

Functionalization of Carboxylated Multi-wall Nanotubes with 1,2-phenylenediamine

H. Tahermansouri^{1,*}, D. Chobfrosh khoei², M. Meskinfam³

¹Department of chemistry, Islamic Azad University, Ayatollah Amoli Branch , Amol, Iran

²Department of Science, Islamic Azad University, Shabestar Branch , Shabestar, Iran

³Department of chemistry, Islamic Azad University, Lahijan Branch , Lahijan , Iran

Received: 19 November 2010; Accepted: 11 December 2010

Abstract

In this paper, the chemical functionalization of carboxylated multi-walled carbon nanotubes (MWNT-COOH) by 1,2-phenylenediamine, have been investigated. MWNT-benzimidazole is obtained through MWNT-Amide reaction with POCl₃ after 72h, which is confirmed by FT-IR, SEM, TGA, and elemental analysis. These functionalizations have been chosen due to -NH₂ and NHCO active sites in MWNT-Amide for future application.

Keyword: Functionalization, 1, 2-phenylenediamine, Carboxylated multiwall nanotubes

1. Introduction

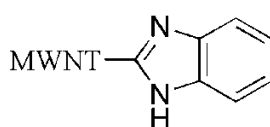
Carbon nanotubes (CNTs) have been attracting much attention from chemists and scientists owing to their electronic, mechanical, optical and chemical characteristics [1-3]. Multiwalled carbon nanotubes (MWNTs) are more attractive than single walled carbon nanotubes because of their relatively low production costs and availability in large quantities.

In recent years, the chemical functionalization of carbon nanotubes has been more interesting because it allows the modification of nanotube surface for subsequent alignment. These surface modifications play an important role for application of nanotubes in composite, sensors and many other fields. The chemical modifications of CNTs have been well summarized in several review articles [4-10].

* Corresponding author: Hasan Tahermansouri
Islamic Azad University, Ayatollah Amoli
Branch, Amol, Iran.
Tel +989127632577
Email Tahermansouri2@gmail.com

Amines are among the reagents that have drawn the greatest attention. Haddon and coworker pioneered the approach of functionalizing the carboxylic groups of CNTs through amidation with amines bearing long alkyl chains [11-14]. On the other hand, acid-chloride-functionalized CNTs are used to attach glucosamine [15] and didecylamine [16]. Also, the amidation of CNTs carried out with aromatic amines [17, 18]. In this paper, we investigated the formation of penta-heterocyclic, MWNT-benzimidazole, on the MWNT in addition to developing the amidation of MWNT with bifunctional aromatic amine.

The products were characterized by FT-IR, SEM, TGA, and elemental analysis. Synthesis of MWNT-benzimidazole **Figure 1A** was reported before for determination of carboxylic group number [19]. But lack of sufficient structural data encouraged us to develop this work. Synthesis route of modified MWNT-COOH is shown in **Figure 2**.



