Chemical Modification of Multiwalled Carbon Nanotube with the Liquid Phase Method

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ABSTRACT: In this study, multiwalled carbon nanotubes (MWNTs) were purified by using chemical method with different proportion of nitric acid and sulfuric acid liquid phase mixture. Carboxyl groups and other functional groups could be modified on the MWNTs surface. However, oxidation can damage the structure of carbon atoms on the surface of the carbon nanotube. Furthermore, the characteristic properties of MWNTs specimens were demonstrated by Raman spectrograph and Fourier transform infrared spectrum. The thermal properties and morphology of MWNTs were checked by Thermogravimetric analysis and Scanning electron microscope. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1655–1660, 2008

Key words: carbon nanotubes; chemical modification; carboxyl groups; Raman spectroscopy; FTIR

INTRODUCTION

Carbon nanotubes were discovered as early as in 1985, when Kroto et al.[1] found the existence of C_{60} by accident. This discovery means a significant breakthrough to the research on carbon compounds. When synthesizing C_{60} using the arc discharge vaporization method, Iijjma[2] from the NEC Japan accidentally observed some acicular things, and Transmission electron microscopy (TEM) observation revealed that they were multiwalled, coaxial and hollow structure. The hollow tube in the multiwalled structure is mainly composed of carbon atoms, and this new structure is referred to as a carbon nanotube, generally represented by CNT. It has two forms, the single-walled carbon nanotubes (SWNTs) and the multiwalled carbon nanotubes (MWNTs).

A multiwalled carbon nanotube is generally composed of several or dozens of SWNTs coaxially. The carbon nanotube has a diameter from less than 1 nm to dozens of nm, the side of each single-walled is composed of hexagons of carbon atoms, the length generally ranges from dozens of nm to micro level, and both ends are covered with pentagon. These SWNTs can have different chiral forms, and concentric SWNTs are bonded by using Van der Waals force. The multiwalled structure of carbon nanotubes makes its more complicated properties, and its outside diameter ranging from 2.5 to 30 nm.[3,4]

The carbon nanotube is characterized by light mass, high strength, high heat resistance, flexibility, large surface area, large surface curvature, high heat conductivity, and unique electric conductivity. Its mechanical properties are far superior as compared with other materials. Excellent Young's modulus and tensile strength enable it to be an optimal filler and reinforcement material in polymers.[5,6]

Featured by high mechanical strength, light mass, and nice flexibility, the carbon nanotube has a high ratio of length to diameter and large specific surface area, and strong action ability for it to combine with polymers physically or chemically. The interface bonding between a particle and matrix can withstand a larger load, thus realizing the purpose of increasing of strength and toughness.[7] Therefore, it can be used as reinforcement material for polymers, ceramics or metals, for the development of advanced multifunctional composites and in high-tech industries of spaceflight or automobile.[8–10]

The carbon nanotube has an excellent as a filler because of its low density, high length-diameter ratio and other features. However, the surface of the carbon nanotube is made up of well-structured hexagonal carbon rings, and there are few functional groups on it. The profile of carbon nanotube is long and susceptible to entanglement, while van der Waals force caused by p electrons increases the attraction between carbon nanotubes which are easy to get together and are not soluble in water or inorganic solvent. Thus, carbon nanotube is not easy to disperse in matrices. If the surface of carbon nanotube is rendered to have the nature of functional

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groups or purified through grafting reaction, this can not only endow the carbon nanotube with solubility and help its dispersion, but also enhances its application values. In general, unpurified carbon nanotubes are entangled and many impurities may exist. However, after purification, the influence of charge repulsion between carbon nanotubes reduces the agglomeration, improves the dispersive effect between carbon nanotubes and decreases the amount of impurities.

When carbon nanotubes are prepared by using the arc discharge evaporization method, both nano particles and impurities are generated, and these impurities, including metal catalyst and amorphous carbon, can be wrapped at the outside layer of carbon. Using TEM, the difference between of carbon nanotubes before and after purification can be studied.[11] Before purification, the outside layer of the carbon nanotube is covered with metal catalyst and amorphous carbon and other impurities; after purification treatment, metal catalyst and amorphous carbon on the carbon nanotube surface become less or disappeared.

