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One-pot Three-component Functionalization of Carboxylated Shortend Multi-wall Nanotubes with Histidine Derivative

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Abstract

In this project, a three-component functionalization of carboxylated shortend multi-walled carbon nanotubes (MWNT-COOH) by Histidine derivative via amidation method have been investigated. The functionalized MWNTs were characterized by Fourier Transform Infrared spectroscopy (FT-IR), Raman spectroscopy, elemental analysis and scanning electron microscopy (SEM).

Keywords: *One-pot, Functionalization, Multi-walled nanotubes, Histidine.*

Introduction

Histidine is an α-amino acid with an imidazole functional group. It is one of the 23 proteinogenic amino acids. Histidine is an essential amino acid in humans and other mammals. The imidazole sidechain of histidine is a common coordinating ligand in metalloproteins and is a part of catalytic sites in certain enzymes. In catalytic triads, the basic nitrogen of histidine is used to abstract a proton from serine, threonine, or cysteine activating it as a nucleophile [1-2]. The group attach to the surface of carbon nanotube in order to take advantage of its outstanding mechanical, optical, solubility, electrical and thermal properties. Carbon nanotubes have unique properties that make them attractive for different engineering applications and many other fields [3-7]. Multiwalled carbon nanotubes are more useful than singlewalled carbon nanotubes because of their relatively low production costs and availability in large quantities.

However, because of their chemical inertness,

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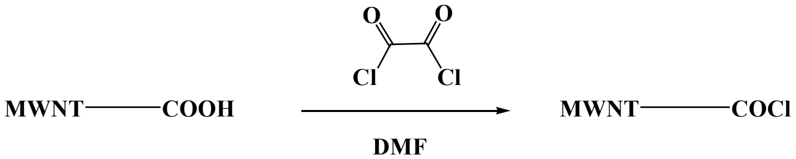
carbon nanotubes have to be functionalized in order to acquire additional physico-chemical properties [8]. Chemically attached to the tubes, these groups, are mostly represented by –COOH groups, less by –C=O, and –OH groups [9, 10]. In this article, we presented a simple route to attach Histidine derivative to MWNT–COOH via esterification method (Scheme 1). The product was characterized by spectroscopy (FT-IR), Raman spectroscopy, elemental analysis and scanning electron microscopy (SEM).

Experimental

All reagents and solvents were obtained from Merck Chemical Inc. (Darmstadt, Germany), and MWCNT–COOH (95% purity, 20–30 nm; Netrino Co. Ltd) were purchased and used as received. The FT-IR spectra were recorded using KBr tablets on a Nexus 870 FT-IR spectrometer (Thermo Nicolet, Madison, WI). FT-Raman spectra were recorded on 960 ES, 1064 Thermo Nicolet. SEM measurement was carried out on the XL30 electron microscope (Philips, Amsterdam, Netherlands) to study the morphology of the MWCNTs. Elemental analyses of carbon, hydrogen, nitrogen and sulphur were performed using a Series II 2400 (Perkin Elmer, Waltham, MA).

Preparation of MWNT-COCl

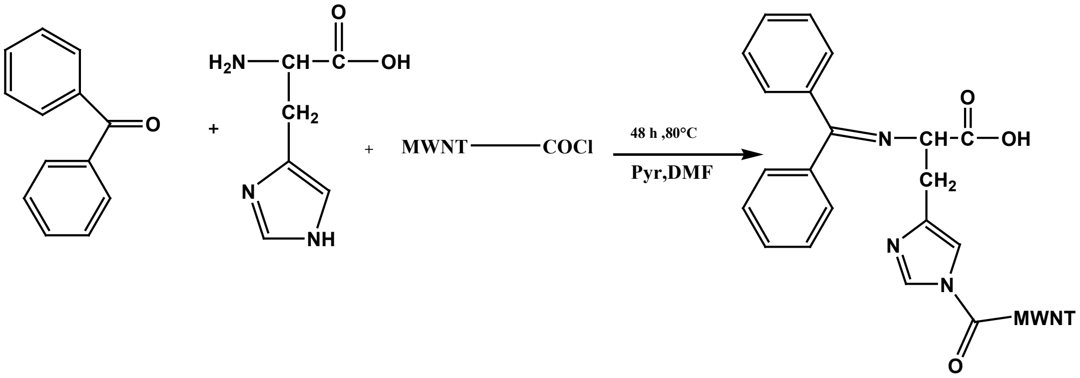
200 mg of the MWNT-COOH were sonicated in 50 ml of DMF for 30 min to provide a suspension. Oxalyl chloride (5 ml) was added drop-wise to the MWNT suspension at 0 ˚C under N_2. The mixture was stirred at 0 ˚C for 2 h and then at room temperature for another 2 h. Finally the temperature was raised to 80 ˚C and the mixture was stirred overnight to remove excess oxalyl chloride. After cooling it to room temperature, the mixture was filtered and washed thoroughly with EtOH.



