Electronic Supplementary Information

Bi-Functional Ion Exchangers for Enhanced Performance of Dye-Sensitized Solar Cells

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Experimental Details and Characterization

*Experimental Details*

Bi-layered TiO$_2$ films were employed in this paper. For an under-layer, a 12-µm-thick transparent nanocrystalline TiO$_2$ film (particle size: ~20 nm) was deposited onto the FTO (F-doped SnO$_2$) glass, and a 6-µm-thick film composed of larger light-scattering TiO$_2$ particles (particle size: ~400 nm) was printed as an over-layer. Then, they were sintered at 500 °C for 30 min. After cooling down to room temperature, the bi-layered TiO$_2$ films were immersed in 40 mM TiCl$_4$ solution at 70 °C for 30 min, and rinsed with deionized water. The TiCl$_4$-treated TiO$_2$ films were heated at 500 °C for 30 min. Finally, the TiO$_2$ films were dipped in two distinct dye solutions: (i) 0.5 mM N719 dissolved in absolute ethanol (for film A and device A) and (ii) 0.5 mM N719 and 0.3 mM AOT in absolute ethanol (for film B and device B). The counter electrode was prepared by dripping a Pt solution (Solaronix, Platisol T) on the FTO glass substrate, which was followed by thermal treatment at 500 °C for 30 min. For the cell assembly, a hot-melt 60-µm-thick Surlyn (Solaronix, Meltonix 1170-60) was used as a spacer between the working electrode and the Pt electrode. The electrolyte composed of 0.7 M BMII-0.03 M I$_2$-0.1 M guanidine thiocyanate-0.5 M 4-tert-butylpyridine in an AC/VN solution was used for devices.

*Characterization*

The TiO$_2$ electrodes were analyzed by attenuated total reflectance FTIR (ATR-FTIR) spectrometry (Hyperion, Bruker). UV-Vis absorption spectra were recorded on an Optizen POP spectrophotometer. The photovoltaic performance was measured under an illumination of a solar simulator (Newport, Oriel class A, 92251A) at one sun (AM 1.5, 100 mW·cm$^{-2}$) with an active area of 0.25 cm$^2$. Electrical impedance spectra were obtained using an impedance analyzer (BioLogic, SP-300), with a frequency ranging from $10^1$ to $10^6$ Hz, and analyzed using Z-view software. The chemical bonding states of the samples were examined by using X-ray photoelectron spectroscopy (XPS, K-alpha (Thermo VG, U.K.) with an Al monochromated X-ray sources (Al Kα line: 1486.6 eV).
**Figure S1.** Chemical structures of (a) N719, (b) N3, and (c) AOT molecules.

**Figure S2.** The amount of the adsorbed N719 dye on the TiO$_2$ surface as a function of the concentration of N719 in absolute ethanol without (film A) and with AOT (film B).
Figure S3. The amount of the adsorbed N3 molecules at various immersion times at 25 °C in absolute ethanol without (film A) and with AOT (film B).

Figure S4. XPS spectra for N1s (a) and O1s (b) of multi-layers of AOT/N719 and N719.
**Figure S5.** Time evolution of the conversion efficiency ($\eta$) of DSCs without (device A*) and with AOT (device B*). 

**Figure S6.** Photovoltaic properties (a. current density; b. voltage; c. fill factor; d. efficiency) at various AOT concentrations under a fixed N719 concentration (0.5 mM). The inset of Fig. 6(a) shows the amount of the adsorbed dye molecules along with the AOT concentration.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device A</td>
<td>802 ± 0.25</td>
<td>13.7 ± 0.11</td>
<td>0.66 ± 0.01</td>
<td>7.3 ± 0.09</td>
</tr>
<tr>
<td>Device A*</td>
<td>796 ± 0.39</td>
<td>15.8 ± 0.19</td>
<td>0.67 ± 0.02</td>
<td>8.4 ± 0.11</td>
</tr>
<tr>
<td>Device B</td>
<td>820 ± 0.12</td>
<td>15.2 ± 0.15</td>
<td>0.66 ± 0.01</td>
<td>8.1 ± 0.12</td>
</tr>
<tr>
<td>Device B*</td>
<td>817 ± 0.36</td>
<td>17.0 ± 0.23</td>
<td>0.66 ± 0.01</td>
<td>9.2 ± 0.08</td>
</tr>
</tbody>
</table>

*: presence of the scattering over-layer