

Electronic Supplementary Information (ESI)

Excellent Optical and Interfacial Performance of a PEDOT-*b*-PEG Block Copolymer Counter Electrode for Polymer Electrolyte-based Solid-state Dye-sensitized Solar Cells

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Experimental

Materials: PEDOT-*b*-PEG block copolymer doped with perchlorate (1 wt% in nitromethane solution), poly(ethylene oxide) (PEO, Mw = 1,000,000 g/mol), poly(ethylene glycol) dimethyl ether (PEGDME; Mw = 500 g/mol), potassium iodide (KI), iodine (I₂), 1-methyl-3-propylimidazolium iodide (MPII), 4-tert-butylpyridine (tBP), guanidinium thiocyanate (GuSCN), chenodexoycholic acid (CDCA), 3,4-ethylenedioxythiophene (EDOT), sodium

dodecyl sulfate (SDS), iron(III) chloride (FeCl_3), acetonitrile (ACN), methanol (MeOH), and dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich. Transparent, conductive, fluorine-doped tin oxide (FTO) glass substrates (TEC-7) were purchased from Pilkington. Titanium dioxide (TiO_2) nanoparticulate paste (18NR-T and WER2-O) and C106 Ru dye were purchased from Dyesol. All chemicals were used as received without further purification.

Preparation of counter electrodes (CEs): Pt CE; FTO glasses were spin-coated with 0.01 M H_2PtCl_6 in isopropanol and sintered at 400°C for 30 min.

PEDOT nanofiber (NF) CE; PEDOT-NFs were prepared according to literature procedures.^{1,2} Briefly, 2 wt% PEDOT NF dispersed in a methanol/DMSO mixture (95:5 wt/wt) was spin-coated onto FTO glass and dried in a vacuum oven at 60°C for 2 h.

PEDOT-*b*-PEG CE; A PEDOT-*b*-PEG solution in nitromethane was filtered (0.2 mm) and sonicated (2 min) to relax aggregation. The solution was spin-coated onto FTO and then dried under ambient conditions.

Preparation of the solid-state polymer electrolyte (SPE): To prepare the PEO-based polymer electrolytes, ACN was used to dissolve a blend of PEO and PEGDME at a molar ratio of $[-\text{O}-]:[\text{MPEI}]:[\text{KI}]:[\text{I}_2] = 10:1:0.05:0.1$, in which the weight ratio of PEO to PEGDME was fixed at 4:6. Thereafter, electrolyte additives of 0.5 mM tBP and 0.1 M GuSCN were dissolved. A detailed description of the process is provided in our previous report.³

Fabrication of DSCs: An FTO glass substrate was cleaned with a detergent solution, DI water, and ethanol in an ultrasonic bath for 15 min per step. The cleaned FTO substrate was used

for both working and counter electrodes. To prepare the working electrodes, a blocking layer of TiO₂ film was formed by immersion of the cleaned FTO glasses in a 40 mM TiCl₄ aqueous solution at 70 °C for 30 min and subsequent sintering at 450 °C for 30 min. A 20.5- μ m-thick TiO₂ nanoparticulate film, in which the light scattering layer was 4 μ m thick, was screenprinted onto a 0.21-cm²-area blocking layer-coated FTO glass before sintering at 450 °C for 30 min. After being cooled to ambient temperature, the substrate underwent the same TiCl₄ treatment described above. For single sensitization, the prepared TiO₂ film was then dipped into a 0.5 mM C106 dye solution for 12 h or into 0.5 mM CDCA. The dye solution consisted of a mixture of ACN and *tert*-butanol (1:1, v/v). To prepare the complete device, a 25- μ m-thick polymer (Surlyn) used as a spacer was thermally attached to the working electrode, and the as-prepared polymer electrolyte was cast and dried. In the final stage, the device was enclosed in a Pt CE using a two-step method.⁴

Characterization

The UV–Vis absorption spectrum was monitored with a JASCO/V-670 spectrophotometer in order to investigate the optical transmittance and reflectance spectra, which were collected by a spectrophotometer equipped with a spherical accessory. The contact angle measurements were obtained with a contact angle analyzer (Drop Shape Analysis System DSA100, Kruss) using 1 μ L droplets of polyethylene glycol (PEG, Mw: 400) on the CEs. Scanning electron microscope (SEM) images were captured using an FE-SEM (JSM-6701F, JEOL) at an acceleration voltage of 5.0 kV and an average working distance of 8.0 mm. The topography of the polymer film was studied using atomic force microscopy (AFM) with a scanning probe microscope equipped with a NanoScope[®] IIIa controller operated in tapping

mode and with the extended electronic module enabling height imaging. The current-voltage (J - V) characteristics of the DSC were obtained under 1 sun illumination conditions (AM1.5G, 100 mW/cm²) with a Newport (USA) solar simulator (300-W Xe source) and a Keithley 2400 source meter. The cell active area was shaded by a 0.24-cm²-area black mask. The incident photon-to-current conversion efficiency (IPCE) of the DSC was measured using a QEX7 (PV Measurements, Inc.). Impedance spectroscopy (IS) using Autolab (Metrohm) measurements was performed under the same illumination conditions as the J - V curves and different bias voltage that ranged from 0.5 to 0.75 V and frequencies between 1 MHz and 0.1 Hz, with an AC perturbation of 20 mV. Tafel polarization measurements were conducted through a symmetric cell assembled with two of the same CEs filled with SPE as used in the DSCs. The active area of the symmetric cell was 0.64 cm² at a scan rate of 50 mV/s using Autolab (Metrohm).

