LETTER

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Highly efficient co-sensitization of nanocrystalline TiO_2 electrodes with plural organic dyes†

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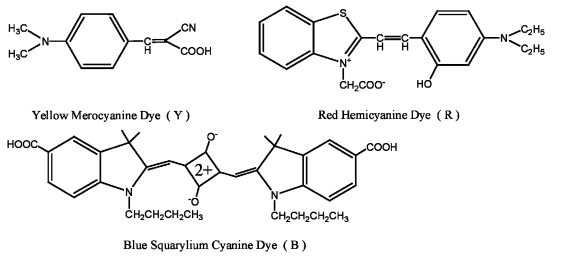
Through cooperative interactions, each of the three organic dyes utilized achieved improved sensitizing abilities on nanocrystalline TiO_2 electrodes in co-sensitization over single-dye-sensitization, which led to a wide (400–700 nm) and highly efficient (exceeding 70%) photocurrent action spectrum in triple-dye-sensitization and an overall power conversion efficiency (η) of 6.5% (AM1.5, 80 mW cm^{-2}), the highest η to date for dye-sensitized solar cells (DSSCs) based on the co-sensitization of plural organic dyes, fully demonstrating the potential of co-sensitization in DSSC applications.

Dye-sensitized nanocrystalline semiconductor solar cells (DSSCs) based on Ru(II) polypyridyl complexes have been actively investigated over the past 15 years since O'Regan and Grätzel's report in 1991.[1–4] Compared with Ru(II) polypyridyl complexes, organic sensitizer dyes generally possess larger molar extinction coefficients and can be prepared and purified more easily and economically, therefore, exhibit promising potential in DSSC applications.[5–8] However, the sharp and narrow absorption bands of organic dyes seriously impairs their light harvesting capabilities, and as a result, the simultaneous adsorption on TiO_2 electrodes of the plural dyes, which have different absorption wavelengths, the so called co-sensitization, was utilized to broaden the absorption spectrum.[9] Though many combinations of organic sensitizer dyes were studied in the context of co-sensitization, success is still very limited.[9–14] The overall photoelectric conversion efficiencies of the DSSCs based on plural organic dyes did not exceed 3.5% under one sun illumination (100 mW cm^{-2}), and in most cases the dye component having the most potent sensitization ability in the dye combination behaved less efficiently in co-sensitization than in single-dye sensitization, which partly accounted for the unsatisfactory photoelectric conversion efficiencies obtained in co-sensitization.[9–14] In this study, three organic dyes, a merocyanine dye (Y), a hemicyanine dye (R), and a squarylium cyanine dye (B) named after their colors respectively (Scheme 1), were combined to co-sensitize TiO_2 electrodes. It was found that all three dyes behaved better in triple-dye sensitization than in single-dye sensitization, consequently a high photoelectric conversion efficiency up to 6.5% was achieved, fully demonstrating the potential of co-sensitization in DSSC applications.

The three dyes absorb light of different wavelengths with absorption maxima at 380 nm for Y, 535 nm for R, and 642 nm for B, respectively, in methanol solutions (Fig. 1). Their molar extinction coefficients at absorption maxima are 3.0×10^4 (Y), 7.2×10^4 (R), and 23.0×10^4 M^{-1} cm^{-1} (B), much higher than those of Ru(II) polypyridyl complexes (*ca.* 1.0×10^4 M^{-1} cm^{-1}).[2] Upon adsorption on TiO_2 electrodes, all the absorption bands were broadened greatly, and a strong shoulder peak appeared at 600 nm for B, suggesting the formation of a dye aggregate, particularly for B, of which the H-type aggregate formed unambiguously.[9] (For clarity, arbitrary units for the absorbance are used in Fig. 1. The absorption spectra of dye-sensitized TiO_2 electrodes with true absorbance are shown in Figure A of the ESI.†) The co-adsorption of the three dyes on TiO_2 electrodes led to an efficient light harvesting over a wide spectrum region covering the whole visible and part of near-IR, a desirable feature for solar cells. It is noted that the shoulder peak intensity of B originating from the H-aggregate decreased significantly with respect to the main peak of B originating from the monomer, indicating that the presence of Y and R restrained the aggregation of B remarkably.

