Microwave single walled carbon nanotubes purification

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A new single walled carbon nanotubes (SWCNTs) purification procedure has been developed; it consists in a combination of air treatment and acid microwave digestion leading to a high purity SWCNTs material; the procedure reaches high metal removal percentages and the operation time is drastically reduced compared to conventional acid reflux treatments.

The production of SWCNTs in macroscopic amounts[1–3] has led to a significant amount of research on the physical and chemical properties of this unique material. Their potential uses range from components in integrated circuits, logic gates, flat panel displays to nanoscale motors.[4–6] Nevertheless, challenges remain in the control of their fabrication and purification before carbon nanotubes can be used for technological applications. Most of SWCNTs purification methods[7] involve oxidation using mineral acids and/or gas phase oxidation to remove catalytic metal particles and amorphous carbon. So far, these processes are not very efficient especially concerning the removal of impurities and require long treatment times.

In this work, a new method to purify SWCNTs is described. The method takes advantage of the ability of microwaves to homogeneously heat a solution while stirring at molecular dipole level. The disruption and recomposition of the dipoles at high frequency considerably improves the diffusion rates and the transport properties.[8] This leads to high percentages of metal removal and drastically reduced operation times compared to the conventional acid reflux methods.

SWCNTs were produced by the arc-discharge method using Ni/Y (4/1 atomic ratio) in the graphite precursor.[1] The as-grown soot sample was subjected to acid treatments in a high performance microwave digestion unit (mls 1200 mega). 3M HNO_3 and HCl (37 wt%) acid solutions at different conditions of time and temperature were used. The resulting suspensions were centrifuged (10000 rpm for 4 h) and the supernatant acids were decanted off. The sediments were re-suspended in deionized water, three times centrifuged and decanted and finally vacuum filtered on 3 μm pore polycarbonate filter membrane.

In order to remove the amorphous carbon after the microwave treatment, the samples were oxidised at 300 °C for 90 minutes and finally annealed for 10 h at 950 °C in a stream of argon. The purified samples were characterised by inductive coupled plasma spectroscopy (ICPS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The Ni and Y content of the raw material as well as the samples treated under different conditions in the microwave reactor were determined by ICPS and are indicated in Table 1.

It can be seen that HNO_3 treatments result in higher removal of Ni and Y than HCl treatments. A temperature increase improved the nickel removal for both the HNO_3 and the HCl treatments, being considerably higher for HNO_3

For HNO_3 treatments at 100 °C, reaction times longer than 2 h led to higher metal concentration in the resultant material. The

Table 1 Microwave treatments carried out on as grown SWCNTs and corresponding metal contents

Acid/temperature/time	Ni (wt%)	Y (wt%)
Raw material	17.5	2.6
3 M HNO_3/100 °C/1 h	6.3	0.8
3 M HNO_3/100 °C/2 h	3.4	0.7
3 M HNO_3/100 °C/3 h	8.0	1.7
3 M HNO_3/200 °C/1 h	3.1	0.7
3 M HNO_3/200 °C/2 h	3.0	1.1
37 wt% HCl/100 °C/1 h	14.2	2.0
37 wt% HCl/200 °C/1 h	12.6	1.9
37 wt% HCl/200 °C/2 h	11.9	2.2

highest metal removal was reached with a 3 M HNO_3 solution at 200 °C for 1 h. By increasing the digestion time from 1 to 2 h no further removal was achieved at this temperature. This indicates that there is a small amount of metals associated to the SWCNTs material difficult to remove as has also been reported by Dujardin *et al.*[9]

To investigate the nature of the metals easily removed and those remaining in the sample after the purification process, the raw and acid treated samples were analysed by XPS. Ni 2p and Y 3d core-level spectra of the raw sample were recorded and are shown in Fig. 1. The most intense peak of nickel, the Ni $2p_{3/2}$, presents two components, one at 854 eV (77%) and another one less intense at 856.5 eV (23%). The first component is located 1.8 eV above the position of metallic nickel. Such a large shift can not be attributed to size effects but rather to the formation of a nickel compound and could correspond to a nickel carbide layer formed at the surface of the metallic nickel particle. The second component is characteristic of Ni^{2+} ions in an oxygen environment[10] and could be due to a very thin layer of nickel oxide since no satellite line is detected. The Y 3d core-level spectrum displays the characteristic Y $3d_{5/2}$/Y $3d_{3/2}$ doublet with the former peak at 156.8 eV (Fig. 1). The binding energy (BE) of the Y $3d_{5/2}$ component is located a little above the usual position of the Y_2O_3 (156.4 eV), which obviously corresponds to Y^{3+} in an environment of oxygen atoms. These results point out that the metal nanoparticles are superficially oxidised or/and are surrounded by a a few layers of metal carbides since no
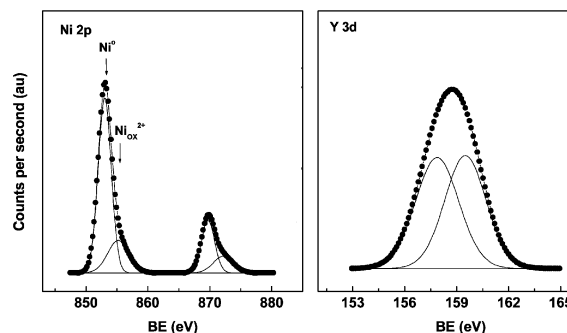

Fig. 1 Ni 2p and Y 3d XPS spectra of the as grown SWCNTs.

binding energies corresponding to metallic states are determined by XPS.

