International Journal of Nanoelectronics and Materials
Volume 15 (Special Issue) December 2022 [213-219]

Oil Palm Lignin Derived Laser Scribed Graphene for Supercapacitor Application

Sathaniswarman Remesh[1,2], Mugashini Vasudevan[1,2], Veeradasan Perumal[1,2,*], Subash C.B. Gopinath[3], Saravanan Karuppanan[2], Pandian Bothi Raja[4], and Mohamad Nasir Mohamad Ibrahim[4]

[1]Centre of Innovative Nanostructures and Nanodevices (COINN), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia
[2]Department of Mechanical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia
[3]Institute of Nano Electronic Engineering, Kangar 01000 & School of Bioprocess Engineering, Arau 02600, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
[4]School of Chemical Sciences, Universiti Sains Malaysia, 11800 Gelugor, Penang, Malaysia

ABSTRACT

Finding a promising material as an alternative resource to replace the consumption of fossil fuels is necessary as the depletion of fossil fuels is increasing annually. A novel approach was explored to produce graphene from natural renewable resources. In this work, a laser scribing technique was conducted to produce large-scale graphene from Empty Fruit Bunches (EFB) of oil palm lignin biopolymer by varying the laser power. The morphology, structure, and electrical conductivity of scribed graphene were investigated at different laser power. Herein, a porous form-like structure with multilayered graphene was obtained at a laser power of 75%. The crystallite size (La) of laser power 75% was 28.4nm which shows a higher degree of graphitization was formed as laser power rises. Furthermore, the resistance was lesser at 75% laser power compared to 50% laser power concluding that 75% laser power has better electrical conductivity than low laser power. Hence, lignin-based laser scribed graphene (LSG) can be a promising and sustainable green substrate material to be utilized in supercapacitor applications.

Keywords: Graphene, laser scribing, lignin, supercapacitor

1. INTRODUCTION

Graphene has been a remarkable material since 2004 when the noble prize was awarded to Geim and Novoselov for identifying graphene just using pencil led and adhesive tape [1]. Graphene induces physiochemical performance in almost all research sectors, especially in the energy sector. Honeycomb morphological structure in a single layer thickness atom of graphene leads to excellent electron mobility and electrical conductivity. Furthermore, a wide surface area with an abundant edge plane site of graphene enhances the electrochemical activity and electrolyte diffusion for supercapacitor application [2], [3].

Chemical vapor deposition (CVD), mechanical exfoliation, and chemical exfoliation are the usual methods used to synthesize graphene. However, these methods have drawbacks in terms of high temperature used complex procedures, time-consuming, and small-scale graphene production. Therefore, a simple laser scribing method was introduced to synthesize graphene. Generally, laser scribing is a direct one-step method in converting polyimide (PI) film into graphene through pulsed ultraviolet laser scribing treatment with parameters such as power and speed involved. Researchers utilize the laser scribing method because it's capable of producing conductive graphene in a short time at a low temperature with excellent productivity and reproducibility.

* veeradasan.perumal@utp.edu.my

The formation of graphene from polyimide (PI) film has opened a new promising platform for discovering graphene [4], [5]. However, this technique has certain limitations in terms of being non-environmentally friendly, preoccupying large resources, and forming large polyimide waste after its service life. So, an alternative environmentally friendly substrate is needed to replace polyimide film. Biomass material is the best candidate to be used as a substrate as it is an abundant renewable resource on earth, low in cost, biodegradable, and environmentally friendly. In precise, natural lignin has remarkable characteristics such as high thermal stability, high carbon content, biodegradability, excellent physical and chemical properties, favorable stiffness, and attractive green polymer material for energy storage applications [6].

In this work, oil palm lignin-derived graphene was fabricated by varying the laser power using CO2 laser system. The morphological, optical, and electrical properties were also studied for further use in green supercapacitor technology.

2. MATERIAL AND METHODS

2.1 Preparation of Lignin Solution

Lignin solution was prepared by adding 10 grams of lignin powder obtained from EFB oil palm little by little into 50 ml distilled water in a beaker. Then, the mixed solution was stirred at 500 rpm on a hot plate using a magnetic stirrer until a homogenous lignin solution was formed. This diluted lignin solution contains 20% lignin and must be kept in a controlled atmosphere to inhibit lignin deterioration.

