

Electronic Supplementary Information

Conjugated porous polymer as precursor for electrocatalyst and storage electrode material

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Experimental section:

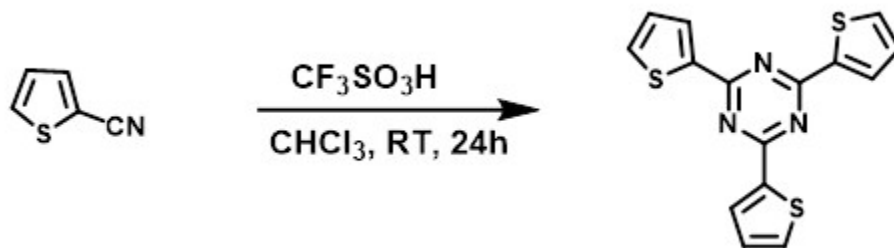
Chemicals Thiophene-2-carbonitrile, N-bromosuccinimide, 1,3,5-Tribromobenzene, Pd(PPh₃)₄, copper iodide and Trimethylsilylacetylene were purchased from Aldrich chemicals. Tri fluoro methane sulfonic acid, NaHCO₃, Triethylamine and KOH were purchased from Avra chemicals. All chemicals were used as received.

Characterization of the prepared samples

¹H NMR spectra were measured on Bruker arx 200 MHz AVANS spectrometer. Nitrogen adsorption-desorption experiments were conducted at 77 K using Quantachrom Quadrasorb automatic volumetric instrument. Raman analysis was done on an HR 800 Raman spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were carried out by VG Microtech Multilab ESCA 3000 spectrometer.

1) Synthesis of 2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine

Synthesis of 2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine was done by reported procedure.¹ The thiophene-2-carbonitrile (2g, 18.3 mmol) was taken in 100 ml of chloroform, then reaction mixture was cooled to 0 °C, then tri fluoro methane sulfonic acid (4.88g, 32.51 mmol) was added drop wise under argon atmosphere, and stirred the reaction mixture at room temperature for 24 h, after that the residue was neutralized with an aqueous NaHCO₃, and the organic layer was washed with water, and concentrated under reduced pressure. The product was obtained by using column chromatography with hexane. (4.3 g, 71%); ¹H NMR (200 MHz, CDCl₃): δ = 8.29 (d, 3H), 7.63 (d, 3H), 7.23 (t, 3H) ppm



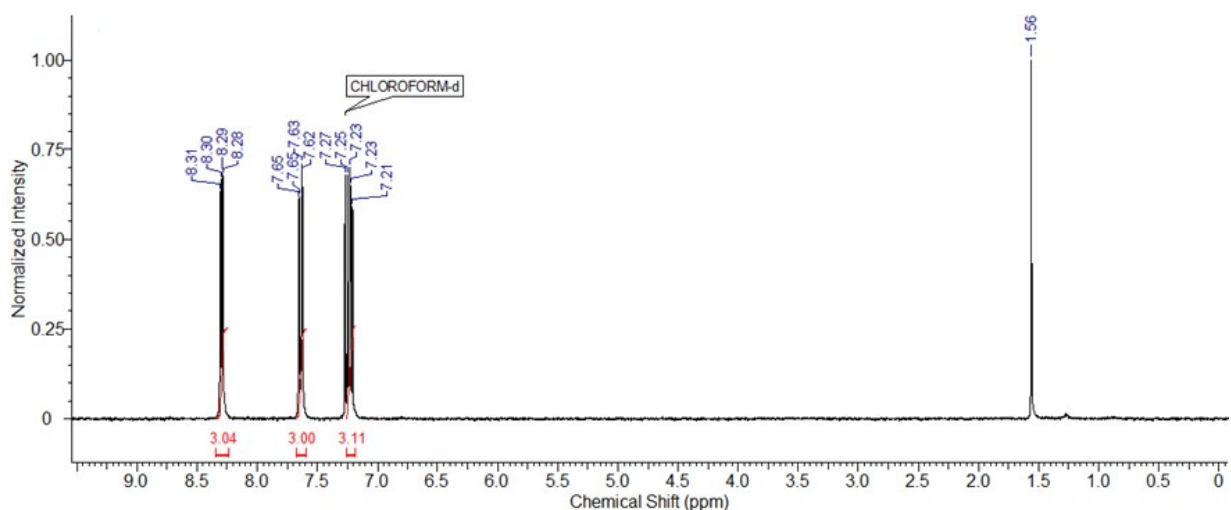
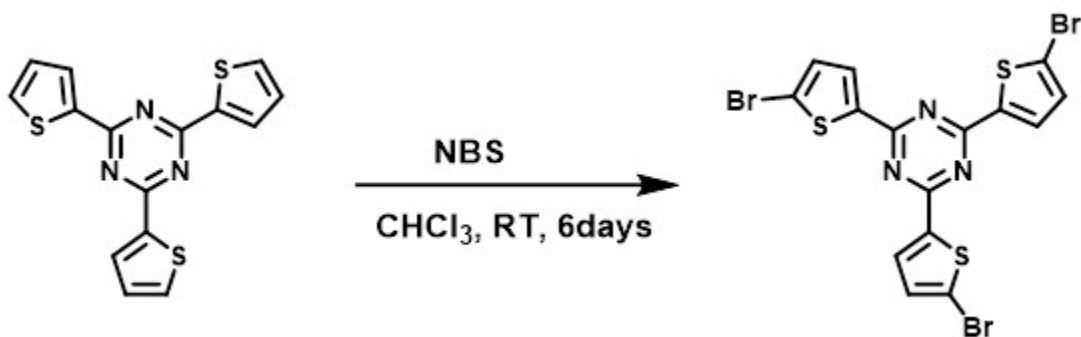


Fig. S1: ¹H-NMR spectrum of 2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine

2) Synthesis of 2,4,6-Tris(5-bromothiophen-2-yl)-1,3,5-triazine

Synthesis of 2,4,6-Tris(5-bromothiophen-2-yl)-1,3,5-triazine was done by reported procedure.¹ The 2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine (1g, 3.05 mmol) was dissolved in 50 ml of chloroform. To this solution N-bromosuccinimide (NBS) was added (5.43 g, 30.5 mmol) and then resulting mixture was stirred at room temperature for 6 days and then reaction mixture was hydrolyzed by adding dilute aqueous hydrochloric acid. The organic layer was separated, washed three times with water and dried over anhydrous sodium sulfate. The reaction mixture was concentrated by evaporating the solvent under reduced pressure and finally product was recrystallized from chloroform. (0.95 g, 55%); ¹H NMR (200 MHz, CDCl₃): δ =7.97 (d, 3H), 7.18(d, 3H) ppm



