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1 **Recycled Red Mud Decorated Porous 3D Graphene for High-Energy Flexible Micro-**
2 **Supercapacitor**

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13 **Abstract**

14 Flexible micro-supercapacitors, with high energy and power density, and using materials with
15 a low environmental impact are attractive for next generation energy storage devices. Carbon-
16 based materials are widely used for supercapacitors but can be increased in energy density via
17 combination with metal oxides. Red mud is an iron-oxide rich by-product of aluminium
18 production, which needs to be more widely utilized to reduce its environmental damage. To
19 achieve a flexible micro-supercapacitor device with increased energy density, we have realized
20 a laser-induced graphene (LIG) supercapacitor from a polyimide substrate, decorated with red
21 mud nanoparticles (LIG-RM), employing a solid-state ionic liquid using a mixture of PVDF,
22 [EMI][TFSI] and [EMIM][BF₄]. The fabricated two-electrode flexible device, in an inter-

1 digitated planar design, with inkjet-printed silver current collectors, has a high energy of 0.018
2 mWh/cm² at a power of 0.66 mW/ cm², with 81 % of capacitance retained after 4000 cycles
3 and good resistance to bending and flexing. The high energy storage performance, brought
4 about through the combination of graphene and red-mud nanoparticles, which would – if not
5 utilized - be an environmental liability, shows a promising material for future energy storage
6 with low environmental impact.

7 **Keywords**

8 Red mud; Flexible supercapacitor; Recycled nanomaterials; Waste management; Waste to
9 wealth.

10

11 **1. Introduction**

12 Future electronics require flexible, fast charging and low-cost power sources, with long service
13 life and a low environmental impact ^[1]. Flexible electronics are sought after for body-worn
14 healthcare ^[2] and smart consumer devices ^[3] and supercapacitors ^[4], which store charges
15 physically at the electrode surface are seen as a promising power source due to their high cyclic
16 stability and power density ^[5].

17 Carbon-based materials are widely used in supercapacitors as they possess high surface area
18 and electrical conductivity ^[6] and there are abundant inexpensive sources with low
19 environmental impact, such as biomass refinery waste ^[7], graphite pencil trace ^[8] and widely-
20 available polymers such as polyimide ^[9]. For example, Lin *et al.* showed that treating
21 polyimide (Kapton) films using a commercial infrared CO₂ laser photothermally converts C—
22 O, C=O and N—C bonds into sp² bonded carbon, with 2D graphene sheets randomly stacked
23 along the c-axis ^[10], termed laser-induced graphene or LIG.

1 Whilst carbon is the most widely used element for supercapacitor electrodes, transition metal-
2 oxides offer potentially higher energy densities ^[11] as they undergo either ultrafast Faradaic
3 reactions at the electrode-electrolyte interface (Faradic pseudocapacitive) ^[12] or by ion
4 intercalation (Intercalation pseudocapacitor). Metal-oxides may suffer, however, from
5 relatively low electrical conductivity ^[13] and poor cyclic stability ^[14] compared with carbon
6 materials. Carbon/metal-oxide hybrid electrodes have thus been employed as supercapacitors
7 which retain high power density whilst increasing the energy density ^[15]. Clerici *et al.* ^[16] coated
8 polyimide in an MoS₂ dispersion, and then CO₂ laser treated to produce metal-oxide decorated
9 LIG, increasing specific capacitance from around ≈ 4 to ≈ 13 mF/cm² at a low scan rate
10 (increasing energy density from ≈ 0.5 μ Wh/cm² to ≈ 4 μ Wh/cm² and power density from ≈ 20
11 μ W/cm² to ≈ 160 μ W/cm²).

12 The route of decorating graphene with metal-oxide nanoparticles is, then, promising in order
13 to increase the energy and power density ^[15a, 17]. However, many of the commonly used metal-
14 oxide materials such as ruthenium, manganese, nickel, and cobalt are becoming increasingly
15 expensive ^[18] and have a high environmental impact due to mining and refining processes ^[19].
16 Whilst the use of low cost, waste-based materials with low environmental impact, for carbon
17 supercapacitor electrodes is very widespread, particularly from waste-derived activated
18 carbons, as recently comprehensively reviewed by Divyashree *et al.* ^[20], the number of waste
19 inorganic sources of metal-oxide pseudocapacitive materials is far smaller, although growing.
20 For example, Fu *et al.* produced micro-particle based supercapacitor electrodes ^[21] and porous
21 Fe₂O₃ micro-rods ^[22] from mill-scale, a waste product from the steel industry.

22 Another common waste, red mud (RM) is an environmentally damaging by-product of bauxite
23 processing which is a mixture of metal-oxides; predominantly Fe₂O₃ and also including Al₂O₃,
24 SiO₂, and Na₂O, amongst others ^[23]. RM had an annual production in the year 2011 of around

1 120 million tonnes ^[24] which is increasing and is often stored or dumped on the land ^[25]. RM
2 is hazardous due to its alkalinity ^[26] and in 2010 caused environmental damage after a large
3 spill in Hungary ^[27]. Since RM is a mass-produced waste, there is a pressing need to further
4 utilize this material to help prevent it from entering and further damaging the environment ^[28].
5 Notable work on the applications of RM mainly focuses on water treatment, including dye ^[29],
6 lead and chromium ^[30], fluoride ^[31], chlorophenols ^[32], and arsenic removal from water ^[33], in
7 catalysis ^[34] and also as building materials ^[35]. These applications have shown the potential to
8 help reduce the amount of RM entering the environment but there is still under-utilization, and
9 further applications, to boost the uptake of red mud in useful products, will limit damage to the
10 environment.