Purification is mainly achieved through the differentiation of physical and chemical properties of metal catalyst, amorphous carbon, and other impurities, and the purification mainly includes the gas phase oxidation method, liquid phase oxidation method and gas-liquid phase method. The study on functional groups of carbon nanotubes begins from the chemical cut-off action of carbon nanotubes. In 1944, Green et al.[12] found that a opening-carbon nanotube could be obtained by chemical cut-off action with strong acid solution. In subsequent researches, Green and coworkers[13] discovered that, after cut-off by using strong acid solution, some stable chemical functional groups, such as (—OH), ($>$C$=$O) and (—COOH) are contained on the top of the carbon nanotube after opening. According to Smalley and coworkers,[14] strong acid oxidation can, on one hand, oxidize little quantity of metal catalysts, and on the other hand, cause the reaction of the side wall with the pentagon defects on the top of carbon nanotube, thus generating functional groups.

In this study, carbon nanotubes are treated in different proportions of nitric acid and sulfuric acid, leading to the carboxylization of carbon nanotubes, and the effect on internal structures is investigated.

EXPERIMENTAL

Purification for multiwalled carbon nanotubes

In this study, with the liquid phase method, MWNTs are purified to remove impurities from the surfaces; meanwhile, carboxylic reaction takes place on the surface of the carbon nanotube, generates

(—COOH), helps the dispersivity of solvents and bonding of matrices, and controls the time of ultrasonic vibration so as to cut off the length of carbon nanotubes by relying on the cavitation action, to avoid entanglement and to increase reaction points.

First, MWNTs mixed with acid of 98% sulfuric acid and 70% nitric acid in the different proportion at 50°C under ultrasonic vibration. Next, carbon nanotubes and acid solvent were separated from those acid solutions through a Teflon filter film (Mesh: 0.5 μm). After that, the filtered carbon nanotubes are rinsed with deionized water until the pH reaches about 6. Finally, the carbon nanotubes heated to 100°C in an oven of for 24 h to remove surplus water.

Instrumental analysis

Fourier transform infrared spectrometer

The sample tested in this study is impenetrable by light, and therefore, the reflective Fourier transform infrared spectrometer (FTIR) can be used. The scanning range of experiment is 400–4000 cm^{-1}, and during the test, the number of scanning with the air as background is kept the same. The resolution of the (FTIR) was about 32 cm^{-1} and the scanning number was 64 in this testing.

Raman spectrograph

The Raman spectrograph used in this study is a Renishaw–inVia Raman, and the light source used is 519.5 nm. The resolution is about 1 cm^{-1} and the scanning number is 1 in this measurement. The light source adopted it has a higher frequency and stronger dispersion strength, and the determinator is more sensitive to blue and green lights. Scanning range was 100–3200 cm^{-1} and time of exposure was 10 s.

Thermograrvimetric analyzer

The thermogravimetric Analyzer used in this study is a Thermal Advantage Software, TGA Q500. Hear rate was 10°C/min, heat range was 50 to 800°C and sample weight was about 9–11 mg in a nitrogen and air heat oven.

Scanning electron microscope

A scanning electron microscope (SEM), model: JEOL, JSM-6360/LV, was used to observe the dispersivity of carbon nanotubes before and after purification. The specimen surface was sputtered with gold. The distance of specimen to detector was 15 mm in the SEM observation.

RESULTS AND DISCUSSION

The removal of the impurities from the carbon nanotubes is not a easy job. In addition, because of the chemical stability and without any functional groups on the surface of carbon nanotubes is not easy to dissolve or disperse in general organic solvent or aqueous solution.

For the purpose of this study, carbon nanotubes are purified with the liquid phase method, by using nitric acid and sulfuric acid on the purified degree of carbon nanotubes in different proportions of 1 : 1, 1 : 3, and 1 : 5. The experimental samples and codes are shown in Table I. The purification method used in the research is to generate oxidation on the surface of the carbon nanotube by using a mixture of nitric acid and sulfuric acid at 50°C and to damage the structures of carbon atoms on the five-membered ring and six-membered ring of graphitic sheets of carbon nanotubes. The oxidation mechanism for carboxylation is that, after treating with a mixture of nitric acid and sulfuric acid, SO_2, NO_2, and free oxygen atoms can be generated. If two free oxygen atoms combine one of the carbon atoms, a molecule of CO_2 gas is formed, and this process gives rise to the damage the structure of carbon nanotubes. On one hand, carbon nanotubes have the cut-off effect and long carbon nanotubes are cut into fullerene pipes with a length of several 100 nm. On the other hand, the carbon atoms at the rupture of carbon nanotubes are increased in terms of reactivity because of unsaturation and are easy to be oxidized into carboxyl groups and other functional groups. When one oxygen combines with one carbon atom, one carbonyl group (C=O) is possibly formed on the carbon nanotube, and further combines with H^+, OH^- and free oxygen atoms in water to form (—COOH) or hydroxyl group (—OH) as well as functional groups containing oxygen. The major chemical reaction for oxidation is as follows:

