Functionalization of multi-walled carbon nanotubes via surface unpaired electrons

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Abstract

The unpaired electrons on multi-walled carbon nanotubes (MWNTs) treated by nitric–sulfuric
mixed acid were detected and characterized by electron spin resonance (ESR). Through
reacting with these unpaired electrons, highly soluble acrylamide-grafted MWNTs were
successfully prepared and characterized by ESR, FT–IR, UV–vis and atomic force microscopy
(AFM), etc. The results indicate that MWNTs could generate more unpaired electrons with
longer mixed-acid treatment time and could be well functionalized by acrylamide. By AFM
analysis, a 'net' structure was formed on MWNTs after grafting with acrylamide. This new
method has some obvious advantages of mild reaction conditions and convenient operation, etc.
Furthermore, the grafting of MWNTs may have great potential for biomedical applications in
drug delivery and regenerative medicine owing to their excellent networks.

1. Introduction

Carbon nanotubes (CNTs) have attracted extensive research
interest since their discovery by Iijima in 1991 [1].
They have been used in many applications, such as
field emission devices [2], nanoelectronics [3], hydrogen
storage [4], electrochemical sensors [5] and delivery systems
for drugs [6, 7], because of their outstanding chemical,
physical, electrical and mechanical properties [8, 9]. However,
a troublesome disadvantage of CNTs is their insolubility in
any solvent. For improved application performance, it was
obvious that modification of CNTs is often necessary [10, 11].
Functionalization of side wall defects, tips, and other
nonhexagonal regions of CNTs has been studied extensively
with regard to their solubilization [12]. Three ways [13]
for chemical modification of CNTs are open to study:
(a) noncovalent functionalization by wrapping the CNTs with
surfactants or polymers; (b) covalent functionalization of
defect sites at the tube ends and side walls by oxidation
and subsequent conversion into derivatives such as amides;
and (c) direct chemical functionalization of the side walls

using addition reactions with direct fluorination, subsequent
nucleophilic substitution and the addition of radicals formed
by reduction.

However, those traditional methods are usually compli-
cated. Therefore, it is still a great challenge to develop new
modification methods for preparing highly soluble CNTs. In
this paper, we developed a new and simple method for func-
tionalizing CNTs, and obtained highly soluble CNTs.

Previous studies have revealed that the acid-oxidized
CNTs exhibited strong ESR signals, which implied that many
unpaired electrons were generated on CNTs [14, 15]. We
inferred these unpaired electrons can react with monomer for
CNT modification, because the free radical polymerization is
popular in polymer chemistry. In order to test and verify
our idea, in this study, we selected acrylamide, monomer
of polyacrylamide, as a model to react with the unpaired
electrons on CNTs for functionalizing CNTs. The highly
soluble acrylamide-grafted multi-walled CNTs (MWNTs)
were prepared and characterized by electron spin resonance
(ESR), FT–IR, UV–vis and atomic force microscopy (AFM),
etc. Some synthesis parameters, such as acid treatment time
and methods, were also investigated in detail.

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2. Experimental details

2.1. Materials

The pristine MWNTs with outside diameters of 10–30 nm, lengths of 5–50 μm and a purity of higher than 95% were purchased from Shenzhen Nanotech Port Co., Ltd. Concentrated sulfuric acid (98%), concentrated nitric acid (65%), anhydrous alcohol, sodium hydroxide, acrylamide and other chemicals were provided by Shanghai Chemical Reagent Company of the Chinese Medical Group. High purity nitrogen was supplied by Shanghai Qingda Gas Fill Plant.

2.2. Grafting acrylamide on MWNTs

Before the acrylamide-grafting reaction, the MWNTs were treated as follows: 15 ml HNO_3, 45 ml H_2SO_4 and 100 mg MWNTs were mixed in a 150 ml flask and subjected to ultrasonic vibration for 2–12 h. The resulting mixture was washed repeatedly with distilled water until the pH of the filtrate turned neutral, and then dried in an oven for 12 h at 100 °C for the next ESR test. The acrylamide-grafted MWNTs were prepared as follows: 20 ml acrylamide (10 wt%) was placed in a 50 ml glass reactor and mixed with 100 mg acid-pretreated MWNTs under ultrasonic vibration. After a reaction for 12 h at 80 °C, the products were repeatedly washed with distilled water to remove the excess acrylamide and dried for 12 h in vacuum oven.