11 In our previous work ^[36], we have used RM from National Aluminum Company Limited
12 (NALCO), India, and used ball-milling to produce ~30-50 nm diameter RM nanoparticles for
13 use as supercapacitor electrodes. RM nanoparticles yielded a specific capacitance of $\approx 317 \text{ F}$
14 g^{-1} , at 10 mV s^{-1} scan rate in 6 M aqueous KOH electrolyte, and cyclic stability of $\approx 97 \%$ after
15 5000 cycles ^[36], demonstrating promising capability as supercapacitor electrodes.

16 Performance of a supercapacitor significantly varies with the choice of electrolyte. Among
17 various electrolytes, ionic liquid has been emerged as a very promising electrolyte for
18 supercapacitor studies ^[37] and particularly, polymer-based gel electrolytes are popular in solid-
19 state micro-supercapacitor owing to the solid nature of electrolytes ^[38].

20 In this present work, we present a working prototype of a flexible RM nanoparticle-decorated
21 LIG supercapacitor, employing environmentally benign ionic liquids ^[39], mixture of
22 [EMIM][BF₄] and [EMIM][TFSI] (1:3), in a PVDF-HFP gel electrolyte (IL: PVDF:HFP=4:1).
23 The addition of RM increases the energy density and a cyclic stability of $\approx 80\%$ after 4000

1 cycles at a current density of 0.3 mA cm^{-2} was achieved. The use of RM is particularly
2 promising as it (i) actively recycles harmful waste material from the environment and (ii) is a
3 promising power source for future flexible electronics.

4 **2. Results and discussion**

5 2.1. Device Fabrication

6 To fabricate a micro-supercapacitor, a $50 \text{ }\mu\text{m}$ thick polyimide substrate was laminated in
7 waterproof masking film (ArCare 90445) and an interdigitated structure outline was laser cut
8 (VLS 230, Universal laser), and the film peeled off (Figure 1(a)). The exposed polyimide was
9 laser-treated (nominal power 8.1 W), which converts the polyimide into a graphene 3-
10 dimensional forest-like structure and was patterned as two interdigitated electrodes (Figure
11 1(b)). Separately, ~ 30 to 50 nm diameter red-mud nanoparticle solution was prepared at 15
12 mg/ml concentration in deionized water and stirred to ensure the dispersion remained uniform,
13 Figure 1(c). We selected the concentration of 15 mg/ml after initially measuring the cyclic
14 voltammetry at varying red mud concentrations (Figure S1 in the supporting information),
15 hereafter LIG-RM is used to refer to the flexible device of LIG decorated with RM at this
16 concentration. The interdigitated electrode was dip-coated in the stirring solution for 15
17 minutes and dried at $50 \text{ }^\circ\text{C}$. Silver current collectors were printed over the electrode edges using
18 a Dimatix 2805 Inkjet printer, using silver nanoparticle ink (NPS-J, Harimatec Ink) and
19 annealed at $180 \text{ }^\circ\text{C}$ in an oven for one hour. The ionogel mixture, at $50 \text{ }^\circ\text{C}$ was viscous but
20 dries like a gel, was micro-pipetted over the interdigitated fingers of the micro-supercapacitor.
21 The whole assembly was dried at room temperature. The schematic of the fabrication process
22 is shown in Figure 1(a-d).