$$H_2SO_{4(l)} + HNO_{3(l)} + C_{(s)} \rightarrow SO_{2(g)} \uparrow + NO_{2(g)}$$
$$\uparrow + CO_{2(g)} \uparrow + H_2O_{(l)}$$
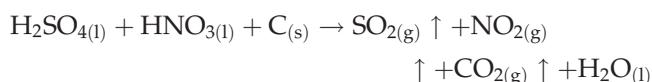
TABLE I
Experimental Samples and Codes

Sample	Code
Multiwalled carbon nanotube	CNT
Noncarboxylic multiwalled carbon nanotube	CNT00
Proportion of acid mixture of carboxylic multiwalled carbon nanotubes[a]	CNT13

[a] HNO_3 : H_2SO_4 / 1 : 3 (vol : vol).

After oxidation, carboxyls are produced at the walls or ends of carbon nanotubes. In combination with cavitation effect caused by ultrasonic vibration, carbon nanotubes are cut into fullerene pipes with a length of several hundred nm. The stronger van der Waals force on the surface of untreated carbon nanotube easily entangles the carbon nanotubes. Depending on the purification treatment, the dispersive effect of carbon nanotubes can be reached.

A thermal analysis controller is used to preliminarily judge whether liquid phase oxidation can increase the purity of carbon nanotubes. Figure 1 represents a thermal gravimetric analysis diagram of nonpurified carbon nanotubes in nitrogen. When the carbon nanotube is heated to 900°C in burning, only 10% of its weight is lost. The 10% weight lost is due to impurities and carbon nanotube with incomplete structure in carbon nanotubes. The steady carbon–carbon structure on the surface became a better heat resistance The perfect hexagon crystal structure formed by sp^2 bonds of carbon nanotube enables the carbon nanotube to bear higher temperatures and have better heat stability. Purified carbon nanotubes are subject to obvious weight loss at about 200°C, especially in nitric acid and sulfuric acid in the proportion of 1 : 3. This demonstrates that more functional groups are obtained in this proportion, and moreover, the surface structure of the carbon nanotube is damaged more seriously. Therefore, in relation to heat stability, the proportion 1 : 3 of nitric acid to sulfuric acid is worse.

Raman spectrograph is the most sensitive instrument to appraise carbon nanotubes.[9,15–19] The carbon nanotubes adopt a characteristic mode of vibration absorption and within the range of 100–400 cm^{-1}, characteristic absorption bands may occur, while the diameter of a single-walled carbon nanotube is inversely proportional to the reciprocal of the length of a characteristic band. Therefore, the characteristic vibration mode can be used to obtain the diameter of a carbon nanotube. MWNTs are formed by coaxial crimping of SWNTs, so the diameter of a multi-walled carbon nanotube cannot be obtained through the characteristic mode of absorption vibration of Raman spectra. A carbon nanotube can be deemed to be formed through the crimping of flat graphite, and has the unsaturated double-bond structure on the graphitic structure, and thus a characteristic band can be measured from Raman spectra. At 1580 cm^{-1} represents the degree of crystallinity of graphitic sheets; and the absorption peak is referred to as G-band (Graphic band), sp^2 bonding of carbon–carbon. A perfect graphitic sheet is composed of hexagons of carbon atoms, and when pentagons and heptagons or defects occur in other positions, defect D-bands (Disorder band) can take place at 1338 cm^{-1}; D-band accounts for the crystal defect degree
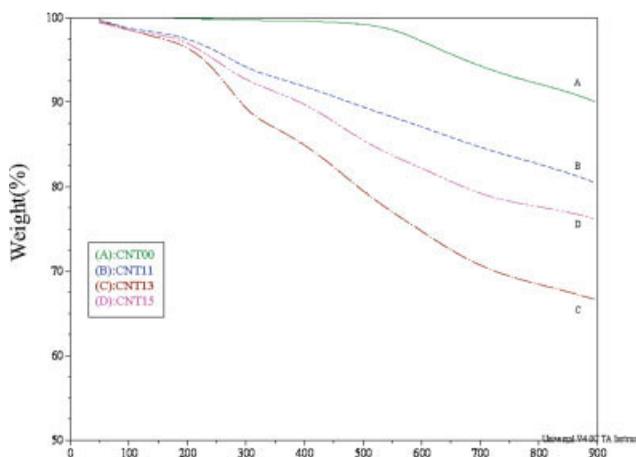
Figure 1 Thermal gravimetric loss of carbon nanotubes in the presence nitrogen environment. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com]

