

Supporting Information

Crystalline Poly(Triazine Imide) based g-CN as an Efficient Electrocatalyst for Counter Electrodes of Dye-Sensitized Solar Cells using a Triiodide/Iodide Redox Electrolyte

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Experimental Section

Materials: FTO-coated glass substrates (TCO22-7, 7 Ω /square), hot melt sealing films (Meltonix 1170-60, 60 μ m thickness) and N719 dyes (Ruthenizer 535-bisTBA) were purchased from Solaronix. TiO₂ paste for transparent layer (DSL 90T, 20 nm) and TiO₂ paste for light-scattering layer (WER2-O, 150~250 nm) were purchased from Dyesol. Super P[®] was purchased from Timcal Graphite & Carbon. Poly(ethylene oxide) (PEO) of M_v ~5,000,000 was purchased from Sigma-Aldrich. A detergent solution (Deconex[®] 12 BASIC) was purchased from Borer Chemie AG. All reagents were used as-received.

Synthesis of cPTI-MCA-LiKCl-550: Synthesis of melamine-cyanuric acid (MCA) complex was performed as previously reported.¹ First, equimolar solutions of melamine and cyanuric acid in dimethyl sulfoxide (DMSO) were mixed at room temperature for 10 min. The resulting white precipitates were then filtered, washed with ethanol, and dried at 100 °C. cPTI-MCA-LiKCl-550 was prepared by using MCA as a precursor in an eutectic mixture of LiCl and KCl.² MCA powder (1 g) was ground with LiCl (1.125 g) and KCl (1.375 g) using a mortar and pestle followed by heating the mixture at 550 °C for 12 hrs in a tube furnace under nitrogen atmosphere. The resulting yellow powder was then washed with water at 90 °C overnight, filtered, washed with water and dried at 110 °C.

Preparation of cPTI-MCA-LiKCl-550 catalyst solution: Four separate catalyst solutions were prepared from varying mass ratios of cPTI-MCA-LiKCl-550 and Super P dissolved in 1 mL of ethanol and 7.5 mg of PEO, followed by 30 min ultrasonication. The actual mass ratios (mg : mg)

of cPTI-MCA-LiKCl-550 : Super P were 15:15, 20:10, 25:5, and 28:2, designated as CC1, CC2, CC3, and CC4, respectively.

Fabrication of cPTI-MCA-LiKCl-550 cathodes: Before assembly of the device commenced, two small holes were drilled into the FTO glass substrate to allow for electrolyte injection into the assembled device. After the holes were drilled, the substrates were cleaned for 20 min in a detergent solution using an ultrasonic bath, followed by rinses with tap water, DI water and lastly, ethanol. 4 pieces of adhesive tape were then applied onto the FTO side to make a confined rectangular area of 0.60 cm^2 (15 mm X 4 mm). $40 \mu\text{L}$ from one of the four freshly prepared cPTI-MCA-LiKCl-550 catalyst solutions was drop-cast onto this defined area and allowed to dry at room temperature followed by removal of the adhesive tape. The FTO glass was then annealed under flowing nitrogen gas in a tube furnace at $450 \text{ }^\circ\text{C}$ for 3 hrs with an increasing ramp rate of $2.3 \text{ }^\circ\text{C}/\text{min}$.

Fabrication of Pt cathodes: FTO glass, which had been drilled and washed as described previously, was coated with a thin layer of a 5 mM solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol, dried at room temperature for 10 min, and then promptly annealed at $450 \text{ }^\circ\text{C}$ in air for 20 min with an increasing ramp rate of $25 \text{ }^\circ\text{C}/\text{min}$.