The solubility of acrylamide-grafted MWNTs in deionized water was investigated. 10 mg functionalized MWNTs were firstly dispersed in 2 ml deionized water via sonication, then stored without shaking for 24 h, and finally 1 ml of the upper solution was dried out; the weight was 2.54–3.10 mg. Therefore, the solubility of acrylamide-grafted MWNTs in deionized water is about ca 2.54–3.10 mg ml^{-1}, depending on experimental conditions.

2.3. Characterizations

Infrared (IR) spectra were recorded by means of an America Nicolet Nexus 7000-C FT–IR spectrometer using KBr wafers. UV–vis spectra were measured with a Shimadzu UV-2501 spectrometer. Transmission electron microscopy (TEM) was carried out on a JEM-200CX electron microscope. Atomic force microscopy (AFM) images were obtained from a Shimazu-9600 AFM operating in tapping mode in air at a scan rate of 1.5 Hz. The AFM probe was a 130 μm-long monocrystalline silicon cantilever with an integrated conical shaped Si tip (NT-MDT Russia) with force constant 5.5 N m^{-1}. The electron spin resonance (ESR) test was measured on a JOEL ESR spectrometer at a modulation frequency of 9.44 kHz, amplitude of 3360 ± 250 G and a microwave power of 1 mW.

3. Results and discussion

3.1. Investigation of ESR on pre- and post-treatment MWNTs

Electron spin resonance (ESR), is resonance absorption induced by the electron spin magnetic moment. ESR is an important method to study material microstructure and motion state. Unpaired electrons can be detected by ESR spectra, and quantitatively analyzed by ESR peak height or peak area. Figure 1(a) shows the ESR spectra of pristine MWNTs. The straight line indicates no ESR signal in the pristine MWNTs, which is in accordance with that reported in the literature [16]. However, the observation of the ESR signal may be complicated by the presence of ferromagnetic catalyst residues which could produce some extraneous lines [17]. ESR spectra of MWNTs after ultrasonic vibration for 2, 4 and 6 h in nitric–sulfuric acid are shown in figures 1(b)–(d). There are two symmetric spin resonance peaks in the center field of *G* in these ESR spectra after nitric–sulfuric acid treatment, due to the presence of unpaired electrons. The relative number of unpaired electrons could be analyzed by the spin resonance peak height of the ESR spectra, as reported in the literature [18, 19]. Hence, we compare the ESR spectra of MWNTs for different ultrasonic vibration times and investigate their relationship. With increasing ultrasonic vibration time, the number of unpaired electrons produced clearly increases (figure 2), which indicates functionalization of MWNTs by reacting to acrylamide with unpaired electrons to enrich ions or proteins etc.

The grafting efficiency mainly depends on the number of unpaired electrons formed after ultrasonic vibration. As shown in figure 2, the longer the ultrasonic vibration time, the larger is the number of unpaired electrons. However, if the reaction time is too long, the basic structures of the MWNTs will be damaged. The experimental results show that we may get sufficient unpaired electrons for the grafting reaction with the structure of MWNTs after ultrasonic vibration for 6 h in nitric–sulfuric acid remaining intact.

The ESR peaks of MWNTs after ultrasonic vibration in nitric–sulfuric acid for 6 h are shown in figure 3. The upper trace (a) was obtained from the sample at room temperature and the lower trace (b) was determined from the sample after heating for 1 h at 80 °C. This suggests that a grafting reaction between MWNTs and acrylamide can also be induced at 80 °C and the solubility of the product in water is about ca 2.54–3.10 mg ml^{-1}, depending on experimental conditions.

