

Project Title:-***Development of Pt-Au-Graphene-Carbon nanotube composites for fuel cells and biosensors applications******Objectives:-***

This project addresses the architectures needed for the processing of Pt-Au-graphene-carbon nanotube (Pt-Au/f-G/f-CNT) nanocomposites and aims at the investigation of suitability of these nanocomposites for the hydrogen and alcohol based fuel cells and to develop novel electrocatalysts for fuel cells. The project also aims at the detection of specific biomolecules in order to develop electrochemical biosensors.

Results and discussion***Fuel cells:-******Graphene and nitrogen doped graphene as catalyst support materials:-***

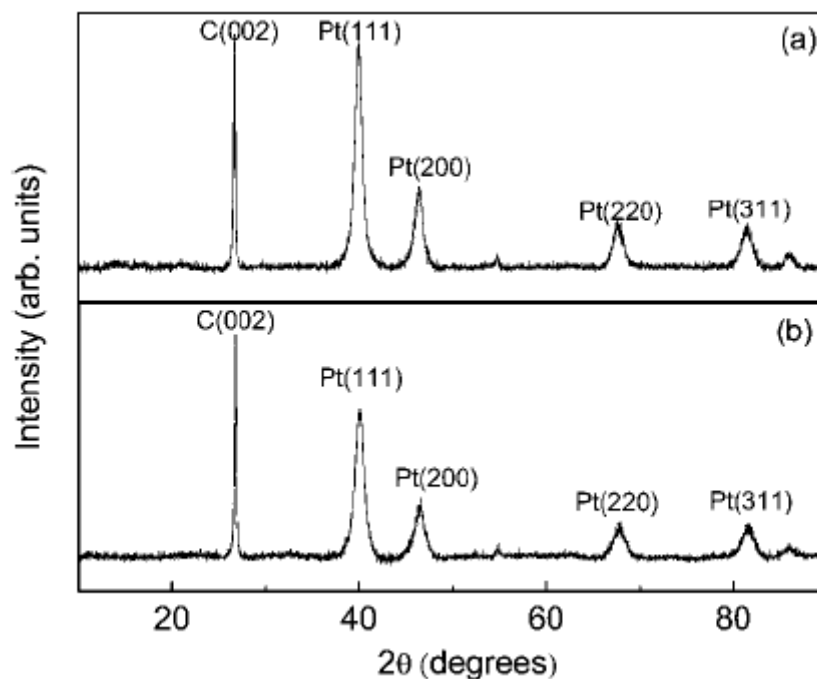
Graphene and nitrogen doped graphene have been used as a catalyst support for platinum nanoparticles for oxygen reduction reactions in proton exchange membrane fuel cells. Platinum nanoparticles were dispersed over these support materials using the conventional chemical reduction technique. The morphology and structure of the graphene based powder samples were studied using X-ray diffraction, Raman spectroscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. A full cell was constructed with platinum loaded nitrogen doped graphene and the results have been compared with platinum loaded graphene. A maximum power density of 440 and 390 mW cm⁻² has been obtained with platinum loaded nitrogen doped graphene and platinum loaded graphene as ORR catalysts respectively. Nitrogen plasma treatment created pyrrolic nitrogen defects, which act as good anchoring sites for the deposition of platinum nanoparticles. The improved performance of fuel cells with N-G as catalyst supports can be attributed to the increased electrical conductivity and improved carbon–catalyst binding.

Graphene was functionalized by sonicating in a solution of conc. sulfuric acid and conc. nitric acid for 30 min. MWNT prepared by pyrolysis of acetylene over AB₃ based alloy hydride catalyst have also been functionalized following a similar process. Nitrogen plasma treatment of G was performed in a Planar R.F Magnetron sputtering system equipped with a high frequency generator

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14. ABSTRACT This project addresses the architectures needed for the processing of Pt-Au-graphene-carbon nanotube (Pt-Au/f-G/f-CNT) nanocomposites and aims at the investigation of suitability of these nanocomposites for the hydrogen and alcohol based fuel cells and to develop novel electrocatalysts for fuel cells. The project also aims at the detection of specific biomolecules in order to develop electrochemical biosensors.					
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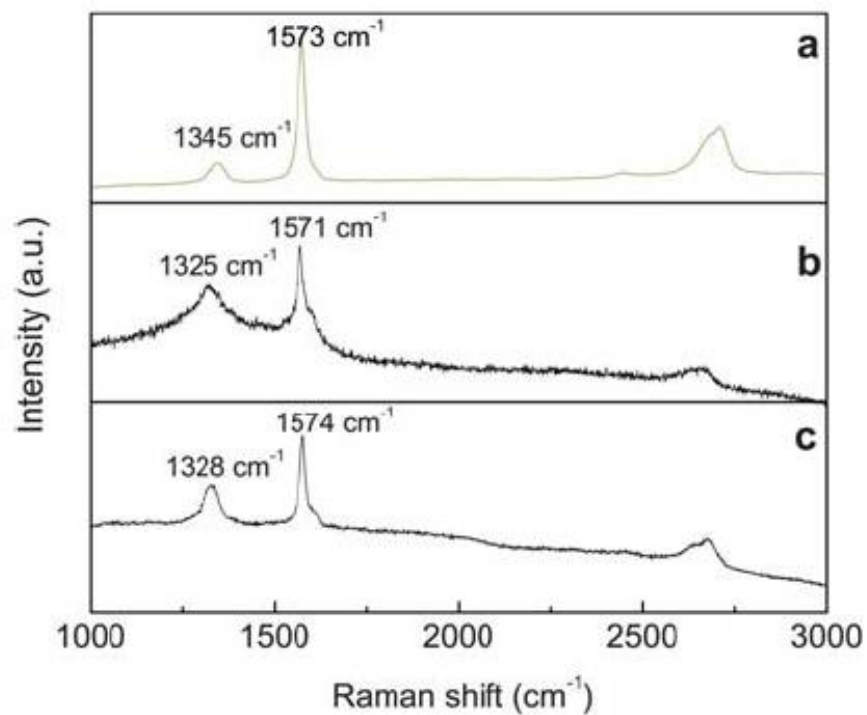
working at a frequency of 13.56 MHz and a power up to 500 W. Platinum loaded MWNT (Pt/MWNT), platinum loaded G (Pt/G) and platinum loaded N-G (Pt/N-G) were prepared by a chemical reduction technique.

