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Study of Stability and Dispersibility of Oxidized Multiwall Carbon Nanotube and Characterization with Analytical Methods for Bioapplication

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Abstract: Nanotechnology is the study of manipulating matter on an atomic and molecular scale. Generally, nanotechnology deals with developing materials, devices, or other structures possessing at least one dimension size from 1 to 100 nanometers. Carbon nanotubes have great potentials for novel applications in industry, drug delivery system and many other uses. In this work after purification, multiwall carbon nanotube was functionalized in acids by liquid phase oxidation method for drug delivery system. The structural and chemical changes after carboxylation of MWNTs improved the solubility and dispersibility of the carboxylated MWNTs in water. Fourier transformed infrared spectroscopy, and transmission electron microscopies were carried out for characterization of these methods of MWCNTs functionalization.

Keywords: Nanotechnology, Dispersibility, Carbon nanotube, Oxidation

INTRODUCTION

Nanotechnology is the ability to produce the materials, tools and new systems at the molecular and atomic measures and taking control and using the features which appear in this dimension. Using this simple definition clears that nanotechnology's applications in several fields of food, medicine, medical diagnosis, biotechnology, electronics and computer related to, transportation, energy, safety, health and environment, materials, aerospace and security can be identified. Clearly, it seems that human is facing another revolution in technology, a revolution much broader and greater than the two other agricultural and industrial revolutions.

Nanometer-scale structures showed the attractive and novel field of study to scientists that permit scientists and engineers manipulate objects at molecular and atomic levels to synthesis and produce new materials for sensing, composite, catalysis and biomedical applications. Carbon nanomaterials such as carbon nanotubes formed a relatively new class of materials, which exhibiting extraordinary electronic and mechanical properties and are also promising candidates for drug delivery (Chung, 2008).

Carbon nanotubes (CNT) have a smooth wall with a high resolution very high thermal conductivity power and potential and special structure, with unique mechanical and electronically properties. Dimensional properties, surface chemistry and electronic properties of Carbon nanotubes make them ideal materials for use in the chemical and biochemical sensors. Carbon nanotubes have very wide surface, which is a good position for the Functionalization of this compound compared with its length scale in diameter, which is capable of adding different functional groups. Their surface is convenient enough for different functionalization of biomolecules or specially drug molecules such as anti-histamines,

Antibiotics, antifungal and anticancer drugs, that can help the medical society for human health care. On the other hand, for the special shape of CNTs as a tube, drug and biomolecules can function and load on the surface or encapsulate into the inner part of this tube shapes nanomaterial without losing their stability (Heister, 2011).

At first for this allotrope of carbon purification with a high percentage is necessary. The purity of the compound is related to method of synthesis if it had metals and impurities such as catalyst particles, amorphous carbons and others. These impurities produce during nanotube synthesis so because of that synthesised CNTs need purification to separate tubes from these kinds of impurities to

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have more purification of this kind of carbons and use in more processing. It seems that the gas phase method (such as CVD) is the best method for synthesis of CNTs, which provided the more potential for growth of CNTs and more proceeding more applications in different fields such as composites, sensor and bioappplicability.

From 1991 when CNTs were first described by Sumio Iijima, Different properties of carbon nanotubes for their unique structure have fascinated scientists to work within their researches that caused a revolution in nanotechnology in various cases such as electronic, mechanic, environment, chemistry and pharmacology. Their physical properties hollow and porous structures, and facile surface functionalization have made the application of the CNTs more attractive as drug delivery vehicles (Reilly,2007),(Iijima,1991). So carbon nanotube as a smart nano career can be functioned and filled with suitable molecules and materials to address the specific goals (Nirajand, 2005).

In the material science, chemical functionalization is a key for improving and inducing the new properties without changing the basic structure. Chemical functionalization of carbon nanotube cause them to be useful Nano objects and Nano careers in biological and biomedical science and a Human body to transfer drug, proteins, peptides, nucleic acid and chemotherapeutics into tissue or cell. Among different functionalization strategies, Oxidation is probably the most widely studied (Bianco, 2005).

