Electronic Supplementary Information (ESI)

Laser-irradiated carbonized polyaniline-N-doped graphene heterostructure helps to improve the cyclability of on-chip micro-supercapacitor

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Materials and Instrumentations

Materials

Highly pure graphite flakes (<20μm), phosphorous pentoxide (P_2O_5, >98%), potassium permanganate ($KMnO_4$), copper sulfate ($CuSO_4$), potassium persulfate ($K_2S_2O_8$) were purchased from Sigma Aldrich and were used as received. Sulphuric acid (H_2SO_4), nitric acid (HNO_3), Aniline, hydrochloric acid (HCl), and perchloric acid ($HClO_4$) were purchased from Merck chemicals India. Poly (vinyl) alcohol (M.W. 89000-98000) was purchased from Alfa Aesar (Thermo Fischer Scientific Chemicals Inc.; US). A high-purity copper foil was purchased from Gelon LIB group, China. PET sheets (d = 0.3 mm) were purchased from the local market. Before use, all the PET sheets were washed with deionized (DI) water and ethanol repeatedly. All other chemicals were at least analytical grade and used without further purification. All aqueous solution was prepared using Millipore water.

Instrumentation details

Raman spectra was collected in a WITEC Focus Innovations Alpha-300 Raman confocal microscope with an excitation laser wavelength of 532 nm. Scanning electron microscopy (SEM) images were obtained in a microscope (SEM Jeol JSMIT300). The elemental composition of rGO-PANI and cPANI-NG was investigated using Bruker XFlash 6130 Energy Dispersive Spectroscopy (EDS). High-Resolution Transmission Electron Microscopy (HRTEM) studies were conducted on a JEM2100 instrument. Laser irradiation of graphene film and patterning was carried out by CO_2 laser (60 W) and near-infrared (NIR) Laser source (30 W), respectively. The material's electrical conductivity was measured by a two-probe and four-probe method using a Keysight B2902A source meter. X-ray photoelectron spectroscopy (XPS) was collected in an ultrahigh vacuum chamber (2×10^{-9} mbar) using monochromatic 6 mA beam current by Kα plus XPS system by ThermoFisher Scientific instruments (UK). Electrochemical measurements like cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and Electrochemical impedance spectroscopy (EIS) were performed on a Biologic VSP electrochemical workstation. A two-electrode Biologic BCS 810 setup was used to measure all-solid-state electrochemical performances of in-plane micro supercapacitor gel electrolyte (PVA-H_3PO_4). Electrochemically deposited three-dimensional reduced graphene oxide (rGO-PANI), copper foam coated copper foil (Cuf) refers to the working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and platinum wire as a counter electrode.

Methods

Synthesis of GO

Graphite oxide was oxidized from graphite powder using a modified Hummer's method. The details of synthesis can be found in the literature.[1] Graphite oxide (1 g) was exfoliated in deionized water to obtain a homogenous solution of graphene oxide, according to our group's previous report.[2]

Electrodeposition of copper foam

The galvanostatic electrodeposition was carried out to depose copper foam (Cuf) in the aqueous solution at room temperature. Briefly, an aqueous solution of 0.4 M with 1.5 M H_2SO_4 was used. A commercially available high-purity copper sheet (>99%) with specified dimensions was used as the substrate (cathode) for copper foam deposition, and another copper sheet of the equal area was used as a counter electrode (anode). Both copper sheets were cleaned with 30 % HNO_3, washed with Millipore water 3-4 times, and finally washed with ethanol. When not used, the cleaned copper sheets were kept in an argon atmosphere to avoid atmospheric oxidation. Copper foam deposition was carried out with a constant current density of 1 A cm^{-2} for 45 s using a DC voltage supply system. A gap of 2 cm was maintained between the electrodes. The as-deposited Cu foam sheet was finally cleaned with Millipore water repeatedly. The formation process of the foam structure is by dynamic hydrogen bubble template mechanism (DHBT).[3]

Electrochemical deposition of rGO-PANI on Cu/Cuf

Electrochemically reduced graphene-oxide (rGO) and PANI networks were grown by electrolysis of GO aqueous solution on the Cu foam. In a typical procedure, bulk electrolysis of

GO aqueous suspension (3 mg ml^{-1}) and aniline in 0.5 M perchloric acid ($HClO_4$) was carried out at an applied potential of -1.1V against Ag/AgCl reference for 180-200 seconds on Cuf electrode. After the electrochemical deposition of ErGO, any unreduced GO suspension or physically absorbed rGO-PANI polymer attached to the surface was removed by repeatedly washing the film with DI water. Electroreduction of the oxygen-containing groups in GO leads to the formation of the conductive rGO sheets with the PANI growth in between the sheets. rGO-PANI membrane deposited onto Cuf was separated by etching Cuf/Cu with 10% ammonium persulfate solution. Typically, the rGO-PANI/Cuf/Cu was placed in the $(NH_4)_2S_2O_8$ solution (with the rGO-PANI side facing up) for overnight under ambient conditions. A stable copper sulfate formed during the oxidation of copper by persulfate to form soluble copper sulfate as,

$$Cu + S_2O_8^{-2} \longrightarrow CuSO_4 + SO_4^{-2}$$

After the complete etching of copper, the rGO-PANI membrane starts floating onto the surface of the solution and the solution turns blue in color. The rGO-PANI film was then transferred by scooping up onto a PET sheet (polyethylene terephthalate) and then washed in Millipore water several times for the complete removal of Cu^{+2} ions that may have adsorbed in the rGO-PANI networks. The rGO-PANI electrode would further be laser-induced to produce N-doping of graphene and carbonization of PANI.

