Electron Field Emission Characteristics and Field Evaporation of a Single Carbon Nanotube

M. S. Wang, L.-M. Peng,* J. Y. Wang, and Q. Chen

Key Laboratory on the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China

Received: August 3, 2004; In Final Form: September 28, 2004

Direct transmission electron microscope (TEM) observations of the field emission and evaporation process of emitting carbon nanotubes (CNTs) shown that the tip structure of the CNT is in general composed of irregular shaped graphitic sheets which extend typically more than 10 nm from the end of the CNT. It is found that the irregular shaped graphitic sheets at the tip of the CNT may greatly enhance the field emission characteristics of the CNT when compared with that having an ideal circular edge. The field evaporation of the CNT proceeds typically via the removal of the irregular shaped graphitic sheets from the tip of the CNT, and field emission characteristics of a CNT depend far more sensitively on the tip structure than on the geometric length of the CNT.

1. Introduction

Extensive studies on the electron field emission characteristics of carbon nanotubes (CNTs) have been carried out in recent years[1−6] due to the potential applications of CNT field emitters in flat TV and large panel display. The detailed emission mechanism of the CNT remains, however, a controversial issue. While Rinzler et al.[3] attributed the excellent field emission characteristics of the CNT to the unravelling of linear chains of carbon atoms from the open edges of the CNT, this unravelling process was not directly observed experimentally and indeed was rejected by Saito et al.[4] based on their field emission microscope (FEM) observations. Instead it was concluded that electron emission results from the circular edges of the graphitic layers of the CNT. Here we present a direct observation of the field evaporation process of the CNT and corresponding field emission characteristics during the process. Although the observed process is not identical with that proposed by Rinzler et al.,[3] many experimental observations of Rinzler et al. may indeed be explained by our observations. In addition we show by directly correlating the tip structure and field emission characteristics of the CNT that the exceptional field emission characteristics result mainly from the irregular shaped graphitic sheets at the tip of the CNT rather than from the ideal circular edges of the graphitic layers.[4]

2. Experimental Section

All transmission electron microscopy (TEM) observations were carried out with a 200 keV Tecnai G20 electron microscope. The vacuum level of the electron microscope is about 10^{-8} Torr. The movement and field emission measurement of the CNT was made by using a Nanofactory sample holder. A maximum of 140 V may be applied between the CNT and counter Pt electrode, and typically the acquisition time for each field emission $I-V$ curve with 1000 data points was 50 ms. All CNTs used in this work were multiwall CNT (MWCNT) prepared by using the chemical vapor deposition (CVD) method. The diameter of these CNTs ranges from 25 to 40 nm, and a typical tube has about 20 walls.[7]

3. Results and Discussions

Using the Fowler−Nordheim theory[8] we may write the field emission current as[9,10]

$$I = A(\beta^2 V^2/\phi)\exp[(-6.53\times 10^7)\phi^{3/2}/\beta V] \qquad (1)$$

where the constant A is proportional to the effective emission area, ϕ is the work function of the CNT, and the local electric field E is related to the potential difference V between the CNT tip and the counter electrode via $E = \beta V$, β being a local field conversion factor. The Fowler−Nordheim (F−N) plot is obtained by plotting $\ln(I/V^2)$ verses $1/V$. For field emission from a metallic object the F−N plot may be fitted by using a straight line. While the slope of the line gives information on both the work function ϕ and the field conversion factor β, the intersection of the line with the $\ln(I/V^2)$-axis provides additional information on the effective emission area. From a practical viewpoint for the same CNT we would like to have a tip structure having low work function ϕ, large local field conversion factor β, and effective emission area. A good emitting tip is therefore the one having a F−N plot with small slope and large intersection with the $\ln(I/V^2)$ axis. However, it should be noted that the Fowler−Nordheim formula (eq 1) was derived for a simple model in which electrons are confined in a simple metal box. Strictly speaking this formula is not expected to be valid for CNTs, and results derived from this and corresponding F−N plots may be used only as a guide. For a CNT emitter the electron emission is affected by many factors that are not considered by the simple Fowler−Nordheim theory, e.g., the influence of the tip structure, the localized electronic states, and finite field penetration into the CNT tip. As a result, the work function ϕ appearing in the Fowler−Nordheim theory should be considered only as an effective quantity that depends both on the geometry of the emitter and the quantum origin of the emitting electrons.

