

The effect of changes in synthesis temperature and acetylene supply on the morphology of carbon nanocoils

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ABSTRACT

Carbon nanocoils (CNCs) with controlled shape, coil diameter and coil pitch have been synthesized in a chemical vapor deposition (CVD) system by changing the reaction temperature and acetylene flow rate. It is found that three-dimensional CNCs are produced at a lower temperature (700–770 °C), while a higher temperature (810 °C) leads to the growth of straight carbon nanofibers (CNFs). CNC–CNF hybrid structures are produced by increasing growth temperature from 750 to 810 °C during a single synthesis run, while CNF–CNC hybrid structures are produced by decreasing the temperature from 810 to 750 °C. Similarly, by changing growth temperature from 750 to 810 °C and then back to 750 °C during a single run, CNC–CNF–CNC complex hybrid structures can be obtained. During the CVD process, the pulsing of acetylene and the changing of acetylene flow rate are also found to be effective in controlling the structure of CNCs. CNCs with periodic helical structures can be produced by interrupting the acetylene flow or changing its flow rate periodically. It is found that the higher the flow rate of acetylene, the smaller the coil pitch and diameter of the grown CNCs.

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1. Introduction

It is well known that the mechanical and electrical properties of carbon materials depend largely on their morphologies. Therefore, the morphology design for carbon nanomaterials is very meaningful and important for its potential applications [1]. So far, researchers have successfully synthesized many kinds of carbon nanomaterials with different morphologies, especially for carbon nanotubes (CNTs) and carbon nanofibers (CNFs), such as carbon nanopipettes [1], CNTs with a zigzag morphology [2], straight CNT Y-junctions [3–5], branched CNTs [6] or CNFs [4], CNT-array double helices [7] and carbon nanocoils (CNCs) [8–12].

As a kind of typical three-dimensional nanostructures, CNCs exhibit outstanding mechanical [11] and electromagnetic properties [12], which can be used as nano-sized

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springs, unit parts in micro/nano electromechanical systems (MEMS/NEMS), electromagnetic wave absorbers, etc. In general, these CNCs are mainly synthesized by thermal chemical vapor deposition (CVD) method, using metals such as Fe, Co, Ni and their alloys as catalysts, acetylene, ethylene and methane as carbon sources. It is noted that, in the growth aspects, most of the researchers were mainly focused on the preparation of CNCs with uniform coil pitch and diameter under the stable reaction conditions. However, the synthesis of CNCs with complex structures has rarely been reported. It is considered that CNCs with novel structures would have some unexpected properties and more special applications than those with uniform structures. Liu et al. have prepared CNCs and CNFs with different morphologies by controlling the delivery of acetylene [4]. They observed that branched CNCs were produced from continuous acetylene flow; pulsed supply of

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acetylene produced branched CNFs; interrupted acetylene flow resulted in half coil and half fiber hybrid structures. However, the formation mechanism of these materials, including CNC/CNF switch and coil branching, has not been clearly explained. In addition, a complex gas transporting system is required in order to realize these carbon nanostructures. Recently, Cheng et al. have obtained carbon microcoils (CMCs) with a fiber cross-section changing from flat to circular by controlling the acetylene flow rate [13]. The change of catalytic anisotropy induced by reaction conditions is considered to be the possible factor for the fiber crosssection changing of CMCs. It is noted that the CNCs and CMCs with novel structures discussed above were both synthesized by controlling the acetylene delivery patterns. However, other methods to obtain these novel structures have not been adequately investigated.

In this work, using a simple temperature controlling method, we have obtained CNCs with unusual structures that include CNC–CNF hybrid structures, CNF–CNC hybrid structures, and CNC–CNF–CNC complex hybrid structures. In addition, CNCs with a periodical changing of coil diameter and coil pitch were obtained by interrupting the acetylene flow or changing its flow rate periodically. It is found that lower acetylene flow rate leads to the growth of CNCs with larger coil pitch and coil diameter, while CNCs with smaller coil pitch and coil diameter can be obtained by introducing acetylene with higher flow rate.

