Differences between carbon nanofibers produced using Fe and Ni catalysts in a floating catalyst reactor

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Abstract

Carbon nanofibers were produced by the catalytic CVD process by the floating catalyst method, in semi-industrial systems at temperatures above 1350 K. Iron-derived carbon nanofibers were produced from natural gas and xylene, using ferrocene as catalyst source, yielding a thickened submicron vapor grown carbon fibers with a core of multi-wall nanotubes. For the production of Ni derived nanofibers, natural gas was used as the carbon feedstock, and the Ni was added in a nickel compound solution. When no sulfur is used, only soot was obtained, but when sulfur is added to the reactive feedstock, a highly graphitic and very nice stacked-cup-type nanofibers with no free-CVD thickened layer were produced. TEM-EDS analysis confirms that this type of stacked-cup carbon nanofiber is produced only with a partially molten catalyst and methane as hydrocarbon source. In fact, very few fibers have either a particle tip at the end or trapped metal particle inside the wide hollow core of this type of produced carbon material.

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1. Introduction

A method for growing catalytically carbon filaments with iron and a hydrocarbon feedstock was first patented in the 19th century [1], but the interest in the structure of these filaments and their properties emerged in the 1970s with the development of the transmission electron microscopy, when the mechanistic proposals of Oberlin et al. [2] and Baker et al. [3] were reported. Basically, these fibrils are produced by the catalytic chemical vapor deposition (CVD) of carbon from a carbon source, and this type of fibers were named vapor grown carbon fibers (VGCF) to differentiate them from other types of carbon fibers (CF). In the 1980s, a great effort was made to develop a contin-

uous method to produce VGCF [4], also named carbon nanofibers (CNF) if the diameter was lower than 500 nm. The discovery of carbon nanotubes (CNT) by Ijima in the early 1990s [5], which are mainly produced by catalytic CVD, increased the interest in the production of different types of carbon nanofilaments (CNT, CNF or VGCF) and their applications, such as in hydrogen storage [6], catalyst supports [7], field emission [8], memory devices [9] and fillers for polymer composites [10,11]. Therefore, there is a very extensive amount of papers in the literature reporting the production of CNT and CNF by different methods, conditions, catalysts (Fe, Ni, Co and Cu) and carbon sources, and often there is some confusion about which material produced is adequate for each application.

As mentioned above, all carbon nanofilaments are produced by catalytic CVD from a carbon feedstock (light or aromatic hydrocarbons, CO) using an elemental transition metal (Fe, Ni, Co and Cu) as catalyst. This process usually

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occurs in a hydrogen atmosphere (partial at least) at temperatures ranging from 500 to 1200 °C. Therefore, the only difference among the various forms of carbon nanofilaments is their chemical structure. The widely accepted forms of carbon nanofilaments are

(i) Carbon nanotubes, which are comprised of graphene layers rolled up in a cylindrical form with the plane parallel to the fiber axis. They can be either a single layer forming a single wall nanotube (SWNT, Fig. 1a), with typical tube diameter of 1–2 nm, or multiple concentric cylinders forming a multi-wall nanotube (MWNT, Fig. 1b), with tube sizes from 10 to above 100 nm, depending on the wall numbers. Since no other element is required to stabilize the structure (except at the extremes), CNTs can be considered an allotropic carbon form. The catalytic solid particle is of the same size as the resulting nanotube, and is located at the tip of the tube.

(ii) Platelet carbon nanofibers, which are composed of small graphene layers, perpendicular to the fiber axis (Fig. 1c). The normal fibril size is at around 100 nm width and the fiber must contain a non-negligible amount of hydrogen or other heteroatoms for the stabilization of the plates. The fibrils can be also coiled, as shown in Fig. 1d [12,13]. Usually, the solid particle is located in the middle of the fiber, yielding bidirectional fibers [14,15].

(iii) Fishbone carbon nanofibers, where the graphene layers are inclined with respect to the fibril axis. Consequently, hydrogen is also required to stabilize the edges. Fishbone carbon nanofibers can have either a hollow core as in Fig. 1e [16] or a solid core [14] as in Fig. 1f. Currently, there is certain disagreement concerning the fibril shape. One group of studies [17,18] suggests that the graphene layers are completely straight due to the catalytic solid particle shape, and the fiber cross-section is polygonal (square,

Fig. 1. Diagram of the different accepted structures of CNT and CNF.

hexagonal, etc.) as shown in Fig. 1e and f, while others [19,20] indicate that the fibril is formed by cones or truncated cones. In fact, Nolan et al. [20] stated that the inclined angle is dependant, among other aspects, on the presence of hydrogen (either molecular or in a hydrocarbon) in the feedstock while only MWNTs are produced when CO was used as the feedstock.

