

Electronic Supplementary Information

Heteroatom facilitated preparation of electrodes for sodium ion batteries

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Experimental section:

Chemicals:

Thiophene-2-carbonitrile, N-bromosuccinimide, 3,4-ethylenedioxythiophene, tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$), and trimethyltin chloride, n-Butyllithium solution (2.5M in hexane) were purchased from Aldrich chemicals. Dimethylformamide, tetrahydrofuran, chloroform were purchased from local chemicals and dried using appropriate drying agent and stored on molecular sieves. Tri fluoro methane sulfonic acid was purchased from Avra chemicals.

Device and material characterization:

^1H Solid state ^{13}C NMR spectra were measured on Bruker arx 200 MHz AVANS spectrometer. Thermogravimetric analysis (TGA) was done using PerkinElmer STA 6000 Thermogravimetric analyser. 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. Field emission scanning electron microscopy (FE-SEM) images were taken using FEI Nova Nano FESEM. The cyclic voltammetry and the charge-discharge experiments were carried out using multi channel autolab MAC 80038 instrument in the potential range of 0.001 - 3 V vs. Na/Na^+ at different current density. Electrochemical Impedance spectroscopy measurements were done in the frequency range of 10 mHz to 40 kHz using Biologic instrument.

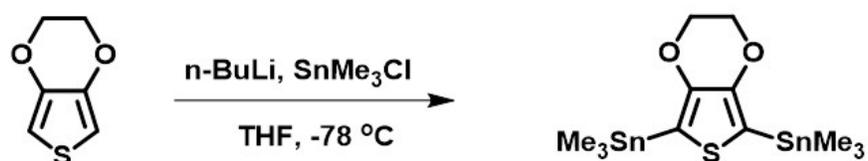
Electrode Preparation:

Electrodes were prepared by mixing C-NOS active material (80 weight %) with carbon black (15 weight %) and Kynar (5 weight %). A paste of these materials was prepared using N-methyl-2-pyrrolidone (NMP) as a solvent. The paste was coated on Aluminum foil and then dried overnight at 80 °C for 10 h under vacuum. The electrodes were then pressed and cut into disks and then transferred into an argon filled glove box and used as working electrode. Coin cells (CR2032) were assembled using sodium foil was used as counter electrode, glass membrane was used as separator and NaPF_6 (1 M) in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 w/w) as the electrolyte. The battery testing was carried out in atmospheric condition.

Synthesis procedure:

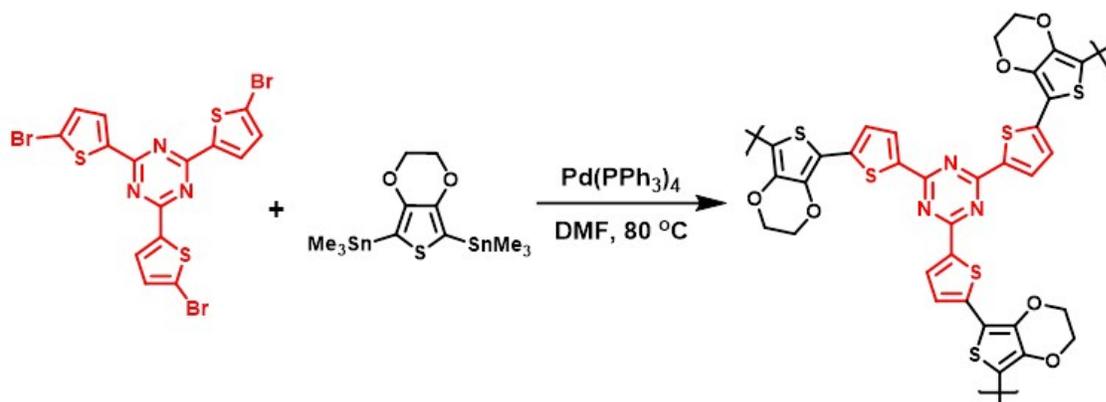
Synthesis of 2,5-Bis(trimethylstannyl)-3,4-ethylenedioxythiophene