2. Experimental

Fe–Sn based binary metals were used as the catalysts for the growth of CNCs. The catalyst preparation process is similar to that previously reported in Ref. [14]. Fe₂(SO₄)₃/SnCl₂ solution with concentration of 0.2 mol/L was selected as the catalyst precursor and the molar ratio of Fe to Sn was maintained at 60:1. The catalyst solution with a volume of 100 μ l was coated on the SiO₂ substrate (size: 10 mm × 10 mm) by a dip-coating method, and dried at 50 °C for 10 min. Then the samples were calcined at 700 °C for 30 min in order to oxidize the catalysts.

Carbon products with different structures were synthesized on these substrates in a thermal CVD system under different patterns of temperature changing or acetylene flow rate changing.

In a typical synthesis procedure, carbon products were prepared under the constant temperatures ranging from 700 to 810 °C for 30 min by introducing acetylene and Ar gases with flow rates of 18 and 320 sccm, respectively. In the temperature changing experiments, keeping the flow rates of acetylene and Ar gases unchanged, the deposition temperature was changed in the following four ways: (1) kept at 750 °C for 10 min, then raised to 810 °C with a heating rate of 6 °C/min and finally kept at 810 °C for 10 min; (2) On the contrary to way (1), kept at 810 °C for 10 min, then decreased to 750 °C with a cooling rate of 6 °C/min, finally kept at 750 °C for 10 min; (3) Combined with ways (1) and (2), the temperature was kept at 750 °C for 10 min, then increased to 810 °C and kept for10 min, finally decreased to 750 °C and kept for 10 min; (4) On the contrary to way (3), the temperature was kept at 810 °C for 10 min, then decreased to 750 °C and kept for 10 min, finally increased to 810 $^\circ C$ and kept for 10 min. The above four ways were successively labeled by S1, S2, S3 and S4.

In the acetylene flow rate changing experiments, reaction temperature of 700 °C and Ar gas flow rate of 320 sccm were kept unchanged, and acetylene was introduced to the Ar flow using the following two modes: (1) 9 pulsed supply of acetylene with a flow rate of 18 sccm, and with pulse duration and pulse interval of 1.5 and 3 min, respectively; (2) periodic feeding of acetylene for 5 periods with alternative flow rates of 6 and 36 sccm for 6 and 3 min, respectively, in a period.

The morphology and structure of synthesized carbon products were analyzed by scanning electron microscopy (SEM; Hitachi, S-4800), transmission electron microscopy (TEM; JEOL, JEM-2000EX) and Raman spectroscopy (Renishaw inVia plus, He–Ne laser, 632.8 nm, 10% laser power: \sim 3.3 mW, 50× magnification, 10 s accumulations and twice accumulations, average of four spectra per sample). The composition of catalyst was analyzed by using energy dispersive X-ray spectroscopy (EDX; Oxford Instruments, ISIS-300) in the TEM.

3. Results and discussion

3.1. Influence of temperature changing patterns

Fig. 1 shows the SEM images of carbon deposits obtained at the growth temperatures of (a) 700 °C, (b) 750 °C, (c) 770 °C, (d) 790 °C, (e) 800 °C and (f) 810 °C. It is found that reaction temperatures affect the structures of the grown carbon products greatly. A high yield of CNCs with a vast variation in coil pitch and coil diameter can be obtained at temperatures ranging from 700 to 770 °C (Fig. 1a-c). These CNCs have an average coil diameter and line diameter of 500 and 300 nm, respectively. When the temperature is raised to 790 °C, small amount of CNCs are observed in the products, and some irregular CNFs with large diameters of approximately 600 nm are formed (Fig. 1d). With the further increase of temperature, the quantity ratio of CNCs/CNFs continues to be reduced. Fig. 1e shows the carbon deposits obtained at 800 °C, where only a few CNCs can be observed. A close examination of Fig. 1e reveals that most of the grown CNCs are twisted forms, differing from those CNCs obtained at lower temperature. It is interesting that when the temperature reaches 810 °C, no CNC but only some straight CNFs with uniform diameter (approximately 300 nm) are grown from the catalysts (Fig. 1f). The above results indicate that higher temperature (810 °C) leads to the growth of straight CNFs, while the helical CNCs can be produced at a lower temperature (700-770 °C). The similar findings also have been presented in the previously published reports [15-17]. For example, Chen and Motojima have prepared CMCs by the Ni-catalysis of acetylene that contained a small amount of thiophene and they found that the regular CMCs could be obtained at temperatures between 760 and 790 °C, while below or above this reaction temperature ranges CMCs with more irregular and larger diameters were obtained, and no coil was obtained when the temperature was very low or very high [15]. Similarly, Chen et al. have successfully synthesized CMCs in 700-800 °C using