2.2 Preparation of Lignin Platform for Laser Scribing

The drop coating method was used to prepare the lignin platform. Firstly, several laboratory glass substrates with a dimension of 100 mm by 178 mm were prepared. Then, the glasses were cleaned with an ethanol solution to avoid contamination before dropping lignin on the glass surface. Lignin solution was dripped until the entire glass was covered, and the glass was dried at 50 ^{0}C for 30 minutes to guarantee the layer was appropriate for the next coating. This coating process was repeated up to 5 layers of lignin film were produced.

2.3 Laser-Scribed Graphene (LSG) Synthesis

The prepared lignin platform then proceeded to the laser process. CO2 laser cartridge with a max power of 30W induces the conversion of lignin into a black product considered graphene. The parameters of the laser scribing process are laser speed, laser power, and pulse per inch (PPI). Therefore, in this experiment laser speed and pulse per inch were fixed to 50% and 500%, respectively. Variations of laser power were fixed at 50% and 75% to determine the quality of the black product formed [7], [8]. The powers below 50% and above 75% were ignored as they failed to convert lignin into graphene and damaged the glass substrate.

2.4 Characterization

Field Emission Scanning Electron Microscopy (VP-FESEM) (Carl Zeiss SUPRA55 VP, Gemini), Raman spectroscopy (514nm laser) (HORIBA Jobin Yvon HR800) and electrochemistry impedance spectra (Metrohm Multi Autolab M204 Potentiostat/Galvanostat) were carried out to determine the morphological, optical and conductivity of the fabricated laser scribed materials.

3. RESULTS AND DISCUSSION

3.1 Field Emission Scanning Electron Microscopy (FESEM)

Figure 1 provides FESEM images of graphene after the laser scribing process at a laser speed of 50% (Figure 1(a) and Figure 1(c)) and 75% (Figure 1(b) and Figure 1(d)) with fixed laser speed at 50% and PPI at 500% at different magnification. Both laser-scribed graphene has porous and foam-like structures at different power similar to past studies [5], [9]. The foam-like appearance is caused by the release of gas during the laser scribing process, which weakens chemical bonds and recombines sublimed atoms into gaseous products that escape via the pores [5], [9]. Therefore, when the power has increased the pores of graphene are greater. The pores diameter in Fig.1c was in the range of 32nm to 950 nm whereas in Figure 1(d) was 65nm to 1500nm. Laser-scribed graphene becomes highly porous as power increases due to carburizing process. The sp3 carbon atom in the lignin molecule was converted to a sp2 carbon atom at an instant heat produced by the laser machine [4], [7]. The oxygen was mainly removed from lignin to form reduced graphene oxide with a 3D structure during the carbonization process. The large porous surface area of laser scribed graphene induces the electrochemical performance by faster diffusion of ion to electrode from electrolyte and mass transportation [9],[10]. Hence, the porous-like structure formed by laser scribing, the graphene will be beneficial for the development of potential supercapacitor and biosensor applications [11],[12].

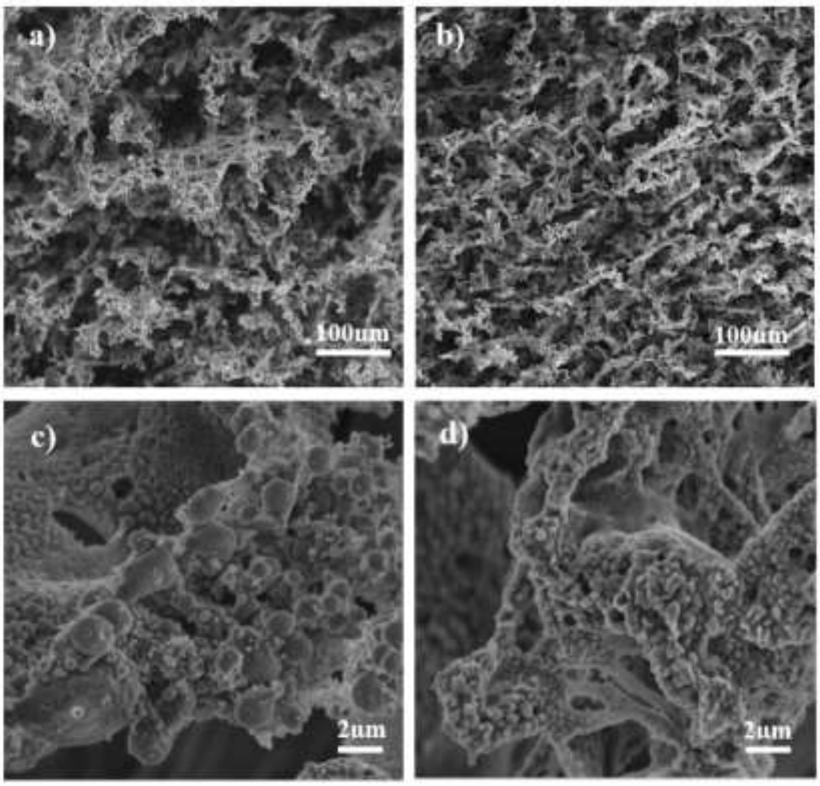

Figure 1. FESEM images of LSG at the power of (a, c) 50% and (b, d) 75%.

