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Co-sensitization promoted light harvesting for plastic dye-sensitized solar cells

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ABSTRACT

A stepwise co-sensitization of a TiO₂ mesoporous film in conjunction with two dye molecules, using different sequences of adsorption for achieving a complementary spectral characteristic, is investigated for application to a low-temperature fabrication plastic dye-sensitized solar cell (plastic DSSCs). The stepwise co-sensitization by monomolecular adsorption of **N719/FL** and **black dye/FL** show enhanced photovoltaic performances for the pertinent plastic DSSCs, compare with that of the cell with the corresponding individual dyes. The optimal conversion efficiencies of plastic DSSCs with **N719/FL** and **black dye/FL** are found to be 5.10% and 3.78%, respectively, which are higher than those of the cells with the corresponding individual sensitizers. The incident photon-to-current conversion efficiency (IPCE) and electrochemical impedance spectroscopy (EIS) are also used to analysis these behaviors.

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1. Introduction

Dye-sensitized solar cells (DSSCs), composed of a dye-adsorbed metal oxide semiconductor, redox electrolyte and counter electrode, have proved themselves as high efficiency and low-cost systems for conversion of visible light into electrical energy [1]. In DSSC, photoelectric conversion is achieved by ultra-fast injection of an electron from a photo-excited dye into the conduction band of a semiconductor and subsequent completion of dye regeneration and holes transportation to the counter electrode. Highest efficiency of DSSC has so far been obtained with glass-based cells using sintered TiO₂ films. To elicit cost-effective performance of DSSC, however, use of plastic substrates with non-sintered TiO₂ films is sought after and has been subject of recent intense study [2–6]. Manufactured by low-temperature printing processes, the plastic-based DSSC provides a lightweight flexible device, which can meet versatile applications in the industry of plastic electronics. The dye sensitizer of the plastic DSSC is required to have especially a high light-harvesting function because a relatively thin semiconductor film is loaded on a conducting plastic in order to ensure high adhesion strength against mechanical bending.

DSSCs based on ruthenium complex dyes generally yield optimum efficiencies with use of a thick TiO₂ film (>15 μ m) because

of maximum molar extinction coefficients being much lower than 20,000 M⁻¹ cm⁻¹ due to metal-ligand charge transfer molecular excitation. Compared with these metal complexes, organic dyes generally have larger molar extinction coefficients. They allow thinner films to be made that minimize the charge transport losses and achieve better pore filling for organic hole-transport materials [7–11]. The sharp and narrow absorption bands of organic dyes, however, seriously weaken the light harvesting capabilities; hence the co-sensitization strategy was applied to broaden the light absorption spectra. Though several groups have examined the combination of two or more dyes in "molecular cocktails" [12-16] while success is still limited. These findings prompted us to investigate the competition of the dye adsorption on the TiO₂ surface that allows formation of a single monolayer on it, considering that the use of multiple dyes gives a lower coverage of each. Thus, sensitizers with higher absorption coefficients require a less amount of adsorbed dye to yield a sufficient optical density with a thin TiO₂ film, thereby providing a sufficient space on TiO₂ for the attachment of other sensitizers yielding a complementary absorption spectrum [17,18].

In this study, a metal-free organic dye (**FL**) and ruthenium complex (**N719** and **black dye**), which chemical structures shown in Fig. 1, were selected to collocate for the complementary in their spectral responses. **FL** ((E)-2-cyano-3-(5-(9,9-diethyl-7-(naphthalen-1-yl(phenyl)amino)-9*H*-fluoren-2-yl)thiophen-2-yl)acrylic acid), which synthesized in the lab [19], is a metal-free organic dye which contains thiophene and fluorine

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Fig. 1. Structures of sensitizers used in this study.

segments, and has a high extinction coefficient of 45,000 M⁻¹ cm⁻¹ at 454 nm. Previously, we have constructed a highly efficient DSSC based on **FL** and achieved a conversion efficiency of about 90% of that obtainable with **N3** dye [19,20]. Based on these studies, we investigated the phenomenon of co-sensitization of TiO₂ films using two collocations: (a) **N719** and **FL**, and (b) **black dye** and **FL** on plastic DSSCs in combination with thin TiO₂ films prepared at low-temperature. The charge transport process at the TiO₂/dye/electrolyte interface was investigated by electrochemical impedance spectroscopy (EIS) [21,22]. To the best of our knowledge, this is the first report on co-sensitization in the case of plastic DSSCs.

