Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Photo and Redox Active Carbon Nitride – Dual Functionality for Energy Storage

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Experimental Section

Chemicals - All chemicals were used as provided without further purification.

Preparation of PCN -: 6 g urea was placed in a quartz crucible and covered with a lid. The sample was heated at 500 ^oC for 1 hr. at 10 K/min. under an inert atmosphere (Ar). Subsequently, the sample was cooled and heated at 550 ^oC for 2 hrs. with a 10 K/min. heating rate.

Preparation of F-PCN -: 6 g urea was placed in a quartz crucible and covered with a lid. The sample was heated at 500 ^oC for 1 hr. at 10 K/min. under an inert atmosphere (Ar). Subsequently, LiCl (1.35 g) and KCl (1.75 g) were added to the cooled sample and heated at 550 ^oC for 2 hrs. at 10 K/min. The sample was repeatedly washed with DI water and vacuum dried at 60 °C.

Protonated F-PCN (H-(F-PCN)) -: 200 mg of F-PCN were mixed with 100 mL 1M H_2SO_4. A solid product was obtained with DI water and vacuum dried after several washes.

Characterization –:

After synthesizing the material using the above-stated synthetic methods, further structural information was gathered using various characterization techniques. Given below are the details of the parameters for each technique that has been used. For FT-IR (Fourier transform infrared) spectroscopy, all the measurements were done with powder samples (pellet of KBr and the material) using the JASCO FT-IR 4600 model. For CHNS measurements, the Thermoscientific Flash 2000 instrument was used. For ICP-MS (Inductively coupled plasma-mass-spectrometry), the sample was digested by keeping it in concentrated nitric acid for two days. Subsequently, the digested samples were diluted 50 times in water. In the end, the diluted sample was filtered with a 0.2 µm filter to get a particle-free solution. For all the ICP-MS measurements, the Agilent 7900 model was used. SEM images were taken on Zeiss Ultra FEG 55 using an accelerating voltage of 5 kV. For Powder XRD (X-ray Diffraction), all the data was obtained with step size (° 2theta) 0.0170 and step time of 50.1650 sec in the range of 2θ = 7° to 80°. UV-DRS (UV–Vis Diffuse Reflectance Spectroscopy) for this study, as all the samples were in the solid phase, UV-Vis DRS was employed to obtain the absorption spectrum of a sample in reflectance mode. In this study, all the samples were thoroughly ground before the measurement. JASCO V-6770 Spectrometer was used for all the data acquisition, and the range of wavelength used was 1200 nm to 200 nm. Steady-state Photoluminescence (PL) measurements for this study were done on solid and water suspensions, and excitation was done at various wavelengths. Subsequently, the emission spectrum was collected using a Fluorolog-3 fluorometer. Data were collected twice for each spectrum, showing the average spectrum. Time-resolved PL measurements were done with TCSPC (Time correlating single photon count) on a solid and a sample suspended in water with an excitation of 295 nm, and emission photons were collected at 460 nm. Electrochemical and photoelectrochemical measurement was done using Bio-Logic SAS VSP 300 potentiostat. EIS measurements reported here were acquired in the frequency range 7 MHz - 10mHz, at a potential of -1.3 V vs Ag/AgCl. Enlitech xenon lamp with 1.5AM spectra 1 Sun is the light source.

Electrode preparation for electrochemical and photoelectrochemical studies -: F-PCN electrodes (working electrode) were prepared by drop-casting 50 µg sample (slurry made by 1 mg sample in 1.2 mL water) on an FTO electrode (5 x 5 mm) for one electrode 60 µL sample was loaded in 4 batches. The electrodes were then heated at 60 °C for 3 hrs.

Electrode preparation for cyclic voltammetry measurement -: F-PCN electrodes (working electrode) were prepared by drop-casting a 2 mg sample (slurry made in ethanol) on a carbon paper electrode (5 x 5 mm), dried through an IR lamp. The electrodes were then heated at 80 °C for a further 3 hrs.

Photoelectrochemical measurement -: A three-electrode system containing a working electrode, reference electrode, and counter electrode was employed. The reference electrode was Ag/AgCl (sat. KCl), and Pt foil was used as a counter electrode. The electrodes were immersed in a 0.1 M electrolyte with 5 mM 4-MBA. The electrolyte was purged with N_2 gas for an inert environment.