The XRD patterns of Pt/G and Pt/N-G show the characteristic (111), (200), (220) and (311) reflections of face centered cubic crystalline Pt along with peak corresponding to hexagonal graphite.



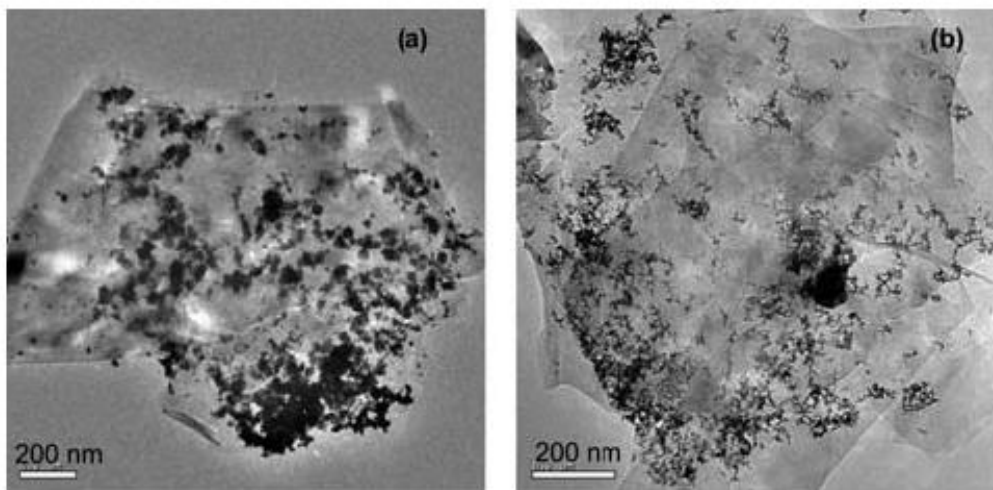
XRD patterns of (a) Pt/G and Pt/N-G

Raman spectra of G and N-G wherein a Stokes G peak occurs at 1571 cm^{-1} and the 2D band occurs at 2661 cm^{-1} which is consistent with the reported Raman spectra of graphene sheets and nitrogen doped graphene sheets. The D band which can be seen at 1325 cm^{-1} arises due to disorder and in contrary to this, highly ordered graphite shows a very weak D-band. The band at 1602 cm^{-1} is a defect induced band (D'-band) and is not found in graphite.



Raman spectrum of (a) graphite, (b) G and (c) N-G

TEM images of Pt/G and Pt/N-G respectively show that the Pt nanoparticles can be seen dispersed over the graphene sheets.



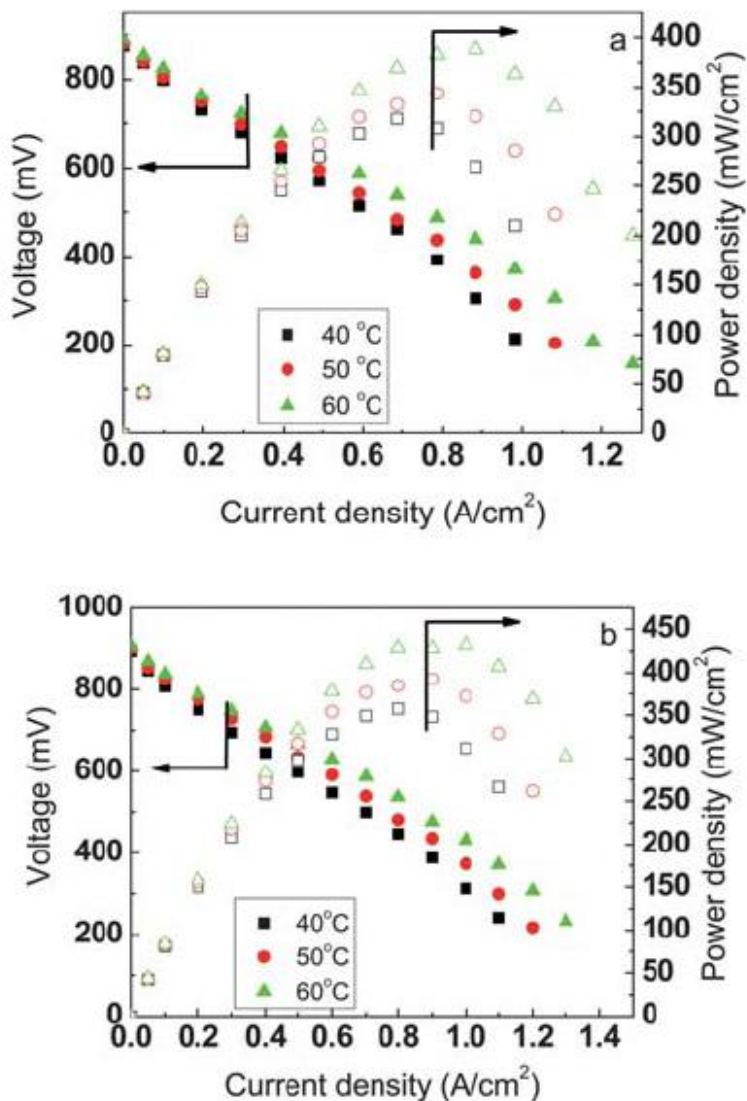
TEM images of (a) G and (b) N-G

Fuel cell measurements were performed using an ElectroChem Fuel Cell Test Station. The membrane electrode assembly (MEA) was prepared by sandwiching a pretreated Nafion 212 membrane between the anode and cathode. Both anode and cathode were made up of a backing layer, a gas diffusion layer and a catalyst layer. The catalyst layer was prepared by ultrasonically dispersing a required amount of catalyst in de-ionized water. Typically, 0.3 ml of 5 wt% Nafion was added to 15 mg of electrocatalyst (Pt/MWNT) at anode side and 0.6 ml of 5 wt% Nafion was added to 30 mg of electrocatalyst (Pt/N-G) at the cathode side maintaining a fixed Nafion to electrocatalyst weight ratio of 1:1. The suspension was coated uniformly over a gas diffusion layer. A mixture of carbon (Vulcan XC 72) and polytetrafluoroethylene (PTFE) was coated on carbon cloth which formed the gas-diffusion layer. For comparison, one more MEA was prepared with Pt/MWNT as anode catalyst and Pt/G as cathode catalyst following the similar procedure mentioned above. The effective electrode area was 11.56 cm². A Pt loading of 0.25 mg cm⁻² and 0.5 mg cm⁻² was maintained at the anode and cathode respectively.