Fig. 1 – SEM images of the carbon products obtained at the growth temperatures of (a) 700 °C, (b) 750 °C, (c) 770 °C, (d) 790 °C, (e) 800 °C and (f) 810 °C.

Ni foam as the catalyst, however, when the reaction temperature was higher than 800 °C or lower than 700 °C, only straight carbon fibers were obtained [16]. The above discussions are mainly focused on the growth of carbon products under the constant temperature conditions. Based on these findings, an idea is proposed that whether we can control the formation of carbon products with novel structures by changing the temperature during the CVD process. For example, CNC-CNF hybrid may be obtained by increasing the temperature; CNF-CNC hybrid would be obtained by decreasing the temperature. Even CNC-CNF-CNC or CNF-CNC-CNF complex hybrid structures could be grown by using the appropriate temperature changes. The design of these novel carbon materials is discussed in detail below.

Carbon nanostructures in CNCs or CNFs obtained under the different temperatures are inspected by Raman spectra analysis with an excitation laser wavelength of 632.8 nm, as shown in Fig. 2. Two main peaks are observed in the Raman spectra, one is around 1324 cm⁻¹ known as D-band originated from structural defects or disorders in carbon nanomaterials, and the other is between 1580 and 1596 cm⁻¹ known as Gband originated from graphite structures (Fig. 2a). With increasing the temperature from 750 to 810 °C, the ratio of I_D/I_G is increased from 0.9 to 1.2, indicating that there is more graphite structures in CNCs than those in CNFs (Fig. 2b). In addition, a red shift happens for the G peaks from 1596 (770 °C) to 1580 (810 °C) cm⁻¹, which reveals that the obtained carbon products gradually change from the nanocrystalline graphite structure to the amorphous carbon structure [18].

In order to obtain the carbon materials with helical CNC on one end and straight CNF on the other end, a simple temperature changing program of S_1 was performed. Fig. 3 shows the SEM images of the carbon products obtained by increasing the temperature from 750 to 810 °C in a single synthesis run. It is observed in Fig. 3a that most of the grown carbon deposits are CNC–CNF hybrid structures (indicated by the arrows), which is similar to that reported by Liu et al. [4]. Fig. 3b-d show the SEM images of a representative single CNC-CNF hybrid structure, and the arrow in Fig. 3b indicates its growth direction. The magnified image of the transition section of this hybrid structure is shown in Fig. 3c. Carbon product gradually changes from a helical CNC to a straight CNF, corresponding to our designed temperature changing program. Interestingly, during the CNF growth its diameter becomes smaller (Fig. 3b), which can be clearly observed at the tip of CNF (Fig. 3d). It is also found that the catalyst particle exists at the CNF tip, indicating a tip growth mechanism for the CNC-CNF hybrid. TEM images of two typical CNC-CNF hybrids (Fig. 4a and e), which are nearly consistent with the SEM images of these hybrids, show that the helical CNC indeed transforms into the straight CNF at some point during the CVD process. The enlarged TEM images shown in Fig. 4b-d indicate that some differences exist in nanostructure between the CNC part and the CNF part. The CNF part is not entirely composed of a solid amorphous structure, but is partially hollow in its center (indicated by the arrows in Fig. 4c, d and f). However, this phenomenon is not clearly observed in the CNC part.

