Electrostatic Functionalization of Carbon Based Nanomaterials and Their Applications in Chemical, Gas and Bio-Sensing

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Sensor Development

1. Sensors based on Nanoparticles Decorated Multi-Wall CNTs

- Electrostatic Functionalization
- Decoration with Nanoparticles

2. Sensors based on Composite Nanomaterials

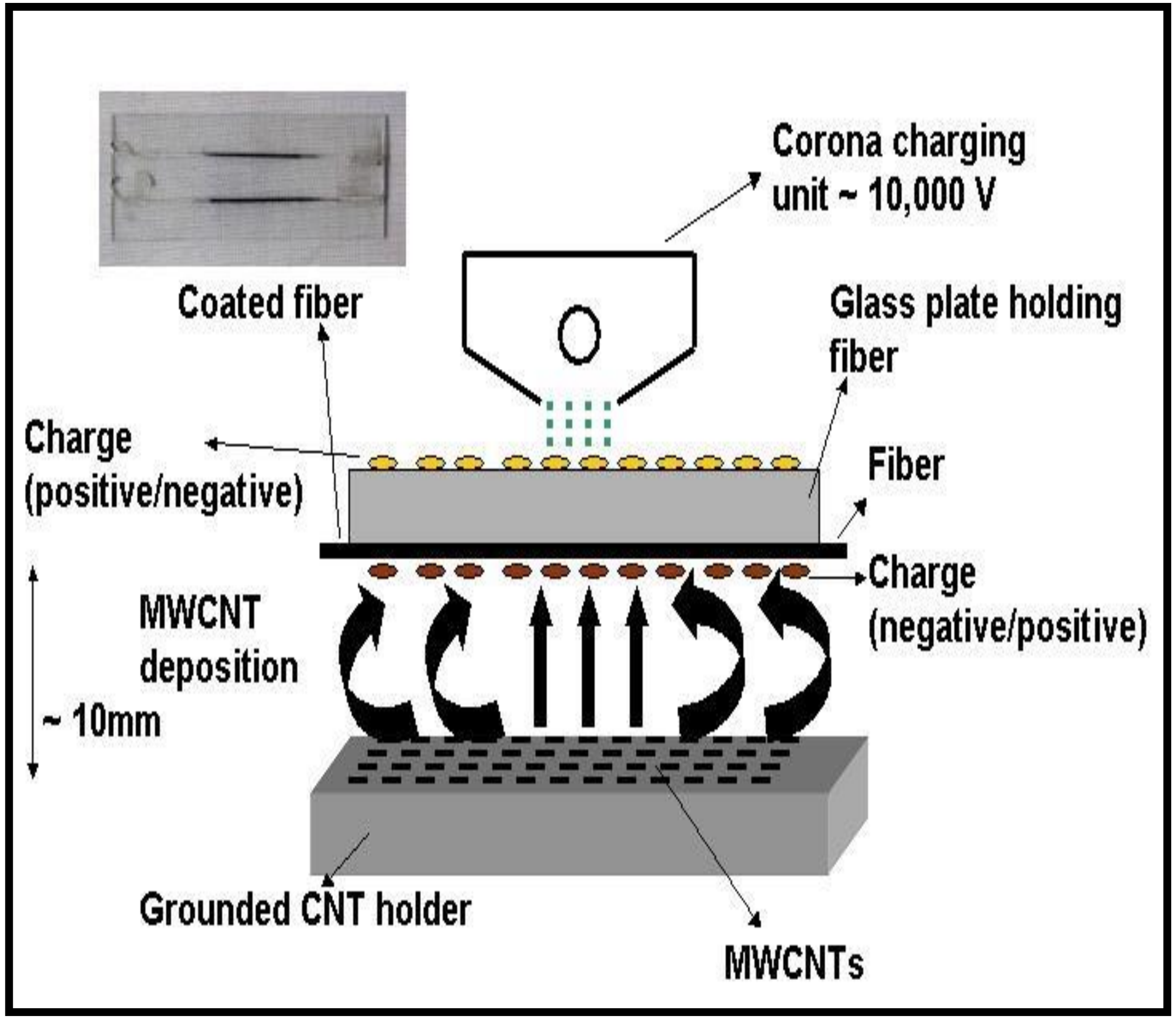
- Polymer Composites
- Amorphous Material Composites

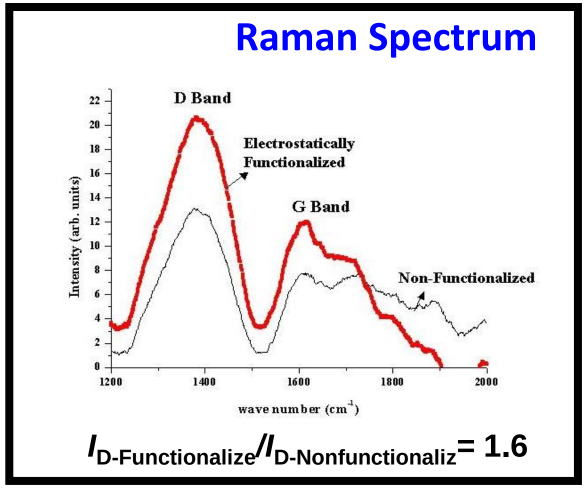
3. Non-enzymatic Bio-Sensors based on Nanomaterials

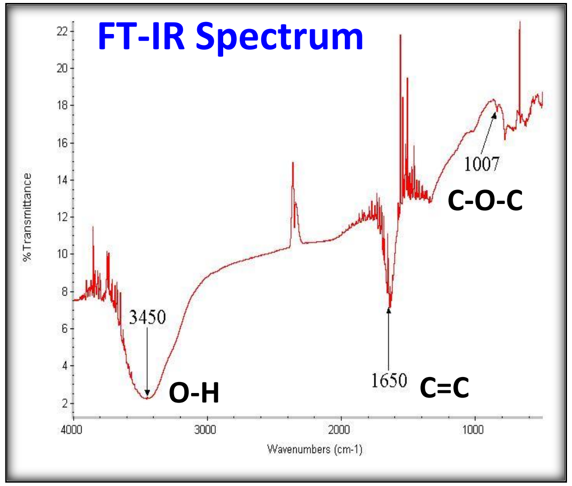
- Glucose Sensor based on CNT
- Cholesterol Sensor based on Nanographitic Oxide