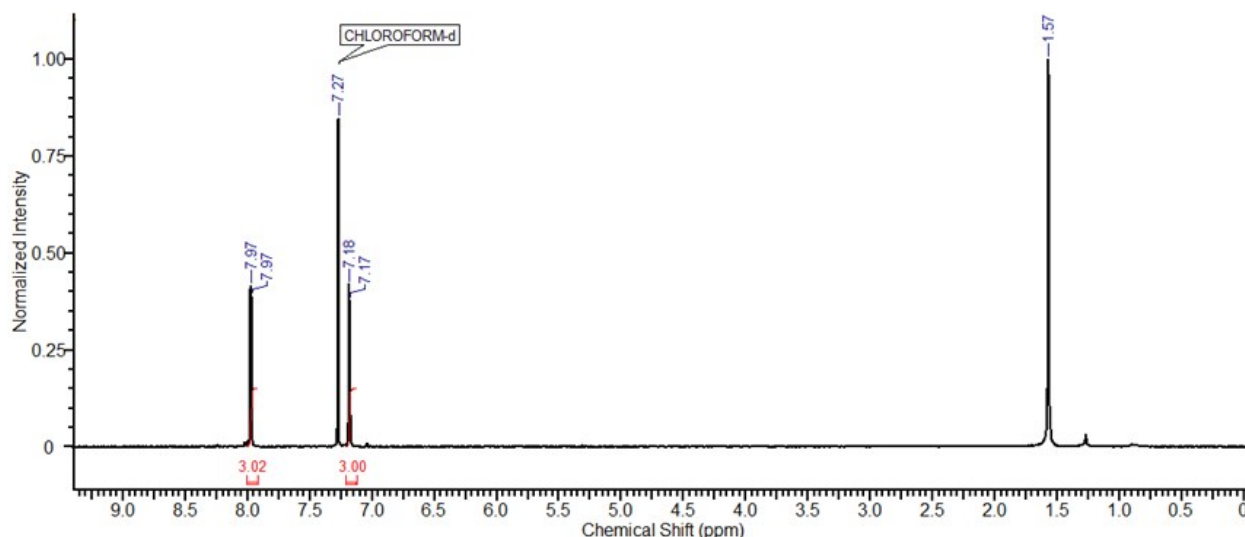
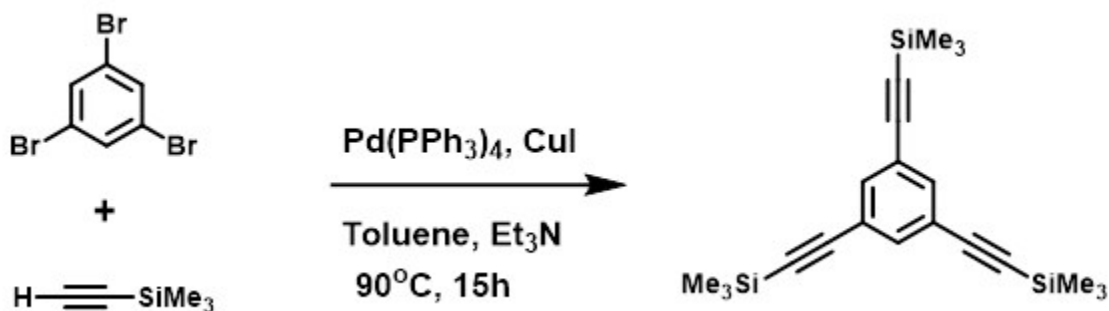


Fig. S2: $^1\text{H-NMR}$ spectrum of 2,4,6-Tris(5-bromothiophen-2-yl)-1,3,5-triazine

3) Synthesis of 1,3,5-tris[2-(trimethylsilyl)ethynyl]benzene

Synthesis of 1,3,5-tris[2-(trimethylsilyl)ethynyl]benzene was done by using reported procedure.² 1,3,5-Tribromobenzene (2 g; 6.3 mmol) was dissolved in dry triethylamine (15 mL) and toluene (15 mL) under argon atmosphere then $[\text{Pd}(\text{PPh}_3)_4]$ (0.73 g; 0.63 mmol) and CuI (0.1 g; 0.52 mmol) were added to the reaction mixture and stirred the reaction mixture under argon atmosphere for 15 minutes. Finally, TMSA (3.55 mL, 25 mmol) was added and stirred the reaction mixture overnight at 90°C under argon atmosphere. The mixture was allowed to cool to room temperature and filtered over celite to remove the solid black particles and filtrate was concentrated under reduced pressure. The product was obtained by using column chromatography with hexane. (1.6 g, 69%); $^1\text{H NMR}$ (200 MHz, CDCl_3): $\delta = 7.50$ (s, 3H), 0.23 (s, 27H) ppm



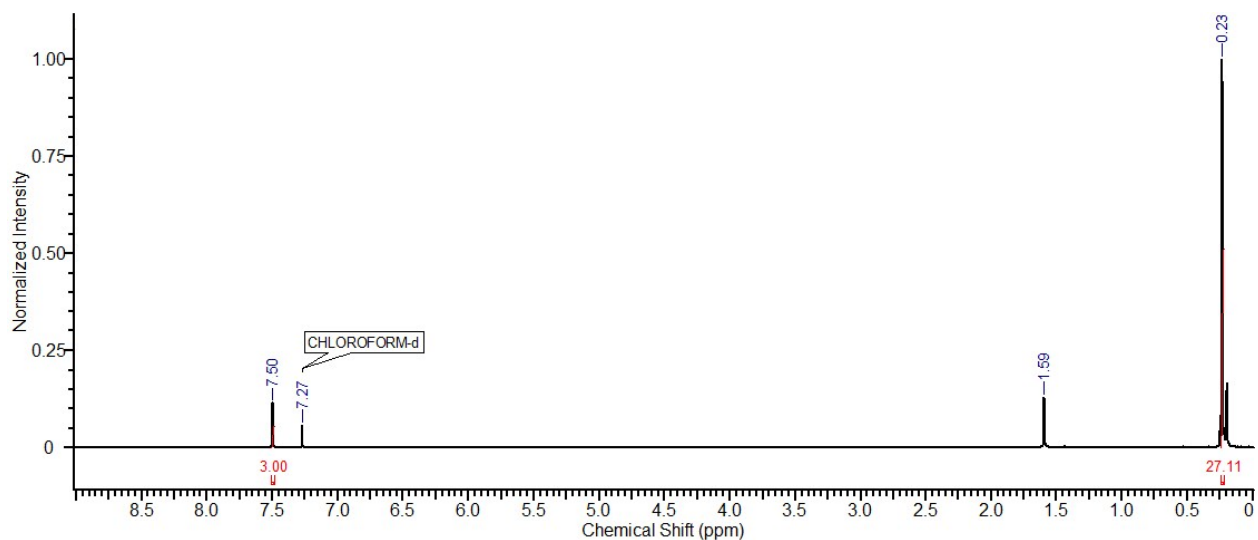
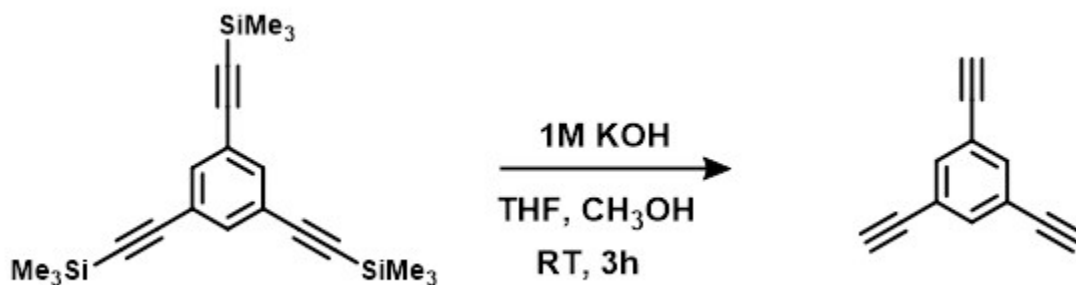


