Supporting Information

A New Cosensitization Method Using Lewis Acid Sites of TiO₂ Photoelectrode for Dye-Sensitized Solar Cells

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Materials and General Measurements

Black dye, NI5, YNI-2 and NI1 were prepared according to the literature.^[1-3] Titanium isopropoxide and deoxycholic acid (DCA) were purchased from Tokyo Chemical Industry Co. 1,2-Dimethyl-3-propylimidazolium iodide (DMPImI) was purchased from Shikoku Kasei. All solvents and reagents were of the highest quality available and were used as received.

The elemental analysis was carried out on a Perkin Elmer 2400II elemental analyzer using acetanilide as a standard material. ¹H NMR spectra were acquired on a Bruker BioSpin AVANCE 400M spectrometer, where chemical shifts in CD₃OD, acetone, and

DMSO were referenced to internal standard tetramethylsilane. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. ATR-IR spectra were recorded on a Shimadzu IRPrestige-21 spectrometer equipped with a single-reflection ATR accessory (MIRacle with a diamond prism plate).

Preparation of TiO₂ photoelectrodes and DSCs

TiO₂ pastes were prepared using titanium isopropoxide.^[4] Nanocrystalline TiO₂ photoelectrodes were prepared by screen printing the TiO₂ paste on fluorine-doped SnO₂ conducting glasses (FTO, Nippon Sheet Glass Co., 10 Ω /square). TiO₂ films were composed of six layers (from the bottom to the third layer: 20 nm TiO₂ particles, the fourth layer: a 8:2 mixture of 20 nm and 100 nm particles, the fifth layer: a 6:4 mixture of 20 nm and 100 nm particles, and the top layer: 400 nm TiO₂ particles; film thickness: approximately 37 µm). TiO₂ photoelectrodes were calcinated at 520 °C after every layer was coated. The active areas of these TiO₂ films were determined using a KEYENCE VHX-200 digital microscope.

Dye-sensitized TiO₂ photoelectrodes were prepared by immersing the TiO₂ photoelectrodes into the 1-propanol solution of 0.2 mM Black dye and 20 mM DCA for 20 h, or the 1-propanol solution of 0.3 mM organic dye (NI5, YNI-2, or NI1) for 10 min at room temperature. Cosensitized TiO₂ photoelectrodes were prepared by immersing the TiO₂ photoelectrodes into the 1-propanol solution of 0.2 mM Black dye and 20 mM DCA for 20 h, and followed by the immersion in the 1-propanol solution of 0.3 mM organic dye (NI5, YNI-2, or NI1) for 10 min at room temperature.

Black dye could be desorbed from TiO_2 photoelectrode by using 50 mM NaOH solution. In the cases of cosensitized TiO_2 photoelectrodes, Black dye could be desorbed selectively by using 0.1 M TBAOH solution (1:1 mixture of H₂O and EtOH). The amounts of Black dye adsorption in the Black-dye-sensitized and the cosensitized TiO_2 photoelectrodes were estimated from the absorption spectra of the resulting NaOH and TBAOH solutions. The amount of organic dye adsorption (NI5, YNI-2 or NI1) in the cosensitized TiO_2 photoelectrode was calculated from the absorption decrease of the organic-dye in solution after immersion of the Black-dye-sensitized TiO_2 photoelectrode because each organic dye could not be desorbed selectively from the cosensitized TiO_2 photoelectrode by the conventional method using a NaOH solution.

Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration composed of the dye-adsorbed TiO₂ photoelectrode, a platinum-sputtering

counter electrode, a spacer film (50 μ m), and an electrolyte solution (0.05 M I₂, 0.1 M LiI, 0.6 M DMPImI and 0.3 M 4-*tert*-butylpyridine (TBP) in acetonitrile).

Photovoltaic measurements

The photocurrent-voltage (I-V) characteristics of the DSCs were measured on a Keithley 2400 source meter under irradiation of AM 1.5, 100 mW/cm² (1 sun) supplied by a solar simulator (Yamashita Denso, YSS-150A). The incident light intensity was calibrated with a grating spectroradiometer LS-100 (EKO Instruments) and Si photodiode (Bunkoh Keiki). The incident photon-to-current conversion efficiency (IPCE) was measured on a PEC-S10 (Peccell Technologies).



Figure S1. Adsorption profiles of Black dye in the absence and the presence of DCA.



Figure S2. ATR-IR spectra of the powder samples of dyes (red) and the dyes adsorbed on TiO_2 particles (blue).



Figure S3. IPCE spectra of the DSCs with NI5, YNI-2, and NI1.

Table S1. Solar cell performances of the organic-dye-based DSCs^a

Sensitizer	JscVocFFηAmount of dye			
				adsorption
(mA/cm^2) (V	7) (%	b)(×10-7 mol/cm ²)		
NI5 2.90.0	61 0.69 1.2	2.1		
YNI-2	3.0 0.62	0.68 1.3	2.5	
NI1	1.0 0.54	0.61 0.3 2.6		

^aTiO₂ film thickness and active area were 37 μ m and 0.25 cm², respectively. Electrolyte was an acetonitrile solution containing 0.05 M I₂, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP. Irradiation was carried out using a solar simulator (AM 1.5, 100 mW/cm²).

References

- Nazeeruddin, M. K., Bessho, T., Cevet, L., Ito, S., Klein, C., De Angelis, F., Fantacci, S., Comte, P., Liska, P., Imai, H., Grätzel, M., *J. Photochem. Photobiol.*, 185, 331-337 (2007).
- [2] Ooyama, Y., Inoue, S., Nagano, T., Kushimoto, K., Ohshita, J., Imae, I., Komaguchi, K., Harima, Y., Angew. Chem. Int. Ed., 50, 7429-7433 (2011).
- [3] Ooyama, Y., Yamaguchi, N., Imae, I., Komaguchi, K., Ohshita, J., Harima, Y., *Chem. Commun.*, 49, 2548-2550 (2013).
- [4] Wang, Z.-S., Yamaguchi, T., Sugihara, H., Arakawa, *Langmuir*, 21, 4272-4276 (2005).