of graphitic sheets. Therefore, purity of carbon nanotube can be judged by means of G-band and D-band. Figure 2(A) shows the Raman spectrum graph of nonpurified carbon nanotubes, the special G-band

of carbon nanotubes is found at 1582 cm^{-1}, while D-band occurs at 1344 cm^{-1}, having the same strength as that of G-band. The two have almost identical absorption strength, indicating that the crystal structure of the surface of the carbon nanotube is not integrated well, which is caused by excessive defects on the graphitic crystal layer. Such excessive defects are mainly attributable to the bending of carbon nanotubes, because the structure of the carbon nanotube is provided with pentagons and heptagons, which cause the bending of carbon nanotubes. The carbon nanotube used in this experiment has a length of about 50 μm, and thus the carbon nanotube bends much more obviously, the D-band show a strong Raman activity. In addition, at 1460 cm^{-1} is due to resonance of C=C bond on the C_{60} of the carbon nanotube of its net structure. From the carbon nanotube structure, at the end of the carbon nanotube, it may be composed of half a C_{60} structure or is one of the impurities in terms of carbon nanotubes. Hence, when there are a number of such substances or structures on carbon nanotubes, producing the G-band. Figure 2(B–D) display the effects of characteristic G-bands of nonpurified
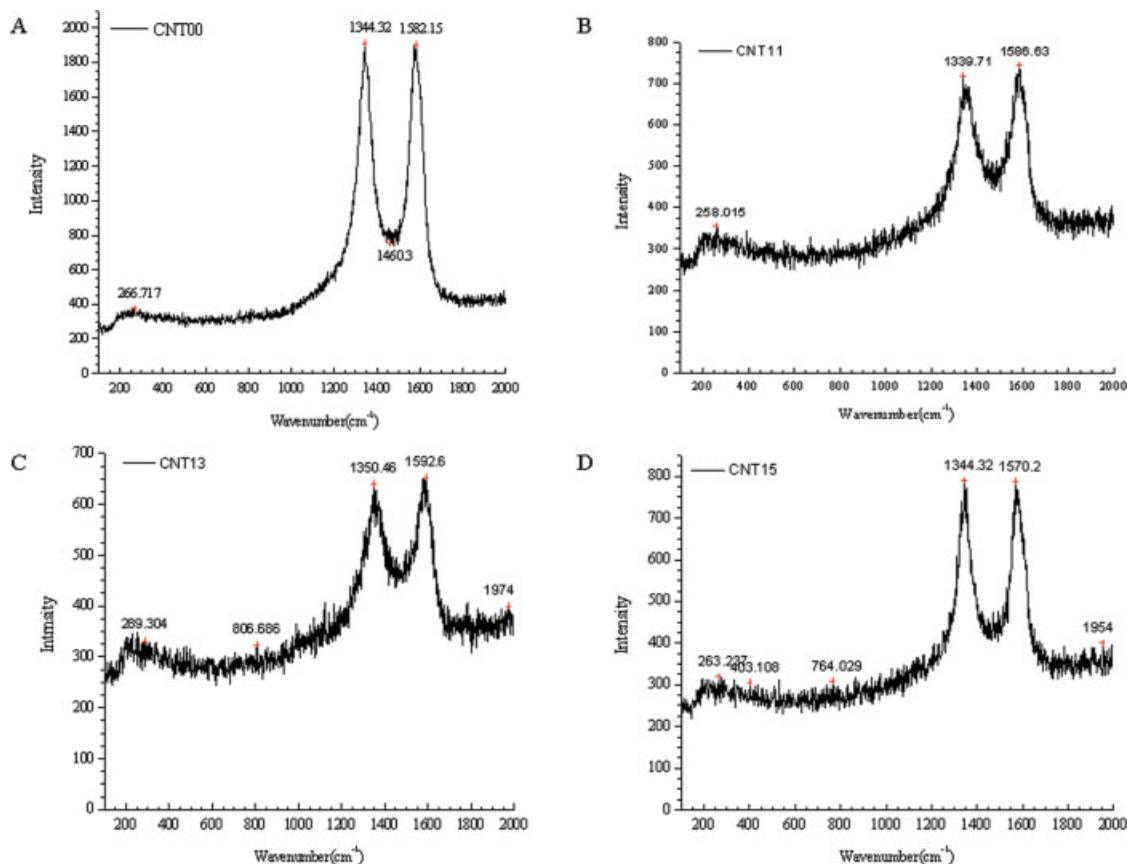
Figure 2 Effects of different proportions of strong oxidants on the characteristic absorption bands of nonpurified and purified carbon nanotubes (A) CNT00, (B) CNT11, (C) CNT13, (D)CNT15. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