Fig. S3: ^1H -NMR spectrum of 1,3,5-tris[2-(trimethylsilyl)ethynyl]benzene

4) Synthesis of 1,3,5-triethynylbenzene

Synthesis of 1,3,5-triethynylbenzene was done by using reported procedure.² 1,3,5-tris(trimethylsilylethynyl)benzene (1 g; 2.7 mmol) was dissolved in a MeOH (25 mL) and THF (25 mL) mixture. Then aqueous solution of 1M KOH (10 mL) was added dropwise to the mixture and stirred the mixture for 3 hours at room temperature. The reaction mixture was diluted in CHCl_3 (100 mL) and then wash with H_2O (100 mL) and brine (100 mL). The organic phase was then dried over Na_2SO_4 and after removing the solvent under reduced pressure, the product was separated by column chromatography using CH_2Cl_2 . (0.38 g, 92%); ^1H NMR (200 MHz, CDCl_3): $\delta = 7.58$ (s, 3H), 3.11 (s, 3H) ppm



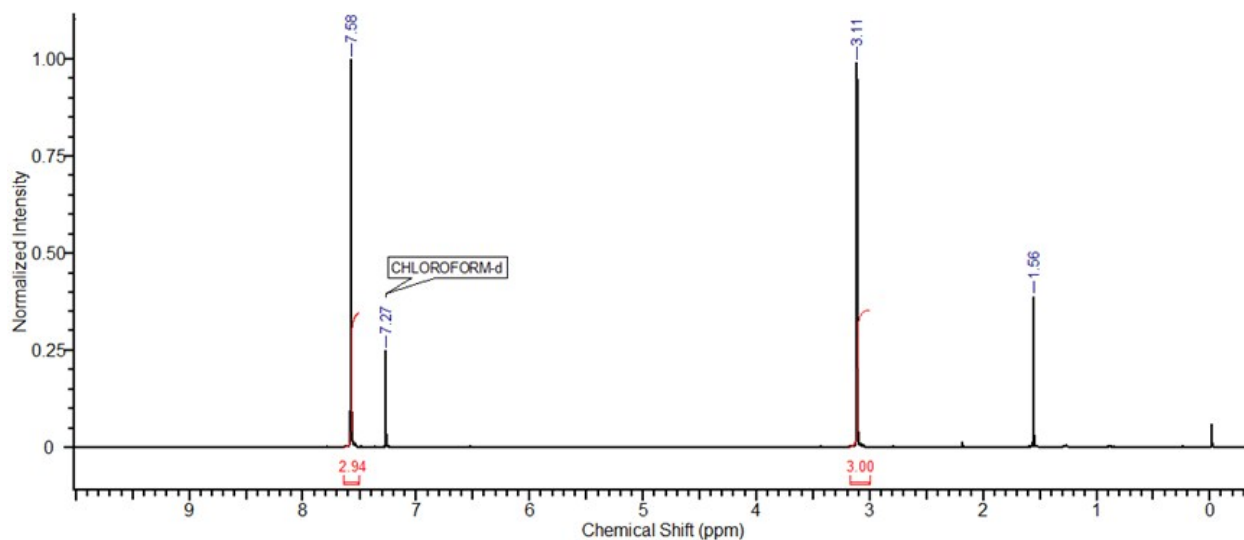
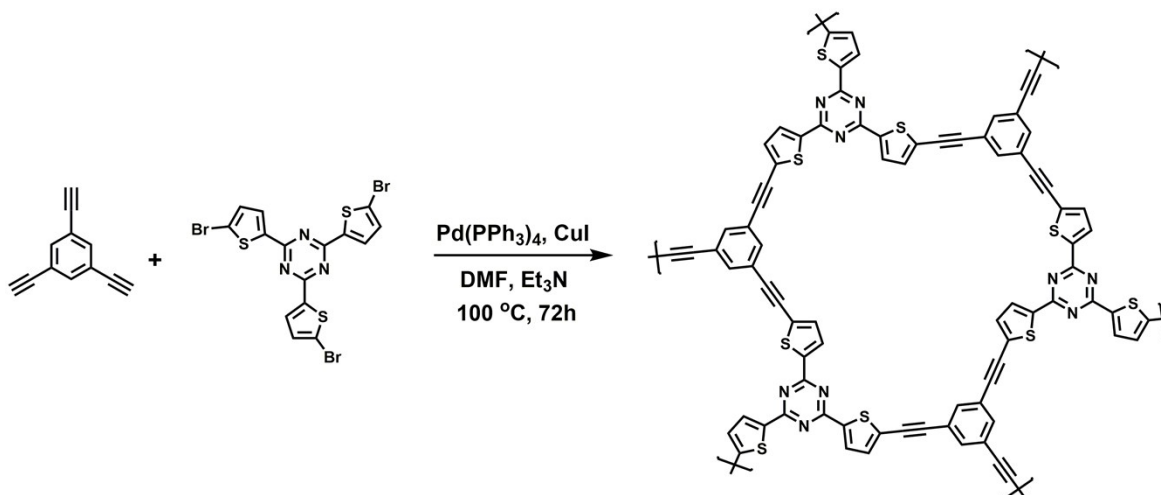


Fig. S4: $^1\text{H-NMR}$ spectrum of 1,3,5-triethynylbenzene

5) Synthesis of Triazine-Thiophene-Benzene CPPs

Synthesis of Triazine-Thiophene-Benzene CPPs was done by using reported procedure.³ 1,3,5-Triethynylbenzene (112 mg, 0.75 mmol) and 2,4,6-Tris(5-bromothiophen-2-yl)-1,3,5-triazine (282 mg, 0.5 mmol), were dissolved in a mixture of anhydrous DMF (5 mL) and Et_3N (5 mL) under argon atmosphere and then tetrakis(triphenylphosphine)palladium (60 mg), and copper(I) iodide (30 mg) was added to the reaction mixture and stirred the reaction mixture at 100 °C for 72 h under argon atmosphere. The mixture was cooled to room temperature, and insoluble precipitated polymer was filtered and washed three times with dichloromethane, water, methanol and acetone (100 ml each) to remove any unreacted monomers or catalyst residues. Further purification of the polymer was done by Soxhlet extraction with methanol and then CHCl_3 for 24h each. The product was then dried under vacuum for 24 h at 100 °C. (0.220 g, 87%)



