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Reduced graphene oxide-Ta3N5 composite: a potential cathode for efficient $Co(bpy)_3^{3+/2+}$ mediated dye-sensitized solar cells

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Synthesis of FNE29. The organic dye **FNE29**, 2-cyano-3-[5"-(4-(diphenylamino)phenyl)-3',3",4-tri-n-hexyl-[2,2',5',2"]terthiophene]acrylic acid, was prepared according to a previous method.[1] The chemical structure and UV-vis absorption spectrum are shown in Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2, δ ppm): 8.32 (s, 1H), 7.29-7.31 (br, 2H), 7.17 (t, *J* = 7.2 Hz, 4H), 6.81-7.01 (m, 11H), 2.63-2.70 (m, 6H), 1.47-1.54 (m, 6H), 1.10-1.30 (m, 18H), 0.73-0.78 (m, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2, δ ppm): 153.68, 140.89, 122.79, 122.71, 122.34, 121.21, 119.61, 118.94, 118.08, 116.80, 116.70, 35.11, 33.57, 25.33, 25.31, 25.22, 25.20, 23.97, 23.77, 23.73, 23.69, 23.66, 23.64, 23.61, 23.59, 23.58, 23.29, 23.22, 22.86, 22.83, 22.77, 22.71, 22.62, 16.13, 14.69, 14.54, 14.47, 13.90, 13.86, 13.81, 11.30. HRMS (ESI, *m/z*): $[M-H]^-$ calcd for ($C_{52}H_{57}N_2O_2S_3$), 837.358; found, 837.359.

Synthesis of $Co(bpy)_3^{3+/2+}$ redox couple: The cobalt complex, $[Co(bpy)_3](PF_6)_2$, and its oxidized form (Co^{3+}) were prepared according to the reported procedure[2]. A mixture of $CoCl_2 \cdot 6H_2O$ (1.0 g, 4.12 mmol, 98% Aldrich) and 2,2'-bipyridyl (2.2 g, 13.94 mmol,) were dissolved in methanol (100 mL) and refluxed for 2 h. After the resulting solution was cooled to room temperature, ammonium hexafluorophosphate (3.4 g, 20.86 mmol) was more added to the reaction mixture. The precipitate was filtrated and the residue was dried under vacuum to obtain $[Co(bpy)_3](PF_6)_2$ (3.1 g, 92% yield) as yellow solid. Additional oxidation of $[Co(bpy)_3](PF_6)_2$ (500 mg, 0.612 mmol) was carried out by using $NOBF_4$ (107 mg, 0.916 mmol) in acetonitrile (15 mL) at room

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temperature for 0.5 h. After removed solvent under reduced pressure, the residue was dissolved in acetonitrile (5 mL) and NH_4PF_6 (502 mg, 3.08 mmol) was more added to the solution. The precipitate of $[Co(bpy)_3](PF_6)_3$ (530 mg) was filtrated, dried under vacuum and used without further purification.

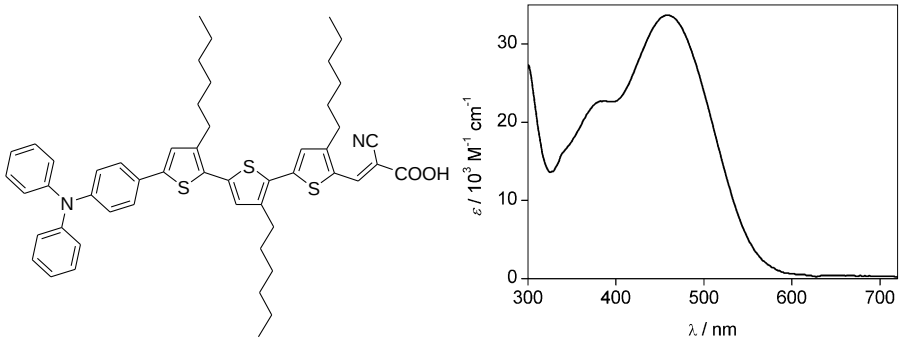

Figure S1. Chemical structure of the **FNE29** dye and its UV-vis absorption spectrum in toluene.