Why does the reaction temperature affect the structures of the grown carbon products so greatly? So far, the mechanism for this phenomenon is not well known. It is considered that the decomposition reaction of acetylene contains two parts, which are the self decomposition (gas-phase reaction) and the catalytic decomposition on the surfaces of catalysts (gas–solid reaction). At higher temperature ($810 \,^{\circ}C$), more reaction gases are consumed by more violent gas-phase reactions [19], which leads to the deposition of amorphous carbon on the surfaces of catalyst particles. The deposited amorphous carbon would have poisoning effect on the catalytic activity of the Fe–Sn catalyst, namely the number of carbon atoms formed by the surface catalytic decomposition would be decreased with the increase of temperature, leading to a lower carbon precipitation rate among the precipitation fac-



Fig. 2 – (a) Raman spectra of the carbon products obtained at temperatures of 750–810 °C. (b) Variation of I_D/I_G ratio for carbon products with reaction temperature.



Fig. 3 – SEM images of the carbon products obtained by continuously feeding acetylene at 750 °C for 10 min and then at 810 °C for 10 min. (a) Low magnification images of the products, (b) a typical CNC–CNF hybrid structure, in which parts 1 and 2 are magnified in (c) and (d), respectively.

ets of catalyst and sequentially a lower CNF growth rate. In addition, from the viewpoint of phase changing, a solubility difference of carbon in the catalyst is another possible reason for affecting the CNF growth.

At lower temperature (700–770 °C), the catalyst exists mainly in the form of $Fe_3C(Sn)$ phase [20], from which CNCs are grown from. With the increase of temperature the composition of catalyst would be gradually transformed into the phase mixture of liquid iron and $Fe_3C(Sn)$, indicating a decreasing of solubility of carbon in the catalyst at higher

temperature. It is considered that the slower growth rate and the smaller diameter of a CNF at higher temperature (Fig. 3b) are caused mainly by the above two possible reasons. On the other hand, similar to the CNT growth [21,22], the plastic distortion for the catalysts may occur during the CVD process. At lower temperature the catalyst particles are polyhedron structured, and the catalytic anisotropy of crystal facets in the catalyst is the driving force for the helical growth of CNC [23]. However, with the increase of temperature the plastic deformation of catalyst particles from



Fig. 4 – (a) TEM image of a typical CNC–CNF hybrid structure, (b) to (d) enlarged TEM images of the CNC part, transition region, and the CNF part marked by dashed circles in (a). (e) TEM image of a large CNC–CNF hybrid structure and (f) the enlarged image of the CNF part in (e).

polyhedron to spherical structures with isotropic property would occur, which leads to the growth of straight CNFs or CNTs at higher temperature. The formation of CNC–CNF hybrid is considered to be resulted from all these discussed reasons.

Similarly, carbon materials with straight CNF on one end and helical CNC on the other end were obtained by using the temperature changing program of S_2 . Fig. 5(a) shows the SEM image of the carbon products prepared by decreasing the temperature from 810 to 750 °C in a single synthesis run. No CNF but only some CNCs with large coil diameters can be observed on the top surfaces of the carbon products, which is considered that the CNF parts exist in the internal of the products. A single representative CNF–CNC hybrid structure is shown in Fig. 5(b). Corresponding to the designed temperature changing program, the straight CNF part is firstly grown out at 810 °C (10 min), then it is gradually transformed into the helical CNC at the cooling stage (10 min), and finally becomes longer in length at 750 °C (10 min). A catalyst particle is observed at the tip of the CNC, indicating a

tip growth mechanism for the CNF-CNC hybrids (Fig. 5c). Fig. 6 shows the TEM images of a CNF-CNC hybrid, which is identical to the SEM image in Fig. 5(b). A close observation in Fig. 6(a) reveals that the CNF-CNC hybrid growth has experienced three stages: straight CNF, twisted CNC, and spring-like CNC. In addition, no large difference is found in nanostructure between the CNF part and the CNC part (Fig. 6b-d), which is different from that of the CNC-CNF hybrid. Inset in Fig. 6(d) shows a magnified image of catalyst particle on the tip of the CNC part, which is diamond-shaped and is covered by a thin layer of approximately 5 nm thick. An EDX spectroscope was employed on the catalyst center in a dot analyst mode to study the elemental constitution of the catalyst particle, as shown in Fig. 6(e). The catalyst is mainly composed of Fe, Sn, O, and C, where the molar ratio of Fe to Sn is approximately 14:5 that is nearly 3:1. It is noted that C accounts for up to 50 at.% of the total element content which is larger than 25% of C in Fe₃C [20], indicating that the thin layer on the particle surface should be covered by carbon.



