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A New purification Way for Multiwalled Carbon Nanotubes

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Abstract. A new purification procedure was used for the purification of multiwalled carbon nanotube (MWCNTs) based on nitric acid oxidation. Using thermogravimetric analysis (TGA), and Energy dispersive X-ray analysis (EDX) to characterize the morphologies of MWCNTs oxidized under various conditions. The TGA provided clear evidence for the presence of carboxylic groups (–COOH) attached to the surface of MWCNTs resulting from the acid treatment.

0 Intorduction

The MWCNTs which were reported by Iijima in 1991[1], have been the focus of worldwide research owing to their outstanding physical properties, such as: their larger aspect ratio, exceptional electrical properties, high strength and high elastic modulus[2]. The potential applications in mechanical, thermo-mechanical, and sensoring is nowadays undisputable[3][4]. Prinstine MWCNTs are generally produced along with amorphous carbon, metal particles and carbon nanoparticle clusters, particularly with a highly hydrophobic surface which seriously hindered their further applications. To date, the removal of impurities and chemical surface modification of carbon materials often processed in the strong oxidant (e.g. HNO_3, HCl or mixtures of H_2SO_4/HNO_3), in which a large amount of acid or a long time of refluxing were used, let alone afterwards wash and separation with high-sped centrifugation. Herein, we report an efficient and simple procedure for the functionalization of MWCNTs based on nitric acid oxidation to overcome the mentioned drawbacks existed in traditional methods.

In this study, the effect of liquid-phase oxidation on the texture and surface properties of carbon nanofibers has been studied using thermogravimetric analysis (TGA), and Energy dispersive X-ray analysis (EDX).

1 Materials and Experimental methods

1.1 Materials

The MWCNTs synthesized by Chemical Vapor Deposition (CVD) with a length of 5-15 μm (purity > 95%, outer diameter 40-60 nm) were purchased from Shenzhen Nanotech Port Co., Ltd. The Prinstine MWCNTs will be referred as p-MWCNTs, and the functionalized MWCNTs will be referred as f-MWCNTs. The concentrated HNO3 (65~68 wt.%) were purchased from Jinan Le Qi Chemical Reagent Co. Ltd.

MWCNTs from commercial sources usually contain some impurities, such as amorphous carbon and metal particles derived from the catalysts used for their growth. These impurities interfere the application of the MWCNTs. It is desirable to obtain MWCNTs as pure as possible without changing their structure. Thus, most of the purification methods are used to remove the metal and unwanted carbon without damaging the structure of the MWCNTs. Different purification methods have been developed to date, and acid treatment is one of the frequently-used methods for MWCNTs oxidation. The most common reagents used for liquid-phase oxidation treatment are HNO_3, H_2SO_4, and $KMnO_4$[5]. Peroxide（H_2O_2）has also been employed to oxidize the carbon surface. Nevertheless, one of the main drawbacks of acid oxidation methods is that the acid may cause MWCNTs fragmentation and defect generation in the graphitic network. Su et al.[6] report on purification of MWCNTs using

different concentrations of HNO_3/H_2SO_4 for 5–20h, observing MWCNTs destruction controlled by the oxidized time. Other researchers have also studied MWCNTs fragmentation adopting strong acid concentrations or long exposure times[7]. Xing et al.[8], however, reported successful sonochemical oxidation of MWCNTs employing a mixture of 8.0M HNO_3 and H_2SO_4 applied for 1–8h without fragmentation or structural damage occurrence of MWCNTs. Using XPS, they found that the great majority oxidation takes place at the first 2h of treatment and reaches oxidative saturation at 4h.
According to the above research, it may be assumed that there is a compromise scheme between the oxidation parameters (acid concentration, treatment time and sonication power) and MWCNTs damage. Therefore, one of the goals of this study was to examine the practicability of several mild acid treatment conditions based on HNO_3, H_2SO_4, and H_2O_2 to functionalize the MWCNTs surface without damaging the MWCNTs structure.

1.2 Experimental methods

1.2.1 The functionalization treatments on MWCNTs

The pristine MWCNTs were dealt with air flow at 450℃ for 2h. Most of iron oxides deposited at the bottom of spherical crucible because of difference densities between iron oxides and MWCNTs, and part of iron oxides was removed before further treatment. And the amorphous carbon were cleared Then, the MWCNTs were carried out using nitric acid, or a combination of nitric acid and sulfuric acid. Table 1 lists the reagents used and their concentrations. All acid solutions were prepared at 10.0 M/L respectively.

For the oxidative treatment “B”, 0.5 g MWCNTs were mixed with 100 ml of HNO_3 by mechanically stirring in a hot plate for 120 min at 150°C. Then, the slurry was distilled at ambient enviroment. This procedure could lighten the post-treatment. Following, the sample was filtered using a 0.1 μm size polytetrafluoroethylene membranes and was washed by deionized water until the pH value approaching 7, and were dried at 200℃ for 6 h. For the scheme “C”, 0.5 g of the agglomerated MWCNTs were mixed with 100 ml of the mixture of H_2SO_4 and HNO_3 solutions in

Table 1 by mechanically stirring in a hot plate for 30 min at 80°C. In order to minimize tube damage, a low power sonicating bath (100 W, 42 kHz) and a relatively low acid exposure time (2h) were used. Then, the slurry was filtered and thoroughly washed with distilled water. Finally, the slurry was dried in a convection oven at 200 °C for 6 h. Treatment “D”, was different to the other treatments. For this treatment, the MWCNTs were oxidized at 150℃ for 120 min, in order to minimize tube damage. Subsequently, the nanotubes were thoroughly washed with distilled water, and the solvent was treated with H_2O_2 (30% v/v) for 60 min. The subsequent oxidation with H_2O_2 was proceeded in order to complete the oxidative process started by HNO_3, but in a gentler way.

