



SYNTHESIS OF GRAPHENE FROM ELECTROCHEMICAL EXFOLIATION OF GRAPHITE UNDER DIFFERENT ORGANIC SOLVENTS

G.D.R. Lakhari^{1,2}, D.P. Dissanayake² and N.P.W. Rathuwadu^{1*}

¹*Institute for Combinatorial Advanced Research and Education,
General Sir John Kotelawala Defence University, Sri Lanka*

²*Faculty of Science, University of Colombo, Sri Lanka*

Researchers are studying the further enhancement of properties of natural graphite. It has led to the development of advanced carbon materials such as graphene. Graphene is utilized in batteries, supercapacitors, and corrosion inhibitors due to its superior characteristics. There are numerous ways to synthesize graphene. The electrochemical exfoliation technique has received significant attention due to its controllable, user-friendly, cost-effective nature compared to existing widely used methods. However, the major drawback of this method is the restacking of exfoliated graphene layers due to the van der Waals forces. One of the most effective strategies for effective exfoliation is to use a compatible solvent that prevents restacking. In this study, organic solvents of DMF, methanol, and chloroform were selected and investigated based on dispersion force and dipolar interaction to determine the best solvent for graphite exfoliation. Different solvent systems were prepared using a water-to-organic solvent ratio of 3:1. The synthesized graphene was characterized structurally through Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and ultraviolet-visible (UV-vis) spectroscopy. FTIR and XRD data confirmed the successful synthesis of graphene by the C=C stretching vibration peak at $\sim 1630\text{ cm}^{-1}$ and the diffraction peak at $\sim 26.50^\circ$ respectively. UV-vis data showed the characteristic peak for graphene at the range of 266-276 nm and confirmed high dispersibility in graphene-DMF, while graphene-methanol was lower. The electrochemical characterization of materials was carried out using cyclic voltammetry (CV) in a three-electrode configuration, where the synthesized graphene material immobilized on FTO was used as the working electrode in a 1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution with 0.1 M Na_2SO_4 as the electrolyte. According to the CV data, the electrode prepared using graphene-DMF showed the highest redox current and the working potential window ($50\ \mu\text{A}$, 2.6 V) compared to the blank ($6\ \mu\text{A}$, 1.8 V). The electrode prepared using graphene-chloroform showed the weakest redox behavior. However, it showed considerable capacitive behavior ($0.712\ \text{F/g}$ for 10 mV/s) compared to others. These findings demonstrated that DMF is the best solvent for graphite exfoliation among investigated solvents due to both dispersion force and dipolar interaction. This method can be successfully developed to synthesize high-quality graphene cost-effectively.

Keywords: graphite, graphene, electrochemical exfoliation, solvents

*Corresponding Author: rathuwadunpw@kdu.ac.lk



SYNTHESIS OF GRAPHENE FROM ELECTROCHEMICAL EXFOLIATION OF GRAPHITE UNDER DIFFERENT ORGANIC SOLVENTS

G.D.R. Lakhari^{1,2}, D.P. Dissanayake² and N.P.W. Rathuwadu^{1*}

¹*Institute for Combinatorial Advanced Research and Education,*

General Sir John Kotelawala Defence University, Sri Lanka

²*Faculty of Science, University of Colombo, Sri Lanka*

INTRODUCTION

Graphite is an abundantly found mineral in Sri Lanka. Researchers are studying further enhancement of properties of natural graphite. It has led to the development of advanced carbon materials such as graphene. Graphene is utilized in batteries, supercapacitors, solar cells, sensors, and corrosion inhibitors due to its superior characteristics. There are numerous ways to synthesize graphene. The electrochemical exfoliation technique has received significant attention due to its controllable, user-friendly, cost-effective nature compared to existing widely used methods. However, the major drawback of this method is the restacking of exfoliated graphene layers due to the van der Waals forces. One of the most effective strategies for effective exfoliation is to use a compatible solvent that prevents restacking. The main objective of this research is to optimize the electrolyte/solvent system to minimize the synthesized graphene layer restacking. In this study, water to organic solvent in the ratio of 3:1 was used and organic solvents of DMF, methanol, and chloroform were selected and investigated based on dispersion force and dipolar interaction to determine the best solvent for graphite exfoliation.