The Cuf@Cu foil was directly used as substrate for rGO-PANI deposition and acts as a working electrode in a three-electrode set-up comprising a Pt wire as counter electrode, Ag/AgCl (3.5 M KCl) a reference electrode in the dispersion solution of GO to PANI in different ratios. The final dispersion solution was named as rGO-PANI. When a potential of -1.1 V was applied, simultaneous reduction of GO, polymerization of aniline into PANI and deposition of rGO-PANI composite happens. The as-prepared sample was transferred into ammonium persulfate (10

wt%) solution heading rGO-PANI film upside. The Cuf@Cu will dissolve into the solution as $CuSO_4$ and a freestanding rGO-PANI film floats on the solution. The freestanding rGO-PANI film was washed thoroughly with distilled (DI) water and transferred to a flexible Poly(terephthalate) (PET) sheet. The transferred film was kept on drying for overnight in a vacuum medium.

Formulas for electrochemical characterization

The area normalized specific capacitance C_{sp} can be calculated from cyclic voltammetry via the equation

$$C_{s\rho} = \frac{I(V)}{2A \cdot \dot{v}V}$$

where A (in cm^2) is the geometric area, ν is the voltage scan rate (V s^{-1}), V (in V) is the potential window of the CV curves, and I (V) is current at different potentials. Dividing areal capacitance by thickness 't' (μm) of the electrode gives volumetric capacitance C_v (F cm^{-3}) as follows.

$$C_v = C_s / t$$

Alternatively, the specific capacitance for the electrodes can be obtained from charge/discharge data according to the following equation

$$C_{sp} = \frac{I}{A\frac{dV}{dt}}$$

Where C_{sp} is the specific capacitance (mF cm^{-2}), I is current (A), dV/dt is the discharge slope after the IR drop, and A is the geometrical area of the single electrode. The volumetric capacitance (F cm^{-3}) can be calculated by normalizing C_{sp} with thickness of the sheet. The area normalized energy density E_A and power density P_A were calculated from

$$E_A = \frac{1 C_{sp} \Delta V^2}{2 \quad 3.6}$$

$$P_A = \frac{E}{\Delta t} 3.6$$

where E_A is the energy density (mWh cm^{-2}), P_A is the power density (kW cm^{-2}), C_{sp} is the specific capacitance, ΔV is the potential window ($\Delta V = V_{max} - V_{drop}$) , Δt is the discharge time (s).

Formula used for Raman analysis

The general expression that gives the crystallite size (L_a) from the integrated intensity ratio I_G/I_D by using any laser line in the visible range is given by the equation.

$$L_a(nm) = (2.4 \times 10^{-10})(\lambda_l^4)\left[\frac{I_G}{I_D}\right]$$

Where λ_l is laser line wavelength (532 nm) and [I_D/I_G] is ratio of D- and G- band intensities.

Table S1: Different parameters calculated from Raman spectra

	D band	**G band**	**2D band**	**I_{2D}/I_G**	**I_G/I_D**	**L_a(nm)**
LIG	1353	1579	2704	0.344	1.465	28.06
cPANI-NG$_3$	1348	1580	2708	0.255	1.180	22.68
cPANI-NG$_4$	1349	1579	2706	0.179	0.943	18.13
cPANI-NG$_6$	1352	1580	2707	0.163	1.113	21.396

Table S2: Nyquist plot equivalent circuit parameters

Equivalent circuit: ESR + $C_{dl}/(Rc_t + W_o)$				
Parameters	ESR	C_{dl}	R_{ct}	W_o
Value	436.5 ohm	1.618 uF	8.621×10^{-3} ohm	2.874×10^{6} ohm $s^{-1/2}$

Table S3: A comparative table showing the different material with the parameters such as cycling stability, Electrolyte and specific capacitance

S.No.	Material	Cycling Stability	Electrolyte	Specific Capacitance	Reference
1.	Graphene/PANI woven fabric	100 % after 2,000 cycles	H_3PO_4/PVA	23 mF cm^{-2}	[4]
2.	Graphene/Sulphonated PANI	85.4 % after 10,000 cycles	H_2SO_4/PVA	3.31 mF cm^{-2}	[5]
3.	rGO/PANI hybrid	97.6 % after 5000 cycles	H_2SO_4/PVA	35.5 mF cm^{-2}	[6]
4.	PANI in graphene electrodes	80.9 % after 500 cycles	H_2SO_4/PVA	7.6 mF cm^{-2}	[7]
5.	rGO/PANI	85 % after 1000 cycles	PVA/H_2SO_4	55.67 mF cm^{-2}	[8]
6.	rGO@PANI	93.5 % after 1000 cycles	H_2SO_4/PVA	72 mF cm^{-2}	[9]
7.	Graphene-PANI Hydrogel	100 % after 10,000 cycles	-	218.26 mF cm^{-2}	[10]
8.	Laser scribed graphene/PANI	90 % after 10,000 cycles	PVA-H_2SO_4	7.6 mF cm^{-2}	[11]
9.	Laser irradiated graphene/Polyimide	96 % after 2,000 cycles	PVA/H_2SO_4	42.6 mF cm^{-2}	[12]
10.	Laser irradiated S,N doped graphene	99 % after 2,000 cycles	PVA/H_3PO_4	13.8 mF cm^{-2}	[13]
11.	**This Work**	**135% after 70,000 cycles**	**PVA/H_3PO_4**	**43.5 mF cm^{-2}**	**-**

