

Electronic Supplementary Information

Metallated Graphene Oxide Foam with Carbon Nanotube Shell for Enhanced Capacitance Device

Rahul Patil^{a†}; Lingaraj Pradhan,^{b,c†}; Babasahab Matsagar^d; Rahul R. Salunkhe^e; Kevin C. W. Wu^{d,f}; Bikash Kumar Jena^{*b,c}; Saikat Dutta^{*a}

^aElectrochemical Energy & Sensor Research Laboratory, Amity Institute of Click Chemistry Research & Studies, Amity University, Noida, India

E-mail: sdutta2@amity.edu

^bMaterials Chemistry Department, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar, India

E-mail: bikash@immt.res.in

^cAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

bikash@immt.res.in

^dNanoporous Materials Laboratory, Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

^eMaterials Research Laboratory, Department of Physics, Indian Institute of Technology Jammu, Jammu, India

^fDepartment of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li, Taoyuan, Taiwan

[†]Equal contribution from authors

Material and methods

All chemicals were purchased from commercial sources and used without further treatment: zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 99%), 2-methylimidazole (Sigma-Aldrich, 99%), cobalt nitrate hexahydrate (Sigma-Aldrich, 99%), nickel nitrate hexahydrate (Sigma-Aldrich, 99%). For hydrosilylation and N-formylation reaction the required chemicals such as triethyl silane (Spectrochem, India), aniline (Spectrochem, India), 1,4-dioxane (Merk, India) were used without further purification.

Powder X-ray diffraction patterns (PXRD) were collected on a Japan Rigaku Miniflex 600 rotation anode X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were performed by using a NEXSA ThermoFisher Scientific with Al K-alpha source. Field-emission scanning electron microscopy (FE-SEM) was carried out with a field emission scanning electron microanalyzer (FESEM- JEOL 7900F at an acceleration voltage of 5 kV. EXAFS spectroscopy data were collected in Taiwan Light Source Beamlines (nsrrc.org.tw) in a beamline which high resolution DCM X-ray beamline with both collimating and focusing mirrors, which will deliver monochromatic photon beams with energy ranging from 6 keV to 33 keV. The transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired on JEOL JEM-2100F. EDS was recorded in OXFORD X-MaxN TSR. The nitrogen isotherms were measured by using automatic volumetric adsorption equipment (Micromeritics ASAP 2020). Prior to gas adsorption/desorption measurement, the samples were dried for 12 h at 433 K under vacuum. Electron paramagnetic resonance spectroscopy (EPR) was recorded in Bruker BiospinEMX^{micro} spectrometer.

Synthesis of Tri-metallic M-ZIF

Tri-metallic ZIF was synthesized via solvothermal method as per our previous report.¹ Typically $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8961; 1 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8770; 1 mmol),

Ni(OAc)₂·4H₂O (1.4955; 2 mmol), in 45ml methanol and mixed together using magnetic stirrer till 45 minutes. This mixture was sonicated for 20 mins. After that 2-methylimidazole (6.8934; 28mmol) was transferred to the trimetallic mixture with continuous stirring. This reaction mixture was transferred to the in 50 ml Teflon vessels and heat it at 90 °C for 21 hrs. The mixture was collected and then Centrifuge the mixture at 8000 rpm for 10 mins. Resuspend the pellet in absolute water and ethanol and centrifuge it at 8000 rpm for 5mins. Repeat this step twice. After that sample was dried at 60 °C for 12 hours in vacuum oven to prevent the oxidation of metallic sites.

Carbonization of M-ZIF to C-ZIF

Typically, the ground Tri-metallic ZIF was homogeneously dispersed in a ceramic boat before placing the ceramic into a tube furnace. After the sample was exposed to a flow of argon at room temperature for 30 min, the furnace was heated to the targeted carbonization temperature 700 °C for 8 hour using a heating rate of 5 °C/min. Then, the resulting sample was extensively washed using a 2M concentration of H₂SO₄ to remove the residual Zn component. Next, the sample was washed several times with deionized water and absolute ethanol before drying in an vacuum oven at 60 °C for 12 hours.

Synthesis of M-rGO-foam

125 mg of graphene oxide and 125 mg of C-ZIF-700 (1:1) were dispersed in 50 ml water. The mixture was sonicated for 60 minutes until the clear suspension is obtained. L-ascorbic acid (vitamin-c) 250 mg was added to the reaction mixture with continuous stirring. Here the vitamin C acts as a reducing agent to convert graphene oxide to reduced graphene oxide. Then the reaction mixture was transferred to the U-shape tube and kept in the oven at 75 °C for 8 hrs.

