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Functionalization and Fabrication of MWCNT on Screen Printed Carbon Eletrode

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Abstract
Carbon nanotubes (CNT) are one of the most widely used nonmaterials. It is applied in various fields due to its special physical characteristics, excellent electronic performance and stable chemical activity. There are two types of CNT occur (a) Single walled carbon nanotube (b) Multiwalled carbon nanotube. As their names shows, SWNTs consist of a single, cylindrical graphene layer, where as MWNTs consist of multiple graphene layers. CNT facilitate electron-transfer between electro-active species and electrode when it used as electrode material. To obtain quick and specific response of electrode, a functional group is attached to the nanotube. Functionalization shows the presence of C-O groups at the open end of nanotubes. Chemical changes were monitored by FTIR. Carboxylated Multi walled CNT treated with mixture of DMF and water to overcome its solubility problem. Now this homogenized mixture was used for fabrication of Screen printed carbon electrode for further use in formation of biosensor.

***Keywords*:** c-MWCNT, CNT, DMF, Screen printed carbon electrode (SPCE) and Ultrasonication.

1. Introduction
Carbon is the basic element of life. It exhibits a richness of allotropes with different carbon-carbon bonds and different physical and chemical properties. In the history of carbon, discovery of CNT is an important milestone (**1).** Sumio Iijima in 1991 discovered CNT which is the allotrope of carbon with cylindrical nanostructure.CNT resemble graphite rolled up to a tube. Rolling of a single layer of graphite into a seamless cylinder composed single walled carbon nanotube (SWCNT) with diameter 1-2 nm (2). Assembly of cylinder of SWCNT one within another formed MWCNT. The three main methods for the production of CNT are (a) arc discharge method (b) laser vaporization and (c) chemical vapor deposition (CVD) (3). Due to their unique structural, physical, chemical and electronic properties many researchers are involved in CNT study. These properties provide a wide range of applications such as DNA biosensor, field emission devices, scanning probe microscopy tips, gas sensors, chemical sensors, potential hydrogen storage material, batteries, nanoelectronic devices etc (4). CNT properties and their applications has been the subject of many studies. It depends on structure, diameter and helicity of carbon nanotube whether it will act as semiconductors or show metallic behaviour. Open end of CNTs originate electro- catalytic properties (5). In recent past CNTs have been used for production of electrodes to improve electron transfer kinetics. So CNTs have acquired broad consideration as an electrode material. In comparison to SWCNT electrode, MWCNT electrode is easy to develop which shows promising electrochemical properties. CNT facilitate electron-transfer between electro-active species and electrode when it is used as electrode material (6). Functionalization of CNTs improve their solubility in physiological solutions and selective binding to biotarget (7).

The walls of CNTs are hexagonal carbon rings and are generally formed in large bundles. The ends of CNTs are domed structures of six membered rings capped by five membered rings (8). But when CNTs are functionalized by different acids, cap and sidewall break in different sites, producing defects on the CNT walls by introducing functional groups. Two types of acid treatments used for CNT are reflex with solution of nitric acid and exposing sample to mixture of HNO_3/H_2SO_4 (1:3) under ultrasonication for 6 h (9). Kyotani *et al.* (10) used nitric acid for oxidation treatment of inner wall of multiwalled carbon nanotubes and claimed that during their experimental conditions no damage to the MWCNTs occurred. A layer of Sp2-bonded carbon atoms form the basic structure of CNT in which each atom in x-y plane is connected to three other carbon atoms and in z-axis by a weakly delocalized- electron cloud. This composition of CNT is responsible for the buildup of strong van der waal's forces that notably obstruct dispersion and solubility of carbon nanoparticles (11). Main disadvantage of CNT is their crucial solubilization. To overcome this problem organic solvent like DMF or DMSO and aqueous solution of nafion are being used. Even highly carboxylated CNTs(c-CNTs) are dissolve in aqueous solutions without using surfactants .Carboxylic groups of c-CNT admit covalent bonding with biomolecules or solid surfaces (12). Three types of SPE are commercially available. SPE have working disk electrode of different nature: carbon, gold/ink high temperature and gold/ink low temperature. The auxiliary electrode imprint on each strip is made up of same ink as working electrode and a silver pseudo-reference electrode was always used (13). To alter the surface of commercially available screen-printed electrode carboxylated multiwall carbon nanotube dissolved in a mixture of DMF & water. Modification begins with dissolving CNT in solution and after that CNT fabricate on

