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Nano-sized double helices and braids: interesting carbon nanostructures

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Abstract

Two interesting carbon nanostructures, the double helices and the nanobraids, have been synthesized by pyrolysis of acetone at 715 °C, using iron nanoparticles as catalysts. The double helix was formed by two nanofibers, strictly coiled together with a strikingly constant pitch. Such a rope-like structure usually extended hundreds of microns in length, and provided excellent strength, stability and flexibility. The nanobraids appeared to be partially rolled up from carbon layers. Electron microscopy was applied to characterize these carbon forms.

Keywords: Nanostructures; Vapor deposition; Electron microscopy

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1. Introduction

Carbon is probably the most versatile element because it can form a number of structures besides diamond and graphite. The discovery of fullerenes [1], carbon nanotubes [2], and carbon onions [3], has excited numerous speculations on the potential applications of these carbons [4–11], and indicated the diversity and variety of nonplanar graphitic structures. Recently, carbon micro-coils [12–14], carbon catabashes [15], onion-like marbles and bats [16], etc. have been fabricated by various methods, such as arc discharge [17] and catalytic decomposition of hydrocarbon [12–14,18]. They all consist of curved graphite planes and possess somewhat twisted morphology. Among them, the coiled carbon filaments or tubes are of particular interest, because they have peculiar spiral structures, thus considered as ideal candidates for electromagnetic wave adsorbents, tunable micro-devices, bioactivators, Li-battery electrodes and hydrogen containers [13,15].

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Coiled carbon fibers have been synthesized by Ni catalyzed pyrolysis of acetylene [12–14]. They were usually coiled regularly with a remarkably constant pitch, and coiled in the right and left clockwise in the same amount. Unfortunately, the processes are generally very accidental with poor reproducibility, and their fiber diameters and coil diameters are basically on the micrometer scale [12–14]. As many researchers are aiming to obtain nano-scale coiled structures, coiled carbon nanofibers have also been reported [19], however, the regularity of their spiral structure is not at all satisfactory. As far as we know, nano-sized double helical carbon structure has not been reported yet.

Here in this letter we report, for the first time, the synthesis of two carbon nanostructures: nano double helices and braids, with fairly good reproducibility by catalytic pyrolysis of acetone at 715 °C. These nano-sized carbon forms are coiled with strikingly constant pitch, or impressively ordered morphology. Their unique morphology and structures are studied, and preliminary discussion on the growth mechanism is presented.

2. Experimental

In the present work, iron nanoparticles embedded in mesoporous silica, were used as the catalyst for pyrolysis of acetone to obtain carbon products. The reaction system is shown as Fig. 1.

The catalyst was prepared by a sol–gel process as the following: 50 ml tetraethoxysilane (TEOS), 52 ml dry ethynol, and 57 ml iron nitrate aqueous solution (0.1 mol/l) were mixed together and magneto-stirred for 30 min. Then 2 ml concentrated hydrogen fluoride was added in, and the mixture were stirred for 15 more minutes. After gelation, the mixture was dried at 60 °C for 1 week, and then calcined at 450 °C under 10^{-2} torr for 10 h. As a result, a silica network embedded with uniformly dispersed iron oxide nanoparticles were obtained [20].

Before used as catalysts, these iron oxide particles were reduced by H_2 (500 sccm) at 550 °C for 5 h. Then the furnace was heated to 715 °C in 10 min, and the H_2 (500 sccm) was forced to flow through acetone to carry the acetone vapor into the reaction system. Typical reaction time was 30 min.

The product was then characterized by transmission electron microscopy (TEM, JEM-200CX, JEOL, Japan), high-resolution transmission electron microscopy (HRTEM, JEM-2010F, JEOL, Japan), energy

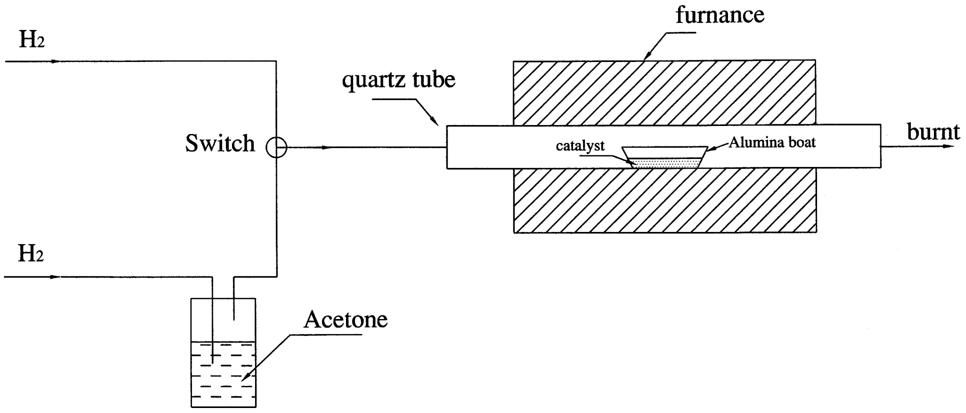

Fig. 1. Schematic layout of the reaction system.

