Efficient co-sensitization of nanocrystalline TiO_2 films by organic sensitizers

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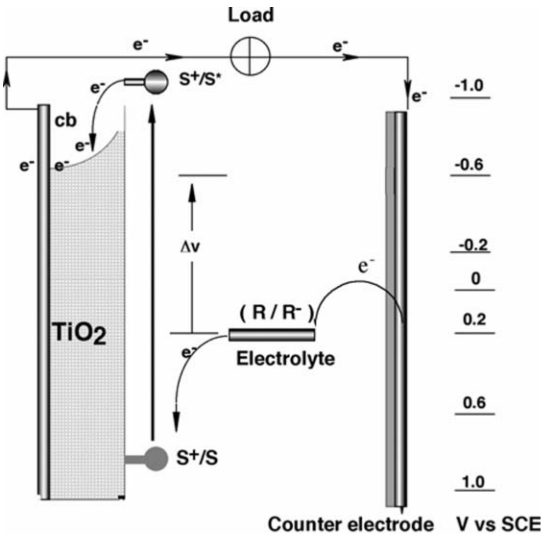
Dye-sensitized solar cells based on co-sensitization of organic dyes having complementary spectral absorption in the visible region resulted in a panchromatic response, which exhibited 86% incident monochromatic photon-to-current conversion efficiency in the visible region; the optimized cell gave a short circuit current density of 15.5 mA cm^{-2}, an open circuit voltage of 685 mV and a fill factor of 0.70 corresponding to an overall conversion efficiency of 7.43% under solar simulated light irradiation of 100 mW cm^{-2}.

The need to develop inexpensive renewable energy sources continues to stimulate new approaches for the production of efficient low-cost photovoltaic devices. In this respect, dye-sensitized mesoporous solar cells (DSSCs) based on nanocrystalline semiconductors and Ru(II) based sensitizers have been investigated extensively.[1] One of the main drawbacks of ruthenium sensitizers is the location of the absorption maximum around 535 nm. The optimal sensitizer for solar cell applications should be panchromatic and absorb all the light from the visible to the near infrared (NIR) domain. Development of such charge transfer sensitizers based on ruthenium presents a challenging task as several requirements have to be fulfilled by the sensitizer, which are very difficult to be met simultaneously. The lowest unoccupied molecular orbital (LUMO) S^+/S^*, and the highest occupied molecular orbital (HOMO) S/S^+, have to be maintained at levels where photo-induced electron transfer to the TiO_2 conduction band (cb), and regeneration of the dye by iodide (R/R^-) can take place at practically 100% yield (see Scheme 1), which restricts greatly the options available to accomplish the desired panchromatic response of the metal-to-ligand charge transfer (MLCT) transitions. This is also pertinent for any single organic sensitizer to be used as a charge transfer sensitizer for TiO_2-based solar cells, necessitating the use of mixed dyes having complementary spectral absorption in the visible region. Various groups have investigated co-sensitized solar cells that often resulted in unimpressive power conversion efficiency when compared to the "single dye" device.[2]

In this communication we report photovoltaic data based on organic dyes 3-{5′-[*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl]-2,2′-bisthiophene-5-yl}-2-cyanoacrylic acid (JK2),[3] which absorbs in 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)[4] that shows intense absorption in the red/near IR region. By combining the JK2 and the SQ1 sensitizers we have obtained higher efficiency than the individual dye cells.

The synthetic strategy used to obtain SQ1 and JK2 is described in our previous work.[3,4] The screen-printed double layer TiO_2 film consisting of a transparent 2.5 μm thick layer and a 4 μm thick scattering layer was prepared and treated with 0.05 M titanium tetrachloride solution using a previously reported procedure.[5] The dye solutions (JK2 in tetrahydrofuran 5×10^{-4} M, and the SQ1 in ethanol, 1×10^{-4} M) were prepared with 10 mM 3a,7a-dihydroxy-5b-cholic acid (cheno) as an additive. Cheno was used for diminishing the aggregation of the sensitizer, which leads to self-quenching and reduces injection into TiO_2. The TiO_2 films were derivatized with the pure dyes and with a mixture of dyes by 4 h of dipping in pure solutions and solution blends, respectively. Alternatively, sequential derivatization of the TiO_2 films was achieved by first dipping for 1 h in the first dye solution followed



Scheme 1 Operating principles and energy level diagram of dye-sensitized solar cell. $S/S^+/S^*$ = Sensitizer in the ground, oxidized and excited state, respectively. R/R^- = Redox mediator (I^-/I_3^-).

