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研究简报

十八醇亲核取代反应修饰溴代多壁碳纳米管

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Modification of Brominated Multiple-walled Carbon Nanotubes with Octadecanol through Nucleophilic Substitution

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Abstract: Octadecanol modified multiple-walled carbon nanotubes, with octadecanol covalently bound to the nanotube surface, have been synthesized by bromination of the carbon nanotubes followed by nucleophilic substitution using octadecanol and sodium hydride. Scanning electron microscopy and transmission electron microscopy images show that the morphologies of the nanotubes are largely intact after functionalization. The brominated carbon nanotubes and octadecanol modified carbon nanotubes were characterized using energy-dispersive X-ray spectroscopy, Raman spectroscopy and Fourier transform infrared spectroscopy. The mechanism of nucleophilic substitution was discussed, and it is believed that the reaction occurs with an S_N1 mechanism.

Key words: multiple-walled carbon nanotubes; brominated; octadecanol; nucleophilic substitution; mechanism

Carbon nanotubes (CNTs) have attracted a great deal of interest since the landmark research of Iijima in 1991[1]. However, if CNTs were to achieve their full potential, chemical modification is often necessary[2~5]. Especially if it was possible to chemically modify the surface of the nanotubes in a controlled manner, this would afford a number of opportunities for the wider use of CNTs[6].

Functionalization of CNTs has commonly conducted by acidic oxidation, employed to purify low quality nanotubes materials[7]. The oxidative functionalization exclusively occurs at high curved sites because of their greater reactivity than that of planar walls[8,9]. To eliminate such a limitation, it is necessary to functionalize nanotube sidewalls directly[10]. Chen et al.[11] reported that CNTs could be purified via bromination, and it appears that the bromination causes a lesser degree of damage and fragmentation of the nanotubes. Bromide is a very useful reagent because it is a good leaving group and can be easily substituted by strong nucleophilic reagents. We report here the preparation of octadecanol modified multiple-walled carbon nanotubes(MWCNTs)

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via first bromination of MWCNTs with element bromine and followed by nucleophilic substitution of brominated MWCNTs (MWCNT-Br) using octadecanol and sodium hydride. The mechanism of the substitution is also discussed and an S_N1 mechanism is proposed.

1 Experimental

1.1 Reagents and instrumentation

MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd..

FTIR, energy-dispersive X-ray spectr-oscopy (EDS), Raman spectroscopy, SEM and TEM were used to characterize the changes in chemical structure and surface morphology of the MWCNTs after each surface treatment step. For the FTIR (Nicolet-Avatar360 FTIR), the MWCNT-Br and octadecanol modified MWCNTs (MWCNT-ODO) samples were pressed into a pellet using spectroscopic grade potassi-um bromide(KBr) and scanned from 400 cm^{-1} to 4 000 cm^{-1}. The elemental composition was analyzed using JEOL JSM-6360LV (operated at 25 kV). The microstr-ucture of the samples obtained was observed with SEM on JEOL JSM-6360LV (operated at 25 kV) and TEM on JEOL JEM-1230 (operated at 100 kV) using a well dispersed small amount of MWCNT-ODO sample in ethanol by sonication for several hours in an ultrasonic bath.

1.2 Functionalzation of MWCNTs with octadecanol

Bromination of MWCNTs was carried out according to reference[11]. A mixture of 2.7 g octadecanol, 15 mL DMF (dimethylformamide), 0.8 g NaH was heated to 50 ℃ for 3 h. And 200 mg MWCNT-Br was added to the reaction solution system and heated to 90 ℃ for 4 d. The solution was distilled to remove DMF, then washed with ethanol (10 min sonication at 40 kHz) for at least four times to remove residual octadecanol. The remaining solid was treated with concentrated hydrochloric acid for 3 h, then filtered and washed with deionized water, dried under vacuum at 40 ℃ to gain 220 mg MWCNT-ODO (Fig.1).

