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Enhancing the crystalline degree of carbon nanotubes by acid treatment, air oxidization and heat treatment

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Abstract: Three approaches of treating carbon nanotubes (CNTs) including acid treatment, air oxidization and heat treatment at high temperature were studied to enhance the crystalline degree of carbon nanotubes. High temperature heat-treatment elevates the crystalline degree of carbon nanotubes. Acid treatment removes parts of amorphous carbonaceous matter through its oxidization effect. Air oxidization disperses carbon nanotubes and amorphous carbonaceous matter. The treatment of combining acid treatment with heat-treatment further elevates the crystalline degree of carbon nanotubes comparing with acid treatment or heat-treatment. The combination of the three treatments creates the thorough effects of enhancing the crystalline degree of carbon nanotubes.

Key words: carbon nanotubes; acid treatment; air oxidization; heat treatment

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1 Introduction

Carbon nanotubes (CNTs) have much potential value for their unique structure, nano-phase dimensions, high and accessible surface, thermal and chemical stability [1]. Bright prospect is placed on carbon nanotubes in the area of engineering material, semiconductor material, electronic devices *etc* [2,3].

CNTs belong to crystalline carbon, their walls are constituted by curled graphite lamina [4]. But much carbonaceous matter with amorphous structure may exist with CNTs and deteriorate their performances.

Heat treatment at high temperature and pressure is one of the effective approaches of elevating the crystalline degree of carbon-based material [5]; Acid treatment is also an effective way for removing amorphous carbonaceous matter [6]; Air oxidization can elevate the dispersity of CNTs and disperse the amorphous carbon [7].

In the present work, CNTs synthesized by catalytic degradation were treated by high temperature heat-treatment, air oxidization, acid treatment and the combinations of two or three of these methods respectively. The effects of these treatments on elevating the crystalline degrees of CNTs are discussed.

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2 Experimental

The CNTs synthesized by catalytic degradation of propylene were treated by hydrofluoric acid and weak nitric acid to remove diatomite and metallic catalyst, and then handed on the ground to properly disperse the block mass in it.

Acid treating CNTs: filling CNTs (10 g) in a mixture liquid of concentrated H_2SO_4 and HNO_3 (100 mL) of 3:1 in volume ratio and heating the mixture at the boiling point temperature for 0.5 h. Then filtering and washing (by distilled water) the CNTs through a glass filler with a aperture range of its ceramic membrane 2-4 μm till pH value being neutrality, drying the CNTs at 100°C for 24 h.

Oxidizating CNTs by air: a quartz tube carrying 25 g of CNTs was placed in the center of a tube furnace with the two ports open. With the temperature being kept at 600°C for 30 min, the furnace tube was rotated at 30 r/min so that the CNTs can be in full contact with air.

Heat treating CNTs at high temperature: CNTs were heated at 2200°C, under 405 kPa (4 atm) in an

inert gas for 4 h in the apparatus of "HIGH MULTI5000 sintering shield furnace (made in Japan)".

"JEOL-200CX" transmission electrical microscopy (TEM) and "H-9000NAR" high resolution transmission electron microscopy (HRTEM) apparatuses were employed to observe the samples; "RM2000" fiber confocal Raman spectrum apparatus and "PERKINELMER Spectrum GX FT-IR System Jeol-200CX" infra-red spectrum apparatus were employed to characterize the samples.

3 Results and discussion

A TEM of as-prepared initial CNTs is shown in **figure 1**, the diameters of CNTs are 30-40 nm. The black and formless clumps existed in the CNT nets are amorphous carbon.

Figure 2 (a) is the Raman spectrum of initial CNTs. The peak strength standing for the crystalline carbon (1572.1 cm^{-1}) is lower than that standing for the carbonaceous matter of amorphous structure (1345 cm^{-1}), and the ratio of them is about 6:10. The result indicates that the amorphous carbonaceous matter is in the majority.

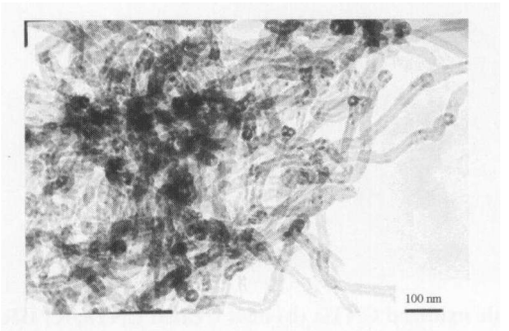

Figure 1 TEM image of initial carbon nanotubes.