Fig. 5 – SEM images of the carbon products obtained by continuously feeding acetylene at 810 °C for 10 min and then at 750 °C for 10 min. (a) Low magnification images of the products. (b) SEM image of a typical CNF–CNC hybrid structure and (c) the enlarged SEM image of the CNC tip marked by a dashed circle in (b).



Fig. 6 – (a) TEM image of a typical CNF–CNC hybrid structure, (b) to (d) enlarged TEM images of the CNF part, transition region, and the CNC tip marked by dashed circles in (a), (e) EDX spectrum of the catalyst particle in Fig. 6d.



Fig. 7 – (a) SEM image of the carbon products obtained by continuous feeding of acetylene successively at 750, 810 and 750 °C for 10 min, respectively. (b) TEM image of a typical CNC–CNF–CNC hybrid structure. Parts 1, 2 and 3 shown in (b) are magnified in (c) to (e), respectively.

Combining the above two temperature changing patterns, more complex carbon nanostructures have been obtained. Fig. 7(a) shows the SEM image of the carbon products obtained by continuous feeding of acetylene successively at 750, 810 and 750 °C for 10 min, respectively. It has been expected that CNC-CNF-CNC hybrid structures should be formed, however, only straight fibers and coiled carbon fibers with coil diameters ranging from a few hundred nanometers to several microns can be observed on the product surfaces. It is considered that the CNFs and CNCs (or CMCs) observed on the surfaces are only the middle parts and the final parts of the CNC-CNF-CNC (CMC) hybrids. Fig. 7(b) shows the TEM image of a typical CNC-CNF-CNC hybrid, which indicates that this complex structure could truly be formed according to our designed program. Fig. 7(c-e) show the enlarged images of parts 1, 2 and 3 (corresponding to the CNC-CNF transitional region, CNF part, and CNF-CNC transitional region, respectively) in Fig. 7(b), where a clear morphology and structural transformation can be observed. Fig. 8 shows the SEM images of the carbon products obtained by continuous feeding of acetylene successively at 810, 750 and 810 °C for 10 min. It is observed in Fig. 8(a) and (b) that some irregular CNFs with large diameters and some CNCs with twisted forms are formed. A careful observation of the CNC tips (Fig. 8c and d) shows that the helical CNC changes into the straight CNF and the fiber diameter becomes smaller, which is similar with the result shown in Fig. 3. It is considered that, at higher temperature (810 °C), only CNFs are grown and the catalytic ability of some catalysts would be decreased. With the decrease of temperature, the catalyst particles with high catalytic ability lead to the growth of CNCs, while the catalyst particles

with low catalytic ability lead to the growth of straight or irregular CNFs. When the temperature is increased to $810 \,^{\circ}$ C once more, the helical CNCs are gradually transformed into the straight CNFs. Therefore, it can be concluded that some irregular CNFs and some CNF-CNC-CNF hybrid structures can be obtained under the temperature changing of $810-750-810 \,^{\circ}$ C.

3.2. Influence of acetylene flow patterns

It is accepted that the concentration or the flow rate of acetylene gas plays an important role in structures of the grown CNCs. Pan et al. have reported that the diameters of CNCs synthesized with the acetylene flow rate of 30 sccm are smaller than those synthesized with the acetylene flow rate of 60 sccm [9]. Cheng et al. found that during the CMC growth the average coil diameter of the CMCs becomes larger when stopping the acetylene supply [6]. However, the relationship between CNC coil diameter/pitch and acetylene flow rate is still not clear, which is very important to understand the CNC growth mechanism. In this section, CNCs with periodic helical structures were obtained by controlling the acetylene delivery patterns.