3.2. Grafting MWNTs with acrylamide via unpaired electrons

As shown in the figure 4(a), the pristine MWNTs contain a lot of impurities and aggregation of nanotubes. After 2 h of ultrasonic vibration in nitric–sulfuric acid, the surface of the CNTs are cleaner and purer after treatment with the mixed acid. This suggests that a large number of metal catalysts, amorphous carbon and other impurities have been removed (figure 4(b)). Figures 4(c) and (d) are the TEM images of MWNTs after 6 h and 12 h ultrasonic vibration in nitric–sulfuric acid respectively. It can be deduced from these pictures that the longer the time these MWNTs were treated with mixed acid, the more ends of nanotubes were opened. The purity and dispersion of these nanotubes were further improved and the length was also further shortened. However, the oxidation of these nanotubes becomes more serious when the ultrasonic treatment time reaches 12 h. It is obvious that the MWNTs
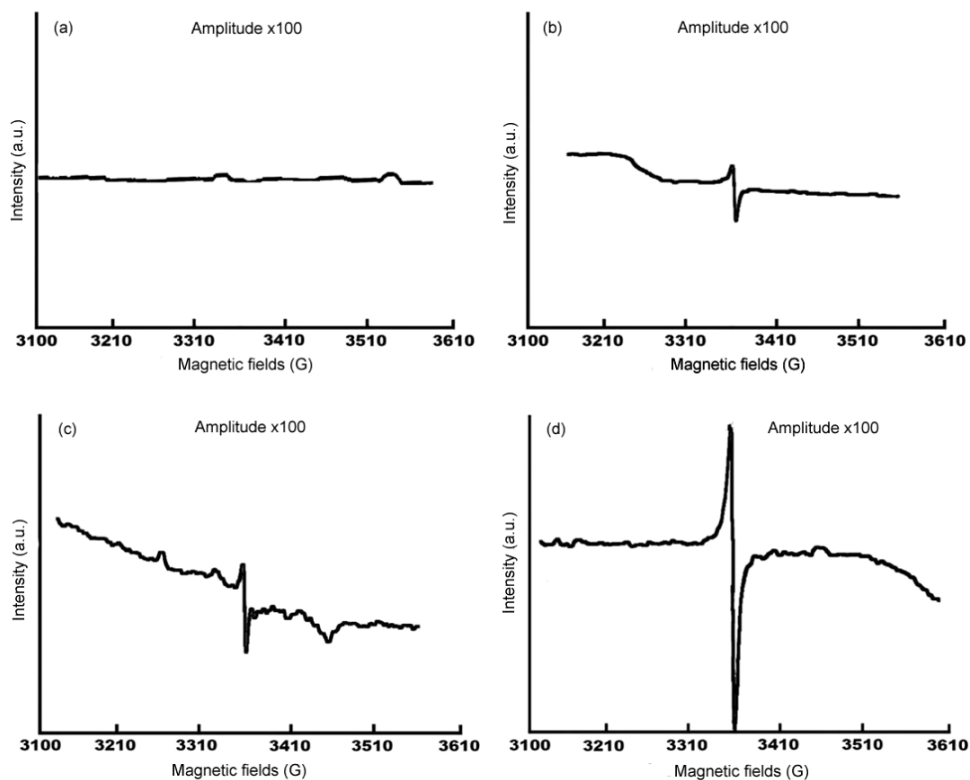
Figure 1. ESR spectra of pristine MWNTs (a), MWNTs after 2 h (b), 4 h (c) and 6 h (d) with ultrasonic vibration in nitric–sulfuric acid.
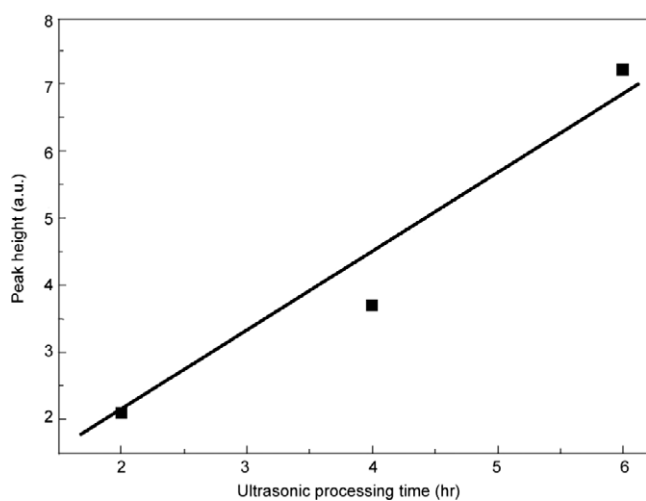