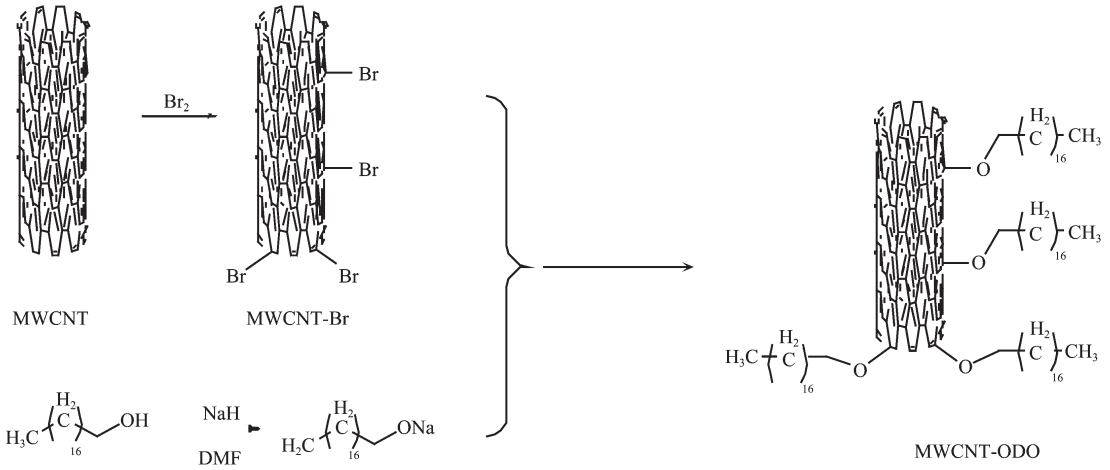

Fig.1 Synthesis route of MWCNT-ODO

2 Results and discussion

2.1 FTIR analysis

The FTIR spectrum of MWCNT-Br shows the presence of a new band at 671 cm^{-1} corresponding to the C-Br stretch (Fig.2A). The FTIR spectrum of MWCNT-ODO shows the presence of new bands at 2 916 cm^{-1} and 2 848 cm^{-1} corresponding to the asymmetric and symmetric C-H stretch, respectively. The two peaks at 1 454 and 1 327 cm^{-1} are in the region of the C-H stretch vibrations. A new peak at 719 cm^{-1} was observed after grafted with octadecanol, typical of the $-(CH_2)_n-$ ($n \geqslant 4$) stretch. The FTIR spectrum confirms the presence of the alkyl functional group grafted to MWCNTs. The two peaks at 1 635 and 1 567 cm^{-1} are typical of the MWCNTs ($-(C=C)_n-(n \geqslant 3)$) (Fig.2B).

