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Synthesis of vapour-grown micrometer-scale carbon fibers

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The growth of micrometer-scale carbon fibers of different morphology was observed in the colder regions of a CVD reactor using Fe-, Co- and Ni-containing catalyst precursors.

Carbon nanotubes and other carbon nanoparticles are in the focus of many researchers. Many of these nanostructures are grown using a CVD method and catalysts (Fe, Co and/or Ni). The iron-group metals catalyze the formation of filamentous carbon particles.[1] The mechanism of filamentous carbon growth has been investigated.[2] Nevertheless, despite a large amount of experimental data, the whole operation mechanism of the catalyst is not revealed completely. The diversity of filamentous carbon structures obtained using CVD and iron-group catalysts is extensive. The CVD method is effective to produce the batches of single-walled and multi-walled carbon nanotubes, where the nanofilament length can be as high as several millimeters.[3] Depending on the catalysts and synthesis conditions, different sorts of nanofibrous carbon structures can be obtained. The difference between the nanotubes and nanofibers is the stacking of graphene sheets of varying shapes: in nanotubes, these sheets are arranged parallel to the long axis, while nanofibers most often have a conical arrangement.[1] The structure of nanofibers may be complex: nanoropes,[4] conical,[5] brushlike,[6] fishbone,[7] *etc*. The nanofibers often grow simultaneously with carbon nanotubes during the synthesis from the gaseous phase.[1] Note that the intensive investigation of fiber-like structures produced by the thermal decomposition of hydrocarbons on the surface of iron-group metals has started prior to the discovery of carbon nanotubes in 1991.[8–11]

The catalyst precursors used in this experiment were iron-group metal nitrates and oxalates. Commercial $Ni(NO_3)_2 \cdot 6H_2O$ (Merck) and the oxalates FeC_2O_4 and CoC_2O_4 prepared by mixing MCl_2 and $H_2C_2O_4$ solutions were used.[12] Schematic diagram of the reactor used for the synthesis of fibrous carbon particles at atmospheric pressure is presented in Figure 1. Methane was used in all experiments; the flow rate of gas stream was 20 ml min^{-1} using a programmable mass flow controller FMA5502 (Omega, USA). Catalyst precursors (1.0 g) in a ceramic boat were placed in a furnace, which was filled with methane; the temperature was gradually increased (2 K min^{-1}) to 850 °C using a programmable temperature controller E5CK-AA1-500 (Omron, Japan). After reaching this temperature, the methane feed was continued for 4 h. Then, the synthesized products were cooled in a methane stream and examined by SEM EVO-50EVP (Carl Zeiss, Germany).

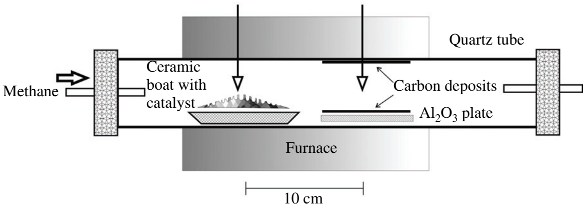

Figure 1 Synthesis of fibrous carbon particles from a methane precursor over metal nitrate and oxalate catalysts.

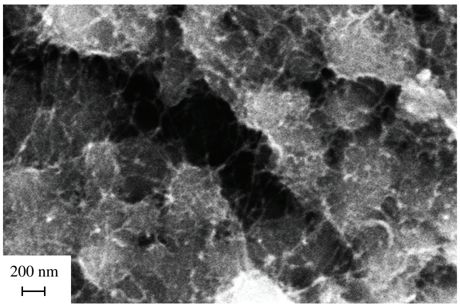

Figure 2 Micrograph of the carbon phase obtained over the CoC_2O_4 catalyst at 850 °C. A network of small-diameter carbon nanotubes (up to 20 nm) is clearly seen.

The morphology of carbon-containing phases was different depending on the catalyst and the location in the furnace. Whenever, [using pure $Ni(NO_3)_2$, FeC_2O_4, CoC_2O_4 or their mixtures] in the zone of the ceramic boat carbon phases rich in carbon nanotubes (either SWNT or MWNT of small diameter) were produced (Figure 2). The Raman spectra (not shown) recorded under 633 nm excitation wavelength confirm the presence of carbon nanotubes in the synthesized samples. Development of the filamentous structure in the zone of carbon deposits at 750 °C depends on the nature of catalyst and the type of surface (Table 1).