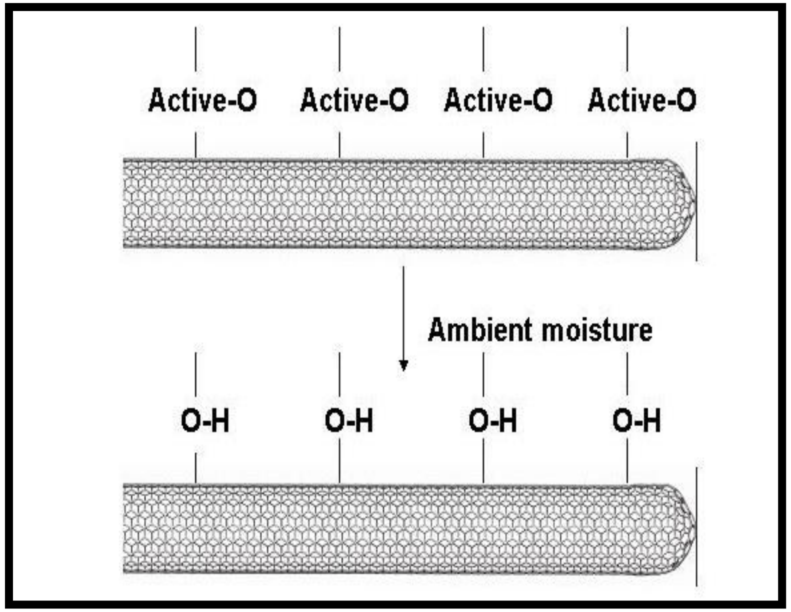
1. Electrostatic Functionalization…

Electrostatic Functionalization of MWCNTs





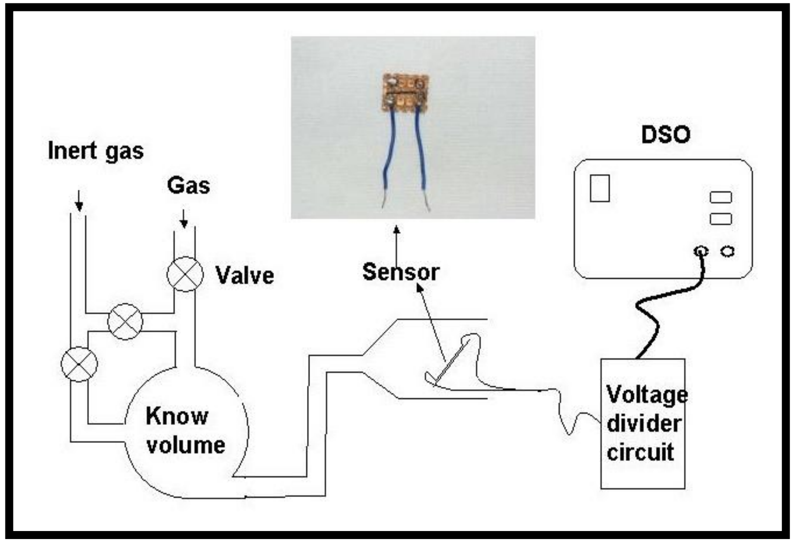


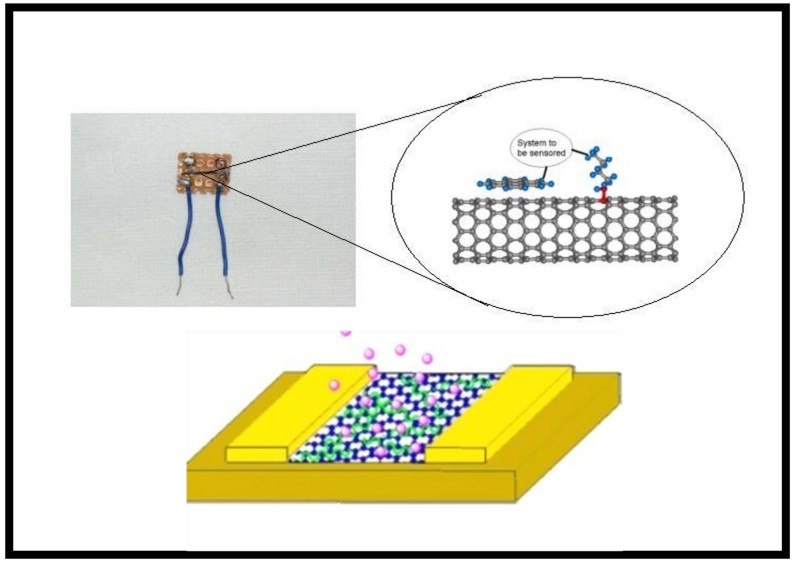


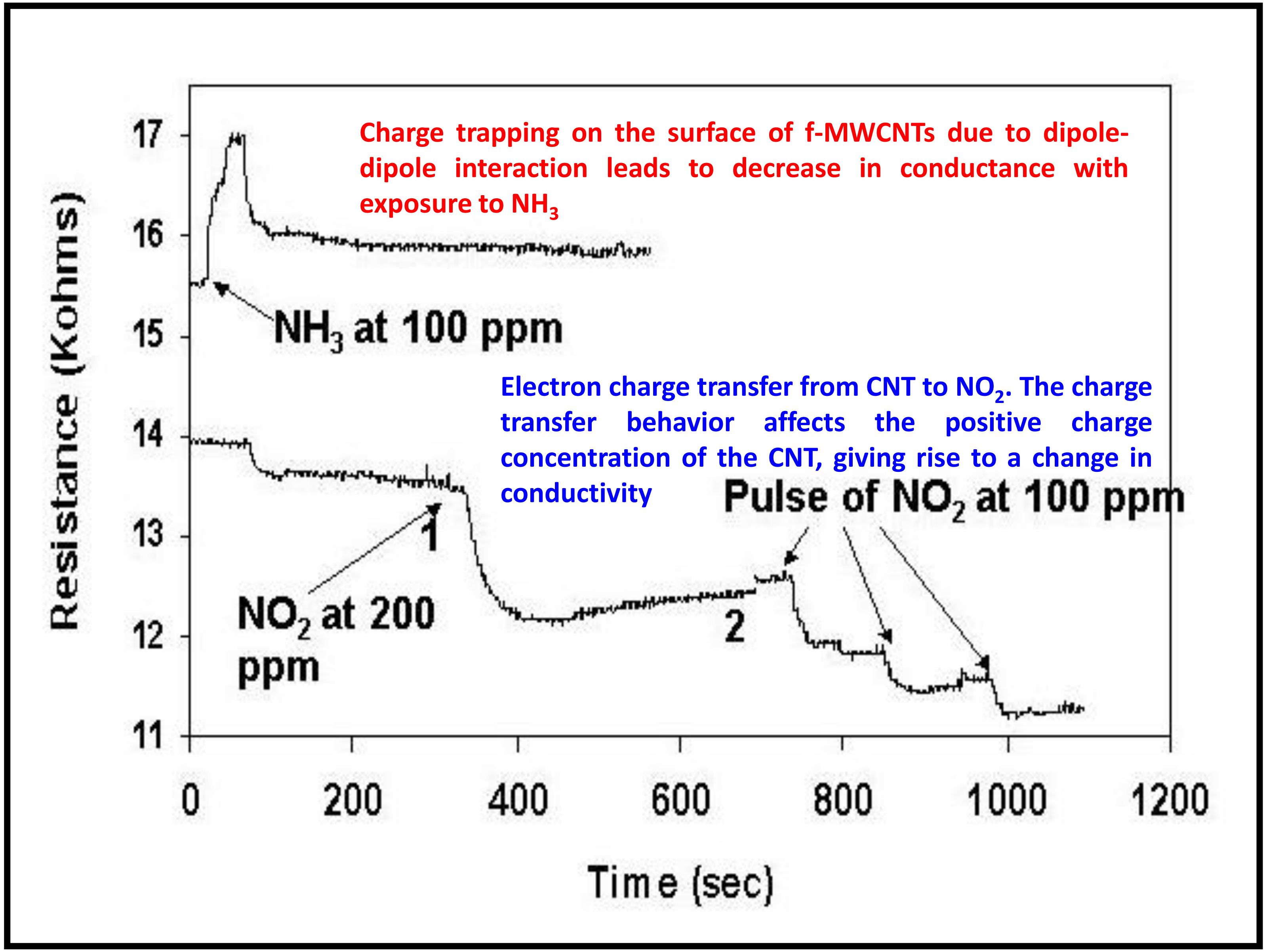
Proposed Functionalization Theory

'New technique to deposit thin films of carbon nanotubes based on electrostatic charge deposition and their applications for alcohol detection', V. Bhatia, V. Gaur, V.K. Jain, *Int. J. Nanosci*, Vol 8, pp 443-453, 2009.

Gas Detection



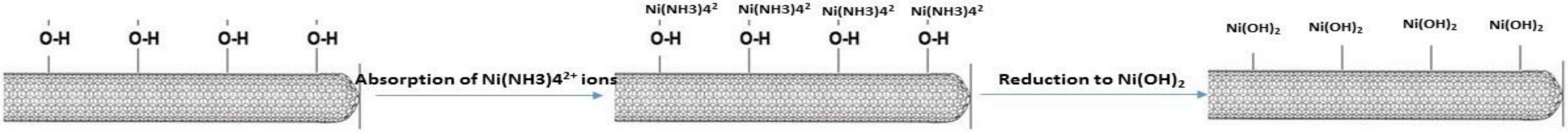




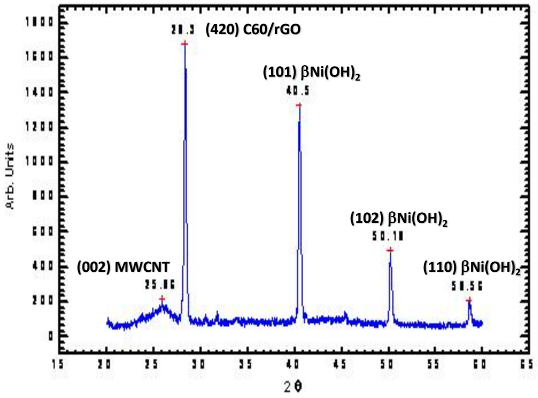
'New technique to deposit thin films of carbon nanotubes based on electrostatic charge deposition and their applications for alcohol detection', V. Bhatia, V. Gaur, V.K. Jain, *Int. J. Nanosci*, Vol 8, pp 443-453, 2009.

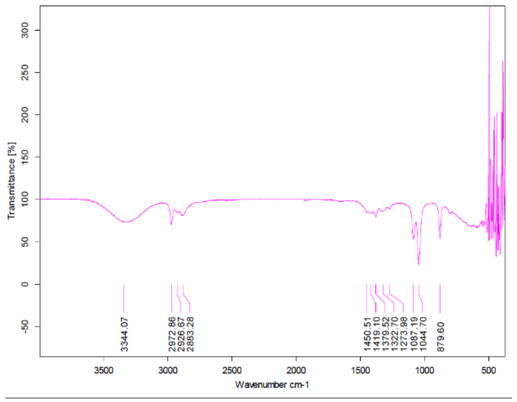
Grafting of Nanoparticles

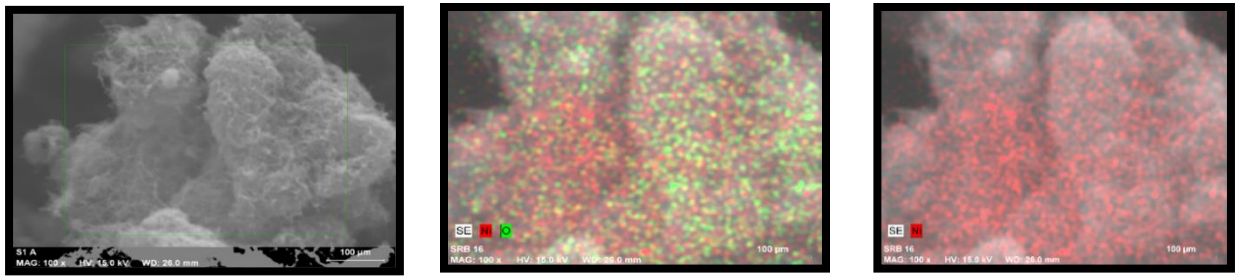
In-Situ Decoration of Electrostatically Functionalized Multiwall Carbon Nanotubes with β-$Ni(OH)_2$ Nanoparticles

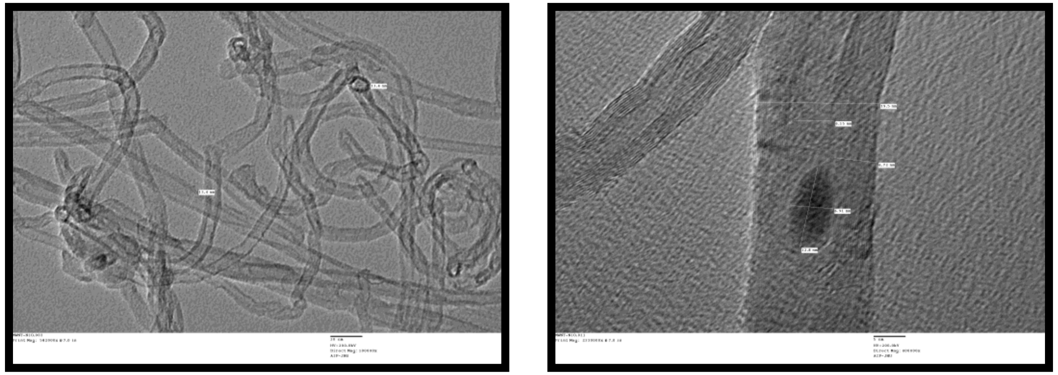


- Sonication of solution of f-MWCNTs and $NiNO_3.6H_2O$ (3:2 ratio by wt.) in presence of KOH. Followed by reduction with sodium hydrogen borate (NaBH4). Finally allowed to sonicate for 7-8 hours in an ice bath to get a homogenous mixture.
- The polar oxygen functional groups introduced by electrostatic functionalization act as nucleation sites. The $Ni(NH3)4^{2+}$ ions in the solution are adsorbed onto these sites. Subsequently, OH− reacts with the $Ni(NH3)4^{2+}$ via electrovalent bonding to form $Ni(OH)_2$ nanoparticles.





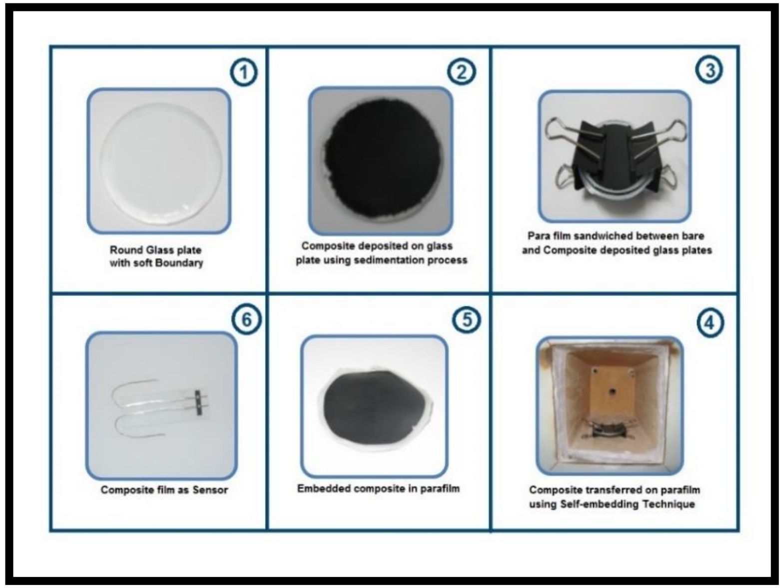




Richa SAGGAR, Vasuda BHATIA, Prashant SHUKLA, Nitin BHARDWAJ, Vinod K JAIN; *Sensors and Transducers*, Vol. 146, pp. 28-35, 2012

Results

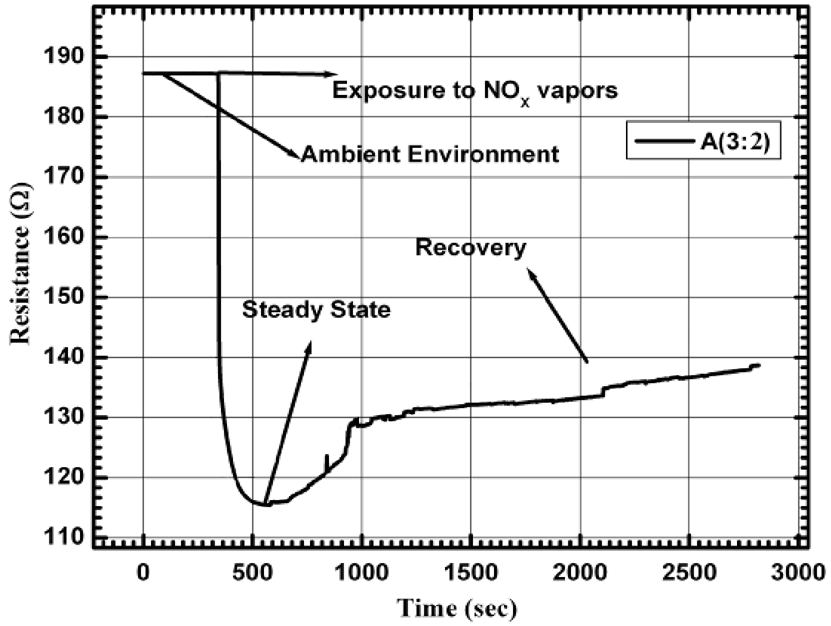
Room Temperature Detection of NO_x Vapors with β-$Ni(OH)_2$ Nanoparticles Decorated Multiwall Carbon Nanotubes