The product mixture is transferred in a 50 ml centrifuge tube and run at 8000 rpm for 10 minutes. The residue was further washed with ammonia and water to remove the unreacted vitamin-C from the foam fragment. After centrifugation, the centrifuge tube was directly kept

in a refrigerator at $-80\text{ }^{\circ}\text{C}$ for 12 hours. The outer wall of centrifuge tube was washed with water and the single piece of foam was collected (kept in petri dish) and again stored in refrigerator for 1 hour at $-80\text{ }^{\circ}\text{C}$. Then the product was freeze-dried at $-70\text{ }^{\circ}\text{C}$ for 12 hours. This process results in the final form of M-rGO-foam.

Electrochemical calculations

Specific capacitance ($\text{F}\cdot\text{g}^{-1}$)²

From cyclic voltammetry (CV),
$$C_{sp} = \frac{\text{Area} \times 1000}{v \times \Delta V \times m} \dots\dots\dots(1)$$

From galvanostatic charge-discharge (GCD),
$$C_{sp} = \frac{I \times \Delta t}{m \times \Delta V} \dots\dots\dots(2)$$

Specific capacitance ($\text{F}\cdot\text{g}^{-1}$)

From cyclic voltammetry (CV),
$$C_{sp} = \frac{2 \times \text{Area} \times 1000}{v \times \Delta V \times m} \text{ (Symmetric device configurations) } \dots\dots\dots(3)$$

Energy density ($\text{Wh}\cdot\text{kg}^{-1}$)

From CV,
$$E.D. = \frac{C_{sp} \times \Delta V^2}{2 \times 3.6} \dots\dots\dots(4)$$

From CD,
$$E.D. = \frac{C_{cd} \times \Delta V^2}{2 \times 3.6} \dots\dots\dots(5)$$

Power density ($\text{W}\cdot\text{kg}^{-1}$)

From CV,
$$P.D. = \frac{C_{sp} \times \Delta V \times v}{2} \dots\dots\dots(6)$$

From CD,
$$P.D. = \frac{3600 \times E}{\Delta t} \dots\dots\dots(7)$$

Where, C_{sp} = Specific capacitance from CV
 C_{cd} = Specific capacitance from CD
 v = Scan rate
 ΔV = Potential window
 m = Mass loading
 I = Current