Scheme 1.

Preparation of MWNT- Histidine derivative

Equimolar quantities of benzophenone (1mmol) and histidine (1mmol) and a few drops of pyridine as a catalyst were refluxed in DMF for 1 h at 80 °C. Then were added 100 mg MWNT–COCl was added and mixture was heated for 2 days. After the completion of the reaction, the mixture was poured into 250 ml of Ethanol and vacuum-filtered through a filter paper (3 µm porosity). This washing operation was repeated five times and followed by washing with petroleum ether three times. The product was then washed with deionized water and acetone, and the functionalized MWCNT was dried in a vacuum oven at 90°C. Scheme 2 shows the synthesis route of the modified MWNT- Histidine derivative.



Scheme 2.

Results and discussion

Figure 1 shows the FT-IR spectrum of the modified MWNTs. In spectrum A, the band at around 1527 cm^{-1} corresponds to the stretching mode of the C =C double bond that forms the framework of the carbon nano tube Sidewall [11]. The peaks at 1704, 3304 cm^{-1} and 1071 cm^{-1} apparently correspond to the stretching modes of the carboxylic acid groups [12]. In spectrum **B**, the C-O and C=O stretching frequencies shifted from 1704 and 1204 cm^{-1} (MWNT-COOH) to at around 1658 and 1016 cm^{-1} (amino functionalized MWNTs), respectively. Peaks at 1574 cm^{-1} of functionalized MWNTs are due to the N–H stretching of amine groups.

