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 m^2 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 ($CoCl_2 \cdot 6H_2O$, 98%) and nitrosyl tetrafluoroborate ($NOBF_4$, 98%) were purchased from Alfa Aesar. Chenodeoxycholic acid (CDCA, $C_{24}H_{40}O_4$, 97%), dimethyl sulfoxide [DMSO, $(CH_3)_2SO$, 99.9%], ethyl cellulose (EC, 30-60 mPa·s, 48%), *tert*-butanol [$(CH_3)_3COH$, 99%] and 4-*tert*-butylpyridine (tBP, $C_9H_{13}N$, 96%) were obtained from Sigma-Aldrich. Lithium perchlorate ($LiClO_4$, 98%) and titanium(IV) chloride ($TiCl_4$, 98%) were purchased from Fluka. Acetonitrile (CH_3CN, 99.5%), ammonium hexafluorophosphate (NH_4PF_6, 99.99%) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 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.

Counter Electrode	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
CB-1-H	11.81	852	0.71	7.14
CB-2-H	11.79	853	0.71	7.14
CB-3-H	11.74	853	0.72	7.21
CB-4-H	11.80	854	0.71	7.15
STCB-1-H	11.72	829	0.63	6.12

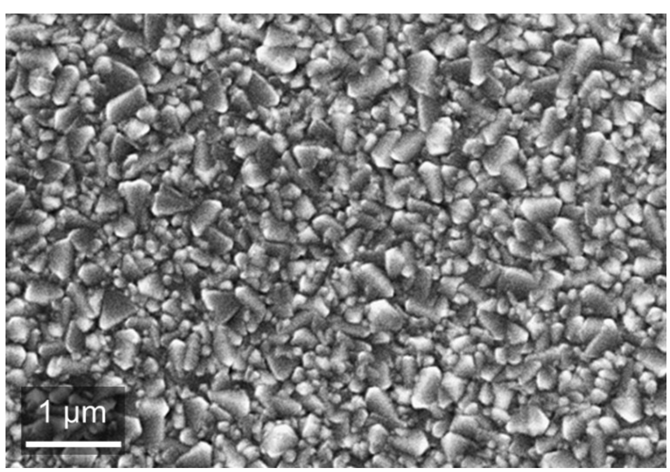

Fig. S1 Top-view SEM image of a pristine FTO conductive glass.

