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Study of purification process of single-walled carbon nanotubes by thermoanalytical techniques

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Abstract

The thermal behaviour of commercial Carbolex single-walled carbon nanotubes (SWCNTs) both as-received and after purification by a novel method has been studied by thermogravimetric/derivative thermogravimetric/difference thermal analysis (TG/DTG/DTA). Purification from metal catalysts (Ni and Y) has been successfully obtained using 0.1 M I_2 in iso-propanol instead of the usual concentrated HNO_3. The final residues of thermal analysis have been characterised by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). The gathered results showed that the as-received SWCNTs burns out in a one-step between 573 and 923 K, whereas the SWCNTs treated with HNO_3 become highly hygroscopic. The I_2-iso-propanol-treated SWCNTs showed three overlapped exothermic peaks between 500 and 973 K in the DTA curve, which allowed separating amorphous carbon from SWCNTs by air-thermal treatment at 573 K. The graphite-like compounds, which are present in both untreated and treated SWCNTs, does not burn up to 1173 K.

Keywords: SWCNTs; Thermal analysis; SEM–EDS; Purification

1. Introduction

Carbon nanotubes (CNTs), discovered in 1991 by Iijima [1] and nowadays produced in large scale, are of increasing interest for their extraordinary and unique mechanical, thermal and electronic properties. Unfortunately, whatever the preparation methods used to produce CNTs they are formed by bundled, which are strictly entangled with a large amount of impurities like others carbonaceous materials (amorphous carbon and graphite) along with small catalytic metal particles. Therefore, in order to evaluate their unique properties for practical use they have to be at first separated and purified.

Although a plenty of purification methods may be found in literature, none of them satisfy fully all the goals. Purification methods are usually based on the use of both gas and wet oxidation or their combination. Oxidation under air, oxygen, ozone, H_2S and CO_2 atmosphere at high temperature has been used to selectively eliminate the unwanted amorphous carbon materials [2–6]. However, owing to the close similarity of the chemical properties of the CNTs with the remained carbonaceous materials the yield is very low with the metal impurities still being encapsulated into CNTs.

Oxidation in the liquid phase at a given temperature using strong oxidative agents such as HNO_3, $HClO_4$ and KMO_4/H_2SO_4 gives rise to higher yield, about 50-wt.%, with respect to gas oxidation [7]. But it has been observed that the strong oxidative conditions of the acids produced damage of the length of the tube with the methods being sometimes very sophisticated and tedious [8]. It is therefore recognised that mild conditions must be found to alleviate the problem of the low yield after purification of CNTs.

It is well known that halogens may be intercalated into carbon at room temperature [9]. The possibility for selective oxidation of unwanted carbonaceous materials at different temperatures by intercalation with bromine of as-prepared CNTs has been reported [10,11]. At lower temperature than the burning of CNTs the intercalated carbonaceous compounds may be selectively volatilised.

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In the present paper, we report a simple methodology to purify as-received Carbolex single-walled carbon nanotubes (SWCNTs) commercialised by Aldrich company. The method consists in the treatment of SWCNTs with 0.1 M I_2 in iso-propanol under heating for the oxidation of the metallic catalyst impurities. The treatment with iodine allows to volatilise selectively the amorphous carbonaceous materials at lower temperature than the burning of CNTs. This study was conducted by thermogravimetric (TG) and differential thermal (DTA) techniques. Flame and graphite atomic absorption analysis, scanning electron microscope (SEM) observation and energy dispersive X-ray spectroscopy (EDS) were also used for CNTs characterization.

2. Experimental

2.1. Instrumentation

Thermal behaviour of samples was investigated by differential-thermogravimetric analysis (DTA-TG apparatus SDT 2960, TA Instruments, Dorking, England). Samples between 3 and 5 mg were heated at 10 K min^{-1} up to 1173 K in dynamic air (flow rate 100 ml min^{-1}). α-Al_2O_3 was used as reference material. Samples were run in platinum crucibles. Temperature scale calibration was carried out by using standard calcium oxalate. After runs, the sample residues were recovered and submitted to further characterization.

Ni and Y metals content in the leached solutions was determined by flame and GF AAS (Varian SpectrAA 220FS).

Morphology was studied by scanning electron microscope (SEM, Jeol JSM-5510LV). Energy dispersive X-ray analysis was performed with an IXRF EDS-2000 System. The conditions were: accelerating voltage 25 kV, spot size 21 and working distance 20 mm. The powder specimens were dispersed separately in iso-propanol by ultrasonication. A drop of the suspension was deposited and allowed to dry onto the metallic face of the SEM slab.

The samples were weighed with a micro balance (AND HM-202) with 0.00001 g accuracy. Flask and reflux condenser system with hot plate were used.