Figure 2. ESR peak height at different nitric–sulfuric acid ultrasonic vibration processing times.
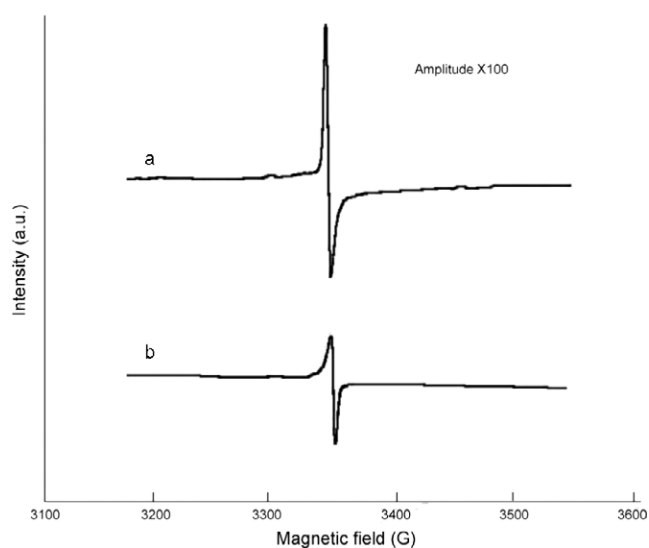

Figure 3. ESR spectra of acid treated MWNTs at (a) room temperature and (b) after heating at 80 °C for 1 h.

have been cut into shorter pieces. This destroys the major characteristics of the MWNTs' aspect ratio. The loss of MWNTs is very serious, with only about 10% yield after 12 h ultrasonic treatment.

