A novel approach to improve the field emission characteristics of printed CNT films

Rujia Zou (邹儒佳)*, Shaolin Xue (薛绍林), and Dayong Li (李大勇)

Department of Applied Physics, Donghua University, Shanghai 201620

**E-mail: rjzou@mail.dhu.edu.cn*

Received June 2, 2008

A novel post-treatment method, including hard hairbrush and electrical treatment, is performed intentionally to improve the field emission capability and stability of screen-printed carbon nanotubes (CNTs). Compared with untreated films, the field emission properties of the treated ones are greatly enhanced. Scanning electron microscopy (SEM) and Raman spectrum studies reveal that field emission properties are enhanced by two factors. Firstly, the improved field emission properties of CNT films can be attributed to the more active CNT surface by removing the organic material cover on the CNTs. Secondly, the generation of a high density of structural defects and the lower resistance contact to the topside CNT emitters after treatment are all helpful to improving the field emission properties of the treated CNTs.

OCIS codes: 160.4760, 240.0310, 310.6870.

doi: 10.3788/COL20090702.0130.

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991[1], CNTs have attracted considerable interest because of their unique physical properties and many potential applications[2,3]. CNTs possess many fascinating properties including concentric planar wall structure, controllable nanometric diameter, high aspect ratio, chemical inertness, extraordinary mechanical strength, and good electric conductivity, which make them a promising candidate as a field emitter[4−6]. Many recent studies have demonstrated that CNTs can be a field emitting material of high performance with a stable current at low electric fields[7,8]. CNT cathodes have been fabricated by both chemical vapor deposition (CVD)[9] and screen-printing[10] techniques. Screen-printing is a low cost process for large-area field emission applications. However, CNTs are randomly distributed in a screen-printed cathode. Compared with highly ordered arrays of vertically aligned CNTs, their emission characteristics are poor in terms of lifetime and uniformity. Therefore, special treatments are often needed to improve the field emission characteristics. Recently, various treatment techniques, such as adhesive taping[11], soft rubber rolling[12], ion irradiation[13], laser irradiation[14], and plasma exposure treatment[15] have been developed to improve the field emission performances of CNT cathodes. Among these methods, adhesive taping and soft rubber rolling are easy methods in removing the paste film on the CNTs, however, these methods tend to leave residue and destroy CNT patterns; therefore, no uniform emission sites can be resulted. In the case of ion irradiation, laser irradiation and plasma exposure, due to the use of vacuum processing, the processing cost is increased in addition to the difficulty in large-area processing. So, it is still challenging for a simple and effective method to improve emission characteristics of printed CNT films. In this paper, we report a new method of fabricating CNT field emitters, which show good field emission characteristics, by using combination treatment. The combination treatment technique of hard hairbrush and electrical treatment is adopted and confirmed as an efficient way of improving the field emission characteristics of screen-printed CNT cathodes.

Multi-walled nano-tubes (MWNTs) prepared with catalytic CVD (Shenzhen Bill Technology Development Ltd.) were used in this study. The paste consisted of MWNTs, ethyl cellulose and terpineol. The preparation process of MWNT paste is as follows. Dispersing MWNTs ultrasonically in terpineol for a long time to get a paste containing MWNTs and terpineol, filtering the paste to remove the large particles, adding ethyl cellulose into the paste, then heating the paste to 80 °C and stirring it until ethyl cellulose is fully dissolved. When the paste was cooled to room temperature, the preparation of MWNT paste for screen-printing was finished. Then the CNT pastes were screen-printed onto aluminum (Al) substrates through the 350 mesh, which was used as the sample. The sample was dried at 100 °C for 1 h and annealed at 300 °C in air for 45 min to burn out the organic binders. When the sample was cooled to room temperature, a thin plastic film was covered on the surface of printed CNT film. A hard hairbrush was applied onto the thin plastic film to-and-fro to crush the organic matter covering on the CNT surface. After hard hairbrush treatment, the thin plastic film was removed from the CNT film. Subsequently the sample was transferred to face an Al anode, where a direct current (DC) electrical treatment was carried out, as shown in Fig. 1. During the treatment, the anode voltage was increased until the emission current reached a current density of

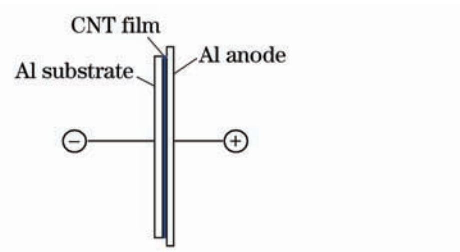

Fig. 1. Schematic diagram of electrical treatment for printed CNT films.

