

# Synthesis and Aromatic Diamine Intercalation of Graphene Oxide to Tailor the Electrochemical Properties

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**ABSTRACT:** Graphene Oxide has been synthesized using Hummer's method by the oxidation of graphite powder using reagents like potassium permanganate, Sulphuric acid, hydrogen peroxide, and distilled water at low temperatures. The filtered suspension of graphene oxide was changed to a dry powder at room temperature. Synthesized Graphene oxide was further modified by functionalizing using diamine 2,6-bis(4-aminophenoxy)benzotrile (BAAP) by ultrasonication and reflux methodology, air-cooled mixture was washed with the equimolar ratio of ethanol and water which was dried at room temperature and followed by drying in the oven at 80 °C. The sample was characterized by Fourier Transform InfraRed (FT-IR) spectroscopy which confirmed all required functional groups and proved the functionalization and modification of Graphene Oxide. Further, UV-Visible spectroscopy confirmed the slight reduction of graphene oxide by the redshift which is due to the chromophoric effect of diamine. X-ray diffraction also confirmed the expected d-spacing due to the covalent reduction of graphene oxide by shifting the peak position towards higher  $2\theta$  values. The cyclic voltammetry results are in a quasi-rectangular shape, due to the pseudocapacitance behaviour of diamine functionalized graphene oxide; successfully synthesised and functionalized graphene oxide showed electrochemical stability and an increase in capacitance with an increase in scan rates which is the promising property for supercapacitance to ensure energy storage and conservation.

**KEYWORDS:** Graphene Oxide; Functionalization; Super capacitance; Hummer's Approach; Electrochemical.

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1021-9986/2023/5/1464-1471 8/\$/5.08

## INTRODUCTION

Graphene is the substance of a monoatomic layered carbon with a single atom thickness, smooth, honeycombs-like structure with tight covalent bonds. The discovery of graphene had a significant influence on science that mirrored the published papers around the world and is still carried out by researchers. We can state that the different structures of Graphene are fullerenes (0D), nanotubes (1D), and piled graphite (3D). The best way to get sheets of graphene or layers of graphene is the method of Stacking (by mechanical exfoliation method). The Manchester University, England team deserves credit for bringing about a substantial change and resolving the two-dimensional materials debate. Graphene has a hexagonal d spacing of 1.42Å, which is less than graphite's 3.37 Å and d-spacing [1]. The C-C bond, which brings the atoms to close together in graphene structure, is perhaps the most basic explanation for this, spacing and bonding indicates that graphene conduction takes place from corner to corner layers, which is why Graphene's mechanical, electrical and optical properties are outstanding. In the graphene valence band, four electrons are present in each sub-level 2s, 2P<sub>x</sub>, 2P<sub>y</sub>, and 2P<sub>z</sub>; these sub-levels overlap to establish the specific material's unique symmetry. 2s orbital overlap and sp<sup>2</sup> hybridization in graphene 2p<sub>x</sub> and 2p<sub>y</sub> by creating stable as well as localized sp<sup>2</sup> hybridization Bond sigma. These connections cause graphene's mechanical strength to increase. In the case of graphene sp<sup>2</sup> hybridization, these orbitals (2s, 2p<sub>x</sub>, 2p<sub>y</sub>) and 2p<sub>z</sub> orbital overlap are meant to hang over neighbouring atoms to form a covalent connection. The bond is primarily important for graphene's efficiency, particularly its electrical characteristics [2].