A

Fig.1. MWNT-benzimidazole structure

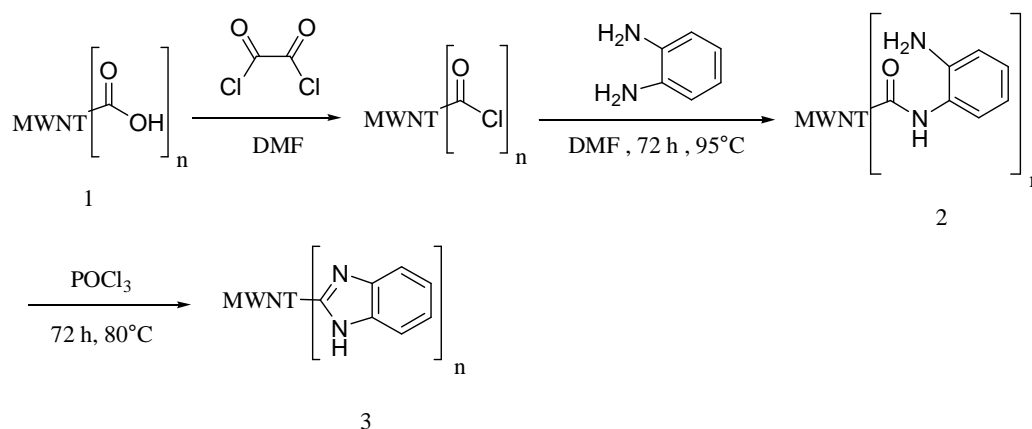


Fig.2. Synthesis route of the modified MWNT-COOH

2. Materials and methods

2.1. Preparation of MWNT-Amide

60 mg of the MWNT-COOH were sonicated in 90 ml of DMF for 45 min to give a homogeneous suspension. Oxalyl chloride (2.5 ml) was added drop-wise to the MWNT suspension at 0 °C under N₂. 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 70 °C and the mixture was stirred overnight to remove excess oxalyl chloride. 100 mg of 1, 2-phenylenediamine dissolved in DMF was added to the MWNT suspension and the mixture was stirred at 95 °C for 72 h. After cooling to room

temperature, the mixture was filtered and washed thoroughly with DMF, ethyl alcohol and THF. Subsequently, the black solid was vacuum dried at room temperature for 5 h.

2.2. Preparation of MWNT-benzimidazole

30 mg of MWNT-Amide was mixed with 10 ml POCl_3 and then was stirred at 80°C for 72h. After cooling to room temperature, the reaction mixture was separated by centrifugation and washed thoroughly with THF. Thus, the obtained solid was dried under vacuum for 4 h.

3. Results and discussion

Elemental analyses of the modified-MWNT 1-3 are shown in Table 1. Apart from the carbon values, the atomic percentages of: H 1.31% and N 2.09% of 2 (as compared to 1) indicated that 1 is functionalized with 1, 2-phenylenediamine. On the other hand, decreasing of percentage of H from 1.31 to 0.96% confirms the five-ring formation. Based on these data coupled with the assumption that the atomic percentages of nitrogen and hydrogen were originated from the employed aromatic amine without elimination, we confirmed the functionalization of MWNT-COOH with 1, 2-phenylenediamine.

Table 1. Elemental analysis of the modified-MWNT 1-3

MWNT	%C	%H	%N
1	96.4	0.04	0
2	89.7	1.31	2.09
3	85.2	0.96	1.47

The Figure 3 presents the FT-IR spectrum of modified MWNTs. In 1, the band at the 1558 cm^{-1} corresponds to the stretching mode of the C=C double bond that forms the framework of the carbon nanotube sidewall. The peak at 1730 and 1045 cm^{-1} apparently correspond to the stretching modes of the carboxylic acid groups. The two bands at $2800\text{-}2950\text{ cm}^{-1}$ which are seen in all spectra are assigned to CH stretching of MWNT-COOH defects. In the spectrum 2, the new strong peaks at $3200\text{-}3500$ can be assigned to the N-H, NH_2 and OH stretching modes.