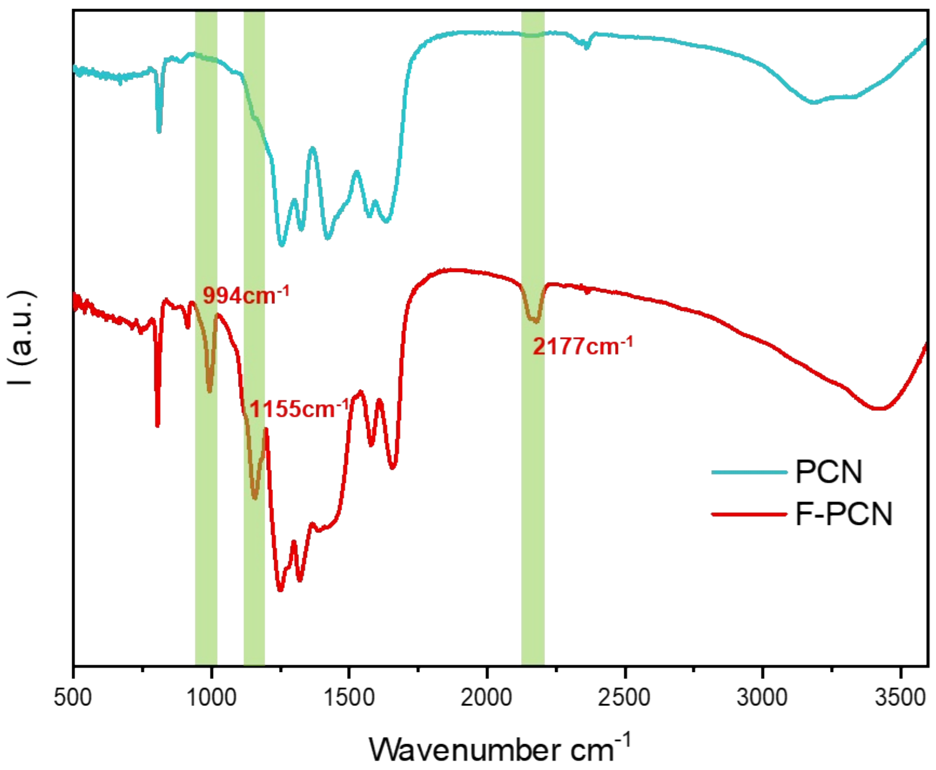
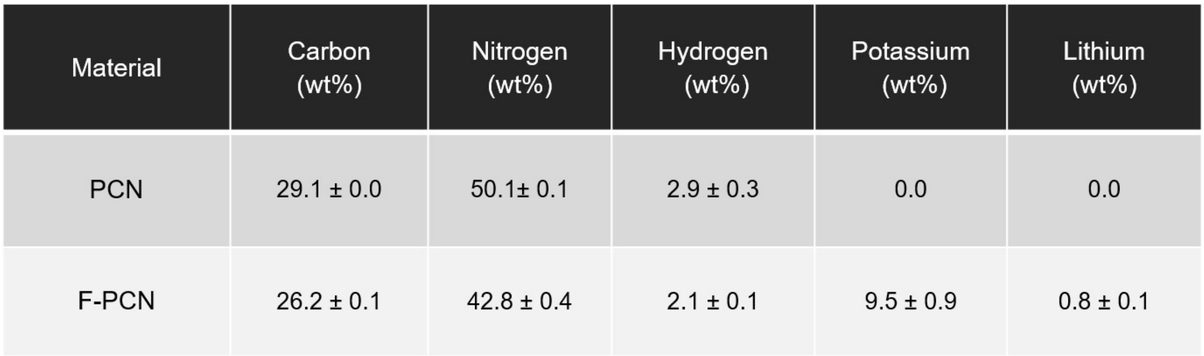


Figure S1. FT-IR Spectra of solid PCN and F-PCN.



Material	Carbon (wt%)	Nitrogen (wt%)	Hydrogen (wt%)	Potassium (wt%)	Lithium (wt%)
PCN	29.1 ± 0.0	50.1± 0.1	2.9 ± 0.3	0.0	0.0
F-PCN	26.2 ± 0.1	42.8 ± 0.4	2.1 ± 0.1	9.5 ± 0.9	0.8 ± 0.1

Table S1. Elemental analysis (CHNS analyses) and ICP-MS data (for Li and K) for PCN and F-PCN.

