context of the sensitization process. This work emphasizes the importance of understanding and engineering the interfaces in DSCs and will provide insights into various optoelectronic fields.

Introduction

Dye-sensitized solar cells (DSCs) are based on a nanoscale-crystalline TiO₂ layer covered with dyes and capable of harvesting sun light.¹ As shown in Fig. 1(a), many photo- and electrochemical reactions take place at the interfaces between the nanoscale TiO₂ crystals, the dyes, and the electrolyte, which includes redox species, such as I⁻ and I₃⁻.²⁻³ Understanding and engineering such interfaces are a key approach to improving the photovoltaic performances of DSCs.⁴⁻⁵ Upon light absorption, the excited dye (D*)injects an electron (e⁻) into the conduction band (Ecb) of TiO₂ (k_{inj}), producing an oxidized dye (D⁺) that is subsequently neutralized by I⁻ (k_{D⁺}). The injected electron may diffuse to the surface states below the Ecb of the TiO₂ electrode and will recombine with oxidized species, such as D⁺ or I₃⁻ (k₁ and k₂), resulting in the decreased charge collection efficiency (ηcc). Katoh

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and Haque, independently, reported\textsuperscript{1a,6} that the dye-regeneration rate (k_{D+}) is \~\mu s time scale which is much longer than the electron injection rate (k_{inj} \sim ps). Meanwhile, the recombination rates (k_1 and k_2) with D^+ or I_3^- are in the range of \~1 ms.\textsuperscript{6,7} Therefore, the dye-regeneration process (\sim k_{D+}) could be considered as a rate-determining step in the electrochemical reactions. In turn, the faster harvesting process (\eta_{lh}) by accelerating the regeneration rate (k_{reg}) is \~1 \times 10^{-6} M/s. We synthesized a novel coadsorbent, 3,4,5-tris-butenyloxy benzoic acid (TD) having three terminal double bonds (Fig. 1(c); 3,4,5-tri-butoxy benzoic acid (TA) without double bonds), which is capable of forming an ionic layer on the TiO\textsubscript{2} electrode surfaces (Fig. 1(b)) through the reversible iodization process (Fig. 1(d)). It is noticed that our novel concept has not been tried by others, although a variety of coadsorbents have been tested in the context of the sensitization process.\textsuperscript{11}

### Experimental Section

#### 3,4,5-Tris-butenyloxy benzoic acid (TD).

**Synthesis of 3,4,5-tris-butenyloxy benzoic acid methyl ester (1).** 1-Bromo-butene (1.35 g, 10 mmol) was added to a suspension of 3,4,5-tri-butenyloxy benzoic acid methyl ester (0.506 g, 2.75 mmol), K\textsubscript{2}CO\textsubscript{3} (5.28 g, 40 mmol), KI (0.2 g, 1.2 mmol) and 4A molecular sieves in dry butanone (50 mL), and the mixture was heated under reflux for 3 days. The reaction mixture was filtered and the butanone distilled off. The crude product was purified by column chromatography (SiO\textsubscript{2}, E.A./hexane = 1/9 v/v), yielding white powder (0.775 g, 2.2 mmol, 80%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta (ppm) = 7.27 (s, 2H), 4.03 (m, 6H), 3.89 (s, 3H), 1.81 (m, 6H), 1.53 (m, 6H), 0.98 (t, J = 7.3 Hz, 9H).

**Synthesis of 3,4,5-tris-butenyloxy benzoic acid (TA).** Compound 1 (0.775 g, 2.2 mmol) was dissolved in THF (8 mL) and methanol (50 mL). A solution of KOH (0.9 g, 15 mmol) in water (5 mL) was then added dropwise to the mixture with stirring. The mixture was stirred at room temperature for overnight, followed by reflux for 4 h. The solvents were evaporated and ice/water (30 mL) was added to the residue. The mixture was acidified with HCl conc. until pH = 3 and the product was filtered off, washed with water and then with hexane (0.67 g, 1.98 mmol, 90%). Crude yield: M = 340.4, \textsuperscript{1}H NMR (400 MHz, DMSO): \delta (ppm) = 7.19 (s, 2H), 3.98 (m, 6H), 1.70 (m, 6H), 1.46 (m, 6H), 0.930 (m, 9H).