2. Experimental

Anhvdrous I2, methanol. ethanol. *tert*-butanol. Nmethylbenzimidazole (NMB), LiI, tetrabutylammonium iodide (TBAI), aectonitrile (AN) and 3-methoxypropionitrile (MPN) were used as received from Wako Chemical (Osaka, Japan). Cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'dicarboxylato)-ruthenium(II)bis-tetrabutylammonium (N719)tris(isothiocyanato)-ruthenium(II)-2,2':6',2"-terpyridineand 4,4',4"-tricarboxylic acid, tris-tertrabutylammonium salt (black dye) were the commercial products obtained from Solaronix.

Indium tin oxide (ITO)-coated polyethylene naphthalate (PEN) $(15 \Omega \text{ sq.}^{-1}, \text{ thickness } 200 \,\mu\text{m}; \text{ Peccell Technologies Inc., Japan})$ was used as the substrate of TiO₂ electrode. A mesoporous TiO₂ layer was coated by the doctor-blade method on an ITO/PEN substrate using the binder-free nanocrystalline TiO₂ paste (PECC-K01, Peccell Technologies, Inc.), followed by heat-drying at 150 °C for 10 min. The thickness of the dried TiO₂ film assembled in the DSSC was ca. $10 \,\mu$ m. The BET surface area of the TiO₂ film was 30–40 $m^2\,g^{-1}$ and the rutile content was less than 50%. For UV–vis spectrum measurement, the thickness of semi-transparent TiO₂ film was needed and coated of ca. 2 µm. The dye solutions were prepared as follows: 5×10^{-4} M FL in THF, 3×10^{-4} M N719 and **black dye** in acetonitrile/*tert*-butanol (50/50, v/v). The TiO₂ films were sensitized with each dye by dipping in the solutions for different times at 40 °C. Stepwise co-sensitization of TiO₂ films was accomplished by dipping the TiO₂-coated substrates for different time intervals in various dye solutions at 40 °C. The flow chart of the preparation of dyed-TiO₂ electrodes is shown in Fig. 2. Electrolyte composition was 0.4 M LiI, 0.4 M TBAI, 0.04 M I₂, and 0.3 M NMB dissolved in a mixture of AN and MPN (50/50, v/v). A platinumsputtered FTO glass was used as the counter electrode.



Fig. 2. The flow chart of co-sensitization process of the TiO₂ electrode in this study.



Fig. 3. The relationship between the quantity of dye adsorption on the TiO_2 film and the soaking times of the TiO_2 film in dye solution at 40 °C.

A sandwich type closed cell was fabricated by using surlyn film (thickness, $25 \,\mu$ m) as a sealant. The effective electrode area was 0.238 cm^2 with a black mask ($\phi = 0.55 \text{ cm}$). J–V curves were recorded on a computer-controlled digital source meter (Keithley 2400) under the illumination of AM 1.5, 100 mW cm^{-2} by a solar simulator (PEC-L11, Peccell Technologies). Incident photonto-current conversion efficiency (IPCE) was measured with an action spectrum measurement setup (PEC-S20, Peccell Technologies). EIS measurements of the DSSCs were carried out using a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie) under illumination of 100 mW cm⁻². The frequency range explored was from 400 mHz to 65 kHz, using the photoanode and the Pt-coated FTO glass as working and counter electrode, respectively. The applied bias voltage and AC amplitude were set at the open-circuit voltage (V_{OC}) of the DSSCs and 10 mV between the ITO/TiO₂/dye working electrode and the FTO/Pt counter electrode, respectively [20]. The measuring temperature was maintained at 25 °C.

3. Results and discussion

The optimal condition for the FL adsorption on the lowtemperature-coated TiO₂ film was initially investigated. The J-V characteristics based on different adsorption periods revealed that the maximum power conversion efficiency for DSSC with the plastic TiO_2 electrode was achieved at $40 \,^{\circ}C$ for 15 min of adsorption, and the amount of adsorbed dye on TiO₂ film was ca. $1.8\times 10^{-7}\,mol\,cm^{-2}$ although the contented of adsorbed dye is about $2.2 \times 10^{-7} \text{ mol cm}^{-2}$. It is also found that the amount of adsorbed FL on TiO₂ film is higher than that of N719 $(1.5 \times 10^{-7} \text{ mol cm}^{-2})$ or **black dye** $(1.3 \times 10^{-7} \text{ mol cm}^{-2})$ owing to FL has a smaller molecular size. These adsorption properties of these dyes were presented in Fig. 3. Furthermore, the photovoltaic performances of plastic DSSCs with the FL sensitized TiO₂ electrodes were assessed by changing the thickness of the TiO₂ film. Fig. 4 shows the dependence of short-circuit current density (J_{SC}) , energy conversion efficiency, and the IPCE spectra behavior on the TiO₂ film thickness. Fig. 4(a) shows that the I_{SC} and the conversion efficiency take maxima with a film thickness of ca. $7 \mu m$. While the **FL** sensitized TiO₂ cell works best with a thinner TiO₂ film, the maximum efficiency for the cell with N719 was achieved with a film thickness of 10 µm. These results are rationalized by the higher molar extinction coefficient of FL, namely, 45,000 M⁻¹ cm⁻¹ at 454 nm, as compared to that of N719 with $13,900 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$ at 541 nm. The IPCE spectra were compared in Fig. 4(b), where the



