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Dye-Sensitized Solar Cells

Stepwise Cosensitization of Nanocrystalline TiO_2 Films Utilizing Al_2O_3 Layers in Dye-Sensitized Solar Cells**

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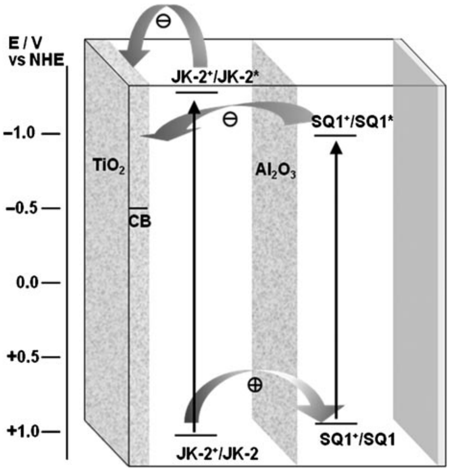
Increasing energy demand and depletion of fossil fuels dictate the development of green, efficient solar energy conversion technology. Dye-sensitized solar cells (DSSCs) have a significant potential as low-cost solar cells[1] and are able to reach sunlight-to-electric power conversion efficiencies of 8–11 %.[2] In these cells, the sensitizer is one of the key elements in achieving a high power conversion efficiency. The design of optimal sensitizers, which combine broad visible light absorption with an excited-state directionality for favorable electron-transfer dynamics, is a key issue in the development of dye-sensitized solar cells. In the first approach, the simultaneous adsorption of the multiple dyes, which have complimentary absorption in the visible region, on TiO_2 electrodes was utilized to broaden the absorption spectrum. This strategy employing blue and red absorbing sensitizers is an attractive route to the panchromatic sensitization of DSSCs.[3] Furthermore, efficient operation of the DSSC device relies upon the minimization of the interfacial charge recombination losses. The general strategy to reduce such losses involves the coating of inorganic barrier layers,[4] saccharides,[5] and metal-assembling dendrimers[6] between the sensitizer and electrolyte. Durrant et al.[7] reported the novel cosensitization based on the controlled construction of the film architecture in which a primary monolayer of dye is spatially separated from a secondary monolayer of another dye using a layer of Al_2O_3, resulting in the configuration TiO_2/Dye1/Al_2O_3/Dye2 (Scheme 1). However, the attempts resulted in unimpressive power-conversion efficiency compared to the single-dye device.



Scheme 1. Charge-transfer processes in multilayer cosensitized nanocrystalline TiO_2 films. CB = Conduction band, NHE = normal hydrogen electrode.

Herein, we revisit the stepwise cosensitization based on organic dyes having complementary spectral absorption in the visible region. Two organic dye sensitizers, were employed: 3-[5′-{*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl}-2,2′-bisthiophene-5-yl]-2-cyanoacrylic acid (**JK-2**)[8] having the blue part of the visible spectrum, and 5-carboxy-2-[{3-[(1,3-dihydro-3,3-dimethyl-1-ethyl-2*H*-indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene}methyl]-3,3-trimethyl-1-octyl-3*H*-indolium (**SQ1**),[9] with intense absorption in the red region. By cosensitizing the multilayer nanocrystalline TiO_2/Al_2O_3 films using **JK-2** and **SQ1** as the sensitizers, we obtained higher efficiency compared to the single-dye

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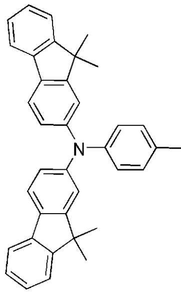
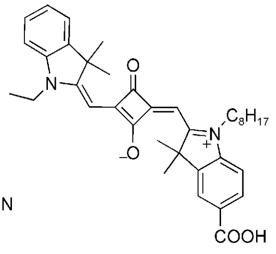


JK-2



SQ1

device and devices in which cosensitization have been employed using a dye cocktail.[11b]

A double-layer TiO_2 film composed of a transparent 10 µm thick layer and a 4 µm thick scattering layer was prepared using the doctor-blade technique and treated with $TiCl_4$.[10] The TiO_2 films were immersed in the dye solution containing **JK-2** in ethanol (0.3 mM) and 3a,7a-dihydroxy-5b-cholic acid in ethanol (10 mM). The secondary Al_2O_3 layer was coated by the hydrolysis of an aluminum isopropoxide on a **JK-2** sensitized TiO_2. The Al_2O_3 coated **JK-2**-sensitized-TiO_2 film was then dipped in the **SQ1** solution in ethanol for the second sensitization step. (Full experimental details are given in the Supporting Information.)