#### 3,4,5-Tributoxy benzoic acid (TA).

**Synthesis of 3,4,5-tributoxy benzoic acid methyl ester (1).** 1-Bromo-butane (1.37 g, 10 mmol) was added to a suspension of 3,4,5-tributoxy benzoate (0.506 g, 2.75 mmol), K\textsubscript{2}CO\textsubscript{3} (5.28 g, 40 mmol), KI (0.2 g, 1.2 mmol) and 4A molecular sieves in dry butanone (50 mL), and the mixture was heated under reflux for 3 days. The reaction mixture was filtered and the butanone distilled off. The crude product was purified by column chromatography (SiO\textsubscript{2}, E.A./hexane = 1/9 v/v), yielding white powder (0.775 g, 2.2 mmol, 80%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta (ppm) = 7.27 (s, 2H), 4.03 (m, 6H), 3.89 (s, 3H), 1.81 (m, 6H), 1.53 (m, 6H), 0.98 (t, J = 7.3 Hz, 9H).

**Synthesis of 3,4,5-tributoxy benzoic acid (TA).** Compound 1 (0.775 g, 2.2 mmol) was dissolved in THF (8 mL) and methanol (50 mL). A solution of KOH (0.9 g, 15 mmol) in water (5 mL) was then added dropwise to the mixture with stirring. The mixture was stirred at room temperature for overnight, followed by reflux for 4 h. The solvents were evaporated and ice/water (30 mL) was added to the residue. The mixture was acidified with HCl conc. until pH = 3 and the product was filtered off, washed with water and then with hexane (0.67 g, 1.98 mmol, 90%). Crude yield: M = 340.4, \textsuperscript{1}H NMR (400 MHz, DMSO): \delta (ppm) = 7.19 (s, 2H), 3.98 (m, 6H), 1.70 (m, 6H), 1.46 (m, 6H), 0.930 (m, 9H).

Here, we demonstrate the enhancement of the light harvesting process by accelerating k_{D+}. We synthesized a novel coadsorbent, 3,4,5-tris-butenyloxy benzoic acid (TD) having three terminal double bonds (Fig. 1(c); 3,4,5-tri-butoxy benzoic acid (TA) without double bonds), which is capable of forming an ionic layer on the TiO\textsubscript{2} electrode surfaces (Fig. 1(b)) through the reversible iodization process (Fig. 1(d)). Fig. 1 (a) Electron transfer processes at the heterogeneous interface of a dye-sensitized solar cell. (b) Illustration of an ionic layer and its role on the surface of TiO\textsubscript{2}. (c) Chemical structures of TA and TD (Fig. S1). (d) Reversible iodization on a terminal olefin.
methanol (50 mL). A solution of KOH (0.9 g, 15 mmol) in water (50 mL) was then added dropwise to the mixture with stirring. The mixture was stirred at room temperature, overnight, followed by reflux for 4 h. The solvents were evaporated and ice/water (30 mL) was added to the residue. The mixture was acidified with HCl conc. until pH = 3 and the product was filtered off, washed with water and then with hexane (0.712 g, 2.106 mmol, 90%). C_{10}H_{12}O_5; M=334.4, 1H NMR (400 MHz, DMSO): δ (ppm) = 7.21 (s, 2H), 5.91 (m, 3H), 5.14 (m, 6H), 4.01 (m, 6H), 2.34 (m, 6H).

Fabrication of DSCs. The nanocrystalline TiO₂ electrode was immediately immersed in the dye solution at room temperature for 18 h. The dye solution consisted of 0.3 mM N719 in acetonitrile and tert-butyl alcohol (1:1 v/v). The coadsorbents, TA or TD, were introduced to the dye solution at constant concentrations (0.3 mM). Coadsorbents were introduced to the dye solutions by transferring appropriate volumes of a 6 mM stock solution to yield the desired final concentrations. The counter electrode was prepared by introducing two holes, using a sandblasting drill, in the FTO glass substrate. The substrate was subsequently washed using the washing method described above. The Pt paste was pasted onto the predrilled FTO glass and subsequently sintered using the programmed heating procedure. The dye-coated photoanode and the counter electrode were assembled and sealed as a sandwich using a transparent 60 µm thick Surlyn spacer (DuPont) by hot pressing. The interelectrode space was filled with the electrolyte solution through the predrilled hole in the counter electrode surface, and the holes were covered with the Surlyn sheet and a thin cover glass followed by heating. The electrolyte consisted of 0.6 M BMII, 0.06 M I₂, 0.1 M guanidinium thiocyanate, 0.5 M LiI, and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (85:15 v/v). More details are included in the electronic supplementary information.

