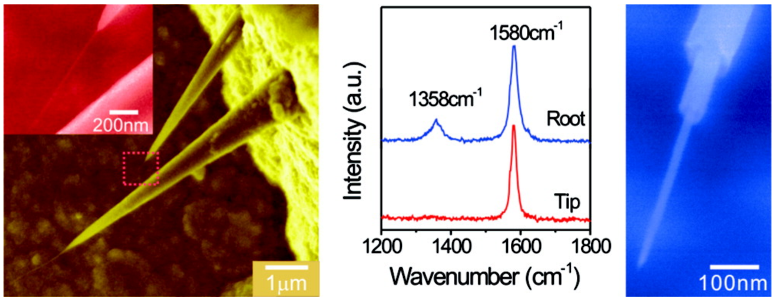
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Tubular Graphite Cones with Single-Crystal Nanotips and Their Antioxygenic Properties

Naigui Shang, William I. Milne, and Xin Jiang

J. Am. Chem. Soc., **2007**, 129 (28), 8907-8911• DOI: 10.1021/ja071830g • Publication Date (Web): 23 June 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

Tubular Graphite Cones with Single-Crystal Nanotips and Their Antioxygenic Properties

Naigui Shang,[†] William I. Milne,*,[†] and Xin Jiang[‡]

Contribution from Electrical Engineering Division, Department of Engineering, Cambridge University, 9 J J Thomson Avenue, Cambridge CB3 0FA, UK, and Insitute of Materials Engineering, University of Siegen, Paul-Bonatz-Strasse 9-11, 57076 Siegen, Germany

Received March 15, 2007; E-mail: wim@eng.cam.ac.uk

Abstract: Tubular graphite cones (TGCs) with a single-crystal nanotip have been achieved by means of microwave plasma-assisted chemical vapor deposition using in-situ-evaporated Fe catalysts. The absence of the disorder-induced D band in Raman spectra revealed the single-crystalline feature of the nanotip. TGCs were found to stem from Fe catalytic carbon spherules on the order of 100 μm diameter, whose critical role in promoting both nucleation and plasma annealing in the formation of highly crystalline TGCs is discussed. The crystalline quality of such TGCs can be further verified by the investigation of their oxidative stability in air. All TGCs can survive up to 600 °C without any structural variations, and a few TGCs still survive with an anisotropic etched and stepped nanotip at temperatures up to 800 °C, much better than CNTs. Thus, TGCs with single crystalline nanotips are potential candidates for scanning probes in high-temperature oxygen-containing environments.

Introduction

Tubular graphite cones (TGCs) have attracted intense attention, because they show not only a fascinating external morphology with a helically faceted cone-shape but also a noticeable internal microstructure with a preferred zigzag monochirality.[1] Recently, we reported large-sized TGCs with straight and long carbon nanotube tips.[2] These are some of the best structures for use as high-resolution scanning probes and are excellent electron emitters compared with both isolated conical and cylindrical structures. This is because of a combination of a conical structure (with better mechanical, thermal stability) and high-aspect-ratio cylindrical structures (with higher lateral resolution and larger field amplification factor). However, structurally robust TGCs have only been successfully grown on sharp metal needles (Fe, Pt, and Au) and planar steel substrates,[3,4] which are very difficult to further manipulate for applications. Direct growth of TGCs on Si substrates is very promising because it is not only compatible with the current Si semiconductor industrial processes but also helps us to understand the growth mechanism due to the noncatalytic nature of the Si substrates. In addition, the growth of highly crystalline carbon materials themselves is a challenge because of the high melting point (3500 °C) of carbon.[5−7] To date, most artificially synthesized carbon materials including single-wall carbon nanotubes (CNTs) are defective or disordered,[8] which is indicated typically by the disorder-induced D band at around 1350 ± 100 cm^{-1} in the Raman spectra. Unquestionably, growing single-crystal carbon nanostructures will greatly improve and stabilize the physical and chemical properties of materials and therefore widen their applications through the exclusion of various defect-induced factors.[9−11] In addition, the oxidative behavior of carbon materials is of significant scientific and technological interest as this is related to carbon combustion, coal gasification, reactions at nuclear reactor walls and re-entry shielding of space craft. It was found that the oxidation of graphite started from surface defect sites and the thermal oxidative stability of carbon-based materials, such as diamond, graphite, and CNTs, was critically related to the amounts of various defects such as edges, dangling bonds, vacancies, dislocations, and steps.[10,12] Therefore, the oxidative stability of such materials directly reveals their crystalline quality, i.e., the greater the oxidative stability the higher the crystalline quality. In this paper, we report the growth of large-area TGCs with a single-crystal nanotube tip on Si substrates by microwave plasma assisted chemical vapor deposition (MPCVD) using in-situ

