

Review on Heterogeneous Electron Transfer in Graphene Electrode with Redox Couple

Betelihem Gesese*

Department of Chemistry, College of Natural and Computational Science, Mekdela Amba University, Ethiopia

***Corresponding Author:** Betelihem Gesese, Department of Chemistry, College of Natural and Computational Science, Mekdela Amba University, Ethiopia, Tel: +251934220868, E-mail: betelihemgesese@gmail.com

Citation: Betelihem Gesese (2021) Review on Heterogeneous Electron Transfer in Graphene Electrode with Redox Couple. *Technolock Mol and Cell Biochem* 1: 1-10

Copyright: © 2021 Betelihem Gesese. This is an open-access article distributed under the terms of Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

ABSTRACT

Graphene is a single sheet of graphite structure and excellent properties, making it attractive for a variety of electrochemical applications. Graphene electrodes are different electrochemical response at varies electrochemical activities such as unique electronic properties, enhance surface area, structure and chemical stabilities. Electrochemistry of grapheme general behavior of grapheme but studies in this review only heterogeneous electron transfer of electrode of graphene such as EPPG, BPPG, q-graphene and ML-GPET with redox probe. Cyclic voltammetry (CV) is a versatile electro analytical technique for the study of electro active species. Heterogeneous electron transfer of graphene in fast at different functionalization or doping of graphene. A detailed study has been conducted using different graphene electrode with redox probe for electron transfer reaction. Edge and base plane graphene electrodes are for different redox couple transfer information different electrochemical response. In the presence of outer sphere redox probe small change electrochemical response in different graphene electrode in other word in the presence of inner sphere redox couple there is different electrochemical response and also PH is affect different heterogonous electron transfer of graphene electrode at different solvent. The voltammetric response of inner redox couple is very inhibited by the presence of COOH-terminated GNF at pH < 8, especially in low ionic strength solution. The very high density of carboxylic acid groups of the c-GNF flakes and the absence of other oxygen-containing functionalities allow us to specifically investigate the effect of these highly charged and acidic groups on electrochemical response.

Keywords: Graphene; Cyclic voltammetry; Hetrognueoes Electron Transfer

Introduction

Graphene is: a single carbon layer of the graphite structure, 2-dimensional, crystalline allotrope of carbon, sp²-hybridized carbon atoms, basic building block for graphitic materials of all other dimensionalities (0D fullerenes, 1D nanotubes, and 3D graphite) and describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size [1].

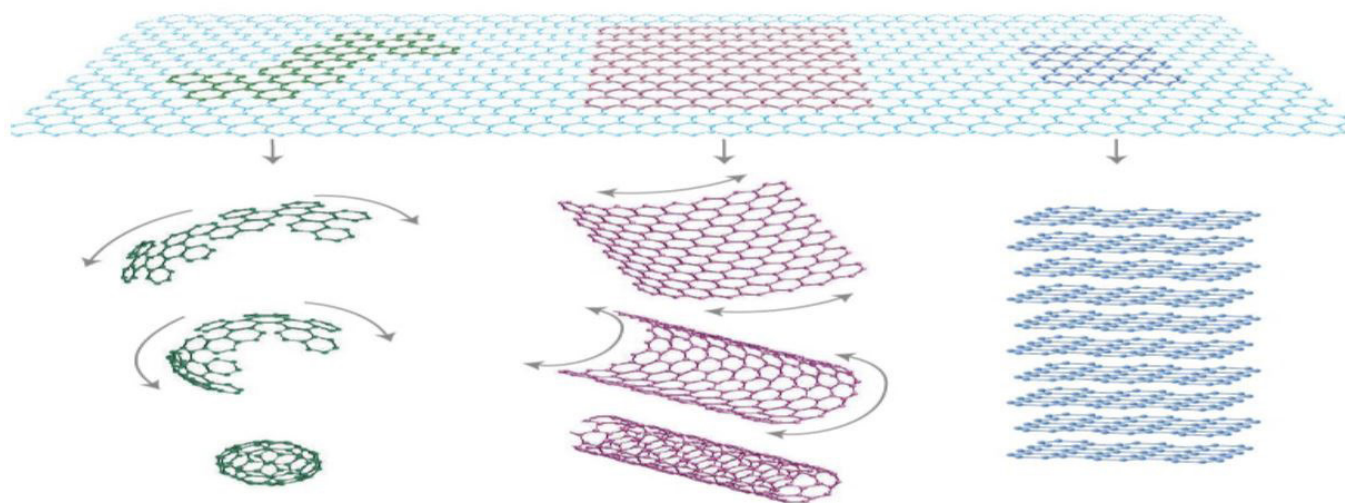


Figure 1: C60 fullerene molecules, carbon nanotubes, and graphite can all be thought of as being formed from graphene sheets, i.e. single layers of carbon atoms arranged in a honeycomb lattice

Graphene have many applications in the world, such as electronics, energy storage and conversion (super capacitors, batteries, fuel cells, solar cells, and bioscience/biotechnology because of its unique physicochemical properties [2].

Property	Details
Electron mobility	200,000 cm ² V ⁻¹ s ⁻¹
Thermal conductivity	5,000 W m ⁻¹ K ⁻¹
Specific surface area	2,630 m ² g ⁻¹
Breaking strength	42 N m ⁻¹
Elastic modulus	0.25 T Pa
Optical transparency	97.7 %
Electrical conductivity of graphene	64 m S cm ⁻¹

Table 1: Properties of Graphene

Studies on graphene electrochemistry have suggested the ability of graphene-based electrodes to carry a large amount of current at electron transfer rates superior to graphite and carbon nanotube (CNT) electrodes [3]. The high conductivity, large surface area and high electron transfer rate of graphene are the underlying reasons for its extensive usage in modern electrochemistry related technologies. The overall aim of this review is to provide a critical overview of our understanding on the electrochemistry of graphene such as electron transfer of graphene in redox probe, doping of graphene and CV electrochemical response of graphene electrode with redox couple. Electrochemistry provides a means to measure electron transfer kinetics, interactions between molecules and electrode surfaces [4].

