

The use of calcination in exposing the entrapped Fe-particles from multi-walled carbon nanotubes grown by chemical vapour deposition

Sreejarani K. Pillai, Letlhogonolo Matlhoko, Chris Arendse, Suprakas Sinha Ray*
and Mathew Moodley

*National Centre for Nano-Structured Materials, Council for Scientific and Industrial Research,
P.O. Box 395, Pretoria 0001, Republic of South Africa*

* To whom all correspondences should be addressed
Tel.: +27 12 841 2388; Fax: +27 12 841 2135
E-mail: rsuprakas@csir.co.za

Abstract

Multi-walled carbon nanotubes (MWCNTs) were synthesized by chemical vapour deposition method. The effect of calcination at temperatures ranging from 300-550 °C, in exposing the metal nanoparticles within the nanotube bundles was studied. The degree of degradation to the structural integrity of the MWCNTs during the thermal process was studied by Raman spectroscopy, X-ray diffraction analysis, field-emission scanning electron microscopy and transmission electron microscopy. The thermal behaviour of the as-prepared and calcined samples was investigated by thermogravimetric analysis. Calcination in air, at 400 °C for 1 hour, was found to be an efficient and simple method to extract metallic impurities from the amorphous carbon shells with minimal damage to the tube walls and lengths. The nanotubes were observed to be damaged at temperature higher than 450 °C.

1. Introduction

MWCNTs have unique mechanical and electrical properties making them attractive materials for fundamental scientific studies, as well as for a wide range of applications [1], such as electron field-emission sources [2–4], nanoscale electronic devices [5,6], chemical filters and storage systems [7], and mechanical reinforcements in polymer composites etc [8,9]. Over the past decade, different synthesis techniques have been developed for carbon nanotubes. The most commonly used approaches include arc discharge [10, 11], laser ablation [12, 13] and chemical vapour deposition (CVD) [14, 15]. Among these techniques, the CVD method attracts wide interest, since the method makes large-scale production of MWCNTs, at relatively low cost, possible. However, to fully exploit the properties of nanotubes, efficient purification is needed to remove all by-products of the synthesis process, such as undesired carbonaceous phases (amorphous carbon, nanoparticles), catalyst particles and catalyst support (if any) while maintaining the original structure and lengths of the CNTs.

In several practical applications, trace-metal catalysts are more harmful than carbon impurities. Various methods have been reported for the removal of metal impurities, such as liquid phase acid

treatment [16-19], and selective thermal oxidation in air or in oxygen environment [20–22]. However, some prior literature indicates that it is hard to dissolve the metal completely when they are encapsulated within the carbonaceous shells and the tips of the nanotubes [23].

Taking advantage of the existence of different oxidation rates for different carbonaceous materials, the aim of this study was to use calcination to expose the metal catalyst residue effectively from the carbonaceous shells and nanotubes, prior to the acid treatments. Various researchers have reported different calcination temperatures to calcine the raw materials by air oxidation [24-27]. An unsuitable oxidation temperature can not fully remove the multi-layered graphitic carbons formed around the metal catalyst which prolongs the purification procedure and eventually degrades the MWCNTs. It is therefore necessary to optimize the calcination temperature and understand how the processes affect the morphology of MWCNTs.

In this work, as-prepared MWCNTs, synthesized by thermal CVD and using ferrocene as a catalyst, were used to study the efficiency of calcination to expose the metal catalyst residues. The effect of different calcination temperatures was evaluated by energy-dispersive X-ray spectroscopy XRD and TGA. The morphology and structure of nanotubes were analyzed by Raman spectroscopy, FE-SEM and TEM.

2. Experimental details

MWCNTs were synthesized by thermal CVD at atmospheric pressure using ferrocene as the catalyst and methane gas as the carbon precursor. The CVD reactor consists of a horizontal quartz tube, with a diameter 30 mm and a length 1500 mm, housed in a two-stage temperature zone split-tube furnace with a length of 90 cm. Ferrocene (1g) was placed in a molybdenum boat in the first temperature zone where it was vaporized at 200 °C. The resultant vapours were transferred to the second temperature zone by the methane gas, where the MWCNTs were grown at a temperature of 800 °C. The methane flow rate and synthesis time amounted to 30 sccm (standard cubic centimeter per minute) and 30 minutes, respectively.

The as-prepared MWCNT material was ultrasonically dispersed in toluene (500 mg / 35 ml) for 10 minutes to remove the fullerenes, filtered washed with acetone and finally, dried at 110°C for 12 h. The sample was then refluxed with 5M HCl (5 ml/10 mg) for 30 minutes to remove the metal particles on the CNT surface if any, filtered, washed with de-ionized water several times and dried at 110°C for 12 h. Calcination was carried out by placing 0.5 g of the as-prepared sample in a silica crucible in a muffle furnace at the desired temperature for 1 h. The effect of calcination was studied by repeating the experiment by varying the temperature between 300°C and 550° C with fresh samples.

