

聚酰胺-胺树状分子接枝到方法修饰多壁碳纳米管

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摘要: 采用聚酰胺-胺树状分子(PAMAM)“接枝到”这一温和而简单易行的方法修饰多壁碳纳米管(MWCNTs), 制备了一种树状分子/碳纳米管(MWCNTs-g-PAMAM)纳米复合材料。在水、甲醇和乙醇等极性溶剂中, 该复合材料具有很好的分散性。通过傅立叶变换红外光谱(FTIR)、X-射线光电子能谱(XPS)、热重分析(TGA)和透射电子显微镜(TEM)等对 MWCNTs-g-PAMAM 纳米复合材料进行了表征。FTIR 表明接枝修饰是 PAMAM 与 MWCNTs 的共价键结合, TGA 数据表明 PAMAM 成功修饰于 MWCNTs 侧壁, 且接枝到 MWCNTs 上 PAMAM 的量随其代数(G1.0~G4.0)的不同而不同, 具体顺序为 G2.0>G1.0≈G3.0>G4.0。

关键词: 多壁碳纳米管; 聚酰胺-胺; 水分散性; 接枝

中图分类号: O633.21

文献标识码: A

文章编号: 1001-4861(2009)06-0973-07

Modification of Multi-walled Carbon Nanotubes with Poly(amidoamine) Dendrimers via “Grafting to” Method

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Abstract: A mild and facile way was used to prepare poly(amidoamine)-grafted multi-walled carbon nanotubes (MWCNTs-g-PAMAM) nanocomposites via “grafting to” method. The MWCNTs-g-PAMAM nanocomposites are well dispersible in polar solvents such as water, methanol and ethanol. Chemical structure of the resulting product was characterized by Fourier transform infrared(FTIR), X-ray photoelectron spectra(XPS), thermal gravimetric analyses(TGA) and transmission electron microscopy(TEM). FTIR showed that the “grafting to” process belonged to covalent attachment mechanisms. TGA data also showed that the PAMAM dendrimers were successfully grafted to the side wall of MWCNTs, and the relative weight of PAMAM grafted onto the MWCNTs surface was in the order G2.0>G1.0≈G3.0>G4.0.

Key words: multi-walled carbon nanotubes; poly(amidoamine); water-dispersible; grafting

Owing to their unique optical, electrical, magnetic and mechanical properties, carbon nanotubes (CNTs) have attracted worldwide attention in the fields of nanoscience, nanotechnology, and bioengineering since

their discovery by Iijima in 1991^[1]. Applications of CNTs, however, are limited by their very strong aggregation tendency and poor dispersibility in solutions or in polymer composites^[2]. Chemical functionalization of