Figure 5(a) is the AFM image of pristine MWNTs. This shows that pristine MWNTs contain a lot of impurities and aggregation, which is in agreement with the TEM result. Figures 5(b) and (c) are AFM images of MWNTs after 2 and 6 h ultrasonic vibration in mixed acid. These pictures are manifestations that the surface of MWNTs becomes cleaner and purer after treatment. A large number of metal catalyst, amorphous carbon and other impurities have been removed, in agreement with the results of TEM. Figure 5(d) shows that the surface of MWNTs after grafting with AAm become rugged, very rough, thicker in diameter and tangled in cross-linking net. This is different from past chemical modification. The reason may be due to cross-linking of acrylamide on the surface of MWNTs which then linked up with one another.
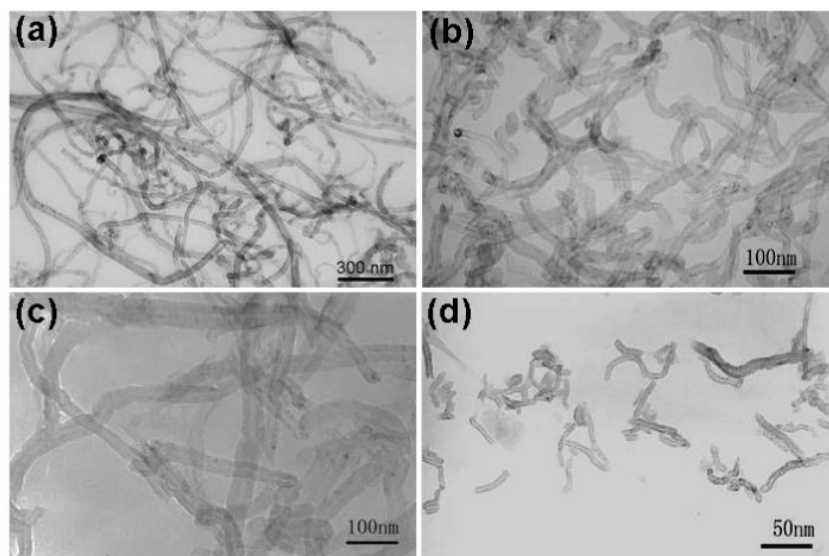
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Figure 4. TEM images of (a) pristine MWNTs, (b) MWNTs after 2 h ultrasonic vibration in nitric–sulfuric acid, (c) MWNTs after 6 h ultrasonic vibration in nitric–sulfuric acid and (d) MWNTs after 12 h ultrasonic vibration in nitric–sulfuric acid.
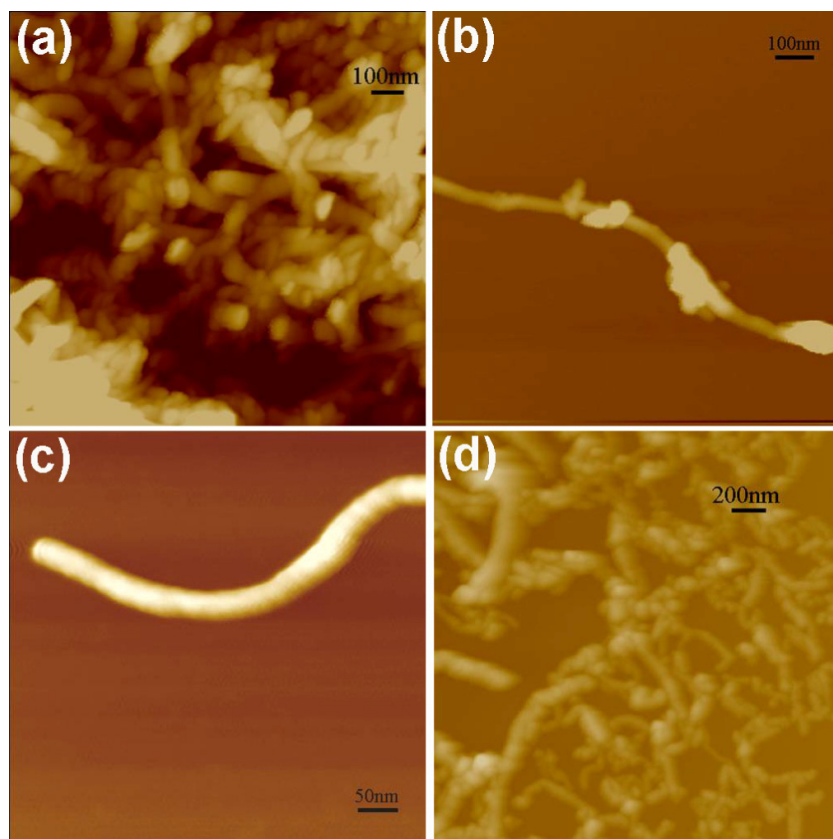

Figure 5. AFM images of MWNTs (a) in pristine state, (b) after 2 h ultrasonic vibration in nitric–sulfuric acid, (c) after 6 h ultrasonic vibration in nitric–sulfuric acid and (d) after grafting with AAm.

(This figure is in colour only in the electronic version)