METHODOLOGY

Material

Natural graphite was obtained from the Bogala mine. Analytical-grade chemicals (NH₄)₂SO₄ (99.5%, VWR chemicals, Belgium), Na₂SO₄ (99%, Sigma Aldrich, India), K₃[Fe(CN)₆] (98%, Alpha Chemika, India), Conc. H₂SO₄ (96%, Sigma Aldrich, India), N,N-Dimethylformamide (DMF) (100%, VWR chemicals, France), Methanol (CH₃OH) (100%, VWR chemicals, France), Chloroform (CHCl₃) (99.99%, Sigma Aldrich, India) Polyvinyl alcohol (PVA) (98%, BP 26, Taiwan) and carbon black (85%, Sasol, Singapore) were used without further purification.

Synthesis of graphene by electrochemical exfoliation of graphite

Natural graphite and a stainless-steel rod were used as the working electrode and the counter electrode, respectively. The electrolyte was 0.1 M (NH₄)₂SO₄ / 1 M H₂SO₄. The electrochemical exfoliation of graphite was carried out in different solvent systems. The solvent systems selected for this study are 3:1 water/methanol, 3:1 water/DMF, and 3:1 water/chloroform. The electrochemical exfoliation process for various solvents was performed by applying 10 V. Synthesized graphene was filtered and washed with deionized water. Then the filtered black powder was kept in the oven to dry. Synthesized graphene material was used for structural characterization by Fourier transform infrared (FT-IR) spectroscopy, Ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), and electrochemical characterization by cyclic voltammetry (CV).

Modified electrode preparation for electrochemical characterization

For the slurry preparation, synthesized graphene, carbon black, and polyvinyl alcohol (PVA) were used in the weight ratio of 80:10:10. These materials were mixed with the respective solvent (deionized water, 3:1 water/methanol, 3:1 water/DMF, and 3:1 water/chloroform) that is used for the synthesis of the active material. The mixtures were stirred using a vortex mixer to achieve a homogenous mixture (slurry). Then they were coated on a Fluorine doped tin oxide (FTO) surface with a coating area of 1 × 1 cm². The prepared electrodes were dried in the oven. Weight was measured before and after the coating was applied. The electrochemical characteristics of the



electrode materials were examined using a three-electrode cell in 1.0 mM $K_3[Fe(CN)_6]$ in 0.1 M Na_2SO_4 electrolyte solution. The Ag/ AgCl electrode was used as the reference electrode, the platinum electrode served as the counter electrode, and the modified electrode served as the working electrode in this cell. CV was carried out at various scan rates (10 mV/s, 25 mV/s, 50 mV/s, and 100 mV/s).

RESULTS AND DISCUSSION

Structural characterization

XRD data analysis - **Error! Reference source not found.** shows the XRD patterns for graphite and synthetic graphene in various solvents. The graphite showed a distinct diffraction peak at 26.50° that corresponded to the graphite's crystal planes. A broad diffraction peak was visible in graphene exfoliated using chloroform, methanol, DMF, and distilled water at 27.24° , 26.64° , 26.62° , and 26.72° respectively. This peak corresponded to the graphene. In the exfoliation process, the peak width broadened as the crystallinity of the graphite decreased. (Abdelkader et al., 2015)