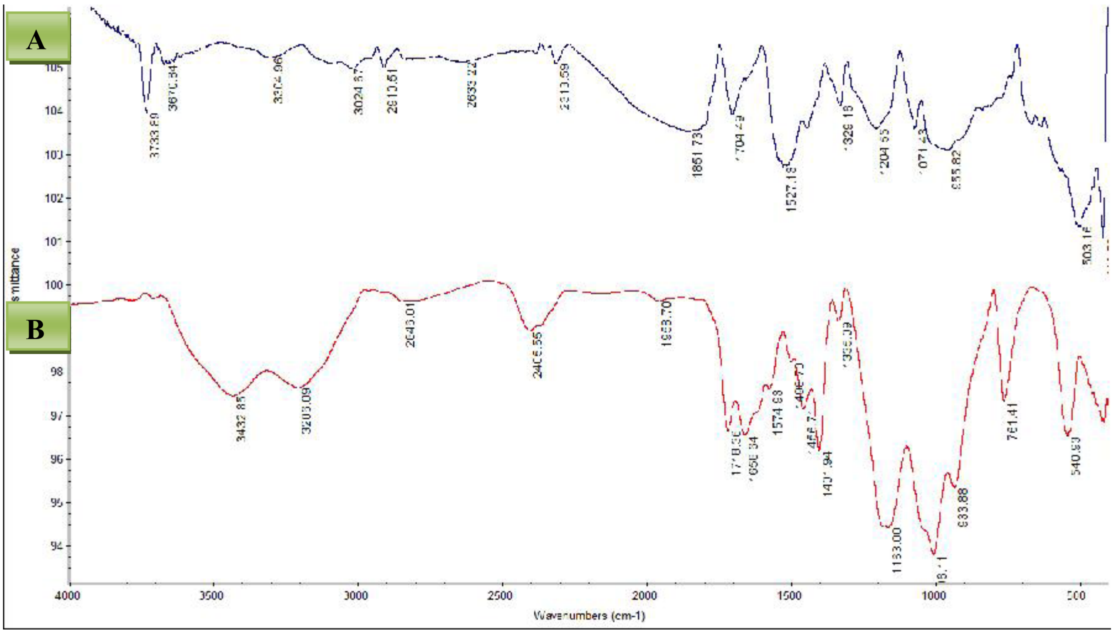


Figure 3. Fourier transform spectra of A; carboxylated shortend multi-walled carbon nanotube (MWNT-COOH) and B; modified multi-walled carbon nanotube (MWNT- Histidine derivative).

Raman spectroscopy is a powerful tool used here to provide structural information about MWNT–COOH before and after functionalization. As shown in Figure 2, the D and G bands of the MWNT at around 1339 and 1596 cm, attributed to defects, disorder-induced peaks, and tangential- mode peaks, (A-B) can be clearly observed for MWNT–COOH and MWNT– Histidine derivative. Additionally, the intensity ratio (ID/IG) of the D and G bands for MWNT– Histidine derivative (B) is 1.38 comparably is greater than that for MWNT–COOH (A) 0.54. The increase in intensity of the defect mode at 1339 cm was related to sp3 hybridization of carbon, and is used as an evidence for the disruption of the aromatic system of π electrons by the attached molecules [13-16].

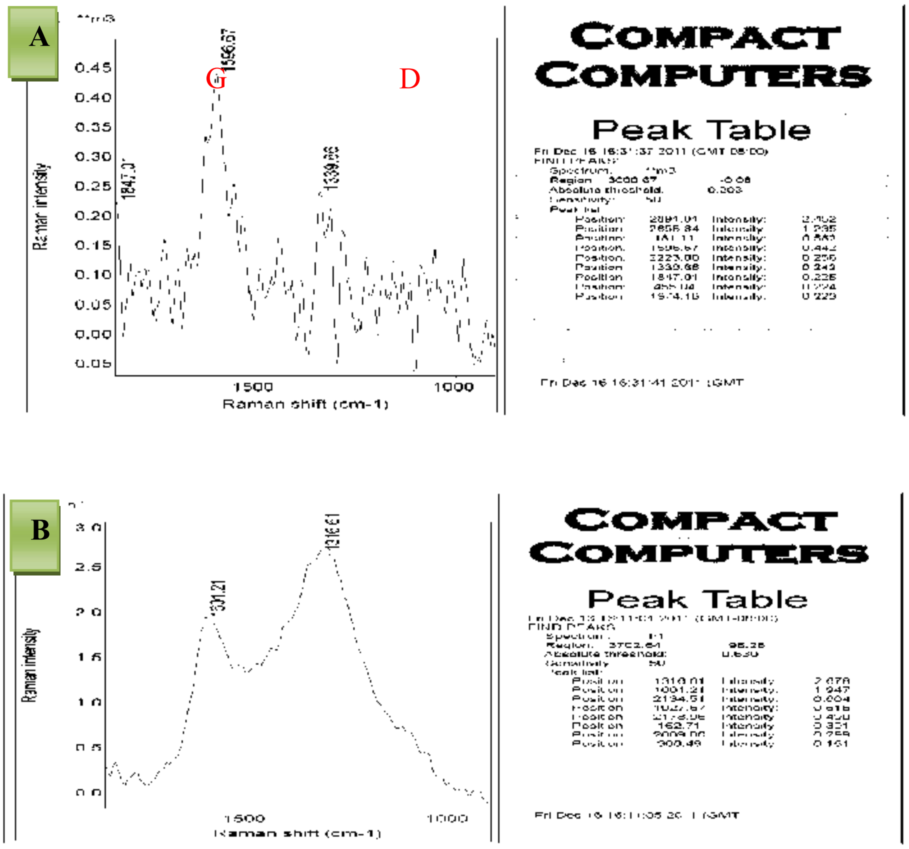


Figure 2. Raman spectroscopy of **A;** carboxylated shortend multi-walled carbon nanotube (MWNT-COOH) and **B;** modified multi-walled carbon nanotube (MWNT- Histidine derivative).

