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A New Cosensitization Method Using Lewis Acid Sites of TiO_2 Photoelectrode for Dye-Sensitized Solar Cells†

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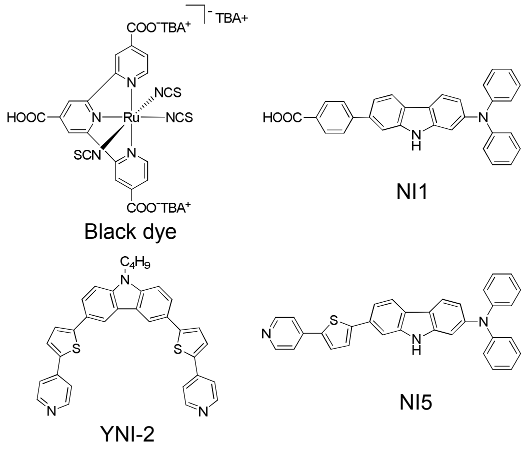
Cosensitized dye-sensitized solar cells using Black dye and a pyridine-anchor dye (NI5 or YNI-2) showing a site-selective adsorption behaviour at the TiO_2 surface have been prepared in the first time to reduce the competitive adsorption between two dyes.

Extensive studies on the efficiency improvement of dye-sensitized solar cells (DSCs) have been carried out during this two decades because DSCs are regarded as promising alternatives to the silicon-based photovoltaic devices.[1] A higher light-to-electrical energy conversion efficiency has been obtained in the DSCs by employing the efficient dyes which can absorb the light at the whole visible and the near IR regions.[2] Among them, Black dye {$(TBA)_3[Ru(Htcterpy)(NCS)_3]$ (TBA = tetrabutylammonium, tcterpy = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine), Scheme 1} is one of the most famous and highly efficient dyes, and more than 11% conversion efficiency was obtained in the Black-dye-based DSCs.[3] For further efficiency improvement of the DSCs, a cosensitization method using two kinds of dyes has been often utilized. For example, effective improvement of the conversion efficiency has been achieved successfully in the cosensitized DSCs with two kinds of organic dyes,[4] Zn porphyrine and organic dyes,[5] and ruthenium-complex and organic dyes.[6] For the effective enhancement of the conversion efficiency of the DSCs by this method, one of the most important points is a combination of two dyes. It is expected that conversion efficiency of the DSC with the main dye is improved effectively by using the additional dye having a complementary absorption feature. However, conversion efficiency decreases quite often by using the additional dye. One of the main reasons is considered to be the decrease of the amount of main dye adsorption at the TiO_2 photoelectrode due to the presence of the competitive adsorption between the main and the additional dyes.[7] Therefore, additional dyes having molecular shapes and molecular sizes different from those of the main dyes were employed to reduce the competitive adsorption between two dyes in the above mentioned studies. However, the obvious guideline for the effective combination of two different dyes for the cosensitization method has been still unclear.



Scheme 1. Structures of Black dye, NI5, YNI-2 and NI1.

On the other hand, a series of organic dyes having a pyridine-anchor unit instead of the conventional carboxyl-anchor one have been synthesized in our group.[8] These pyridine-anchor dyes were confirmed to adsorb dominantly at the Lewis acid sites of the TiO_2 surface (the sites of exposed Ti atoms).[9] Generally, most of dyes having the conventional carboxyl anchor unit adsorb at the Brønsted acid sites of the TiO_2 surface (the sites of hydroxyl-group-bound to Ti atoms) via dehydration reactions. Therefore, it is expected that competitive adsorption does not occur between pyridine-anchor dyes and conventional carboxyl-anchor dyes, such as Black dye. In this study, pyridine-anchor dyes (NI5 and YNI-2, Scheme 1) were employed as additional dyes for the Black-dye-based DSCs[10] to obtain the insights into the guideline for the effective combination of two different dyes for the cosensitization method. As far as we know, this is the first example of the cosensitized DSC employing the two dyes showing a site-selective adsorption behaviour. Conversion efficiency of the Black-dye-based DSC was improved successfully by employing pyridine-anchor dyes without decreasing the amount of Black dye adsorption. Here we communicate a new effective cosensitization method using Lewis acid sites at the TiO_2 surface for the efficiency improvement of the DSCs.

