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## Self-assembly of carbon nanohelices: Characteristics and field electron emission properties

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We report the synthesis of self-assembled carbon nanohelices on iron needles using microwave plasma assisted chemical vapor deposition. The catalytic growth can be explained by the vaporliquid-solid theory. Their morphologies and microstructures are investigated by scanning electron microscopy, high-resolution transmission electron microscopy, nanobeam diffraction, and Raman spectroscopy. The field-emission investigations show a rather low turn-on electrical field and high emission current. © 2004 American Institute of Physics. [DOI: 10.1063/1.1695198]

Carbon nanotubes and nanofibers have attracted much attention in both academic and industrial research in recent years. Among their various structures and morphologies, nano- or micron-scaled helix-shaped carbon tubules and fibers<sup>1-8</sup> are kinds of fascinating structures. They have potential application for many aspects such as chiral catalyst, generator of magnetic beams, electromagnetic wave absorbers or filters, and the building blocks of the nanodevices, etc. Moreover, they would be better anchored in their embedding matrix than the straight ones when used in composites. Here we show catalytically grown self-assembled carbon nanohelices (CNHs). A similar carbon structure has been reported before, but less investigation including microstructure characteristics, growth mechanics, and FEE properties was performed.9 The microstructures and morphologies of CNHs were characterized by scanning electron microscopy, highresolution transmission electron microscopy (HRTEM), nanobeam diffraction (NBD), and Raman spectroscopy measurements. Their field-emission properties were investigated.

Carbon nanohelices were fabricated using microwaveplasma assisted chemical vapor deposition (MPCVD) method. This MPCVD system (Astex 2100) is equipped with a 2.45 GHz microwave source and a movable graphite table, which can be heated up to 1000 °C. On the graphite table, we placed an additional graphite sample holder drilled with holes ( $\Phi$ =0.5 mm) on the upper surface. Iron needles ( $\Phi$ =0.25 mm) were used as substrates and inserted into the holes in the graphite sample holder. The base pressure is less than 10 mTorr. During growth, we controlled the growth parameters as the reactive gas composition of  $N_2$  and  $CH_4$  at a flow rates ratio of 50:1, substrate temperature at  $\sim$ 900 °C measured by infrared thermometer, microwave power at 750 W, total pressure at 15 Torr, and bias voltage at -150 V between the substrate and the chamber (ground). The experimental setup and the growth parameters are similar to that of growing tubular graphite cones we reported before.<sup>10</sup> The growth of CNHs occurred with the help of very little impurities of boron by pretreating the chamber with H<sub>2</sub> and  $B(CH_3)_3$  plasma. The as-grown area located at the lower regions of the iron tips are roughly between the iron wire and the holes in graphite. The -150 to -300 V bias voltage plays a key role at the orientation of them. We have tried to use nickel needle as substrate under the same experimental setup. The as-grown carbon nanohelices are similar to those grown on iron needles except for a rather bigger diameter and poor alignment.

Aligned carbon helices are not grown from the needle surfaces perpendicularly but tilted with an angle of  $30^{\circ}-40^{\circ}$ to the normal of the surface [Fig. 1(a)]. The average diameter of the CNHs are about 200 nm, and the average length of the CNHs is about 20  $\mu$ m after growing for 30 min [Fig. 1(b)]. That each CNH has an iron catalyst particle on the tip reveals a catalytic tip-growth. Enlarged SEM photos and TEM images [Figs. 1(c) and 1(e)] show that all catalyst particles have compressed droplet-like shapes. They are capsulated aslant within the CNHs except for the top surfaces. Unlike the carbon nanotubes with a hollow pore, the CNHs are wrenched by ribbon-like carbon into helical shapes. And the average thickness of the carbon ribbon is roughly 50 nm. The helical directions viewed from their top, either clockwise or counterclockwise, are randomly distributed among various CNHs. The spiral degree has little difference among different CNHs, and usually the repeated length along the axial direction is roughly 2/3 the diameter. Viewing them from their roots, we found that, unlike the upper part of helical structures, their roots are rod-like fibers, although they are not very straight, with a length up to several microns [Figs. 1(d) and 1(f)].

