

Controlling Interfacial Recombination in Aqueous Dye-Sensitized Solar Cells by Octadecyltrichlorosilane Surface Treatment**

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Abstract: A general and convenient strategy is proposed for enhancing photovoltaic performance of aqueous dye-sensitized solar cells (DSCs) through the surface modification of titania using an organic alkyl silane. Introduction of octadecyltrichlorosilane on the surface of dyed titania photoanode as an organic barrier layer leads to the efficient suppression of electron recombination with oxidized cobalt species by restricting access of the cobalt redox couple to the titania surface. The champion ODTs-treated aqueous DSCs (0.25 mM ODTs in hexane for 5 min) exhibit a V_{oc} of 821 ± 4 mV and J_{sc} of 10.17 ± 0.21 mA cm⁻², yielding a record PCE of 5.64 ± 0.10 %. This surface treatment thus serves as a promising post-dye strategy for improving the photovoltaic performance of other aqueous DSCs.

In recent years, aqueous electrolytes have come under investigation as promising alternatives for dye-sensitized solar cells (DSCs) to traditional organic electrolytes owing to the non-toxicity, non-flammability, and safety of water. Efforts have been made to bridge the gap in the power conversion efficiency (PCE) of aqueous based DSCs and the more than 12 % PCE achieved with an organic electrolyte.^[1]

Quite recently, there have been a number of reports of significant improvements in the performance of DSCs based on aqueous electrolytes.^[2] An iodide-based electrolyte reported by O'Regan et al. achieved a PCE of 2.4 %, ^[3] whereas Sun and co-workers reported a PCE of 3.5 % for a water-soluble organic redox couple (TT⁻/DTT) with organic dye (D51).^[4] For our own part, we reported that DSCs assembled with aqueous electrolytes based on [Fe(CN)₆]⁴⁻³⁻ and [Co(bpy)₃]^{2+/3+} achieved PCEs of 4.1 % and 5.0 %, respectively.^[5,6] The PCEs of aqueous electrolyte-based DSCs, however, are still lower than their organic counterpart owing to the low open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}),^[7] which can be partially attributed to electron recombination processes occurring at the dye/TiO₂ hetero-interface. Modification of the surface properties of TiO₂ nanoparticles is an attractive approach to suppress this unfavorable back-reaction. Selective encapsulation of the dye-free titania surface with an insulating layer, such as an inorganic barrier layer, the introduction of adsorbents or polymer passivation, has been investigated to minimize photogenerated electron loss in the organic electrolyte-based DSCs.^[8] However, there has been no report on the less extensively studied DSCs based on aqueous electrolytes.

Herein, we report a general and facile route for achieving significant improvements in aqueous DSC performance by utilizing octadecyltrichlorosilane (ODTS). Reaction of ODTs with exposed titania surface sites creates an insulating layer on the surface of the semiconductor nanoparticles, which reduces electron recombination by restricting access of cobalt redox couples to the titania surface. A simultaneous increase in V_{oc} and J_{sc} is observed, which has resulted in a record aqueous DSCs PCE of 5.74 %. Furthermore, the V_{oc} of the devices could be controlled or modulated by varying the ODTs treatment method, and values approach those achieved for organic cobalt electrolytes (V_{oc} = 861 mV at one sun). We believe that this approach provides a post-dye treatment strategy for enhancing the photovoltaic performance of other aqueous DSCs.

To treat the dyed photoanodes with alkyl trichlorosilane, they were immersed in an ODTs hexane solution for different time intervals at room temperature (a plausible mechanism by which an alkyl siloxane is attached to the titania surface is described below). FTIR spectroscopy was employed to confirm the presence of the alkyl siloxane on the ODTs-treated electrodes (Supporting Information, Figure S1). Vibrations arising from the CH₂ (ν_a (CH₂)) were observed at about 2922 cm⁻¹, and Si-O stretching vibrations (ν (Si-O)) at circa 1050 and 1091 cm⁻¹, consistent with the previous studies applying ODTs surface treatment.^[9] Based on these data,

