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Microwave-assisted purification of HIPCO carbon nanotubes

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A very easy way for improving the purity of carbon nanotubes using a domestic multimode microwave oven is reported, in which selective burning of metal particles helps remove most of the iron content.

Carbon nanotubes (NTs) are under intense investigation owing to their spectacular mechanical and electronic properties.[1–3] In fact, not only do single-walled carbon nanotubes (SWNTs) show a very high aspect ratio (length-to-diameter ratio),[4–6] high strength and extraordinary flexibility and resilience,[7] but they can also be used as nanoelectronic components[8–12] and as nanotips for microscopy.[13] Many ways are currently available for the production of SWNTs, which include arc-discharge,[14] HIPCO process[15] or pulsed laser vaporization (PLV).[16] The HIPCO material, produced by Carbon Nanotechnologies, Inc. (CNI),[17] consists of a very high quality material, in which the major impurity is the iron catalyst. Since a reasonable purity is required for applications of SWNT, several methods have been recently devised to purify nanotubes from either metal catalysts and/or amorphous carbon.[18] Attempts to remove the metal catalyst from the soot include treatment with strong oxidizing acids, such as concentrated nitric acid,[19,20] or air oxidation at high temperatures.[21] Here we report a new method, based on the treatment of the raw nanotubes in a microwave oven, under air and with no solvent, which has led to a strong depletion of the iron content in the soot. We also report an accurate estimate of the iron content using atomic absorption analysis.

As declared by CNI, the raw HIPCO tubes contain between 20 and 30% of iron content in weight. In fact, we have measured the content of iron using atomic absorption analysis, finding an average value of 26% (w/w).† A typical transmission electron micrograph (TEM), obtained with the raw material, is shown in Fig. 1. Several dots are clearly visible, indicating the presence of iron particles overcoated with carbon clusters.

In order to remove most of the iron content in the HIPCO tubes, we have devised a method consisting of two fundamental steps: (i) the raw nanotubes were subjected to microwave heating under ambient air conditions, (ii) the resulting powder was then washed with concentrated hydrochloric acid to remove the soluble oxidised iron.

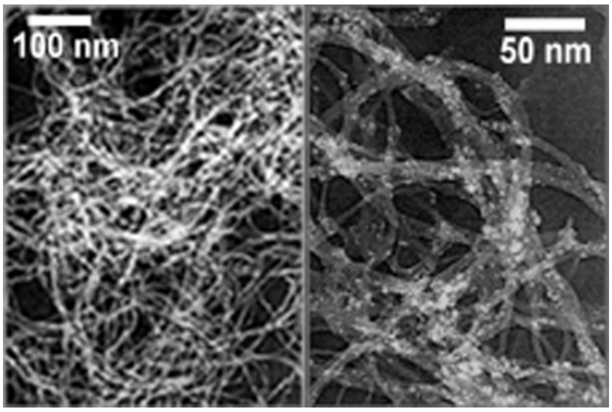

Fig. 1 Transmission electron microscopy image of raw HIPCO tubes, at low (left) and high (right) magnification.

A standard multimode microwave oven for domestic use was employed (MIELE M 638 EC). Raw HIPCO tubes as obtained from CNI appear as a very light ash. In order to obtain a more compact material to handle, the SWNT were soaked in diethyl ether. After evaporation of the solvent, the tubes consisted of a packed solid, which could be easily weighed. Therefore, 50 mg of tubes in an Erlenmeyer flask, covered with a glass plate, were placed inside the oven. The flask was then subjected to microwave heating using a power of 80 W. An immediate lightening occurred, which tended to decrease until a complete stop after 5 sec. The flask was removed from the oven; the mass was shaken gently with a spatula and then resubmitted to microwave heating. This process was repeated for a total time of 5 min of microwave irradiation. Each time that the sample was placed in the oven, lightening restarted to occur. The sample was then washed with concentrated HCl (35%): a typically yellow colour developed, due to dissolved Fe^{3+}. The mixture was centrifuged and the solution was removed. The solid was then washed with water, methanol and ethyl ether and then dried. After the washings, the material amounted to 25 mg. The entire process (microwave treatment and acid washings) was repeated twice, to ensure the maximum removal of iron. After the second treatment, the total weight was reduced to 19 mg. The resulting material was analysed by atomic absorption for the determination of iron,‡ while the quality of the tubes was checked by TEM analysis.