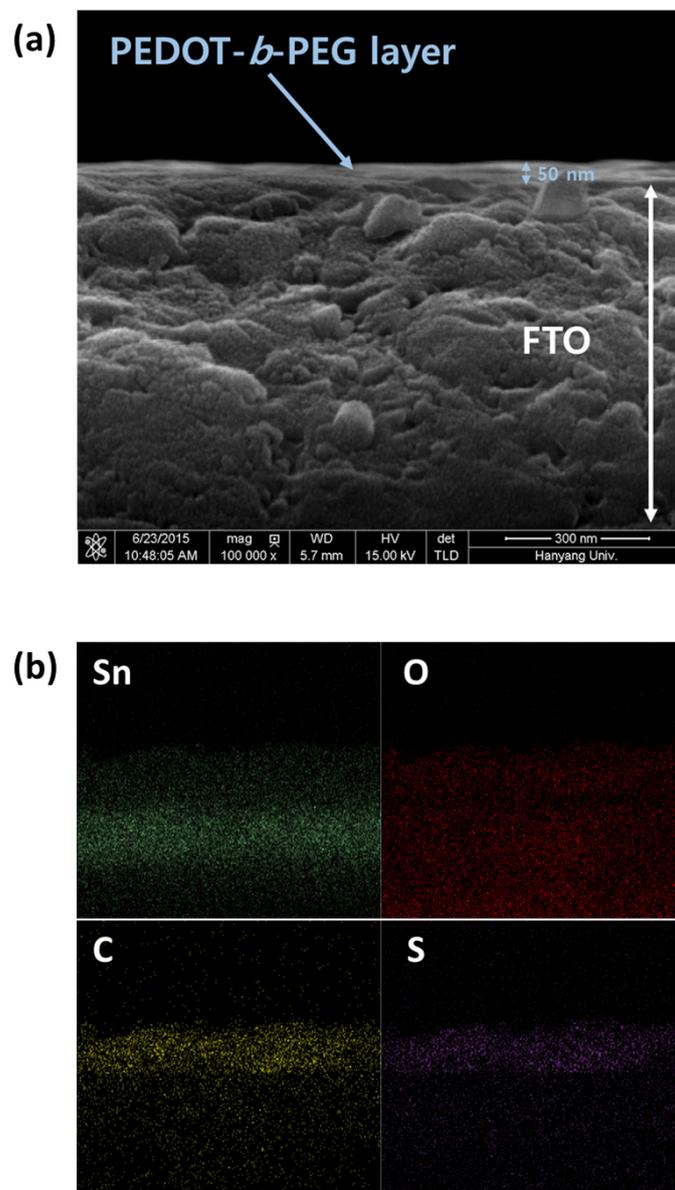


Fig. S1 (a) Cross-sectional SEM image and (b) cross-sectional energy dispersive X-ray (EDS) spectral mapping of the Sn, O, C, and S elements in PEDOT-*b*-PEG CE on FTO.

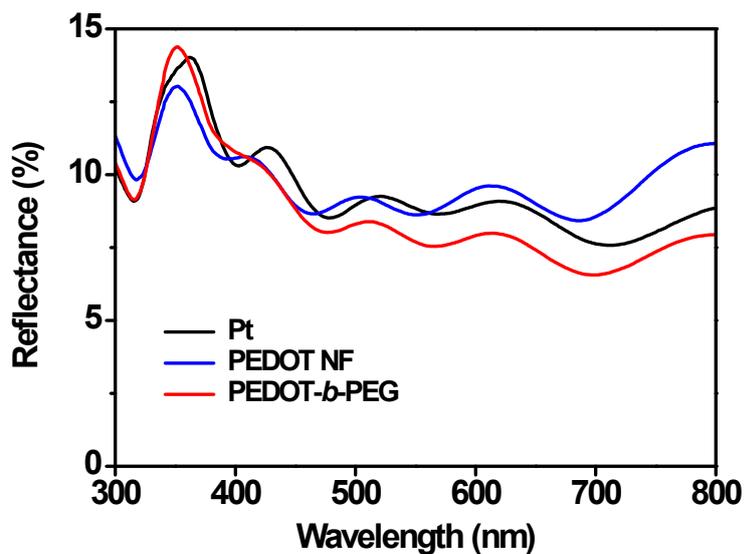


Fig. S2 Reflectance spectra of Pt (black-line), PEDOT NF (blue-line), and PEDOT-*b*-PEG block copolymer (red-line) CEs.