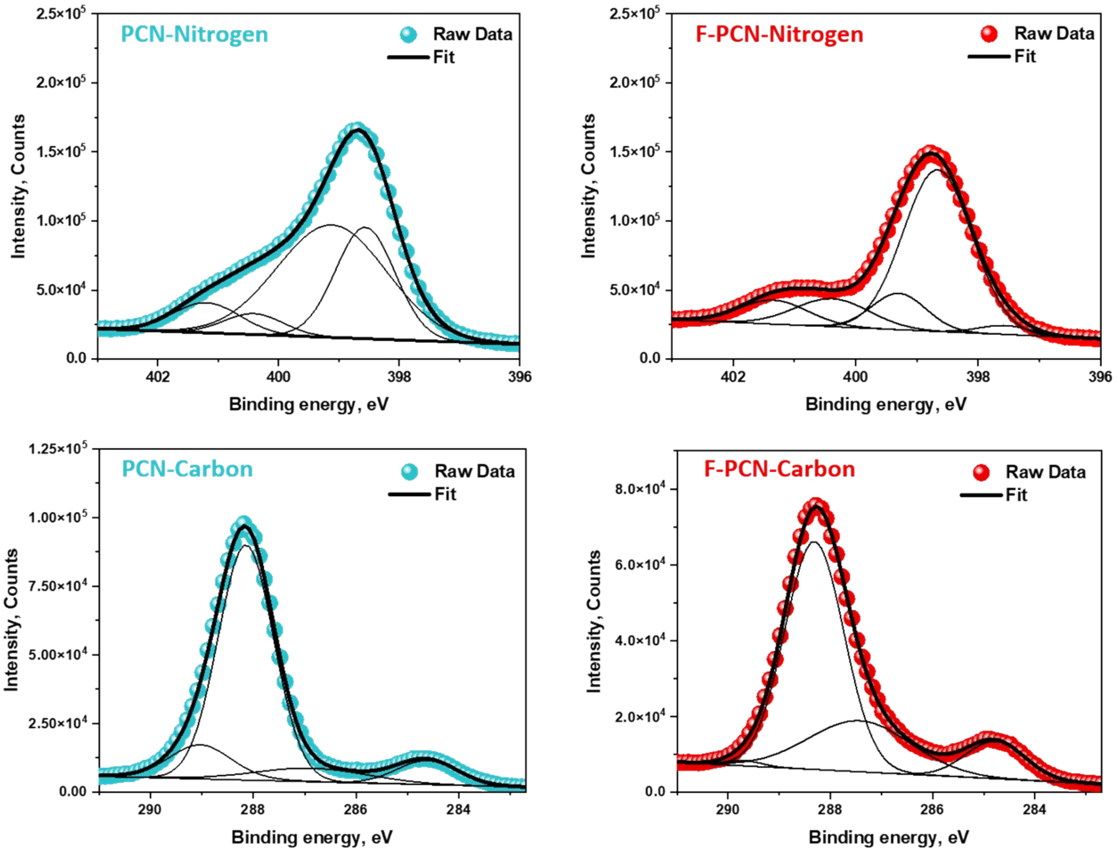


Figure S2. XPS spectra of PCN and F-PCN.

Nitrogen XPS	R_3-N	R_2-NH	R-NH_2	Pyridinic	Deprotonated Nitrogen (N^-)
PCN	401.2 (9%)	400.4 (6%)	399.1 (55%)	398.6 (30%)	-
F-PCN	401.3 (10%)	400.4 (12%)	399.3 (11%)	398.7 (64%)	397.6 (3%)

Table S2. Nitrogen XPS peak fitted data for PCN and F-PCN.

Carbon XPS	**Heptazine Sp^2 carbon**	**C≡N**	**C-C**	**C=O**
PCN	288.1 (72%)	286.9 (8%)	284.6 (8%)	289.0 (12%)
F-PCN	288.3 (64%)	287.4 (25%)	284.8 (10%)	289.7 (1%)

Table S3. Carbon XPS peak fitted data for PCN and F-PCN.

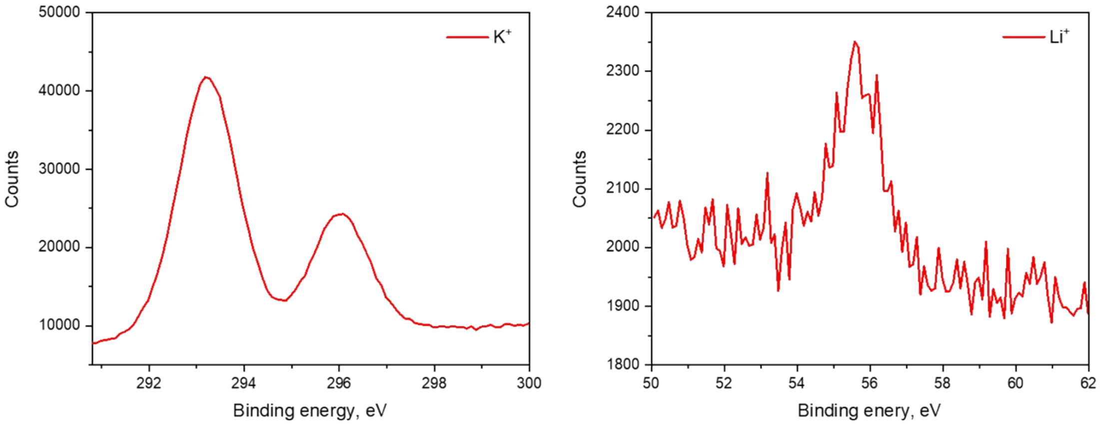


Figure S3. XPS spectra of K^+ (2p) and Li^+ (1s) for F-PCN.

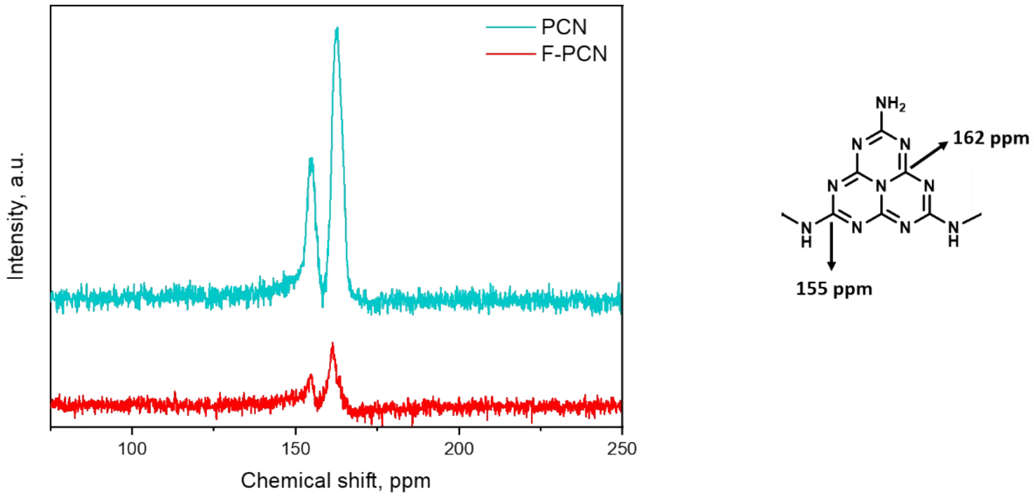


Figure S4. ^{13}C Solid State CP NMR for PCN and F-PCN.