---

[†] Cambridge University.

[‡] University of Siegen.

(1) Zhang, G. Y.; Jiang, X.; Wang, E. G. *Science* **2003**, *300*, 472−474.

(2) Shang, N. G.; Jiang X. *Appl. Phys. Lett.* **2005**, *87*, 163102−163102−3.

(3) Li, J. J.; Gu, C. Z.; Wang, Q.; Xu, P.; Wang, Z. L.; Xu, Z.; Bai, X. D. *Appl. Phys. Lett.* **2005**, *87*, 143107−143107−3.

(4) Mani, R. C.; Li, X.; Sunkara, M. K.; Rajan, K. *Nano Lett.* **2003**, *3*, 671−673.

(5) Charrier, A.; Coati, A.; Argunova, T.; Thibaudau, F.; Garreau, Y.; Pinchaux, R.; Forbeaux, I.; Debever, J. M.; Sauvage-Simkin, M.; Themlin, J. M. *J. Appl. Phys.* **2002**, *92*, 2479−2484.

(6) Gogotsi, Y.; Libera, J. A.; Kalashnikov, N.; Yoshimura, M. *Science* **2000**, *290*, 317−320.

(7) Badzian, T.; Badzian, A.; Roy, R. *Appl. Phys. Lett.* **2000**, *76*, 1125−1127.

(8) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza-Filho, A. G.; Saito, R. *Carbon* **2002**, *40*, 2043−2061.

(9) Bockrath, M.; Liang, W. J.; Bozovic, D.; Hafner, J. H.; Lieber, C. M.; Tinkham, M.; Park, H. *Science* **1991**, *291*, 283−285.

(10) Lee, S. M.; Lee, Y. H.; Hwang, Y. G.; Hahn, J. R.; Kang, H. *Phys. Rev. Lett.* **1999**, *82*, 217−220.

(11) Endo, M.; Saito, R.; Dresselhaus, M. S.; Dresselhaus, G. Carbon Nanotubes: Preparation and Properties, edited by Ebbesen, T. W. (CRC Press, Boca Raton, FL, 1997), P. 35.

(12) Bom, D.; Andrews, R.; Jacques, D.; Anthony, J.; Chen, B.; Meier, M. S.; Selegue, J. P. *Nano Lett.* **2002**, *2*, 615−619.