Based on the ground state oxidation potentials (0.84 V, 0.80 V, and 0.72 V *vs.* SCE for Y, R, and B, respectively) and 0–0 transition energies (2.94 eV, 2.20 eV, and 1.92 eV for Y, R, and B, respectively, calculated from the wavelength where the normalized absorption and fluorescence spectra intersect),[2] the oxidation potentials of Y, R, and B in their excited states are estimated to be −2.1 V, −1.4 V, and −1.2 V *vs.* SCE, respectively, far more negative than the conduction band edge potential of the nanocrystalline TiO_2 electrodes (*ca.* −0.8 V *vs.* SCE),[15] indicating that the electron injection processes from the excited dyes into the TiO_2 conduction band are energetically permitted. This is confirmed by the photocurrent efficiencies of the three dyes shown in Fig. 2 (A), where the monochromatic incident photon-to-current conversion efficiencies (IPCEs) are plotted as the function of wavelength.[2] The TiO_2 electrodes sensitized by Y, R, and B alone exhibited



Scheme 1 Molecular structures of the three dyes.

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† Electronic supplementary information (ESI) available: the absorption spectra of dye-sensitized TiO_2 films with true units of absorbance and the adsorption amount and ratio of the dyes on TiO_2 films. See http://www.rsc.org/suppdata/nj/b5/b502725j/

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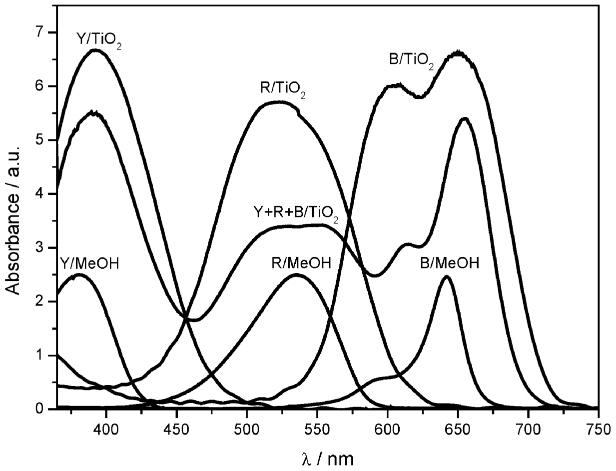

Fig. 1 Absorption spectra of TiO_2 electrodes sensitized by the individual dye alone (Y/TiO_2, R/TiO_2 and B/TiO_2) and by their combination ($Y+R+B/TiO_2$, the molar ratio of Y : R : B in the dye solutions was 10 : 20 : 1). The absorption spectra of the three dyes in methanol are also included.

effective photoelectric conversion abilities in the regions 400–500 nm, 500–600 nm, and 600–700 nm, respectively. As a result, their combination as sensitizers gave rise to a wide photoelectric response spectrum (Fig. 2 (A), $Y+R+B/TiO_2$). Though the molar ratio of the three dyes was 10 : 20 : 1 (Y : R : B) in the dye solution, the dye ratio of Y : R : B desorbed from the electrode was 4.1 : 1.0 : 1.3 (see Table 1 and Table A in the ESI†), indicating the stronger adsorbing abilities of Y and B than that of R, which probably results from the smaller size of Y (allowing its entrance to the small pores in the electrode) and the presence of two carboxyl anchoring groups in B.

It is worthy of note that the three dyes all exhibited higher IPCEs in their corresponding spectrum regions in co-sensitization than in single-dye sensitization, despite the fact that the adsorbed amount of each kind of dye decreased in the co-sensitization cases (see Table A in the ESI†). Such a cooperative effect may result from two possibilities. First, the co-adsorption of the three kinds of dyes may result in a more compact coverage of the TiO_2 surface, which blocks the approach of I_3^- in the electrolyte to the TiO_2 surface, and therefore decreases the dark current originating from the combination of injected electrons with I_3^- ions. Secondly, the aggregation behaviors of the individual dyes may be varied in co-adsorption conditions so that their injection efficiencies take positive changes. The sharpening and narrowing occurred for the photoelectric response band coming from the contribution of B (650–750 nm) may reflect the suppression of B aggregation, which is in line with the observation in Fig. 1, and supports the second explanation. The decrease in the adsorbed amount of B in the co-sensitization did not favor its aggregation either.

It is well known that the simultaneous adsorption of deoxycholic acid (DCA) onto a TiO_2 surface with organic sensitizer dyes can improve the photocurrent efficiencies (IPCEs) of the organic sensitizers due to a blocking effect which stops the dark current and/or the isolating effect which suppresses dye aggregation.[9,16] Fig. 2 (B) indicates that DCA can also improve the IPCEs of R and B remarkably, suggesting that in triple-dye-sensitization Y and B or Y and R may serve as DCA for R or B, respectively. The "DCA effect" was also observed in double-dye-sensitized solar cells (Fig. 2 (C)), where the IPCEs of each dye were improved over the single-dye sensitization cases.