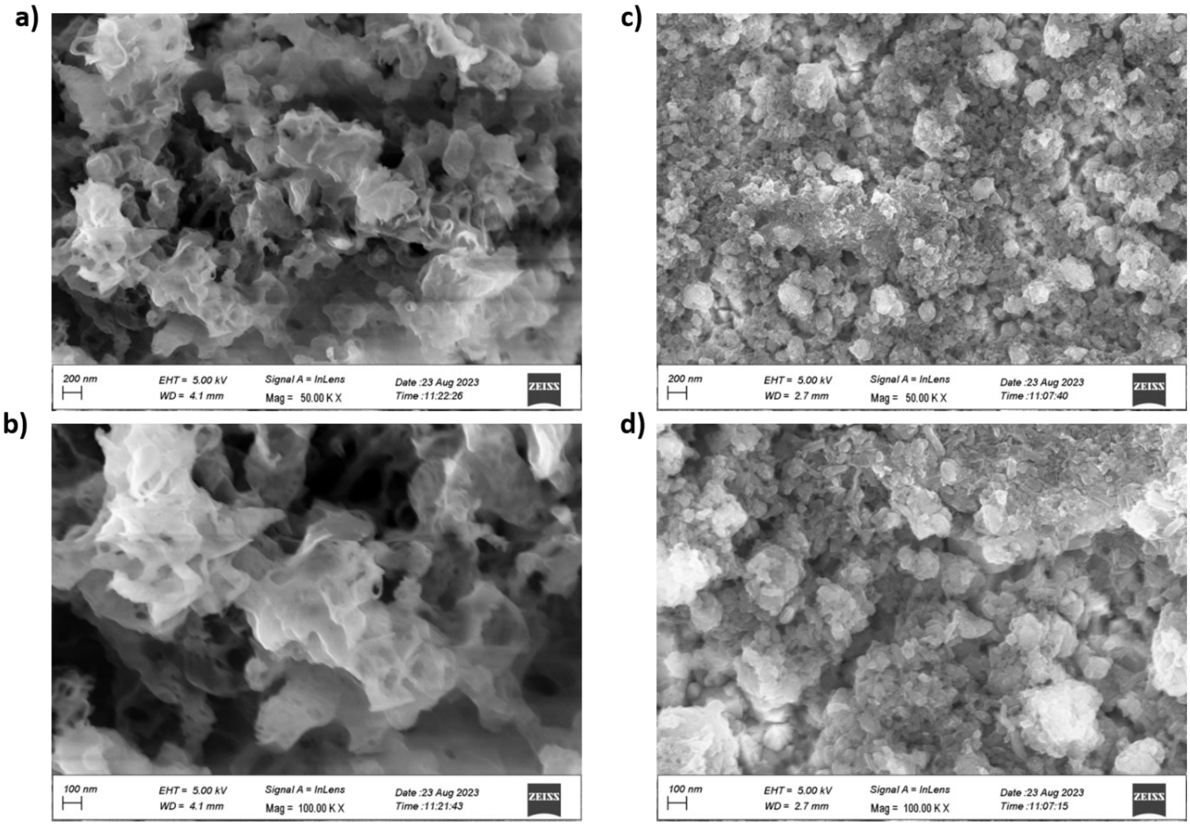


Figure S5. SEM image of the PCN (a,b) and F-PCN (c,d).

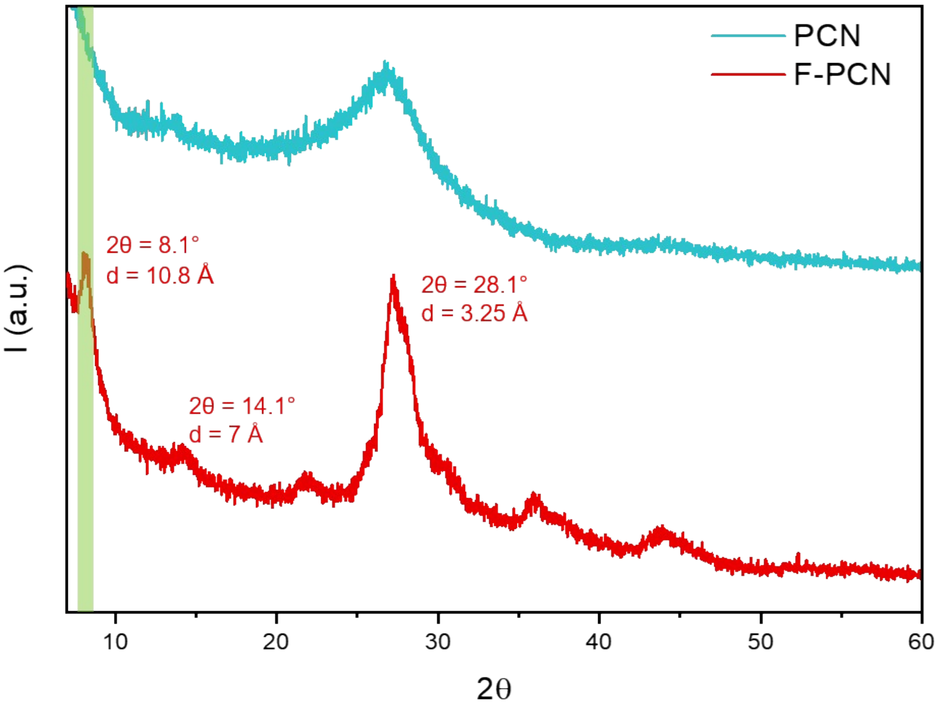


Figure S6. Powder XRD pattern for PCN and F-PCN.