dispersive spectrum (EDS, Link ISIS, Oxford, UK), and electron energy loss spectrum (EELS, GIF, Gatan, US).

3. Results

After the reaction, a black wool-like layer was formed on the inner wall of the quartz tube. In this product, two interesting carbon forms (Figs. 2 and 3, respectively), as well as some carbon nanotubes, were found.

As in Fig. 2, two nanofibers were strictly coiled together to form a double helix, which is very much like the twisted pairs extensively used in electronics and telecommunications. It can be found from Fig. 2 that the outer diameter of the twisted pair is ~50 nm and each single fiber is about 21 nm in diameter. With strikingly constant pitch, this rope-like structure shows great flexibility and usually extends up to several microns long. The component nanonfibers remain closely twisted together all the length, even toward the end. And partially unfastened twisted pair has not been found. Because of its flexibility, stability and possible electromagnetic properties, this double helical structure is promising as the connection wires for the Micro/Nano Electronic and Mechanical System (MEMS/NEMS) or as the reinforcement in the nanocomposites.

In the EDS of the double helices, with a detection limit of approximately 1%, only carbon was detected. It is thus believed that these double helices are composed of pure carbon, although existence of a small amount of hydrogen is still arguable. It should be noted that, metal catalysts could often be found on the end of carbon nanotubes/nanofibers in other reports [21,22], which is usually explained with a VLS growth mechanism. Nevertheless, in our work, metal catalyst was not observed on the end, or any other part, of the double helices, suggesting a different growth mechanism. EELS of an individual twisted pair also confirms its composition (Fig. 4a). In the near-edge fine structure, it exhibits the onset of the leading peak at $\Delta E = 284$ eV, corresponding to C 1s $\rightarrow \pi^*$ transitions, and the following peak up from 290 eV, mainly due to transitions from C 1s $\rightarrow \pi^*$ states. This near-edge fine

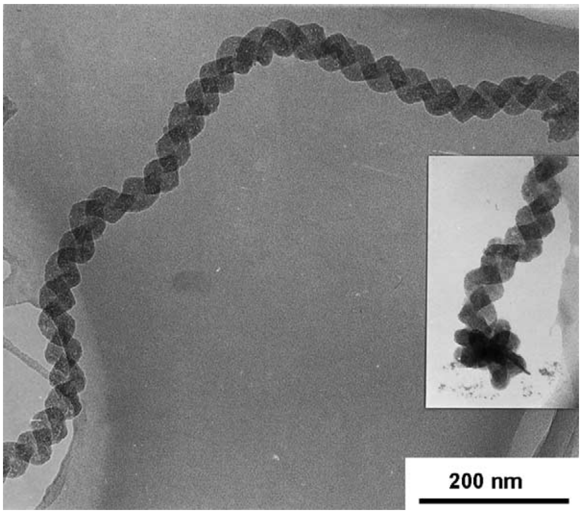

Fig. 2. Morphological image of the double helix.

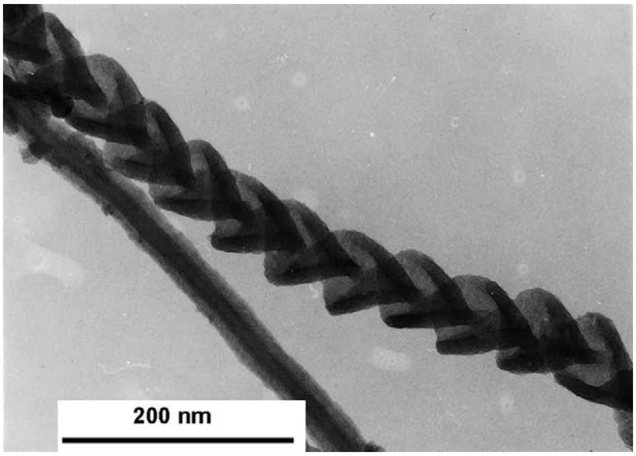

Fig. 3. Morphological image of the nanobraids (together with a carbon nanofiber).