10.1021/ja071830g CCC: $37.00 © 2007 American Chemical Society

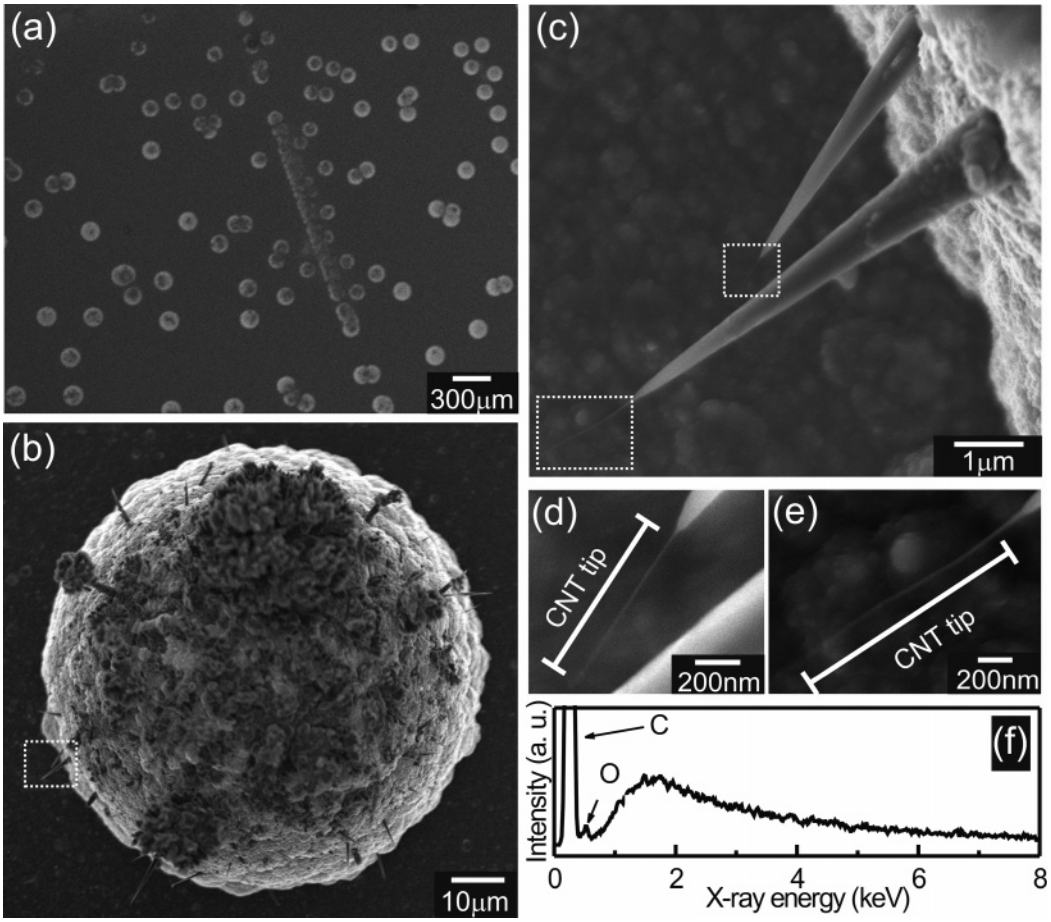


Figure 1. Different magnification SEM images of TGCs grown on Si substrates (a−e) and EDS spectrum (f). The dashed rectangles show corresponding enlarged areas. (d and e) TGCs having a long straight CNT tip.

evaporated Fe catalysts. The thermal oxidative stability is also studied using high-temperature air heating at temperatures between 500 and 900 °C.

Experimental Section

A 2.45 GHz, 5 kW MPCVD system was used to grow the TGCs with single-crystal nanotips. Two 15 × 15 mm Si wafers, one covered solely with a native oxide layer and the other coated with a 160 nm thick Fe film, were put side by side at the center of a circular stainless steel holder. The substrates were first pretreated in a hydrogen (85 sccm) atmosphere by using a microwave power of 1500 W at 60 mbar and a negative bias of 150 V for 10 min. After pretreatment, the hydrogen flow and the bias were switched off and the TGC growth was started by flowing in a gas mixture of methane and nitrogen (N_2:CH_4 = 30:30 sccm) at a working pressure of 40 mbar. The substrate temperature was measured by an infrared optical pyrometer and found to increase from 900 °C during the pretreatment to 1150−1200 °C during the growth, which enabled the Fe evaporation, condensation, and catalytic growth of TGCs on the bare Si wafer. The thermal oxidation effects on as-grown TGCs were measured in a tubular furnace in air. The samples were heated with a time ramp of 45 min and kept at the desired temperature between 500 and 900 °C for 30 min. They were taken out after 1−2 h when the furnace had cooled down to 400 °C. The morphology and structure of all TGC samples were characterized by using scanning electron microscopy (SEM) and micro-Raman scattering spectroscopy, respectively.

