

One Pot Chemically Attachment of Amino Groups on Multi walled Carbon Nanotubes Surfaces

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Abstract

Functionalization of multiwalled carbon nanotubes (MWCNTs) with NH_2 groups under a one pot reaction is studied. During the first step of the reaction, Cl and CHCl_2 groups were attached to the surfaces of MWCNTs through an electrophilic addition reaction. In the second step of process, Cl atoms were replaced with NH_2 and amino groups (ethylene diamine and butyl amine) under a nucleophilic substitution reaction. The aminated MWCNTs have high solubility and dispersion stability in organic solvents and polymeric matrixes. FTIR, XRD, TGA and Raman spectroscopy were used for characterization of the achieved products. The analysis results indicate that the MWCNTs functionalized with high concentration of amino groups. Also, treated CNTs show good dispersity and interfacial compatibility when used to make MWCNT/polymer composites. Proposed method is an efficient route to introduce of amino groups onto the surfaces of MWCNTs and the process is a very effective, clean, safe and easy to operate, and the scale up of this method is easy.

Keywords: Amination, Functionalization, Multiwalled carbon nanotubes, One Pot, Solubilization

1. INTRODUCTION

Carbon nanotubes (CNTs) have mechanical [1], thermal [2], optical and electrical [3] properties that make them ideal nanoscale materials. However, all the proposed applications have been limited by their practical insolubility in aqueous and organic solvents. One way to overcome to these barriers is functionalization of CNTs. Chemical reactions, such as direct oxidation [4-8], sulfonation [9-10], thiolation [11] and amination [12-14] have been used to modify the CNTs as means to enhance their workability. In fact, chemical modification of CNT surfaces can be effected in promoting the performance of CNTs and expanding their industrial applications. In recent years, Functionalization of CNTs

with different amines has been widely investigated by researchers [15,16]. Aminated nanotubes are typically easy to disperse in organic solvents [17], water [18] and polymeric matrixes [19,20], due to the nitrogen lone valence electrons are easily available for bonding to other molecules, the amino functionalized CNTs can be used in composites [21-23], membranes [24], biosensors [25] and so on.

In the most methods of amination of carbon nanotubes, amino groups react with acylated or carboxylated CNTs [26-31]. The preparation of CNT-COOH or CNT-COCl requires hazardous materials such as strange acid and reagents (sulfuric acid, nitric acid and thionyl or oxalyl chloride), and also

these procedures must be performed in anhydrous solvents and inert gases with long reaction times. In the present study, we have proposed a one pot method for amination of MWCNTs without using strong acids via a simple and clean method with high degree of functionalization.

In continues of our researches about the amination of MWCNTs [32-33], here we present a method for functionalization of MWCNTs with -NHR or -NH₂ groups in a simple one-pot procedure (Scheme 1). Moreover, our methodology does not comprise acid treatment, which is common in the conventional methods. The MWCNTs samples were characterized from the viewpoint of functionality and morphology through FTIR, Raman, TGA and determining the dispersion stability.

2. EXPERIMENTAL

2-1. Materials

Pristine MWCNTs (purity>95%) were purchased from Shenzhen Nanotech Port Co. Ltd. with diameters and lengths ranging between 20-40nm and 5-15 μ m, respectively. AlCl₃, ethylene diamine, ammonium acetate, ammonia, buthylamine and all solvents were purchased from Merck and Sigma Aldrich Companies.