The MEAs were tested in a fuel cell test station by fixing them between two graphite plates which had a serpentine type flow provision for gas flow. The gas streams of pure hydrogen and oxygen were controlled by their respective mass flow controllers, and the flow rates were kept at 100 sccm respectively. Hydrogen and oxygen were humidified using respective humidifiers before feeding into the anode and cathode. The performance of the fuel cell was studied at three different temperatures (40, 50 and 60°C) under 15 psig back pressure.

The polarization plots were recorded using a d.c. load box. The reactant gases were humidified with water to maintain the water content in the membrane electrolyte. Prior to the polarization studies, the electrodes were activated between an open circuit potential and high current densities which are necessary to activate the catalyst for the oxygen reduction reaction. The polarization curves taken at three different temperatures (40, 50 and 60°C) with cathode containing Pt/G and Pt/N-G respectively showed a maximum power density of 440 mW cm⁻² with Pt/N-G whereas the MEA with Pt/G showed a maximum power density of 390 mW cm⁻². The improved performance with Pt/NG as an ORR catalyst can be attributed to the formation of pentagons and heptagons and increase in the reactivity of neighboring carbon atoms because of nitrogen doping. It has been reported that nitrogen doping introduces disorder in the graphene stacking and these disorder

structures and the defects can act as good anchoring sites for deposition of Pt particles. Besides, the oxygen defects in the surface of graphene formed by exfoliation of graphite may also act as anchoring sites for the deposition of the Pt particles. N-doping of graphene increases the binding energy of Pt atom to the substrate. In general, the more N atoms and the closer they are to the C atom which bonds directly to the Pt, the stronger the binding energy. The improved performance can also be attributed to the improved carbon–catalyst binding and increased electrical conductivity brought about by nitrogen doping. It has also been hypothesized that a synergistic support effect is with N-G because the nitrogen doped carbon nanostructures are known to decompose reactive intermediates such as hydrogen peroxide into oxygen formed during ORR.

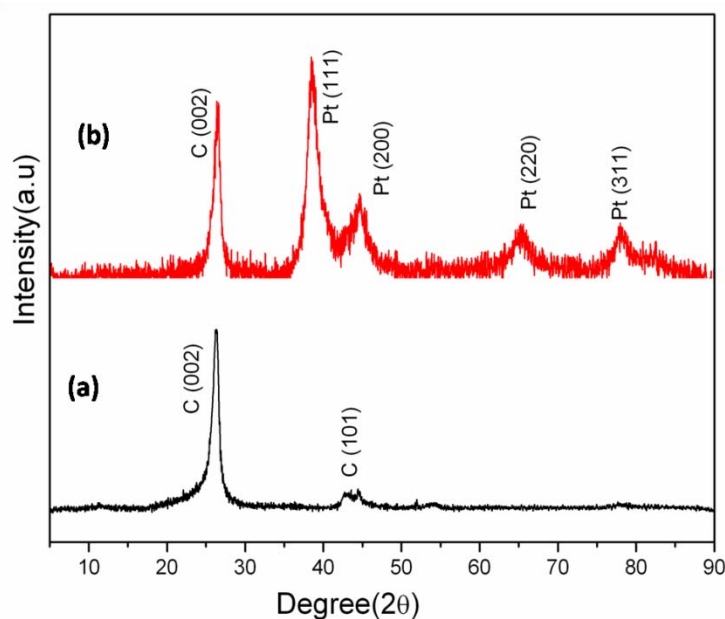


Polarization graphs with (a) Pt/G and (b) Pt/N-G as cathode catalysts

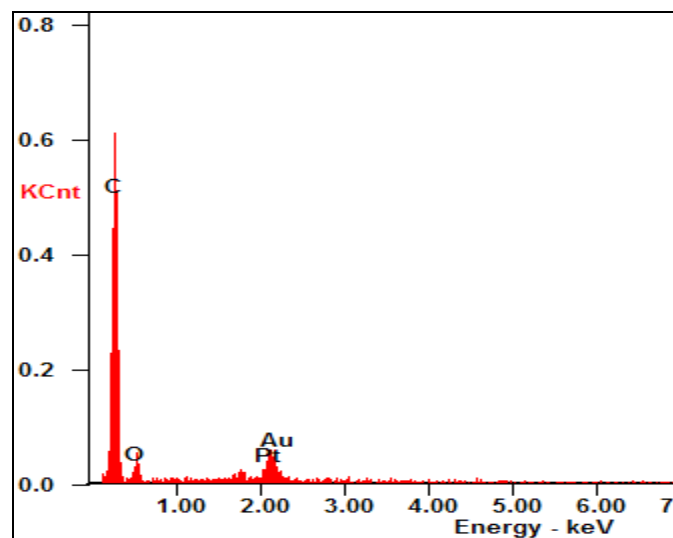
Graphene + MWNT as catalyst support materials:-

Initially 200 mg of (f-MWNT+f-G) was dispersed in 200 ml of a mixture of ethylene glycol (EG) and water by ultrasonication for 1 h and followed by stirring for 6 hr. After that the appropriate amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution were added to the suspension dropwise and stirred for 24h. The molar ratio of Pt and Au was taken in 3:1 ratio. The pH of the entire solution was adjusted to 13 by adding a NaOH solution (2.5 M) and the solution was refluxed at 100°C for 2hr to ensure that entire Pt and Au were completely reduced. The water to EG ratio was controlled 1:4 ratio throughout the reaction. In this reaction ethylene glycol acts as a reducing, stabilizing and dispersing agent. Finally the solid was filtered and washed with DI water and after dried at 70°C for 8 h. The prepared samples were labeled as $\text{Pt}_3\text{Au}/(\text{f-MWNT}+\text{f-G})$.

