In-situ Mg-Al Delaminated Layered Double HydroxideInfused Lignin-Derived Laser Scribed Graphene for Facilitated Ion Transport in Flexible Supercapacitor Application

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Abstract

Background: Innovations in the synthesis of hybrid materials have led to technology advancement of the microsupercapacitor. Delaminated layered double hydroxide (LDH) reduces self-agglomeration and increases energy density in graphene-based supercapacitors. The incorporation of delaminated LDH with oil palm lignin derived laser scribed graphene in neutral PAAS/K_2SO4 gel electrolyte for flexible microsupercapacitor applications was investigated.

Method: Various concentrations of positively charged sucrose-delaminated Mg-Al LDH nanosheets produced through the coprecipitation method were hybridised with negatively charged oil palm lignin-derived laser scribed graphene (L-LSG) through electrostatic interaction.

Significant Findings: Hybrid laser scribed graphene developed from delaminated Mg-Al LDH at a concentration of 10 gL^{-1} (L-LSG/D-MgAl-10) had the largest surface area of 49.335 m^2g^{-1}. It also had the highest areal capacitance and energy density, measuring 40 $mFcm^{-2}$ and 0.00296 $mWhcm^{-2}$, respectively, at a current density of 0.08 $mAcm^{-2}$. The fabricated microsupercapacitor has exceptional bending capabilities and capacitance retention of 89.2 % after 5000 cycles. In summary, by inducing additional pseudocapacitance, delaminated Mg-Al LDH improved the overall effectiveness of the oil palm lignin derived graphene electrode compared to pristine graphene.

Keywords: Delaminated layered double hydroxide, Oil palm lignin, Laser scribed graphene, Flexible microsupercapacitor

1.0 Introduction

Supercapacitors have high power density, rapid charging and discharging, long cyclic stability, and low environmental impact [1]. It fills the energy gap between Li-ion batteries and typical capacitors for next-generation flexible electronics and comes in various sizes, shapes, and functionality [2,3]. There are two distinct charge transfers for supercapacitors: electrode/electrolyte interaction for electric double layer capacitor (EDLC) and near-surface redox reaction for pseudocapacitor (PC) [4]. The electrode material is very important when choosing the type of energy storage mechanism. Carbon variants with large surface area and high ion adsorption and desorption rates, including activated carbons, carbon nanotubes, nano horns, and graphene, are typically used as the electrode material in electrical double-layer capacitors (EDLC), while the electrode for pseudocapacitive (PC) supercapacitors are made of components from faradaic active battery materials, such as transition metals (Fe, Co, Ni, and Mn) oxide/ hydroxides, and polymers [4,5]. These EDLC and PC electrode materials are frequently coupled to form hybrid nanomaterials such as RGO/MnO_2 [6], C-Fe/PANI/Ni-GF [7], rGO-CuS [8], MoS2@rGO [9], RuO_2-P-rGO [10], V_3S_4/RGO [11] and GNF/$NiCo_2S_4$/$Co_xNi_{(3-x)}S_2$ [12], which typically have better intrinsic conductivity and superior electrical double layer capacitance [13].

Single sheet graphene is usually used as the primary EDLC material due to its large theoretical surface area (2600 m^2g^{-1}) [14], steady electrical conductivity (10^3-10^4 Scm^{-1} facile) [5], good carrier mobility (> $2*10^5$ $cm^2V^{-1}s^{-1}$ at $2*10^{11}$ cm^{-2}, electron density) [4], and chemical and mechanical stability. Tour et al. recent discovery of 3D graphene by laser irradiation has greatly facilitated graphene synthesis, since it is much easier to print microelectrodes for microsupercapacitors, biosensing and gas sensing application without the need for any toxic materials and high temperatures [2,15]. Their simple one-step approach is suitable for developing a variety of doped and infused materials, including Phosphorus [16],

Sulphur/Nitrogen [17], Boron [18], Cobalt [19], and TiO_2 [20], for functionalized or hybrid graphene.