Chemical and morphological features of MWCNTs were analyzed by FE-SEM, HR-TEM, EDS, XRD, Raman Spectroscopy, and TGA. Raman spectra of samples were recorded by a Raman spectroscopy (Jobin-Yvon T64000 spectroscope), equipped with an Olympus BX-40 microscope attachment. The excitation wavelength was of 514.5 nm with energy setting 1.2 mW from a Coherent Innova Model 308 Argon ion laser. The crystalline phases of the samples were determined by X-ray diffraction (PANalytical XPERT-PRO diffractometer) measurement, using Fe filtered Co K α radiation ($\lambda = 1.789 \text{ \AA}$), with variable slit at 35 kV, 50 mA. The thermal behaviour of the pristine and calcined samples was investigated by TGA using a Q500 TGA instrument under air environment. The samples were heated in platinum crucibles with an air flow of 50 ml. min⁻¹. The dynamic measurement was made between ambient and 1000° C, with a ramp rate of 10 °C min⁻¹. The surface morphology and EDS measurements were done by a Leo 1525 FE-SEM instrument. HRTEM images of the samples were obtained by a Philips CM200 electron microscopy which was operated at 100 kV.

3. Results and discussion

Raman spectroscopy is an exceedingly powerful tool for the characterization of CNTs. It can reveal the structural imperfections and information on the electronic and phonon properties of CNTs. **Fig. 1** represents the Raman spectra of pristine and calcined CVD samples. In the spectrum of the raw sample, the peak of nearly 1340cm⁻¹, the so-called D-band, indicates disordered sp²-

hybridized carbon atoms. In contrast, the peak near 1580cm^{-1} is the G-band and is related to the graphitic E_{2g} symmetry of the interlayer mode. This mode reflects the structural integrity of the sp^2 -hybridized carbon atoms of the nanotubes. These peaks are characteristics of MWCNTs. Raman spectrum may also be used to qualitatively describe the purity of the MWCNTs. An increase in the intensity ratio of the primary G-peak to that of the D-peak, i.e. I_G/I_D ratio, correlates with increasing the graphite crystallite size and a decrease in the amount of ‘unorganized’ carbon in graphitic materials in the sample. The Raman spectrum of the raw sample showed a relatively intense and broad peak at around 1340 cm^{-1} due to the presence of non-CNT carbonaceous impurities [28-30]. After calcination, the intensity of the D-band decreased gradually up to $400\text{ }^\circ\text{C}$, which points to the removal of amorphous carbon. The calcination above $450\text{ }^\circ\text{C}$ drastically reduced the intensity of the G-band, which indicates the possible destruction of MWCNTs at higher temperatures. This can be attributed to the exposure of metal particles (Fe, in this case) from the multi-shell graphitic carbons that can act as catalysts for oxidative cutting of MWCNTs, which eventually leads to structural degradation.