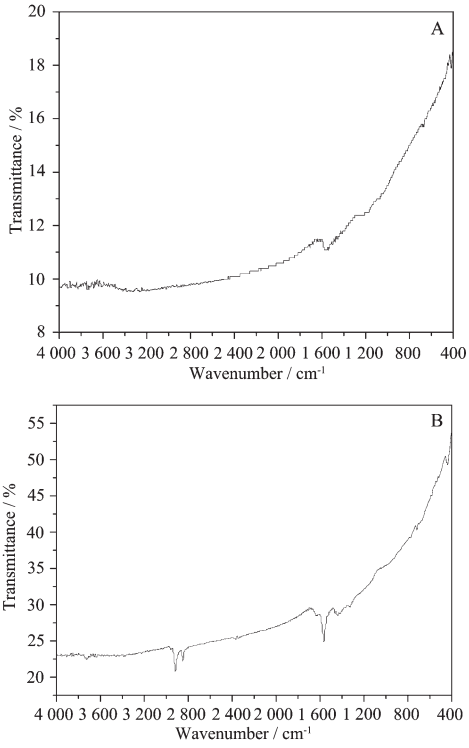

Fig.2　FTIR spectra of samples: (A) MWCNT-Br; (B) MWCNT-ODO

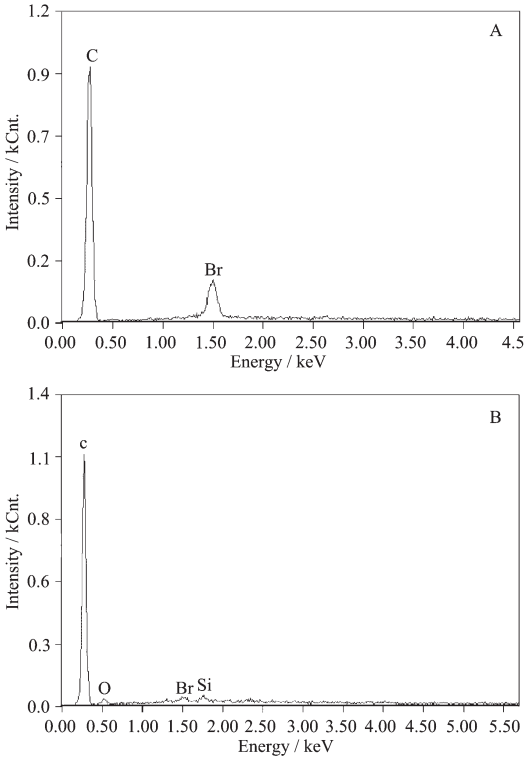

Fig.3　EDS of MWCNT samples: (A) MWCNT-Br; (B) MWCNT-ODO

2.2 EDS analysis

EDS of the MWCNT-Br (Fig.3A) shows that the weight percentage of bromine in the product is about 6%. Fig.3B shows the EDS spectrum obtained from MWCNT-ODO. The spectra show that the weight percentage of bromine in the products is decreased to about 0.94%, and the weight percentage of oxygen is increased to about 4.23% due to the introduction of octadecanol. The Si peak originates from the NaH reagent. The EDS analysis clearly indicates that octadecanol is reacted with MWCNT-Br and octadecyl-ether bonds are formed.

2.3　TEM analysis

Fig.4 shows the TEM images of pristine MWCNTs and MWCNT-ODO. The octadecanol modified MWCNT (Fig.4B) is nearly clean as that of pristine MWCNT(Fig.4A). In this regard, it should be mentioned that modific-ation of MWCNTs through nucleophilic substitution does not change their surface microstructures.

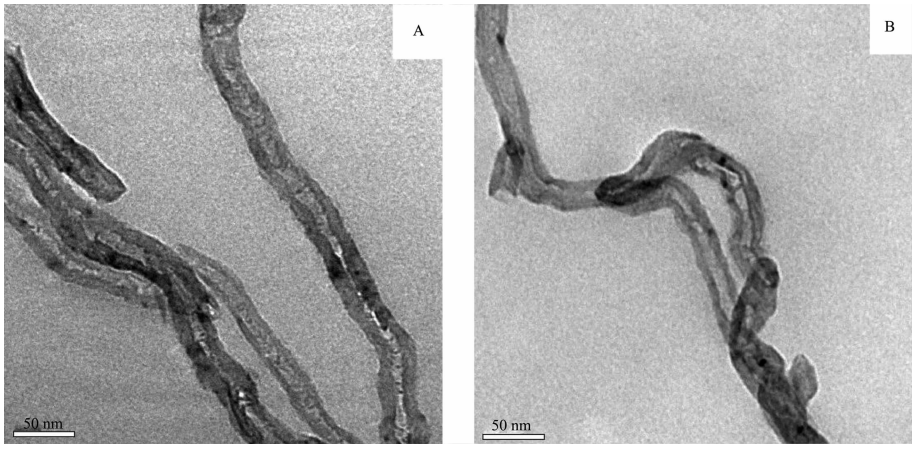

Fig.4　TEM images of MWCNT samples: (A) pristine MWCNT; (B) MWCNT-ODO

2.4 SEM analysis

Fig.5 shows the SEM images of pristine MWCNTs, MWCNT-Br and MWCNT-ODO. Both MWCNT-Br and MWCNT-ODO are still keeping their normal morphology and the tubes are not shortened after modification. Simultaneously MWCNT-Br or MWCNT-ODO is somewhat enlarged because of attached bromine or octadecanol.