Results and Discussion

After deposition for 2 h, the two Si wafers were covered by a layer of black-shape, perfect carbon spherules with a diameter of 85−120 μm, which can be seen by the naked eye (Figure 1a). These relatively large carbon spherules are essentially uniformly distributed on the Si surface, but some of them accumulate together to form a straight line. Unlike the radially textured carbon nanoflake spherules covered by nanometer-sized thick carbon nanoflakes,[13] there are many TGCs and tree-like carbon nanostructures standing on the top of each carbon spherule on the Si substrates which have not been pre-coated with a Fe film (Figure 1b), while neither TGCs nor any other especially interesting carbon structures were found on the top of such carbon spherules on the Fe pre-coated Si wafer. The average

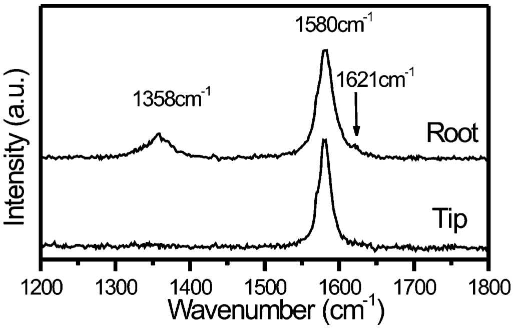


Figure 2. Raman scattering spectra taken from the TGC root and tip, showing the single crystalline feature of the tip.

---

(13) Shang, N. G.; Staedler, T.; Jiang, X. *Appl. Phys. Lett.* **2006**, *89*, 103112−103112−3.