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by 3 h of dipping in the second dye solution. The dye loading was measured by desorbing the adsorbed sensitizers from the TiO_2 films using an alkaline solution. The fabrication procedure for solar cells, the testing conditions, and the equipment used were reported before.[5]

Fig. 1 shows the molecular structures of sensitizers JK2 and SQ1. The absorption spectrum of JK2 displays a lowest energy band at 452 nm (ε = 42 000 $dm^3 mol^{-1} cm^{-1}$), while the maximum absorption for SQ1 is at 636 nm and manifests a very high molar extinction coefficient (ε = 158 500 $dm^3 mol^{-1} cm^{-1}$) corresponding to the π–π transitions of the conjugated molecule.[3,4]

Fig. 2 shows absorption spectra of the solution after desorbing the sensitizers from a 2.5 μm thick TiO_2 film in 0.01 M tetrabutylammonium hydroxide in ethanol. The spectral absorption features are identical to the superposition of the solution spectra of the corresponding individual dyes. Knowing the concentrations of desorbed sensitizers, the dye loading onto the oxide film can be calculated using the Beer–Lambert law. For separate adsorption of JK2 and SQ1 on a 2.5 + 4 μm thick TiO_2 film we obtain surface concentrations of 3.7×10^{-8} and 8.5×10^{-9} mol cm^{-2}, respectively. The co-sensitized electrode showed lower dye uptake for JK2 (2.8×10^{-8} mol cm^{-2}) and SQ1 (3.7×10^{-9} mol cm^{-2}) compared to the electrode covered with the individual sensitizers. However, the total dye loading of the co-sensitized film was 3.2×10^{-8} mol cm^{-2} which is very close to the pure JK2 loading indicating that the TiO_2 surface coverage by the two sensitizers is almost complete. Based on the molar extinction coefficients of sensitizers SQ1 and JK2, adsorption for SQ1 is ≈7.5 times lower than for JK2. The reason for low SQ1 adsorption on TiO_2 is due to the reduced free surface area of TiO_2 available for SQ1 after JK2 adsorption and shows that JK2 is not significantly desorbed from the TiO_2 surface during adsorption of SQ1.

In Fig. 3 we present the IPCE spectra of solar cells using the individual dyes as well as the co-sensitizers JK2 and SQ1. In the latter case the dyes were sequentially adsorbed on the TiO_2 film consisting of a transparent 2.5 μm thick mesoporous layer and a 4 μm thick scattering layer. The data were obtained using an electrolyte consisting of 0.6 M *N*-methyl-*N*-butylimidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate and 0.28 M tertiary butylpyridine in a 15 : 85 (v/v) mixture of valeronitrile and acetonitrile solution. The incident monochromatic photon-to-current conversion efficiency plotted as a function of excitation wavelength shows impressive panchromatic response. Co-sensitization broadens the photocurrent action spectrum covering the entire visible domain with peak efficiencies of 86 and 76% at 530 and 660 nm, respectively, corresponding to the highest absorption of JK2 and SQ1.

The current–voltage characteristics of the cells using JK2, SQ1 or the mixed dyes demonstrate the advantage of co-sensitization. Table 1 displays the photovoltaic performance of the pure solar cells as well as co-sensitized cells for different TiO_2 film thicknesses. As can be inferred from Table 1, co-sensitized solar cells based on the 2.5 μm thin transparent layer yielded a remarkably high photocurrent density (J_{sc}) of 14.3 ± 0.2 mA cm^{-2} under standard global AM 1.5 solar irradiation conditions due to high molar extinction coefficients of the sensitizers. The cell showed an open circuit voltage (V_{oc}) of 680 ± 10 mV and a fill factor (*ff*) of 0.72 ± 0.02, corresponding to an overall power conversion efficiency (η) of 7.03 ± 0.02%.[6] When the thickness of the TiO_2 film was increased from 2.5 to 7 μm the dye loading was higher and correspondingly the photocurrent rose from 14 to 16 mA cm^{-2}. The open circuit voltage was 655 ± 10 mV and the fill factor attained 0.70 ± 0.02, corresponding to an overall conversion efficiency of 7.38%. Further increasing the TiO_2 film thickness to 10 + 4 μm left the power conversion efficiency at approximately the same value as for the 7 + 4 μm TiO_2 film. Under similar conditions, the individually sensitized cell efficiencies were 7.00 and 4.23%, using JK2 and SQ1, respectively, showing inferior performance as compared to the co-sensitized cell.