(iv) Ribbon carbon nanofibers are comprised of straight, unrolled graphene layers that are parallel to the fibril axis with non-cylindrical cross-sections (Fig. 1g). TEM images of MWNTs and ribbon carbon nanofibers would bear a striking resemblance. While there is an agreement about the position of the catalytic solid particle in one extreme, some authors claim that the graphite layers are completely parallel to the fibril axis [14], while others state that the layers are slightly inclined [21].

(v) Stacked cup carbon nanofibers: This form of carbon nanofiber is a continuous layer of rolled (spiral) graphene along the fiber axis. The spiral orientation of these nanofibers yields a truncated cone arrangement along the axis with a wide internal hollow space, as shown in Fig. 1h. Although these nanofibers were previously described as either a Pd catalyzed product [22] with small diameters around 20 nm or a Fe derived nanofiber with a huge hollow space [23], Kim et al. [24] recently stated that the stacked-cup nanofibers have a circular cross-section and are different to fishbone nanofibers even though the TEM pictures look like the same. These authors also stated that stacked-cup carbon nanofibers, with a huge hollow space, are catalyzed with a molten particle.

(vi) Thickened carbon nanofibers are the last form of carbon nanofilaments. This form of carbon nanofibers is comprised of a base structure of one of the previously mentioned catalytic nanofilaments (CNF or CNT) with a variable coating of amorphous carbon produced by non-catalytic CVD. If the carbon thickened layer, which is deposited after the catalytic filament is formed, produces a fibril which diameter is greater than 500 μm , then it is considered to be a VGCF. In fact, Endo et al. communicated in 1995 [25] that the catalytic inner core of the VGCFs mentioned in 1980s [26], which were reported prior to the discovery of the nanotubes, turned out to be a MWNT. Nevertheless, these thickened MWNTs cannot be considered a MWNT because the term nanotube implies pure carbon graphite layers in cylinders along the axis with no impurities, including amorphous carbon. There are also thickened carbon nanofibers whose base structures are another of the previously listed nanofiber types. For example, Kim et al. [24] reported the stacked-cup nanofiber covered by a CVD coating.

The methods for producing the carbon nanofilaments have been developed and are in use since the early 1980s, due to the great effort carried out especially by Endo and co-workers [4] and Tibbetts's group [27]. Most of the filaments exposed can be produced by the substrate method, a batch process where the catalytic particle is first precipitated from a solution over a substrate, calcined, and then

reduced to its elemental state with H_2 . Once the seeds are in their elemental state, a hydrocarbon source (methane, ethylene, acetylene, carbon monoxide and aromatics) is fed into the reactor at high partial pressures of hydrogen and moderate temperatures (700–1000 K). In short, Fe yields platelet nanofibers [15,17,18] at low temperatures (ca. 700 K) and ribbon or 'tubular' fibers at higher temperatures (950 K) [14] regardless of the particle size, although the particle size and shape might play a crucial role [28] in the structure. Multi-wall carbon nanotubes are normally produced from iron substrates and aromatic vapors at temperatures above 1000 K [25,29], which can often lead to the problems of parallel soot formation or MWNT thickening. On the other hand, using a Ni catalyst or a bimetallic Ni–Fe [17,21] yields mostly fishbone nanofibers (both solid [12,14,21] and hollow [16,20,30]). Moreover, a Ni catalyst may also yield platelet CNF at very specific conditions (big particles, temperature above 900 K) [12,30].