Fabrication of TiO_2 /dye anodes: A washed FTO glass was heated in a 40 mM aqueous TiCl_4 solution at $70 \text{ }^\circ\text{C}$ for 30 min, and rinsed with DI water and ethanol. Two TiO_2 layers consisting of a $\sim 11 \mu\text{m}$ thick transparent layer (from 20 nm TiO_2 paste diluted with terpineol) and a $\sim 4 \mu\text{m}$ thick light-scattering layer (from 200 nm TiO_2 paste diluted with terpineol) were successively deposited onto the FTO glass by doctor blade technique followed by drying at $110 \text{ }^\circ\text{C}$ for 10 min on a hot plate after each subsequent deposition step. Then, the FTO glass was annealed at $450 \text{ }^\circ\text{C}$ for 20 min at an increasing ramp rate of $25 \text{ }^\circ\text{C}/\text{min}$ in an ambient oven. The active area of 0.20 cm^2 was defined with a razor blade, and the substrate was again treated in a 40 mM aqueous TiCl_4 solution at $70 \text{ }^\circ\text{C}$ for 30 min. After cleaning, it was annealed at $25 \text{ }^\circ\text{C}/\text{min}$ to $450 \text{ }^\circ\text{C}$ with a 30 min hold. Once the TiO_2 anode was cooled to $80 \text{ }^\circ\text{C}$, the substrate was dye-coated by immersing for 12 hrs in a 0.2 mM solution of an N719 dye in ethanol.

Assembly of DSSCs: A cathode and an anode were sealed around their perimeter using a thermal melt polymer film ($60 \mu\text{m}$ thickness) such that a $60 \mu\text{m}$ space was created between them upon assembly. Liquid electrolyte (0.1 M I_2 , 0.1 M lithium iodide (LiI), 0.6 M tetrabutylammonium iodide, 0.5 M 4-*tert*-butylpyridine in acetonitrile) was injected into the space between the electrodes through one of the holes predrilled in the cathode. The drilled holes were then sealed with thermal melt polymer films and microscope cover slips.

Characterization: PXRD was carried out in reflection mode (Cu K α radiation) on a Scintag X2 θ - θ diffractometer. Elemental analysis was performed using a Vario EL 3 elemental analyzer manufactured by Elementar. FT-IR spectra were collected on a JASCO FT-IR 470 plus using an average of 12 scans with a resolution of 4 cm⁻¹ from 4000 cm⁻¹ to 600 cm⁻¹. XPS spectra were obtained on an ESCALAB250 spectrometer. SEM images were obtained with an FEI XL30 Sirion FEG Digital Electron Scanning Microscope at an acceleration voltage of 5 kV and TEM images were obtained on a JEOL FB-2100F (HR) operating at an accelerating voltage of 200 kV. Nitrogen sorption analysis was conducted at -196 °C using a Micromeritics ASAP 2020. A Dektak 6M Profilometer was used to measure thickness for the TiO₂ anode and cPTI-MCA-LiKCl-550 cathode films. EIS measurements were obtained with a Bio-Logic VSP potentiostat at 0 V bias potential. The impedance studies were carried out by simulating open circuit conditions, and a sinus amplitude of 10 mV in the dark conditions. The frequency range was 0.01 Hz ~ 0.3 MHz for Pt symmetric cells, and 0.2 Hz ~ 0.2 MHz for cPTI-MCA-LiKCl-550 symmetric cells. The resultant impedance spectra were analyzed using the Z Fit in EC-Lab software provided by Bio-Logic. For EIS analyses, two identical electrodes were sealed to make an active area of 0.60 cm² and filled with the same composition of the redox electrolyte that was used in the DSSCs. Photovoltaic measurements were carried out using a Newport Air Mass 1.5 Global (AM 1.5 G) full spectrum solar simulator as source at an irradiation intensity of 100 mW cm⁻². Current density-voltage (J-V) measurements were carried out using a Keithley 2400 Digital Source Measure Unit.