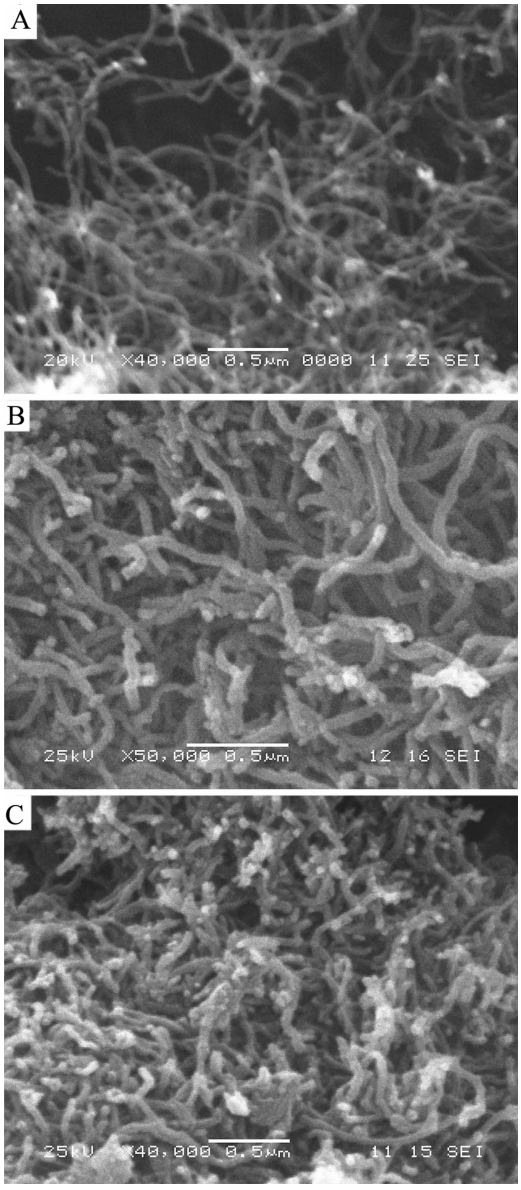

Fig.5 SEM images of MWCNT samples: (A) pristine MWCNT; (B) MWCNT-Br; (C) MWCNT-ODO

2.5 Raman spectroscopy

The Raman spectra of pristine MWCNTs exhibit three usual bands of MWCNTs: the D-line at 1 315 cm^{-1} (amorphous carbon and disorder induced line), the G-line at 1 566 cm^{-1} (in-plane stretching E_{2g} mode) and a shoulder around 1 594 cm^{-1} assigned to the D-line (disorder line). As shown in Fig.6A, the peak intensity ratio I_D/I_G is close to 2, indicating that there exist many defects in pristine MWCNTs. For MWCNT-Br and MWCNT-ODO (Fig.6B and 6C), these three usual bands of MWCNT can still be observed, except that the ratio of the peak intensity changes a little, especially for MWCNT-ODO. The intensity enhancement of D-line and D-line in octadecanol-grafted MWCNT samples proves the covalent bonding of octadecanol to MWCNTs. The Raman results indicate that the chemical structure of the MWCNTs has mainly been remained intact.