3,4-ethylenedioxythiophene (5 g, 35.1 mmol) was added in dry THF (40 mL) and cooled to -78 °C in a mixture of liquid nitrogen and methanol under argon atmosphere. Then, *n*BuLi (2.5M in hexane, 28 mL) was added dropwise to the reaction mixture, and the temperature of the reaction mixture was kept constant below -55 °C. A solution of trimethyltin chloride (14 g, 70 mmol) in dry THF (20 mL) was slowly added to the reaction mixture, after which the temperature was allowed to reach room temperature and stirred the reaction mixture for 12 hours. After that, solvent was removed under reduced pressure and the residue was extracted with dichloromethane water mixture. The organic fraction was dried and filtered, and the solvent was removed under reduced pressure to give the product (11.2 g, 70 % yield).



Synthesis of Triazine-Thiophene-EDOT CPP

2,5-Bis(trimethylstannyl)-3,4-ethylenedioxythiophene (746 mg, 1.5 mmol) and 2,4,6-Tris(5-bromothiophen-2-yl)-1,3,5-triazine (400 mg, 0.7 mmol), were dissolved in anhydrous DMF (30 mL) under argon atmosphere and then tetrakis(triphenylphosphine)palladium(105 mg) was added to the reaction mixture and stirred the reaction mixture at 80 °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, methanol and acetone (200 ml each) to remove any unreacted monomers or catalyst residues. Further purification of the polymer was done by Soxhlet extraction with methanol and then CHCl₃ for 24h each. The product was then dried under vacuum for 24 h at 100 °C.