The fundamental understanding of electron transfer at graphitic electrode materials indicates that they are electronically anisotropic in nature [5]. This review can be considered electron transfer of graphene originates from two heterogeneous structures such as edge and base plane. In order to investigate the heterogeneous electron transfer properties of graphene electrode that performed cyclic voltammetric measurements in the presence of redox couples and this redox couple that describe electrochemical response. Cyclic voltammetric studies of redox couples in the presence of GNF function of graphene that have different effects for different solvents and doping of graphene functionalization. This review generalized compare and contrast electrochemistry of graphene structure and different electrode of graphene depends on electrochemical response for example conductance, rate of reaction, peak to peak separation, current, potential, electron transfer effect etc.

Objective of the review

General Objective

- To review heterogeneous electron transfer in graphene electrode with redox couple

Specific Objective

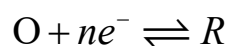
- To review electrochemistry of graphene
- To review different graphene electrode with redox couple electrochemical response by using cyclic voltammetric study
- To review electrochemical response of edge and plane-electrodes with electrochemical probe
- To review doping of graphene

Electrochemistry of Graphene

For the potential application of a certain kind of carbon material in electrochemistry, the basic electrochemical behaviors should be first studied to determine several important parameters of carbon electrodes such as: electrochemical potential window, electron transfer rate, redox potentials, density of state, peak to peak separation etc.

Redox Couple

Redox Couple is consists of reduction and oxidation reaction for example;



Where O is oxidized and R reduced in redox couple.

Redox couple can be classifieds in to two this are outer and inner redox couple or classifieds based on electrode surface such as surface sensitive, surface sensitive and oxide-sensitive and surface in sensitive [6]. Cyclic voltammetry is the most extensively used technique for acquiring qualitative information about electrochemical reactions. It kinds the rapid identification of redox potentials distinctive to the electro active species under investigation, providing considerable information about the thermodynamics of a redox process, kinetics of heterogeneous electron-transfer reactions and analysis of coupled electrochemical reactions or adsorption processes.

This review can be study electrochemical response/activity of graphene toward different kinds of redox systems such as $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$, $[\text{Fe}(\text{CN})_6]^{3-/4-}$, and $\text{Fe}^{3+/2+}$. As is known, $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ is a nearly ideal outer-sphere redox system that is insensitive to most surface defects or impurities on electrodes and can serve as a useful benchmark in comparing electron transfer of various carbon electrodes; $[\text{Fe}(\text{CN})_6]^{3-/4-}$ is "surface-sensitive" but not "oxide-sensitive"; $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ is surface in sensitive ; $\text{Fe}^{3+/2+}$ is both "surface-sensitive" and "oxide-sensitive" [7].

Compare Different Graphene Electrode with Redox Couple Electrochemical Response by Using Cyclic Voltammetric Study

Hetrognueoes electron transfer of graphene can be determined redox mediator and biological molecules. Redox mediator by using cyclic voltammetry was indicated different electrochemical response/activities. Inner redox mediator most of the time more expressed electrochemical response for different structure of graphene [6]. Electron transfer kinetics with inner sphere redox couple can be affected by density of electron state (DOS) and micro surface structure. Edge plane defect on graphitic structure that accelerate rate of recreation and more electrochemical response than other graphene electrode. In cyclic voltammetry study different graphene electrode are different electrochemical response for example multilayer graphene poly(ethylene terephthalate) (PET) electrode (ML-G-PET), edge-plane pyrolytic graphite (EPPG), and basal-plane pyrolytic graphite (BPPG) electrodes are different rate of reaction, peak to peak separation ,DOS etc.

In addition to inner sphere redox couple outer redox couple and biological molecule have affected electrochemical response in cyclic voltammetry. Generally, the following figure can be compare and contrast electrochemical response of more than two graphene electrodes.