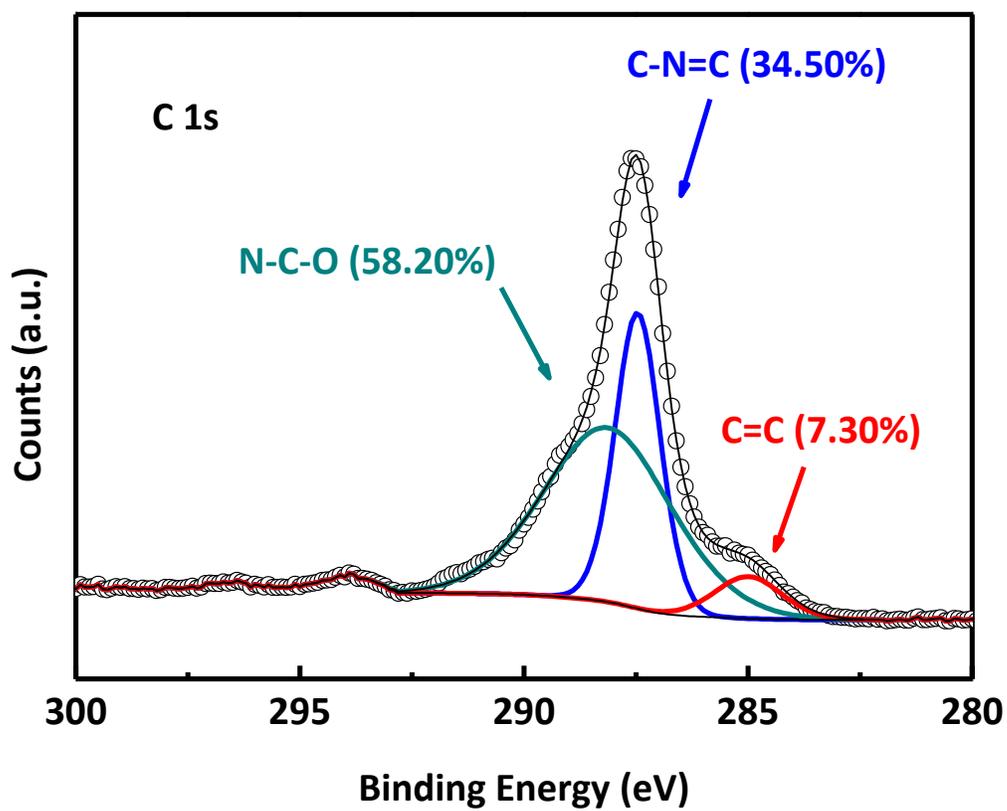


Figure S1. High resolution C 1s XPS spectrum of cPTI-MCA-LiKCl-550. The corresponding chemical structure of three peaks is indicated, with the percent area.