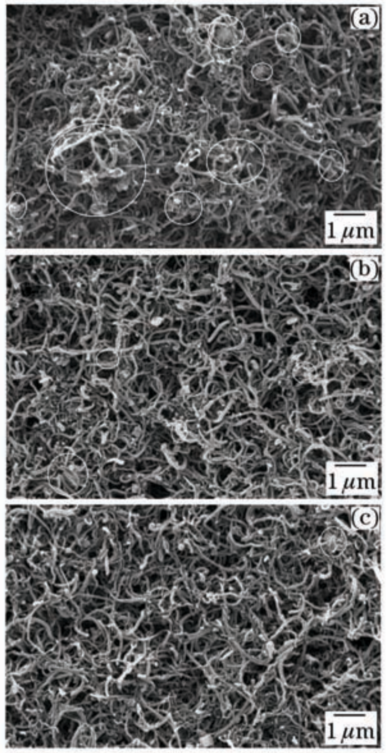

Fig. 2. SEM images of three kinds of CNT films. (a) Untreated; (b) after hard hairbrush treatment; (c) after hard hairbrush and electrical treatment.

$\sim$ 30 mA/cm^2 and then maintained for 5 min. Finally, when the electrical treatment was finished, the cathode of CNT film was obtained. Morphological analyses were made by scanning electron microscopy (SEM). Raman spectroscopy was used to characterize the CNT microstructure before and after the hard hairbrush and electrical treatment.

Figures 2(a)—(c) show the SEM images of three kinds of CNT film cathodes. As shown in Fig. 2(a), all the surface of untreated CNT cathode was almost covered by nubbly organic binder materials, which restrained the field emission dramatically because it prevented the CNTs from protruding from the surface of the CNT film. The hard hairbrush treated sample is shown in Fig. 2(b). The big blocks of organic binder materials were removed, but there were still organic binder materials covering on CNT surfaces. Obviously, this morphology is not advantageous for field emission since the CNTs do not perfectly protrude from the material. Figure 2(c) presents a homogeneous and clean surface of CNT cathode after treated by hard hairbrush and electrical treatment. Obviously, the organic contaminants were removed and more active CNT emitters were formed. The marked differences in surface morphology of films after and before treatment, as shown in Fig. 2, should have a major impact on the electron emission characteristics.

It is well known that Raman spectroscopy is highly sensitive to microstructure, especially for carbon materials. In the experiment, Raman spectroscopy was carried out to further characterize the microstructure and defect density of CNTs after treatment. Figure 3 exhibits the Raman spectra taken with 632.8 nm excitation for the samples before and after hard hairbrush and electrical

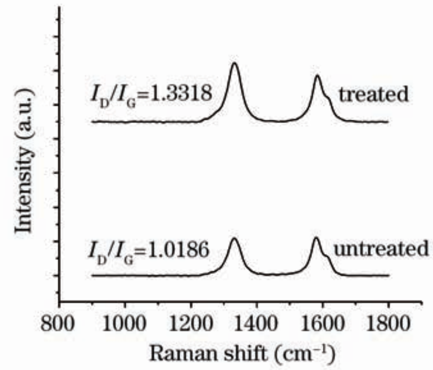

Fig. 3. Raman spectra for CNT films before and after hard hairbrush and electrical treatment.

treatment, respectively. The spectra were dominated by two intensity peaks at 1332 and 1580 cm^{-1}, which are referred to as D and G line, respectively. The G line corresponds to the tangential stretching mode of highly oriented pyrolytic graphite (HOPG) and indicates the presence of crystalline graphitic carbon in the MWNT films. The D line originates from a resonant coupling of the excitation laser with electronic states associated with disordered graphite materials. The ratio of the intensity of D peak to that of the G peak, $I_{\rm D}/I_{\rm G}$, is an indication of the amount of disorder in the nanotube materials[16,17]. The $I_{\rm D}/I_{\rm G}$ ratios were 1.0186 and 1.3318 for untreated and treated samples, respectively. According to the results of Raman spectroscopy characterization, hard hairbrush and electrical treatment generated a large amount of structural defects. Experiments have shown that the defects on the CNT wall have predominant effects on field emission of the CNTs[18,19].

