

## Supporting Information

### **Highly Conductive and Stable Graphene/PEDOT:PSS Composite as Metal Free Cathode for Organic Dye-Sensitized Solar Cells**

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## Preparation of Counter Electrodes

The aqueous dispersion of PEDOT:PSS was diluted in ethanol (1:3 v/v) and sonicated for 30 min. After then, GnP powder with different weight percent (0.02, 0.1, 0.5, and 1 %) were added into the diluted PP solutions and sonicated for another 30 min. The well dispersed pure GnP (1 wt%) solution was prepared in 2-propanol by sonication for 30 min. The resulting solutions were deposition directly onto FTO glass (8  $\Omega$ /Sq. TEC-8, Pilkington) by using an electro-spray (e-spray) technique. Briefly, GnP, PP, and GnP/PP (with varying wt% of GnP) solutions were loaded into a plastic syringe equipped with a 23-gauge stainless steel hypodermic needle, which was connected to a high voltage power supply (ESN-HV30). A voltage of  $\sim$  9 kV was applied between a metal orifice and the FTO substrate at a distance of 3.5 cm. The feed rate was controlled by the syringe pump (KD Scientific, KDS220) at a constant flow rate of 50  $\mu$ L/min. The sample electrodes were obtained by an e-spray for 2 min, and then they were sintered at 80  $^{\circ}$ C for 30 min under vacuum. The GnP, PP, and different wt% GnP mixed PP-modified FTO electrodes were denoted as GnP, PP, PPG<sub>x</sub> (x = 1-4). As a reference, the Pt CEs were also prepared by spin coating of 5 mM ethanolic solution of chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) on FTO and sintered in an electric muffle furnace at 400  $^{\circ}$ C for 20 min.

## Fabrication of a Symmetrical Dummy cell

A symmetrical dummy cell was fabricated with two identical Pt-, GnP-, PP-, or PPG<sub>x</sub> (x = 1-4)-FTO sheets, which were separated by 60- $\mu$ m thick Surlyn (Solaronix, Switzerland) tape as a sealant and spacer (active area, *ca.* 0.36 cm<sup>2</sup>). The sheet edges were coated by an ultrasonic soldering system (USS-9200, MBR Electronics) to improve the electrical contacts.

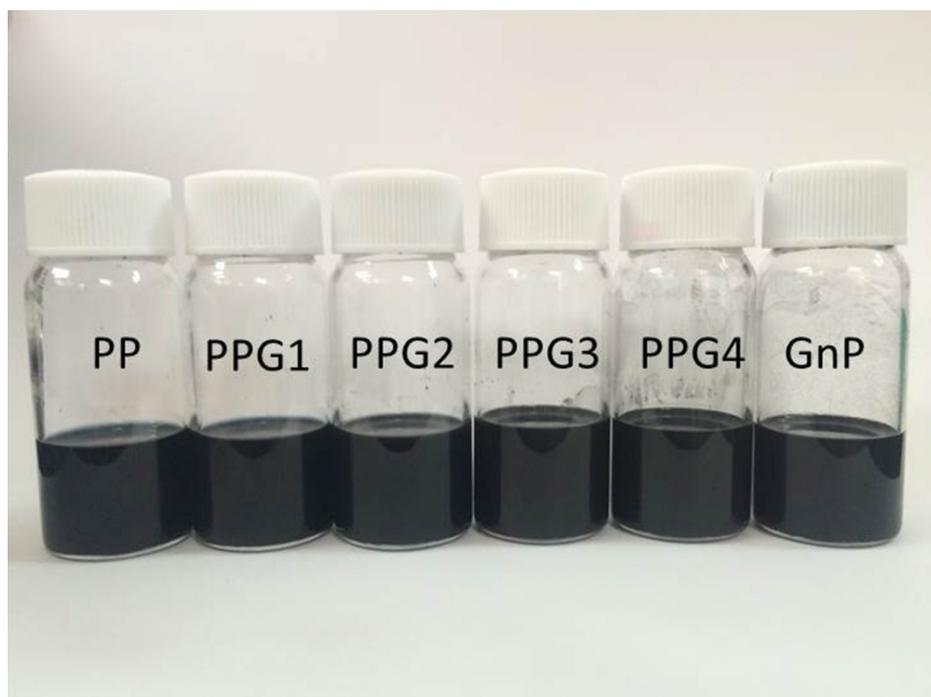
The cell was filled with the Co-complex electrolyte solution through a hole in one FTO support, which was finally sealed by Surlyn.

