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DERIVATIZATION OF CARBON NANO MATERIAL

Seema Manchanda*[1]

[1*]B.K. Birla College (Autonomous), Kalyan, Maharashtra, India.

ABSTRACT

In the present work, the effort was focused on trying the use of Nano materials for drug delivery and Carbon Nano material (CNM) was chosen, because surface of CNMs can be functionally modified, also it has potential biocompatibility. Carbon Nano Tube was functionalized by acid treatment. Surface morphology of the Carbon Nano material after acid treatment was assessed by SEM and TEM characterization. FTIR of functionalized CNT showed the introduction of –COOH and –OH groups which was thought to be suitable for attachment of drug molecules by non-covalent bonding.

KEYWORDS

Nano materials, SEM and TEM.

Author for Correspondence:

Seema Manchanda,

B. K. Birla College (Autonomous),

Kalyan, Maharashtra, India.

Email: seema231106@gmail.com

INTRODUCTION

Carbon nanotubes (CNT) (Bacon *et al*, 1960[1], Oberlin *et al*, 1976[2] and Iijima 1991[3]) are considered ideal materials for several applications (Baughman *et al*, 2002)[4], ranging from ultra-strong fibers (Ericson *et al*, 2004)[5] to field emission displays (Milne *et al*, 2004)[6]. Recently, CNT have generated great interest in biology (Martin *et al*, 2003)[7], where suitably modified CNT can serve as vaccine delivery systems (Bianco *et al*, 2003)[8] or protein transporters (Shi Kam *et al*, 2005)[9].

Biological properties of Carbon nano tubes are being studied in terms of toxicity (Colvin 2003)[10]. The development of efficient methodologies for the chemical modification of CNT has stimulated the

preparation of soluble CNT that can be employed in several biological applications, among which drug delivery appears to be particularly promising (Lin *et al*, 2004[11], Bianco *et al*, 2005[12], Kostarelos *et al*, 2005[13] and Bianco *et al*, 2004[14]).

To improve solubility and biocompatibility of CNTs, functionalization of CNT was done Cationic functionalized CNTs (f- CNTs) can be bound to active molecules via stable covalent bonds or supramolecular assemblies based on electrostatic attractions. Two possibilities exist: (1) the more energetically feasible attachment onto the sidewalls either by covalent or noncovalent interactions, and (2) the encapsulation of these molecular assembilies within CNTs. Chemical reactions forming bonds with nano tube walls are carried out in the covalent functionalization case, while noncovalent functionalization exploits favourable interactions between the hydrophobic domains of an amphiphilic molecule and the CNT surface, affording aqueous nanotube wrapped by surfactant.

***Covalent* functionalization of nanotubes**

Various covalent reactions have been developed to functionalize CNT, oxidation being one of the most common. CNT oxidation is carried out with oxidizing agents such as nitric acid (Niyogi *et al*, 2002[15] and Rosca *et al*, 2005[16]). During the process, Carboxyl groups are formed at the ends of the tubes as well as at the defects on the sidewalls. Zeng et al observed sp3 Carbon atoms on SWNTs after oxidation and further covalent conjugation with amino acids (Zeng *et al*, 2008)[17]. Further modification can be achieved by attaching hydrophilic polymers such as poly (ethylene glycol) (PEG) to oxidized CNTs, yielding CNT-polymer conjugates stable in biological environments. (Liu 2007[18], Schipper 2008[19], Zhao 2005[20]).

***Noncovalent* functionalization of carbon nanotubes**

In contrast to covalent functionalization, noncovalent functionalization of CNTs can be carried out by coating CNTs with amphiphilic surfactant molecules or polymers. Since the chemical structure of the π-network of carbon nanotubes is not disrupted, except for shortening of length due to the sonication employed in the functionalization process. Consequently, aqueous solutions of CNTs, especially SWNTs, engineered by noncovalent functionalization are promising for multiple biomedical applications including imaging (Chen 2001 and 2002)[21,22]. Carbon Nano tubes have been dissolved in aqueous solutions using amphiphiles (Richard 2003)[23].