Lignin is a well-known biopolymer that may be used as an alternative to cellulose, chitosan, and pectin to produce functionalized graphene. It is a biowaste with multiple aromatic rings and is an excellent carbon precursor [21]. Graphene can been synthesized using laser scribing as the primary technique and lignin as the primary precursor [22–24]. Laser scribing is a viable technology for synthesizing graphene from lignin since many variables, such as laser intensity and speed, can be tuned to obtain the desired graphene quality. The C-O, C=O, and N-C bonds in lignin could be easily broken by localised high temperature pulses from lasers, resulting in rearranged structured graphene [15].

Bimetallic Layered Double Hydroxides (LDH), also known as anionic clay, with a general chemical formula of $[M^{2+}_{1-x}M^{3+}_{X}(OH)_2]^{x+}$ $[A^{n-}_{x/n}]^{X-}$. mH_2O (M^{2+}/ M^{3+} - Divalent / trivalent metal cations; A^{n-} interlayer anion) have attracted considerable attention, due to its ease of preparation, environmental friendliness, and accessibility to a wide range of ions for electrochemical reactions [25,26]. The octahedral, brucite-like layers of the LDH crystallites can be detached into a positively charged 2D single-layer nanosheet for thin layer application and nanocomposite formation [4,13]. Delaminated LDH possesses a much higher surface area (1000 m^2g^{-1}) with highly exposed ions for enhanced redox reaction [5]. CF@Cu-BDC@NiCo [27], $MoSe_2$-$CoSe_2$@CoAl [28], and CoFe-LDH/GO/NF [29], CC@Co2CH/NM-LDH-Ag [30] are a few of the recently synthesized LDH for electrocatalytic and supercapacitor applications. However, the agglomeration of LDH nanosheets impairs electrical conductivity and cyclic performance [26]. A promising solution is incorporating delaminated LDH to overcome agglomeration through electrostatic interaction. Various types of delaminated LDH, including Ni-Al [4,26,31], Co-Al [5,32], Co-Ni [5,13,33], Ni-Fe [34], Co-Fe [35] and Mg-Al [36] have been electrostatically assembled with graphene-based materials using mixing,

dropwise and laser assisted technique to create a useful nanocomposite for supercapacitor applications.

In this work, we have developed a novel sucrose-delaminated Mg-Al layered double hydroxide nanosheets (D-MgAl) using a simple coprecipitation approach. The positively charged D-MgAl was subsequently used alongside surface reduced in-situ oil palm lignin-derived laser-scribed graphene (L-LSG) microelectrodes on a flexible substrate to form a synergized composite held together by electrostatic interaction.The embedding of D-MgAl on top of grown graphene was evident in both FESEM and TEM imaging, and characterization studies supported these findings. Further investigation on the electrochemical performance of the composite using PAAS/K_2SO_4 gel electrolyte confirmed that delaminated LDH boosted the conductivity, capacitance, energy density, and power density of pure L-LSG microsupercapacitor. The L-LSG/D-MgAl electrode yielded a remarkable areal capacitance of 40 $mFcm^{-2}$ at 0.08 $mAcm^{-2}$ with outstanding cyclic stability of 89.2 % over 5000 charge-discharge cycles and 94.9 % capacitance retention at 5 different angles. The in-situ laser scribing technique has successfully infused D-MgAl on top of L-LSG.

2.0 Methodology

2.1 Materials

Extracted oil palm lignin [37]. Magnesium Nitrate (Mg $(NO_3)_2$), Aluminum Nitrate (Al $(NO_3)_3$), Sodium Hydroxide (NaOH), Sodium Polyacrylate (PAAS), Potassium Sulphate (K_2SO_4), Polypropylene Glycol and sucrose were purchased from Sigma-Aldrich. Polyimide film (5 mil) was purchased from Avantis Laboratory Supply. Deionized (DI) water was used throughout the experiment.

2.2 Preparation of Delaminated Mg-Al LDH

An eco-friendly coprecipitation method was employed to synthesize delaminated Mg-Al LDH. First, a 50 ml mixture solution containing 30 mmol of magnesium nitrate and 15 mmol of aluminium nitrate was prepared. While stirred, the solution was added dropwise to a 100 ml mixture of deionized water and polypropylene glycol solution containing 1 g sucrose. The reaction mixture was maintained at pH 9 using a 1 M NaOH solution while being purged by nitrogen gas. The slurry product was centrifuged for 3 minutes at 3500 rpm. The finalized product was dried into a powder in a freezer dryer for 24 hours for further dilution.