### **DSSCs Fabrication**

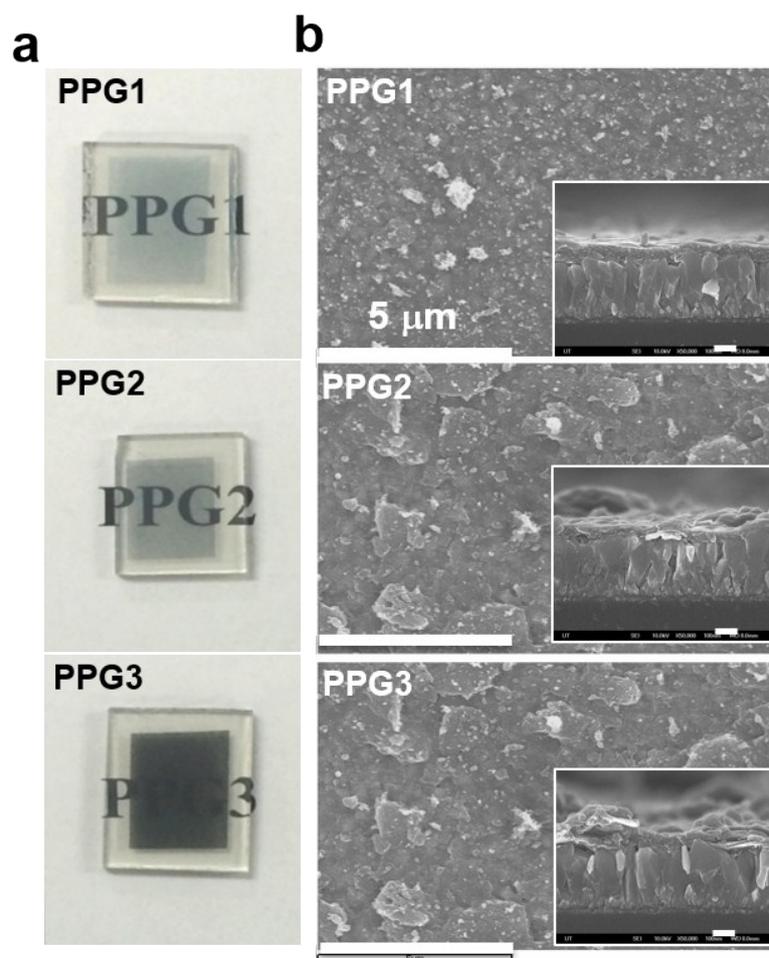
FTO glass plates were cleaned in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. The FTO glass plates were immersed in  $\text{TiCl}_4$  (40 mM) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline  $\text{TiO}_2$  layer on the FTO glass plates was prepared by screen printing  $\text{TiO}_2$  paste (Dyesol, 18NR-T) and then drying at 120 °C. The  $\text{TiO}_2$  electrodes were gradually heated under an air flow at 350, 375, 450, and 500 °C for 5, 5, 15, and 15 min, respectively. A paste for the scattering layer containing 400 nm anatase particles (CCIC, PST-400C) was deposited by screen printing and then dried for 1 h at 120 °C. Then, the  $\text{TiO}_2$  electrodes were gradually heated under an air flow at 350, 375, 450, and 500 °C for 5, 5, 15, and 15 min, respectively. The resulting layer was composed of a 6- $\mu\text{m}$  thick transparent layer and a 4- $\mu\text{m}$  thick scattering layer. The  $\text{TiO}_2$  electrodes were treated again with  $\text{TiCl}_4$  at 70 °C for 30 min and sintered at 500 °C for 30 min. A solar simulator equipped with a 200 W Xenon lamp (McScience, Polaronix® K201) was used to generate the simulated light AM 1.5G. A photovoltaic power meter (McScience, Polaronix® K101 LAB20) was used to measure the current density-voltage ( $J$ - $V$ ) curves. The incident light intensity was adjusted to 100  $\text{mW cm}^{-2}$  (1 sun) by a standard mono-Si solar cell (PV Measurement Inc, PVM 396) being certified by US National Renewable Energy Laboratory. Incident-photon-to-current conversion efficiency (IPCE) spectra were measured by an IPCE measurement system (McScience, Polaronix® K3100) with 300 W xenon light source. The intensity of the incident

