

MODIFICATION OF GRAPHENE OXIDE AS EFFICIENT CATALYST SUPPORT
FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

by
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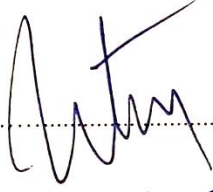
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Materials Science and Engineering, M.Sc. Thesis, 2016

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Electrocatalyst Support, Modified Polyol Process, PEMFC

ABSTRACT

Since 2004, graphene has gained immense popularity due to its unique properties and structure but graphene as a bulk material, rarely depicts surface properties needed for energy conversion and storage owing to the irreversible aggregation of the nanosheets. Electrocatalysts are often synthesized on supports by solution based methods that require the supports to have high surface area with excellent solubility and processibility in solvents e.g. organic solvents for uniform dispersion and growth of ultra-small platinum nanoparticles for high electrocatalytic activity in PEM fuel cells. As a remedy, graphene oxide can act as a precursor which has many chemically reactive oxygenated functional groups at edges and basal planes giving an opportunity for covalent and non-covalent functionalization with

many functional materials like organic compounds, biomaterials, polymers and nanoparticles. As a result, functionalized graphene oxide (f-GO) can have many applications because of their interesting properties such as chemical stability, tunable modification, high electrical conductivity and multifunctional structures.

In this research, the successful modifications of graphene oxide via covalent functionalization with novel functional reagents p-phenylenediamine (GO-NH₂) and Gly-Arg-Gly-Asp-Ser-Pro (GO-RGD) was achieved to overcome the graphene issues mentioned before while imparting desirable properties, as evidenced by the different characterization techniques employed such as FTIR, TGA, XRD and Raman. Subsequently, these f-GO were utilized as effective electrocatalyst supports for anchoring platinum nanoparticles using the well-known polyol reduction process along with Vulcan XC-72, GO and N doped GO for comparison purposes and further characterized by XRD, TGA, TEM and CV. Pt/GO-RGD showed the highest hydrogen adsorption/desorption peaks with large areas under them indicating increased number of available Pt catalyst active sites for charge transfer which in turn gave high ECSA value of 147 m²/g about 83% higher than synthesized Pt/Vulcan XC-72 (80 m²/g) and 48% higher than Pt/GO (99 m²/g) which can be attributed to smaller Pt nanoparticles' size with homogeneous distribution on the support material with large surface area to anchor metal nanoparticles. While the runner-up in ECSA values was Pt/GO-NH₂ (130 m²/g) due to small Pt nanoparticles' size (3.9 nm) with excellent dispersion as evidenced by TEM which increased the Pt utilization. These results showed that the as-synthesized Pt/f-GO are promising electrocatalysts for high performance PEM fuel cells which would be the future task of our investigation. This concluded the first part of our work.

Secondly, graphene oxide was modified via non-covalent functionalization with incorporation of polypyrrole/carbon nanocomposite by solution intercalation to yield hybrid nanocomposite. Subsequently, Pt nanoparticles were reduced on the catalyst supports i.e. graphene oxide (GO), polypyrrole/carbon black nanocomposite (PPy/CB) and polypyrrole/carbon black/graphene oxide hybrid nanocomposite by three different methods based upon modified polyol process to see their effects on the size of Pt nanoparticles, their dispersion on supports and electrocatalytic activity by employing different characterization

techniques such as XRD, TGA, TEM, and CV. Method 2 i.e. modified polyol process with FeCl_3 proved to be the best among the three compared methods owing to the utilization of FeCl_3 which acted as an effective stabilizer and retardant in the Pt seed growth leading to smaller particle size with high surface area available for electrocatalytic activity. While the hybrid nanocomposite support i.e. Pt/PPy/CB/GO synthesized by the method 2 showed the highest ECSA value of $153 \text{ m}^2/\text{g}$ about 30% higher than Pt/PPy/CB ($117 \text{ m}^2/\text{g}$) and 20% higher than Pt/GO ($128 \text{ m}^2/\text{g}$). The improved electrocatalytic activity of Pt loaded hybrid nanocomposite as compared to other supports could be explained due to the increased electrical conductivity, increased number of charge carriers with their free mobility. Since the oxygen containing groups which acted as insulators, were partially reduced during Pt synthesis on the hybrid nanocomposite, which resulted in less resistance for electron and mass transfer. In addition to this, the inclusion of PPy/CB into layers of GO inhibited the aggregation of graphene sheets during partial reduction of GO which in turn provided large surface area for uniformly distributing Pt nanoparticles on the heterogeneous nucleation sites formed by the PPy/CB. Thus Pt loaded hybrid nanocomposite synthesized by method 2 could serve as potential candidate for PEM fuel cell application which would be our future task of investigation. This concluded the second part of our work.

PEM YAKIT HÜCRELERİ İÇİN KULLANILAN GRAPHEN OKSİT KATALİZ DESTEK MALZEMENİN MODİFİYE EDİLMESİ

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Anahtar Kelimeler: Grafen işlevselleştirilmesi, Grafen - Polipirrol Hibrid nanokompozit, elektrokatalizörü Destek, Modifiye Poliol Süreci, PEM Yakıt Hücreleri

ÖZET

2004 yılından itibaren grafen, kendine mahsus özellikleri ve yapısından dolayı yoğun bir popülerlik kazanmıştır. Ancak bulk bir malzeme olarak kullanıldığında, enerji depolama ve dönüşümü için gerekli yüzey özelliklerini nadiren göstermektedir çünkü grafen nano levhalar bir araya gelerek kümelenmeler oluşturmaktadır. Elektrokatalizler, çözelti hazırlama tekniği ile sentezlenirler ve yüksek yüzey alanına ek olarak çözeltilerdeki çözünürlükleri ve işlenebilirlikleri mükemmel olmalıdır ki PEM yakıt hücrelerinde yüksek bir elektrokatalitik aktivasyon sağlamak için kullanılan platin nanoparçacıkların büyütülmesi ve homojen dağılımı elde edilebilsin. Çözüm olarak, grafen oksit preskursör olarak kullanılabilir çünkü ana yapıda ve kenarlarda bulunan ve kimyasal olarak aktive edilmiş oksijenlendirilmiş fonksiyonel gruplar, organik yapılar, biyomalzemeler ve nanoparçacıklar ile kolay bir şekilde kovalent ve kovalent olmayan bağlar kurabilirler. Bunun sonucu olarak, kimyasal

kararlılığı, ayarlanabilir modifikasyonu, yüksek elektrik iletkenliği ve birçok farklı yapıda bulunmasından dolayı fonksiyonlandırılmış grafen oksit (f-GO) birçok uygulama alanına sahip olabilir.

Bu çalışmanın ilk kısmında, grafenin negatif etkilerinden kurtulmak için grafen oksit, p-phenylenediamine (GO-NH₂) ve Gly-Arg-Gly-Asp-Ser-Pro (GO-RGD) ile başarılı bir şekilde modifiye edilmiştir ve elde edilen yapıların karakterizasyonu FTIR, Raman, XRD ve TGA ile yapılmıştır. Buna ek olarak, elde edilen f-GO malzemesi, platin nanopartikülleri daha kolay yapıya katabilmek için efektif bir elektrokatalist destekleyici olarak kullanılmıştır. Vulcan XC 72, GO ve nitrojen ile doplanmış GO kullanılarak polyol indirgeme prosesi sayesinde elde edilen yeni malzeme XRD, TGA, TEM ve CV ile karakterize edilmiştir. Pt/GO-RGD malzemesi en yüksek hidrojen tutma/bırakma pikleri göstermiştir çünkü piklerin altında kalan alanlar yük transferi için gerekli olan Pt kataliz aktif noktaların arttığını göstermektedir. Böylece ECSA değeri 147 m²/g olarak hesaplanmış ve bu değer Pt/Vulcan XC-72 (80 m²/g) den %83 ve Pt/GO (99 m²/g) den %48 daha fazladır. ECSA daki bu artış Pt nanoparçacıkların Pt/GO-RGD malzemesi içinde homojen bir şekilde dağıldığını göstermektedir. Pt/GO-NH₂ malzemesi 130 m²/g yüzel alanına sahiptir ve bu artış 3.9 nm büyüklüğe sahip Pt nanoparçacıklarının dağılımının mükemmel olduğunu göstermektedir ve TEM kullanılarak elde edilen resimler bu dağılım kanıtıdır. Bu sonuçlar; Pt/f-GO yapılı malzemelerin yüksek performanslı PEM yakıt hücreleri için ideal bir elektrokataliz olduğunu göstermektedir.

Çalışmanın ikinci kısmında ise, grafen oksit ve poliprol/karbon kullanılarak kovalent olmayan fonksiyonlaştırma yöntemi ile hibrid nanokompozitler oluşturulmuştur. Daha sonra polyol prosesi ile Pt nanoparçacıkların, GO, PPy/CB ve PPy/CB/GO malzemeleri ile üç farklı yöntem kullanılarak hibrid nanokompozitleri oluşturulmuştur. Burdaki amaç ise Pt nanoparçacıkların büyüklüğünün ve dağılımının destek malzeme üzerine etkisi ve PEM yakıt piline olana elektrokatalitik etkisini incelemektir. Tüm bu etkiler XRD, TGA, TEM, ve CV karakterizasyon yöntemleri ile incelenmiştir. Kullanılan üç farklı FeCl₃ modifiye edilmiş polyol prosesinden Method 2 en efektif method olmuştur çünkü FeCl₃ efektif bir sabitleyici olarak rol almış ve Pt parçacıkların biraraya gelerek büyümesine engel olmuştur. Method 2

kullanılarak sentezlenen Pt/PPy/CB/GO, 153 m²/g ile en yüksek ECSA sahip olmuştur ve bu değer yaklaşık olarak Pt/PPy/CB (117 m²/g) den %30 ve Pt/GO (128 m²/g) den %20 daha fazladır. Pt ile hazırlanan hibrid nanokompozit yapıların diğer destek malzemeler ile kıyaslandığında daha iyi elektrokatalitik etki göstermesinin nedeni elektriksel iletkenlikteki artış ve yük taşıyıcıların sayısındaki artış ile açıklanabilir. Yalıtkan olarak davranan oksijenli fonksiyonel gruplar, hibrid nanokompozit sentezi sırasında Pt ile kısmen indirgenmektedir ve böylece elektron ve kütle transferi için ortamdaki direnç azaltılmaktadır. Bu bilgilere ek olarak, PPy/CB yapısının GO katmanları arasına dahil edilmesi grafen katmanlarının yığılmasını kısmende olsa azaltmıştır ve sonuç olarak Pt nanoparçacıkların daha homojen dağılımı elde edilerek yüzey alanı geniş bir malzeme elde edilmiştir. Ayrıca Method 2 ile elde edilen Pt yapılı hibrid nanokompozit malzemeler PEM yakıt hücre uygulaması için ideal aday olarak görülmektedir.

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1. INTRODUCTION

Mother earth will care for us until we are good to it. We have consumed earth resources (fossil fuels) to an extent that they will vanish soon. As a consequence, our environment is too much polluted to live in and the price of everything is skyrocketing due to elevated cost of energy, making it almost impossible for a common man to survive. The current scenario accentuates to alleviate the energy crisis issues. Since research provides a vehicle in addressing these issues, some reliable alternative energy systems need to be developed for implementing at utility scale to inhibit the adversity stricken due to energy crisis, especially in the developing countries. Among these alternative energy systems, fuel cell technologies especially PEM fuel cells are very promising candidates that can provide cheap and green energy systems to the society.

1.1. Proton Exchange Membrane Fuel Cell and its Working Principle

Also known as Polymer Electrolyte Membrane Fuel Cell (PEMFC) is an electrochemical energy device that directly converts chemical energy of fuel i.e. hydrogen and oxygen into DC electrical energy [1]. At the very core of the PEM fuel cells, there is a membrane electrode assembly (MEA) which has polymer membrane e.g. nafion which acts as solid electrolyte that is impermeable to reactant gases but conducts protons. This membrane is sandwiched between two porous and electrically conductive anode and cathode electrodes called gas diffusion layer (GDL) which are usually carbon fiber paper or cloth. Electrochemical reactions takes place at the interface between the electrodes and membrane where has an electrocatalyst layer, mostly platinum supported on carbon materials e.g. carbon black. Hydrogen gas is fed from anode side which splits into protons and electrons. Protons goes through the membrane while electrons travel through the electrodes and current collectors to the external circuit. Oxygen is fed on the cathode side where it meets with the protons coming through the membrane and electrons from external circuit to form water which is discharged with excess flow of oxygen. These reactions results for flowing direct current through the external circuit [1].

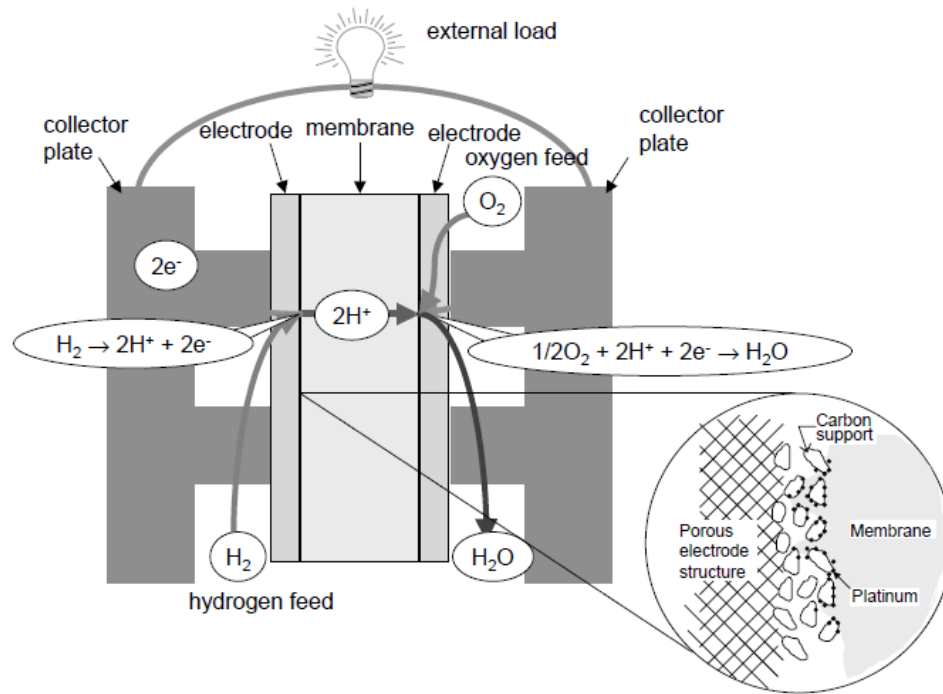


Figure 1: Working principle of PEM fuel cells [1]

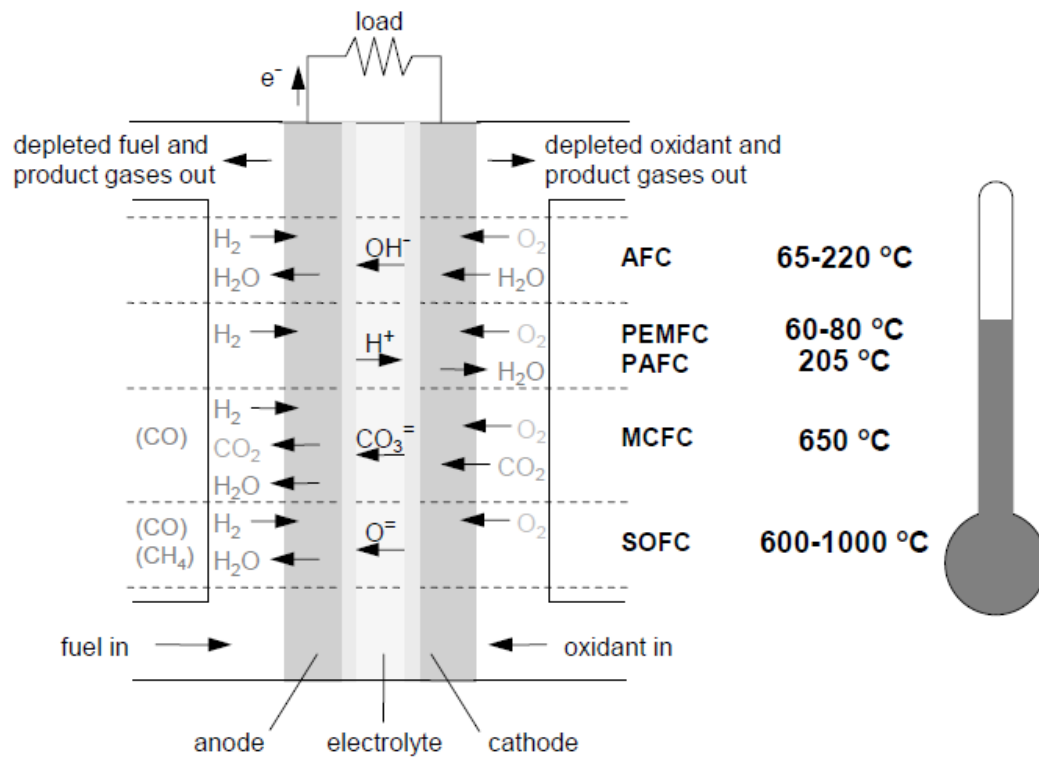


Figure 2: Different types of fuel cells, their operating temperatures and reactions [1]

Table 1: Fuel cell types, their reactions, electrolytes, catalyst, merits and demerits [4]

Fuel cell type and reaction	Electrolyte	Catalyst	Advantages	Disadvantages
AFC A: $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$ C: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	Aqueous alkaline solution (KOH)	A: Raney nickel, Pt, Pd, Ru, Rh, Pt-noble metal alloys C: Ag, perovskites and spinels, silica, carbon	Cheapest to manufacture, low-cost KOH electrolyte	Poor lifetime, intolerant to impurities in gas stream (CO_2 and CO)
PEMFC A: $\text{H}_2 \rightarrow 2\text{H} + 2\text{e}^-$ C: $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	Polymer electrolyte membrane (proton exchange membrane)	A and C: Pt/C, Pt-M alloy (M = Pd, Fe, Co, Ni, Ru)	Compact, high efficiency	Expensive catalyst, fast catalyst poisoning, H_2O management essential, H_2 storage tanks
PAFC A: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ C: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	Phosphoric acid	A and C: Pt/C, Pt-M alloy (M = Co, Al, Ce, Si, Sr, Ti, W, V)	CO_2 -tolerant (CO tolerant up to 1.5%), fuel flexibility	Low power density, aggressive electrolyte
SOFC A: $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ C: $1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$	Solid oxide (Zr, Ca) or ceramic	A and C: Ni, Rh, Ru, Ru/CeO ₂	High efficiency, long-term stability, fuel flexibility, relatively low cost	Operate on high temperature (800–1,000 °C), sulfur poisoning
DMFC A: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + 6\text{e}^- + \text{CO}_2$ C: $3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$	Proton exchange membrane	A and C: Pt/C, Pt-M (M = Ru, Au, Pd)	High energy density, ease of transport	Low efficiency, methanol hazardous, CO catalyst poisoning
DEFC A: $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 12\text{H}^+ + 12\text{e}^- + \text{CO}_2$ C: $3\text{O}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow 6\text{H}_2\text{O}$	Proton exchange membrane	A: Pt, Pt-M alloy (M = Ru, Mo, Fe, Co, Ni, Sn) C: Pt/C, Pt-Ni, Pt-Co,	Not toxic, higher specific energy (8.0 kWh/kg) compared to methanol (6.1 kWh/kg), obtainable from biomass	Catalyst poisoning, expensive catalyst
DFAFC A: $\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ C: $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	Proton exchange membrane	A: Pt-Pd, Pt-Ru C: Pt/C, Pt-M (M = Pd, Ru, Au)	Easily handled and stored, fuel does not cross the PEM, environmentally friendly	Lower energy density, expensive catalyst

1.1.1. Major Components of PEM Fuel Cells

1.1.1.1. Polymer Electrolyte Membrane

The primary function of the electrolyte includes proton conductance, electronic isolation of electrodes and separation of the reactant gases. Commercially available membrane e.g. Nafion's structure consists of tetrafluoroethylene and sulfonyl fluoride vinyl ether which brings long term stability. When the membrane is hydrated, proton conducting channels are formed which are facilitated by the sulphonic groups of the polymer which in turn increases its protonic conductivity to a certain level of water content. After this water tolerance limit is reached, conductivity starts to deteriorate [2].

Nafion is suitable for low temperature operation in PEMFC i.e. less than 80 °C after which its degradation starts happening. Alternatively, high temperature resistant membranes e.g. polybenzimidazole (PBI), sulfonated polyethersulphone (PES) or polyetheretherketone (PEEK) membranes can be used to increase the reaction kinetics of electrodes and decrease the carbon monoxide poisoning effect.

Main features of polymer electrolyte e.g. Nafion and other fluorosulphonate ionomers include high chemical resistance, mechanical strength, flexibility, thinness, acidic in nature, absorbance of large quantities of water which allows free protonic conductivity. [3]

1.1.1.2. Electrodes

Platinum is most widely used electrocatalyst material for both the anode and cathode electrodes which is usually supported on Carbon based materials to get good dispersion, increased surface area and reduced amount of Platinum e.g. 0.2mg of Pt per cm². This catalyst layer can be applied on the gas diffusion layer or membrane, for example by spraying, brushing, etc. [2].

1.1.1.3. Gas Diffusion Layer

GDL can be carbon fiber paper or carbon cloth which has porous morphology. It should have good electronic contact with the bipolar plates and should be hydrophobic in nature. One side of GDL is in contact with the flow channels of bipolar plates to effectively transport the reactant gases to the electrocatalyst layer on the other side while providing minimum electronic resistance [2].

1.1.1.4. Bipolar Plates

Bipolar plates supplies and distribute the reactant gases to the GDL through its flow channels which cover the entire area of GDL for equal distribution of gases. The material is usually graphite because its light weight, stable and less corrosive but it's hard and expensive to manufacture the flow channels for large scale productions. The other purpose of the bipolar plates is to provide electrical connection between the individual cells [2].

