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Microwave Induced Reactive Base Wash for the Removal of Oxidation Debris from Carboxylated Carbon Nanotubes

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Abstract

Removal of oxidation debris for generating high purity functionalized carbon nanotubes (CNTs) has been a challenge, where base washing has been found to be an effective purification treatment. In this paper we report microwave induced reactive base wash (MRW) as a fast, green alternate to conventional filtrate washing. Carboxylated CNTs of three different dimensions were subjected to MRW and the results were compared to conventional base-wash. The results showed that MRW was an effective method for the removal of oxidation debris which reduced the reaction time from 4 hours to 20 min and alkali consumption by 75%. The CNTs from MRW were similar to those from conventional base wash in terms of dimensions, elemental composition, BET surface area and colloidal stability in aqueous media.

1 Introduction

Since their first discovery in 1991 [1], carbon nanotubes (CNTs) have attracted much attention due to their unique structural, optical, mechanical and electronic properties. Since the pristine CNTs are chemically inert and do not dissolve in solvents, covalent or non-covalent functionalization is usually required to render them soluble, and also for attaching other chemical moieties [3-7]. Introduction of carboxylic functional groups on CNTs is usually the first important step prior to conversions such as those to amines, esters, amides and for developing polymer linkages [8-10]. Acid treatment is the most common method for carboxylation [11, 12].

Many applications such as photovoltaics and drug delivery require high purity CNTs [2] and much effort has gone into purification of raw CNTs. It has been reported that oxidation debris are generated during carboxylation via acid treatments. The debris comprises of partially oxidized polyaromatic fragments that attach to the CNT surface by π -stacking, and are not easily removed by washing with water [13, 14]. These impurities adversely affect physical and chemical properties such as dimensions, surface properties, dispersibility and

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stability in chemical and biological environments [13]. Dilute base-washing has been used to remove the debris [13] where the acidic groups are converted into their conjugate salts and washed out. Chemical, physical and structural properties of carboxylated CNTs are known to improve after the base wash because it eliminates the impurities from the surface [13, 15].

The conventional approach to debris removal is to wash the oxidized CNTs with dilute base followed by water. Finally, a dilute acid wash is used to reinstate the surface carboxylic groups [14-16]. The first step usually needs a large amount of base and it takes several hours (or days) to wash the debris out and also generates much waste. Moreover, during long filtrations some CNTs are lost. Therefore, it is important to develop efficient base wash techniques that require less time and chemicals.

CNTs are known to be microwave active and the latter has been used for purification and functionalization [17]. These processes have been carried out with less reagents and in significantly shorter time. The objective of this research is to study microwave induced reactive base wash (MRW) of carboxylated CNTs as a fast, green method for the removal of oxidation debris.

2 Experimental

2.1 Chemicals

Three types of multi-walled carbon nanotubes were purchased from Cheap Tubes Inc (Branford, VT). Purity of each was higher than 95%. The CNTs were categorized based on size. Those which had relatively shorter length and diameter (0.5-2 μm long and 10-20 nm OD) were referred to as CNT_{SS}; shorter length and relative larger diameter (0.5-2 μm long and 30-50 nm OD) were referred to as CNT_{SL}, and longer length and smaller diameter (10-30 μm long and 10-20 nm OD) were referred to as CNT_{LS}. All other chemicals were purchased from Sigma Aldrich (St Louis, MO) with purity higher than 95%.

2.2 Preparation of the F-CNTs

The preparation of the functionalized multiwall carbon nanotubes (F-CNT_{SS}, F-CNT_{SL}, and F-CNT_{LS}) were carried out in a microwave accelerated reaction system (CEM Corp. Mars System). Pre-weighed amounts of CNTs were treated with a mixture of concentrated H₂SO₄ and HNO₃ under microwave radiation at 140°C for 20 minutes. After cooling down to room temperature, the products were vacuum filtered and washed by Milli Q water through 10 μm filter paper until a neutral pH was obtained. The F-CNTs were then dried under vacuum oven at 70 °C until a constant weight was achieved.