In addition, Multilayered Graphite Oxide (MGO) and graphene oxide (GO) has received much interest in disciplines like physics, chemistry, biology, and materials science in general since they are crucial building blocks for graphene material, the "wonder material" and they are easy to make. Because graphene is very inert and thermally stable, rehybridizing its -conjugated carbon structure necessitates high-energy procedures. The oxidation of graphite and subsequent exfoliation in acid to create Graphene Oxide (GO) with Oxygenated Organic Functions (OF) such as carboxyl, epoxy, hydroxyl, carboxyl, phenol, lactone, and quinine is the most prevalent approach for functionalizing graphene. This results in the creation of a substantial density of sp<sup>3</sup> hybridized carbons in the

graphene complex, which breaks the delocalized  $\pi$  electronic cloud, transforming graphene into an insulator material [3]. One of the major obstacles to efficiently capturing, storing, and using energy from different renewable energy sources is energy storage. It is also the most important constraint to the widespread adoption of hybrid electric vehicles. Supercapacitors and secondary batteries are two main devices for storing electricity. The interfacial capacitance and surface area of a supercapacitor electrode dictate its energy storage capacity. To date, increasing the surface area of graphene materials with more active sites has been the primary focus. GO produced from one of the well-known principal Hummer's method that is hydrophilic because of oxygen containing moieties that in turn disturb the aromatic graphene network result in insulating that reduce the utilization of GO [13-15]. Partial restoration of GO into graphitic structure can be done by different electrochemical and chemical reduction methods. Functionalization may be of chemical bonding, hydrogen-bonding and  $\pi$ - $\pi$  interactions with available unoxidized parts of GO. The pH conditions are evaluative likewise incompletely removed oxygen functionalities are negatively charged under high pH and induced repulsion which facilitates intercalation Nitrogen in amine groups are more nucleophilic as compared to oxygen atoms. Studies shows that amine functionalized GO are better to increase interfacial binding sites. Under the different condition the chemical 2,6- bis(4-amino phenoxy) benzonitrile (BAAP) which includes both aromatic ring and amino group attach with GO in multiple ways like hydrogen bonding and nucleophilic substitution on GO surface with epoxy groups and behave as connecting bridge between the nanosheets [16-18]. The Covalently functionalized GO with BAAP have multiple possible applications including a material can be used in energy storage conversion devices, a suitable electrode material, co-existing inorganic-organic composite and a suitable host for many materials like metal-organic frame work to provide excellent electrical properties with stability [19-21]. In this paper, we quantify the interfacial capacitance on both sides of single-layer graphene for the first time, indicating that graphene's electrical properties, in addition to the surface area, play a crucial role in its storage capacity [21-22]. Understanding the factors that influence interfacial capacitance and the amount of charge that may be stored is critical for graphene's future growth

in electrical energy storage applications[4]. Graphene has a theoretical surface area of 2630 m<sup>2</sup>/g, as well as several graphene-derived materials for supercapacitor electrodes, have been reported, such as chemically reduced graphene oxide (CGO), graphene oxide (GO) reduced in propylene carbonate, microwave exfoliated graphite oxide, and a novel carbon produced by the chemical activation of graphene [5, 22-23]. Understanding the factors that influence interfacial capacitance and the charge that can be trapped in high-surface-area materials like graphene is crucial. A space charge component has been reported in interfacial capacitance for high surface area carbons, and this component could be a significant factor in determining the energy storage capacity of revolutionary carbon materials like graphene and ultrathin layers of other carbon utilized in supercapacitors [6].

## EXPERIMENTAL SECTION

All the chemicals (Sulfuric acid, graphite powder, Potassium permanganate, Hydrogen peroxide, 2,6- bis(4-amino phenoxy)benzotrile, Ethanol), utilized during this work were of analytical grade and purchased from Sigma Aldrich, Fluka and Merck. Solvents were also of high purity and were used without any prior treatment.

### *Synthesis of Graphene Oxide (GO)*

Hummer's method was adopted for the synthesis of graphene oxide this method was selected for the high quality (fewer defects) of the desired material and size of produced flakes. 50 mL of H<sub>2</sub>SO<sub>4</sub> was taken in a beaker set in the ice bath into which 2g of graphite powder was added on stirring. The 6 g of KMnO<sub>4</sub> was added slowly at stirring (600rpm), the temperature was kept constant at < 20 °C for 3 hours, followed by the slow addition of distilled water (100 mL) by keeping the temperature of the reaction mixture up to 50 °C to start the oxidation process. After some time, a colour change to dark brown was observed which indicated the formation of graphene oxide (GO). In addition of 200 mL of water ensured the oxidation of any unoxidized graphite (UOG). Finally, the reaction was quenched through the addition of 10 mL of H<sub>2</sub>O<sub>2</sub>, to remove the excess of KMnO<sub>4</sub>. The suspension was subjected to filtration, washed repeatedly to remove any unreacted species and dried at room temperature. Colour change during the process was a clear confirmation about the reaction proceeding effectively and clearly.