1.1.2. Platinum Deposition Methods

Platinum, a precious metal and good catalyst for various chemical and electrochemical reactions, can be deposited either by chemical or electrochemical method. In the latter method, the operating parameters such as pH, temperature and current density can affect the structure of the deposited material to get different particle size and surface morphology. Thus the reduction of the precursors into metallic state nanoparticles has been a focus in material science. [5]

In **electroless deposition or chemical method**, the metal precursor is chemically reduced in a controlled way to obtain a desired coating on to the substrate. The reducing agent supplies the electrons for the reduction process and redox reaction sites are inseparable.

In **electrochemical deposition**, the desired metal precursor in aqueous solution is electrolyzed to obtain thin metallic coating on the surface of another metal. The external current is supplied for the reduction to occur and redox reaction sites are separable. These redox reactions take place on the catalytically active surface of platinum. [5]

Table 2: Nature of reactions and their sites occurring in electrochemical and chemical depositions [5]

Property	Electrochemical deposition	Chemical deposition
1. Driving force	External power supply	Reducing agent [RA] and auto-catalytic property of the deposited metal
2. Cathode reaction	$M^{n+} + ne^- \rightarrow M$	$M^{n+} + RA \rightarrow M$
3. Anodic reaction	$M - ne^- \rightarrow M^{n+}$	$RA - ne^- \rightarrow [RA]_{\text{Oxidized form}}$
4. Overall reaction	$M_{\text{anode}} \rightarrow M_{\text{cathode}}$	$M^{n+} + RA \rightarrow M + [RA]_{\text{Oxidized form}}$
5. Anodic site	Anode itself	Work piece
6. Cathodic site	Work piece	Work piece

1.1.3. Catalyst Support Materials

Platinum is scarce and expensive material. Since it's required for oxygen reduction reaction at cathode of PEM fuel cells, there is a need to either replace the platinum or provide catalyst support that can enhance its performance [5]

At the cathode of PEM fuel cell, the oxygen reduction reaction (ORR) can either proceed by fast procedure i.e. by directly combining oxygen with four electrons and protons to form water or by slow two step procedure which involves formation of hydrogen peroxide ions as an intermediate step which reduces the reaction kinetics. Platinum nanoparticles are good catalyst for ORR but has several demerits such as deactivation by CO poisoning, low durability and high cost. [6]

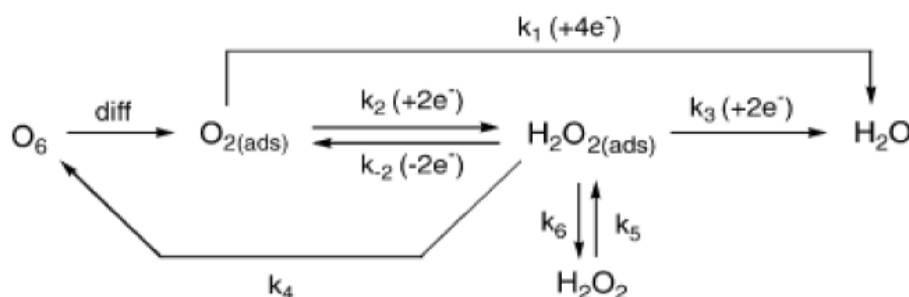


Figure 3: Damjanovic's oxygen reduction reaction (ORR) mechanisms for noble metal electrocatalyst in PEM fuel cells.

Catalyst supports are known to reduce the metal loading and increase the catalyst activity with high durability. However, different properties of these supports e.g. surface area, electrical conductivity, corrosion resistance, mechanical strength and pore structure affect the performance of the catalysts in PEM fuel cells.

For instance, among carbon based catalyst supports, Vulcan XC-72 has high surface area ($237 \text{ m}^2/\text{g}$) but the microporous structure ($<2\text{nm}$) tends to sink the catalyst nanoparticles making them less electrochemically active due to poor accessibility of reactant gases and insufficient formation of the triple phase boundaries which drastically reduces the catalytic activity. Moreover, Vulcan XC-72 has high electrical conductivity (4 S/cm) which ensures increased catalytic activity of catalyst but it is also known to be less durable i.e. less mechanically strong and corrosion resistant as it forms surface oxides at the cathode side of PEM fuel cells during electrochemical oxidation due to which the platinum nanoparticles either loss or aggregate, resulting in decreased performance of the catalyst [6].

Therefore, new support materials with improved properties are being investigated to replace carbon blacks. For instance, carbon nanotubes (CNTs) are promising support materials for PEM fuel cells. Most of the drawbacks of Vulcan XC-72 are overcome by CNTs which provides higher surface area enabling high and uniform dispersion of catalyst nanoparticles while avoiding sinking of catalyst nanoparticles into the micropores due to their higher mesoporosity which facilitates the formation of triple phase boundaries. Also, CNTs support, with their higher electrical conductivity and corrosion resistance for durability, can improve the catalytic activity of catalyst and hence the performance of PEM fuel cells. However, the production cost of CNTs is still a barrier in its commercialization [6].

Graphene oxide (GO) has unique properties (discussed in detail in following sections) such as high surface area which make them particularly appealing for supporting and uniformly dispersing nanoparticles of platinum which is non-covalently immobilized on the basal plane which enhances its electrocatalytic activity due to reduced aggregation [9]. Also, the conductive GO sheets anchor platinum nanoparticles on the electrode surface providing better electron transfer and mass transport of reactants to the electroactive region [8].

Table 3: Comparison of properties of Graphene and CNTs [6]

Properties	Graphene	CNTs
Fracture strength (GPa)	≈ 124 (Modulus: ≈ 1100 GPa)	45
Density (g cm^{-3})	>1	1.33
Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	≈ 5000	3000
Electrical Conductivity (S cm^{-1})	10^6	5000
Charge mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	200 000	100 000
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	2630	400 (for nano-tube "paper")

1.2. GRAPHENE OXIDE AND ITS FUNCTIONALIZATION

1.2.1. Graphene: Properties and Synthesis

Since 2004, graphene has gained immense popularity due to its unique 2D structure and properties. It has sp^2 bonded crystalline carbon structure with thickness of one atomic layer. It depicts extraordinary physiochemical properties such as very high theoretical surface area for single layer ($2630 \text{ m}^2/\text{g}$), high charge mobility ($20000 \text{ cm}^2/\text{V.s}$), high mechanical strength (Young's modulus of 1 TPa), and excellent thermal (5000 W/m.K) and electrical conductivities (10^6 S/cm) etc. [8, 9].

Graphene can be synthesized by various techniques such as chemical vapor deposition on metal surfaces, mechanically splitting graphite by scotch tape method, epitaxial growth on single crystal SiC, chemical coupling reactions, chemically exfoliating graphite powder by solution oxidation, ultrasonication/intercalation or ball milling [9].

1.2.2. Functionalization of Graphene

Since graphene as a bulk material, rarely depicts surface properties needed for various applications, so controlled functionalization of the edge and basal plane is needed for which different covalent and noncovalent chemistries have been designed to modify the surface properties that can utilized in energy conversion and storage applications [9].

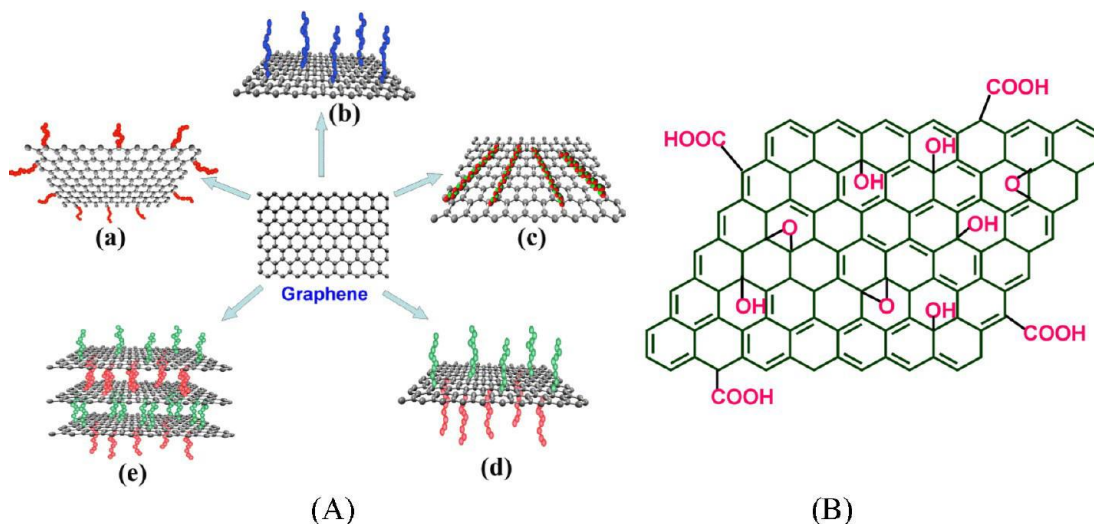


Figure 4: Left (a) functionalization of the edge, (b) functionalization of the basal plane, (c) non covalent adsorption on the basal plane, (d) asymmetrical functionalization of the basal plane, (e) functionalized graphene sheets self-assembly, (f) and Right graphene oxide chemical structure [9]

The above figure shows different possibilities for functionalizing graphene sheets at molecular and supra molecular scale. The dangling bonds at the edges of the graphene sheet arising from the highly delocalized π electrons are more reactive than the basal plane formed by the strong covalent bonding among the sp^2 hybridized carbon atoms. Different chemical moieties can covalently bond with these dangling bonds at the edges to increase solubility, film forming ability, and increase reactivity for more chemical functionalization. However the covalent functionalization of the basal planes, the π - π conjugation becomes distorted causing deterioration of the physical and chemical properties. Sometimes, non-covalent functionalization of the basal plane is favored as it does not change the basal plane's structure. Functionalizing the top and bottom of an individual graphene sheet asymmetrically, with different moieties results in graphene sheets self-assembling [9].

1.2.3. Graphene Oxide and its Structure

Pristine graphene sheets cannot be functionalized because of poor solubility and processability which limit them to certain applications. To overcome this problem, graphene oxide (GO) and edge functionalized graphene (EFG) derived from the exfoliation of graphite powders, have emerged as possible precursors for functionalization of graphene.

Graphene oxide has reactive carboxylic acid groups at the edges and epoxy and hydroxyl groups on the basal planes [9]. Due to these oxygen functional groups with structural defects in the basal planes, GO demonstrates higher chemical reactivity than pristine graphene. These chemically reactive oxygen functional groups give opportunity for chemical functionalization with other groups or materials. Further, GO can be reduced to graphene by reducing agents, thermal annealing or electrochemical techniques [8].

1.2.4. Functionalization of Graphene Oxide and its Techniques

GO can be functionalized by many functional materials like organic compounds, biomaterials, polymers and nanoparticles and these functionalized GO have many applications because of interesting properties such as chemical stability, tunable modification, high electrical conductivity and multifunctional structures [8].

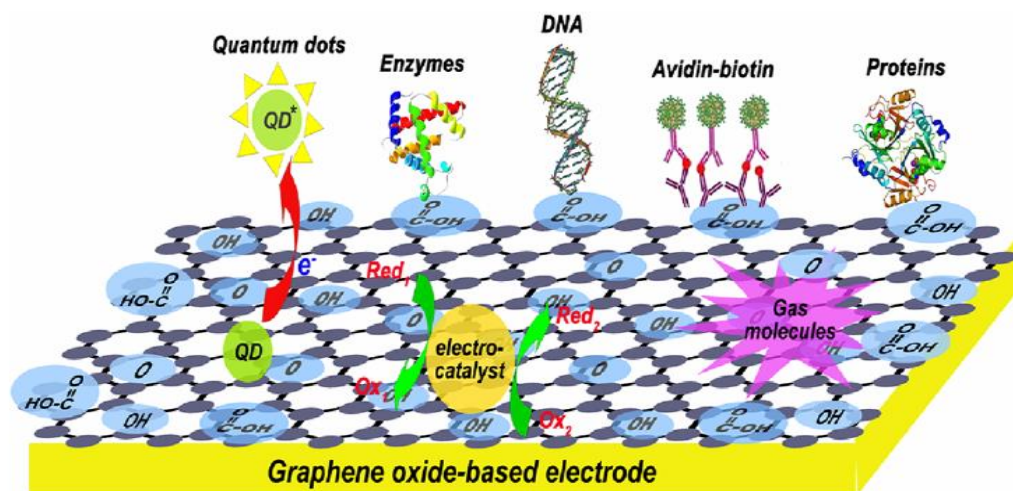


Figure 5: GO based electrodes for various electrochemical applications [8]

1.2.4.1. Covalent Functionalization of Graphene Oxide

Small molecules or polymer can be used to covalently functionalize the carboxyl or hydroxyl groups on GO by activation and amidation/esterification via coupling reactions. Also, amine can be used to covalently functionalize the epoxy groups on GO by nucleophilic attack at the α -carbon via ring opening reactions. [8]

For example, GO can be functionalized with **organic compounds** to improve its solubility and processability in water and organic solvents. The resulting durable hybrid materials can be applied in different electrochemical applications. In covalent functionalization of GO, the organic compound diffuses on the surface of GO and reacts with oxygen-containing functional groups to chemically modify the surface [8].

Also, GO has excellent biocompatibility which means it can incorporate **biomolecules** to increase the electrochemical reactivity and rate of electron transfer of biomolecules. Amine groups on the biomolecules can covalently attach to the hydrophilic oxygenated functional groups of GO such as carboxylic acid [8].

A lot of surface modification techniques have been developed to improve GO or RGO dispersibility and to avoid irreversible aggregation of sheets through surface functionalization. Non-covalent techniques to functionalize GO/RGO with metal oxides, conducting polymers, etc. have some demerits like molecules slippage, difficult to control and unstabilty. Hence, covalent functionalization of GO/RGO is more promising technique to overcome the issues [15].

Since reduced GO (RGO) tends to irreversibly agglomerate or restack through van der Waal interactions among the individual sheets and loose the unique properties. This can be avoided by dispersing RGO in polar organic solvents such as DMF, NMP, etc. but RGO has poor solubility in non-polar organic solvents like toluene which limits its application areas [10].

To overcome this issue, Jang, Jinhee et al. [10] functionalized GO with **alkylamines** like octylamine, dodecylamine and hexadecylamine and found out that all of these were very well dispersible in organic solvents. The amine groups of alkylamines reacted with the epoxide groups present on the basal planes of GO and carboxylic groups on the edges of GO. After reduction with hydrazine, the alkylamine with the shortest chain exhibited best electrical conductivity. The as-synthesized RFGO could be utilized in various applications due to their high solubility and processibility.

Yang, Xuyu et al. [11] reported similar (as above) alkylamine functionalization of GO then reducing it to RGO to make it compatible with non-polar organic polymer e.g. polyolefins to synthesize alkylamine functionalized RGO/low density polyethylene nanocomposites via solution blending. The results showed that the dodecylamine functionalized RGO/LDPE has the best mechanical properties and thermal stability.

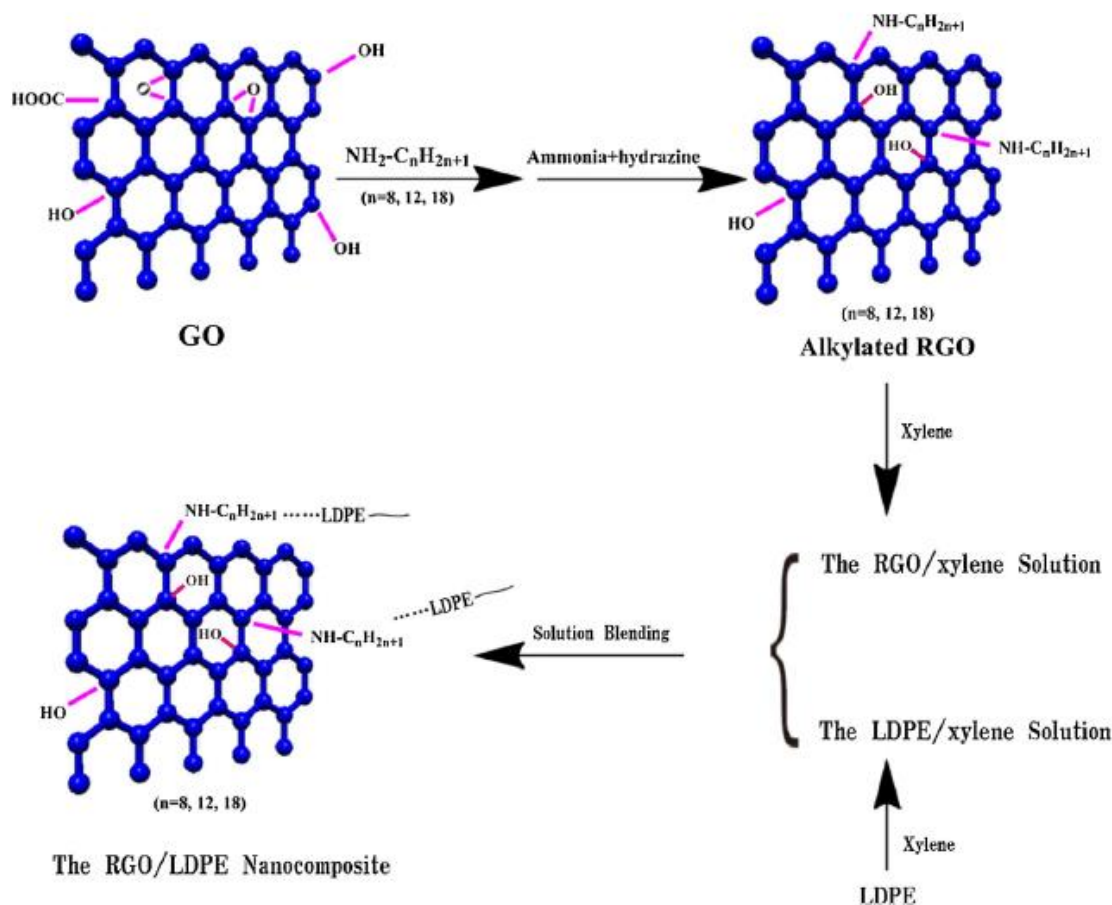


Figure 6: Alkylamine functionalized RGO/LDPE nanocomposite [11]

Yang, Huafeng et al. [12] utilized dicyclohexylcarbodiimide (DCC) as catalyst and coupling agent to covalently react amino group of 3-aminopropyltriethoxysilane (APTES) with the epoxy groups present on the GO basal plane and carboxylic groups on the edges to expose Si-O-R while functionalizing GO to increase dispersibility of graphene sheets. However, the exposed groups are relatively inactive to anchor foreign materials like biomolecules, metal nanoparticles etc. or to graft organic materials like polymers on GO nanosheets.

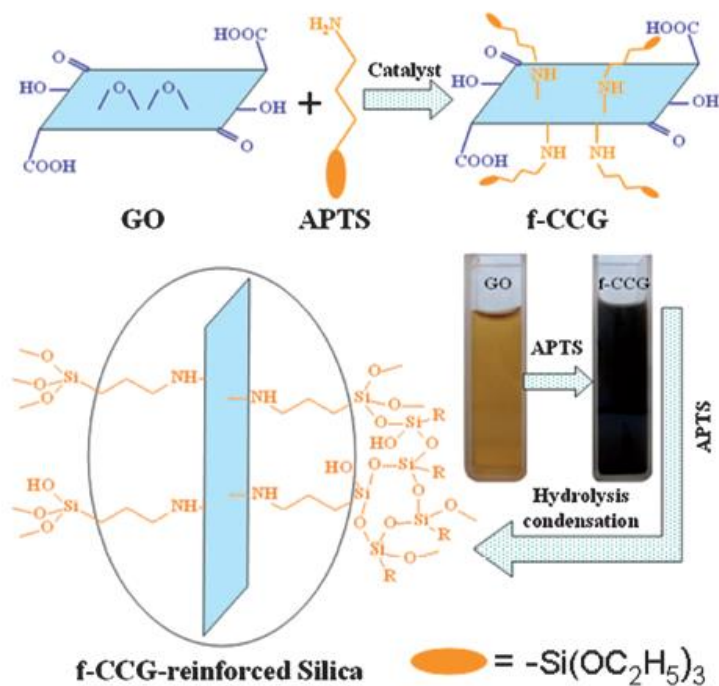


Illustration of the reaction between GO and 3-amino-propyltriethoxysilane (APTS), and incorporation of f-CCG sheets into the silica matrix. R = $-\text{OH}$ or $-\text{CH}_2(\text{CH}_2)_2\text{NH}_2$.

Figure 7: APTS functionalized GO with Si-O-R exposed [12]

Liu, Zhiting et al. [13] instead exposed nucleophilic amino groups of APTES by using one pot hydrothermal method which can find wide range of applications which were not possible by exposed inactive Si-O-R of APTES functionalized GO. In this method, water first reacted with ethoxy groups of APTES generating silanols which further reacted with hydroxyl groups of GO to dehydrate and expose free amino groups of APTES. Further thermal reduction caused polycondensation of APTES silanols to form siloxane network which prevented aggregation of graphene nanosheets.

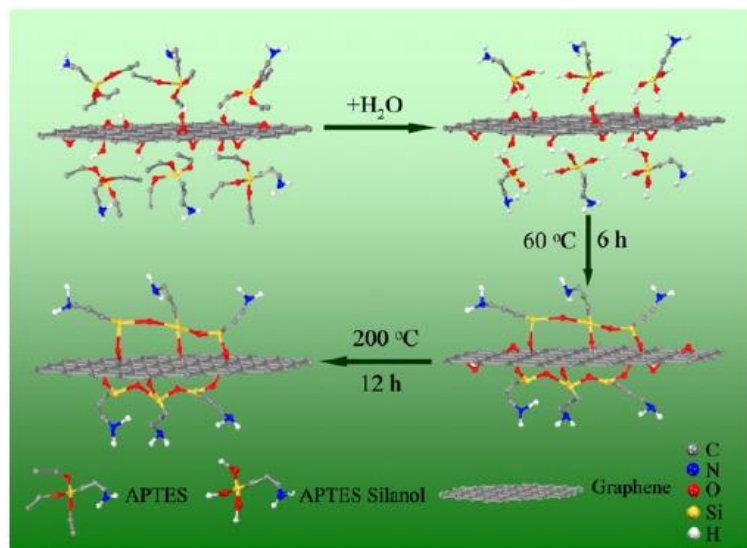


Illustration of the synthesis route of A-FGs. For clarity, minor functional groups, e.g. carboxyl groups and carbonyl groups, have been omitted at the edges.

