A High Performance Selectively Grown Nano-octahedral Mn_3O_4 on Lignin Derived Laser Scribed Graphene for Microsupercapacitor Applications

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Abstract

~~Porous graphene infused with mixed valency metal oxide as a supercapacitor material has received much attention. However, t~~The existing approach to directly infusing mixed valency metal oxide such as Mn_3O_4 on graphene electrodes results in poor electrochemical performance. We report the facile fabrication of oil palm lignin derived laser scribed graphene with sol-gel hydrothermal grown nano-octahedral shaped Mn_3O_4 nanoparticles to boost the electrochemical performance of the flexible hybrid microsupercapacitor. The newly formed Mn_3O_4 nanoparticles (Mn_3O_4 NPs) were octahedral shaped and 15 to 30 nm in size, without any agglomeration and detrimental effect on the porosity of the laser scribed lignin-graphene. Further, the addition of ~~high performance~~ Mn_3O_4 NPs grown for 3 hours increased the specific surface area of the lignin-graphene by 66%, which improved the microsupercapacitor's areal capacitance by five times to 136.19 $mFcm^{-2}$ at 0.08 $mAcm^{-2}$ measured in PAAS/K_2SO_4 gel electrolyte. The resulting highly stable and pliable microsupercapacitor retained 93.4 of its initial capacitances over 5000 charge-discharge cycles at 0.5 $mAcm^{-2}$ and 97% over 400 bending cycles at 50 mVs^{-1}, respectively. The direct synthesis of Mn_3O_4 on IDE-patterned lignin-derived LSG electrodes presents new possibilities in energy storage applications.

Keywords: Oil palm lignin, laser scribed graphene, Mn_3O_4, Flexible Microsupercapacitors

1.0 Introduction

Supercapacitors are electrochemical energy storage devices~~,~~ consisting of conducting plates and electrolytic solutions~~,~~ with extraordinarily long ~~-~~life cycles, high energy and power densities ~~at~~ across a wide range of operating temperatures [1]. They can be classified into three categories based on their energy storage mechanism. Electric double-layer capacitors (EDLC) contain carbon-based materials (activated carbon, graphene, carbon nanotubes) at both terminals. Similar to an electrolytic capacitor, EDLC stores energy electrostatically at the electrode-electrolyte interface. It has a higher power density [2] but limited energy density~~,~~ because the electrostatic charges are only retained at the surface of the carbon-based electrode [3]. The surface area and porosity of the electrode directly determine~~s~~ the energy density of the EDLC supercapacitor [4]. In contrast, the charge storage mechanism of a pseudocapacitor or faradaic capacitor, which has electrodes based on pseudocapacitive materials, is through intercalation or redox reactions [5]. During charging, the electrolyte ions tunnel into the electrode material without causing an expansion of the crystal structure. During discharge, the ions are released from the electrode surface, releasing energy [5]. On the other hand, redox supercapacitors store and discharge charges through the electrode-electrolyte interface at the electrode surface without ion penetration [5]. Hybrid supercapacitors, made of carbon-based electrodes doped with pseudocapacitive materials, exploit the fast charge kinetics of EDLC and the enhanced energy density of pseudocapacitors [6].

The use of porous graphene infused with mixed valency metal oxide as a supercapacitor material has received much attention. Graphene is a one-atom-thick carbon atom arranged in a hexagonal lattice. Pristine single-layer graphene was first ~~synthesised~~ synthesized by Andre Geim and Konstantin Noveselov through mechanical exfoliation of graphite [7]. However, this method of graphene synthesis is tedious. Instead, the reduction of graphene oxide to reduced graphene oxide (rGO)~~, can be considered as it~~ is a more cost-efficient, simple and feasible method, especially for energy storage and sensing applications [8], [9]. The combined effect of rGO's high surface area and outstanding electrical characteristics makes it an ideal material ~~in~~ for ~~the construction~~ constructing ~~of~~ supercapacitor electrodes [10]. Thermal, chemical, and electrochemical reduction methods are commonly used to reduce a carbon precursor into multilayered ~~functionalised~~ functionalized graphene [8], [9]. For device integration, laser-scribed carbon precursors have emerged as a new avenue of rGO synthesis~~,~~ due to their simplicity compared to chemical and electrochemical reduction [11].

For carbon precursors, ~~Polymers~~ polymers are often used ~~as carbon precursors due to their~~as it has excellent thermal stability and mechanical properties [12]. For laser scribed graphene's (LSG), ~~Synthetic~~ synthetic polymers such as polyimide offer more control over the properties of the starting material and allow a greater degree of performance tuning ~~of the laser scribed graphene's (LSG) performance~~ [13], [14]. Recently, biopolymers have been used in the synthesis of LSG [15]–[17]. Compared to synthetic polymers, biopolymers are renewable and sustainable. ~~Besides that, biopolymers~~They may also contain certain functional groups that enhance the reduction process of the material and result in a higher quality LSG [18].