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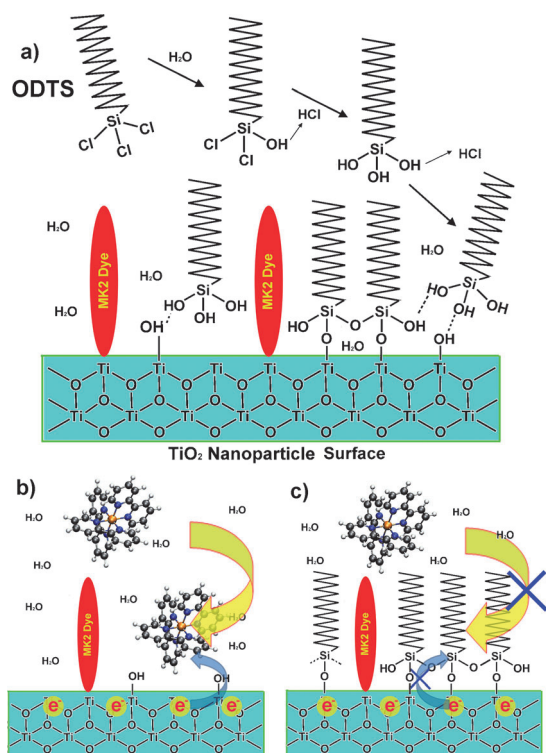
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ODTS treatment can be postulated to result in the attachment of an alkyl siloxane to exposed surface sites in the dyed TiO_2 photoanode.^[9,10] The successful coating of the dyed photoanode is also supported by energy-dispersive X-ray spectroscopic analysis (EDS; Supporting Information, Figure S2), which showed the introduction of Si and also indicated that some chloro groups are retained after treatment.

Scheme 1a shows a plausible reaction process for the surface modification of the dyed TiO_2 nanoparticles. The



Scheme 1. a) Plausible reaction process for alkyl siloxane attachment to dye-coated TiO_2 nanoparticles following treatment with an ODTS solution; b) electron recombination in non-ODTS treated aqueous DSCs; c) inhibition of electron recombination by aqueous DSCs made with ODTS treated photoanodes.

ODTS molecules are first partially hydrolyzed by traces of water present in the hexane solution, and they can then condense with OH groups on the TiO_2 surface.^[9,10] Alternatively, condensation can occur directly between surface Ti–OH groups and the octadecyltrichlorosilane. Either way the alkyl groups can intercalate or insert between the MK2 dye molecules, resulting in an insulating layer on the titania surface, which can be strengthened through the formation of Si–O–Si and Si–O–Ti cross-linkages induced by further hydrolysis and condensation processes occurring on introduction of the aqueous electrolyte during device assembly. This layer, in principle, prevents species present in the aqueous electrolyte, such as the cobalt complexes, from approaching the TiO_2 surface, as the octadecyl chains protrude out from the TiO_2 surface into the electrolyte solution. Thus, recombination between injected electrons in

the semiconductor and $[\text{Co}(\text{bpy})_3]^{3+}$ ions in the electrolyte can be suppressed.

The electrolyte used in this study contained 0.20 M $[\text{Co}(\text{bpy})_3]^{2+}$, 0.040 M $[\text{Co}(\text{bpy})_3]^{3+}$, 0.70 M N-methylimidazole (NMBI) and PEG 300 (1 wt %).^[5] The photoanodes consisted of a 1 μm transparent layer (30 nm TiO_2 nanoparticles) and a 3 μm scattering layer (400 nm TiO_2 nanoparticles). For 1 μm layer, screening experiments with a fixed treatment time (20 min) revealed best photovoltaic performances for dye-sensitized films post-treated with a 0.25 mM ODTS solution (Supporting Information, Table S2). When the 1 μm transparent layer was replaced with a thicker 2 μm layer, lower efficiencies (Supporting Information, Table S1) were produced. An examination of the effect of the ODTS treatment time on the aqueous DSCs photocurrent density–voltage (J – V) characteristics (Figure 1a) showed that devices made with