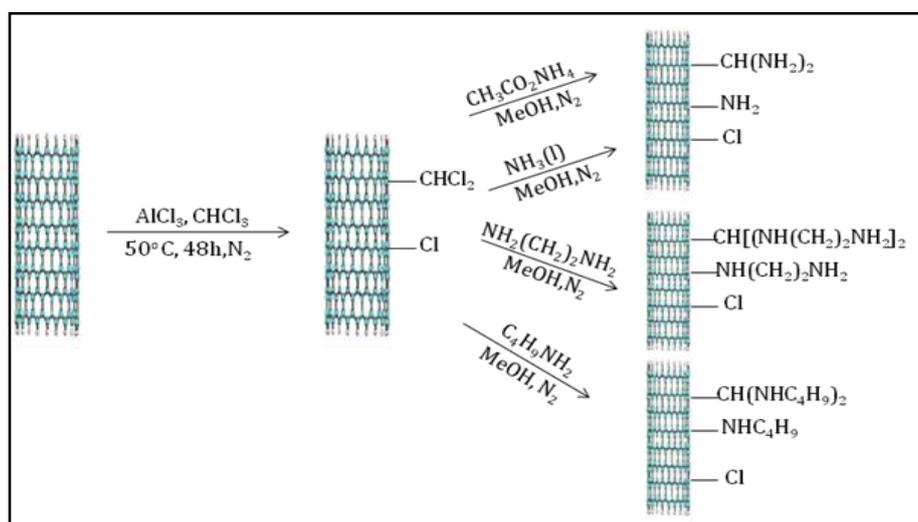
2-2. Apparatuses

Functionalization of MWCNTs were confirmed by FTIR spectra recorded on Bruker ISS-88 instrument, TGA performed in oxygen atmosphere with a 10°C/min rate, using a METTLER- 810 analyser. ASTRA 3-D. Bath sonicator was applied for debundeling of MWCNTs, and Raman spectroscopy occurred with FRA/106/S instrument. The exciting source was a Nd:YAG laser operating at 1064nm.

2-3. Amination of MWCNTs

2-3-1. Attachment of NH₂ groups on MWCNTs surfaces using ammonium acetate

In a typical experiment, 0.25 gr of MWCNTs and 2 gr of AlCl₃ were mixed and ground for 15 minutes. This mixture was then transferred into a 150ml round bottom 3 necked flask filled with 70ml chloroform and sonicated for 10 minute to achieve a completely dispersed solution. Then, the reaction mixture was refluxed under nitrogen atmosphere in 50°C for 48h. After this time, about 4gr ammonium acetate as NH₃ source (dissolved in 30 ml of methanol) was added to the reaction mixture and reflux continued at 80°C for 72h. After that, the reaction mixture was filtered and washed with warm ethanol for several times, and dried overnight at 70°C.



Scheme 1. Functionalization procedure for chemically attachment of NH₂ and amino groups on MWCNTs.

2-3-2. Attachment of NH₂ groups using aqueous NH₃

In a simple procedure, after chlorinating MWCNTs (step 1 of one pot reaction), 25ml of aqueous ammonia was added (instead of ammonium acetate) and reflux continued at 80°C for 72h under N₂ atmosphere. After that, the reaction product was separated according to the previous section.

2-3-3. Attachment of NH₂ groups using ethylene diamine

After chlorinating MWCNTs (step 1 of one pot reaction), 25ml of Ethylene diamine was added (instead of ammonium acetate) and reflux continued at 80°C for 72h under N₂ atmosphere. After that, the reaction product was separated according to 2-3-1 section.

2-3-4. Attachment of NHR

After chlorinating MWCNTs (step 1 of one pot reaction), 1.5 gr buthyl amine (dissolved in 20 ml MeOH) was added to the mixture and the reaction continued for 72 hours under N₂ atmosphere. After this time, the mixture was cooled to room temperature and filtered. Then, the product was added to 50 ml warm ethanol and sonicated for 10min to remove remained unreacted amines, and then the mixture was filtered and the resulting products were dried at 80°C for 10 hours. This procedure can be used for attachment of amines with various chain longs on CNT surfaces.

3. RESULTS AND DISCUSSION

3-1. FTIR Spectroscopy

Figure 1 shows IR spectra of raw and modified MWCNTs. For raw sample, the weak band around 1600cm⁻¹ is attributed to the graphitic structure of MWCNT (Fig.1A).

In contrast to pristine MWCNTs, all the treated samples show several peaks according to functional groups attached to their surfaces. The peaks at the ranges of

1554-1627cm⁻¹ and about 3400cm⁻¹ are consistent to -N-H bending and stretching vibration of amine groups, respectively. A couple of peaks at the ranges of 2850-3000 cm⁻¹ (special for aminated with EDA and buthyl amine), are due to stretching vibration of aliphatic C-H bonds. Also, the peaks at the range of 1060-1070cm⁻¹ are related to the C-N stretching vibrations. Furthermore, peaks at the range of 630-730cm⁻¹ are attributed to C-Cl bands.