2.2. Samples

As-received Carbolex SWCNTs were supplied from Aldrich. The CNTs were prepared according to the catalytic process, based on arc discharge, using Ni(Y) as catalysts without any purification. The pristine carbon deposit (named collaret) was a mixture of graphitic carbon (usually encapsulating metallic particles of Ni and Y), amorphous carbon, SWCNT bundles and metallic particles of Ni and Y.

2.3. Procedure

An accurately weighed amount of CNTs (about 200 mg) was introduced in a 25-ml flask, added 3 ml 0.1 M I_2 in iso-propanol and refluxed at 240 °C for 12 h. Simultaneously, the same amount of CNTs was treated with 3 ml 6 M HNO_3 and refluxed at 120 °C for 4 h. Then the suspension was filtered through a Teflon filter with pore size of 1 μm in a Millipore filtration apparatus under vacuum and washed thoroughly with deionised water and then with iso-propanol. The filtrates and the water washings were transferred to a 25 ml volumetric flask and made up to volume with 1 M HNO_3. The solutions were analysed for the metallic catalyst content.

3. Results and discussion

3.1. Ni and Y removal from SWCNTs by wet chemical treatment

The results of the AAS analysis of the washing water after treatment of the as-received SWCNTs with I_2 in iso-propanol give rise to 7.0 wt.% Ni and 5.1 wt.% Y (Table 1). For comparison purpose the carbon nanotubes have been treated with HNO_3 and the analytical results are also shown in Table 1. The two-oxidant reagents are able to eliminate metal catalysts from CNTs. Thus, metal purification may be obtained with I_2/isopropanol solution, which is a milder oxidant than nitric acid.

3.2. Thermal behaviour of SWCNTs

The TG/DTG/DTA curves of the as-received SWCNTs sample are shown in Fig. 1. The TG curve shows one well-defined weight loss between 573 and 923 K. The weight loss corresponds to about 68 wt.% of total mass, which indicates

Table 1
Results (wt.%) of AAS analysis of washing water after wet digestion in different oxidants of commercial Carbolex SWCNTs

AAS	Ni	Y
I_2/isopropanol	7.0 ± 0.2[a]	5.1 ± 0.2[a]
HNO_3	6.9 ± 0.2[a]	5.0 ± 0.2[a]

[a] Mean ± standard deviation of five measurements.

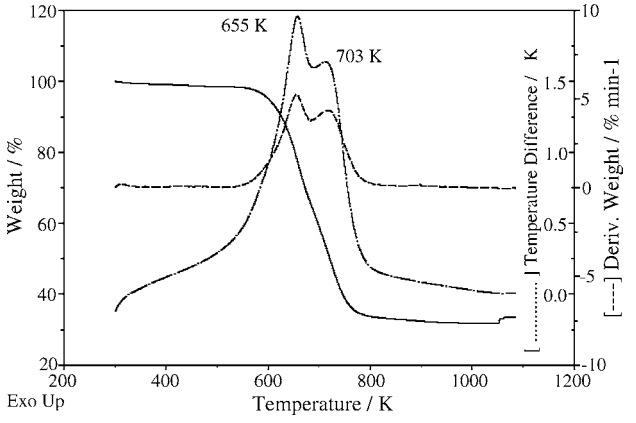

Fig. 1. TG/DTG/DTA curves of the as-received Carbolex SWCNTs. Heating rate at 10 K min^{-1} under fluxing air.

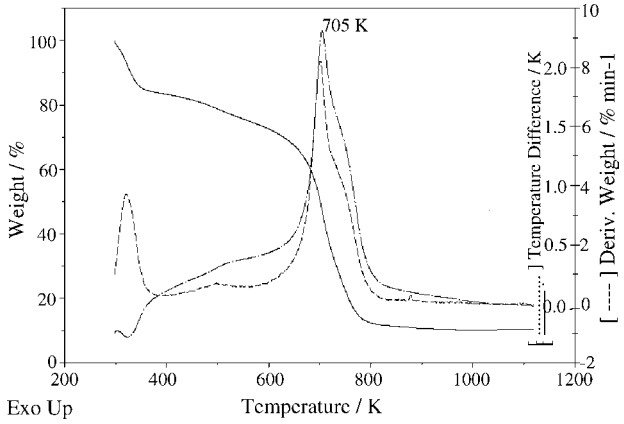

Fig. 2. TG/DTG/DTA curves of the HNO_3-treated Carbolex SWCNTs. Heating rate at 10 K min^{-1} under fluxing air.