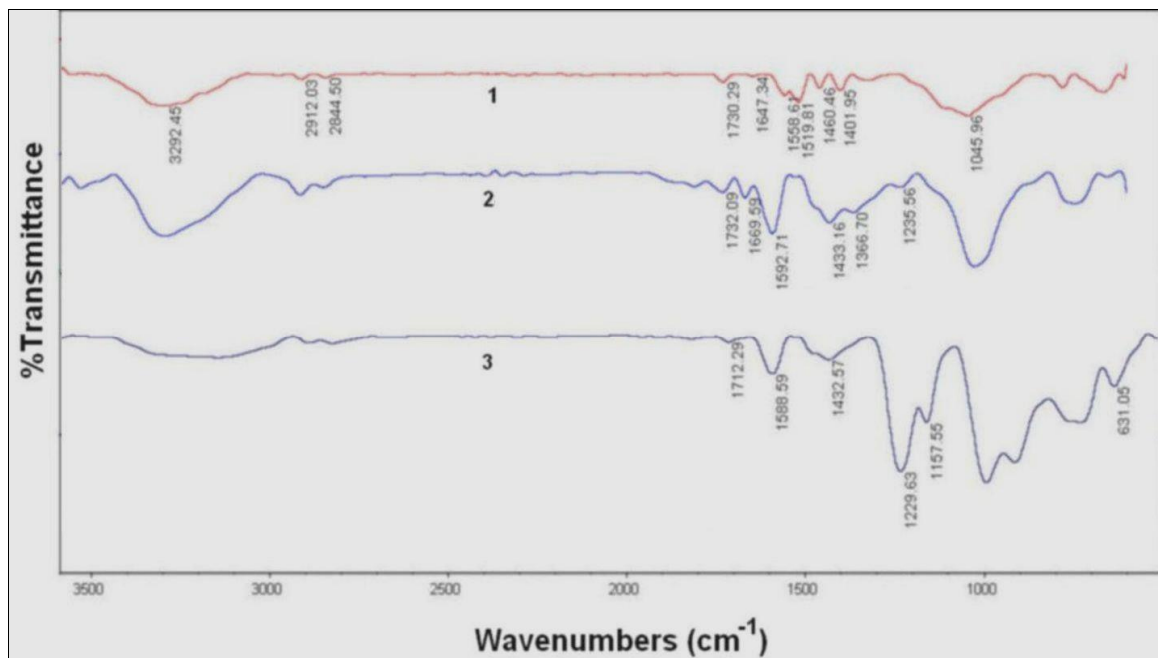


Fig.3. FT-IR spectra (after baseline correction) of functionalized carbon nanotubes: (1) MWNT-COOH ; (2) MWNT-Amide ; (3) MWNT-benzimidazole

The carbonyl peak in 2 shift to 1669 cm^{-1} (as compared to 1730 cm^{-1} for 1) as a result of the amide $\text{C}(=\text{O})\text{NH}$ linkage formation. The other peak at around 1620 cm^{-1} can be assigned to the NH_2 scissoring mode in 2 that overlap with $\text{C}=\text{C}$ mode. The peaks at around $1540\text{--}1590$, $1400\text{--}1480$, $1200\text{--}1380$ and 1100 cm^{-1} correspond to $\text{C}=\text{C}$ stretching nanotube, aromatic ring modes, $\text{C}-\text{N}$ and $\text{C}-\text{O}$ stretching modes, respectively. In the spectra 3 the peaks of amide group disappear and three peaks at around 1580 , 620 and 1150 cm^{-1} are appeared which can be assigned to imidazole-ring stretching. The two peak at 1732 and 1712 cm^{-1} in 2 and 3, respectively can be related to residual carboxylic acids on the nanotube. Thus, FT-IR spectra confirm that MWNT-COOH has been successfully modified by aromatic amine. Two obvious bands at $1320\text{--}1350\text{ cm}^{-1}$ (D band) and $1550\text{--}1600\text{ cm}^{-1}$ (G band) can be seen in the Raman spectra of modified MWNTs in the solid state with the excitation at 1064 nm which are similar to those of insoluble nanotubes.

More direct evidence for the functionalization of MWNTs is manifested by SEM images. In Figure 4, SEM images of 1 and 3 are shown. It indicates that the 1 has a smooth surface. The changes in the morphology for 3 are remarkable. A uniform tubular layer due to covalently bonded aromatic amine on the surface of the MWNT (the rough part) is observable. It seems that the diameters of 3 are slightly increased in comparison to 1.