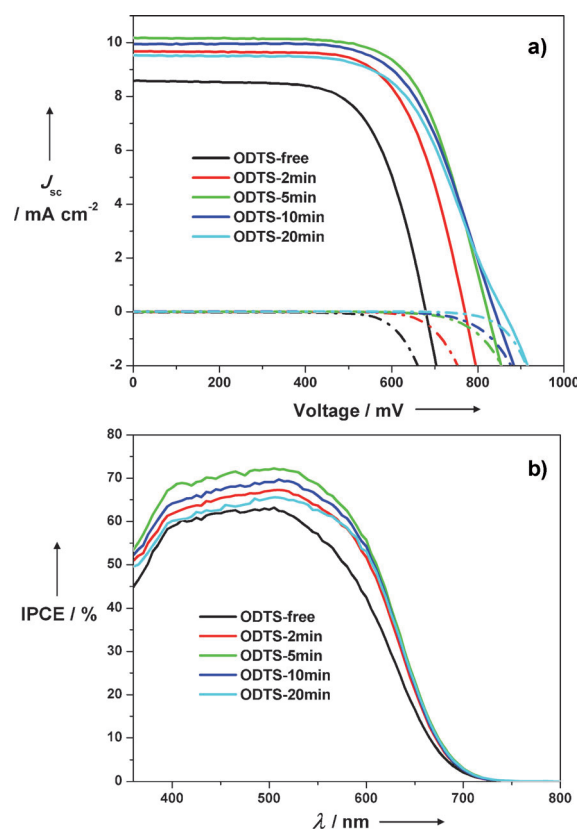


Figure 1. a) J – V curves and b) IPCE spectra of DSCs based on untreated and ODTS-treated dyed photoanodes with various soaking times in a 0.25 mM ODTS solution under AM 1.5 G simulated sunlight irradiation (100 mW cm^{-2}). The dark-current onset of ODTS-treated dyed TiO_2 nanoparticles is significantly shifted to a higher potential, suggesting efficient suppression of electron recombination.^[11]

the 5 min ODTS-treated photoanodes exhibit a V_{oc} of $821 \pm 4 \text{ mV}$ and J_{sc} of $10.17 \pm 0.21 \text{ mA cm}^{-2}$, and yield a record PCE of $5.64 \pm 0.10 \%$. The best performing device had an efficiency of 5.74%. Thus, ODTS treatment resulted in increases of about 20% in V_{oc} and J_{sc} and 38% in PCE of at one sun, whereas little effect was observed for corresponding organic electrolyte based DSCs (Table 1).

Table 1: Photovoltaic performance of DSCs based on aqueous^[a] and organic^[b] DSCs assembled with ODTS-free and -treated dyed photoanodes in 0.25 mM ODTS in hexane under one sun irradiation.

Treatment time [min]	V_{oc} [mV]	J_{sc} [mA cm ⁻²]	FF	PCE [%]
0	687 ± 1	8.45 ± 0.13	0.70 ± 0.01	4.09 ± 0.01
2	773 ± 3	9.76 ± 0.10	0.68 ± 0.01	5.04 ± 0.04
5	821 ± 4	10.17 ± 0.21	0.68 ± 0.01	5.64 ± 0.10
10	844 ± 4	9.84 ± 0.11	0.66 ± 0.01	5.31 ± 0.07
20	861 ± 2	9.52 ± 0.10	0.63 ± 0.01	5.16 ± 0.08
organic	912 ± 4	10.88 ± 0.12	0.71 ± 0.01	7.06 ± 0.20
5 min treatment				
organic	913 ± 5	10.88 ± 0.17	0.72 ± 0.01	7.13 ± 0.10
no treatment				

[a] Aqueous electrolyte contained 0.20 M [Co(bpy)₃](NO₃)₂, 0.040 M [Co(bpy)₃](NO₃)₃, 0.70 M NMBI, and 1 wt% PEG 300. [b] Organic electrolyte contained 0.20 M [Co(bpy)₃](TFSI)₂ (bpy = 2,2'-bipyridine, TFSI = bis(trifluoromethane)sulfonimide), 0.040 M [Co(bpy)₃](TFSI)₃, 0.70 M NMBI in CH₃CN. Two devices were tested for the organic electrolyte based DSCs and ODTS treatment was for 5 min. Photoanodes consisted of a 1 μm transparent TiO₂ layer and a 3 μm scattering layer.

Interestingly, the V_{oc} of DSCs based on ODTS-treated photoanodes increases with soaking time (Table 1). A 20 min ODTS treatment results in a V_{oc} 861 mV for the aqueous DSCs, which is only 60 mV lower than that observed for DSCs based on an organic cobalt electrolyte (Table 1). Thus, ODTS concentration and soaking time can be used to modulate the V_{oc} of the devices (Table 1; Supporting Information, Tables S1, S2). Notably, the fill factor (FF) decreases with increasing ODTS soaking time. Transient photocurrent spectroscopy, using on/off modulation of the incident light (Supporting Information, Figure S3), indicated that this detrimental effect may be reflecting mass transport limitations in the titania mesopores.^[12] In the untreated DSCs, the photocurrent rapidly reaches a maximum upon light switch-on, and remains constant thereafter. In contrast, as the ODTS soaking time increases, constant photocurrent is reached more slowly indicating that diffusion of the redox couple into the titania mesopores is affected.

