SYNTHESIS OF POROUS GRAPHENE MATERIAL FOR SUPERCAPACITORS IN THE PRESENCE OF NITROGEN-BASED ADDITIVES

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Developing high-performance and environment-friendly energy storage devices has become a crucial requirement in this technologically expanding world. Supercapacitors play a key role in modern energy-storing technology and graphene is considered an ideal electrode material for such applications due to its extraordinary properties. A single layer of sp^2 hybridized C atoms arranged as a honeycomb lattice makes a graphene sheet, however, tends to aggregate because of the π-π restacking and strong van der Waals interactions. This aggregation inhibits its inherent properties, electron diffusion rate, and electrolyte penetration power. In addition, most graphene synthesis methods are sophisticated, expensive, and need toxic, oxidative chemicals. Therefore, this study aims to produce high-quality porous graphene (PG) with reduced restacking via economically and environmentally friendly novel electrochemical pathways. PG was synthesized via electrochemical exfoliation while having Ethylenediamine-N,-N'-disuccinic acid (EDDS), and iminodiacetic acid-disodium salt (IDA) as the additives to facilitate the PG synthesis. Synthesized PG was fully characterized electrochemically and structurally. UV-visible data confirmed the synthesis of graphene due to the absorbance peak near the 270 nm wavelength range. Raman spectroscopic analysis data indicating the synthesis of porous graphene. The Cyclic voltammetry data illustrated the electric double-layer capacitive behavior of synthesized PG by having the rectangular shapes within the respective potential window even at higher scan rates such as 100mV/s. The specific capacitances of PG-EDDS and PG-IDA are 13.93 Fg^{-1} and 14.72 Fg^{-1} respectively at a scan rate of 10mV/s. This improvement is 240% and 254% compared to the graphene sample. The electrochemical impedance spectroscopy and galvanostatic charge-discharge also showed the improved capacitive behavior of the PG material. These data confirm the successful synthesis of PG with improved electrochemical performances by using a greener and cost-effective pathway.

Keywords: Graphene, electrochemical exfoliation, Porous graphene, restacking, supercapacitors

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INTRODUCTION

Developing high-performance and environment-friendly energy storage devices has become a crucial requirement in this technologically expanding world. (Ahmad et al., 2023) Supercapacitors play a key role in modern energy-storing technology and graphene is considered an ideal electrode material for such applications due to its extraordinary properties. (Lu et al., 2019) A single layer of sp^2 hybridized C atoms arranged as a honeycomb lattice makes a graphene sheet, however, it tends to aggregate because of the π-π restacking and strong van der Waals interactions. (Lu et al., 2019; Zhang et al., 2019) This aggregation inhibits its inherent properties, electron diffusion rate, and electrolyte penetration power. (Zhang et al., 2019) In addition, most graphene synthesis methods are sophisticated, expensive, and need toxic, oxidative chemicals. (Ahmad et al., 2023; Li et al., 2017) Therefore, this study aims to produce high-quality porous graphene (PG) with reduced restacking via economically and environmentally friendly novel electrochemical pathways. PG was synthesized via electrochemical exfoliation while having Ethylenediamine-N, -N'-disuccinic acid (EDDS), and iminodiacetic acid-disodium salt (IDA) as the additives to facilitate the PG synthesis. Synthesized PG was fully characterized electrochemically using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD).

MATERIALS AND METHODS

Electrochemical exfoliation and electrochemical characterization were done by using the Metrohm Autolab potentiostat/Galvanostat instrument and NOVA 2.1 software. Sonication was done by using Lab Companion ultrasonic cleaner. Structural characterization was done by using the ThermoFisher Scientific UV-Visible spectrophotometer, PerkinElmer FTIR spectrophotometer, and Bruker Senterra Raman Microscope. All chemicals were purchased from Sigma Aldrich. Graphite was purchased from Bogala Graphite Lanka PLC.

1. Synthesis of graphene

Anodic electrochemical exfoliation was done by using two electrode systems to synthesize graphene. Graphite rod was taken as the working electrode (WE/anode) and stainless-steel rod was taken as the counter electrode (CE/cathode). A +10 V bias voltage was applied for the graphite exfoliation in 0.5 M Na_2SO_4 as the electrolyte. Synthesized graphene solution was sonicated. Synthesized graphene was filtered and oven-dried.