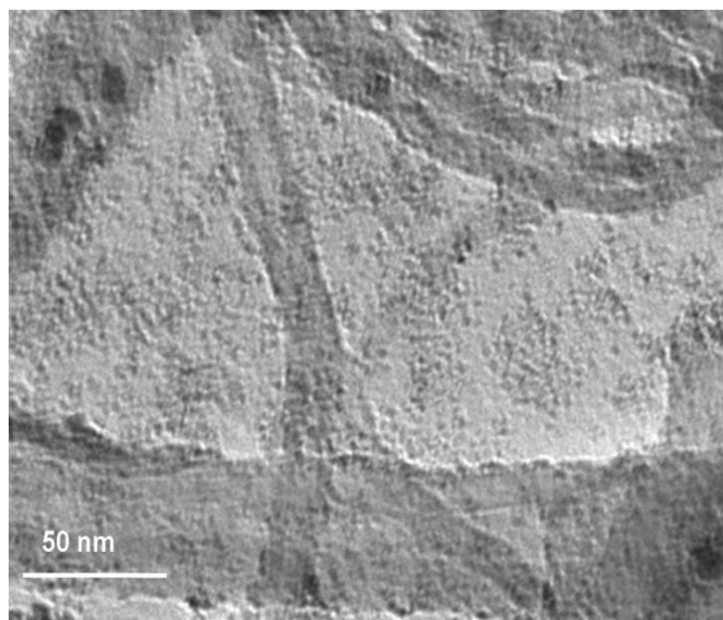
The XRD shows the fcc crystal structure of Pt_3Au alloy catalyst along with the peaks of graphene and MWNT. EDX shows the presence of Pt and Au within the nanocomposite in the ratio (3:1).



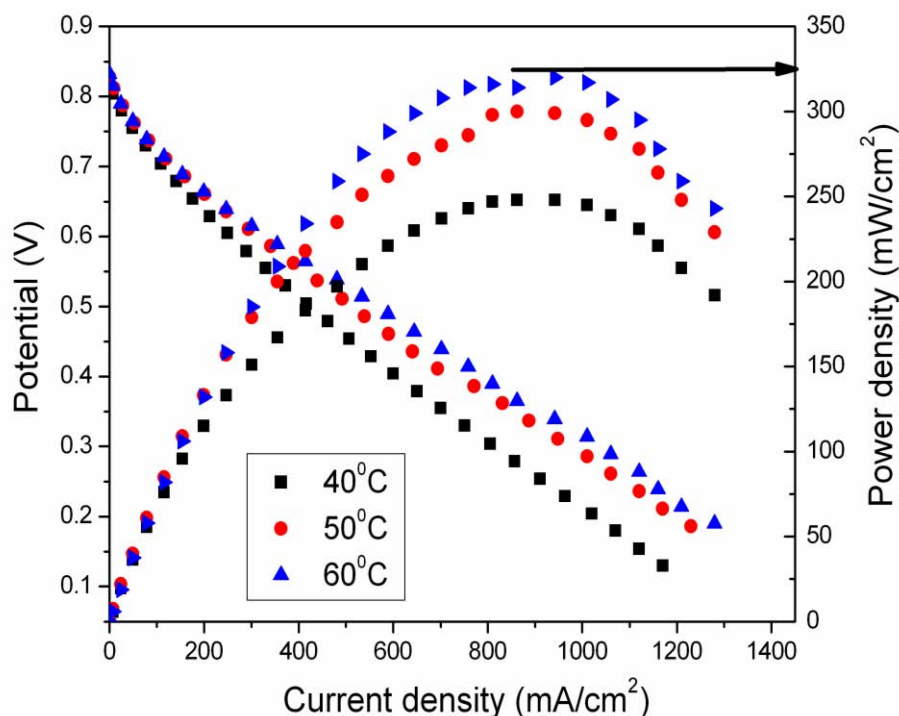
XRD of (a) (f-G + f-MWNT) (b) $\text{Pt}_3\text{Au}-(\text{f/G} + \text{f/MWNT})$



EDX of $Pt_3Au-(f/G + f/MWNT)$



TEM image of $Pt_3Au-(f/G + f/MWNT)$



Polarization curve of Pt₃Au dispersed (f/G + f/MWNT) electrocatalyst

Pt₃Au-(f/G + f/MWNT) shows a maximum power density of 320 mW/cm². Aggregation of graphene sheets during drying of graphene dispersions leads to a loss of its ultrahigh surface area, advantage as a two-dimensional nanomaterial. In this regard, addition of MWNT to graphene dispersions during the synthesis of Pt₃Au/f-(Graphene + MWNT) retains its high surface area because these MWNT can act as spacers in between graphene bundle sheets and prevent the restacking of graphene bundle sheets due to van der Waals forces. So these hybrid nanostructure give high surface area to the uniform dispersion Pt₃Au catalyst nanoparticles. Also the high electrical conductivity of MWNT can enhance the conductivity of hybrid nanostructure.

Also when we are alloying platinum (Pt) with gold (Au) in the ratio 3:1 compositions, the fcc geometry of Pt is slightly distorted with Au atoms tending to occupy the corner positions (surface sites). The orientation of Au atoms at surface sites is attributed to (a) the relative cohesive metal energies, (b) electronegativities, and (c) electronic/steric effects. Cohesive of 565 kJ/mol for platinum is much larger than its value of 368 kJ/mol for gold, implying that platinum atoms occupy interior sites having maximum coordination with the other metal atoms. The relative

electronegativity values for Pt and Au are 2.2 and 2.54, respectively. Owing to the higher electronegativity value of Au, there is a partial charge-transfer from Pt to Au resulting in enrichment of electron density on Au surface. These electronic effects can enhance the ORR activity of the Pt₃Au alloy catalyst. Also the stability of the Pt-Au cluster increases substantially upon alloying Au with Pt. This may be responsible for the increased durability of Pt-Au alloy in relation to Pt in fuel cells.