2.3 Preparation of base-washed samples

F-CNT samples were washed by dilute base via conventional washing through filtration as well as by MRW. For conventional washing, F-CNT samples were filtered through a 10 μm filter paper and washed with 0.01M NaOH until the filtrate turned from brown to colorless. This method has been reported before [15, 16]. The wash was continued with Milli Q water until a filtrate of neutral pH was obtained. Finally, the F-CNTs were washed by 0.01M HCl, and then washed with Milli Q water to obtain a neutral pH. These filter-washed samples and

filtrates were referred to as BW-F-CNT_{SS}, BW-F-CNT_{SL}, BW-F-CNT_{LS} and W-CNT_{SS}, W-CNT_{SL}; W-CNT_{LS}

For MRW, the F-CNT samples were treated with different volumes 0.01M NaOH under microwave irradiation at 100° C for different periods of time. The resulting solids were filtered and washed using additional 5 ml of 0.01M NaOH to determine if the oxidation debris had been completely removed. Then the resulting products were washed with Milli Q water until a neutral pH was obtained. Once again the products were washed with 0.01M HCl and then washed with Milli Q water to obtain a neutral pH. These microwave-washed samples and filtrates were referred to as MRW-F-CNT_{SS}, MRW-F-CNT_{SL}, MRW-F-CNT_{LS} and W-MRW-CNT_{SS}, WMRW-CNT_{SL}, W-MRW-CNT_{LS}.

2.4 Characterization

Scanning electron microscopy (SEM) and energy-dispersive X-ray analyzer (EDX) were carried out using a LEO 1530 VP, (Carl Zeiss SMT Inc., Peabody, MA) equipped with EDX (Oxford Instruments, Concord, MA). For FTIR analysis, the samples were mixed with purified KBr and pressed into pellets, and then the analysis was carried out using a Perkin-Elmer instrument (Waltham, MA) instrument. Raman spectra were obtained using a DXR Raman microscope (Thermo Fisher Scientific Inc., Madison, WI). Specific surface areas of the samples was carried out using a Quantachrome NOVA 3000 series (Model N32-11) High Speed Gas Sorption Analyzer at 77.40 K (Boynton Beach, FL). Before each experiment, the samples were heated and degassed at 300°C in a vacuum oven for three hours. Particle size and zeta-potential were measured at 25 °C by Zetasizer nano ZS90 (Malvern Instruments Ltd., Worcestershire, UK) at a 90° detector angle.

3 Results and Discussions

3.1 Sample preparation

MRW was tested under different conditions. Based on previous studies [13, 15], the turning of filtrate color from brown to colorless was used as an indicator for complete removal of the debris. In initial screening reactions, 50 ml 0.01M NaOH was used to treat 0.2 g F-CNTs by MRW for reactions times of 5, 10, 15 and 20 min. For 5 min reaction time, the filtrate showed a light yellow color which was attributed to incomplete reaction. For reactions times of 10, 15 and 20 min, the filtrates showed brown color. An additional wash using 5ml NaOH still showed brown solution which implied that the oxidation debris remained in the sample. The ratio of the base to F-CNTs was doubled to complete the reaction within a shorter time period. Now 50 ml of 0.01M NaOH was used to treat 0.1g F-CNTs for 15 and 20 min. The filtrate of these two batches showed brown color. A wash with an additional 5ml NaOH was clear for the 20 min MRW while the one from 15 min still showed light brown color. Therefore, 50ml of 0.01 M NaOH and 20 min reaction time was considered to be the optimum condition for removing oxidation debris from 0.1g F-CNT by MRW.

