



CHARACTERIZATION OF FUNCTIONALIZED COMPOSITE SWCNT FOR SENSING APPLICATION.

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ABSTRACT

It has been seen that an individual carbon nanotube can be bent and tangled within a bundle, increasing the difficulty of exfoliation and debundling of SWCNTs aggregates. As the surface area of untangled SWCNTs are quite high as compared to those exist in bundles, efforts have been made to debundle the SWCNTs and make the use of its unique properties. Increase in surface area increases the sensing ability of the CNTs. Since the most common gas sensing principle is the adsorption and desorption of gas molecules on sensing materials, it is quite understandable that by increasing the contact interfaces between the analytes and sensing materials, the sensitivity can be significantly enhanced. Functionalization can improve the sensitivity and selectivity of the CNTs based gas sensors. Chemical bonds might be used to facilitate the interaction of the nanotube with other analytes such as solvents, polymers and biopolymers matrices. The adsorption of these molecules on the nanotubes is associated with a partial charge transfer, who alters the charge-carrier concentration as the electronic properties of semiconducting CNTs are very sensitive to certain analytes. After interaction with gas molecules and charge transfer, the resulting change in the electrical resistance of the nanotube is utilized as a sensor signal. Functionalization of CNTs with PANI makes it selective towards NH₃ gas, with PEI makes it selective towards NO₂ gas and HFIP derivatives makes it selective towards DMMP gas. Thus functionalization can provide a better pathway for the CNTs for utilization in potential applications. Further characterization using FTIR and Raman of the given samples were done to ensure the potential of the samples as gas sensor.

KEYWORDS :

Experimental Details:

A requisite amount of carboxylated SWCNT was taken in a bottle and dissolved in 50 ml DI water. Now the prepared sample was ultrasonicated by bath sonicator (Blackstone-NEY-Ultrasonics) for one and half hour between 40 kHz to 80 kHz. After ultrasonication, appropriate amount of aqueous solution of PEI was added to the dispersed solution. Now the dispersed solution was kept under stirring for approximately 24 hours. The resultant solution was again ultrasonicated for approximately 1 hr. and then filtered over 0.2µm polycarbonate millipore membrane through vacuum filtration pump to obtain desired composite. The sample was taken for FTIR and Raman analysis. The description of the samples which were prepared is shown in table 1.0:

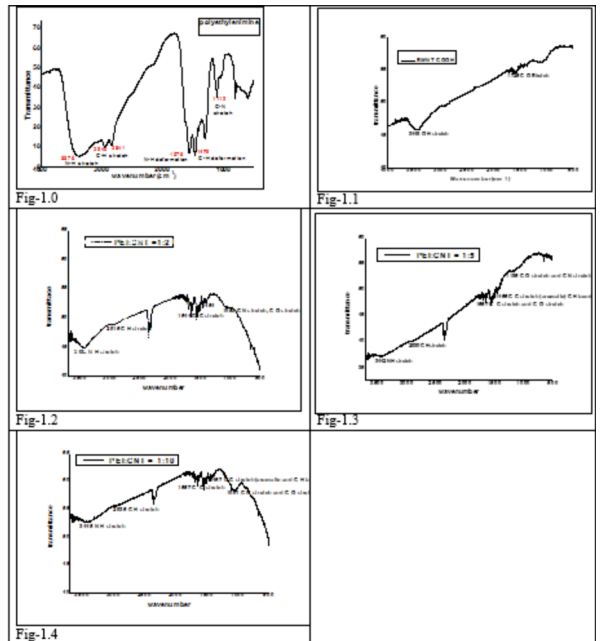
TABLE 1.0:

S.No.	Description of the Sample	Composition of the Sample (PEI:CNT)
1.	SWNT-COOH + PEI (DI water)	PEI:CNT = 1 : 10
2.	SWNT-COOH +PEI (DI water)	PEI:CNT = 1 : 5
3.	SWNT-COOH +PEI (DI water)	PEI:CNT = 1 : 4
4.	SWNT-COOH +PEI (DI water)	PEI:CNT = 1 : 3.33
5.	SWNT-COOH +PEI (DI water)	PEI:CNT = 1 : 2.5
6.	SWNT-COOH +PEI (DI water)	PEI:CNT = 1 : 2