monochromatic light was also calibrated with the same standard mono-Si solar cell.

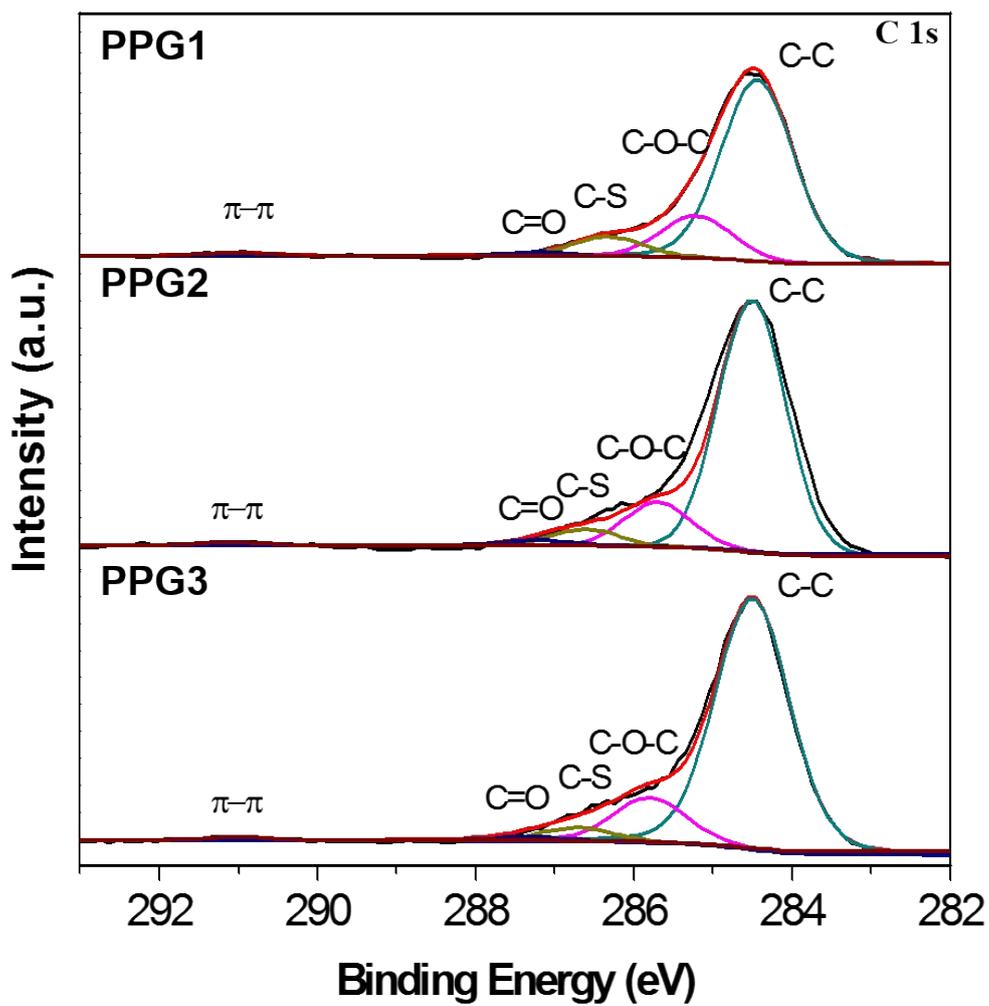
The sintered TiO<sub>2</sub> electrodes were dipped into a THF/ethanol (v/v, 1/2) solution containing 0.1 mM Y123 dye (Dyename, Sweden) and 5 mM chenodeoxycholic acid (CDCA) (Sigma-Aldrich) co-adsorbent and kept at room temperature for 12 h. The dye loaded photoelectrodes (active area *ca.* 0.25 cm<sup>2</sup>) and the Pt, GnP, PP, and PPG<sub>x</sub> (x=1-4) CEs were sandwiched by heating at 80 °C with a hot-melt film (40-μm thickness, Surlyn) as a spacer and sealing between the electrodes. The liquid-type Co-complex electrolyte was injected into the cells through the drilled holes at the CE and the holes were sealed with cover glass using surlyn.