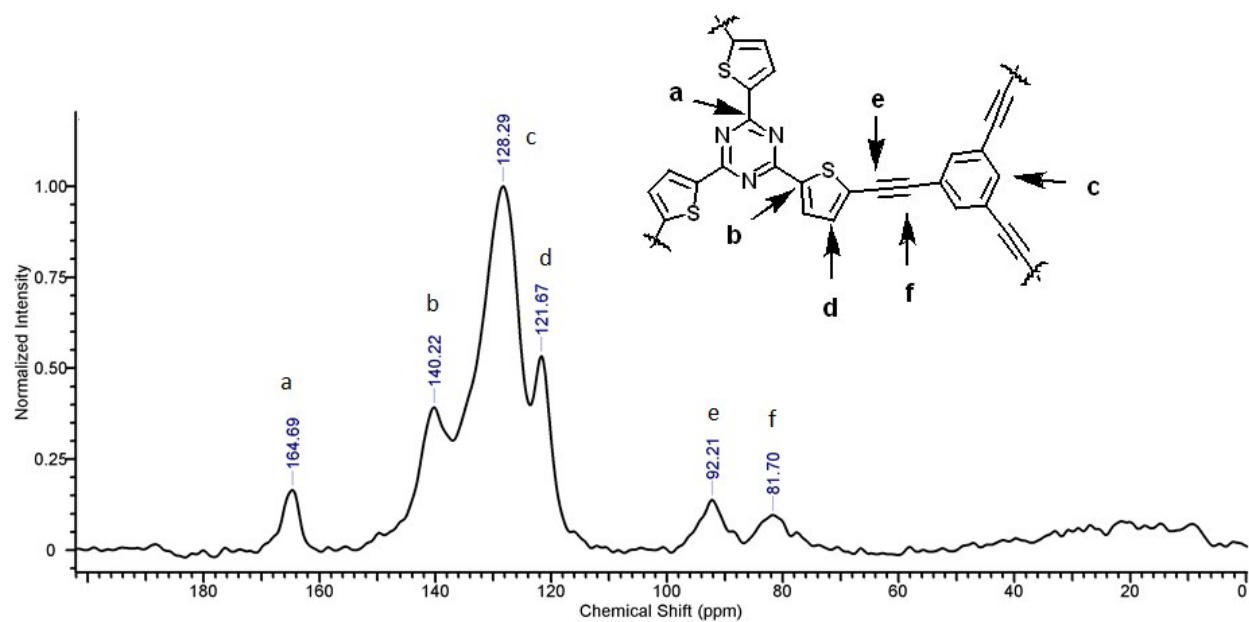


Fig. S5: Solid state ^{13}C NMR spectrum of TTB-CPP

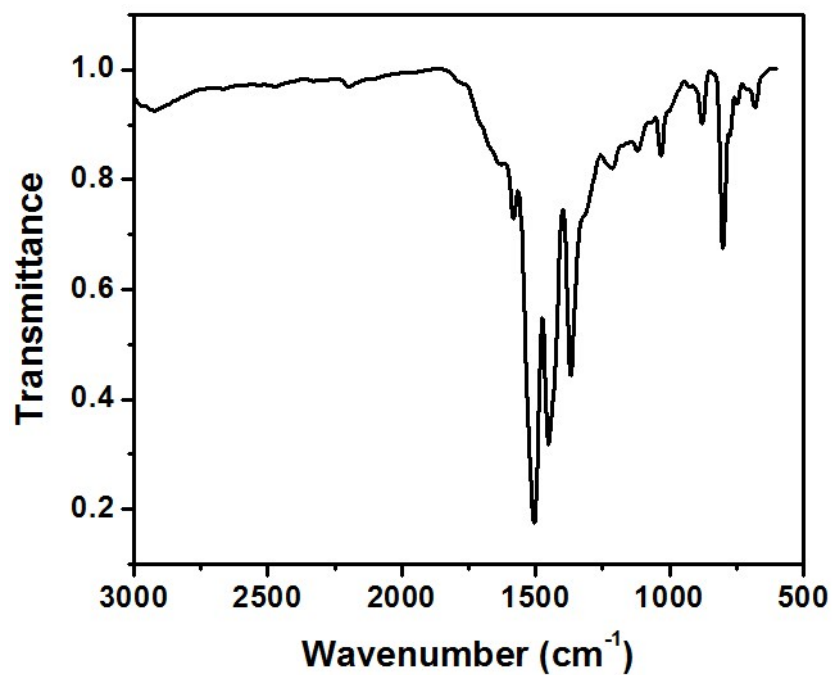


Fig. S6: FT-IR spectrum of TTB-CPP

Synthesized conjugated porous polymer (TTB-CPP) was pyrolyzed at different temperature 700, 800 and 900 °C under argon atmosphere in a tube furnace for 2h at a heating rate of 5 °C per minute and which were labeled as NS-G@700, NS-G@800 and NS-G@900 respectively.