Figure 1 shows absorption spectra of **JK-2**, **SQ1**, **JK-2/SQ1**, and **JK-2**/Al_2O_3/**SQ1** absorbed onto 4 µm TiO_2 film. The absorption spectra of **JK-2** and **SQ1** have a visible band at 492 and 652 nm, respectively, arising from π–π* transitions of the conjugated molecule. The high optical density of the **JK-2**/Al_2O_3/**SQ1** film is attributed to an increased dye adsorption caused by the presence of Al_2O_3 layer compared to that obtained by cosensitization.[11] The absorbance of **JK-2**/Al_2O_3/**SQ1** is the exact sum of the constituent chromophores.

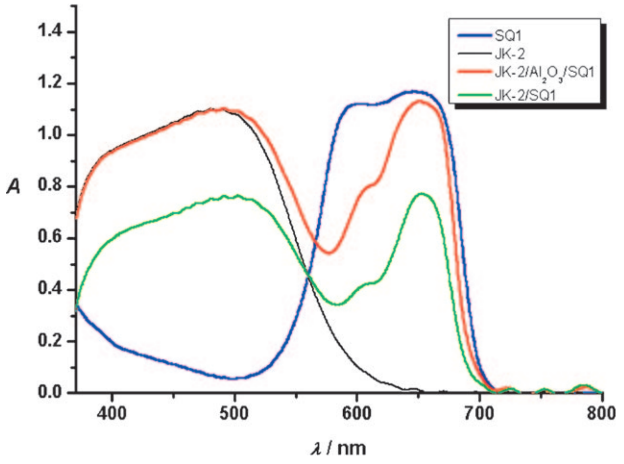


Figure 1. Absorption spectra of **SQ1** (blue line), **JK-2** (black line), **JK-2/SQ** (green line) and **JK-2**/Al_2O_3/**SQ1** (red line) absorbed onto 4 µm TiO_2 films.

Figure 2a shows action spectra of monochromatic incident-to-current conversion efficiencies (IPCEs) for DSSCs based on **JK-2**, **SQ1**, **JK-2/SQ1**, and **JK-2**/Al_2O_3/**SQ1** (electrolyte: 0.6 M DMPImI, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile). The IPCE for the **JK-2**/Al_2O_3/**SQ1** cell reached about 85 % at 453 nm. Furthermore, the photoresponse of the cell extends to 700 nm with photon-to-electron conversion efficiencies of 79 % at 660 nm, which corresponds to the absorption band of **SQ1**. The cell has an enhanced photocurrent compared to the **JK-2**- and the **JK-2/SQ1**-sensitized solar cells. The *J–V* curves for the cells based on **JK-2**, **SQ1**, **JK-2/SQ1**, and **JK-2**/Al_2O_3/**SQ1** are presented in Figure 2b. Under standard global air mass 1.5 solar conditions, the **JK-2**/Al_2O_3/**SQ1** cell resulted in the short-circuit current density (J_{sc}) of $(17.6 \pm 0.20)\,mA\,cm^{-2}$, the open-circuit voltage (V_{oc}) of (0.696 ± 0.01) V, and a fill factor (FF) of 0.70 ± 0.01, corresponding to an overall conversion efficiency (η) of $(8.65 \pm 0.15)\,\%$. Under the same conditions, the **JK-2/SQ1**-sensitized cell gave $J_{sc} = (16.9 \pm 0.15)\,mA\,cm^{-2}$, $V_{oc} = (0.662 \pm 0.01)$ V, and FF $= 0.71 \pm 0.01$, corresponding to $\eta = (8.01 \pm 0.15)\,\%$.