Thin film fabrication

- Thermal embedding technique on a parafilm.
- Ni(OH)2-f-MWCNTs was dispersed in ethanol and sonicated for several hours to provide a uniform suspension.
- The dispersed solution of nanocomposite was cast on cleaned glass surface and allowed to dry under ambient conditions for several hours.
- The cast film was then self-assembled on to the surface of non-conducting parafilm by thermal embedding technique while heating at oven temperatures for a few minutes to achieve a desired thickness of about 100 μm of the film.
- Thin strips of specified area were and electronic grade silver paste was used for wire bonding with the strips

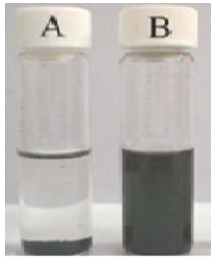
- Film response to 75 ppm of NO_2 vapors.
- A sensitivity of about 38 % observed.
- The average τ_{90} of the sample was observed to be 65.48 sec

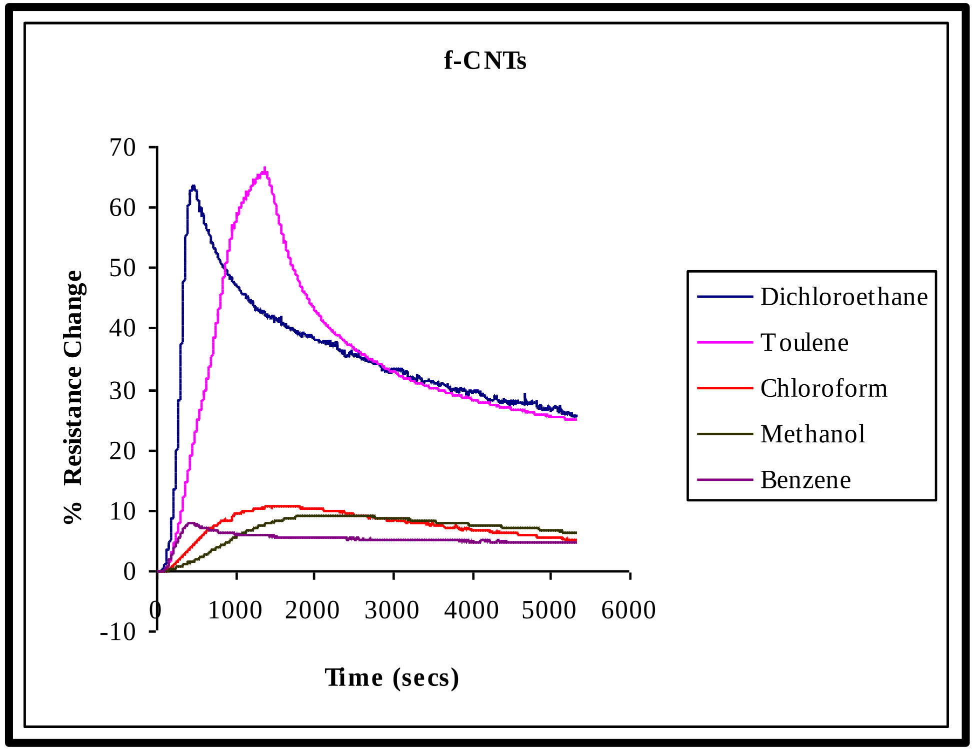


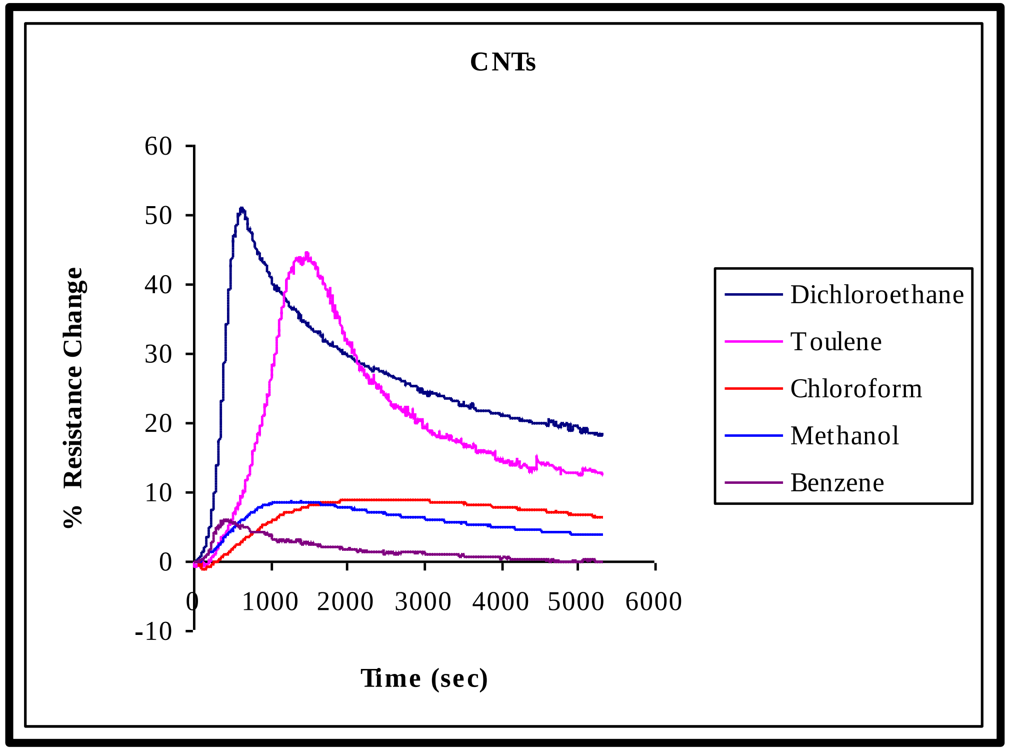
2. Composite based …

Organic Vapor Detection using MWCNTs/PMMA (poly (methyl methacrylate)) Composites

- Hydroxyl and oxygenated functional groups physically interact with the matrix of PMMA, resulting
- in a strong interfacial adhesion and a better dispersion of electrostatically functionalized CNTs in the polymer matrix.
- Composite dispersed in dichloroethane and drop coated.
- PMMA and f-MWCNTs :: 33.33:1 (by wt.)
- Higher sensitivity for f-MWCNTs-PMMA films.



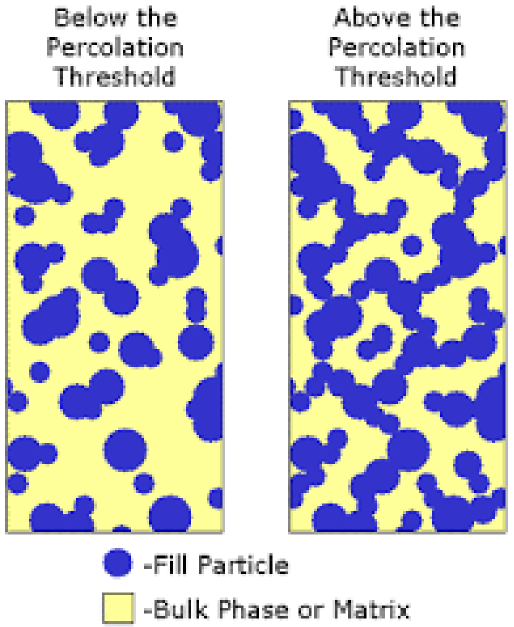


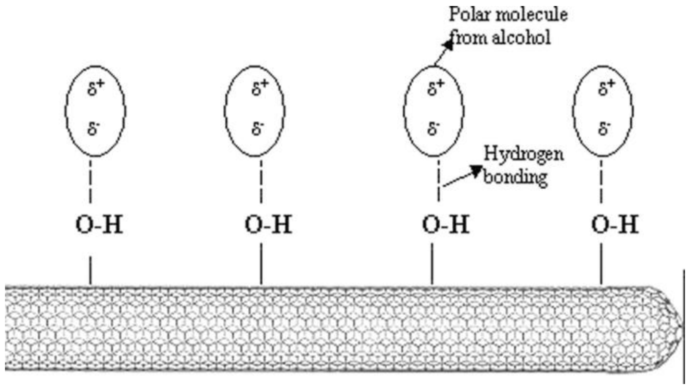


Electrostatically Functionalized Multiwalled Carbon Nanotube/ PMMA Composite Thin Films For Organic Vapor Detection, P. Shukla, V. Bhatia, V. Gaur, V. K. Jain, *Polymer-Plastics Technology and Engineering*, 50, 1179-1184, 2011.

Detection Theory

- CNTs in polymer matrix reduce the percolation threshold to a much lower filler volume
- Enhancement of physical interaction between nanotubes and polymers and dispersion in the polymer matrix can be achieved by surface modification of nanotubes
- Detection based on swelling of polymer matrix on absorption of organic vapors that increases the distance between adjacent nanotubes.
- Change in conductivity of MWCNT/polymer upon exposure to chemical vapors occurs as a result of the charge transfer induced by adsorption of polar organic molecules.
- f-MWCNTs introduced hydroxyl and oxygenated functional groups interfacial adhesion and a better dispersion of f-MWCNTs in the polymer matrix. Thus, the volume of the conducting channel through the PMMA matrix was large so that a small swelling of the matrix induced a large increase in resistance. This explains the large increase in response for f-MWCNT composite when exposed to toluene, dichloroethane and chloroform that could swell the polymer matrix to a large extent. The polar groups on the nanotube surface also increase by adsorption of solvent molecules, and give a better response.