Figure 8: APTS functionalized GO with NH_2 exposed [13]

Mallakpour, Shadpour et al [14] used different **aromatic and aliphatic amino acids** to covalently bio-functionalize GO by nucleophilic substitution and condensation reactions between amine group and carboxylic/epoxy groups of GO. The structure, functional groups and chain lengths of these amino acids had different effects on the structure and morphology of the amino acid functionalized GO which resulted in better dispersibility in organic solvents.

Aryl groups are known to improve conductivity of graphene. Liu, Zanhui et al. [15] produced reduced graphene oxide – poly p-phenylenediamine (PPD) composite. GO was reacted with thionyl chloride (GO-COCl), then p-phenylenediamine was covalently functionalized on GO-COCl through amidation reaction. Then it was polymerized using ammonium persulphate and reduced with sodium borohydride to get RGO-PPD composite. TEM results showed that PPD nanoparticles incorporation on the RGO surface with increased interlayer spacing in RGO-PPD composite as compared to RGO due to which it showed enhanced performance in supercapacitors.

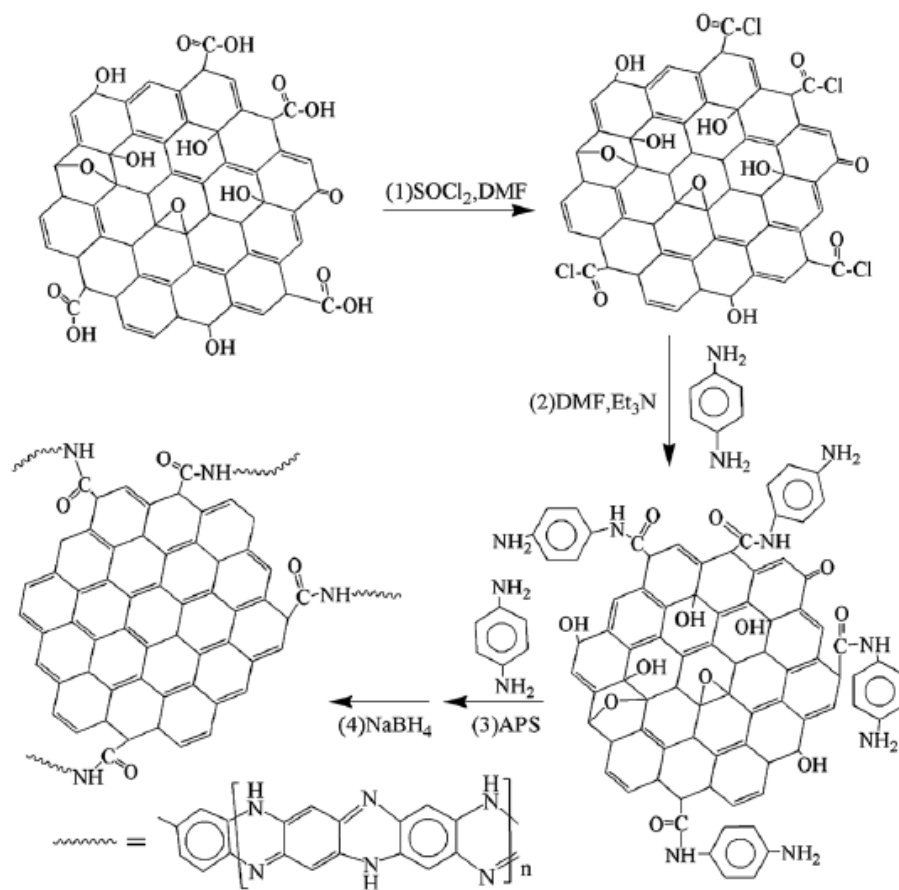


Figure 9: Synthesis of RGO-PPD composite [15]

Lu, Y et al. [16] also employed the same aromatic organic molecule p-phenylenediamine (PD) as spacer and nitrogen source to functionalize and dope GO simultaneously, by one-step solvothermal which resulted in high specific capacitance and cyclic stability process for supercapacitors application.

Since nitrogen doping is known to introduce chemically active sites for anchoring metal nanoparticles to enhance catalytic reactions, Jafri, R. Imran et al. [17] reported nitrogen doped graphene prepared by thermal solid state and hydrothermal method as catalyst support for dispersing platinum nanoparticles using polyol method with MWCNTs as spacers to avoid aggregation of graphene nanosheets and studied their oxygen reduction reaction (ORR) for PEM fuel cells and methanol oxidation reaction (MOR) and found that these Pt/N doped graphene performed better than commercial Pt/C.

Zhang, Xiang et al. [18] covalently grafted arginine-glycine-aspartic (RGD) acid peptide on to surface of apatite/wollastonite (AW) ceramic with synthesized silane coupling agent APTS-E and synthetic cross linker 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) in two step chemical reaction process. First APTS-E was covalently attached to AW surface by silanization reaction via free hydroxyl groups to expose carboxyl groups on the surface. Then immobilizing linear RGD peptides on to the surface of AW-E with EDC which resulted in improved cell adhesion and proliferation.

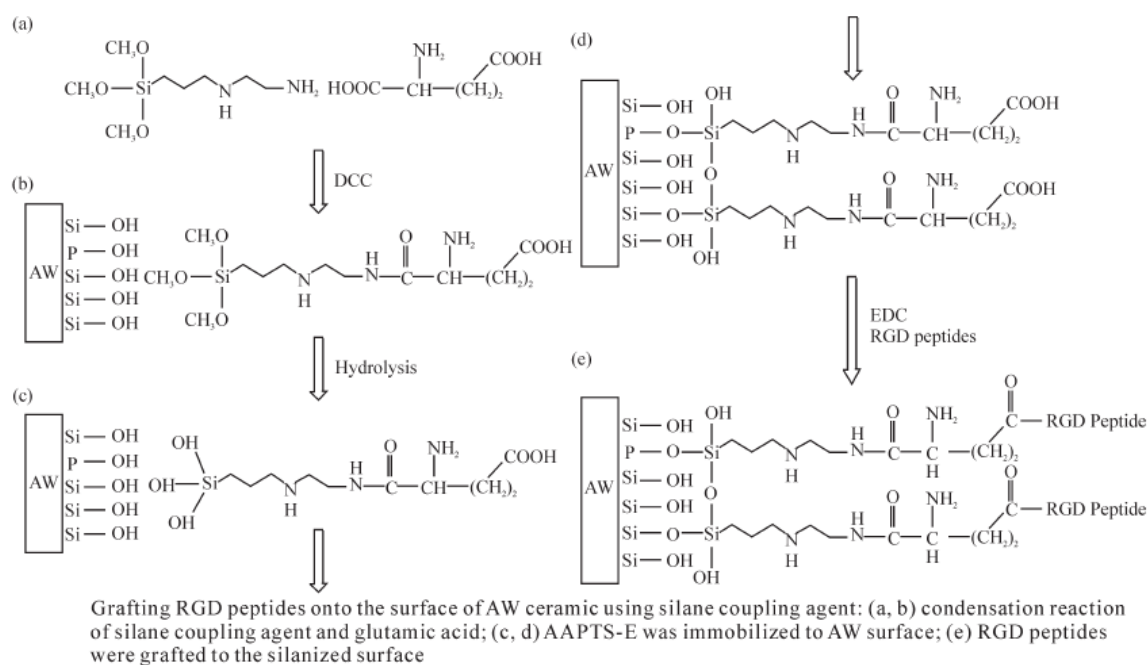


Figure 10: Grafting RGD peptides onto the surface of AW ceramic [18]

1.2.4.2. Non-Covalent Functionalization of Graphene Oxide

Non covalent functionalization of GO can be achieved by π - π stacking, cation- π , van der Waals interactions, or hydrogen bonding [8]. For example, in non-covalent functionalization, **organic aromatic compounds** are strongly adsorbed on the GO sheets by π stacking and hydrophobic interactions between GO and organic molecules. Other example is the **biomolecules** which can be non-covalently immobilized on to the GO sheets by physical

entrapment or adsorption. This can be done by incorporating biomolecules in GO suspension which results in non-covalent interactions.

Guo, Chun Xian et al. [19] used single strands of biological molecule deoxyribonucleic acid's (DNA) base pairs to non-covalently functionalize graphene surface through π - π conjugation which eliminated graphene sheets' agglomeration and improved dispersion to uniform distribute and support palladium nanoparticles on graphene by polyol process for direct formic acid fuel cells. The Pd-DNA@graphene showed high electrochemical surface area as compared to Pd-graphene.

1.2.4.3. Doping of Graphene Oxide

Metal free catalyst can substitute platinum for ORR at cathode. This can be done by doping the basal plane of graphene with heteroatoms during graphene synthesis (in-situ doping) or after (post doping). Post treatment with precursor containing heteroatoms, for instance, ammonia for nitrogen doping, results in surface functionalization only whereas the in-situ doping results in homogeneous distribution of heteroatoms into the basal plane. These doping cause electron modulation to provide electronic structure (due to intramolecular charge transfer) that results in good ORR performance without CO poisoning effect and better catalytic activity with long term stability in alkaline medium than the commercial Pt/C catalysts [9]

1.3. GRAPHENE OXIDE – CONDUCTING POLYMER NANOCOMPOSITE

1.3.1. Conducting Polymer

Conducting polymers combine the electronic properties of metals and mechanical properties and processibility of conventional polymers due to which they are also known as synthetic metals. Typical examples are poly (p-phenylene), polythiophene, polyaniline and polypyrrole. Conducting Polymers have polyconjugation in the π -system of their backbone structure [7].

1.3.1.1. Doping of Conducting Polymer

With doping in their matrix, they acquire high conductivity in the range of semiconductors or metals (1 to 10^5 S/cm). The p-doping or n-doping can be done by chemical/ electrochemical oxidation or reduction, respectively, due to which their polymeric chains acquire positive or negative charges. As a whole, their electro-neutrality is preserved by the dopants counterions. The process of doping is reversible and can be adjusted to get the electrical conductivity ranging from no conductivity to very high conductivity. Due to these properties, they have been used in wide variety of fields e.g. electrode materials for energy storage and conversion, electrocatalyst, etc. [7]

1.3.1.2. Polypyrrole and its Synthesis

Polypyrrole is one of the representatives of the conducting polymers with unique features such as ease of synthetic procedures, availability of initials monomers, high conductivity, stability in oxidized state and interesting redox properties.

It can be synthesized by **chemical polymerization** by oxidizing its monomers with chemical oxidants to form black powder. Several parameters such as dopants, choice of solvent (water, methanol, etc), oxidants Fe(III) or Cu(II), initial pyrrole/oxidant ratio (optimal ratio 1:2.4),

duration (shorter times) and temperature (0 to 5 °C) of reaction can positively affect the yield and conductivity of the polypyrrole produced [7].

The other synthesis method is **electrochemical polymerization** which has several advantages over the former synthesis method, for instance, the resulting product is in the form of highly conductive and electroactive thin film on to the electrode surface. Moreover, yield can approach to 100% providing the ability to control thickness and mass of the deposited film while controlling the properties of the film during preparation. Electropolymerization of pyrrole can be done by various methods including galvanostatic, potentiostatic, potentiodynamic and pulsed one. The resulting films' mechanical properties, surface morphology and electrochemical behavior depend upon various factors such as solvent, electrolyte pH, electrolytic salt, initial monomer purity and concentration [7].

1.3.2. Graphene Oxide – Polypyrrole Nanocomposite and its Synthesis

Combination of two or more components namely, a selected filler or reinforcing agent and a compatible matrix binder which results in formation of a new material with specific characteristics and properties. If dimensions of one of the constituents lies below 100nm, then it's called **nanocomposite**. These nanocomposites exhibit different mechanical, electrical, optical, electrochemical, catalytic, and structural properties than those of the individual components.

GO based conducting polymer nanocomposites are promising new materials for electrochemical applications since they show properties which cannot be achieved with the individual components alone such as high electrical conductivity, chemical stability, etc. The improvement in the properties depends upon various parameters such as type of polymer, morphological organization, interface control, and the level of dispersion of nanofillers inside the matrix. Usually very low loadings of GO nanofillers are incorporated into the polymer matrix without the agglomeration [8].

Generally, there are two routes of preparing such nanocomposites. **In-situ intercalative polymerization** involves swelling GO in the liquid monomer and then some initiator is used to start polymerization under some reaction conditions e.g. **in-situ chemical or electrochemical polymerization**. The other method is called **solution intercalation** involves sonication or mechanical agitation to disperse and swell GO sheets in polymer solution. The result is the adsorption of polymer onto the GO sheets. When the solution is evaporated, the polymer is sandwiched between the reassembled sheets of GO, forming nanocomposites [8].

When graphene is non-covalently functionalized by polymers by weak interactions, there is rather no change in the electronic properties and basal plane of graphene. The resulting polymer adsorbed onto graphene sheets shows better ORR electrocatalytic activity due to intermolecular charge transfer phenomenon [9]. For instance, Bose, Saswata et al. [20] prepared graphene oxide/polypyrrole nanocomposite by in-situ chemical polymerization and employed hydrazine monohydrate for chemical reduction of GO. The structural analysis revealed removal of oxygen containing groups and increased number of sp^2 domains which resulted in better electrical conductivity and thermal stability.

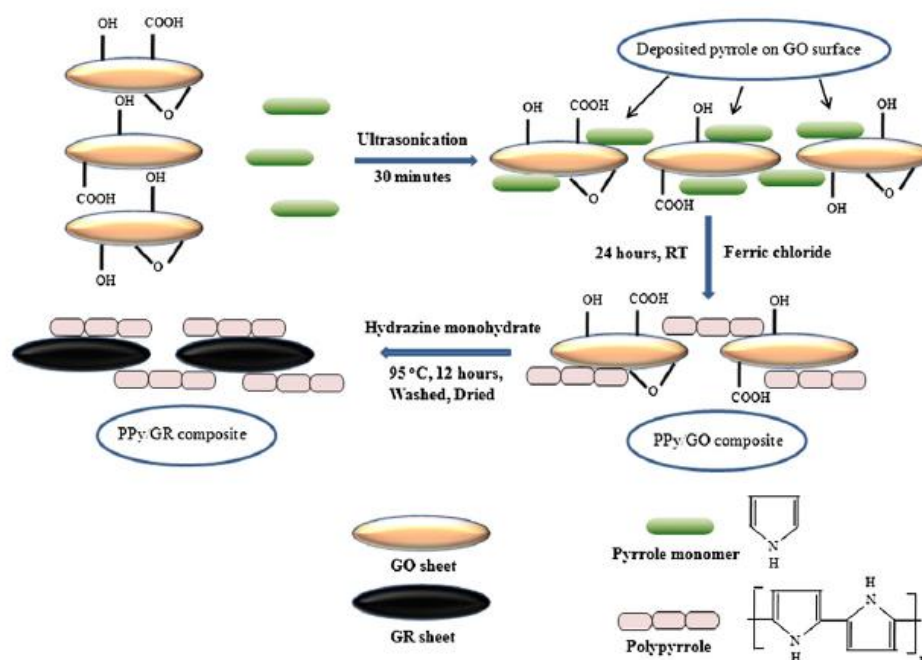


Figure 11: Synthesis of polypyrrole/reduced graphene oxide by chemical polymerization [20]

Memioğlu, Fulya et al. [21] reported **polypyrrole/carbon composite** prepared by in-situ chemical oxidative polymerization of pyrrole monomer on carbon black while investigating effects of different dopants such as p-toluenesulphonic acid and sodium dodecyl sulfate and reaction temperatures on the properties of the composites. The results showed that PPy/C composites prepared at 0 °C with p-TSA as dopant has higher oxidation resistance than carbon for **fuel cell** applications. Similarly, Zhao, Hongbin et al. [22] prepared Vulcan XC-72 carbon/polypyrrole catalyst support by in-situ chemical polymerization at room temperature in the presence of ammonium persulfate as oxidant and naphthalene sulfonic acid solution for doping. Further depositing platinum nanoparticles by sodium borohydride. The resulting Pt/PPy/CB doped with NSA was used as an anode to test hydrogen and methanol oxidation for fuel cells which showed better catalytic activity than Pt/C which can be attributed to higher electronic conductivity, electroactive surface area and better charge transfer at conducting polymer/carbon interfaces with well dispersed platinum nanoparticles.

Yang, Sudong et al. [23] prepared **graphene oxide/polypyrrole nanocomposite** (2:1 by weight) catalyst support by in-situ chemical oxidation polymerization. Further palladium nanoparticles were loaded by microwave assisted polyol process. The resulting electrode exhibited high catalytic activity and stability for the application of formic acid electro-oxidation. Jiang, Shu et al [24] synthesized graphene oxide/polypyrrole nanocomposite by in-situ chemical polymerization and further incorporated cobalt (II) nitrate on the nanocomposite by annealing heat treatment to make non-precious metal based ORR electrocatalyst (Co-N-GN) in alkaline solution which showed better electrocatalytic activity as compared to commercial Pt/C electrocatalyst. Kumar, G Gnana et al. [25] synthesized polypyrrole/reduced graphene oxide by in-situ polymerization and bioreduction techniques for durable and improved microbial **fuel cell** performance.

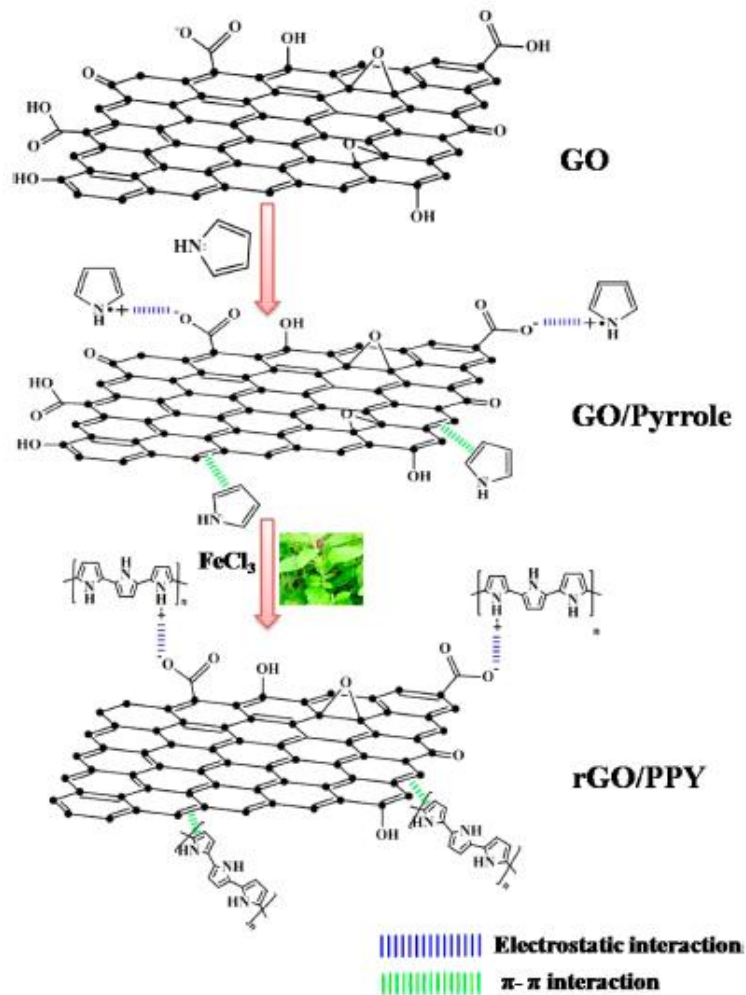


Figure 12: Polypyrrole/reduced graphene oxide synthesis and their interactions [25]

Zhang, Dacheng et al. [26] prepared **graphene/polypyrrole nanocomposite** by in-situ polymerization of pyrrole monomer on graphene under acidic conditions for application in supercapacitors which outperforms pure polypyrrole in terms of specific capacitance, rate capability and cyclic stability which can be attributed to hydrogen bonding and π - π stacking interactions between polypyrrole and graphene. Wang, Jingping et al. [27] worked on reduced graphene oxide and polypyrrole synthesized by in-situ galvanostatic polymerization for **supercapacitors** with high power density. The nanocomposite electrode exhibited high capacitance attributed to its porous structure having high protonation level on PPy ring while having improved cyclic stability due to incorporation of rGO.

Lim, Su Pei et al. [28] worked on **reduced graphene oxide/ polypyrrole nanocomposite** supported on ITO conducting glass as platinum free counter electrode synthesized by in-situ electrochemical polymerization for **dye sensitized solar cell (DSSC)**. The energy conversion efficiency of as prepared electrode was comparable to the high cost DSSC with platinum counter electrode. Chen, Lijia et al. [29] also worked on DSSC but doped graphene quantum dots (GQD) on polypyrrole on F-doped tin oxide glass. The as-synthesized electrode had porous structure with higher catalytic current density and lower charge transfer resistance towards I_3^-/I^- redox reaction than the densely packed pure PPy. The power conversion efficiency of 10% doped GQDs on PPy counter electrode was found to be comparable to Pt based counter electrode for DSSC. These studies suggest graphene oxide based polypyrrole nanocomposites have wide range of electrochemical applications which can be extended to PEM fuel cells also.

1.4. Aim of the Research

Graphene has gained immense popularity due to its unique 2D structure and properties but graphene as a bulk material, rarely depicts surface properties needed for various applications, so controlled functionalization of the edge and basal plane is needed for which different covalent and noncovalent chemistries have been designed to modify the surface properties that can utilized in various energy conversion and storage applications [9].

Since, pristine graphene sheets cannot be functionalized because of poor solubility and processability which limit them to certain applications. Graphene oxide (GO) can act as a precursor which has carboxylic acid groups at the edges and epoxy and hydroxyl groups on the basal planes [9]. These chemically reactive groups give opportunity for chemical functionalization with many functional materials like organic compounds, biomaterials, polymers and nanoparticles. As a result, functionalized GO have many applications because of their interesting properties such as chemical stability, tunable modification, high electrical conductivity and multifunctional structures [8].