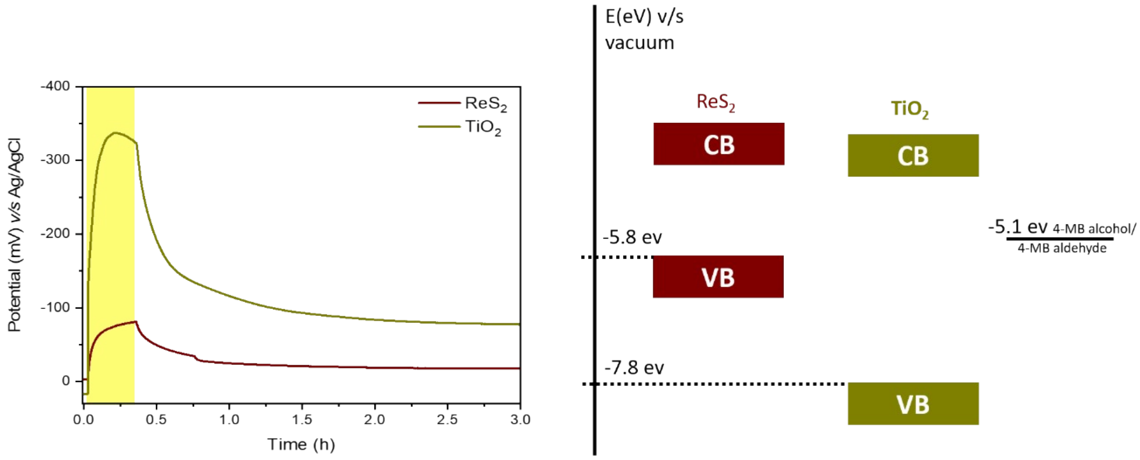


Figure S7. OCP measurements on TiO_2 and ReS_2 using 0.1 M Na_2SO_4 and 4-MBA (inert atmosphere).

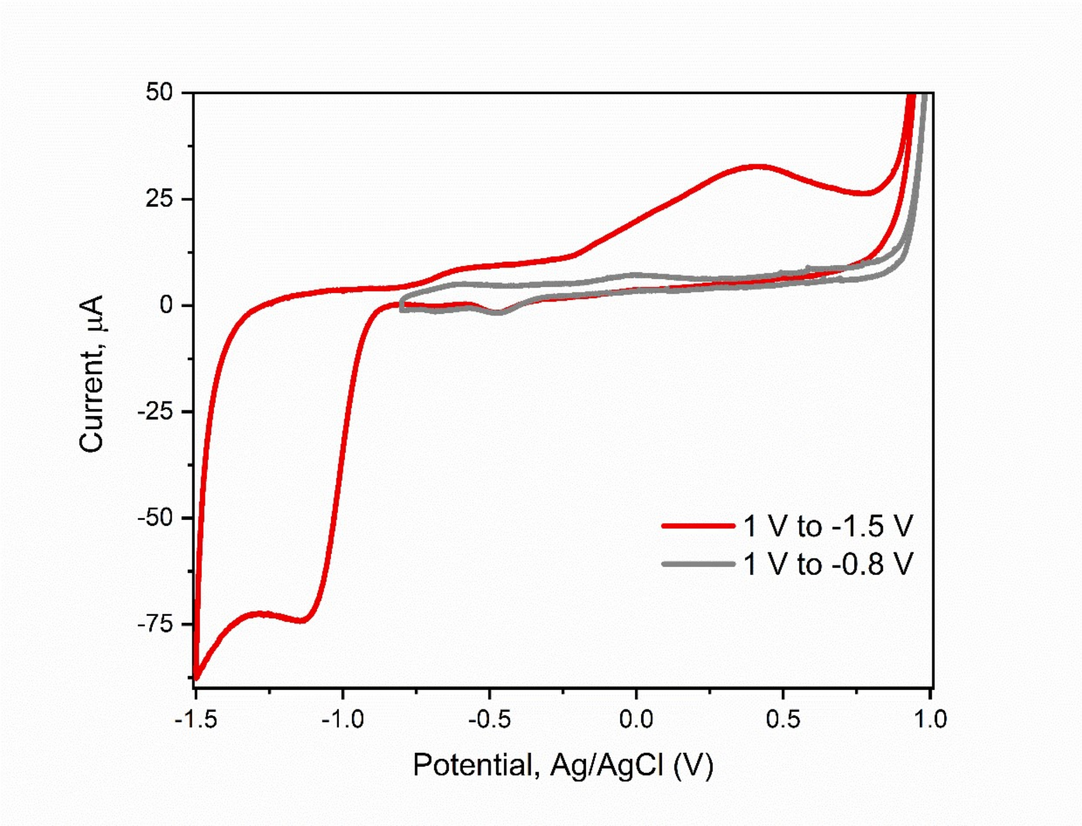


Figure S8. Cyclic voltammetry on F-PCN at different potential windows with a scan rate of 5mV/sec in 0.1 M Na_2SO_4 and 4MBA electrolytes. The red curve provides the full CV cycle showing both the oxidized and reducted species. The grey curve shows that unless F-PCN is reduced by accessing voltages below -0.85V, no oxidized feature will be observed.