The wet chemical methods of oxidation of CNTs such as photo-oxidation, gas phase treatment or oxygen plasma has gained a lot of attention in an attempt to purify and enhance the chemical reactivity of this graphitic network. Typically, through the treatments not only the pristine CNTs can be purified but also oxygen-containing groups such as carboxyl and hydroxyl, can find to decorate the graphitic surface (Datsyuka,2008). The presence of oxygen-containing groups can simplify the exfoliation of CNT bundles, and increases the solubility of these compounds in polar media.

From the chemical reactivity point of view, CNTs can be differentiated with two zones; the tips and the sidewalls. The tips are reminiscent of the structure of a fullerene hemisphere and are relatively reactive. The sidewalls can be approximately considered as curved graphite, the degree of curvature, of course, depending on the diameter of the tube.

Technique of surface functionalization of CNTs is performed by covalent and non-covalent methods, each of them has advantages and disadvantages. Non-Covalent method can guarantee electrical properties and structure of CNTs that can bind to these graphene sheets bye van der waals and π-stacking interactions. Covalent functionalization can save strong and stable bond formation which oxidation with acid treatment is one of the covalent functionalization methods (Sim,2011). Figure 1 shows some interactions and benefits of these two methods of functionalization.

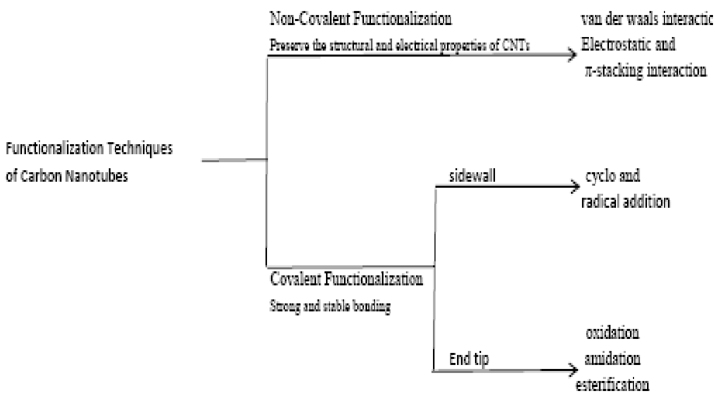


Fig. 1. Covalent and Non-Covalent methods of Carbon nanotube Functionalization

METHODOLOGY

In this work, we use liquid phase as an oxidation method with HNO3 and H2SO4 to function the surface of MWCNT. Which is the most effective and accepted method for biological application of CNTs.

We use two refluxing and sonicating techniques for functionalization. By oxidation of CNTs carboxyl groups can appear and become useful sites for more modifications, such as covalent coupling of molecules by creation of amide and ester bonds. By this method, the nanotubes can connect with a wide range of molecules and functional moieties (Balasubramanian,2004; Benito, 2008).

The oxidation of MWCNTs is to provide sites for anchoring drug molecules and to give more dispersibility effect in the simulated biological fluids. Oxidation of carbon nanotubes is created opportunities to connect the drug molecules as well as solubility and dispersibility in water and solvent emissions (Marianna, 2008; Wenrong, 2007; Wang, 2009).

The MWCNT used as raw material had been prepared by chemical vapor deposition (CVD) With purity more than 90%, length 10-30mm and the diameter 10-30 nm. In first method the raw CNTs (MWCNT) refluxed in nitric acid (HNO3 with 30%) at 130 ºC for three hours. Then the mixture filtered after cooling down and washed with deionized water, and the treated MWCNT collected by filtering through polycarbonate membranes. This process carried out continuously. Final material dried overnight at 110 ºC in a thermostated oven and became a powder. In second method, we use this kind of nanocopound (Multi-wall Carbon nanotube MWCNT) with The 3:1 concentrated H2SO4:HNO3 mixture used for oxidizing in this work. The suspension of two acids and MWCNT sonicated in one hour at less than 150 ºC to avoid structure damage. After adding the distilled water to suspension, separation and then filtration carried out by centrifugation, the resulting solid washed with deionize water until pH=7, and the sample dried in a vacuum oven. In the second technique (sonication), we use this process in spite of reflux, we did sonication.