Figure 1b shows the incident photon to electron conversion efficiencies (IPCE) of DSCs employing the untreated and ODTS-treated photoanodes. The ODTS-treated DSCs display a broader plateau over the visible spectral region (350–700 nm). Furthermore, the IPCE maxima of DSCs with ODTS-treated photoanodes are higher than those made with the untreated films. In particular, the IPCE of DSCs made from films treated for 5 min shows a plateau of about 70% from 420 to 550 nm, leading to the highest J_{sc} , compared with about 60% for the untreated DSCs. Thus, we conclude that ODTS treatment results in a higher charge collection efficiency.

The improved performance of ODTS-treated DSCs, and in particular the V_{oc} , could arise from: 1) a negative shift in the conduction band edge of the TiO₂ photoanode; or 2) a suppression of interfacial electron recombination of injected electron with oxidized cobalt species.^[13] Electrochemical impedance spectroscopy (EIS) was used to explore these possibilities. A series of bias voltages ranging from –0.50 V to –0.75 V were applied to ODTS-free and ODTS-treated

DSCs under dark conditions. The slope of the plot chemical capacitance (C_{μ}) versus applied voltage is related to the trap distribution in TiO₂.^[14] Figure 2a shows that solar cells assembled using untreated and ODTS-treated photoanodes have similar slopes and capacitance at the same bias voltage, indicating that the titania conduction band edge is not changed by the ODTS treatment. Therefore, the enhanced photovoltaic properties may be attributed to efficient suppression of electron recombination, which were explored by EIS analysis and molecular dynamics simulations.

To confirm the effect of ODTS treatment on the performance of DSCs, the recombination resistance (R_{cr}) at one sun and in the dark was investigated, respectively, which is an indicator of electron recombination occurring at electrolyte/TiO₂ interface. The R_{cr} is extracted from EIS plot in Figure 2b by fitting Nyquist plot using the equivalent circuit model (Bisquert no. 2).^[15] Upon treatment with ODTS, the R_{cr} at one sun increases (from 11 Ω for 2 min to 21 Ω for 5 min to 48 Ω for 10 min), and is higher than for the untreated photoanode (5.4 Ω). This indicates that the resistance to electron recombination gradually increases with ODTS soaking time, in line with the trend of V_{oc} values (Table 1), owing to an increasing coverage of exposed (or undyed) titania surface sites by the alkyl siloxane. Figure 2c shows that at a fixed bias, ODTS-treatment results in two-orders of magnitude increase in R_{cr} . At the same time, the J_{sc} values for ODTS-treated DSCs are higher than that for ODTS-free DSCs (Table 1). Therefore, higher V_{oc} (up to 861 mV) and J_{sc} (up to 10.17 mA cm⁻²) were achieved for the aqueous DSCs when an ODTS treatment was applied. The improvement in V_{oc} and J_{sc} of ODTS-treated DSCs can be attributed to the formation of a barrier layer comprised of octadecyl groups on exposed regions of the titania nanoparticles, which hinders the ability of oxidized cobalt(III) species to approach the titania surface, where they can promote recombination with injected electron. EIS also suggests that the effective electron diffusion length (L_n) for the ODTS-treated devices is much greater than that for the untreated photoanodes (Figure 2d), thereby yielding higher IPCE and PCE. These results reveal that ODTS treatment can improve the performance of aqueous DSCs by modifying the nature of dyed titania surface. The stability of aqueous DSCs assembled with the ODTS-treated films matched that of corresponding devices constructed using an organic electrolyte over a period of more than 500 h of storage in the dark (Supporting Information, Figure S4). These results are in good agreement with our previous studies on DSCs based on [Co(bpy)₃]^{2+/3+} aqueous electrolytes but lacking ODTS treatment.^[6]

Intensity-modulated photovoltage spectroscopy (IMVS) was also used to examine the dynamics of electron recombination with oxidized cobalt(III) species for untreated and ODTS-treated DSCs (Supporting Information, Figure S5). The ODTS-treated DSCs clearly exhibit much longer electron lifetimes compared to untreated DSCs, indicating that electron recombination is significantly suppressed. This is in agreement with the above EIS analysis and again supports the conclusion that electron recombination is suppressed in the ODTS-treated DSC, and leads to the improved V_{oc} , J_{sc} , and PCE.