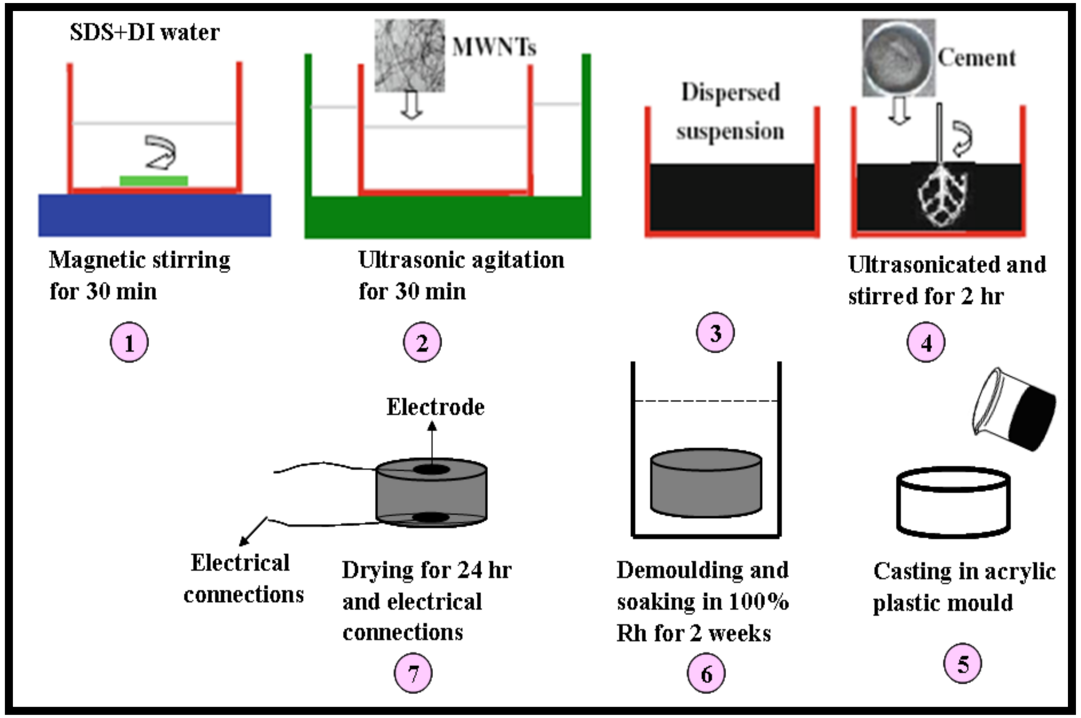


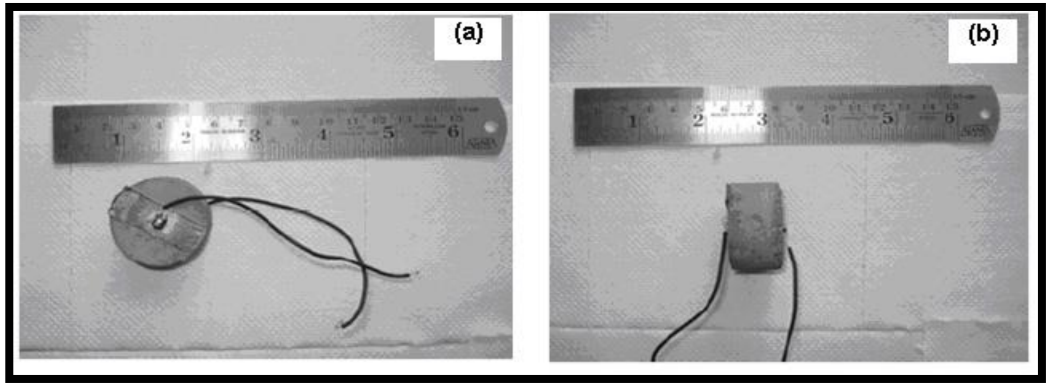


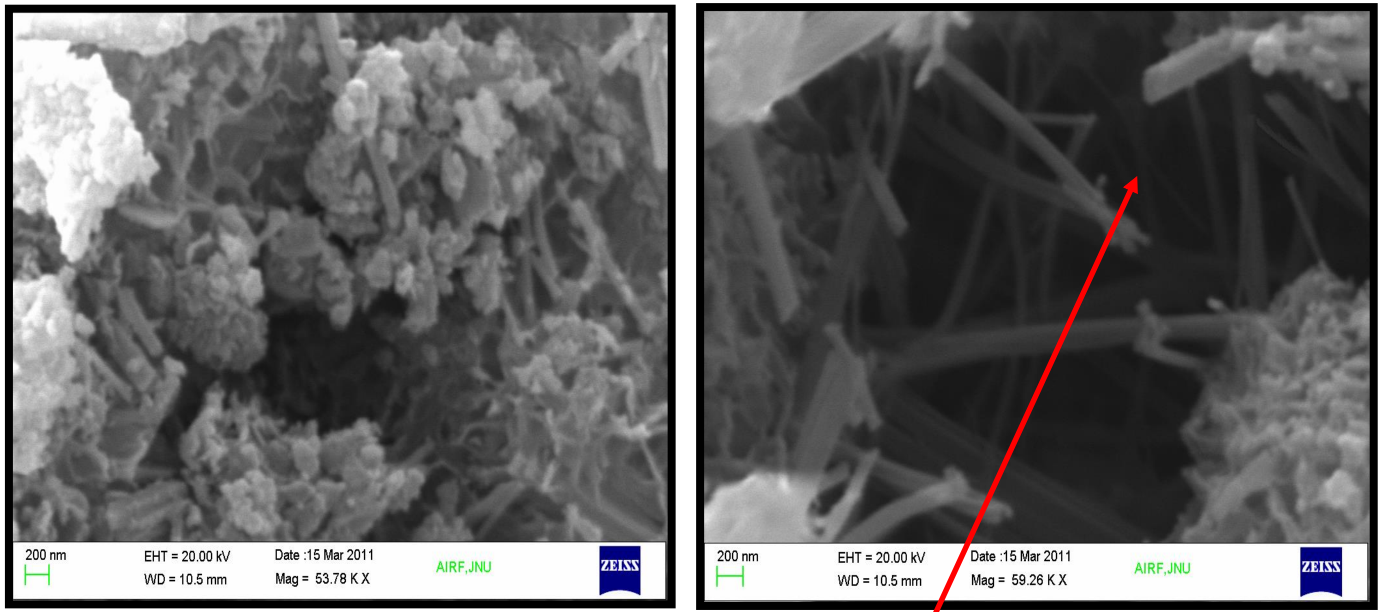
Electrostatically Functionalized Multiwalled Carbon Nanotube/ PMMA Composite Thin Films For Organic Vapor Detection, P. Shukla, V. Bhatia, V. Gaur, V. K. Jain, *Polymer-Plastics Technology and Engineering,* 50, 1179-1184, 2011.

Multiwalled Carbon Nanotubes Reinforced Portland Cement for Smoke Detection

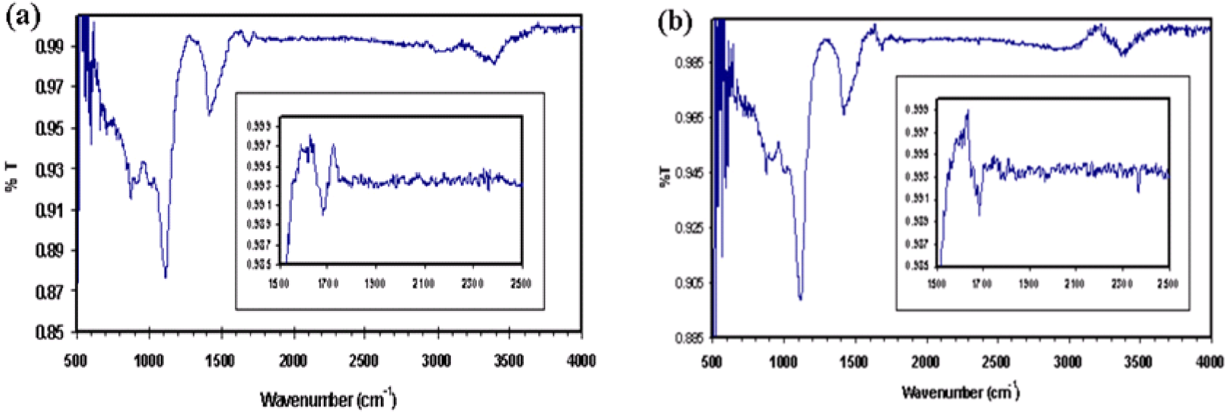
P. Shukla, **V. Bhatia**, V. Gaur, R. K. Basniwal, B. K. Singh, V. K. Jain; ***Solid State Phenomena*, Vol. 185, pp. 21-24, 2012**.





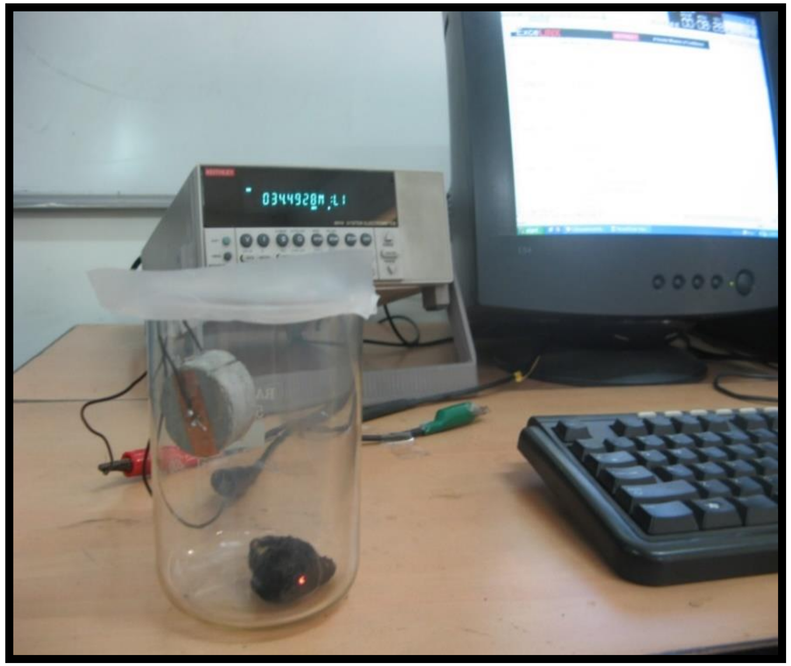


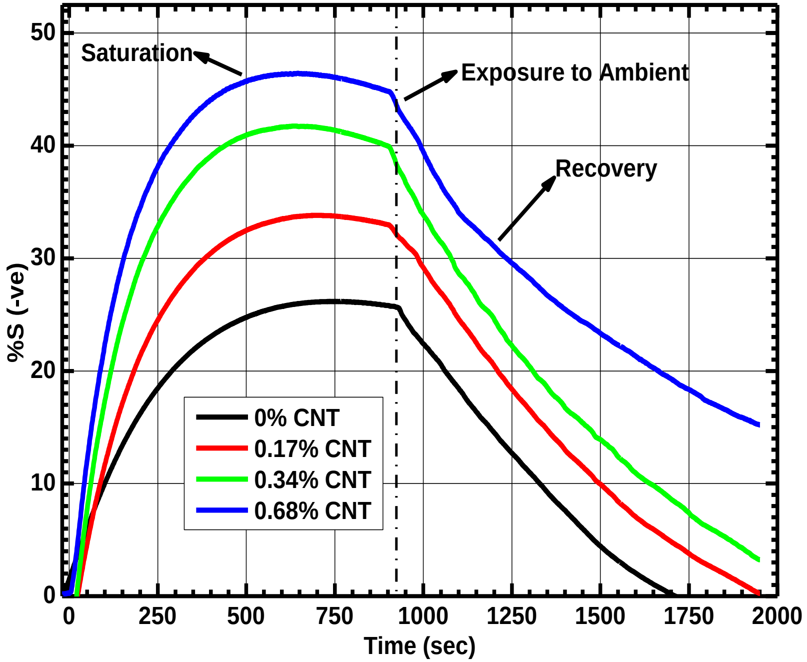
MWCNTs in the Pores of Cementitious Material



