



Removal of some impurities from carbon nanotubes

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Abstract

A non-destructive mild oxidation method of removing some impurities from as-grown carbon nanotubes (CNTs), including single-wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes (MWNTs), by H₂O₂ oxidation and HCl treatment, has been investigated, and somewhat pure carbon nanotubes have been prepared. The CNTs from which some impurities were removed have been evaluated by transmission electron microscopy (TEM) and temperature programmed oxidation and gas chromatography (TPO–GC).

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1. Introduction

Carbon nanotubes (CNTs), with excellent electronic, mechanical, and structural characteristics, can be applied to new functional materials and devices, such as field emission displays, supercapacitors, secondary batteries and various composites [1–5]. Since Iijima discovered the CNTs [6] in 1991, many methods of synthesizing CNTs have been discovered [7–12]. However, most as-grown CNT powders contain not only CNTs but also other carbonaceous impurities such as amorphous carbon, fullerenes, nanocrystalline graphite, and metallic catalysts. These impurities have limited the superior performance of CNTs, and resulted in a serious impediment to their application to new

functional materials and devices. To speed up the CNTs' application, the problem of removing the impurities should be addressed first. The purification process should not destroy the structure of CNTs when the impurities are removed. In the literature [13–18], two methods are generally proposed to purify the as-grown CNTs, the dry and the wet method. The dry method refers mainly to the oxidation by air, oxygen or carbon dioxide at certain temperatures; the wet method commonly refers to the oxidation using a solution of KMnO₄, K₂Cr₂O₇ or concentrated HNO₃. These processes are either difficult to control or easy to damage the integrity of the CNTs' walls.

This Letter reports a novel process of removing some impurities from CNTs synthesized by the catalytic chemical vapor deposition (CCVD). It contains two steps. The first step is H₂O₂ oxidation for removing the carbonaceous impurities, which are produced as a byproduct when the CNTs are synthesized; and a final step with an HCl treatment

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for removing the catalyst metal, predominantly the Ni nanoparticles addressed in this Letter. As a result, carbon and catalyst from CNTs were removed without a damage of the nanotubes. The catalysts in the CCVD act mainly to catch and absorb the C atoms, and then catalyze the atoms to form CNTs. The residual catalyst particles are considered as impurities once the CNTs have formed. In addition, we found that transmission electron microscopy (TEM) plus TPO–GC could characterize the purity of CNTs more closely and more adequately than TEM, SEM, TGA, XRD, Raman Spectrum, or others [19–21] when they are applied separately.

2. Experimental

The as-grown MWNTs and SMNTs were produced by CCVD, in which the CH_4 or C_2H_2 were converted into CNTs at 700 and 1000 °C in the presence of the Ni– La_2O_3 catalyst. The impurities of as-grown CNTs thus prepared can be categorized in two types, the carbonaceous ones, such as amorphous carbon, fullerenes, nanocrystalline graphite, and the metallic catalysts. The procedure for the removal of some impurities was as follows: First, the prepared CNTs were submerged into an H_2O_2 solution and simultaneously ultrasonified for 12 h at 60 °C, and then the solution was centrifuged and filtered. The carbonaceous impurities were removed from the as-grown CNTs at this step. Next, the CNTs treated in the aforesaid way were successively submerged into an HCl solution, ultrasonified for more than 6 h, then centrifuged and filtered again. The metallic catalyst impurities were removed in the final step. This results in somewhat pure carbon nanotubes. The as-grown

CNTs and pure CNTs were characterized by TEM and TPO–GC.

3. Results and discussion

Fig. 1b shows the TEM image of purified multi-wall carbon nanotubes (MWNTs) in which some impurities have been removed by H_2O_2 oxidation and HCl treatment. Fig. 3b shows the TEM image of purified single-wall carbon nanotubes (SWNTs), which were treated by the same method. By all appearances they are cleaner than those in Figs. 1a and 3a, which are the TEM images of as-grown MWNTs and SWNTs. Contrasting the four images we can conclude that the carbon and catalyst impurities are almost completely removed in this process. In addition, the cleaned CNTs have been evaluated by TPO–GC, in which the quantity of released CO_2 at each stage is plotted and calculated while the examined CNTs (purified or unpurified) are oxidized by pure O_2 or air. Because the oxidation temperature of CNTs differs from other carbonaceous substances, the quantities of the CNTs and other carbonaceous substances can be determined by calculating the amount of the released CO_2 in the TPO process. Figs. 2a and 4a show the TPO–GC spectra of as-grown MWNTs and SWNTs. The peaks from 300 to 550 °C in Fig. 2a and those from 250 to 400 °C in Fig. 4a are due to the oxidation of amorphous carbon in as-grown MWNTs and SWNTs, whereas there are no noticeable peaks from 300 to 550 °C in Fig. 2b and from 250 to 400 °C in Fig. 4b which are the TPO–GC spectra of cleaned MWNTs and SWNTs. The peaks at 620 °C in Fig. 2a and at 640 °C in Fig. 2b result from the oxidation of MWNTs, and the weak peak at 740 °C in Fig. 2a is due to the oxi-

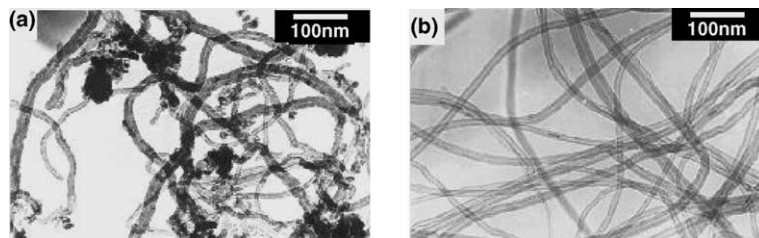


Fig. 1. TEM images of as-grown MWNTs (a), and cleaned MWNTs (b).