收稿日期: 2009-02-20。收修改稿日期: 2009-04-13。

天水师范学院“青蓝”人才工程基金、甘肃省高校研究生导师基金(No.07-08-12)和甘肃省自然科学基金(No.3ZS061-A25-028)资助项目。

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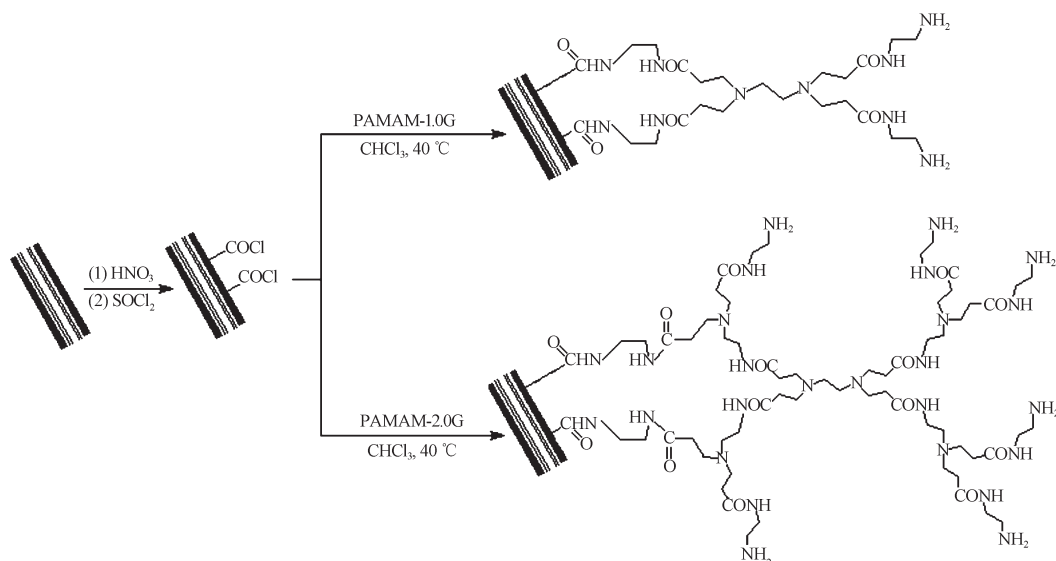
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carbon nanotubes surfaces is expected to play a vital role in tailoring the structure and properties, especially improving the solubility, biocompatibility and the ability of reacting with other species. Among the modification of CNTs, covalently attaching polymer chains onto the surfaces of CNTs has recently attracted considerable attention because it endows the surface with novel structure and properties. Therefore, many groups have focused their research on the functionalization of CNTs and have successfully reported surface functionalization of single-walled carbon nanotubes(SWNTs)^[3-8] as well as multi-walled carbon nanotubes(MWNTs)^[9-12].

So-called “grafting to” and “grafting from” approaches have been employed to attach polymer chains onto the surface of CNTs. The “grafting to” route, which allows full control over polymer length and architecture, involves the bonding of the readymade end-functionalized polymer chains to the reactive surface of the CNTs by amidation, esterification, radical coupling, or other reactions^[13]. And it could be physical adsorption or covalent attachment mechanism^[14]. Not long ago, synthetic and bioactive macromolecules were grafted to form covalent bonded or chemiadsorbed polymer

chains onto the CNTs surface^[15-21]. In fact, issues regarding the functionalizations and solubilizations of carbon nanotubes are relevant topics in the rapidly growing fields^[14,22-29].

Dendrimers are characteristic synthetic macromolecules with highly branched structure and globular shape. They possess unique properties such as high density of active groups, good structural homogeneity, intense internal porosity, and good biocompatibility. Among the various types, polyamidoamine (PAMAM) dendrimers are of particular interest because of their globular structure, mimicking the three-dimensional structure of biomacromolecules, and their good biocompatibility. To the best of our knowledge, only few experimental studies are available in the literature about dendrimers modified MWCNTs^[30]. In the present study, we describe a mild and facile way to prepare PAMAM-grafted multi-walled carbon nanotubes(MWCNTs-g-PAMAM) by grafting to method. Here, PAMAM dendrimers contain generations of 1.0, 2.0, 3.0 and 4.0. The detailed process is shown in Scheme 1(only grafting process of G1.0 and G2.0 are given as examples).



Scheme 1 Outlines for PAMAM modification of multi-walled carbon nanotubes

1 Experimental

1.1 Materials

The MWCNTs used in this study were purchased

from Shenzhen Nanotech Port Co. Ltd., with the purity higher than 95%. Chloroform and sulfurous chloride were purchased from Shanghai Chemical Reagent Factory. Anhydrous methyl alcohol, 1,2-ethylenedi-

amine and Methyl acrylate were all redistilled before use. All other reagents were used without further purification.

1.2 Synthesis of poly (amidoamine) dendrimers (PAMAM)

Poly (amidoamine) dendrimers were synthesized following the procedure described by Tomalia et al.^[31] where ethylenediamine was used as a nitrogen core (Scheme 2).

