Preparation and Characterization of Valine Functionalized Multi-walled Carbon Nanotubes

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Abstract— The valine functionalized multi-walled carbon nanotubes were prepared and characterized by using Ultraviolet-visible, Fourier transform infrared, Scanning electron microscopy, Energy dispersive X-ray analysis and Electron paramagnetic resonance spectroscopic techniques. UV-Vis study shows the formation of valine functionalized MWCNTs. Fourier transform infrared study confirms the presence of functional groups of oxidized MWNTs and valine functionalized MWCNTs. The morphology study was carried out for oxidized MWCNTs and valine functionalized MWCNTs by using Scanning electron microscopy. The Energy dispersive x-ray spectra revealed that the high purity of oxidized MWCNTs and valine functionalized MWCNTs. The ESR line shape analysis indicates that the observed ESR line shape is a Gaussian line shape. The g-values indicate that the systems are isotropic in nature.

.**Index Terms**— EPR, EDX, Functionalization, Multi-walled carbon nanotubes, SEM, UV-Vis, Valine

1 INTRODUCTION

CARBON nanotubes (CNTs) have unique electrical properties, high chemical stability and high surface to volume ratio have lead to many investigations in the field of chemical and biological applications [1]. The functionalized MWCNTs can have higher sensitivity and good response towards electrochemical detection than pristine MWCNTs [2]. The acid treatmented carbon nanotubes functionalized with carboxylic groups leads to manufacturing new derivatives of nanotubes via covalent functionalization, which changes the optical, thermal and electrical properties of nanotubes [3]. Functionalization of CNTs with the assistance of biological molecules remarkably improves the solubility of nanotubes in aqueous or organic environment and, thus, facilitates the development of novel biotechnology, biomedicine, and bioengineering [4].

Amino acids are an elementary unit for composing biomolecules and can also reflect the common chemical properties of complicated biomolecules. So, the interaction between CNTs and amino acid is very important for understanding the interaction mechanism between CNTs and biomolecules [5]. Valine is an essential amino acid important for smooth nervous system and cognitive functioning, which is particularly important for gall bladder and liver function, as well as balancing nitrogen levels in the body. Hence, Valine functionalized MWCNTs has been researched because Valine has a high reactivity and wealth of chemistry. The aim of the present work is to develop a relatively simple and effective process of functionalizing MWCNTs and carry out the characterization study. Here we report, the preparation and characterization of oxidized MWCNTs and valine functionalized MWCNTs.

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2 MATERIALS AND METHODS

The multi-walled carbon nanotubes, valine, H_2SO_4, and HNO_3 were purchased from Aldrich Chemical Co. The various concentrations of valine functionalized MWCNTs were prepared [5].

3 RESULTS AND DISCUSSION

3.1 UV-VIS ANALYSIS

The UV-Vis spectra of oxidized MWCNTs and valine functionalized MWCNTs were shown in Fig. 1. The characteristic peak was appeared at 276 nm for oxidized MWCNTs [6]. The blue shift was observed for valine functioned MWCNTs. Another broad peak was observed around ~327 nm for valine functionalized MWCNTs, which is attributed to the formation of charge transfer complex, valine functionalized MWCNTs.

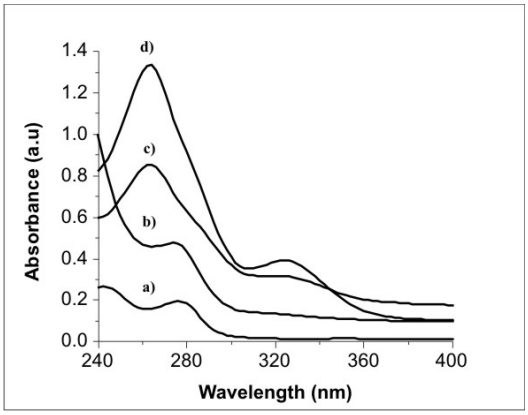

Fig. 1. UV-Vis spectra of a) oxidized MWCNTs b) 0.3 M c) 0.6 M and d) 0.9 M valine functionalized MWCNTs.

3.2 FT-IR ANALYSIS

The FT-IR spectra of oxidized MWCNTs and valine functionalized MWCNTs were shown in Fig. 2. The FTIR study confirms the presence of functional groups in oxidized MWCNTs and valine functionalized MWCNTs. The carbonyl stretching mode, N-H stretching mode, C-N stretching mode, C-O stretching mode, C-H bending mode C-OH stretching mode and O-H bending modes were identified and assigned.

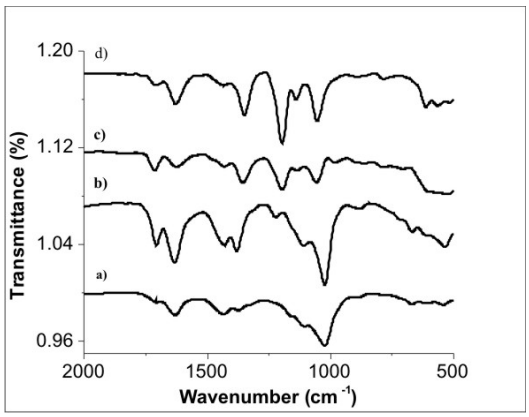

Fig. 2. FTIR spectra of a) oxidized MWCNTs b)0. 3M c) 0.6 M and d) 0.9 M valine functionalized MWCNTs.

