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A study of the Characterization and Synthesis of MWCNTs under a Magnetic Field via an Arc Discharge Technique

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Multi-walled carbon nanotubes (MWCNTs) were synthesized by arc discharge in a magnetic field and a low pressure helium gas using mixtures of FeS/Co, FeS/Ni and FeS/Co/Ni catalysts. The synthesized carbon materials indicated a high-purity of MWCNTs related to decreasing the metal catalysts results from applying the magnetic field which was investigated by X-ray diffraction (XRD) analysis and a high-yield of MWCNTs with less amorphous carbon in the presence of the magnetic field for all mixtures as shown by scanning electron microscopy (SEM). Raman spectroscopy was used to characterize the MWCNTs. The ratio of intensity of the graphitic mode to the defect mode (I_G/I_D) showed that the quality and crystallity of MWCNTs, which were synthesized using FeS/Ni and FeS/Co/Ni decreased in the presence of magnetic field while the quality of MWCNTs, synthesized using FeS/Co increased. Thermo gravimetric analysis (TG/DTA) was performed for quantitative MWCNTs purity assessment. Results showed that the purity of MWCNTs was increased for all cases in the presence of a magnetic field. This was attributed to the concentration of carbon monomers in the arc plasma with the magnetic field.

Key words: Multi-Wall Carbon Nanotubes (MWCNTs), Arc Discharge, Magnetic Field, Catalysts.

Introduction

Since the discovery of multi-walled carbon nanotubes (MWCNTs) [1], researchers have investigated their use in various applications due to their remarkable electrical, mechanical, and chemical properties [2-4]. Carbon nanotubes have emerged as an attractive material for electronic applications [5]. Specifically, CNTs are suitable for nanosized electric wires, MWNTs and SWNTs [6, 7] were used in electronic devices, such as scanning microscopy probe tips and energy storage materials [8]. Several techniques have been developed for CNT synthesis such as arc discharge, chemical vapor deposition (CVD) and laser ablation [9-15]. Arc discharge is the most practical method of MWCNTs synthesis. Because of its low cost and simplicity, the electric arc is still widely used, including for commercial production, despite some drawbacks. In spite of the efforts that have been devoted to the electric arc technique to understand the influence of the main and numerous physical parameters (typically: arc current, pressure, anode composition and mobility, type of catalysts…) [11-16]. CNTs produced by an arc discharge have less structural defects than those produced by low temperature techniques. Most likely, this is due to the rapid growth that prevents defect formation [9]. The as-synthesized nanotubes usually contain impurities such as amorphous carbon, and metal nanoparticles. The fabrication of CNT devices requires high-purity CNTs. Purification of CNTs, therefore, is an important issue in carbon nanotubes research [17, 8]. To improve the purity of MWCNTs from soot, adjusting the experimental conditions, such as the configuration of the magnets and different mixtures of catalysts are used [5]. In this study we focus on the specific role of the magnetic field on the yield and purity of MWCNTs that were synthesized with different mixtures of catalysts.

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Experimental

Our synthesis set up was similar to the one used by Anazawa et al [5], arc discharging with a magnetic field around the arc plasma. The chamber was vertical and had cylindrical geometry, it was 30 mm in diameter and 350 mm in length, graphite rods were used as electrodes. The process consisted of the evaporation of an anode which was 8 mm in diameter with a hole of 5 mm diameter and 5 mm depth filled with carbon powder with various mixtures of catalysts. The total amount of catalyst was 10 wt%, FeS : Co = 1 : 1, FeS : Ni = 1 : 1 and FeS : Ni : Co = 1 : 1 : 1.

The other graphite rod used as a cathode was 12 mm in diameter and had a flat surface to keep a uniform arcing during experiments. The vacuum was applied to the chamber (1 torr (133.32 Pascal)) and then filled with helium at (400 torr (53328 Pascal)). The run was

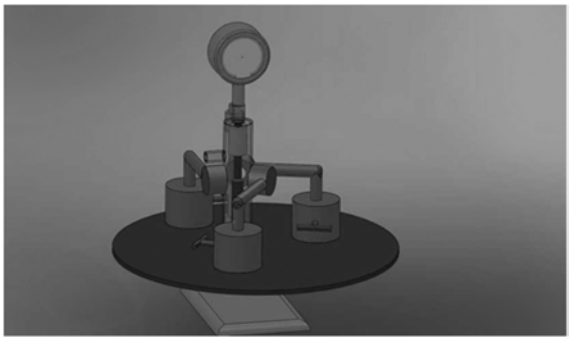

Fig. 1. A schematic of the arc discharge system with the magnets around the chamber.