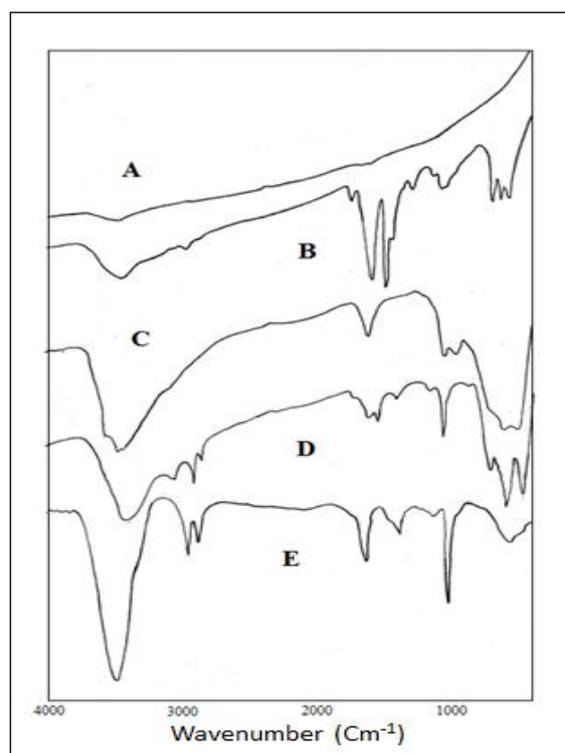


Figure 1. FTIR Spectra of: A) Raw, aminated derivatives with B) ammonium acetate, C) aqueous NH₃, D) ethylene diamine, E) buthylamine.

3-2. TGA Analysis

TGA measurements were performed in oxygen atmosphere at a rate of 10°C/min (from 50 to 700°C). This analysis method provides quantitative estimation of the degree of the functionalization. TGA curve of the pristine and modified MWCNTs, are shown in Figure. 2. While there is no significant mass loss for pristine MWCNTs, a significant mass loss in the temperature range of 100-500°C for the treated samples is observed. All four graphs of modified

materials show that decomposition was performed successfully between 150–500°C (the temperature range that organic groups were removed from the CNT surfaces) and show that treated MWCNTs are about 12 to 25 percent of functional groups.

3-3. Dispersion stability

Figure. 3 shows the dispersed states of raw and modified CNT samples in Ethanol after 30 days. The amino groups attached on the nanotubes surfaces enable the CNTs to repel from each other and keep the solution dispersed, and also the hydrogen bonds between aminated CNTs and ethanol enhance the stability of the dispersion. In contrast, the suspension stability of the pristine CNTs was poor and they easily sediment because of the lack of hydrogen bonding. Nevertheless, functionalized CNTs presented the best stability, concluding a higher percentage of functional groups.

3-4. Raman Spectroscopy

Raman spectroscopy has been extensively used to characterize the various carbon materials. Figure. 4 shows the Raman spectra of the MWCNTs before and after functionalization. The G band at about 1572.8cm^{-1} is the E_{2g} model corresponding to the movement in opposite direction of two neighboring carbon atoms in a graphitic

sheet. This model indicates the presence of crystalline graphitic carbon in MWCNTs. The D band at approximately 1345.9cm^{-1} is an A_{1g} breathing mode. This mode is generally attributed to the defects in the curved graphite sheet, sp^3 carbon, or other impurities. After functionalization treatment, the intensity of D bands changed. In fact, the creation of a covalent bond between a carbon of carbon nanotube surfaces and functional groups converts the hybridization of these carbons towards sp^3 character, so the number of surface defects increases and hence contributes to increase the intensity of the D-band. The ratio of the intensity of the D to G bands, ($R=I_D/I_G$) can be used to evaluate the relative extent of functionalization (Figure.4). The enhancement of R values for modified MWCNTs can be attributed to the chemically attachment of amino groups on CNT surface and end caps.