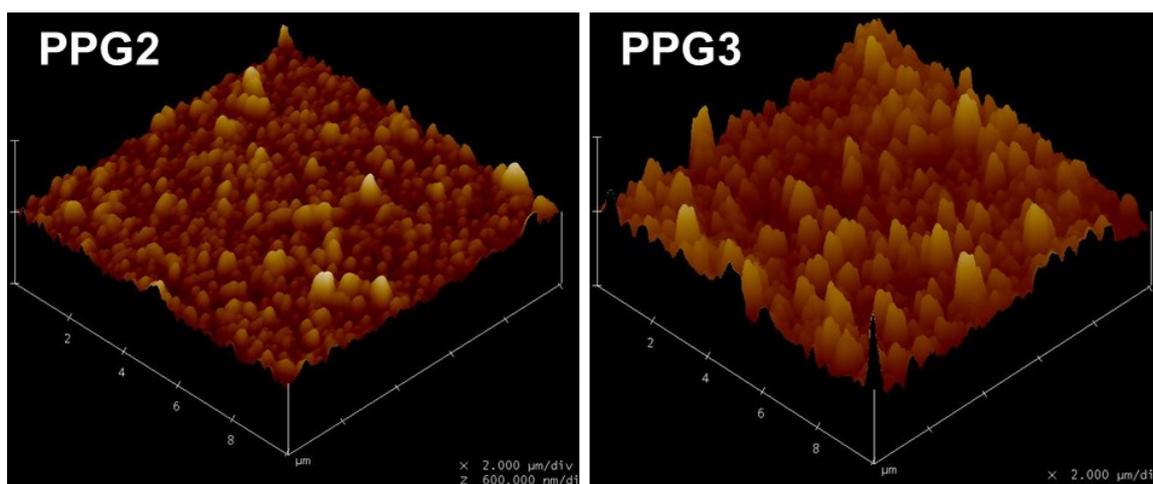
**Figure S1.** Photographic images of the dispersed PP, PP/GnPs (PPG<sub>x</sub>, x = 1, 2, 3, 4).