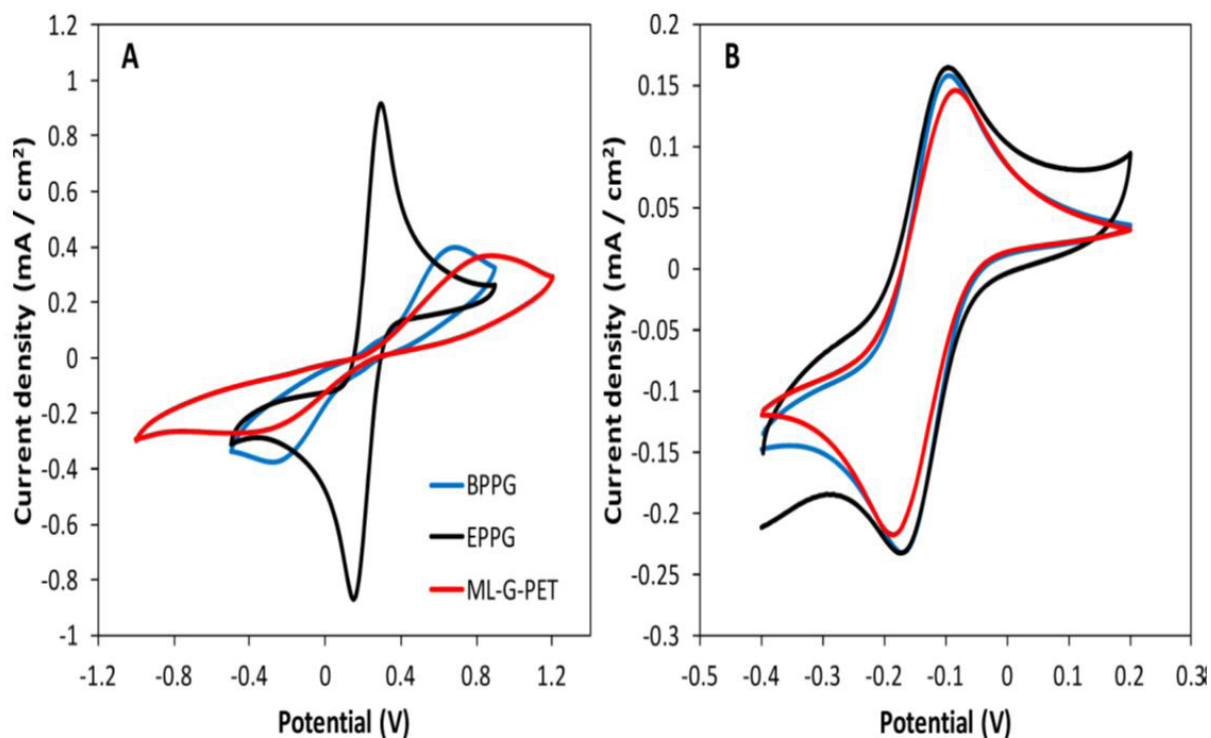


Figure 2: Representative cyclic voltammograms in the presence of (A) $\text{Fe}(\text{CN})_6^{3-/4-}$ and (B) $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ redox probes and using BPPG (blue), EPPG (black), and multilayer graphene transferred to PET (ML-G-PET) (red) electrodes. Supporting electrolyte 0.1 M KCl; scan rate 0.1 V s^{-1} (vs Ag/AgCl)

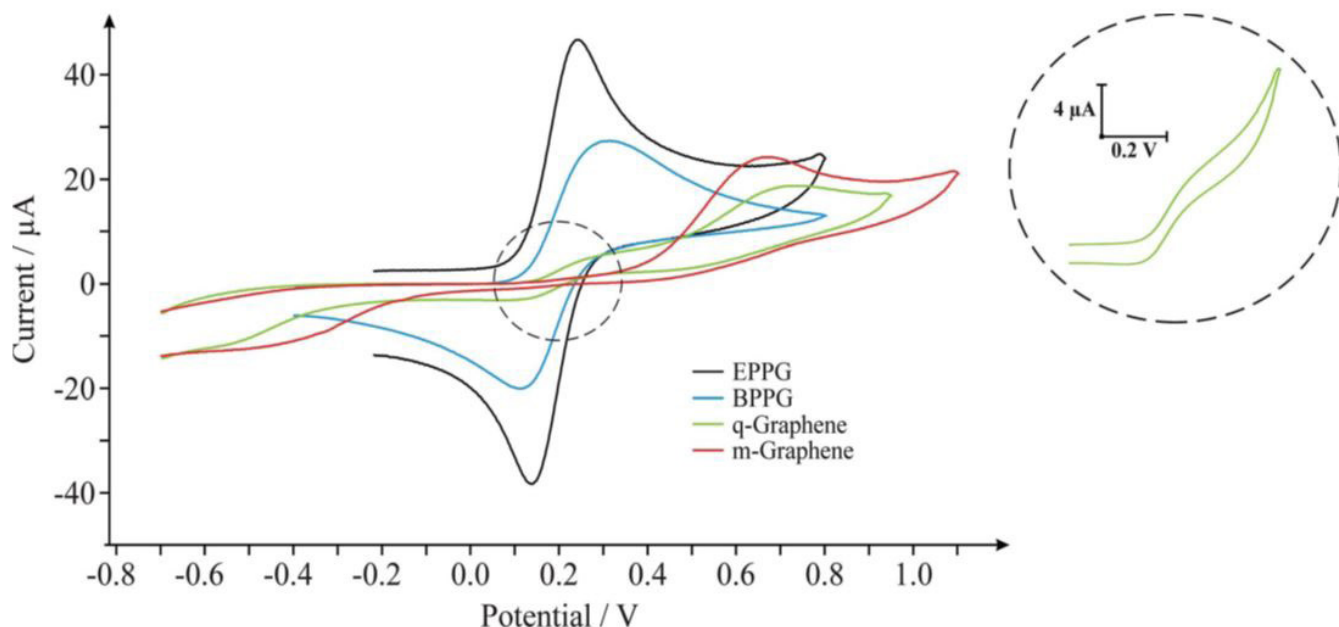


Figure 3: Cyclic voltammetric signatures obtained using potassium ferrocyanide(II) at EPPG (black), BPPG (blue), quasi-graphene (q-graphene, green) and monolayer graphene (m-graphene, red) electrodes. Scan rate shown for each electrode: 100 mV s^{-1} (vs. SCE)

The dotted circle area is a zoomed in portion of the voltammetric window, highlighting the heterogeneous electrode response of the quasi graphene which gives rise to two distinctive voltammetric signatures. Shown is a separate scan of the region indicated with quasi-graphene using the same parameters except with limiting the potential window. q-graphene is contains four layers of graphene this layer have edge and base plan where edge plane sites are active and neglect any defects upon the basal sheets ,such types of electrode which is nanoscopic in width and microscopic in length; akin to a nanoband type electrode. Faradaic current can be predicted by the following equation for the current at a hemicylinder of equivalent [8].

$$i = 2\pi nFDCl[1 / (\ln 4\Theta)] \quad (1)$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, D is the diffusion coefficient of the electro active species, C the concentration of the redox probe, l (cm) is the length of the micro/nanoband, and $\Theta = Dt / (w / \pi)^2$ where w (cm) is the width of the band and $t = RT / Fv$, where v is voltammetric scan rate.

Electrochemical response of edge and plane-electrodes with electrochemical probe

Single-layer graphene sheet can be classified in to two different structural regions: (1) the basal plane, consisting of two dimensional conjugated sp^2 carbon atoms; (2) the edge, making of one-atom thick defective graphitic line of carbon atoms with dandling bonds and various capping moieties (oxygen containing organic compounds) [7].