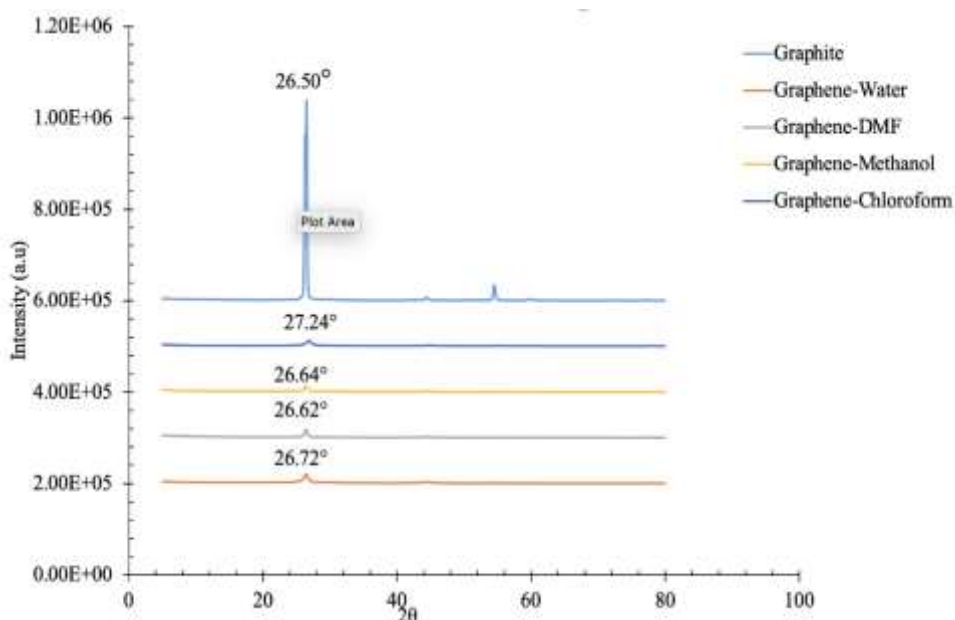


Figure 1: XRD patterns for graphite and graphene exfoliated in various solvents

FT-IR data analysis - The synthesis of graphene from graphite in various solvents is depicted in the FTIR spectra (Figure 2). All the graphene samples that have been exfoliated in various solvent systems exhibit a peak at $\sim 1630\text{ cm}^{-1}$ which is assigned for the C=C stretching vibration of graphene. Graphene exfoliated in DMF, methanol, and, chloroform shows the C-O-C stretching vibration at $1030\text{-}1050\text{ cm}^{-1}$ and the O-H stretching vibration at $3500\text{-}3200\text{ cm}^{-1}$. Therefore the peaks suggested the presence of graphene and graphene oxide as well. (Alkhouzaam et al., 2020)

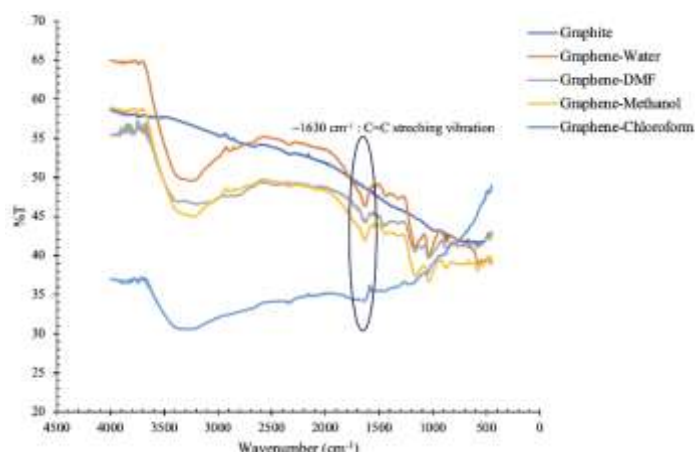


Figure 2: FTIR spectra for graphite and graphene exfoliated in various solvents

UV-vis data analysis- UV-vis spectroscopy data was used to analyze the dispersibility of graphene in different solvents. Figure 3 shows UV-vis spectroscopy data of the 1st, 15th, and 30th day. In DMF solvent, the peak wavelength of 274 nm did not change over time. However, the sample of graphene in chloroform showed a slight change in the peak wavelength value over time, and graphene in methanol showed a significant change in the peak wavelength indicating the restacking of the graphene layers. (Kurniawan et al., 2019)

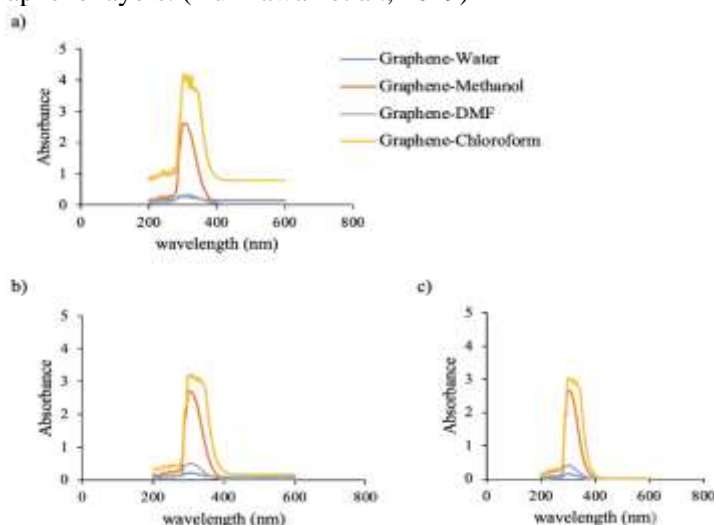


Figure 3 : UV-visible spectrum for the graphene sample in different solvents at a) day 1 b) day 15 c) day 30