Δt = Discharge time
E= Energy density

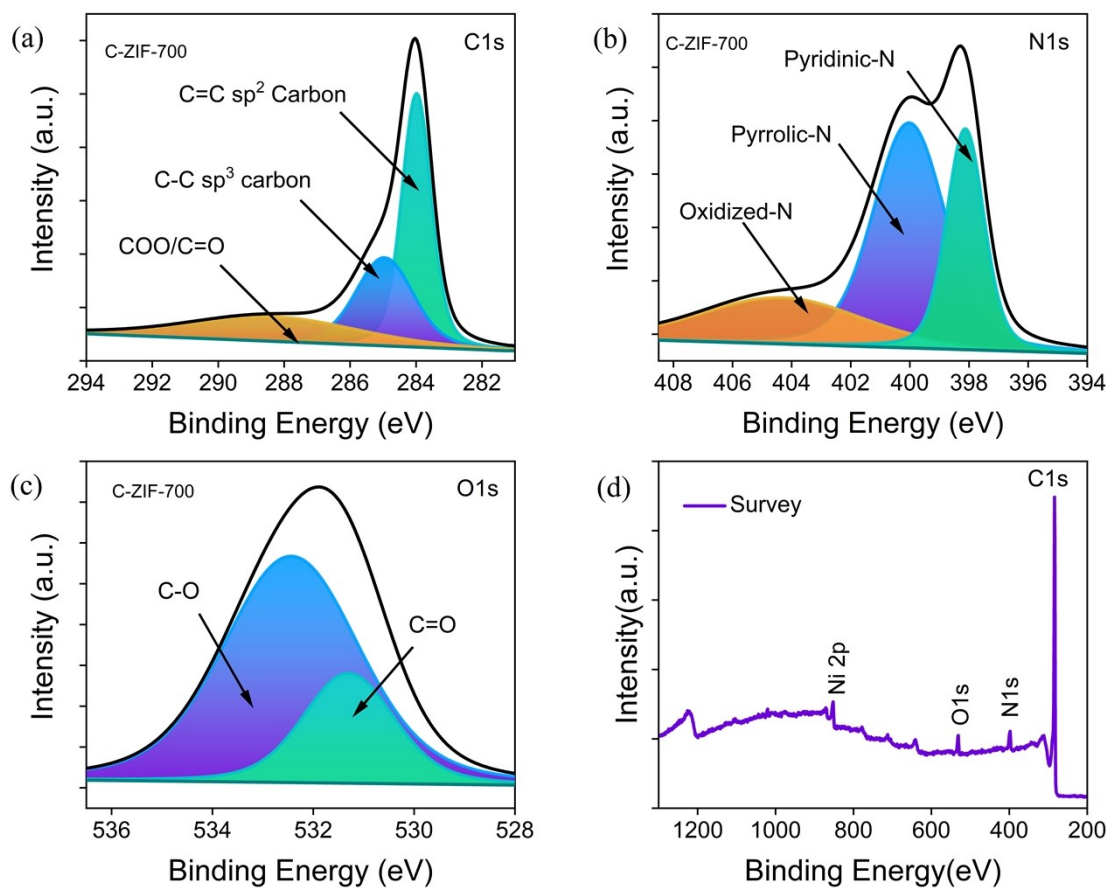


Figure S1. Deconvoluted XPS for C-ZIF-700 XPS spectra (a) C 1s (b), N 1s (c), O1S (d) Survey. (e) Raman spectra of C-ZIF700.

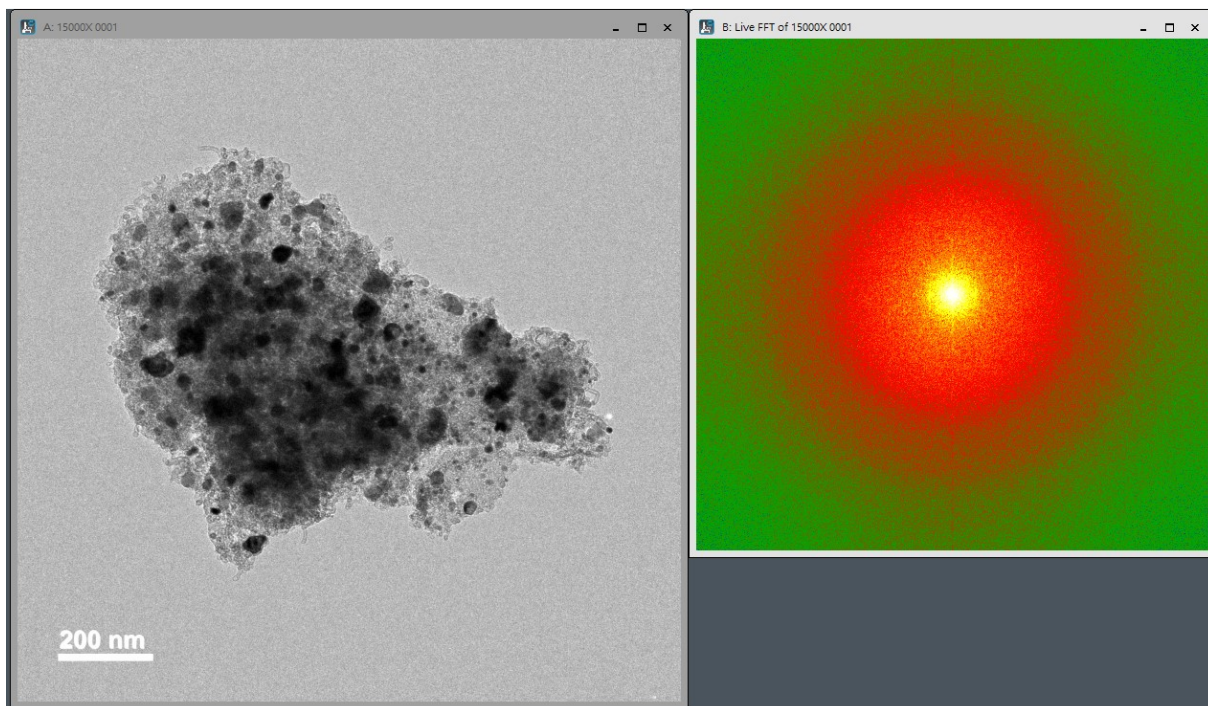


Figure S2. Tubular morphology in C-ZIF-700 at 200 nm resolution and corresponding FFT image.

