INFLUENCE OF PLASMA AND ACID TREATMENTS ON ELECTRICAL PROPERTIES OF MULTI-WALL CARBON NANOTUBES

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Introduction

Carbon nanotubes (CNTs) tend to agglomerate to form bundles via strong van de waals interactions between nanotubes. This is a challenge in the most applications because it reduces their efficiency. Therefore, functionalization of CNTs that leads to increase of interactions between nanotubes and other materials is necessary. What must be considered during functionalization of CNTs, is that functionalization must not considerably diminish their excellent properties.

Generally, CNTs are functionalized covalently or noncovalently. In noncovalent functionalization approach, such as molecular wrapping in which long molecules are wrapped around the nanotubes, the nanotubes structure is not altered. However, the interaction between the wrapping molecules and nanotubes is weak.

In covalent functionalization approach, functional groups are attached to the nanotubes surface. The nanotubes are usually functionalized by the current methods including wet chemistry and exposure to high temperature vapors [1]. However, due to the rather harsh conditions involved, these methods can damage the structure of the nanotubes and considerably affect their properties, such as electrical property [2, 3].

Acid treatment is a wet chemistry method that is widely used to functionalize nanotubes. It has been showed that this method not only destroys graphical structure of the nanotubes but also cuts the nanotubes and shortens their length [3, 4]. The intensity of these damages depends on treatment conditions (time, temperature, acid concentration etc.).

Destroying graphical structure of nanotubes can lead to increase of their electrical resistivity. This can reduce the efficiency of nanotubes in many applications like conductive polymer nanocomposites [5]. Plasma treatment is another approach to functionalize nanotubes covalently. Nanotubes can be functionalized by plasma treatment without any large change in their structural integrity [6] because plasma treatment can be performed at low temperature even as low as room temperature and with very short treatment duration.

The aim of this work is to investigate and compare electrical properties of multi-wall carbon nanotubes (MWCNTs) functionalized by oxygen plasma and also by nitric acid treatments, respectively. For this purpose the surface electrical resistivity of the entangled networks of nanotubes, also known as buckypapers, is reported.

Experimental

Purified MWCNTs were provided by Shenzhen Nanotech Port Co. Ltd (China). Prior to functionalization, MWCNTs were annealed by exposing to a flow of He and heating to 1000^{o}C at a rate of 5.0^{o}C /min. They were retained at 1000^{o}C for 30 minutes. The temperature was then reduced to room temperature under He flow. By this pretreatment most of the defects and functional groups, formed on the surface of the nanotubes during synthesis and purification processes, can be removed. In plasma method MWNTs were functionalized by dielectric barrier discharge (DBD) plasma in air under a power of 90 W and treatment time of 5 min. Details of the used plasma set-up have been described in our previous work [7]. In order to functionalize MWCNTs by acid treatment, they were refluxed in a concentrated nitric acid for 4 h.

The annealed and functionalized MWCNTs buckypapers were prepared through multiple steps of nanotubes dispersion and suspension filtration. For this purpose 100 mg of MWNTs were dispersed in 20 ml of deionized water and were sonicated for 30 min. The suspension was then immediately filtered. In order to measure the surface electrical resistivity, the buckypapers were cut into rectangular shapes (10 mm × 3 mm). A two-point method was used with contacts formed by a silver paint.

Results and discussion

A typical scanning electron microscopy (SEM) image of the annealed MWCNTs demonstrating nanotubes with a high degree of purification is shown in Figure 1.

The Fourier transform Infrared (FT-IR) spectra of functionalized nanotubes shown in Figure 2 indicate the formation of oxygen-containing functional groups on the surface of nanotubes functionalized by both the plasma and

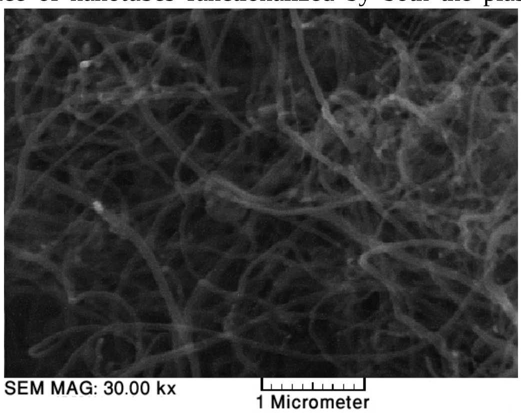

Fig. 1 SEM image of annealed MWCNTs.