Lignin, one of the most abundant biopolymers, is a heavily researched biopolymer in ~~the synthesis of~~synthesising graphene. The complex structure of lignin, consisting of benzyl and phenolic hydroxyl groups, could be converted into a quinone group to significantly boost the capacitive performance of graphene ~~significantly~~. [19]. The chemical properties of lignin can vary depending on the source of the lignin [20], with multiple sources of lignin, e.g., pulpwood, kraft, and wood used in the synthesis of graphene [21]–[23]. Among these, EFB oil palm lignin is one of the potential materials.

In terms of ~~Pseudocapacitive~~ pseudocapacitive materials, they can be classified into three categories, i.e., metal-based compounds (metal oxides, sulfides, nitrides, chalcogenide, hydrides, and many more), conducting polymers, and metal-organic framework (MOFs). Metal compounds undergo faradaic redox reactions or ion intercalation. Conducting polymers exhibit pseudocapacitive behaviour due to the movement of electrons at the polymer backbone owing to the addition of electrons. Metal frameworks have organic linkers and metal centers that enable redox reactions at their interface [24], [25]~~.~~. Mixed valency metal oxide are usually directly infused on graphene electrodes. In particular, nanostructured manganese oxides such as Mn_3O_4 with various valance states have been explored widely in the synthesis of energy storage materials, due to their low cost, environmentally friendliness, high abundance, large potential window, and high specific capacitance [26], [27]. ~~Mn_3O_4~~ It is one of the most stable oxides and possesses a standard spinel structure in which Mn^{2+} cations occupy the tetrahedral positions~~,~~ and Mn^{3+} cations occupy the octahedral positions. Mixed valency of manganese element can aid the pseudocapacitive behaviour of the material [28], [29]. It has the potential for high theoretical capacity and cycle stability in neutral solution ~~D~~due to ~~Mn_3O_4's~~ the reversible conversion between distinct redox states~~, it has the potential for high theoretical capacity and cycle stability in neutral solution~~ [3]. However, the poor electrical conductivity (10^{-7} – 10^{-8} S cm^{-1}) of Mn_3O_4 further limits its potential to be an electrode material in energy

storage applications [29], [30]~~. This~~ which could be effectively resolved by including more channels for electrolyte diffusion ~~by~~ using highly conductive porous carbon material, notably LSG [31]. ~~As of now~~Currently, the most common technique for coupling LSG with Mn_3O_4 for microsupercapacitors application is in-situ laser scribing. Nevertheless, the areal capacitance is very low (< 75 $mFcm^{-2}$) ~~from what is expected~~ from a commercial standpoint [32]–[34].

In our previous work, laser parameters were ~~optimised~~ optimized to produce high-quality oil palm lignin derived laser scribed graphene for a microsupercapacitor [35]. However, the supercapacitor performance declined over several cycles ~~as a result of~~due to graphene detachment, which reduced the electrode's total surface area [36]. A possible solution is the use of manganese oxides to increase the surface area, while restricting self-agglomeration [37]. This work reports the facile ~~synthesise~~ synthesize of a hybrid supercapacitor from oil palm lignin derived laser scribed graphene (L-LSG) and nano-octahedral shaped Mn_3O_4 nanoparticles (Mn_3O_4 NPs) through a hydrothermal process for microsupercapacitor application. The microsupercapacitor ~~is~~ was constructed in-plane with interdigitated electrodes using a one-step laser lithography process on a lignin-polyimide precursor. Further, ~~the~~ Mn_3O_4 was ~~synthesised~~ synthesized via one-step sol-gel hydrothermal growth using manganese acetate as the seed solution and manganese nitrate as the growth solution. This fabrication approach enables Mn_3O_4 to grow directly onto the in-plane ~~functionalised~~ functionalized LSG supercapacitor electrodes for improved adhesion while maintaining its ideal octahedral structure. To our knowledge, the direct synthesis of Mn_3O_4 NPs on a~~n~~ lignin based LSG electrode ~~comprised of lignin~~ has never been reported.

2.0 Methodology

2.1 Materials

The ~~Lignin~~ lignin was extracted from EFB ~~Oil~~ oil ~~Palm~~ palm [38], the ~~0.127 mm~~ polyimide film was purchased from Avantis Laboratory Supply, Manganese (II) Acetate Tetrahydrate ($Mn(C_2H_3O_2)_2.4H_2O$), Hexamethylenetetramine, HMT ($C_6H_{16}N_2$), and Manganese (II) Nitrate Tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) were purchased from Sigma-Aldrich, and Ethanol (C_2H_5OH) and Monoethanolamine, MEA (C_2H_7NO) were purchased from R&M chemicals.

2.2 Fabrication of L-LSG electrode

The ~~Lignin~~ lignin solution (20 % V/V) was drop-coated and spread evenly on the~~a~~ polyimide sheet using the doctor's blade technique. The lignin coated substrate was then dried at 50 °C for an hour inside an oven. The cured substrate was subjected to CO_2 laser engraving system (V-460, Universal Laser System) with 21 W laser power and 300 mm/s speed. The ~~decarbonised~~ decarbonized layer of lignin was removed using a water bath. The lignin derived laser scribed graphene (L-LSG) electrode was dried at 50 °C for an hour.