Table 1 shows that the formation of glass-like and coral-like coatings predominates at the presence of various catalyst precursors (Figure 3). Glassy coatings are often found on the quartz surface, while coral-like structure is observed on the surface of Al_2O_3 ceramic plate. The morphology of coral-like structure is visible in the fracture of the coating [Figure 3(*a*)], while the surface area is covered by a layer of spherical clusters.

Table 1 Catalyst precursors used in the synthesis, surfaces upon which the carbon phases were grown, and morphologies of the carbon phases.

Catalyst precursor	Surface	Morphology of carbon phase
$Ni(NO_3)_2$	Al_2O_3 plate	Filamentous
$Ni(NO_3)_2 + FeC_2O_4$	Al_2O_3 plate	Filamentous
CoC_2O_4	Quartz	Filamentous
$Ni(NO_3)_2$	Quartz	Coral-like
$Ni(NO_3)_2 + FeC_2O_4$	Quartz	Glass-like
CoC_2O_4	Al_2O_3 plate	Coral-like
FeC_2O_4	Al_2O_3 and quartz	Coral-like
$Ni(NO_3)_2 + CoC_2O_4$	Al_2O_3 and quartz	Coral-like / Glass-like
$FeC_2O_4 + CoC_2O_4$	Al_2O_3 and quartz	Coral-like / Glass-like

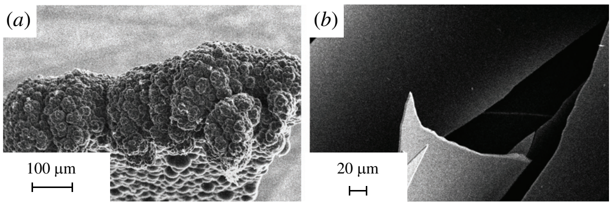

Figure 3 Morphology of the (*a*) coral-like [catalyst, $Ni(NO_3)_2$] and (*b*) glass-like [catalyst, $Ni(NO_3)_2 + CoC_2O_4$] carbon coatings produced on the quartz surface in the furnace behind the catalyst zone at 750 °C.

Nevertheless, in some cases, the formation of filamentous particles was observed. The thickness of individual filaments was 5–20 μm, dependent on the catalyst precursor. Formation of such thick filaments had never been observed in other locations of the reaction zone, *e.g.*, over the boat with catalyst precursor.

The presumptive structure of the micrometer-scale filamentous carbon formations should be similar to the structures of carbon nanofilaments, which are described in more detail elsewhere.[1] In the presence of $Ni(NO_3)_2$ catalyst precursor the filamentous carbon particles with the sheets of graphene stacked parallel to the long axis of the fiber were formed (Figure 4). The inner fracture of filament clearly seen in the micrograph can serve as an argument for that structure. We see that this sort of filament is produced from the coral-like carbon phase [Figure 3(*a*)]. The only difference between the conditions, under which these two carbon coatings are obtained, is the nature of the substrate: coral-like structure is emerged on the quartz surface, while the filaments are produced on the alumina plate. The morphology of inner structure of these filaments is similar to the structure of the carbon fiber obtained from the polymer filament precursor by carbonization.[13] In a number of cases, spherical particles appear to develop into the filaments. Therefore, we guess these spheroids should have a layered onion-like structure.[14] The growth of micron-scale diameter carbon filaments is comparable to that of capped single-walled carbon nanotubes derived from the fullerenes.[15] Consequently, there should be a reasonable correspondence between the mechanisms of growth of these structures in the presence of the metal catalyst.

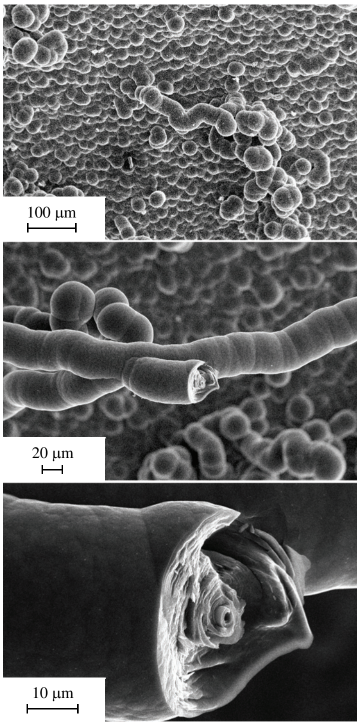

Figure 4 SEM image of the filamentous carbon particles grown on the Al_2O_3 ceramic plate using a $Ni(NO_3)_2$ catalyst precursor.

