

Solubility of functionalized carbon nanotubes in different solvents

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Abstract: The solubilization of multi-walled carbon nanotubes (MWNTs) had been a research goal for the past few years. Carbon nanotubes could be solubilized in different solvents to promote their potential applications in the form of polymers, copolymers, ceramics, and gasoline, etc. In this work, solubility of the functionalized carbon nanotubes were studied in different solvents such as THF, dichloromethane, ethanol, deionized water and n-hexane. Carboxylic acid groups and amide groups were applied for functionalization of multi-walled carbon nanotubes. Octadecylamine and dodecylamine were used for functionalization of carbon nanotubes to study solubility of them in gasoline, for the first time, and compared the results with those of the other solvents. The results showed that amido-functionalized carbon nanotubes had the best solubility in the dichloromethane, ethanol, and gasoline. In addition it was observed that the solubility of these carbon nanotubes was stable for several days. The resulting materials were characterized by Fourier-transform infrared spectroscopy (FT-IR), and thermal gravimetry analysis (TGA).

Keywords: *Carbon nanotubes, Dispersity, Amidation, FT-IR, TGA*

Introduction

Carbon nanotubes (CNTs) can be used as ideal building blocks in nanotechnology. Extraordinary properties have been attributed to CNTs, so that a plethora of diverse technological applications ranging from wiring in integrated circuits and nano-scale components to composite materials with improved functional characteristics are being investigated [1-3]. However, many of these interesting and unique properties can only be realized once the CNTs are integrated into more complex assemblies. A common technique to incorporate MWNTs into such assemblies is through

chemical functionalization of the MWNTs, which leads to chemical covalent bonding between the MWNTs and the material of interest. Functionalized carbon nanotubes are typically easy to disperse in organic solvents and water. Therefore, functionalization of carbon nanotubes can improve the dispersion and homogeneity of these compounds in the desired solvents [4-5]. Numerous methods for chemical functionalization of carbon nanotubes, either at the tips or sidewall of CNTs, have already been reported [5-10]. The chemical covalent bond mechanism is proved to be very useful to maintain the stable bonds, and

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significant efforts have been directed towards the establishment of chemical functionalities on the surface of CNTs. Amido-functionalized CNTs have been studied because amide groups has a high reactivity, and can react with many chemicals [6].

In this paper, we report the solubilization of functionalized carbon nanotubes containing carboxylic acid and amide groups. Therefore, we are mainly concerned with functionalization of carbon nanotubes containing amide groups by modifying the MWNTs with 2 different amines (Figure1). It was shown that amido- functionalized carbon nanotubes have stable solubility in the gasoline.

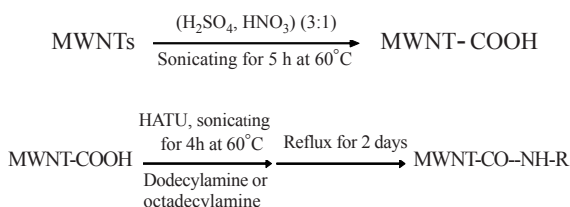


Figure 1 the procedures used in this study for the functionalization of MWNTs

Experimental

Materials

Multi-walled carbon nanotubes (MWNTs) with 90-95 % purity were prepared in our group by CVD method over Co-Mo/MgO catalyst [7]. The average diameter of the nanotubes varies from 10 to 20 nm and their lengths from 5 to 15 μm . Octadecylamine with 90%, dodecylamine with 98%, thionyl chloride with 99%, dimethyl formamide (DMF) with 98%, and coupling agent-[(dimethylamino)-1H-1,2,3-triazolo[4,5,6]pyridin-1-ylmethylene]-N-methylmethanaminium hexafluorophosphate N-oxide (HATU) with 98% purity were purchased from Merck Company.

Equipments and techniques

The functionalized MWNTs were characterized by FT-IR spectra recorded on Perkin-Elmer Spectrum-GX, and TGA in a nitrogen atmosphere, with a $10^{\circ}\text{C}/\text{min}$ rate using a METTLER-810 analyser. For sonicating the samples a Fugilab sonicator was used (49- 59 kHz).

Oxidation of carbon nanotubes

500 mg of carbon nanotubes were added to 250 ml of a mixture of concentrated sulfuric acid (95%), and nitric acid (52%) (with a volume ratio of 3:1). The mixture was sonicated in a bath for 5h at 60°C . After cooling to room temperature the reaction mixture was diluted with 250 ml of deionized water. Then this mixture was filtered and washed with deionized water for several times until pH 7 was obtained. The product was dried in an oven at 100°C .

Amidation of carbon nanotubes

Twenty milligrams of the oxidized nanotubes were dispersed by sonication in 10 ml of DMF and 100 milligrams of desired amine (having a formula of $\text{C}_{12}\text{H}_{25}\text{NH}_2$ (dda) or $\text{C}_{18}\text{H}_{37}\text{NH}_2$ (oda)). One milligram of the coupling agent HATU was added to the mixture and sonication continued for 4 h. Then the mixture was refluxed at $\sim 70^{\circ}\text{C}$ for 2 days in N_2 atmosphere. The obtained mixture was diluted with methanol and filtered through polycarbonate filter paper and then the product was washed with ethanol to remove excess amine. The product was dried in an oven at 70°C for 24 h.