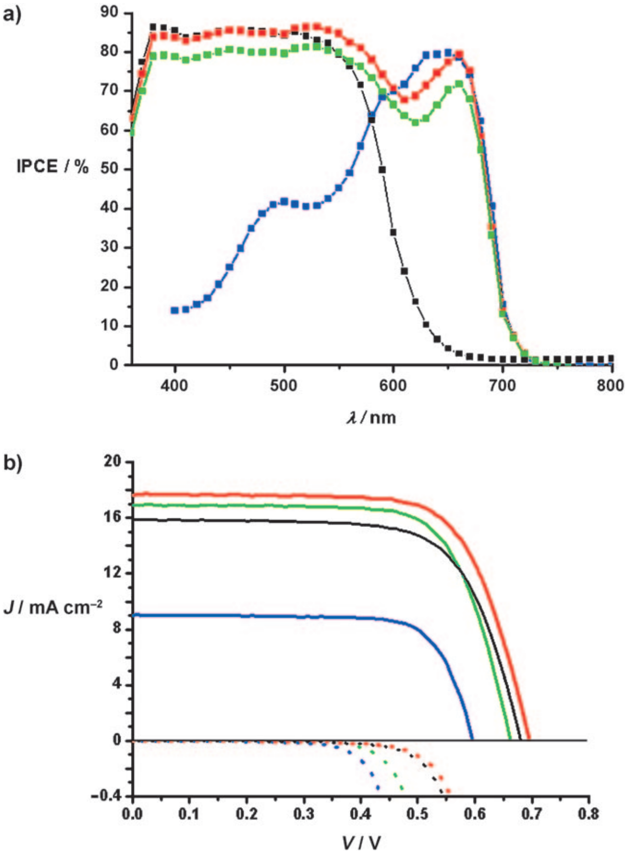


Figure 2. a) IPCE spectra and b) *J–V* curve of **SQ** (blue line), **JK-2** (black line), **JK-2/SQ** (green line) and **JK-2**/Al_2O_3/**SQ** (red line). The dark-current–bias-potential relationship is shown as dotted curves.

From these results (Table 1), we note that the η of **JK-2**/Al_2O_3/**SQ1** cell was higher than those of other cells. Neither **JK-2** nor **SQ1** devices could reach this high value of device efficiency as a single dye solar cell or as a dye solar cocktail cell **JK-2/SQ1**. Of particular importance is the 30 mV increase in V_{oc} of the **JK-2**/Al_2O_3/**SQ1** cell under illumination. This result can be interpreted as the suppression of the charge-

Table 1: Photovoltaic performance of the DSSCs.

Dye	J_{sc} [mAcm^{-2}]	V_{oc} [V]	FF	η [%]
JK-2	15.8	0.680	0.69	7.48
Al_2O_3/**JK-2**	13.7	0.740	0.76	7.80
SQ1	9.0	0.596	0.74	4.02
JK-2/SQ1	16.9	0.662	0.71	8.01
JK-2/Al_2O_3/**SQ1**	17.6	0.696	0.70	8.65

recombination reaction, as the physical separation of injected electrons and oxidized dye increases. In the present cell, the energetics of two dyes were such that a charge-transfer cascade was formed, whereby subsequent electron transfer from **JK-2** to the TiO_2 conduction band, the resultant hole is channeled from **JK-2** to **SQ1,** which resides further away from the TiO_2 surface, thus increasing the distance between injected electron in the TiO_2 film and the oxidized dye. Minimization of interfacial charge recombination losses in the device is also evident from the dark-current data for the cell.

Transient absorption spectroscopy was used to investigate the electron-transfer dynamics in the cosensitized films (TiO_2/**JK-2**/Al_2O_3/**SQ1**). The excitation of **SQ1** in the cosensitized film TiO_2/**JK-2**/Al_2O_3/**SQ1** yields recombination kinetics that are slower than those of **SQ1** on bare TiO_2 (see Supporting Information, Figure S1) indicating that the **SQ1** dye is anchored further away from the TiO_2 surface in the former (TiO_2/**JK-2**/Al_2O_3/**SQ1**) relative to the latter (TiO_2/**SQ1**). These results indicate that the cosensitized TiO_2 film does indeed possess a configuration (TiO_2/**JK-2**/Al_2O_3/**SQ1**), in which the two dye layers are spatially separated from one another, with **JK-2** significantly closer to the TiO_2 surface than **SQ1**.

Transient absorption spectroscopy was also used to investigate the desired electron-transfer cascade capable of laterally translating holes between the different dyes away from the TiO_2 surface. Figure 3 shows the transient absorption data of TiO_2/**JK-2**/Al_2O_3/**SQ1** following excitation at 470 nm (the absorbance maximum of the **JK-2** band), in which the transient kinetics is monitored using a probe beam of 660 nm wavelength (the maximum of the ground-state absorption bleach of **SQ1**). Despite having excited the **JK-2** band at 470 nm (where **SQ1** does not absorb at all), the resulting difference absorbance spectrum obtained is in fact that of **SQ1**, indicating efficient hole-transfer from **JK-2** to **SQ1**. From the size of the signal we estimate a hole-transfer yield from **JK-2** to **SQ1** of almost unity. The transient in Figure 3 also indicates that the hole-transfer is rapid, and is more than 50% complete before the fastest time resolution of our measurement apparatus (1 μs).