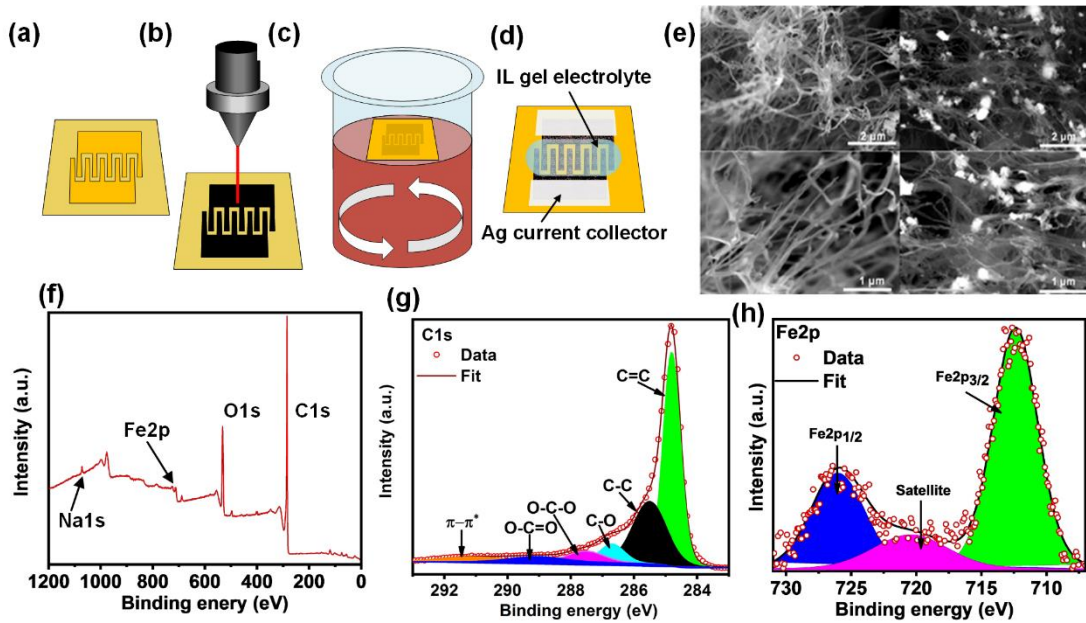
23 3.2. TEM and FESEM analysis

1 TEM images of RM nanoparticles are represented in Figure S2, here the spherical morphology
2 of the nanoparticles is clear, and an average size of $49 \text{ nm} \pm 9 \text{ nm}$ (S.D) was measured. In order
3 to visualize the decoration of red mud particles over the LIG nanofibers, FESEM analysis was
4 carried out and is represented in Figure 1e and cross sectional images (60° tilt angle) are shown
5 in Figure S3(a-b) which helps to demonstrate the 3D porous nature of LIG. Images of pure LIG
6 and LIG-RM show a relatively uniform dispersion of RM nanoparticles over the LIG forest.
7 SEM EDX elemental mapping is represented in Figure S4 to exhibit the presence and
8 homogenous distribution of carbon, iron, oxygen, aluminium, silicon and sodium within the
9 LIG-RM sample. BET analysis (Figure S5), was used to calculate the surface area of LIG-RM
10 as $120 \text{ m}^2/\text{g}$.

11 2.3. XPS analysis

12 X-ray photoelectron spectroscopy was carried out to probe the presence of different elements
13 in the composite assembly as shown in Figure 1(f-h). The survey scan of the red mud embedded
14 LIG structure shows the presence of Fe_2O_3 and oxides of aluminium, silicon, sodium and trace
15 amounts of oxides of magnesium, titanium and manganese in agreement with our previous
16 work [36] and is also similar to the red mud XPS data taken by Xu *et al.* and Liu *et al.* [40]
17 respectively. The high resolution XPS graphs display the C1s and Fe2p spectra, and the
18 presence of both components confirms the formation of the LIG-RM nanocomposite. The
19 presence of sp^2 C=C, sp^3 C-C, CO, O-C-O, O-C=O and π - π^* in the carbon XPS spectra
20 matches with the previously reported literature on LIG [41]. The high conductivity of LIG has
21 been correlated with the presence of high amount of sp^2 carbon ($\sim 284.8 \text{ eV}$) and minimal
22 residual oxygen functionalities. The high-resolution XPS result for iron showed the presence
23 of the doublet state of $2\text{p}^{1/2}$ (725.8 eV) and $2\text{p}^{3/2}$ (712 eV) levels which confirms the presence
24 of hematite phase in red mud nanoparticles [40b].

1



2

3 Figure 1. Fabrication of LIG-RM supercapacitor (a) Patterning and peeling of protecting layer
4 (b) Laser-induced graphene formation with CO₂ laser (c) dip-coating in RM solution (d) Silver
5 electrode printing and use of an ionic liquid electrolyte solution; (e) SEM images of pure LIG
6 film (left-hand side) and LIG-RM and XPS spectra of (f) RM decorated LIG, (g) C 1S spectrum
7 of LIG and (h) Fe 2p spectrum of red mud.

8

9 2.4. Cyclic Voltammetry

10 The Cyclic voltammogram for a two-electrode symmetric cell assembly for pristine LIG and
11 LIG-RM electrodes in IL mixture electrolyte at a scan rate 20 mVs⁻¹ is represented in
12 Figure 2(a). From the figure it is quite evident that for the LIG-RM electrode, there is a
13 significant 2-fold improvement in the specific current density as compared to the pristine LIG,
14 along with a higher area under the CV curve.

1 The variation in the cyclic voltammogram data of LIG-RM sample as a function of scan rate
2 (from 10 to 200 mVs⁻¹) is shown in Figure 2(b). The specific cell capacitance, C_{cell} , is assessed
3 from the CV graphs using equations (1 – 2):^[36]

$$4 \quad C_{cell} = 0.5(I/v) \quad (1)$$

5 where I is the total current (in Amperes), v is the scan rate (in Volt/sec). The total current I
6 can also be obtained from integration of the CV curve as ^[36, 42].

$$7 \quad I = \int_{V_i}^{V_f} \frac{i(V)dV}{(V_f - V_i)} \quad (2)$$

8 where V_i and V_f represent the upper and lower bounds of the voltage range. The cell capacitance
9 from $v = 5$ to 200 mVs⁻¹ is shown in Figure S6(a). At $v = 5$ mV s⁻¹ a cell capacitance of ~18
10 mF was obtained. At a sweeping potential of 50 mVs⁻¹, a cell capacitance of ~ 4 mF was
11 calculated for LIG-RM which is double to that for the pristine LIG device (~ 2 mF).