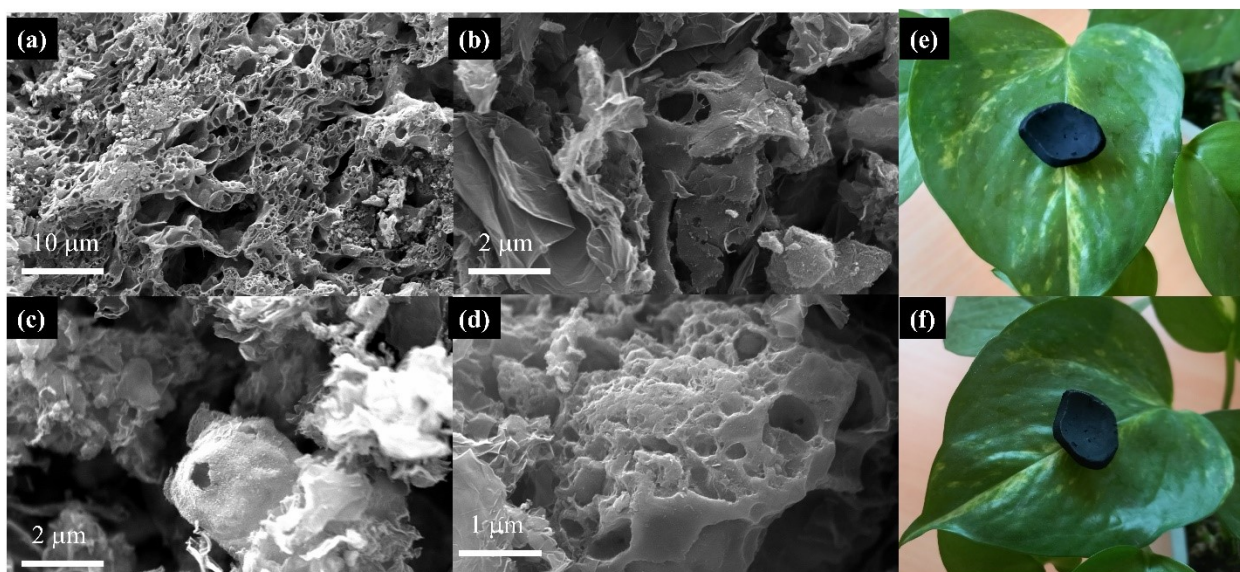


Figure S3. (a-d) SEM image of M-rGO foam and (e-f) picture of M-rGO foam after freeze synthesis.

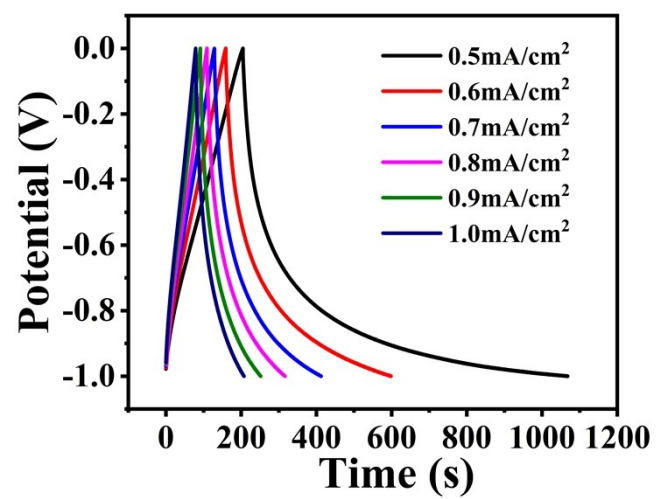


Figure S4. GCD profile at different current densities,

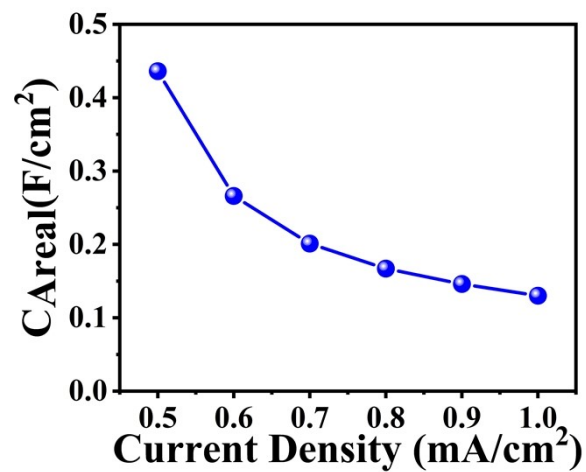


Figure S5. Areal capacitance vs. Current density plot.