2.3 Preparation of L-LSG/Mn_3O_4

The procedure was ~~acquired and~~ modified ~~from~~based on previous studies [39]. ~~First, a~~A seed sol-gel of 0.2 M $Mn(C_2H_3O_2)_2.4H_2O$ was prepared using 50 ml of ethanol. The solution was heated and stirred for 30 minutes at 60 °C and 800 rpm. MEA at a 1:1 concentration ratio was gradually dropped into the Manganese Oxide (MnO) seed solution. The pitch-dark brown solution was aged for one day before the second phase of the experiment. The MnO seed solution was spin coated at 3000 rpm for 20 s onto the L-LSG microsupercapacitor fabricated earlier. The coated L-LSG IDE was dried at 60 °C for 20 minutes, followed by 150 °C for 10 minutes. After allowing the sample to cool, the ~~experiment~~ process was repeated three times to ensure the MnO seed solution completely covered the sample. An equal concentration of HMT and $Mn(NO_3)_2 \cdot 4H_2O$ at 0.025M were prepared in distilled water as the hydrothermal growth medium for Mn_3O_4 NPs. The ~~finalised~~ finalized L-LSG IDE sample was subjected to a hydrothermal growth of Mn_3O_4 NPs at 93 °C for varying~~ied~~ hours. The sample was placed in the growth solution upside down for 2, 3 and 5 hours using a Teflon sample holder. The samples were carefully removed and left to dry at room temperature. Finally, the samples were labelled as L-LSG/Mn_3O_4-2, L-LSG/Mn_3O_4-3, and L-LSG/Mn_3O_4-5 corresponding to 2, 3 and 5 hours of exposure.

2.4 Assembly of L-LSG/Mn_3O_4 microsupercapacitors

Microsupercapacitors consisting of 6 pairs of microelectrodes with an active area of 0.5 cm^2 were drawn on Corel DRAW software before laser scribing. After connecting ~~them~~ these to current collectors, the hydrothermally treated L-LSG/Mn_3O_4 IDE microsupercapacitor was coated with PAAS/K_2SO_4 gel electrolyte. The sample was left to dry for 4 hours (current collectors only) before conducting the electrochemical test with the ~~given~~ electrolyte.

2.4 Material ~~characterisation~~ characterization

The surface morphology and microstructure of the ~~material~~ electrode ~~were~~was examined using Field Emission Scanning Electron Microscopy, FESEM (TESCAN CLARA, UHR SEM), and Transmission Electron Microscopy, TEM (Hitachi, HT7830). PANalytical X'Pert3 Powder was used to obtain the X-ray diffraction and XRD patterns of the ~~material~~ electrode at 0.02 °/step and 2 s/step. The Raman Spectrometer (Horiba, HR800) with a laser excitation of 514 nm provided the Raman Spectra of the tested material. The Tristar 3020 Plus was used to evaluate the specific surface area (SSA) and pore diameter distribution of the electrode based on the Brunauer-Emmett-Teller (BET) technique and the Barrett Joyner Halenda (BJH) model ~~were applied by Tristar 3020 Plus to evaluate the specific surface area (SSA) and pore diameter distribution of the material~~. The ~~material's~~ electrode's elemental composition was ~~studied~~ analyzed using X-ray photoelectron spectroscopy, XPS spectra using Thermo Scientific K-X-ray Alpha's photoelectron spectroscopy. Fourier-transform infrared spectroscopy (FTIR) readings were ~~collected~~ taken to identify the functional groups present in the material (Perkin Elmer Spectrum One).

2.5 Electrochemical ~~characterisation~~ characterization

A 2-electrode system (Metrohm, Autolab) consisting of a pair of working electrodes was ~~utilised~~ used ~~in this study~~ to evaluate Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD) and Electrochemical impedance spectroscopy with a voltage potential of -0.4 V to 0.4 V for all the CV and GCD curves. The CV curves were evaluated at a scan rate of 10 to 200 mVs^{-1} and a current density of 0.08 to 1.0 $mAcm^{-2}$ for GCD curves. The EIS spectra were measured from ~~at a frequency of~~ 10 mHz to 100 kHz. The areal capacitance, energy density, and power density were~~as~~ calculated based on measurements from CV and GCD curves using equations in the supplementary material.

3.0 Results and Discussion

3.1 Fabrication techniques and materials ~~characterisations~~ characterizations

Fig. 1 illustrates the sol-gel hydrothermal growth of Mn_3O_4 NPs on laser-scribed lignin graphene at different stages of the synthesis process. ~~Initially, t~~The lignin solution was drop-coated onto a polyimide sheet and lithographed via an optimized laser beam~~.~~ ~~Once~~ once the lignin layer dried~~, it was lithographed via an optimised laser beam~~. A three-layer MnO seed solution ~~spin coating~~ was applied on L-LSG via spin coating. The L-LSG was then inverted

and heated to 93 °C for 2, 3, and 5 hours to promote hydrothermal development, resulting in evenly coated manganese composites with ~~diverse~~ various forms and quantities. The ~~finalised~~ finalized interdigitated electrodes were assembled into a complete microsupercapacitor.