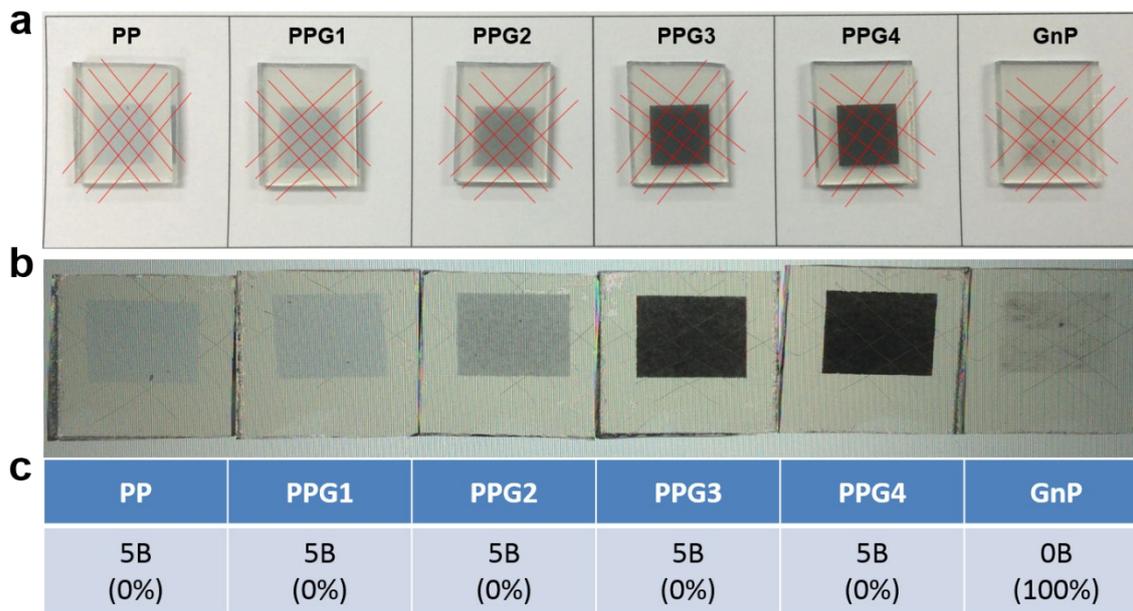
**Figure S2.** (a) Photographic images of the dispersed PP, PPG<sub>x</sub> ( $x = 1, 2, 3$ ), and GnP samples. (b) Top view SEM images of PPG<sub>x</sub>,  $x=1, 2, 3$ . The insets are cross-section view SEM images of same films.



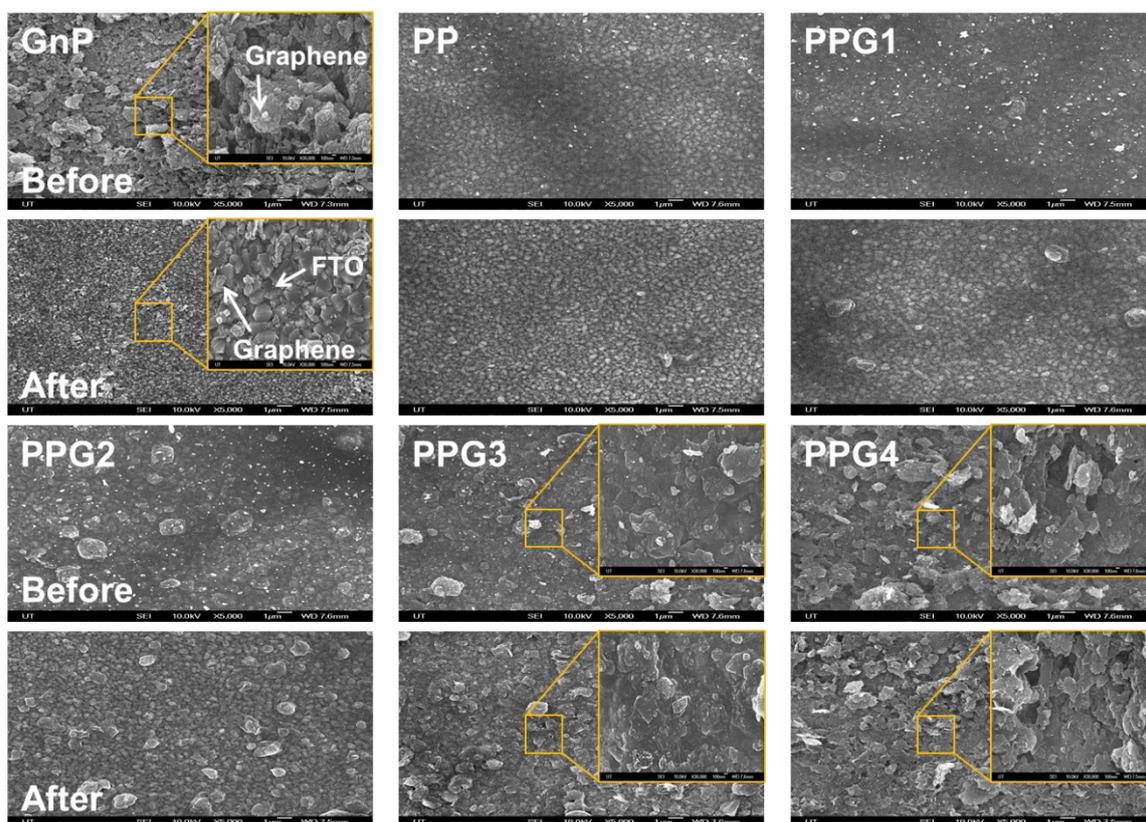
**Figure S3.** C 1s XPS peaks of PPG<sub>x</sub> (x = 1, 2, 3) samples.