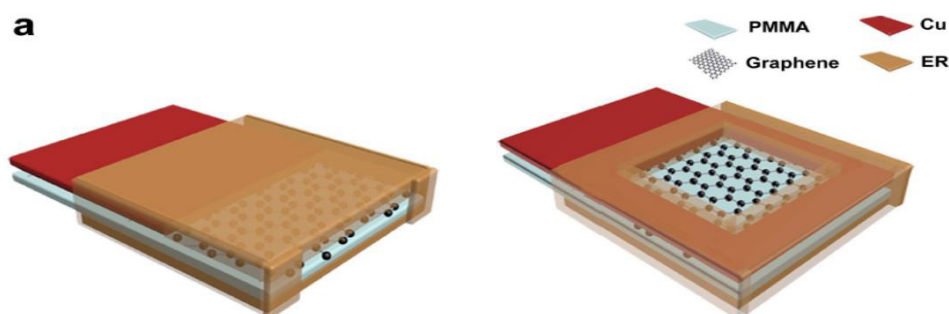


Figure 4: Configurations of plane- and edge-electrodes, and the structure of a CVD graphene sheet

Electrochemistry at two structure of graphene was studies by using cyclic voltammetry in the presence of buffered solution and electrolyte ;but electrolyte is pure cyclic voltamogram both electrode rectangular in shape that indicated pure capacitive behavior (figure 5) .Edge electrode higher specific capacitance than base plane electrode because graphene edge electrode was formed by mechanical cutting leading to the formation of structural defect with dandling bond and this dandling bond unstable in reactive species or air.

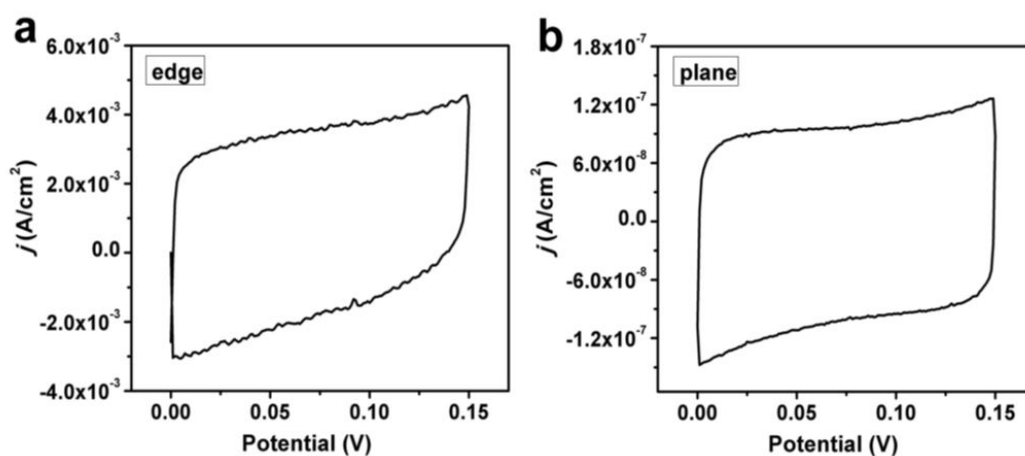


Figure 5: Capacitive comparison of graphene edge and basal plane. (a, b) Cyclic voltammograms of the edge- (a) and plane- (b) electrodes in a 0.1 M PBS solution containing 0.1 M KCl at a scan rate of 50 mV /s

Edge and base electrode have different properties in electrochemical redox probe. Edge and base plane electrode studies charge transfer in the presence of surface sensitive redox probe that follow different response for example different scan rate and current density. Electrochemical response can be controlled by diffusion electro active species (figure 6): like linear diffusion-based system and the peak current or wave current (i_p) can be given by Randles-Sevcik equation.

$$i_p = 2.69 \times 10^5 n^{3/2} ACD^{1/2}V^{1/2} \quad (2)$$

Where n is the number of electrons involved in the redox reaction, A is the area of the electrode, C is the concentration of the electrochemical probe, D is the diffusion coefficient and v is the scan rate. For equation 1 that indicates current density directly proportional to square root of scan rate.

Anodic and cathodic peak currents in the CVs are linear with the square root of the scan rate, which suggest that the redox processes on graphene-based electrodes are predominantly diffusion controlled [9]. The peak-to-peak potential separation is related to the electron transfer (ET) coefficient [10] and a low ΔE_p value indicates a fast electron transfer for a single-electron electrochemical reaction on grapheme. Edge and plane graphene electrode have different oxidation time for function of graphene and different electrochemical response [11]. Oxidation of graphene in CV experiment that have faster electron transfer, lower peak to peak separation and larger DOS than unoxidized graphene electrode (figure 6).

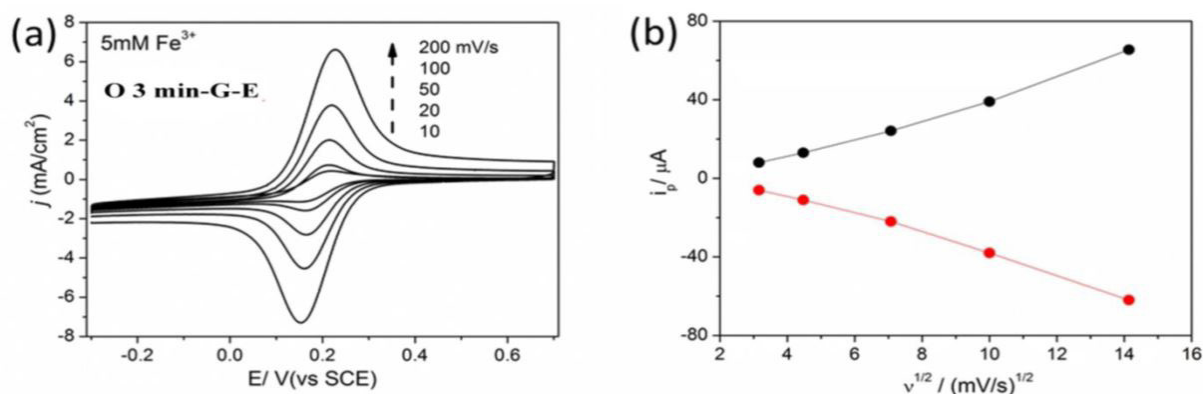


Figure 6: (a) CVs of 5 mM K3 [Fe(CN)6] in 0.1 M PBS (pH 6.5) at a scan rates scope of 10, 20, 50, 100 to 200 500 mV/s, (b) shows the relationship of plot of peak current and the square root of the scan rate

Convergent diffusion used to induce a faster mass transfer to contribute a stronger wave current density [12]. The steady current (i_s) for ultramicroband electrode can be approximately calculated by equation 3

$$i_s = 2\pi nFDCL \left[1 / \left(\ln 4Dt\pi^2 / w^2 \right) \right] \quad (3)$$

Where t is time, D is the diffusion coefficient, L is length of edge-electrode W is width electrode, C is concentration, n is number of electron and F is Faraday constant.