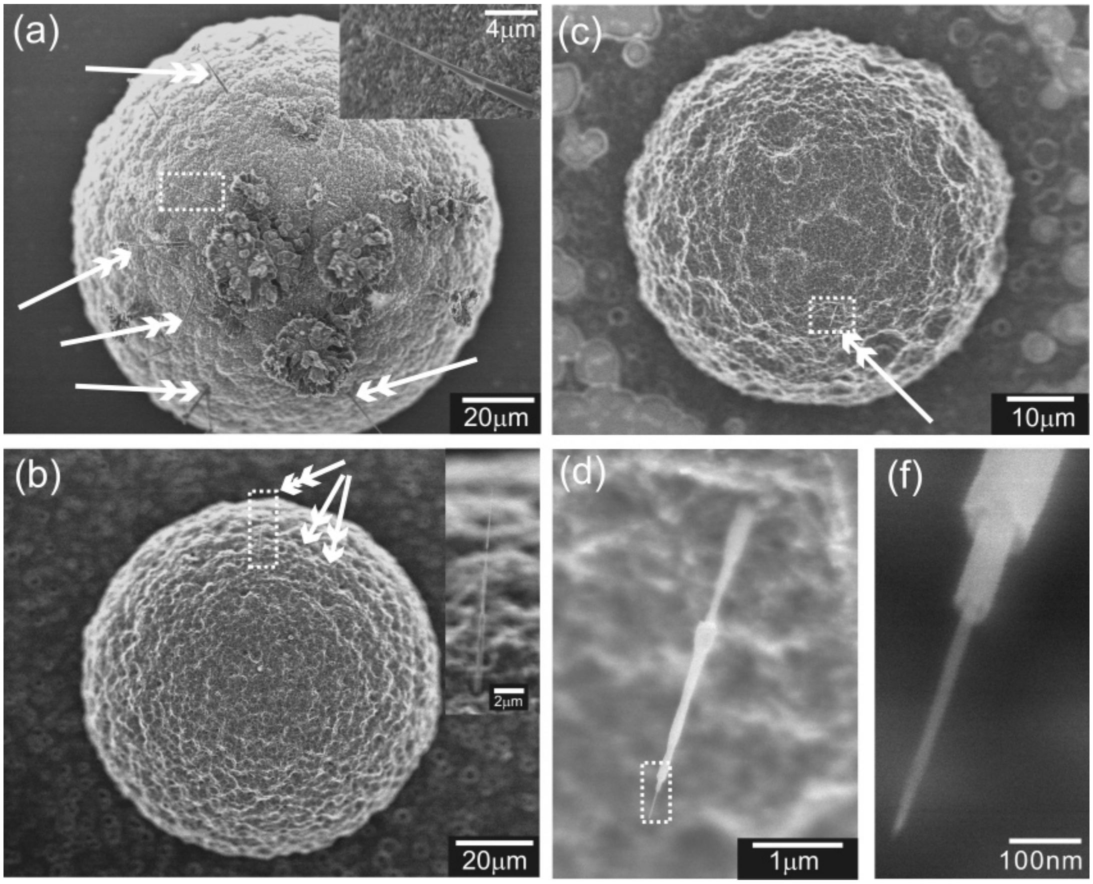


Figure 3. SEM images of thermally oxidized TGCs at the temperature of 600 °C (a), 700 °C (b), and 800 °C (c); the insets are the corresponding enlarged images of marked rectangles in a and b; (d) an enlarged SEM image of single TGC in the marked area of c; (f) enlarged images of marked area of d.

length of the TGCs is about 4−18 μm with a root diameter of 0.3−1 μm.

The majority of TGCs are slender, having a small-angle sharp apex (Figure 1c). As we reported previously,[2] many TGCs have a straight or slightly bent tip with a length in the range of 0.6−1 μm and a diameter of 10−20 nm (Figure 1d,e). The chemical composition of such carbon spherules and TGCs including their roots and tips was analyzed by energy dispersive X-ray spectroscopy (EDS) with an electron energy of 20 KeV. Figure 1f indicates that they are mainly made of carbon and small amounts of oxygen (∼1−5 wt %). No metal (Fe) catalyst was found on the surfaces of the Si and all as-deposited structures. However, after removing the top carbon structures by high-temperature oxidation, we were able to find a number of several-hundreds-micrometers sized Fe clusters to catalytically grow the TGCs.

Raman spectroscopy is a nondestructive and powerful technique and has been used to characterize the crystalline quality and phonon and band structure of various carbon materials. Figure 2 shows typical Raman spectra of the root and tip of a single TGC over a wave number range from 1200 to 1800 cm^{-1}. The Raman spectra were excited with a 514 nm Ar^{+} laser and collected in a backscattering geometry with a spatial resolution of 1 μm at room temperature. The TGC root shows a typical microcrystalline graphite structure with a strong G peak at 1580 cm^{-1}, a small D band at 1358 cm^{-1}, and a D′ shoulder at 1621 cm^{-1}. However, the tip shows a single crystalline graphite feature with only one G peak at 1580 cm^{-1} and no D and D′ bands which are both directly correlated to the defects and degree of disorder in carbon materials. The full width at half-maximum of the G peak decreases from 26 cm^{-1} at the root down to 18 cm^{-1} at the tip, which is very close to that of natural single-crystal graphite, highly oriented pyrolytic graphite (HOPG), and graphite polyhedral crystals (14 cm^{-1}).[6,14,15] The slight broadening could be due to the size effect. The tip is highly graphitized and defect-free compared to the root.