In Raman spectrum, the peak standing for carbonaceous matter with amorphous structure is led by follow factors: First, the amorphous carbon larded with CNT nets, which is also constituted by hexacyclic planes, but many hexacyclic planes do not align in order but form disorganized laminate structures that are not crystalline graphite; Second, parts of nanotube-walls, such as defects and curvatures *etc.*, may also be irregular structure of hexacyclic planes due to discontinuous cracked graphite sheets [8].

3.1 Effects of acid treatment on CNTs

Figure 2(b) is the Raman spectrum of acid treated CNTs. The peak strength of 1571.0 cm^{-1} is basically equal to the peak strength of 1344.6 cm^{-1}. This result indicates that the ratio of the amorphous carbonaceous matter of acid treated sample declines.

Concentrated acid decomposes to generate free oxygen atoms during heating process. Amorphous carbonaceous matter has unstable structure relative to CNT walls with regular laminate structure, its oxidation rate is also faster than that of CNTs, resulting in the ratio of amorphous carbonaceous matter decreasing.

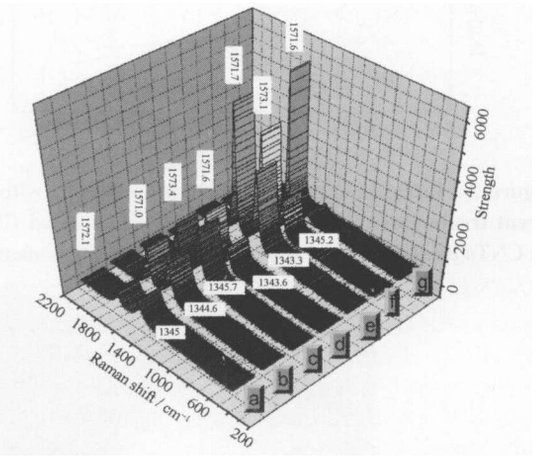

Figure 2 Raman spectra of CNTs treated by different ways: (a) initial CNTs; (b) acid treated CNTs; (c) air oxidized CNTs; (d) heat treated CNTs; (e) combination of air oxidization and heat treatment; (f) combination of acid treatment and heat treatment; (g) combination of acid treatment, air oxidization and heat treatment.

The infrared transmission spectra of initial and acid treated CNTs are shown in **figure 3** (a) and (b). The broad band centered around 3450 cm^{-1} associates with hydroxy groups (–OH), and the band centered on 1198 cm^{-1} associates with C–O stretching in ethers, hydroxys or carboxylic anhydrides. The peaks of 1582 cm^{-1} reflect the vibration of carbocyclic plane and should be hold by both acid treated and untreated CNTs. The signature of >C=O functional groups in carboxyls or carboxylic anhydrides is evident at about 1718 cm^{-1}. It is evident that there are much more carbonyl groups, carboxylic groups and hydroxyl groups *etc.* in acid treated CNTs than that in initial CNTs [9,10].

Free oxygen atoms generated during the heating process of concentrated acid can combine with water molecules to generate free radicals of –OH that can be connected to π bonds and hook-bonds of carbon atoms on the outer walls of CNTs to generate hydroxy functional groups. Free oxygen atoms can also connect two adjacent carbon atoms with hook-bonds to generate ethers (C–O–C). For those carbon atoms with two or three free bonds in the defects of CNT walls, the former can be connected to free oxygen atoms to form carbonyl (>C=O) and the latter be connected to oxygen atoms to form carboxy (–COOH). Carbonyl (>C=O) can also be connected to H^+, OH^- and free

oxygen to form carboxy (–COOH) or –C–OH. Dehydration reaction may occur between the adjacent carboxyls to generate carboxylic anhydrides.

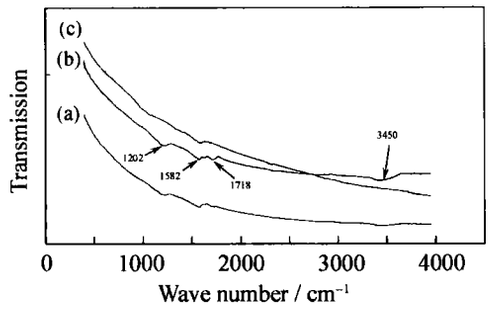

Figure 3 Infrared spectra of carbon nanotubes with different treatments: (a) initial CNTs; (b) acid treated CNTs; (c) CNTs treated by acid and followed by heat treatment.

3.2 Effects of air oxidizing on CNTs

Carbon can react with air to generate CO_2. But the structures with pentagons, heptagons and amorphous carbonaceous matter have higher reactivities relative to CNTs, oxygen molecules oxidize at first the curvatures and the defects containing pentagons, heptagons, irregular hexacyclic planes or greater strains, finally resulting in the breaking of CNTs. Amorphous carbon jammed in CNT nets is also etched away or stripped off by air oxidation. Then the cross-entangled nanotubes disassemble, and become short, low curvature ones. It can be seen by comparing figure 1 with **figure 4** (a), a TEM image of air oxidized CNTs, that after oxidization, the dispersity of CNTs is enhanced.