To determine the amount of solvent needed in an equivalent conventional base wash, 0.1g F-CNT was dispersed in 50ml NaOH, put on a shaker and shaken for 20 min, after which the sample was filtered. If the filtrate was brown, the F-CNT was redispersed in another 50ml NaOH, and the shaking/filtration was repeated till a clear filtrate was obtained. It was found

that four rounds of 20 min shaking batch with a total 200 ml NaOH was needed to complete the base wash. In another experiment, the CNT solution was shaken overnight and filtered, with a NaOH consumption of 150 ml. The process of filtration took one hour per round, so the whole process required an additional 3 to 4 hours.

It is quite evident that the MRW required shorter reaction times and significant less amounts of base. The faster reaction in MRW was due to the molecular heating in microwave irradiation which directly heated the reactive species. In the absence of microwave radiation, the reaction was slower and this led to higher base requirement. In general, faster reaction time and less reagent usage make MRW a more environmental friendly approach to remove the oxidation debris.

3.2 Characterization

The characteristics of the BW-F-CNT and MRW-F-CNT samples were studied and compared. The MRW-F-CNT prepared from the 10 min reaction and 0.2g F-CNT_{SL} and 50 ml of the base was used as the benchmark where the oxidation debris had not been removed completely (referred as MRW-F-CNT_{SL10}). SEM images of BW-F-CNT and MRW-F-CNT samples are presented in Figure 1. All CNTs remained intact with minimal visible tube defect. The elemental analysis of CNTs (Table 1) was carried out by EDX. The oxygen content decreased after base wash due to the removal of oxidation debris, which is in line with what has been reported before [15]. The percentage of oxygen decreased by 38, 53, and 47% in BW-F-CNT_{SS}, BW-F-CNT_{SL}, BW-F-CNT_{LS} respectively, and 44, 53, and 33% for the corresponding MRW-F-CNT samples. The C/O ratio were 22, 20, 18 for BW-F-CNT_{SS}, BW-F-CNT_{SL}, BW-F-CNT_{LS} and 24, 20, 14 for the corresponding MRW-F-CNT samples. This showed that the final product from MRW was similar to conventional base wash. On the other hand, the C/O ratio of MRW-F-CNT_{SL10} (which was 10) was closer with that of F-CNT_{SL} (8.3). This was attributed to the incomplete removal of oxidation debris. This implied that optimal process conditions were necessary for successful MRW.

The dimensions of the F-CNT, BW-F-CNT and MRW-F-CNT samples are presented in Table 2. The length and diameter showed minor differences before and after MRW, which confirmed that the MRW did neither fragment nor cause excessive tube damage. Also the dimension of BW-F-CNTs and their corresponding MRW-F-CNT samples showed similar results. The length of BW-F-CNT_{SS}, BW-F-CNT_{SL}, were shortened by 10 and 4% while 12 and 4% for the corresponding MRW-F-CNT samples. At the same time MRW-F-CNT_{SL10} showed only 1% decrease of length compare with F-CNT_{SL}. Figure 2 shows the Raman spectra of the different CNT samples. The intensity ratio of D (defect band) and G band (graphite band) (I_D/I_G) is shown in Table 2. I_D/I_G decreased by 16, 15, 28% with base washing for BW-F-CNT_{SS}, BW-F-CNT_{SL}, BW-F-CNT_{LS} respectively and 16, 14, 28% for the corresponding MRW-F-CNT samples. This shows that the two methods produced similar results.

FTIR spectroscopy (Figure 3) was used to qualitatively analyze functional groups on the functionalized and base washed CNTs. The presence of C=C stretching around 1583 cm^{-1} which was present in the original carbon skeleton of the CNTs, the carbonyl stretching frequency (C=O) around 1726 cm^{-1} , stretching vibration (C-O) around 1220 cm^{-1} and (O-

H) around 3473 cm^{-1} provided the evidence of carboxyl groups in all the F-CNTs. The FTIR analysis showed the same peaks by both conventional and MRW (including MRW-F-CNT_{SL10}). This implied that the base-wash did not affect the attachment of carboxylic groups on the surface of CNTs. Fig. 3 (a) and (b) shows the FTIR spectra of BW-F-CNT_{SL} and MRW-F-CNT_{SL}. Other F-CNTs, BW-F-CNTs and MRW-F-CNT samples showed similar spectra and are not shown here for brevity.