TABLE II
The Effect of CNT on the Corresponding I_D/I_G Ratio Upon Treatment with Deferent Acid Concentration

| CNT of different acid concentration treatment	[a]I_D/[b]I_G ratio
CNT00	0.96
CNT11	0.90
CNT13	0.89
CNT15	1.01

[a] I_D, Intensity of the D-band peak.
[b] I_G, Intensity of the G-band peak.

and purified carbon nanotubes in different proportions of strong oxidant. Apparently, in the proportions of 1 : 1, 1 : 3, and 1 : 5 of nitric acid to sulfuric acid, no absorption signal is observed at 1460 cm^{-1}, and it can be inferred that no C$_{60}$ structure appears on the surface of the carbon nanotube, for example, this may be caused by the damage to the cover of the top of the carbon nanotube or C$_{60}$ in the carbon nanotube.

Within the low-frequency zone of Raman spectra, faint absorption signals are found respectively, at 258 and 252 cm^{-1}, indicating the existence of little SWNTs. On the basis of the research done by Bandow et al.,[20] if the number of waves from the low-frequency zone of Raman spectra is divided by a constant, the diameter of a carbon nanotube can be obtained as follows, $d = 234/v$, where d: diameter, v: number of waves, the diameter being 0.91 and 0.93 nm respectively. When the proportion of nitric acid to sulfuric acid is 1 : 5, more absorption signals are generated in the low-frequency zone because of the destruction of MWNTs. According to the information on D-band and G-band, at the position of 1582 cm^{-1}, the nonpurified carbon nanotube has a larger absorption peak than that of a purified carbon nanotube, this is because functional groups are produced on the surface of the purified carbon nanotube because of the breakage of the double-bond (C=C) by strong acid solution, resulting in weaker G-band signal is than that of nonpurified carbon nanotube. It is also found from D-band that, due to the strong acid solution, the carbon nanotube decreases the defects of structure, and absorption peak is obviously weaker than that before purified. Table II shows the valves of I_D/I_G intensity of the D-band peak to the G-band peak on CNT by different acid treatments. We obtain CNT13 with minimum value (0.89) of the intensity ratio of the D-band peak to the D-band peak (I_D/I_G ratio) of the Raman spectrum. The smaller I_D/I_G ratio shows fewer defects in this purified carbon nanotube. Among them, the proportion of 1 : 3 of nitric acid to sulfuric achieves a satisfactory result (proven in TGA drawing).

In the course of reaction, the wall or ends of the carbon nanotube can turn into functional groups containing oxygen, including carboxylic acid (—COOH), carbonyl groups (>C=O) and hydroxyl groups (—OH). By means of FTIR, the functional groups of purified carbon nanotubes have been studied. Figure 3 shows the FTIR spectrum of a purified carbon nanotube. Because there are no reactive functional groups on the surface of the carbon nanotube, the spectrum displays only noise without any absorption feature. According to Figure 3(B), in the proportion of 1 : 1 of nitric acid to sulfuric acid, signals remain unclear under FTIR. Figure 3(C) displays a purified carbon nanotube in the proportion of 1 : 3 of nitric acid to sulfuric acid. Obviously, the carbonyl group (C=O) absorption band is seen at 1740 cm^{-1}, and hydroxy stretching (O—H) is observed at 3500 cm^{-1}. Mainly after the treatment, carboxylic acid generated on the carbon nanotube surface forms a characteristic functional group.