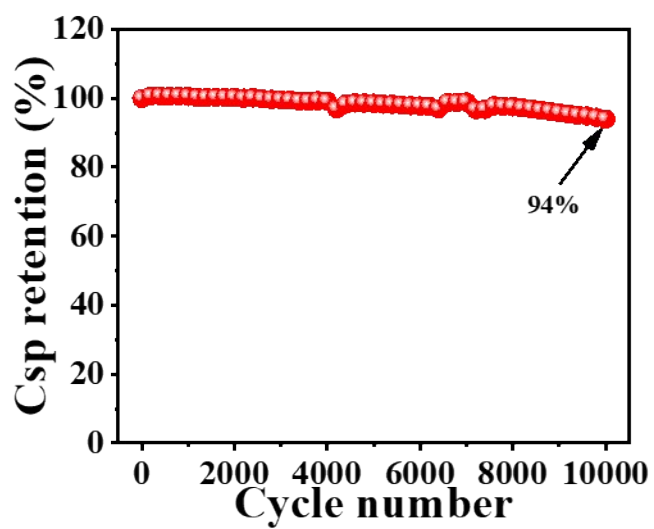


Figure S6. Three-electrode EIS plot of as-synthesized M-rGO-foam.

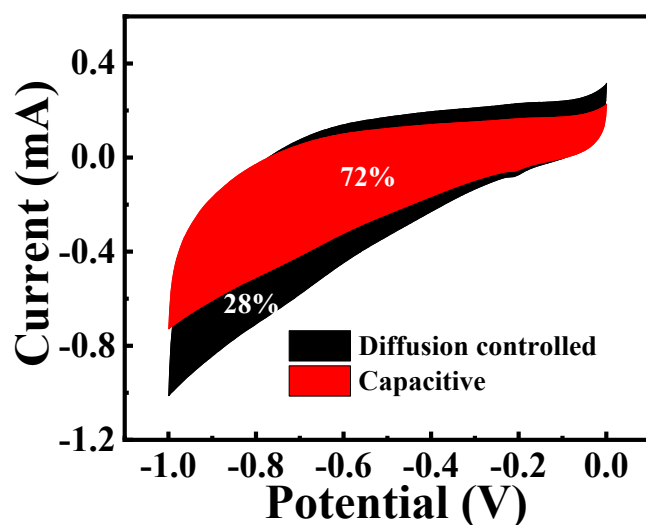


Figure S7. Percentage contribution of surface capacitance and diffusion-controlled capacitance for M-rGO-foam in 6 M KOH electrolyte at a scan rate of 2 mV/s.

Table S1. Energy density performance compares our fabricated SSD with previous related literature for graphene-foam and porous materials in a supercapacitor device.

S. No.	Sample	Electrolyte	Energy density	Capacitance retention	reference
1.	M-rGO Foam//M-rGO Foam (Symmetric Supercapacitor Device)	6M KOH	44.93 Wh/kg (1 A/g)	87% (20000 cycles)	This work
2.	PPy/Graphene foam	gel electrolyte	24 $\mu\text{Wh cm}^{-2}$	75% (10000 cycles)	3
3.	Core-Shell Nanowire Arrays on Graphene-Decorated Nickel Foam	3M KOH	27.8 wh/kg	93.4% (5000 cycles)	4
4.	ZnCo ₂ O ₄ /reduced graphene oxide (rGO)	PVA-KOH electrolyte	11.4 Wh/kg	93.4% (5000 cycles)	5
5.	Nitrogen doped graphene	PVA-KOH gel electrolyte	27.7 Wh/kg	-	6
6.	GF	PVA-KOH gel	11.4 Wh/kg	89% (5000 cycles)	7

7.	GO supported ZnS nanoweb	2M KOH	20.29 Wh/kg	-	8
8.	Graphene foam based SC	H ₃ PO ₄	3.4 μ W h cm ⁻²	-	9
9.	GP/MnO ₂	1 M Na ₂ SO ₄	26.7 W h kg ⁻¹	85% (5000 cycles)	10
10.	rGO-NPC	[bmim][BF ₄]	17.6 W h kg ⁻¹	-	11

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