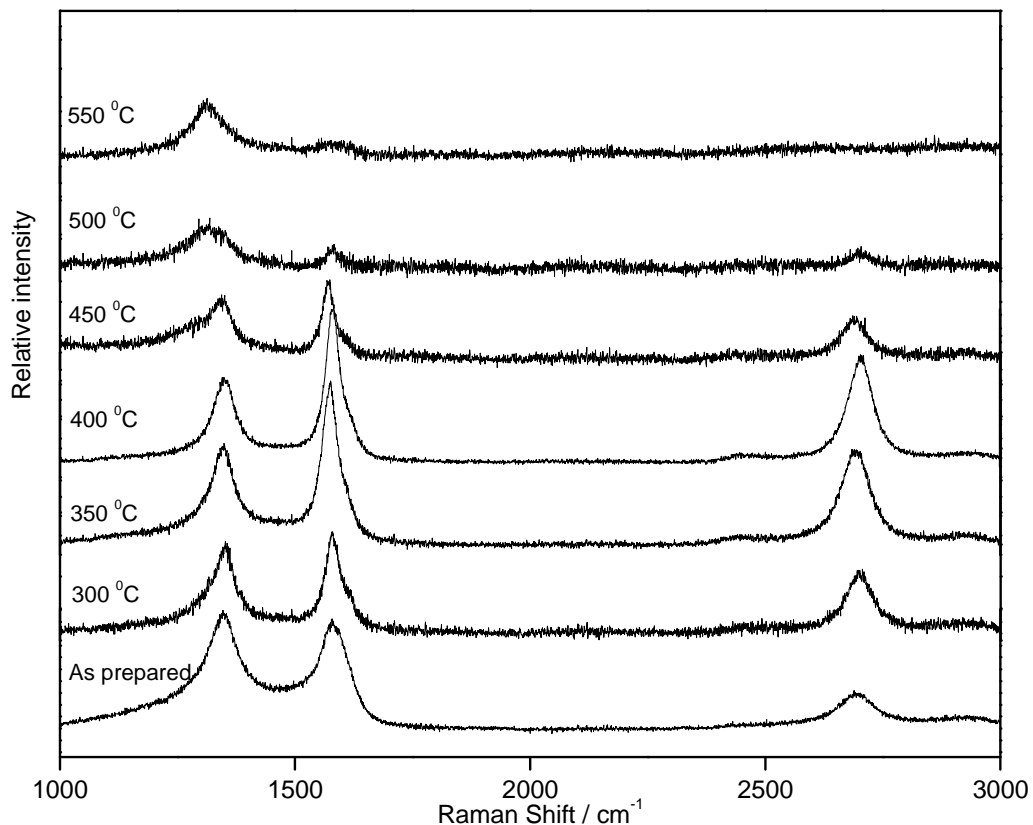


Fig. 1. Raman spectra of as prepared and various calcined MWCNTs samples.

EDS was employed to identify the concentration of the Fe-catalyst before and after calcination. Several regions of about 1 mm² were chosen to measure the elemental distribution and the results for the products before and after calcination at different temperatures are shown in **Fig. 2**. All the spectra showed Fe as the main element, an impurity from the ferrocene used during MWCNT synthesis, besides C and O. Comparing different spectra, the Fe and O peaks kept on increasing in intensity with calcination temperature. The C-peak intensity remained unchanged up to the calcination temperature of 450 °C. At higher calcination temperatures, the peak intensity decreased significantly. From the integral calculations, the weight percentage of carbon decreased from 69.9 % to 20.2 %, while that of Fe increased from 24.1 % to 57.1 % and oxygen from 5.9% to 22.8 % (see **Table 1**). These results imply that with an increase in calcination temperature, the carbon coating on the entrapped Fe-particles gradually burn off, exposing the Fe to an oxidative environment which eventually converts it to iron oxide. The appearance of a brownish-red colour on the sample after calcination, at a temperature higher than 450 °C supports the above observations.