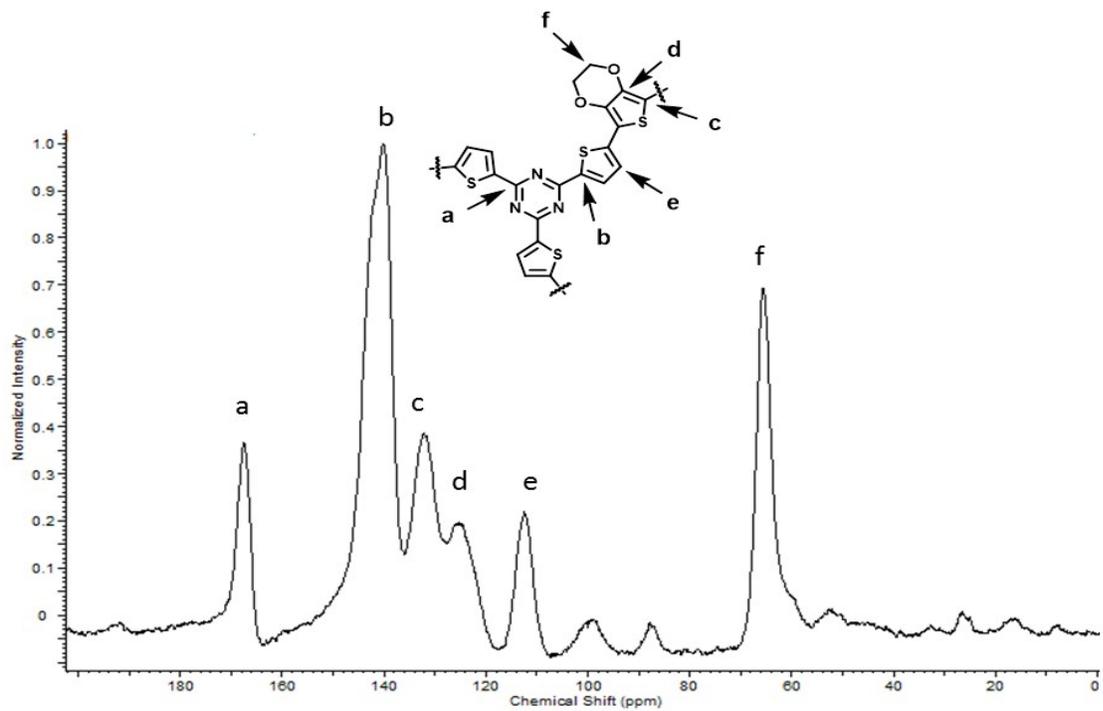


Fig. S1: Solid state ^{13}C NMR spectrum of CPP

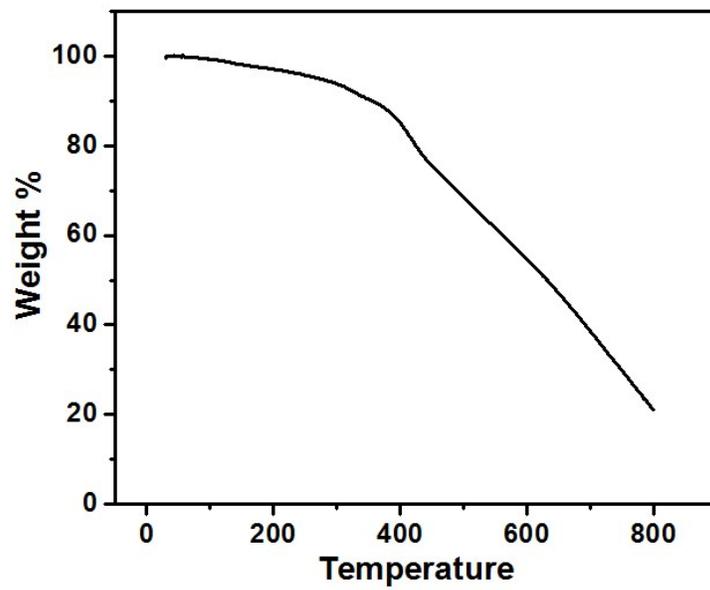


Fig. S2: TGA of CPP

Synthesized conjugated porous polymer (CPP) was pyrolyzed at different temperature 800, 1000 and 1200 °C under argon atmosphere in a tube furnace for 2h at a heating rate of 5 °C per minute and which were labeled as C-NOS@800, C-NOS@1000 and C-NOS@1200 respectively.