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SPE. The morphology of MWCNT-COOH and modified SPE are characterized by scanning electron microscopy SEM (14). Such screen printed CNT electrodes offer large scale mass production of highly reproducible low-cost electrochemical biosensors (15). In this study functionalization of CNT and then fabrication on Screen printed carbon electrode which is further used for biosensor preparation have been elucidated.

2.Materials and Method

2.1 Materials and instruments

Multiwalled carbon nanotube (MWCNT) was purchased from Nanostructured and Amorphous Materials, Inc. Houston, USA. DMF was procured from Sisco Research Laboratory, India. Other chemicals were of Analytical Reagent (AR) grade. Commercially available screen printed carbon electrode (SPCE) was obtained from Dropsens, Spain. Screen printed electrode include three-electrode configuration in which carbon (working), platinum (counter) and silver (reference) electrodes are printed in close proximity. Ultrasonicator (SCIENTZ Biotechnology Co. Ltd.) used for sonication. Fourier transformed infrared spectroscopy (Model: IRAffinity -1 Shimadzu) was conducted at Guru Jambheswar University of Science & Technology, Hissar. Scanning electron microscopy (Model: JEOL JSM-6510) was conducted at IIT Delhi.

2.2 Functionalization of multiwalled carbon nanotubes

This experiment was conducted with a mixture of nitric acid and sulfuric acid. 10mg Multiwalled carbon nanotube was suspended into 13 ml mixture of concentrated H_2SO_4 and HNO_3 in 3:1 ratio and ultrasonicated them at 34°C for 8 h to obtain a homogeneous mixture (Fig.1). After sonication MWCNT dispersion was filtered through milipore nylon filter membrane. Now the supernatant of MWCNT was washed thoroughly with distilled water until the pH of the washing discard was 7 and then dried overnight in a vacuum oven at 120 °C. Functionalized MWCNT was characterized by FTIR.

2.3 Fabrication of functionalized CNT on SPCE

Carboxylated multiwalled carbon nanotubes (6.0 mg) were dispersed in 10 ml solution of Dimethylformamide (DMF) & Water(1:1) and ultrasonicated at room temperature for 6 h to obtain a completely homogenized solution. 5 µl of the c-MWCNT solution was coated on the surface of working electrode (carbon) of SPCE and kept for 12 h at room temperature (Fig.2). The excess unbound c-MWCNTs were removed by 2-3 washing with water. Then, c-MWCNT/SPCE was dried completely at room temperature. The fabricated electrode was characterized by scanning electron micrograph (SEM).

3. Results and Discussions

3.1 FTIR Spectra

FTIR samples prepared by grinding multiwalled carbon nanotube into potassium bromide powder. Low concentration of MWCNT is necessary due to high absorption of the nanotubes. Spectra performed at 120 °C in absorption mode. Fig.3 shows the FTIR spectra of carboxylated MWCNTs. Peak at 1570 cm^{-1} can be associated with the stretching of carbon nanotubes backbone. Chemical treatment with the acid mixture introduces additional peaks in the spectra. Peak obtained at 1635 cm^{-1} is associated with the stretching of CNT backbone. Peak at 3022 cm^{-1} shows the O-H stretching. One small peak appearing at 1404 cm^{-1} is possibly associated with O–H bending deformation in carboxylic acid groups whilst increased strength of the signal at 1226 cm^{-1} may be associated with C–O stretching in the same functionalities. In addition, a small peak appears at 945 cm^{-1}, which can be associated with ether R–O–R functionalities, for H_2SO_4 & HNO_3 treatment. The FTIR spectrum of c-MWCNT shows a peak at 2360 cm^{-1} associated with O-H stretch from strongly hydrogen bonded –COOH.

3.2 SEM studies

The morphology of fabricated c-MWCNT/SPC electrode was characterized by SEM studies Fig.4 shows the presence of c-MWCNT on SPCE.

