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Comparative study of thermal stability of filled and un-filled multiwalled carbon nanotubes

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ABSTRACT

Filled or un-filled multiwalled carbon nanotubes (CNTs) used in this study have been synthesized by the floating catalyst method and fixed catalyst method, respectively. The thermal stability of filled/un-filled carbon nanotubes has been investigated by using Thermogravimetric analysis (TGA) and Derivative thermogravimetric (DTG) analysis. In this report, we have developed a methodology to distinguish between filled and un-filled carbon nanotubes. Filled-CNTs are found to be more resistant to oxidation than the un-filled carbon nanotubes. The calculated activation energy of as-grown filled CNTs, by using differential method, determined to be 3.29 ± 0.04 eV, which is higher than that of highly ordered pyrolytic graphite (HOPG). Carboneous impurities; amorphous carbon, catalyst and CNT of different diameter, which are structurally different, are identified by their reactivity and the resistance to oxidation. Copyright © 2016 VBRI Press.

Keywords: Carbon nanotubes; thermogravimetric analysis; derivative thermogravimetric analysis; highly ordered pyrolytic graphite.

Introduction

Carbon nanotubes since their discovery in 1991 **[1]** owing to their distinctive electronic and mechanical properties have raised much interest. Their astonishing properties: electrical conduction beyond copper, thermal conduction beyond diamond, tougher than diamond, and stronger than steel, etc. have generated a huge interest and engendered innumerous potential applications in various fields **[2–6]**. Besides these well-known applications recently much research interest has been shifted to 3D carbon nano-network [**7**], where CNT are connected through either by coating of amorphous carbon [**8**] or reduced graphene [**9**]. Recently this network has been envisioned as a superior architecture for lithium ion battery [**7**]. Further, development of carbon based 3D materials include aerographite [**10**] as well as 3D graphene networks [**9**] have been demonstrated their utilization in flexible magnetic aerogels [**11**], stiff magnetic nanopaper [**11**], ultralight and flexible supercapacitor electrodes[**12**], Li batteries [**7, 13**], conducting composite materials for sensor and photonic applications [**14**]. Most promising application of CNTs is reported by Mecklenburg Matthias *et al.* [**10**]. They have reported the synthesis of 3D interconnected structure of carbon microtube called as aerographite of remarkable enhanced mechanical strength and conductivity. In order to further explore the applications CNTs possess high thermal stability, high mechanical strength, electrical or thermal conductivity as well as purity are prerequisite. Thus, many research groups have used various methods for the synthesis of CNTs, for example, thermal chemical vapor deposition **[15-17]**, plasma enhanced chemical vapor deposition **[18, 19]**, laser ablation **[20]** and arc discharge **[21]**. But, so far, synthesis of CNTs having quality and purity as needed for specific application is still a challenge. So, we need a simple method not only for synthesis but also to ensure the purity and quality of carbon nanotubes.

Carbon nanotubes grown by using either physical or chemical routes have mainly two kinds of impurities one being the metallic impurities and the other being carbonaceous impurities **[22]**. Carbonaceous impurities include graphitic particles, amorphous carbon and CNT of different wall numbers. From the existing methods of analysis Thermogravimetric analysis (TGA) technique seems to be the most promising technique as it gives information about the presence of the metallic impurities, amorphous carbon and other carbonaceous structures and even the defect contents in carbon nanotubes. Thermogravimetric technique not only provides the metal contents, but also thermal stability of the contents can be studied in detail. However, oxidation temperature and thermal stability of un-filed CNTs have been studied in many reports **[23-29]**. Among all the reports to date, no reports have been published on how to identify the carbon impurities present in the as-grown CNT sample by using TGA. Furthermore, thermal stability of filled-CNT is also not much explored **[30]**. In filled-CNT, concave geometry of hollow core with confined space offers the tremendous possibility to generate the nanomaterial of superior electronic, physical or chemical properties [**31**]. This has been attributed to the fact that in filled-CNT, tube-walls not only protect the filled nanomagnets against harsh

environment but also prohibit coalescence. In previous reports [**32,33**], CNTs filled with ferromagnetic materials have been proposed as a novel material and have numerous potential applications such as biomedicine [**34**], spintronics [**35**], magnetic recording media [**36**] and magnetic force microscopy (MFM) [**37**]. Hence comparative study of thermal stability of filled as well as un-filled CNTs is desirable.