made with a direct current at 60 A, and voltage of 25 V. A schematic of the apparatus is shown in Fig 1. The magnetic field was formed around the discharging region by three cylindrical magnets (magnetic flux density ~ 250 mT).The structure of MWCNTs and possible impurities were characterized by XRD with 2θ within the range of 10-80 ×.The MWCNTs produced were examined under a SEM, using a VG2080573IR SEM system with an accelerating voltage of 15 kV, to investigate the morphology of the MWCNTs. Raman spectroscopy was also performed to evaluate the graphitization of the products. We measured the Raman spectra with an Nd-yittrium-aluminum-garnet (YAG) laser (1064 nm). TG/DTA was also performed to know the amount of catalytic metals and the phases of carbon materials in a synthesized sample.

Results and Discussion

All different samples are shown in table 1.The XRD results of MWCNTs produced in the absence of the magnetic field are shown in Fig. 2. A peak appeared at around 2θ = 26.3 × in all samples is a characteristic of MWCNTs, the peaks at 2θ = 54.5 × in (b) is related to MWCNTs as well. The peaks at 2θ = 53 ×, 2θ =45 × and 2θ = 42.2 × are characteristics of FeS, Ni and Co respectively. It could be observed that in presence of the magnetic field in Fig. 3. the peak intensities of FeS, Co and Ni are removed and the peaks at 2θ = 26.3 × and 2θ = 54.5 × related to MWCNTs still remained.

Table 1. The sample synthesized at different reaction conditions.

MWCNTs Samples	Synthesized Samples	Conditions
I	Carbon Powder + FeS : Co = 1/1	B = 0
II	Carbon Powder + FeS : Co = 1/1	B ≠ 0
III	Carbon Powder + FeS : Ni = 1/1	B = 0
IV	Carbon Powder + FeS:Ni = 1/1	B ≠ 0
V	Carbon Powder + FeS : Ni : Co = 1/1	B = 0
VI	Carbon Powder + FeS : Ni : Co = 1/1	B ≠ 0

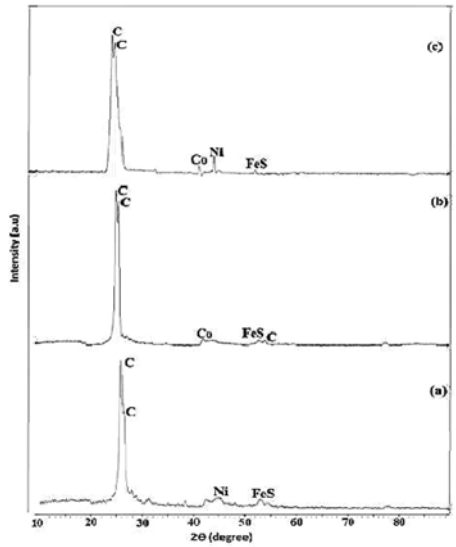

Fig. 2. XRD patterns of MWCNTs synthesized without applying a magnetic field (a) sample III, (b) sample I, (c) sample V.

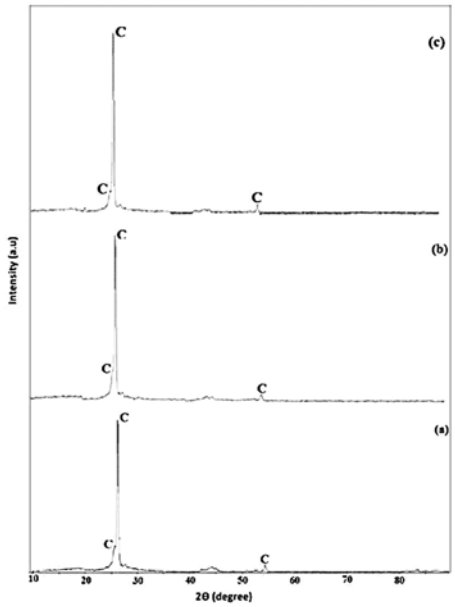

Fig 3. XRD patterns of MWCNTs synthesized in the magnetic field (a) sample VI, (b) sample II, (c)sample IV.