Fig. 4. Cell performances of the plastic DSSCs, using **FL** to sensitize the low temperature-fabricated TiO₂ films of various thicknesses: (a) J_{SC} and energy conversion efficiency, each as a function of TiO₂ film thickness; (b) IPCE spectra of the cells with different TiO₂ film thicknesses.

solid line represents the absorption spectrum of **FL** on a TiO₂ film as a reference. A high IPCE value of more than 60% was reached with the optimal thickness of TiO₂ film, although the action spectrum was constrained between 350 and 650 nm.

For the study of co-sensitization using **FL**, initially, two configurations of DSSCs, i.e., with **N719/FL** and **black dye/FL** were examined. The co-sensitized TiO_2 films were prepared by dipping first in the dye solutions of **N719** or **black dye**, as the case may be, followed by dipping them in **FL** solution. The effects of dipping periods in different dye solutions are discussed below. The *J*–*V*



Fig. 5. J-V curves of the plastic DSSCs with co-sensitized TiO₂ films and with films sensitized with individual dyes.

curves of cells with two collocations are shown in Fig. 5, and the corresponding photovoltaic parameters are included in Table 1. The conversion efficiencies of DSSCs based on individual **FL**, **N719** and **black dye** were 2.67%, 4.89%, and 2.66%, respectively. Interestingly, both the DSSCs with co-sensitized photoanodes of **N719/FL** and **black dye/FL** showed greater photocurrents than those of DSSCs with the corresponding individual dyes.

In the case of N719/FL, the UV-vis spectra of the films corresponding to the sensitization conditions were shown in Fig. 6(a). The absorption of co-sensitized with N719/FL showed a broader range than that adsorbed individual dyes. Meanwhile, at beginning, we controlled the dipping period in N719 to be 10 min and varied the dipping period in FL from 5 to 20 min. As a result, J_{SC} do not change significantly and reached a constant level when the dipping time in **FL** reached 10 min; the values of V_{OC} and FF showed an increase from 0.685 to 0.715V and 0.553 to 0.629, respectively. The IPCE spectra of the cells corresponding to this co-sensitization were plotted in Fig. 6(b) and the performance parameters were listed in Table 1. The IPCE indicates that there were still some unoccupied sites on the TiO₂ surface when the dipping time in FL solution was kept only for 5 min, leading to an increased recombination of I₃⁻ with the injected electrons at the surface of TiO₂ and thereby reducing V_{OC}. With the increase of dipping time, the dyes presumably are in close contact with each other on the TiO₂ surface, thus suppressing the electron recombination process. Alternatively, the dipping time in **FL** was maintained at 10 min and was varied in N719 dye solution; the corresponding photovoltaic data and the IPCE spectra were presented in Table 1

Table 1

Photovoltaic parameters and fitting data of EIS of plastic DSSCs with various sensitized-TiO₂ films under the illumination of 100 mW cm⁻².

Cell no.	Dye	$J_{\rm SC}$ (mA cm ⁻²)	$V_{\rm OC}$ (V)	FF	η (%)	$R_{\rm ct2}\left(\Omega\right)$	τ_e^{a} (ms)
А	N719 (1 h)	10.48	0.755	0.619	4.89	18.5	15.9
В	BD (1 h) ^b	7.60	0.650	0.539	2.66	30.0	11.8
С	FL (15 min)	6.40	0.655	0.636	2.67	25.6	11.8
F	N719 (10 min)/FL (5 min)	8.73	0.685	0.553	3.31	-	-
G	N719 (10 min)/FL (10 min)	8.85	0.715	0.629	3.98	-	-
Н	N719 (10 min)/ FL (20 min)	8.60	0.710	0.631	3.85	-	-
Ι	N719 (20 min)/FL (10 min)	9.65	0.715	0.626	4.32	-	-
J	N719 (40 min)/FL (10 min)	11.42	0.715	0.625	5.10	19.2	15.9
K	BD (10 min)/ FL (10 min)	8.05	0.650	0.590	3.09	-	-
L	BD (20 min)/ FL (10 min)	9.77	0.650	0.595	3.78	15.3	14.9
М	BD (40 min)/ FL (10 min)	8.65	0.645	0.559	3.12	-	-

^a τ_e : electron lifetime.