Besides the "DCA effect", we cannot exclude energy and/or electron transfer among the three dyes when they closely contact each other on the TiO_2 surface. It has been recognized that the energy and/or electron transfer among different dyes will make all of them exhibit the electron injection efficiency of the dye having the smallest band-gap.[9] Owing to the highly efficient electron injection efficiency of B (approaching unity when one considers the loss of the incident light caused by the

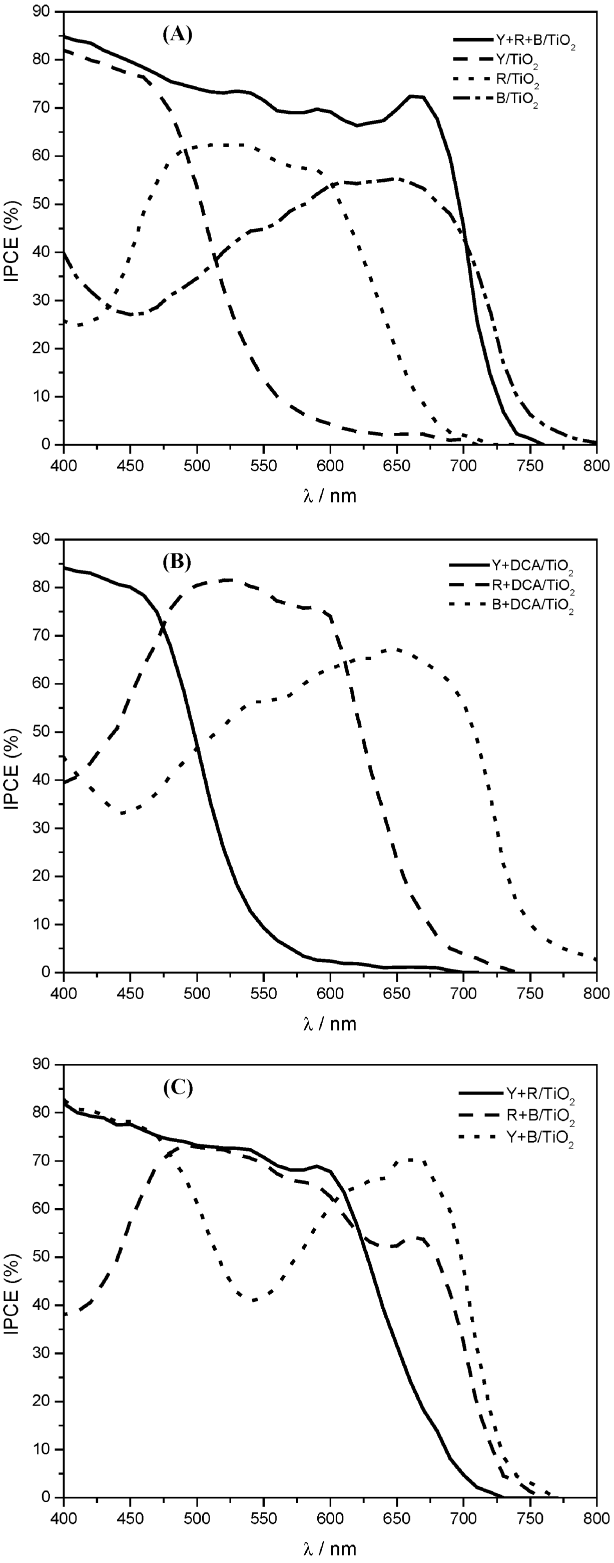

Fig. 2 Photocurrent action spectra of TiO_2 electrodes **(A)** sensitized by the individual dye alone (Y/TiO_2, R/TiO_2 and B/TiO_2) and by their combination ($Y+R+B/TiO_2$); **(B)** sensitized by the individual dye alone with deoxycholic acid (DCA) adsorbed simultaneously ($Y+DCA/TiO_2$, $R+DCA/TiO_2$ and $B+DCA/TiO_2$); and **(C)** sensitized by the double dyes ($Y+R/TiO_2$, $R+B/TiO_2$ and $Y+B/TiO_2$). The total dye(s) concentrations in the dye solutions were kept at 0.5 mM. The molar ratios of the dyes in solution were 10 : 20 : 1 for $Y+R+B/TiO_2$, 10 : 20 for $Y+R/TiO_2$, 20 : 1 for $R+B/TiO_2$, 10 : 1 for $Y+B/TiO_2$. The concentrations of DCA were fixed at 1.0 mM in the dye solutions.