3.2 Raman Spectroscopy

Figure 2 shows Raman spectroscopy of LSG at laser power 50% and 75%. Both spectra displayed the three major bands which are the D band, G band, and 2D band. The LSG at 50% power revealed a D, G and 2D band at 1340 cm-1, 1575 cm-1, and 2675 cm-1. However, the LSG at 75% power has a D band at 1360 cm-1, a G band at 1573 cm-1, and a broad 2D band from 2300 cm-1 to 2700 cm-1. The D band is due to out-of-plane vibrations attributed to the presence of structural defects, edge effects and dangling sp2 carbon bonds that break the symmetry while the G band shows the presents of in-plane vibration of sp2 bonded carbon atoms like graphene. The 2D band is referred to the stacking order of graphene layers. Additionally, it can be seen that laser power influences band intensity due to the increased graphitization degree caused by heat ablation [7],[13]. The Raman results of both spectra were shown in Table 1. The ID / IG ratio of laser power of 50% is higher than the ID / IG ratio of laser power of 75% indicating that the crystallinity of graphitic is better at 50%. Furthermore, both laser powers synthesized multi-layered graphene as the I2D / IG ratio is less than 1 meanwhile the crystallite size (La) of 75% power is greater than 50% power. Most importantly, the crystalline size of current findings is comparable to and better than previous studies carried out with other types of lignin [2], [9].

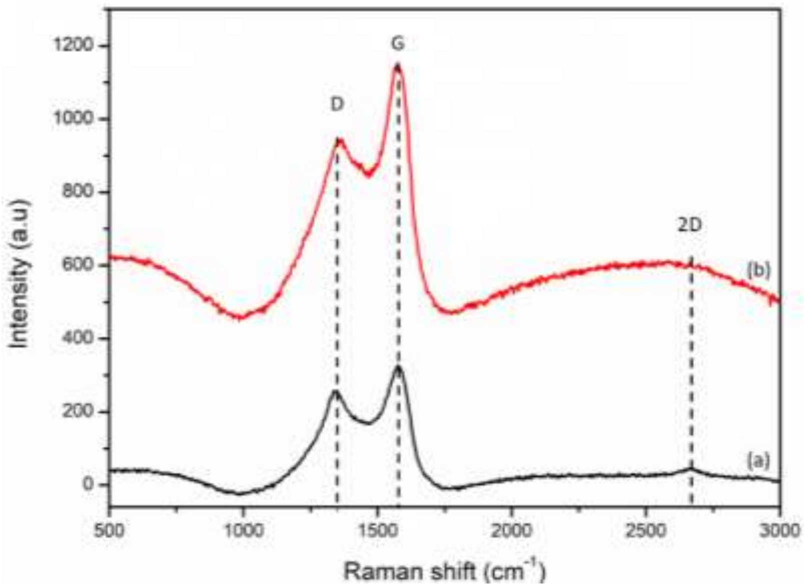

Figure 2. Raman spectrum of LSG at the power of (a) 50% and (b) 75%.

Table 1 Raman Spectroscopy result of LSG by different power

Power (%)	I_D / I_G	I_{2D} / I_G	La (nm)
50	0.8	0.15	24.3
75	0.7	0.16	28.4

3.3 Electrochemical Impedance Spectroscopy (EIS)

The electrical conductivity of the fabricated LSG was identified through EIS analysis as shown in Figure 3. The laser-scribed graphene was deposited on Screen-Printed Electrode (SPE) to determine whether the LSG material affects the performance of the commercially developed electrode. The intercept on the Z' axis and semicircle diameter of the EIS curves in the high frequency area region represent the equivalent series resistance (ESR) and charge transfer resistance (Rct) of a material indicating the sum of the electrode's natural resistance and the electrolyte's ionic resistance [14], [15]. The semicircle of 75% laser power graphene is smaller than 50% laser power graphene with a difference of 400 Ohm shows the lower resistivity of 75% laser power graphene. Ultimately, 75% laser power graphene has a superior electrical conductivity compared to the 50% laser power graphene due to excellent interfacial properties, crystallinity, and morphology. The FESEM results of 75% laser power graphene containing numerous micropores and micropores are the clear evidence for the enhancement of electron transfer efficiency between laser scribed graphene and carbon filled SPE surface [2]. The experiment was repeated on 5 different SPE electrodes as shown in Figure 4.