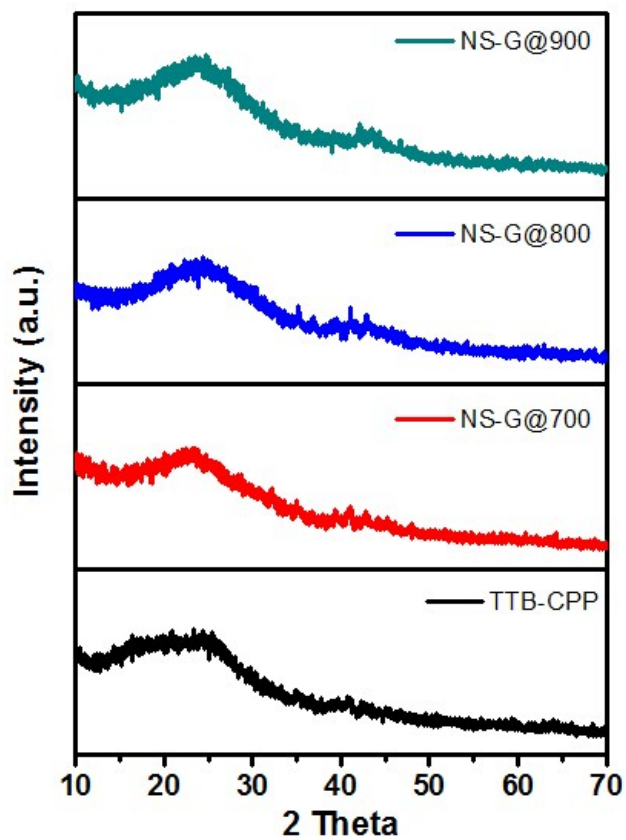


Fig. S7: Powder X-ray diffraction pattern of TTB-CPPs and NS-Gs

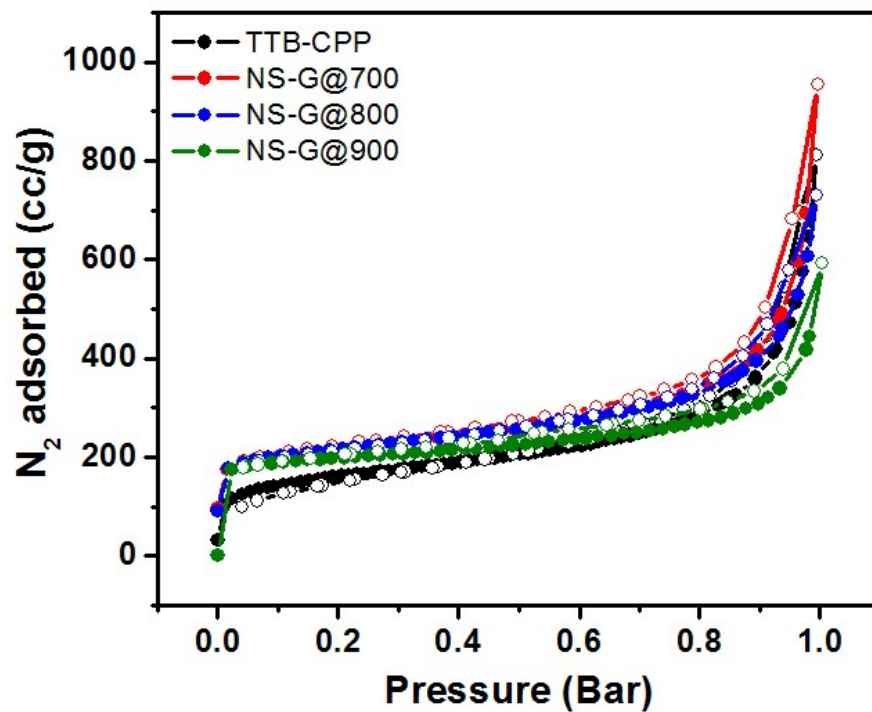


Fig. S8: N₂ adsorption desorption isotherm of TTB-CPPs and NS-Gs

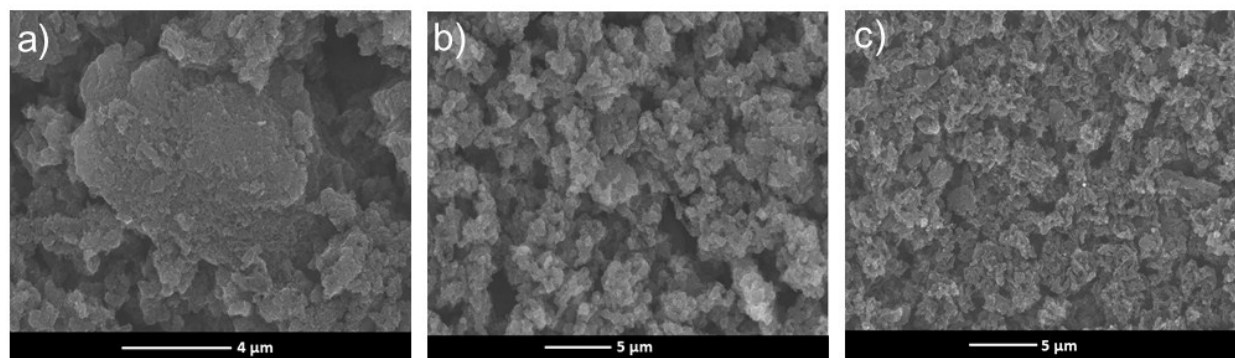


Fig. S9: SEM images of a) NS-G@700, b) NS-G@800 and c) NS-G@900

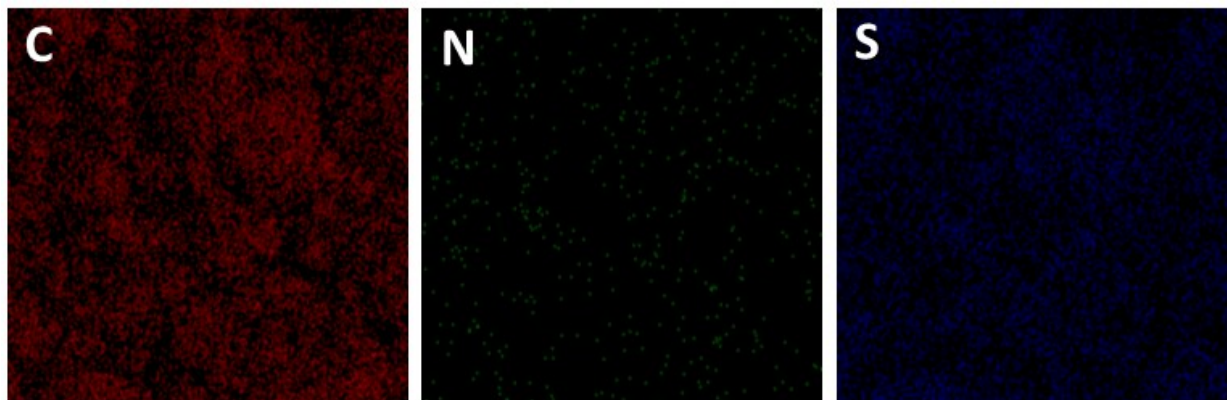


Fig. S10: SEM elemental mapping images of NS-G@800

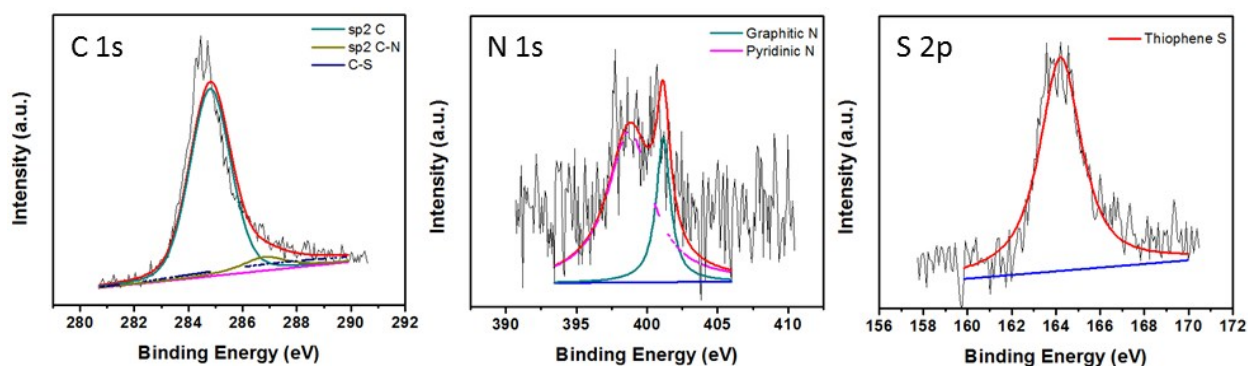


Fig. S11: Deconvoluted C 1s, N 1s and S 2p XPS spectra of NS-G@800

Supercapacitor measurement:

Cyclic voltammetry and galvanostatic charge discharge experiments were carried out using multichannel autolab MAC 80038 instrument with three electrode configuration in the potential range of -1 to 0V using 6M KOH solution as an electrolyte and in the potential range of 0 to 3V using 1M LiPF₆ in ethylene carbonate and diethyl carbonate as an electrolyte with two electrode configuration. Working electrodes were prepared by mixing NS-G(80 weight %) with carbon black (15 weight %) and Kynar (5 weight %), platinum foil as counter electrode and Hg/HgO as reference electrode.