12 The specific gravimetric and areal capacitance of the system was also calculated as ^[43]:

$$13 \quad C_{sg} = 2 \frac{C_{cell}}{m} \quad (3)$$

$$14 \quad \text{and,} \quad C_{sa} = 2 \frac{C_{cell}}{A} \quad (4)$$

15 where C_{sg} is the specific gravimetric capacitance; C_{sa} is the specific areal capacitance, m is the
16 active mass and A is the total device area. The variation of specific areal and gravimetric
17 capacitance as a function of scan rate is represented in Figure 2(c) and Figure S6(b)
18 respectively.

19 The primary charge storage mechanism of an electrode is governed by the amalgamation of
20 capacitive and intercalation. The appearance of both the processes can be evaluated and

1 distinguished by monitoring the CV scans at different scan rates rendering to the following
2 power law ^[36, 44],

$$3 \quad i = av^b \quad (5)$$

4 Where a and b are adjustable parameters. A value of $b \approx 1$, shows a capacitance-dominated
5 current, and b value of ≈ 0.5 shows the current flow at that potential is dominated by
6 diffusion^[45].

7 The b values between the potentials -1.2 to 1.5 V were obtained for LIG-RM, and the variation
8 of b with applied potential is plotted in Figure 2(d) with a considerable variation in “ b ” values
9 from 0.3 to 0.85, which suggests that the charge storage mechanism is an amalgamation of both
10 capacitive and diffusion which arises from intercalation/de-intercalation phenomena ^[36, 46].

11 As it has been shown that the obtained capacitance is a combination of adsorption and diffusion
12 processes, the next aim was to quantify each element. According to a power-law relationship,
13 when the storage is driven by surface controlled phenomena the current (i_{cap}) varies linearly
14 with the scan rate (v) ^[46a, 47] and thus

$$15 \quad i_{cap} = k_1v \quad (6)$$

16 where, k_1 is a constant.

17 If the current is controlled by semi-infinite diffusion, then the current (i_{dif}) varies linearly to
18 the square root of scan rate ^[46a, 47]:

$$19 \quad i_{dif} = k_2v^{1/2} \quad (7)$$

20 thus, the total current, ^[46a, 47-48]

$$21 \quad i_T = i_{cap} + i_{dif} \quad (8)$$

1 $= k_1 v + k_2 v^{1/2}$

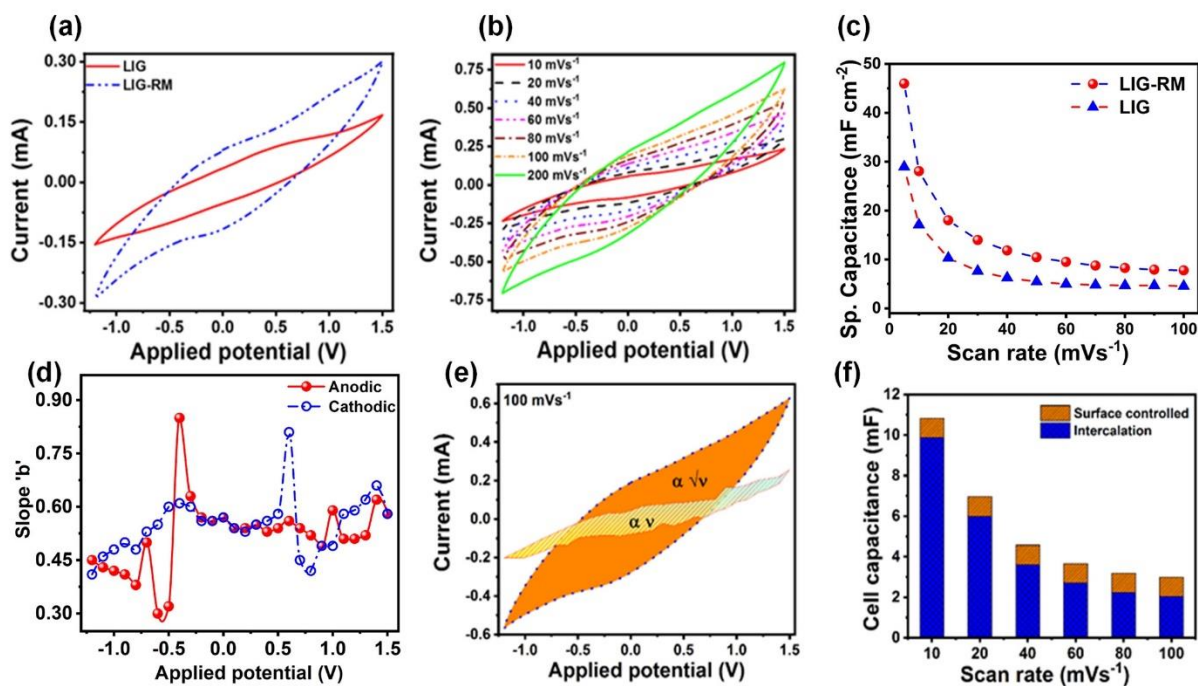
2 $\therefore \frac{i_T}{v^{1/2}} = k_1 v^{1/2} + k_2$ (9)

3 Therefore, the current values at different potential were calculated from CV at different scan
4 rate (200 to 5 mV s⁻¹) and then was plotted with $v^{1/2}$ for different potentials. The plot was
5 linearly fitted and the values of k_1 and k_2 were obtained from the slope and the intercept of the
6 graph respectively [46a]. The contribution of each component may be evaluated from the as-
7 obtained values of k_1 and k_2 . The resultant plots at scan rates 20 mV s⁻¹ and 100 mV s⁻¹ where
8 these components are distinguished are shown in Figure S7 and Figure 2(e) respectively.