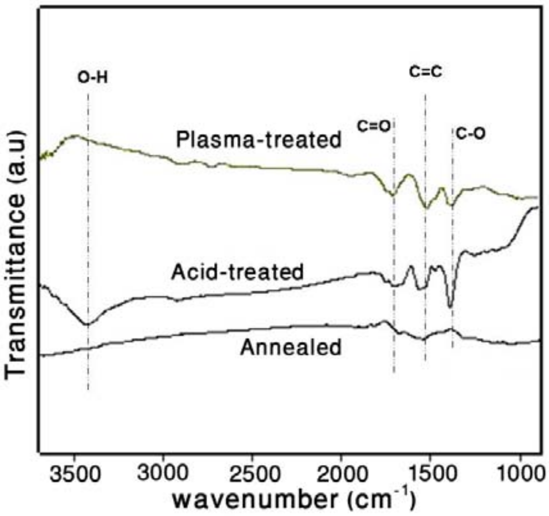

Fig. 2 The FT-IR spectra of annealed and functionalized MWCNTs.

acid treatments and absence of these groups in the annealed sample. All three samples show a peak around 1538 cm^{-1}, corresponding to C=C stretching band of the nanotubes. This peak indicates the presence of functional groups and defects on the nanotubes surface. As is observed, functionalization of the annealed MWCNTs by either plasma or acid treatment leads to an increase in the intensity of this peak. Two peaks at 1660 and 3330 cm^{-1} which are seen in spectrum of acid-treated MWCNTs, are attributed to acidic carbonyl and hydroxyl groups, respectively. The multiple peaks seen at 1660–1720 cm^{-1} can be assigned to different functional groups such as carboxyls, ketones and lactones. The peak at 1383 cm^{-1} characterizes acidic C–O bond. In the spectrum of plasma-treated MWCNT, the multiple peaks at 1680–1740 cm^{-1} can be attributed to carbonyl group of the oxygen-containing groups such as lactone and carboxylic anhydride, and the peak at 1375 cm^{-1} can be attributed to esterified C–O bond [7].

Figure 3 shows the electrical surface resistivity of the buckypapers prepared from the annealed, acid-treated and

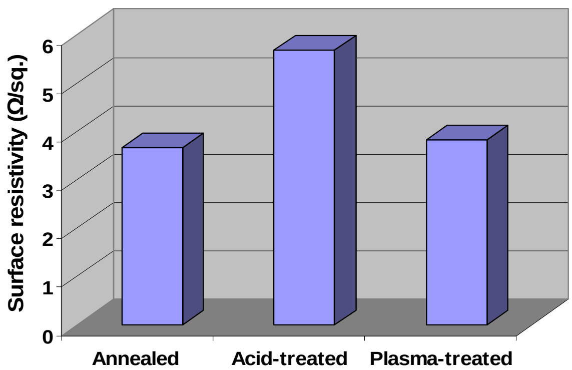

Fig. 3 Electrical surface resistivity of the buckypapers prepared from annealed, acid and plasma-treated MWCNTs.

plasma-treated MWCNTs. As it is seen, the acid treatment increases the electrical surface resistivity while the plasma treatment does not change it considerably. It has been accepted that the acid treatment destroys the graphical structure of the nanotubes and cuts them to shorter length [2-4]. It seems that destroying graphical structure of nanotubes and shortening their length have led to increase of the electrical surface resistivity of the buckypapers prepared from acid-treated MWCNTs. It also seems that the plasma treatment has not considerably changed the electrical surface resistivity as compared to the acid treatment because it has very less damaging effect on structure of nanotubes [2-4, 6]. According to other researcher's findings [8], it looks that the plasma treatment functionalizes only the uppermost surface layers of the nanotubes.

Conclusions

In this study, MWNTs were functionalized by DBD plasma in air and also by refluxing in concentrated nitric acid for 4 hour, respectively. The influence of these two types of treatments on the electrical properties of the nanotubes was investigated. Our results showed that the acid treatment increases the electrical surface resistivity of buckypapers made from these nanotubes, while the plasma treatment does not change it considerably. Based on these results one can conclude that our plasma treatment approach is more suitable than the traditional acid treatment for making functionalized nanotubes with superior electrical properties.

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