(a) Portland Cement, (b) f-MWCNT-Cement Matrix

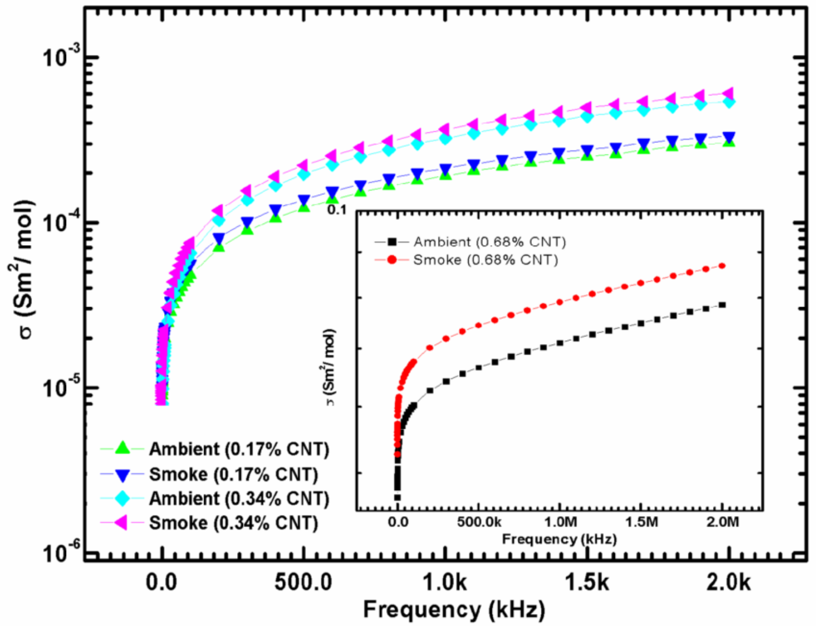
Results

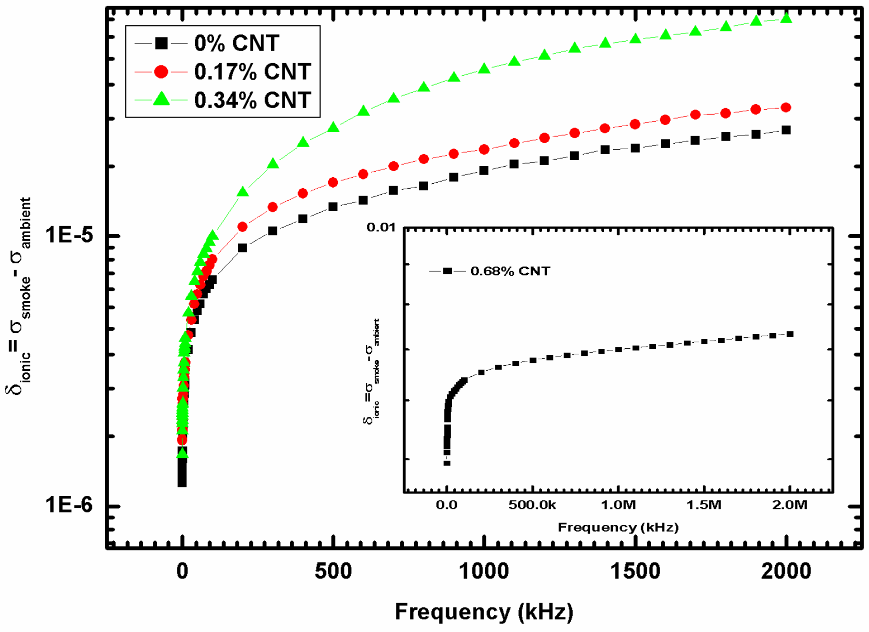




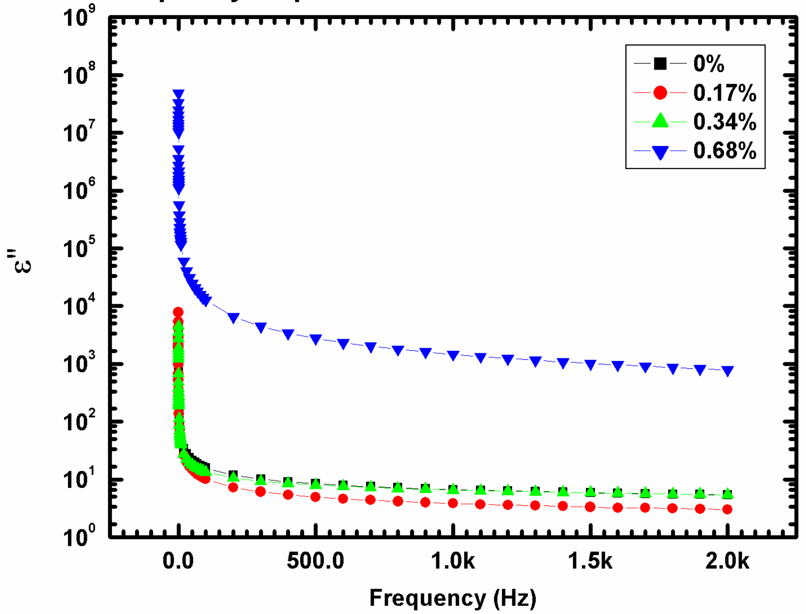
- **DC Transient measurements - Keithley Electrometer 6514**
- **AC Impedance measurements - Agilent E4890A Impedance Analyzer**
- **Smoke Generation- 30 ml Paraffin Oil of Mol Wt. 325 gm/mol & r 0.8gm/cc**

Responsivity of the MWCNTs reinforced cement pellets of different concentrations of MWCNTs under smoky environments





Frequency response of ε'' for different CNT% in Smoke

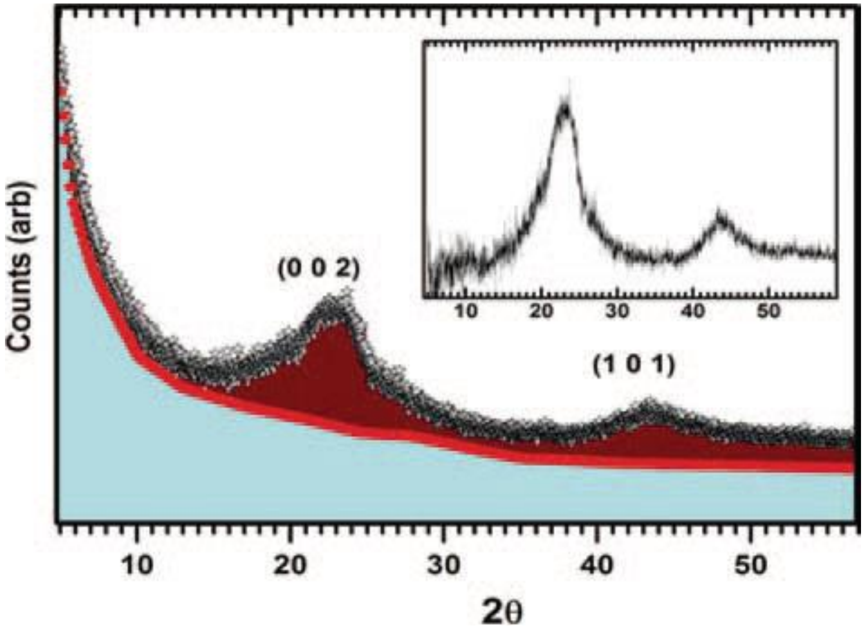


$$\sigma(\omega) = \sigma_{dc} + A\omega^{s}$$

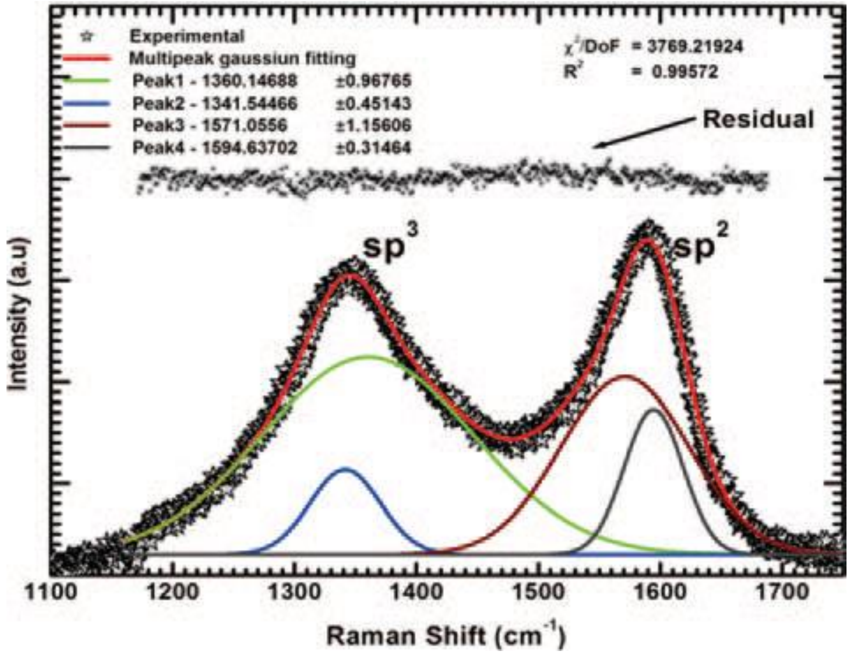
- **Jonscher Equation for Ionic Conductivity**
- **Dimensionless frequency parameter, S : 0.14-0.28**
- **In cementitious material conduction through flow of ions: Ca^{2+}, Na^{+}, K^{+} or OH^{-} through the porosity of the material.**
- **In MWCNTs conduction through flow of free electrons.**
- **In MWCNTs/Cement conduction via: continuous network of conductive fiber in series with flow of ions.**
- **Under smoky environment : charged particles interact with MWCNTs and provide enhanced ionic conductivity**

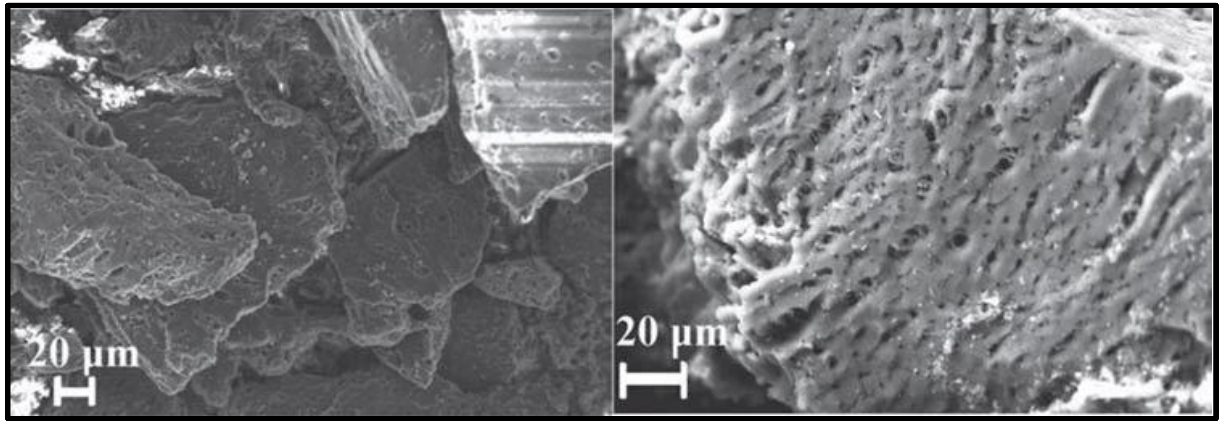
3. Amorphous Carbon based …

Low Cost Liquefied Petroleum Gas (LPG) Sensor Based on Activated Carbon for Room Temperature Sensing Application



- LPG chemical analytes are essential for environment monitoring, human and homeland security.
- LPG is a flammable mixture of hydrocarbon gases and is used as a fuel in heating appliances and vehicles.
- It is increasingly used as an aerosol propellant and a refrigerant, replacing chlorofluorocarbons in an effort to reduce damage to the ozone layer.
- Due to its highly flammable characteristics, even low level concentration (ppm) poses a serious threat.

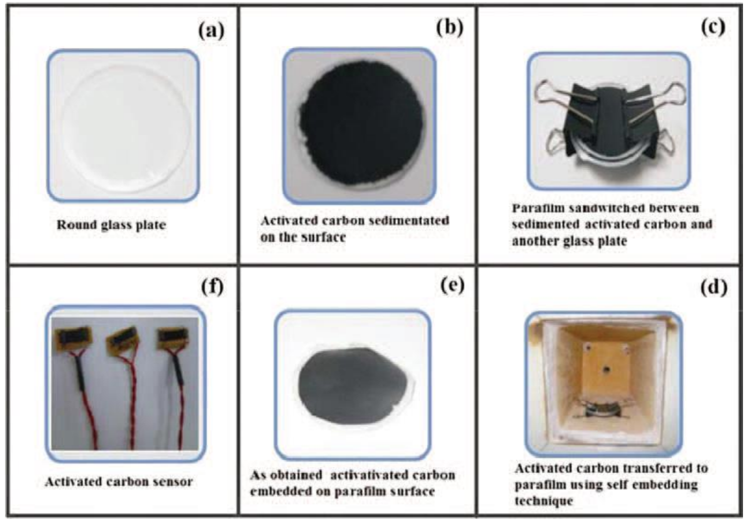


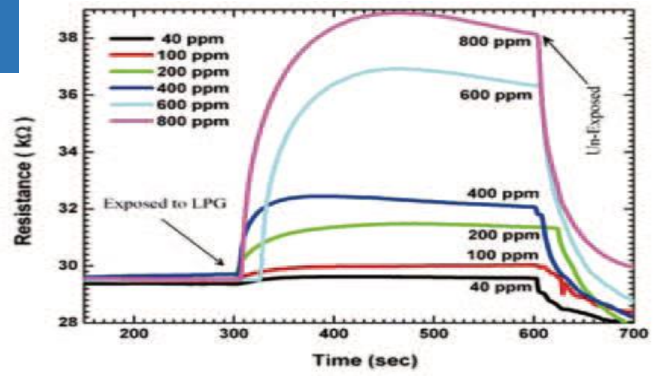


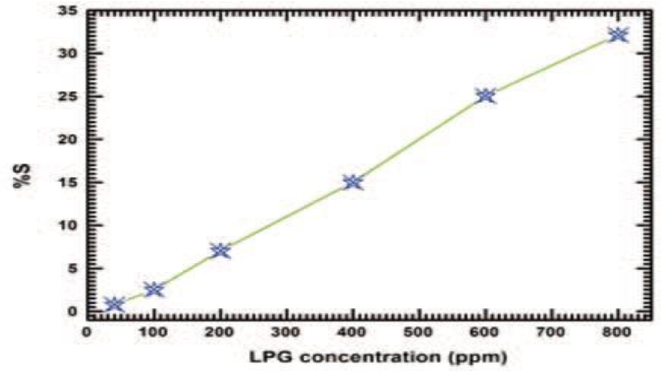
Activated amorphous carbon of particle size 100 μm and pore surface area 10 μm^2