2.3 Preparation of D-MgAl incorporated L-LSG electrodes.

A 20 % v/v lignin solution was mixed with D-MgAl in varying concentrations from 6 gL^{-1} to 10 gL^{-1} in a 4:1 ratio at 1000 rpm. The solution was then drop-coated on a sterilized polyimide sheet using the blade coating method. The prepared thin film was dried in an oven (50 °C) for an hour, with the solution with higher D-MgAl concentration taking longer to dry completely. The 10.6 µm CO2 laser engraving system (V-460, Universal Laser System) was on a raster mode at a constant intensity of 21 W (70 % of max 30 W). All samples were handled with the same laser parameters, including laser speed, z-axis, and PPI. After laser writing 45 samples per batch for ~20 mins, the resulting lignin only layer was removed using a water bath. The final composite was denoted as L-LSG/D-MgAl-X, where X represents the D-MgAl concentrations (6,8, and 10 gL^{-1}).

2.4 Fabrication of L-LSG/D-MgAl microsupercapacitors

A CorelDRAW drawing of a microsupercapacitor comprising six pairs of electrodes and a current collector with an area of 0.5 cm^2 was designed before laser scribing (Fig. S1a). Conducting wires, silver paste, and polyimide tape were used for connection. The resulting device was covered with a PAAS/K_2SO_4 (0.5 M) gel electrolyte and allowed to soak overnight for complete electrode immersion. PAAS/K_2SO_4 (0.5 M) gel electrolyte was prepared by

adding 5 ml of prepared 0.5 M K_2SO_4 dropwise into PAAS crystals until a gel-like substance was formed (Fig. S1b - S1c).

2.5 Material Characterization

A few 10 X 10 cm samples of L-LSG/D-MgAl-X have been prepared and scraped carefully until a sufficient amount of powder is obtained for the following material characterizations: Field Emission Scanning Electron Microscopy, FESEM (TESCAN CLARA, UHR SEM) and Transmission Electron Microscopy, TEM (Hitachi, HT7830) were used to study the surface morphology of the material. The Raman spectra (514 nm) were obtained from the Raman Spectrometer (Horiba, HR800) to analyze the crystalline size (L_a) of a material. Specific surface area (SSA) and pore size distributions were evaluated using the Brunauer-Emmett-Teller (BET) technique and Barrett Joyner Halenda (BJH) model by Tristar 3020 Plus, respectively. The X-ray diffraction (XRD) patterns were obtained to study the material's crystal structure at 0.02 °/step and 2 s/step (PANalytical X'Pert3 Powder). Charges on the material surface were identified via Zeta potential measurements from Malvern, Zetasizer Nano-ZSP. XPS readings from Thermo Scientific K-X-ray Alpha's photoelectron spectroscopy were used to analyze the composition of materials, while Fourier-transform infrared spectroscopy, FTIR was used to analyze the functional groups of ordinary and composite material (Perkin Elmer Spectrum One).

2.6 Electrochemical characterization

A two-electrode system was used to evaluate the cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) of the microsupercapacitors (Metrohm, Autolab). Cyclic voltammetry (CV) was performed with a scan rate of 10-200 mVs^{-1} and voltage window size of 0.8 V. Galvanostatic charge/discharge (GCD) measurements were taken with current densities ranging from 0.08 to 1.0 $mAcm^{-2}$. EIS

data were collected in the frequency range of 0.01 Hz to 10 kHz with an amplitude of 0.01 V. The detailed calculations of areal capacitance, energy density and power density obtained from CV and GCD readings are shown in the supplementary document.

3.0 Results and Discussion

3.1 Fabrication and characterization of L-LSG/D-MgAl electrodes

Fig. 1 illustrates the in-situ laser scribing process of lignin-derived laser-scribed graphene decorated with delaminated MgAl LDH. A fixed ratio of oil palm lignin powder from the soda pulping procedure was combined with varied concentrations of gel-like delaminated MgAl LDH. The brown solution was then coated on clean polyimide and cured for an hour at 50 °C. Electrostatic interaction infused positively charged delaminated MgAl LDH with negatively charged LSG. The changes in the morphological structure of 3D porous graphene anchoring nanosheets composite before (lignin and D-MgAl) and after (L-LSG/D-MgAl) laser scribing are highlighted in the FESEM insets. Microelectrodes were subsequently integrated into a supercapacitor with connecting wires and a PAAS/K_2SO_4 electrolyte for further electrochemical measurements.