Equation 3 is the limitation of its diffusion law. For example, the flux in memory diffusion that based on the Fick's first law is generated with a delay from the formation of concentration gradient. Furthermore, a fast electrochemical process can cause a delay of diffusion; the actual diffusion velocity is much slower than the theoretical value [13]. The electro catalytic activities of the edge- and plane-electrodes have been studied by using three electrochemical probes, including ascorbic acid (AA), beta-nicotinamide adenine dinucleotide (NADH) and oxygen so in this electrochemical probe that transfer information different electrochemical response [13].

Traditional consensus has been that electron transfer at graphitic materials is dominated by the edge plane [14, 15] and it has been shown that the intentional generation of oxygen-containing defects increases reactivity. The basal plane of the GNF is predominantly defect free and hence contains negligible oxygen content. In contrast, the edges of the flakes are decorated with carboxylic acid (COOH) functionalities.

The high density of edge COOH groups makes this an ideal material which to study the role of oxygen species on electrochemical response, as their influence is greatly amplified due to the small size of the flakes. Modification of the edge groups by transformation into amide groups also allows us to probe the influence of the edge group acidity and ability to hydrogen bond. COOH-terminated GNF (c-GNF) and amide-terminated GNF (a-GNF) modified electrodes interact with the common redox probes such as FcMeOH (figure 7), ferricyanide (figure 8) and hydroquinone (figure 9) give different electrochemical response at different PH effect.

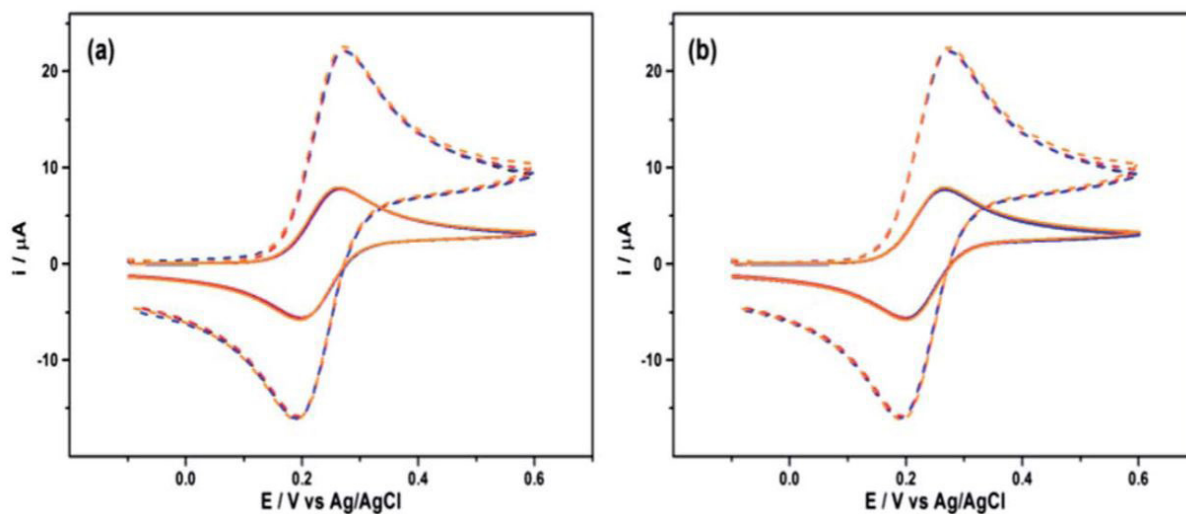


Figure 7: CVs of 0.5 mM FcMeOH (a) at clean BDD in 0.1 M KH_2PO_4 (pH 4.6) (black line) and 0.1 M K_2HPO_4 (pH 9.2) (red line); at c-GNF modified BDD in 0.1 M KH_2PO_4 (pH 4.6) (blue line) and 0.1 M K_2HPO_4 (pH 9.2) (orange line); (b) at clean BDD in 0.1 M KH_2PO_4 (pH 4.6) (black line) and 0.1 M K_2HPO_4 (pH 9.2) (red line); at a-GNF modified BDD in 0.1 M KH_2PO_4 (pH 4.6) (Blue line) and 0.1 M K_2HPO_4 (pH 9.2) (orange line) scan rate 100 mV s^{-1} (solid line), 1 V s^{-1} (dashed line)