4. Conclusion

Treatment with mixture of nitric acid & sulphuric acid (1:3) for 8 h show relevant effect on side walls of multiwalled carbon nanotubes. Results show the presence of C-O groups at the open end of nanotubes. Modification of electrodes with CNT is used to increase the rate constant for electron transfer and electro active area. Fabrication of functionalized MWCNT on screen printed carbon electrode results in a mesoporous coating where original electrode surface become an electrical contact.

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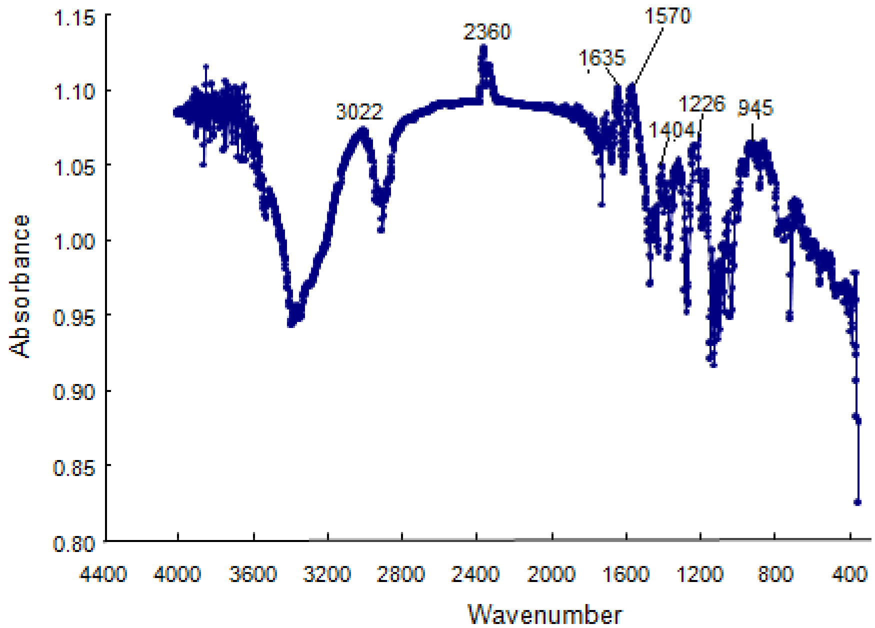
Legends
Fig 1. Image of a stable solution of carboxylated multiwalled CNT after sonication.
Fig 2. Fabricated Screen Printed Carbon Electrode with carboxylated multiwalled CNT.
Fig 3. FTIR Spectrum obtained for c-MWCNT
Fig 4. SEM Images of c-MWCNT/SPC electrode

Fig 1.

Fig 2.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3200
2800
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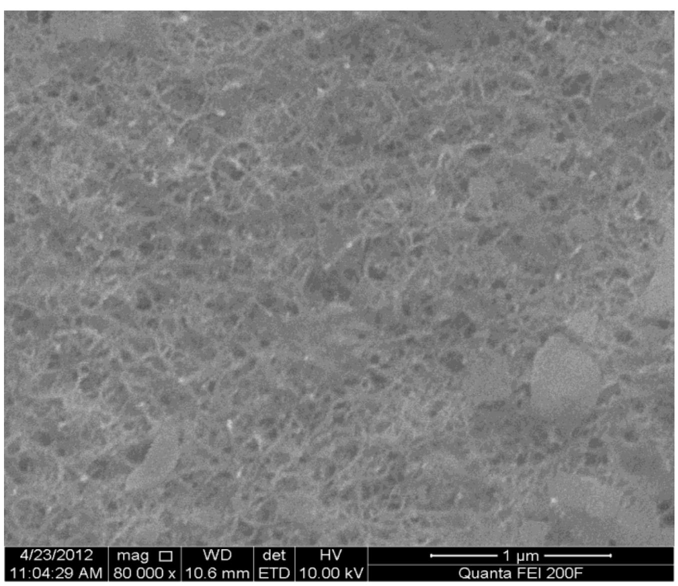
2000
1600
1200
800
400
3022
2360
1635
1570
1404
1226
945

Fig 3.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WD 10.6 mm
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Fig 4.