Electronic Supplementary Information (ESI)

Ultralong cycle life and outstanding capacitive performance of 10.8 V metal-free micro-supercapacitor with highly conducting and robust laser-irradiated graphene for integrated storage device

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Materials and Instrumentations

Materials

Highly pure graphite flakes ($<20\mu$ m), phosphorous pentoxide (P₂O₅, >98%), potassium permanganate (KMnO₄), copper sulphate (CuSO₄), potassium persulfate (K₂S₂O₈) were purchased from Sigma Aldrich and were used as received. Sulphuric acid (H₂SO₄), nitric acid (HNO₃), hydrochloric acid (HCl), and perchloric acid (HClO₄) 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 local market. Before use, all the PET sheets were washed with deionized (DI) water and ethanol repeatedly. All other chemicals used were at least of analytical grade and were used without any further purification. All aqueous solution was prepared using Millipore water.

Instrumentation details

X-ray Diffraction (XRD) spectroscopy was used to determine the structural information of electrochemically reduced graphene oxide (ErGO) and laser irradiated graphene (LIG) on a Bruker D8 Advances diffractometer using Cu- K α ($\lambda = 1.5406$ Å) radiation. Raman spectra were collected in a WITEC Focus Innovations Alpha-300 Raman confocal microscope with an excitation laser waveleng th of 532 nm. Scanning electron microscopy (SEM) images were obtained in a microscope (SEM Jeol JSMIT300). Elemental composition of ErGO and LIG were investigated using Bruker XFlash 6130 Energy Dispersive Spectroscopy (EDS). High-Resolution Transmission Electron Microscopy (HRTEM) studies were carried out on a JEM2100 instrument. Laser irradiation of graphene film and patterning was carried out by CO₂ laser (60 W) and near infra-red (NIR) Laser source (30 W), respectively. The electrical conductivity of the material was measured by a two-probe method using a Keithley 2635B source meter. X-ray photoelectron spectroscopy (XPS) was collected in an ultrahigh vacuum chamber (2 $\times 10^{-9}$ mbar) using (Monchromatic) with 6 mA beam current by Ka plus XPS system by ThermoFisher Scientific instruments (UK). Electrochemical measurements like cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), were performed on a CHI 760E electrochemical workstation and electrochemical impedance spectroscopy (EIS) was performed with FRA 32M module of Metrohm Autolab (M204 multichannel potentiostat galvanostat). Electrodeposition of three-dimensional reduced graphene oxide (ErGO) networks, copper foam coated copper foil (Cuf) refers to working electrode, Ag/AgCl (3 M KCl) as the reference electrode and a platinum wire as a counter electrode. A two electrode set up was used to measure all solid-state electrochemical performances of the in-plane microsupercapacitor device in a solid-state gel electrolyte (PVA-H₃PO₄). A 6V mini solar panel was purchased from local market to hybrid with supercapacitor.A 400W Xenon lamp (ORIEL Instruments; OPS-A1000) with Newport (FSQ-GG400) filter was used to charge the solar panel.

Methods

Synthesis of GO

Graphite oxide was oxidized from graphite powder using 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 previous report. ²

Electrodeposition of copper foam

The galvanostatic electrodeposition was carried out for the deposition of copper foam (Cuf) in the aqueous suspension at room temperature. Briefly, an aqueous solution of 0.4 M CuSO₄ with 1.5 M H₂SO₄ was used. 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 equal area was used as counter electrode (anode). Both copper sheets were cleaned with 30 % HNO₃ followed by washing with Millipore water 3-4 times and finally washed with ethanol. When not in use, the cleaned copper sheets were kept in 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 can be mechanistically described as a reason of hydrogen gas evolution as described in our previous paper.³