2. Synthesis of Ethylenediamine-N, N'-disuccinic acid additive PG (PG-EDDS), and iminodiacetic acid disodium salt additive PG (PG-IDA)

Anodic electrochemical exfoliation was done by using two electrode systems to synthesize graphene. Graphite rod was taken as the working electrode (WE/anode) and stainless-steel rod was taken as the counter electrode (CE/cathode). A +10 V bias voltage was applied for the graphite exfoliation in the presence of 0.025M of EDDS in 0.5 M Na_2SO_4 as the electrolyte. Synthesized graphene solution was sonicated. Synthesized PG-EDDS was filtered and oven-dried.

The same procedure was used to synthesize the PG-IDA in the presence of 0.025 M IDA.

1. Structural characterization

Synthesized PG-IDA and PG-EDDS were characterized using UV-visible spectroscopy and Raman spectroscopy. UV absorbances were taken in the range 200 nm-800 nm after 1:5 dilution. The same procedure was used to take the absorbance of graphite. Raman spectra were recorded using an Ar^+ laser beam of 532 nm.

2. Electrochemical characterization

Synthesized material, carbon black, and PVDF were taken as 80:10:10 mass ratios. The slurry was prepared in NMP by using a vortex for proper mixing. The prepared slurry was coated on 1 cm x 1 cm Al foil and dried. This was used as the working electrode.

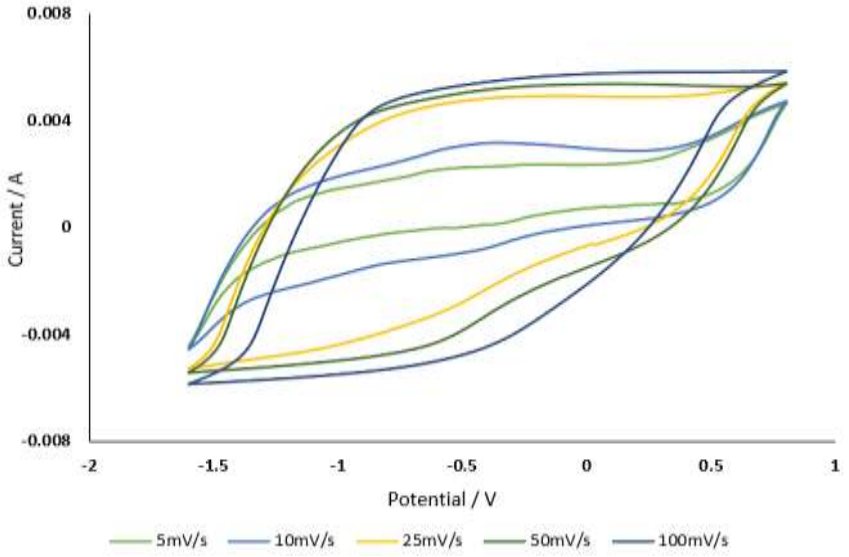
A three-electrode system with the synthesized porous graphene/graphite working electrode (WE), Pt counter electrode (CE), and Ag/AgCl reference electrode (RE) was used for the experiments. A 0.1 M potassium hydroxide solution was used as the electrolyte. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) were performed.

RESULTS AND DISCUSSION

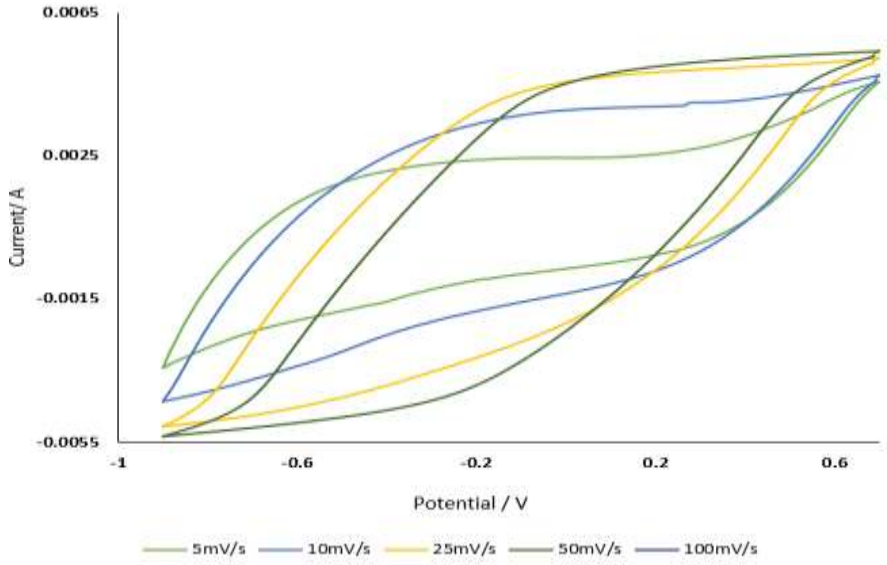
Cyclic voltammetry data illustrate the electric double-layer capacitance (EDLC) behavior of synthesized porous graphene materials by keeping the rectangular shapes within the respective potential window even at higher scan rates like 100 mV/s.