9 After deconvolution of the contribution of surface controlled capacitance and intercalation-
10 dominated capacitance, the contributions at different scan rates were plotted in Figure 2(f). The
11 graph exhibits that at lower scan rate the storage is dominated by the intercalation where at a
12 low scan rate of 10 mVs⁻¹, only ~ 9% of the capacitance originates from surface adsorption
13 and the rest is intercalation [49]. Correspondingly, at a scan rate of 100 mVs⁻¹ ~32% capacitance
14 comes from the surface. This is consistent with the fact that at higher scan rate the ions of the
15 electrolyte have less time to intercalate in the electrode assembly [49-50]. The porous nature of
16 the electrode is responsible for intercalation-dominated pseudocapacitive charge storage in the
17 system [51]. The uniform decoration of the RM nanoparticles over 3D hierarchical LIG forest
18 configuration can allow complete exposure of the LIG-RM composite to the ILs [52].
19 Additionally, the high surface area of LIG provides enhanced contact with both the silver
20 current collector and the IL electrolyte. As a result, the electrolytes can easily penetrate and
21 enhances diffusion domination [53].

22 Trasatti's method was utilized to differentiate the specific capacitance from either surface or
23 diffusion-driven storage [54] which have different responses to the change in scan rate v [55]. At

1 a higher scan rate, the charge is stored at the outer surface since this is more immediately
2 accessible to the electrolyte (the surface may be accessed even at high scan rate). However at
3 lower scan rate, there is a combination of both surface and diffusion-driven storage, since the
4 ions have a longer period to diffuse to the inner electrode surface. Figure S8(a) shows a plot of
5 $1/C_s$ as a function $v^{1/2}$ between $v = 10$ to 100 mV s^{-1} , here both storage mechanisms (surface
6 and diffusion-driven) yield a significant contribution ^[46a]. The intercept of this line with best
7 fit of this line $1/C_s$ was used to calculate the specific capacitance as $\sim 55.5 \text{ mF cm}^{-2}$ at infinitely
8 slow scan rate. Figure S8(b) shows the graph C_s as a function of $v^{-1/2}$ which is used to calculate
9 the surface-controlled capacitance ^[55]. In this graph (S8b), the intercept ^[55] of the plot with the
10 C_s forecasted the surface controlled capacitance at infinitely high scan rate as $\sim 4.3 \text{ mF cm}^{-2}$.
11 The results predict that only $\sim 8\%$ of the capacitance is surface controlled and 92% is diffusion-
12 dominated; the dominant mechanism is thus diffusion-dominated pseudocapacitance. The
13 presence of iron oxide and other metal oxides in RM contributes towards the diffusion-driven
14 storage mechanism and the presence of porous LIG backbones enhances the diffusion ^[56].
15



1

2 Figure 2. (a) Cyclic voltammogram response of LIG and LIG-RM in IL electrolyte with a scan
 3 rate of 20 mV s^{-1} , (b) Cyclic voltammogram of LIG-RM in IL electrolyte at different scan rates
 4 (c) the variation of specific areal capacitance of the two-electrode LIG-RM supercapacitor (d)
 5 “ b ” (fitting parameter which shows storage mechanism) dependence as a function of applied
 6 potential (e) deconvolution of two different storage mechanisms: surface controlled ($\propto v$) and
 7 diffusion controlled ($\propto v^{1/2}$) from CV at scan rate 100 mV s^{-1} and (f) the contribution of surface
 8 controlled and intercalation cell capacitance after deconvolution of the CV graph at different
 9 scan rates.

10

11 2.5. Charging /discharging analysis

12 To determine the specific capacitance and cyclic stability, the LIG-RM two-electrode
 13 symmetric capacitor was galvanostatically charged and discharged between the applied

1 potential of -1.2 to 1.5 V, in the same ionogel electrolyte. The specific cell capacitance was
2 calculated using ^[57]:

$$3 \quad C_{cell/CD} = -[i/\{(dV/dt)\}] \quad (10)$$

4 Where $C_{cell/CD}$ is the cell capacitance and dV/dt is average gradient during the discharge
5 cycle. A steady device performance outlined by the quasi-symmetric charging/ discharging
6 cycles. ^[58] whereas the appearance of pseudocapacitance is confirmed from the curvature in
7 the discharge cycle. ^[59]. The charging/discharging plot (at a specific current density of 0.3 mA
8 cm^{-2}) for pristine LIG and LIG-RM devices are presented in Figure 3(a). The charge/discharge
9 period in case of the composite device is significantly higher than its pristine counterpart, and
10 consequently shows improved charge storage. The presence of RM nanoparticles not only
11 provide pseudocapacitive contribution and more accessible surface area but also provides a
12 better attachment of electrode-electrolyte assembly which can be attributed towards higher
13 storage in the composite device ^[15a].

14 The specific areal capacitance of the electrode material (LIG-RM) ($C_{sp/elec}$) was calculated as
15 ^[60]:

$$16 \quad C_{sp/elec} = 4 \frac{C_{cell/CD}}{A} \quad (11)$$

17 where A is the total device area (77.25 mm^2).