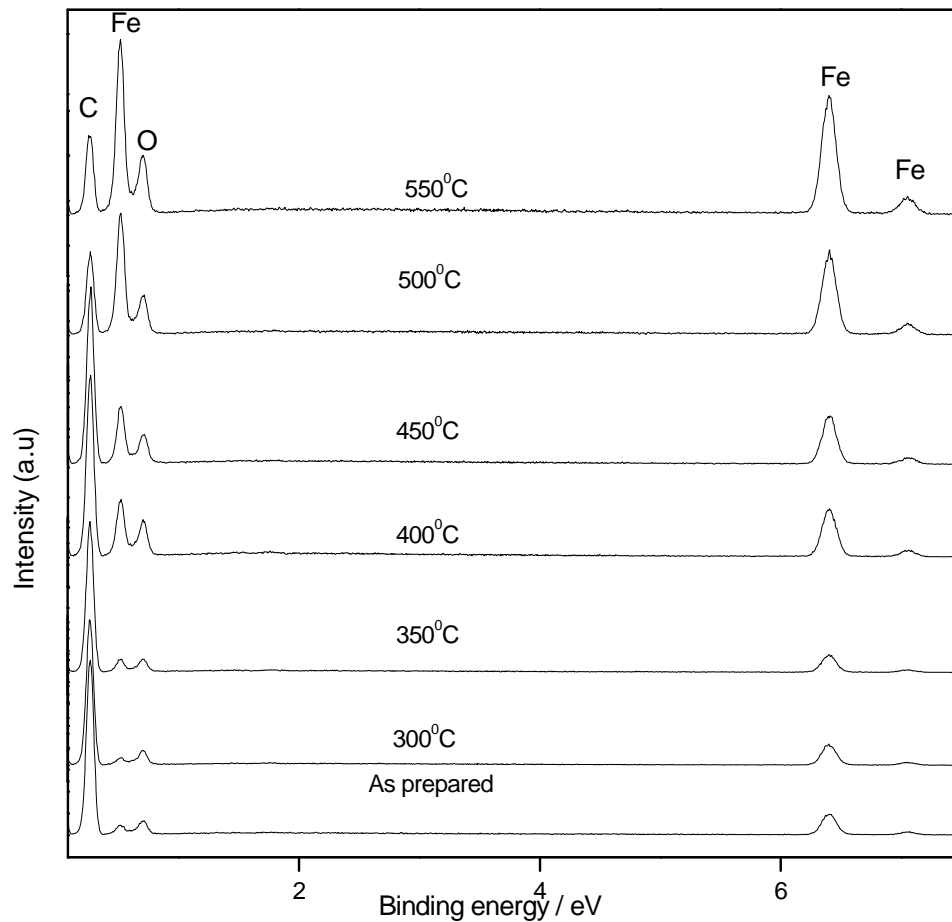


Fig. 2. EDS spectra of different CVD samples

Table 1 Weight % of different elements for CVD samples from EDS spectra

Sample	Elements weight %		
	C	Fe	O
As prepared	69.95	5.93	24.12
300 °C*	64.27	6.8	28.93
350 °C	59.18	9.93	30.89
400 °C	48.35	16.54	35.11
450 °C	44.14	17.86	38
500 °C	37.68	20.62	41.7
550 °C	20.19	22.81	57

* Sample calcined at a particular temperature

To confirm the above results, the samples calcined at different temperatures were analyzed by XRD and the diffractograms are presented in **Fig. 3**. The sample calcined at 300 °C (**Fig. 3a**) showed relatively intense peak of C (002) phase with d_{002} values of 0.34 nm characteristic of MWCNTs. In addition, peaks corresponding to Fe_2O_3 (hematite), Fe_3O_4 (magnetite) and Fe_3C (*syn*

cohenite) were detected in all the samples. Several authors have detected this Fe_3C phase as a sub product of CNTs obtained by ferrocene pyrolysis [31, 32]. From a relative peak intensity comparison of XRD patterns of these three samples, it is noteworthy that the amount of iron oxide (both Fe_2O_3 and Fe_3O_4) increases with calcination temperature with substantial reduction in the C (002) peak intensity and the results support other experimental data.