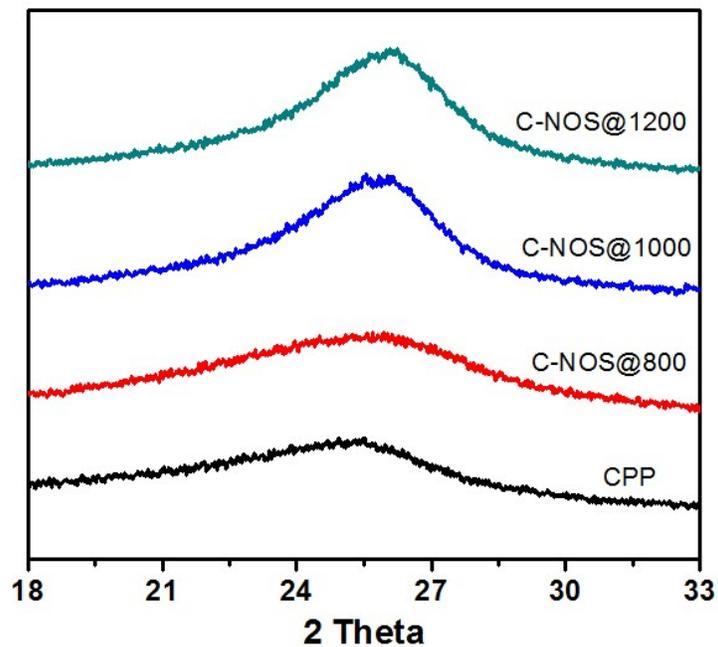


Fig. S3: Powder X-ray diffraction pattern of CPP and C-NOS

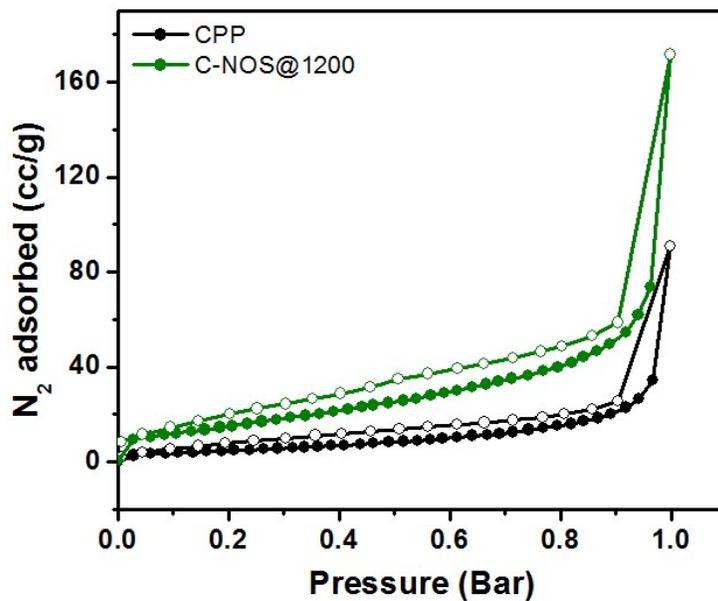


Fig. S4: N₂ adsorption desorption isotherm of CPP and C-NOS@1200

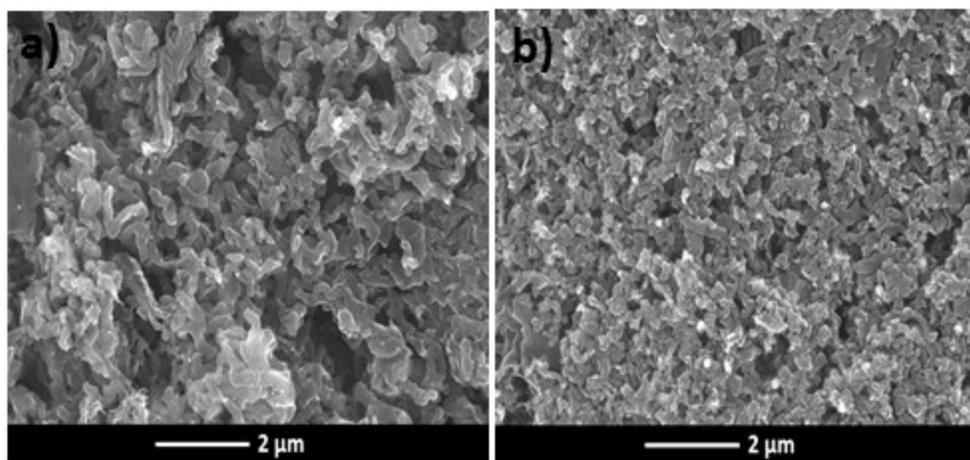


Fig. S5: SEM images of a) C-NOS@800, b) C-NOS@1200

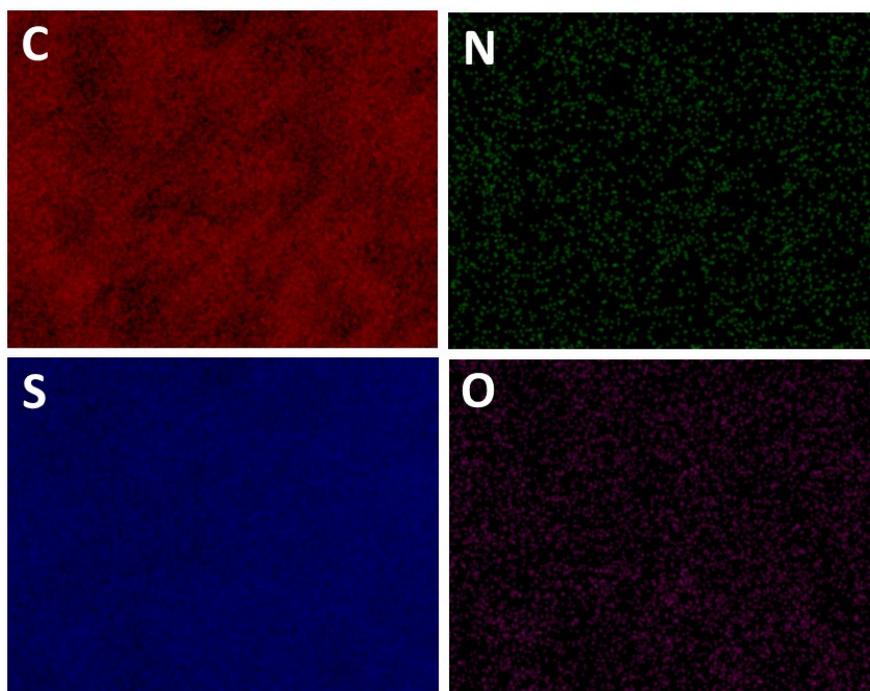