Characterization of given samples-

1. Fourier Transform Infrared Spectroscopy:

FTIR spectroscopy was used to monitor both molecular interactions and concentration of volatile organic chemicals adsorbed onto CNTs surface. These includes minimal preparation, the ability to use neat samples, observation of useful overtone and combination bands, and that most bands were visible in a single FTIR spectrum without sample dilution or spectral scaling. For FTIR measurements, the specimens were submitted with a powder, using KBr as background. In order to eliminate the influence of water and other contaminations, both the KBr and the sample tablets were pretreated in-situ with temperature of 80 °C for 2 h. The background of KBr and the atmosphere in the cell were deduced. All the spectra baselines were corrected. The measurements were done using FTIR spectrometer (Varian-680-IR spectrometer) The FTIR spectrum of SWCNT-COOH, PEI and their composite are shown from figure 1.0 to figure 1.4:



FTIR Spectrum of Fig.1.0-PEI, Fig.1.1-SWNT-COOH, Fig.1.2-composite having PEI: CNT=1:2, Fig.1.3- the sample having PEI: CNT = 1: 5 and Fig.1.4-the sample having PEI: CNT = 1: 10

The IR spectra of SWCNT-COOH+PEI composite shows the bands at 1737 cm⁻¹ related to C=O Stretch which indicates the presence of carboxyl group. At 1650 cm⁻¹, peak of C=C stretch is observed which indicates the presence of carbon bonds of SWCNTs as well as indicates the N-H bend due to the presence of amine group in PEI. At around 2920cm⁻¹ peak of C-H Stretch is observed due to presence of aliphatic chain in PEI. At 3440 cm⁻¹, peak of N-H stretch indicates the presence of amine group due to PEI. Peaks of C-H deformation at nearly 1460cm⁻¹ and C-N stretch at nearly 1066 cm⁻¹ and 1186 cm⁻¹ were also observed. Peak at 1737cm⁻¹ are due to carboxyl group of SWCNT-COOH.

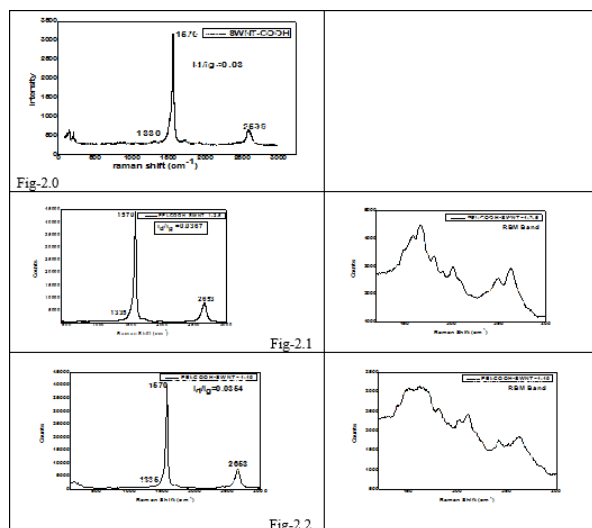
The FTIR spectroscopy was carried out for the samples to confirm the functionalization of SWCNTs-polymer composites

obtained. From the spectra it can be concluded that non-covalent functionalization has taken place between carboxyl SWCNTs and PEI as no new bond formation has taken place. Non-covalent functionalization occurs simply by the adsorption of polymer over the surface of the material. Some of the PEI got adsorbed onto CNT surface via electrostatic charge interaction between NH^+ of PEI and COO^- of carboxylic group of SWCNT.

For covalent functionalization to take place, formation of some new bonds must be evident. In the case of carboxyl SWCNT-PEI composite, covalent functionalization must take place via amide bond formation via nucleophilic substitution where nitrogen donates its lone pair to the carboxyl carbon atom of SWCNTs. As in the spectra, no evidence of amide bond has been observed so there must be very feeble chances of covalent functionalization.