In relation to the production by the continuous floating catalyst method, the process with the most appealing potential for industrial scale up, most of the work is carried out with iron in the form of zero valence compounds such as $\text{Fe}(\text{C}_5\text{H}_5)_2$ or $\text{Fe}(\text{CO})_5$ to favour and control the adequate catalyst particle size [31,32]. Pure MWNTs are produced when using an aromatic hydrocarbon with ferrocene at around 1000–1100 K [33] and also in a modified reactor at slightly lower temperatures (900–1000 K) where the reactants are fed continuously and the nanotubes begin to grow when the iron particles are seeded on the substrate [34,35]. A similar system also yields MWNTs when acetylene and iron pentacarbonyl are fed in an argon atmosphere [36]. Increasing temperature to increase the kinetics of the reaction (and reduce the costs) yields thickened carbon nanofibers (non-catalytic CVD coated MWNTs). A sulfur compound (regularly, thiophene or H_2S) is required for increase kinetics, in order to reduce residence time, and consequently, to reduce soot [37]. The effect of sulfur seems to be the formation of a pseudo-liquid state of iron particles that enhances a VLS mechanism formation, possibly due to an eutectic formed between iron and iron–sulfur compounds at 1271 K [38]. Nevertheless, Tibbetts and Balogh [39] reported that together to the role of sulfur, a liquid Fe–C intermediate in the catalytic particle is also necessary. Most of the carbon nanofibers produced with iron by the floating catalyst method with sulfur were thickened MWNTs until it was recently communicated that stacked-cup nanofibers [23,24] and fishbone nanofibers [40] can also be produced by the floating catalyst method with an iron organometallic and a sulfur–hydrocarbon source. Consequently, the literature is not clear when differentiating between when each type of carbon nanofiber is produced.

This work presents carbon nanofibers produced at pilot plant scale by the floating catalyst method using iron and nickel as catalysts. The deep characterization of these products may clarify how each nanofiber is formed. In addition, the first Ni-based CNFs produced by the floating catalyst

method at industrial scale are presented. For comparison purposes, two commercial carbon nanofibers were also characterized.

2. Experimental

2.1. Production of carbon nanofibers

Both Fe and Ni catalyzed carbon nanofibers were produced at the facilities of Grupo Antolín (Burgos, Spain). Fe-based CNFs, denoted as HM4, were produced in a vertical furnace, using ferrocene as catalyst, xylene as main hydrocarbon feedstock, an operating temperature above 1350 K, and natural gas and hydrogen as carrier gas. More information about this system is given elsewhere [41]. Ni catalyzed CNF, denoted as GANF1, were produced on the semi-industrial reactor. Ni, from a cheap nickel chemical precursor, was solved and introduced continuously into the reactor. A sulfur compound was added to the liquid solution for the production of GANF1. Nevertheless, an experiment with no sulfur source was done to analyse the effect of sulfur (denoted as NSS). Natural gas was used as carbon feedstock with H_2 as carrier gas at temperatures above 1400 K. Both reactors were externally heated through electrical resistance.

For comparison, commercial carbon nanofibers manufactured by the floating catalyst method at industrial scale were studied: VGCFTM from Showa Denko (Tokyo, Japan), a graphitized material produced by ferrocene/benzene/thiophene [42]; and PyrografTM III—PR24 from Applied Sciences Inc. (Cedarville, OH, United States), which was produced from iron pentacarbonyl, natural gas, H_2S , air and NH_3 [43,44].

2.2. Characterization techniques

Several characterization techniques were applied to each of the three samples of the present work and to the two commercial products. Proximate analysis were determined according to standards and CHNS elemental analysis was performed using a Carlo Erba (CHNS-OEA1108) equipment. The metal composition of the residual ashes from the calcined samples (1173 K overnight) were determined by X-ray fluorescence using a Philips model PW1480. BET surface area and micropore volume were determined through the 77 K nitrogen adsorption isotherm, measured in a Quantachrome Autosorb 6 apparatus.

In addition, the polyaromatic hydrocarbon (PAH) content was determined for the samples of iron-based CNFs (HM4) and both nickel-based materials (GANF1 and NSS) because these were as-grown samples (as opposed to commercially prepared) and furthermore, their composition could give information about the chemical reactions taking place in the furnace. These compounds were separated and quantified from each CNF sample and later quantified by heat treating them in an inert atmosphere at 300 °C (a temperature which evaporates the PAHs but

does not produce cracking). This pyrolysis technique was carried out in a horizontal tubular reactor where the samples, placed in a crucible, were automatically introduced by a magnetic feeder after the furnace reached already the required temperature. All the exhaust gases evolved from the samples were trapped at the outlet with a polymeric resin fixed bed (XAD-2 resin). Then, the PAHs were extracted from the resin and analyzed by GC–MS (Fisons Instruments model MD800/GC8000) following US Environmental Protection Agency (EPA) method 8270C. More information about the reactor and the analysis procedure can be found elsewhere [45].