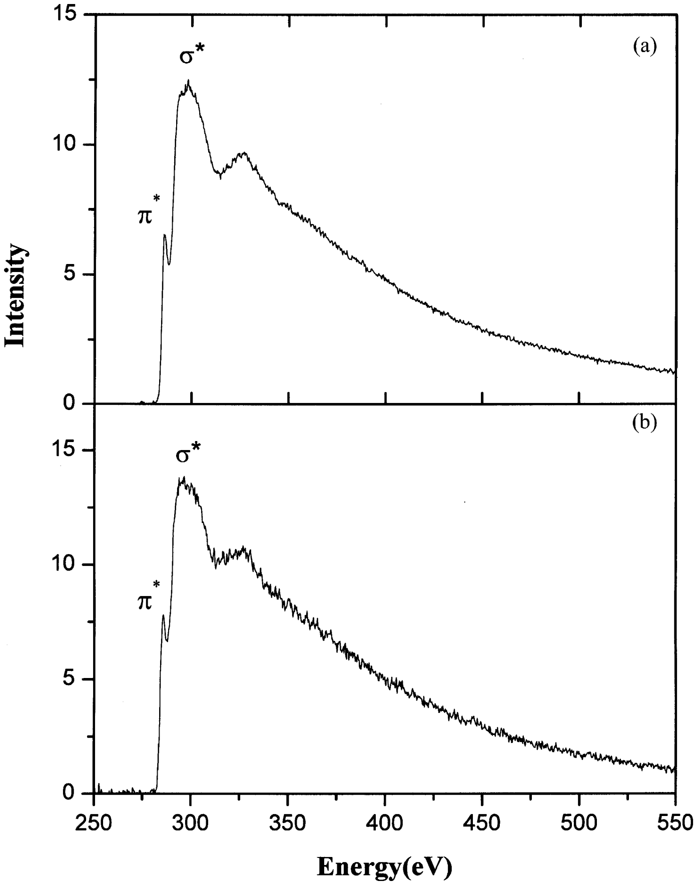

Fig. 4. EELS of (a) the double helices; (b) the nanobraids.

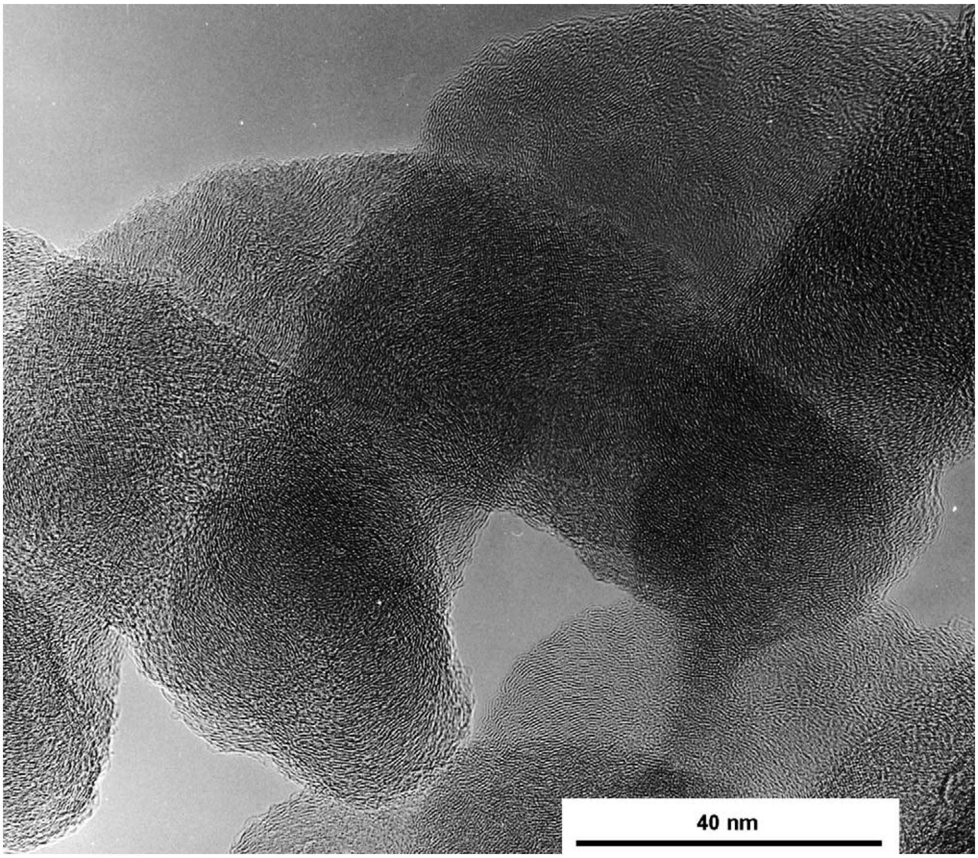

Fig. 5. HRTEM image of the double helix.

structure, which is very similar to that of carbon onions [16], confirms that carbon is in sp^2 hybridization state, and consequently a graphitic short-range ordering.