Electrochemical biosensors

In addition to the novel catalytic support material for fuel cells, there are various advantages that graphene-CNTs nanocomposites bring to electrochemical-sensor design; the most attractive feature of the graphene-CNT enzyme-based biosensor may be their improved operational stability. The improvement in the electrochemical activity of graphene-CNT-based electrochemical sensors for DNA, Glucose, Cholesterol and protein is anticipated mainly due to the introduction of functional groups on the surface of the graphene-CNTs nanocomposites and the anticipated changes in the morphology of graphene due to the introduction of CNTs.

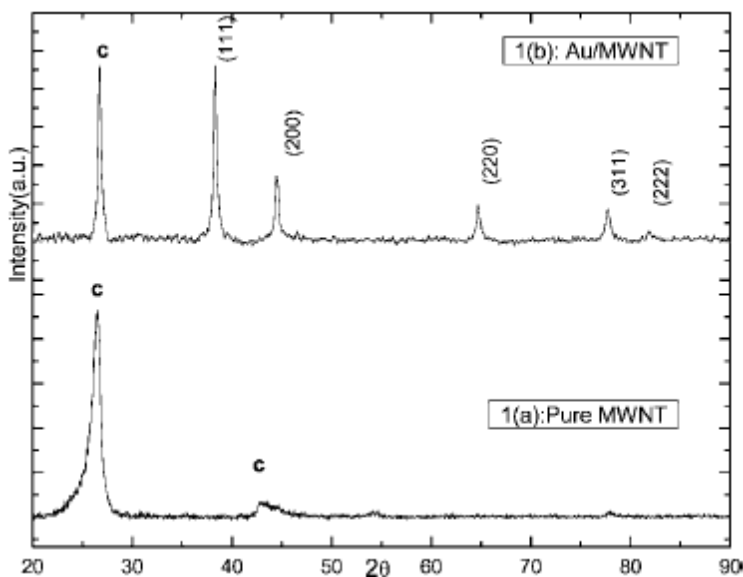
In most of the glucose biosensors, glucose oxidase (GOD) is employed as the enzyme as it is of practical use, stable, and inexpensive. GOD catalyzes the electron transfer from glucose to oxygen accompanying the production of gluconolactone and hydrogen peroxide. From the electrochemical detection of the enzymatically liberated H₂O₂, the quantification of glucose can be achieved. However, the overvoltage necessary for the oxidation or reduction of H₂O₂ at solid electrodes is rather high. Therefore, the modification of the electrode surface is carried out such that the H₂O₂ oxidation/reduction overvoltage is considerably lowered. This can be achieved by the deposition of nanocrystalline metal clusters of noble metals such as palladium, platinum, gold (Au), copper, and iridium on to the surface of the electrochemical transducers, the MWNT.

A new amperometric biosensor, based on deposition of glucose oxidase (GOD) onto crystalline gold (Au) nanoparticle modified MWNT electrode has been prepared. Chemical reduction method is a simple and effective technique to deposit nanocrystalline Au metal particles on the surface of MWNT. With the immobilization of 32 U of GOD on the Au-MWNT/Nafion film, a novel glucose biosensor was fabricated by a simple deposition technique and exhibited many advantages at a

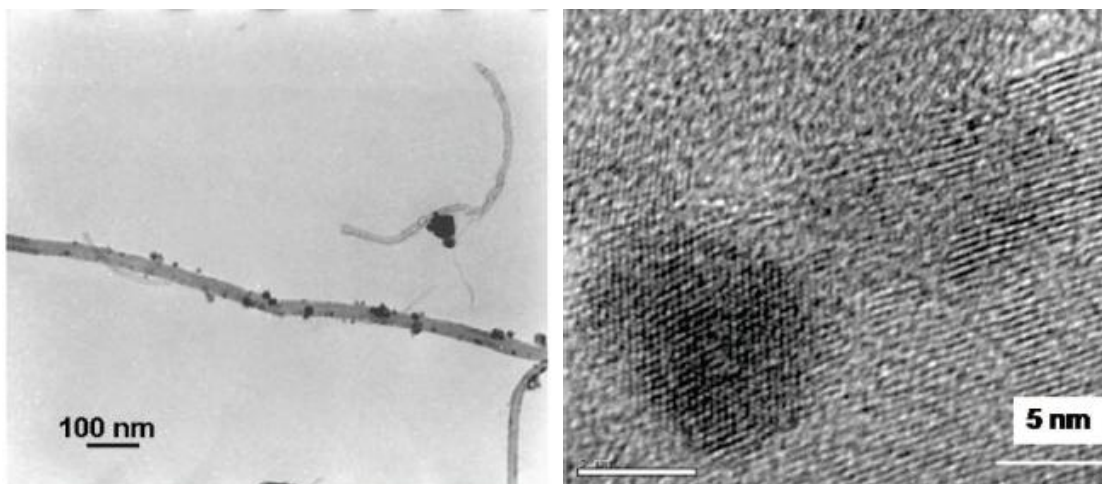
low applied potential, such as high sensitivity, low detection limit, good reproducibility, long-term stability, and fast current response.

Preparation of Au-MWNT Composite:-

In order to decorate the purified MWNT with nanocrystalline Au clusters, a chemical reduction method was used. Nearly 0.02 g of purified MWNTs were treated with 0.075 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ followed by magnetic stirring for 12 h. Au salt is reduced by adding a reducing solution, which is a mixture of 0.1 M NaBH_4 and 1M NaOH , during stirring. After the reaction is over, the solution is washed three times with deionized water and filtered using cellulose membrane filters having a pore size of $0.1 \mu\text{m}$. The material left out is collected and dried in a vacuum oven at 80°C for 2 h. The sample was then characterized using XRD, SEM, and energy dispersive analysis of X-rays (EDAX).