There is a stronger van der Waals force on the surface of the treated carbon nanotube, and thus the carbon nanotube is susceptible to entanglement. By means of SEM, morphological changes have been studied, as shown in Figure 4, which shows that purified treatment of acid solution can achieve dispersive effect of carbon nanotubes. Figure 4(B–D) represent the morphological images of fixed time of ultrasonic vibration in the different proportions of nitric acid to sulfuric acid. It is known that acidic treatment can remove impurities from the carbon nanotube and help the carbon nanotube to achieve better results of dispersion.
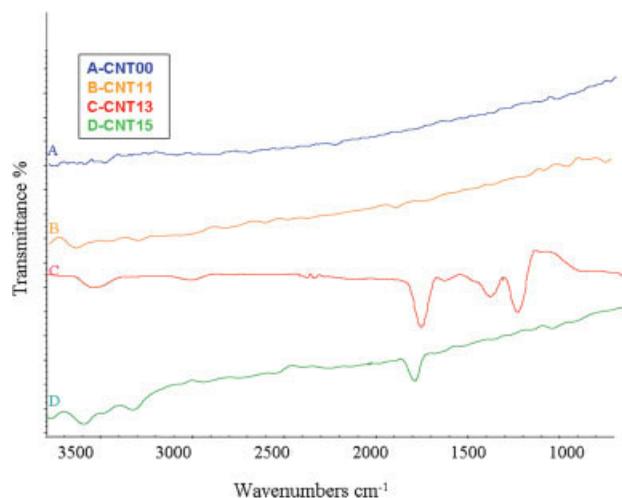
Figure 3 FTIR spectra of nonpurified and purified carbon nanotubes in different proportions of strong oxidant. (A) CNT00, (B) CNT11, (C) CNT13, (D) CNT15. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
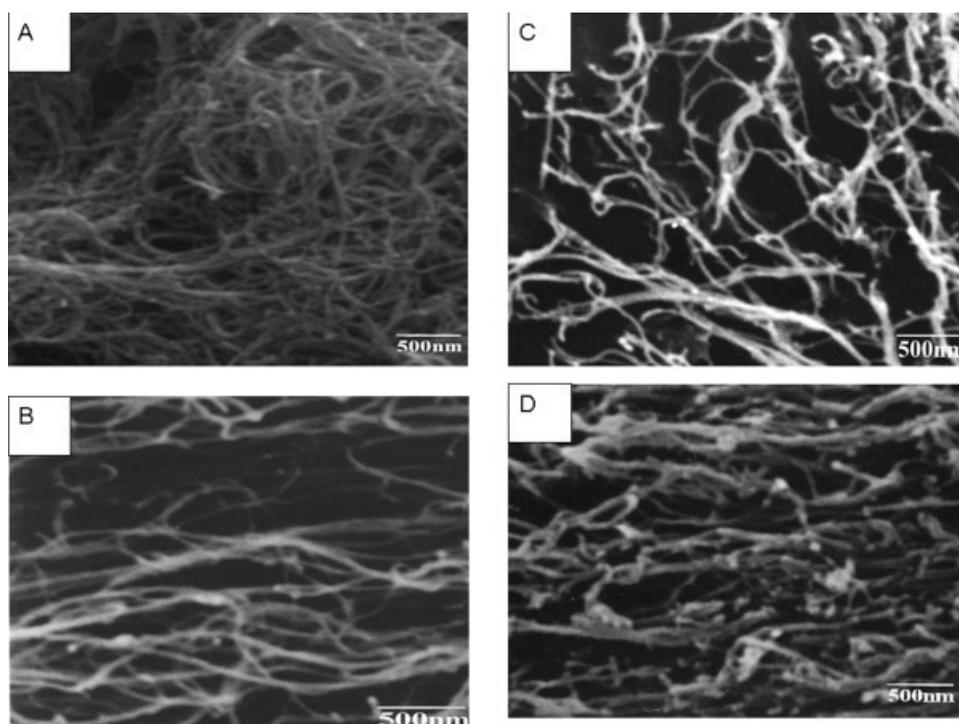
Figure 4 SEM images (×20,000) showing the morphological changes in nonpurified and purified carbon nanotubes. (A) CNT00, (B) CNT11, (C) CNT13, (D) CNT15.

CONCLUSIONS

In this study, carboxyl groups and other functional groups are modified on the surface of the carbon nanotube by using nitric acid and sulfuric acid in different proportion. However, oxidation can damage the structure of carbon atoms on the surface of the carbon nanotube. Carboxylic carbon nanotubes can be steadily dispersed into polar solvents to improve the agglomeration because of van der Waals force attraction. Therefore, the carboxylation can enable the multiwalled carbon nanotube be soluble to enhance the dispersivity of carbon nanotubes.

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