Supplementary Material (ESI) for Energy and Environmental Science
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Electronic Supplementary Information

For

A novel quasi-solid state dye-sensitized solar cell fabricated using a multifunctional network polymer membrane electrolyte

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Experimental Details and Measurements

Chemicals. Methylmethacrylate (MMA), 1,6-hexanediol diacrylate (HDDA), *tert*-butanol, iodine (I2), guanidinium thiocyanate (GuSCN), 4-*tert*-butylpyridine (tBP), ethylene carbonate (EC), propylene carbonate (PC) and acetonitrile (AN) were purchase from Sigma-Aldrich. MMA and HDDA were passed from the basic alumina column to eliminate inhibitor. 4-Aminobutyric acid, methacryloyl chloride, and tetrabutylammonium iodide (TBAI) were purchased from Tokyo Chemical Industry Co., LTD. Fluorine-doped SnO2 (FTO) glass, Ti-nanoxide T/SP. Ti-nanoxide R/SP, *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (N719), 1-butyl-3-methylimidazolium iodide (BMII) were purchased from Solaronix SA. 3-(2-Methyl-acryloylamino)propionic acid (MAP) was synthesized by following literature.[S1]

Field emission scanning electron microscopy (FE-SEM). The morphologies and diameters of nanoporous network polymer films on the surface of N719-sensitized TiO_2 films were determined by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800).

Ionic conductivities of nanoporous network polymer film. For the ionic conductivity, symmetric cells were fabricated by following procedure. The electrodes prepared from the surface-indcued polymerization and FTO conducting glass were assembled and sealed as a sandwich using a transparent 60 μm thick surlyn spacer (DuPont) by hot pressing. The interelectrode space was filled with the electrolyte solution through the predrilled hole in the FTO conducting glass surface, and the holes were covered with the Surlyn sheet and a thin cover glass, followed by heating. The electrolyte was consisted with 0.6 M BMII, 0.05 M LiI, and 0.03 M I_2 in a mixture of AN and VN (85:15 *v*/*v*). Ionic conductivity was measured by AC impedance spectroscopy a computer-controlled potentiostat(SP-200, BioLogic) under dark conditions. The frequency range examined was 1 MHz to 1 Hz at room temperature, and the impedance spectra were recorded at a potential of 0 V with an amplitude set at 50 mV. A conductivity (σ) was calculated using the equation ($\sigma = d / (R_b \times A)$, where where d is the distance between the two electrodes (42 μm), A is the active area of the device (0.25 cm^2), and R_b is the bulk resistance obtained from the electrochemical impedance spectrum). From the measured spectra, bulk resistances of nanoporous network polymer film were taken at the intercept of the Nyquist plot with the real axis of the impedance spectra [imaginary (-Z") v.s. real (Z')], then, the ionic conductivities were obtained from the bulk resistances found in the impedance diagrams.

Fabrication of DSCs. The FTO conducting glass for the substrate was washed using the washing method described above. The prepared FTO conducting glass was treated with 40 mM $TiCl_4$ aqueous solution at 70°C for 30 min and rinsed with deionized water and ethanol to support good mechanical and chemical adhesion at the interface between the transparent TiO_2 layer and the FTO conducting glass. The nanocrystalline TiO_2 photoanode consisted of a double-layered film. A 20 nm sized TiO_2 particles were screen-printed onto the $TiCl_4$-treated FTO surface. The transparent film thickness was controlled by reapplication using a similar printing process. The second light-scattering layer was prepared by screen-printing 400 nm anatase particles onto the transparent layer. For liquid junction DSCs, the thicknesses of the transparent layer and scattering layer was 6 μm and 2 μm, respectively, measured using an Alpha-Step 500 Surface Profilometer (Tencor Instruments, USA). The double layer prepared on the FTO glass was sintered at 500°C for 15 min according to a programmed heating procedure. After cooling to 60°C, the nanocrystalline TiO_2 electrode was immediately immersed in a dye solution to minimize moisture adsorption. The dye solution consisted of 0.3 mM N719 sensitizer in AN and *tert*-butanol (1:1 *v/v*). The control electrode was prepared by the TiO_2 electrodes were immediately immersed in the dye solution for 18h. The counter electrode was prepared by introducing two holes, using a sandblasting drill, into the FTO conducting glass for the substrate. The substrate was subsequently washed using the washing method described above. The Pt paste was spread onto the predrilled FTO conducting glass and subsequently sintered using a programmed heating procedure. The dye-coated photoanode encapsulated with nanoporous network polymer film and counter electrode were assembled and sealed as a sandwich using a transparent 60 μm thick surlyn spacer (DuPont) by hot pressing. The inter-electrode space was filled with the electrolyte solution through the predrilled hole in the counter electrode surface, and the holes were covered with the Surlyn sheet and a thin cover glass, followed by heating. The electrolyte was consisted with 0.6 M BMII, 0.03 M I_2, 0.1 M guanidinium thiocyanate, 0.05M, LiI, and 0.5 M 4-*tert*-butylpyridine in a mixture of AN and VN (85:15 *v*/*v*). In case of EC and PC based DSCs with liquid and quasi-solid electrolyte, the thicknesses of the transparent layer and scattering layer was 9 μm and 6 μm, and the electrolyte was consisted with 0.1 M I_2, 0.4 M TBAI, 0.6 M BMImI, 0.1 M GuSCN, and 0.5 M tBP in a mixture of EC and PC (4:1 *v*/*v*). For quasi-solid state DSSCs, the electrolyte was soaked onto polymer network membrane. The Pt coated FTO glass were covered on a working electrode and pressed.