Therefore, the first aim of our research is the modification of graphene oxide via covalent functionalization with novel functional reagents (p-phenylenediamine and Gly-Arg-Gly-Asp-Ser-Pro) which is expected to eliminate irreversible aggregation of graphene nanosheets to improve its solubility, dispersion and processibility in water and organic solvents. Subsequently, utilizing these functionalized GO as effective electrocatalyst supports for anchoring platinum nanoparticles using the well-known polyol reduction process along with Vulcan XC-72, GO and N doped GO for comparison purposes by different characterization techniques for the application of PEM fuel cells. This concludes the first part of our work.

The second aim of our research is the modification of graphene oxide via non-covalent functionalization with incorporation of conducting polymer/carbon nanocomposite by solution intercalation to yield hybrid nanocomposite. Subsequently, Pt nanoparticles are reduced on the catalyst supports i.e. graphene oxide (GO), polypyrrole/carbon black nanocomposite (PPy/CB) and polypyrrole/carbon black/graphene oxide hybrid nanocomposite by three different methods based upon modified polyol process to see their effects on the size of Pt nanoparticles, their dispersion on supports and electrocatalytic activity by different characterization techniques for the application of PEM fuel cells. This concludes the second part of our work.

2. FUNCTIONALIZATION OF GRAPHENE OXIDE AS CATALYST SUPPORT

2.1. EXPERIMENTAL

2.1.1. Materials

Flagship Graphene Oxide (GO), Carbon Black Vulcan XC-72R (CB), Dichloromethane (DCM, 99.8%), N,N'-Dicyclohexylcarbodiimide (DCC, 99%), p-Phenylenediamine (PPD, 99%), Gly-Arg-Gly-Asp-Ser-Pro (GRGDSP, 97%; RGD Peptide Content 60%), Chloroplatinic acid hexahydrate (Pt Precursor, 37.5% Pt Basis), Sulfuric Acid (98%), Nafion® perfluorinated resin solution (20 wt. % in mixture of lower aliphatic alcohols and water, contains 20% water), Nafion® perfluorinated resin solution (5 wt. % in mixture of lower aliphatic alcohols and water, contains 15-20% water), Ethylene Glycol (EG, 99.8%), N,N-Dimethylformamide (99%) and Ethyl Alcohol (99.5%) were purchased from Sigma Aldrich. Carbon Paper (AvCarb MGL190 μm) was purchased from Fuel Cell Store while Nafion® PFSA NR211 membrane from Fuel Cell Earth. Deionized Water (18.2M Ω -cm, Milli-Q Reference) was used in all the experiments. All the chemicals were used without further purification.

2.1.2. Methods

2.1.2.1. Synthesis of Functionalized Graphene Oxide

For functionalization of graphene oxide (GO) with p-phenylenediamine (**GO-NH₂**) and gly-arg-gly-asp-ser-pro (**GO-RGD**), commercial GO (500mg) was ultrasonically dispersed in dichloromethane (150mL) for 1 hour in icy water to avoid evaporation of solvent and then mixed with N,N'-dicyclohexylcarbodiimide (100mg) which acted as a catalyst. Subsequently p-phenylenediamine (5g) and gly-arg-gly-asp-ser-pro (5g) were mixed with the homogeneous mixture above respectively. The reaction was continued for 48 hours with constant stirring (300rpm) and heating (60⁰ C). After the completion of the reaction,

dichloromethane was evaporated. The resulting mass was washed and centrifuged with ethanol (thrice) and then dried for 24 hours at 70⁰ C in an oven.

The ammonia doping of graphene oxide (**GO-N Doped**) was pursued through a multi-step thermal treatment of the GO. This process result a synergistic effect of higher layer-exfoliation in the material as it undergoes thermal reduction as well as chemical functionalization during a single in-situ process. During the doping process, GO was poured into zirconium cuvettes into a quartz tube furnace. The passing atmosphere was set to be composed of a mixture of 9:1 argon to ammonia gas, respectively. A combination of heating ramps accompanied with two isotherm steps were optimized for operation on the material during the preparation. The detailed process includes heating the sample up to 500°C, an isotherm step at the mentioned temperature for 10 minutes, a heating ramp up to 900°C, and the final isotherm step at 900°C for another 10 minutes was conducted. After heating at this desired temperature for 10 min the furnace was cooled down in NH₃. The samples were taken out of the tube reactor after the furnace temperature was below 50°C. [5]

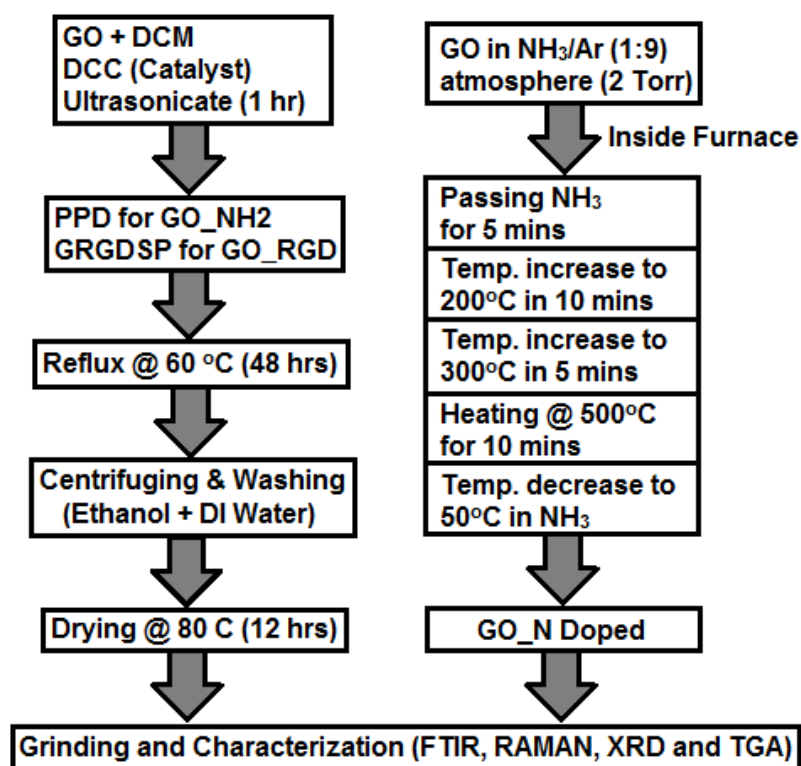


Figure 13: Functionalization of GO and nitrogen doping of GO

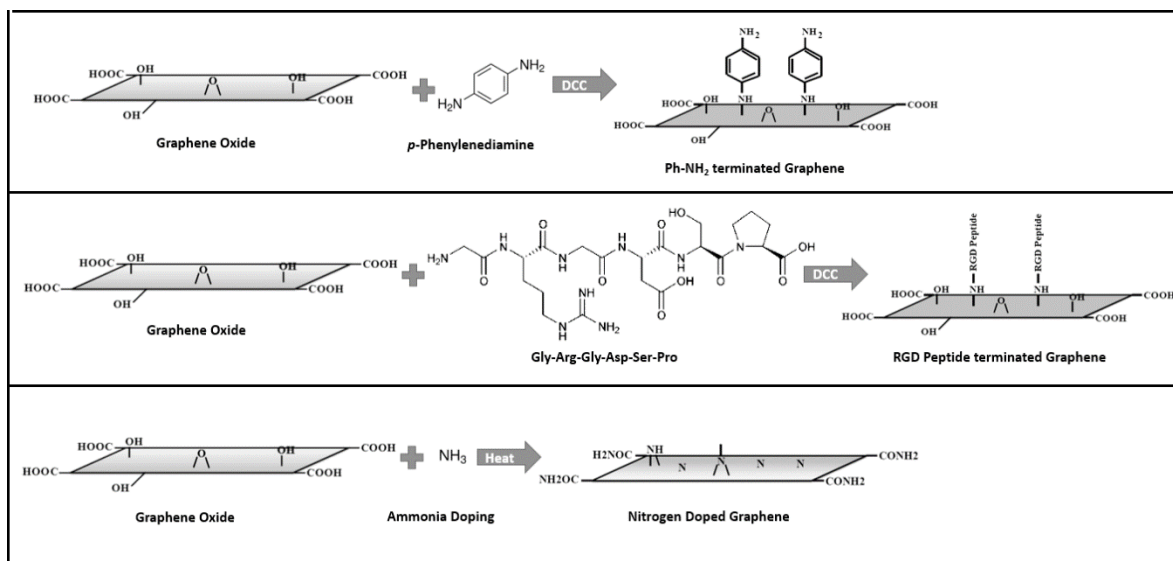


Figure14: Schematic representation of functionalized GO and N doped GO

2.1.2.2. Synthesis of Platinum Nanoparticles on Functionalized Graphene Oxide

A chemical method known as polyol reduction process was used to synthesize platinum nanoparticles on the catalyst supports i.e. carbon black vulcan XC-72, graphene oxide, GO-N Doped, GO-NH₂ and GO-RGD due to its versatility and easiness in carrying out the experiments. This polyol mediated synthesis allows better distribution i.e. non-agglomeration, uniform shape and size control-ability of nanoparticles on catalyst supports [1].

Ethylene glycol was used as solvent and reducing agent. Catalyst supports were separately ultrasonicated in ethylene glycol for 30 mins (conc. of 1mg/mL) to get homogeneous dispersions. The ratio of ethylene glycol to DI Water was kept 9:1 (v/v). Meanwhile, platinum precursor i.e. chloroplatinic acid hexahydrate was dissolved in DI Water and mixed with the above homogeneous mixture and stirred for 1 hour. The ratio of catalyst support to platinum precursor was 2:1 (w/w) which makes the platinum weight in the final products equal to 15.8% by weight. The resulting mixture was put in the round bottom reaction flask and refluxed for 12 hours at 130⁰ C with constant stirring of 300 rpm. After 12 hours, the heat was turned off to allow it to cool to the room temperature. Afterwards, the solid product was

centrifuged and washed with ethanol and DI Water several times and dried in an oven at 70⁰ for 12 hours.

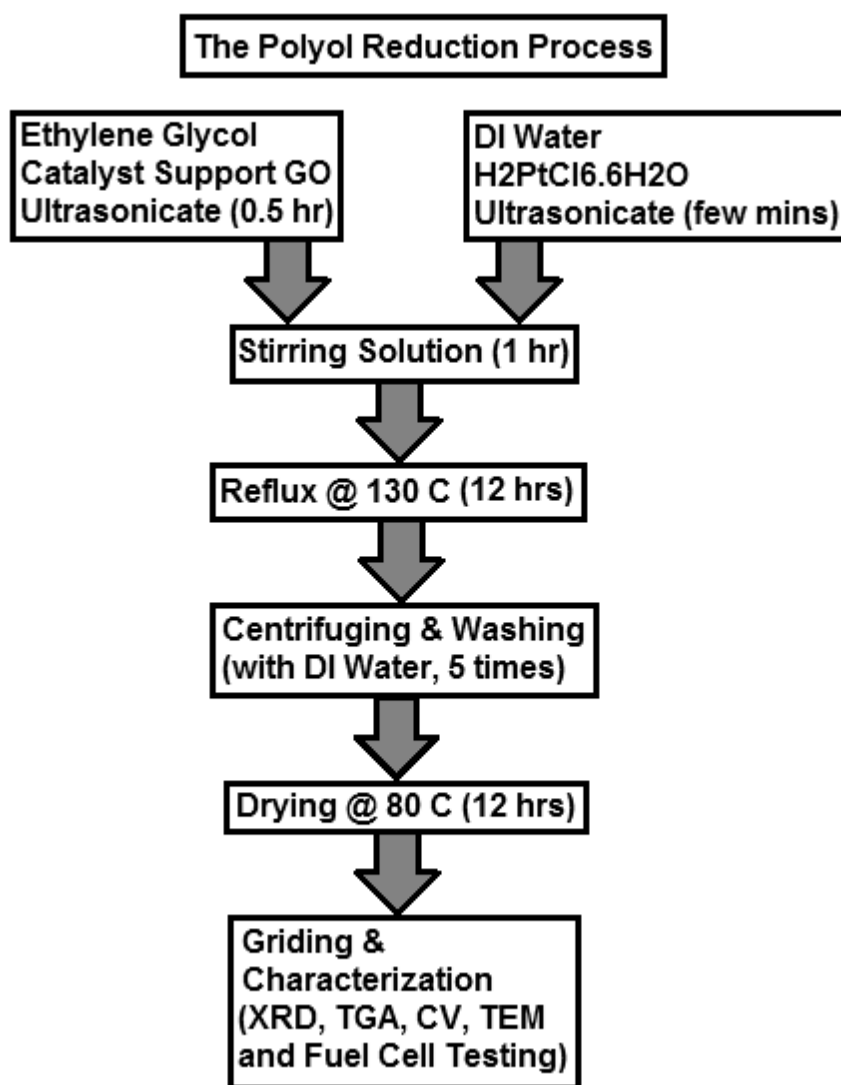


Figure 15: The polyol reduction process

2.1.3. Characterization Methods

2.1.3.1. Materials Characterization

Fourier Transform Infrared Spectroscopy

FT-IR spectra of the powdered samples were tested at room temperature with germanium crystal using ThermoScientific Nicolet iS-10 FT-IR spectrometer.

Raman Spectroscopy

Raman spectral analysis of the powdered samples were done by visible laser with an excitation line at 532 nm and spectral range from 100 to 3200 cm^{-1} using Renishaw inVia Raman Microscope.

Thermogravimetric Analysis

TGA Measurements was done by Shimadzu Corp. DTG-60H. Aluminum pans were used in all of the experiments. Powdered samples were put in crucible and heated from 30 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ with a heating ramp of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen and air flows.

X-Ray Diffraction Analysis

The XRD measurements were performed by Bruker D8 Advance X-Ray Diffractometer which uses $\lambda_{\text{Cu-K}\alpha} = 1.54 \text{ \AA}$ and operating voltage of 40KV and current of 40mA. The measurements were done at 2θ angles ranging from 5° to 90° with the scan rate of $0.04^{\circ}/\text{s}$. The Pt crystallite size was measured by Eva software which uses Scherer equation.

Transmission Electron Microscopy (TEM)

High resolution images of Platinum loaded samples were taken by JEOL JEM-2100F Transmission Electron Microscope to observe the Pt nanoparticles' size and their distribution. The images were further processed to calculate the Pt particle size using ImageJ software.

2.1.3.2. Electrochemical Characterization

Cyclic Voltammetry

Catalyst Ink Preparation: Catalyst (4mg) was dispersed in 950 μL DMF and 50 μL nafion (5 wt% in low aliphatic alcohols) mixture for 2 hours using ultrasonication to get homogeneous catalyst ink (4mg/mL)

Electrode Preparation: Glassy carbon working electrodes (diameter 3mm and area 0.07065 cm^2) were pre-polished with 1 micrometer diamond polish, rinsed with ethanol and dried with nitrogen gas. Calculated amount of catalyst ink was applied on the working electrodes and dried, to get the fixed platinum loading of 20 $\mu\text{g}/\text{cm}^2$. Ag/AgCl, glassy carbon and platinum wire were used as reference, working and counter electrodes respectively.

Experimental Conditions: The measurements were performed using Gamry Inc. Reference 3000 in a three electrode setup under room temperature with a scan rate of 50mV/s between -0.2V to 1.2V vs Ag/AgCl. 0.5M H_2SO_4 was used as an electrolyte which was purged with nitrogen gas for 30 mins prior experiments.

2.1.3.3. In-situ Fuel Cell Characterization

Catalyst Ink Preparation: Pt/catalyst support (100mg) and nafion® (49.25mg) (20 wt. % in mixture of lower aliphatic alcohols and water) were ultrasonically dispersed in N,N-

dimethylformamide (3mL) and then stirred for 3 hours to get homogenous catalyst ink. The weight ratio of Pt/catalyst support to nafion was kept 2:1.

Electrode Fabrication: The catalyst ink was tape casted on one side of 5x5 cm² carbon paper (AvCarb MGL190 μm) by using M.S.E. Tape Caster equipment and dried in an oven at 60 °C for 15 minutes. This process of applying catalyst ink on the carbon paper and drying was repeated until the platinum loading of 0.24 mg/cm² was achieved.

Electrocatalyst Layer Thickness: The thickness was measured using KLA-TENCOR P6 Surface Profiler which gave an average value of 7 μm for the electrocatalyst layer thickness which was in accordance with the theoretical calculation done prior to the measurements.

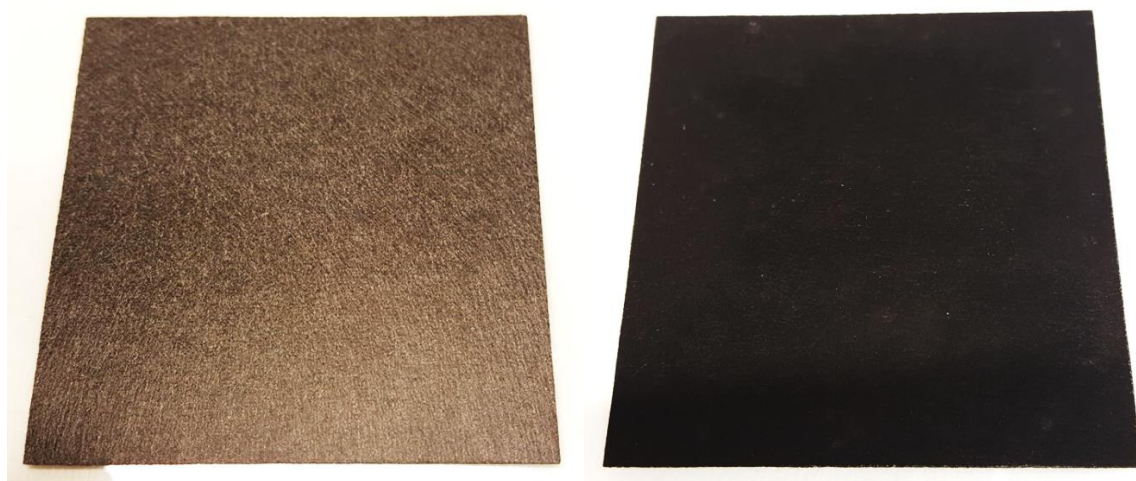


Figure 16: Plain Carbon Paper (Left) and Tape Casted Electrode (Right)

Membrane Electrode Assembly Fabrication: MEA with an area of 25cm² was fabricated by hot pressing the anode and cathode electrodes to a Nafion®-NR211 membrane at 120°C at 533.8 KPa for 3 minutes. Prior to this, the membrane was preconditioned by putting it into 3% solution of hydrogen peroxide, DI water, 0.5 M sulfuric acid. Finally, putting in DI water at 80°C.

2.2. RESULTS AND DISCUSSIONS

2.2.1. Synthesis of Functionalized Graphene Oxide

2.2.1.1. FTIR Results

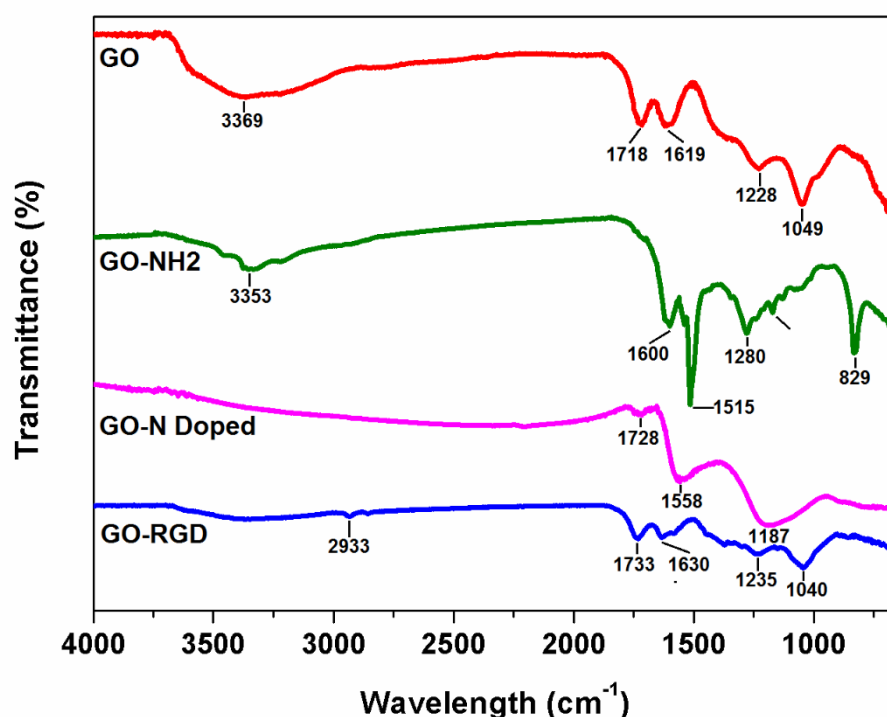


Figure 17: FTIR spectra of GO, GO-N Doped, GO-NH₂ and GO-RGD

FTIR spectra can be used to analyze the chemical structures of GO and functionalized GO samples. The FTIR spectrum of GO shows a broad absorption peak at 3369 cm^{-1} corresponding to O-H stretching vibration of carboxyl group with the characteristic peak at 1718 cm^{-1} for C=O stretching vibration of carbonyl group. The peaks 1619 cm^{-1} , 1228 cm^{-1} and 1049 cm^{-1} are ascribed to C=C stretching vibration of the aromatic ring, C-OH stretching vibration of carboxyl group and C-O stretching vibration of epoxy group, respectively [10]. In case of ammonia doping of GO with simultaneous thermal reduction (GO-N doped), all of the oxygen containing groups e.g. carboxyl, hydroxyl, epoxy are removed leaving only a weak peak at 1728 cm^{-1} (C=O) and two new peaks at 1558 cm^{-1} and 1187 cm^{-1} corresponding to C-N stretching vibration of aliphatic amines.