Elemental analyses of the MWNT-COOH (A) and MWNT- Histidine derivative (B) are shown in Table 1. Apart from the carbon values, the atomic percentages of nitrogen B (as compared with A) indicated that A is functionalized with Histidine derivative.

Table 1. Elemental analysis of **A;** carboxylated shortend multi-walled carbon nanotube (MWNT-COOH) and **B;** modified multiwalled carbon nanotube (MWNT- Histidine derivative).

Sample	%C	%H	%N	%S
A	96.4	0.04	0	0
B	70.6	0.2	1.3	0

The morphology of the resulting MWNT-Histidine Derivative was observed with SEM. In Figure 3, SEM images of A and **B** are shown. They indicate that the MWNT–COOH (A) has a smooth surface. The changes in the morphology for MWNT- Histidine Derivative (**B**) are remarkable. A uniform tubular layer is observable due to ester group on the surface of the MWNT (the rough part) is observable. It seems that the diameter of **B** is slightly increased in comparison to those of A [17-21].

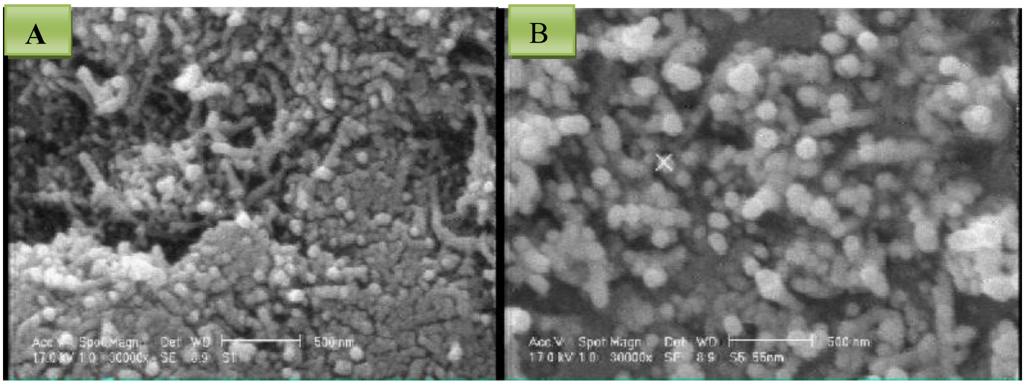


Figure 3. Scanning electron microscopy images of **A** carboxylated multiwalled carbon nanotubes and **B** MWCNT- Histidine derivative.

As a result of this functionalization, the solubility of MWNT- Histidine derivative was improved significantly, and they were easily dispersed in deionized water. A dispersion test gives a fair idea whether the modification of the carbon nanotubes has been achieved or not. Figure 4 presents a photograph of two vials containing MWNTCOOH and MWNT- Histidine derivative dispersed in deionized water. As can be seen from Figure 6, MWNT-COOH is insoluble in deionized water while the modified CNTs can be directly dispersed in deionized water (without sonication) homogeneously and no precipitation was found even after it was sealed for 2 month at room temperature.

Figure 4. The images of MWNT-COOH and MWNT- Histidine Derivative in deionized water (1mg/6ml) after standing for 1 month.

Conclusion

Functionalized carbon nanotubes have played and will continue to play an important role in the research and development of based materials and systems. Carbon nanotubes can be functionalized via amidation of the nanotube-bound carboxylic acids. A detailed methodology for the modification and functionalization of multiwalled carbon nanotube (MWCNT) via Amidation has already been presented. The solubility of the carbon nanotubes associated with the functionalization and chemical modification offers excellent opportunities not only in the characterization and understanding of carbon nanotubes but also in the utilization of carbon nanotubes for various nanomaterials.

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