Orthogonal experiment analysis of Carbon nanotubes oxidation process

Hongwei LU^a, Liming ZOU^b, Yizhe WEI^c and Yongjing XU^d

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials,

College of Materials Science and Engineering, Donghua University, 2999 North

People Road, Shanghai 201620, People's Republic of China

^aemail: luhw0801@sina.com, ^bemail: lmzou@dhu.edu.cn,

^cemail: ln_2008@163.com, ^demail: kittyxyj@163.com

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Abstract. The application of carbon nanotubes (CNTs) in biomaterials field was limited by its poor dispersion in water solution. In this paper, a specific methodology based on potassium permanganate (KMnO₄)/concentrated sulfuric acid (H₂SO₄) hydrothermal oxidation was used to modify the surface of multi-walled carbon nanotubes (MWCNTs). The orthogonal experiment results indicated that MWCNTs/ KMnO₄/ concentrated H₂SO₄ at 1:3:100 (g/g/g), stirring under 150°C for 7h was the optimal oxidation process. FT-IR and TGA results demonstrated that carboxyl groups were introduced to the surface of MWCNTs. Raman spectra and SEM, TEM showed that structure of MWCNTs were damaged after been oxidized.

Introduction

Carbon nanotubes (CNTs) hold promise as one of the key nanomaterials since it was discovered by Iijima in 1991[1]. CNTs have attracted much interest due to their unique properties such as excellent mechanical strength, high electrical conductivity, chemical stability [2] and CNTs have been widely applied in composite [3], hydrogen storage materials[4], field emission devices[5], biomaterials[6] and other fields.

The preparation of promising nanomaterials based on CNTs requires high dispersibility of CNTs in solvent or base materials. CNTs are easily aggregated in water solution for the predominantly hydrophobic nature of carbon materials. Covalent modification is an efficient method to improve the dispersion of CNTs in solvents. Typical hydrothermal oxidation method are based on sulphuric acid (H₂SO₄), nitric acid (HNO₃), HNO₃-H₂SO₄ mixtures or potassium permanganate (KMnO₄) [7].

In this paper, a specific methodology based on potassium permanganate (KMnO₄)/ concentrated sulfuric acid (H₂SO₄) hydrothermal oxidation was used to modify MWCNTs. Orthogonal experiment were taken to study the process. The as prepared functional MWCNTs show excellent dispersion in water. This work can offer us a systematic method to prepare functional CNTs and realized its application in many fields.

Materials and method

Pristine MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd with purity of 90%, lengths>1.5μm and diameters <10nm. H₂SO₄ KMnO₄ were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used as received. HCl and H₂SO₄ were purchased from Shanghai daruifine-chemical Co., Ltd (China).

Fourier transform infrared spectral (FT-IR) in the range of 400-4000cm⁻¹ were obtained by a Nicolet 8700 Fourier transform infrared spectrometer (thermo Electron, American) with KBr pellets of MWCNTs, and under the averaging of 32 scans at a resolution of 4 cm⁻¹. Thermogravimetric analyses (TGA) were performed by heating the sample under nitrogen flow from 30°C to 900°C at 20 K/min using a TG 209 F1 Iris thermogravimetric analyzer (Netzsch-Geraetebau GmbH,

Germany). The Raman spectra were performed using a Renishaw inVia-Reflex spectrometer (UK) with excitation line set to $\lambda=633$ nm, and the measurements were recorded from 600 cm^{-1} to 4000 cm^{-1} on each MWCNTs sample. Scanning electron microscopy (SEM) was carried out on a JEOL JSM-5600 LV instrument (Japan) operating at 5KV. Transmission electron microscopy (TEM) was taken using a NEC2100F transmission electron microscopy (Japan).

MWCNTs have been purified before we used [8]. 10 g concentrated H_2SO_4 (98%) were diluted to 0.5 mol/L and added to a 1000 ml round-bottom flask, then 100 mg MWCNTs and 300 mg KMnO_4 followed. The mixture were treated under a refluxed condenser for 7 h at 150 $^\circ\text{C}$. After that, 10 ml HCl (37%) were added to the mixture to neutralize superfluous KMnO_4 . Then the product was filtrated and washed by water until neutral. Finally, the functional MWCNTs were dried in a vacuum oven at 75 $^\circ\text{C}$ over night.

Result and Discussion

Orthogonal experiment analysis

In this paper, $\text{H}_2\text{SO}_4/\text{KMnO}_4$ were used as oxidant. Ratio of $\text{H}_2\text{SO}_4/\text{KMnO}_4$ influence the oxidability of KMnO_4 . Ratio of MWCNTs/ KMnO_4 , reaction temperature, reaction time influence the oxidation results of MWCNTs. So the effect factors of oxidation process were designed as follows.