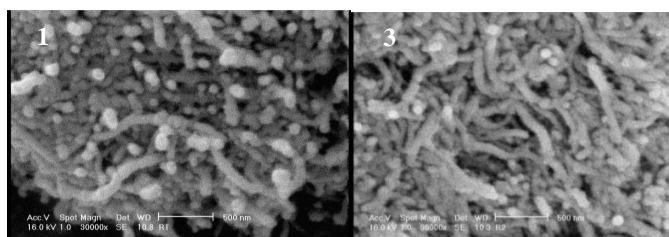


Fig.4. SEM images of (1) MWNT-COOH and (3) MWNT-benzimidazole

Figure 5 provide quantitative information on the nanotube functionalization by using TGA results. In TGA graphs of MWNT-Amide and MWNT-benzimidazole, two distinct decompositions are observable. The first one (below 360 °C) can be assigned to aromatic amine and benzimidazole of MWNT Amide and MWNT-benzimidazole, respectively, while the second one (above 360 °C) is related to nanotube as comparing to MWNT- COOH thermogram. If the mass loss of the MWNT-COOH at 360 °C (%0.88) is used as the reference, the mass loss of functionalized MWNT by 1, 2-phenylenediamine and benzimidazole of MWNT-Amide and MWNT-benzimidazole at 360 °C is about %19 and %11.4, respectively.

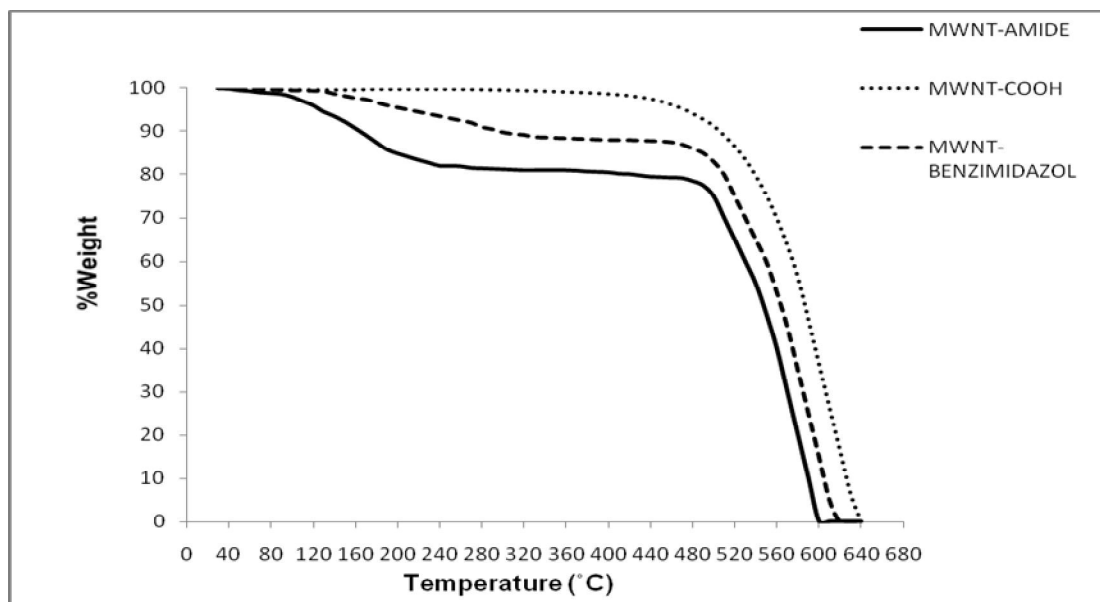


Fig.5. TGA curves of modified-MWNT in the air.(ramp10°C/min)

These results indicate that there is one amide group for MWNT-Amide per 47.9 and one benzimidazole group for MWNT-benzimidazole per 75.8 carbon atoms of MWNT, respectively.

In summary, we have introduced benzimidazole groups onto the surface of nanotubes via reaction of MWNT-Amide with POCl_3 . Functionalization was demonstrated by their SEM images and analyses by FT-IR, elemental analysis and TGA.

Acknowledgements

The financial and encouragement support provided by Research vice Presidency of Science and Research branch, Islamic Azad University and Iranian Nanotechnology Initiative (Govt. of Iran).

References

- [1] Bonard , J-M., Kind , H., Stöckli , T., Nilsson , L.-O.(2001). Field emission from carbon nanotubes: The first five years. *Solid-State Electron* ,45,893-914.