In this work, we report a simple procedure to identify the crystallinity as well as purity of the plethora of CNT by merely studying the thermal stability and differentiating the activation energy of oxidation for various carbonaceous structures present in sample. In presented study we have identified the type of impurities present in the sample and activated energy was calculated for the different variants of MWCNTs. The calculated values of activation energy of filled-CNTs have been compared with activation energy for the oxidation of highly oriented pyrolytic graphite (HOPG) **[38]**. Here HOPG is used as reference to access the crystallinity of CNT because HOPG possess high crystallinity as well as low defect concentration. If the activation energy of CNTs is found to be of the order of HOPG, then one can claim that the CNTs are of high purity and have low defect concentration. Furthermore, present work intend to confirm that thermogravimetric analysis (TGA) could be considered as a reliable technique to identify the crystallinity and purity of the plethora of CNT unlike Raman spectroscopy and high resolution transmission electron microscopy (HRTEM) which only probe the individual CNT.

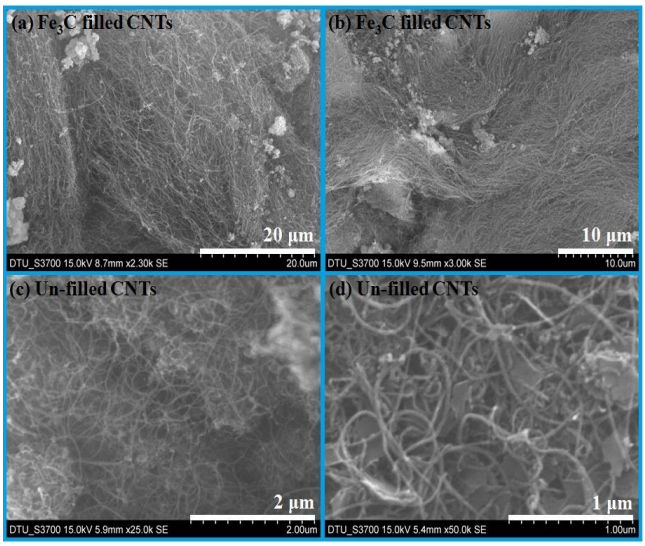

Fig. 1. SEM images (a) & (b) for Fe_3C filled CNTs synthesized by floating catalyst method, (c) and (d) un-filled CNTs synthesized by fixed catalyst method.

Experimental

The Fe_3C filled as well as un-filled CNTs were grown by thermal chemical vapor deposition method. The Fe_3C filled CNTs were synthesized using ferrocene as a floating catalyst. The precursor solution of ferrocene/toluene was made to flow in the system's pre heating zone with argon as a carrier gas. The temperature of the heating zone is kept 825 °C. More details are given in **[39]**. The un-filled CNTs were grown by using Fe: Mo: MgO (1:1.5:10) as a catalyst. Ethanol was used as carbon precursor. Synthesis temperature for un-filled CNT is 840 °C. To carry the vapors of ethanol, argon gas of optimized flow rate 150 sccm was used. The morphology and structure of CNTs were analyzed by XRD (Bruker D8 – Advance) and SEM (Hitachi S-3700N).

Results and discussion

Microstructural analysis

SEM micrographs of Fe_3C filled CNTs and un-filled CNTs have shown in **Fig. 1**, where plenty of CNTs can be clearly seen. CNTs in **Fig. 1**(**a**, **b**) are found to be straight in comparison to that in (**c**) and (**d**) in which the CNTs are twisted. This may be due to the fact that either CNTs are un-filled or are of lower diameter. The quality of CNT depends upon the growth parameters (temperature, precursor and catalyst).