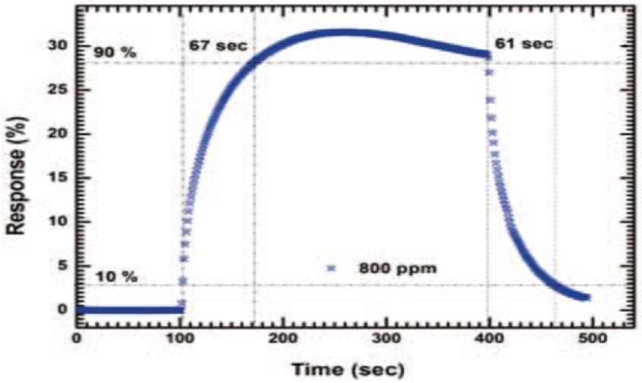
A Novel Low Cost Liquefied Petroleum Gas (LPG) Sensor Based on Activated Carbon for Room Temperature Sensing Application
Budhendra Singh, Abhishek Verma, Ajay Kaushal, Igor Bdikin, Somik, Nitin Bhardwaj, Prashant Shukla, Vasuda Bhatia, and V. K. Jain,
Accepted Sensors Letters, Vol 12, 1-7, 2014

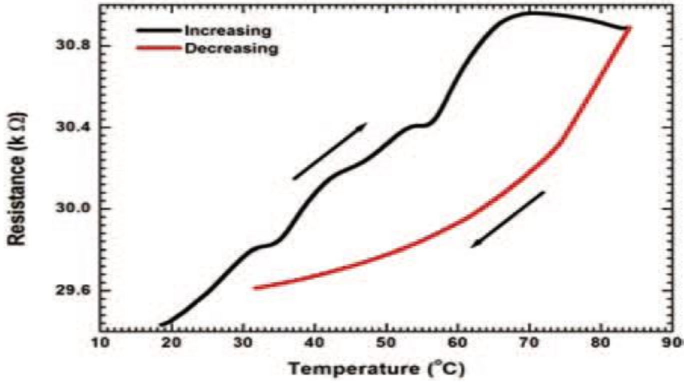
Sensing of LPG with Activated Carbon Film







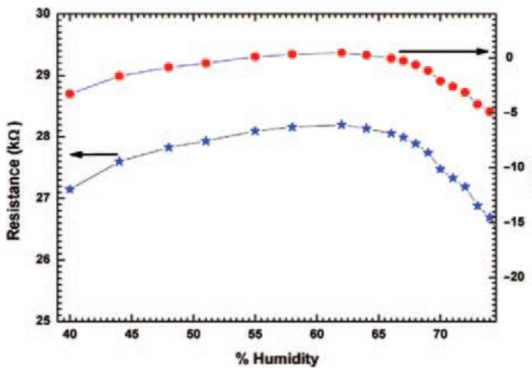


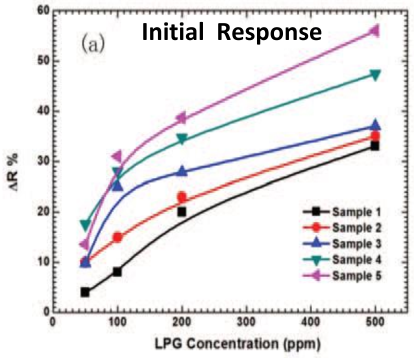


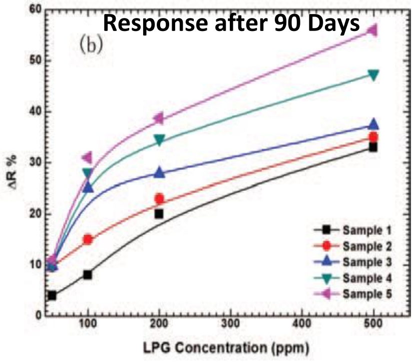
Interaction of hydrocarbons (C*n* H2*n*+2) of LPG and chemisorbed oxygen on the surface of the film

$2CnH2n+n\ \ +2O^{-}_{2}\ \ \rightarrow 2CnH2nO+2H2O+2e^{-}$

By products such as water vapor provides a potential barrier to charge transport leading to an increase in resistance of the sensing film with time.

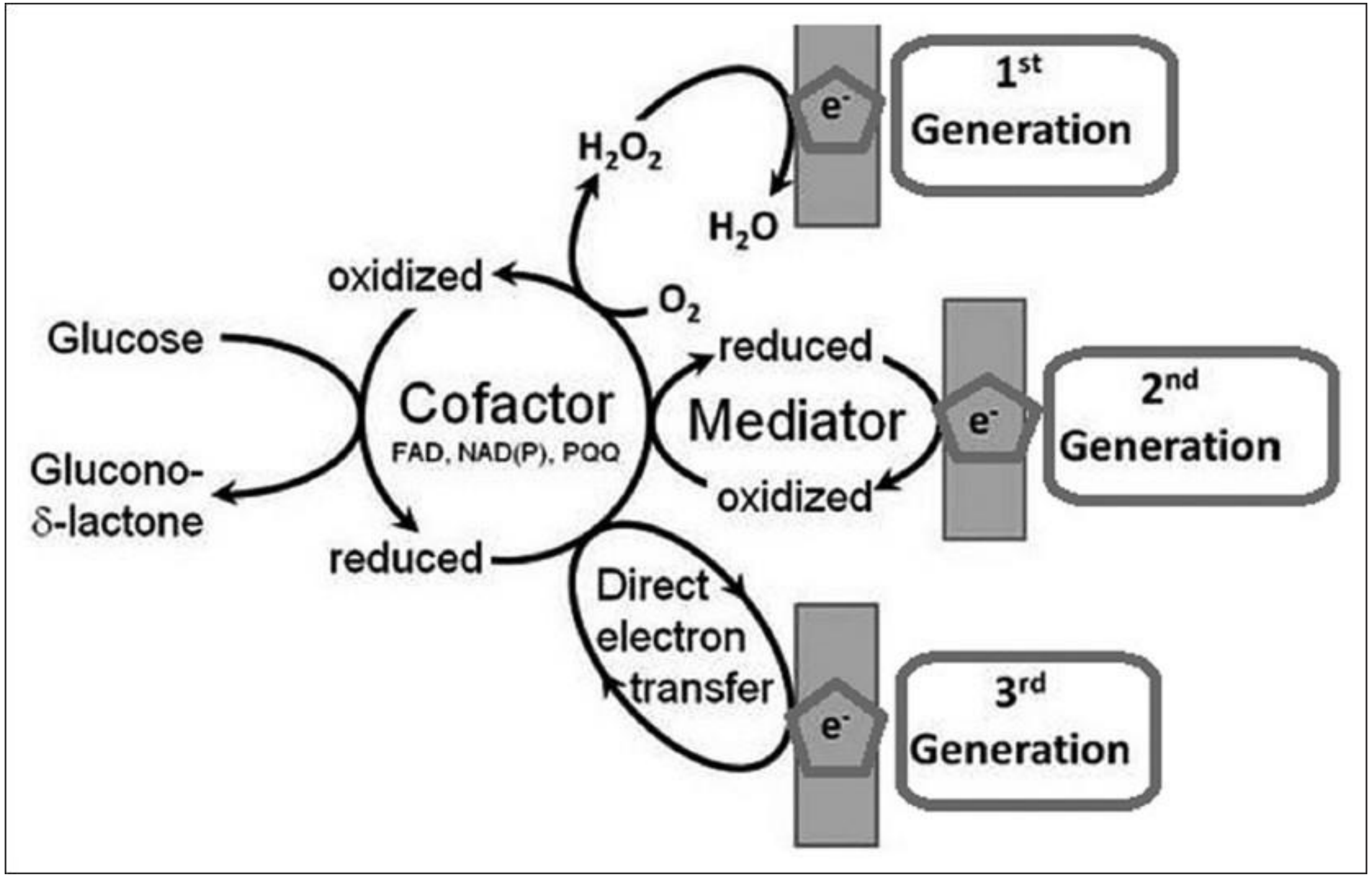






4. Biosensors …

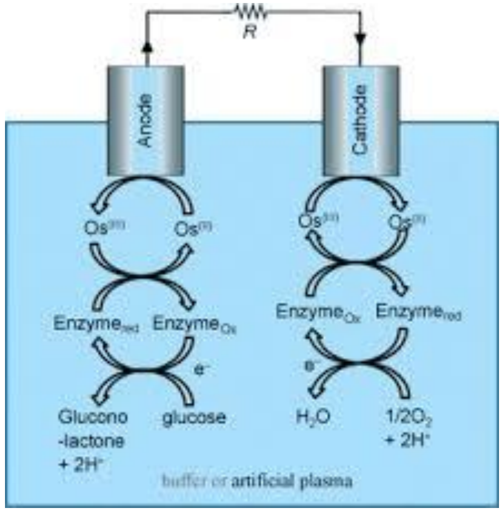
Glucose



- Biggest biosensor success story!
- Motivation to develop enzyme – less systems

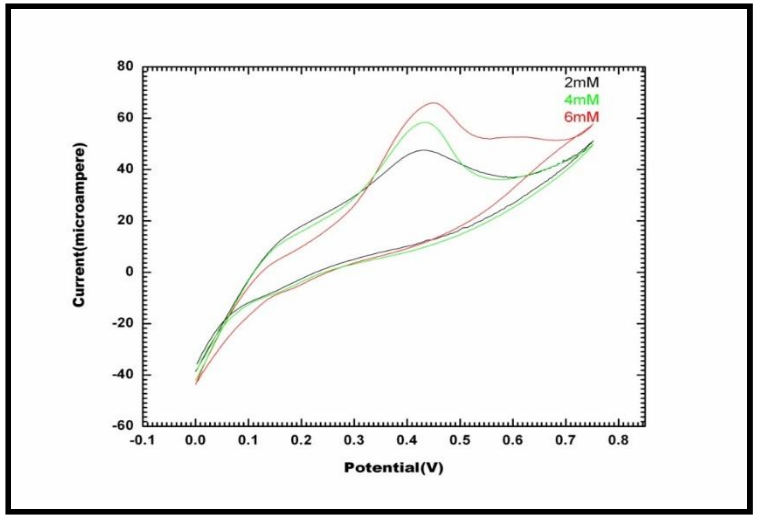
Bhawana SINGH, Vasuda BHATIA, V. K. JIAN; Sensors and Transducers, Vol. 146, pp. 69-77, 2012.