Fig. 2a-d shows Field Emission Scanning Electron Microscopy (FESEM) images of Mn_3O_4 NPs formed over 3 and 5 hours. The forest-like fibrous structure of L-LSG (Fig. S1, S2) formed under the evaporation of gases (H_2O and CO_2) has been partially covered by Mn_3O_4 NPs, ~~developed~~ resulting in L-LSG/Mn_3O_4-3, as illustrated in Fig. 2a, b [40]. However, the Mn_3O_4 NPs produced in L-LSG/Mn_3O_4-5 have agglomerated and ~~coated~~ densely coated the~~on~~ L-LSG, as seen in Fig. 2c, d. ~~Furthermore, the~~ The magnified images of L-LSG/Mn_3O_4-3 in Fig. S3, S4 reveal the 3D structure of produced Mn_3O_4 NPs with an ~~shape similar to~~ octahedron shape, consistent with ~~reported in the~~ previous studies [41]–[44]. The L-LSG/Mn_3O_4-2 in Fig. S5, S6 indicate the early stage formation of the Mn_3O_4 nanorods ~~at early stages~~ and their subsequent transition into a nano octahedron crystalline structure~~ in contrast with earlier images~~. It is evident that the newly established sol-gel hydrothermal process at a constant temperature over an increasing reaction time ~~utilises~~ utilizes the "Ostwald ripening" mechanism of nanorod dissolution and nano octahedron ~~recrystallisation~~ recrystallization ~~at a constant temperature over an increasing reaction time~~ [41], [45]. The elemental mapping (EDS) pictures of L-LSG/Mn_3O_4-3 ~~shown~~ in Figs. 2e-i show~~s~~ the uniform dispersion of Manganese and Oxygen elements (Mn_3O_4) on top of the carbon element (L-LSG). The addition of evenly coated highly conductive Mn_3O_4 NPs enhances the surface area of the graphene and considerably improves the flow of electrons through crosslinked pathways within the framework [46].

To further ~~analyse~~ analyze the morphological structure of hausmannite Mn_3O_4 NPs produced, Transmission Electron Microscopy (TEM) images were taken, as shown in Fig. 3a-f. TEM photos provide sharper imaging for a better understanding of the ~~interaction~~ correlation between Mn_3O_4 NPs aggregation and the porosity of the L-LSG material. Although the Mn_3O_4 NPs' size or shape remained unchanged as the hydrothermal treatment period was extended from 3 to 5 hours, L-LSG/Mn_3O_4-3 (Fig. 3a, b) has a far more visible meso and micropore than L-LSG/Mn_3O_4-5 (Fig. 3d, e) due to the lower quantity of Mn_3O_4 NPs ~~the~~ at lower ~~the~~ reactive time. The detrimental effect of the absence of porosity in the material could be readily seen in more detailed electrochemical studies~~,~~ since variation in porosity plays an essential part in electrolyte ion diffusivity for optimal electrochemical performance [47]. Both Mn_3O_4 NPs decorated on L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 have a cubic-like shape (Inset in Fig. 3c, f)) and have been reported to be similar or smaller in size compared to those from earlier

investigations, ranging from 15 to 30 nm [41]–[44]. The presence of Mn_3O_4 NPs ~~additionally~~ prevented L-LSG from stacking, increasing the surface area accessible to ions (Fig. S7) [48]. The lattice fringes of L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 are 0.49 nm, corresponding to the (101) plane of Mn_3O_4 nano-octahedron (Fig. 3c, f) [48]. As a result of the ~~previously mentioned~~ "Ostwald ripening" process, it is possible to achieve the ~~crystallisation~~ crystallization of Mn_3O_4 nano-octahedrons through the dispersion of Mn_3O_4 nanorods (L-LSG/Mn_3O_4-2), as depicted in Fig. S8, S9 [41], [45].

The specific surface areas of L-LSG and L-LSG/Mn_3O_4-3 have been determined using nitrogen (N_2) adsorption-desorption isotherms (Fig. 4a). L-LSG has macro porous hysteresis type III loop, ~~in accordance with~~ based on IUPAC classification. In contrast, L-LSG/Mn_3O_4-3 ~~had~~ has a typical type IV form with a type H4 hysteresis loop, suggesting the presence of mesopores ~~presence~~ in the form of a narrow slit [3], [49]. The narrow, steep rise in the loop that appeared at a relatively low pressure ~~suggests the presence of micropores, which~~ would facilitate a more rapid capillary evaporation process compared to the capillary condensation of nitrogen [50], [51]. The Brunauer-Emmett-Teller (BET) specific surface area of L-LSG has ~~been~~ doubled from 37.13 m^2g^{-1} to 61.67 m^2g^{-1} following the addition of Mn_3O_4 NPs. According to the Barrett Joyner Halenda (BJH) model, the L-LSG/Mn_3O_4-3 pore size distribution curve in Fig. 4b reveals an additional pore diameter peak at 15.9 nm on top of other micropores and mesopores at less than 4 nm. Mesoporous Mn_3O_4 octahedrons and microporous fibrous L-LSG in L-LSG/Mn_3O_4-3 with a total pore volume of 0.159 cm^3g^{-1} provide low resistance, wider ion paths, and the availability of an ion-buffering zone for rapid ion facilitation [3], [50]. The complete porous combinations found in L-LSG/Mn_3O_4-3 indicate enhanced supercapacitor properties of L-LSG.