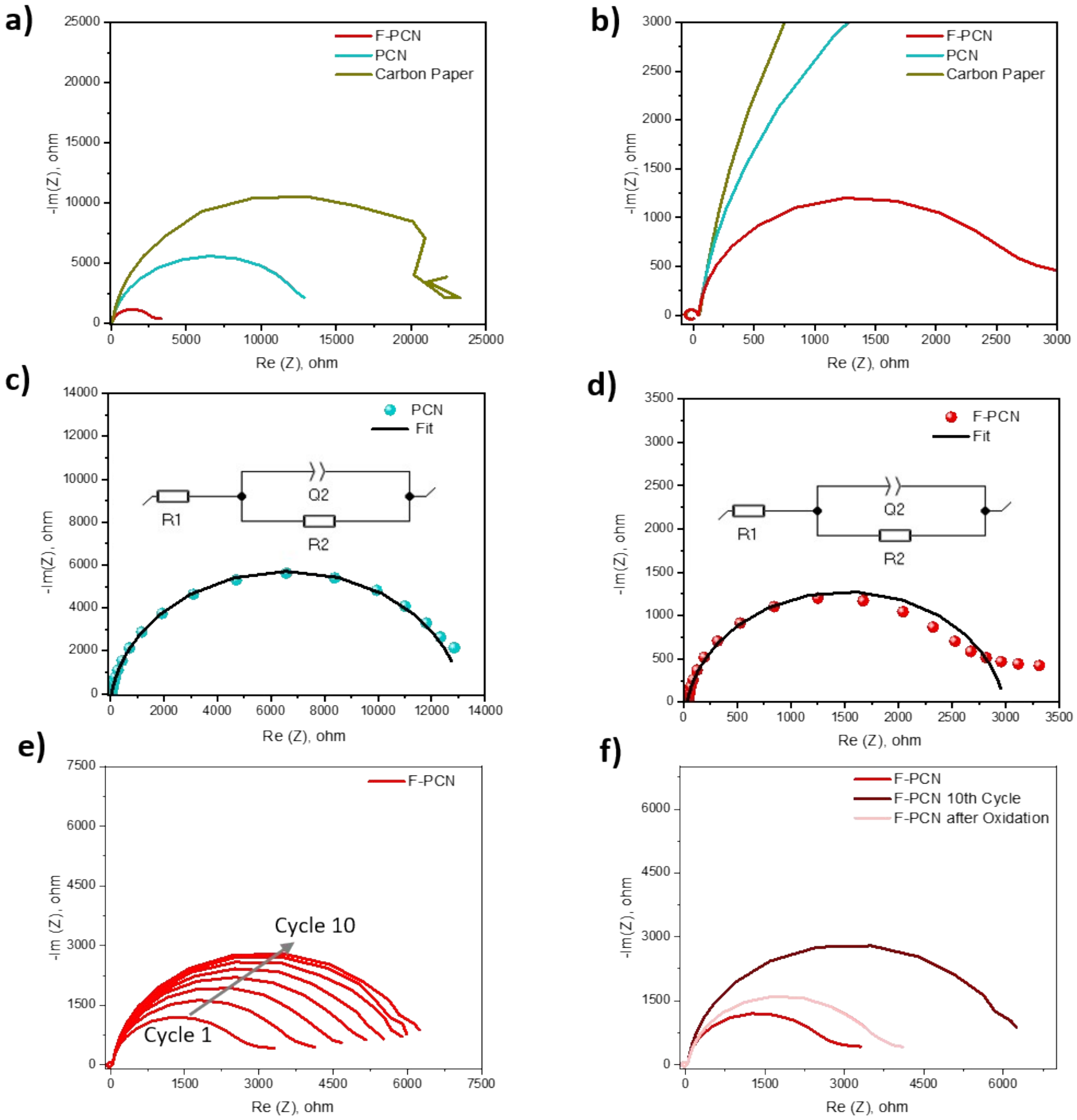


Figure S9. a) Nyquist plot for PCN, F-PCN, and Carbon paper in a 0.1 M Na2SO4 and 4MBA electrolyte at a potential os -1.3 V v/s Ag/AgCl. b) Nyquist plot of F-PCN zoomed in version c) Nyquist plot fitting and corresponding equivalent circuit for PCN d) Nyquist plot fitting and corresponding equivalent circuit for F-PCN e) Multiple cycles of Nyquist plot for F-PCN at -1.3 V potential f) Nyquist plot for F-PCN at -1.3 V potential as synthesized, after 10th cycle and after oxidizing it back.

Material	**Solution Resistance (R_s), ohm**	**Constant Phase element (Q), μF.s$^{(a-1)}$**	**Charge transfer Resistance (R_{ct}), ohm**
Carbon Paper	49	29	23,173
PCN	41	117	13,110
F-PCN	37	237	2,947