2 Raman Spectroscopy:

Raman Spectroscopy is frequently employed to study the quality of the Carbon Nanotubes. It also provides information about the number of the walls, and the presence of crystalline or amorphous carbon, including the diameter of SWCNT. As the D-band is the diagnostic of disruptions in the hexagonal framework of the SWCNTs, the variation of the relative intensity of the D band to the G band can provide direct evidence for the covalent modification of SWCNTs.



Raman Spectra of Fig. 2.0 -SWCNT-COOH, Fig. 2.1- Functionalized PEI Composite (PEI: SWCNT-COOH = 1:2.5) and Fig. 2.2- Functionalized PEI Composite (PEI: SWCNT-COOH = 1:10)

The non-covalent attachment can be also confirmed by Raman spectroscopy (Fig. 2.0 and 2.2). Spectra of SWCNTs-PEI composites having concentration (PEI: SWCNT-COOH=1:2.5 and 1:10) after functionalization contained the following characteristic peaks: the D band located at 1335 cm^{-1} which is corresponds to the sp_3 hybridized carbon atoms in rings which are correlated with the extent of nanotubes sidewalls defects and chemical sidewall functionalization and the G band centered at 1575 cm^{-1} which arises due to bond stretching of all pairs of sp_2 atoms in both rings and chains. The multiple peaks observed in the radial breathing mode (RBM) of SWCNTs could be ascribed to a distribution of diameters in the SWNT samples. From the RBM band, the diameter of SWCNTs used were calculated by the equation:

$$\omega_{\text{RBM}} (\text{cm}^{-1}) = \frac{224 (\text{cm}^{-1})}{d_t (\text{nm})}$$

Thus the diameter of carboxylated SWCNTs used in our work ranges from 0.8nm to 1.2nm. No variation in Id/Ig ratio of the

composite means defects were not increased after the functionalization. This confirms that there is non-covalent attachment of PEI on surface of carboxylated SWCNT. Thus non-covalent attachment can also be confirmed by Raman spectroscopy. From the above figures it can be clearly seen that the nanotubes of different chiralities are present in the carboxylated SWCNTs used in making composite as many peaks arises in the RBM band of the composites. These peaks refer to the different diameter of the nanotubes corresponding to which one or more chirality may be present.

After functionalization, G band and the D band shifted from their position and located at 1570 cm^{-1} and D band at 1335 cm^{-1} respectively. G' band is also shifted from its position and located at 2653 cm^{-1} . This shows that non covalent functionalization has taken place. In Raman spectra G'band in PEI-SWCNT has a higher Raman shift by 54 cm^{-1} compared to that of carboxylated SWCNTs. On functionalization of CNTs, heavy atoms get attached to the CNTs so this causes change in the vibrations between the bonds and hence there is upshift of the band. The id/ig ratio in SWCNT-COOH is 0.03 and in composite id/ig ratio is also nearly 0.03. Thus the Raman results also confirm the non covalent type of functionalization between PEI and carboxylated SWCNT.

CONCLUSION-

The FTIR spectroscopy was carried out for the samples to confirm the functionalization of SWCNTs-polymer composites obtained. From the spectra it can be concluded that non-covalent functionalization has taken place between carboxyl SWCNTs and PEI as no new bond formation has taken place. Non-covalent functionalization occurs simply by the adsorption of polymer over the surface of the material. Some of the PEI got adsorbed onto CNT surface via electrostatic charge interaction between NH^+ of PEI and COO^- of carboxylic group of SWCNT.

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Thus the diameter of carboxylated SWCNTs used in our work ranges from 0.8nm to 1.2nm. No variation in Id/Ig ratio of the composite means defects were not increased after the functionalization. This confirms that there is non-covalent attachment of PEI on surface of carboxylated SWCNT. The id/ig ratio in SWCNT-COOH is 0.03 and in composite id/ig ratio is also nearly 0.03. Thus the Raman results also confirm the non covalent type of functionalization between PEI and carboxylated SWCNT.

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