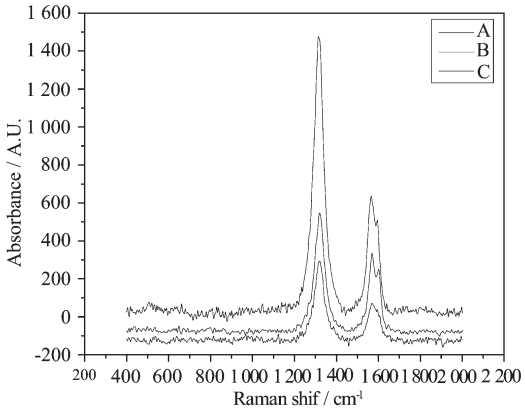

Fig.6 Raman spectra of MWCNT samples: (A) pristine MWCNT; (B) MWCNT-Br; (C) MWCNT-ODO

2.6 The mechanism of nucleophilic substitution

This striking new reaction of MWCNT-Br and sodium octadecanolate can be accommodated by assuming the intermediate formation of MWCNT cation and octadecyloxygen anion. The mechanism is believed to be an S_N1 nucleophilic substitution. If octadecy-loxygen anion attacks the carbon atom grafted with a Br group, S_N2 mechanism will be proposed. However, huge resistance between MWCNT-Br and Octadecyloxygen anion will prevent the reaction.

Cleavage of the already polar C-Br bond allows the loss of the good leaving group, a halide ion, to give a carbocation intermediate, which is the rate determining step. Then the oxygen anion of the octadecanol molecule attacks the carbocation intermediate to form objective molecule, and the reaction speed is very quick and not reversible (Fig.7).

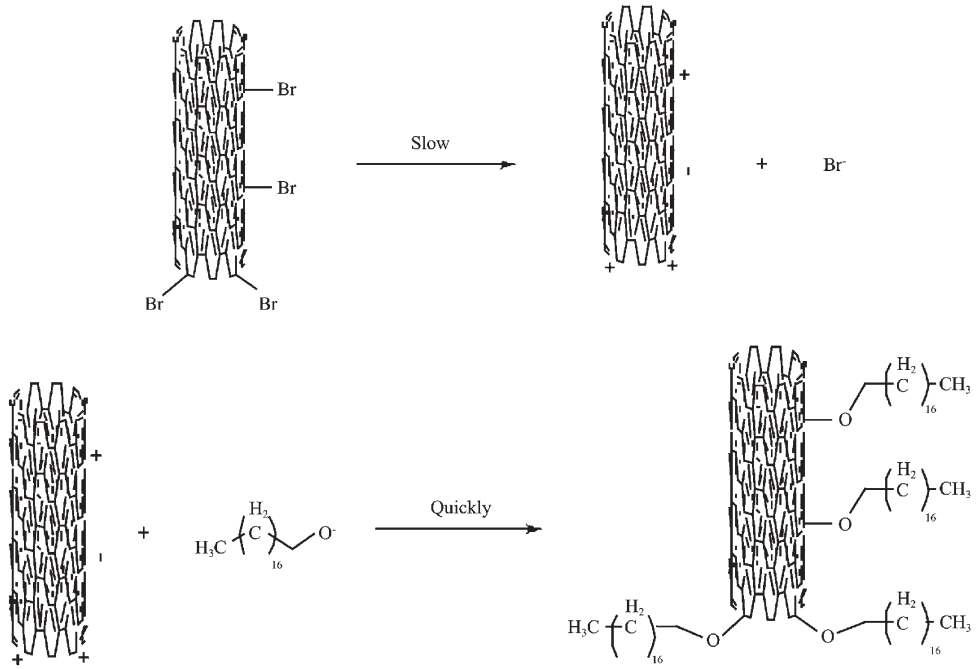

Fig.7　Reaction mechanism of nucleophilic substitution between MWCNT-Br and sodium octadecanolate

3　Conclusion

Octadecanol modified MWCNTs have been synthesized by first bromination of MWCNTs with element bromine followed by a nucleophilic substitution using octadecanol and sodium hydride. We believe that the nucleophilic substitution occurs with an SN1 mechanism. SEM and TEM images show that the morphologies of the nanotubes are largely intact after functionalization. FTIR spectroscopy, Raman spectroscopy and EDS analysis confirm the presence of octadecyl-ether bonds. The ability to form C-O bonds on the surface of carbon nanotubes opens up a range of possibilities to carry out further reactions on the bromine-functionalized nanotube materials.

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