Powder X-ray diffractogram of (a) purified CNTs and (b) Au-MWNT.



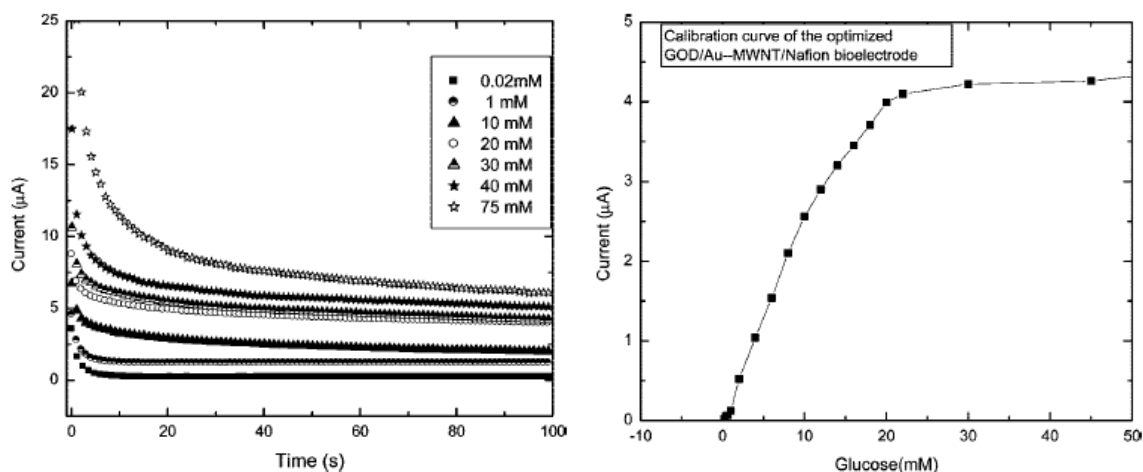
TEM and HRTEM images of Au-MWNT

Fabrication of GCE/GOD/Au-MWNT/Nafion Electrode:-

Before electrode modification, the bare GCE was polished with 0.05 μm alumina slurry, sonicated in deionized water, and dried with a high-purity nitrogen stream to obtain a mirror surface. The Au-MWNTs were sonicated in 0.5% Nafion solution to give a concentration of ~ 1 mg/ml. Four microliters of the CNT suspension was film-cast onto the surface of the GCE and allowed to dry slowly. Films formed from Nafion-solubilized MWNT are more uniform and stable than those cast from organic solvents. Nafion assists the dispersion of MWNT, whereby the MWNT remain well-dispersed on prolonged standing. A 4 μL portion of 32 U GOD solution was film-cast onto the surface of the GCE/GOD/Au-MWNT/Nafion electrode and allowed to dry slowly at 4°C. The obtained GOD/Au-MWNT/Nafion electrode was washed carefully with double-distilled water and dried at less than 4°C. These GCE/Au-MWNT/GOD/Nafion bioelectrodes were coated with an extra 2.5 μL layer of 0.5% Nafion. The electrodes were rinsed with pH 7 buffer.

Determination of Glucose Using Fabricated GOD/Au-MWNT/Nafion Electrode:-

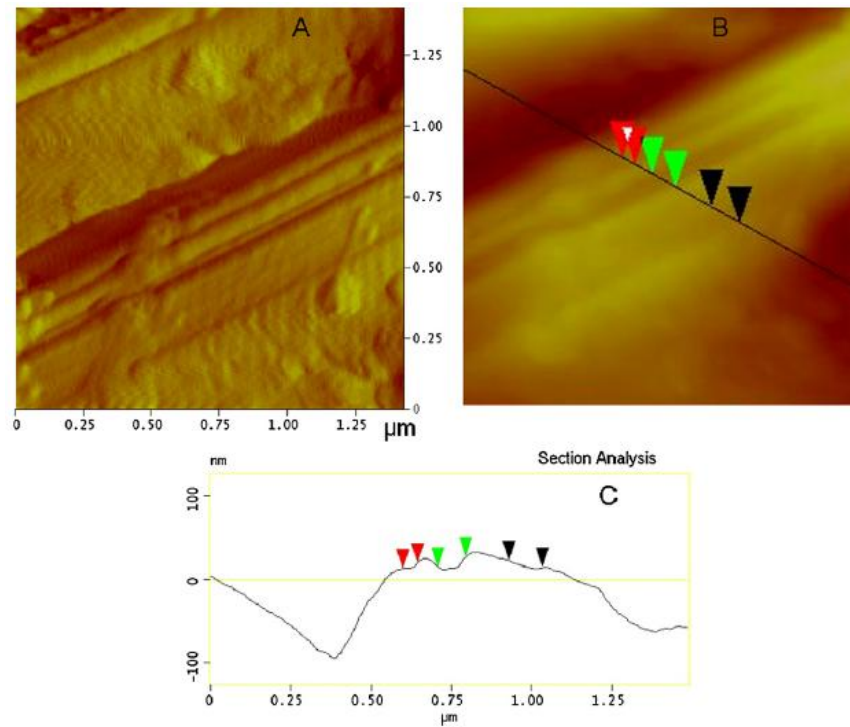
The typical amperometric i - t curves for the fabricated GOD/Au-MWNT/Nafion electrode at a constant voltage of +0.3 V and using this, the steady-state calibration curve has been drawn using the steady-state current values corresponding to different glucose concentrations.