### *Synthesis of Functionalized Graphene Oxide (FGO)*

FGO synthesized using in the above-mentioned step was weighed GO equivalent to 0.6 g and ultrasonicated for 2 hours in 500 mL deionized water. 0.8g BAAP was added to GO dispersion and further ultrasonicated for 15 minutes. The dispersion was then set to reflux on magnetic stirring for 24 hours. Later the mixture was cooled down to room temperature, filtered, washed with EtOH: and H<sub>2</sub>O. The solid product was air dried followed by oven drying at 80 °C [7].

## RESULT AND DISCUSSION

### *Analysis techniques*

Synthesis of amine-Functionalized Graphene Oxide (FGO) was confirmed for structural and functional modifications using various analytical techniques. FT-IR spectra were recorded in 4000-500 cm<sup>-1</sup> for functional group analysis. XRD spectra were recorded for plane arrangement; UV visible spectroscopy has been applied for the determination of wavelength with maximum absorption, also the peak shift was investigated to confirm the functionalization of Graphene Oxide using diamine. CV was carried out to investigate the electrochemical properties of the synthesized functionalized graphene oxide (FGO). Synthesis of FGO was confirmed from the analytical techniques required plane formation and d spacing of graphene oxide sheets. The techniques that determines the functionalization of graphene oxide has been studied through these techniques like FT-IR, XRD, UV Visible and CV [8].

### *Fourier Transform InfraRed (FT-IR) spectroscopy*

FT-IR was carried out for functional group analysis in the range of 500 to 4000 cm<sup>-1</sup>. Fig. 3 displays the FT-IR absorption spectrum of 2,6- bis(4-amino phenoxy) benzotrile functionalized graphene oxide. The characteristic peak for OH has been observed at 3410 cm<sup>-1</sup>, which confirms the presence of OH in functionalized GO. All the functional groups of the material were confirmed through the respective signals observed in the spectra. C=O; stretch has been noticed at 1720 cm<sup>-1</sup>. A resonance peak allocated to the stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide is the sharp peak noticed at 1615 cm<sup>-1</sup>. The peak at 1354 cm<sup>-1</sup> shows the aromatic stretch of C-N and 1087 cm<sup>-1</sup>, 790cm<sup>-1</sup> corresponding signals for the vibrational mode of the C-O