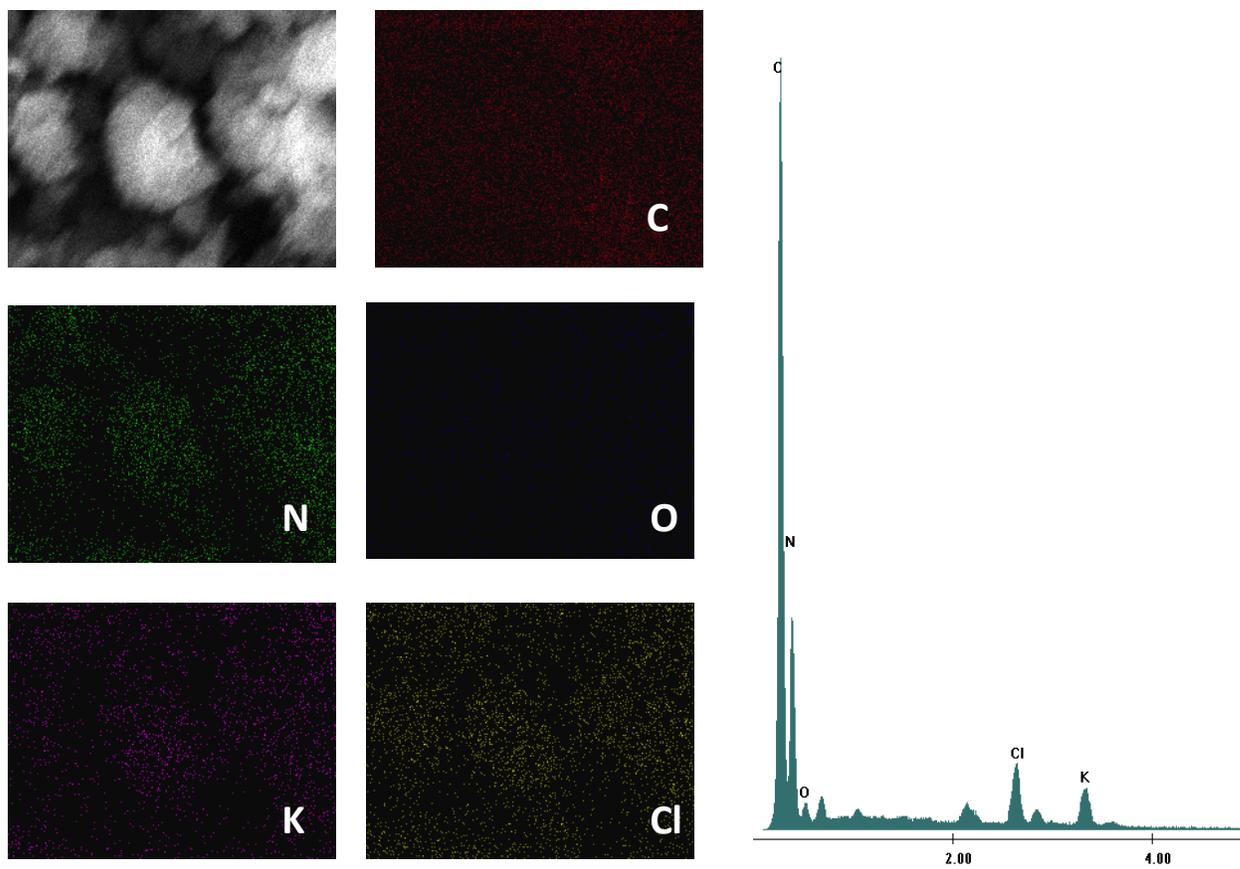
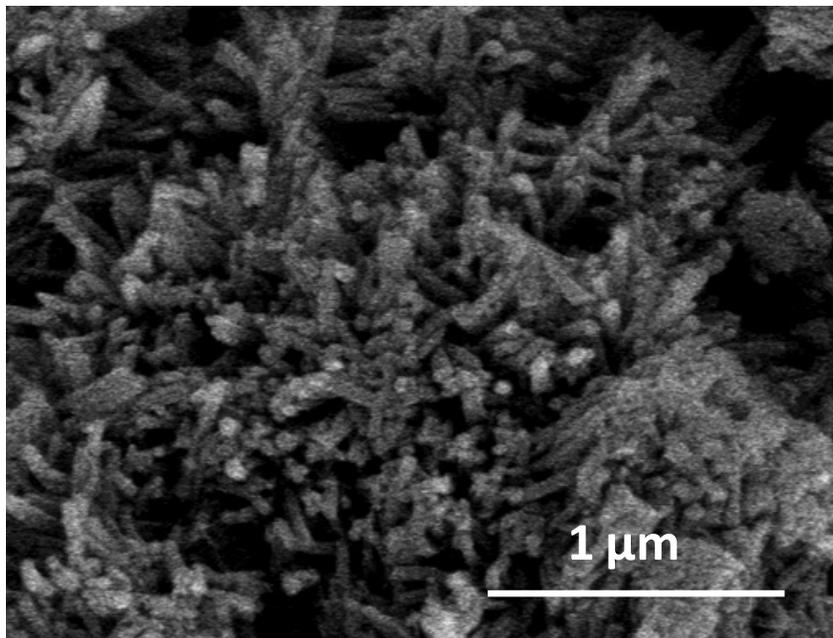


Figure S2. Elemental mapping and EDX spectrum of cPTI-MCA-LiKCl-550.