Table 1 Photovoltaic performances of the dye-sensitized solar cells[a]

Y : R : B (dye solution)[b]	Y : R : B (TiO_2 film)[c]	[TBP][d]/M	J_{sc}/mA cm^{-2}	V_{oc}/mV	Fill factor	η (%)
10 : 10 : 5	2.2 : 1.0 : 2.9	0.1	15.8	512	0.56	5.7
10 : 10 : 1	5.0 : 1.0 : 1.5	0.1	17.1	505	0.58	6.3
10 : 20 : 1	4.1 : 1.0 : 1.3	0.1	16.8	510	0.57	6.1
10 : 30 : 1	3.5 : 1.0 : 1.2	0.1	15.1	503	0.57	5.4
10 : 50 : 1	2.5 : 1.0 : 0.9	0.1	13.9	497	0.55	4.7
10 : 10 : 1		0.2	15.8	525	0.63	6.5
10 : 10 : 1		0.3	13.8	535	0.67	6.2
10 : 10 : 1		0.5	11.5	552	0.68	5.4
1 : 0 : 0[e]		0.1	6.4	518	0.67	2.8
0 : 1 : 0[e]		0.1	12.2	508	0.60	4.6
0 : 0 : 1[e]		0.1	11.6	492	0.54	3.9

[a] Measurement conditions: AM1.5 Global simulated light (80 mW cm^{-2}); electrolyte contained 0.1 M LiI, 0.05 M I_2, 0.1–0.5 M *t*-butylpyridine (TBP), and 0.3 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI) in methoxypropionitrile. [b] The dye ratios in the dye solutions, where the total dye concentrations were fixed at 0.5 mM. [c] The dye ratios adsorbed on the TiO_2 film. [d] The concentration of TBP in the electrolyte. [e] 1.0 mM of DCA was present in the dye solutions.

conducting glass substrate) in the co-sensitization cases, the energy and/or electron transfer, if any, will not deteriorate the electron injection efficiencies of Y and R to a detectable extent.

It is found that the IPCEs of the co-sensitized electrodes depended greatly on the ratio of the three dyes on the TiO_2 surface (Fig. 3 and Table 1), and the electrode soaked in a solution of the three dyes with the molar ratio of 10 : 10 : 1 (Y : R : B) achieved the best IPCE curve over the wavelength region 400–800 nm, of which the dye ratio on the TiO_2 surface was detected to be 5.0 : 1.0 : 1.5 after dye desorption.

The photovoltaic performances including the short-circuit photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (ff), and the overall power conversion efficiency (η) of solar cells based on the three dyes are collected in Table 1, from which the potent ability of the co-sensitization approach in improving the efficiencies of the solar cells is clearly demonstrated. The power conversion efficiencies of the solar cells were affected remarkably by the components of the dye solutions. Also, as expected, the power conversion efficiencies depended greatly on the concentration of *t*-butylpyridine in the electrolyte, an additive often used in DSSCs for improving V_{oc} and optimizing η.[3] As a result, a maximum power conversion efficiency of 6.5% was obtained (Fig. 4 inset and Table 1), representing up to now the most efficient DSSC based on the co-sensitization of plural organic sensitizer dyes. The short-circuit photocurrent obtained in the most efficient solar cell was 15.8 mA cm^{-2}, in good agreement with the calculated value (16.4 mA cm^{-2}) from the overlap integral of the corresponding IPCE curve (Figs. 3 and 4) with AM1.5 Global solar spectrum (normalized to 80 mW/cm^2).

In summary, we demonstrate in this study a remarkable promotion of J_{sc} and η of the solar cells by co-sensitization of plural organic sensitizer dyes. The "DCA effect", involving both the blockage of I_3^- ions at the TiO_2 surface and the restriction of dye aggregation, play an important role in achieving the cooperation of the three dyes upon TiO_2 sensitization.