Transient absorption spectrophotometer. Pulsed laser excitation was applied using Continuum Surelite-II Q-switched Nd:YAG laser (λ=355 nm, 10 Hz repetition rate). The output of the optical parametric oscillator (OPO, pulse width at half-height 5 ns) was tuned at 532 nm and attenuated to 75 µJ/cm²-pulse. The analyzer light, produced by a 150 W Xe arc lamp, was passed through the sample, and was detected by the amplifier equipped Si photodiode. A 1 GHz band-pass digital signal analyzer was employed to record the time course of the optical absorbance changes induced by laser excitation of the films. Satisfactory signal-to-noise ratios were typically obtained by averaging over 512 laser shots.

Results and Discussion

The iodization process was monitored by 1H NMR, using 1-hexene as a model compound. The olefinic active site in 1-hexene provided three peaks, H₆ and two diastereotopic H₅ and H₆ peaks (Fig. 2(a)).

The addition of I₂ to the 1-hexene solution (d-chloroform) generated three new peaks (H₅₁, H₆₁, and H₆₂), in addition to the peaks corresponding to 1-hexene at equilibrium. The latter pattern was identical to the peaks provided by propylene oxide, indicating that the two protons (H₅ and H₆) retained their diastereotopic environments (see Supporting information for details, Fig. S2). In d-acetonitrile solution, further reactions were expected, as d-acetonitrile is competitive and contains greater amounts of water molecules than d-chloroform; however, indistinguishable results were obtained in d-acetonitrile and d-chloroform, after the removal of residual water (Fig. 2(b) and Fig. S3). Interestingly, the presence of water shifted the peak positions of the diastereotopic protons (H₅₁ and H₆₁) (see Supporting information for details, Fig. S4), which were more exposed to water molecules than H₅₁, down-field. The positive charge on I⁻ would then have been stabilized by dispersing the charges across the carbon atom connected to H₅₁ and H₆₁ (Fig. S5).

Water contact angle (θc) measurements supported the conclusion that ionic complexes were generated at the double bonds of TD, as shown in Fig. 2(c) (see also Fig. S6). Unlike the case of TA, the θc value for the TiO₂ electrode covered with TD, after treatment with a dried acetonitrile (AN) solution containing I₂ and KI, decreased significantly from 66 to 28°. This result indicated that the double bonds reacted with I₂ and were then solvated with water, consistent with the 1H NMR experiments.
Fig. 3 Normalized decay profiles of D⁺ in devices prepared with TA or TD (N719+TA or N719+TD), in comparison with the control device (N719-only), probed at 790 nm using transient absorption spectroscopy in the presence (a) or absence (b) of redox species. The 790 nm absorption profile examined the metal-to-ligand charge transfer (MLCT) transition associated with the ligand-localized D⁺,ⁱ⁰a upon excitation at 532 nm (the maximum absorption of the N719 dye) (Fig. S7). (c) Bode plots obtained from devices prepared with TA or TD (N719+TA or N719+TD), in comparison with the control device (N719-only), using electrochemical impedance spectroscopy under dark conditions in the vicinity of V_{OC} (0.63 V) (Fig. S8).

We examined the rapid regeneration of D⁺ by the ionic complexes, including I⁻. The rate of dye regeneration (ca. ~ 10⁶/s) typically exceeds the recombination reaction rates (ca. ~ 10⁻³/s),⁶⁻¹² therefore, in the presence of redox species, most D⁺ species could be regenerated by I⁻.¹⁰a Fig. 3(a) shows the normalized decay profiles of D⁺ probed at 790 nm using TAS (D⁺ + e⁻ (TiO₂) → D). The estimated regeneration time at 0.5 ΔO.D. for TiO₂/N719 (with TD)/AN (I⁻+I₃⁻) was 0.2 ± 0.03μs, one order of magnitude shorter than those for TiO₂/N719 (with TA)/AN (I⁻+I₃⁻) or the control device, demonstrating that in situ-generated I⁻ on TD participated in the regeneration of D⁺.