Fig. 2a depicts a FESEM image of a composite (L-LSG/D-MgAl) comprising a forest-like lignin-derived laser-scribed graphene structure with an extra-thin layer of delaminated Mg-Al LDH coating. Due to the instantaneous evaporation of water molecules during the carbonization process, the composite has numerous macro and mesopores, facilitating ion diffusion [24,33]. The numerous conductive networks provided by the 3D hierarchical structure of laser-derived graphene enable the flow of electrons during electrochemical reactions. Further addition of D-MgAl LDH increased the LSG's electroactive sites for redox reactions without reducing its original porosity [2,33]. The initial agglomeration of LDH first seen in Fig. S2 has been minimized, and it is dispersed homogeneously on LSG, as shown in Fig. 2b and c. The Energy dispersive spectroscopy (EDX) elemental mapping results from Fig. 2d further demonstrated the uniform distribution of the Mg and Al metal particles across the LSG layer containing carbon and oxygen. By introducing metal nanosheets as an effective charge

191 holder, in-situ laser scribing technology has successfully increased the conductivity of
192 graphene layers by avoiding agglomeration [4]. The composite consists of carbon, oxygen,
193 magnesium, and aluminium in decreasing order of weight across a large scanning region based
194 on the EDX Spectrum (Fig. 2e).

195 The TEM image of L-LSG/D-MgAl shows a wrinkled layer of graphene attached to translucent
196 D-MgAl LDH at the top, bottom, and side edges (Fig. 3a). TEM images of agglomerated LDH
197 particles before (Fig. S3) and after (Fig. S4) laser scribing shows that in-situ laser scribing has
198 affected the morphology and structure of the delaminated LDH particles, resulting in a more
199 uniform and well-defined pattern. The laser energy induced a local thermal effect, which
200 caused the LDH particles to melt and resolidify, forming a more compact and homogeneous
201 layer [38]. This local thermal effect has led to a reduction in the size of the LDH agglomerates
202 (single sheet ranges from 50- 100 nm) and an increase in their surface area, which can have
203 significant implications on the faradaic reactions of L-LSG/D-MgAl [13,32]. L-LSG with a
204 homogeneous distribution of MgAl LDH exhibits a similar overall increase in surface area after
205 being prevented from restacking, as shown in Fig. 3b. The selected area electron diffraction
206 (SAED) patterns of L-LSG/D-MgAl in the inset of Fig. 3b exhibits well-defined diffraction
207 patterns for L-LSG and diffused rings for D-MgAl LDH, indicating the overlapping of
208 crystalline and amorphous structure [39].

209 The crystalline structure of the composite has been studied using the XRD pattern, as shown
210 in Fig. 3c. L-LSG featured an obvious diffraction peak at 25.9° corresponding to (002) with
211 minimal interference from adjacent peaks [21]. Due to its amorphous state, D-MgAl exhibited
212 a broader 2θ peak from 20° to 30° degrees, closely aligned with SAED data. Since the LDH
213 nanosheets dissolved in water, the diffraction of water can be seen clearly in the XRD patterns
214 of D-MgAl [40]. Furthermore, the L-LSG/D-MgAl 's diffraction pattern exhibited peaks from

both parental and an extra (003) peak at 11.3°, demonstrating that D-LDH constructed a layer-by-layer ordered structure with L-LSG utilizing electrostatic interaction [41].

In Fig. 3d, the zeta potential data shows that the delaminated MgAl LDH has a positive zeta potential (+5 mV), while L-LSG has a negative zeta potential (-30 mV). This difference in charge between the two materials is attributed to the absence of oxygenated functional groups on the MgAl LDH and the presence of these groups on the surface of L-LSG [42,43]. The opposite charges on the two materials are believed to be the primary contributor to producing a stable nanostructure when the two materials are combined. The formation of a stable composite material is demonstrated by the shift of L-LSG/D-MgAl towards the positive region (-26 mV) when negatively charged L-LSG sheets and positively charged MgAl LDH nanosheets are mixed [42,44].