Table 1. Oxidative reagents conducted on the MWCNTs.

Method	Reagents
A	No treatment (pristine)
B	HNO_3 10.0 M/L
C	Mixture of H_2SO_4 and HNO_3, 10 M/L
D	HNO_3 3.0 M/L +H_2O_2 30% v/v

1.2.2 Characterization of the oxidized MWCNTs

In order to estimate the purity of the MWCNTs, the thermogravimetric analysis (TGA) was done using a thermal gravimetric analyzer (SDT Q600 V8.3). TGA is a technique of thermal analysis in which the variation of sample mass is evaluated as a temperature function. The analyse of MWCNTs powder were processed under air flow, which indicates that a thermal oxidation is detected and the remnant at the end of burning is substantially iron oxide. In each experiment, MWCNTs samples (5 mg) were heated from 30℃ to 800 ℃ at a rate of 20℃/min.

2 Results and discussion

2.1 TGA

TGA is used to detect the purity and thermal stability of MWCNTs. After undergoing a procedural increase in temperature, the variation of the mass is proposed as a function of temperature. The main parameters of TGA curves include the initiation temperature, the oxidation temperature, the final temperature and the residual mass percent. Generally, the peaks of MWCNTs thermal oxidation distributes around 500–700°C. Amorphous carbon takes on a lower degradation temperatures (<400 °C). Fig. 1 shows TGA curves of the MWCNT samples after: non-oxidative treatments (pristine MWCNTs), oxidative treatments with HNO_3 , and the mixture of HNO_3 and H_2SO_4 respectively.

The treatments “A”, the pristine MWCNTs presented an onset degradation temperature around 580°C and a final degradation temperature around 680°C, with high oxidizing temperature at 600°C. The temperature of thermal oxidation of graphitic structures depends on their ordering or presence of impurities. At the end of these analyses (around 690 °C), the residual content (iron oxide) was around 15%. Hence, pristine MWCNTs have a purity degree of around 85%.

The treatments “B”, which oxidized by HNO_3 promoted to remove the iron. The percentage of residual weight registered after thermal degradation was only 1%. Moreover, the onset temperature had a slight decrease (around 520℃) in this case. It implies that the oxidative acids can damage the surface of MWCNTs with incorporation of functional groups.

The treatments “C”, the mixed acid caused serious damage to the carbon tube, which can be seen from the TGA curve. The onset temperature had a significant decrease (around 480℃) in this case. It implies that the oxidative acids damage the internal structure of MWCNTs, which reduces the initial temperature of degradation.

The effect of treatments “D” closes to the treatment “B”.

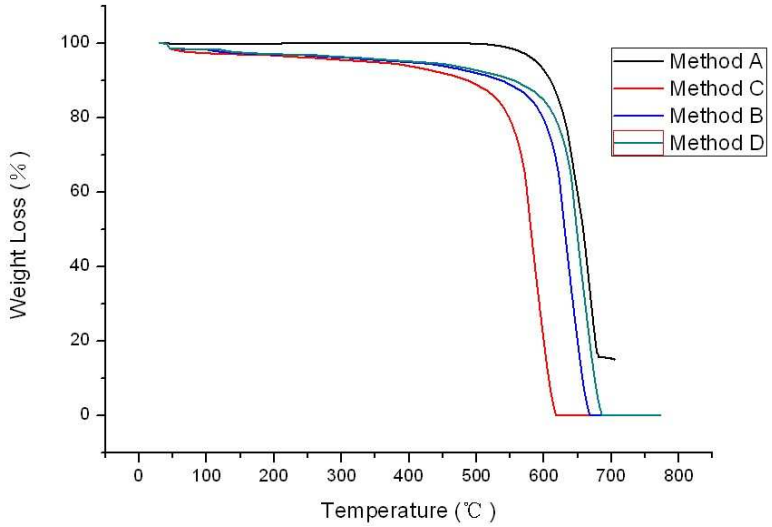

Fig. 1. TGA curves of the MWCNTs samples treated by method A, B, C, and D.

2.2 Assessment of functionalization by EDX

Energy dispersive X-ray analysis (EDX) was conducted on several zones of the treated and non-treated MWCNTs. The main elements and concentrations found in a representative analysis are listed in Table 2. As observed in this table, by far, the largest element in the as-received material (A) is carbon (either graphitic or amorphous), with significant oxygen content and a few metal impurities such as Mg, Al, Mn, and Co. Small traces of Fe and Na (not listed in the Table) were also detected in some samples. After the oxidation treatments, it is observed that the amount of impurities diminishes significantly, given the established role of nitric and sulfuric acids as purification agents. For the objective of this work, the oxygen content is of particular interest. For treatment B (sulfuric acid), it is

observed that the oxygen content increases only moderately respect to the as-received sample. A more marked increase in the oxygen content is observed for treatments C–F. Interestingly, the largest amount of oxygen was observed in samples E (treated with a mixture of nitric and sulfuric acid at 8.0 M) and F (treated with 3.0 M nitric acid followed by H_2O_2). These results suggest that oxidation of the MWCNTs surface has been promoted by the chemical treatments.

Table 2. EDX chemical composition of representative CNT samples (atomic %).

Element	Treatment			
	A	B	C	D
C	94.75	92.85	93.04	92.40
O	3.32	4.96	5.94	6.25
S	/	0.05	/	/
Al	0.18	/	0.02	0.03
Co	0.13	0.05	0.01	0.01

3 Conclusions

The surface modification of MWCNTs was successfully performed by means of a HNO_3 hydrothermal functionalization method.The result showed the best reflux temperature is 150℃ and the optimal reflux time is 2 hours. Therefore, method D is more effective to remove impurities and protect MWCNTs from being damaged than other methods.

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