Electrochemical characterization

CV data analysis - The redox behavior of ferrocyanide /ferricyanide was studied using the CV. Figure 4 shows the CV of the bare FTO electrode and the modified electrode, which was prepared using graphite and synthesized graphene in different solvents. The electrode that has been modified using graphene-DMF was shown to have the corresponding redox peak for ferrocyanide/ferricyanide compared to the electrodes that were modified using graphene-methanol and graphene-chloroform. The electrode modified by the graphene graphene-chloroform was shown with a shoulder appearance instead of a peak. The electrode prepared using graphene-DMF showed the highest redox current and the working potential window (50 μ A, 2.6 V) compared to the blank (6 μ A, 1.8 V). Therefore, graphene exfoliated using a DMF solvent has better electrochemical performance than the others.



However, electrodes modified using graphene-chloroform have shown considerable capacitive behavior (0.712 F/g for 10 mV/s) compared to others.

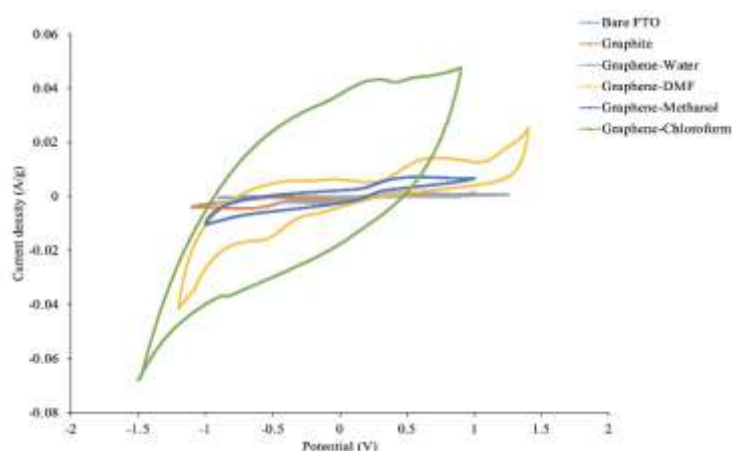


Figure 4: CV overlay for electrodes at 25 mV/s scan rate.

CONCLUSION

This study was conducted to understand the solvent effect on the electrochemical exfoliation of graphite. FTIR and XRD data confirmed the successful synthesis of graphene by electrochemical exfoliation. UV-vis data showed the characteristic peak for graphene at the range of 266-276 nm. Graphene in DMF showed high dispersibility, while graphene in methanol was lower. According to the CV data, the electrode prepared using graphene-DMF showed the highest redox current and the working potential window (50 μ A, 2.6 V) compared to the blank (6 μ A, 1.8 V). The electrode prepared using graphene in chloroform showed the weakest redox behavior. However, it showed considerable capacitive behavior (0.712 F/g for 10 mV/s) compared to others. These findings demonstrated that DMF is the best solvent for graphite exfoliation among investigated solvents due to both dispersion force and dipolar interaction. This method can be successfully developed to synthesize high-quality graphene cost-effectively.

REFERENCES

- Abdelkader, A. M., Patten, H. V., Li, Z., Chen, Y., & Kinloch, I. A. (2015). Electrochemical exfoliation of graphite in quaternary ammonium-based deep eutectic solvents: a route for the mass production of graphene. *Nanoscale*, 7(26), 11386–11392. <https://doi.org/10.1039/c5nr02840j>
- Alkhouzaam, A., Qiblawey, H., Khraisheh, M., Atieh, M., & Al-Ghouti, M. (2020). Synthesis of graphene oxide particles of high oxidation degree using a modified Hummers method. *Ceramics International*, 46(15), 23997–24007. <https://doi.org/10.1016/j.ceramint.2020.06.177>
- Kurniawan, T., Anwar, M. A., Oktiani, R., Ragadhita, R., Nandiyanto, A. B. D., & Aziz, M. (2019). Influences of solvent types on the formation of graphene in the electrochemical exfoliation method. *Materials Physics and Mechanics*, 42(1), 151–157. https://doi.org/10.18720/MPM.4212019_13

ACKNOWLEDGMENTS

This work was supported by the General Sir John Kotelawala Defence University Research grant (KDU/RG/2021/CARE/003).