Raman spectra were obtained to assess the degree of graphitization for the L-LSG/D-MgAl composites for various D-MgAl LDH concentrations (Fig. 3e). All the measured samples have three major peaks at 1350 cm^{-1}, 1585 cm^{-1}, and 2700 cm^{-1}, which correspond to the peaks for the D (breathing modes of sp^2 carbon atoms), G (E_{2g} vibrational mode of sp^2-bonded carbon atoms) and 2D (a double-resonance process of two phonons) bands [1,45]. I_D/I_G intensity was measured to evaluate the degree of disorder and defects in the crystalline domains of the fabricated composite [25]. The decrease in the average size of the sp^2 graphitic domains is evidenced by the I_D/I_G ratio of LSG to L-LSG/D-MgAl-10, which gradually climbed from 0.66 to 1.07. The reduction of L-LSG's crystalline size from 25.3 to 15.7 nm provides further evidence to support this. The unrepaired defects in the hybrids promote the formation of strong chemical bonds, which can prevent the aggregation of delaminated LDH and ensure that they are uniformly distributed on L-LSG [25]. Interestingly, the M-OH (M= Mg, Al) stretching band at 475 cm^{-1} with L-LSG and D-Mg Al LDH is capable of forming a hybrid [31].

According to Fig. 3f, the FTIR Spectra measured between 500 and 4000 cm^{-1}. The existence of the C-O and N-O bonds (Nitrate anions), through a prominent absorption band, is seen in the IR spectra of D-MgAl at 1092 cm^{-1} and 1375 cm^{-1} [26,46]. D-MgAl exhibits bands from 2867 to 2950 cm^{-1} that indicate the presence of C-H stretching vibrations spurred on by polypropylene glycol, whereas hydroxyl groups and intercalated water molecules had vibration bands at 3400 cm^{-1} and 1636 cm^{-1}, respectively [26,47,48]. When comparing the IR spectra of L-LSG/D-MgAl to L-LSG from Fig. S5, the strength, and the existence of additional peaks from D-MgAl are obvious. The presence of C-O and hydroquinone functionality groups could be observed at 1070 and 1045 cm^{-1} [49,50]. Interestingly, the intensity of the peaks steadily increases as the D-MgAl concentration rises.

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Fig. 4a shows the N_2 adsorption/desorption isotherms of L-LSG/D-MgAl-10 exhibiting type - III shaped isotherm due to water vapour in the basal panel of the composite [51]. LSG/D-MgAl-10 has 30 % greater Brunauer-Emmett-Teller (BET) measured specific surface area of 49.335 m^2g^{-1}, with enhanced adsorption volume at high and low relative pressure in comparison to L-LSG (Fig. S6). There is only a small increase in surface area relative to the anticipated surface area, primarily as a result of D-MgAl's melting and solidification process during laser lithography covering a portion of the porous structure of L-LSG [38]. L-LSG/D-MgAl-10 has an apparent peak at a pore diameter of 2.4 nm (mesopores) and an increasing pore volume from 1 nm to 260 nm, indicating a wide variety of pore diameters, which promotes the diffusion of ions in the composite materials [26]. The L-LSG/D-MgAl surface's chemical composition was further studied using XPS, as shown in Fig. 4c. According to the survey spectra of L-LSG/D-MgAl, the composite primarily consists of major carbon and oxygen peaks at binding energies of 286.08 eV and 533.08 eV. The inset from Fig. 4c illustrates the formation of minor Al 2p and Mg 1s at binding energies of 75.08 eV and 1304.58 eV [52,53]. D-MgAl and L-LSG contribute to the oxygen peak with the presence of exfoliated hydroxyl group and uncarbonized

lignin compound, and L-LSG is the main contributor to the carbon peak. The breakdown of the C 1s spectrum revealed four bond peaks, which correspond to the functional groups of C-C, C-O, C=O, and O-C=O, at binding energies of 284.4 eV, 285.6 eV, 287.07 eV, and 288 eV, respectively [22] (Fig. 4d). In addition, the high-resolution spectra of Al 2p and Mg 1s as a sharp peak resembles the presence of Al^{3+} and Mg^{2+} species as metal oxides or hydroxides compound within the composite (Fig. 4e and f) [52–55].