Experimental

The three dyes, Y, R, and B, were synthesized according to the reported procedures[17–20] and characterized by ^1H NMR, EI-MS and MALDI-TOF MS. The TiO_2 paste (Nanoxide-T from Solaronix, Switzerland) was coated by means of the doctor blade technique on fluorine-doped tin oxide (FTO) conducting glass, followed by sintering at 450 °C in air for 30 min.[2] The thickness of the TiO_2 film was 9 μm determined by a Dektak 3 Profilometer. The obtained TiO_2 electrodes were dipped in a 0.5 mM dye solution with or without the presence of 1 mM DCA in *t*-BuOH/CH_3CN (1 : 1 volume ratio) for 8 h at room temperature and rinsed with CH_3CN and dried under a stream of hot air. A sandwich-type solar cell was constructed by introducing the redox electrolyte containing 0.1 M LiI, 0.05 M I_2, 0.1–0.5 M *t*-butylpyridine (TBP), and 0.3 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI) in methoxy-

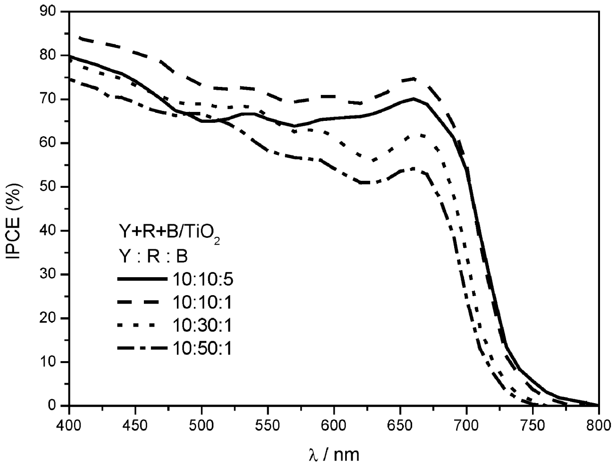

Fig. 3 Photocurrent action spectra of the TiO_2 electrodes co-sensitized by the three dyes at different dye ratios. The total dye(s)' concentrations in dyeing solutions were kept at 0.5 mM. The ratios of Y : R : B in dyeing solutions were 10 : 10 : 5, 10 : 10 : 1, 10 : 30 : 1, and 10 : 50 : 1, respectively.

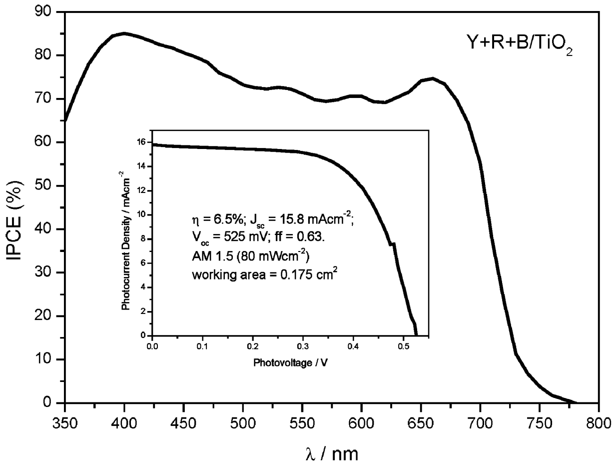

Fig. 4 Photocurrent action spectrum of the TiO_2 electrode sensitized by the three dyes at the dye ratio of 10 : 10 : 1 (Y : R : B) in the dye solution. Inset shows its photocurrent–photovoltage curve under AM1.5 Global simulated light (80 mW cm^{-2}) irradiation.

propionitrile between a dye-sensitized TiO_2 electrode and a counter electrode of Pt-coated FTO conducting glass. The dye-sensitized TiO_2 film was illuminated through the conducting glass support and the effective irradiated area was 0.175 cm^2. The photovoltaic performance of the solar cell was taken from a computer-controlled digital sourcemeter (Keithley 2400) under illumination from a AM1.5 Global simulated light (80 mW cm^{-2}) from an Oriel 91192 Solar Simulator. During the measurement of the photocurrent action spectra, the solar cell was irradiated by monochromatic light, obtained from a 500 W Xe lamp in combination with a SpectraPro-150 monochromator (Acton Research Co.), in the range 400–800 nm at 10 nm intervals, and the generated short-circuit photocurrents were recorded on a model 283A potentiostat/galvanostat. The incident monochromatic light intensity was measured with a S370 single-channel optometer equipped with a Model 262 flat response sensor head (Graseby Optronics). The electrolyte of 0.1 M LiI, 0.05 M I_2, and 0.3 M DMPImI in methoxypropionitrile was used in the IPCE measurements.

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