The crystalline quality of the TGCs can be further evaluated by its oxidative stability by virtue of the mechanism of defect-induced oxidation in carbon structures.[10] Figure 3 shows the SEM images of the TGC samples oxidized at temperatures between 600−800 °C. Compared with the as-deposited TGCs, there are no changes observed in the morphology, size, and number of the TGCs oxidized at 600 °C except for the disappearance of some tree-like structures, which mainly consist of amorphous carbon. When the TGCs underwent oxidation at 700 °C for 30 min, no carbon structures were found on the carbon spherules other than some TGCs, which had greatly decreased in number from 20−30 to 3−5. They had also decreased in length and diameter. Meanwhile, many etched pits with diameters of 0.5−1 μm size were found on the surface of the spherules. After oxidation at 800 °C, these etched pits further increased in size to 3−5 μm while the carbon spherules decreased from typically 60−100 μm at 700 °C down to 30−60 μm. However a few TGCs with a length of 3−4 μm survived on top of the carbon spherules. Thus, TGCs have a superthermal oxidative stability in air compared to those as-grown and high-

---

(14) Tuinstra, F.; Koenig, J. L. *J. Chem. Phys.* **1970**, *53*, 1126−1130.
(15) Nemanich, R. J.; Solin, S. A. *Phys. Rev. B* **1979**, *20*, 392−401.

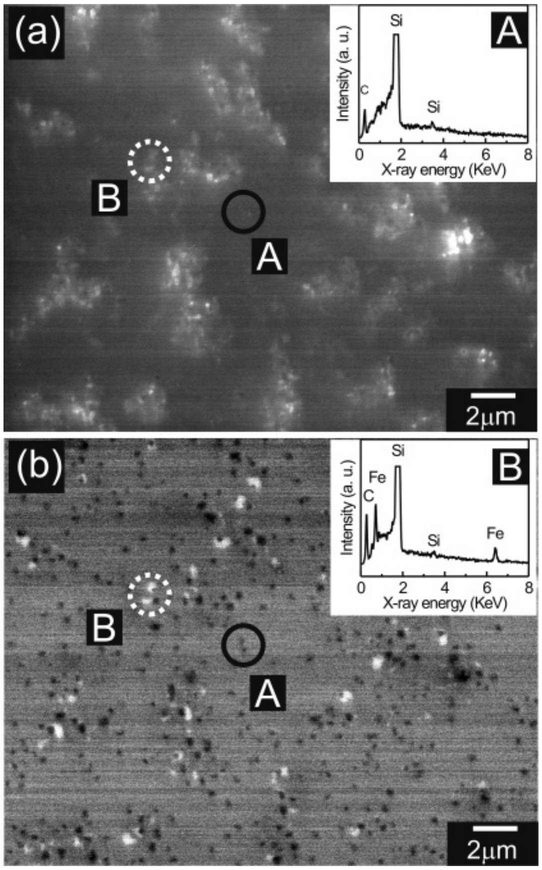


Figure 4. SEM images of the secondary (a) and backscattering (b) electron taken from the sample after the oxidation at 900 °C. The insets are EDS spectra taken from different spots (marked with solid and dash line circles, and upper case letters A and B), showing the presence of 100 nm sized Fe clusters on the Si wafer.

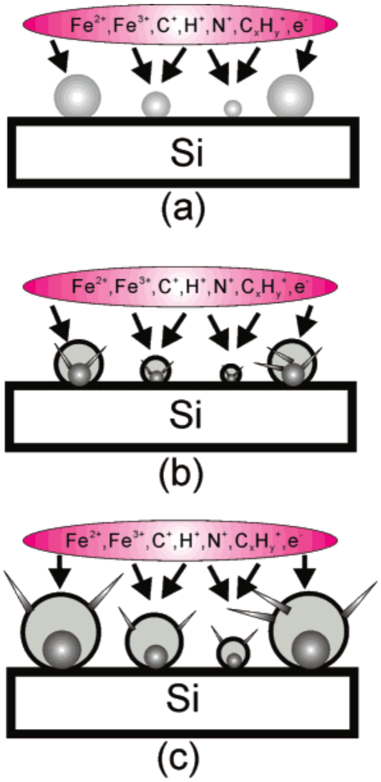


Figure 5. Schematic diagram of the growth model of TGCs with single-crystalline nanotips: (a) The formation of highly condensed Fe−C eutectic droplets on the Si substrate by the vapor-phase precipitation of dissociated carbon and evaporated Fe clusters from the plasma ball; (b) the nucleation of TGCs on the supersaturated droplet by phase separation; (c) growth of TGCs with the growth of carbon spherules, which enhanced not only the nucleation of TGCs but also plasma annealing of all defects in TGC tips due to a tip-discharge effect.