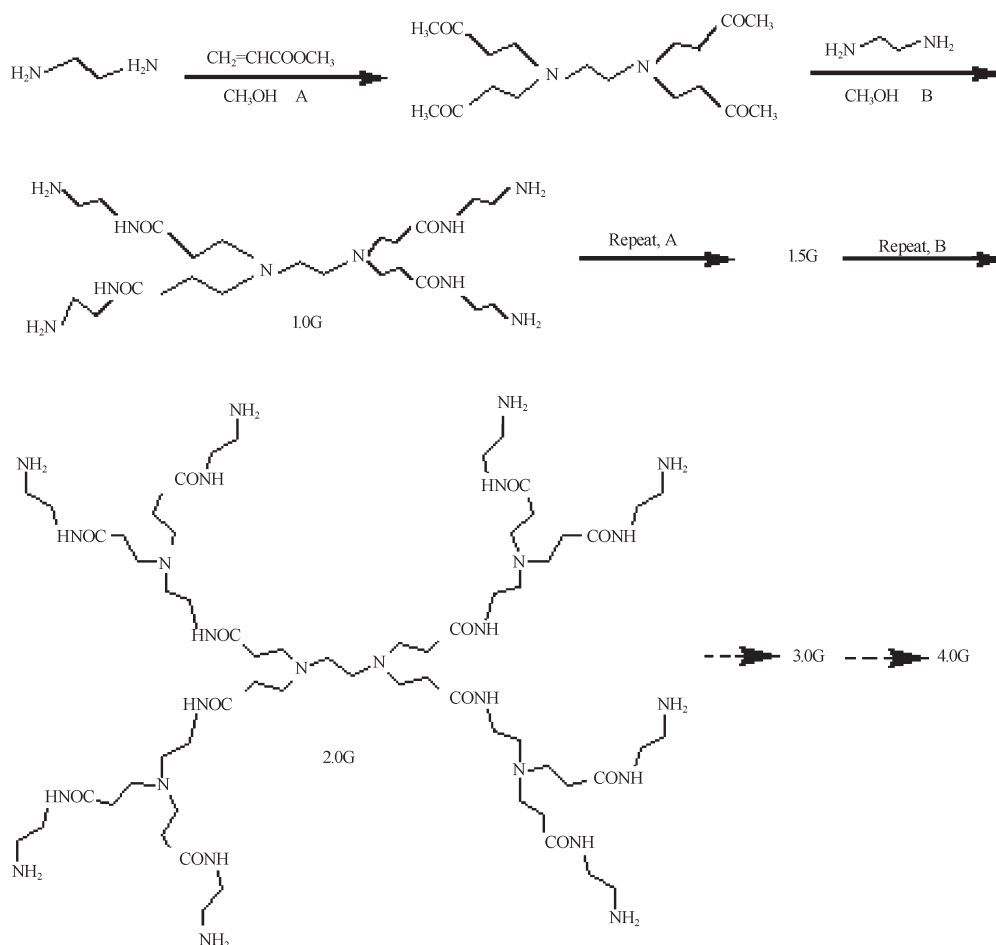
1.3 Oxidation of MWCNTs^[29]

A 100 mL flask charged with 2.0 g of pristine MWCNTs and 30 mL of 70% HNO₃ aqueous solution was sonicated in a bath (20 kHz) for 30 min and stirred for 24 h under refluxing. Then following the method described in literature^[29], about 1.3 g of carboxylic acid-modified MWCNTs (MWCNTs-COOH) was obtained.

1.4 Modification of MWCNTs with PAMAM

In order to enhance the activity of -COOH groups,

it is necessary to convert carboxylic groups into carboxylic chloride. Dried MWCNTs-COOH (1.0 g) was reacted with excess of neat SOCl₂ (20 mL) at 65 °C for 24 h. The residual SOCl₂ was removed under vacuum. The remaining solid (MWCNTs-COCl) was washed three times with anhydrous Tetrahydrofuran (THF) and was dried under vacuum at room temperature for 4 h, yielding 80% MWCNTs-COCl (0.8 g). The last step was solubilization of PAMAM (1.0G, 2.0G, 3.0G and 4.0G) (5.0 g) in 40 mL of CHCl₃ and adding MWCNTs-COCl (0.1015 g), sonicating (20 kHz) for 30 min, and stirring at 40 °C for 24 h. After cooling to room temperature, the resulting solid was separated by vacuum filtration using a 0.22 μm polycarbonate membrane filter, washed with anhydrous methyl alcohol for five times to remove excess PAMAM. To ensure that no ungrafted PAMAM is mixed in the product, the filtered solid was redispersed in anhydrous methyl alcohol by ultrasonic



Scheme 2 Outlines of PAMAM synthesis^[31]

for 15 min, and filtered using a 0.22 μm polycarbonate membrane again, then washed with distilled water for many times. Finally, the black solid was dried at room temperature overnight under vacuum, yielding MWCNT-g-PAMAM.