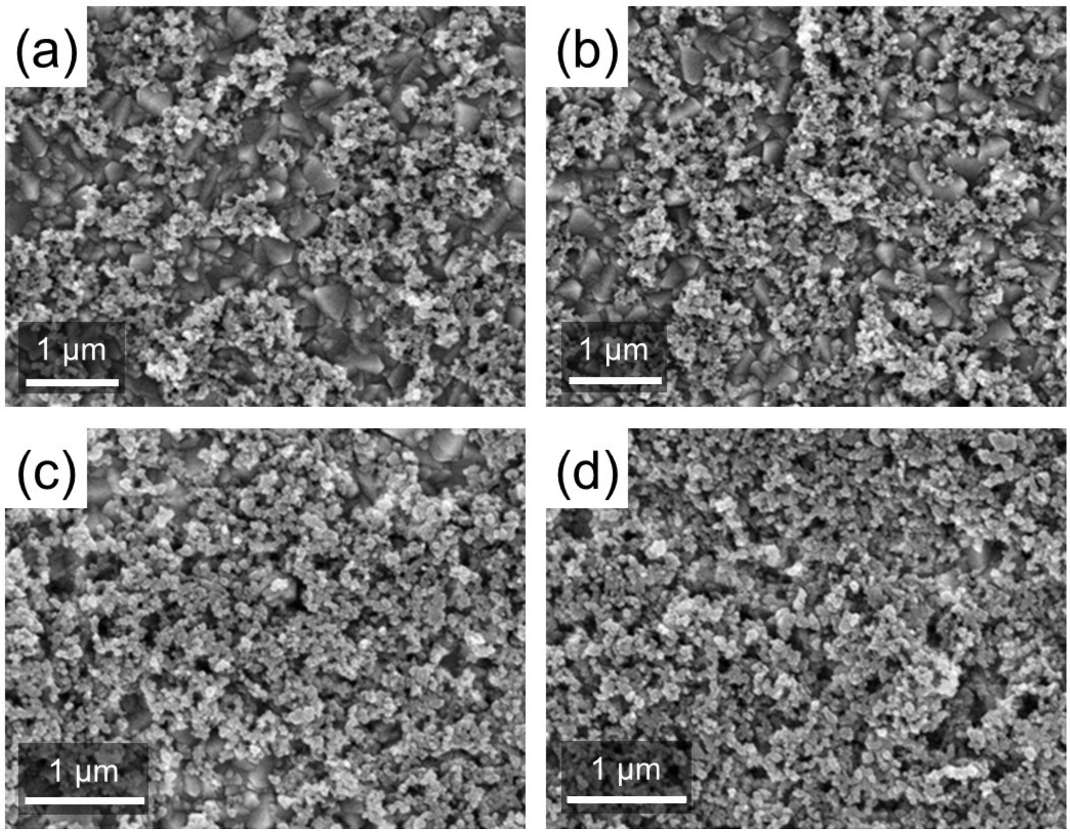

Fig. S2 Top-view SEM images of (a) CB-1-H, (b) CB-2-H, (c) CB-3-H and (d) CB-4-H films.

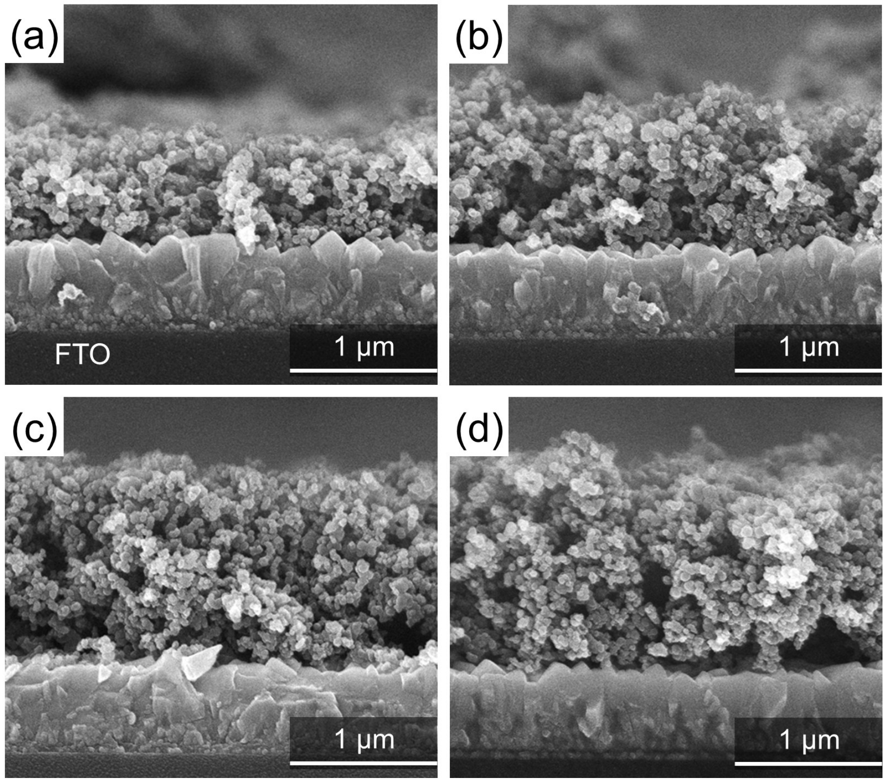

Fig. S3 Cross-sectional SEM images of (a) CB-1-H, (b) CB-2-H, (c) CB-3-H and (d) CB-4-H films.

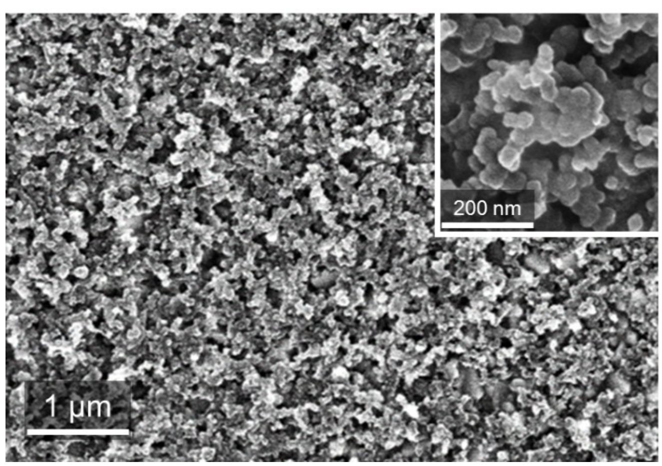

Fig. S4 Top-view SEM image of the CB-1 film with its magnified structure.