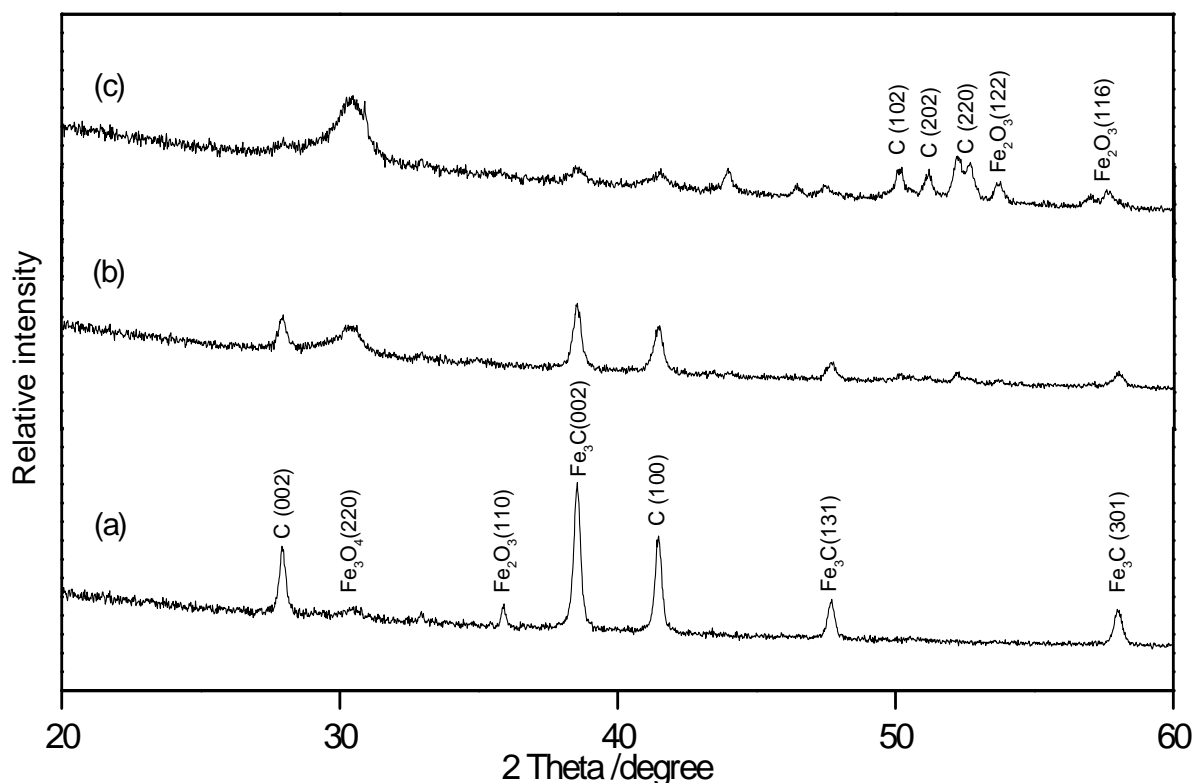
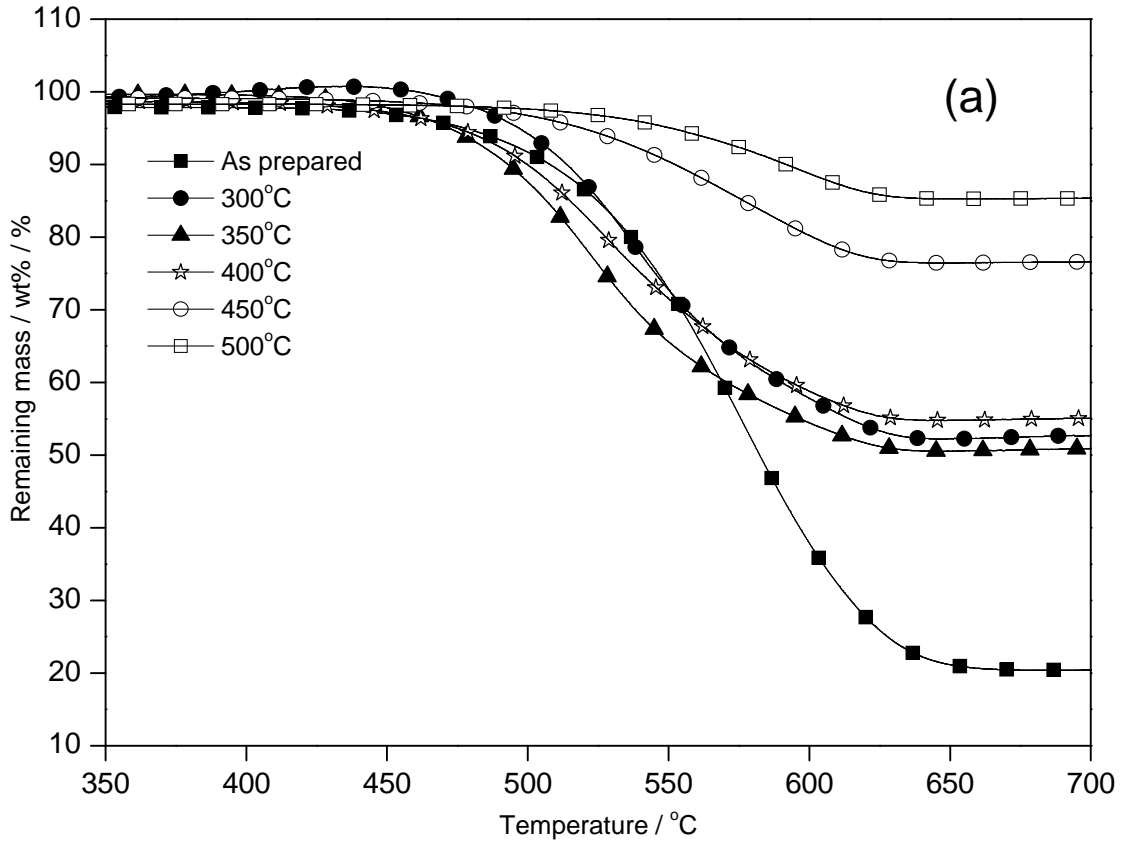


Fig. 3. XRD patterns of CVD samples calcined at different temperatures

(a) 300 °C (b) 450 °C (c) 500 °C

Figs. 4a & b represent the TGA curves and differential TGAs, respectively, obtained for the as-prepared and calcined samples. For all the samples there was only one main combustion region which may be credited to the decomposition of carbonaceous materials along with the CNTs. The weight started to reduce at nearly 420 °C for the as-prepared sample and for the samples calcined up to 400 °C. From the DTG (derivative-TGA) curves of the samples (**Fig. 4b**), it is obvious that the temperatures for nanotube combustion slightly shifted to lower temperatures after calcination at 300-400 °C. This is due to the catalytic oxidation effects of the metal present in the nanotube

sample. The metal particles from the graphitic shells exposed on calcination act as catalysts that enhance the rate of oxidation of MWCNTs. However, calcination at temperatures above 400°C, increased the oxidative stability of the tubes (Note that the nanotube burning temperatures increased to higher temperatures.), but resulted in the loss of a larger percentage of MWCNTs.