Fig. 9 shows the SEM images of a representative CNC that was obtained by 9 pulsed supply of acetylene with a flow rate of 18 sccm, having pulse duration and pulse interval of 1.5 and 3 min, respectively. The long white arrow in Fig. 9(a) indicates the direction of the CNC growth, and the yellow arrows point to the parts of CNC that was grown during the paused supply of acetylene gas. It can be seen that both the coil pitch and coil diameter of the CNC become larger when stopping



Fig. 8 – SEM images of the carbon products obtained by continuous acetylene feeding successively at 810, 750 and 810 °C for 10 min, respectively. (a) and (b) Low magnification images of the products, (c) and (d) the enlarged SEM images of two areas marked by the dashed circles in (a) and (b).



Fig. 9 – (a) SEM image of a representative CNC obtained at 700 °C with 9 acetylene pulses, (b) an enlarged SEM image of the coil tip in (a).

the acetylene supply, and with the restoration of acetylene supply the coil pitch and diameter of the CNC are changed back. Fig. 9(b) is the corresponding magnified image for the tip of CNC in Fig. 9(a), where the small catalyst particle can be observed.

Acetylene supply with periodic changes of flow rates is the other simple way to obtain CNCs with periodic helical structures. Fig. 10 shows the SEM images of a typical CNC obtained at 700 °C by periodic feeding of acetylene for 5 periods with alternative flow rates of 6 and 36 sccm for 6 and 3 min, respectively, in a period. It is observed in Fig. 10(a) that the coil pitches and diameters of CNC are varied periodically. According to the structural change features, the CNC can be divided

into five sections (marked with the double arrows and Arabic numerals), which is corresponding to our designed acetylene delivery pattern. Fig. 10(b–d) show the enlarged images of the third, the fourth, and the fifth sections of the CNC, and each section is composed of two parts. It is found that CNC with large coil diameter and large coil pitch is grown with acetylene flow rate of 6 sccm (yellow arrows), when the flow rate of acetylene is increased to 36 sccm the coil pitch and coil diameter of the CNC decrease (red arrows). This result indicates that the coil pitch and coil diameter are determined by the concentration or the flow rate of acetylene. It can be concluded that lower acetylene flow rate leads to the growth of CNCs with larger coil pitch and coil diameter, while CNCs



Fig. 10 – SEM images of a typical CNC obtained at 700 °C by periodic feeding of acetylene for 5 periods with alternative flow rates of 6 and 36 sccm for 6 and 3 min, respectively, in a period. Parts 3, 4 and 5 shown in (a) are magnified in (b) to (d), respectively.

with smaller coil pitch and coil diameter can be obtained by introducing acetylene with higher flow rate.

It is well known that the helical growth of CNCs or CMCs is due to the nonuniformity of the carbon extrusion speed at different parts of the catalyst particles at the coil tips [24,25]. The coil diameter and coil pitch of a CNC or a CMC is considered to be determined by the catalytic anisotropy. The smaller the anisotropy, the larger the coil diameter and coil pitch of the CNC. In this experiment, stopping acetylene supply or decreasing acetylene flow rate (concentration) would reduce both the catalytic acetylene decomposition rate and the difference of carbon precipitation rate from different facets of a catalyst particle, which then causes a decrease of catalytic anisotropy. Therefore, CNCs with large coil pitch and diameter can be obtained by feeding acetylene with a low flow rate, while acetylene with a high flow rate leads to growth of CNCs with small coil pitch and diameter.

4. Summary

CNCs with novel structures have been synthesized by using a simple temperature changing method or by controlling acetylene flow patterns. By changing the temperature in a single synthesis run, various CNC–CNF hybrid structures are produced. The formation of these hybrids is considered to depend on several possible factors that include the poisoning effect of amorphous carbon on the catalytic activity of Fe– Sn catalysts, the solubility difference of carbon in the catalyst and the plastic deformation of catalyst particles from polyhedron to spherical structures. By interrupting the acetylene flow or changing its flow rate periodically, CNCs with periodic changes of coil pitch and coil diameter can be obtained. These kinds of CNCs with periodic helical structures may be developed as novel nano-sized springs, nano inductance coils, and nano resistance components for NEMS or MEMS. The ability to control the morphology of carbon nanomaterials provides better insight into the formation mechanism of these new materials, based on which carbon materials with more complex structures and new properties may be developed.

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