Photoelectrochemical measurements. A 150 W xenon light source (Model No. 94022A, Oriel) was used to apply an illumination power of 100 $\mathrm{mWcm^{-2}}$ (the equivalent of one sun at AM 1.5) to the surface of the solar cell to simulate solar light irradiation. The incident light intensity was calibrated with reference to a Si solar cell equipped with an IR cutoff filter (KG-5, Schott). Comparison of the simulated light to the true solar spectrum in the region 350–750 nm determined a spectral mismatch of less than 2%. The I–V characteristics were obtained by measuring the photocurrent generated by the cells (under an applied external bias) using a Keithley model 2400 digital source meter (Keithley, USA). The voltage step and delay time for the measurement were 10 mV and 40 ms, respectively. For the influence of the temperature on the long-term stability of DSC, devices are aged in hot-air ovens at 65°C in dark condition.

Diffusion coefficients. The steady-state voltammograms were carried out on a SP-200 (BioLogic) electrochemical workstation at room temperature and scan rate was 10 mV/s. The electrolyte was consisted with 0.1 M I_2, 0.4 M TBAI, 0.6 M BMImI, 0.1 M GuSCN, and 0.5 M tBP in a mixture solvent of nonvolatile EC/PC (4:1 *v*/*v*), and was sandwiched between two identical platinized conducting glasses. Thicknesses of electrolyte were controlled to 15, 30, 45, and 60 μm.