According to TGA and Raman results, aqueous NH_3 is one of the suitable reagents for the amination of CNT-Cl materials. As shown in Figure. 2, the weight loss in aminated CNT with ammonium acetate is lower than functionalized CNT with aqueous NH_3 . Also, the I_D/I_G ratio in Raman spectra for CNT- NH_2 from aqueous NH_3 ($I_D/I_G=0.75$) in comparison to ammonium acetate method ($I_D/I_G=0.82$) show that the functionalization with aqueous NH_3 is a better approach.

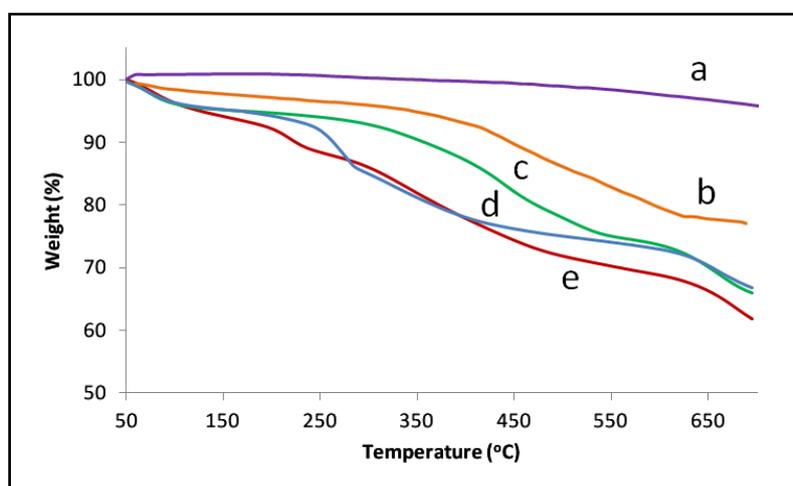


Figure 2. TGA graphs of a) raw MWCNTs, aminated derivatives with b) ammonium acetate, c) aqueous NH_3 d) ethylene diamine and e) butylamine.

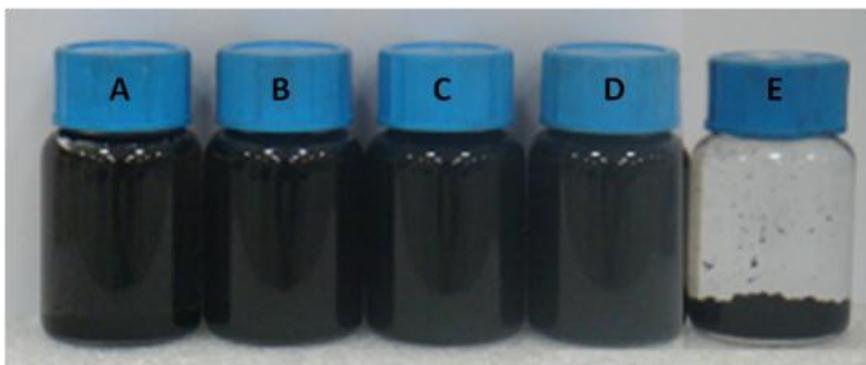


Figure 3. Dispersion stability of 10 mg in 10 ml EtOH of modified MWCNTs with: A) ammonium acetate B) aqueous NH_3 , C) ethylene diamine and D) buthylamine compared with raw CNTs (E), after 30 days.