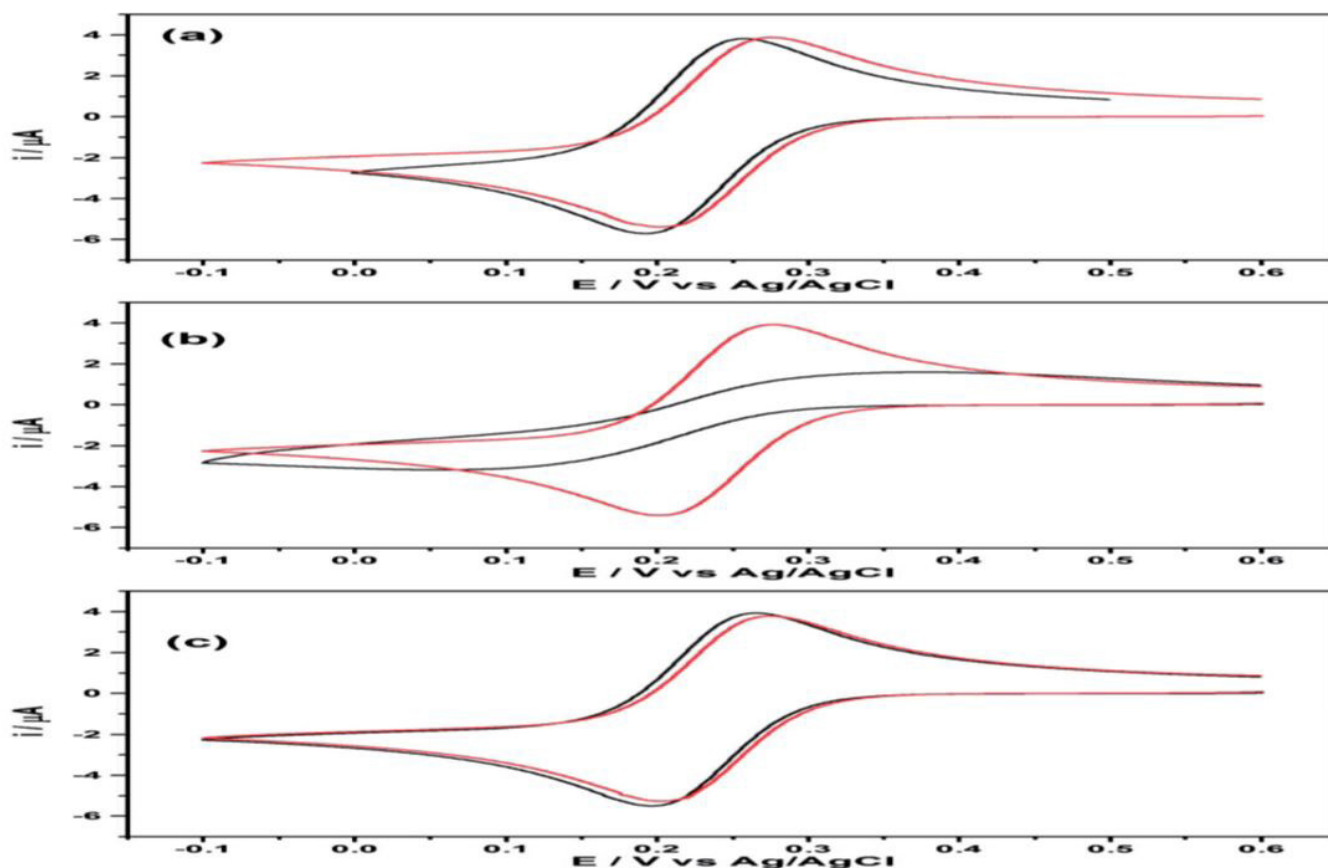


Figure 8: The influence of pH on the ferri/ferrocyanide redox reaction at different electrodes (a) Clean BDD; (b): BDD modified with c-GNF; (c): BDD modified with a-GNF. Supporting electrolyte: 0.1 M KH_2PO_4 (pH 4.6) (black line); 0.1 M K_2HPO_4 (pH 9.2) (red line). Potassium ferricyanide concentration $0.5 \times 10^{-3} \text{ M}$. Scan rate: 50 mV s^{-1}

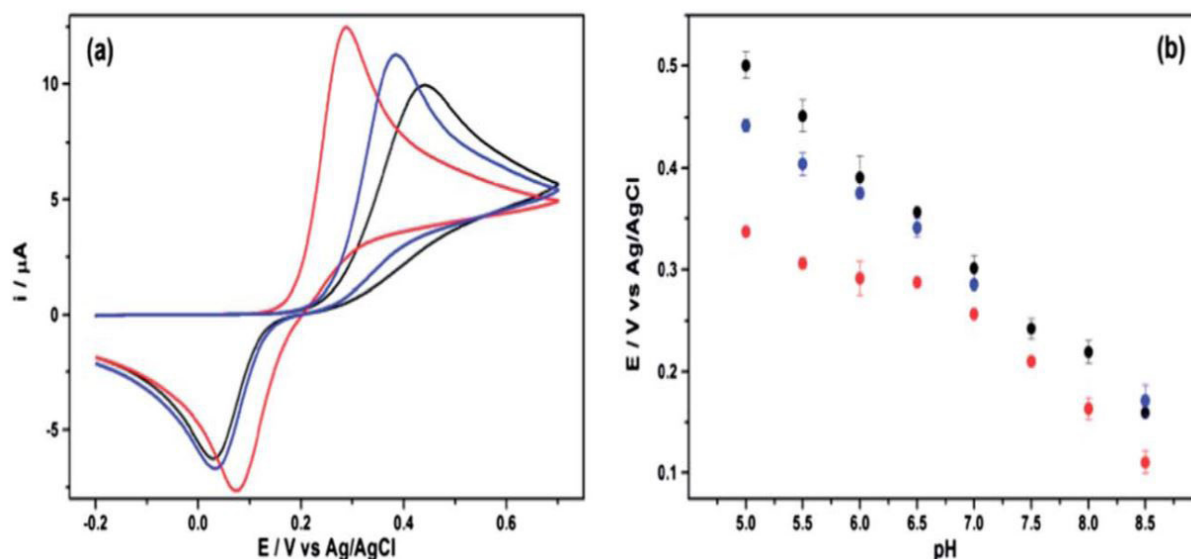


Figure 9: (a) CV of 0.5 mM hydroquinone at clean BDD electrode (black line), c-GNF (red line) and a-GNF (blue line) supporting electrolyte: 0.1 M pH 5.5 PBS. Scan rate: 50 mV s^{-1} . First scans shown. (b): Peak potential of hydroquinone oxidation as a function of pH at clean BDD electrode (black), c-GNF (red) and a-GNF (blue)

GNF in solution form that affected redox probe and electrochemical response can be induced for these effects. In case of $\text{Ru}(\text{CN})_6^{3+/4+}$ that indicates small increasing peak to peak separation and small decreasing peak height in other words in case of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ peak height drastically reduced, voltammogram has sigmoidal shape that indicated electrode blocking (figure 10). This is the same response as we obtained when COOH-terminated GNF were immobilized directly on the electrode surface [16].