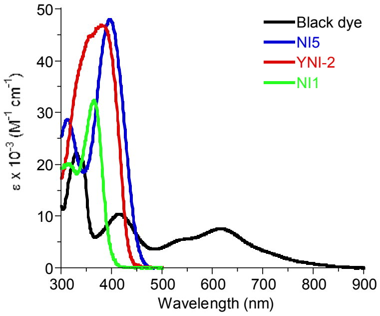


Figure 1. Molar absorptivity spectra of Black dye, NI5, YNI-2 and NI1 in 1-propanol.

Pyridine-anchor dyes (NI5 and YNI-2) showed strong absorption bands centered at around 400 and 380 nm, respectively (Figure 1). These absorptions correspond to the intramolecular charge transfer (ICT) bands from the donor units (carbazole units) to the acceptor ones (pyridine groups). Since the incident photon-to-current conversion efficiency (IPCE) of the Black-dye-based DSCs at around 400 nm was relatively lower due to the presence of I_3^- in the electrolyte, which has a molar absorptivity much larger than that of Black dye at this wavelength range (ε_{353} = 26400 cm^{-1}M^{-1}),[11] NI5 and YNI-2 seem to be suitable additional dyes for the Black-dye-based DSCs toward the effective panchromatic sensitization. A structural analogue dye (NI1) having a carboxyl-anchor unit also displayed ICT bands at this wavelength range even though the molar absorptivity was relatively smaller than those of NI5 and YNI-2.

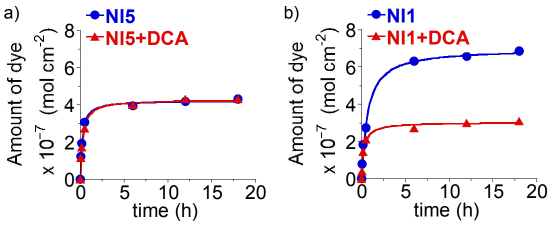


Figure 2. Adsorption profiles of NI5 in the absence and the presence of DCA (a), and those of NI1 in the absence and the presence of DCA (b).

Adsorption behaviour of NI5 to the TiO_2 surface in the absence and the presence of deoxycholic acid (DCA), which has a carboxyl-anchor unit and is often used as a coadsorbent to disperse the dye aggregation at the TiO_2 surface, has been investigated to know whether competitive adsorption occurs or not. As shown in Figure 2a, the adsorption behaviour of NI5 having a pyridine-anchor unit was not changed at all by adding DCA, clearly indicating that competitive adsorption does not occur between NI5 and DCA. In comparison, the maximum amount of dye adsorption of NI1 having a carboxyl-anchor unit was decreased drastically by adding DCA (Figure 2b). In addition, adsorption rate and the maximum amount of dye adsorption of Black dye were also decreased by adding DCA (Figure S1). These results indicate that competitive adsorption occurs between NI1 and DCA, and Black dye and DCA. In other words, competitive adsorption occurs between the molecules having a carboxyl-anchor unit.

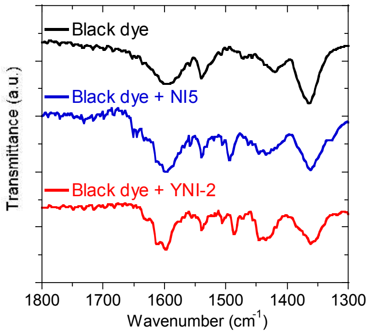


Figure 3. ATR-IR spectra of the dyes adsorbed on TiO_2 films; Black dye (black line), Black dye and NI5 (blue line), and Black dye and YNI-2 (red line).