Sample dispersion in the solvents

Dispersibility of MWNTs in different solvents was semi-qualitatively determined by mixing 5 mg of functionalized MWNTs in 25 ml of desired solvent, followed by sonication for 10 min at room temperature.

Results and discussion

Infrared Spectroscopy

Figure 2 shows the FT-IR spectra of carboxylated carbon nanotubes (MWNT-COOH) and amido-functionalized MWNTs. In figure 2(A), spectrum of carboxylated MWNTs, peaks at 1704cm^{-1} and 1206cm^{-1} correspond to $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ asymmetric stretches, respectively. These stretching frequencies shifted to 1650 and 1144cm^{-1} for amido-functionalized MWNTs (figures 2(B) and 2(C)). The peaks at 1507cm^{-1} (in figure 2(B) and 2(C)) are due to the

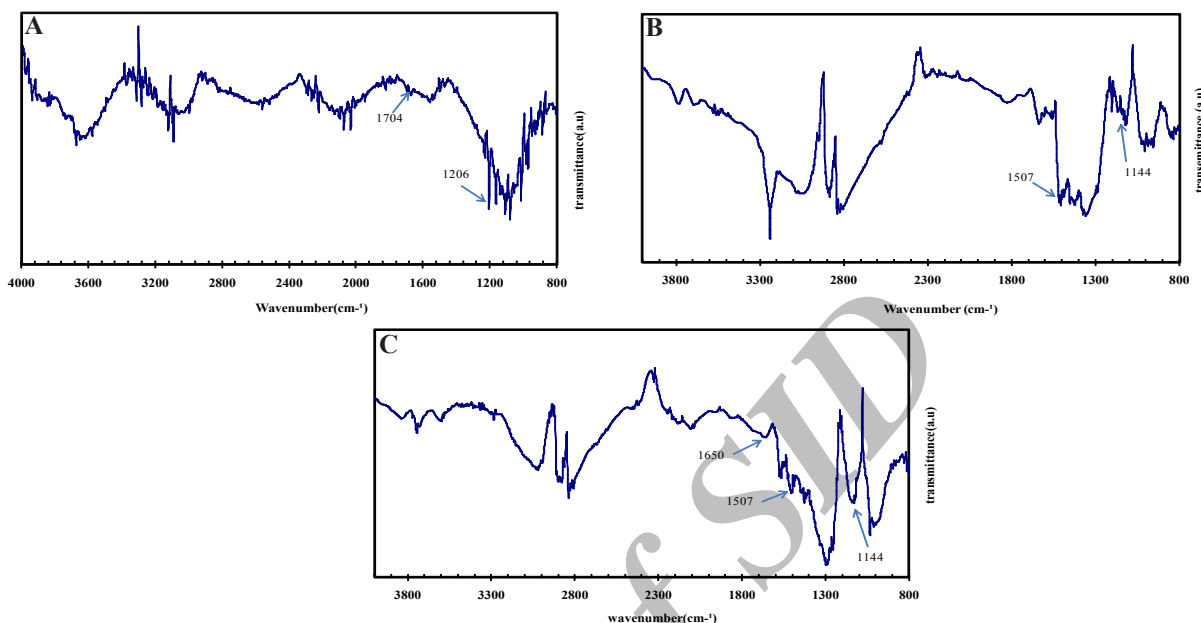


Figure 2 FTIR spectra of functionalized carbon nanotubes: (A) MWNT-COOH; (B) MWNT-dda; (C) MWNT-oda

N-H stretching of amide groups [6]. These spectra confirm that the MWNTs have been functionalized by amine group.

TGA analyses

TGA measurements performed in N_2 atmosphere at a heating rate of $10^\circ C/min$. Oxygen-containing functional groups present on the surface of the nanotubes are expected to decompose with the concomitant

evolution of CO_2 , CO, and water [11]. The composition of gases depends on the type of surface groups. Thus, carboxylic groups are expected to decompose as CO_2 and water between $200-600^\circ C$. Figure 3(A) indicates a broad peak between 280 and $700^\circ C$ with a long tail related to the decomposition of acidic surface groups. Figure 3(B) exhibits a derivative peak in the range of $240-360^\circ C$, which can be ascribed to the reacted octadecylamine. This degradation involves