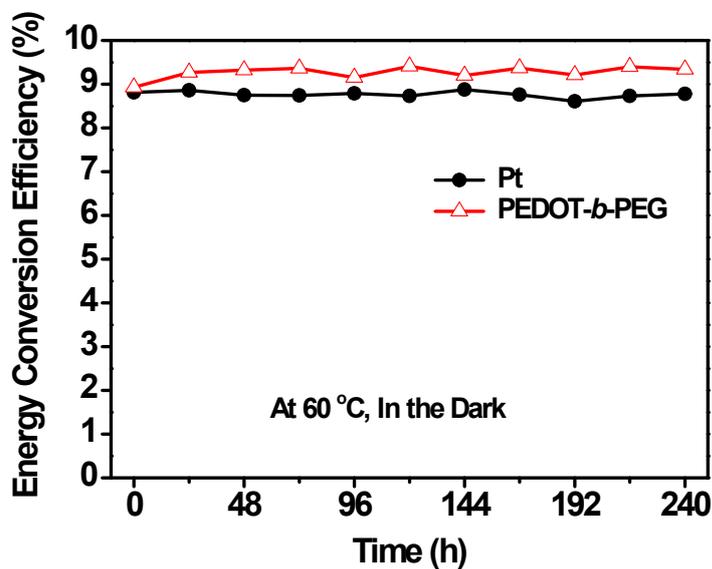


Fig. S3 Long-term stability of DSCs assembled with Pt (black-squares), and PEDOT-*b*-PEG block copolymer (red-triangles) coated counter electrodes until 240 hours of storage in the dark at 60 °C (measured on the 1 sun illumination conditions).

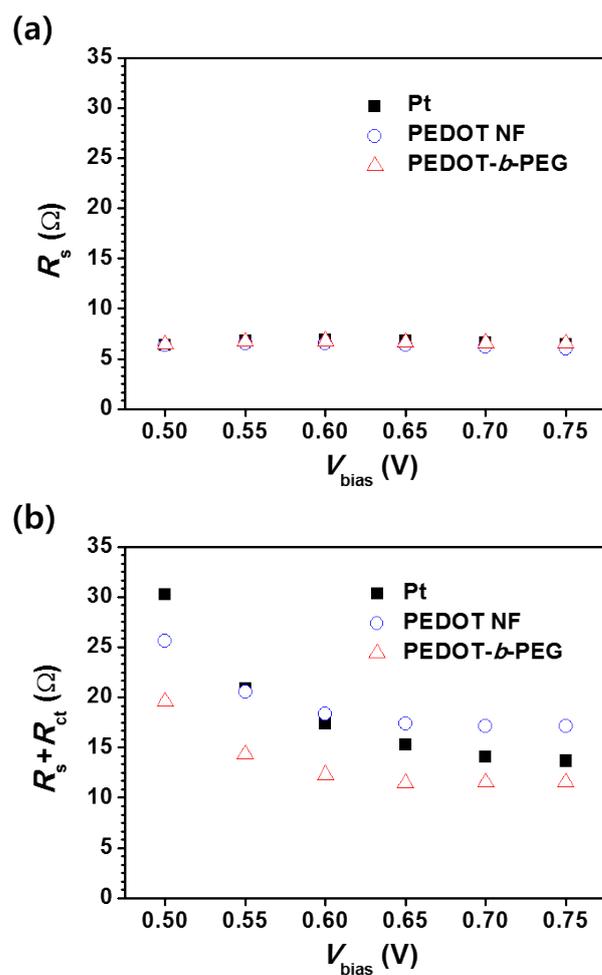


Fig. S4 (a) Sheet resistance (R_s), and (b) the sum of both parameters ($R_s + R_{ct}$) with respect to applied voltage (V_{app}) for Pt (black squares), PEDOT NF (blue circles), and PEDOT-*b*-PEG block copolymer (red triangles) coated CEs in DSCs according to IS measurements at 1 sun conditions.

References

1. M. G. Han and S. H. Foulger, *Small*, 2006, **2**, 1164.
2. T. H. Lee, K. Do, Y. W. Lee, S. S. Jeon, C. Kim, J. Ko and S. S. Im, *J. Mater. Chem.*, 2012, **22**, 21624.

3. H. Chae, D. Song, Y.-G. Lee, T. Son, W. Cho, Y. B. Pyun, T.-Y. Kim, J. H. Lee, F. Fabregat-Santiago, J. Bisquert and Y. S. Kang, *J. Phys. Chem. C*, 2014, **118**, 16510.
4. J. H. Kim, M.-S. Kang, Y. J. Kim, J. Won, N.-G. Park and Y. S. Kang, *Chem. Commun.*, 2004, 1662.