Coadsorption of Black dye and the pyridine-anchor dye to the TiO_2 photoelectrode has been carried out by a stepwise adsorption method because the ligand substitution reaction of NCS ligands of Black dye by a pyridine-anchor unit of NI5 or YNI-2 would occur in a mixed solution. In the cases of NI5 and YNI-2, enough amount of dye adsorption could be obtained within only 10 minutes. While, much longer immersion time (about 20 hours) was required to obtain enough amount of Black dye adsorption. Therefore, Black-dye adsorption to the TiO_2 photoelectrode was carried out at first, and then pyridine-anchor dye adsorption was carried out for only 10 minutes to avoid proceeding the ligand substitution reaction between the NCS ligands of the adsorbed Black dye by the pyridine-anchor unit of NI5 or YNI-2. ATR-IR spectroscopic measurements of the cosensitized TiO_2 particles have been conducted to know whether site selective adsorption of Black dye and pyridine-anchor dye was achieved or not. As shown in Figures 3 and S2, the absorption band at 1695 cm^{-1} corresponding to the stretching vibration mode of carbonyl groups of Black dye disappeared, and the peak intensities of absorption bands at 1361 and 1600 cm^{-1} increased in the case of the Black-dye-sensitized TiO_2 particles. As reported previously, these results indicate that Black dye adsorbs at the Brønsted acid sites of the TiO_2 surface (the sites of hydroxyl-group-bound to Ti atoms) via dehydration reactions.[12] On the other hand, several absorption bands corresponding to the stretching vibration mode of C=C or C=N of pyridine-anchor dyes as well as the absorption bands of terpyridine ligand of Black dye were observed at around 1590, 1485, 1445, and 1415 cm^{-1} in the cases of coadsorbed TiO_2 particles. In addition, characteristic absorption bands at around 1615 cm^{-1} were observed in both cosensitized TiO_2 particles. These absorption bands are assigned to be absorptions of the pyridine ring of NI5 or YNI-2, which coordinates to the Ti atom at the TiO_2 surface (Lewis acid sites of the TiO_2 surface).[13] These results suggest that site selective adsorption is achieved successfully by using the combination of Black dye and the pyridine-anchor dye. It is noted here that the adsorption rate of pyridine-anchor dyes (NI5 and YNI-2) is quite faster, and they can also adsorb at the Brønsted acid sites of the TiO_2 surface if the Brønsted acid sites are not occupied. Therefore, adsorption of dye which has the conventional carboxyl anchor unit should be carried out at first to occupy the Brønsted acid sitesof the TiO_2 surface.

Table 1. Solar cell performances of the Black-dye-based and cosensitizedDSCs[a]

Entry	Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	Amount of Black dye ($\times 10^{-7}$mol/cm^2)	Amount of organic dye ($\times 10^{-7}$mol/cm^2)
1	Black dye	18.7	0.69	0.73	9.5	2.1	
2	Black dye + NI5	20.7	0.68	0.71	10.0	2.1	1.6
3	Black dye + YNI-2	20.1	0.67	0.72	9.8	2.0	1.2
4	Black dye + NI1	18.3	0.67	0.72	8.8	1.7	0.5

[a]The electrolyte was an acetonitrile solution containing 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 film thickness: 37 µm, active area: 0.25 cm^2). Irradiation was carried out by using the solar simulator (AM 1.5, 100 mW/cm^2).

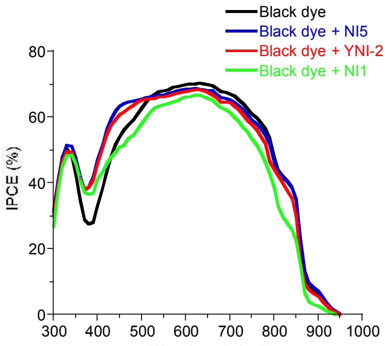


Figure 4. IPCE spectra of the Black-dye-based and the cosensitized DSCs.