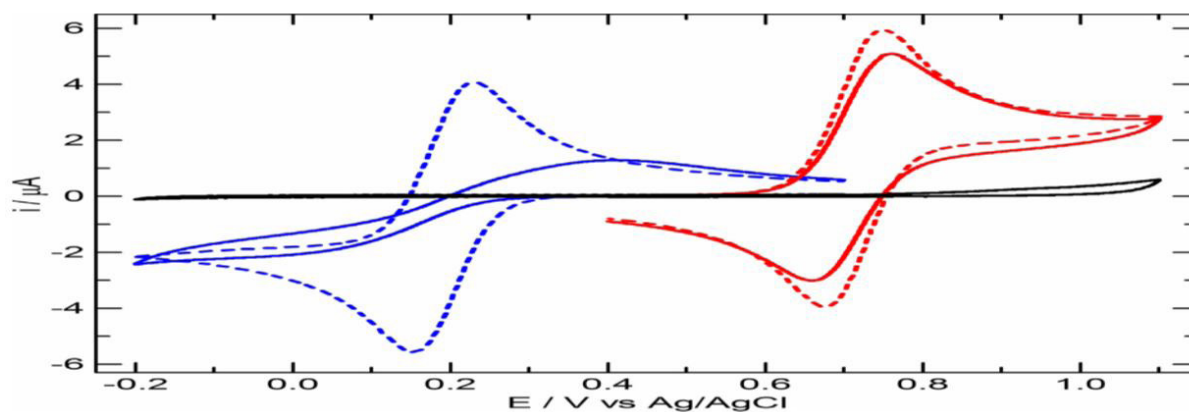
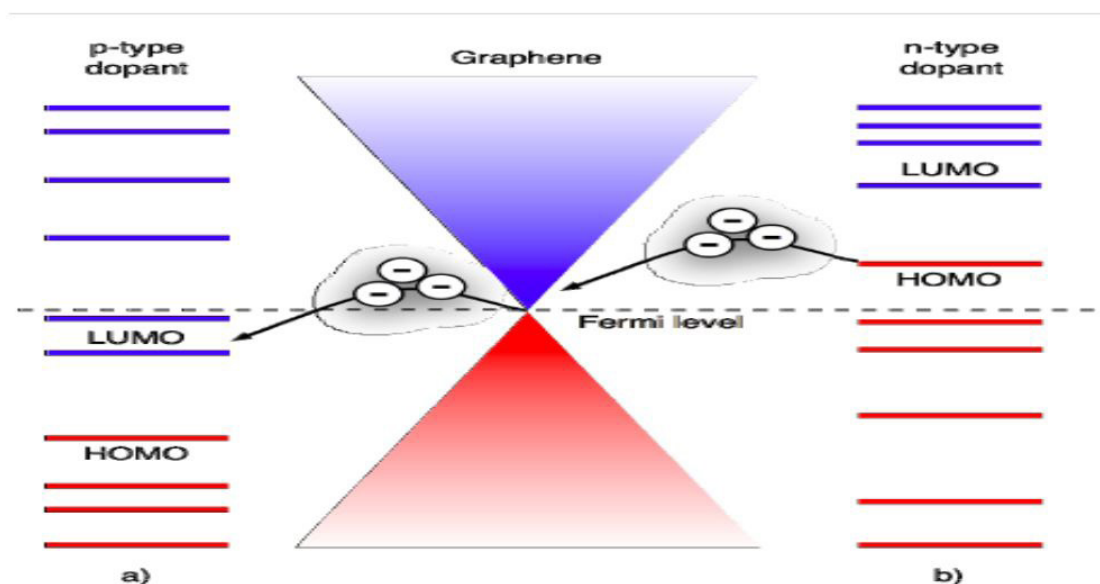


Figure 10: CVs of GNF only (black); 0.5 mM $[\text{Fe}(\text{CN})_6]^{3-}$ (dashed blue); 0.5 mM $[\text{Fe}(\text{CN})_6]^{3-}$ and 34 $\mu\text{g ml}^{-1}$ GNF (solid blue); 0.5 mM $[\text{Ru}(\text{CN})_6]^{4-}$ (dashed red); 0.5 mM $[\text{Ru}(\text{CN})_6]^{4-}$ and 34 $\mu\text{g ml}^{-1}$ GNF (solid red). Electrolyte: 0.01 M KCl. Scan rate: 50 mV s^{-1}

Having acid functionality $[\text{Fe}(\text{CN})_6]^{3-/4-}$ CV experiments carried out low ionic strength solution with GNF immobilized electrode surface and either H_2O or D_2O used as a solvent. For CV experiment H_2O used as CV significant inhibition first cycle and repeated cycle increasing peak height reversible of redox reaction and in case of D_2O first cycle show inhibition electron transfer kinetics and repeated cycle increasing peak height, decreasing peak separation and reaction will be more reversible reaction. GNF in H_2O used as a solvent that explained constant protonation and deprotonating carboxylic acid group and D_2O used as a solvent inhibition redox, good proton exchange and electron closing species inhibition electron transfer.

Doping of graphene

Doping can modify the electronic structure of graphene, and can also bring interesting physicochemical properties to the graphitic system [17]. Doping of graphene can be classified in to two such as chemical and electronic doping. Chemical doping involves interactions of graphene with other chemical species or occurs due to charge transfer between graphene and surface adsorbates. Whether the charge transfer will take place is determined by the relative position of density of states (DOS) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dopant and the Fermi level of graphene (Scheme 1).