The specific capacitance (C, F g⁻¹) was calculated from the discharge curve by using the following equation

$$C = (I \times t) / (m \times V)$$

Where I = discharge current in the unit of A,

V is the discharge voltage in the unit of V

t is the discharge time in the unit of s

m is the mass of the active material in the unit of g

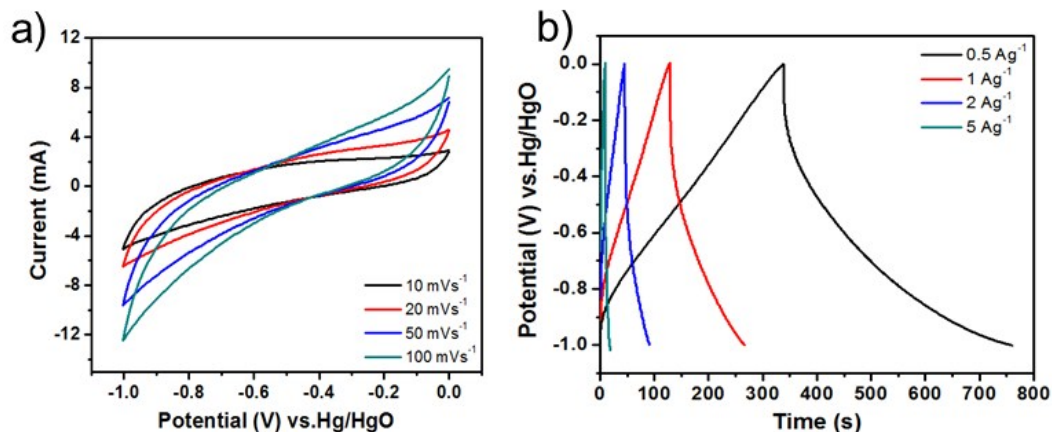


Fig. S12: Cyclic voltammogram a) and charge/discharge curves b) of NS-G@700

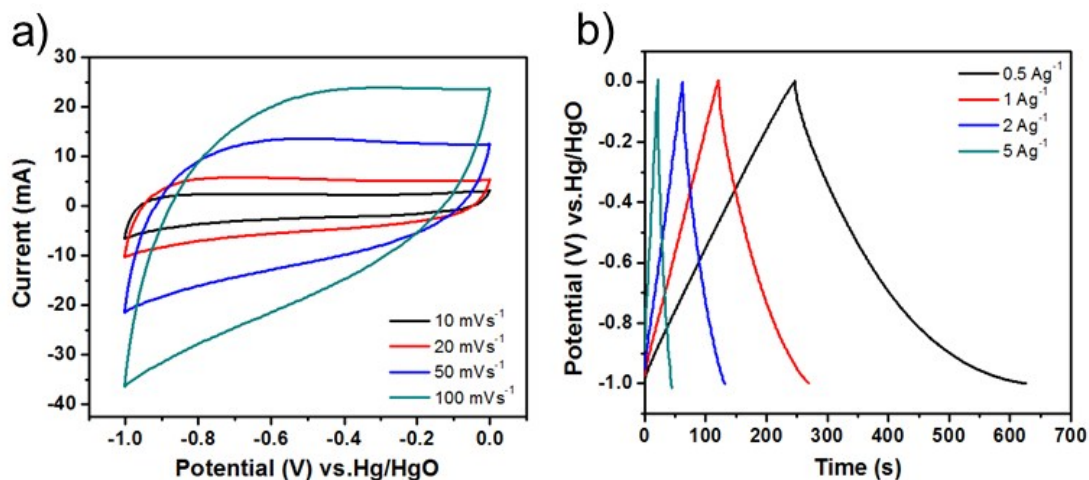


Fig. S13: Cyclic voltammogram a) and charge/discharge curves b) of NS-G@900

Oxygen Reduction Reaction (ORR) Measurement:

Using the conventional three electrode setup, oxygen reduction reaction (ORR) analysis was carried out by using the Bio-Logic instrument. Here, Glassy carbon (5 mm diameter) was used as

the working electrode, Hg/HgO was used as the reference electrode and graphite rod was used as the working electrode. The following procedure has used for making the catalyst ink for the ORR analysis. 5 mg of the catalyst was mixed with a 3:1 water-isopropyl alcohol mixture (1 mL), subsequently added 40 μL of 5 wt. % Nafion to it and sonicated in a bath sonicator for 1h. 20 μL of the catalyst ink was drop coated on the Glassy carbon working electrode surface and kept it for drying. The commercial 40 wt. % Pt/C (Johnson Matthey) slurry was made in the same procedure and a Pt loading of 100 $\mu\text{g cm}^{-2}$ was maintained in the analysis. The ORR analysis was carried out in 0.1M KOH solution under N_2 saturated and O_2 saturated atmospheres with a scan rate of 50 mV s^{-1} for Cyclic voltammetry (CV) and 5 mV s^{-1} for Linear sweep voltammetry (LSV) experiments respectively.

The Koutecky-Levich (K-L) equation has been used to find out the kinetic parameters and the K-L equation can be given as below,

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L}$$

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

Where,

$$j_k = nFAkC_0$$

$$B = 0.62 nFAC_{\text{O}_2}D_{\text{O}_2}^{2/3}\nu^{-1/6}$$

Where, j is the measured current density, j_k is the kinetic current density, j_L is the limiting current density, ω is the angular rotation ($\omega = 2\pi f/60$, f is the rotation speed), n is the number of electron transferred in the oxygen reduction, F is the Faradays constant (96485 C mol^{-1}), A is the area of the electrode, C_{O_2} is the bulk concentration of O_2 , ν is the kinematic viscosity of the electrolyte, and k is the electron transfer rate constant.

The H_2O_2 yield was found out by using the rotating ring disc electrode (RRDE) study by keeping the ring potential at 0.6 V. The glassy carbon disc (0.2826 cm^2) having a platinum ring was used as the working electrode, Hg/HgO was used as the reference electrode and graphite rod was used as the counter electrode. The below formula was used to calculate the H_2O_2 percentage.

$$\text{H}_2\text{O}_2\% = \frac{200 * I_r/N}{I_d + I_r/N}$$

The number of electron transfer during ORR was calculated by using the equation,

$$n = \frac{4 I_d}{I_d + I_r/N}$$

Where, 'Ir' is the Faradaic ring current, 'Id' is the Faradaic disc current, 'N' is the collection efficiency (0.37) and 'n' is the number of transferred electrons.