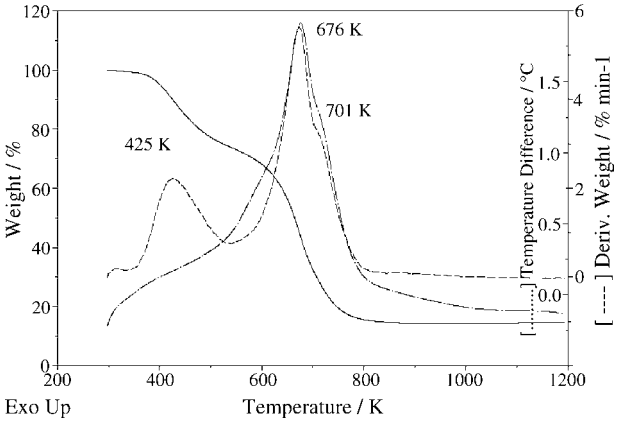

Fig. 3. TG/DTG/DTA curves of the I_2-iso-propanol-treated Carbolex SWCNTs. Heating rate at 10 K min^{-1} under fluxing air.

that mostly of carbon is burning out at temperature below 923 K. The DTG curve shows two overlapped peaks at 657 and 707 K, respectively, which may indicate the superimposition of two thermal events in this temperature range. The corresponding DTA curve shows two exothermic overlapped peaks at 657 and 703 K, respectively. According to literature data [12] the combustion of amorphous carbon occurs between 573 and 673 K, whereas the burning temperature of carbon nanotubes is between 673 and 873 K. The final residue at 1173 K corresponds to about 32 wt.% of total mass and it is composed of nickel and yttrium oxides along with carbon as computed by SEM–EDS analysis.

The TG/DTG/DTA curves of the HNO_3-treated SWCNTs sample are shown in Fig. 2. The TG curve shows an abrupt weight loss at temperature below 373 K, which was immediately followed by a weight loss up to 573 K. The weight loss is about 22 wt.% of total mass. These findings are in accordance with the results of others authors [13], who have found that the CNTs became hygroscopic after treatment with nitric acid, while some acid may intercalate into carbon nanotubes and released at temperature of about 573 K [14]. The third weight loss occurs between 573 and 923 K. The weight loss corresponds to about 67 wt.% of total mass, which indicates that mostly of carbon is burning out at temperature below 923 K. The DTG curve shows one peak at 705 K with shoulder at 723 K on the right side. One exothermic peak at 703 K with shoulder at 753 K on the right side is evidenced on the corresponding DTA curve. It is worthy to note that the beginning of combustion of carbonaceous materials occurs at temperature (onset temperature 678 K) higher than the untreated sample. The final residue at 1173 K is 11 wt.% of the total mass and it is composed of only carbon as computed by SEM–EDS analysis.

The TG/DTG/DTA curves of the I_2-iso-propanol-treated SWCNTs sample are shown in Fig. 3. The TG curve shows a weight loss between 393 and 493 K along with a peak at 425 K in the corresponding derivative curve. The total mass loss corresponds to about 25 wt.%. This effect is due to evaporation of I_2 [15], which has been not completely removed during the washing step. The I_2-iso-propanol-treated SWCNTs starts to burn in one step with onset temperature of about 513 K. The total weight loss corresponds to 58 wt.% of total mass. The DTG curve shows one major peak at 676 K, accompanied with a right-shoulder at 701 K. The corresponding

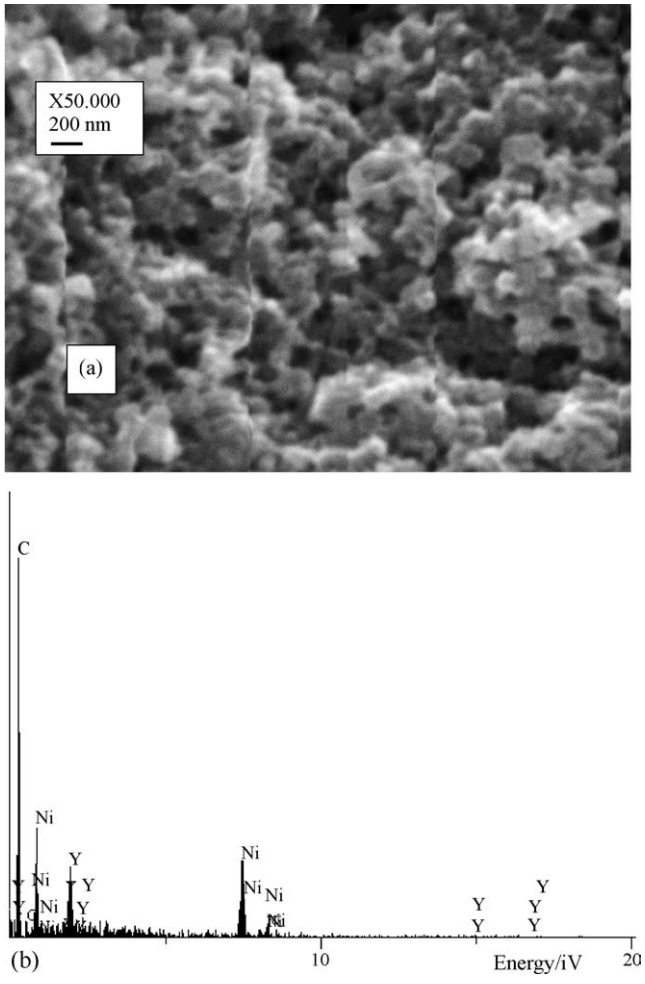

Fig. 4. SEM image of the as-received SWCNTs (a), and corresponding EDS spectrum (b).