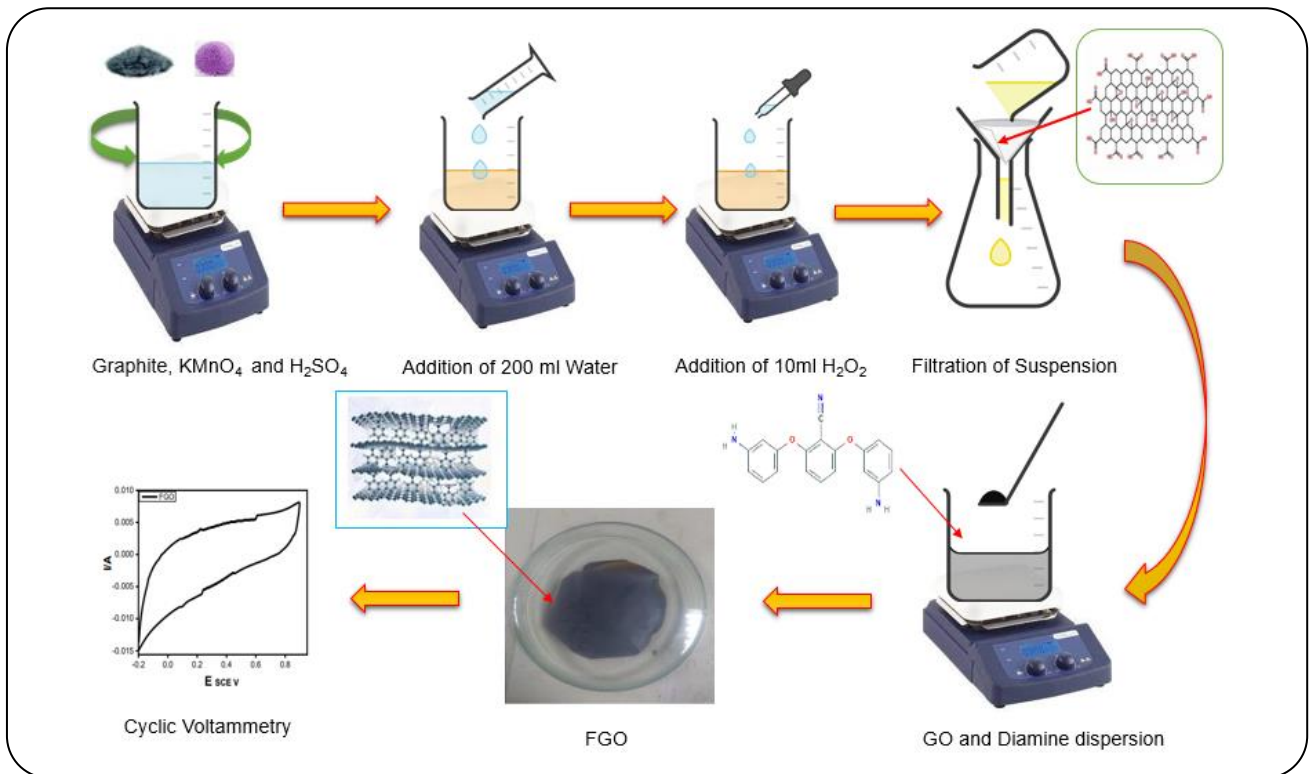


Fig. 1: Schematic illustration of graphene oxide synthesis and functionalization.