Electrochemical deposition of ErGO on Cu/Cuf

Electrochemically reduced graphene-oxide (ErGO) networks were grown by electrolysis of GO aqueous solution on the Cu foam³. In a typical procedure, bulk electrolysis of GO aqueous suspension (3 mg ml⁻¹) in 0.5 M perchloric acid (HClO₄) was carried out at an applied potential of -1.0 V against Ag/AgCl reference for 60-120 seconds on Cu foam electrode. After electrochemical deposition of ErGO, any unreduced GO suspension or physically absorbed rGO 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 of thickness approximately 25 μ m in the form of three-dimensional porous networks (Fig. S1). ErGO membrane deposited on to Cuf was separated by etching Cuf/Cu with 10% ammonium persulfate solution. Typically, the rGO/Cuf/Cu was placed in the (NH₄)₂S₂O₈ solution (with the rGO side facing up) for overnight under ambient conditions. A stable copper sulfate formed during oxidation of copper by persulfate to form soluble copper sulfate as, Cu + S₂O₈⁻² \longrightarrow CuSO₄ + SO₄⁻²

 $Cu + S_2O_8^{-2} \longrightarrow CuSO_4 + SO_4^{-2}$ After complete etching of copper, the rGO membrane starts floating onto the surface of the solution and the solution turns blue in color. The rGO film was then transferred by scooping up on to a PET sheet (poly ethylene terephthalate) and then washed in Millipore water several times for the complete removal of Cu^{+2} ions that may have adsorbed in the ErGO networks. The ErGO electrode would further be laser induced for production of graphene like characteristics.

Formula used for Raman analysis

The general expressions that gives the crystallite size (L_a), defect density (n_D) from the integrated intensity ratio I_G/I_D by using any laser line in the visible range ⁴ is given by equation 1 and 2.

$$L_{a}(nm) = (2.4 \times 10^{-10})(\lambda_{l}^{4}) \left[\frac{I_{G}}{I_{D}}\right]$$

$$n_{D}(cm^{-2}) = \frac{(2.4 \times 10^{22})}{\lambda_{l}^{4}} \left[\frac{I_{D}}{I_{G}}\right]$$
[1]
[2]

Where λ_l is laser line wavelength (532 nm) and $[I_D/I_G]$ is ratio of D- and G- band intensities.⁵ The calculated crystallite size corresponding to the ErGO and LIG is 18.4 nm and 309 nm, respectively and the calculated parameters are listed in table S1.

Optimization of laser speed and power in Raman measurement

The LIG formation is more likely to be caused by photothermal effects owing to the long wavelength (10.6 μ m) and relatively long pulses of the CO₂ laser ⁶. The energy from laser irradiation results in lattice vibrations, which could lead to the extremely high localized temperatures. High temperature generated by laser irradiation could easily break the C-O, C=O bonds as confirmed by the dramatically decreased oxygen contents in LIG (Fig. S4). The effect of laser power (51 W-60 W) and speed (1.4 m s⁻¹-2.2 m s⁻¹) on various properties of sample was investigated. A direct relationship between sheet resistance (Rs)/crystallite size vs power/speed of laser is shown in Fig. S7 (b, c, e and f). Optimization gives a threshold power and speed of 60 W and 1.6 m/s respectively, where the sheet resistance reduces to a minimum value of 0.1 k Ω sq ¹. and the translated conductivity is ~60 S cm⁻¹, higher than in laser-reduced GO.⁴ Above the threshold speed, R_s gradually increased to 1 k Ω sq⁻¹. This suggests that when the laser speed is > 1.6 m/s, thermal influence is less. Therefore, decreasing laser speed would give strong thermal effects which lead to higher degree of graphitization⁷. Raman spectra corresponding to speed and power of laser is illustrated in Fig. S7a and d, showing sharp increase in 2D peak and decrease in defect density occurs in the sample. The laser irradiated graphene at threshold power 60 W and speed (1.6 m/s) shows minimum defect density and maximum crystallite size. All calculated parameters are listed in table S1-S3.

Formula for electrochemical characterization

The area normalized specific capacitance C_{sp} (mF cm⁻²) can be calculated from cyclic voltammetry via the equation (3)

$$C_{sp} = \frac{I(V)}{2.A.\nu.V}$$
[3]

where A (in cm²) is the geometric area, v is the voltage scan rate (V s⁻¹), V (in V) are the potential window of the CV curves, and I(V) is current at different potentials. Dividing areal capacitance by thickness 't' (μ m) of the electrode gives volumetric capacitance C_v (F cm⁻³) as follows (equation 4),

$$C_{\nu} = \frac{C_{sp}}{t}$$
[4]

Alternatively, the specific capacitance for the electrodes can be obtained from charge/discharge data according to the following equation 5.