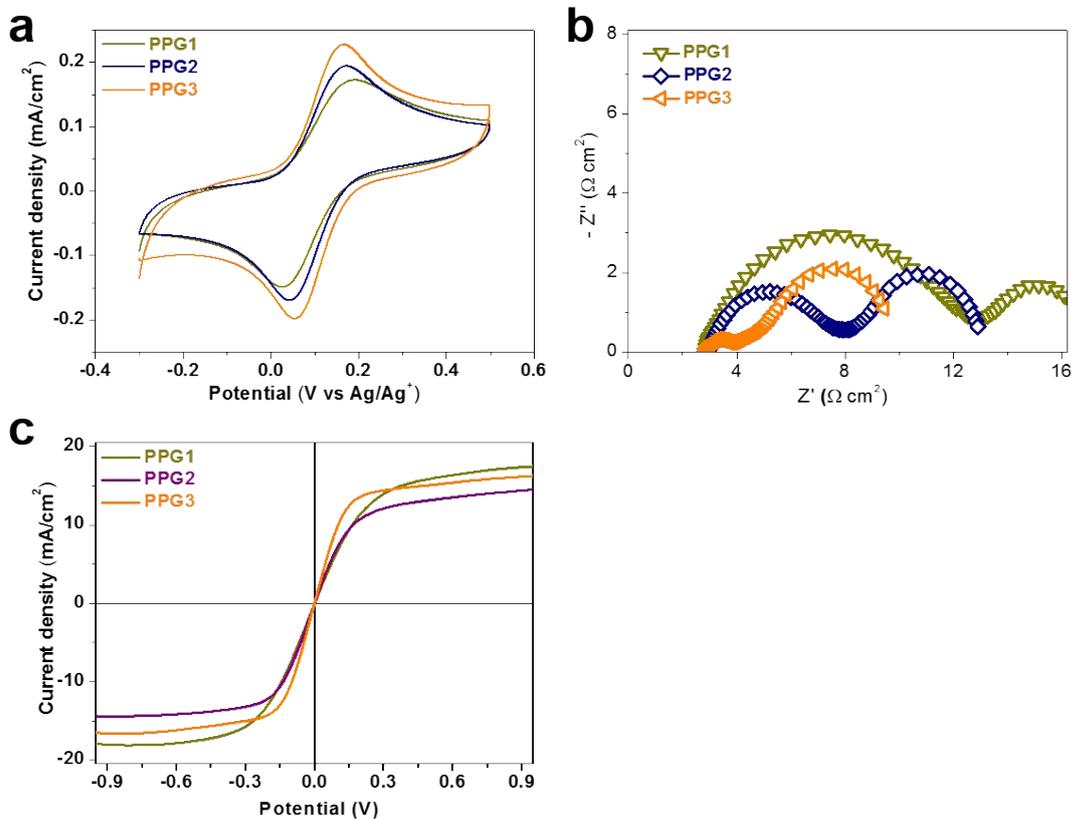
**Figure S4.** Topographical AFM images of the GnP, PP, and PPGx (x=2, 3) samples on FTO.



**Figure S5.** Top-view potgraphic images of the PP, PPG<sub>x</sub> (x = 1-4), and GnP films (a) as prepared, (b) after adhesion test using scotch tape, and (c) the percent of their peeling off from the FTO surface.



