Adsorption Modification of Carboxylated Carbon Nanotubes with Aniline in Aqueous Solution

Xiaofeng Xie and Lian Gao*
State Key Laboratory of High Performance Ceramics and Superfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

(Received March 7, 2006; CL-060280; E-mail: liangaoc@online.sh.cn)

Aniline-modified multi-walled carbon nanotubes (MWNT) have been obtained through interaction between carboxylated MWNT and aniline in aqueous solution. The influence of three species carboxylation treatment on the interaction has been studied. FT-IR spectra bands detectable in this case implied the generation of amide bonds and the conjugation of aromatic ring in samples. The results show that citric acid serves as super intermediate medium in the course of aniline-modified MWNT. Moreover, higher temperature can promote the modified procedure significantly.

Physicochemical modification of carbon nanotubes (CNTs) is a promising way to make them more amenable to rational and predictable manipulation. Modified CNTs exploit widely application in molecular electronics, biological sensors, catalyst support, superior sorbent, and CNTs–polymer composites.[1] The routes of modification can rely upon either chemical covalent-bond formation or multiple adsorptions on CNTs via non-covalent interactions.[2]

Recently, amidation of CNTs attracts many scientific interests because of their favorable chemical processibility and high reactivity. Amino-functionalized CNTs are typically easier to disperse in organic solvents and water, which can also improve the interface binding of CNTs within polymer matrix and biological system.[3] Different approaches to produce the amino-functionalized nanotubes have been reported.[4] Most of them are based on chemical manipulation of carboxyl groups, which can be easily introduced onto CNTs by various methods. Interaction of amino group with carboxylated CNTs has been studied both from experimental and theoretical views.[5] Obviously, generation of oxygenated functional groups has been a crucial fundament to further CNTs chemistry. However, the effect of different oxidation methods on the interaction has not been detailed reported so far as we know.

Here, oxygen-containing groups were introduced onto pristine multi-walled carbon nanotubes (MWNT) by diverse chemical treatment, and then the treated MWNT reacted with aniline in aqueous solution at different temperatures. As a representative aromatic amine, aniline possesses feasibility to form diazotabile amide link with MWNT and then could be applied in biosensor and photoelectrical devices.[6] Exploration of oxidative groups' influence on this modification methods would be valuable for improving the functionalized MWNT's properties. In addition, effect of temperature on this strategy will also be briefly discussed.

We used aligned MWNT commercially available from Shengzhen Nanoport Co., Ltd., China. The BET surface area of pristine MWNT is approximately 180 m^2/g according to the manufacturer. Figure 1 shows the TEM images of pristine MWNT, which have inner diameter around 10 nm with lengths ranging from several to tens of micrometer.

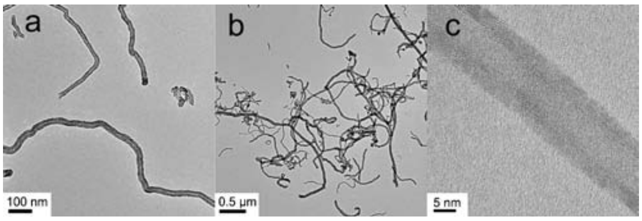

Figure 1. TEM images of pristine MWNT.

In a typical treatment, 1.0 g of MWNT was added in 200 mL of 0.3 M potassium permanganate (PP), 3 M nitric acid (NA) and 1 M citric acid (CA) solutions, respectively. The solution containing MWNT was heated at 140 °C for 20 h. Then, the MWNT was separated through filtering with 0.2 μm membrane filter. The filter residue was rinsed by distilled water four times and dried in vacuum oven at 60 °C, referred as "PP–MWNT", "NA–MWNT", and "CA–MWNT", respectively. Afterward, 50 mg treated MWNT was added in 25 mL 60 mg/L aniline solution and ultrasonicated for 10 min at room temperature. These suspensions were placed in thermostat water bath at 25, 50, and 75 °C for 24 h, respectively. Finally, aniline-modified MWNT were obtained through filtration, washing and vacuum oven-drying. The amount adsorbed was calculated by measuring the UV–vis absorption (Perkin-Elmer Lambda 950) of the filtrate before and after the procedure.[7]

The influence of temperature on the interaction between MWNT and aniline can be observed in Figure 2. Gradually raising temperature represents positive effects on the aniline adsorption capacity of CA–MWNT sample. Simultaneously, the capacity of NA–MWNT and PP–MWNT has minor change, a small quantity of increase and decrease, respectively. Pristine MWNT keep nearly constant capacity during all temperature regions. The highest adsorptive capacity of citric acid indicates that it can serve as super intermediate medium in the course of aniline-modified MWNT. The potential mechanism can be con-