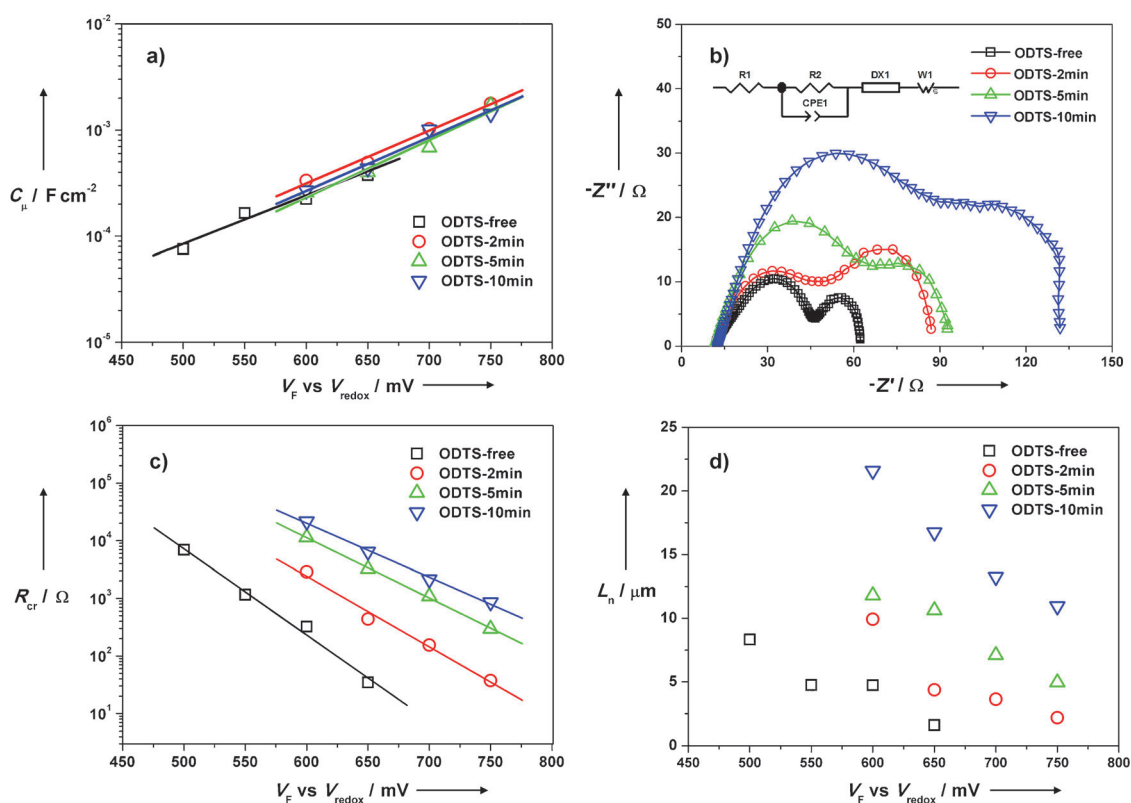


Figure 2. a) Chemical capacitance (C_μ), b) recombination resistance (R_{cr}), and c) electrochemical impedance spectroscopy under AM1.5 G simulated sunlight irradiation, and d) effective electron diffusion length (L_n) for DSCs employing ODTS-free and -treated photoanodes.