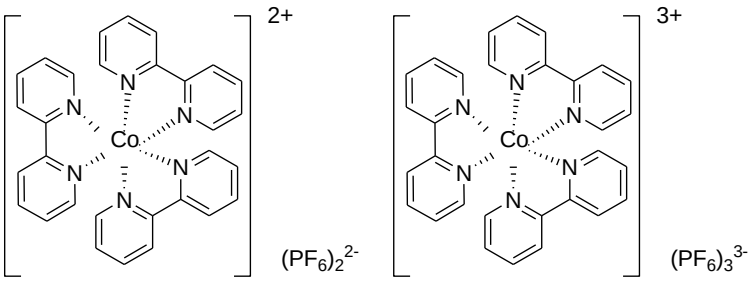

Figure S2. Chemical structures of the Co(II)/Co(III) redox couple.

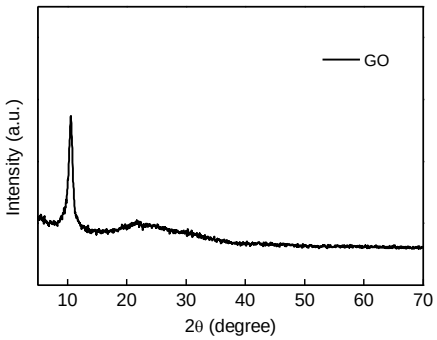

Fig. S3 XRD pattern of GO.

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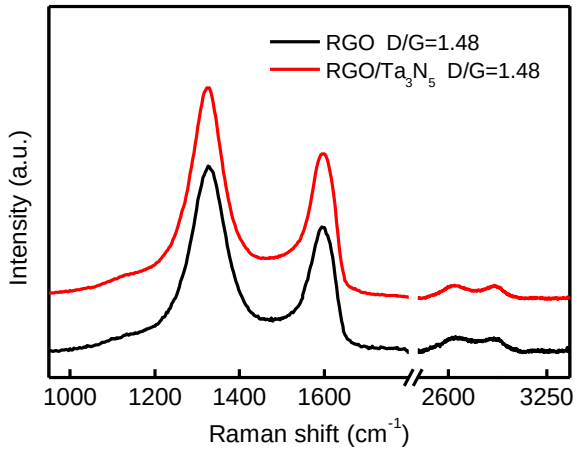

Fig. S4 Raman spectra for RGO and PGOT film.

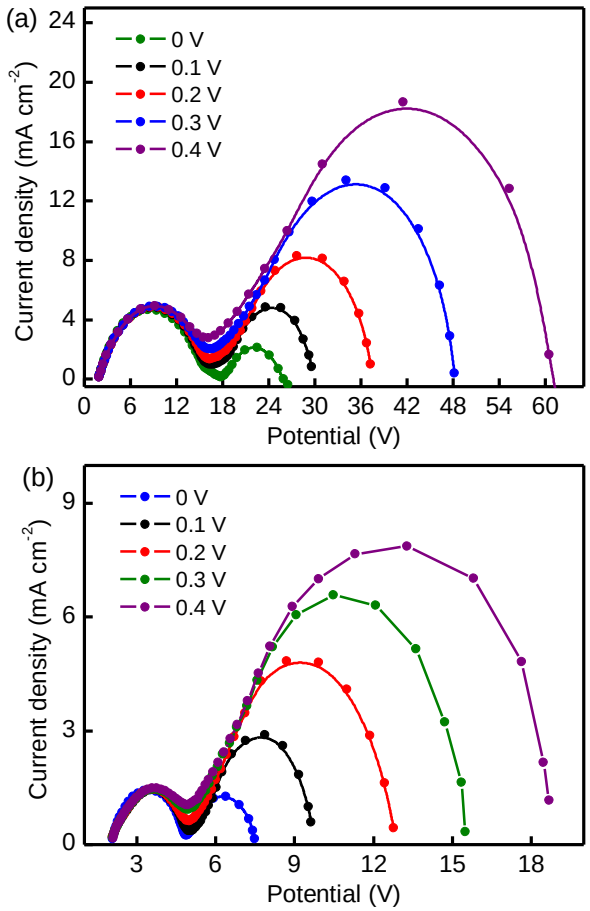

Fig. S5 Nyquist plot of electrochemical impedance spectra measured from 100 mHz to 100 kHz on symmetrical dummy cell with (a) RGO and (b) RGO-Ta_3N_5 electrodes under different bias voltages of 0, 0.1, 0.2, 0.3 and 0.4 V, respectively. As bias is applied, Z_n increases dramatically as a result of depletion of Co-ions from the bulk electrolyte.