PANI-Polyaniline, rGO- reduced graphene oxide

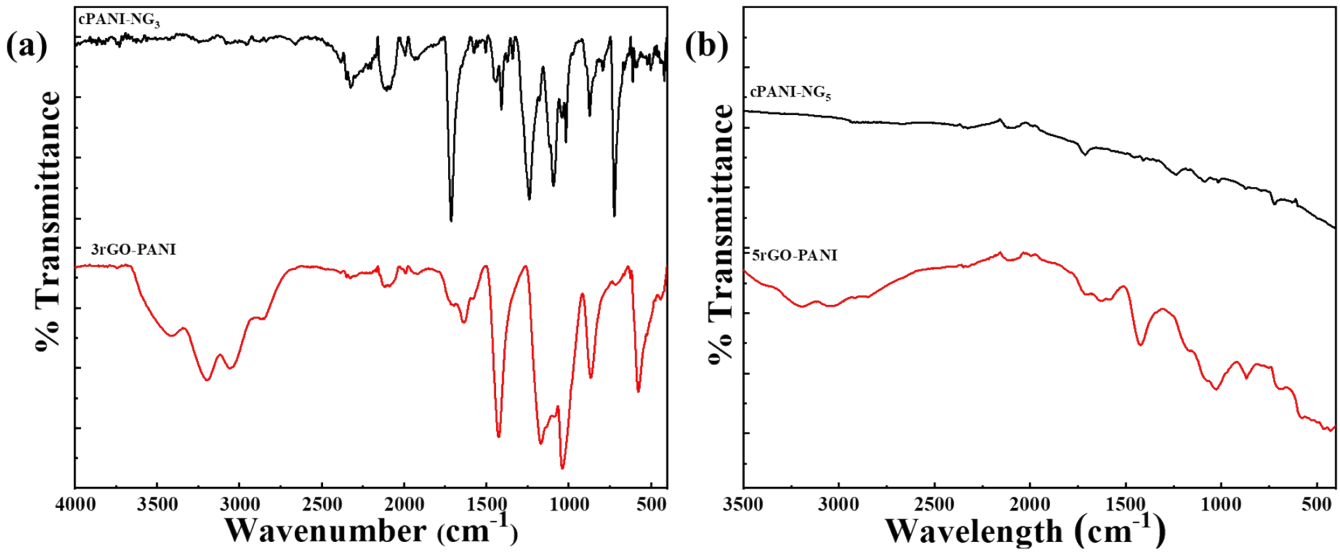


Figure S1: FT-IR spectra of (a) cPANI-NG_5 5rGO-PANI and (b)cPANI-NG_3, 3rGO-PANI, respectively.

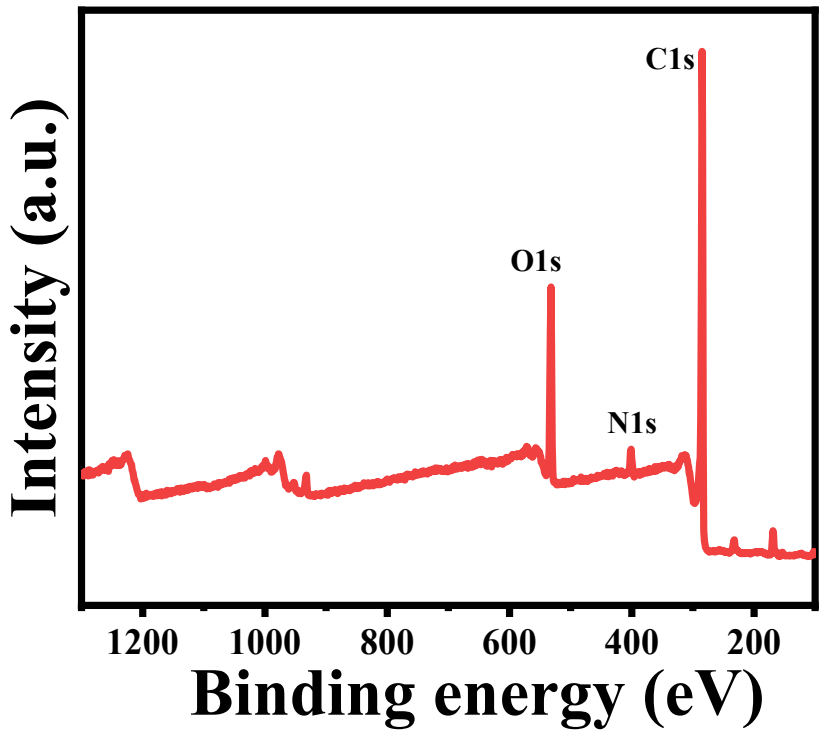


Figure S2: X-Ray photoelectron full survey spectra of cPANI-NG$_4$.