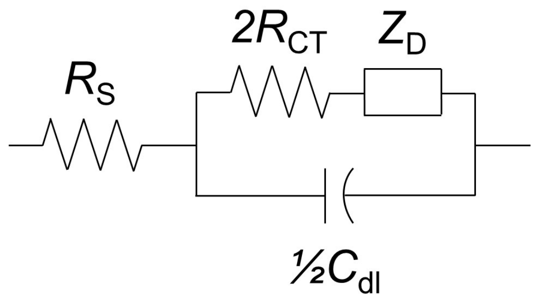

Fig. S5 Equivalent circuit employed for fitting the Nyquist spectra of dummy cells.

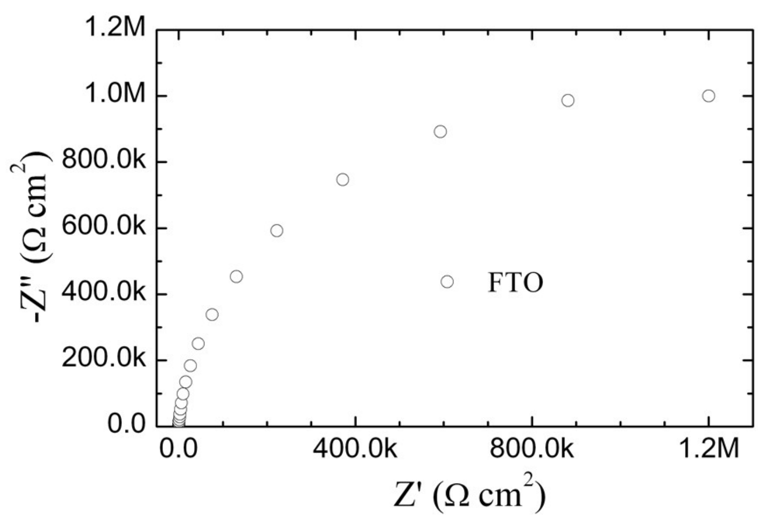

Fig. S6 Nyquist plot at 0 V of a bare FTO symmetrical dummy cell.

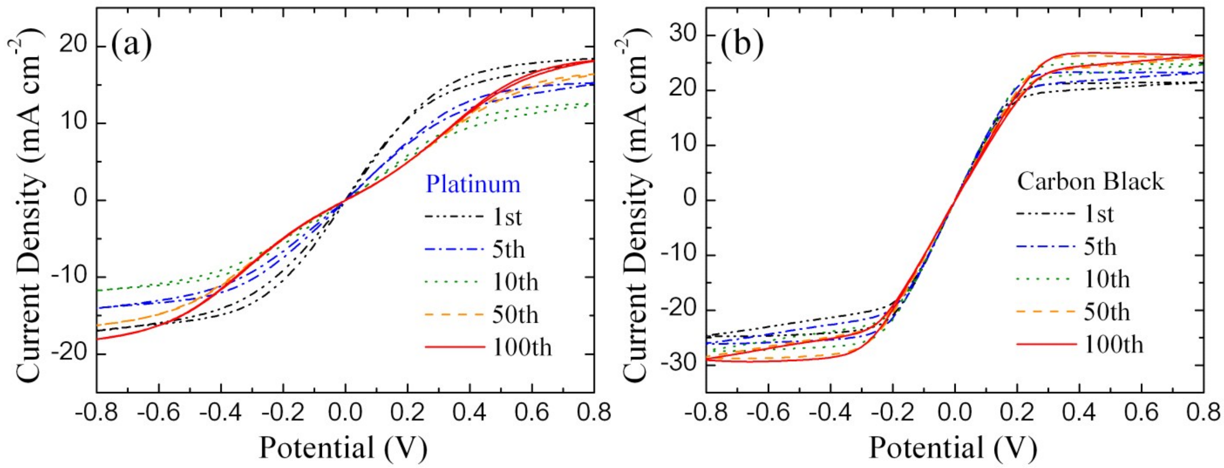

Fig. S7 Cyclic voltammograms of (a) Pt-105 and (b) CB-1-H electrodes measured using symmetrical dummy cells at a scan rate of 50 mV sec^{-1} with repeated potential cycles.