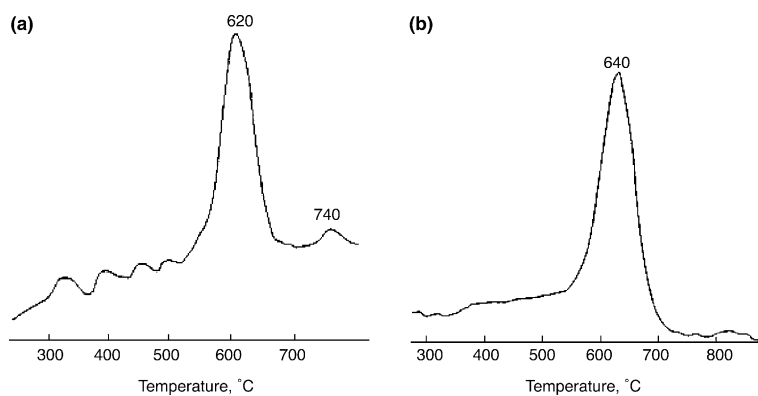


Fig. 2. TPO-GC spectra of as-grown MWNTs (a), and cleaned MWNTs (b).

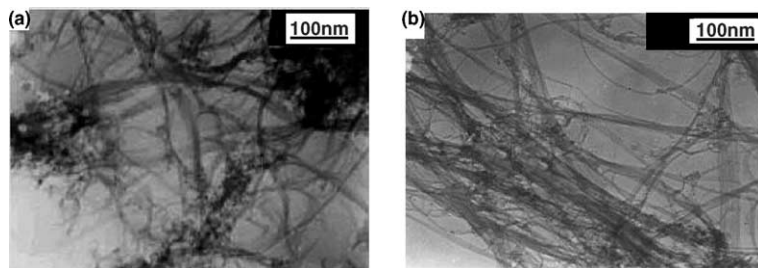


Fig. 3. TEM images of as-grown SWNTs (a), and cleaned SWNTs (b).

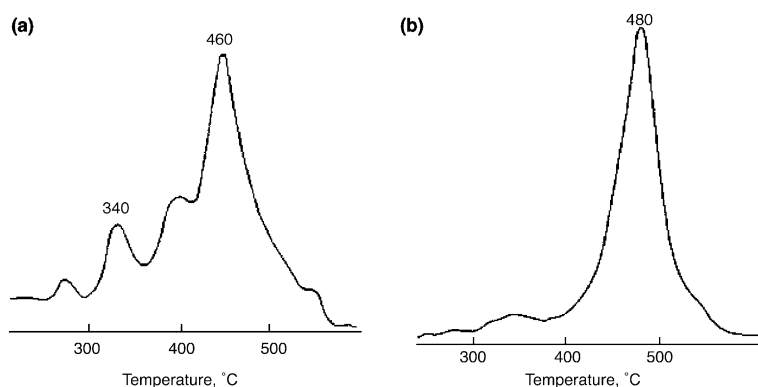


Fig. 4. TPO-GC spectra of as-grown SWNTs (a), and purified SWNTs (b).

of graphite particles. The peaks at 460 °C in Fig. 4a and at 480 °C in Fig. 4b show the oxidation peaks of MWNTs. Figs. 2 and 4 indicate that the oxidation temperature of CNTs before removing the catalysts is a little lower (about 20 °C) than that

of CNTs after removing the catalysts. This revealed that the residual catalysts speeded up the oxidation process of the CNTs. From these comparisons we can confirm that those carbonaceous impurities have been removed from the as-grown CNTs.

Furthermore, the percentage of CNTs within the raw CNTs admixture, namely the composition of CNTs, can be calculated from the characteristic peak areas of CNTs in the TPO–GC spectra.

The oxidation ability of the H_2O_2 is moderate, so the CNTs would not be eroded and the removal process of some impurities is easy to control. Moreover, the only byproducts produced in this process are H_2O and CO_2 . In addition, we found that the effectiveness of removing the impurities within the as-grown CNTs admixture by H_2O_2 oxidation and HCl treatment was better than if the steps were reversed. Perhaps this is because the residual catalyst particles within as-grown CNTs also act as the catalysts when removing the carbonaceous impurities.

4. Conclusion

In conclusion, the H_2O_2 oxidation followed by HCl treatment is a useful and suitable method for the removal of some impurities within as-grown CNTs (including MWNTs and SWNTs). The integrity of the CNTs' structure is not compromised and there are no byproducts except H_2O and CO_2 . Cleaner carbon nanotubes can be obtained by this method. Moreover TPO–GC plus TEM has proven to be a suitable method for checking the cleanness of CNTs, as it is able to measure both the cleaning of CNTs qualitatively and the percentage of each component of the examined CNTs admixture quantitatively.

Acknowledgements

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