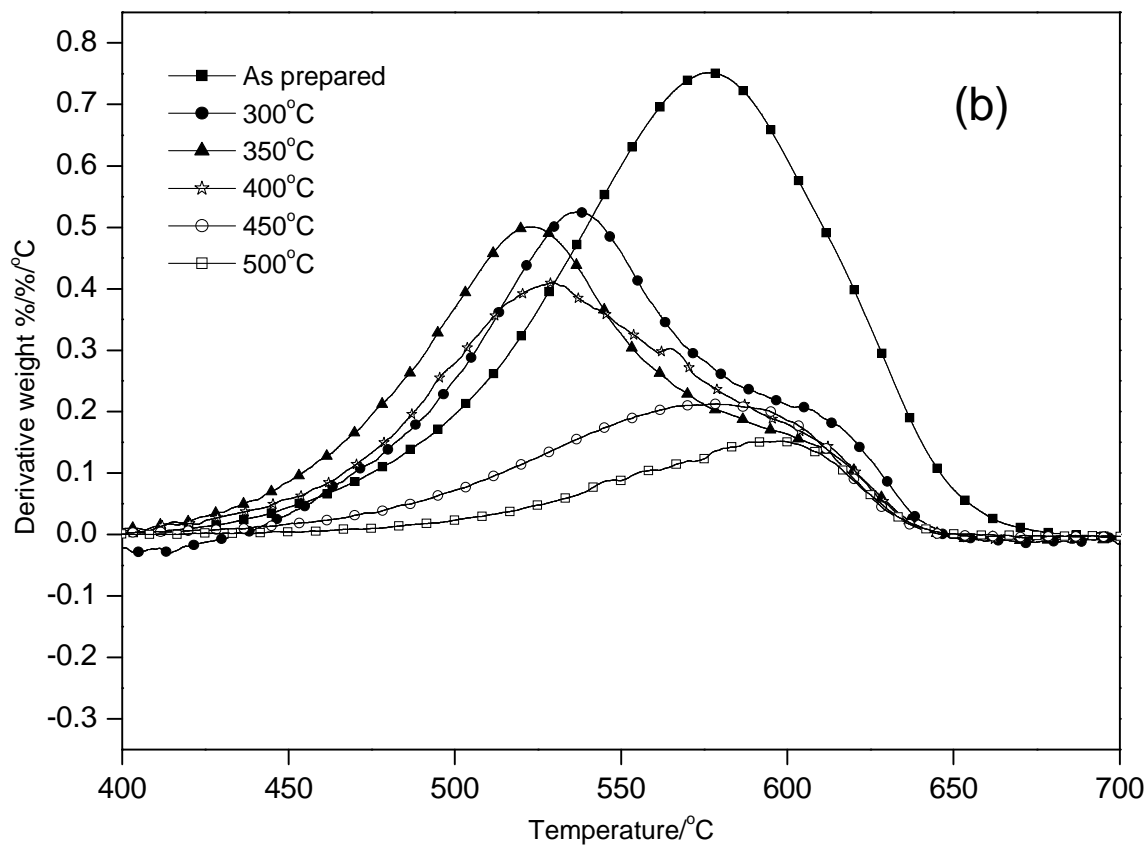


Fig. 4. (a) TGA and (b) DTG curves of different samples.