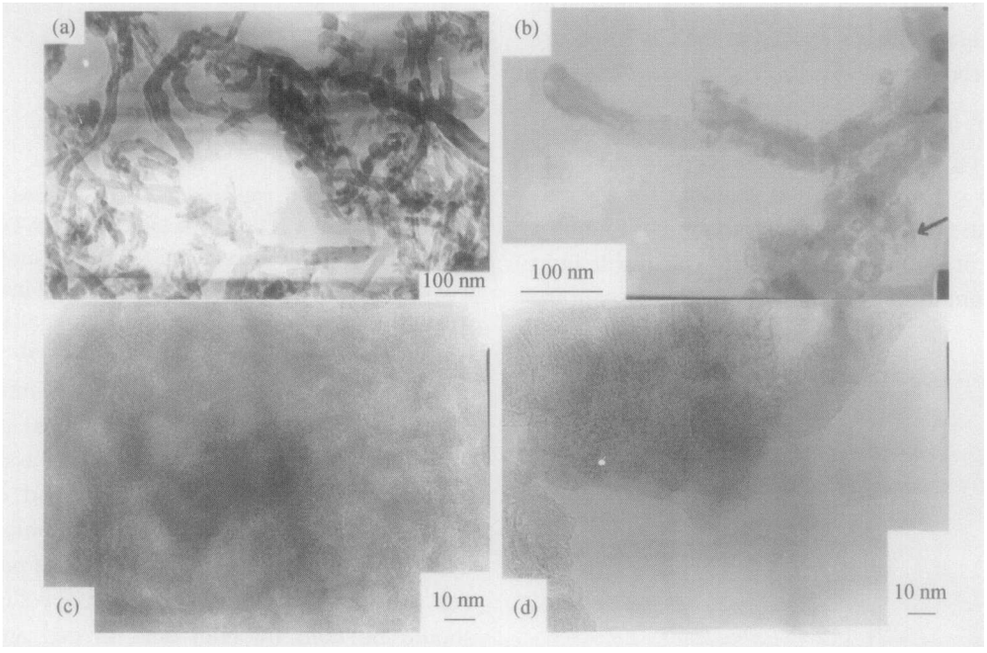

Figure 4 TEM and HRTEM images of differently treated CNTs: (a) air oxidized CNTs; (b) heat treated CNTs; (c) HRTEM of amorphous carbon; (d) HRTEM of crystalline carbon.

Figure 2(c) is the Raman spectrum of air oxidized CNTs. The peak strength of 1573.4 cm^{-1} is still obviously lower than that of amorphous structure (1345.7 cm^{-1}). This result indicates that air oxidization has not obviously enhanced the crystalline degree of CNTs. The reason is that both amorphous carbonaceous matter and CNTs are fast oxidized due to the acute oxidization reaction. Though the dispersity of CNTs is elevated and amorphous carbon is dispersed from CNT nets, the concentration of amorphous carbonaceous matter in CNTs has not obviously changed.

3.3 Effects of heat treating on CNTs at high temperature

As introduced above, the hexacyclic planes of the carbonaceous matter with amorphous structure do not align in order. Enough energy supplied by high temperature and pressure is needed to make these disorder hexacyclic planes approach and unite each other to form regular align in three-dimension.

A HRTEM image of the amorphous carbon in initial CNTs is shown in figure 4(c), the compact stripes are cross section of laminated carboncycle planes. It can be seen that these carboncycle planes are irregularly arraying and thus constituting the amorphous inner structure.

A TEM image of heat treated CNTs, shown in figure 4(b), preliminary indicates that amorphous carbon has become crystal with regular shapes and edges, as arrow pointing. A HRTEM image at the arrow pointed site is shown in figure 4(d), and indicates that carboncycle planes tend to be regular and parallel array, *i.e.*, the characteristic of crystalline graphite.

The Raman spectrum of heat treated CNTs is shown in figure 2(d). The peak strength of 1571.6

cm^{-1} is obviously higher than that of 1343.6 cm^{-1}, and the ratio of the two peak strengths is about 2:1. The result means that much amorphous carbonaceous matter has changed into crystalline structure and the latter is in the majority.