Finally, the texture and structure of the carbon nanofibers were analyzed by electron microscopy. Scanning electron microscopy (SEM) studies were carried out with JEOL-JSM 840 and HITACHI S-3000 N models, both provided with EDS analysis. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2010 model provided with a EDS system OXFORD instruments INCA Energy TEM100.

3. Results

Fig. 2 shows a SEM image of iron derived HM4. Well formed and thin filaments can be picked out among the other much wider nanofibers and even soot. The specimen does not contain free soot, but the non-uniformity of the amorphous carbon coating on some fibers results in the formation of soot-like nanoballs along the fibers. As previously reported by Masuda et al. [46], this is caused by metal particles seeded over an already formed nanofilaments. Generally, there are large differences in the fiber diameters and, regardless of these stuck balls, the fibers are quite straight. On the other hand, Fig. 3 shows a SEM image of GANF1 sample. There is neither soot nor irregularities along the length of the nanofibers, and the fiber sizes appear quite uniform. Nevertheless, it must be also noted that the nanofibers are more entangled than those of

Fig. 2. SEM picture of HM-4 sample.

Fig. 3. SEM picture of GANF1 sample.

Fig. 4. TEM picture of HM-4 sample, a closer look to a individual fiber, with a clear different core and a thickened coating.

HM4, although their aspect ratio is good. On the contrary, the NSS sample, produced in the same conditions as GANF1 but without a sulfur feedstock, yielded soot with some isolated fibril structures. Thus, it can be pointed out that the sulfur is critical for the effect of producing carbon nanofibers and inhibiting soot formation.

Table 1 contains the CHNS and proximate analysis as well as other parameters. It is noted that the iron-based material has a very low ash content of 2%, whereas this amount is higher for Ni-based GANF1 and NSS (13.5% and 8%, respectively). In relation to the commercial products, Showa Denko has no ash content at all, which is indicative that the graphitization treatment volatilized all the metal content. The ash content of Pyrograf III is close to that of HM4 as well as both the proximate and ultimate analysis (except for sulfur). X-ray fluorescence of the ashes indicated that the compositions of the ashes from HM4 and Pyrograf III are 99.5% iron oxides, and those of GANF1 are composed of NiO in a similar concentration, which is indicative of the original sulfur content of the ashes (i.e. sulfides do not evolve into sulfates but are evolved as SO₂ and quantified as S in the CHNS analysis). The amount of hydrogen in NNS (mostly soot) is very high and different from all the others. BET specific surface area for GANF1 is higher than those of the other nanofibers studied, as commented below.

TEM analysis shows large differences in the structures of HM4 and GANF1. Fig. 4 shows a fiber of the HM4 sample. The image clearly shows a small metal particle, that

forms catalytically the core of the nanofiber consisting of a bundle of MWNTs. This catalytic core is covered with a coating of amorphous carbon. Consequently, the low surface area of HM4 could be expected since the nanofibers are solid and the texture of the soot coating is non-porous and has short-length crystallinity.

Fig. 5 shows TEM images of different magnifications of GANF1. From a general overview in Fig. 5a, it is clear that the pipe-type structure of these nanofibers with huge hollow cores is completely different. In addition, it seems that the extremes of the nanofibers are opened and very few catalytic particles were detected. A higher magnification image (Fig. 5b) confirms the wide, hollow core structure and reveals a wide distribution of nanofiber diameters. Large metal particles, which appear independent of the nanofibers, are also present in Fig. 5b. The structure of GANF1 is stacked-cup nanofiber type for carbon nanofibers with both large diameters (100 nm), as seen in Fig. 5c and d, and small diameters (40 nm), as seen in Fig. 5e with a bamboo-type cone. It is very clear from Fig. 5a–e that all the fibrils are highly graphitic and there is no CVD thickening. These nanofibers exhibit clearly a cylindrical cross-section, as observed in Fig. 5f, which shows a nice perspective of the structure.