Organic compounds with aryl groups such as p-phenylenediamine, are known to improve conductivity of graphene [15]. After functionalization of GO with p-phenylenediamine (GO-NH₂), the intensity of broad peak at 3369 cm⁻¹ (O-H) and peak at 1049 cm⁻¹ (C-O) deteriorated. While new peaks appeared at 3353 cm⁻¹ due to N-H stretching vibration of secondary amines, 1600 cm⁻¹ due to N-H bending vibration of primary amines, 1515 cm⁻¹ due to C-N stretching vibration, 1280 cm⁻¹ due to C-N stretching vibration of the aromatic amines and 829 cm⁻¹ due to N-H wagging of primary amines. These results suggest that the amino groups of p-phenylenediamine (PPD) were covalently attached to carboxyl groups on the edges of GO to form amide bonds with activation via coupling reagent i.e. dicyclohexylcarbodiimide (DCC). Also, the amino moieties of PPD were covalently attached to the epoxy groups on the basal planes of GO by ring opening reactions (S_N2 nucleophilic substitution) of amines.

GO is known to have excellent biocompatibility to incorporate biomolecules [8]. Arginine-glycine-aspartic acid (RGD) is a well-known short amino acid sequence peptide present in integrin used for promoting cell adhesion and growth for surface modification in biological applications [18]. After functionalization of GO with RGD peptide (GO-RGD), the intensity of broad peak at 3369 cm⁻¹ (O-H) decreased with characteristic peaks of RGD peptide appearing at 1733 cm⁻¹ (amide I) and 1634 cm⁻¹ (amide II) which can be related to C=O stretching vibration of carboxyl group and N-H bending vibration of primary amines, respectively [38]. While the peaks at 2933 cm⁻¹ and 1227 cm⁻¹ can be ascribed to C-H stretching vibration of alkanes and C-N stretching vibration of aliphatic amines in the backbone of RGD peptide. The last peak at 1050 cm⁻¹ belongs to C-O stretching vibrations of epoxy group. Based on these it can be concluded that the amino moieties of RGD peptide were covalently attached to the carboxyl groups on the edges of GO with activation via coupling reagent, to form amide bonds.

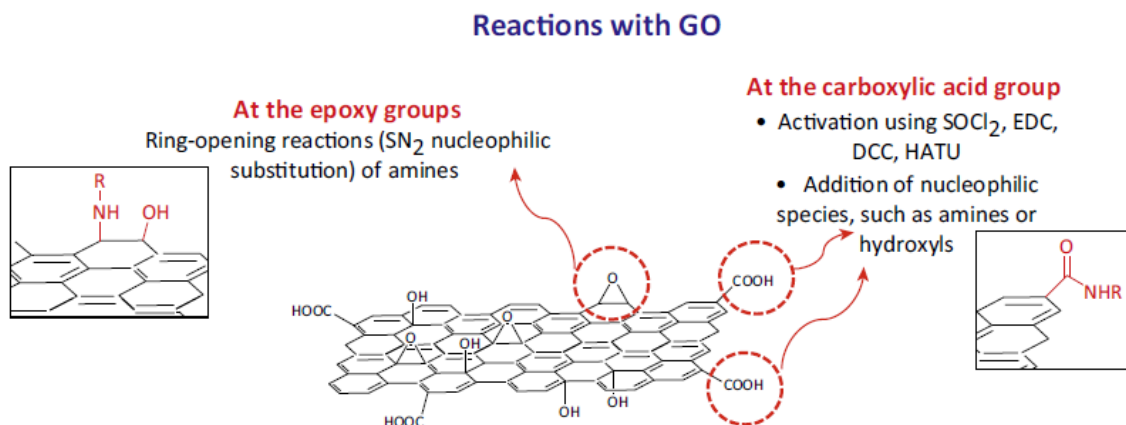


Figure 18: Scheme of reactions between amino moieties with GO [39]

2.2.1.2. TGA Results

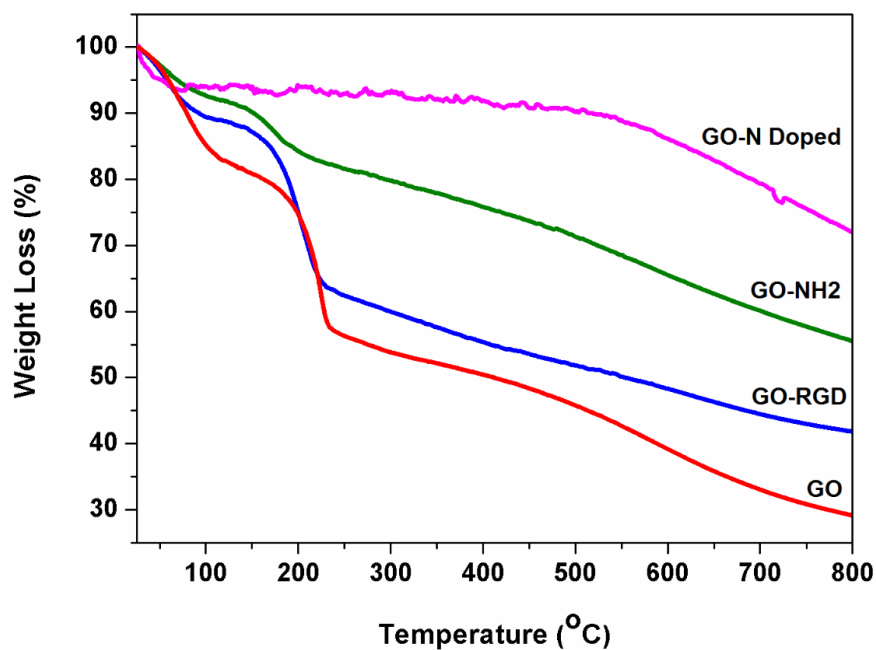


Figure 19: TGA curves of GO, GO-N Doped, GO-NH₂ and GO-RGD under N₂ atmosphere

The thermal stabilities of GO, GO-RGD, GO-NH₂ and GO-N Doped under N₂ atmosphere can be observed by the TGA curves with approx. 15%, 10.5%, 7.3% and 6% first major weight loss respectively, at 100⁰ C due to evaporation of entrapped water [36]. The second major weight loss for GO occurred between 150⁰ C to 250⁰ C because of the decomposition

of labile oxygen functional groups like hydroxyl, carboxyl, etc. Final major weight loss started about 550⁰ C due to the pyrolysis of the carbon skeleton [12, 13].

GO-NH₂ and GO-RGD also showed weight loss between 150⁰ C to 250⁰ C (but lower than GO) which are due to the decomposition of the residual oxygen functional groups while GO-N Doped showed almost no weight loss in this range suggesting complete removal of the said groups during thermal reduction. Thereafter, the functionalized GO samples gradually loss weight due to thermal stripping of covalent bonds formed by the functionalizing moieties and subsequently, the pyrolysis of the carbon skeleton starts to happen.

The residual weights of GO, GO-RGD, GO-NH₂ and GO-N Doped are 29.1%, 41.8%, 55.5% and 71.9%, respectively, corresponding to 800⁰ C. Therefore, GO-N Doped is thermally most stable, followed by GO-NH₂, GO-RGD and GO. From the residual weights of the TGA curves, the degree of doping and functionalization can be estimated at 800⁰ C to be 42.8%, 26.4% and 12.7% for GO-N Doped, GO-NH₂ and GO-RGD, respectively, which is consistent with the results of XRD and FTIR, demonstrating successful functionalization of GO.

2.2.1.3. Raman Results

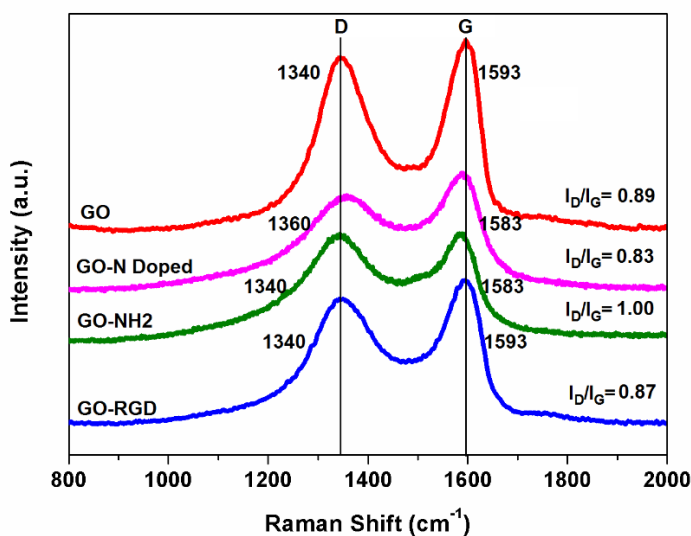


Figure 20: Raman spectra of GO, GO-N Doped, GO-NH₂ and GO-RGD

Raman spectroscopy is a non-destructive technique for studying structural changes of GO. The GO spectrum shows two characteristics peaks at D (1340 cm^{-1}) and G (1593 cm^{-1}) with I_D/I_G ratio of 0.89 [37]. The D band is attributed to sp^3 hybridized carbon or structural defects and G is assigned to the first order scattering of the E_{2g} mode of vibrational mode of sp^2 carbon graphitic domains, respectively [11, 20]. The I_D/I_G ratio shows the quality of carbon materials. The slight red shifting of G bands of GO-NH₂ and GO-N doped to 1583 cm^{-1} implies some restoration of the conjugated structure upon reduction [17]. While GO-NH₂ shows higher I_D/I_G ratio (1.00) due to unrepaired sp^3 defects or structural disorder as a result of the removal of oxygenated functional groups during functionalization and partial reduction. Normally, the I_D/I_G ratio of GO-RGD (0.87) and GO-N doped (0.83) should be higher than GO (0.89) as a result of functionalization but this can be explained as when new sp^2 carbon or graphitic domains are formed that are more in number and have smaller average size compared to the ones present in GO before functionalization, then this happens [11].

2.2.1.4. XRD Results

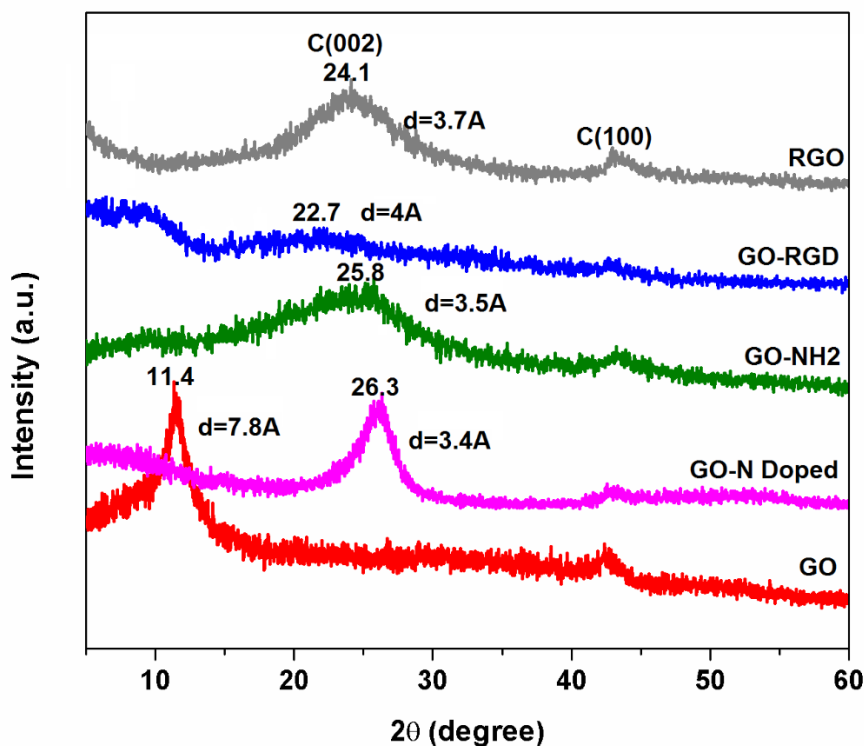


Figure 21: XRD patterns of GO, RGO, GO-N Doped, GO-NH₂ and GO-RGD

The XRD Spectrum of GO shows a high intensity peak at 11.4° corresponding to C(002) plane with interlayer spacing of 0.778 nm and another small peak at about 43° corresponding to C(100) plane of the hexagonal carbon structure [41]. The broadness of the peak represents the disorder in the graphitic structure which is due to the inclusion of oxygenated functional groups on the basal planes and edges of graphene surface. This results in the increase of interlayer spacing as compared to graphite [35]. While RGO shows a shifted peak at 24.1° with interlayer spacing of 0.368 nm. The decrease in the interlayer spacing resulted from partial removal of oxygen containing groups during the reduction process which enhanced the van der waals' interactions between the nanosheets.

After functionalization of GO with p-phenylenediamine (GO-NH₂) and ammonia doping of GO (GO-N Doped) with simultaneous thermal reduction, the C(002) peaks are shifted to 25.8° and 26.3° with decrease in the interlayer spacing to 0.345 nm and 0.338 nm, respectively, as in case of RGO due to π - π stacking. While functionalization of GO with RGD peptide, the C(002) peak is shifted to 22.7° with interlayer spacing of 0.401 nm. The enhanced interlayer spacing suggests the intercalation of RGD peptides between the graphene nanosheets. The Raman and XRD results show that the graphene structure have been maintained after the functionalization of GO.

2.2.1.5. Dispersibility and Stability Results

The samples GO, GO-N doped, GO-NH₂ and GO-RGD were dispersed in DMF (2mg/mL) with ultrasonication for 60 minutes to check their dispersibility and stability in the organic solvent after one month. Except for GO-N doped, the as-prepared functionalized showed excellent stability after one month.

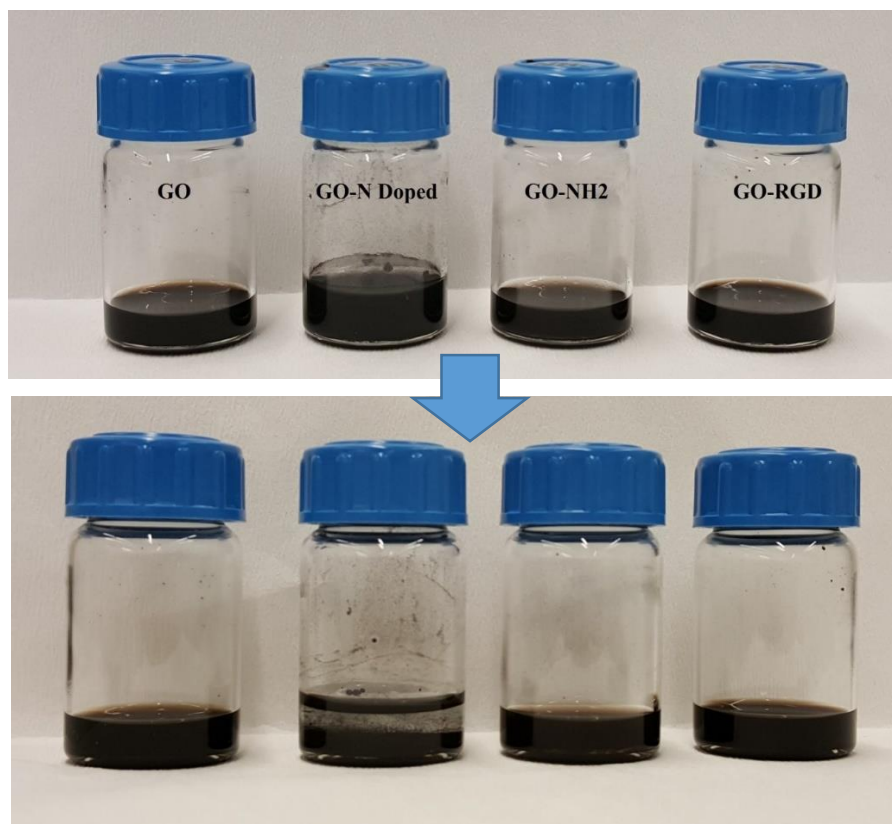


Figure 22: (Top) GO and f-GO dispersed in DMF (2mg/mL), (bottom) after one month

2.2.2. Synthesis of Platinum Nanoparticles on Functionalized Graphene Oxide

2.2.2.1. XRD Results

The diffraction peak C(002) of GO previously at 11.4° shifted to higher angles at 23.8° after Pt deposition by ethylene glycol which implies that the GO was also partially reduced to graphene and restacked into an ordered crystalline structure [23, 41]

For all samples, the diffraction peaks at the Bragg angles 39.9° ($d_{\text{spacing}}=0.226$ nm), 46.1° , 67.5° and 81.4° correspond to (111), (200), (220) and (311) planes of face centered cubic (fcc) crystalline structure of Pt. These peaks shows successful reduction of Pt nanoparticles on the catalyst supports. The peak intensity of the dominating Pt(111) plane suggests the degree of reduction of Pt on catalyst supports while its broadness gives information about of the crystallite size i.e. broader means smaller grain size.

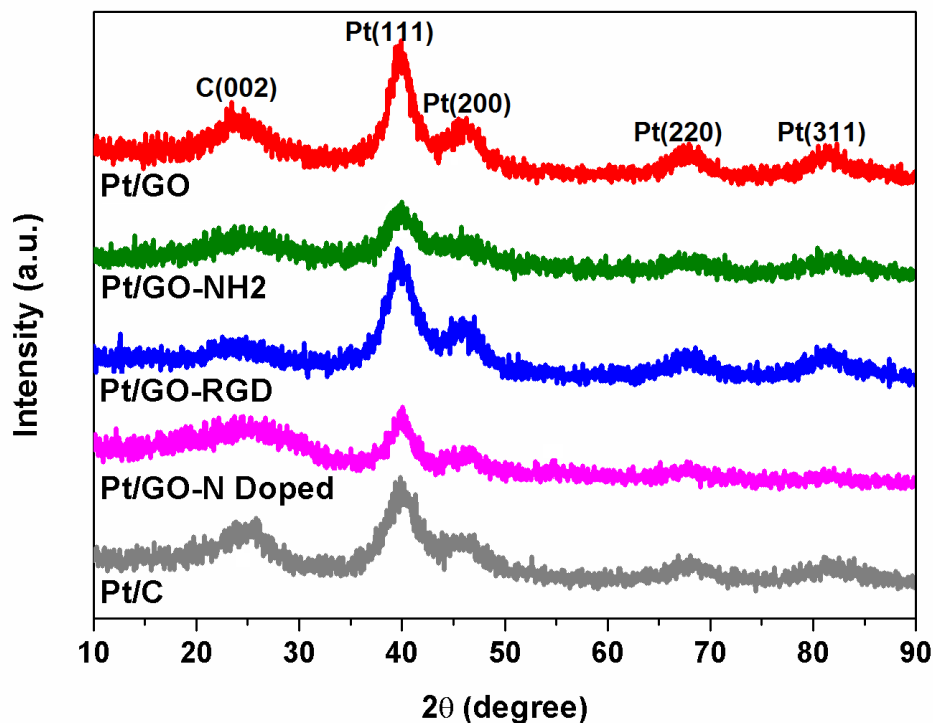


Figure 23: XRD spectra of different Pt loaded f-GO

The average Pt crystallite size was measured using Pt(111) plane using Scherer equation: $d = (0.89\lambda)/(\beta\theta)$ where 0.89 is constant for spherical Pt particles, λ is the wavelength of incident X-rays (0.154 nm for Cu-K α radiation), β is the full width at half maximum (FWHM) in radians and θ is the Bragg angle at the position of peak maximum in radian [41].

Table 4: Calculated average particle size of Pt on various catalyst supports by XRD data

Samples	Average Pt particle size (nm)
Pt/C	3.7
Pt/GO	3.8
Pt/GO-N Doped	4.6
Pt/GO-NH ₂	3.9
Pt/GO-RGD	3.4

2.2.2.2. TGA Results

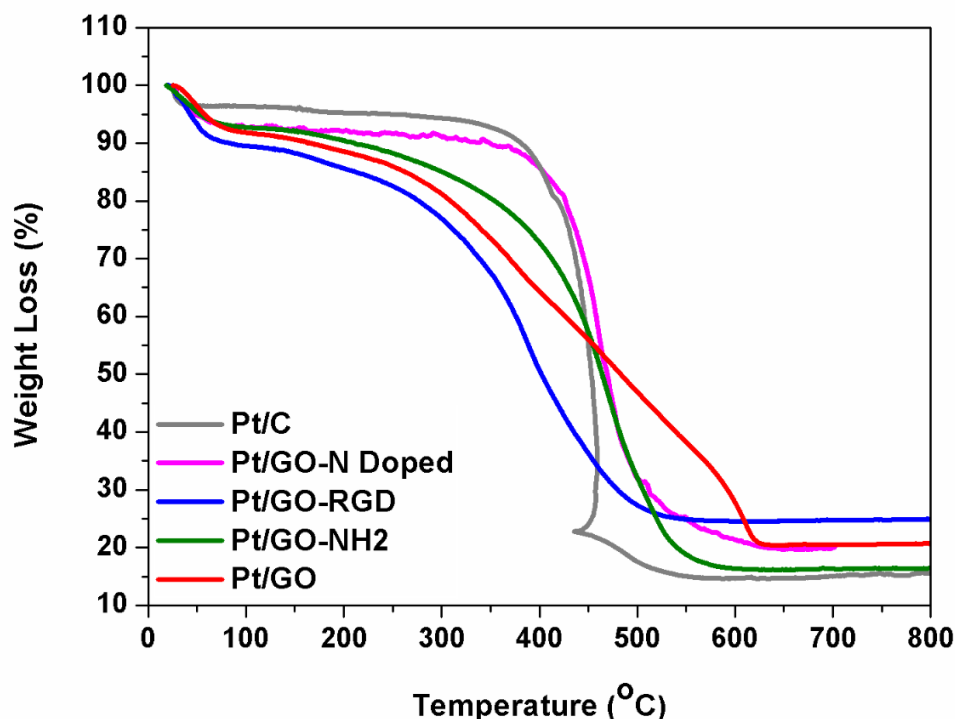


Figure 24: TGA curves of Pt loaded f-GO (under air atmosphere)

The TGA analysis was done under air atmosphere to estimate the platinum amount deposited on the various catalyst supports namely: Vulcan XC-72, GO, GO-N Doped, GO-NH₂ and GO-RGD, with approx. 3.6%, 8.1%, 7.3%, 7.2% and 10.5% first major weight loss respectively, at 100⁰ C due to evaporation of entrapped water. After this temperature, Pt/GO, Pt/GO-NH₂ and Pt/GO-RGD samples showed gradual weight loss due to decomposition of different functional groups and combustion of carbon structure in the presence of air while Pt/C and Pt/GO-N doped showed sudden weight loss between 350⁰ C and 550⁰ C indicating combustion of the carbon structure in the presence of air.