Cross-sectional SEM images of neat TiO_2 and TiO_2 encapsulated network polymer

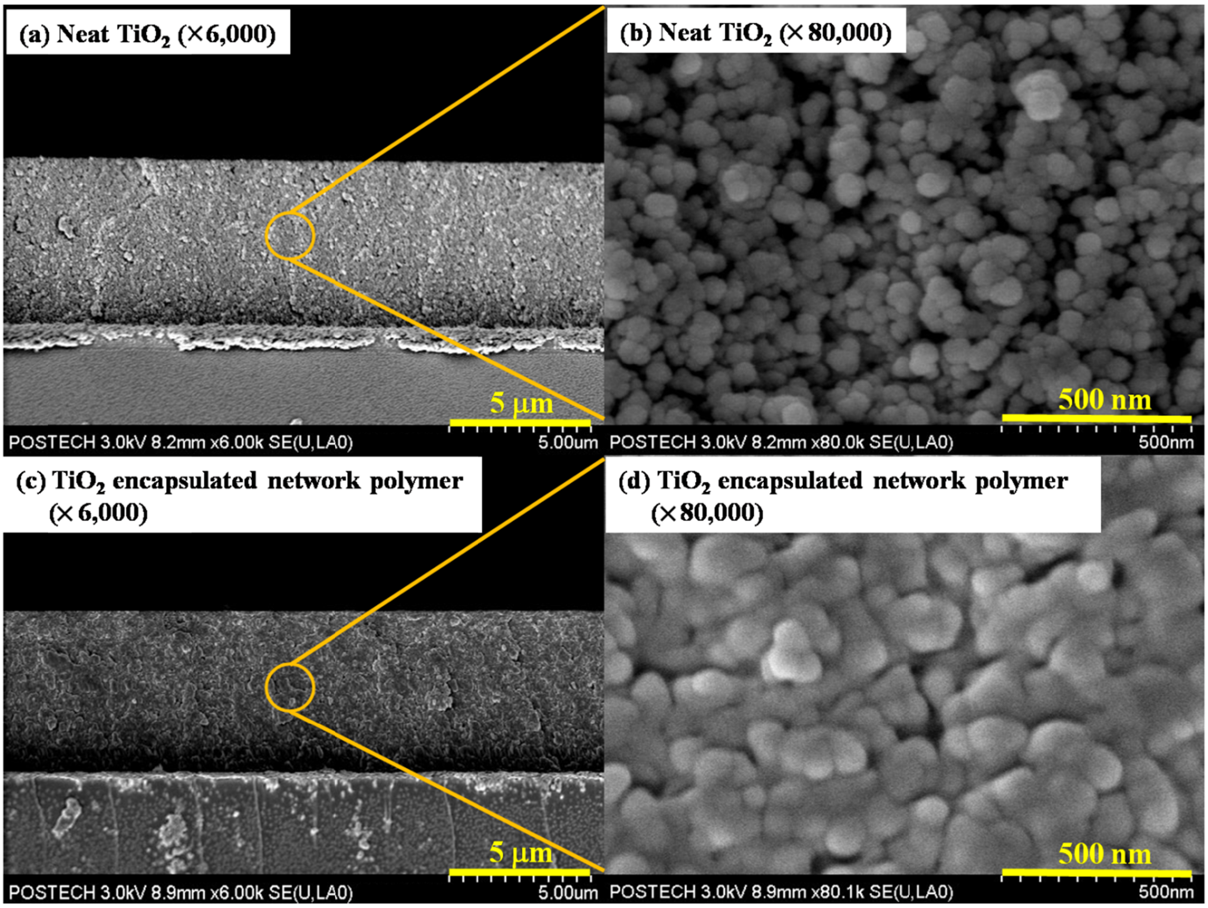

Fig. S1 (a) Field emission scanning electron microscopy (FE-SEM) photographs of the cross-section views of neat TiO_2 ((a) and (b)) and TiO_2 encapsulated network polymer ((c) and (d)).

Transmittances of electrodes; dye-sensitized TiO_2, dye and MAP treated TiO_2, and encasulated TiO_2