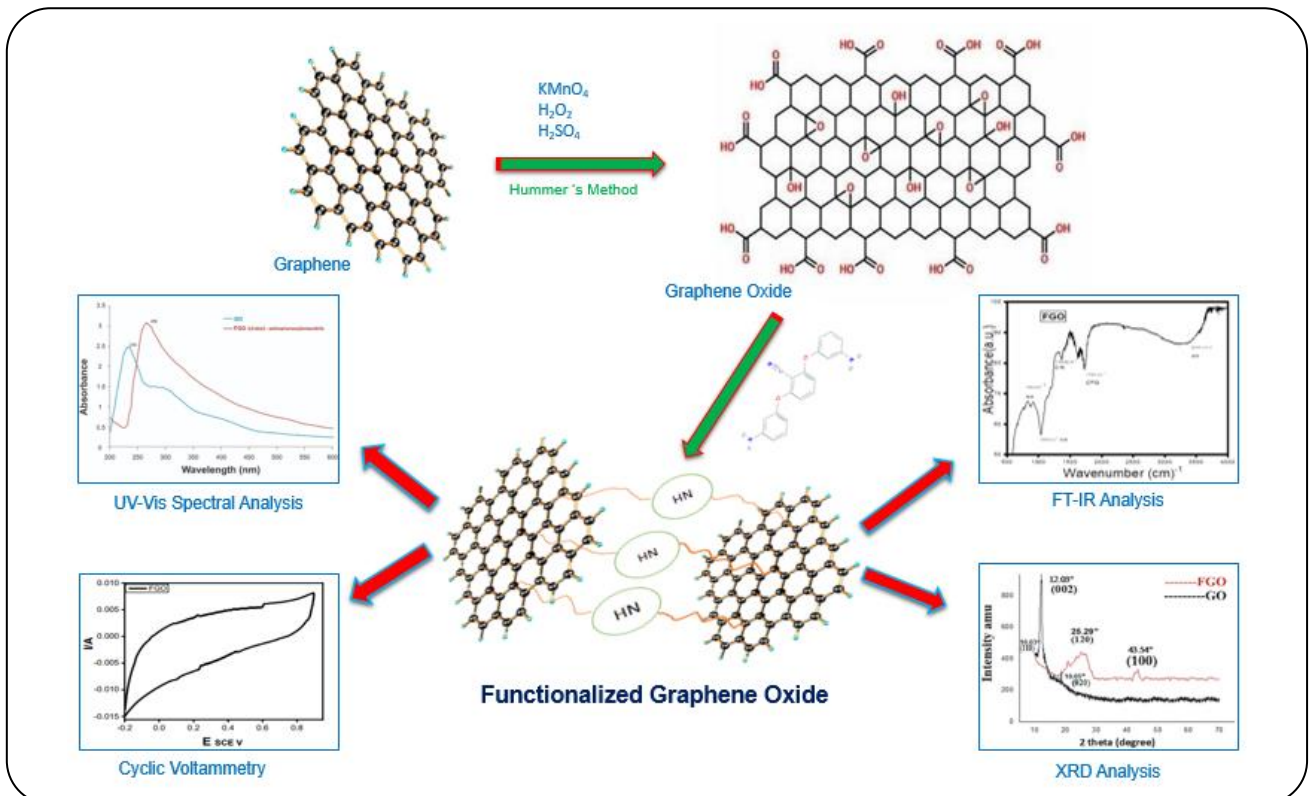


Fig. 2: Schematic representation of Graphene conversion into Graphene Oxide (GO) and Functionalized Graphene Oxide (FGO) and Characterization through various techniques.

group and basic aromatic amine N-H stretch respectively [9]. Hence structural modification has been confirmed by the characteristic peaks appearing in the spectrum.

#### X-Ray Diffraction (XRD) analysis

XRD patterns of GO and FGO both are shown in Fig. 4. The Graphene Oxide shows a sharp peak of reflection at  $12.03^\circ$  (002), corresponding to interlayer d-spacing which attributes the oxygen containing functional groups [10].

The Functionalized graphene oxide (FGO) composite with 2, 6- bis(4-amino phenoxy)benzotrile a narrow peak at  $43.54^\circ$  (100), shows the oxidation of the graphite to shape graphene -oxide (GO) in the sample and shows a broad peak at  $25.29^\circ$  (120) to understand that some oxygen containing functional groups are partially reduced because of diamine and increase in interlayer spacing between GO layers because of aromatic diamines act as bridge, that also increase active sites and surface area. The peak at  $10.03^\circ$  (111), represents there are still small quantities of graphite phases present in the Functionalized graphene Oxide [11].

#### UV-Visible spectroscopy

Characteristics peaks of GO from graphite flakes have been confirmed, with one of the absorbance peaks in the range of 320–360 nm, of graphene oxide is to identify that peak appeared at the 234 nm wavelength corresponding to  $\pi$ - $\pi^*$  transition in the aromatic C-C bond. The second peak shoulder was observed at a range of approximately 280 - 300 nm; transition attributed to  $n$ - $\pi^*$  in

C=O. Owing to C-N, they often have a small peak or only fluctuation of it about 266 nm transition electron from  $n$ - $\pi^*$ . These transitions and absorption maxima confirmed the formation of functionalized graphene oxide [12].