For biomedical application of carbon nanotubes, we can use different methods of functionalization and modification for enhancement of solubilization and dispersion of carbon nanotubes in water whether they have low solubility. This modification also enhanced their biocompatibility. This type of using CNTs cause improvement of nanomedicine (Vivek, 2010). So in this way and after these processes, we must analyze and make characterization for oxidized multi-wall carbon nanotubes to make sure of functionalization.

Carbon nanotube does not describe simple because of its chemical structure, the difference in their numbers of walls, purity, diameter distribution, catalyst material, length distribution, impurity species, chirality and defects. Thus, it is essential to do the characterization of this kind of applied material is to make sure of the quality. Although various techniques have been used to characterize CNTs, In order to study the structural characteristics of The nanotubes (Khanh, 2002; Haipeng, 2008; Russier, 2011).

In this work, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) completed under control conditions. Fourier transformed infrared spectroscopy (FTIR) use to characterize the mesoporous carbon nanotube materials and shows the formation of oxygen containing groups such as C=O and COOH and used to characterize surface of functionalized CNTs and in this work, MWCNT. MWCNTs sample taken KBr added in the ratio of 1:100 (sample: KBr), mixed thoroughly and ground together in the mortar until it becomes a "fine homogenous" powder (Mohd Yosuf,2010). The mixture pressed under high pressure obtained the sample pallet. The pallet placed in the instrument and scanned.

Transmission electron microscopy (TEM) is a microscopy technique which mainly used to display general morphology, The biocompatibility and crystallinity of CNT and improve the information with high quality about the structure, size and shape of composites and carbonaceous materials. In this kind of scanning, we can see defect of CNT (if there is), the form of tips shows the changes also pieces of nanotubes and carbonaceous nanoparticles belong to the graphitic tubular structure detected by TEM.

RESULTS AND DISCUSSION

For biological and biomedical applications of carbon nanotubes, there are many ways to functionalize and optimize them to increase the solubility and biological properties when they have not solubility and dipersibility or their solubility is low. This functionalized and optimization method (oxidization) is used to increase their biological properties. Use of this kind of carbon nanotubes causes the increase of efficiency and improves the use of these compounds in nano-medicine. After this stage, analytical characterization must be done. Preparation of carboxylated multi-wall carbon nanotube with different ratio and different conditions of acids have done in this work, which this kind of oxidation is common for bio application of CNTs