Table S4. EIS fitted parameters for PCN, Carbon paper, and F-PCN

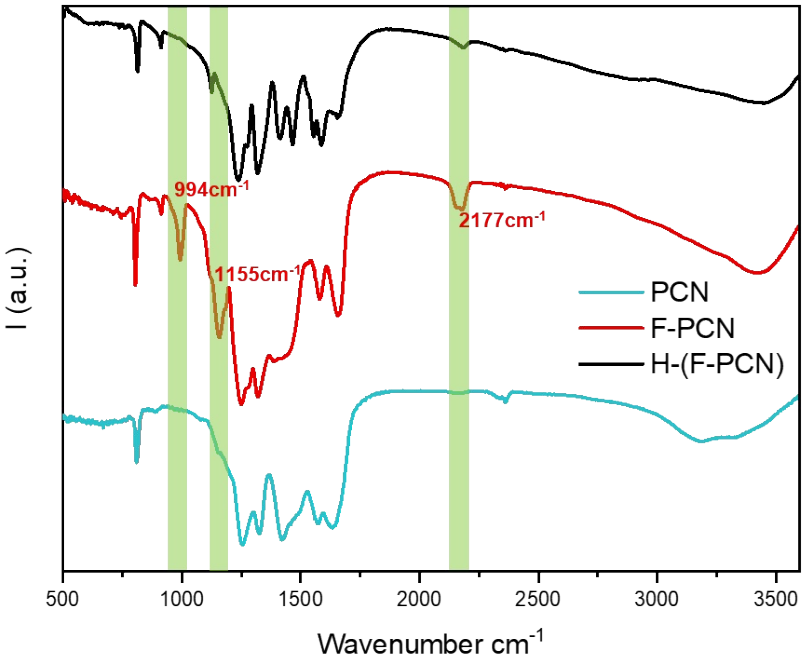


Figure S10. F-PCN IR spectra after and before protonation.

Material	Carbon (wt%)	Nitrogen (wt%)	Hydrogen (wt%)	Potassium (wt%)	Lithium (wt%)
PCN	29.1 ± 0.0	50.1± 0.1	2.9 ± 0.3	0.0	0.0
F-PCN	26.2 ± 0.1	42.8 ± 0.4	2.1 ± 0.1	9.5 ± 0.9	0.8 ± 0.1
H-(F-PCN)	27.2 ± 0.0	44.6 ± 0.1	2.8 ± 0.1	-	-

Table S5. Elemental analysis of (H-(F-PCN)) F-PCN structure after protonation.

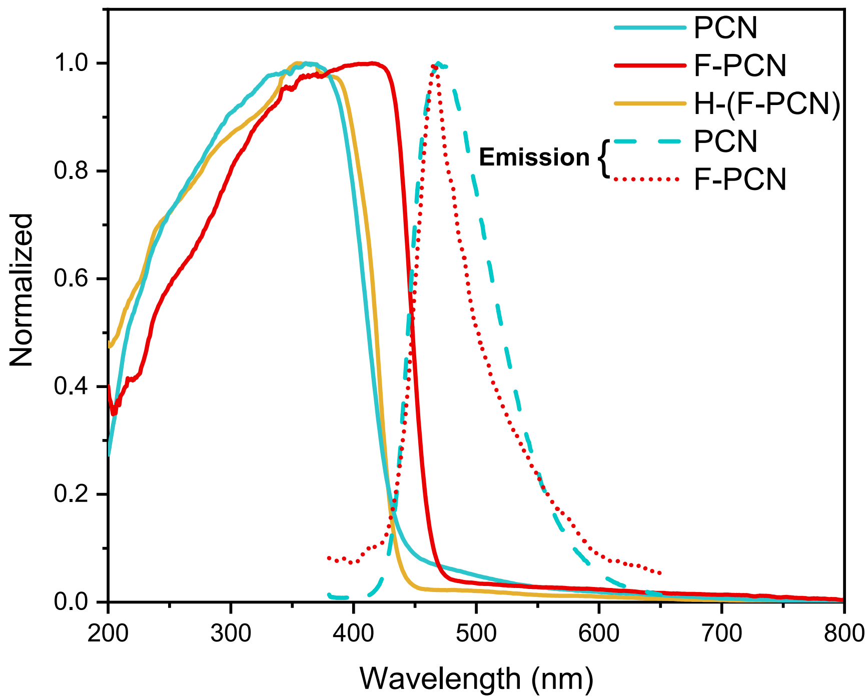


Figure S11. Absorption for solid PCN, F-PCN, and Protonated F-PCN (H-(F-PCN)) and Emission spectra (excitation 350 nm) of solid PCN and F-PCN.