Fig. 6. (a) The absorption spectra of **FL**, **N719** and **FL/N719** co-anchored on 2 μ m TiO₂ film; (b) IPCE spectra of the plastic DSSCs obtained with TiO₂ films which were dipped, first in **N719** solution for 10 min and then in **FL** solution for different periods; (c) IPCE spectra of the plastic DSSCs obtained with TiO₂ films which were dipped, first in **N719** solution for different periods and then in **FL** solution for 10 min.

and Fig. 6(c), respectively. The photocurrents increased from 8.60 to a range of 8.85–11.42 mA cm⁻² with an increase of dipping times of **N719** to 10, 20 and 40 min. The corresponding energy conversion efficiency increased from 3.85% to 5.10% under illumination of 100 mW cm⁻². An important change is that the IPCE spectra treated with the N719 dipping exhibited a remarkable increase in the longer wavelength region (550-800 nm) without causing a reduction in the shorter wavelength region (350-500 nm). As the **N719** dipping time reached 40 min, the co-sensitization gave similar IPCE values at the longer wavelength 550-800 nm to those of a reference DSSC with N719 (1 h) alone, while the IPCE values at the shorter wavelength region (350-500 nm) keeping almost the same value with plain FL (15 min), amply exceed the values of N719 alone. By analyzing these results, it is now clear that the optimal co-sensitization condition for this system is dipping first in N719 solution for 40 min and then in FL solution for another 10 min.

On the other hand, the **black dye**/**FL** system was also investigated regarding the influence of dipping period in different dye solutions on the cell performance. First, the **black dye** was allowed to adsorb onto the TiO₂ surface with different dipping times in order to control the distribution of the dye on the TiO₂ surface; then the TiO₂ films were dipped in **FL** solution and the dipping period in this solution was maintained for 10 min. It was revealed that the photocurrent varied from 8.05 mA cm⁻² to 9.77 and 8.65 mA cm⁻² by changing the dipping time from 10 min to 20 and 40 min, respectively. The corresponding energy conversion efficiency was improved from 3.09% to 3.78% and 3.12%, respectively, which all surpass the performances of individual **FL** or **black dye**. The V_{OC} values of these co-sensitization systems did not show a significant change, probably due to the fact that the V_{OC}s achieved by the individual dyes have the same value of *ca*. 0.65 V.

Fig. 7(a) shows the UV-vis spectra of the FL and black dye cosensitization system, the absorption of co-sensitized with N719/FL also showed a broader range than that adsorbed individual dyes. Fig. 7(b) demonstrates that the plastic DSSC based on only black dye has a broad action spectrum extended up to 900 nm [18]; however, the low molar extinction coefficient of **black dye** (7640 M⁻¹ cm⁻¹ at 600 nm in DMF solution) in combination with a thin TiO₂ film has resulted in a poor IPCE value of only ca. 30%. By controlling the dipping time in the black dye solution from 10 to 40 min, it was found that the IPCE values in the region of 600-900 nm increased slightly and the values in the region of 350-600 nm decreased which owing to the less amount of FL on TiO₂ electrode. Consequently, the employed optimal condition for black dye/FL system was dipping in black dye solution for 20 min and then in FL solution for 10 min. In addition, we also have studied the cell performances in conjunction with the co-sensitization by reversing the sequence of dye adsorption, in which the TiO₂ films were dipped first in FL solution and then in N719 or black dye solutions. Lower performances were observed by this strategy, due to desorption of FL dye while dipping the FL dyed-TiO₂ films in N719 or black dye solutions.

From the previous studies, we adopted a strategy of cosensitization intending to control the distribution of **black dye** or **N719** (broad action spectrum) at the outer layer and that of **FL** (narrow action spectrum but high extinction coefficient) at the inner layer. The configuration of this two-layer-like TiO₂ film is similar to that of a two-layer film of TiO₂/Al₂O₃ [23], where the inner layer was sensitized by a wide band gap dye. Therefore, the panchromatic sensitization could be achieved in one layer TiO₂ film by controlling the co-sensitized time and sequence. It is also suggested that not only the sensitizers with complementary absorption regions but also molar extinction coefficients could be considered to improve the cell performance of the DSSC via the co-sensitization.