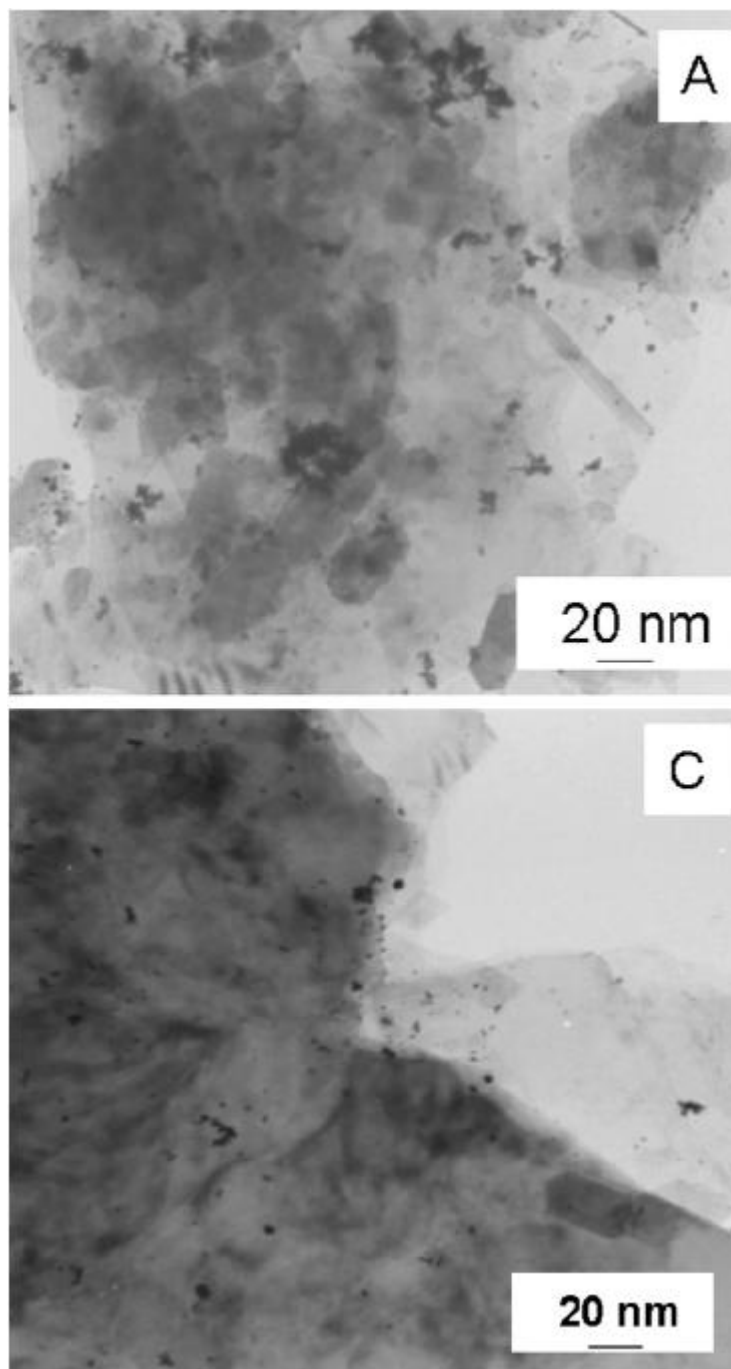
Amperometric *i-t* curves for different glucose concentrations and the calibration curve of the fabricated GOD/Au-MWNT/Nafion electrode

A more controllable, stable, and reproducible deposition of Au-MWNT film onto GCE can be achieved using a homogeneous solution of (0.5%) Nafion/Au-MWNT. The fabricated GOD/Au-MWNT/Nafion electrode has a good glucose-biosensing capability, and it exhibits a linear response up to 22 mM glucose and a detection limit of 20 μM .

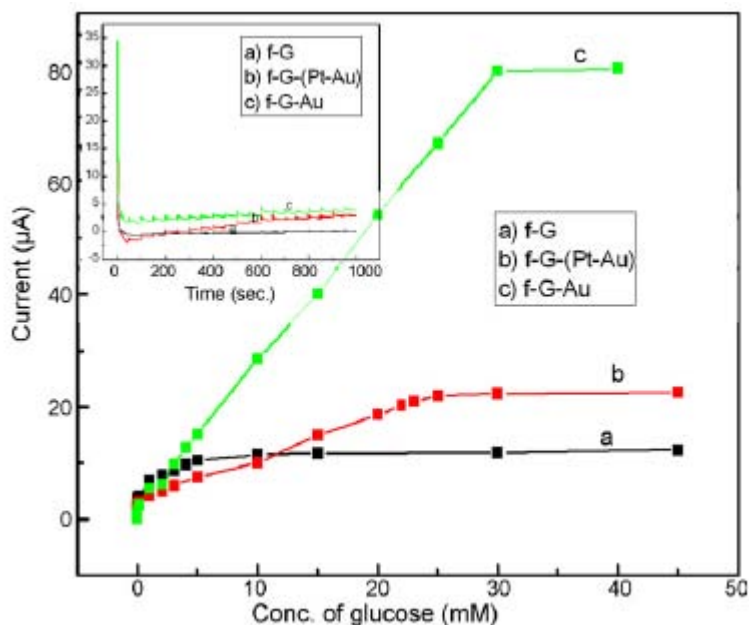
In addition, Amperometric glucose biosensors have been fabricated by using platinum–gold (Pt–Au) and gold (Au) nanoparticle spacers decorated graphene nanosheets. The immobilization of glucose oxidase (GOD) over Nafion-solubilized metal nanoparticles dispersed graphene f-G-(Pt–Au) and f-G-(Au) electrode has been achieved by physical adsorption. The resultant bioelectrode retains its biocatalytic activity and offers fast and sensitive glucose quantification. The performances of the biosensor have been investigated by electrochemical method at an optimum potential of +0.8V in pH 7.0 phosphate buffer. The fabricated f-G-(Au) based glucose biosensor exhibits best sensing performance with a linear response up to 30 mM with an excellent detection limit of 1 μM . The elimination of restacking of f-G by using (Pt–Au) and (Au) nanoparticle spacers resulted in the increase in the surface area and glucose sensing performance.



AFM images of graphene layers: (A) a 5_μm×5_μm square showing the layered structure of graphene. (B) A zoomed image of graphene layers. (C) A line scan taken through the image.