1.5 Characterization instruments

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer FTIR spectrometer using the KBr disk method. X-ray photoelectron spectra (XPS) were performed on a PHI-5702 instrument using Mg $K\alpha$ radiation with a pass energy of 29.35 eV. Thermal gravimetric analyses (TGA) was made with a Perkin-Elmer TGA-7 instrument under nitrogen at a heating rate of 5 $^{\circ}\text{C} \cdot \text{min}^{-1}$. Transmission electron microscopy (TEM) analyses were conducted on a Hitachi Model H-600 electron microscope at 100 kV.

2 Results and Discussion

In FTIR measurements, the amount of sample added to the KBr must be strictly controlled (the weight ratio of KBr:sample is not less than 2000:1) because the black MWCNTs absorb the infrared rays if the amount of MWCNTs were too much^[32]. Fig. 1 shows the FTIR spectra of pristine MWCNTs and MWCNTs-g-PAMAM. Because the reaction between amino groups in PAMAM and carboxylic chloride groups in MWCNT forms MWCNT-PAMAM hybrid with large amount of amide, amino and carbonyl groups on the surface of the hybrid, one can see from the infrared absorption spectrum in Fig. 1 that MWCNTs-g-PAMAM (G1.0 ~G2.0) have similar infrared spectra. Compared with the FTIR spectra of pristine MWCNTs (Fig. 1(a)), the FTIR spectra of MWCNTs-g-PAMAM (Fig. 1(b ~e)) clearly shows the peaks at 1775 cm^{-1} and 1638 cm^{-1} , which are due to the acylamide groups (acylamide band I and II, respectively). And the peaks at 3404 cm^{-1} and 2921 cm^{-1} are due to N-H and C-H stretching, respectively. Other characteristic absorption peaks of PAMAM, such as C=O at 1616 cm^{-1} , can be found in Fig. 1(b~e). These results indicate that PAMAM successfully grafted to the surface of MWCNTs. The absorption from the carboxylic groups (root from hydrolyzation of the remain-

ing carboxylic chloride during wash process) at MWCNT surface, though also contributes the absorbance increase in this region, is too weak to give appreciable peaks. Fig. 2 shows the XPS full-scan spectra of the MWNCT-g-G3.0. The peaks at the electron binding energies of about 284.6, 399.2 and 533.2 eV are attributed to the C1s (-C=O), N1s (-N-H) and O1s (O=C-), respectively. Judging by combination of FTIR and XPS results, it can be concluded that the PAMAM dendrimers have covalently bound to the surface of MWCNTs.

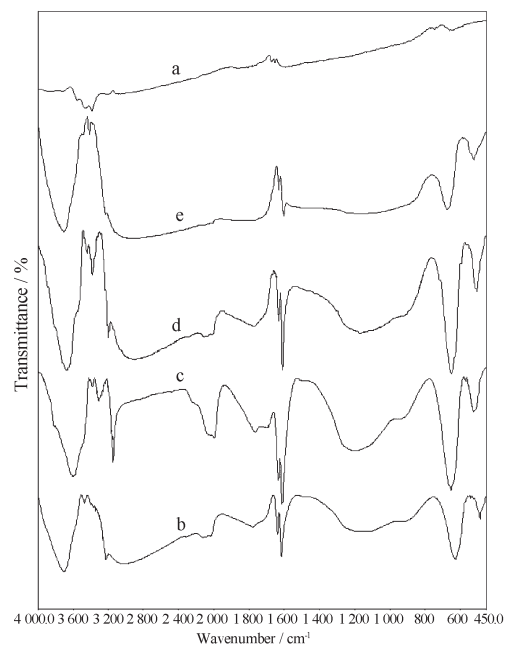


Fig. 1 FTIR spectra of (a) pristine MWCNTs; (b) MWCNTs-g-G1.0; (c) MWCNTs-g-G2.0; (d) MWCNTs-g-G3.0; (e) MWCNTs-g-G4.0