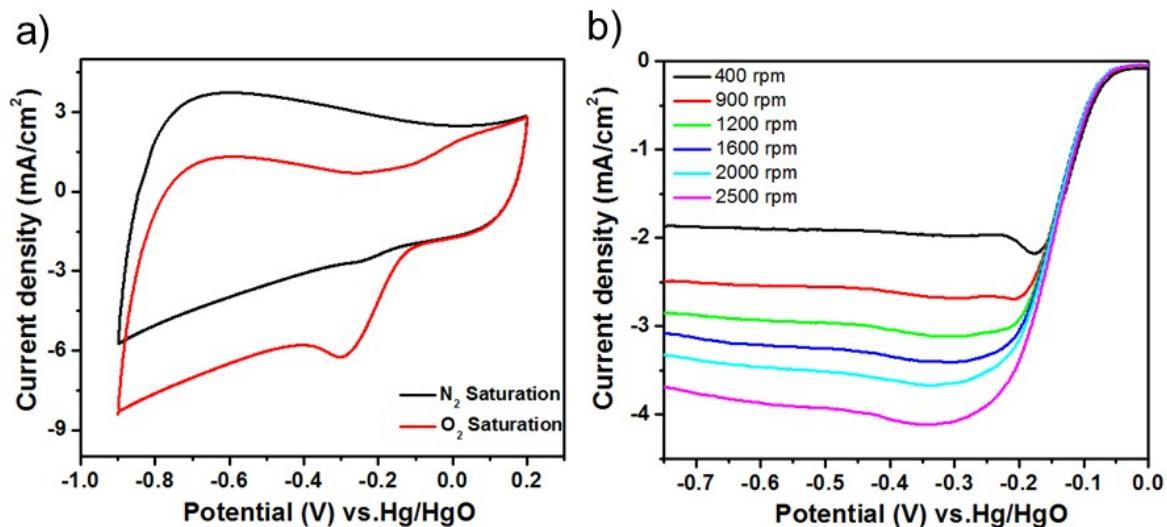


Fig. S14: Cyclic voltammogram a) and LSV of NS-G@700

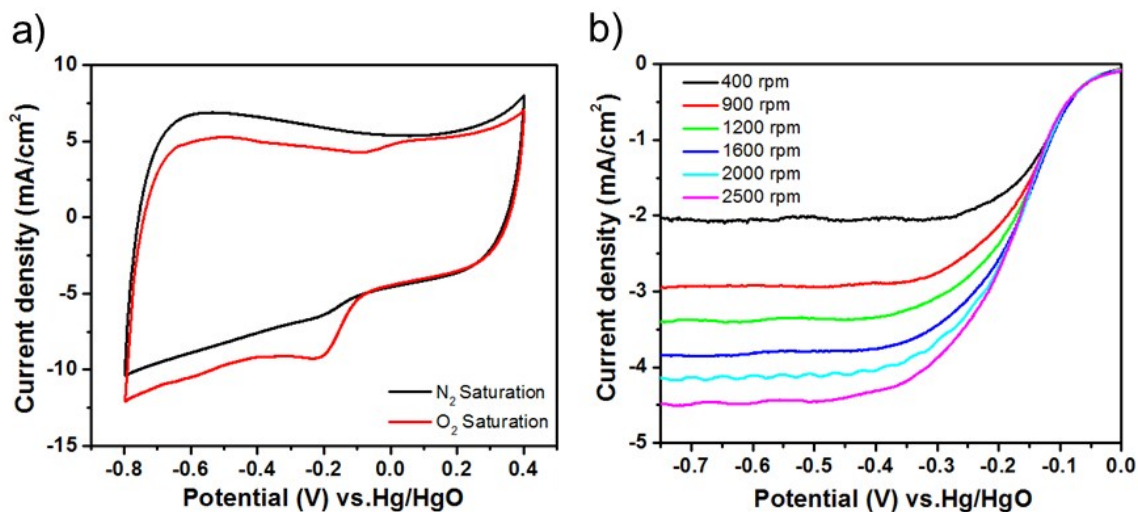


Fig. S15: Cyclic voltammogram a) and LSV of NS-G@900

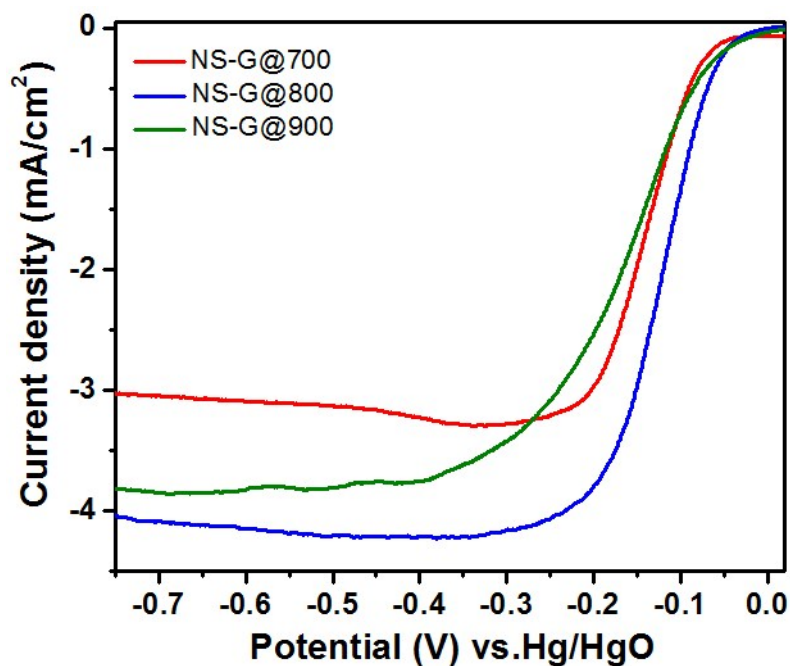


Fig. S16: LSV curves of NS-Gs in O₂-saturated 0.1M KOH solution at 1600 rpm at a scan rate of 5 mVs⁻¹