Shown in Figure 1 are four TEM images and corresponding field emission $I-V$ curves and F−N plots. Figure 1a shows a

* Corresponding author. E-mail: lmpeng@pku.edu.cn.

10.1021/jp046526d CCC: $30.25
Published on Web 12/04/2004

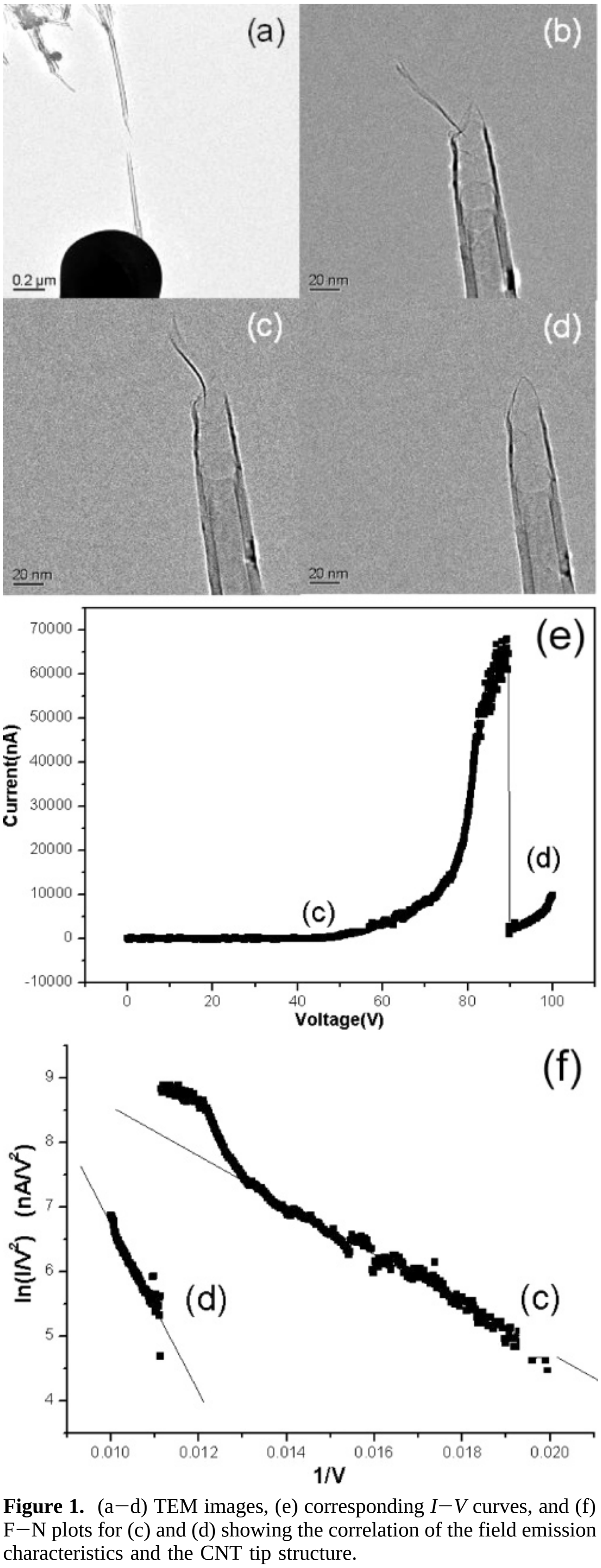

Figure 1. (a−d) TEM images, (e) corresponding $I-V$ curves, and (f) F−N plots for (c) and (d) showing the correlation of the field emission characteristics and the CNT tip structure.