3.3 SEM AND EDX ANALYSIS

The SEM images of oxidized MWCNTs and valine functionalized MWCNTs are shown in Fig. 3. The oxidized MWCNTs and valine functionalized MWCNTs were composed of CNTs with uniform size, shape and the surface appeared as large bundles with a length of ~3 µm. The agglomeration of the MWCNTs was not observed by SEM images, which indicates the higher dispersing ability of CNTs in solvents. The SEM image of oxidized MWCNTs was observed with an average diameter of ~80 nm. After the functionalization of a valine molecule on the oxidized MWCNTs, which resulted in an increase of the average diameter of ~100 nm. The quantitative EDX elemental microanalysis was carried out for oxidized MWCNTs and valine functionalized MWCNTs using EDX technique.

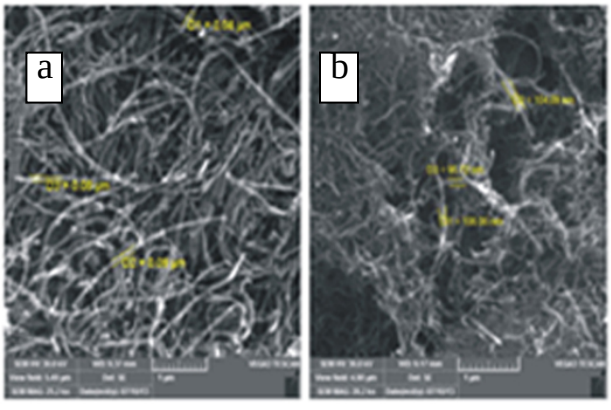

Fig. 3. SEM image of a)oxidized MWCNTs b) valine functionalized MWCNTs.

rbon and oxygen were identified in the oxidized MWCNTs sample,

TABLE 1
EDX ELEMENTAL MICROANALYSIS (WT. %) OF OXIDIZED AND VALINE FUNCTIONALIZED MWCNTS

Samples	Elements (%)		
	C	O	N
Oxidized MWCNTs	98.24	1.76	-
Valine functionalized MWCNTs	94.58	2.37	3.05

but the valine functionalized MWCNTs sample contains the elements carbon, oxygen and nitrogen. The EDX elemental micro analysis (wt. %) of oxidized MWCNTs and valine functionalized MWCNTs were listed in Table 2. EDX analysis confirms that the valine molecules are functionalized on the oxidized MWCNTs.

3.4 EPR ANALYSIS

The EPR spectra of oxidized MWCNTs and valine functionlized MWCNTs, their corresponding absorption spectra and the Gaussian fit were shown in Fig. 4. The EPR parameters were obtained from the spectra and listed in Table 1. The lineshape analysis was carried out using Origin 8 software, which reveals that the EPR absorption spectra have a Gaussian lineshape. The line width broadening arises due to the dipolar-interaction. Hence, the dipolar interaction can be explained in terms of the FWHM values of Gaussian line shape. The FWHM line width increases with increasing concentration of valine, which reveals that the dipole-dipole interaction increases with increasing concentration of valine. The g-value was calculated using the magnetic field B_0, which is obtained from the central position of the EPR spectral line. The observed g value is close to the free electron g value, which indicates that the isotropic nature of the system [7]. The g-value is independent of the magnetic field direction only in isotropic systems. The spin concentration values were obtained from the area of the Gaussian lineshape of the EPR spectral line. The spin concentration value decreases with increasing concentration of valine, which reveals that the unpaired electrons in carbon nanotubes undergo reduction process in valine functionlized MWCNTs.

TABLE 2
EPR PARAMETERS OF OXIDIZED MWCNTS AND VALINE FUNCTIONALIZED MWCNTS

Sample		R^2 from Gaussian fit	Spin concentration from Gaussian fit (a.u)	FWHM (mT)	g-factor
Pure MWCNTs		0.97	9.16×10^9	42.14	2.0072
Valine functionalised MWCNTs	Valine concentration 0.3M	0.95	1.72×10^9	48.79	2.0111
	0.6M	0.95	1.22×10^9	49.27	2.0122
	0.9 M	0.96	9.81×10^8	50.92	2.0122

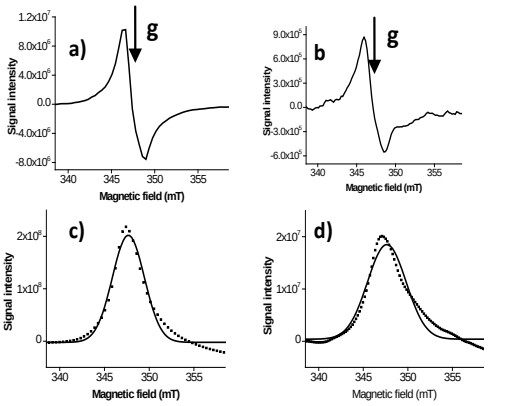

Fig. 4. EPR Spectra of a)oxidized b) valine functionalized MWCNTs, c) and d) the corresponding absorption spectra and Gaussian fit.

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4 CONCLUSION

FTIR study confirms the presence of functional groups in oxidized MWCNTs and valine functionalized MWCNTs. UV-Vis study reveals that the formation of valine-MWCNTs charge transfer complex. The surface morphology of the samples was analyzed by SEM. EPR study revealed that the EPR absorption data found to be best fit for the Gaussian lineshape. The g-value indicates that the system was found to be isotropic in nature. The spin concentration value decreases with increasing concentration of valine, which reveals that the unpaired electrons undergo reduction process in valine functionalized MWCNTs. The line width increases with increasing concentration of valine, which reveals that the dipole-dipole interaction increases with increasing concentration of valine.

4 ACKNOWLEDGMENTS

The authors thank the management for encouragement and permission to carry out this work. This work was supported by the UGC Research Award scheme, New Delhi (F.No.30-35/2011 (SA-II).

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