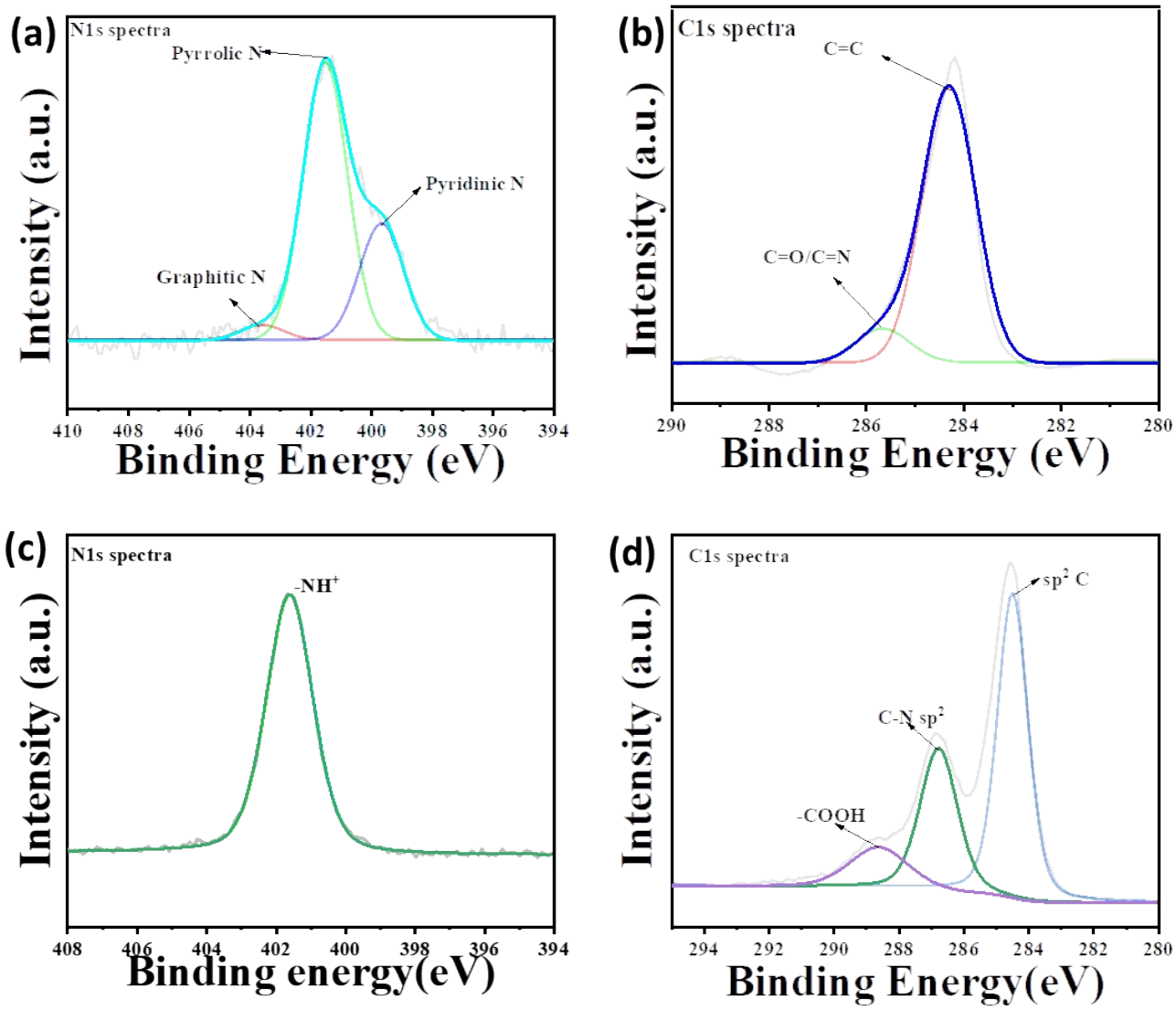


Figure S3: (a) N1s spectra of cPANI-NG$_5$ (b) C1s of cPANI-NG$_5$ (c) N1s of 5rGO-PANI (d) C1s of 5rGO-PANI