The TA and TD coadsorbents could have formed a physical barrier, which would be expected to increase the interfacial resistance at the TiO₂/D/electrolyte interface and decrease $k_1$ and $k_2$, as has been observed previously.⁴c,¹¹c,¹² The effects of the coadsorbents on $k_1$ and $k_2$ were characterized using TAS,¹d,⁸,¹³ and electrochemical impedance spectroscopy (EIS),¹⁰a respectively. In the absence of redox species (I⁻ and I⁻), the photoinduced electrons were expected to recombine with D⁺ (thus, $k_1$: D⁺ + e⁻ (TiO₂) → D). The estimated life time of D⁺ time at 0.5 ΔO.D. in the electrodes prepared with the TA and TD coadsorbents (~5.0 ms) were longer than the lifetime of D⁺ in the control electrode (2.5 ms) as revealed by the decay kinetics of the $k_1$ (Fig. 3(b)). In the presence of the electrolytes (I₃⁻ and I⁻), the photoinduced electrons mainly recombined with I⁻ ($k_2$: I₃⁻ + e⁻ (TiO₂) → I⁻). The electron lifetimes ($\tau_e$) in the electrodes prepared with TA and TD (38 ms) were longer than that in the control electrode (28 ms), as shown in the bode plots (Fig. 3(c)).

Table 1. Photocurrent–voltage characteristics of devices prepared with TA or TD (N719+TA or N719+TD), or with a control device (N719 only), under AM 1.5 irradiation.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Relative [dye][b]</th>
<th>V_{OC} [V]</th>
<th>J_{SC} [mA/cm²]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N719 only</td>
<td>1.00</td>
<td>0.735</td>
<td>16.2</td>
<td>69.9</td>
<td>8.3</td>
</tr>
<tr>
<td>N719 + TA</td>
<td>0.84</td>
<td>0.773</td>
<td>16.3</td>
<td>73.2</td>
<td>9.2</td>
</tr>
<tr>
<td>N719 + TD</td>
<td>0.85</td>
<td>0.783</td>
<td>17.7</td>
<td>73.2</td>
<td>10.2</td>
</tr>
</tbody>
</table>

[a] Values obtained using the average over 4 devices, for 5 individual experiments (Fig. S9).[b] The values were determined by measuring UV-Vis absorption spectra (see insert in Fig. 4(a)).

Finally, the role of the ionic layer in the photoelectrochemical reaction was examined in the context of device operation, as shown in Fig. 4(a) and Table 1. The quantities of N719 adsorbed onto the electrodes cosensitized with TA or TD were measured using UV-Vis spectrophotometer and were found to be 15 or 16% lower, respectively, than the quantity adsorbed onto the control electrode.
(N719 only, see insert in Fig. 4(a)), indicating that N719 and the coadsorbents (TA and TD) competed for anchoring sites on the Ti+ active sites of the nanocrystalline TiO2 electrodes.11c, 11f

The power conversion efficiency (\( \eta \)) of the device prepared with TD was 10.2%, 23% improvement compared to the control device (\( \eta = 8.3\% \)).14 The improvement was ascribed to the increased \( J_{SC} \) as well as \( V_{OC} \) values, even in 15% low dye-loading in the device prepared with TD. The \( V_{OC} \) values of the devices prepared with TA and TD are ca. 40 mV higher than that obtained in the control device, probably due to the increased interfacial resistance at the TiO2/D/electrolyte interface as demonstrated in the EIS experiments (Fig. 3(c)). The increased interfacial resistance could minimize the \( J_{SC} \) loss caused from the recombination reactions, resulting in the relative increase in \( V_{OC} \) according to the equation:15

\[
V_{OC} \sim \left( \frac{n k T}{q} \right) \ln\left( \frac{J_{SC}}{J_S} \right)
\]

\( n \): the device ideality factor, \( k \): the Boltzmann constant, \( T \): the temperature in Kelvin, \( q \): the fundamental charge, \( J_S \): the saturation current density). In addition, we measured the density-of-states (DOS) on the TiO2 surfaces using cyclic voltammetry (Fig. S10).

As Grätzel16 and we,11b independently, reported, the capacitive currents in the electrodes at the TiO2 / 1-butyl-3-methylimidazolium bromide (BMIB)17 interface displayed gradual onsets under a forward potential. The lower-energy surface states, in which photoinduced electrons were trapped, resulted in fewer recombination reactions. The electrode prepared with TA and TD indicated that the edge of the TiO2 conduction band was shifted ca. 63 mV toward the vacuum level compared to the control electrode (Fig. 5). Therefore, the coadsorbents (TA) present on the TiO2 electrode surface reduced \( k_1 \) and \( k_2 \).