Molecular dynamics (MD) simulations were performed to explore how the ODTS treatment inhibits electron recombination in aqueous DSCs at the atomic level. The dyed TiO_2 photoanode for MD simulations was constructed by attaching MK2 molecules onto a TiO_2 cluster ($30.6 \text{ \AA} \times 30.2 \text{ \AA}$). Cross-linked hydrolyzed ODTS molecules were introduced on undyed regions on the TiO_2 surface to model the ODTS-treated system (MK2-hydrolyzed ODTS molecules; Supporting Information, Figure S6). For recombination to occur with the electrolyte, the oxidized cobalt(III) species have to approach the TiO_2 surface to capture the injected electrons. The ODTS coating introduces a physical barrier, as well as an energy barrier, between the TiO_2 and the electrolyte, both of which make it more difficult for the electrons in the TiO_2 to recombine with the $[\text{Co}(\text{bpy})_3]^{3+}$ ion. To evaluate the possibility of electron recombination in the aqueous electrolyte, the distance of the cobalt atom normal to the TiO_2 surface ($d_{\text{Co-TiO}_2}$) can be considered an important parameter. For the untreated system, $d_{\text{Co-TiO}_2}$ decreases significantly with the dynamic simulation time from about $25 \text{ \AA}$ in the initial state to about $8 \text{ \AA}$ in the final state (Supporting Information, Figure S7). In contrast, after 40 ps of simulation $d_{\text{Co-TiO}_2}$ remains almost constant at about $20 \text{ \AA}$ normal to TiO_2 surface for the ODTS-treated system. To highlight these differences, snapshots of the simulated system were taken during the dynamic process (Figure 3). As the simulation time increases, the $[\text{Co}(\text{bpy})_3]^{3+}$ ion moves towards the bare surface of the TiO_2 cluster in the untreated system and finally

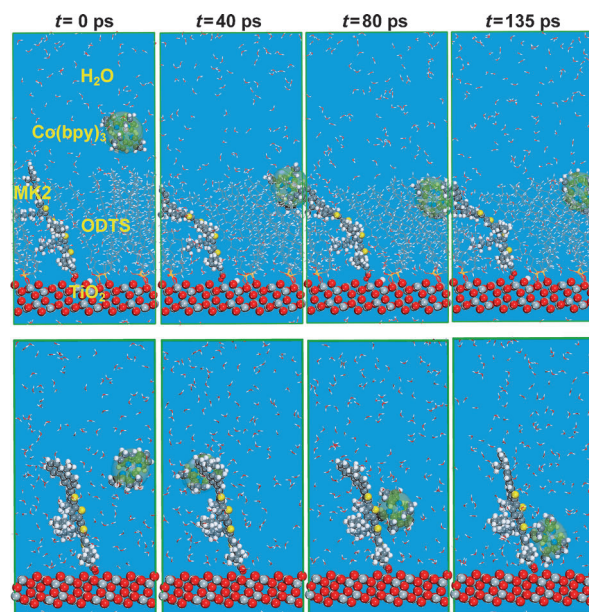


Figure 3. Snapshot of the simulated systems of the ODTS-untreated and treated dyed TiO_2 cluster as a function of simulation time. In the ODTS-untreated system (bottom), the MK2 molecule was attached on TiO_2 cluster, whereas the ODTS-treated dyed TiO_2 photoanode (top) was obtained by attaching the cross-linked hydrolyzed ODTS molecules in the vacant sites. Both systems were immersed in an explicit water environment.

reaches exposed regions on the surface of the dyed TiO_2 cluster ($d_{\text{Co-TiO}_2} \approx 7.5 \text{ \AA}$ at $t = 135 \text{ ps}$). As the $[\text{Co}(\text{bpy})_3]^{3+}$ ion approaches the titania surface an increase in recombination probability would be expected. For the ODTS-treated system, on the other hand, the $[\text{Co}(\text{bpy})_3]^{3+}$ ion is prevented from getting close to the TiO_2 cluster surface, owing to the assembly of octadecyl on exposed TiO_2 regions. Therefore, the MD simulation results suggest that ODTS treatment forms an insulating layer that can reduce electron recombination in aqueous DSCs, in line with above EIS and IMVS analysis.

In summary, a general route for improving the performance of aqueous DSCs is proposed which involves the modification of the surface of the TiO_2 photoanodes by treatment with an organic silane after the films had been dyed with the organic sensitizer. We postulate that the silane can react with exposed regions on the titania surface, contributing to the formation of an organic barrier layer, which prevents redox-active species present in the electrolyte from approaching the surface. As a result, electron recombination is significantly suppressed resulting in an aqueous DSCs record energy conversion efficiency of $5.64 \pm 0.10\%$. Use of EIS and theoretical simulations to probe the effect of ODTS treatment on DSC performance indicated that this treatment reduces recombination by preventing oxidized cobalt(III) redox species from reaching the titania surface. Such a surface modification is a very promising approach for improving the photovoltaic performance of aqueous DSCs, and a useful alternative to commonly applied strategies,^[8] such as core-shell photoanodes. Moreover, such a strategy could be readily applied in photoelectrochemical water splitting devices where the use of aqueous electrolytes is mandatory.^[16]

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