Fig. S6: SEM elemental mapping images of C-NOS@800

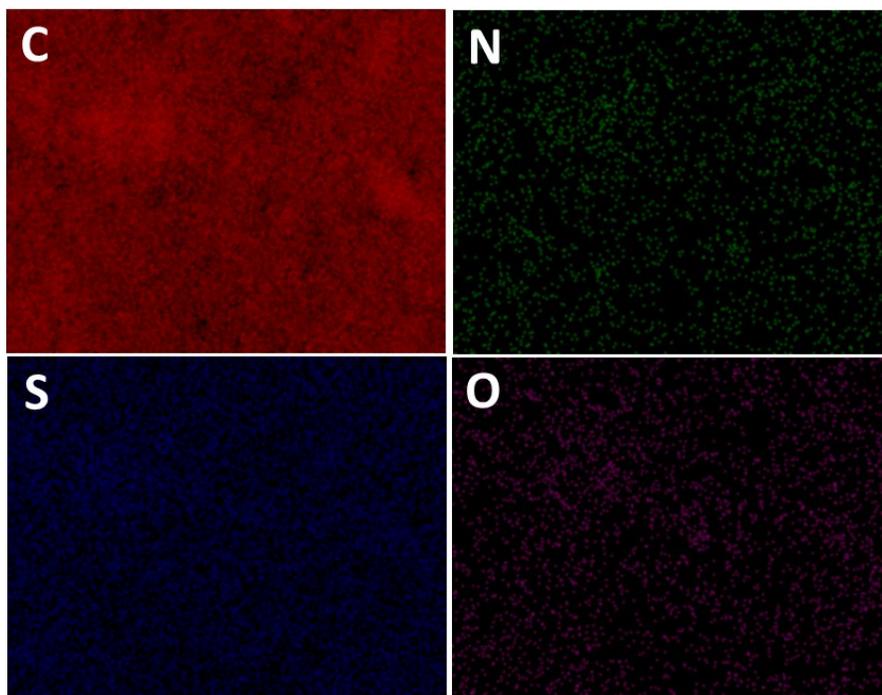


Fig. S7: SEM elemental mapping images of C-NOS@1200

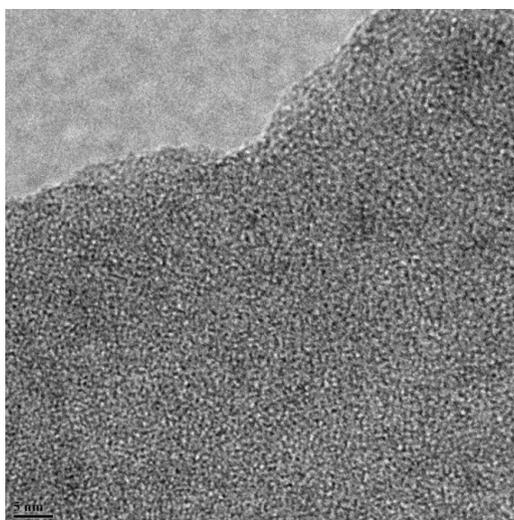


Fig. S8: TEM image of CPP

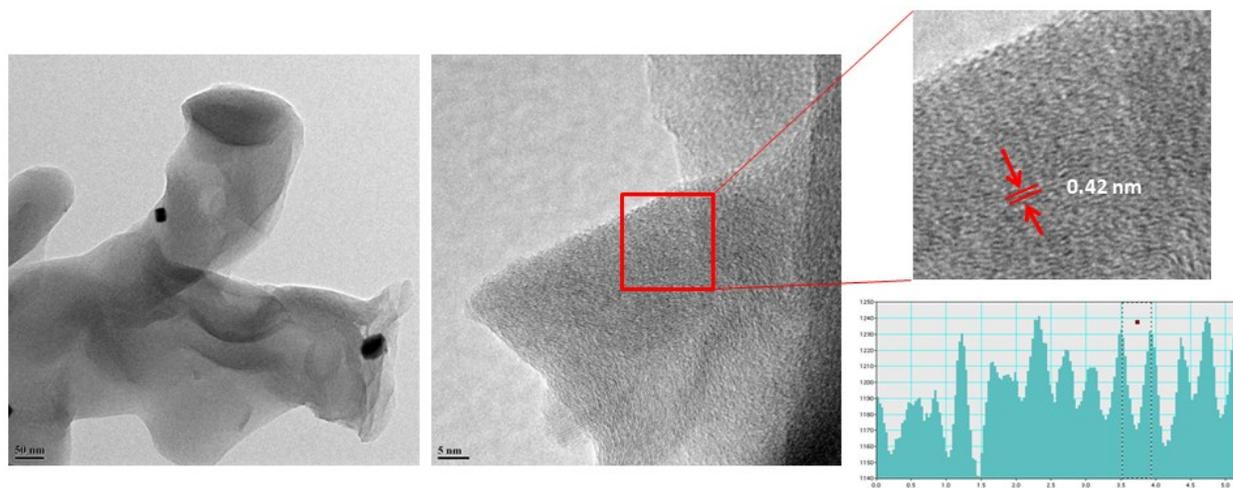


Fig. S9: TEM images and line profile of C-NOS@800