temperature (up to 2800 °C) annealed CNTs, where at least 95% weight loss was found at 800 °C and catalysts dominated the residual materials.[12,16] However, unlike the as-deposited and low-temperature oxidized TGCs, all of the TGCs oxidized at 800 °C no longer have a perfect conical structure and seem to be made of two TGCs grafted together. In the middle area, there is a protruding hump with a diameter slightly larger than that of the TGC root. This means that the thicker root has been preferentially etched away, and this is of poorer crystalline quality compared with the middle area of the TGC. Another noticeable phenomenon is that the oxidized nanotip shows a probe structure with a regular step (see Figure 3f). The narrowest section is about 15 nm in diameter and about 300 nm in length while the widest one is about 100 nm thick and 500 nm long and the two etched steps like in the cleaved HOPG are very clear. This is evidence of anisotropic etching, which in general takes place in single crystalline materials, e.g., in Si chemical etching. Thus, the nanotips are unequivocally single crystals, consistent with the Raman results.

When the samples were oxidized at 900 °C, no carbon spherules and TGCs were found on the Si substrate except for some residual granular hillocks as shown in Figure 4(a). In order to further clarify the nanostructures after high-temperature oxidation, a SEM was used in back scattering mode, based on its powerful ability to distinguish between chemical elements with different atomic numbers. Figure 4b is a typical image taken from the same area of the sample as shown in Figure 4a. A large quantity of black spots and a few white spots were observed on the Si surface. Because of the atomic number of Fe being larger than that of carbon, the white spots will be Fe while the black ones are made of carbon. This can be further confirmed by the EDS microprobe. The insets of Figure 4a,b show the EDS spectra taken from the marked area in Figure 4a,b and reveal the presence of Fe which was deeply embedded in the deposited carbon structures as the catalyst for the growth of TGCs. Note the size of the Fe clusters is about 200−700 nm, much larger than the catalysts commonly used to drive the CNT growth. However, these bigger clusters could be evidence of the growth mechanism of TGCs we suggested previously,[2] where the growth of catalysts themselves results in the formation of tapered structures.

The forming mechanism of various conical carbon structures is an interesting subject.[17−19] The specific conical structure of TGCs implies that the growth of TGCs should differ from the one-dimensional mode of CNTs, in which the diameter of CNTs critically depends on the size of the liquid droplet or localized liquefied zone of the catalyst. The TGC can instead follow a nonsymmetrical two-dimensional growth mode: a faster axial

---

[16] Ajayan, P. M.; Ebbesen, T. W.; Ichihashi, T.; Iijima, S.; Tanigaki, K.; Hiura, H. *Nature* **1993**, *362*, 522−525.

[17] Merkulov, V. I.; Guillorn, M. A.; Lowndes, D. H.; Simpson, M. L. *Appl. Phys. Lett.* **2001**, *79*, 1178−1180.

[18] Bhimarasetti, G.; Sunkara, M. K.; Graham, U. M.; Davis, B. H.; Suh, C.; Rajan, K. *Adv. Mater* **2003**, *15*, 1629−1632.