**Figure S6.** Top-view FE-SEM images of the GnP, PP, and PPG<sub>x</sub> (x = 1-4) samples before and after ‘scotch tape test’.

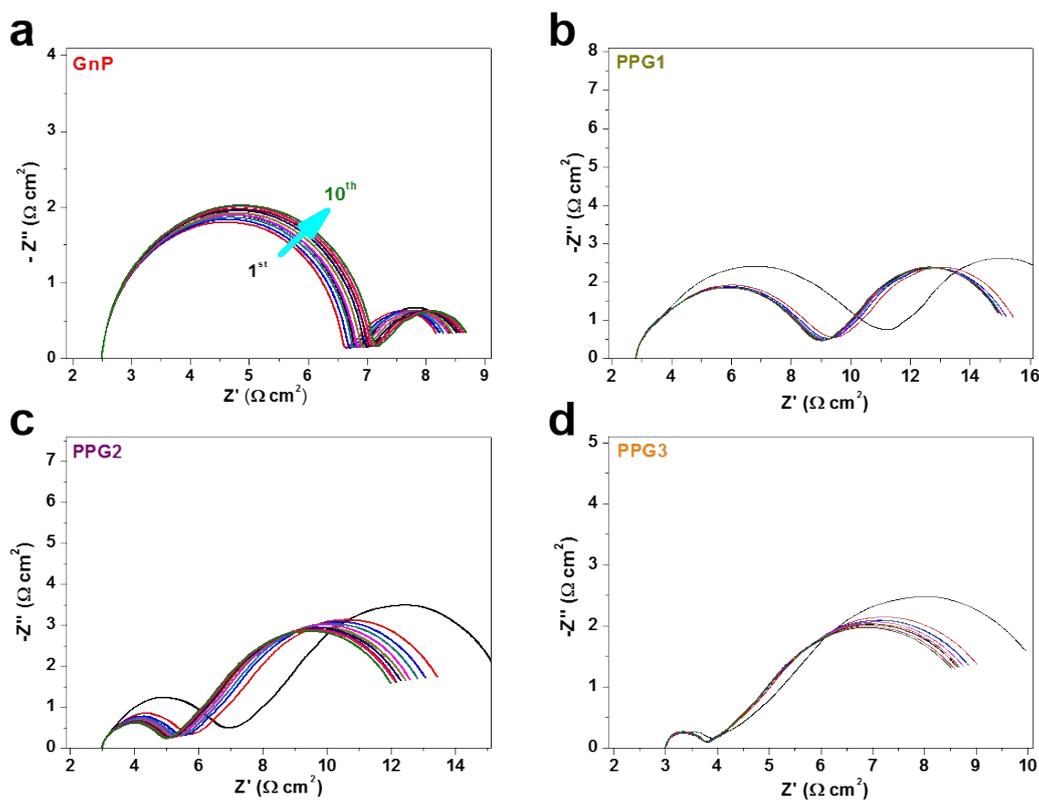


**Figure S7.** (a) CV plots of the PPG<sub>x</sub> (x=1, 2, 3) CE in 100 times lower concentration of Co(bpy)<sub>3</sub><sup>2+/3+</sup> redox couples used for a typical performance test in DSSC, and 0.1 M LiClO<sub>4</sub> as the supporting electrolyte; scan rate:10 mV/s. (b) Nyquist plots of the PPG<sub>x</sub> (x=1, 2, 3) symmetrical dummy cells. (c) Linear sweep voltammograms (LSV) of Co(bpy)<sub>3</sub><sup>2+/3+</sup> redox couples at PPG<sub>x</sub> (x=1, 2, 3) dummy cells; scan rate 10 mV/s.