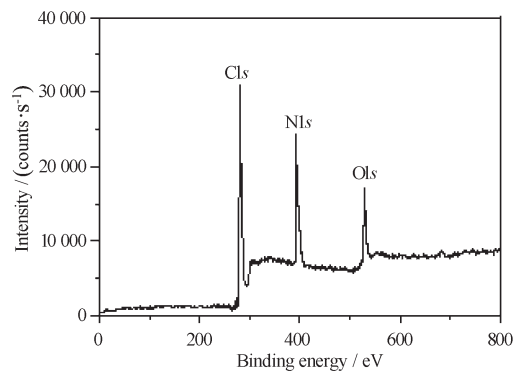


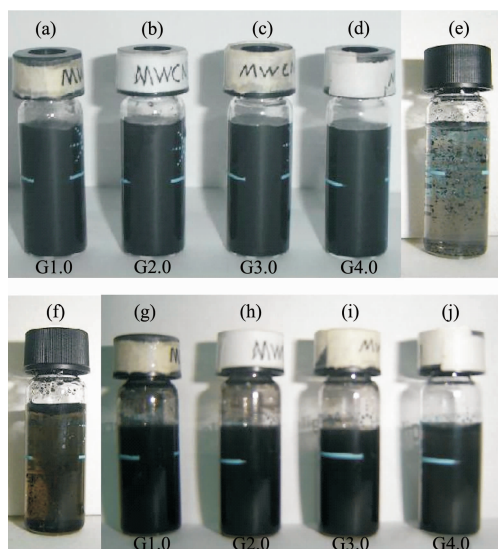
Fig. 2 XPS full-scan spectrum of the MWNCT-g-PAMAM(G3.0)

Generally, the solubility or dispersibility of the functionalized MWCNTs strongly depends on the struc-

ture and amounts of the grafted moieties. Dispersion of pristine MWCNTs into aqueous solution or organic solvent is very difficult even after it is sonicated. However, dispersion of MWCNTs-g-PAMAM into polar solvents such as water, methanol and ethanol is very easy. Fig.3 gives the digital photos of pristine MWCNTs in distilled water and MWCNTs-g-PAMAM in distilled water. It is clear that the pristine MWCNTs are insoluble in distilled water, and there is obvious sedimentation at the bottom of the vial(Fig.3e). However, MWCNTs-g-PAMAM (G1.0~G4.0) can well disperse in distilled water, forming a homogeneous system, and there is no sedimentation observed even after one month as shown in Fig.3 (a~d). For comparison, the dispersion of the mixture of pristine MWCNTs(2%) and pure PAMAM (G2.0, 98%) into distilled water has been studied, but it is shown that PAMAM is a poor dispersant for MWCNTs in distilled water(Fig.3f). In order to further investigate the stability of different generation PAMAM modified MWCNTs' dispersibility in water, the digital photos of MWCNTs-g-PAMAM (G1.0~G4.0) dispersed in distilled water are also presented after setting for 3 months(Fig.3 (g~j)), the results show that MWCNTs-g-PAMAM(G1.0, G2.0 and G3.0) still have good dispersibility, but the sample of MWCNTs-g-PAMAM

(G4.0) has a small quantity of sedimentation in bottom of the bottle, this probably because PAMAM(G4.0) has more terminal $-NH_2$ than other generations, and much more MWCNTs surround the same PAMAM(G4.0) dendrimer molecule. This could decrease the hydrophilic character of MWCNTs-g-PAMAM. All of these evidences indicate that PAMAM dendrimers have successfully grafted onto the surface of MWCNTs.