DTA curve shows one major peak at 676 K with two shoulders at 623 and 717 K on the low and high-temperature side, respectively. The final residue at 1173 K is about 15 wt.% of the total mass and it is composed of only carbon as computed by SEM–EDS analysis.

3.3. SEM characterization of purified SWCNTs

Fig. 4 shows the SEM picture of the as-received SWCNTs sample and the corresponding EDS spectrum. The typical morphology of as-received SWCNTs is bulky particles agglomerates, whereas the corresponding EDS analysis indicates the presence of carbon with along Ni and Y particles catalysts. Any evidence of SWCNTs on the surface of the pristine SWCNTs air-thermally-treated at 603 K for 1 h (here not shown) has been found. Fig. 5 shows the SEM picture of the I_2-isopropanol treated SWCNTs sample after treatment in air at 603 K for 1 h and the corresponding EDS spectrum. As it can be seen a modified morphology is evident and tube-like structure of single-wall carbon nanotubes with along some graphitic-like compounds appears. The EDS analysis confirmed the presence of only carbon.

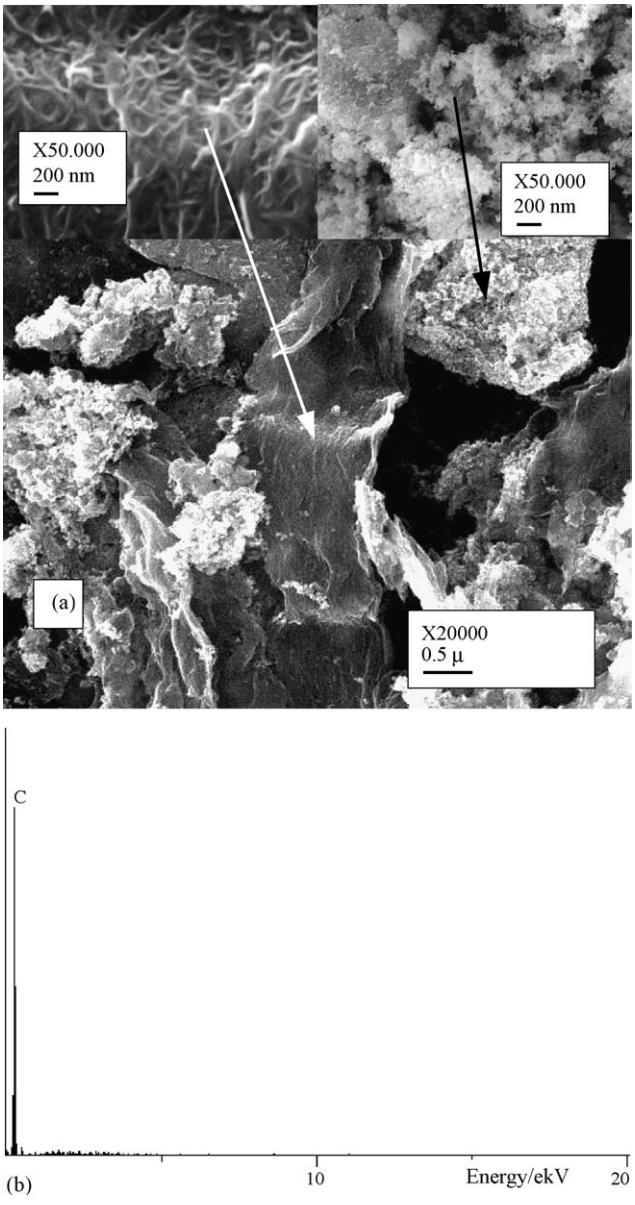

Fig. 5. SEM image of the I_2-isopropanol/air-treated SWCNTs (a) after thermal treatment at 573 K for 2 h, and corresponding EDS spectrum (b).

4. Conclusions

The treatment of SWCNTs with I_2 in iso-propanol allows the purification from metal catalysts. The burning out of amorphous carbon particles occurs at lower temperature than untreated SWCNTs. The TG/DTG/DTA techniques are powerful tools to study the purification process of SWCNTs.

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