Fig. 4c reveals the X-ray diffraction (XRD) patterns of pristine L-LSG, L-LSG/Mn_3O_4-3, and LSG/Mn_3O_4-5 powder. The presence of (002) crystal plane at 25.9° indicates the existence of graphene sheets in L-LSG and its composites [42]. The diffraction peaks at 18.08°, 28.89°, 31.05°, 32.48°, 36.14°, 38.18°, 44.56°, 50.89°, 53.80°, 56.10°, 58.55°, 59.95°, and 64.71°, which ~~are assigned~~corresponds to the (101), (112), (200), (103), (211), (004), (220), (105), (312), (303), (321), (224) and (400) planes~~,~~ respectively [42], [52], [53] ~~is~~ are indicative of the highly crystalline structure of the hausmannite Mn_3O_4 nano-octahedron in L-LSG/Mn_3O_4-3, and LSG/Mn_3O_4-5. Most notably, the newly formed nano octahedral Mn_3O_4 NPs' XRD patterns ~~is~~ are consistent with JCPDS Card No. 24-0734 and previous literature [42], [45]. ~~Both~~ L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 demonstrate sharper, wider, and lower intensity peaks,

~~which~~ reflecting strong crystallinity and relatively smaller particle sizes [31], [54]. The absence of additional characteristic peaks at L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 indicates the high purity of Mn_3O_4 nano-octahedron formed in this study [26], [55].

The Fourier-transform infrared spectroscopy (FTIR) spectra of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 in the 4000-400 cm^{-1} zone are shown in Fig. 4d. The FTIR spectra of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 materials show the chemical properties and key functional groups of the material. All the fabricated compounds have peaks at 3405-3445, 1714, 1628, and 1084 cm^{-1}, which may be attributed to O-H vibration and deformation bands [52], stretching vibration of C=O at carbonyl/carboxyl groups [54], aromatic rings of C=C [52] and C-O in C-OH/C-O-C functional moieties [54], respectively. The vibration of the Mn-O stretching modes of the tetrahedral and octahedral sites of newly formed L-LSG composites are denoted by the extra peaks detected at 611 and 503 cm^{-1} [52], [54]. Additionally, an absorption peak of 1383 cm^{-1} for L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 ~~at imply~~implies increased moisture (O-H) and carbonate ions in the atmosphere with Mn atoms [50], [56]. The L-LSG/Mn_3O_4-5 composite film is abundant in nano-octahedrons of Mn_3O_4 NPs, as evidenced by the difference in band strength of Mn-O stretching between L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5, denoting a rise in the number of Mn functional groups due to the difference in hydrothermal exposure [50], [52].

Raman spectroscopy ~~is~~ was used to ~~analyse~~ analyze the variation of graphene-based material structure encompassing disorder and defect frameworks [47]. The Raman spectra of L-LSG, L-LSG/Mn_3O_4-3, and L-LSG/Mn_3O_4-5 in Fig. 4e show two prominent peaks of D (breath of the sp^2 -rings/ K-point phonons of A_{1g} symmetry) and G (bond stretching motion of C sp^2/ E_{2g} phonons) at ~1348 and ~1580 cm^{-1} respectively [47]. The D and G peak intensities (I_D/I_G) ratios were evaluated to identify the degree of disorder and crystalline size of graphitic material. The I_D/I_G value of L-LSG/Mn_3O_4-3 (0.74) and L-LSG/Mn_3O_4-5 (0.77) is relatively higher than L-LSG (0.611) in Fig. 4f due to the ~~development of~~ presence of unrepaired surfaces following the further reduction of graphene and the inclusion of Mn_3O_4 NPs to the graphene material during the hydrothermal process [1], [57], [58]. In addition, the new major peak at 644 cm^{-1} corresponds to the stretching A_{1g} mode of Mn^{2+} ions at the tetrahedral site in manganese oxide [26]. These spectrum findings show that the ~~synthesised~~ synthesized composites were produced via sol-gel hydrothermal method combining L-LSG and Mn_3O_4.

The chemical compositions of the L-LSG composites were further ~~studied~~ analyzed using XPS analysis. Fig. 5a depicts the survey spectra of L-LSG/Mn_3O_4-3, which include three significant peaks: C 1s, O 1s, and Mn 2p. The functional groups C-C, C-O, C=O, and O-C=O ~~may be~~correspond ~~attributed~~ to the deconvoluted C 1s peaks at 284.43, 285.49, 286.67, and 288.2 eV, respectively (Fig. 5b) [59]. The graphene structure has been successfully preserved after the hydrothermal treatment, based on the C-C peak's high intensity [4]. A spin energy gap of 11.8 eV distinguishes the two primary peaks of Mn 2p, Mn $2p_{3/2}$, and Mn $2p_{1/2}$ [4] (Fig. 5c). A further validation of manganese's oxidation state as Mn_3O_4 can be confirmed by the binding energy of 5.5 eV found in the Mn 3s spectrum [30], [31] (Fig. S10). ~~According to~~Based on Fig. 5d, the Mn-O-Mn, Mn-O-H, and H-O-H fitting curves for the O 1s peaks at 529.86 eV, 531.06 eV, and 532.51 eV, respectively, ~~and can be assigned~~corresponding to anhydrous oxide, hydroxide, and residual water [4], [26]. Similar XPS findings for C 1s, O 1s, Mn 2p, and Mn 3s ~~is~~ are apparent for L-LSG/Mn_3O_4-5 in Fig. S11, S12.