3.2 *Electrochemical performance L-LSG/D-MgAl microsupercapacitor*

The electrochemical properties of the L-LSG and D-MgAl incorporated composites assembled into a 2-electrode IDE in a 0.5 M PAAS/K_2SO_4 gel electrolyte were evaluated by CV, GCD, and EIS tests. Understandably, the microelectrode exhibits a different operating potential range due to the different types of electrolytes [56–58]. Fig. 5a shows the CV curves of the samples measured at a scan rate of 50 mVs^{-1} from -0.4 V to 0.4 V. All the composites exhibited a quasi-rectangular curve with two strong redox peaks at anodic and cathodic regions, indicating the presence of Mg^{2+} metal ions through the reversible equation (1) below [14,26]. D-MgAl is denoted as LDH-Mg $(OH)_2$ as Al metal is electrochemically inert [59].

$$\text{LDH-Mg (OH)}_2 + OH^- \leftrightarrow \text{LDH- MgOOH} + H_2O + e^- \qquad (1)$$

Aromatic compounds (quinone/hydroquinone groups) discovered on lignin are responsible for the synergistic impact of EDLC and pseudocapacitance observed in L-LSG curves [50,60]. At the corresponding oxidation and reduction potentials, hydroquinone is oxidised into quinone during charging with $2H^+$ and $2e^-$ and is reduced back into hydroquinone during discharge by gaining $2e^-$ from $2H^+$ [61]. The electrode L-LSG/D-MgAl shows a greater integral area of the CV curves when compared to pure graphene and other composites, indicating that an increase in D-LDH concentration is necessary to improve the electrical conductivity of the porous

graphene surface. The areal capacitance ($mFcm^{-2}$) for L-LSG/D-MgAl, determined from CV curves, is 3.13, 3.4, 3.73, and 3.81 for the lowest to the highest concentration.

The CV tests were run at different scan rates for L-LSG and L-LSG/D-MgAl composite electrodes to assess the redox processes further, as shown in Fig. 5b and Fig. S7 – S10. Slight shifts in the redox peaks could be seen for all the composites, in addition to L-LSG/D-MgAl-10, due to the access limitation of ions to the interior and exterior sections of the electrode material [62]. Higher areal capacitance at lower scan rates and lower areal capacitance at higher scan rates are influenced by the rate of ion movement in the electrolyte [36]. L-LSG/D-MgAl-10 has the maximum capacitance at each scan rate, as shown in Fig. 5c. The capacitance of L-LSG/D-MgAl-10 is 10.43, 6.74, 3.81, 2.39, and 1.36 $mFcm^{-2}$ at scan rates of 200, 100, 50, 20, and 10 mVs^{-1}.

Fig. 5d compares the galvanostatic charge-discharge (GCD)patterns of L-LSG and L-LSG/D-MgAl at various concentrations. The appearance of non-symmetrical triangles in the GCD curves at 0.1 $mAcm^{-2}$ suggests pseudocapacitive behaviour caused by hydroquinone from the oil palm lignin and delaminated metal ions present on L-LSG and L-LSG/D-MgAl, respectively [33,63]. All of the curves display slightly more than 100 % coulombic efficiency due to remaining electronegative oxygen functions that resist being discharged during GCD characterization [64,65]. Due to the synergistic effects of EDLC from the graphene electrode and the faradaic reaction of Mg and Al from the LDH nanosheets, the GCD peak of the L-LSG coupled with delaminated LDH is noticeably broader than that of pristine L-LSG. The easily accessible delaminated MgAl nanosheets linked on top of graphene composed of lignin boosted the surface area and improved the charge transfer mechanism at a uniform distribution [31]. The L-LSG and L-LSG/MgAl areal capacitances are 27.7, 32.57, 35.4, and 36.9 $mFcm^{-2}$, respectively, for concentrations of 0, 6, 8, and 10 gL^{-1}. The L-LSG/MgAl-10 composite with the highest capacitance was subsequently examined using different current densities, as shown

in Fig. 5e. The overall charge-discharge time of L-LSG/MgAl-10 reduces with increasing current density, due to the reduced ion penetration rate into the electrode surface. At a current density of 0.08 $mAcm^{-2}$, L-LSG/MgAl has a maximum areal capacitance of 40 $mFcm^{-2}$, followed by 36.9, 22.22, 14.29, 10.51, 6.4, and 2.63 $mFcm^{-2}$ at 0.1, 0.2, 0.4, 0.8, and 1.0 $mAcm^{-2}$. The capacitance measurements for the other composites are shown in Fig. 5f. All L-LSG/MgAl composites exhibited an overall improvement in areal capacitance until saturation at 8 gL^{-1}.