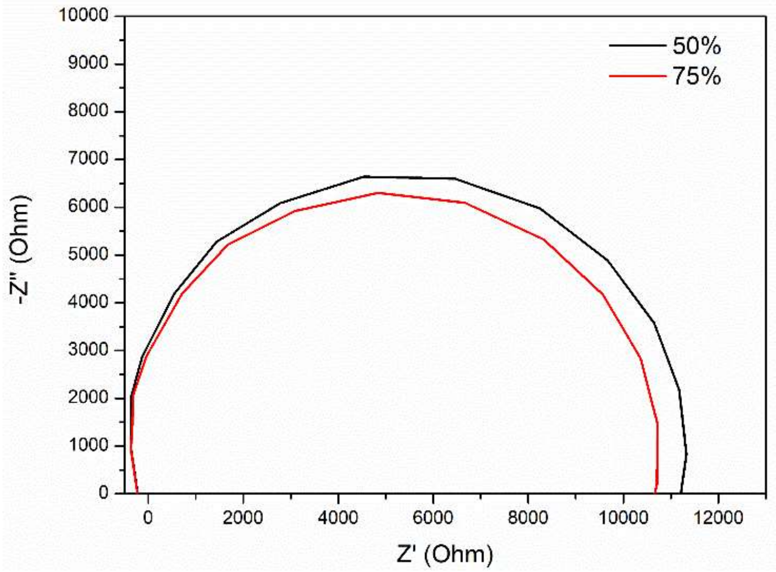

Figure 3. Electrochemical Impedance Spectroscopy of LSG at the power of 50% and 75%.

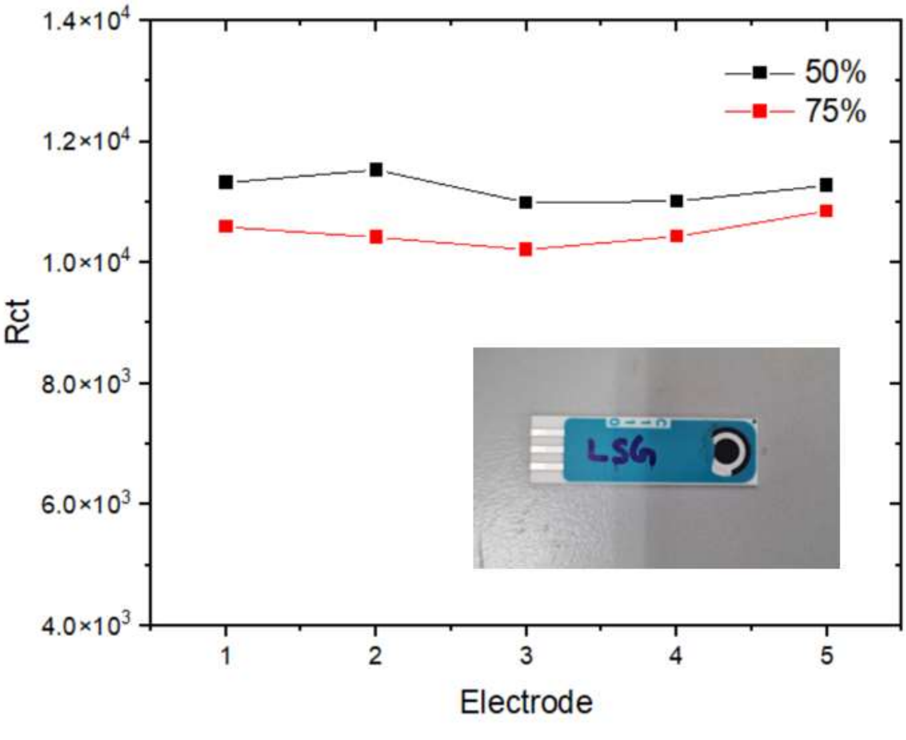

Figure 4. Repeatability of the EIS reading using five different SPE electrodes. The inset image represents the picture of Screen-Printed Carbon Electrode (SPCE).