The high-resolution TEM images (Fig. 5) reveals the detailed arrangement of these graphitic layers in the double helices. The uneven contrast and defocus of the adjacent part of the nanofibers reflects the unflatness of the entire structure. And the abrupt contrast change around the nodes distinctively reveals the three-dimension spiral nature of the double helix structure. The short-range ordered graphitic layers could be clearly observed, aligned to the shape of twisting nanofibers. These layers are incontinuously curved, due to the twist and strain of the carbon nanofibers.

The other interesting carbon structures found in the product looks really like a braid, as shown in Fig. 3. It seems to be partially rolled up from a layer, but what is intriguing is its periodic and regular morphology. These braids range from 10 nm to hundreds of nanometer in width, and usually extend as long as tens of micrometer. They are also made of pure carbon, in sp^2 hybridization state, which is confirmed by EDS and EELS (Fig. 4b).

The HRTEM image (Fig. 6) reveals the detailed structure of the braided carbon, which is closer to graphite than the double helix. The graphitic layers stack more orderly, and the (0 0 2) spacing is calculated to be 0.34 nm, in good consistence with that of standard graphite.

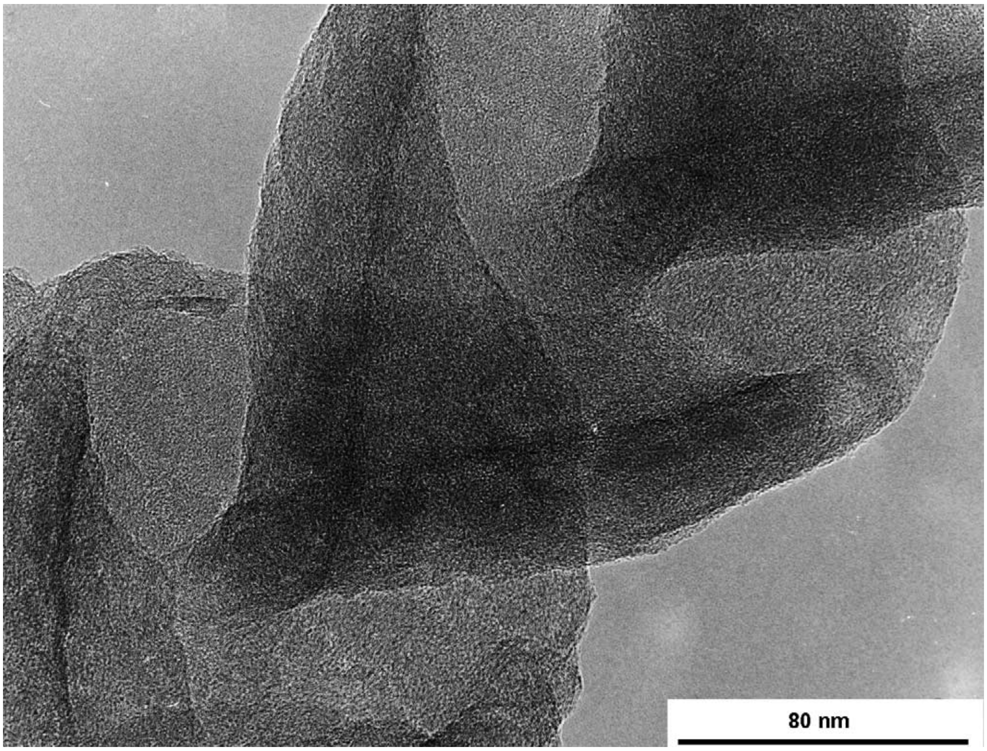

Fig. 6. HRTEM image of the carbon nanobraids.