After 650⁰ C, all the samples showed straight lines with some residual weights which can be attributed to platinum amounts in the samples. Initially, while reducing the platinum precursor on carbon supports, the amount of platinum was kept about 15.8% by weight (theoretical), but the TGA curves shows different residual weights. These discrepancies can be attributed to the entrapped water and some instrumentation errors.

Table 5: Platinum amounts in various catalyst supports by TGA under air atmosphere

Samples	Pt amounts (weight %)
Pt/C	14.6
Pt/GO	20.4
Pt/GO-N Doped	19.6
Pt/GO-NH ₂	16.2
Pt/GO-RGD	24.5

2.2.2.3. Cyclic Voltammetry Result

In cyclic voltammetry (CV), during the forward scan, H⁺ ions are reduced and adsorbed on Pt surface providing cathodic current while in the reverse scan, the hydrogen is desorbed resulting anodic current. The area under the adsorption and desorption peaks give the total columbic charge transfer (Q_H). The mean of these two peaks' area excluding the double layer charge can be used in the calculation of electrochemically active surface area (ECSA) which provides vital information about the number of available catalyst active sites for charge transfer [40]. CV was used to find ECSA of platinum on different supports namely: Vulcan XC-72, GO, GO-N doped, GO-NH₂ and GO-RGD synthesized by the polyol reduction process. ECSA can be calculated by the following equation [40].

$$\text{ECSA}[\text{cm}^2\text{Pt/gPt}] = \frac{\text{charge}[Q_H, \mu\text{C}/\text{cm}^2]}{210[\mu\text{C}/\text{cm}^2] \times \text{electrode loading}[\text{g Pt}/\text{cm}^2]}$$

Where Q_H is the mean charge integrated from the cyclic voltammogram of the adsorption and desorption hydrogen peaks, 210 is the charge to oxidize a single hydrogen layer adsorbed on platinum surface, electrode loading is the amount of Pt deposited on the electrode surface.

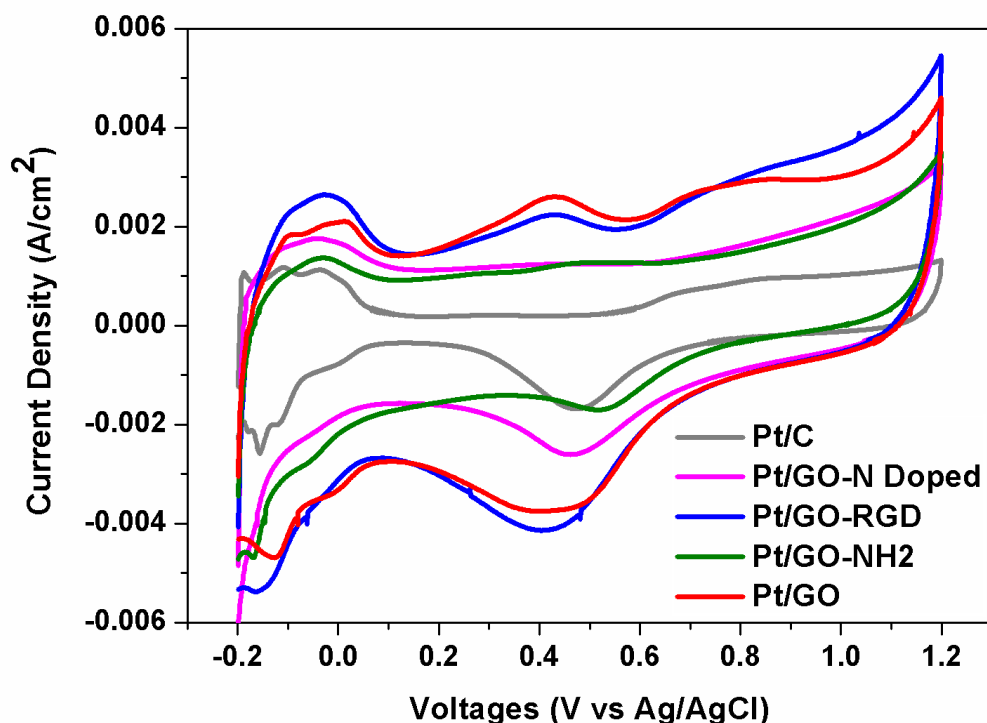


Figure 25: Cyclic voltammograms of Pt/Vulcan XC-72, Pt/GO and Pt/f-GO synthesized by polyol reduction process.

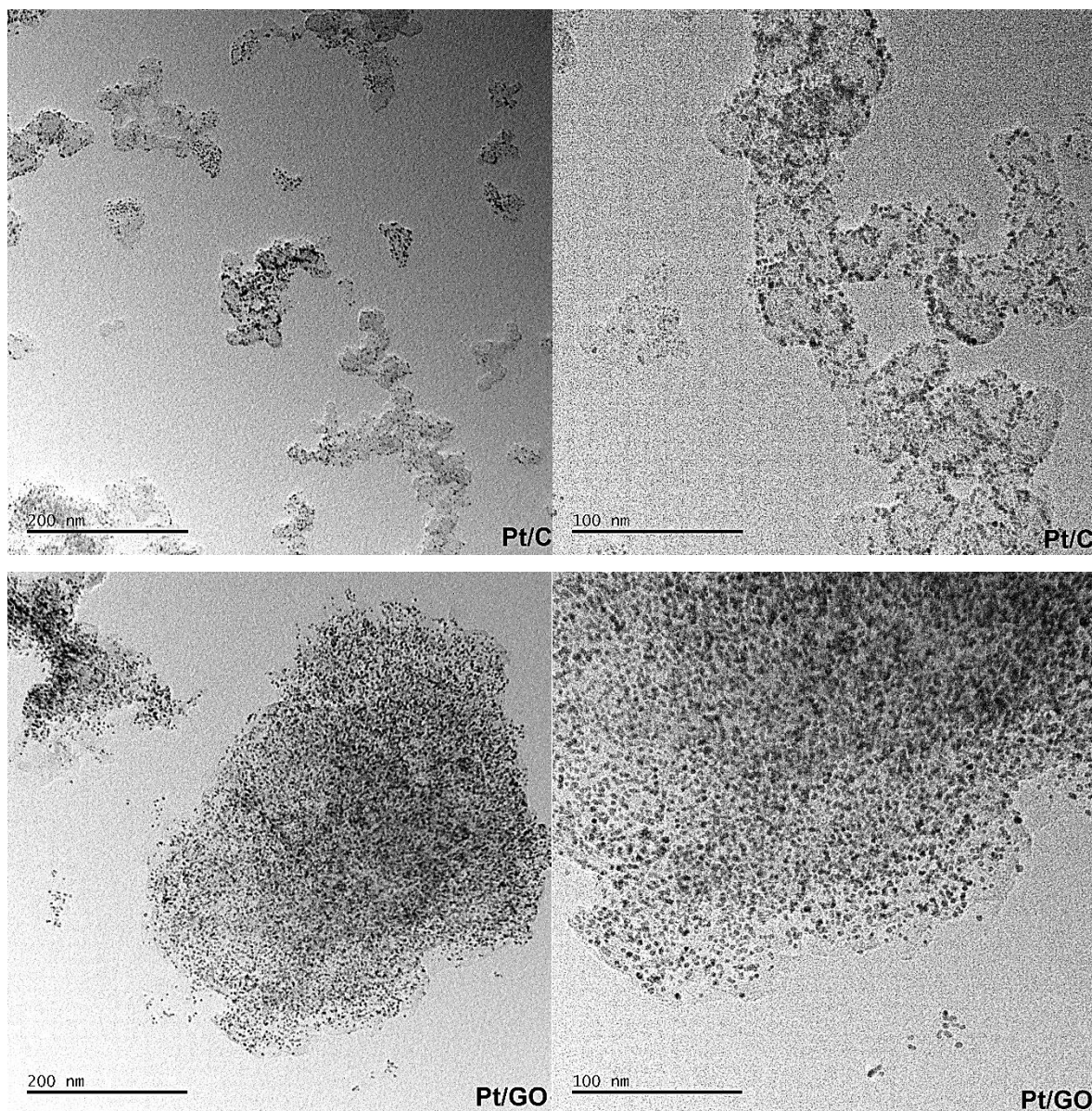
Table 6: Calculated ECSA values of different Pt loaded f-GO

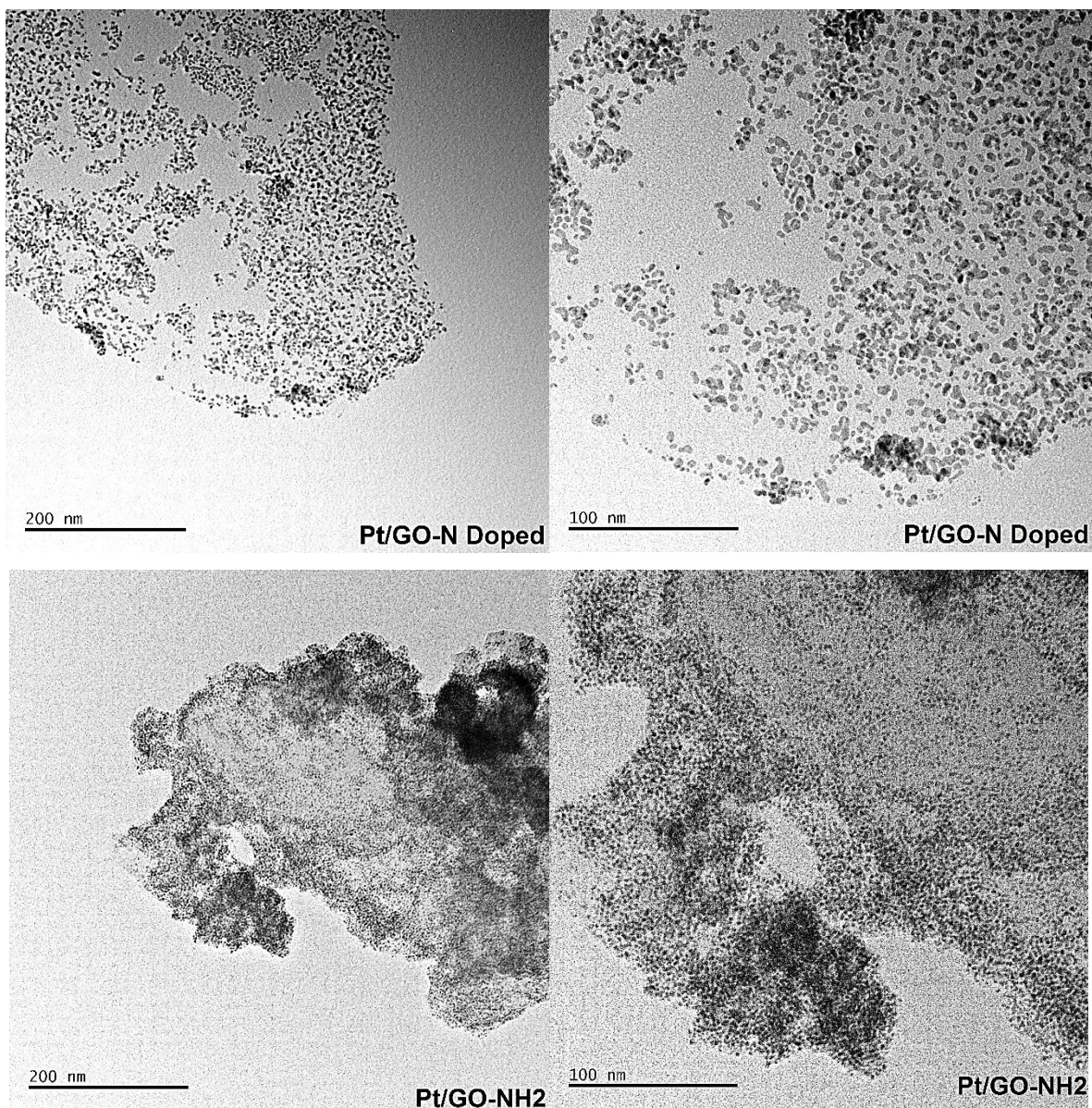
Samples	ECSA ($\text{m}^2/\text{g Pt}$)
Pt/C	80
Pt/GO	99
Pt/GO-N Doped	105
Pt/GO-NH ₂	130
Pt/GO-RGD	147

Although Pt/GO showed high cathodic and anodic current densities but the area under the hydrogen adsorption/desorption peaks is less. Similar trend is observed for Pt/GO-N doped with larger Pt nanoparticle size (4.6 nm) and non-homogeneous dispersion as seen in TEM images, restricting its ECSA value to 105 m^2/g . While the runner-up in ECSA values is Pt/GO-NH₂ (130 m^2/g) due to smaller Pt nanoparticle size (3.9 nm) with excellent dispersion which increases the Pt utilization.

The CV voltammogram of Pt/GO-RGD showed the highest hydrogen adsorption/desorption peaks with large areas under them indicating increased number of available Pt catalyst active sites for charge transfer which in turn gives high ECSA value of $147 \text{ m}^2/\text{g}$ about 83% higher than synthesized Pt/Vulcan XC-72 ($80 \text{ m}^2/\text{g}$) and 48% higher than Pt/GO ($99 \text{ m}^2/\text{g}$) which can be attributed to smaller Pt nanoparticles' size (3.4 nm) with homogeneous dispersion on the support with large surface area to anchor metal nanoparticles.

2.2.2.4. TEM Results





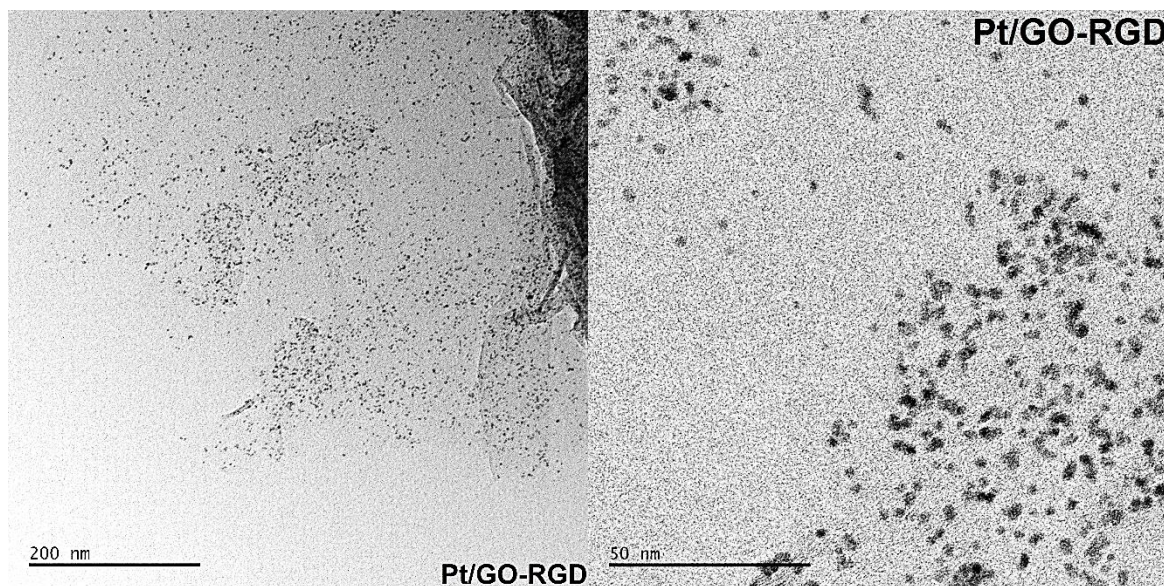


Figure 26: TEM images of Pt loaded functionalized GO

TEM imaging was used to observe Pt nanoparticles' incorporation, size, distribution as well as the surface morphology of the supports. As it can be seen that the polyol reduction method successfully incorporated Pt nanoparticles on the supports. The Pt nanoparticles size calculated from XRD data matches quite well with the TEM results. Although Pt/C has particle size in the midrange (3.7 nm) but has small surface area to support Pt nanoparticles with some agglomerations which results in lowest ECSA value. Similarly Pt/GO shows very good dispersion of Pt nanoparticles (3.8 nm) but with slight agglomerations. Pt/GO-N Doped has non-homogeneous distribution of large Pt nanoparticles (4.7 nm) but still manages to have slightly higher ECSA value ($105 \text{ m}^2/\text{g}$) than Pt/GO ($99 \text{ m}^2/\text{g}$) which can be attributed to the change in chemical and electronic structure due to N doping which increases its electrical conductivity. Among these Pt/GO-NH₂ serves as the good support for anchoring highly dispersed Pt nanoparticles (3.9 nm) resulting in slightly lower ECSA value ($130 \text{ m}^2/\text{g}$) than Pt/GO-RGD ($147 \text{ m}^2/\text{g}$) which has smallest Pt nanoparticles size (3.4 nm).

2.2.2.4. In-situ Fuel Cell Test Results

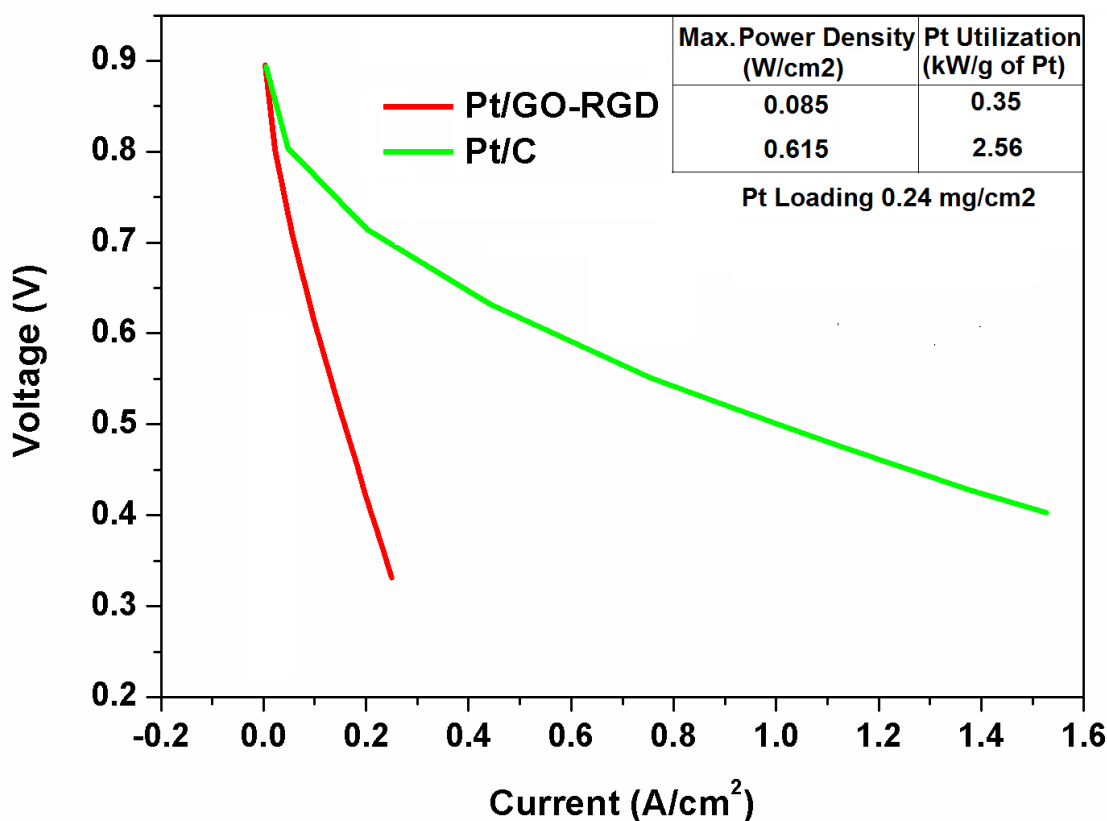


Figure 27: Polarization curves of Pt/C and Pt/GO-RGD

As-synthesized Pt/C and Pt/GO-RGD with Pt amount of 15.8% and Pt loading 0.24mg/cm² on carbon paper were used as cathodes. On the anode side, commercial electrode were used. These fuel cell testing were performed at 60⁰C. Both of the samples started at same open circuit voltage. Pt/C showed very good fuel cell performance as shown in the inset table in the figure above. This can be attributed to tape casting electrode fabrication method with electrocatalyst layer thickness of 7 μ m. But Pt/GO-RGD showed rapid deterioration of current density resulting in lower fuel cell performance, since the catalyst ink homogeneity of the Pt/GO-RGD was not as good as the former one. However, these are preliminary results which will be improved in our future work.

2.3. CONCLUSIONS

The functionalization of graphene oxide (GO) was successfully carried out by p-phenylenediamine and Gly-Arg-Gly-Asp-Ser-Pro by activating via coupling reagent N,N'-Dicyclohexylcarbodiimide, to yield phenyl amine terminated graphene (GO-NH₂) and RGD peptide terminated graphene (GO-RGD). GO was also nitrogen doped by annealing it with ammonia gas (GO-N doped). FTIR structural analysis of as-synthesized functionalized GO (f-GO) evidenced the successful GO reactions with the corresponding amino moieties of functional reagents while in case of chemical doping of GO, FTIR showed simultaneous thermal reduction of GO with nitrogen doping. These results were further supported by TGA by estimating the degree of functionalization and doping, demonstrating successful functionalization of GO. Also TGA results showed that f-GO were thermally more stable than the plain GO while Raman and XRD results showed that the graphene structure have been maintained after the functionalization of GO. These f-GO had excellent dispersibility and stability in organic solvents like DMF.