18 The areal capacitance was calculated from the charging-discharging graphs for different
19 specific current densities as plotted in Figure 3(b). The maximum areal capacitance of 203 mF
20 cm^{-2} was achieved at a specific current density of 0.1 mA cm^{-2} , whereas at an extremely high
21 specific current density of 1 mA cm^{-2} , a steady capacitance of 15 mF cm^{-2} was obtained. The

1 retention of a moderate capacitance even in such ultra-high specific current density highlights
2 the stability of the cell and supports its suitability as a supercapacitor electrode material.

3

4 2.6. Long-term cyclic stability

5 The performance of the supercapacitor in-terms of its stability over long-term cyclic usage was
6 also investigated through the charging/discharging measurement for 4000 cycles at specific
7 current density of 0.3 mA cm^{-2} . The capacitance retention as a function of cycle number is
8 plotted in Figure 3(c) and shows ~81 % retention of initial capacitance after 4000 cycles. The
9 retention initially increases to ~110 % of the initial value because of the surface chemical
10 activation of the composite electrode and subsequently better access of the electrolyte ions into
11 the porous LIG assembly during the charging-discharging cycle; a similar behavior has also
12 been reported in the literature ^[61]. The measurements were carried in an ambient atmosphere
13 and without any encapsulation and thus establish the suitability of the two-electrode device as
14 a long-term energy storage module.

15 The higher charge retention of the device is due to the porous LIG structure created during the
16 laser treatment ^[62, 63] of the polyimide precursor. Mixed ionic liquid brings forth the short-range
17 rearrangement of ions which plays a dominant role in electrolyte dynamics and electrosorption;
18 the different anions of the electrolytes dampens the alternating layer configuration and reduces
19 the excluded volume effect and in turns enhances the electrostatic interaction in the system and
20 improves the electrolyte dynamics and expand the effective potential window (2.7 V) and
21 charge storage capability of the device ^[64]. Favorable cyclic performance has previously been
22 observed in other mixed-metal oxide-based supercapacitors such as mixed-metal hydroxide
23 nanosheets ^[52], nickel–manganese oxide (NMO) and cobalt–manganese oxide ^[65] and mixed

1 V_2O_5 - TiO_2 supercapacitor electrodes.^[66] Additionally, the IL and ionogel electrolytes interlock
2 with the porous electrode and minimize material leaching and also improves the robustness of
3 the flexible device^[67]. The direct inkjet printing of silver current collector on top the LIG-RM
4 assembly provides better attachment and efficient contact for fast charge transport and current
5 collection^[68].

6

7 2.7. Energy and power density

8 Energy and power densities are the two most fundamental parameters of any energy storage
9 devices. The specific energy density E_{elec} ($mW\ h\ cm^{-2}$) of an electrode in a 2-electrode cell
10 configuration can be calculated as^[43b]:

$$11\ E_{elec} = \frac{1}{8} C_{cd/cell} V^2 \quad (12)$$

12 Where the cell capacitance and the effective potential windows are represented by $C_{cell/CD}$
13 and V , respectively. The specific power density P_{elec} ($mW\ cm^{-2}$) was calculated using the
14 following equation^[57]:

$$15\ P_{elec} = E_{elec} / t_d \quad (13)$$

16 where, E_{elec} is the specific energy density of the electrode and t_d is the discharge time.

17 Performance of the LIG-RM electrodes is presented in a Ragone plot (Power density vs. Energy
18 density) as shown in Figure 3(d). It exhibited the highest energy density of $\sim 51\ \mu Wh/cm^2$ of
19 energy density at a power density of $0.14\ mW/cm^2$ (specific current density $0.1\ mA\ cm^{-2}$) and
20 retained an energy density of $\sim 2\ \mu Wh/cm^2$ at a very high power density of $1.36\ mW/cm^2$
21 (current density of $1\ mA\ cm^{-2}$), which indicates better stability of the electrode at high current

1 density. In order to compare the performance of different similar flexible supercapacitors, a
2 comparative Ragone plot was drawn. The performance of LIG-RM was compared with highly
3 stretchable supercapacitors enabled by interwoven CNTs ^[69], coiled fibrous CNT-MnO₂-
4 polymer solid-state supercapacitors ^[70], porous LIG films from polymers ^[71], in-situ MoS₂
5 decorated flexible LIG electrodes ^[16]. Though the energy density was very high for the
6 interwoven CNT electrode its power density was very poor ^[69]. On the other hand in spite of
7 having very high power density porous LIG film on polyimide substrate lacks in terms of low
8 energy density.^[71] Energy and power densities of the MoS₂ decorated LIG ^[16] and coiled CNT-
9 MnO₂-polymer electrodes ^[70] falls in between and suitable for a high-performance flexible
10 device. Our result in terms of both power and current densities is better in comparison to these
11 two electrodes, which further confirms the suitability of our device as an effective storage
12 device. In our device higher energy density was achieved without sacrificing its inherent higher
13 power density.

14

15 2.8. Electrochemical impedance analysis

16 The nature of charge transfer kinetics and ionic diffusions have been probed using
17 Electrochemical impedance spectroscopy (EIS). ^[72]. During the EIS measurement a 10 mV AC
18 perturbation of between applied frequencies 0.1–100 kHz. The Nyquist plots of pristine LIG
19 and LIG-RM samples in IL composite electrolytes are represented in Figure S9. The charge
20 transfer resistance can be qualitatively evaluated by the semicircular diameter of the Nyquist
21 plot. ^[57, 73]. The reduction in the charge transfer resistance of the composite electrode indicates
22 a favorable diffusion of the electrolyte in the LIG-RM surface ^[73].