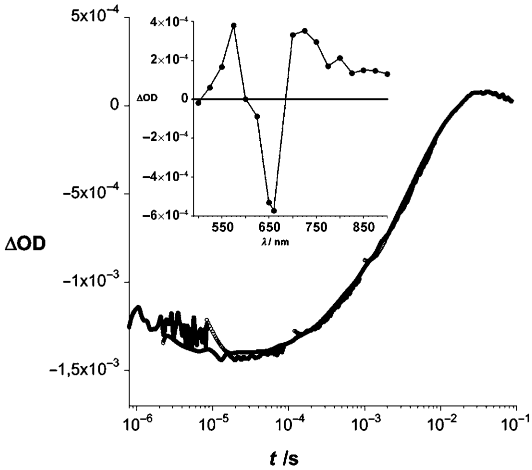


Figure 3. Transient absorption kinetics for a cosensitized film TiO_2/**JK-2**/Al_2O_3/**SQ1** (excitation beam: $\lambda_{ex} = 470$ nm, probe beam: $\lambda_{pr} = 660$ nm). The inset shows the difference absorption spectrum of TiO_2/**JK-2**/Al_2O_3/**SQ1** recorded at 100 μs.

The existence of such a hole-transfer process in cosensitized films without the Al_2O_3 interlayer was also investigated. However, following excitation of **JK-2,** no hole-transfer kinetics to **SQ1** was evident, which may be due to the time-resolution of our measuring system. Furthermore, we observed that in 1:1 mixed solutions of **JK-2** and **SQ1**, the excitation of **JK-2** results in energy transfer to **SQ1** (see Supporting Information, Figure S2). This energy transfer can also be expected to occur on the surface of TiO_2 films cosensitized with both dyes in the normal manner, clearly demonstrating the importance of the Al_2O_3 layer to the functionality of the hole-transfer cascade in our cosensitized model.

To understand the electron-injection properties and the change in V_{oc} of **JK-2**, **SQ1**, **JK-2/SQ1**, and **JK-2**/Al_2O_3/**SQ1**, we measured the electron diffusion coefficients and lifetimes of the electrode. Figure 4 shows the electron diffusion coefficient (D_e) and lifetime (τ_e) of the DSSCs employing different dyes (i.e. **JK-2**, **SQ1**, and **JK-2/SQ1**) as a function of J_{sc}. The D_e and τ_e values were determined by the photocurrent and photovoltage transients induced by a stepwise change in the laser light intensity controlled with a function generator.[12] The D_e value was obtained by a time constant (τ_c) determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_c)$, and the TiO_2 film thickness (ω) using $D_e = \omega^2/(2.77\tau_c)$.[12a] The τ value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau)$.[12a] The D_e values of the photoanodes adsorbing the organic dyes are very similar each other at the identical short-circuit current conditions. This result indicates that the D_e values are hardly affected by the nature of the dye molecules; the values are similar to those of the coumarin dyes.[13] However, the difference in the τ_e values was observed among the cells employing different dyes. The τ_e values of **SQ1** in particular were much smaller than those of **JK-2** owing to the relatively poor dye adsorption onto the TiO_2 surface. The electron recombination can be facilitated along with the insufficient coverage on the TiO_2 surface, resulting in the decrease in the τ_e values. However, the τ_e values were enhanced by the insertion of Al_2O_3 layer between the different dyes without loss of the photocurrent, demonstrating that the electron recombination processes were effectively retarded by the Al_2O_3 shell coupled with the successful multistep electron transfer. The results of the electron lifetime are also consistent with those of V_{oc} (Table 1). The D_e and τ_e values of **JK-2** were observed at relatively low current ranges compared with those of others, owing to its low molar extinction coefficient at 635 nm.