Furthermore, polyol reduction process with ethylene glycol as reducing agent was used to synthesize platinum nanoparticles on the catalyst supports (Vulcan XC-72, GO, GO-N doped, GO- NH₂ and GO-RGD) and characterized with different characterization techniques. XRD results showed that oxygen containing functional groups were simultaneously reduced with the successful incorporation of Pt nanoparticles on the catalyst supports as evidenced by the characteristic Pt peaks with the Pt nanoparticles' size lying around 3.9 nm. TGA results were used to estimate the Pt amounts while TEM images were used to observe the size and dispersion of Pt nanoparticles immobilized onto the catalyst supports. Among these Pt/GO and Pt/GO-NH₂ showed excellent dispersion with minimal agglomeration while Pt/GO-RGD showed the smallest Pt nanoparticle size (3.4 nm) consistent with XRD results. The CV voltammogram of Pt/GO-RGD showed the highest hydrogen adsorption/desorption peaks with large areas under them indicating increased number of available Pt catalyst active sites for charge transfer which in turn gives high ECSA value of 147 m²/g about 83% higher than synthesized Pt/Vulcan XC-72 (80 m²/g) and 48% higher than Pt/GO (99 m²/g) which can be attributed to smaller Pt nanoparticles' size with homogeneous distribution on the support

material with large surface area to anchor metal nanoparticles. While the runner-up in ECSA values is Pt/GO-NH₂ (130 m²/g) due to small Pt nanoparticles' size (3.9 nm) with excellent dispersion which increases the Pt utilization. These results show that the as-prepared Pt/f-GO are promising electrocatalysts for high performance PEM fuel cells which is our future task of investigation.

3. GRAPHENE OXIDE – POLYPYRROLE NANOCOMPOSITE AS CATALYST SUPPORT

3.1. EXPERIMENTAL

3.1.1. Materials

Flagship Graphene Oxide (GO), Polypyrrole (30 S/cm) composite with 20% Carbon Black (PPy/CB doped with organic sulfonic acid), Chloroplatinic acid hexahydrate (Pt Precursor, 37.5% Pt Basis), Iron (III) Chloride Anhydrous (99.99%), Sodium hydroxide (97%), Sodium Borohydride (99%), Sulfuric Acid (98%), Nafion® perfluorinated resin solution (20 wt. % in mixture of lower aliphatic alcohols and water, contains 20% water), Nafion® perfluorinated resin solution (5 wt. % in mixture of lower aliphatic alcohols and water, contains 15-20% water), Ethylene Glycol (EG, 99.8%), N,N-Dimethylformamide (99%) and Ethyl Alcohol (99.5%) were purchased from Sigma Aldrich. Carbon Paper (AvCarb MGL190 μm) was purchased from Fuel Cell Store while Nafion® PFSA NR211 membrane from Fuel Cell Earth. Deionized Water (18.2M Ω -cm, Milli-Q Reference) was used in all the experiments. All the chemicals were used without further purification.

3.1.2. Methods

3.1.2.1. Synthesis of Polypyrrole/Carbon Black/Graphene Oxide Hybrid Nanocomposite

Polypyrrole/carbon black/graphene oxide (**PPy/CB/GO**) hybrid nanocomposite was prepared by dispersing graphene oxide in ethanol for 30 minutes under ultrasonication and then adding commercial polypyrrole composite with 20% carbon black which is doped with organic sulfonic acid (30 S/cm), in the homogeneous dispersion of graphene oxide. This mixture was further ultrasonicated for 30 mins and stirred for 1 hour. Subsequently the solution was centrifuged and dried in an oven at 70⁰ C for 12 hours. The weight ratio of PPy/CB/GO was kept as 4:1:1.

3.1.2.2. Synthesis of Platinum Nanoparticles on Catalyst Supports by Method 1

The polyol reduction process as outlined by Lim, Bo-Rami et al. [2] was used with some changes for optimized results and labelled as Modified Polyol Process (Method 1).

Catalyst supports GO, PPy/CB and PPy/CB/GO were separately ultrasonicated in ethylene glycol for 30 mins (conc. of 1mg/mL) to get homogeneous dispersions. The ratio of ethylene glycol to DI water was kept 9:1 (v/v). Meanwhile, platinum precursor i.e. chloroplatinic acid hexahydrate was dissolved in DI water and mixed with the above homogeneous mixture and stirred for 1 hour. After which the pH of the solution was adjusted to 10 by 0.5 M sodium H hydroxide. The ratio of catalyst support to platinum precursor was 2:1 (w/w) which makes the platinum weight in the final products equal to 15.8% by weight. The resulting mixture was put in the round bottom reaction flask and refluxed for 4 hours at 130⁰ C with constant stirring of 300 rpm. After 4 hours, the heat was turned off to allow it to cool to the room temperature and further stirred for 12 hours at room temperature. Afterwards, the solid product was centrifuged and washed with ethanol and DI water several times and dried in an oven at 70⁰ for 12 hours.

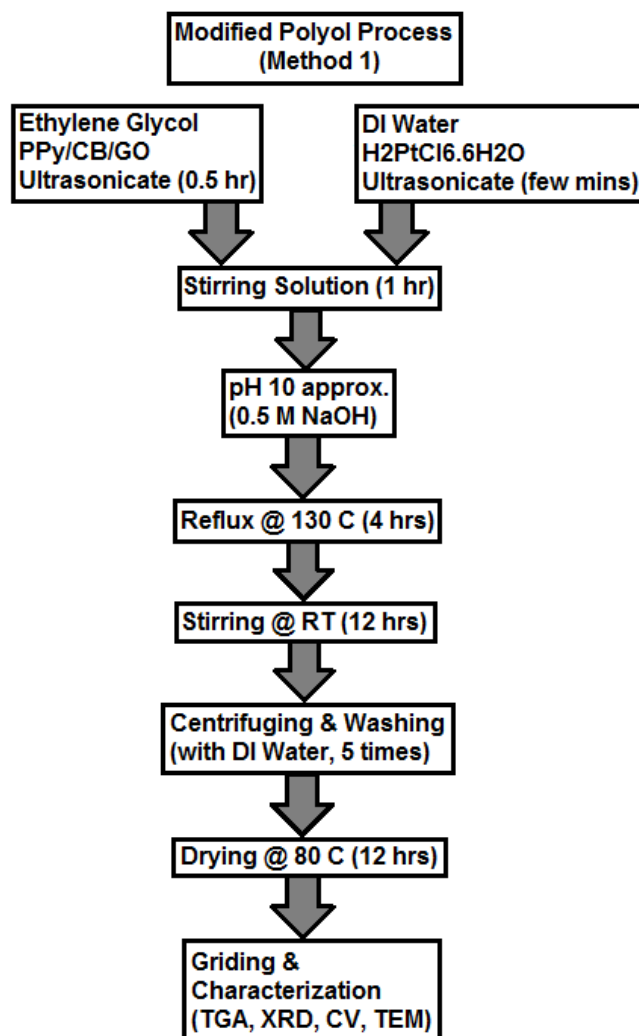


Figure 28: Modified polyol process (Method 1)

3.1.2.3. Synthesis of Platinum Nanoparticles on Catalyst Supports by Method 2

The polyol reduction process as outlined by Kim, Joung Woon et al. [3] was used with some changes for optimized results and labelled as Modified Polyol Process with FeCl_3 (Method 2).

Catalyst supports GO, PPy/CB and PPy/CB/GO were separately ultrasonicated in ethylene glycol for 30 mins (conc. of 1mg/mL) to get homogeneous dispersions. The ratio of ethylene glycol to DI water was kept 9:1 (v/v). Meanwhile, platinum precursor i.e. chloroplatinic acid hexahydrate and iron (III) chloride were dissolved in DI water and mixed with the above

homogeneous mixture and stirred for 1 hour. The mole ratio of Pt:Fe was kept as 1:3. After this the pH of the solution was adjusted to 10 by 0.5M sodium hydroxide. The ratio of catalyst support to platinum precursor was 2:1 (w/w) which makes the platinum weight in the final products equal to 15.8% by weight. The resulting mixture was put in the round bottom reaction flask and refluxed for 4 hours at 130⁰ C with constant stirring of 300 rpm. After 4 hours, the heat was turned off to allow it to cool to the room temperature and further stirred for 12 hours at room temperature. Afterwards, the solid product was centrifuged and washed with ethanol and DI water several times and dried in an oven at 70⁰ for 12 hours.

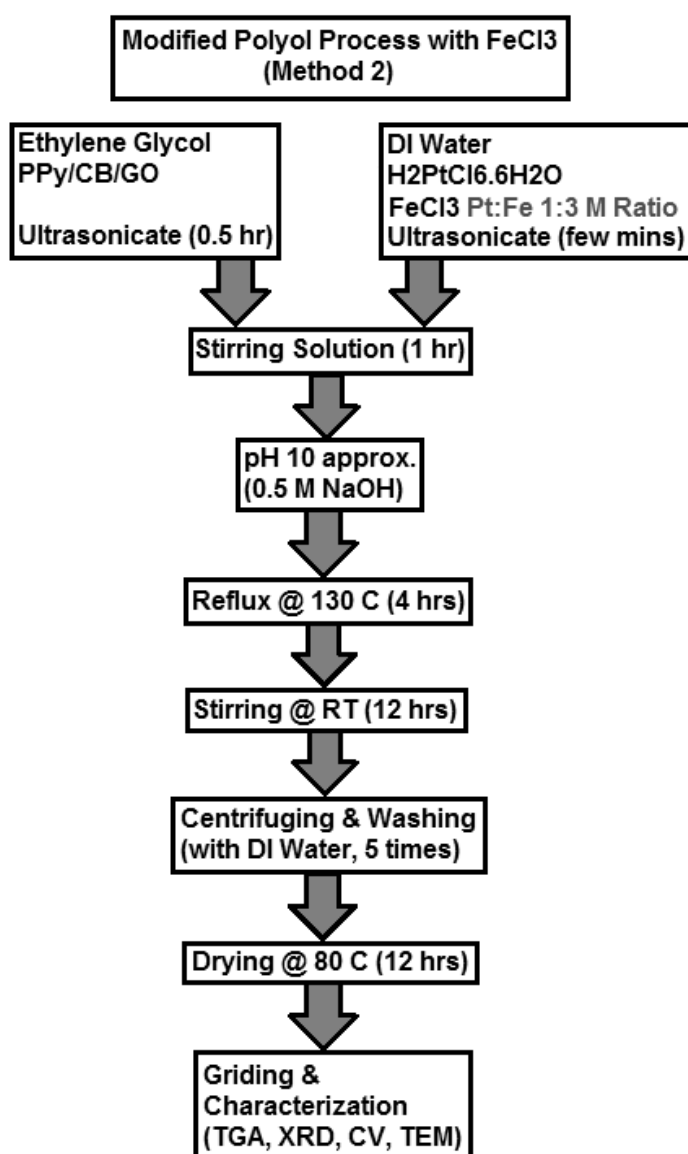


Figure 29: Modified polyol process with FeCl₃ (Method 2)

3.1.2.4. Synthesis of Platinum Nanoparticles on Catalyst Supports by Method 3

The polyol reduction process as outlined by Ha, Hyung-Wook et al. [4] was used with some changes for optimized results and labelled as Modified Polyol Process with NaBH_4 +EG Complex (Method 3).

Catalyst supports GO, PPy/CB and PPy/CB/GO were separately ultrasonicated in ethylene glycol for 30 mins (conc. of 1mg/mL) to get homogeneous dispersions. The ratio of ethylene glycol to DI water was kept 9:1 (v/v). Meanwhile, platinum precursor i.e. chloroplatinic acid hexahydrate was dissolved in DI water and mixed with the above homogeneous mixture and stirred for 1 hour. After this the pH of the solution was adjusted to 10 by 0.5M sodium hydroxide. The ratio of catalyst support to platinum precursor was 2:1 (w/w) which makes the platinum weight in the final products equal to 15.8% by weight. The resulting mixture was put in the round bottom reaction flask and the temperature was raised to 130 °C with constant stirring. Meanwhile certain amount of NaBH_4 dissolved in EG (20mg/mL) was added dropwise in the mixture with vigorous stirring. The mixture was refluxed for 4 hours with constant stirring of 300 rpm. After 4 hours, the heat was turned off to allow it to cool to the room temperature and further stirred for 12 hours at room temperature. Afterwards, the solid product was centrifuged and washed with ethanol and DI water several times and dried in an oven at 70° for 12 hours.

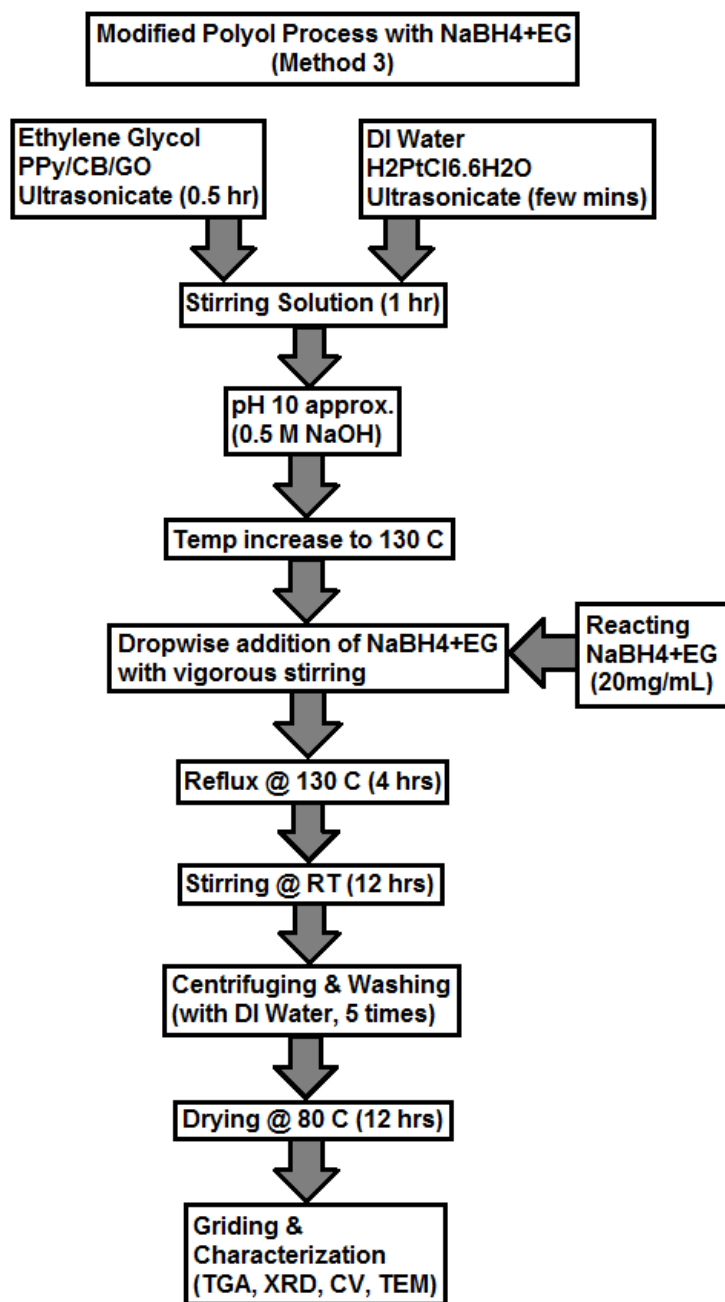


Figure 30: Modified polyol process with NaBH₄+EG (Method 3)

3.1.3. Characterization Methods

(Same as last chapter)

3.2. RESULTS AND DISCUSSION

A simple chemical method known as polyol reduction process with ethylene glycol (EG) as reducing agent is used to synthesize platinum nanoparticles on the catalyst supports due to its versatility and easiness in carrying out the experiments. This polyol mediated synthesis allows better distribution i.e. non-agglomeration, uniform shape and size control-ability of nanoparticles on catalyst supports [1]. However, different synthesizing parameters such as EG to water ratio, EG concentration, solution pH, experiment duration, reaction temperature, additives, etc. have profound effects on as-synthesized Pt catalyst on carbon based supports such as size of metal nanoparticles, their dispersion and electrocatalytic activity [31].

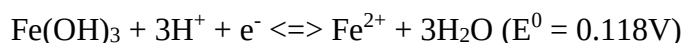
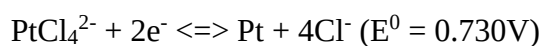
In this study, Pt nanoparticles are reduced on catalyst supports i.e. graphene oxide (GO), polypyrrole/carbon black nanocomposite (PPy/CB) and polypyrrole/carbon black/graphene oxide hybrid nanocomposite by three methods to see their effects on the size of Pt nanoparticles, their dispersion on supports and electrocatalytic activity by different characterization techniques. For comparison purposes, the reaction parameters such as EG to water ratio, solution pH, reaction time and temperature, etc. in all three methods have been maintained as outlined in the previous experimental section. The three methods are further discussed below.

Modified Polyol Process (Method 1) Studies have shown that higher pH values of solution (EG and water mixture) in polyol process results in smaller catalyst nanoparticle size leading to high surface area with good dispersion which in turn increase the electrochemically active surface area [42]. The modified polyol reduction process as outlined by Lim, Bo-Rami et al. [2] has been used with some changes for consistent and optimized results and extended to new catalyst support materials.

Modified Polyol Process with FeCl₃ (Method 2) It has been shown by using FeCl₃ as an additive in the mixture of EG and Water during polyol process influences the Pt particle size resulting from the interference of Pt reduction rate by Fe³⁺ ions [3]. Unlike most other studies, the role of FeCl₃ here as an additive is not to act as an etchant or adsorbate but to act as a

retardant and stabilizing agent in addition to EG itself to control the size of Pt nanoparticles formed. Briefly, the mechanism of FeCl₃ as a retardant is as follows:

Fe³⁺ ions form Fe(OH)₃ in the presence of water and pH (10) adjustment by NaOH, which has standard reduction potential (E⁰) of 0.118V to Fe²⁺ ions while the standard reduction potential (E⁰) for PtCl₄²⁻ is 0.73V.



This means Fe(OH)₃ has no ability to oxidize the Pt particles to Pt²⁺ to act as an etchant and decrease its particle size. Instead Fe(OH)₃ is adsorbed onto the platinum seed to retard its growth isotropically by slowing down the surface reaction during synthesis to produce small sized spherical Pt nanoparticles. Also Fe has not been alloyed with Pt which is confirmed by XRD (next section) as the Pt(111) peak at 39.9° showed no shift to other angles. The modified polyol reduction process as outlined by Kim, Joung Woon et al. [3] has been used with some changes for consistent and optimized results and extended to new catalyst support materials.

Modified Polyol Process with NaBH₄+EG Complex (Method 3) In this method, sodium borohydride first reacts with ethylene glycol to form a complex Na⁺B⁻(OCH₂CH₂OH)₄ which serves as a reducing agent for the platinum precursor as well as a stabilizer to control the size and dispersion of Pt nanoparticles alongside EG itself in the solution. The reducing strength and stabilization effect of this complex is stronger than the EG alone which can not only completely reduce Pt precursor at room temperature to produce fine Pt nanoparticles with homogeneous dispersion on carbon based supports [43] but can also reduce most of the oxygen containing groups on GO [4]. However, for the sake of comparison with other methods, the reaction parameters such as reaction temperature (130° C) was made consistent with the other methods. The modified polyol reduction process as outlined by Ha, Hyung-Wook et al. [4] has been used with some changes for consistent and optimized results and extended to new catalyst support materials.

3.2.1. Synthesis of Platinum Nanoparticles on Graphene Oxide – Polypyrrole Nanocomposite

3.2.1.1. XRD Results

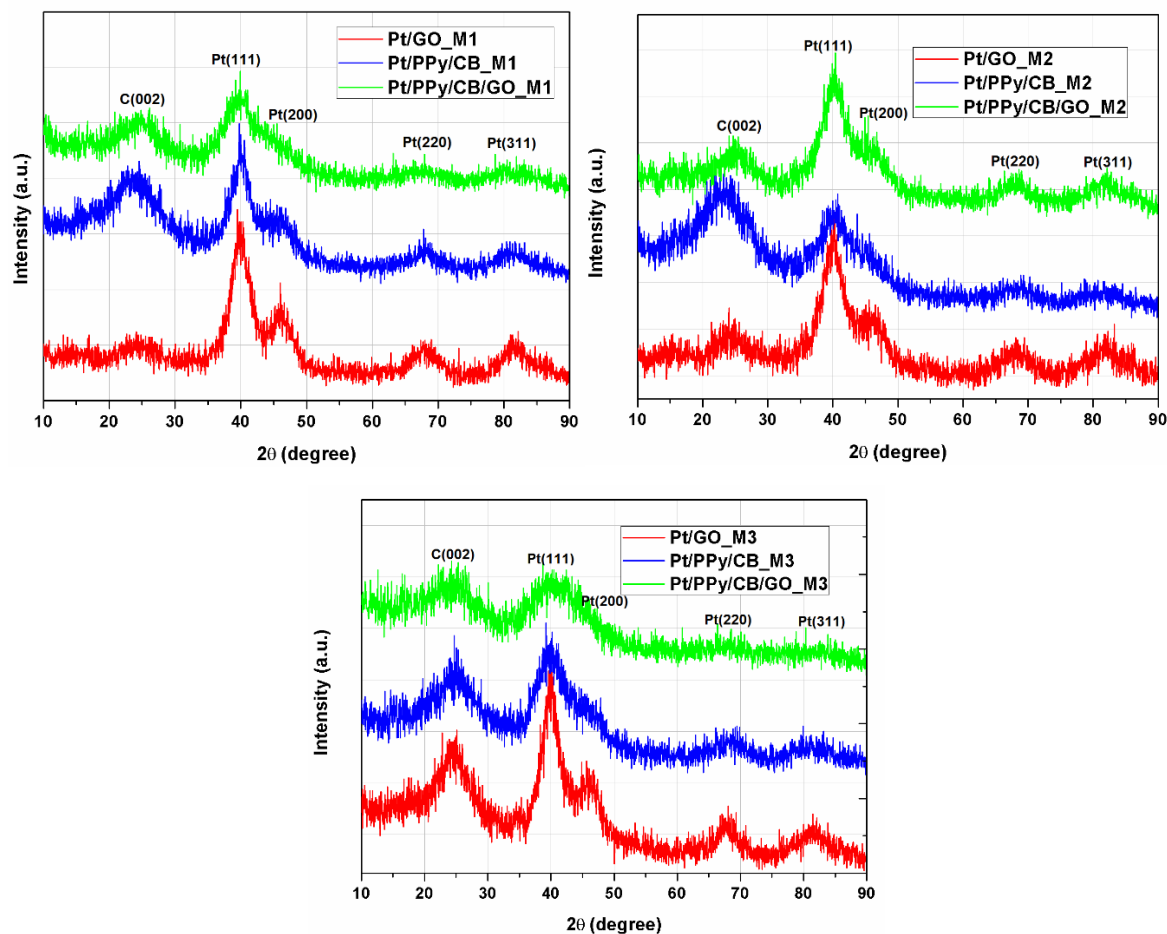


Figure 31: XRD spectra: (top left) Pt loaded nanocomposites by Method 1, (top right) Pt loaded nanocomposites by Method 2 and (bottom) Pt loaded nanocomposites by Method 3

In all three methods (M1, M2 and M3), the characteristic diffraction peak C(001) of GO previously at 11.4° shifted to higher angles at about 24° after Pt deposition on GO (Pt/GO, red color spectra) which implies that the GO was also partially reduced to graphene and restacked into an ordered crystalline structure [23, 41]. The Pt loaded hybrid nanocomposite (Pt/PPy/CB/GO, green color spectra) synthesized by the three methods showed slightly shifted peaks of C(002) to higher angles with lower intensities (as compared to Pt/PPy/CB, blue color spectra), demonstrating successful incorporation of GO in PPy/CB.