Further evaluation was conducted using EIS analysis on the graphene composite L-LSG/D-MgAl at 100 kHz to 0.01 Hz. Fig. 6a depicts the Nyquist plot, which has steeper slopes at low frequencies and compressed semi-circles at high frequencies. The resistance of the electrochemical system, Rs, consists of the resistance of the electrode, the electrolyte, and the contact resistance between the electrode and is indicated by the intersection of the curve at the real axis, while the charge transfer resistance during the electrochemical process, Rct, is the diameter of the semicircle [66]. The slope denotes the resistance due to the diffusion of ions in the electrolyte into the surface of the electrode [31]. The inset shows that the Rct value of L-LSG/D-MgAl increases at increasing concentrations due to interfacial resistance between L-LSG and D-MgAl [67]. The vertical lines, however, clearly demonstrate the improvement in Warburg impedance in the low-frequency region. Crucially, the EIS spectra of L-LSG/D-MgAl-10 have a comparable Rs value of 98.28 while retaining a steeper slope towards the imaginary axis at higher LDH concentration. L-LSG/D-MgAl-10 is superior to standard L-LSG due to improved ion/ electron diffusivity through a faradaic reaction.

To determine the long-term durability of the microsupercapacitors, the capacitance retention of the L-LSG/D-MgAl-10 electrode was evaluated at 0.5 $mAcm^{-2}$ for 5000 cycles, as shown in Fig. 6b. A remarkable retention rate of 89.2 % was achieved by L-LSG/D-MgAl-10 following an early peak in the capacitance measurements due to an ‘’electro-activation’’, or the steady

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increase in the infiltration of electrolyte into electrode material [68,69]. The flexibility of the L-LSG/D-MgAl-10 was investigated using CV measurement at 50 mV/s and varied bending angles to assess its feasibility for applications involving wearable and malleable electronics. The wide CV curves with redox peaks observed in Fig. 6c at bending angles of 0°, 45°, 90°, 135°, and 180° imply minor capacitance loss of 5.1 % at increasing bending angles. These support LSG/D-MgAl-10 's potential for flexible and wearable applications.

The microsupercapacitors were subsequently upgraded and linked in series and parallel configurations to generate the required capacitance, energy, and power densities for practical applications. The electrical measurements of microsupercapacitors at an increasing CV area and charge-discharge duration as the number of supercapacitors in the parallel increased are shown in Fig. 6d and e. Fig. 6f and g show an increase in voltage for microsupercapacitors connected in a series circuit of up to 1.2 V for 2 devices and 2.0 V for 3 devices, while retaining almost the same discharge period. The three microsupercapacitors connected in series were used to switch on a light-emitting diode (LED). As observed in Fig. 6h and Fig. S11, the microsupercapacitors demonstrate their potential in turning on a red LED, which is very similar to prior studies [70,71].

While having comparable power densities to L-LSG, L-LSG/D-MgAl-10 microsupercapacitor recorded the highest energy density of 0.00296 $mWhcm^{-2}$ at 0.055 $mWcm^{-2}$. Although the highest power density of L-LSG/D-MgAl-10, 0.25 $mWcm^{-2}$ is consistent with L-LSG, there is a significant increase in energy density in the higher current density region of Fig. S12 due to the additional surface area and electrical conductivity provided by delaminated LDH nanosheets. Fig. 6i shows the Ragone plots of the L-LSG/D-MgAl-10 and other previously reported LSG microsupercapacitor to highlight the overall improvement in areal energy and power densities. The L-LSG/D-MgAl-10 microsupercapacitor has higher energy and power densities than several previously published composites, including the LIG [15], LSG-P24-Au

[21], 3D-GF [72], M-PBRV-RGO [73] , PA-PBI-LIG [74] and Paper LIG [75] composites. Ph-ddm/LIG [76] and KOH-LIG [77] composites however, continued to have greater power densities. Further comparison regarding electrochemical performance of microsupercapacitors can be seen in Table S1.