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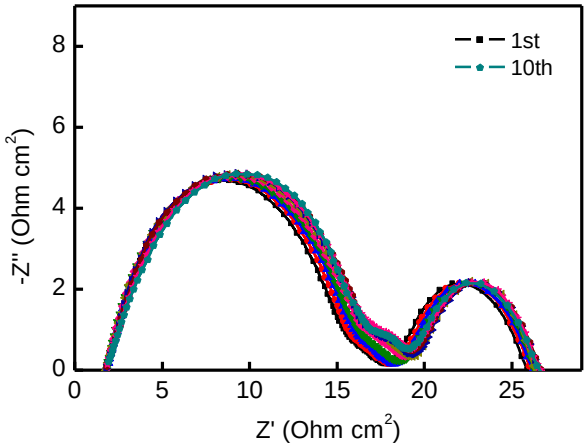

Fig. S6 Nyquist plots of EIS for the potential cycling stability of the symmetric cells with RGO electrode. The dummy cell was first subjected to cyclic voltammetry scanning of -1 to 1 V with a scan rate of 50 mV s^{-1}, followed by 20 s relaxation at 0 V, and then EIS measurement at 0 V form 50 mHz to 1 MHz was performed. This sequence of eectrochemical tests was repeated 10 times.

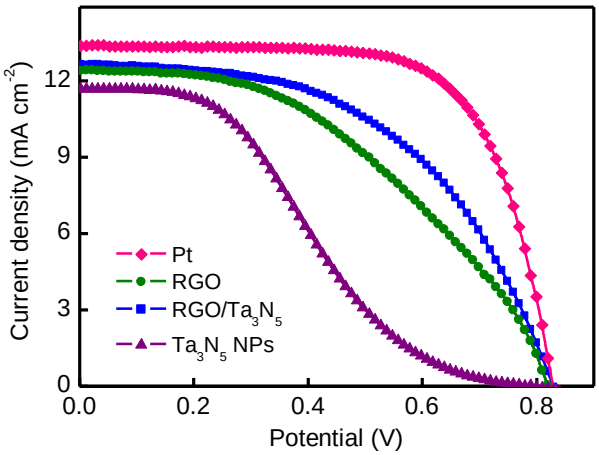

Fig. S7 Photocurrent density-voltage characteristics of DSSCs with different CEs of Pt, RGO, Ta_3N_5 NRs and PGOT measured at 1 sun illumination.

Table S1 Photovoltaic performance of the DSSC fabricated with CE of physical composited RGO/Ta_3N_5.

Counter Electrode	V_{oc}/mV	J_{sc}/mA cm^{-2}	FF	η/%
RGO/Ta_3N_5	829	12.63	51.7	5.41

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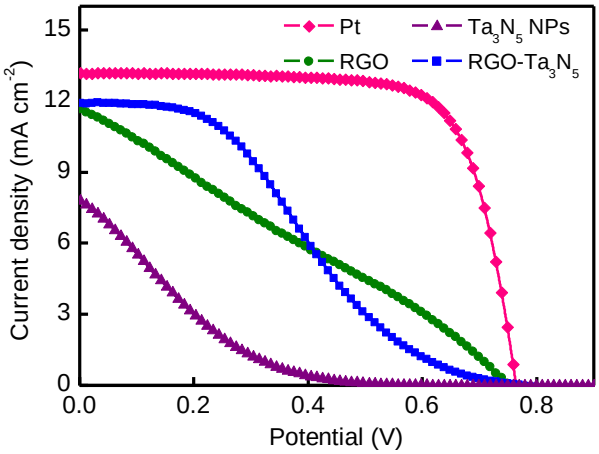

Fig. S8 Photocurrent density-voltage characteristics of N719-sensitized solar cells with I_2^-/I_3^- in acetonitrile as electrolyte and RGO-Ta_3N_5, RGO, Ta_3N_5, and Pt as CEs measured at AM 1.5G illumination (100 mW cm^{-2}).

Table S2 Photovoltaic performance of the DSSCs fabricated with CEs of Pt, RGO, RGO-Ta_3N_5 and Ta_3N_5 NPs, using N719 dye as the sensitizer and I^-/I_3^- in acetonitrile as the electrolyte.

Counter Electrode	V_{oc}/mV	J_{sc}/mA cm^{-2}	FF	η/%
Ta_3N_5 NPs	714	7.10	12.6	0.64
RGO	749	11.62	26.7	2.33
RGO-Ta_3N_5	762	11.89	31.8	2.88
Pt	763	13.18	73.3	7.38