(a)



(b)

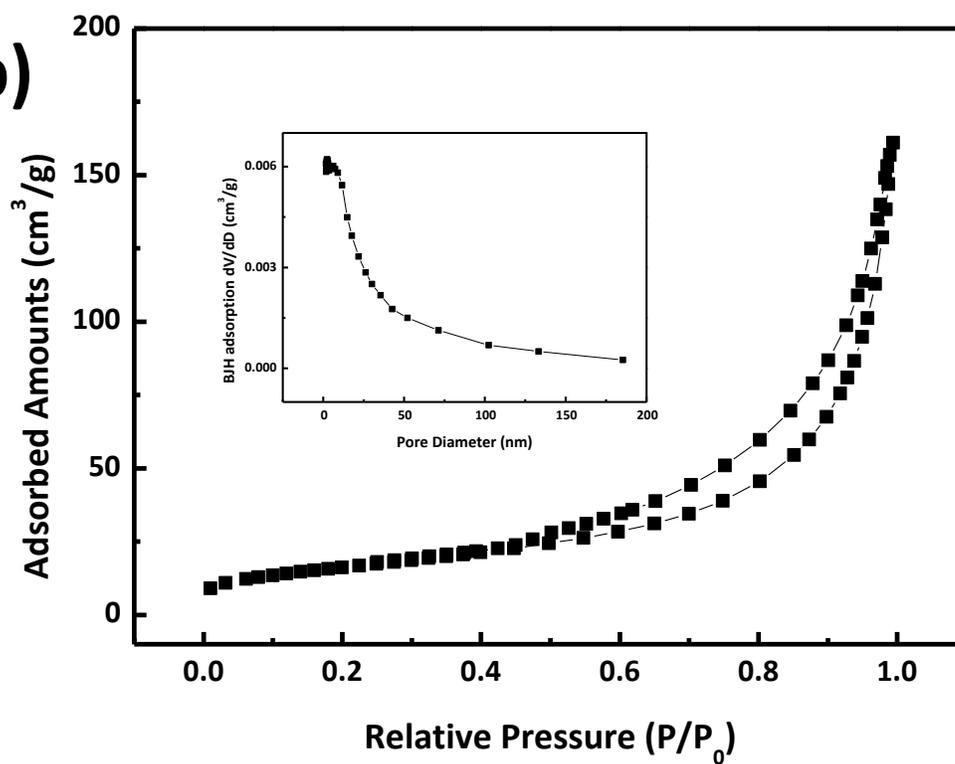


Figure S3. (a) SEM image and (b) nitrogen sorption isotherm of cPTI-MCA-LiKCl-550. Inset is a pore size distribution diagram derived from adsorption isotherm.