4. CONCLUSION

In short, optimizing the parameters of laser scribed machines according to the number of layers and thickness of each layer was the biggest challenge to obtain valuable graphene. It was found that through laser scribing foam-like structure graphene was able to obtain which will effectively enhance the surface area for faster ion diffusion from the electrolyte to the electrode. Furthermore, it also provides an opportunity to bind nanomaterials on LSG for an enhanced supercapacitor with high energy and power density. Raman spectroscopy proves that lignin can be converted into graphene when heat treatment was applied and act as an alternative renewable resource of graphene. Furthermore, laser power affects the quality of graphene, therefore optimizing the laser power is much required for supercapacitor application.

ACKNOWLEDGEMENTS

The corresponding authors thank the Minister of Higher Education Malaysia for supporting the research with Fundamental Research Grant Scheme (FRGS) REF CODE FRGS/1/2020/TKO/UTP/03/7 and Universiti Teknologi PETRONAS.

REFERENCES

[1] K. S. Novoselov, Electric Field Effect in Atomically Thin Carbon Films, Science, Vol. 306, no. 5696 (2004) pp. 666–669.

[2] W. Zhang, Y. Lei, F. Ming, Q. Jiang, P.M.F.J. Costa, and H.N. Alshareef, Lignin Laser Lithography: A Direct-Write Method for Fabricating 3D Graphene Electrodes for Microsupercapacitors, Advanced Energy Materials, vol 8, no. 27 (2018).

[3] M.R. Bobinger et al., Flexible and robust laser-induced graphene heaters photothermally scribed on bare polyimide substrates, Carbon, vol. 144 (2019) pp. 116–126.

[4] Z. Wan, N.T. Nguyen, Y. Gao, and Q. Li, Laser induced graphene for biosensors, Sustainable Materials and Technologies, vol 25 (2020).

[5] Y. Lei, A. H. Alshareef, W. Zhao, and S. Inal, Laser-Scribed Graphene Electrodes Derived from Lignin for Biochemical Sensing, ACS Applied Nano Materials, vol. 3, no. 2 (2020) pp. 1166–1174.

[6] J. Zhu, C. Yan, X. Zhang, C. Yang, M. Jiang, and X. Zhang, A sustainable platform of lignin: From bioresources to materials and their applications in rechargeable batteries and supercapacitors, Progress in Energy and Combustion Science, vol. 76 (2020). pp. 100788.

[7] M.J.Y. Tai et al., Laser-scribed graphene nanofiber decorated with oil palm lignin capped silver nanoparticles: a green biosensor, Scientific Reports, vol. 11, no. 1 (2021) pp. 1–9.

[8] I. G. Subramani, V. Perumal, S.C. Gopinath, N.M. Mohamed, M. Ovinis, and L.L. Sze, 1,1'-carbonyldiimidazole-copper nanoflower enhanced collapsible laser scribed graphene engraved microgap capacitive aptasensor for the detection of milk allergen, Scientific Reports, vol. 11, no. 1 (2021).

[9] F. Mahmood, F. Mahmood, H. Zhang, J. Lin, and C. Wan, Laser-Induced Graphene Derived from Kraft Lignin for Flexible Supercapacitors, ACS Omega, vol. 5, no. 24 (2020) pp. 14611–14618.

[10] N. Tasić et al., Insights into electrochemical behavior in laser-scribed electrochemical paper-based analytical devices, Electrochemistry Communications, vol. 121 (2020).

[11] V. Perumal and U. Hashim, Advances in biosensors: Principle, architecture and applications, Journal of Applied Biomedicine, vol. 12, no. 1 (2014) pp. 1–15.

[12] F. Mahmood, C. Zhang, Y. Xie, D. Stalla, J. Lin, and C. Wan, Transforming lignin into porous graphene via direct laser writing for solid-state supercapacitors, RSC Advances, vol. 9, no. 39 (2019) pp. 22713–22720.

[13] K. Singh, S. Kumar, K. Agarwal, K. Soni, V. Ramana Gedela, and K. Ghosh, Three-dimensional Graphene with MoS 2 Nanohybrid as Potential Energy Storage/Transfer Device, Scientific Reports, vol. 7, no. 1 (2017) pp. 1–12.

[14] S. Wang, Y. Yu, S. Luo, X. Cheng, G. Feng, Y. Zhang, Z. Wu, G. Compagnini, J. Pooran, and A. Hu, All-solid-state supercapacitors from natural lignin-based composite film by laser direct writing, Applied Physics Letters, vol. 115, no. 8 (2019) p. 083904.

[15] X. Sun, X. Liu, and F. Li, Sulfur-doped laser-induced graphene derived from polyethersulfone and lignin hybrid for all-solid-state supercapacitor, Applied Surface Science, vol. 551 (2021) p. 149438.