An ideal noncovalent functionalization coating on CNTs for biological applications should have the following characteristics. The amphiphilic coating molecules should have very low critical micelle concentrations (CMC) values so that the nanotube coating is stable after removal of most of the excess coating molecules from the CNT suspension. Lastly, the coating molecules should have functional groups which are available for bio conjugation with antibodies or other molecules to create various functional CNT conjugates for different biological applications.

Acid – functionalization technique is being used for derivatization of CNTs. The Salient characteristics of an efficient drug delivery system include its ability to perform controlled and targeted drug delivery, which CNT have been shown to exhibit (Heilmann 1983)[24]. CNTs and pharmaceutically active components are possible in drug delivery. One method of interaction is as porous absorbent to entrap active components within a CNT mesh or CNT bundle; and the other is through functional attachment of the compound to the exterior walls of the CNTs. The third approach involves the use of CNT channel as nano-catheters.

MATERIAL AND METHODOLOGY

CNT was functionalized by adding 0.5g of MWCNT in 100ml of 3: 1 ratio of 2M Nitric-Sulphuric acid mixture and then refluxed for 1 hr followed by keeping at room temperature for 24 hrs. It is then filtered through Millipore filtration apparatus with membrane of Nylon 6, 6 of 0.2µm pore size and 47mm diameter. Functionalized CNT (f-MWCNT) was dried and its FTIR was recorded. To know whether their structure is damaged due to

acid treatment, scanning electron micrographs and transmission electron micrographs were taken.

RESULTS AND DISCUSSION

FTIR Analysis

Was used as a tool to study whether CNTs are functionalized or not. The FTIR results of CNT and functionalized CNT are presented in Figure No.1.

Peak at 3430.14cm^{-1} in the FTIR of functionalized-MWNT (F-MWCNT) corresponds to –OH stretching absorption band and also shows intra-molecular H- bonding.

Peak at 2918.76cm^{-1} corresponds to C-H stretching

Peak at 1633.82cm^{-1} corresponds to C=O stretching. This lowering of peak is due to conjugations of C=O with the ring and also due to intra-molecular H- bonding stabilized by resonance.

FTIR of functionalized CNT shows the introduction of –COOH and –OH group on the surface of CNT.

SEM Characterization of CNTs

To know whether the surface morphology of CNT is damaged due to acid treatment during functionalization, Scanning Electron Micrographs were taken before and after functionalization (Figure No.2a and No.2b and Figure No.3c and No.2d). The SEM micrographs reveal that there is no damage to the structure of CNT due to acid treatment.

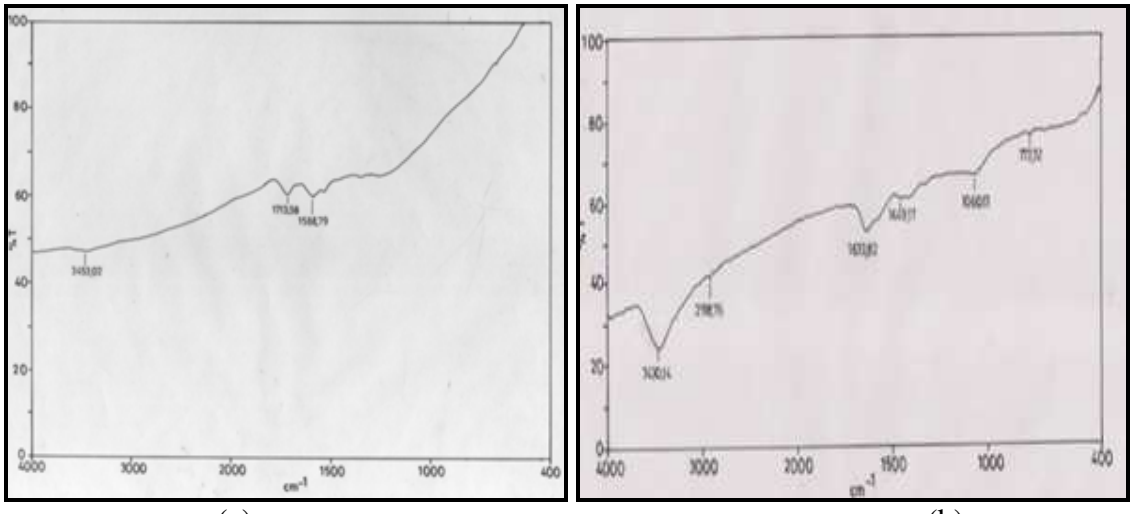
TEM Characterization of CNTs

Confirmed that the surfaces were not damaged (Figure No.4).