These results declare a decrease of the impurities such as FeS and metal catalysts. Fig. 4. shows the SEM images of samples grown without and with the symmetrical magnetic field using different catalysts according to table 1. By comparison, soot synthesized without the magnetic field consisted of not only MWCNTs but also a large amount of byproducts. The SEM images of Fig. 4 indicate that the amount of MWCNTs grown with the magnetic field is larger than the MWCNTs grown without the magnetic field and also their purity shows a significant increase. According to Fig. 4a, b the ratio of MWCNTs to the particles in sample II was much higher than in sample I. We can also see these results in Fig. 4c, d and e,f. in which

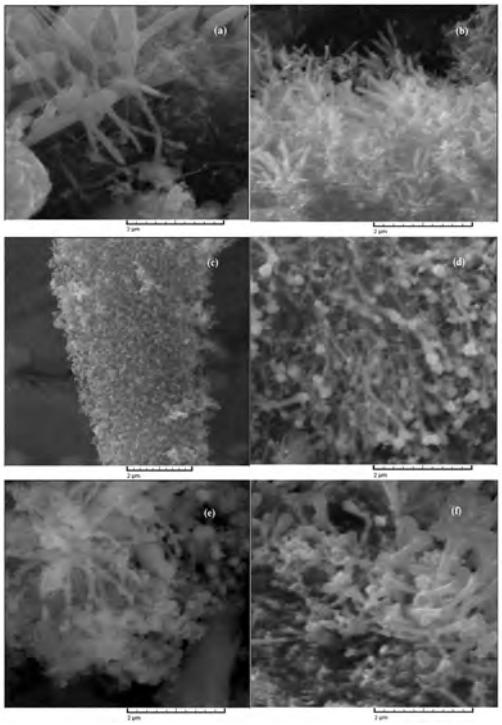

Fig. 4. SEM images of samples grown without and with the magnetic field using different mixtures of catalysts. (a), (b) samples of I,II. (c), (d) samples of III, IV (e), (f) samples of V, VI, respectively.

FeS/Ni and FeS/Ni/Co were used. This is in good agreement with previous reports [5], that the samples with the highest yield and purity were obtained under a magnetic field. In our experiments, the arcing was achieved under the magnetic field. The magnetic confinement of the plasma resulted in increasing the collision probability among charged particles, so that the reaction of the MWCNTs growth was extended. Comparison between two conditions in Fig. 4 shows the yield of MWCNTs in sample IV seems to be improved and the diameters of bundles also became smaller than in sample III. This clearly demonstrates that applying a magnetic field takes an important role for a high yield of MWCNTs synthesized, Fig. 4c, d. Nanotubes with large diameters around 120 nm are mostly shown in Fig. 4e, f. and nanotubes with holes in their centers, where obtained using a mixture of FeS,Ni and Co as catalysts (samples V and VI). The empty inner (in the bottom of images) is mostly shown in Fig. 4a, b. for the samples of I and II. In Fig. 4c, d, samples of III and IV MWCNTs bundles and nanoparticles are shown, the bundles are often covered with amorphous carbon. As it is known amorphous carbon could be formed during the cooling process, where the transition metals no longer act as catalysts and, therefore, amorphous particles may be formed near the metal