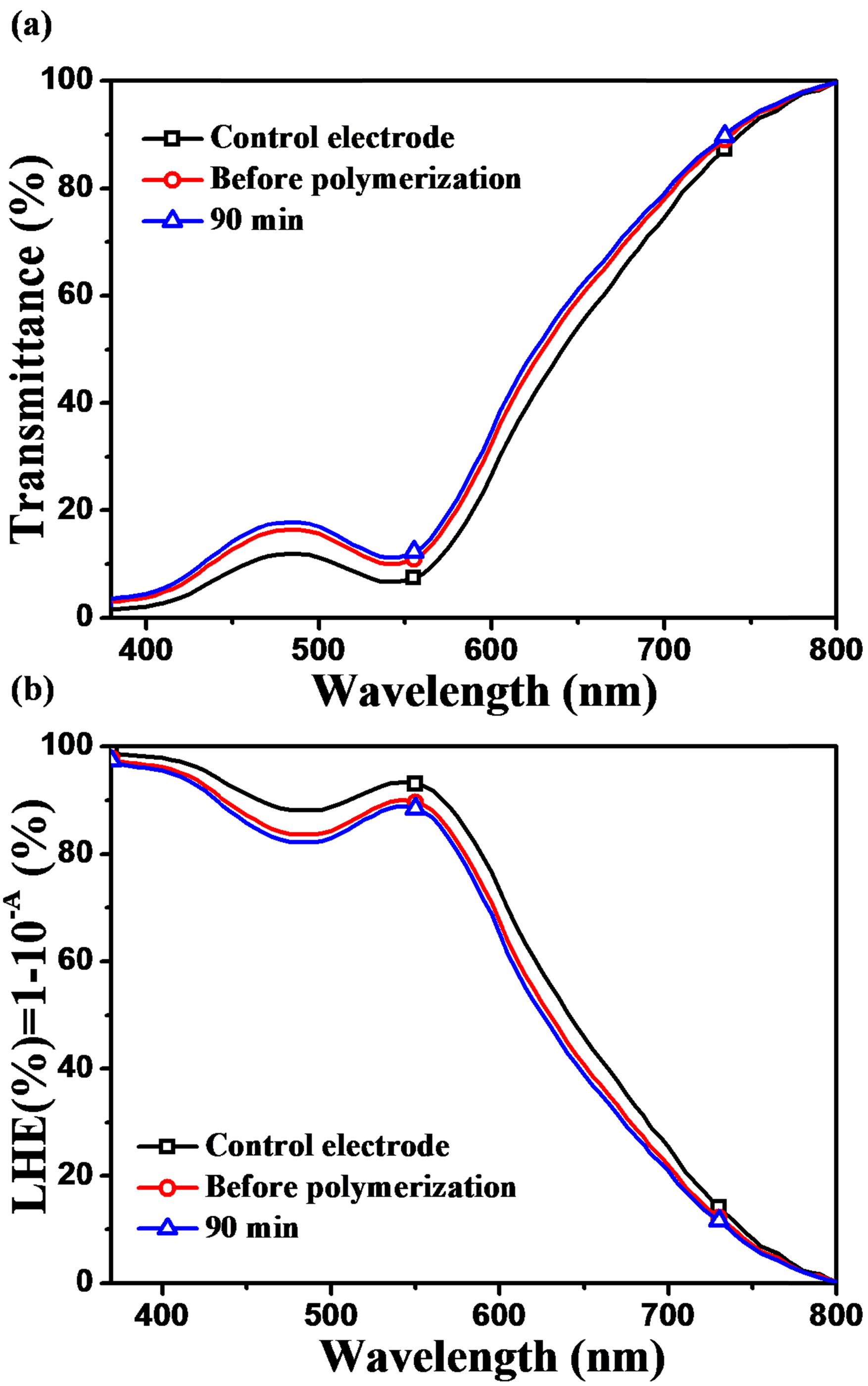

Fig. S2 (a) Transmittances and (b) light harvesting efficiencies of the dye (N719) of neat electrode (without scattering layer) sensitized with dye only, electrode prepared by the coadsorption of the dye and MAP, and electrodes after the surface-induced polymerization reaction of MMA and HDDA (90 min). LHE data were calculated by the equation of $1\text{-}10^{-A}$. (A: absorption intensity).

Nyquist plots and Bode plots of devices employing liquid (control) and network polymer electrolyte (Q-DSC)