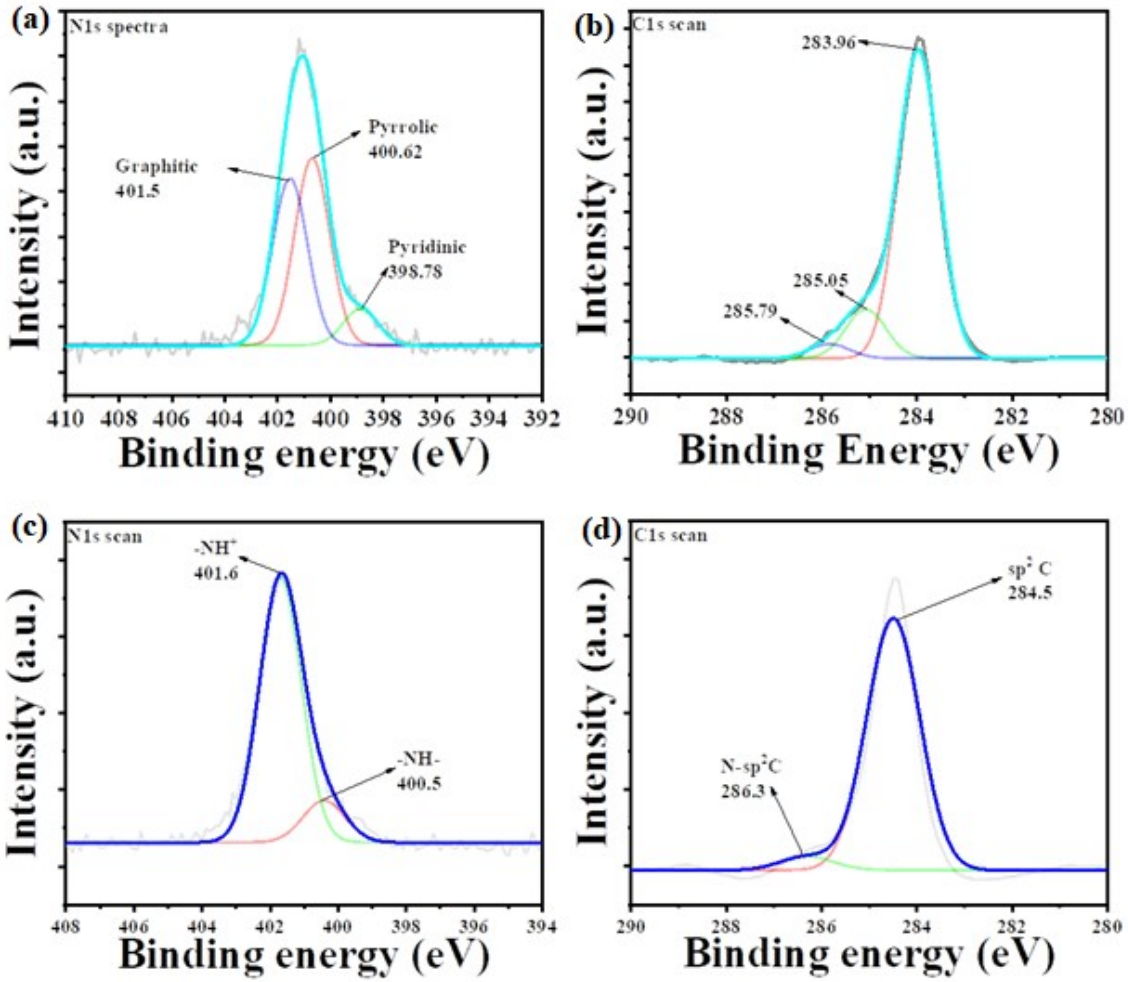
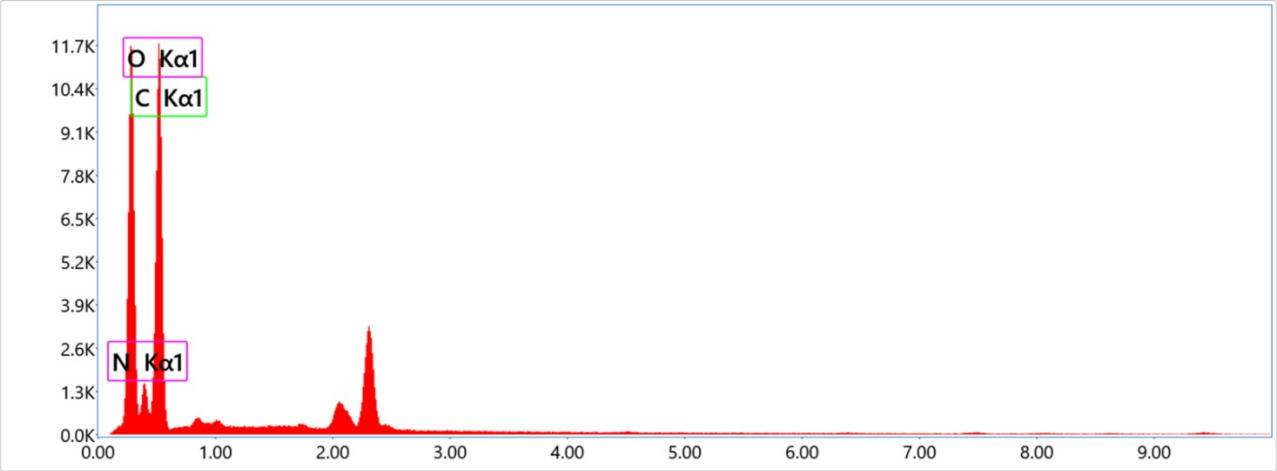


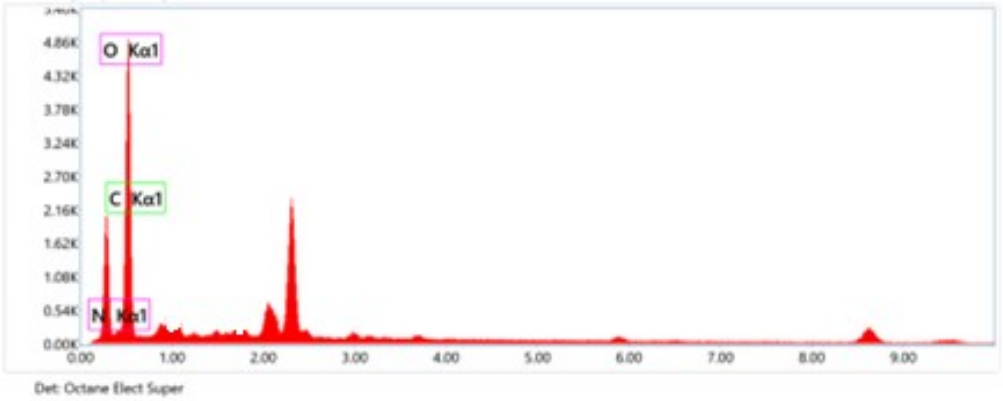
Figure S4: (a) N1s spectra of cPANI-NG_3 (b) C1s of cPANI-NG_3 (c) N1s of 3rGO-PANI (d) C1s od 3rGO-PANI