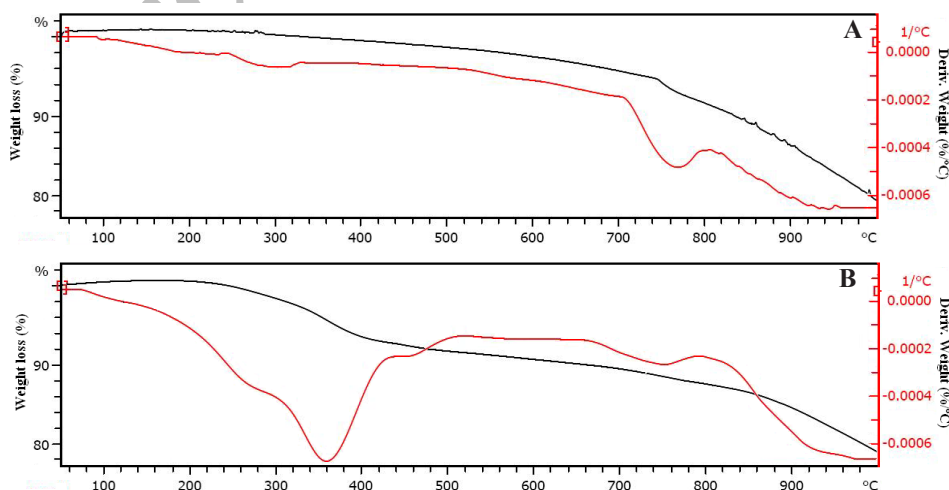


Figure 3 TGA and corresponding differential curves of modified MWNTs: (A) MWNT-COOH; (B) MWNT-oda

high temperatures that can be due to adsorbed amine, because free oda presents the derivative peak at $\sim 185^{\circ}\text{C}$ [12]. Both samples (MWNT-COOH and MWNT-oda) present a peak above 700°C due to MWNTs combustion.

Dispersibility of the samples

The dispersibility of the samples in the different solvents is shown in figure 4. It is observed that the dispersibility of MWNTs in the solvents is remarkably changed after the modification of these compounds. The results indicate that amido-func-

tionalized MWNTs are relatively easily dispersed in the solvents except in deionized water while carboxylated carbon nanotubes are easily dispersed in deionized water. This result can be due to hydrogen bonding between carboxylic acid groups and water. Table 1 shows that even after 2 weeks, the dispersibility of the samples is still stable. Further study indicated that dispersion of amido-functionalized MWNTs in gasoline was stable for more than 2 months. Therefore, these compounds are capable for improving the quality of gasoline.

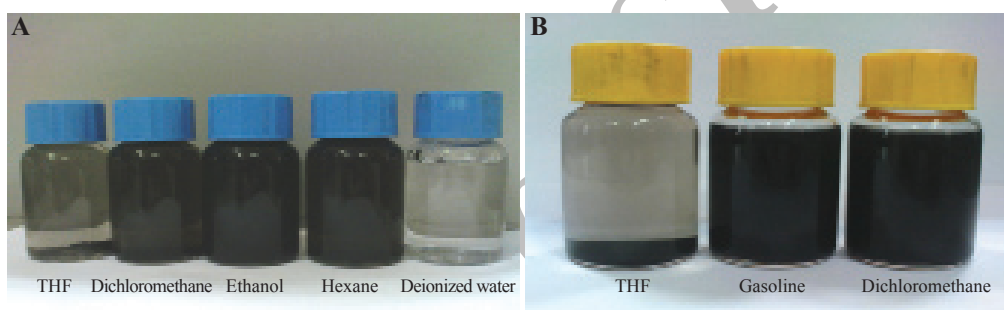


Figure 4 (A) dispersibility of the amido-functionalized carbon nanotubes in different solvents; (B) comparison of the sample dispersion in the gasoline with that of in THF and dichloromethane.

Table 1 The dispersibility of the functionalized carbon nanotubes; (+++) completely dispersed; (++) partially dispersed; (+) mostly precipitated; (—) completely precipitated

Compounds	Time	THF	Dichloromethane	Ethanol	Hexane	Deionized water	gasoline
MWNTs	1h	—	—	—	—	—	—
MWNT-COOH	1h	+++	+++	—	—	+++	—
MWNT-amide	1h	+	+++	+++	+++	—	+++
MWNTs	24h	—	—	—	—	—	—
MWNT-COOH	24h	+++	+++	—	—	+++	—
MWNT-amide	24h	+	+++	+++	++	—	+++
MWNTs	3days	—	—	—	—	—	—
MWNT-COOH	3days	++	+++	—	—	+++	—
MWNT-amide	3days	+	+++	+++	++	—	+++
MWNTs	1week	—	—	—	—	—	—
MWNT-COOH	1week	++	+++	—	—	+++	—
MWNT-amide	1week	+	+++	+++	++	—	+++
MWNTs	2weeks	—	—	—	—	—	—
MWNT-COOH	2weeks	++	+++	—	—	+++	—
MWNT-amide	2weeks	+	+++	+++	+	—	+++

Conclusion

The FT-IR spectra of the samples confirmed that amido-functionalized MWNTs were successfully prepared. Thermal behavior of the nanotubes was studied by TGA. In the corresponding curves some peaks were observed in the range of 240- 360 °C, which were due to combustion of reacted amines. Dispersibility of MWNTs in different solvents was determined semi-qualitatively. The results indicated that amido-functionalized MWNTs were relatively easily dispersed in the solvents except in deionized water and the solubility of these carbon nanotubes were stable for several days. Further study indicated that amido-functionalized MWNTs could be capable for improving the quality of gasoline, because their dispersion in gasoline was stable for more than 2 months.

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