According to the CV experiments, potential windows of graphite, graphene, PG-EDDS, and PG-IDA were 1.6, 1.2, 1.6, and 2.4 respectively.

Graphite, graphene, PG-EDDS, and PG-IDA show specific capacitance values of 5.30 Fg^{-1}, 5.80 Fg^{-1}, 13.93 $Fg^{-1,}$ and 14.72 Fg^{-1} respectively at a scan rate of 10 mV/s. For PG-EDDS and PG-IDA the improvement is 240% and 254% compared to the graphene sample.



(a)



(b)

Figure 1 - CV curves at different scan rates (a) PG-EDDS (b) PG-IDA

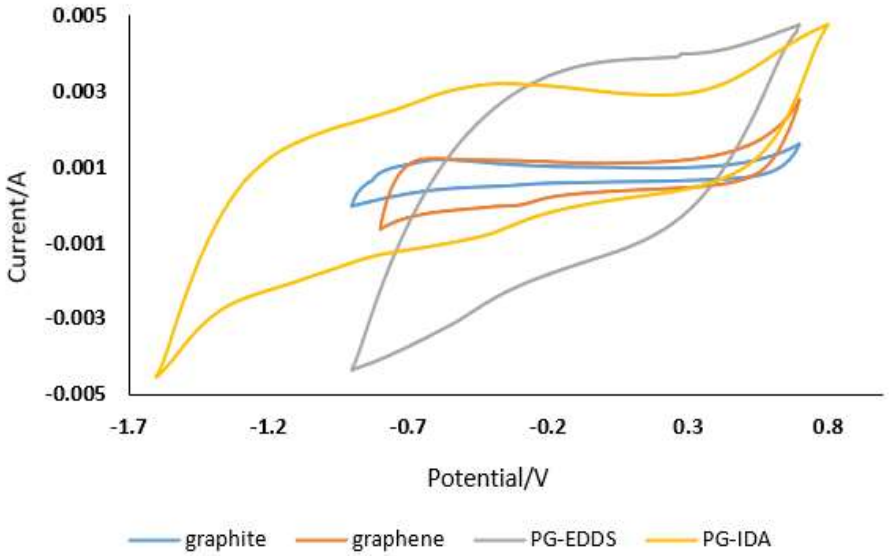


Figure 2 - CV overlay for graphite, graphene, PG-EDDS, and PG-IDA at a scan rate of 10 mV/s.

In addition, EIS and GCD also showed improved electrochemical performance for synthesized PG.

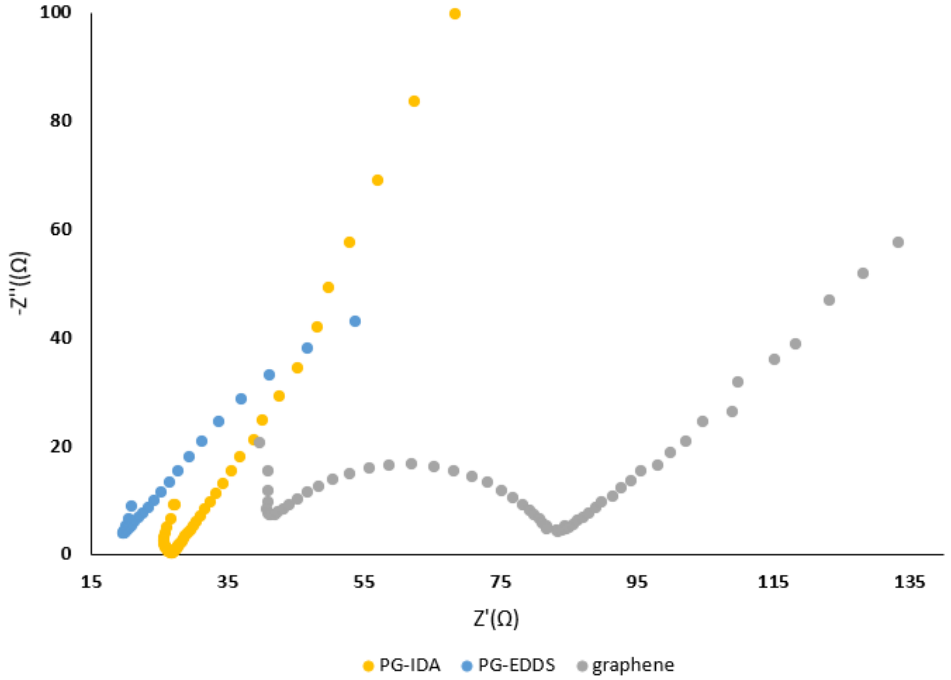


Figure 3 – EIS, Nyquist plot overlay for, PG-IDA PG-EDDS, and graphene

UV absorption peaks appeared for PG-EDDS and PG-IDA were near 272 nm and 267 nm respectively and indicate the synthesis of graphene.