4. Discussion

As mentioned before, the double helices are very stable, although some strain and stress might have been introduced from the twisted structure. They can maintain this structure after 3030 min' ultrasonic oscillation, and remain unchanged for at least 6 months in air. As the high activity of carbon nanotubes or nanofibers has generally been explained with the large surface areas and huge number of dangling bonds [23,24]. Accordingly, the stability of the double helices might have resulted from pairing of these dangling bonds, which leads to a strong interaction between the two nanofibers and greatly lowered the energy of the system. Thus, by coupling the two nanofibers, the twisted structure was stabilized.

As in other work, the micro-sized catalysts produced only micro-coiled carbon [12,25], thus the key to the synthesis of nano-sized coiled fibers/tubes could be the nano-sized catalyst particles used to decompose acetone. The VLS mechanism is not likely working here, as mentioned before, because catalyst particles were not found on the ends of the double helices. The growth might be in two processes: first, H_2 and acetone vapor were adsorbed on the catalyst surface, then the acetone was reduced, and carbon left on the catalyst. The iron particles simply supplied surfaces for reaction, and no catalyst liquid was formed, just as in the VLS mechanism. Therefore, the interaction between double helices and catalysts was very weak, and they were detached during ultrasonic oscillation. And the newly reduced iron catalysts kept the regular crystal shape, thus when two carbon nanofibers were growing from different faces, such as (1 0 0) and (0 0 1), they got twisted with each other to reduce dangling bonds. Otherwise, if one predominating nanofiber rose from a catalyst particle, it would just grow into carbon nanotubes. However, the way to a controlled production has not been found, although the double helices could be obtained with fairly good reproduction.

On the other hand the braided carbon with regular graphite structure, seems to be partially rolled up from a carbon layer. It is believed to be the mid-products of the growth of carbon nanotubes, although the growth mechanism and its relationship with carbon nanotubes are yet to be studied.

In summary, two interesting carbon nanostructures, the double helices and braids, have been synthesized by catalytic pyrolysis of acetone and characterized with TEM, EDS and EELS, etc. They were all made of pure carbon of sp^2 hybridization state. Preliminary discussion on the growth mechanism was presented. These carbon structures were fabricated in the same reaction system where carbon nanotubes were produced, further studies on their structure, property and growth processes could reveal the growth mechanism of carbon nanotubes. The carbon double helices are promising for applications in MEMS/NEMS, or nanocoposites.

References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.
[2] S. Iijima, Nature 354 (1991) 56.
[3] D. Ugarte, Nature 359 (1992) 707.
[4] J.W. Mintmire, B.I. Dunlap, C.T. White, Phys. Rev. Lett. 68 (1992) 631.
[5] M.S. Dresselhaus, Nature 358 (1992) 195.
[6] P.M. Ajayan, S. Iijima, Nature 361 (1993) 333.
[7] W.A. de Heer, A. Chatelain, D. Ugate, Science 270 (1995) 1179.
[8] E.W. Wong, P.E. Sheehan, C.M. Lieber, Science 277 (1997) 1971.
[9] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[10] P.G. Collin, Z. Zettl, H. Bando, A. Thess, R.E. Smalley, Science 278 (1997) 100.
[11] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Ceerligs, C. Dekker, Nature 386 (1997) 377.
[12] S. Motojima, M. Kawaguchi, K. Nozaki, H. Iwanaga, Appl. Phys. Lett. 56 (1990) 321.
[13] X. Chen, S. Motojima, Carbon 37 (1999) 1817.
[14] W.I. Hwan, H. Yanagida, S. Motojima, Mater. Lett. 43 (2000) 11.
[15] Z.L. Wang, J.S. Yin, Chem. Phys. Lett. 289 (1998) 189.
[16] C. Moschel, A. Reich, W. Assenmacher, I. Loa, M. Jansen, Chem. Phys. Lett. 335 (2000) 9.
[17] Y. Saito, Carbon 33 (1995) 979.
[18] D. Jiang, N. He, Y. Zhang, C. Xu, C. Yuan, Z. Lu, Mater. Chem. Phys. 69 (2001) 246.
[19] K. Hernadi, A. Fonseca, J.B. Nagy, D. Bernaerts, A.A. Lucas, Carbon 34 (10) (1996) 1249.
[20] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
[21] S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V. Ivanov, J.B. Nagy, Science 265 (1994) 635.
[22] R.T.K. Baker, Carbon 27 (3) (1989) 315.
[23] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tománek, J.E. Fischer, R.E. Smalley, Science 273 (1996) 483.
[24] P.M. Ajayan, V. Ravikumar, J.C. Charlier, Phys. Rev. Lett. 81 (1998) 1437.
[25] S. Motojima, Y. Itoh, S. Asakura, J. Mater. Sci. 30 (1995) 5049.