The Brunauer, Emmett, and Teller (BET) surface area of all samples are shown in Table 2. All CNTs had large surface area. For all three sizes, the specific surface areas (SSA) of carboxylated carbon nanotubes were lower than those of samples after base wash, which was in line with what has been reported before [15]. The SSA increased after base wash by 8, 13, 10% for BW-F-CNT_{SS}, BW-F-CNT_{SL}, BW-F-CNT_{LS} and 6, 13, and 11% for the corresponding MRWF-CNT samples. It implies that during MRW as well as conventional base wash, the SSA increased due to the removal of oxidation debris. Once again, the SSA from the two base wash approaches were quite similar, which implied that MRW was as effective as the conventional method. The SSA of MRW-F-CNT_{SL10} also increased somewhat compared to F-CNT_{SL} but not as much as those from MRW or conventional base wash, where the removal of oxidation debris was complete.

The colloidal behavior of BW-F-CNTs and MRW-F-CNTs was studied using dynamic light scattering. Particle size and zeta-potential of the CNT samples are presented in (Table 2). Both BW-F-CNTs and MRW-F-CNTs were stable in water. The difference of zeta potential was 7, 6, and 1% for BW-F-CNT_{SS}, BW-F-CNT_{SL}, BW-F-CNT_{LS} and 8, 6, 1% for MRW-F-CNT_{SS}, MRW-F-CNT_{SL}, MRW-F-CNT_{LS} for the corresponding F-CNT samples. Once again it can be seen from Table 2 that the MRW and conventional base washed samples showed similar agglomerate size. The difference of particle size was 9, 11, and 5% for BW-F-CNT_{SS}, BW-F-CNT_{SL}, BW-F-CNT_{LS} and 9, 11, and 4% for MRW-F-CNT_{SS}, MRW-F-CNT_{SL}, MRW-F-CNT_{LS} for the corresponding F-CNT samples. This again showed that the difference between F-CNTs and corresponding BW-F-CNTs and MRW-F-CNTs was insignificant. The presence of the oxidation debris did not affect the stability or dispersibility of carbon nanotubes. MRW-F-CNT_{SL10} also showed similar colloidal properties compared to F-CNT_{SL}.

The SEM images of the oxidation debris W-CNT_{LS} and W-MRW-CNT_{LS} presented in Fig 1 (h, i). Images of debris for other two sizes are not presented here for brevity. The oxidation debris from both methods (including W-MRW-CNT_{SL10}) showed similar morphology, but no tube fragments. The elemental analysis of the wash is presented in Table 3. The results showed low C/O ratios in the range of 1.8 to 3.0. This implied that over-functionalized fragments were present in the wash. The results from MRW and conventional wash were somewhat similar, which was further evidence that the two methods were comparable. The FTIR analysis of the wash residues from the two methods showed the presence of conjugated C-C with C=O stretching at 1610 cm^{-1} , C-H bending vibrations at 1338 cm^{-1} and 1434 cm^{-1} . In addition, C-O stretching (1114 cm^{-1}) and O-H stretching (3440 cm^{-1}) were observed, which implied the removal of oxidation debris, which was attributed to partially oxidized polyaromatic fragments. O-H (3440 cm^{-1}) vibration may due to the extra NaOH from washing procedure.

4 Conclusions

MRW was developed for removing the oxidation debris generated during CNTs functionalization. CNTs of different dimensions were tested where the decreases of oxygen content in F-CNTs after MRW were between 33 to 53%, reduction in length was between 4 and 12%, and specific surface area increased by 6 to 13%. The zeta potential of MRW samples were between -40 and -45 mV, which was similar to the original F-CNTs. The dimensions, elemental composition, surface area and colloidal properties of MRW and base-washed samples by conventional method were similar. The chemical properties of the debris from the two methods were also similar. In summary, MRW is an effective method for the removal of oxidation debris that is much faster and consumes less reagents than the conventional approach.