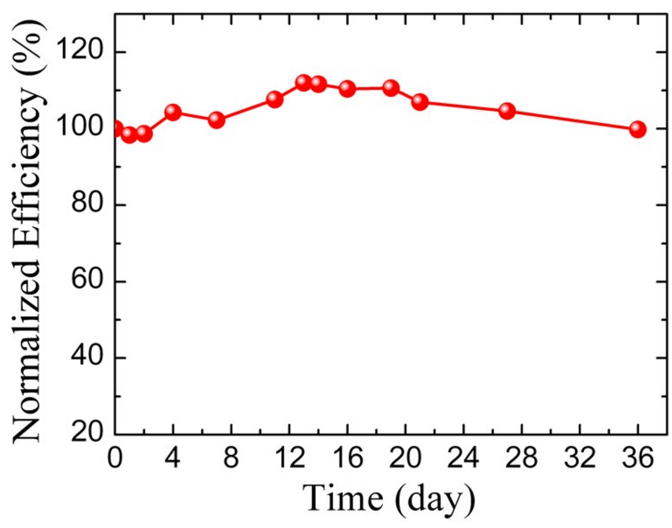

Fig. S8 Long-term stability of Z907 DSSC equipped with a CB-1-H counter electrode measured under ambient conditions.

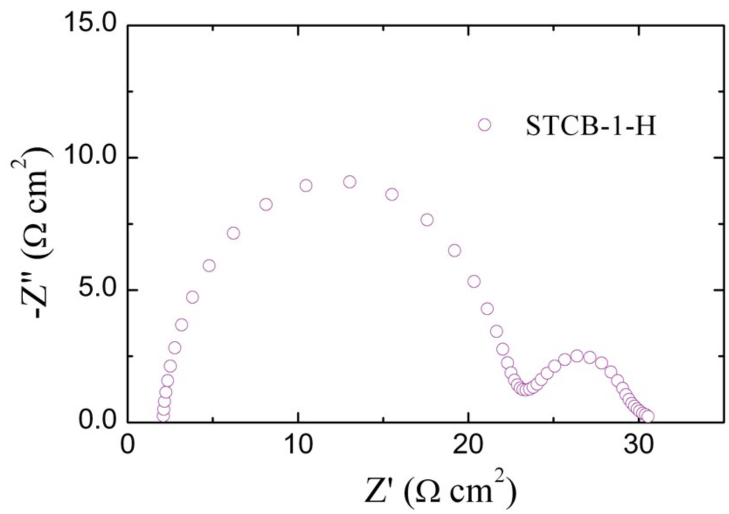

Fig. S9 Nyquist plot at 0 V of a dummy cell fabricated using STCB-1-H electrodes.

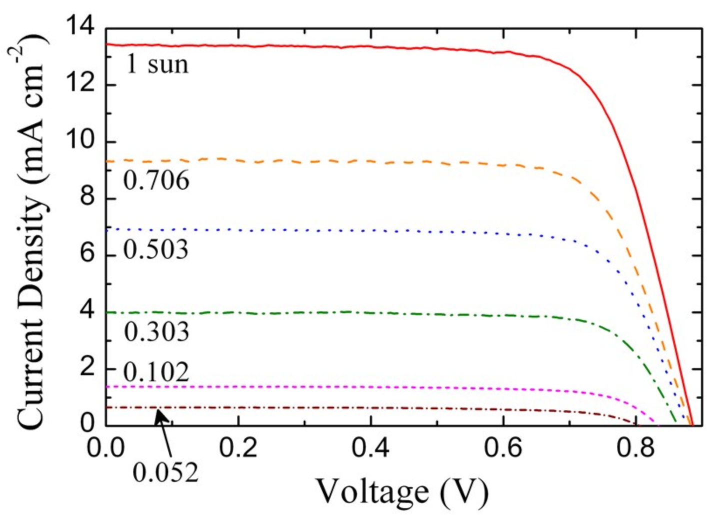

Fig. S10 Photovoltaic J–V curves of Y123 DSSC employing a CB-1-H counter electrode measured under different light intensities (in sun).