The iron analysis gave 16% (w/w) for the first run and 9% (w/w) after the second heating and washing. Further treatment with microwave and acid did not lead to any change in weight or to any substantial decrease of the iron content.

In a second, parallel procedure, 50 mg of raw tubes were exposed to the microwave treatment for 20 min, followed by washing with concentrated HCl, water, methanol and ethyl ether. In this case, no intermediate washings were applied and the time of exposure to microwave heating was extended. The sample was analysed by atomic absorption, which gave a content of iron of 7% (w/w or 1.5% atomic percent).

The purification process and the quality of the resulting tubes were checked by TEM. Fig. 2 shows that, while the quality of the tubes had remained similar to the original material, most of the iron spots had disappeared.

It has already been shown that metal catalysts from the production of SWNT accelerate the oxidation of carbon.[21] It is clear that the microwave heating is selectively directed to the iron particles. We therefore expect that the high temperatures, which are locally reached under microwave irradiation, should be able to selectively oxidise the carbon shells that surround the metal particles, while the more distant nanotubes should remain intact. In the presence of air, Fe is oxidised to Fe_2O_3, which can therefore be removed with acid washings, without prolonged refluxing or sonication-assisted extractions. At the same time, amorphous carbon is converted to CO_2,[21] thus explaining the decrease of weight in the sample.

We have also attempted the purification of SWNT or MWNT supplied by other companies. For instance, a sample of SWNT purchased from Bucky-USA did not show the same behaviour

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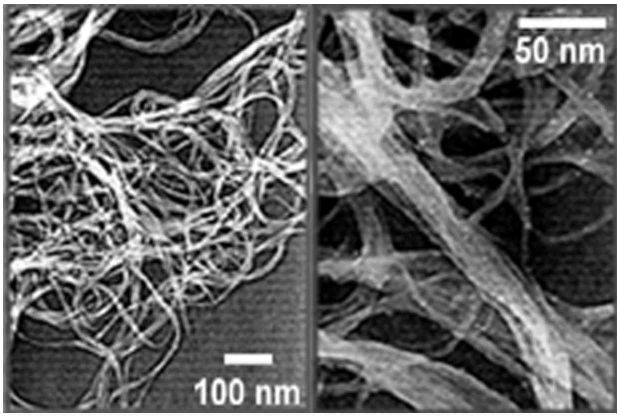

Fig. 2 Transmission electron microscopy image of HIPCO tubes after microwave and acid washing treatment, at low (left) and high (right) magnification.

as the HIPCO nanotubes when subjected to the microwave treatment. The difference could be that only samples of nanotubes with a high content of metal may be purified using the procedure reported in this paper.

In conclusion, we report a very simple new method for decreasing the iron content in raw HIPCO nanotubes. In principle, this technique can be scaled up to reasonable amounts to make the process competitive with existing purification techniques.

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Notes and references

† 1 mg of nanotubes (raw or purified) was treated with 2 ml of concentrated nitric acid (65%) for 24 h at reflux temperature. After this, 3 ml of hydrochloric acid was added and the mixture was stirred for an additional 6 h. The yellow solution was transferred into a volumetric flask and analysed by atomic absorption.

‡ A suspension of SWNT in diethyl ether was sonicated for 30 sec. One drop of the resulting mixture was deposited onto a copper grid (3 mm, 200 mesh, coated with formvar film). After evaporation of the solvent, the grid was introduced in the TEM microscope. The analysis was performed using a TEM Philips 208 at an accelerating voltage of 100 kV.

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