Discussion

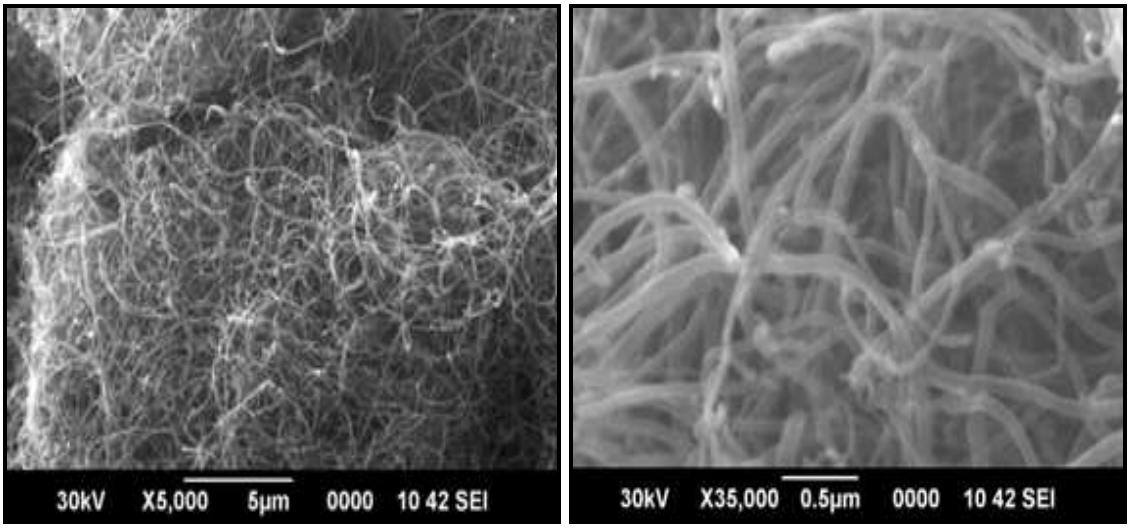
Organic functionalization has opened new horizons in the study of the biological properties of CNT.

Various covalent reactions have been envisaged regarding functionalized Carbon Nano tubes, Oxidation being one of the most common. CNT oxidation is carried out with oxidizing agents like nitric acid, sulphuric acid etc. (Niyogi *et al*, 2002[15] and Rosca *et al*, 2005[16]). During the process carboxyl groups are formed at the ends of the tubes as well as at the defects on the sidewalls (Figure No.5).



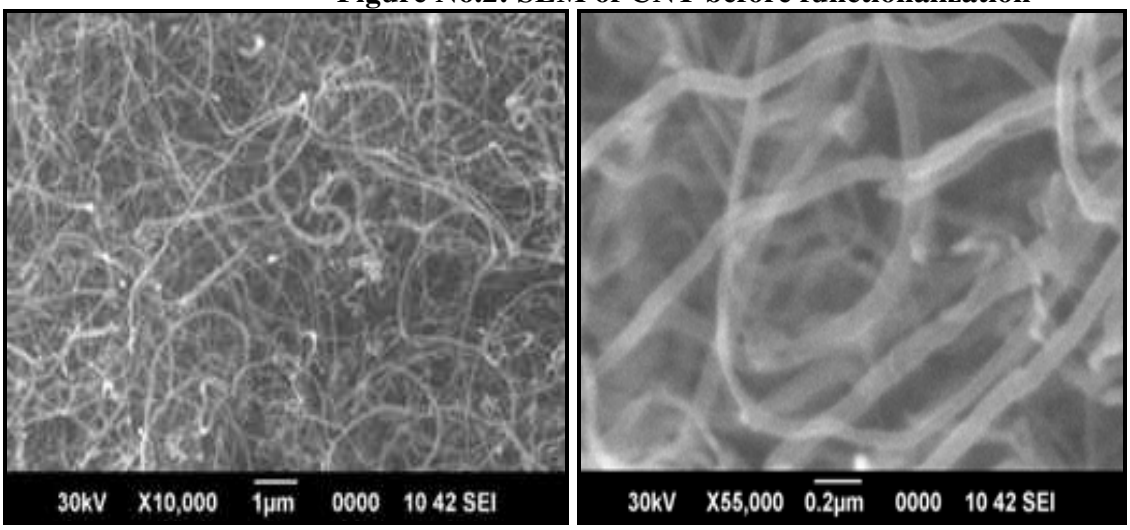
(a) (b)