[19] Xia, W.; Su, D. S.; Schlögl, R.; Birkner, A.; Muhler, M. *Adv. Mater* **2005**, *17*, 1677−1679.

growth and a slower radial growth. The fast axial growth can be driven by the same mechanism as the CNTs while the slow radial growth can be demonstrated by either the thickening of inner diameters or the increasing number of outer shells. The thickened inner diameters could be due to the increase of catalyst sizes, and the increased outer shells could be due to the improved carbon supply. Here, we suggested the TGC growth originated from the gradual extension of the boundary diffusion interlayer of the solid−liquid around the catalyst surface, allowing the graphitic shell to grow along two directions. Figure 5 shows a schematic growth model for the TGCs. At high temperature, the Fe film was evaporated and reacted with the vapor-phase carbon, forming eutectic clusters in the plasma ball. After supersaturation, the eutectic clusters can precipitate onto the bare Si substrate to a form a liquid droplet. Because of the very large temperature gradients from the plasma ball to the substrate surface, the highly condensed droplet would become an active seed leading to the nucleation of TGCs with a cap-like structure by phase separation. When a large amount of carbon and Fe clusters from the plasma condense onto the liquid nuclei, the boundary diffusion interlayer between the solid and liquid will thicken and spread out as a result of seeds increasing in size, making the growth of new graphitic shells because of the increased carbon supply. Note the carbon supply cannot simply be considered as an essential factor but the variation of the boundary diffusion interlayer is also necessary, as this could lead to the carbon sources for the axial growth only.[20] The variation in the boundary interlayer could be due to two reasons. One is the increase of the catalyst size, which can be demonstrated by a tapered inner cavity in the conical structure.[21] Another is the increased viscosity of the condensed matter due to the decrease of the temperature gradient. This is similar to the shoulder process in the Czochralski method of growing various single crystals.[22] Meanwhile, the seed could gradually grow up to form the big carbon spherules with the TGC growth due to an excessive amount of carbon supply. Alternatively, it is possible that the large sized carbon spherules preferred to grow and then enhance the nucleation of TGCs due to the tip-discharge effect which induces a local strong electric field, as found for such sharp needles vertically standing in a plasma after its diameter achieved a specific size.[1,3,4] Similar cases have been found from such TGCs previously grown on planar steel substrates,[2] where there is a layer of coalesced carbon spherules with a size of 10−25 μm underneath the TGCs. As far as the formation of single crystalline nanotips is concerned, it is possible that the temperature of the plasma around the carbon spherules, particularly around such grown TGC tips, could close to the carbon melting point based on a same principle as the tip-enhancement effect. This could anneal out all defects in the nanotip, forming a single crystal.

Conclusions

In summary, large-area TGCs with single crystalline nanotips have been grown on Si substrates by MPCVD using in-situ evaporated Fe catalysts. D band-free Raman spectra indicated that the nanotip of the TGCs is a single crystal. The as-deposited TGCs show excellent thermal oxidative stability in air up to 800 °C, better than CNTs. A Fe catalytic mediated growth mechanism for the TGCs with single crystalline nanotips is suggested based on the carbon spherules enhancing the TGC nucleation in the presence of high-temperature plasma annealing. This study enables us not only to control the growth of TGCs but also to open a new application field for carbon nanostructures.

Acknowledgment. The authors thank V. Scardaci and A. Ferrari in the Engineering Department of Cambridge University for their help in Raman measurements and K. Zhang in the Second Physical Department of Göttingen University, Germany, for providing the Fe-coated Si substrates. This work was financially supported by the Engineering and Physical Science Research Council (EPSRC) under Grant GR/S975901, UK, and the Ministry for Education and Research (BMBF), Germany, under Project CHN 05/002 of WTZ.

JA071830G

---

(20) Ren, W. C.; Li, F.; Chen, H. M. *J. Phys. Chem. B* **2006**, *110*, 16941−16946.

(21) Gogotsi, Y.; Dimovski, S.; Libera, J. A. *Carbon* **2002**, *40*, 2263−2267.

(22) Scheel, H. J.; Fukuda, T. *Crystal Growth Technology*; Wiley Press: New York, 2003; p 293.