4.0 Conclusion

In conclusion, in-situ laser-scribed sucrose delaminated Mg-Al LDH infused with lignin-derived graphene is a more efficient electrode material than pure lignin-derived graphene. The remarkable overall supercapacitor performance surpassed that of previous studies (LIG [15], 3D-GF [72], PA-PBI-LIG [74] and Paper LIG [75]) due to the strong electrostatic coupling and synergistic effect of the laser-derived graphene and pseudocapacitor (PC) properties of delaminated LDH. Delaminating LDH into nanosheets greatly improved capacitance, since it increased the surface area accessible for rapid ion reactions on graphene's exterior and interior surfaces. Laser scribed graphene developed from delaminated Mg-Al LDH at a concentration of 10 gL^{-1} (L-LSG/D-MgAl-10) has a maximum areal capacitance of 40 $mFcm^{-2}$ and an energy density of 0.00296 $mWhcm^{-2}$, with a current density of 0.08 $mAcm^{-2}$, In addition, L-LSG/D-MgAl-10 showed exceptional flexibility and reliability with outstanding cyclic and angle bending retentions of 89.2 % and 94.9 %, respectively. This study not only showcases the considerable potential of this material as an electrode material for microsupercapacitors but also lays the groundwork for the research and development of electrostatically assembled LDH on biopolymer derived graphene for energy storage application.

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Figure legends

Fig. 1. Schematic illustration of the L-LSG/D-MgAl LDH preparation for microsupercapacitor application

Fig. 2. (a-c) FESEM images of L-LSG/D-MgAl at different magnification. (d) FESEM elemental mapping of L-LSG/D-MgAl and the corresponding elements. (e) EDX spectrum of L-LSG/D-MgAl

Fig. 3 Low (a) and high (b) magnification TEM images of L-LSG/D-MgAl (Inset: SAED pattern). (c) XRD and (d) Zeta potential patterns of L-LSG, D-MgAl and L-LSG/D-MgAl. (e) Raman Spectra and (f) FTIR of L-LSG, D-MgAl and L-LSG/D-MgAl-X.

Fig. 4. (a) Nitrogen adsorption–desorption isotherms and (b) corresponding BJH Pore size distribution of L-LSG/D-MgAl-10. (c) XPS survey spectra, (d) C 1s, (e) Al 2p and (f) Mg 1s of L-LSG/D-MgAl-10 (The insets represent magnified survey image of Mg 1s and Al 2p).

Fig. 5 (a) CV curves of L-LSG/D-MgAl-X at 50 mVs^{-1}. (b) CV curves of L-LSG/D-MgAl-10 at scan rates ranging from 10 to 200 mVs^{-1}. (c) Correlation of L-LSG/D-MgAl-X capacitance at different scan rates. (d) GCD curves of L-LSG/D-MgAl-X at 0.1 $mAcm^{-2}$. (e) GCD curves

of L-LSG/D-MgAl-10 at current densities ranging from 0.08 to 1 $mAcm^{-2}$. (f) Dependence of L-LSG/D-MgAl-X capacitance at different current densities

Fig. 6 (a) Nyquist plots of L-LSG/D-MgAl-X (Inset: magnified image of Nyquist plots). (b) Cyclic stability of L-LSG/D-MgAl-10 at 0.5 $mAcm^{-2}$. (c) Capacitance retention of L-LSG/D-MgAl-10 measured at different bending angle (The inset represents CV measurements of L-LSG/D-MgAl-10 at different bending angle). (d) CV curves at 50 mVs^{-1} and (e) GCD curves at 0.5 $mAcm^{-2}$ of L-LSG/D-MgAl-10 parallel devices. (f) CV curves at 50 mVs^{-1} and (g) GCD curves at 0.5 $mAcm^{-2}$ of L-LSG/D-MgAl-10 series devices. (h) Photograph of L-LSG/D-MgAl-10 series devices powering up a LED bulb (side view). (i) Ragone plot comparing energy density and power density of L-LSG/D-MgAl-10 with previously reported articles.