eZAF Quant Result - Analysis Uncertainty: 99.00 %

Element	Weight %	Atomic %	Net Int.	Error %
C K	49.1	55.5	682.6	2.6
N K	10.6	10.3	81.3	3
O K	40.2	34.1	722.2	1.1

Figure S5: Elemental dispersive X-Ray analysis of cPANI-NG$_4$.



eZAF Quant Result - Analysis Uncertainty: 99.00 %

Element	Weight %	Atomic %	Net Int.	Error %
C K	41.3	48.1	123.4	9.5
N K	14.6	13.6	9.8	7.8
O K	44.1	38.3	297.8	2.8

Figure S6: Elemental dispersive X-ray analysis of 4rGO-PANI

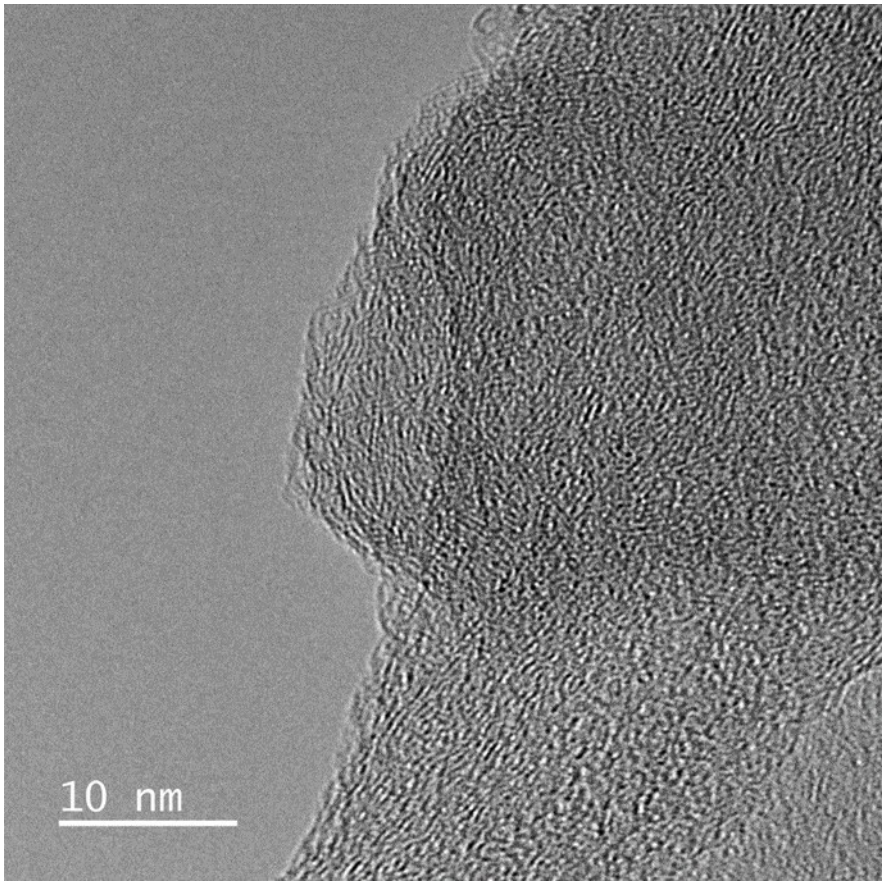


Figure S7: HRTEM of 4rGO-PANI

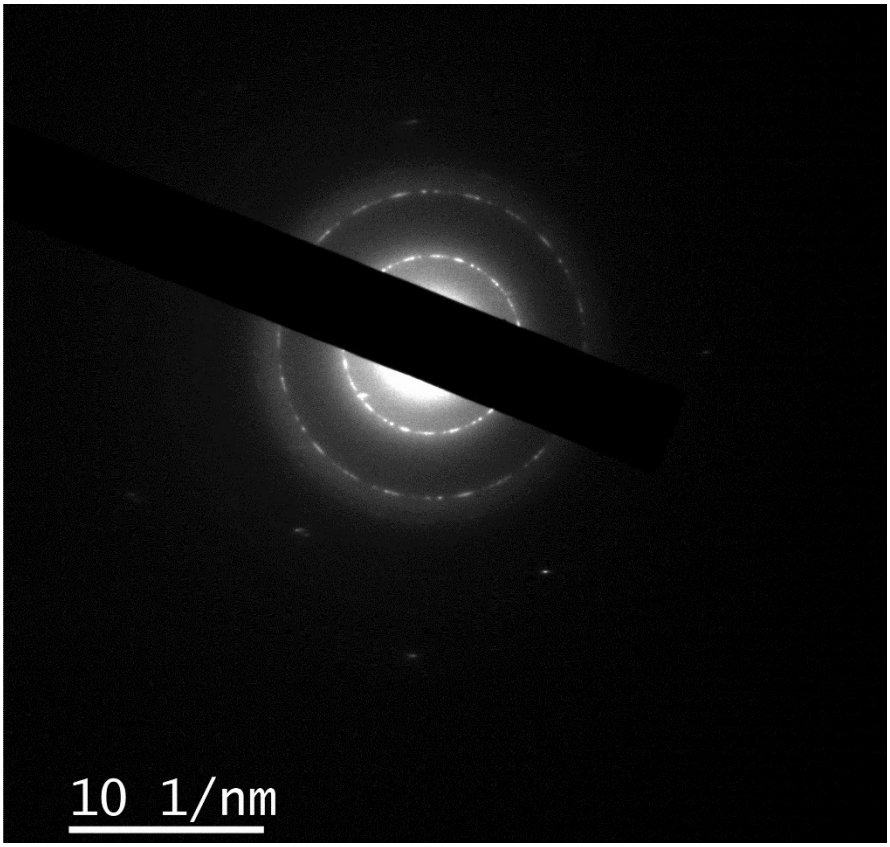


Figure S8: Selected area electron diffraction (SAED) pattern for cPANI-NG$_4$

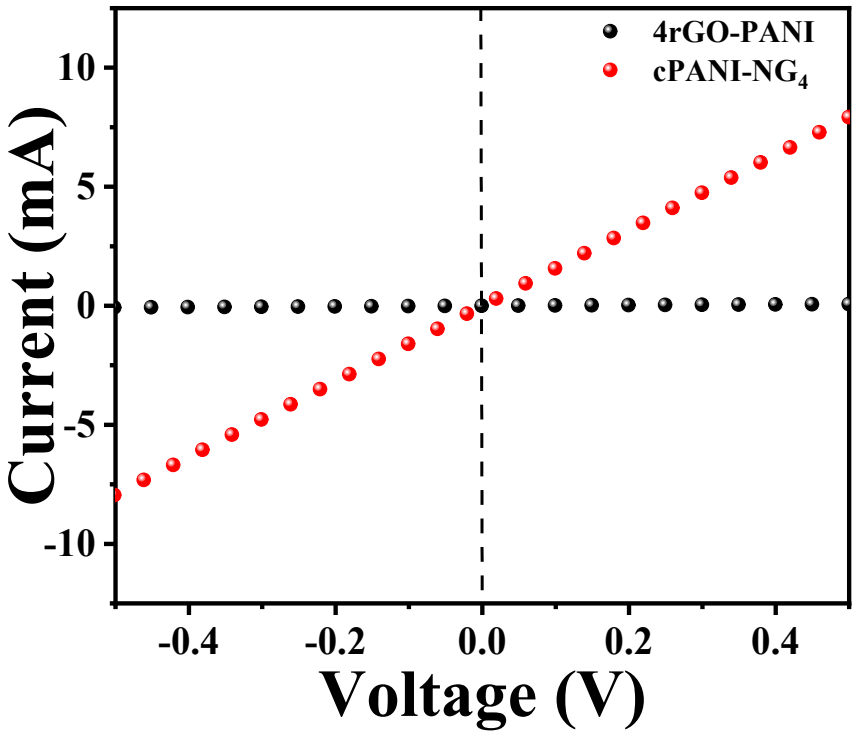


Figure S9: I-V characteristics of 4rGO-PANI and cPANI-NG_4