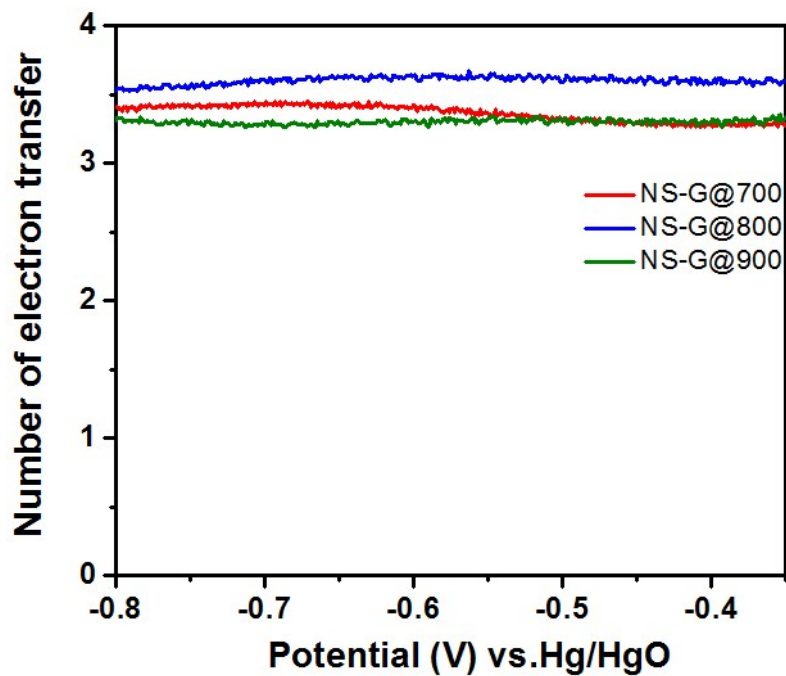


Fig. S17: Number of electron transfer of NS-Gs from RRDE

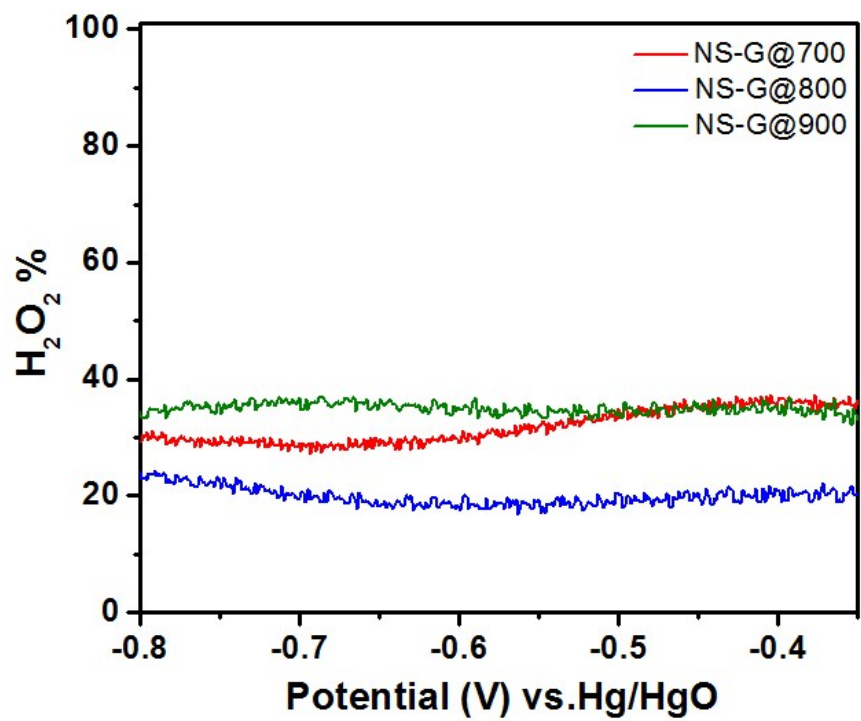


Fig. S18: Yield of H₂O₂ formed during RRDE analysis of NS-Gs

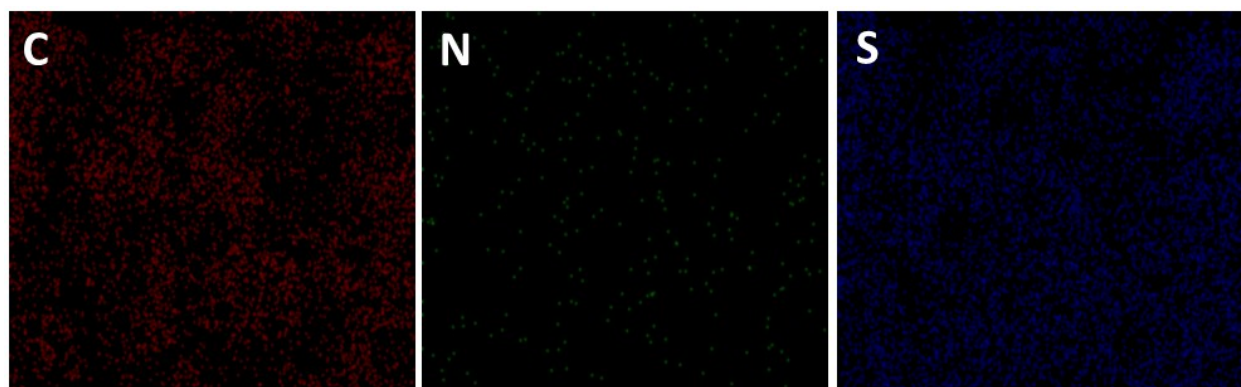


Fig. S19: SEM elemental mapping images of TTB-CPP

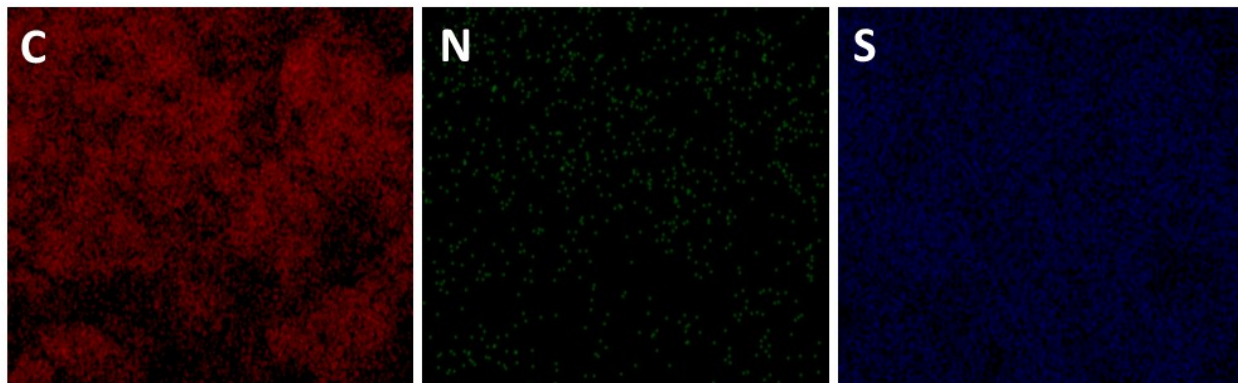


Fig. S20: SEM elemental mapping images of NS-G@700

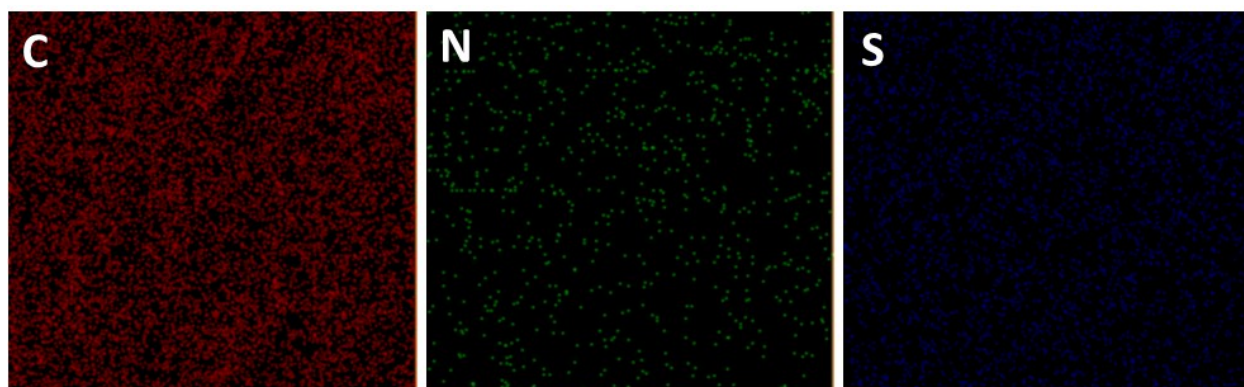


Fig. S21: SEM elemental mapping images of NS-G@900

Table1. Comparison of the onset potential and the half wave potential obtained from RDE

SI.No.	Sample	Onset Potential (V)	$E_{1/2}$ (V)
1	NS-G@700	-0.041	-0.135
2	NS-G@800	-0.005	-0.121
3	NS-G@900	-0.028	-0.163
4	40% Pt/C	0.1	0.030

Table2. Elemental analysis of TTB-CPPs and NS-Gs

Sample	Carbon	Nitrogen	Sulphur
Polymer	64.38	4.52	14.20
NS-G@700	63.64	1.20	7.81
NS-G@800	69.55	1.15	6.54
NS-G@900	64.19	0.28	6.33

References:

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- 2 K. Yoosaf, A. Llanes-Pallas, T. Marangoni, A. Belbakra, R. Marega, E. Botek, B. Champagne, D. Bonifazi and N. Armaroli, *Chem.–Eur. J.*, 2011, **17**, 3262.
- 3 S. Ren, R. Dawson, A. Laybourn, J.-X. Jiang, Y. Khimyak, D. J. Adams and A. I. Cooper, *Polym. Chem.*, 2012, **3**, 928.