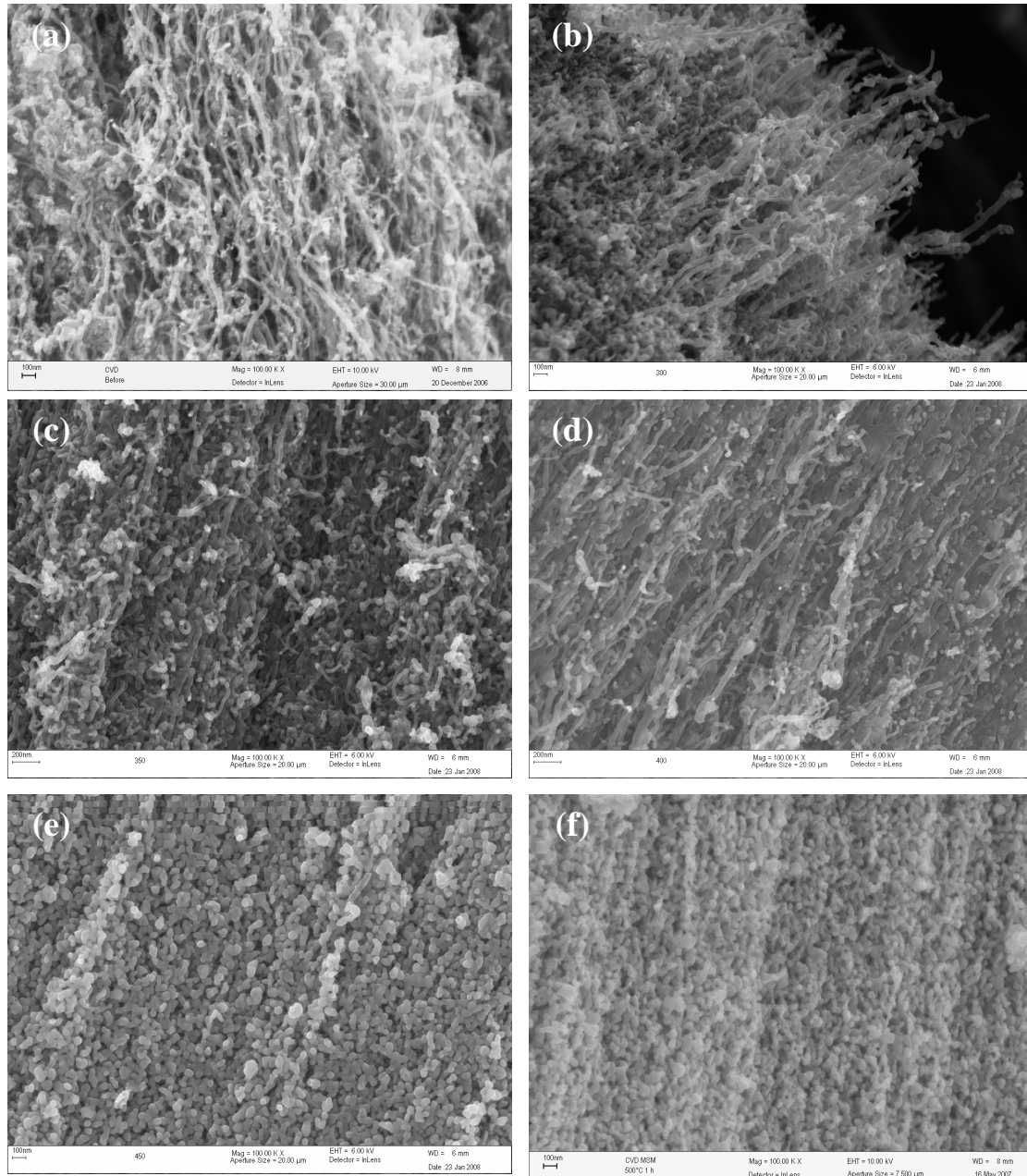


Fig. 5. FE-SEM micrographs of different samples, (a) as-prepared and (b)-(f) calcined, at different temperatures: (b) 300 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C, (f) 500 °C.

Fig. 5 presents the FE-SEM images of the as-prepared and calcined material. The raw soot contained bundles of aligned MWCNTs and a considerable amount of amorphous carbon and embedded metal particles (**Fig. 5a**). **Figs. 5 (b-h)** show the effect of calcination on the morphology of MWCNT bundles in the temperature range of 300-500 °C. It is to be noted that the tubular structure and the rope-like arrays of MWCNTs were preserved up to the calcination temperature of

400°C. With an increase in the calcination temperature from 450°C to 500 °C, changes in the morphology were observed. Many broken MWCNTs were seen with open tips in the temperature range of 450°C to 550 °C. This may be due to the oxidation-induced cuttings of CNTs. This implies that higher temperature generates damages to nanotube walls, which can accumulate to produce low-quality nanotubes. At 450-500 °C, the tubular nature of the sample was entirely lost. The weight of the sample reduced to 50% after calcination at 400 °C. A weight loss, up to 80%, was noticed at higher temperatures because of the over-oxidation of the samples. The weight loss observed were less at lower temperatures which can be ascribed to insufficient oxidation of the sample. The results indicate that the calcination temperature is crucial and should be carefully controlled during purification of MWCNTs.