3.2 Electrochemical performance of L-LSG/Mn_3O_4 microsupercapacitors

The CV, GCD, and Nyquist plots were ~~examined~~ used to ~~analyse~~ analyze the electrochemical performance of the L-LSG and L-LSG/Mn_3O_4 electrodes with the microsupercapacitor fully assembled. The CV and GCD ~~characterisation~~ characterizations were ~~carried out~~performed at -0.4V to 0.4V to achieve the best electrochemical performance. Fig. 6a ~~displays~~ shows the CV curves of the L-LSG, L-LSG/Mn_3O_4-3, and L-LSG/Mn_3O_4-5 electrodes at a scan rate of 50 mVs^{-1} in a K_2SO_4 gel electrolyte. The characteristic of the hybrid capacitor developed by combining the double-layer capacitance of LSG and pseudocapacitance of Mn_3O_4 NPs and lignin hydroquinone groups were observed in all samples as a quasi-rectangular CV peak with evident weak redox peaks [32], [60], [61]. Mn_3O_4 ~~utilises~~ utilizes proton-electron energy storage mechanism, where the pseudocapacitance reaction of oxymanganese species at various redox state, $MnO_x(OH)_y$ and $K_\delta MnO_x(OH)_y$ ~~can be deduced~~is ~~as follows~~ [31], [37], [62]:~~.~~

$$MnO_x(OH)_y + \delta K^+ + \delta e^- \leftrightarrow K_\delta MnO_x(OH)_y \quad (1)$$

~~In the meantime,~~ L-LSG ~~continues to~~ store charges electrostatically on its surface and serves as an electron conductive network for Mn_3O_4 NPs [31]. The areal capacitance ~~of the tested materials~~ corresponds to the integral area of CV. L-LSG/Mn_3O_4-3 had the highest integral area ~~and~~ with an areal capacitance of 5.06 $mFcm^{-2}$ at a scan rate of 50 mVs^{-1}, followed by L-LSG/Mn_3O_4-5 and L-LSG with areal capacitances of 4.39 and 3.15 $mFcm^{-2}$, respectively. A similar trend in the areal capacitance of the fabricated composites could be observed at scan

rates (mVs^{-1}) of 10, 20, 100, and 200 in Fig. S13. The exceptional capacitance behaviour of L-LSG/Mn_3O_4-3 is apparent by the uniformity in the shape of its CV curves at various scan rates, as shown in Fig. 6b [1], [48]. Based on Fig. 6c, at lower scan rates (10–20 mVs^{-1}), L-LSG/Mn_3O_4-3 and other samples had substantially greater areal capacitance, ~~as a result of~~due to ion intercalation at more gradual rates [46]. At a 10 mVs^{-1} scan rate, L-LSG/Mn_3O_4-3 had the highest areal capacitance of 16.5 $mFcm^{-2}$.

The electrochemical performance of the L-LSG, L-LSG/Mn_3O_4-3, and L-LSG/Mn_3O_4-5 electrodes based on galvanostatic charge-discharge (GCD) measurements performed at 0.1 $mAcm^{-2}$ are shown in Fig. 6d. All the GCD peaks suggested an asymmetric profile and high columbic efficiency that was impaired by the pseudocapacitive Mn_3O_4 NPs and lignin hydroquinone [37], [60], [61]. The charge-discharge duration correlates with a material's capacitance. L-LSG/Mn_3O_4-3 achieved the longest charge discharge cycle among all the samples with an areal capacitance of 134.91 $mFcm^{-2}$, which is consistent with the findings from Cyclic Voltammetry. The areal capacitances ($mFcm^{-2}$) of L-LSG and L-LSG/Mn_3O_4 nanocomposites at 0.1 $mAcm^{-2}$ in increasing order are: L-LSG (27.7), L-LSG/Mn_3O_4-3 (95.23) and L-LSG/Mn_3O_4-5 (134.91). L-LSG/Mn_3O_4-3's areal capacitance is more than 5-fold greater than L-LSG's~~,~~ due to the evenly distributed high surface area nano-octahedrons of Mn_3O_4 NPs on the surface of L-LSG, mixed valency of Mn_3O_4 metal oxide and additional conductive pathways provided by the porous L-LSG to Mn_3O_4 nano-octahedrons for the electron and ion transmission [28], [41]. Additionally, Mn_3O_4 inhibits graphene from restacking, ~~resulting in an increased~~increasing surface area [63]. A further increase in Mn_3O_4 NPs in L-LSG/Mn_3O_4-5 reduced the areal capacitance~~,~~ due to the composite's overall ~~drop~~ decrease in graphene content [1], [31]. L-LSG/Mn_3O_4-3's GCD curves showed minimal variation in shape under a range of current densities (Fig. 6e). All ~~of~~ the specimens ~~studied~~ considered had ~~an~~ increased ~~in~~ areal capacitance at lower current densities due to higher electrode-electrolyte interaction at the maximum time interval [37]. L-LSG/Mn_3O_4-3 had maximum areal capacitance ($mFcm^{-2}$) of 136.19, 91.74, 65.79, 44.12, 33.76, and 23.04 at current densities ($mAcm^{-2}$) of 0.08, 0.2, 0.4, 0.6, 0.8, and 1.0 respectively, compared to all the nanocomposites in Fig. 6f.