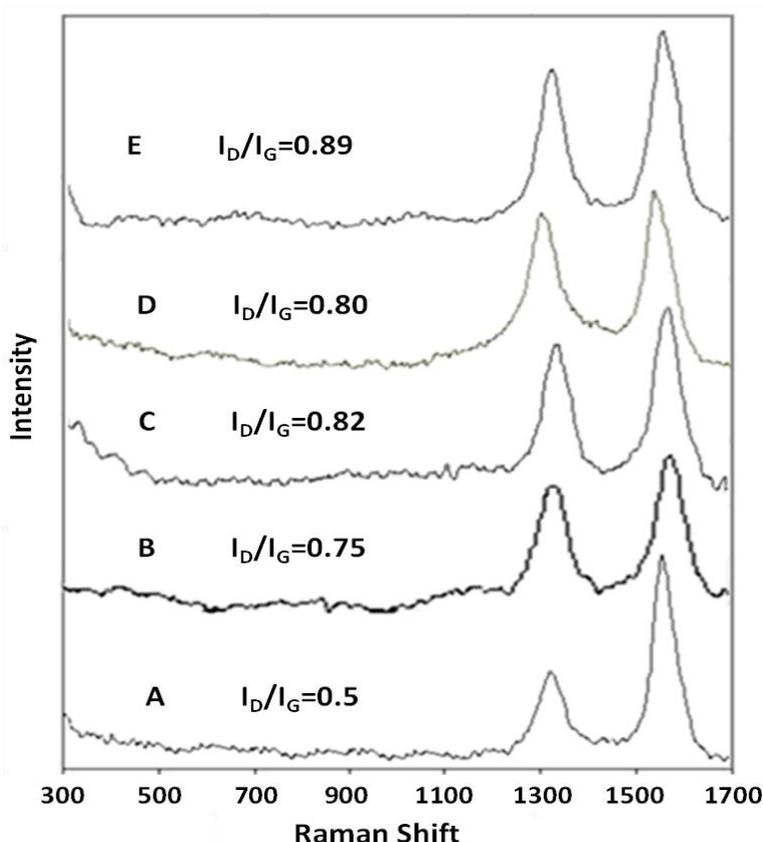


Figure 4. Raman spectra of: A) raw MWCNTs, aminated derivatives with B) ammonium acetate, C) aqueous NH_3 , D) ethylene diamine and E) buthylamine..

3.5- XRD

XRD was used to measure the crystal size and interlayer spacing of CNTs. Due to the CNT's intrinsic nature, the main features of the X-ray diffraction pattern of CNTs are close to those of graphite. Figure. 5 shows the XRD profiles of the MWCNTs. It can be found that the pristine and modified

samples possess a structure similar to that of graphite crystal, which indicates that the functionalization process did not change the structure of the MWCNTs. The strongest and sharpest diffraction peak for all samples at around $2\theta = 26.9^\circ$ could be indexed as the C (002) reflection of graphite. The sharpness of the C (002) peak indicates that the graphite structure of aminated

MWCNTs was remained without significant damage.

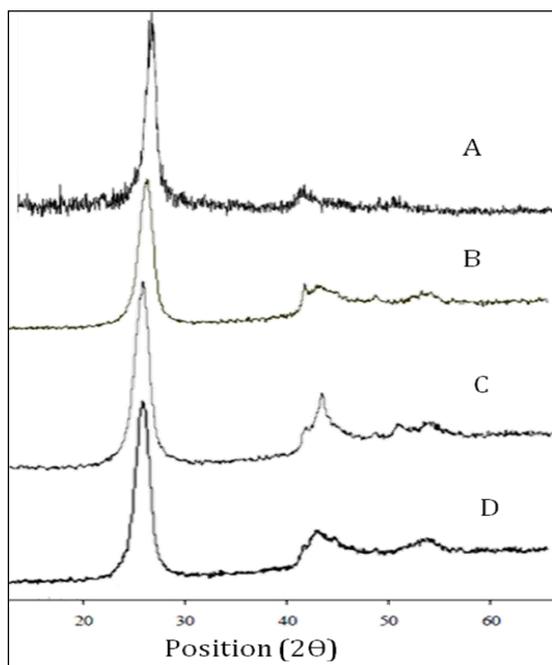


Figure 5. XRD patterns of raw CNT (A), aminated derivatives with B) ammonium acetate, C) aqueous NH_3 and D) ethylene diamine..

4. CONCLUSION

Amino and NH_2 groups are introduced onto MWCNTs surfaces by using a facile one pot method. The analysis results of FTIR, TGA and Raman spectra indicate that the MWCNTs functionalized with high concentration of amino groups. In addition, treated CNTs show good dispersity and interfacial compatibility when used to make MWCNT/polymer composites. Proposed method is an efficient route to introduce amino groups onto the surfaces of MWCNTs.

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