Structural analysis

In order to confirm the crystallinity of both CNT as well as filled nanocrystal, XRD was performed. Peaks shown in XRD pattern (**Fig. 2**) are originating only from two components which are MWCNT and iron carbide. The peak which corresponds to the (002) crystallographic plane of graphitic structure of MWCNT (PCPDF: 89-8487), was observed at 26.2º.

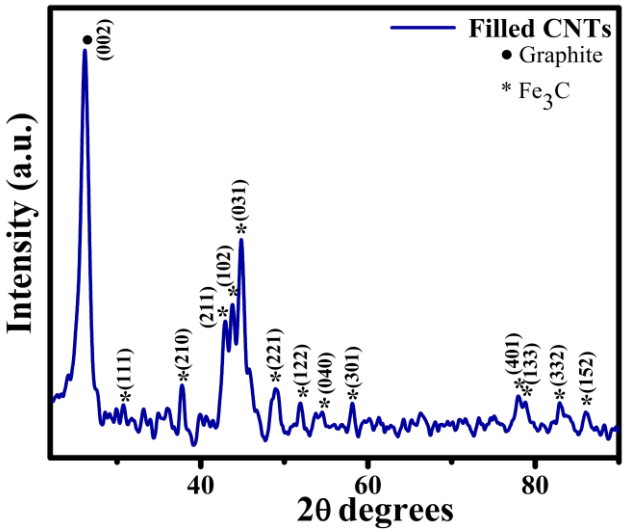

Fig. 2. X-ray diffraction pattern of Fe_3C filled CNTs collected from the inner walls of the quartz tube. (Orthorhombic structure of Fe_3C (PCPDF: 89-7271)).

This peak is known as the characteristic peak of MWCNTs. The diffraction peaks at 2θ position of 30.2º, 37.72º, 42.82º, 43.61º, 45.01º, 49.04º, 51.87º,54.42º, 58.00º, 77.86º, 78.79º, 83.04º and 85.96º identified and found corresponding to the planes (111), (210), (211), (102), (031), (221), (122), (040), (301), (401), (133), (332) and (152) respectively of orthorhombic structure of Fe_3C (PCPDF: 89-7271) are associated with Fe_3C (indexed in **Fig. 2**). Hence, presence of Fe_3C is clearly confirmed. No other peaks related to other phases of carbide and iron was

found. This confirms that MWCNT are filled with pure Fe_3C.