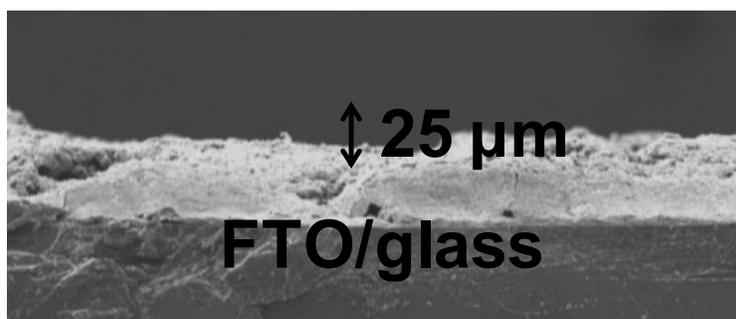
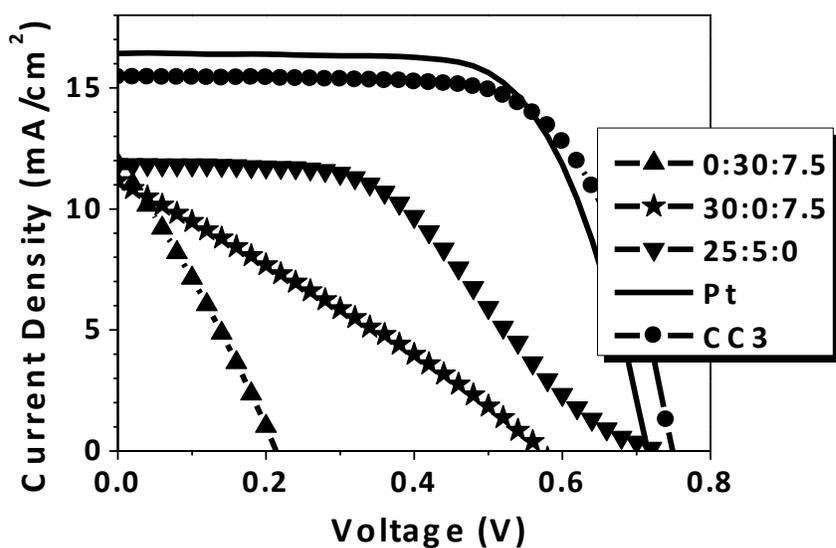
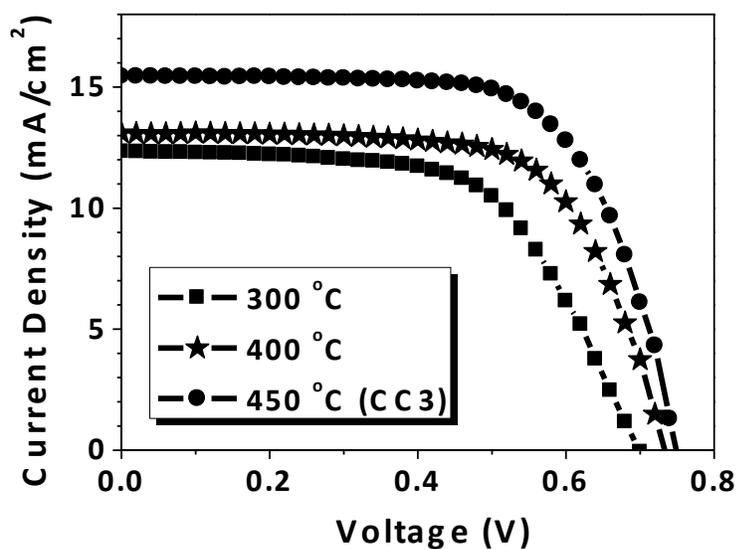


Figure S4. SEM image of the FTO glass counter electrode with cPTI-MCA-LiKCl-550 film annealed at 450 °C under N₂.



CE	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
0:30:7.5	0.214	11.9	0.29	0.7
30:0:7.5	0.571	11.2	0.28	1.8
25:5:0	0.726	11.8	0.45	3.9
Pt	0.715	16.4	0.67	7.9
25:5:7.5 (CC3)	0.749	15.4	0.68	7.8

Figure S5. J - V characteristics in case any of the three components of the catalyst solution is absent. The numbers in a CE name represent the respective milligram weight of cPTI-MCA-LiKCl-550, Super P, and PEO in 1 mL catalyst solution. Pt and CC3 are also shown for comparison.



CE	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
300 °C	0.699	12.3	0.61	5.2
400 °C	0.733	13.1	0.67	6.4
450 °C (CC3)	0.749	15.4	0.68	7.8

Figure S6. *J-V* characteristics of DSSCs with CEs heated at different temperatures. The higher the annealing temperature, the higher the *PCE*.

References

- 1 Y. S. Jun, E. Z. Lee, X. Wang, W. H. Hong, G. D. Stucky and A. Thomas, *Adv. Funct. Mater.*, 2013, **23**, 3661.
- 2 M. J. Bojdys, J. O. Müller, M. Antonietti and A. Thomas, *Chem. Eur. J.*, 2008, **14**, 8177.