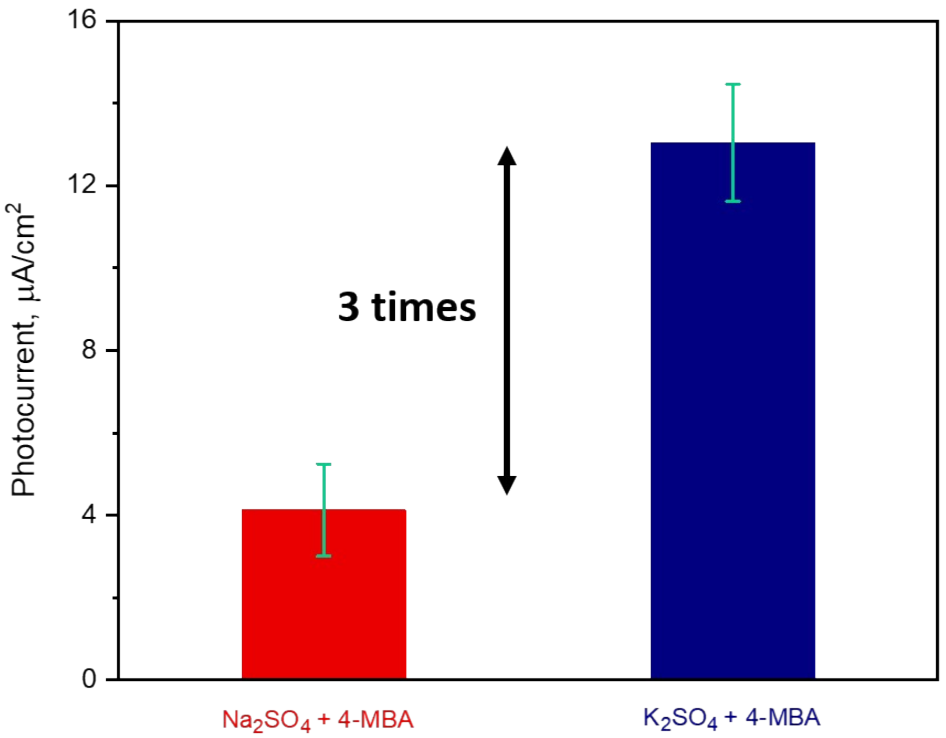


Figure S12. Photocurrent measurement in Na_2SO_4 and K_2SO_4 with 4MBA.

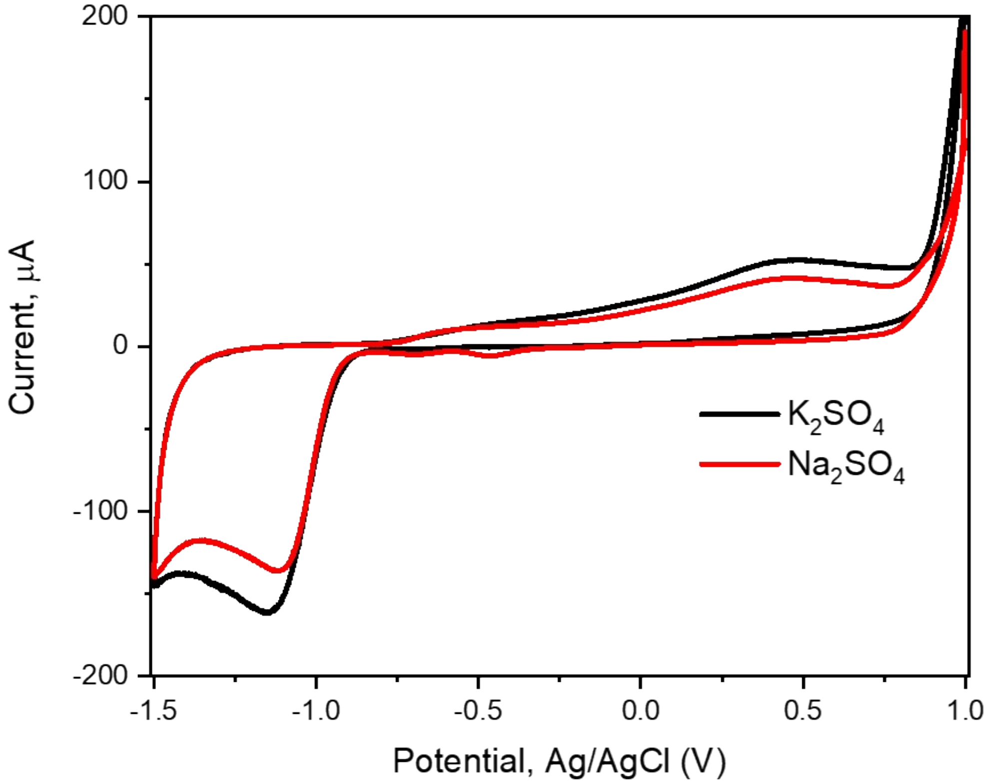


Figure S13. CV of F-PCN in different electrolytes Na_2SO_4 and K_2SO_4 with 4MBA.

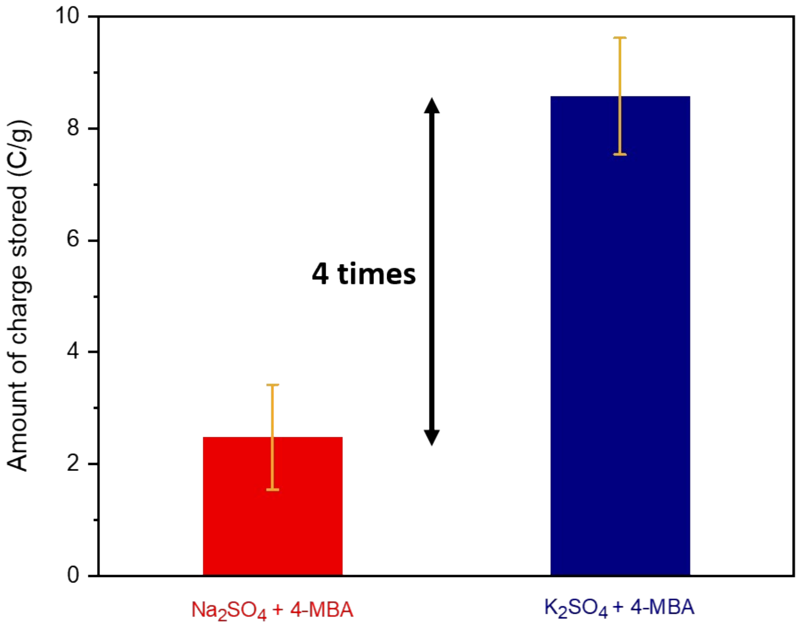


Figure S14. Amount of charge stored within 20 min of light irradiation in 0.1M Na_2SO_4 and 4MBA and 0.1M K_2SO_4 and 4MBA.