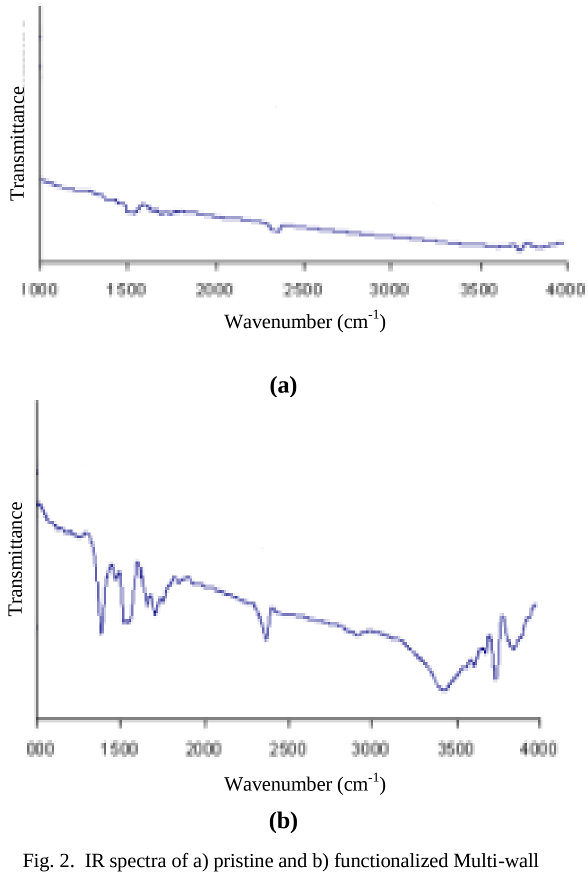
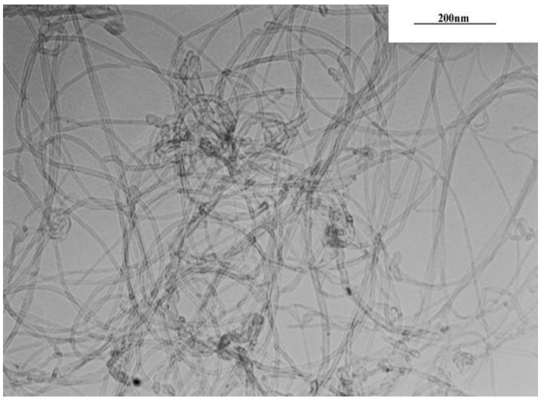


Fig. 2. IR spectra of a) pristine and b) functionalized Multi-wall carbon nanotube by acids

and it is more efficient. Functional groups on the structure of nanotubes such as the carboxylic group provide sites for anchoring drug molecules. The main problem is purification of material without structural defect or damage. It observed that in the process, several functional groups such as carboxyl (-COOH), carbonyl (-CO), and hydroxyl (-OH) formed on the surface of nanotubes (Masera,2008), which is typical of carbon materials. This function method changes the reactivity of nanotubes and modifies their wetting characteristics, which increase their properties and their ability for different application.

Fourier Transformed Infrared Spectroscopy (FTIS) is used to characterize mesoporous materials such as carbon nanotube. With IR spectra in oxidize carbon nanotube; observer can demonstrate the presence of different functional groups on the surface of CNT, including carbonyl, hydroxyl and carboxyl groups. The peak at different ranges of wavelength and different points shows various kinds of functional groups. Figure 2 shows the IR spectra of raw and oxidized CNTs. Transmission electron microscopy (TEM) can provide resolution to observe the morphology length, diameter and defects (Haipeng, 2007). Figure 3 shows the TEM images of pristine and functionalized MWCNTs. After treatment, more individual MWCNT appeared under TEM, and seems that some tubes have open cavities, and some have broken end cap because of chemical oxidation in functionalization. In sonication method tubes have less damage as shown in figure 3 b) the outer surface of MWCNT is smooth and after acid treatment, tubes are shortened and MWCNTs are dispersed. So in this way,



(a)

(b)

Fig. 3. TEM images of a) pristine MWCNT , b) Functionalized MWCNT after acid treatment

TEM can help and show us the truth of an experiment and make us sure about the result and complete oxidation in the best and efficient method.

From these results, we can state that the formation of other surfaces functional groups, like hydroxyl and carbonyl groups (–OH, –CO), is considerable under the oxidation conditions**.**

CONCLUSION

This paper presented some methods of carboxylation of MWCNT, which are useful and efficient in biological applications. Chemical oxidation of these materials (MWCNTs) has studied with reagents of different oxidation power. Oxidation with nitric acid under reflux conditions increases the defect and broken tube's population formation on the CNTs also causes the length shortening, having this result is because of refluxing method, which damages the structure of CNT. Application of a mixed acid solution with sonication technique showed better structure, more acid content and absence of a defect on graphitic modified surface in comparison with nitric acid oxidation by refluxing method**.**

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