FT–IR spectra of MWNTs in the pristine state, before and after grafting with acrylamide (AAm) are shown in figure 6. There are distinct absorption peaks at 1582, 2920, 2850 and 3446 cm^{-1} in figure 6(a). The spectrum shows a band around 3446 cm^{-1} which can be attributed to the hydroxyl group (νOH). Bands around 2920 and 2850 cm^{-1} are due to asymmetric and symmetric C–H stretching. The band around 1582 cm^{-1} can be attributed to the structure of graphite in MWNTs. There are obvious differences between pristine (figure 6(a)) and treated MWNTs (figures 6(b) and (c)), which
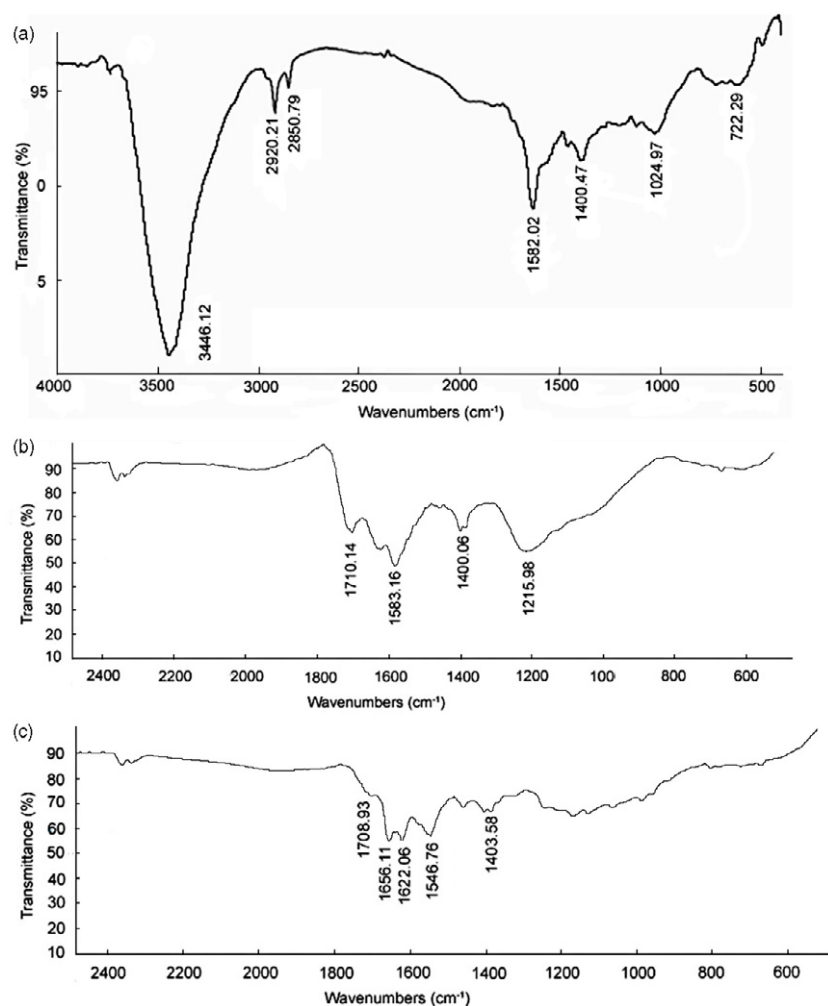
Figure 6. FT–IR spectra of MWNTs in (a) pristine state, (b) before grafting with AAm, and (c), after grafting with AAm.
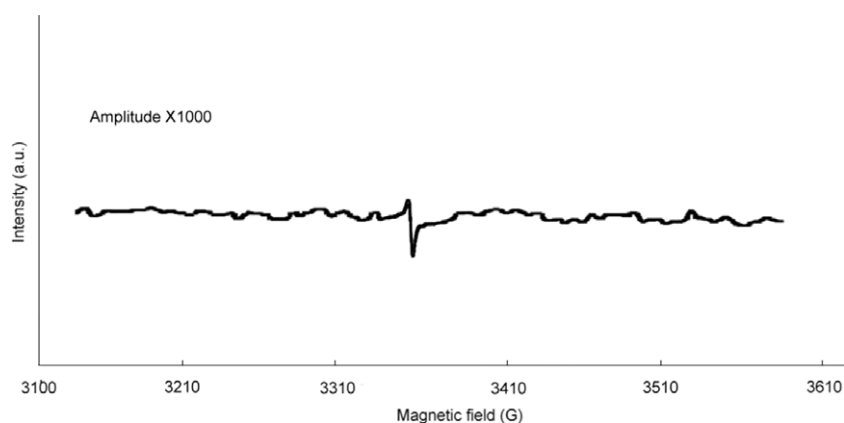

Figure 7. ESR spectra of MWNTs after grafting with AAm.

implies that the structure of MWNTs was changed. Compared to figure 6(b), there are two new absorption peaks appearing at 1656 and 1622 cm^{-1} in figure 6(c), which could be attributed to amide bond stretching, confirming that MWNTs were grafted by AAm successfully.

Further evidence of successful grafting of MWNTs by AAm is the weak ESR signal of the product even when the amplitude is magnified by 1000× (figure 7). This shows that most unpaired electrons obtained by acid treatment have successfully reacted with AAm, leaving only a few unsuccessful electrons to give a weak ESR signal.