#### Cyclic voltammetry analysis

Cyclic voltammogram (CV) of the FGO samples were carried out in 1.0 M KOH solution at a scan rate of 10, 20, 30, 50 mV/s, displayed in Fig. 6; The output of the CV showed asymmetrical and quasi-rectangular curves, the shape is a clear depiction of the performance of the strong capacitance of double layers (HDLC). This is representative of the capacitance of 2,6- bis(4aminophenoxy)benzotrile and the shape of the curves in synthesized FGO was retained up to 500 mV/s [13]. The shapes are identical to some tiny hump suggesting a little overcharging at high voltage. To assess the charge

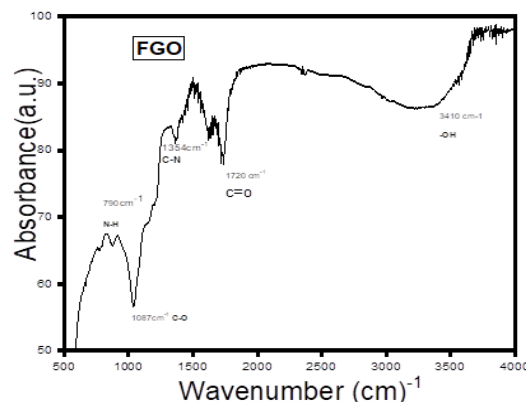


Fig. 3: FT-IR Spectrum of FGO.

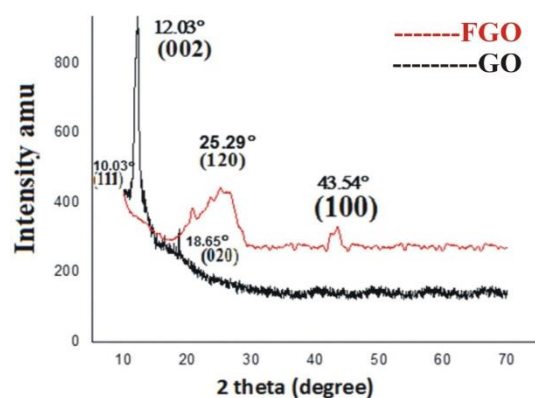


Fig. 4: XRD Spectrum of GO and FGO.

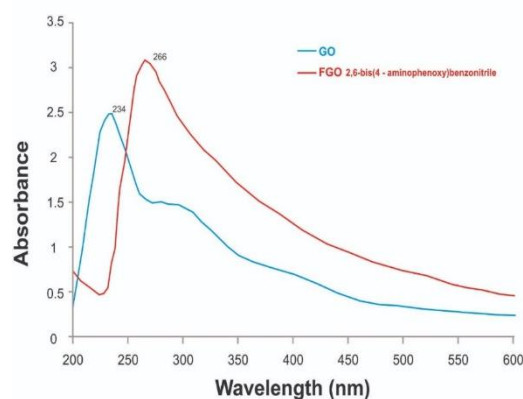


Fig. 5: UV-Visible Spectrum GO and FGO.

transfer resistance potential ranged from 10 mV to 50 mV. This is a modern standard method of cycling that is a more reliable and effective way to test super-capacitors for stability. This suggests that there was strong intercalation of electrolyte materials between 10 and 18 hours,