We have also investigated the photovoltaic performance of co-sensitization by reversing the sequence of dye adsorption. In this case SQ1 was first adsorbed by dipping the TiO_2 film in the dye solution for 1 h followed by 3 h of dipping in a JK2 dye solution. The co-sensitized solar cells under standard global AM 1.5 solar

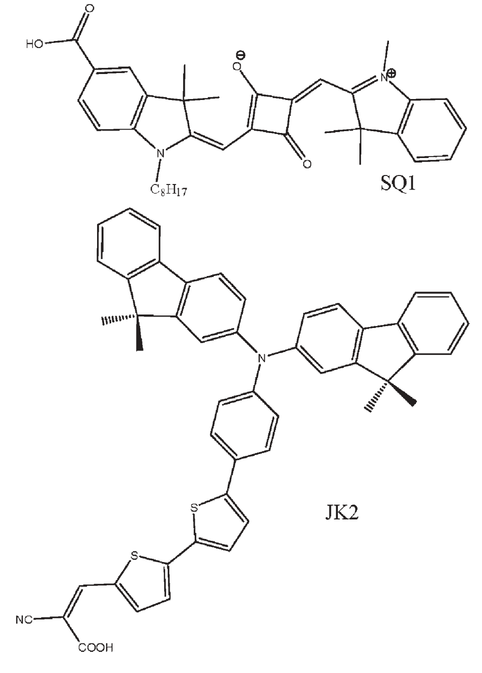

Fig. 1 Molecular structures of the JK2 and SQ1 sensitizers.

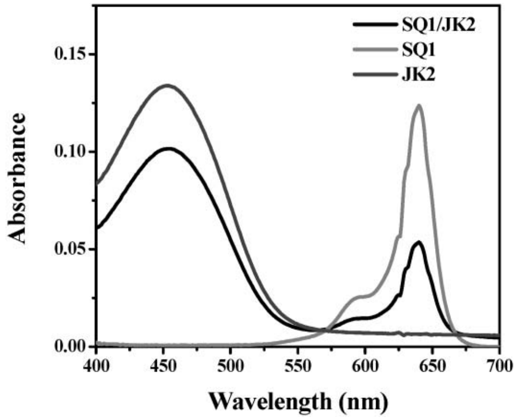

Fig. 2 Absorption spectra of SQ1 (light grey line), JK2 (dark grey line), and SQ1/JK2 (black line) in solution (0.01 M tetrabutylammonium hydroxide in ethanol) obtained by desorption from a TiO_2 film.

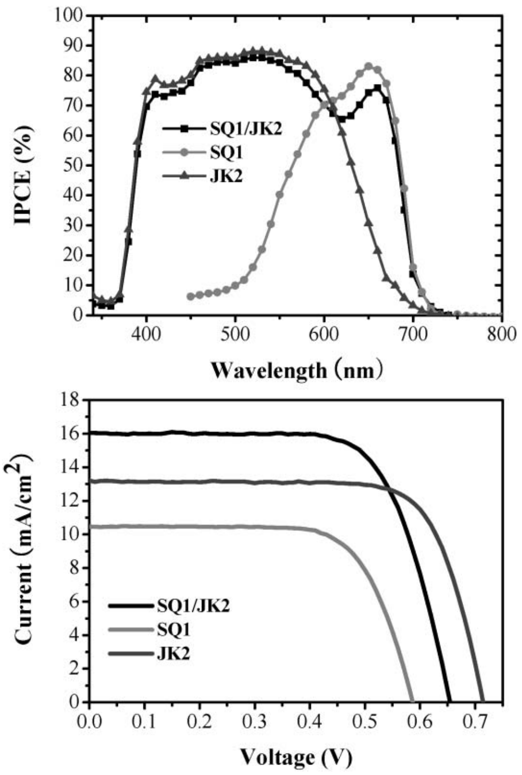

Fig. 3 Photocurrent action spectrum (top) and current–voltage characteristics (bottom) of solar cells sensitized with SQ1 (light grey line), JK2 (dark grey line), and SQ1/JK2 (black line) co-adsorbed by sequential solution dipping.