UV–vis spectra of (a) acid modified MWNTs, (b) graft acrylamide (AAm) MWNTs and (c) high temperature treatment to dehydro-acrylamide MWNTs are shown in
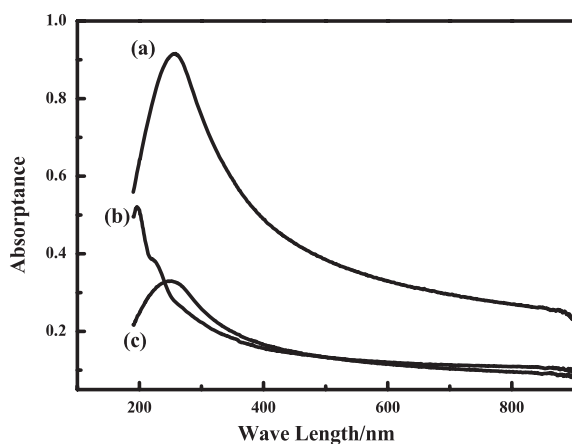
Figure 8. UV–vis spectra of (a) acid modified MWNTs, (b) AAm-MWNTs and (c) De-AAm-MWNTs.

figure 8. There is a fine structure characteristic peak of acidification MWNTs at 260 nm, which weakens after grafting AAm and strengthens after removing AAm at high temperature. The modification of MWNTs was completed by unpaired electron transfer from sp^2 hybridization of partly side wall carbon atom to sp^3, which could change the electronic structure. That is why the fine structure peak of MWNTs weakens after grafting AAm but the original characteristic peak appears again when AAm was removed from the grafted AAm-MWNTs by high temperature treatment in nitrogen atmosphere.

The possible mechanism of grafting MWNTs with acrylamide via unpaired electrons has been indicated as in figure 9. There are two stages in this reaction, acidification and grafting. Firstly, a lot of unpaired electrons are produced by ultrasonic treatment destroying C–C bonds. Then, acrylamide is linked to MWNTs via unpaired electrons which attack the double bonds of vinyl monomers.

Seen from figure 2, the number of unpaired electrons produced clearly increases with increasing ultrasonic vibration time, which further confirms that the free radicals exist (namely unpaired electron for MWNT). Many researchers reported that free radicals can remain active from 10^{-2} s to several days, we think that the surface structure of MWNT has effects on stabilizing unpaired electrons. According to the results of ESR analysis (figure 3), the ESR signal of acid modified MWNTs is still strong even after heating at 80 °C for 1 h, which indicates unpaired electrons can still be active under higher temperature.

There exists various degree of polyacrylamide modified MWNTs, which can be observed as a net structure of MWNTs

by AFM. That is considered as an ideal structure of functional materials for various application.

4. Conclusions

In summary, we developed a new and simple method for functionalizing CNTs. Using the unpaired electrons on CNT surface, highly soluble acrylamide-grafted MWNTs were successfully prepared and characterized. It is interesting to find that more unpaired electrons on MWNTs can be produced by increasing the ultrasonic treatment time of the mixed acid and reacting well with acrylamide. The new method for modifying CNTs has some advantages, such as mild reaction conditions, convenient operation, etc. We anticipate that these scientific merits will motivate further study and development of MWNTs, resolve the problem of shortage of effective functionalization methods, and culminate in technological advances of major significance.

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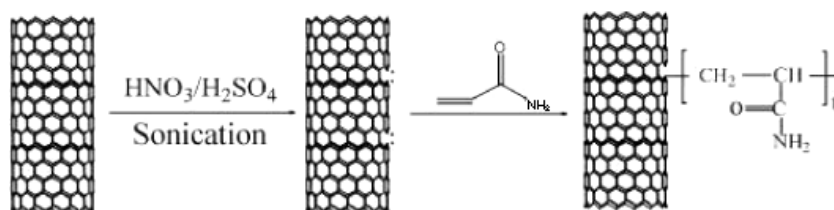[10] Lin T, Bajpai V, Ji T and Dai L M 2003 *Aust. J. Chem.* **56** 635–51

Figure 9. Scheme for the fabrication of acrylamide-grafted MWNTs.

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