Supplementary Information

Highly Electrocatalytic Counter Electrodes Based on Carbon Black for Cobalt(III)/(II)-Mediated Dye-Sensitized Solar Cells

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Experimental section

Materials

Carbon black powders (PRINTEX®L, furnace black, 99%) were obtained from Orion Engineered Carbons; according to the manufacturer’s specifications, the properties of this powder include BET surface area of 150 m² g⁻¹, DBP absorption of 120 ml per 100 g CB, pH value of 9.0, toluene extraction less than 0.1% (8 h), sieve residue less than 25 ppm (45 µm residue) and a particle diameter of ~23 nm. The amphiphilic ruthenium Z907 dye, cis-bis(isothiocyanato)-(2,2’-bipyridyl-4,4’-dicarboxylato)-(4,4’-di-nonyl-2’-bipyridyl) ruthenium(II), was acquired from Solaronix, and the organic Y123 dye, 3-{-6-{-4-[bis(2’,4’-dihexyloxybiphenyl-4-yl)amino]-phenyl}]-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b’]dithiphene-2-yl]-2-cyanoacrylic acid, was purchased from Dyenamo. Titanium dioxide pastes of PST-18NR and PST-400C were obtained from JGC C&C (JGC Catalysts and Chemicals Ltd., Japan), and the 30 NR-D paste was acquired from Dyesol. 2,2’-Bipyridyl (99+%), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, 98%) and nitrosyl tetrafluoroborate (NOBF₄, 98%) were purchased from Alfa Aesar. Chenodeoxycholic acid (CDCA, C₂₄H₄₀O₄, 97%), dimethyl sulfoxide [DMSO, (CH₃)₂SO, 99.9%], ethyl cellulose [EC, 30-60 mPa·s, 48%], tert-butanol [(CH₃)₃COH, 99%] and 4-tert-butylpyridine (tBP, C₉H₁₃N, 96%) were obtained from Sigma-Aldrich. Lithium perchlorate (LiClO₄, 98%) and titanium(IV) chloride (TiCl₄, 98%) were purchased from Fluka. Acetonitrile (CH₃CN, 99.5%), ammonium hexafluorophosphate (NH₄PF₆, 99.99%) and tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%) were acquired from Riedel-de Haën, Aldrich Chemistry and Tokyo Chemical Industry, respectively. Ethanol (99.9%) and methanol (99.8%) were purchased from J. T. Baker. All chemicals were used as received without further purification.

Preparation of Dye-Sensitized Photoelectrodes
Mesoporous titanium dioxide (TiO$_2$) films were screen-printed onto the cleaned FTO substrates. Prior to printing the TiO$_2$ films, a pre-treatment was adopted to coat a compact layer on the FTO substrates. This was performed by immersing the cleaned FTO in a 40 mM aqueous TiCl$_4$ solution at 70ºC for 30 min and then rinsing it with deionized water and ethanol. The TiO$_2$ films with a double-layered architecture, consisting of a transparent layer and a light scattering layer, were employed. Pastes of PST-18NR and 30 NR-D were introduced to prepare the transparent layers of 4.0 ± 0.2 and 7.5 ± 0.4 μm-thick for the Z907 and Y123 photoelectrodes, respectively. A 4.0 ± 0.2 μm-thick scattering layer was further printed onto transparent layers using the PST-400C paste. A sintering process at 500ºC was applied to all as-prepared TiO$_2$ electrodes, after which the electrodes were immersed in the Z907 dye solution for 6 h or in the Y123 solution for 15 h to perform the dye sensitization. The Z907 solution was composed of 0.5 mM Z907 dye and 50 mM CDCA in a tert-butanol/acetonitrile/DMSO mixture (9/9/2 by volume), and the Y123 solution was 0.1 mM Y123 dye in a tert-butanol/acetonitrile mixture (1/1 by volume).
Table S1. Comparison of efficient Z907 DSSCs using various CB counter electrodes in conjunction with the Co(bpy)$_3^{2+/3+}$ redox couple irradiated under standard 1 sun.

<table>
<thead>
<tr>
<th>Counter Electrode</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB-1-H</td>
<td>11.81</td>
<td>852</td>
<td>0.71</td>
<td>7.14</td>
</tr>
<tr>
<td>CB-2-H</td>
<td>11.79</td>
<td>853</td>
<td>0.71</td>
<td>7.14</td>
</tr>
<tr>
<td>CB-3-H</td>
<td>11.74</td>
<td>853</td>
<td>0.72</td>
<td>7.21</td>
</tr>
<tr>
<td>CB-4-H</td>
<td>11.80</td>
<td>854</td>
<td>0.71</td>
<td>7.15</td>
</tr>
<tr>
<td>STCB-1-H</td>
<td>11.72</td>
<td>829</td>
<td>0.63</td>
<td>6.12</td>
</tr>
</tbody>
</table>
**Fig. S1** Top-view SEM image of a pristine FTO conductive glass.

**Fig. S2** Top-view SEM images of (a) CB-1-H, (b) CB-2-H, (c) CB-3-H and (d) CB-4-H films.
Fig. S3  Cross-sectional SEM images of (a) CB-1-H, (b) CB-2-H, (c) CB-3-H and (d) CB-4-H films.

Fig. S4  Top-view SEM image of the CB-1 film with its magnified structure.
**Fig. S5** Equivalent circuit employed for fitting the Nyquist spectra of dummy cells.

**Fig. S6** Nyquist plot at 0 V of a bare FTO symmetrical dummy cell.
**Fig. S7**  Cyclic voltammograms of (a) Pt-105 and (b) CB-1-H electrodes measured using symmetrical dummy cells at a scan rate of 50 mV sec$^{-1}$ with repeated potential cycles.

**Fig. S8**  Long-term stability of Z907 DSSC equipped with a CB-1-H counter electrode measured under ambient conditions.
Fig. S9  Nyquist plot at 0 V of a dummy cell fabricated using STCB-1-H electrodes.

Fig. S10  Photovoltaic $J-V$ curves of Y123 DSSC employing a CB-1-H counter electrode measured under different light intensities (in sun).