Fig. 6g shows the L-LSG, L-LSG/Mn_3O_4-3, and L-LSG/Mn_3O_4-5 Nyquist plots generated from high to low frequency. Warburg resistance (Rw) is the long tail at low frequency, which reflects ion mobility in a material. ~~Meanwhile, i~~In the high frequency zone, the initial intersection point and diameter of a small semi-circle are known as the Equivalent Series Resistance (ESR) and the Charge Transfer Resistance (Rct)~~,~~ respectively [27], [59]. L-LSG ~~obtained~~ had the lowest

Rct value, indicating low resistance at the charge accumulation site between active material and electrolyte, despite a minor shift in ESR from 60.1 to 74 after being ~~transformed~~ converted into L-LSG/Mn_3O_4-3 (Fig. 6h). The steeper and shorter tail of L-LSG/Mn_3O_4-3, close to 45° articulates~~,~~ reduced Warburg resistance due to the inclusion of EDLC L-LSG with a sufficient amount of pseudocapacitive Mn_3O_4 NPs to boost the overall conductivity of the material [28]. Fig. 6i shows the cycle stability of the L-LSG/Mn_3O_4-3 electrode for 5,000 cycles at a current density of 0.5 $mAcm^{-2}$. The curve starts with a slight increase in capacitance retention due to the "electro-activation" process, which promotes slow penetration of electrolyte during charge and discharge cycles ~~to~~ and further access to the fibrous surface of graphene [64], [65]. Despite a steady decline, L-LSG/Mn_3O_4-3 was able to retain 93.4% of its capacitance, as Mn_3O_4 nano-octahedrons served as a buffer for the volume expansion in L-LSG electrode, ~~where it mitigates~~ mitigating the fall off phenomenon of electrode material reported in previous studies [28], [35]. The newly developed method increases the capacitance retention of L-LSG/Mn_3O_4-3, owing to Mn_3O_4 NPs' long-lasting solid adhesion to the L-LSG surface.

The XRD, XPS and FESEM investigations were performed to examine the phase development and structural integrity of the L-LSG/Mn_3O_4-3 electrode after 5,000 cycles. The FESEM images in Fig. S14, 15 ~~display~~ show Mn_3O_4 agglomeration on the surface of L-LSG caused by constant OH^- insertion throughout an extended charge-discharge process [66]. ~~The~~ This agglomeration ~~described above~~ may be one of the primary factors affecting L-LSG/Mn_3O_4-3's performance ~~in the course of~~over time. ~~Furthermore, t~~The XPS survey spectra ~~depicted~~ in Fig. S16 ~~demonstrate~~ indicate the existence of supplementary impurities, namely sulfur (S), potassium (K), silver (Ag), and sodium (Na), at energy levels of ~168, ~294, ~368, and ~1071 eV respectively. These ~~observation of~~ additional elements and the gradual increase in the intensity of the O 1s peak can be attributed to the use~~utilization~~ of PAAS/K_2SO_4 and silver paste during the assembly process of the supercapacitor. High-resolution spectra of Mn 2p and Mn 3s indicate that the L-LSG surface continues to hold a similar manganese phase (Fig. S17, 18). ~~In the meantime, the f~~Four noticeable peaks at 38.28° (111), 44.45° (200), 64.63° (220), and 77.48° (311) in the XRD patterns further ~~demonstrate~~ confirm the existence of silver within L-LSG/Mn_3O_4-3 (Fig. S19) [67]. The presence of crystalline peaks of the Mn_3O_4 after a long cyclic activity ~~naturally~~ suggests that the L-LSG/Mn_3O_4-3 electrode has a very long lifespan. ~~It is significant to understand that the utilisation of a~~The neutral electrolyte~~, as supported by prior research [35],~~ has ~~effectively~~ mitigated the onset of corrosion in the sample [35]~~. This is~~ evident from the absence of ~~any~~ additional elements ~~observed~~ in the XPS and XRD readings.