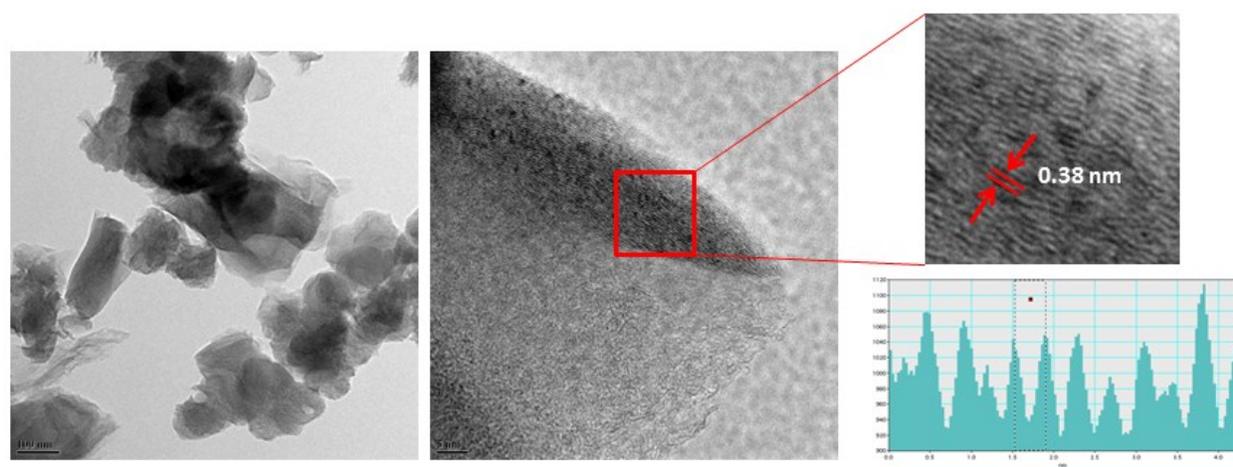


Fig. S10: TEM images and line profile of C-NOS@1000

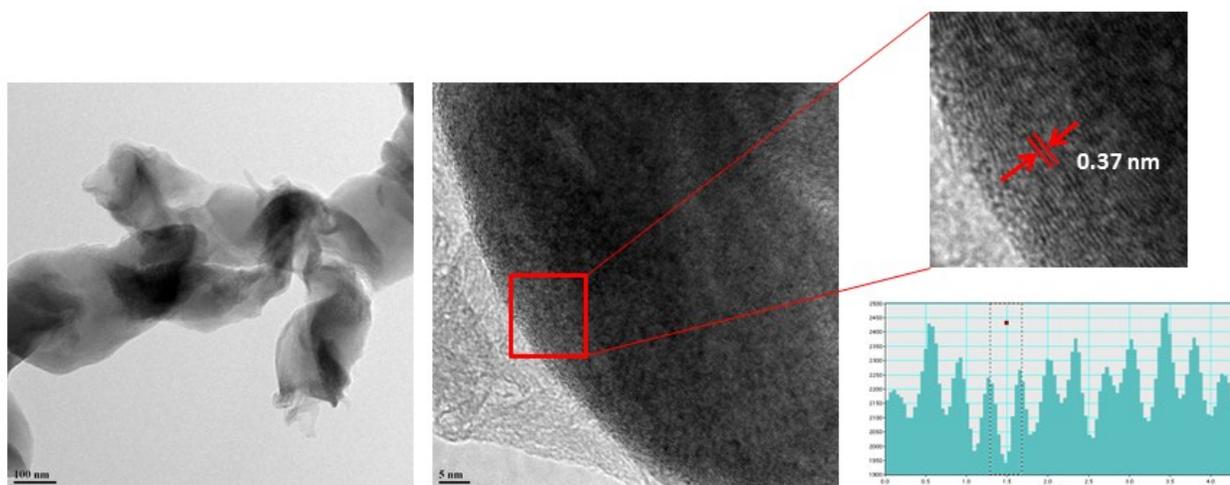


Fig. S11: TEM images and line profile of C-NOS@1200

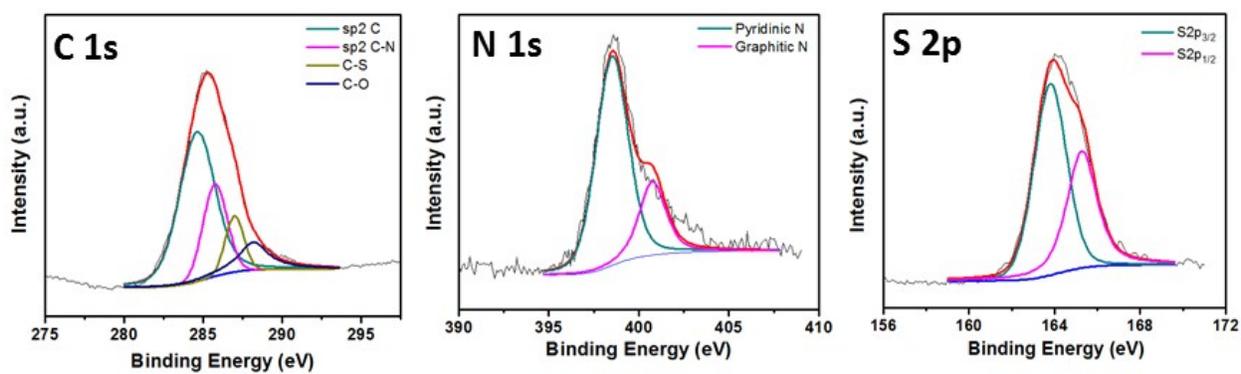


Fig. S12: Deconvoluted C 1s, N 1s and S 2p XPS spectra of CPP

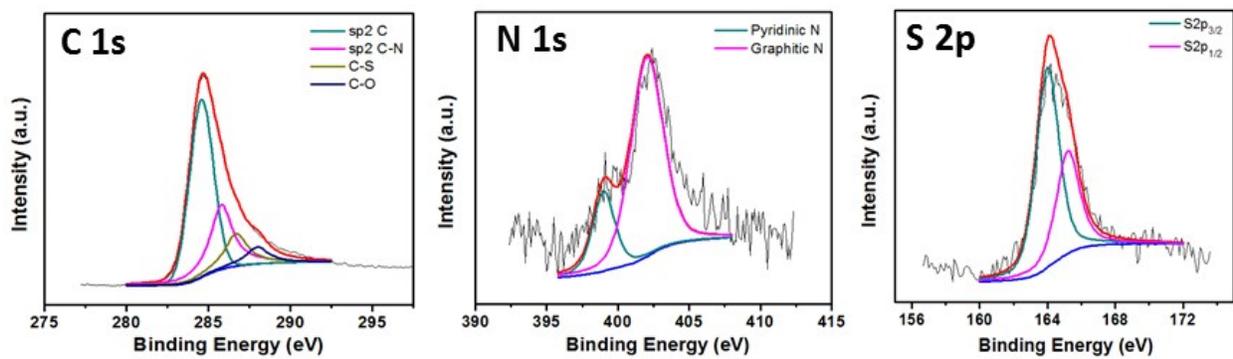