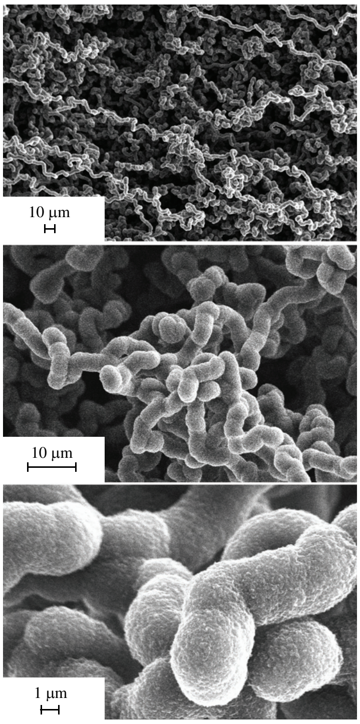

Figure 5 SEM image of the filamentous carbon particles grown on the Al_2O_3 ceramic plate using a $Ni(NO_3)_2 + FeC_2O_4$ catalyst precursor.

Different morphology of produced micrometer-scale carbon filaments is observed, when the synthesis is carried out in the presence of $Ni(NO_3)_2 + FeC_2O_4$ catalyst precursor (Figure 5). Equally, as in the case of $Ni(NO_3)_2$ precursor, the filamentous structure was obtained on the surface of Al_2O_3 ceramic plate. The thickness of filaments (~5 μm) is less, and the network of the filaments formed is much closer in comparison with that from the previous experiment. The filaments themselves are more curled and fuzzy. The SEM analysis suggests that the fuzzy coating on the surface of these filaments must be composed of carbon nanotubes. This suggestion is confirmed by the Raman spectra. Considering that the difference between these two experiments is only in the presence of FeC_2O_4 catalyst precursor, a consequent suggestion about the influence of Fe can be done. It is well known that Fe acts as a catalyst in the formation of carbon nanotubes on numerous occasions.[16] Similar fuzzy nanotube coatings on the surface of carbon fibers can be produced using a ferrocene catalyst.[17] Moreover, the Fe particles absorbed on the surface decreased diffusion of the catalyst into the fiber.

The third case when we succeeded to synthesize the filamentous carbon formations was using a CoC_2O_4 catalyst precursor (Figure 6). The SEM analysis shows that the structure of the carbon filament there is quite different from that obtained in the previous two experiments. The filaments are growing perpendicularly to the base surface; they are straight and brittle. This sort of carbon filaments is growing directly from the glass-like phase, which is formed on the quartz surface, differently from the previous two cases. The arrangement of graphene layers in these filaments should be axial, leading to the increase in brittleness. Nanometer-scale carbon fibers with the same type of structure obtained using thin Co film were described.[18]

According to the conventional theory, which is used to explain the catalytic growth of carbon nanotubes, the process begins from the formation of carbon radicals in gaseous phase. In the presence of the iron-group metal, carbon radicals are dissolved in the metal phase to form super-saturated solution.[19] This

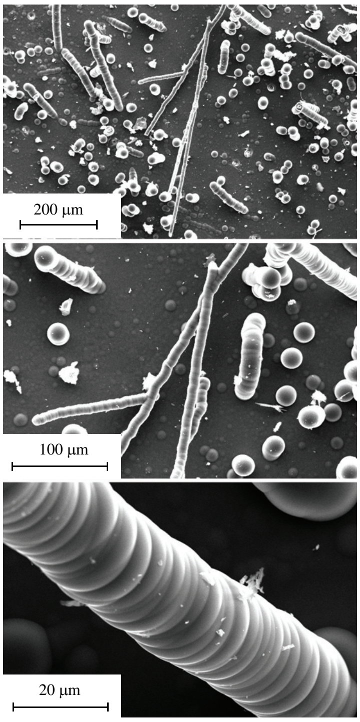

Figure 6 SEM image of filamentous carbon partices grown on the quartz substrate using a CoC_2O_4 catalyst precursor.

stage, which is the most important in the whole sequence of the carbon nanotube formation, remains largely obscure. A lot of chemical reactions have been established taking place in this process: formation of Fe–C phases (austenite, pearlite, ferrite, cementite, *etc*.),[20] as well as those including Co[21] and/or Ni[22].

The diameter of carbon nanotube is directly proportional to the size of a catalyst particle used for the synthesis.[23] The single-walled carbon nanotubes can reach up to 2.5 nm in diameter.[24] The SWNTs of a higher diameter are unstable due to the large vibrational energy of the nanotube walls. The growth mechanism of small-diameter MWNTs (up to several tens of nanometers) is similar to that of SWNTs.[25] Nevertheless, the growth mechanism of microscale-diameter carbon nanofibers remains incompletely elucidated.