Fig.4 displays the TGA weight loss curves of the pristine MWCNTs, MWCNTs-g-PAMAM (G1.0~G4.0) and pure PAMAM(G3.0 and G4.0). The weight loss of pristine MWCNTs below 1 200 °C is less than 10.0%. In fact, the sample of pristine MWCNTs is steady without evident weight loss below 600 °C(Fig.4a). On the contrary, the sample of MWCNTs-g-PAMAM(G1.0) displays weight loss of about 72% between 400 and 800 °C. This weight loss mainly results from the losing of PAMAM (G1.0) on the surface of MWCNTs; the sample of MWCNTs-g-PAMAM (G4.0) displays weight loss of about 66% between 400 and 1 200 °C. As for MWCNTs-g-PAMAM(G2.0) and MWCNTs-g-PAMAM(G3.0), there are weight loss of about 75% and 72% in the temperature of 600~1 000 °C, respectively. Compared to pure PAMAM, it is clearly seen that the PAMAM dendrimers grafted onto the surface of MWCNTs have higher thermo-decompose temperature. That means MWCNTs-g-PAMAM nanocomposite has better thermo stability than that of pure PAMAM. Further more, it is interesting to find that the thermo-decompose velocity of the four PAMAM grafted MWCNTs is in the order of MWCNTs-g-G1.0>MWCNTs-g-G2.0>MWCNTs-g-G3.0>



(a~d) MWCNTs-g-PAMAM (G1.0~G4.0) after 1 month; (e) pristine MWCNTs alone; (f) pure PAMAM (G2.0, 98%) and MWCNTs(2%); (g~j) MWCNTs-g-PAMAM(G1.0~G4.0) after 3 months

Fig.3 Digital photos of MWCNTs dispersed in distilled water

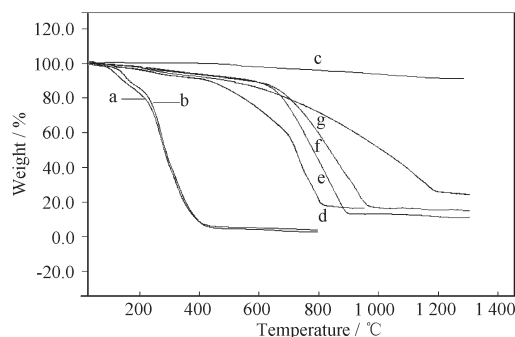


Fig.4 TG curves of (a) PAMAM G3.0; (b) PAMAM G4.0; (c) pristine MWNTs; (d) MWCNTs-g-G1.0; (e) MWCNTs-g-G2.0; (f) MWCNTs-g-G3.0; (g) MWCNTs-g-G4.0

MWCNTs-g-G4.0, this probably because higher generation of PAMAM has more terminal -NH_2 than the lower ones, and much more MWCNTs would surround the same PAMAM dendrimer molecule with higher generation, thus the thermo stability would be enhanced. In addition, it can be conclude from the TG curve that the weight of PAMAM grafted onto the MWCNTs surface is in the order of $\text{G2.0} > \text{G1.0} \approx \text{G3.0} > \text{G4.0}$.

The derivative thermogravimetric (DTG) curves of the partial samples are given in Fig.5, and the results show that the DTG curves of the PAMAM with different

generations are similar (Fig.5 (a) and Fig.5 (b)). Both in Fig.5(c) and Fig.5(d), the first peak point at 220°C can be observed, and then in the range of $350\sim 500^\circ\text{C}$, the DTG curves keep horizontal and close to zero, this illuminates that the covalent bonding existence between MWCNTs and PAMAM. Further more, the maximum DTG value of the MWCNTs-g-G2.0 is larger than that of MWCNTs-g-G3.0, this attributes to the much more weight content of PAMAM G2.0 in MWCNTs-g-G2.0 than that of PAMAM G3.0 in MWCNTs-g-G3.0. The more grafted PAMAM, the more sensitive to temperature.