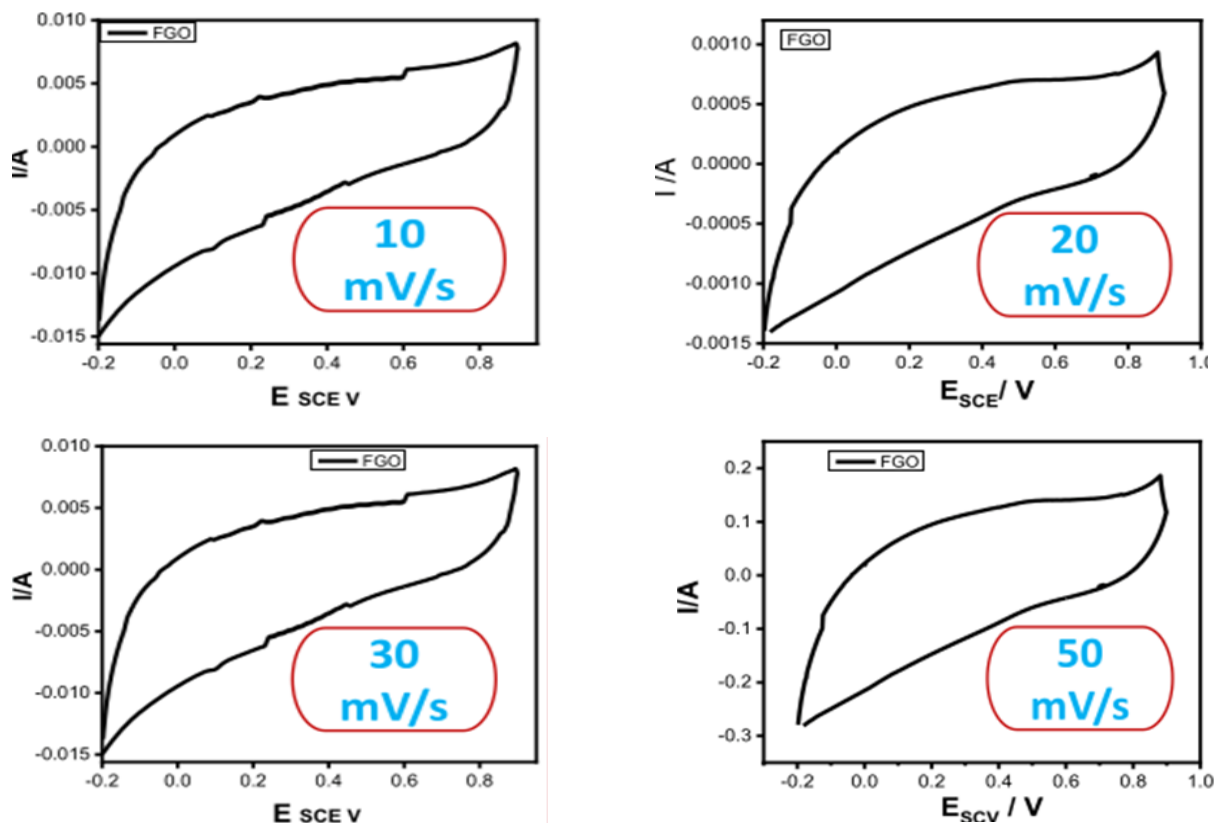


Fig. 6: Cyclic Voltammogram at the Various Scan Rate.

which may be due to high-potential interactions of electrolytes. This may also be due to the interaction of  $K^+$  ions with functional groups of oxygen on the surface of the material triggering Faradaic reactions. The amount of current depends not only on the voltage magnitude but also on the material properties that the current is flowing through. The specific capacitance of GO/FGO is considered for each scan rate and it is found that a high value is achieved for a high scan rate of 50 mV/s. The difference of specific capacitance with scan rate is displayed in Fig. 6. FGO is perfect in that capacitance value increases with increases in the scan rate. This is owing to the production of a large number of active sites on the electrode surface and consequently improved charge transfer reactions at a higher scan rate [14].

## CONCLUSION

Graphene Oxide was successfully synthesized from graphite- flakes, by the Hummer process. The functionalization of synthesized GO is done by Ultrasonication. The materials have been characterized by various techniques, including UV-Vis spectroscopy,

checking FT-IR, XRD and electrochemical properties in supercapacitors and their application for energy storage and production devices. The methods of characterization verified the presence of various functional groups which are essential in Graphene oxide and Functionalized Graphene Oxide. That involve C-O, C-O and main elements such as oxygen and carbon. Besides, the presence of functional groups such as C=O and C-O in the GO materials approves that GO oxidized the graphite flakes and can be used for further electrochemical applications. The output of the Cyclic Voltammetry revealed asymmetrical and quasi-rectangular behavior. These shapes display the performance of the strong capacitance of double layers (HDLC).

Received : May 17, 2022 ; Accepted : Aug. 28, 2022

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