As summarized in Table 1, conversion efficiency of the Black-dye-based DSC was improved by cosensitization with pyridine-anchor dye (NI5 or YNI-2), while it was decreased by cosensitization with carboxyl-anchor dye (NI1). In the cases of the cosensitized DSCs with NI5 or YNI-2, *J*sc value increased effectively without changing *V*oc and *FF* values. On the other hand, *J*sc value decreased slightly in the case of the cosensitized DSC with NI1. As shown in Figure 4, IPCE values of the cosensitized DSCs with NI5 or YNI-2 between 350 and 500 nm were higher than those of Black-dye-based DSC, while those at the wavelength range above 500 nm were almost the same. Since NI5 and YNI-2 exhibit relatively higher IPCE values at around this wavelength region(Figure S3), these two dyes must contribute to this improvement of IPCE values of the cosensitized DSCs. In the case of the cosensitized DSC with NI1, IPCE values at the wavelength region beyond 420 nm were lower than those of Black-dye-based DSC even though those at around 400 nm were higher. In order to obtain further insights into the IPCE spectra, the amounts of dye adsorption of the cosensitized DSCs were investigated. In the case of Black-dye-based DSC, the amount of Black dye adsorption was estimated to be 2.1 × 10^{-7}mol/cm^2 (Table 1). In the cases of cosensitized DSCs with NI5 or YNI-2, the amounts of organic dye adsorption were calculated to be 1.6 × 10^{-7} and 1.2 × 10^{-7}mol/cm^2, respectively. YNI-2 has two pyridine-anchor units within a single molecule, and has a molecular size larger than NI5, therefore, the amount of dye adsorption of YNI-2 seems to be smaller than that of NI5. The most important point is that the amount of Black dye adsorption did not decrease at all in each cosensitized DSC. These results clearly indicate that effective cosensitization of Black dye and pyridine-anchor dye (NI5 or YNI-2) without a competitive adsorption was achieved successfully by using the combination of dyes showing a site-selective adsorption behaviour. On the other hand, the amount of Black dye adsorption decreased to 1.7 × 10^{-7}mol/cm^2 in the case of the cosensitized DSC with NI1, as expected from the results of adsorption behaviour. Smaller amount of Black dye adsorption would be a main reason for the lower IPCE values of the cosensitized DSC with NI1 at the wavelength range above 420 nm.

In conclusion, cosensitized DSCs with Black dye and pyridine-anchor dye (NI5 or YNI-2) have been prepared to obtain the insights into the guideline for the effective combination of two different dyes for the cosensitization method. Effective cosensitization of Black dye and pyridine-anchor dye to the TiO_2 surface without a competitive adsorption was achieved successfully for the first time due to the site-selective adsorption behaviour of two different dyes. The conversion efficiency of the Black-dye-based DSC was improved by cosensitization with NI5 or YNI-2. This study provides a new effective cosensitization method using Lewis acid sites at the TiO_2 surface for the efficiency improvement of the DSCs.

Notes and references

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†Electronic Supplementary Information (ESI) available: [details of experimental procedures, adsorption profiles, ATR-IR spectra, IPCE spectra, and solar cell perfomrances]. See DOI: 10.1039/c000000x/

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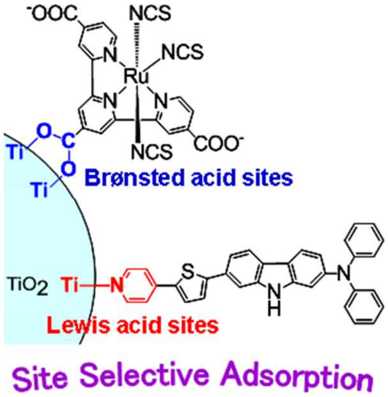

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