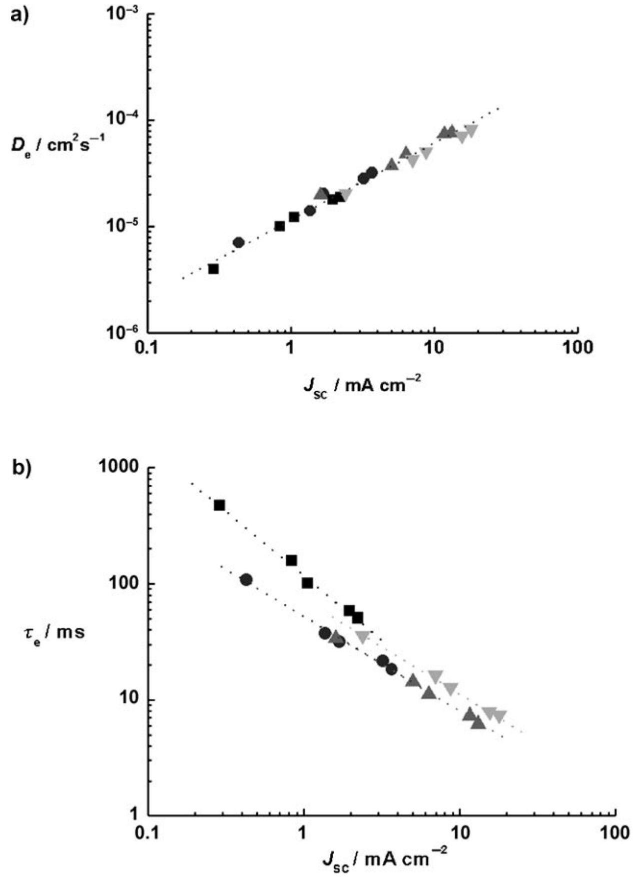


Figure 4. a) Diffusion coefficients and b) lifetimes of electrons in the photoelectrodes adsorbing different dyes. ■ **JK-2**, ● **SQ1**, ▲ **JK-2/SQ1**, and ▼ **JK-2**/Al_2O_3/**SQ1**.

The ac impedances of the cells were measured under the illumination conditions. Figure 5 shows the ac impedance spectra measured under open-circuit conditions and under illumination of 100 mW cm^{-2}, in which the radius of the intermediate-frequency semicircle in the Nyquist plot decreased in the order of **SQ1** (131.9 Ω) > **JK-2** (64.8 Ω) > **JK-2/SQ1** (52.6 Ω) > **JK-2**/Al_2O_3/**SQ1** (45.0 Ω), indicating the improved charge generation and transport, which corresponds to the overall device efficiency.

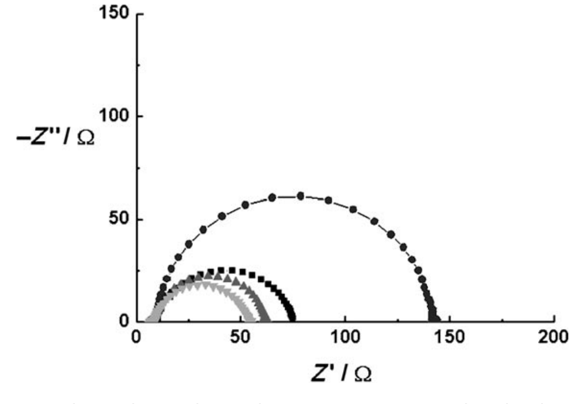


Figure 5. Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) and open-circuit conditions for the devices employing different dyes. ■ **JK-2**, ● **SQ1**, ▲ **JK-2/SQ1**, and ▼ **JK-2**/Al_2O_3/**SQ1**.

In conclusion, we have attempted the stepwise cosensitization of nanocrystalline TiO_2 films using Al_2O_3 layers based on two organic dyes having complementary spectral absorption in the visible region. This coating resulted in both impressive improvement in device performance and retardation of the interfacial recombination dynamics. The data unambiguously demonstrate that our approach results in a panchromatic response, yielding higher efficiency than the devices based on the individually sensitized oxide layers and a cosensitization using a cocktail of dyes. We believe that the results are an improvement towards efficient cosensitization of DSSCs based on a system of dyes with extended spectral response.

Experimental Section

Details regarding the synthesis of **JK-2** and **SQ1** are published elsewhere.[8,9] Nanocrystalline TiO_2 films (4 μm) for transient absorption measurements were sensitized in 0.3 mM solutions of **JK-2** and **SQ1** in tetrahydrofuran and ethanol, respectively. The Al_2O_3 layer was deposited by immersion of a **JK-2**-sensitized TiO_2 film in a 15 mM solution of aluminum 2-propoxide in 2-propanol at 25 °C.

The electron diffusion coefficients and lifetimes were measured by the stepped light-induced transient measurements of photocurrent and voltages (SLIM-PCV).[12] The transients were induced by a stepwise change in the laser intensity. A diode laser ($\lambda = 635$ nm) as a light source was modulated using a function generator. The initial laser intensity was a constant 90 mW cm^{-2} and was attenuated up to approximately 10 mW cm^{-2} using a neutral density filter which was positioned at the front side of the fabricated samples (0.04 cm^2). For the measurement of SLIM-PCV, the TiO_2 thickness of the photoelectrode was controlled as approximately 3.3 μm. The photocurrent and photovoltage transients were monitored using a digital oscilloscope through an amplifier. A total of 5 points were measured to determine the electron diffusion coefficients and lifetimes.

The ac impedance measurements were carried out under illumination (1 sun) using an impedance analyzer (1260 A, Solartron, UK).

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