The PAHs present in the as-grown products are shown in Table 2, and the compound distribution gives an idea

Table 1
Ultimate analysis, proximate analysis, ash, metal content, and BET specific surface area of the carbon samples studied

Sample	C (%)	H (%)	N (%)	S (%)	Ash (%)	Metal (%)	Surface (m ² /g)
HM-4	95.7	0.3	0.0	0.0	2.0	1.4	14.2
GANF1	84.1	0.5	0.9	0.9	13.5	10.6	178.4
NNS	86.5	2.1	1.3	0.0	8.0	5.6	N/A
SDK	99.9	0.0	0.0	0.0	0.0	0.0	18.0
Pyrograf III	93.4	0.48	1.1	0.6	2.1	1.4	41.9

Fig. 5. TEM pictures of GANF1. (a) and (b) general overview, with a clear hollow core, with no metal on the tips, (c) a wide CNF of over 100 nm of diameter, (d) the border of previous 100 nm diameter with stacked cup structure and no coating, (e) a 40 nm CNF with same structure and a bamboo closing and (f) a clear cylindrical cone form of the fibril.

about how the gas-phase cracking reactions, which finally yield soot or CVD coating, were taken place (PAHs are intermediates in the formation of soot). Table 2 shows the 16 most toxic and harmful PAHs according to the

US-EPA. As expected, NSS contains multiple PAHs since it is primarily comprised of soot. It must be pointed out that most of the PAHs have over three rings, especially pyrene (1% concentration). Pyrene is considered to be the

Table 2

PAH concentration on the as-grown materials studied, expressed in milligrams of compound per kilogram of carbon sample

Compounds	HM-4	GANF1	NNS
Naphthalene	90	700	110
Acenaphthylene	175	1.6	340
Acenaphthene	19	0.1	100
Fluorene	3	0.1	170
Phenanthrene	0	0.5	630
Anthracene	45	0.3	6300
Fluorantene	50	0.1	6400
Pyrene	658	0.2	10 400
Benzo[<i>a</i>]anthracene	0	1.1	130
Chrysene	1	0.1	150
Benzo[<i>b+j+k</i>]fluorantene	0	0.3	360
Benzo[<i>a</i>]pyrene	0	0.6	720
Indeno[1,2,3- <i>cd</i>]pyrene	0	0.1	110
Dibenzo[<i>a,h</i>]anthracene	0	0.1	4.50
Benzo[<i>ghi</i>]perilene	0	0.2	430

precursor or initiator of homogeneous gas phase soot formation and its presence undoubtedly means that amorphous carbon formation (free or thickening) is taking place [47]. For HM4, which has a CVD coating and soot formation, pyrene is again the prevalent PAH, but in a much lower concentration (658 mg/kg). Nevertheless, naphthalene is the only predominant PAH in GANF1, with a negligible amount of other compounds. There is a negligible amount of the other PAHs. This aspect clearly indicates that the reaction includes no hydrocarbon cracking where soot formation is highly inhibited, a marked difference with respect to NNS sample (run without sulfur feed).

In relation to the commercial fibers, Showa Denko carbon nanofibers have a structure of thickened nanofibers based on MWNT coating, which have been clearly graphitized according to the TEM exploration (as published in the product datasheet¹). On the other hand, Pyrograf III has a stacked-cup carbon nanofiber structure with a light CVD coating. From TEM exploration, it can be said that Pyrograf III and the stacked-cup carbon nanofibers characterized by Endo et al. [23] have the same structure and, in fact, both materials were produced using iron pentacarbonyl, natural gas and hydrogen sulfide as a sulfur source.

4. Discussion

GANF1 carbon nanofibers yield a stacked cup structure when using natural gas as hydrocarbon feedstock. Both GANF1 and Pyrograf III share a similar graphene structure with a wide hollow core except that GANF1 has no CVD coating resulting in a much higher surface area. While the type of catalyst (Fe vs Ni) does not seem important for producing this type of CNFs, the presence of sulfur seems to be indispensable to produce of this unique structure. Kim et al. [24] suggested that the catalyst particle must be molten, and according to Tibbetts et al. [38], the