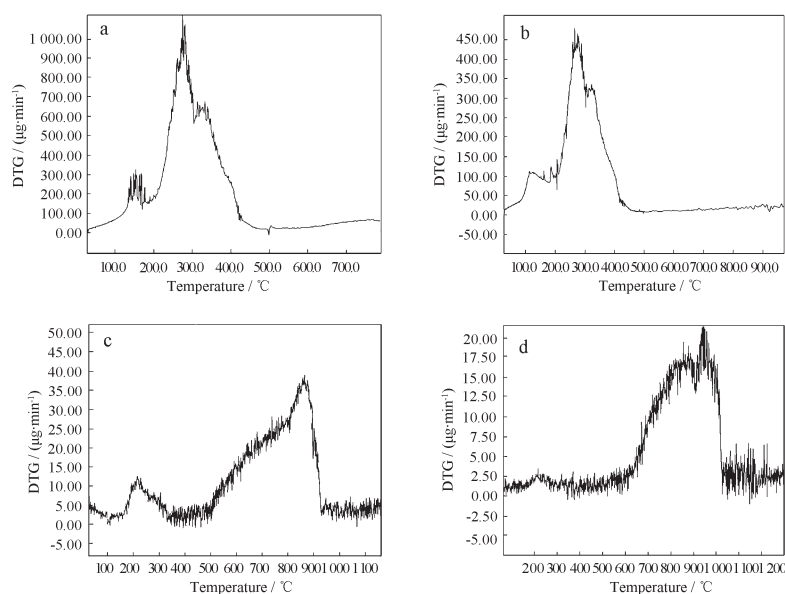


Fig.5 DTG curves of (a) PAMAM G3.0; (b) PAMAM G4.0; (c) MWCNTs-g-G2.0; (d) MWCNTs-g-G3.0

The MWCNTs-g-PAMAM(G3.0) is further characterized with TEM. TEM images provide a direct description for the samples. The TEM images of the pris-

tine and modified MWCNTs are shown in Fig.6. The average diameters of the pristine nanotubes are $30\sim 40\text{ nm}$, and the surface of pristine MWCNTs is feature-

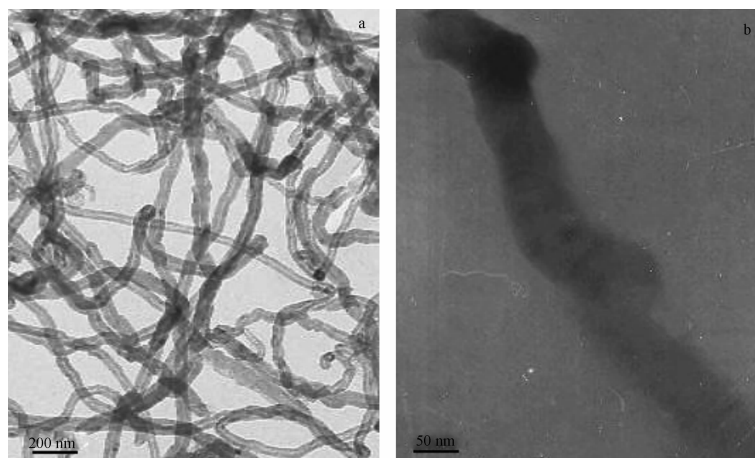


Fig.6 TEM images of (a) pristine MWNTs and (b) MWNTs-g-G3.0

less. The average length of the MWNT is several micrometers. In the image of pristine MWCNTs (Fig.6a), many jointed tubes mass together seriously. From the image of MWCNTs-g-PAMAM(G3.0) (Fig.6b), it can be found that the diameters of PAMAM (G3.0) modified MWCNTs reach about 60 nm. In addition, the images also indicate that the thickness of the PAMAM layer coated on the MWCNTs is uniform.

3 Conclusions

The modification of MWCNTs with poly (amidoamine) dendrimers(PAMAM) via the “grafting to” method was investigated in this work. After the MWCNTs were treated with HNO_3 and SO_2Cl_2 , PAMAM dendrimers were successfully grafted onto the surface of MWCNTs via side group reaction, forming a nanocomposite. The product of MWCNT-g-PAMAM has excellent water dispersibility. FTIR results show that the “grafting to” process could be explained by covalent attachment mechanism. TGA data also indicate that the PAMAM dendrimers are successfully grafted to the side wall of MWCNTs, and the weight of PAMAM grafted onto the MWCNTs surface is in the order of $\text{G2.0} > \text{G1.0} \approx \text{G3.0} > \text{G4.0}$.

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