Electron energy loss spectroscopy analysis reveals that

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FIG. 1. SEM and TEM images of the carbon nanohelices. (a)–(c) The aligned CNHs growing on an iron needle surface, enlarged images of aligned CNHs, and the catalyst particles on their tips, respectively. (d) is taken from the roots of the CNHs by scratching some of the CNHs off. (e) and (f) The TEM image of the tip and the root of a CNH.

the CNHs are made of pure carbon in  $sp^2$  hybridization state. NBD patterns of a CNH at different position with the incident electron beam roughly normal to its axis are presented in Fig. 2(a). The selected position such as edge areas I and II (or core areas III and IV) gives a similar pattern. The (002) spot always appears in both patterns although the diffraction spots diffuse to a large angle, which manifests an ordered layer-like structure of graphite. In the edge regions I and II, the direction of 002 is roughly normal to the rotation direction of the carbon ribbon, while the 002 spots divide into two groups in the center regions III and IV where the upper and lower half carbon ribbon is overlapped. Considering these features combined with the geometrical structure of them, we conclude that the graphite sheets are roughly parallel to the rotation direction of the carbon ribbon. This conclusion is also confirmed by the HRTEM image in the edge area such as that taken from region I or II. The HRTEM image reveals an obviously layer-like structure of graphite, although it is more like a turbostacking structure with layer



FIG. 2. (a) NBD pattern from different selected position in a CNH. (b) HRTEM image of a CNH edge, which shows a graphite layer stacking. Layer overlap can be clearly seen and is attributed to the bending of the carbon ribbon of the upper and lower parts.



FIG. 3. Raman spectrum of the CNHs with a selected region size of  $1{\times}1~\mu m^2.$ 

buckling and bending. The interlayer spacing is  $0.34\pm005$  nm calculated from the diffraction spots of 002.

Figure 3 shows a Raman spectrum (selected area is about 1  $\mu$ m<sup>2</sup>) of the CNHs sample [Fig. 2(a)]. Two peaks appeared approximately at 1353 cm<sup>-1</sup> (*D* band) and 1585 cm<sup>-1</sup> (*G* band), while the *D*-band peak is stronger than that of *G* band. Crystalline graphite, such as highly oriented pyrolitic graphite, can be characterized by the Raman peak at 1580 cm<sup>-1</sup>, whereas the disorder in carbon materials would induce an intense peak at 1350 cm<sup>-1</sup>, which is called the defect-induced Raman band.<sup>11</sup> The origin of the *D* band as well as the broader half-width (43 cm<sup>-1</sup>) for the as-grown samples is possibly caused by two factors, one is the amorphous carbon deposited on the CNH surface and the other is the rather strong disorder or distortion existing in this material. The two peaks in Fig. 3 are upshifted by several cm<sup>-1</sup>. This reveals that compress stress exists within the CNHs.

The growth mechanism of CVD-grown carbon fibers or carbon nanotubes is known as the vapor-liquid-solid growth mode,<sup>12,13</sup> that is, the liquid catalyst droplet absorbs the building block material from the surrounding vapor then deposits carbon on their surface. This mechanism can also be applicable here quite well. We can get some direct proofs from observing the roots and the catalyst particles of the CNHs to understand the microscopic growth mechanism. The SEM and TEM results [Figs. 1(c)-1(f)] of their roots suggest a two-stage growth model, that is, growing carbon fibers first then growing carbon helical structures second. The catalyst particles are near spherical in the first stage and then are compressed into the droplet-like shape in the second stage. In the second stage, the helical features of the CNHs suggest that the particles are rotating when growing. It is still unknown what is the impetus for the catalyst particles transferring their shapes of the two stages and rotating in the second stage. Our understanding is that the inhomogeneous plasma located in the growth area plays a key role. To verify this, we used flat iron plates as substrate placed on the same sample holder and used the same growth parameters as described before. The as-grown carbon materials then are all rod-like carbon nanofibers. In some samples, we observed the mixture of carbon nanohelices and carbon nanotubes. Most of these carbon nanotubes are not straight and have coil-like structures. The tube or catalyst particle diameters are rather small, about 70 nm or smaller, suggesting that



FIG. 4. (a) A field emission I-V curve of an iron wire (cutting off the tip without CNHs) at different gaps. (b), (c) The optimized I-E curves and FN plots corresponding to (a), (d)  $d-\beta$  curve.

smaller catalyst particles are difficult to transform into droplet shape, which is essential to grow helical structures. The alignment of the CNHs is supposed to be caused by the high bias voltage added as has been reported for carbon nanotubes/fibers or micro coils (such as Refs. 14 and 15).