Figure No.1: FTIR of (a) CNT and (b) functionalized CNT



(a) (b)

Figure No.2: SEM of CNT before functionalization



(a) (b)

Figure No.3: SEM of CNT after functionalization

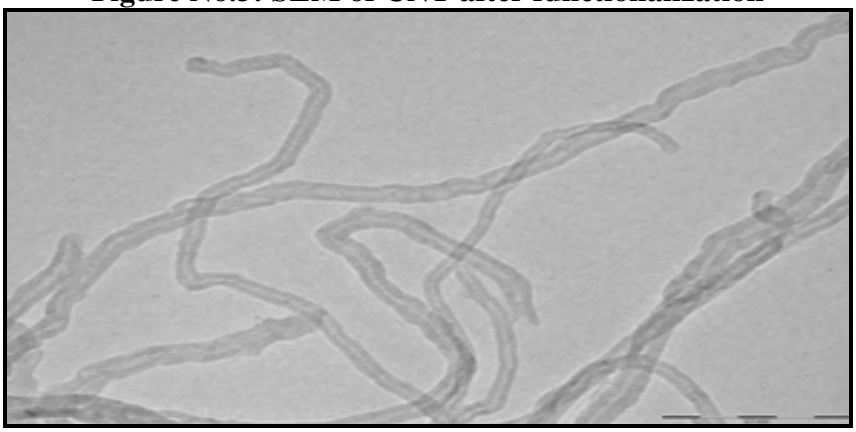


Figure No.4: TEM of functionalized CNT

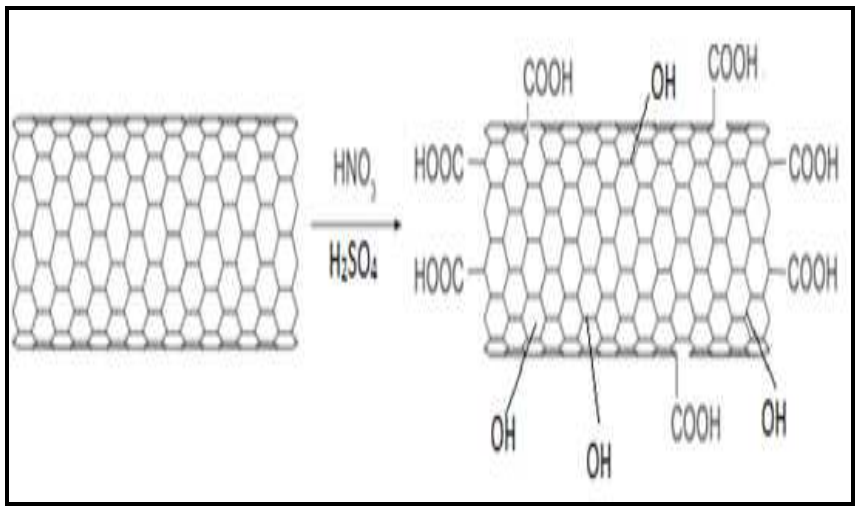


Figure No.5: Covalent functionalization of Carbon Nano tubes with -COOH and -OH

CONCLUSION

SEM and TEM images reveal that there is no damage to the structure of CNT due to acid treatment for functionalization.

FTIR of functionalized CNT shows the introduction of –COOH and –OH group on the surface of CNT. Due to derivatized CNM, drug molecule can be attached to- COOH or - OH group of CNM by non-covalent bonding.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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