1 The EIS spectra of the prototype device were measured and the EIS data was fitted using a
2 model equivalent circuit and is represented in Figure 3(e). The equivalent circuit consists of a
3 series resistance which is in series with a Warburg impedance. These circuit components are
4 in series with two parallel circuits (in series with each other). The parallel circuit consists of a
5 charge transfer resistance and a constant phase element (CPE) ^[74]. All the parameters obtained
6 from the circuit fitting is represented in Table S1 in the supporting information. The as-obtained
7 series and charge transfer resistances of the solid-state supercapacitor device are similar to that
8 of the impedances recorded for similar supercapacitor devices ^[16]. The presence of Warburg
9 impedance and CPE validates the coexistence of capacitive and diffusion controlled charge
10 storage processes which is in agreement with the diffusion-dominated pseudocapacitive charge
11 storage mechanism.^[36]

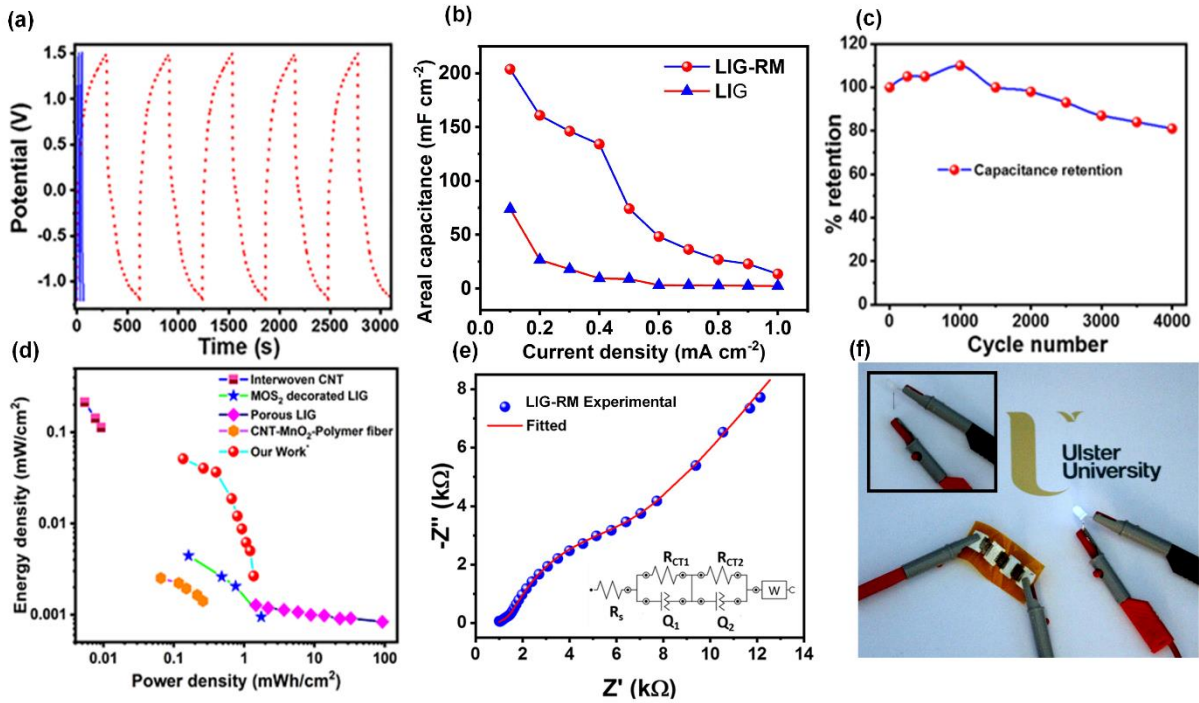
12

13 2.9. Bending test and flexible prototype device testing

14 In order to prove the suitability of the flexible device, a bending test was carried out. The
15 prototype device was bent to an arbitrary angle (Figure S10) and the cyclic voltammogram was
16 recorded at a scan rate of 20 mVs⁻¹. It is evident that the shape of the CV graph remains almost
17 intact after the bending, Figure S10 inset. The cell capacitance before bending was calculated
18 as ~4.4 mF and after the bending, the value was also found to be ~4.8 mF. The change is
19 minimal, and the results also indicate the acceptance and reliability of the flexible device ^[75].

20 Finally, to demonstrate the real-time application of the fabricated flexible device, the glowing
21 of the white LED experiment was performed (Figure 3(f)). Three prototype cells were printed
22 in series and charged using ~7 V using a constant voltage source. After charging the device
23 was connected to a white LED which requires 3.5 V for illumination. The prototype device was

1 able to power up the LED and a bright illumination was achieved, which demonstrates the
 2 successful fabrication of a prototype device.