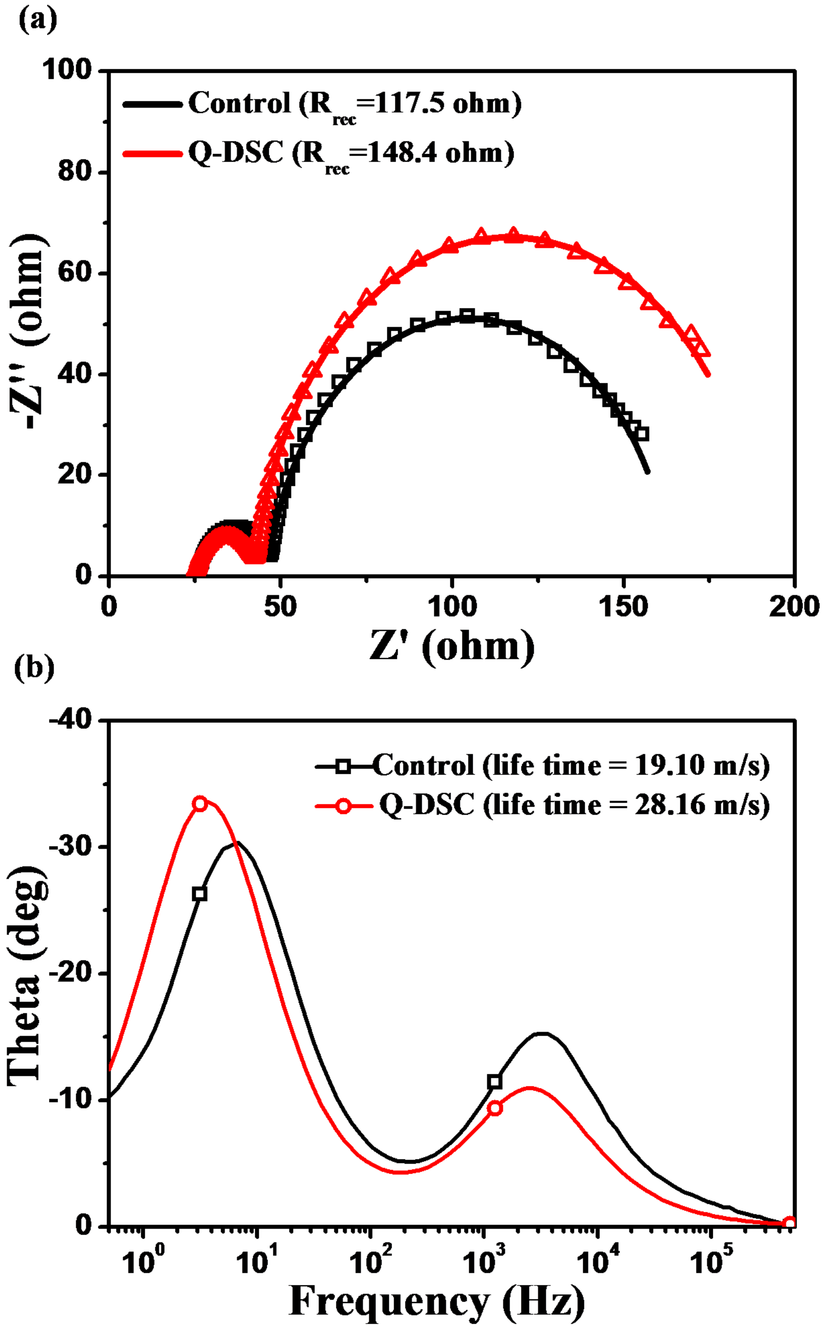

Fig. S3 (a) Nyquist and (b) Bode plots for devices employing liquid (control) and multifunctional network polymer membrane electrolytes (Q-DSC) as measured using electrochemical impedance spectroscopy (EIS) in the dark under -0.75 V applied voltage and 50 mV amplitude.

I-V curves of devices having TiO^2/Pt interface and TiO^2-polymer/Pt interface

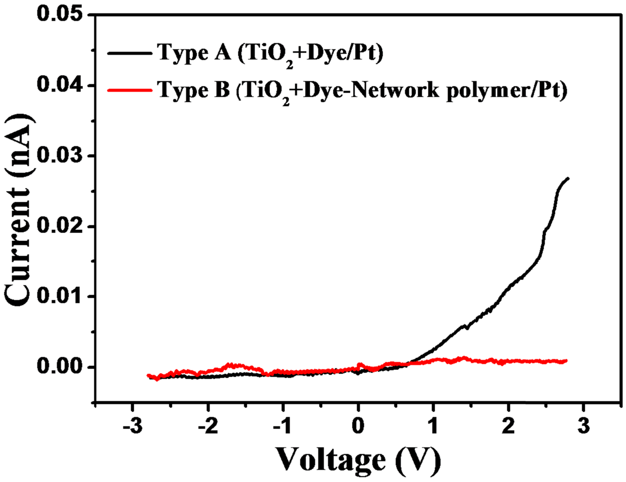

Fig. S4 *I-V* curves of Device A and Device B. Device A was consisted with N719 sensitized TiO2 anode and Pt electrode, and Device B was consisted with N719 sensitized anode encapsulated network polymer film and Pt electrode. Then, two electrodes were sandwiched by clips. Scan rate was 50 mV/s.

Summary of recombination resistances (R_{rec}) and electron life times (τ_n) at the interfaces of TiO_2 anodes

Table S1. Summary of recombination resistances (R_{rec}) and electron life times (τ_n) at the interfaces of TiO_2 anodes.

Device	R_{rec} (Ω)	τ_n (ms)
Control	117.5	19.10
Q-DSC	148.4	28.16

Reference

S1 S. Varghese, A. K. Lele, D. Srinivas and R. A. Mashelkar, *J. Phys. Chem., B* 2001, **105**, 5368.