Fig. S13: Deconvoluted C 1s, N 1s and S 2p XPS spectra of C-NOS@1000

Table1. Atomic percentage obtained from XPS spectra

Sample	Carbon	Nitrogen	Oxygen	Sulfur
Polymer	74.24	4.63	14.77	6.35
NOS Carbon-800	87.19	3.57	6.27	2.95
NOS Carbon-1000	90.64	2.07	5.86	1.43
NOS Carbon-1200	94.14	0.90	4.68	0.30

Electrochemical measurements:

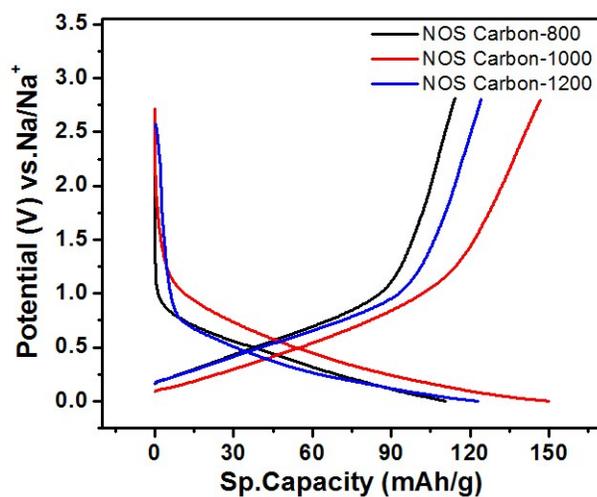


Fig. S14: Comparative charge discharge curves of C-NOS at a current density 100 mA/g

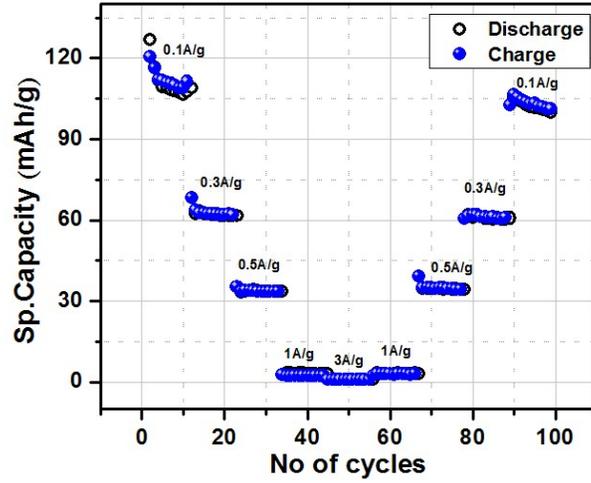


Fig. S15: Rate performance of C-NOS@1200 at different current densities

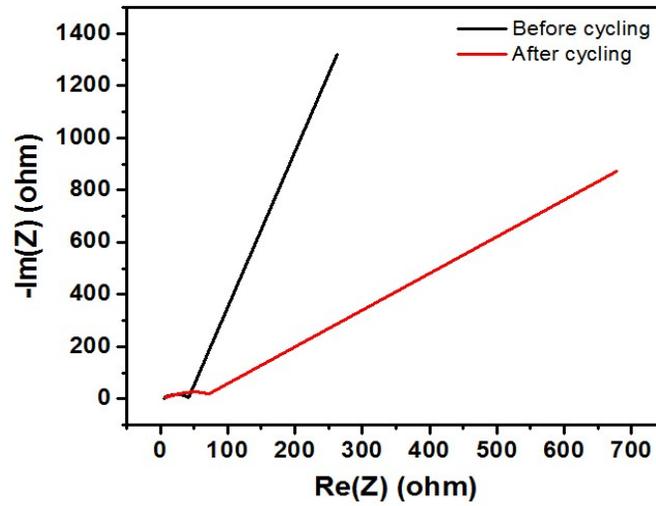


Fig. S16: Impedance spectra of C-NOS@1000 before and after cycling