$$C_{sp} = \frac{I}{A \cdot \frac{dV}{dt}}$$
[5]

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 galvanostatic charge/discharge curves by the following equations 6 and 7:

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

$$P_A = \frac{E}{\Delta t} \times 3.6$$
[6]
[7]

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). The volumetric energy density (E_v) and power density (P_v) was calculated from E_A and P_A divided by thickness of the electrode shown in equations 8 and 9.

$$E_{v} = \frac{E_{A}}{t}$$
[8]

$$P_{v} = \frac{r_{A}}{t}$$
[9]



Fig. S1. SEM images showing cross-sectional image of ErGO (a) and LIG (b) samples. ErGO and LIG supported on flexible PET sheet, shows a cross-sectional length of 25 μ m and 7 μ m, respectively



Fig. S2. TEM image of ErGO and LIG material.



Fig. S3. High-resolution SEM image showing the fused graphene sheets revealed after laser irradiation

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Total	100	100						
Fig. S4. Energy dispersive spectra (EDS) for laser irradiated graphene film. (a) EDS spectra obtained from LIG film. (b) Elemental mapping of sample obtained from								

selected area. Individual elemental distribution of carbon (c) and oxygen (d). Table shows the atomic and weight percent of C and O in the sample



Fig. S5. XRD analysis of GO, LIG and ErGO. XRD pattern of GO gives a sharp peak at $2\theta = 11^{\circ}$ with d-spacing 0.398 nm. ErGO and LIG shows a broad peak at $2\theta = 24.6^{\circ}$ (d-spacing 0.190 nm). However, the intensity of the peak is sharp for LIG sample.



Fig. S6. (a) Raman spectra of GO and LIGO. (b) Comparison of Raman spectra obtained from GO, ErGO and LIG.

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Fig. S7. (a) Raman spectra obtained from LIG sample with different power of laser. (b, c) Statistical analysis of the I_G/I_D ratio, sheet resistance and crystalline size with laser power. (d) Raman spectra obtained from LIG sample with different laser speed. (e, f) Variation of I_G/I_D ratio, sheet resistance and crystalline size with laser speed.



Fig. S8. A comparison of electrical conductivity of ErGO and LIG sheet measured by two-probe technique. I-V characteristics for ErGO and LIG shows linear plot, indicating ohmic behavior. The calculated electrical conductivity values for ErGO and LIG are 2123 S m⁻¹ and 5963 S m⁻¹, respectively



Fig. S9 (a) Optimization of potential window of LIG-MSC avoiding oxygen evolution reaction. (b, c) Galvanostatic charge-discharge plot for LIG-MSC at higher current densities. (d) A plot of capacitance retention versus current density showing a 42% retention at a current density of 0.23 mA cm^{-2} of its initial capacitance. (e) Impedance analysis for LIG microsupercapacitor. Nyquist plot obtained for LIG-MSC and the inset shows the Randles equivalent circuit used to fit the data. It shows a linear straight line parallel to y-axis, indicating highly capacitive behavior of the active material.



Fig. S10. (a) Area-normalized Ragone plot obtained from LIG-MSC and comparison with various carbonaceous materials reported in literatures from reference $^{12,14-17}$ (b) Mechanism model illustrates the ionic and electronic transport occurs in three-dimensional networks of LIG material.



Fig. S11. CV response obtained from before and after 1,00,000 cycling test.



Fig. S12. (a) Cyclic voltammetry showing flexibility of the device in vertical and horizontal bending mode, (b) Free-standing reduced graphene oxide film, (c) Optical image of Laser induced film $(1.5 \times 1.5 \text{ cm}^2)$ deposited on PET sheet, (d) Optical image of the same device at bended state, (e) Patterned LIG micro device on PET and (f and g) shows flexibility of the MSC device in vertical and horizontal directions



Fig. S13. Schematics of various shapes of LIG-MSC (Interdigital, Rectangular, Linear and Circular) with size parameters.



Fig. S14 Cyclic voltammetry (inset shows the digital image of linear LIG-MSC) and GCD profile (a, b) of linear shape micro supercapacitor at different scan rates and current densities, respectively.