Electrostatically Functionalized Multi-Walled Carbon Nanotubes Based Flexible and Non-Enzymatic Biosensor for Glucose Detection

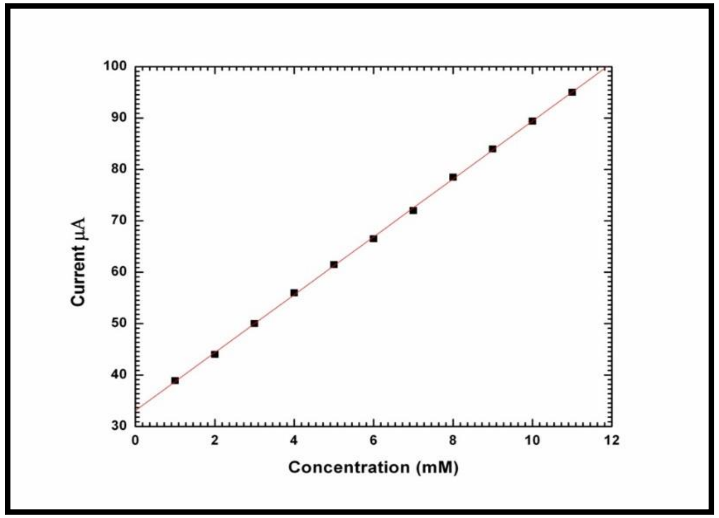


- Gamry electrochemical workstation with a conventional three-electrode setup, including f-MWCNTs as a working electrode and an Ag/AgCl (3MKCl) electrode and a platinum wire as reference electrode and counter electrode respectively.
- The electrolyte solutions were purged with high purity nitrogen for at least 30 minutes prior to each electrochemical measurement and the nitrogen environment was maintained over the electrolyte to protect the solution from oxygen.
- All the measurements were performed under a continuous magnetic stirring at 250 rpm of 5 ml electrolytic solution to provide convective mass transport at the electrodes.

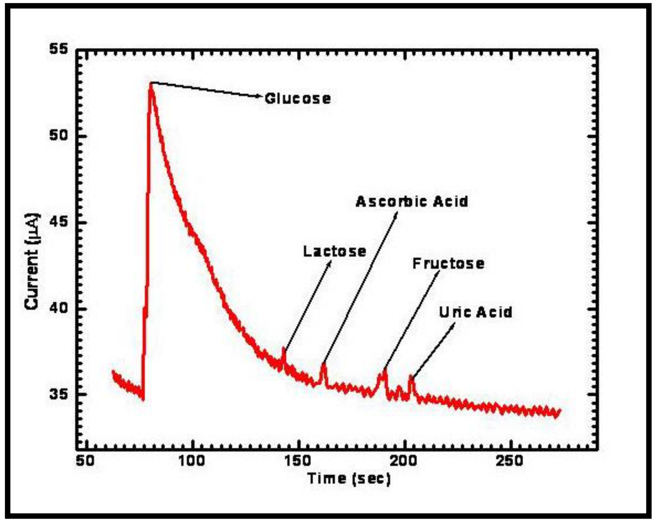
Cyclic voltammetric response in 0.1M NaOH solution at a scan rate of 50 mV/s



Calibration Curve

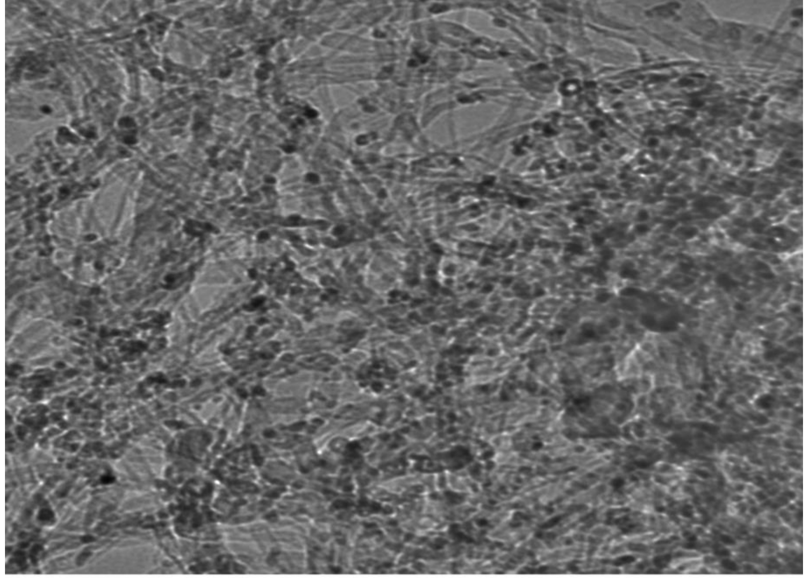


Interference Response



Bhawana SINGH, Vasuda BHATIA, V. K. JIAN; Sensors and Transducers, Vol. 146, pp. 69-77, 2012.

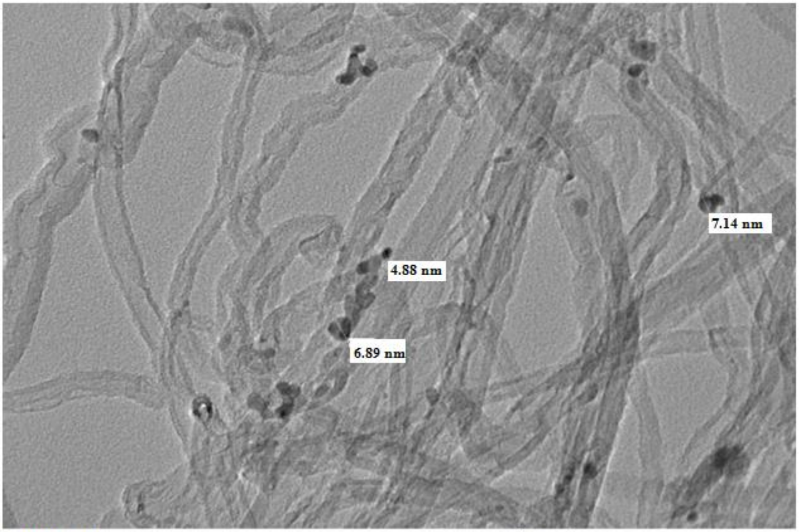
Enzyme Free Detection with Nanoparticles Grafted…..



20 nm
HV=200.0kV
Direct Mag: 60000x
AIF-JNU

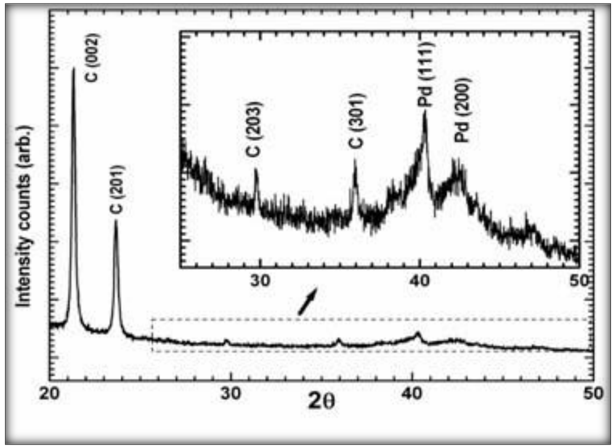
Pd Nanoparticles Decorated Electrostatic Functionalized MWCNTs

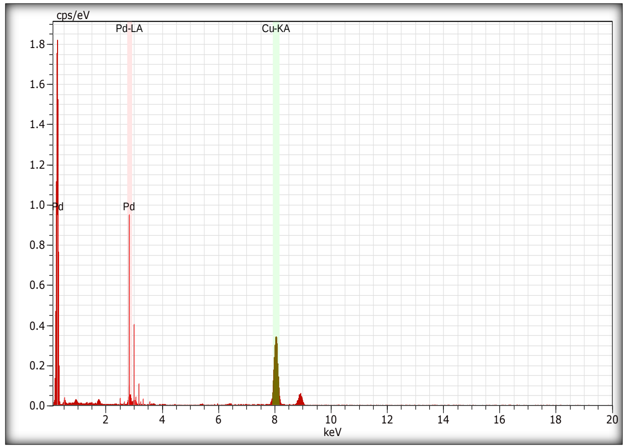
- **In-situ decoration of Pd nanoparticles achieved by reducing $PdCl_2$.**
- **Electrodes have been fabricated by self-assembly method during thermal embedding onto para-film.**
- **XRD and EDX data showed peaks of C and Pd only.**
- **SEM and TEM microscopy revealed uniform dispersion of Pd-nanoparticles on the side walls of MWCNTs. The average size of the nanoparticles was determined to be < 10 nm.**



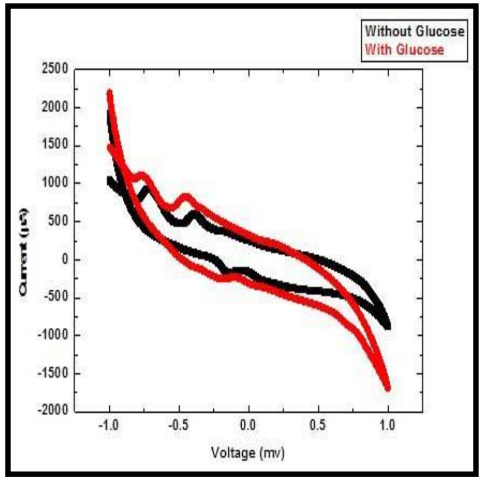
MWCNT-pd

20 nm
HV=200.0 kv
Direct Meg: 600000 x
AIF=JNU

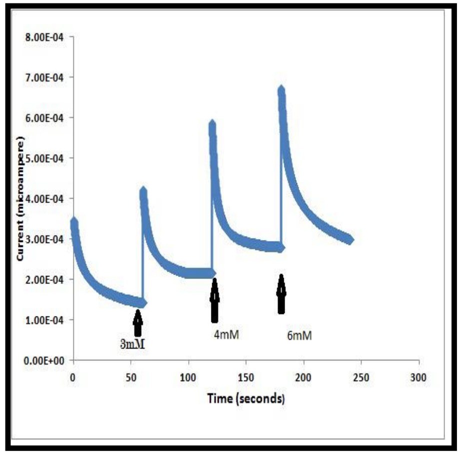




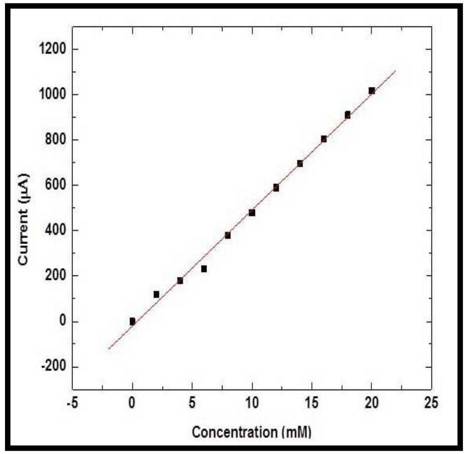
Palladium Nanoparticles Decorated Electrostatically Functionalized MWCNTs Non Enzymatic Glucose Sensor



Cyclic voltammogram of Pd loaded MWCNT in the absence and presence of 1mM glucose

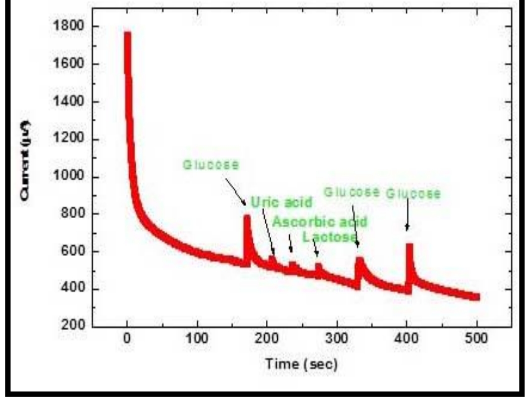


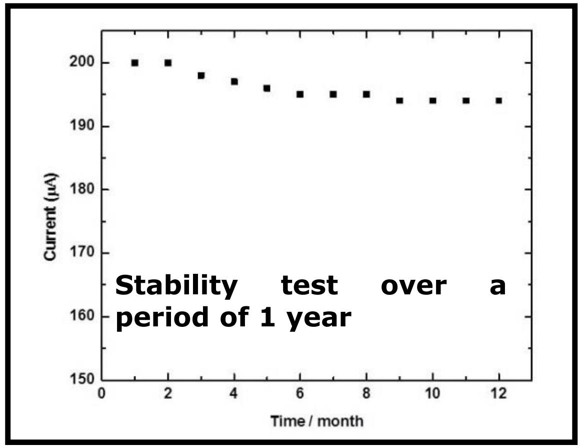
Amperometry response of glucose at different concentration of glucose