~~To further demonstrate the flexibility and stability of L-LSG/Mn_3O_4-3, bending~~ Bending tests were performed to determine the flexibility and stability of L-LSG/Mn_3O_4-3, as shown in Fig. 7a. After 400 cycles of bending, L-LSG/Mn_3O_4-3 exhibited exceptional mechanical stability with slight variation in the CV curves (measured at 50 mVs^{-1}) while retaining 97% of its initial value. ~~A series/parallel integrated system has been developed with laser scribing~~, as microsupercapacitors struggle to achieve high operating voltage and capacitance for practical applications, a series/parallel integrated system has been developed. ~~Both t~~The charge-discharge duration in GCD curves recorded at 0.5 $mAcm^{-2}$ and the CV area measured at 50 mVs^{-1} improved by a factor of two and three in parallel-arranged microsupercapacitors (Fig.7 b, c). As illustrated in Fig. 7d and 7e, series-connected microsupercapacitors have enhanced the working voltage to power up light-emitting diodes (LEDs). The newly developed L-LSG/Mn_3O_4-3 microsupercapacitor can attain a remarkable maximum energy and power density of 0.0106 $mWhcm^{-2}$ and 0.266 $mWcm^{-2}$~~,~~ by exploiting uniformly distributed high pseudocapacitive nano-octahedrons of Mn_3O_4 NPs on the surface of L-LSG. Fig. 7f compares the electrochemical performance of the L-LSG/Mn_3O_4-3 microsupercapacitor to other previously reported microsupercapacitors. Crucially, compared to other microsupercapacitors fabricated from an identical approach, which include OPL-LSG 7030 [35], sLIG-O/S14 [68], LSG/MnO [33], LWG-ONS 1.5 [69], S-LrGO/S-MnO-Mn_3O_4 [32] and LIG/MnOx [34], L-LSG/Mn_3O_4-3 has greater or comparable energy density. However, Ppy@FeOOH//Mn_3O_4 [70], ZIHMSC [71], CNTs@MnO2 //MXene/BC@PPy [72] and MnO_2/LIG [73] outperformed L-LSG/Mn_3O_4-3 electrochemically owing to the integration of conductive polymers and the us~~c~~~~age~~ of an alternative manganese oxide group (Table S1).

4.0 Conclusion

In summary, an ~~high performance~~ octahedral shaped Mn_3O_4 NPs grown on oil palm lignin derived laser scribed graphene was developed for high performance microsupercapacitor applications. Laser scribed lignin-graphene electrode with Mn_3O_4 NPs reached maximal performance ~~with laser scribed lignin graphene electrode~~ at 3 hours reaction time following a robust one-step sol-gel hydrothermal growth through dissolution and ~~recrystallisation~~ recrystallization via "Ostwald ripening". The evenly coated and high surface area nano-octahedral Mn_3O_4 NPs retained the lignin graphene's porosity and delivered a high areal capacitance and energy density of 136.19 $mFcm^{-2}$ and 0.0106 $mWhcm^{-2}$ respectively, at 0.08 mAcm-2. In addition, the microsupercapacitor exhibited an extended life cycle (93.4% @ 5000 cycles) and excellent mechanical flexibility (97% @ 400 bending cycles). The enhanced

charge-discharge period and operating voltage of the microsupercapacitor through parallel and series connections further increase~~s~~ the efficiency and capabilities of interconnected energy storage systems. ~~This study revealed that o~~Oil palm lignin derived laser scribed graphene decorated with Mn_3O_4 NPs is a durable electrode material for a flexible, high performance microsupercapacitor with a simple and affordable manufacturing technique.

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Figure Legends

Fig. 1 Fabrication of L-LSG/Mn_3O_4 microsupercapacitors

Fig. 2 (a-b) FESEM images of L-LSG/Mn_3O_4-3. (c-d) FESEM images of L-LSG/Mn_3O_4-5. (e-i) Elemental mapping images of L-LSG/Mn_3O_4-3

Fig. 3 (a-b) Low magnification and (c) High magnification TEM images of L-LSG/Mn_3O_4-3; inset shows overlay of imaginary cubic shapes. (d-e) Low magnification and (f) High magnification TEM images of L-LSG/Mn_3O_4-5; inset shows overlay of imaginary cubic shapes.

Fig. 4 (a) N_2 adsorption-desorption isotherms and (b) Pore size distribution of L-LSG and L-LSG/Mn_3O_4-3. (c) XRD patterns, (d) FTIR (e) Raman spectra and (f) I_D/I_G ratio of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5.

Fig. 5 (a) XPS survey spectrum, (b) High resolution C 1s, (c) High resolution Mn 2p and (d) High resolution O 1s of L-LSG/Mn_3O_4-3.

Fig. 6 (a) CV curves of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 at 50 mVs^{-1}. (b) CV curves of L-LSG/Mn_3O_4-3 at various scan rates from 10 to 200 mVs^{-1}. (c) Corelation of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 capacitance at different scan rates. (d) GCD curves of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 at 0.1 $mAcm^{-2}$. (e) GCD curves of L-LSG/Mn_3O_4-3 at various current densities from 0.08 to 1.0 $mAcm^{-2}$. (f) Dependence of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5 capacitance at different current densities. (g) Low and (h) high frequency nyquist plots region of L-LSG, L-LSG/Mn_3O_4-3 and L-LSG/Mn_3O_4-5. (i) Cyclic performance of L-LSG/Mn_3O_4-3.

Fig. 7 (a) Bending performance of L-LSG/Mn_3O_4-3; inset shows CV curves for 400 bending cycles. (b) CV and (c) GCD curves of L-LSG/Mn_3O_4-3 microsupercapacitor arranged in parallel. (d) CV and (e) GCD curves of L-LSG/Mn_3O_4-3 microsupercapacitor arranged in series; inset shows LED powered by L-LSG/Mn_3O_4-3 microsupercapacitor. (f) Ragone plot of L-LSG/Mn_3O_4-3 compared with other reported microsupercapacitor devices.