W-tip (to the bottom of the figure) and a broken CNT. Initially the CNT was attached to the W-tip and its counter Pt-tip (above the W-tip but not shown in the figure). The CNT was then broken inside the TEM and two separate CNT tips were formed. Figure 1b shows a high resolution image of the CNT tip attached to the W-tip. The tip structure of the CNT is seen to be far from the ideal circular edge shape, and an irregular shaped graphitic sheet is clearly visible at the tip. On applying a voltage between the CNT and the counter Pt-tip, the irregular shaped graphitic sheet was seen to align with the electric field (Figure 1c) and over 50 μA stable emission current was obtained with a bias of about 80 V (Figure 1e). At higher voltage the emission current became unstable and dropped substantially at about 85 V and the sharp irregular shaped graphitic sheet seen in Figure 1c was removed from the tip. Although the new tip structure (Figure 1d) also gave field emission current, the onset voltage of field emission became much larger than that shown in Figure 1c. Shown in Figure 1f are corresponding F−N plots. The F−N plot associated with Figure 1c is seen to have a smaller slope and larger intersection with the $\ln(I/V^2)$ axis than that associated with Figure 1d. Note that the two CNTs shown in parts c and d of Figure 1 have identical geometry (i.e. length, aspect ratio), and the different field emission characteristics results entirely from the different tip structures, suggesting the important quantum nature of the field emission mechanism of the CNT. The tip structure shown in Figure 1d is similar to the slant-cut structure discussed by Han and Kim,[11] strongly supporting the ideas that the dangling bond states at the edges of the graphitic sheets are most efficient in contributing to the field emission current.[11,12]

Shown in Figure 2 are a series of TEM images recorded during field emission and evaporation process, demonstrating clearly that irregular shaped graphitic sheets at the emitting tip of the CNT are subject to a large electric field or force. Previous study has shown that on electron emission the tip temperature of the CNT may increase substantially up to 2000 K,[13] and this heating also contributes to the instability of the tip structure leading to the removal of carbon atoms from the tip. The series of TEM images shown in Figure 3 were recorded during the field emission process of a CNT at a constant bias. The whole process lasted about 30 min and the CNT shortened from about 420 nm to less than 150 nm. This process is very similar to that proposed by Rinzler et al.[3] The CNT became short via the field evaporation or removal of irregular shaped graphitic sheets at the tip of the CNT rather than via the unravelling of linear chains of carbon atoms, and the excellent field emission characteristics of the CNT resulted mainly from the irregular shaped graphitic sheet having many dangling bond states around its edges rather than from the linear chains as originally proposed by Rinzler et al.[3]

Shown in Figure 3 are field emission $I-V$ curves and corresponding F−N plots for the different CNT and tip structures shown in Figure 2, with curves K, I, J, etc., correspond respectively to panels K, I, J, etc. in Figure 2. The important point to note here is that there exists no one-to-one correspondence between the field emission characteristics and CNT length. For example, although the CNTs shown in panels B and D in FIgure 2 are longer than that shown in panels K and I in Figure 2, the field emission characteristics exhibited by the latter two are seen to be much better than that shown in panels B and D in Figure 2. The $I-V$ curves and corresponding F−N plots of Figure 3 therefore demonstrate amply that although the geometric field enhancement at the tip of the CNT (determined largely by the length and aspect ratio of the CNT) is a very important factor determining its field emission performance, the tip structure is perhaps a far more important factor that determines ultimately how good electron emitter a CNT may become. For a CNT with almost the same length over 100% change on the onset voltage has been observed for different tip structures, while the change due to the geometric length