The electro-active surface area was calculated according to the following Randles-Sevcik equation: <sup>S1,S2</sup>

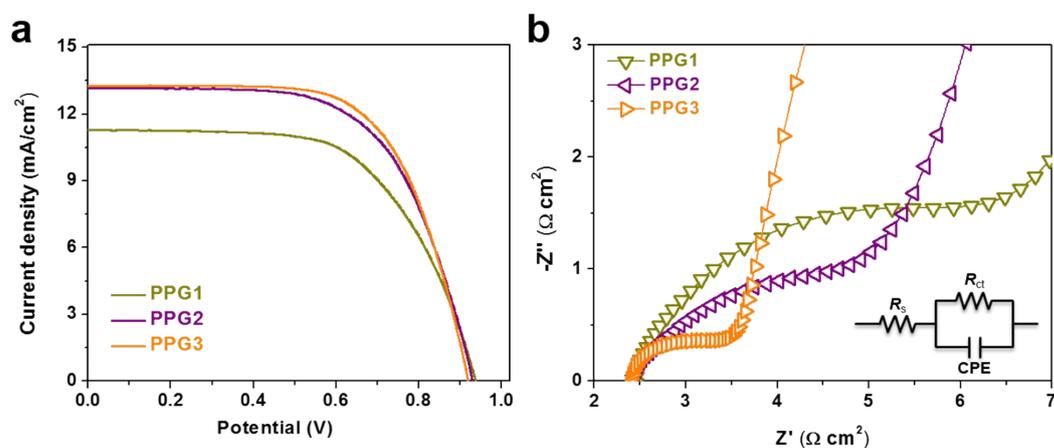
$$A = \frac{I_p}{2.69 \times 10^5 \times n^{3/2} \times D^{1/2} \times v^{1/2} \times C} \quad (\text{S1})$$

where,  $A$  is the electro-active surface area ( $\text{cm}^2$ ),  $I_p$  is the peak current ( $A$ ), and  $n = 1$ ,  $D$  is the diffusion coefficient obtained from the chronoamperometry (Figure 2c),  $V$  is the scan rate ( $\text{V/s}$ ),  $C$  is the concentration of  $\text{Co}(\text{bpy})_3^{2+/3+}$  ( $\text{mol/ml}$ ).



**Figure S8.** Nyquist plots of the PPGx ( $x=1, 2, 3$ ) CEs-based dummy cells under potential cycling in an acetonitrile solution of  $\text{Co}(\text{bpy})_3^{2+/3+}$ . The sequence of measurements was as follows:  $100 \times \text{CV}$  scans (from  $0 \text{ V} \rightarrow 1 \text{ V} \rightarrow -1 \text{ V} \rightarrow 0 \text{ V} \rightarrow 1 \text{ V}$ ; scan rate  $50 \text{ mV/s}$ );  $30 \text{ s}$

relaxation at 0 V; EIS measurements at 0 V from  $10^6$  to 0.1 Hz. This sequence of electrochemical stability testing was repeated 10 times.



**Figure S9.** The  $J-V$  characteristics of the DSSCs-based on PPGx ( $x = 1, 2, 3$ ) CEs under one sun illumination (AM 1.5G).

**Table S1.**  $R_{CT}$  of the symmetrical dummy cells of the Pt, GnP, PP, and PPG<sub>x</sub> (x =1-4) CEs with respect to the potential cycling together with the  $R_{CT}$  of those CEs-based DSSCs.

CEs	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> ) after 1 <sup>st</sup> CV cycle	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> ) after 10 <sup>th</sup> CV cycle	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> ) in real DSSCs
Pt	3.17	7.38	3.40
GnPs	2.34	2.52	4.95
PP	3.0	1.93	6.68
PPG1	3.97	3.01	7.72
PPG2	1.89	0.98	5.67
PPG3	0.53	0.41	2.15
PPG4	0.1	0.3	0.94

## References

- S1. N. Papageorgiou, *Coord. Chem. Rev.*, 2004, **248**, 1421-1446.
- S2. Y. Xue, J. Liu, H. Chen, R. Wang, D. Li, J. Qu, L. Dai, *Angew. Chem. Int. Ed.*, 2012, **51**, 12124-12127.