EIS is a useful technique for the analysis of electronic and ionic transport processes in an electrochemical device. It is a



Fig. 7. (a) The absorption spectra of **FL**, **black dye** (**BD**) and **FL/BD** co-anchored on $2 \,\mu$ m TiO₂ film; (b) the IPCE spectra of plastic DSSCs based on sequential dipping, first in **black dye** solution for different dipping times and then in **FL** solution for 10 min.

steady state method measuring the current response based on the application of an ac voltage at different frequencies [24–26]. Fig. 8 shows the Nyquist plots of EIS of plastic DSSCs with various sensitized systems. Herein, we utilized EIS to analyze the charge transport resistance at the TiO₂/dye/electrolyte interface (R_{ct2}), intermediated-frequency semicircle (1–10³ Hz), with different sensitizers in plastic DSSCs. The equivalent circuit plot is shown in Fig. 8(a). All the spectral exhibit three semicircles, which are assigned to electrochemical reaction at Pt/electrolyte, charge transfer at the TiO₂/dye/electrode and Warburg diffusion process of I^-/I_3^- in the electrolyte. The equivalent circuit employed for the curves fitted the impedance spectra of the DSSCs are also shown in Table 1.

Meanwhile, the electron lifetime (τ_e) can be obtained via Eq. (1)

$$\tau_e = R_{\rm ct2} \times C_{\mu 2} \tag{1}$$

where R_{ct2} and $C_{\mu 2}$ are the charge transfer resistance and the chemical capacitance at TiO₂/dye/electrolyte interface, respectively. The chemical capacitance ($C_{\mu 2}$) is an equilibrium property that relates the variation of the carrier density to the displacement of the Fermi level. The $C_{\mu 2}$ is a positive quantity, as it represents the equilibrium property.



Fig. 8. (a) The equivalent circuit used in this study. The EIS analysis of DSSCs based on various co-sensitized systems: with (b) **N719** and **FL**, and (c) **black dye (BD)** and **FL**.

It was found that the plastic DSSCs based on **N719** (40 min)/**FL** (10 min) system and **N719** dye alone have the same R_{ct2} value of *ca*. 18.5 Ω . In contrast, the DSSC based on **FL** has a larger value of *ca*. 25.6 Ω . In Fig. 8(b), the cell based on **black dye** (20 min)/**FL** (10 min) shows R_{ct2} a value of *ca*. 15.3 Ω which is smaller than that of the individual dyes. Correspondingly, the electron lifetime (τ_e) of cells based on **N719** (40 min)/**FL** (10 min) and **N719** alone are *ca*.15.9 ms, while that of cell based on **FL** alone is *ca*.11.8 ms. This implies that the TiO₂ films adsorbed with **N719** (40 min)/**FL** (10 min) and with only **N719** have similar adsorption conditions. The collection and transport of electrons in the TiO₂ film adsorbed with **N719** (40 min)/**FL** (10 min) and **N719** alone are faster than those with plain **FL**, which leads to a reduction in the electron recombination and extension of the electron lifetime in the TiO₂ film. In addition,

the τ_e of cells based on **black dye** (20 min)/**FL** (10 min) and **black dye** alone are 14.9 and 11.8 ms, respectively. Surprisingly, the cell based on **black dye** (20 min)/**FL** (10 min) showed a longer electron lifetime than that of cell with individual dyes. This behavior maybe either due to a higher surface coverage of dye on the TiO₂ surface after co-sensitization that blocks the approach of I₃⁻ to the TiO₂ surface and decreases the recombination of injected electrons with I₃⁻ ions, or due to the less aggregation of individual dyes in co-sensitized conditions that improves their injection efficiencies. Meanwhile, it is important in the co-sensitization process to limit the dye aggregation. Indeed, limited aggregation could occur, if the binding sites for neighboring dyes were greater than Van der Waals distances, thereby causing the molecules aggregate themselves by leaning upon each other [12].

4. Conclusions

The co-sensitization with various collocations of dyes was examined for achieving complementary spectra in the case of lowtemperature fabricated plastic DSSCs. The plastic DSSCs based on **N719/FL** and **black dye/FL** systems showed remarkable improvements in the active spectra and photocurrents, compared with the cells based on individual dyes. It was also found that a good cosensitization of DSSC can be achieved by combining the dyes with complementary parameters with respect to both absorption spectra and molar extinction coefficient. With this strategy, we can regulate the active absorption spectrum simply by the stepwise cosensitization and the strategy also provides an alternative choice for screening dyes.

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