The overall increase in \( J_{SC} \) (16.2 to 16.3 mA/cm²) for the device with TA was negligible due to the decrease in the dye loading level by 16%, in spite of the less recombination. On the other hand, the device prepared with TD exhibited an increase in \( J_{SC} \) (16.2 to 17.7 mA/cm²) as well as \( V_{OC} \) (0.735 to 0.783 V). We also confirmed the tendency in a thinner TiO2 active layer (Fig. S11). Highly ionic coadsorbents

**Fig. 4** (a) Representative photocurrent–voltage curves and (b) incident photon-to-current efficiency (IPCE) spectra for devices prepared with TA or TD (N719+TA or N719+TD), in comparison with a control device (N719 only). Insert in (a): comparison of amounts of N719 adsorbed on the TiO2 electrodes calculated using UV-Vis spectrophotometer. Insert in (b): comparison of \( J_{SC} \) values calculated from IPCE (%) spectra and \( J-V \) curves. \( J-V \) curves measured under AM 1.5 irradiation (DSCs: 12 μm thickness of TiO2 and 0.078 cm² active areas defined using a black metal mask).

**Fig. 5** The energy levels at the TiO2/film/BMIB interface in the electrodes prepared with TA or TD (N719+TA or N719+TD), or with a control electrode (N719 only), were estimated using cyclic voltammetry using a 0.05 V/s scan rate.
(e.g., 4-guanidinobutyric\textsuperscript{1b} or chenodeoxycholic acid\textsuperscript{18}) have been tested previously, but these coadsorbents only increased either the $V_{oc}$ or $J_{sc}$ value. The increase in $J_{sc}$ as well as $V_{oc}$, as observed in the device prepared with TD, could not be ascribed to the ionic character or the alcohol groups generated by scavenging water molecules. We verified the $J_{sc}$ values of the devices by comparison with the calculated $J_{sc}$ values obtained from the incident photon-to-current efficiency (IPCE) spectra (Fig. 4(b)).\textsuperscript{19} Therefore, we concluded that the dye regeneration reaction ($\sim \eta_{sq}$) occurred efficiently through the reaction between the $I^-$ species generated on TD and $D^+$, thereby facilitating the light harvesting process ($\sim \eta_{ph}$), even at a low dye loading level.

Conclusions

we demonstrated that TD, which includes three terminal double bonds, reacted with $I_2$ and generated ionic complexes on the surfaces of a TiO$_2$ electrode. The in situ-generated ionic layer accelerated the neutralization (or regeneration) rate ($k_1$) of $D^+$ and decreased the recombination reactions with $D^-$ ($k_2$) and $I^-$ ($k_3$) due to coadsorbent effects. The device cosensitized with TD provided 10.2 $\%$ of power conversion efficiency, 22$\%$ higher due to the simultaneous improvements in $J_{sc}$ and $V_{oc}$, even at 15$\%$ low dye loading levels, compared to the values obtained from a conventional device under identical experimental conditions. This work demonstrated the importance of understanding and engineering the interfaces between nanoscale TiO$_2$ crystals, dyes, and electrolytes at the molecular level and will provide insights into various optoelectronic fields.

Acknowledgements

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Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental details, Extra 1H NMR spectra, EIS spectra, cyclic voltammograms and $J-V$ characteristics for 7.0 $\mu$m TiO$_2$ thicknesses]. See DOI: 10.1039/b000000x/


14. Notice that the control value ($\eta = 8.3\%$) is still greater than those ($\eta = 6 \sim 8\%$) reported in literatures in the identical condition employing 12 $\sim$ 15 $\mu$m thickness of TiO$_2$ and N719 sensitizer. a) M. Kimura, H. Nomoto, N. Masaki and S. Mori, Angew. Chem. Int. Ed., 2012, 51,


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A novel coadsorbent which includes three terminal double bonds, reacted with I$_2$ and generated ionic complexes on the surfaces of a TiO$_2$ electrode. The in situ-generated ionic layer accelerated the neutralization rate of dye$^+$ and decreased the recombination reactions with dye$^+$ and I$^-$ due to coadsorbent effects, resulting in the 22% higher power conversion efficiency ($\eta$), even at 15% low dye loading levels, compared to the values obtained from a conventional device.

Keyword

Dye-sensitized solar cells • Iodization on olefin • Rate-determining step • Neutralization • Transient absorption spectroscopy

Jongchul Lim, Taewan Kim, and Taiho Park *

Fast cascade neutralization of an oxidized sensitizer by an in situ-generated ionic layer of I$^-$ species on a nanocrystalline TiO$_2$ electrode

TOC figure