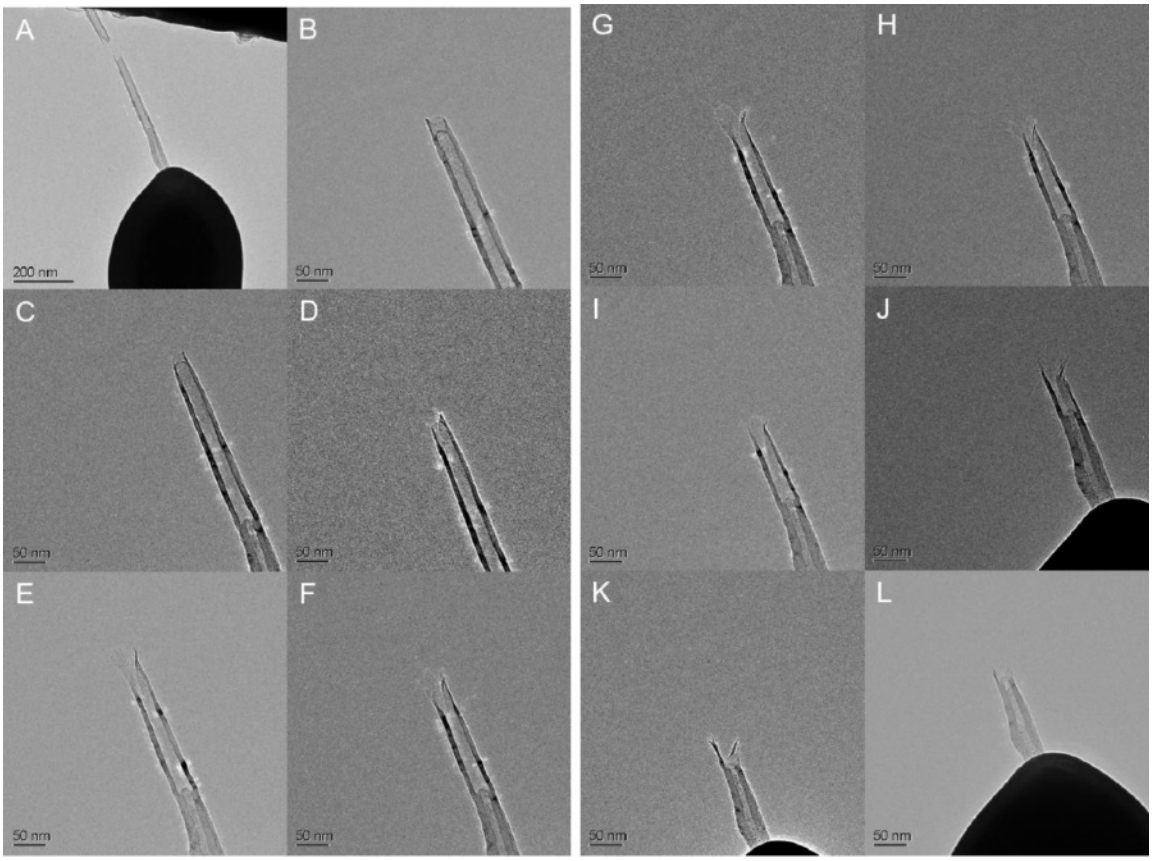

Figure 2. TEM images showing the evolution of a MWCNT during the field emission and evaporation process.

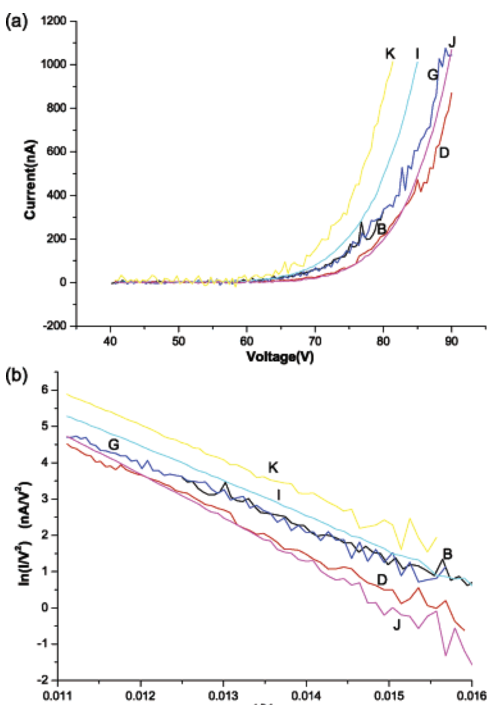

Figure 3. (a) Field emission $I-V$ curves and (b) corresponding F−N plots. The curves marked with K, I, etc. correspond to TEM images of K, I, etc. of Figure 2.

difference is much more moderate, especially when the CNT is longer than a certain length, say more than 200 nm.