TEM images of f-G-(Pt-Au), f-G-Au

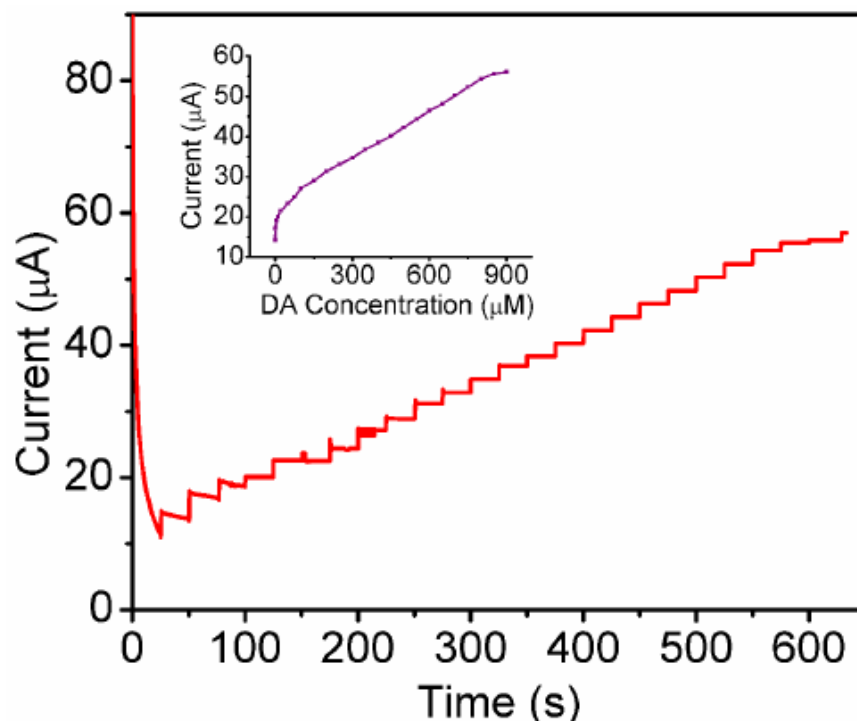


Amperometric I-T curves of the fabricated (a) Nafion/GOD/f-G/GC (b) Nafion/GOD/f-G-(Pt-Au)/GC (c) Nafion/GOD/f-G-Au/GC electrode for different glucose concentrations (inset) calibration curve of the fabricated (a) Nafion/GOD/f-G/GC (b) Nafion/GOD/f-G (Pt-Au)/GC and (c) Nafion/GOD/f-G-Au/GC bioelectrode

The fabricated f-G-(Au) based cost effective glucose biosensor exhibits best sensing performance with a linear response up to 30mM with excellent detection limit of 1_μM and also has excellent selectivity for the anionic interference and stability.

Pt/f-MWNT immobilized ss-DNA for selective detection of dopamine:-

A hybrid nanocomposite consisting of Pt nanoparticles decorated functionalized multiwalled carbon nanotubes (f-MWNT) immobilized with single strand-DNA (ss-DNA) has been devised for the selective detection of dopamine (DA). AFM and TEM analyses show that wrapping of ss-DNA over Pt/f-MWNT reduces the aggregation of the nanotubes arising from van der Waals interaction. In addition to serving as a noncovalent dispersion agent, ss-DNA facilitated electron transfer towards dopamine, as analyzed by cyclic voltammetric studies (CV) and amperometry. The sequence dependency of ss-DNA for DA detection has been analyzed using AC and GT ss-DNA. The hybrid nanocomposite biosensor consisting of AC/ss-DNA exhibits linearity of detection upto ~315 μ M, with a detection limit 0.8 μ M towards dopamine. The best sensing performance with linearity of ~800 μ M and detection limit ~0.45 μ M has been obtained with GT/ss-DNA immobilized Pt/f-MWNT sensor.



Amperometric response of Pt/f-MWNT/ss-DNA(GT)/NA electrode for the addition of 25 μM dopamine in 0.1 M PBS at a constant applied potential of 0.23 V. Inset shows the calibration curve for dopamine

The Pt/f-MWNT/ss-DNA/NA/GCE electrode exhibits excellent electrocatalytic activity towards DA, repelling signals from AA and UA. The detection limit and linearity of AC and GT/ss-DNA immobilized Pt/f-MWNT sensors are $\sim 0.8 \mu\text{M}$, 315 μM and 0.45 μM , 800 μM respectively which are superior to that of pure AC/ss-DNA immobilized sensor. The advantage of the modified electrodes was attributed to the separation and controlled alignment of Pt/f-MWNT by ss-DNA wrapping as well as the good conductivity of Pt together with high surface area of f-MWNT, which in turn increased the overall electron transfer rates.

Deliverables:

1. *G, N-G and (G+MWNT) as excellent catalyst support materials for fuel cells.*
2. *Novel Pt/f-MWNT, Au/G electrodes as biosensors for determination of glucose and dopamine.*

Publications:-

A Glucose Biosensor Based on Deposition of Glucose Oxidase onto Crystalline Gold Nanoparticle Modified Carbon Nanotube Electrode

Raghavan Baby Rakhi, Kanikrishnan Sethupathi, and Sundara Ramaprabhu

J. Phys. Chem. B (2009), 113, 3190–3194

Nitrogen doped graphene nanoplatelets as catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell

R. Imran Jafri, N. Rajalakshmi and S. Ramaprabhu

J. Mater. Chem., 2010, 20, 7114–7117

Metal decorated graphene nanosheets as immobilization matrix for amperometric glucose biosensor

Tessy Theres Baby, S.S. Jyothirmayee Aravind, T. Arockiadoss, R.B. Rakhi, S. Ramaprabhu

Sensors and Actuators B 145 (2010) 71–77

Noble metal dispersed multiwalled carbon nanotubes immobilized ss-DNA for selective detection of dopamine

S.S. Jyothirmayee Aravind, S Ramaprabhu

Sensors and Actuators B, in press (2011)

Performance of polymer electrolyte membrane fuel cell with novel Pt₃Co/f-MWNTs electrocatalyst for oxygen reduction reaction

B. P. Vinayan, R. Imran Jafri, N. Rajalakshmi, K. Sethupathi, and S. Ramaprabhu

J power sources, communicated (2011)