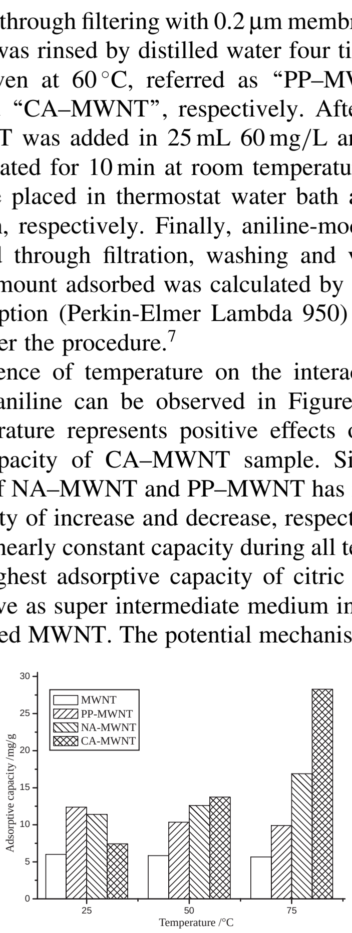

Figure 2. Aniline adsorptive capacity of MWNT at different temperature.

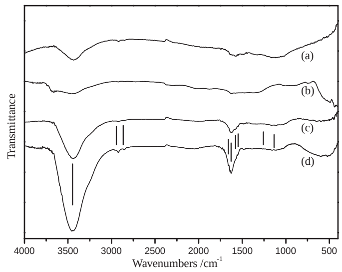

Figure 3. FT-IR spectra of aniline treated pristine MWNT (a); PP–MWNT (b); NA–MWNT (c); CA–MWNT (d).

sidered that the citric acid molecule and its derivant, which can be physicochemically adsorbed on the nanotube surface, posses a rather amidation reactivity with aniline. Higher temperature can promote the amide reaction because of the endothermic process. The minor increase of NA–MWNT capacity can be observed at the meantime. As a stronger acid, NA can increase diverse functional groups on the MWNT and improve the dispersion of MWNT in aqueous solution, so the NA–MWNT show higher adsorptive capacity at 25 °C. However, at higher temperature, simplex physical adsorption can be suppressed and chemical adsorption, meaning the amidation reactivity, would generate at more quickly reaction rate. CA can selectively increase the carboxyl groups on MWNT, and then accelerate the chemical adsorption. The reason of PP–MWNT capacity decreased with increasing temperature can be presumed to the existence of additional disturbance. Many researches show that FT-IR spectra can be utilized for detailed studying the variant functional groups on CNTs.[8] Therefore, we surveyed the aniline-treated samples' FT-IR spectra (obtained on Nicolet 7000-C with 4 cm^{-1} resolution) for further reaction detail.

Figure 3 illustrates the FT-IR spectra of aniline treated MWNT with different pre-processing. It is well known that oxidation of CNTs introduces weakly acidic surface groups such as carboxylic, carbonyl, phenolic, and lactonic groups. The carboxylic groups are considered having higher reactivity and larger quantity than the others.[7] Table 1 summarizes the main bands obtained in these spectra, together with the corresponding assignment. These bands have been marked as A–G in the wavenumbers descent sequence. A clear trend is observed in the spectra as the aniline is attached on MWNT. The C=O stretching vibration in ketone and/or carboxylic groups which usually at 1710–1734 cm^{-1} has not been observed, meanwhile, there is a sharp peak at 1643 cm^{-1} in NA–MWNT (Figure 3c) and CA–MWNT (Figure 3d) samples which indicate the C=O stretching vibration in amide. It can be interpreted that amide bonds gradually replace the carboxylic groups of the samples. The conjugation of aromatic ring with amide bonds makes the C=O bond vibrational frequency (1680 cm^{-1}) migrates to lower values. An interesting observation is that there are very low peak of C=O stretching vibration in pristine MWNT (Figure 3a) and PP–MWNT (Figure 3b), meaning that aniline is almost unavailable to them. For pristine MWNT, it can be easily known that there are only few oxygen-containing groups to react with aniline. For PP–MWNT, it is imaginable that small quantities of residual oxidant, which can be firmly adsorbed on MWNT despite of well rinse, will interact with aniline and represses the amide formation. It has been confirmed by the peaks at 418, 610, and 898 cm^{-1} in Figure 3b, means Mn–O, Mn=O, $[MnO_4]^{2-}$ stretching vibration, respectively. The sharp peaks at 1627 and 1550 cm^{-1} of NA–MWNT and CA–MWNT can be inferred to the amide N–H deformation and amide C–N stretching vibration, respectively. In the high frequency region, a broadened band at around 3451 cm^{-1} with distinctly overlapping peaks can be observed, especially in CA–MWNT. The O–H stretching vibration and N–H stretching vibration is considered at this region. Obviously, the CA–MWNT shows the most efficient interaction between aniline and MWNT because of its stronger amide bands than the others. The logical cause is that the citric acid molecule has been attached on MWNT though physicochemical adsorption process, thus the oxygen-containing groups on MWNT is increased significantly. Accordingly, the abundance of carboxylic groups is very helpful to amidation process.