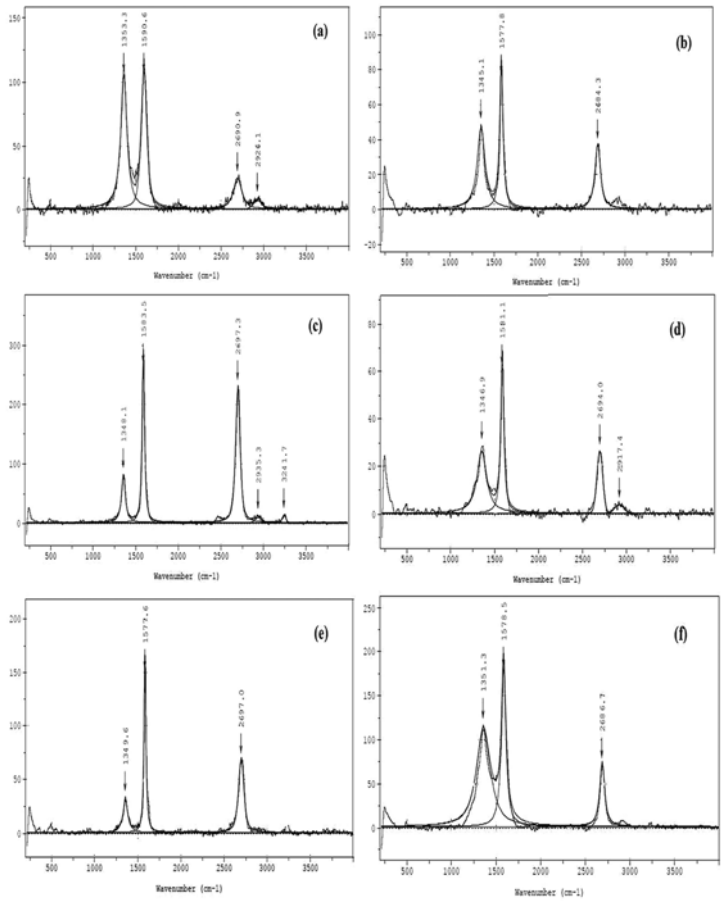

Fig. 5. Raman spectroscopy of grown, (a) sample II, (b) sample I, (c) sample IV, (d) sample III, (e) sample VI, (f) sample V.

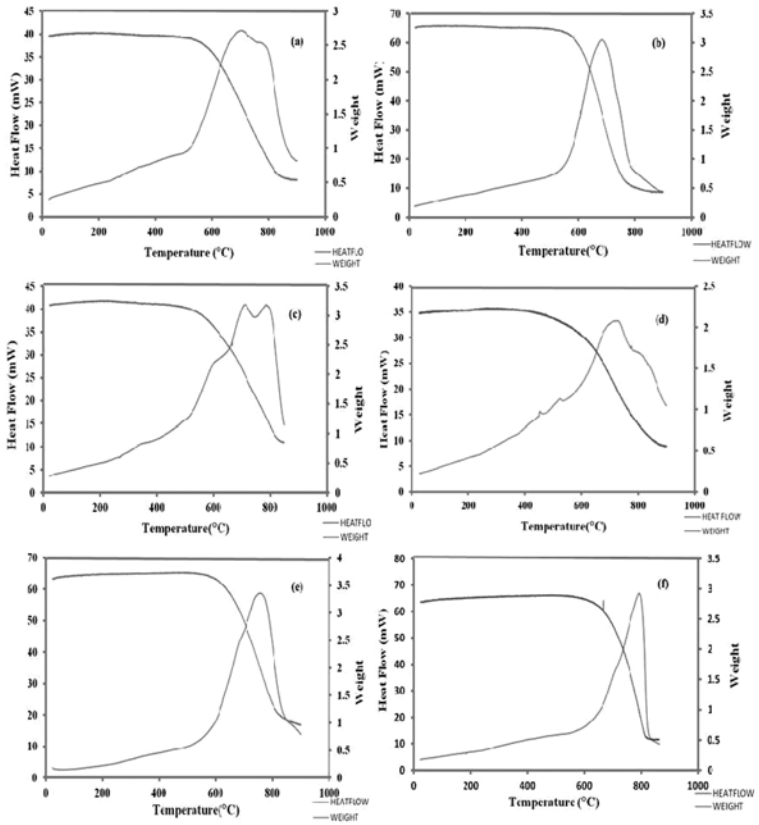

Fig. 6. Thermogravimetric analysis (TGA) & (DTA) of grown (a) sample I, (b) sample II, (c) sample III, (d) sample IV, (e) sample V, (f) sample VI.

particles [15]. As a result of the effects of the magnetic field on the synthesis of MWCNTs by an arc discharge, in particular, the yield of MWCNTs of sample II, as shown in Fig. 4b is much higher than for samples IV, and also VI, see Fig. 4d, f. The diameters of the bundles of VI as shown in Fig. 4f are large, compared with the samples of II and IV in Fig. 4b and d. where the ratio of FeS/Ni, and FeS/Co was 1 : 1. Fig. 4d is an image of the sample IV, here the MWCNTs have a large amount of impurities such as amorphous carbon, metal catalysts and carbon nanoparticles, compared with two other cases, II and VI in Fig. 4b and f.

Raman spectroscopy was used to characterize the MWCNTs and as shown in Fig. 5. This gives information about sp^2 hybridization, disorders in the sp^2 network (diamond-like carbon, amorphous carbon), nanostructured carbon and the degree of crystallinity of carbon materials [16]. All graphite-like materials, including MWCNTs show bands within the range of 1250-1450 (D), 1500-1600 (G) and bands in the range of 2450-2705 cm^{-1} (G') corresponding to the second-order Raman scattering. The D, G and G' bands are related to lattice defects, a finite crystal size (nano-carbons), the tangential mode vibrations with a sp^2 orbital structure of the C atoms and intrinsic property of well ordered sp^2 carbons, respectively[17]. Fig. 5a, b show the Raman spectra of the samples of II, I. In Fig. 5a. we can see the peak position at 1590.6 cm^{-1}

Table 2. The results of DSC and TGA for the synthesized MWCNTs without and with the magnetic field.