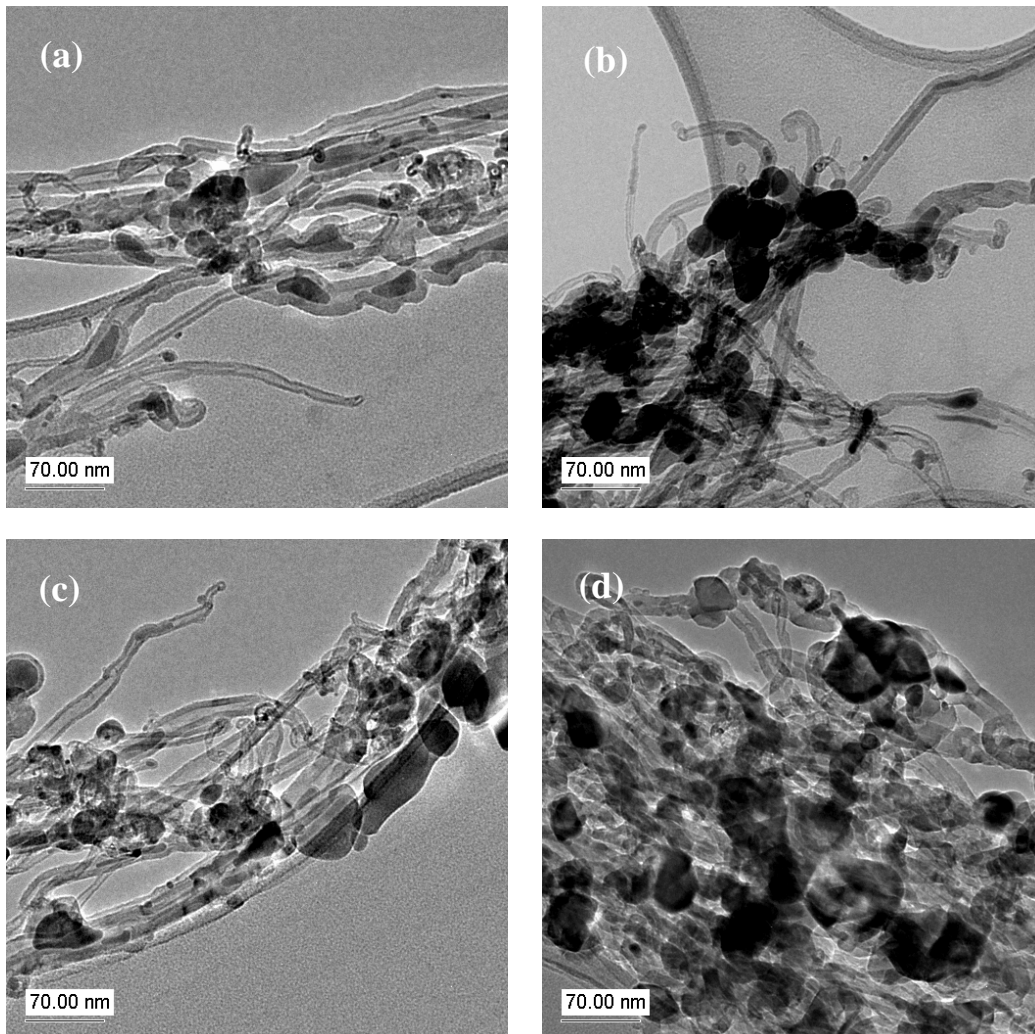


Fig. 6. TEM images of different samples (a) as prepared and (b)-(f) calcined at different temperatures: (b) 400 °C, (c) 450 °C, (d) 500 °C.

TEM observations (**Fig. 6**) were used to clarify the effect of calcination temperature on MWCNTs. The TEM image of the original sample (**Fig. 6a**) shows the presence of a network of MWCNTs, along with clusters of amorphous carbon that surrounds the metallic nanoparticles (black dots). The calcined samples show a higher concentration of metallic particles (as is evident in the numerous black dots) where the amorphous carbon layer is removed. After calcination at 400 °C, it was observed that the nanotubular morphology was preserved with minimal defects on the walls (see **Fig. 6b**). The nanotube- ends were found to be open which even gives a possibility to extract the metal particles trapped within the core of the nanotubes by mild acid treatment. A higher calcination temperature exposes more and more catalyst particles from within the carbon shells but aggravates damages to MWCNTs or their disintegration. The SEM and TEM analyses support the Raman spectroscopy, XRD and TG-DTA results.

4. Conclusions

In this paper we have demonstrated that calcination at 400 °C is an effective method for exposing Fe metal residues from MWCNT bundles produced by the CVD method. The procedure is simple; does not require large equipment and can be applied in laboratory-sized quantities of MWCNT samples. The Raman spectroscopy, FE-SEM and HR-TEM results revealed that proper/meticulous control of the calcination temperature is crucial for preserving the structural integrity of MWCNTs. Calcination at temperatures higher than 450 °C produced more damage in carbon nanotubes. The catalyst impurities from a properly pre-treated CNT sample can easily be removed by mild acid treatments.

Acknowledgement: Authors thank the CSIR executive and DST, South Africa for the financial support. Thanks to Dr. Sabine Verryn (University of Pretoria) for the XRD measurements.

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