In contrast to the ICPS data, the XPS analysis on the treated samples did not show any signal corresponding to Ni and Y.

This shows that the Ni and Y content, as determined by ICPS, was in the form of nanoparticles covered by carbon layers which prevent their detection by a surface sensitive technique such as XPS. This suggests that this carbonaceous material covering the metal nanoparticles hinders their removal by the acid treatments.

Going one step further, the acid treated sample was sputtered with Ar$^+$ ions at 2 keV for 5 min to pull up the carbon layers covering the metallic nanoparticles. After this treatment, the XPS technique detected the presence of Ni with the same BE as the raw sample; the Ni $2p_{3/2}$ peak showed two components at 854 eV (69%) and 856.5 eV (31%) and Y in trace amounts. This indicates that the remaining metal nanoparticules not removed by the acid treatment were in the same oxidation state as those removed in the purification step clearly pointing out that the carbonaceous material covering the metal particles prevents their elimination.

To make the metal nanoparticles more accesible to the acid treatment, the raw samples were oxidised in air at 350 °C before the microwave treatments. In Table 2, the metallic contents of the air pre-treated and subsequently microwave treated samples are shown.

Table 2 Microwave treatments carried out on air oxidised SWCNTs

Oxidation/acid/temperature/time	Ni (wt%)	Y (wt%)
350 °C, 10 min/37 wt% HCl/100 °C/1 h	6.1	1.2
350 °C, 10 min/3 M HNO$_3$/100 °C/1 h	3.7	0.6
350 °C, 1 h/3 M HNO$_3$/100 °C/1 h	1.7	0.4
350 °C, 1 h/3 M HNO$_3$/200 °C/1 h	2.4	1.2

The best results were obtained after air treatment for 1 h at 350 °C and 3 M HNO$_3$ at 100 °C for 1 h. It can be seen that by increasing the temperature to 200 °C the amount of metal after the microwave treatment is higher than after the treatment at 100 °C. This is due to a higher destruction of carbonaceous material under more severe conditions as can be deduced from the lower yields of material recovered, 56 wt% at 100 °C and 39 wt% at 200 °C.

As general result, the combined treatment enhances the metal removal considerably. Nevertheless, some metal nanoparticules remain, probably those covered by defect-free graphitic material not oxidised during the thermal pre-treatment.

The yields of the remaining material after each purification step were: 55 wt% for the pre-oxidation treatment, 56 wt% for the microwaves acid digestion, 34 wt% for the post-oxidation step and 85 wt% for the annealing.

The evolution of the carbonaceous material with the purification process was followed by Raman spectroscopy. The Raman spectra (excitation line 514 nm) in Fig. 2, show in all cases the radial breathing modes (RBM) in a range of frequencies from 140 to 210 cm^{-1} characteristic of the SWNTs as well as the splitted tangential modes at 1500–1600 cm^{-1} indicating the presence of SWCNTs in all samples. After the microwave acid treatment, an increase of the D band around 1350 cm^{-1} can be seen indicating the presence of amorphous carbon probably formed due to the partial destruction of the SWNTs. However, subsequent thermal treatments result in a decrease of the D band pointing out the removal and reorganisation of amorphous carbon with the oxidation steps.
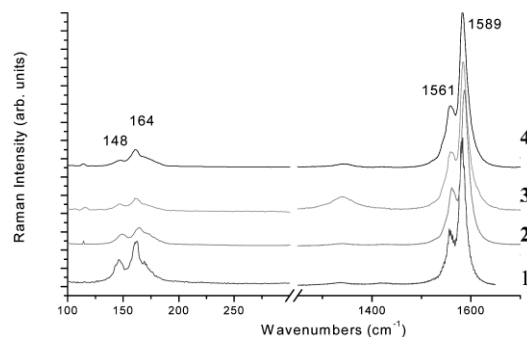

Fig. 2 Raman spectra at 514 nm of the raw SWCNT sample (1), the pre-oxidised sample (2), the microwave treated sample (3), and the post-oxidised sample (4).
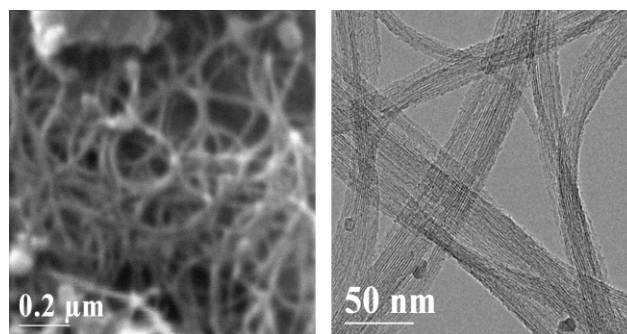

Fig. 3 SEM and TEM images of the purified SWNT material.

After the final annealing step, a high purity SWCNT material has been obtained as can be seen by SEM and TEM (Fig. 3).

Summarising, we have developed an efficient purification procedure that drastically reduces the treatment time to 1 h compared to conventional acid reflux times of 45 h and this process results in high purity SWNT material.

Notes and references

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