3
 4 Figure 3. (a) Galvanostatic charging/discharging curve of pristine LIG (solid blue) and LIG-
 5 RM (dotted red) at a specific current density of 0.3 mA cm^{-2} , (b) variation of specific
 6 capacitance with specific current for LIG-RM, (c) the cycling performance of LIG-RM at a
 7 specific current density of 0.3 mA cm^{-2} for 4000 cycle, (d) Ragone plot related to energy and
 8 power density of the LIG-RM supercapacitor device, 2.7 V operation window in comparison
 9 to interwoven CNT [87], MoS_2 decorated LIG [19], CNT-MnO_2 -polymer fiber [88] and Porous
 10 LIG [89], (e) Nyquist plots of experimental and fitted impedance data for prototype LIG-RM
 11 device), the red line corresponds to fitted data and (f) the glowing of a white LED using a
 12 prototype device [The inset represents the open circuit (no supercapacitor was connected)].

13

1

2 **3. Conclusions**

3 The LIG-RM supercapacitor based 2 electrodes flexible all-solid-state micro-supercapacitor
4 with polymer ionogel was successfully fabricated. The waste red mud, an abundant source of
5 iron oxide was decorated over the laser-induced graphene. The two-electrode cell exhibits
6 promising and stable supercapacitor behavior. The stored charge in the supercapacitor device
7 was dominated by intercalation governed pseudocapacitance. The device displayed
8 significant specific capacitance along with high energy and power densities. The long-term
9 cyclic performance at ambient condition was also promising. Bending tests confirm its
10 suitability as a flexible device. Finally, the prototype device was able to power up a white LED.
11 The present approach does not involve any harsh chemicals and also deals with industrial waste
12 material, the fabrication process is inexpensive and is an encouraging route towards
13 sustainability.

14

15 **Experimental Section**

16 **Materials**

17 Raw red mud was collected from National Aluminum Company Limited (NALCO), India. The
18 polyimide sheet of 50 μm thickness was purchased from Printed Electronics (PEL), UK. 1-
19 Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI], 1-Ethyl-3-
20 methylimidazolium tetrafluoroborate ([EMIM][BF₄]) and Poly(vinylidene fluoride-co-
21 hexafluoropropylene) (PVDF-HFP) of high purities were purchased from Sigma-Aldrich and
22 were used without any further purification. All aqueous solutions were prepared using ultrapure
23 de-ionized (DI) water (Millipore-Q system).

1 **Synthesis of Red mud nanoparticles**

2 Red mud nanoparticles were synthesized from the as-received red mud powder according to
3 the process already reported in the literature [43]. Briefly, the powders were at first dried inside
4 an oven for 1 hour at an elevated temperature (383K) and crushed using a motor-pastel to obtain
5 dehydrated, and homogenous microparticles. RM nanoparticles were synthesized using a
6 planetary ball mill (Retsch, PN200) and pulverized inside a 60ml chrome steel bowl filled with
7 RM powders and spherical steel balls (diameter 5mm). An optimum ball to RM mass ratio of
8 8:1 was employed and the milling was carried out at a rotation speed of 150 rpm for 10 hours.

9

10 **Synthesis of LIG**

11 Kapton polyimide of 50 μm thickness (Printed electronics ltd. UK) was used as received for
12 the LIG production. Laser treatment was performed with a Universal Laser 230 VLS under
13 ambient conditions. The power throughout was 8.1 W (32.5 % of the maximum of this 25 W
14 system), speed was 570 mm s^{-1} (50 % of the maximum speed of the system) and at a density
15 of 1000 PPI. The device was fabricated as an in-plane interdigitated structure, the electrode
16 ‘fingers’ were 0.5 mm wide, 2.5 mm long, and with a 0.5 mm separation between fingers. The
17 total area was 77.25 mm^2 and this is used in calculations for cell capacitance

18 **Synthesis of ionogel electrolyte**

19 In order to prepare the ionogel, the ILs [EMI][TFSI] and [EMIM][BF₄] were mixed in a 3:1
20 ratio. Separately, PVDF-HFP was dissolved in acetone as a 1 mg/ml concentration. The RTIL
21 solution was then mixed with the PVDF-HFP solution (3:1), heated at 50 °C and stirred to
22 produce a homogenous mixture.

1 **Characterization**

2 TEM imaging was performed using JEOL 2100F. RM nanoparticles were dispersed in
3 methanol, sonicated until the dispersion was uniform, and micro-pipetted over a copper grid.
4 Scanning electron microscopy was completed using a Hitachi SU5000, acceleration voltage
5 10kV, working distance ~6 mm. The Brunauer–Emmett–Teller (BET) analysis was employed
6 to measure the specific surface area of LIG-RM with a Quantachrome Autosorb-1 BET surface
7 analyzer at 77K. X-ray photoelectron spectroscopy was performed using a Kratos Axis Ultra
8 using a monochromatic Al K α X-ray source ($\hbar\nu$ 1486 eV). The survey scan window was 287
9 to 1892 eV with a dwell time of 0.2 seconds. The 28 eV window high-resolution scans were
10 performed in triplicate with a dwell time of 0.5 seconds. The active mass was measured by
11 producing 252 cm² each of both LIG and LIG-RM and delaminating these from the substrate
12 before measuring using an analytical balance. The CV, charging-discharging and EIS
13 measurements were carried out in a 2-electrode cell configuration using an Autolab
14 Potentiostat/ Galvanostat (PGSTAT3, Metrhom, Netherlands). The equivalent circuit elements
15 were extracted from the Nyquist plots using the vendor-supplied Nova software.

16

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23

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