Scheme 1: A schematic showing the relationship between positions of the HOMO–LUMO levels of dopants with respect to the Fermi level of graphene relevant for n- and p-type doping of graphene

Adsorbates or substrates used to controlled type and concentration of carriers in graphene during transfer charge to graphene. P-type and n-type doping simply forming the difference between the highest occupied molecular level (HOMO) and the lowest unoccupied molecular level (LUMO) of the adsorbate and graphene. Charge is transferred from the dopant to the graphene layer, if the HOMO of the dopant is above the Fermi level of graphene resulting in n-type doping and for dopants with LUMO below the Fermi level of graphene, charge transfer occurs from the graphene layer to the dopant amounting to p-type doping. Electronic dopants are ability to dope graphene either n- or p-type has been demonstrated for various atomic and molecular adsorbates for example electropositive elements that easily donate their outer shell electrons are expected to be n-type dopants. Given the relatively low work function of graphene (-4.6 eV), n-type doping is perceived to be more challenging than p-type. P-type electronic doping is disparity between the work function of graphene and the electron affinity of the adsorbate.. The electrochemical doping of graphene occurs when certain surface adsorbates participate in electrochemical redox reactions in which graphene plays the role of an electrode. The total Gibbs free energy change is given by $\Delta G + W$ for p-doping and $\Delta G - W$ for n-doping, where ΔG is the free energy for the molecular reaction and W is the work function of graphen [18, 19].

Conclusion

In summary, can be conclude Hetrognueoes electron transfer of different graphene electrode with redox couple. Redox couple is a redoxing species and it corresponding oxidized form .There are two types of redox couple such as inner and outer redox couple .Inner redox couple is sensitive to surface of graphene electrode but outer sphere redox couple is in sensitive to surface of graphene electrode .Electron transfer kinetics in graphene electrode that defect less base plane graphite and slower electron transfer toward the surface sensitive redox probe compared to that of base plane graphene electrode which is known to possess a certain density of edge plane defect site. In varies functionalization derivative of doped and undoped graphene oxide surface to probe the role of defects in determining the net electron transfer kinetics. Graphene basal plane and edge carbon atoms play a different role in electrochemistry at the graphene flak eelectrodes because of the used electrochemical species. Edge plane graphene electrode compared to BPPG, ML-GPET and quasi-graphene in CV study faster electrochemical properties in terms of HET kinetics.

References

1. Geim KA, Novoselov SK (2007) *Nature Materials* 6: 183.
2. Pumera M (2009) *Electrochemistry of Graphene: New Horizons for Sensing and Energy Storage*. *Chem Rec* 211-23.
3. Ning Xia, Lin Liu, Zhifang Sun, Binbin Zhou (2015) *Nanocomposites of Graphene with Ferrocene or Hemin: Preparation and Application in Electrochemical Sensing*. *J Nanomater* 892674.
4. Bard AJ, Faulkner LR (2000) *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York.
5. McCreery RL (2008) *Advanced carbon electrode materials for molecular electrochemistry*. *Chem Rev* 108: 2646-87.
6. Ambrosi A, Pumera M (2013) *Electrochemistry at CVD Grown Multilayer Graphene Transferred onto Flexible Substrates*. *J Phys Chem C* 117: 2053-8.
7. Pumera M, Ambrosi A, Bonanni A, Chng E L K, Poh HL (2010) *Graphene for electrochemical sensing and biosensing*. *TrAC, Trends Anal. Chem.* 29: 954-65.
8. Dale AC, Brownson Sarah, A Varey, Fiazal Hussain, Sarah J Haighb, et al. (2014) *Electrochemical properties of CVD grown pristine graphene: monolayer- vs. quasi-graphen*. *Nanoscale* 6: 1607.
9. Lin JW, Liao SC, Jhang HJ, Tsai CY (2009) *Electrochem Commun* 11: 2153
10. Shang GN, Papakonstantinou P, McMullan M, Chu M, Stamboulis A, et al. (2008). *Adv Funct Mater* 18: 3506.
11. Feifei Zhang, Lin Lu, Min Yang, Cuili Gao, Zonghua Wang (2017) *Electrochemistry of Graphene Flake Electrodes: Edge and Basal Plane Effect for Biosensing*. *Int J Electrochem Sci* 12.
12. Le Drogoff B, El Khakani MA, Silva PRM, Chaker M, Vijn AK (2001) *Effect of the Microelectrode geometry on the diffusion behavior and the electroanalytical performance of Hg-electroplated iridium microelectrode arrays intended for the detection of heavy metal traces*. *Electro analysis* 13: 1491-6.
13. Wenjing Yuan, Yu Zhou, Yingru Li, Chun Li, Hailin Peng, et al. (2013) *The edge- and basal-plane-specific electrochemistry of a single-layer graphene sheet*. *Scien Rep* 3: 2248.
14. DAC Brownson, CAD, Munro JL, Kampouris KD (2011) *Banks RSC Adv* 1: 978-88.
15. Lim XM, Hoh YM, Ang KP, Loh PM (2010) *Anal Chem* 82: 7387-93.
16. Lounasvuori MM, Rosillo-Lopez M, Salzmann GC, Caruana JD (2014) *Holt, Electrochemical characterisation of graphene nanoflakes with functionalized edges*, *Faraday Discuss* 172: 293-310.
17. Sidhureddy Boopathi, Tharangattu N, Narayanan, Shanmugam Senthil Kumar (2014) *Improved heterogeneous electron transfer kinetics of fluorinated graphene derivatives*. *Nanoscale* 6: 10140.
18. Kunal S Mali, John Greenwood, Jinne Adisojoso, Roald Phillipson, Steven De Feyter (2015) *Nanostructuring graphene for controlled and reproducible functionalization*. *Nanoscale*, 7: 1566-85.
19. Shouvik Banerjee, Jiwook Shim, Jose Rivera, Xiaozhong Jin, David Estrada, et al. (2013) *Electrochemistry at Edge of Single Graphene Layer in a Nanopore*. *ACS Nano* 7: 834-43.