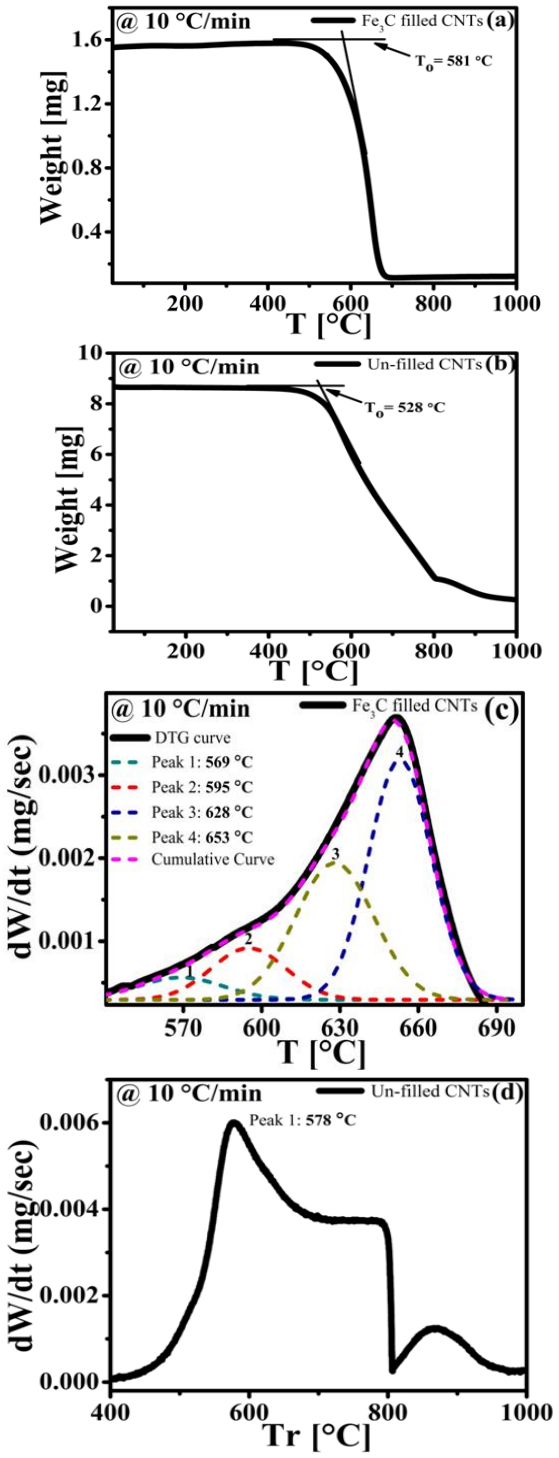

Fig. 3. TGA curves (a) Fe_3C filled CNTs (b) Un-filled CNTs; (c) and (d) DTG curve for Fe_3C filled CNTs and un-filled CNTs.

Thermal analysis

The thermogravimetric analysis on both filled and un-filled CNTs sample was performed at a constant heating rate (10 ºC/min) and has plotted in **Fig. 3** (**a**) and (**b**). From the TGA curves it is clearly depicted that oxidation process for both filled and un-filled CNTs is a single step process. The onset temperatures (T_o) were found to be 581 ºC and 528 ºC for filled and un-filled CNTs respectively. With consideration of the onset temperatures, it can be confirmed that un-filled CNTs are less thermally stable because they started to oxidize early at 528 ºC as compared to filled CNTs which start to oxidize at 581 ºC. The DTG curve of the Fe_3C filled sample is plotted in **Fig. 3**(**c**), it features four stepwise weight-losses which correspond to the peak oxidation temperatures for each sample fraction. Analysis of the DTG curve can be done by considering two temperatures being initialization temperature and oxidation/peak temperature. The peak temperature is the oxidation temperature and the initialization temperature is the temperature at which carbonaceous impurities start to decompose. Gaussian fitting was applied to do the quantitative analysis of each part. Peak 1 at 569 ºC corresponds to the oxidation temperature of amorphous carbon. The other peaks were found to correspond to the different types of CNTs present in the sample: peak 2 at 595 ºC of SWCNTs, peak 2 at 628 ºC of thin-MWCNTs (TWCNT) and peak 4 at 653 ºC of MWCNTs. Higher thermal stability for MWCNT may be due to the presence of low defects or low curvature i.e. to pure sp^2 structure. The DTG curve for un-filled CNTs is shown in **Fig. 3** (**d**) in which there is only one peak at 578 ºC corresponding to the un-filled CNTs.