The SEM analysis shows that the growth of the micrometer-scale carbon filaments occurs through the solid phase (either coral-like or glass-like). A comparison between the diameters of micrometer-scale and nano-scale filamentous carbon particles (the ratio of ~1000), on the one hand, and the densities in solid and gaseous phases (bears approximately the same ratio; ~1000), on the other hand, can serve as an additional argument for the solid-state mechanism. The reasons and exact circumstances of the tubular structure formation are not completely clear. The tubular structure of SWNTs ant MWNTs is thermodynamically favourable, since tubular structures have less surface energy due to the absence of dangling bonds in comparison with the nano-scale graphite crystals. Gain in the energy comparing the tubular and the crystal-shaped particles in the micrometer scale should be less. To drive these solid-state reactions, there must be additional forces, which become active under certain conditions.

Presumably, during the temperature raising process, the small fractions of FeC_2O_4, CoC_2O_4 or $Ni(NO_3)_2$ thermal decomposition products should be transferred to the colder zone of the reactor by methane stream. However, it is not clear why the growth of filamentous carbon particles have ever been in the reactor zones where the catalyst concentration is not very high. The role of the substrate surface is not passive; since the filaments can be grown only on the certain surfaces under the certain conditions.

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References

1 A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes and M. L. Simpson, *J. Appl. Phys*., 2005, **97**, 041301.
2 M. S. Dresselhaus and H. Day, *MRS Bull*., 2004, **29**, 237.
3 M. L. Terranova, V. Sessa and M. Rossi, *Chem. Vap. Deposition*., 2006, **12**, 315.
4 M. J. Peters, L. E. McNeil, J. P. Lu and D. Kahn, *Phys. Rev. B*, 2000, **61**, 5939.
5 W. Xia, D. Su, R. Schlogl, A. Birkner and M. Muhler, *Adv. Mater*., 2005, **17**, 1677.
6 L. Qu, Y. Zhao and L. Dai, *Small*, 2006, **2**, 1052.
7 W. Xia, O. F.-K. Schluter and M. Muhler, *Carbon*, 2004, **42**, 2735.
8 S. T. Robertson, *Carbon*, 1969, **8**, 365.
9 P. A. Tesner, E. Y. Robinovich, I. S. Rafalkes and E. F. Arefieva, *Carbon*, 1970, **8**, 435.
10 A. Tomita, K. Yoshida, Y. Nishiyama and Y. Tamai, *Carbon*, 1972, **10**, 601.
11 B. Granoff, H. O. Pierson and D. M. Shuster, *Carbon*, 1973, **11**, 177.
12 J. A. Allen and C. J. Haigh, *J. Am. Chem. Soc*., 1954, **76**, 5245.
13 B. Reznik, D. Gerthsen and K. J. Hüttinger, *Carbon*, 2001, **39**, 215.
14 S. Erkoc, *Nano Lett*., 2002, **2**, 215.
15 N. de Jonge, Y. Lamy and M. Kaiser, *Nano Lett*., 2003, **3**, 1621.
16 C. H. See and A. T. Harris, *Ind. Eng. Chem. Res*., 2007, **46**, 997.
17 Y. Xia, L. Zeng, W. Wang, J. Liang, D. Lei, S. Chen and H. Zha, *Appl. Surf. Sci*., 2007, **253**, 6807.
18 S. P. Somani, P. R. Somani, M. Tanemura, S. P. Lau and M. Umeno, *Curr. Appl. Phys*., 2009, **9**, 144.
19 J. Gavillet, A. Loiseau, F. Ducastelle, S. Thair, P. Bernier, O. Stéphan, J. Thibault and J.-C. Charlier, *Carbon*, 2002, **40**, 1649.
20 S. Takenaka, M. Serizawa and K. Otsuka, *J. Catal.*, 2004, **222**, 520.
21 A. A. Khassin, T. M. Yurieva, V. I. Zaikovskii and V. N. Parmon, *React. Kinet. Catal. Lett*., 1998, **4**, 63.
22 F. Banhart, J.-C. Charlier and P. M. Ajayan, *Phys. Rev. Lett*., 2000, **84**, 686.
23 A. G. Nasibulin, P. V. Pikhitsa, H. Jiang and E. I. Kauppinen, *Carbon*, 2005, **43**, 2251.
24 A. Moisala, A. G. Nasibulin and E. I. Kauppinen, *J. Phys.: Condens. Matter*, 2003, **15**, S3011.
25 M. Pinault, M. Mayne-L'Hermite, C. Reynaud, V. Pichot, P. Launois and D. Ballutaud, *Carbon*, 2005, **43**, 2968.

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