MWCNTs Samples	Onset, Inflection and Offset Temperatures (C)	Weight Loss (%)
I	434, 700 and 897	79/79
II	441, 690 and 892	86/94
III	466, 710 and 840	72/75
IV	366, 720 and 840	74/46
V	523, 750 and 892	73/75
VI	499, 790 and 860	82

referred to the G-band with a triplet of A1g, E1g and E2g modes. In this case, the G band has a narrow and strong spectral peak, indicating a good arrangement of the hexagonal lattice of graphite [18, 19]. The weak D band at 1353.3 cm^{-1} in the spectrum reveals the high purity of sample II, while the spectrum in Fig. 5b shows the two characteristic peaks of the sample I:The ratio of I_G/I_D in these conditions show that the crystalinity of the sample and pristine arrangement of atoms in the sample of II is improved. Figure 5 c, d shows the Raman spectra of the samples IV and III, respectively. Comparison of the ratio of I_G/I_D in this case shows that the crystalinity and the graphitic nature of the sample in the presence of the magnetic field has decreased. Also according to Fig. 5e, and f the Raman

spectra of two characteristic peaks of samples VI, and V are shown.The ratio of I_G/I_D in this condition shows that the magnetic field causes a small decrease in the quality of MWCNTs which can be ignored.The second-order Raman spectra for the pristine and treated MWCNTs are shown as well. The G' bands are observed around 2700 cm^{-1} (G2') for all carbon structures [20-24]. Researches indicate that the G2' band is attributed to the larger crystallite structures.As result, the results obtained are in good agreement with the previous analyses. The effect of the magnetic field on the crystalinity and graphitic nature of samples was not good when FeS/Ni and FeS/Ni/Co were used, but the crystality of MWCNTs synthesized with FeS/Co was increased.

Thermo gravimetric and differential thermal analyses (TG/DTA) were used to determine the carbon structure and other impurities. We performed a TG/DTA for all the samples. The TG/DTA data were measured under an air ambient in the temperature range from 20 to 900 °C. The percentages of the amorphous carbon and the sp^2 hybridization of carbon are obtained according to the weight loss at 300-400 °C and 500-800 °C, respectively. The results are shown in Table 2 and Fig. 6. According to Table 2, the yield of MWCNTs produced without and with the magnetic field with FeS/Co, FeS/Ni, FeS/Co/Ni is 79.79, 86.94, 72.75, 74.46 and 73.75 and 82% respectively. The onset, inflection and offset temperatures indicate the temperatures at the initial, maximum, and the end of weight loss in TGA, respectively. The results showed that the samples of II and I consisted of 86.94 and 79.79 wt%,MWCNTs respectively, as shown in Figure 6b and a. and the product weight percent of as-synthesized MWCNTs increased with the magnetic field. For the sample II the MWCNTs started to burn around 550 °C and all MWCNTs are consumed around 850 °C. The remaining materials were less than 14 wt%. which were transition metals introduced during the synthesis. The derivative of the weight considering the temperature is also shown. Fig. 6c and d and Fig. 6e and f show the product weight percent of the samples of III,IV,V and VI, respectively. Fig. 6. shows DTA curves of MWCNTs obtained with the arc-discharge method. According to Fig. 6, a main exothermic peak at around 750-800 °C is detected in the DTA curves for all samples. The exothermic peak at around 750-800 °C shows the chemical reaction and crystallization temperature of the MWCNTs in this process. The weight loss remains constant while the DTA curves decrease with an increase in the temperature because this weight loss depends on the intrinsic value of the material and is realized in a special temperature range and is independent of an increase in the temperature.

The above results indicate that the MWCNTs produced by the arc-discharge method in the sample II had a higher purity compared with other samples, IV, VI.

Conclusions

We investigated the influences of the magnetic field on the purity and yield of MWCNTs in an arc reactor using different catalysts. Indeed, these measurements, coupled with SEM analysis and XRD, indicated clearly that the nanotube yield was increased by the magnetic field, especially when FeS/Co was used. The calculated MWCNTs qualities derived from the Raman ratios, demonstrated a high quality of MWCNTs in the case of FeS/Co. Conventionally TGA showed an increasing percentage of MWCNTs synthesized with the magnetic field. A clear message therefore comes out from this study towards MWCNTs production when arc-discharge processes are used and controlled by the magnetic field: increasing the MWCNTs yield and selectivity and purity should be achieved by providing a magnetic field using FeS/Co as catalysts.

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