Fig. S15. CV at a scan rate of 100 mVs⁻¹ and GCD at a current of 10 μ A obtained from 1 to 5 cells configured in parallel fashion.



Fig. S16. Digital images of integrated solar cell-supercapacitor system. (a)LIG-Module was charged with solar cell through an open-circuit voltage of 5.082 V as can be seen on multimeter. (b) After unplugging the solar cell, supercapacitor attain an open-circuit potential of 5.004 V.

Table S1:

Various physical parameters of ErGO and LIG obtained from Raman characterization technique.

Sample	D-	G-	2D -	I _{2D} /I _G	I _G /I _D	L _a (nm)	$n_{\rm D} \times 10^{11}$
	band	band	band	ratio	ratio		(cm ⁻²)
GO	1350	1604	-	-	0.71	13.8	4.2
LIGO	1356	1593	2696	0.080	0.75	14.4	3.9
ErGO	1347	1583	2693	0.083	0.94	18.4	3.1
LIG	1350	1582	2696	0.72	16.1	309	0.2

Table S2:

Variation of sheet I_D/I_G , sheet resistance and crystallite size with speed of laser power.

speed of laser power	I _G /I _D	Sheet Resistance	L _a (nm)
(m/s)		(kΩ)	
2.5	0.88	2.0	16.9
2.2	1.22	1.2	23.4
1.9	2.94	0.4	56.5
1.6	16.1	0.1	309
1.4	3.4	0.25	65.3

Table S3:

Variation of sheet I_D/I_G , sheet resistance and crystallite size with percentage of laser power.

laser power (W)	I _G /I _D	Sheet Resistance	L _a (nm)	
		(kΩ)		
51	0.89	4.0	17.1	
54	1.27	1.4	24.4	
57	3.80	0.2	73.0	
60	16.1	0.1	309	

S. No.	Electrode material	electrolyte	Potential Window	Capacitance C _{sp}	Energy Density	Power density	Stability (Cycle)	Reten tion	Ref.
1	Graphene	PVA-H ₂ SO ₄	1V	>9 mF cm ⁻² (3.6 F cm ⁻³)	0.5 mWh cm ⁻³	5 W cm ⁻³	8000	98 %	8
2	Graphene/gra phite paper	1M H2SO4	1 V	15.6 mF cm ⁻²	0.001 mWh cm ⁻²	4 W cm ⁻²	10000	100%	9
3	LSG-SWCNT- MSC	PVA-H3PO4	1V	3.10 F cm ⁻³	0.84 mWh cm ⁻³	1 W cm ⁻³	5000	88.6 %	10
4	Graphene foam	НЗРО4	2V	38 mF cm ⁻²	3.4 mWh cm ⁻ 2	0.27 mW cm ⁻²	25000	68 %	11
5	3D- cellular graphene film	PVA-H3PO4	1V	2.47 mF cm ⁻²	$0.22 \mu\text{Wh cm}^{-2}$	0.37 mW cm ⁻²	10000	97.6 %	12
6	3D- graphene	Gel ele trolyte	1V	2.63 mF cm ⁻²	0.38 μ Wh cm ⁻²	0.86 mW cm ⁻²	3000	90%	13
7	LIG-MSC	Ionic liquid	1V	>4mF cm ⁻²	0.8 μ Wh cm ⁻²	9 mW cm ⁻²	8000	100%	7
8	LIG-MSC	PVA-H3PO4	1.2 V	2.32 mF cm ⁻² (3.3 mF cm ⁻³)	459 μ Wh cm ⁻² (655 μ Wh cm ⁻³)	576 mW cm ² (822 W cm ³)	100000	100%	This wor k

Table S4: A comparative study of electrochemical performance of carbon based microsupercapacitor

SWCNT- single walled carbon nanotube, PVA- poly (vinyl alcohol, LIG- laser induced (irradiated) graphene

Supplementry video S1.

Supporting video describes the device performance; two LED's were lightening up by LIGmodule charged at 5V for 3 minutes through DC power supply and LED's glow continuously till 30 seconds.

Supplementry video S2.

Supporting video describes a solar cell/supercapacitor hybrid power system. Supercapacitor was charged through solar cell in light and the stored charge was further used to lighten up a LED continuously for 35 seconds in dark.

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