presence of sulfur causes the catalyst particles to melt due to an eutectic in the Fe–S system at 1271 K and at a 42 at.% of S. This molten state increases the catalytic activity, which allows to reduce the residence time considerably and, in turn, mitigates the non-catalytic CVD coating (or soot) formation. The quantity of sulfur in the feedstock cannot be random and must be on a similar atomic ratio to iron. Higher concentrations of sulfur have been reported to cause a negative effect [37]. Metallic Ni has a very high melting point of 1728 K, but the melting point of NiS is only 1063 K and there is an eutectic point between Ni and NiS at 908 K which corresponds to a 32 at.% of sulfur in the mixture [48]. Both eutectic and NiS melting points are lower than the operating temperature and, consequently, metallic nickel might be present in equilibrium with a molten particle. Fig. 6a shows a TEM image of a catalytic particle that has grown a short nanofiber. This image shows that the particle has a long shape, and the variable darkness suggests that the composition is not uniform across the particle. EDS analysis of a magnified image (Fig. 6b) shows that the portion of the particle on the left (darker) is composed of only Ni, whereas the other side (lighter) is composed of S and Ni with a sulfur concentration of 46.1 atomic %, which would be molten at reaction conditions. Other examples may confirm this feature. It appears that the external portion of the catalytic particle, which adsorbs the hydrocarbon source, is elemental and solid Ni, but it is not clear if (1) the fiber grew from the dark region of the particle formed by Ni (and not molten) while attaining its shape from the union with the molten portion; or (2) the fiber began to grow from the molten portion because of its special shape and, due to this feature, the stacked cup might have a circular cross-section. In either case, it must be stated that it is uncommon to find catalytic particles at the tips of nanofibers like those observed probably because they flow out of their molten state leaving only opened the hollow core. However, in those nanofibers containing catalytic particles, which are scarce, a carbon layer always surrounds the particle as shown in Fig. 6b, which prevents any possible fluid from flowing out.

As a consequence, it seems that the catalytic activity of the metal is related to sulfur through the formation of a molten state, which has also been shown to occur with phosphorous [49]. The combination of methane (natural gas) and sulfur yields this unique stacked-cup structure from a partially molten particle regardless of the catalyst (Fe, Ni or Co) [50]. Nevertheless, sulfur has always been considered to be poisonous for the metal transition catalyst (i.e. sulfur coverage and particle breakage prevent hydrocracking reactions from occurring) [51]. When producing carbon nanofibers at much higher temperatures, the sulfur continues to have a negative effect since the elemental form of metal, not the sulfide, is critical to the reaction. However, a critical amount of sulfur may have benefits as an agent for partially melting the particle and preventing sintering.

¹ <http://www.sdkc.com/documents/VGCF-H.pdf>.

Fig. 6. TEM pictures of GANF1 fibril with a metal on the tip at two different magnifications.

The present work shows that thickened nanofibers with a MWNT core can be produced from an aromatic feedstock with and without the presence of sulfur (Showa Denko is produced with thiophene; HM4 is produced without sulfur). In addition, the sulfur precursor type was previously reported to be independent of sulfur's effect on floating catalyst production systems [52]. The present work also confirms that stacked-cup structure is formed when using the same catalyst and sulfur with simpler carbon sources, such as methane (natural gas), like occurred with Pyrograf III. Similar results were reported by Otsuka et al. [53], where methane and *n*-hexane yielded fishbone nanofibers whereas benzene and cyclopentadiene yielded MWNTs.

5. Conclusions

1. Highly graphitic, stacked-cup-type carbon nanofibers without amorphous carbon coatings were obtained from a feedstock of natural gas and inexpensive nickel precursor by the floating catalyst method. The presence of sulfur is critical to form the appropriate active catalyst particles, which appear to be partially molten on one side. This molten state is responsible for yielding the stacked-cup structure.

2. Thickened carbon nanofibers with MWNT bundles on the core of the filament are produced when using xylene as a carbon source and ferrocene as a catalyst.

3. These results, and those previously reported, lead to the conclusion that methane (natural gas) with the presence of sulfur at high temperatures yields a stacked-cup nanofiber structure regardless of the metal catalyst (Fe, Ni and Co). Furthermore, the same carbon feedstock without sulfur can yield other nanofiber structures at lower temperatures (platelet, fishbone and ribbon), but the influence of the metal catalyst is more important in this case.

4. Regardless of the presence of sulfur and the metal nature, a feedstock of an aromatic compound or acetylene will form a MWNT structure. The intermediate chemical complex that forms over the metallic particle, which is similar for both acetylene and an aromatic compound, probably

yields the MWNT structure, whereas the complex formed from methane (or other linear hydrocarbons) feedstock is different and yields carbon fibrils of other structures.

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