Table 1. FT-IR spectra bands of the different aniline-treated MWNT

	Region (cm^{-1})	Band assignments
A	3500–3200	O–H stretching vibration and/or N–H stretching vibration
B	2920, 2854	C–H stretch vibration
C	1643	amide C=O stretching vibration
D	1627	amide N–H deformation
E	1550	amide C–N stretching vibration (amide II band)
F	1523	Aromatic C–C stretching vibration
G	1246	amide out-of-plane N–H deformation (amide III band)

In summary, we have successfully generated aromatic amine-modification MWNT through interaction of aniline with carboxylated samples. Meanwhile, short chain polybasic carboxylic acid, citric acid in this experiment, has shown impressive effect as intermedium between aniline and CNTs. This is the first step towards the synthesis of diazotization CNTs. Further research will be carried on the possibility of preparing functional CNTs for both photoelectric and biological devices.

References

1 S. Banerjee, T. Hemraj-Benny, S. S. Wong, *Adv. Mater.* **2005**, *17*, 17; Y. Yan, M. Zhang, K. Gong, L. Su, Z. Guo, L. Mao, *Chem. Mater.* **2005**, *17*, 3457.

2 E. V. Basiuk, E. V. Rybak-Akimova, V. A. Basiuk, D. Acosta-Najarro, J. M. Saniger, *Nano Lett.* **2002**, *2*, 1249.

3 M. A. Hamon, J. Chen, H. Hu, Y. S. Chen, M. E. Itkis, A. M. Rao, P. C. Eklund, *Adv. Mater.* **1999**, *10*, 11; T. Ramanathan, F. T. Fisher, R. S. Ruoff, L. C. Brinson, *Chem. Mater.* **2005**, *17*, 1290; M. H. Liu, Y. L. Yang, T. Zhu, Z. F. Liu, *Carbon* **2005**, *43*, 1470.

4 J. Kong, H. Dai, *J. Phys. Chem. B* **2001**, *105*, 2890; J. J. Ge, D. Zhang, Q. Li, H. Q. Hou, M. J. Graham, L. Dai, F. W. Harris, S. Z. D. Cheng, *J. Am. Chem. Soc.* **2005**, *127*, 9984.

5 F. Pompeo, D. E. Resasco, *Nano Lett.* **2002**, *2*, 369; V. Georgakilas, N. Tagmatarchis, D. Pantarotto, A. Bianco, J. P. Briand, M. Prato, *Chem. Commun.* **2002**, 3050; C. A. Dyke, J. M. Tour, *J. Am. Chem. Soc.* **2003**, *125*, 1156; E. V. Basiuk, M. Monroy-Pelaez, I. Puente-Lee, V. A. Basiuk, *Nano Lett.* **2004**, *4*, 863; J. J. Stephenson, J. L. Hudson, S. Azad, J. M. Tour, *Chem. Mater.* **2006**, *18*, 374.

6 L. Valentini, D. Puglia, I. Armentano, J. M. Kenny, *Chem. Phys. Lett.* **2005**, *403*, 385; C. H. Hu, Z. Chen, A. Shen, X. C. Shen, J. Lei, S. S. Hu, *Carbon* **2006**, *44*, 428.

7 D. M. Nevskaia, E. Castillejos-Lopez, A. Guerrero-Ruiz, V. Munoz, *Carbon* **2004**, *42*, 653.

8 L. Q. Jiang, L. Gao, *Carbon* **2003**, *41*, 2923; T. Wang, G. C. Zhao, X. W. Wei, *Chem. Lett.* **2005**, *34*, 518; U. J. Kim, C. A. Furtado, X. M. Liu, G. G. Chen, P. C. Eklund, *J. Am. Chem. Soc.* **2005**, *127*, 15437.

Published on the web (Advance View) May 20, 2006; doi:10.1246/cl.2006.624