It should be noted that all our observations were carried out using a 200 keV Tecnai G20 TEM, which is able to resolve individual walls of the CNT.[7] In principle our observations may also be carried out in a field emission high-resolution TEM with atomic resolution to better characterize the tip structure and to map the electrostatic field distribution at the tip using the method of electron holography.[14] One possible difficulty preventing higher resolution characterization of the emitting tip structure is that the emitting CNT tip is usually heated to a rather high temperature, e.g. up to 1500−2000 K,[13] during electron field emission and at such a high temperature it is usually not possible to obtain near-atomic resolution images of the emitting tip of a CNT having a finite length of, say, a few hundred nanometers due to the large thermal vibrating amplitude of the tip.[15] Nevertheless, high-resolution characterization of the CNT tip should be possible when the tip is not emitting a large current of electrons and therefore not heated to a very high temperature.

The emitting tip evaporation process reported here occurs only when the emission current exceeds a large value, say tens of μA, and the field used for extracting electrons is very strong. For a less strong field and small emission current excellent current stability was observed by many groups around the world.[6] From a practical viewpoint, the main advantage of the CNT field electron emitters over the conventional metal tips[9,16] is that the emission current of the CNT would not become runaway and therefore break down as a result of the tip heating. This is because the CNT is extremely stable at temperatures as high as 2000 K and, unlike metals, the resistance of the CNT decreases with increasing temperature[13] leading to a negative feedback to heating and runaway of the emitting tip.

4. Conclusions

In summary, we have shown that the open edge of an emitting CNT is in general far from the ideal circular shape, and the irregular shaped graphitic sheet often found at the tip of the CNT extends typically more than 10 nm from the end of the tube and sometimes as much as more than the diameter of the

CNT. Evaporation or removal of the irregular shaped graphitic sheet from the emitting tip of the CNT was often accompanied by a large change in emission current, and the tip structure was found to play a far more important role in determining the emission current than geometric factors, e.g. the length of the CNT.

Acknowledgment. The authors are grateful for the support by the Ministry of Science and Technology (Grant No. 001CB610502), National Science Foundation of China (Grant Nos. 90206021 and 10434010), the Chinese Ministry of Education (Key Project, Grant No. 10401), and the National Center for Nanoscience and Technology of China.

References and Notes

(1) de Heer, W. A.; Chatelain, A.; Ugarte, D. *Science* **1995**, *270*, 1179.
(2) Collins, P. G.; Zettl, A. *Appl. Phys. Lett.* **1996**, 69, 1969.
(3) Rinzler, A. G.; et al. *Science* **1995**, *269*, 1550.
(4) Saito, Y.; et al. *Nature* **1997**, *389*, 554.
(5) Dean, K. A.; Chalamala, B. R. *Appl. Phys. Lett.* **2000**, *76*, 375.
(6) Bonard, J.-M.; Kind, H.; Stockli, T.; Nilsson, L. O. *Solid-State Electron.* **2001**, *45*, 893.
(7) Liang, X. L.; Peng, L.-M.; Chen, Q.; Che, R. C.; Xia, Y.; Xue, Z. Q.; Wu, Q. D. *Phys. Rev. B* **2003**, *68*, 073403.
(8) Fowler, R. H.; Hordheim, L. W. *Proc. R. Soc. London A* **1928**, *119*, 173.
(9) Spindt, C. A.; Brodie, I.; Humphrey, L.; Westerberg, E. R. *J. Appl. Phys.* **1976**, *47*, 5248.
(10) Carroll, D. L.; Redlich, P.; Ajayan, P. M.; Charlier, J. C.; Blas, X.; De Vita, A.; Car, R. *Phys. Rev. Lett.* **1997**, *78*, 2811.
(11) Han, S.; Kim, J. *Phys. Rev. B* **2000**, *61*, 9986.
(12) Tada, K.; Watanable, K. *Phys. Rev. Lett.* **2002**, *88*, 127601.
(13) Purcell, S. T.; Vincent, P.; Journet, C.; Thien Binh, V. *Phys. Rev. Lett.* **2002**, *88*, 105502.
(14) Cumings, J.; Zettl, A.; McCartney, M. R.; Spence, J. C. H. *Phys. Rev. Lett.* **2002**, *88*, 056804.
(15) Treacy, M. M.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, *381*, 678.
(16) Qian, W.; Scheinfein, M. R.; Spence, J. C. H, *J. Appl. Phys.* **1993**, *73*, 7041.