Table1. Effect factors of MWCNTs oxidation process

	A	B	C	D
	$\text{H}_2\text{SO}_4/\text{KMnO}_4$ (g/mg)	MWCNTs/ KMnO_4 (g/g)	Temperature ($^\circ\text{C}$)	Time (h)
1	10/200	1/1	100	7
2	10/300	1/2	125	9
3	10/400	1/3	150	11

According to Table1 we designed a series of orthogonal experiment as shown in Table2.

Table2. Design of orthogonal experiment

Experiment Number	A	B	C	D
1	A1	B1	C1	D1
2	A1	B2	C2	D2
3	A1	B3	C3	D3
4	A2	B1	C2	D3
5	A2	B2	C3	D1
6	A2	B3	C1	D2
7	A3	B1	C3	D2
8	A3	B2	C1	D3
9	A3	B3	C2	D1

According to Table2 we prepared a series of functional MWCNTs, Boehm titration were used to detect the content of carboxyl groups on the surface of MWCNTs and evaluate the effect of oxidation process. The results were presented in Table3 and the result analyses were displayed in Table4.

Table3. Content of carboxyl groups on the surface of MWCNTs

Experiment Number	content of carboxyl groups (mmoL/g)
1	2.68
2	2.44
3	1.94
4	2.94
5	4.67
6	2.86
7	2.42
8	1.56
9	1.30

Table4. Orthogonal experiment analysis result of content of carboxyl groups

	A	B	C	D
K1	821.2	694.0	881.9	786.9
K2	661.8	775.1	741.6	739.9
K3	796.8	810.7	656.3	753.0
K1	273.7	231.3	294.0	262.3
K2	220.6	258.4	247.2	246.6
K ₃	265.6	270.2	218.8	251.0
Rang (R)	53.1	38.9	75.2	15.7
Effect sequence	C>A>B>D			
Optimal level	A2	B1	C3	D1
Optimal combination	A2 B1 C3 D1			

From the Orthogonal experiment analysis result, we got the optimal combination A2-B1-C3-D1, which means that at a $\text{H}_2\text{SO}_4/\text{KMnO}_4$ (g/mg) 1:300, MWCNTs/ KMnO_4 (g/g) 1:3, reaction temperature 150°C , reaction time 7h MWCNTs got the best oxidation effect.

Characterization

The FT-IR spectra were taken to characterize the functional groups on the surface of MWCNTs as showed in Figure 1. After modification O-MWCNTs shows a peak at 1740cm^{-1} which is the stretching vibration for $\text{C}=\text{O}$, it means that MWCNTs has been modified and carboxyl groups were introduced to the surface of MWCNTs. In addition, obvious CH_3 bending vibration peak and C-O stretching vibration peak appear at 1380cm^{-1} and $1000\sim 1100\text{cm}^{-1}$, it means that some other kind of oxygen containing groups were also introduced and the surface defect increased.

Figure 1. FT-IR spectra of MWCNTs and O-MWCNTs

TGA is a practical thermal analysis technique that can be used to evaluate the thermal stability and content of a materials. Figure 2 showed the TGA curves of MWCNTs and O-MWCNTs at a

temperature range from 30-500°C. O-MWCNTs have a significant mass loss at 200-500°C, which is the functional groups decompose temperature range. It can be used to prove that functional groups have been introduced to the surface of MWCNTs after been modification.

Figure 2. TGA curves of MWCNTs and O-MWCNTs

The morphology of MWCNTs and O-MWCNTs were observed using SEM and TEM (Figure 3). As can be seen from Figure 3a and 3b, MWCNTs aggregated together while O-MWCNTs homogeneous dispersed due to the functional groups introduced to the surface of O-MWCNTs. Figure 3c and 3d demonstrated that after modification, diameter of MWCNTs decreased and the port of tubes were opened, it proves that the structure of O-MWCNTs were damaged.

Figure 3. SEM (a, b) and TEM (c, d) of MWCNTs and O-MWCNTs

Conclusion

Orthogonal experiment analysis offered us an efficient and quickly method to determine the optimal oxidation process, and the optimal process is: $\text{H}_2\text{SO}_4/\text{KMnO}_4$ (g/mg) 1:300, MWCNTs/ KMnO_4 (g/g) 1:3, reaction temperature 150°C, reaction time 7h. FT-IR, TGA and SEM, TEM measurement were taken follow by the optimal process. The result indicate that carboxyl groups were introduced to the surface of MWCNTs, structure of MWCNTs were damaged and MWCNTs became homogeneous dispersed.

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