The field-emission characteristics are studied in homemade instrument, which used a phosphorus glass plate coated with indium tin oxide as anode. The iron needle coated with aligned CNHs acts as cathode. In order to eliminate the influence of the iron tip when emitting, we cut off the iron tip (where it is not grown with CNHs) and aligned the iron wire axis normal to the transparent anode. The I-V curve shown in Fig. 4(a) is measured at different gaps between the anode and cathode. Due to the rather small size of the cathode and large gap between the anode and cathode, the electrical field on the near sample surface is not uniform and can no longer be calculated as in the works done for large-area samples before. Two extreme conditions should be considered, one is that the gap distance is very small and another is the gap distance is very large. In the first case, the average electrical field is proportional to V/d, where V is the applied electrical field and d is the gap distance. In the second case, the electrical field (near the sample surface) is roughly proportional to V(1/d+1/r) when adopting a sphere approximation for the cathode tip, where r is the radius of the tip. At present the experimental parameters are between these two extreme conditions, and we assume that the average electrical field (E) is roughly equal to  $V(1/d+1/\alpha)$ , where  $\alpha$  is a parameter. Given that the turn-on electrical fields  $(E_t)$  at different gaps are roughly the same, we set the optimized  $\alpha$  value of 6 based on the I-V data [Fig. 4(a)]. And we can get the  $E_t$  of  $\sim$ 0.6 V/ $\mu$ m, which is similar or smaller compared to that of carbon fibers or nanotubes.<sup>16–20</sup> The optimized I-E curve is shown in Fig. 4(b), and the corresponding Fowler-Nordheim (FN) plots [Fig. 4(c)] are straight lines for different gap distance. According to the Fowler–Nordheim theory,<sup>21</sup> we calculated the field enhanced factor  $\beta$  at different gaps [Fig. 4(d)]. That the  $\beta$  increases with increasing *d* can be attributed to the increasing emission area. A field emission current density of 1 mA/cm<sup>2</sup> is achieved at ~1700 V and the current density of 10 mA/cm<sup>2</sup> can be achieved at ~2100 V when the gap distance is set to be 2 mm. The well performance of the field-emission properties to these materials may be attributed to the large number of emission sites formed by the tips and edges of the CNHs.

In summary, we successfully fabricated the aligned carbon nanohelices "film" on iron needle and find that the alignment is directly related to the bias voltage added on the substrate. The microstructure analysis shows that they have graphite layer-like structure with amounts of layer bending coupled with lattice stress. The field emission properties are very good and comparable to that of carbon nanotubes. The work for characterizing the mechanical, electrical, and chemical properties are on the way.

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- <sup>1</sup>R. T. K. Baker, P. S. Harris, and S. Terry, Nature (London) 253, 37 (1975).
- <sup>2</sup>A. Oberlin, M. Endo, and T. Koyama, J. Cryst. Growth 32, 335 (1976).
- <sup>3</sup>S. Motojima, M. Kawaguchi, K. Nozaki, and H. Iwanaga, Carbon **29**, 379 (1991).
- <sup>4</sup>M. Jos-Yacaman, M. Miki-Yoshida, L. Rendon, and J. G. Santiesteban, Appl. Phys. Lett. **62**, 657 (1993).
- <sup>5</sup>D. S. Bethune, C. H. Kiang, M. S. De Vries, G. Gorman, R. Savoy, and R. Beyers, Nature (London) **363**, 605 (1993).
- <sup>6</sup>S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov, and J. B. Nagy, Science **265**, 635 (1994).
- <sup>7</sup>Z. L. Wang and Z. C. Kang, Philos. Mag. B 74, 51 (1996).
- <sup>8</sup>S. Motojima and Q. Chen, J. Appl. Phys. **85**, 3919 (1999).
- <sup>9</sup>J. Liu, X. Zhang, Y. J. Zhang, X. H. Chen, and J. Zhu, Mater. Res. Bull. 38, 261 (2003).
- $^{10}\mbox{G.}$  Y. Zhang, X. Jiang, and E. G. Wang, Science  $300,\,472$  (2003).
- <sup>11</sup>A. Cuesta, P. Dhamelinocourt, J. Laureyns, A. Martinez-Alonso, and M. D. Tascon, Carbon **32**, 1523 (1994).
- <sup>12</sup>R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. 4, 89 (1964).
- <sup>13</sup>W. L. Holstein, J. Catal. **152**, 42 (1995).
- <sup>14</sup>Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, Science **282**, 1105 (1998).
- <sup>15</sup> W. In-Hwang, X. Q. Chen, T. Kuzuya, K. Kawabe, and S. Motojima, Carbon **38**, 565 (2000).
- <sup>16</sup>G. Y. Zhang, X. C. Ma, D. Y. Zhong, and E. G. Wang, J. Appl. Phys. **91**, 9324 (2002).
- <sup>17</sup> W. A. de Heer, A. Chatelain, and D. Ugarte, Science 270, 1179 (1995).
- <sup>18</sup>Y. Chen, S. Patel, Y. Ye, D. T. Shaw, and L. Guo, Appl. Phys. Lett. 73, 2119 (1998).
- <sup>19</sup>Z. W. Pan, Frederick C. K. Au, H. L. Lai, W. Y. Zhou, L. F. Sun, Z. Q. Liu, D. S. Tang, C. S. Lee, S. T. Lee, and S. S. Xie, J. Phys. Chem. B **105**, 1519 (2001).
- <sup>20</sup> D. Y. Zhong, G. Y. Zhang, S. Liu, T. Sakurai, and E. G. Wang, Appl. Phys. Lett. **80**, 506 (2002).
- <sup>21</sup> R. H. Fowler and D. L. Nordheim, Proc. R. Soc. London, Ser. A **119**, 173 (1928).