Table 1 Current–voltage characteristics obtained for various TiO_2 thicknesses (l) and using sequential adsorption of co-sensitizers, SQ1 and JK2

Dye	l/μm	J_{sc}/mA cm^{-2}	V_{oc}/mV	ff	η (%)
JK2 + SQ1	2.5 + 4	14.3	680	0.72	7.03
JK2 + SQ1	7 + 4	16.1	655	0.70	7.38
JK2 + SQ1	10 + 4	16.2	649	0.70	7.36
JK2	7 + 4	13.2	714	0.74	7.00
SQ1	7 + 4	10.2	590	0.70	4.23

conditions yielded lower efficiency 6.53% (photocurrent of 13.4 ± 0.2 mA cm^{-2}, open circuit voltage of 660 ± 10 mV and fill factor of 0.74 ± 0.01) as compared to the cells prepared by the initial dye adsorption sequence. The low efficiency obtained in co-sensitization using the reverse sequence is due to desorption of SQ1 while dipping the cell in the JK2 dye solution. The incident monochromatic photon-to-current conversion efficiency (the data are not shown) of SQ1 was only 50%, compared to 76% obtained in the previous case.

Table 2 Current–voltage characteristics obtained for 7 + 4 μm thick TiO_2 films using simultaneous adsorption of SQ1 and JK2 sensitizers from a mixed solution with various concentrations

JK2 conc./M	SQ1 conc./M	J_{sc}/mA cm^{-2}	V_{oc}/mV	ff	η (%)
3×10^{-4}	1×10^{-4}	15.5	685	0.70	7.43
2×10^{-4}	3×10^{-5}	13.0	649	0.71	6.00
1×10^{-4}	6×10^{-5}	12.2	646	0.72	5.66
6×10^{-5}	8×10^{-5}	11.4	644	0.71	5.27

Of substantial technological interest is co-adsorption of JK2 and SQ1 from a mixed solution. Using different dye concentrations (see Table 2), we found that the optimum molar ratio of JK2 and SQ1 for obtaining highest efficiency is 3 to 1, respectively. Measured under AM 1.5 solar conditions, the sensitized cells prepared from a cocktail dye solution (3×10^{-4} M of JK2 and 1×10^{-4} M of SQ1 in ethanol) showed a photocurrent of 15.5 ± 0.2 mA cm^{-2}, an open circuit voltage of 684 ± 10 mV and a fill factor of 0.70 ± 0.02, corresponding to an overall conversion efficiency of 7.43%. Further increasing the TiO_2 film thickness from 7 + 4 μm to 10 + 4 μm did not ameliorate the total efficiency since most of the incoming light is already absorbed in the thinner film due the high extinction coefficients of sensitizers SQ1 and JK2.

In conclusion, we have demonstrated co-sensitized solar cells yielding very high incident monochromatic photon-to-current, and power conversion efficiency under 1 sun. Our data unambiguously demonstrate that co-adsorbed dyes having complementary spectral absorption in the visible region result in a panchromatic response yielding higher efficiency than the cells based on the individual sensitizers. Advantageously the mixed dye layer can be adsorbed from a solution blend using a single dipping step.

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Notes and references

1 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382; G. Schlichthörl, N. G. Park and A. J. Frank, *J. Phys. Chem. B*, 1999, **103**, 782; M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, C. Le, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, 2001, **123**, 1613; Z.-S. Wang, T. Yamaguchi, H. Sugihara and H. Arakawa, *Langmuir*, 2004, **20**, 4246; M. K. Nazeeruddin, Q. Wang, L. Cevey, V. Aranyos, P. Liska, E. Figgemeier, C. Klein, N. Hirata, S. Koops, S. A. Haque, J. R. Durrant, A. Hagfeldt, A. B. P. Lever and M. Grätzel, *Inorg. Chem.*, 2006, **45**, 787; C. Klein, M. K. Nazeeruddin, D. D. Censo, P. Liska and M. Grätzel, *Inorg. Chem.*, 2004, **43**, 4216.

2 A. Ehret, L. Stuhl and M. T. Spitler, *J. Phys. Chem. B*, 2001, **105**, 9960; K. Sayama, S. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga and H. Arakawa, *Sol. Energy Mater. Sol. Cells*, 2003, **80**, 47; Y. Chen, Z. Zeng, C. Li, W. Wang, X. Wang and B. Zhang, *New J. Chem.*, 2005, **29**, 773; V. P. S. Perera, P. K. D. D. P. Pitigala, M. K. I. Senevirathne and K. Tennakone, *Sol. Energy Mater. Sol. Cells*, 2005, **85**, 91.

3 S. Kim, J. K. Lee, S. O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, Md. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2006, **128**, 16701.

4 J.-H. Yum, P. Walter, S. Huber, T. Geiger, F. Nüesch, F. De Angelis, M. Grätzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2007, **129**, 10320–10321.

5 M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, T. Bessho and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835.

6 The overall conversion efficiency is derived from the equation: $\eta = (100 \times J_{sc} \times V_{oc} \times ff)$/light intensity.