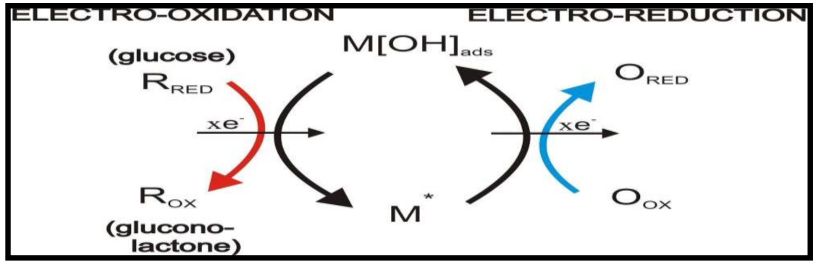
Calibration plot of glucose sensor based on Pd-fMWCNT electrode

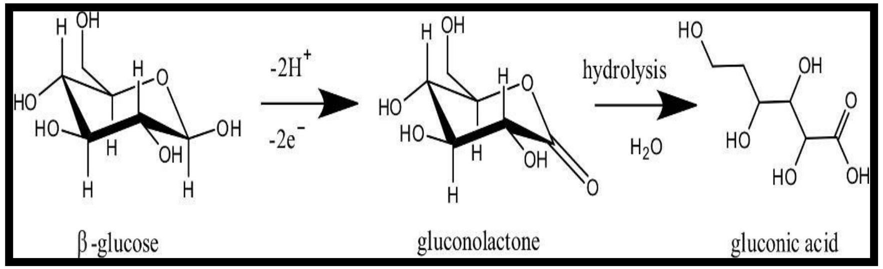
Interference study at -0.4V



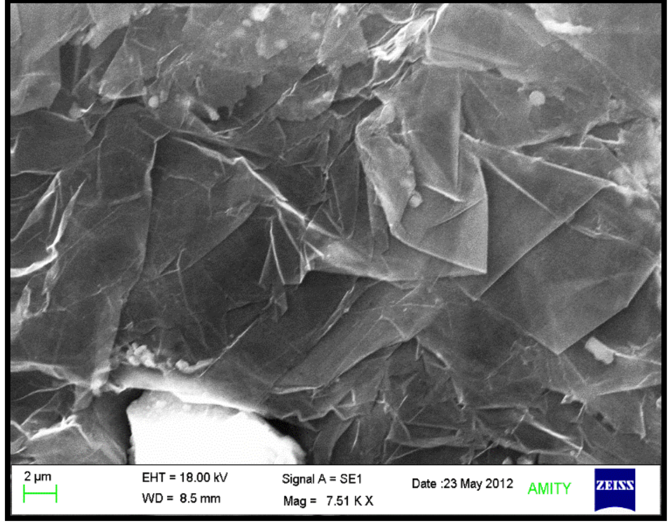


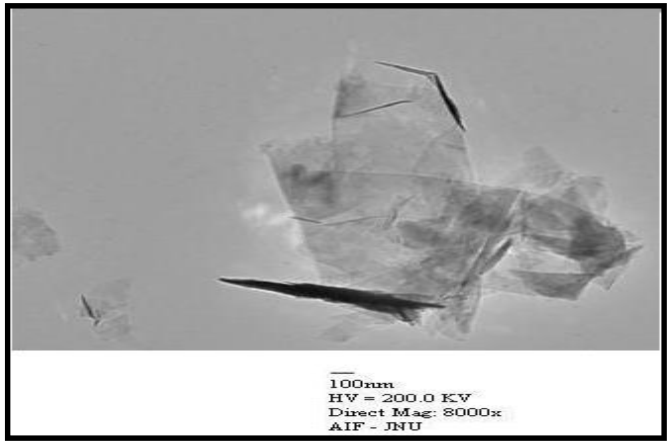
Stability test over a period of 1 year

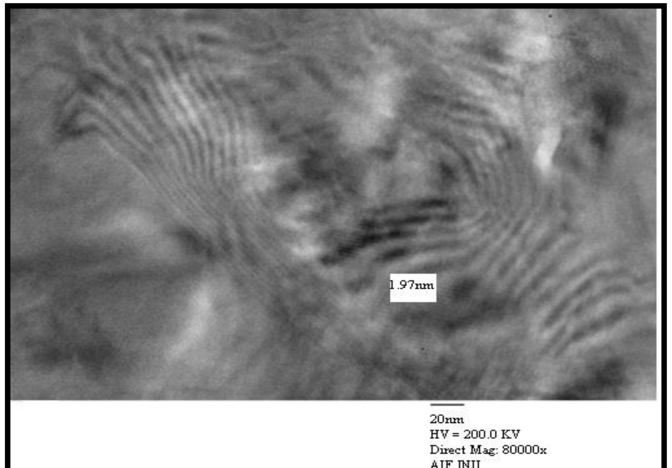




Cholesterol Sensor-Enzyme Free

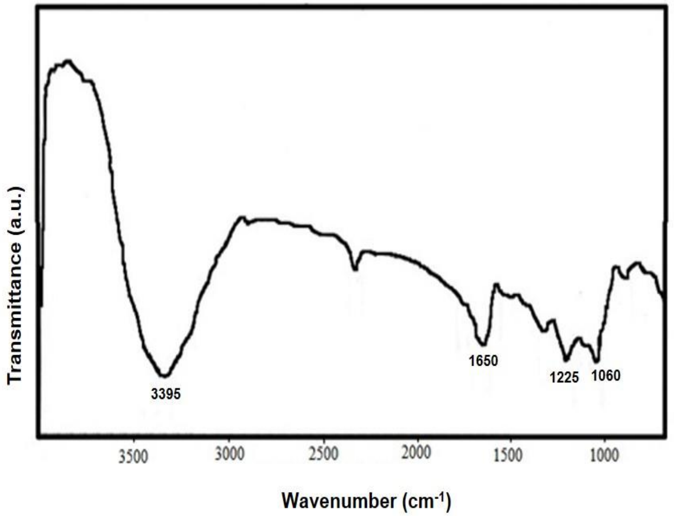


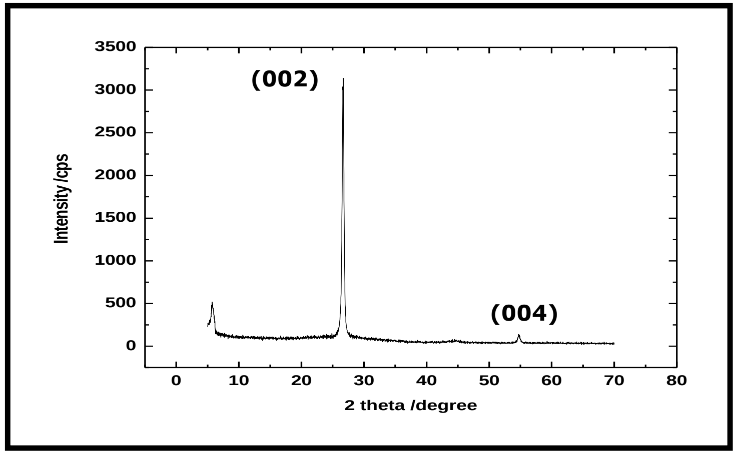




Synthesis of Nano-Graphitic Oxide:

- Nano-graphite oxide was prepared by modified Hummers' process.
- Vacuum dried graphite was subjected to concentrated sulfuric acid in a three-neck flask under appropriate cooling and stirring conditions for a duration of 16 hours.
- Graphite intercalation compound was then obtained and subjected to a thermal shock at 1050 ^{0}C for 15 seconds in a muffle furnace to form exfoliated graphite (EG).
- The EG was further saturated with alcohol and ultra-sonicated to get a uniform dispersion of foliated graphite (FG).
- FG was filtered and dried to obtain FG powder for fabricating the electrodes for the electrochemical analysis of cholesterol.



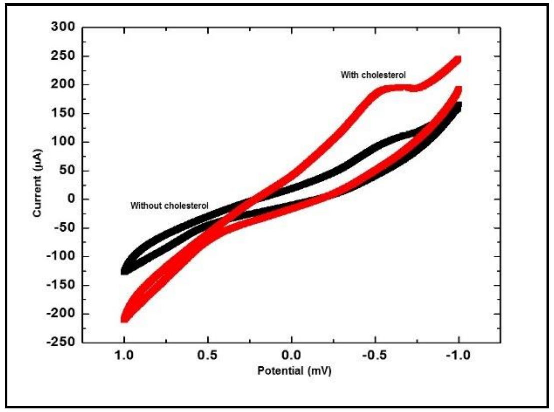


A Novel Nanographite Based Non-Enzymatic Cholesterol Sensor, Bhawana, Nitin Bhardwaj, Vinod K. Jain and Vasuda Bhatia; *Physics of Semiconductor Devices;* 17th International Workshop on Physics of Semiconductor Devices 2013; Springer International Publishing; pp. 531-534, 2014.

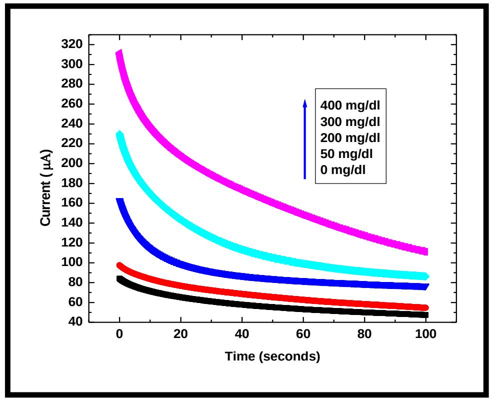
Electrochemical Results: Experiments were performed with a conventional three-electrode setup, using nano-graphite oxide as working electrode, Ag/AgCl (3 M KCl) electrode as reference electrode and platinum wire as counter electrode in 0.1 M NaOH electrolyte. CV measurements with and without addition of 200 mg/dl cholesterol displayed enzyme-free oxidation at -0.6 V. The electrode provided sensitivity of 1.0587 μA/mg and a correlation coefficient, R, as 0.99784 was obtained. Response to interfering species was negligible.

Cholesterol + O (-attached to nano-graphite oxide) $\longrightarrow$ *4- Cholesten-3-one +* H_2O_2

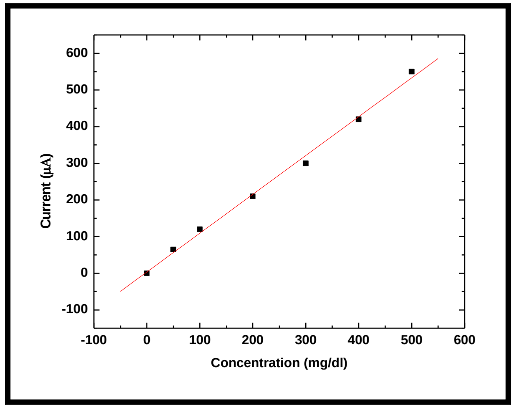
$$H_2O_2 \xrightarrow{\text{Electrode}} O_2 + 2H^+ + 2e^-$$

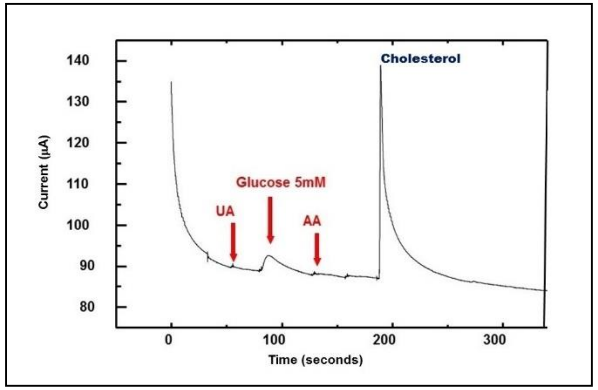


Cyclic voltammograms of graphite oxide modified electrode in the absence and presence of 200 mg/dl cholesterol in 0.1M NaOH



Amperometric response of the electrode at different concentrations of cholesterol in 0.1M NaOH solution at an applied potential of -0.6V





Interference response

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