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Fig. 1.
SEM Images of a)BW-F-CNT_{SS}, b)BW-F-CNT_{SL}, c)BW-F-CNT_{LS}, d)MRW-F-CNT_{SS},
e)MRW-F-CNT_{SL}, f)MRW-F-CNT_{LS}, g)MRW-F-CNT_{SL10}, h) W-CNT_{LS}, i) W-MRW-
CNT_{LS}

Fig.2.
Raman spectra of a) F-CNT_{SL}, b) BW-F-CNT_{SL}, c) MRW-F-CNT_{SL}

Fig. 3. FTIR spectra of a) BW-F-CNT_{SL}, b) MRW-F-CNT_{SL}, c) W-CNT_{SL}, and d) WMRW-CNT_{SL}

Table 1

Elemental analysis of CNT samples

	C (%)	O (%)	C/O ratio
CNT _{SS} (0.5-2 μm long and 10-20 nm OD)			
F-CNT _{SS}	90.7	9.3	13
BW-F-CNT _{SS}	94.2	5.8	22
MRW-F-CNT _{SS}	94.8	5.2	24
CNT _{SL} (0.5-2 μm long and 30-50 nm OD)			
F-CNT _{SL}	86.1	13.9	8.3
BW-F-CNT _{SL}	93.5	6.5	20
MRW-F-CNT _{SL}	93.5	6.5	20
MRW-F-CNT _{SL10}	87.7	12.3	10
CNT _{LS} (10-30 μm long and 10-20 nm OD)			
F-CNT _{LS}	87.1	12.9	11
BW-F-CNT _{LS}	93.2	6.8	18
MRW-F-CNT _{LS}	91.3	8.7	14

Table 2

Dimension, specific surface area, particle size and zeta potential of F-CNT samples

	Length (nm)	Diameter (nm)	Surface area (m ² /g)	I _D /I _G	Particle size(nm)	Zeta potential (mV)
CNT _{SS} (0.5-2μm long and 10-20 nm OD)						
F-CNT _{SS}	898±431	25±6	156	1.02±0.01	104.4	−43.4
BW-F-CNT _{SS}	806±396	24±5	169	0.86±0.02	113.3	−40.5
MRW-F-CNT _{SS}	792±307	24±3	166	0.84±0.03	113.3	−40.1
CNT _{SL} (0.5-2 μm long and 30-50 nm OD)						
F-CNT _{SL}	761±519	33±9	234	1.37±0.01	92.3	−43.5
BW-F-CNT _{SL}	731±451	32±5	265	1.16±0.05	82.1	−46.3
MRW-F-CNT _{SL}	734±309	32±3	264	1.18±0.01	81.9	−46.2
MRW-F-CNT _{SL10}	750±248	33±4	240	1.34±0.04	89.6	−45.0
CNT _{LS} (10-30 μm long and 10-20 nm OD)						
F-CNT _{LS}	-	23±6	240	1.41±0.01	99.9	−43.7
BW-F-CNT _{LS}	-	23±4	264	1.01±0.04	95.2	−44.3
MRW-F-CNT _{LS}	-	23±4	266	1.01±0.05	95.9	−44.1

Table 3

Elemental analysis of filtrate

	C (%)	O (%)	C/O ratio
CNT _{SS} (0.5-2µm long and 10-20 nm OD)			
W-CNT _{SS}	57.6	42.4	1.8
W-MRW-CNT _{SS}	58.5	41.5	1.9
CNT _{SL} (0.5-2 µm long and 30-50 nm OD)			
W-CNT _{SL}	65.8	34.2	2.6
W-MRW-CNT _{SL}	69.1	30.9	3.0
W-MRW-CNT _{SL10}	67.1	32.9	2.7
CNT _{LS} (10-30 µm long and 10-20 nm OD)			
W-CNT _{LS}	59.9	40.1	2.0
W-MRW-CNT _{LS}	60.6	39.4	2.1