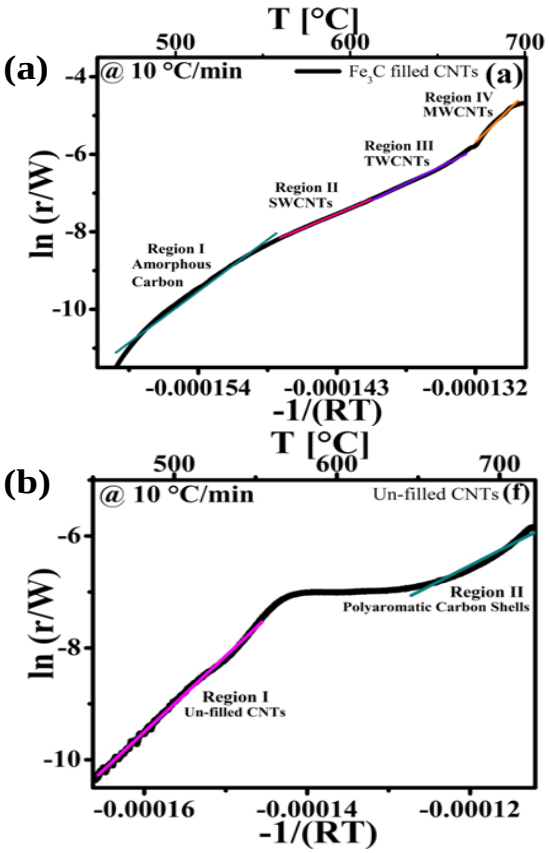

Fig. 4. The (ln(r/W) vs. (1/RT) and T) curve at heating rate 10 ºC/min (a) The regions I, II, III, and IV represents the dominating oxidation of amorphous carbon, SWCNTs, TWCNTs and MWCNTs (b) The region I represent oxidation of un-filled CNTs and region II of polyaromatic carbon shells.

A ln(r/W) vs. 1/RT curve is plotted (as shown in **Fig. 4**) for determining the activation energies for the oxidation of

un-filled and filled CNTs together with the impurities of amorphous carbon, SWCNTs, TWCNTs as shown in **Fig. 4(a)**. By using equation (1) (differential method) **[40]** the activation energies can be calculated for both Fe_3C filled CNTs and un-filled CNTs.

$$\ln\left(\frac{r}{w}\right) = E\left(-\frac{1}{RT}\right) + \ln A \quad (1)$$

where, W: Weight, R: rate of change of weight with respect to time, A: constant

Table 1. Determined values of activation energy for filled as well unfiled CNT by using differential method.

Type of Sample	Regions in the Curve	Activation Energy (eV)
	Amorphous Carbon	2.50 ± 0.019
Fe_3C Filled CNTs	SWCNTs	1.42 ± 0.002
	TWCNTs	1.65 ± 0.009
	MWCNTs	3.29 ± 0.04
Un-filled MWCNTs	Un-filled MWCNTs	1.41 ± 0.002
	Polyaromatic Carbon Shells	0.77 ± 0.005

For Fe_3C filled CNTs curve can be fitted with four regions representing region I for amorphous carbon, region II for SWCNTs, region III for TWCNTs and region IV for MWCNTs similarly, for un-filled CNTs the curve is fitted with two regions: region I for un-filled CNTs and region II for polyaromatic carbon shells **[41]**. The calculated activation energies are tabulated in **Table 1**. However, the calculated activation energies for filled CNTs are very high and not comparable to HOPG. Therefore, in order to calculate the accurate values of activation energy differential method have to be improvised to integral method **[42]**. An integral method cannot be applied to this data because it comprises only of one heating rate (10 ºC/min) and for better studies it is required to employ it for various heating rates.

The comparative study of Fe_3C filled CNTs and un-filled CNTs confirmed that the filled CNTs have a higher oxidation temperature than un-filled CNTs so it can be stated that the filled CNTs are more thermally stable. Un-filled CNTs presumed to have one open-end while another may be open or have a carbon cap at the tip **[43]**. Tip of CNT or open-end are reported to be energetically favored to initiate the oxidation **[28, 44-47]**. This may be a possible cause of low thermal stability in comparing to filled CNTs. In filled-CNT the open end is blocked by the filler and has minimum possibility of shortening the tubes at higher temperature. This possibility is high for un-filled CNTs. We believe that factors discussed above mainly affect the thermal stability of filled/un-filled CNTs.

Conclusion

A comparative TGA and DTG study on both filled and un-filled CNTs has been made. Filled CNTs are found to be more thermally stable and have high resistance to oxidation. This study reveals that different variant of MWCNTs do not exhibit same thermal stability but nearly same activation energy. This activation energy is found comparable to reported values of activation energy for HOPG. Detailed analysis of the DTG profile for the plethora of filled-CNTs reveals that different carbonaceous structures can be identified. These structures have followed systematic order of the thermal stability. We have demonstrated that TGA/DTG technique can be used to identify the nature of different variants of MWCNTs.

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