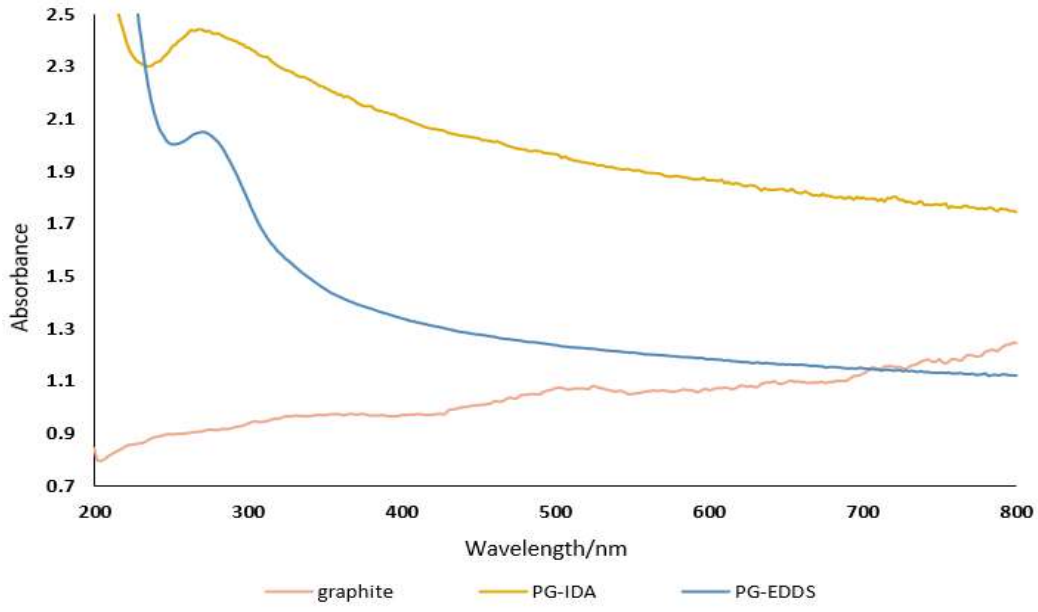


Figure 4 - UV spectrum for PG-IDA, PG-EDDS, and graphite

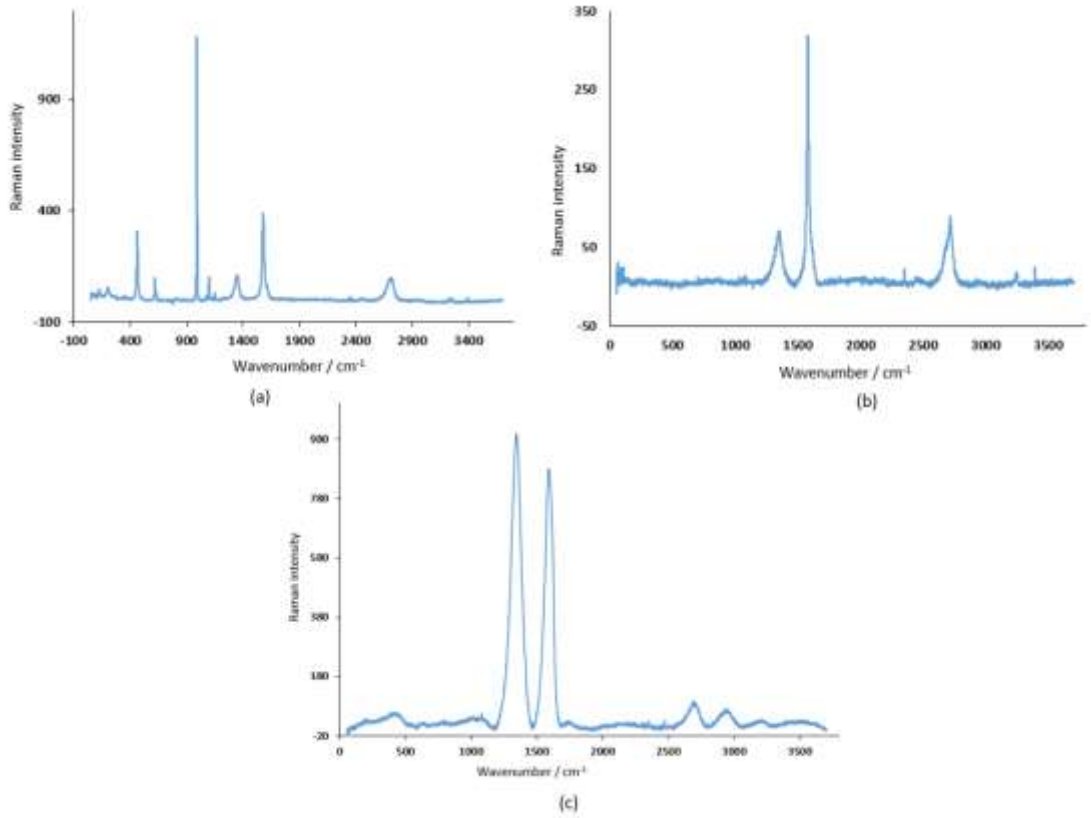


Figure 5 - Raman spectrum for (a) graphite (b) graphene (c) PG-IDA

According to the Raman analysis data, the G peak (1580 cm^{-1}) is associated with the ordered in-plane sp^2 carbon structure, and the D peak (1347.5 cm^{-1}) reveals disordered defects.

I_D/I_G = 1.14 of PG-IDA indicates the synthesis of porous graphene

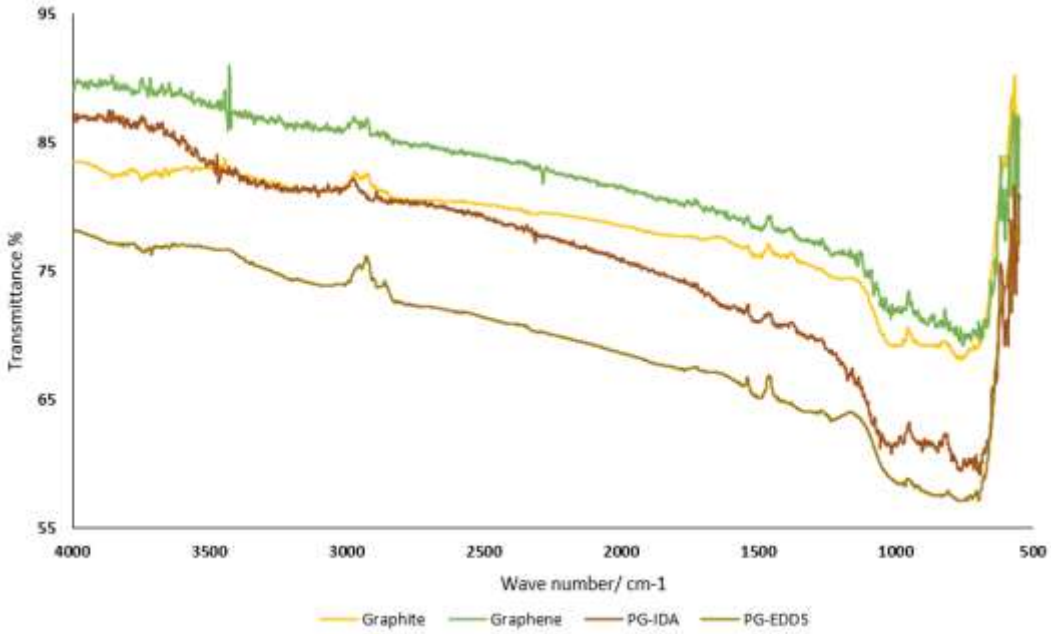


Figure 6 - FTIR spectrum overlay for the graphite, graphene, PG-IDA, and PG-EDDS

According to the FTIR analysis data, the obtained peaks for PG-IDA and PG-EDDS same as the peaks obtained from graphene and graphite.

CONCLUSIONS/RECOMMENDATIONS

A novel, green, and cost-effective method was developed for the synthesis of porous graphene with improved electrochemical performance. This novel method is based on electrochemical exfoliation in the presence of additives to facilitate PG synthesis. The specific capacitance enhancement values of PG-IDA and PG-EDDS were 254% and 240% higher than graphene. UV-Visible spectrum and Raman spectrum analysis data confirm the synthesis of PG graphene. FT-IR spectra verify that used additives only help to make defects to enhance electrochemical performance and that nitrogen atoms are not incorporated into the PG structure.

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