Supporting Information

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

Naoyuki Shibayama, a,b Hironobu Ozawa, a Masahiro Abe, b Yousuke Ooyama, c and Hironori Arakawa* a

aDepartment of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 12-1, Ichigaya-Funagawara, Shinjuku, Tokyo, 162-0826, JAPAN
E-mail: h.arakawa@ci.kagu.tus.ac.jp; Fax: (+81) 3 5261 4631; Tel: (+81) 3 5228 8311

bTechnical Research Institute, Toppan Printing Co., Ltd., 4-2-3, Takanodaiminami, Sugito, Saitama, 345-8508, JAPAN

cDepartment of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima, 739-8527, JAPAN

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 acetonilide 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 TiO$_2$ photoelectrodes and DSCs**

TiO$_2$ pastes were prepared using titanium isopropoxide.$^{[4]}$ Nanocrystalline TiO$_2$ photoelectrodes were prepared by screen printing the TiO$_2$ paste on fluorine-doped SnO$_2$ conducting glasses (FTO, Nippon Sheet Glass Co., 10 Ω/square). TiO$_2$ films were composed of six layers (from the bottom to the third layer: 20 nm TiO$_2$ 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 TiO$_2$ particles; film thickness: approximately 37 μm). TiO$_2$ photoelectrodes were calcinated at 520 °C after every layer was coated. The active areas of these TiO$_2$ films were determined using a KEYENCE VHX-200 digital microscope.

Dye-sensitized TiO$_2$ photoelectrodes were prepared by immersing the TiO$_2$ 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 TiO$_2$ photoelectrodes were prepared by immersing the TiO$_2$ 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 H$_2$O 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 TiO$_2$ photoelectrode, a platinum-sputtering
counter electrode, a spacer film (50 μm), and an electrolyte solution (0.05 M I₂, 0.1 M LiI, 0.6 M DMPIml 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.](image-url)
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

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta$</th>
<th>Amount of dye adsorption $(\times 10^{-7} \text{ mol/cm}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI5</td>
<td>2.90</td>
<td>0.69</td>
<td>0.69</td>
<td>1.2</td>
<td>2.1</td>
</tr>
<tr>
<td>YNI-2</td>
<td>3.0</td>
<td>0.62</td>
<td>0.68</td>
<td>1.3</td>
<td>2.5</td>
</tr>
<tr>
<td>NI1</td>
<td>1.0</td>
<td>0.54</td>
<td>0.61</td>
<td>0.3</td>
<td>2.6</td>
</tr>
</tbody>
</table>

$^a$TiO$_2$ film thickness and active area were 37 µm and 0.25 cm$^2$, respectively. Electrolyte was an acetonitrile solution containing 0.05 M I$_2$, 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/cm$^2$).

References