3.4 Effects of combination of several treatments on CNTs

The Raman spectrum of CNTs treated by air oxidization and followed by heat treatment at high temperature is shown in figure 2(e). The ratio of the peak strengths of 1571.7 cm^{-1} and 1343.3 cm^{-1} is not obviously different from that shown in figure 2(d), the Raman spectrum of only heat treated CNTs. This result indicates that the crystalline degree of such CNTs is basically equal to that of only heat treated CNTs. As discussed above, the concentration of amorphous carbonaceous matter in CNTs is not obviously changed after air oxidization, the increase of the crystalline degree is mainly caused by heat treatment.

The Raman spectrum of CNTs treated by acid and followed by heat treatment is shown in figure 2(f). The ratio of the peak strength of 1573.1 cm^{-1} to that of 1345.2 cm^{-1} is about 2.7:1, which is higher than the ratio of the two peaks of figure 2(d).

According to the theory of carbon material [11], parts of the hexacyclic planes of amorphous carbonaceous matter approximatively parallel array and can be easily changed into entirely order alignment in three dimensions. The other hexacyclic planes or plane-dumps are seriously disorderly orientating and cross-linking reciprocally. This seriously cross-linking microstructure is difficult to be changed even in high temperature, thus lead to the contacting process of adjacent plane-dumps being disturbed.

On the other hand, the reactivity of the amorphous carbonaceous matter with cross-linking and seriously disordered orientation microstructure is higher than that of the amorphous carbonaceous matter with approximatively parallel array hexacyclic planes. The former can be firstly oxidized by strong acid. The latter has the reactivity being close to CNT walls for reason that their approximatively parallel array hexacyclic planes are close to the microstructure of graphite, thus this part of amorphous carbonaceous matter can not be seriously consumed during the process of acid boiling, but can be easily changed into crystalline structure during heat treatment at high temperature.

For the CNTs treated by acid and followed by heat treatment, strong acid eliminates the amorphous carbonaceous matter with cross-linked and seriously disorder microstructure, heat treatment transfers the amorphous carbonaceous matter with approximate parallel microstructure into crystalline structure. However, the third reason may help to further elevate the crystalline degree of CNTs. Figure 3(c) shows the infrared spectrum of such CNTs, and indicates that no other functional groups exist except the intensive absorption at wave number of about 1582 cm^{-1} that reflects the vibration of carbocyclic plane and should be hold by CNTs themselves. The functional groups generated during acid treatment decompose during heat treatment, and remain the vacancies, which can make carbocycle planes more easily array and unite over again till reaching the graphitic structure.

For the CNTs being firstly boiled in the mixture of H_2SO_4 and HNO_3, then oxidized by air, and finally treated at 2200°C, the corresponding Raman spectrum is shown in figure 2(g), the peak of amorphous carbonaceous matter is basically vanished, only left the peak of crystalline structure (1571.6 cm^{-1}) with the shape being sharp and strong. The complementarity of these three treatments creates the thorough effects of enhancing the crystalline degree of CNTs. Strong acid eliminates the amorphous carbonaceous matter with cross-linked and seriously disorder microstructure, heat treatment transfers the amorphous carbonaceous matter with approximate parallel microstructure into crystalline structure. However, air oxidization, the middle process between acid treatment and heat treatment, breaks the CNTs at the curvatures and defects, disperses the amorphous carbon and the CNT nets. The process of disorganized laminate structures transferring into crystalline structure can thus be more easy in the latter heat treatment, results in the amorphous structures being thoroughly eliminated.

4 Conclusions

The approaches of treating carbon nanotubes including acid treatment, air oxidization, heat treatment and the combinations of two or three of them were experimented. Their effects on enhancing the crystalline degree of carbon nanotubes were studied. Following conclusions are drawn:

(1) Amorphous carbonaceous matter exists in the generally prepared CNTs.

(2) Acid treatment eliminates the amorphous carbonaceous matter with cross-linked and seriously disorder microstructure, and adds many groups to CNTs.

(3) Heat treatment transfers the amorphous carbonaceous matter with approximate parallel microstructure into crystalline structure.

(4) Air oxidization breaks the CNT walls, disperses

the amorphous carbon and CNT nets, and enhances the dispersity of CNTs.

(5) The combination of air oxidization and heat treatment has almost the same effects of enhancing the crystalline degree of CNTs as the single heat treatment has.

(6) The approach of combining acid treatment and heat treatment has the merits of the two approaches of removing the amorphous carbonaceous matter. Moreover, the decomposing process of functional groups during the heat treatment also help to elevating the crystalline degree of CNTs. Thus the combination of acid treatment and heat treatment further enhance the crystalline degree of CNTs relative to single acid treatment or single heat treatment.

(7) The approach of combining acid treatment, air oxidization and heat treatment has the merits of the three methods, entirely remove the amorphous structure.

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