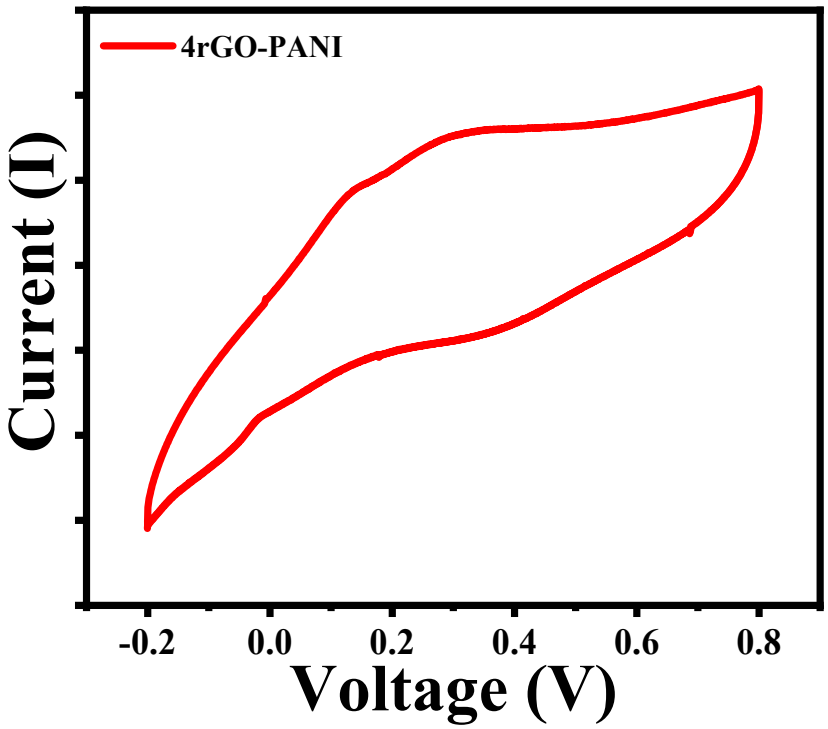


Figure S10: CV plot of 4rGO-PANI in 1.5 M H_2SO_4 solution

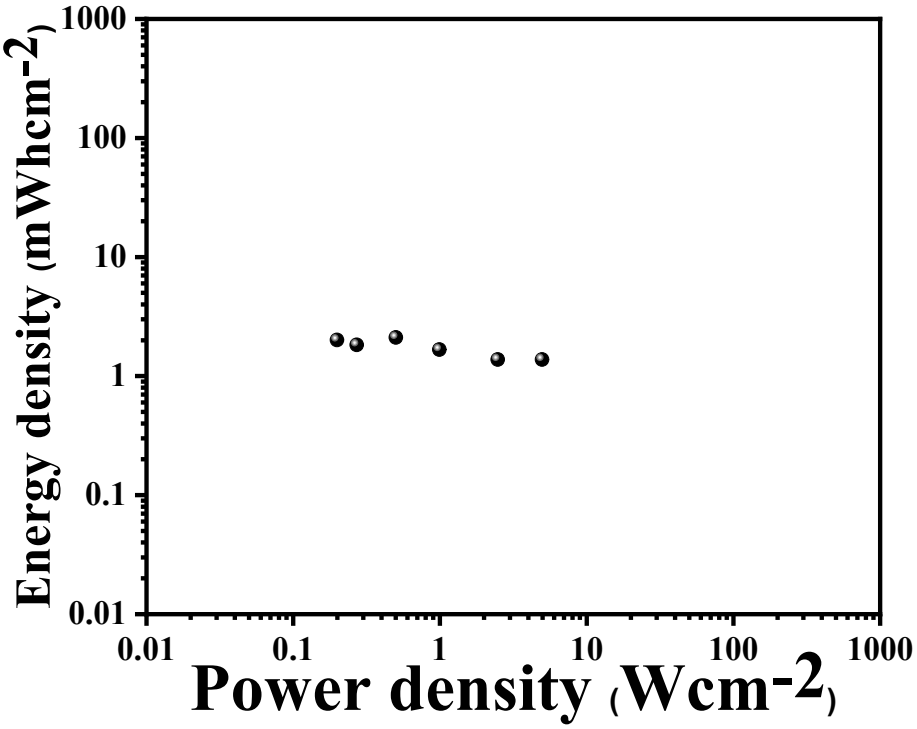


Figure S11: Ragone plot of NG-MSC

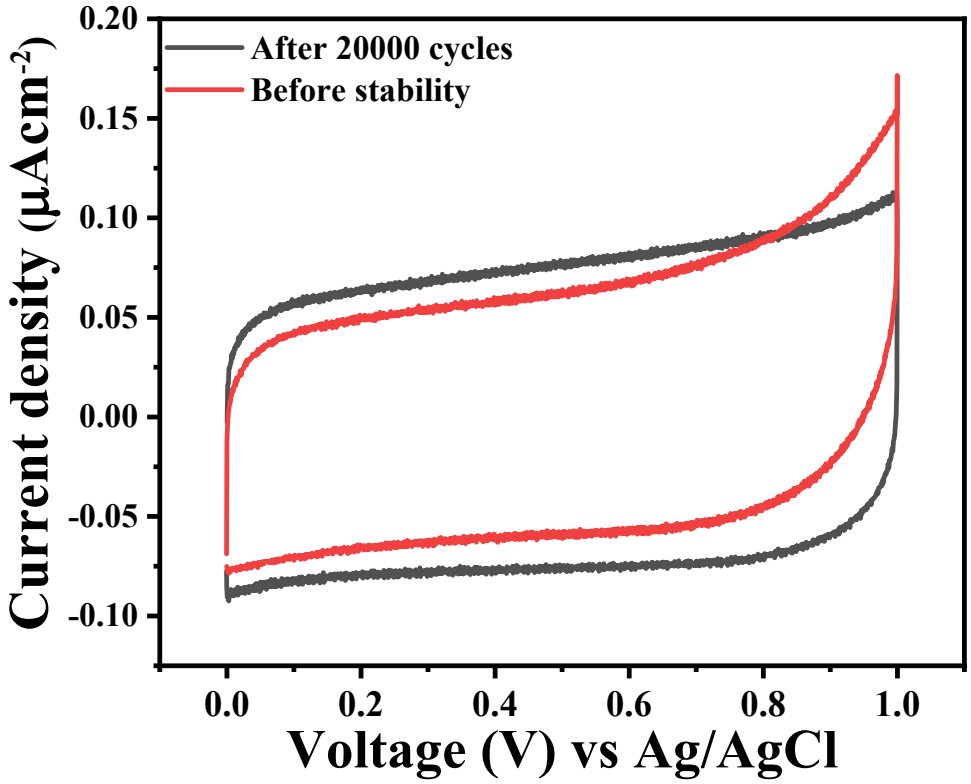


Figure S12: CV curves of NG-MSC before and after 20,000 GCD cycles

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