For all samples, the diffraction peaks at the Bragg angles 39.9° ($d_{\text{spacing}}=0.226$ nm), 46.1° , 67.5° and 81.4° correspond to (111), (200), (220) and (311) planes of face centered cubic (fcc) crystalline structure of Pt. These peaks shows successful reduction of Pt nanoparticles on the catalyst supports. However, the peak intensity of the dominating Pt(111) plane suggests the degree of reduction of Pt on catalyst supports, in which case, method 2 proved to be the best method for reducing Pt precursor on the hybrid nanocomposite (PPy/CB/GO). For the same support, method 1 and 3 showed Pt(200) peaks almost merged with Pt(111).

The Pt(111) peak broadness gives information about the crystallite size i.e. broader means smaller grain size. The average Pt crystallite/particle size was measured using Pt(111) plane using Scherrer equation. Pt(220) plane was used instead, where the Pt(200) was infused with Pt(111). The calculated average particle size of Pt on various catalyst supports is shown in the table which are consistent with the TEM results. A general trend has been observed in the Pt particle size i.e. for any given catalyst support, the Pt reduced by method 2 gives the smallest Pt particle size (e.g. 3.1 nm for Pt/GO_M2), method 1 gives the largest Pt particle size (e.g. 3.9 nm for Pt/GO_M1), and method 3 gives a value in between these methods (e.g. 3.8 nm for Pt/GO_M3).

Table 7: Calculated average particle size of Pt on various catalyst supports by XRD data

Samples	Average Pt particle size (nm)
Pt/GO_M1	3.9
Pt/GO_M2	3.1
Pt/GO_M3	3.8
Pt/PPy/CB_M1	5.3
Pt/PPy/CB_M2	4.7
Pt/PPy/CB_M3	4.9
Pt/PPy/CB/GO_M1	3.8
Pt/PPy/CB/GO_M2	3.7
Pt/PPy/CB/GO_M3	2.7

3.2.1.2. TGA Results

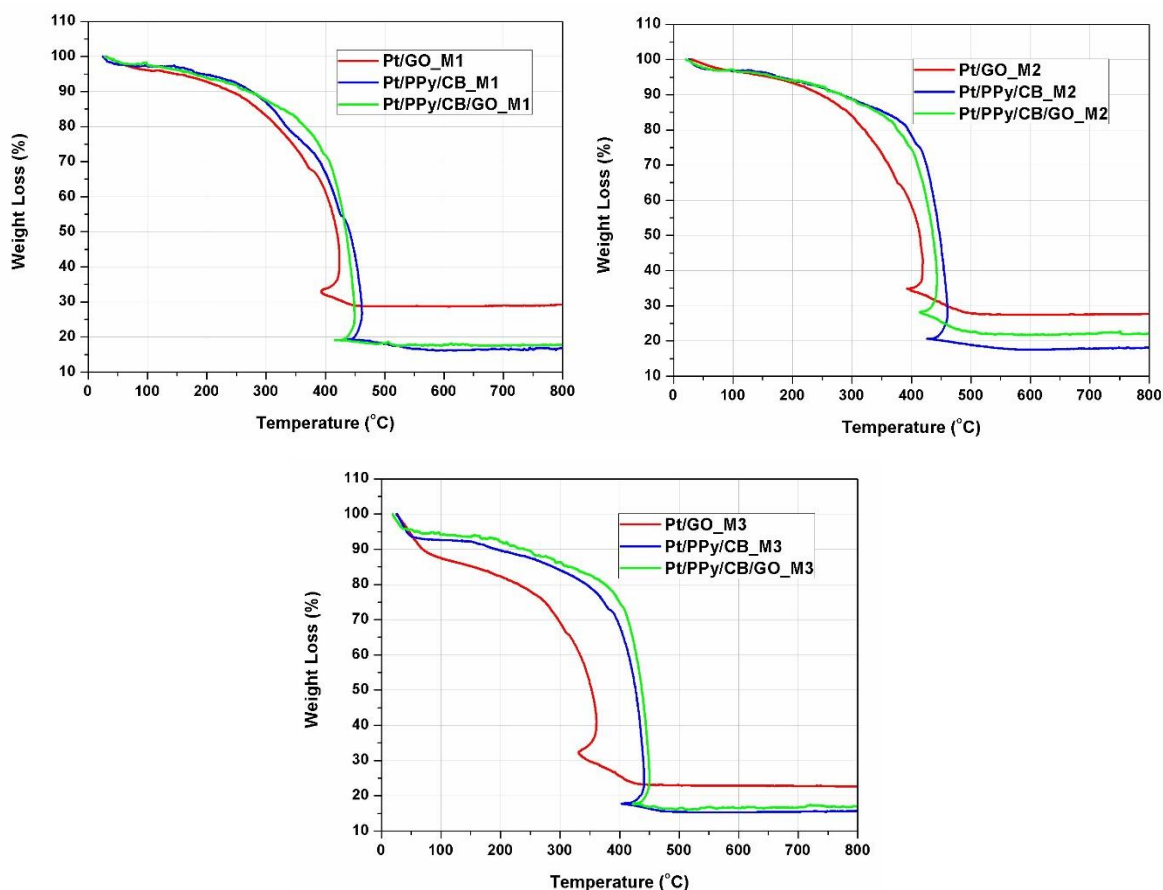


Figure 32: TGA curves: (top left) Pt loaded nanocomposites by Method 1, (top right) Pt loaded nanocomposites by Method 2, (bottom) Pt loaded nanocomposites by Method 3

The TGA analysis was done under air atmosphere to estimate the platinum amount deposited on the various catalyst supports namely: GO, PPy/CB and PPy/CB/GO by method 1, 2 and 3. The first weight loss occurred at 100⁰ C due to evaporation of entrapped water. After this temperature, the samples showed gradual weight loss due to combustion in the presence of air. After 550⁰ C, all the samples yielded straight lines with some residual weights which can be attributed to platinum amounts in the samples. Initially, while reducing the platinum precursor on carbon supports, the amount of platinum was kept about 15.8% by weight (theoretical), but the TGA curves shows different residual weights. These discrepancies can be attributed to the entrapped water contents and some instrumentation errors.

Table 8: Platinum amounts in various catalyst supports by TGA under air atmosphere

Samples	Pt amounts (weight %)
Pt/GO_M1	28.7
Pt/GO_M2	27.4
Pt/GO_M3	22.6
Pt/PPy/CB_M1	16.2
Pt/PPy/CB_M2	17.5
Pt/PPy/CB_M3	15.3
Pt/PPy/CB/GO_M1	17.5
Pt/PPy/CB/GO_M2	21.6
Pt/PPy/CB/GO_M3	16.1

3.2.1.3. Cyclic Voltammetry Results

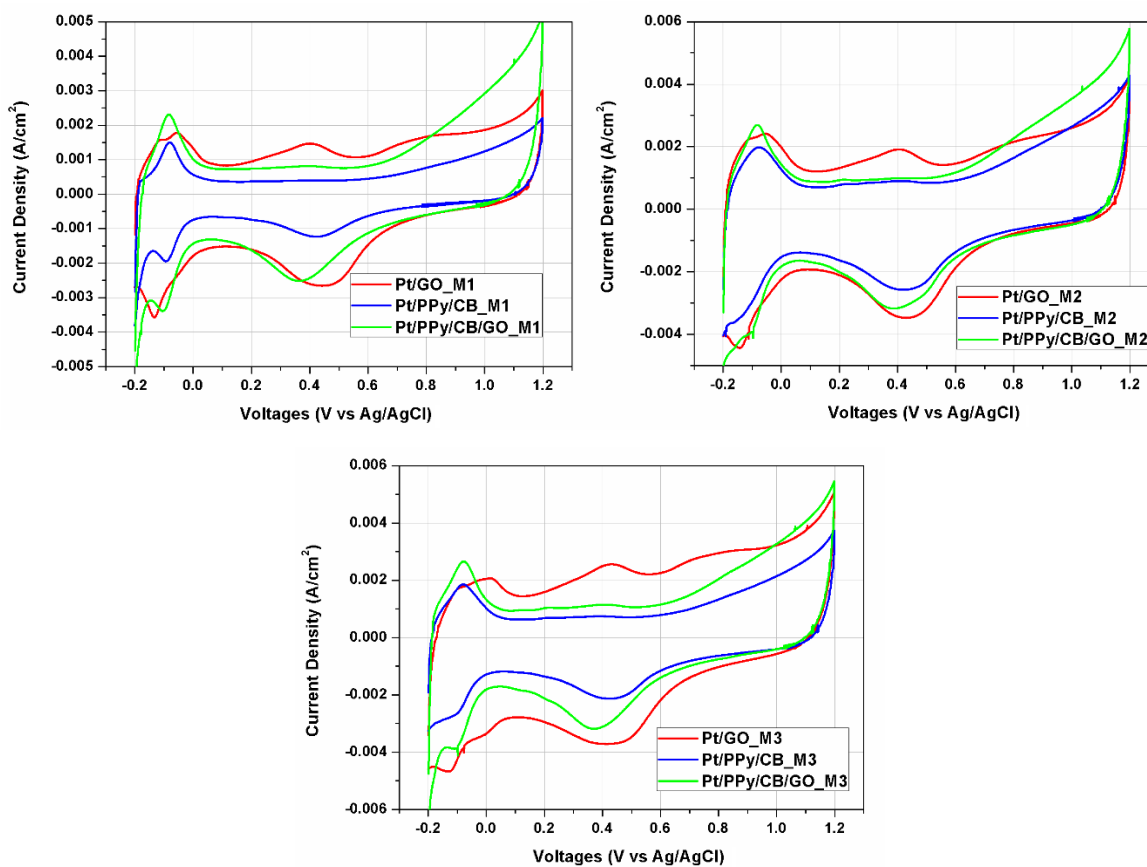


Figure 33: Cyclic voltammograms: (top left) Pt loaded nanocomposites by Method 1, (top right) Pt loaded nanocomposites by Method 2 and (bottom) Pt loaded nanocomposites by Method 3

Cyclic Voltammetry was used to find electrochemical surface area (ECSA) of platinum on different supports namely: GO, PPy/CB and PPy/CB/GO synthesized by method 1, method 2 and method 3. ECSA can be calculated by the formula mentioned in the previous chapter.

Table 9: Calculated ECSA values of different Pt loaded nanocomposites by method 1, method 2 and method 3

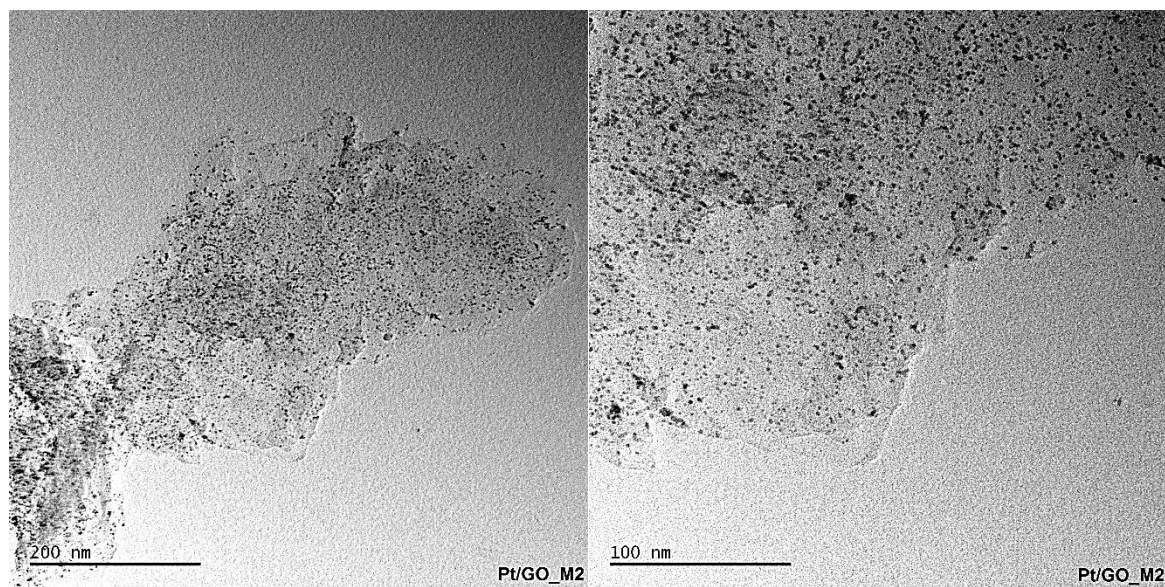
Samples	ECSA (m ² /g Pt)
Pt/GO_M1	97
Pt/GO_M2	128
Pt/GO_M3	101
Pt/PPy/CB_M1	84
Pt/PPy/CB_M2	117
Pt/PPy/CB_M3	95
Pt/PPy/CB/GO_M1	126
Pt/PPy/CB/GO_M2	153
Pt/PPy/CB/GO_M3	142

Two trends have been observed by the CV voltammograms. First, for a particular support e.g. GO, Pt synthesized by method 2 gives the highest ECSA value, e.g. 128 m²/g for Pt/GO_M2. This is because FeCl₃ acts as an effective stabilizer and retardant in the Pt seed growth leading to smaller particle size with high surface area available for electrocatalytic activity (3.1 nm). Followed by this, method 3 also gives good ECSA values owing to the use of the complex Na⁺B⁻(OCH₂CH₂OH)₄ which acts as an additional stabilizer e.g. 101 m²/g for Pt/GO_M3. While method 1 gives the lowest ECSA value.

Second trend is, for a particular method e.g. method 2, the CV voltammogram of the hybrid nanocomposite support i.e. Pt/PPy/CB/GO shows the highest hydrogen

adsorption/desorption peaks with large areas under them indicating increased number of available Pt catalyst active sites for charge transfer which in turn gives high ECSA value of $153 \text{ m}^2/\text{g}$ about 30% higher than Pt/PPy/CB ($117 \text{ m}^2/\text{g}$) and 20% higher than Pt/GO ($128 \text{ m}^2/\text{g}$). The improved electrocatalytic activity of Pt loaded hybrid nanocomposite (Pt/PPy/CB/GO) as compared to other supports can be explained due to the increased electrical conductivity, increased number of charge carriers with their free mobility. Since the oxygen containing groups which act as insulators, were partially reduced during Pt synthesis on the hybrid nanocomposite, which results in less resistance for electron and mass transfer. In addition to this, the inclusion of PPy/CB into layers of GO inhibits the aggregation of graphene sheets during partial reduction of GO which in turn provides large surface area for uniformly distributing Pt nanoparticles on the heterogeneous nucleation sites formed by the PPy/CB.

3.2.1.4. TEM Results



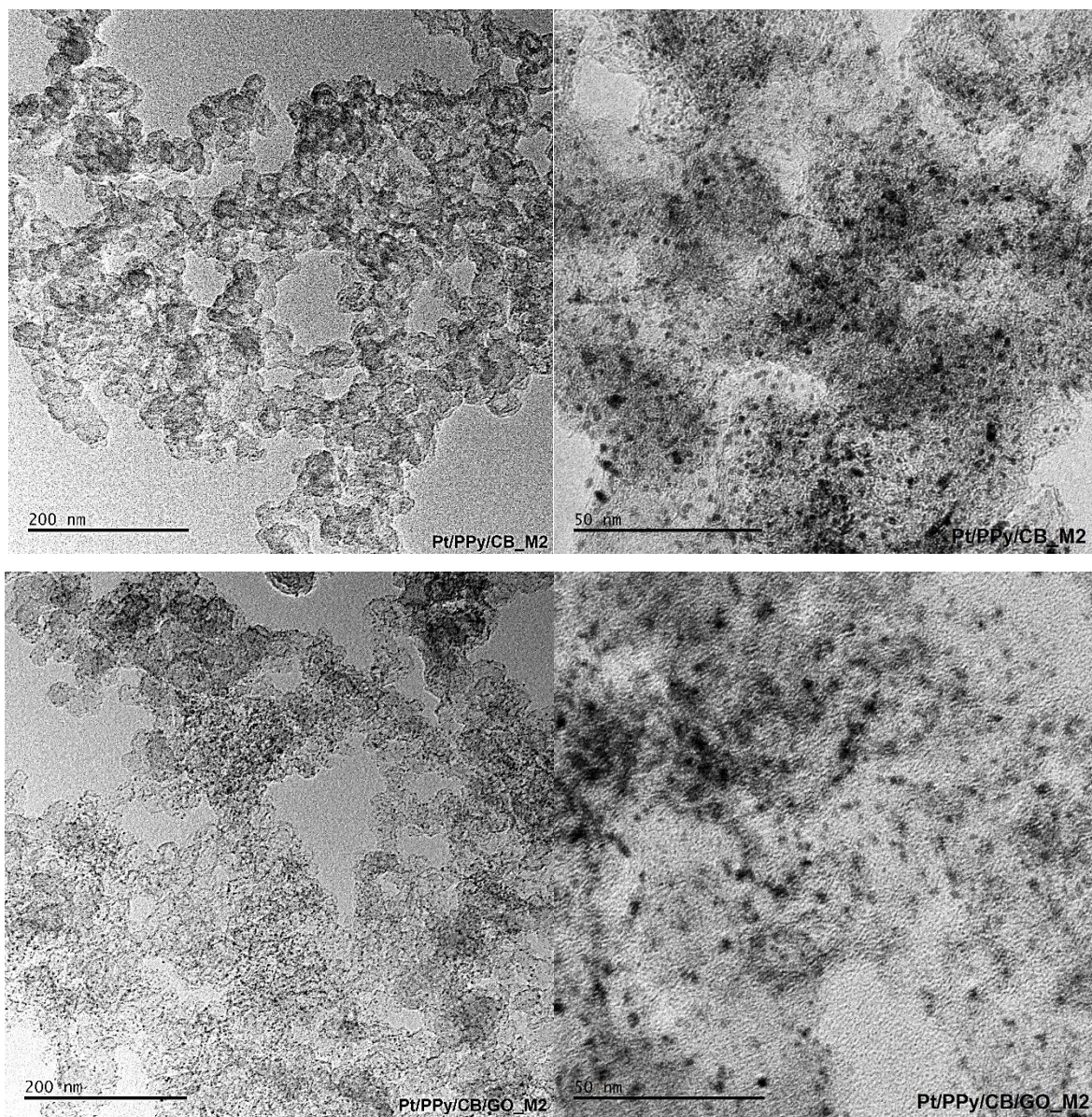


Figure 34: TEM images: (top) Pt/GO by method 2, (middle) Pt/PPy/CB by method 2 and (bottom) Pt/PPy/CB/GO by method 2.

From the results of XRD and CV, the samples Pt/GO, Pt/PPy/CB and Pt/PPy/CB/GO synthesized by method 2 were selected for TEM imaging to see their Pt nanoparticles' incorporation, size, distribution as well as the surface morphology of the supports. As it can be seen that method 2 successfully incorporated Pt nanoparticles on the supports with uniform dispersion with almost no Pt agglomerations. Also the Pt nanoparticle size calculated from XRD data (i.e. Pt/GO 3.1 nm, Pt/PPy/CB 4.7 nm, Pt/PPy/CB/GO 3.7 nm) matches quite well with the TEM results.

3.3. CONCLUSIONS

Pt nanoparticles were reduced on catalyst supports i.e. graphene oxide (GO), polypyrrole/carbon black nanocomposite (PPy/CB) and polypyrrole/carbon black/graphene oxide hybrid nanocomposite by three methods to see their effects on the size of Pt nanoparticles, their distribution on supports and electrocatalytic activity with different characterization techniques. For comparison and consistency purposes, the reaction parameters in all the three methods were maintained. XRD results showed the successful incorporation of Pt nanoparticles on the catalyst supports by all three methods as evidenced by the characteristic Pt peaks with the smallest Pt nanoparticles' size yielded by method 2. TGA results were used to estimate the Pt amounts in the catalyst supports. TEM imaging was used to observe the Pt nanoparticles' incorporation, size, distribution as well as the surface morphology of the samples Pt/GO, Pt/PPy/CB and Pt/PPy/CB/GO synthesized by method 2, which showed small Pt nanoparticles' size with homogeneous dispersion and minimal agglomeration. Two trends were observed by the CV voltammograms. First, for a particular support e.g. GO, Pt synthesized by method 2 gave the highest ECSA value while method 1 gave the lowest. Method 3 gave ECSA values intermediate to these. Second trend was, for a particular method e.g. method 2, the CV voltammogram of the hybrid nanocomposite support i.e. Pt/PPy/CB/GO showed the highest ECSA value about 30% higher than Pt/PPy/CB and 20% higher than Pt/GO. The results showed that Pt loaded hybrid nanocomposite (Pt/PPy/CB/GO) synthesized by method 2 was the best among all the catalyst supports and methods due to which it is promising electrocatalyst for high performance PEM fuel cells. This would be our future task of investigation.

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