- [2] Baughman , R. H., Zakhidov , A.A., Heer , W.A.(2002). Carbon Nanotubes--the Route Toward Applications. *Science*,297,787-792.
- [3] Avouris , Ph.(2002).Carbon nanotube electronics.*Chem. Phys*, 281, 429-438.
- [4] Niyogi , S., Hamon ,M.A., Hu ,H., Zhao , B., Bhowmik , P., Sen , R.(2002) . Chemistry of Single-Walled Carbon Nanotubes. *Acc Chem Res*, 35, 1105-1113.
- [5] Hu , C-Y., Xu , Y-J., Duo ,S-W., Zhang , R-F., Li , M-S.(2009). One-step Electrodeposited Carbon Nanotube /Zirconia / Myoglobin Film. *J. Chin. Chem. Soc*, 56,234-238.
- [6] Holzinger , M., Vostrowsky ,O., Hirsch , A., Hennrich , F., Kappes , M., Weiss, R.(2001). *Angew Chem Int Ed* ,40,4002-4005.
- [7] Sun , YP., Fu , K., Lin , Y., Huang ,W.(2002). Functionalized Carbon Nanotubes: Properties and Applications. *Acc Chem Res*,35,1096-1104.
- [8] Banerjee , S., Hemraj-Benny , T., Wong , SS.(2005) . Covalent Surface Chemistry of Single-Walled Carbon Nanotubes. *Adv Mater*,17,17-29.
- [9] Banerjee , S., Kahn , MGC., Wong , SS.(2003). Rational Chemical Strategies for Carbon Nanotube Functionalization.*Chem Eur J* , 9,1898-1908.
- [10] Hirsch , A.(2002) . Functionalization of Single-Walled Carbon Nanotubes.*Angew Chem Int Ed*, 41,853-1859.
- [11] Hamon , M.A., Chen , J., Hu , H., Chen , Y., Itkis , M.E., Rao , A.M., Eklund , P.C., Haddon , R.C.(1999). Dissolution of Single-Walled Carbon Nanotubes. *Adv. Mater*,11,834-840.
- [12] Hamon , M.A., Hu , H., Bhowmik , P., Niyogi , S., Zhao , B., Itkis ,M.E., Haddon , R.C.(2001). End-group and defect analysis of soluble single-walled carbon nanotubes. *Chem. Phys. Lett*, 5, 347-348.
- [13] Chen , J., Hamon , M.A., Hu , H., Chen , Y., Rao , A.M., Eklund , P.C., Haddon , R.C.(1998). Solution. Properties of Single-Walled Carbon Nanotubes. *Science* ,282,95-98.
- [14] Zhao , B., Hu , H., Niyogi ,S., Itkis , M.E., Hamon , M.A., Bhowmik , P., Meier , M.S., Haddon , R.C.(2001). Chromatographic Purification and Properties of Soluble Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc*, 123, 11673-11677.
- [15] Pompeo , F.,Water , D.E., Resasco.(2002). Water Solubilization of Single-Walled Carbon Nanotubes by Functionalization with Glucosamine . *Nano Lett* , 2, 369-373.
- [16] Liu , L., Zhang , S., Hu , T., Guo , Z-X., Ye , C., Dai , L., Zhu , D.(2002). Solubilized multi-walled carbon nanotubes with broadband optical limiting effect. *Chem. Phys. Lett* , 359,191-195.
- [17] Chen , W-Y., Chen , C-Y., Hsu , K-Y., Wang , C-C., Ling ,Y-C.(2004). Reaction monitoring of polyaniline film formation on carbon nanotubes with TOF-SIMS. *Applied Surface Science*, 231-2, 845-849 .
- [18] D'Este , M., Nardi , M., Menna , E.A.(2006). Co-functionalization approach to soluble and functional single-walled carbon nanotubes. *Eur. J. Org. Chem*, 4, 2517-2522.
- [19] Kirikova , M.N., Ivanov , A.S., Savilov , S.V.(2008). Modification of multiwalled carbon nanotubes by carboxy groups and determination of the degree of functionalization.*Russ. Chem. Bull, Int. Ed*, 57(2),298-303.