Besides the above-mentioned reason, we considered that the tight pileup structure on the cathode surface is another influence factor in the emission characteristics of printed CNT films. Figure 4 is a schematic drawing of the pileup structure. The topside CNT clusters of the pileup structure created the main sites of electron emission. Therefore, the electron conductive channel from the CNT to the topside CNT emitter was indispensable. As shown in Fig. 4(a), the higher and looser the pileup structure is, the lower the electron conductive probability from the CNT to the CNT emitter is. After treatment, a lot of CNT clusters being removed made the height of the pileup structure decreased, and the press appearing in the hard hairbrush process condensed the CNT layer, as shown in Fig. 4(b). These resulted in increase of electron conductive probability from CNT to the topside CNT emitter. Once a lower resistance contact was formed, the barrier on the CNT-CNT junction was removed. Electrons could pass through CNT-CNT junction easily. During the whole process of field emission,

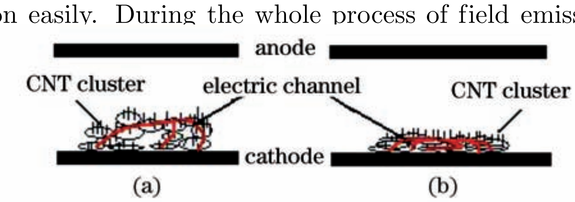

Fig. 4. Schematic drawing of the electron conductive channel in the pileup structure of the CNT films. (a) Before and (b) after hard hairbrush and electrical treatment.

electrons need to overcome only CNT-vacuum barrier. Therefore, a very low voltage bias would result in a considerable electron emission. The low resistance can also reduce the joule heat released from tunneling current and avoid the burning of CNTs.

The field emission characteristics of the CNT cathode films before and after combination treatment was tested in a diode setup using DC power supply. The cathode area was 1×1 (cm) and the distance between the anode and the CNT cathode was 200 μm which was maintained by a glass fiber. The anode was a glass substrate with indium tin oxide (ITO) coating and fluorescence layer on top of it. This construction was installed into the vacuum chamber with the base pressure of 5×10^{-5} Pa. To study the behavior of CNT emitters, the voltage was ramped up and down and the current-voltate (I-V) data were obtained. Figure 5 shows the I-V curves. We can see that enhanced field emission can be achieved by hard hairbrush and electrical treatment. After the treatment, the turn-on voltage decreased from 2.4 to 1.6 V/μm, the emitting current increased from 0.1177 to 1.642 mA/cm^2 under the same condition of 3.1 V/μm. This result revealed that hard hairbrush and electrical treatment played an important role in the improvement of field emission properties. The inset of Fig. 5 illustrates that typical stability of the field emission capacity for the CNT film was observed when the films were operated continuously at 3.1 V/μm for 300 min. Comparing Fig. 5(b) with Fig. 5(a), the ramp-down and time curves of treated CNT film have a smaller fluctuation than the untreated CNT film. The results indicate that this method could improve the lifetime and stability of field emission for screen-printed CNT film cathode effectively. The emission current I can be represented by the Fowler-Nordheim (F-N) equation as[20]

$$I = aV^2 \exp(-\frac{b}{V}), \tag{1}$$

$$b = \frac{0.95B\phi^{3/2}}{\beta'}, \tag{2}$$

where a is a constant, b is the slope of the F-N plot, V is the electric field, β' is the local field conversion factor at the emitting surface, $B = 6.87 \times 10^7$, ϕ is the work function of CNTs ($\sim$ 5 eV). The electric field enhancement factor β can be estimated from

$$E_{\rm loc} = \frac{\beta V}{d}, \tag{3}$$

where d is the distance between the anode and the cathode. Combining these relationship gives

$$\beta = \frac{0.95B\phi^{3/2}d}{b}. \tag{4}$$

After being treated, the electric field enhancement factor β increased from about 2200 to 3700. This result reveals that the hard hairbrush and electrical treatment plays an important role in the improvement of field emission characteristics.

In order to compare the emission uniformity of CNT films before and after combination treatment, the emission images were recorded by a digital camera and the results are shown in Fig. 6. The field emission images were all obtained at an applied anode voltage of 620 V (3.1 V/μm). Before treatment, the image uniformity was poor and the CNT films had only a few randomly distributed emission sites (Fig. 6(a)). After hard hairbrush treatment, the image uniformity was poor and lots of sites do not perform lighting behavior. There still exists dark image in local positions. Such quality is not good enough to be adopted in the display technology (Fig. 6(b)). After hard hairbrush and electrical treatment, the CNT films show more uniform and homogeneous emission over the whole film area without the presence of hot emitting sites (Fig. 6(c)). Therefore, the good uniformity of field emission was obtained after

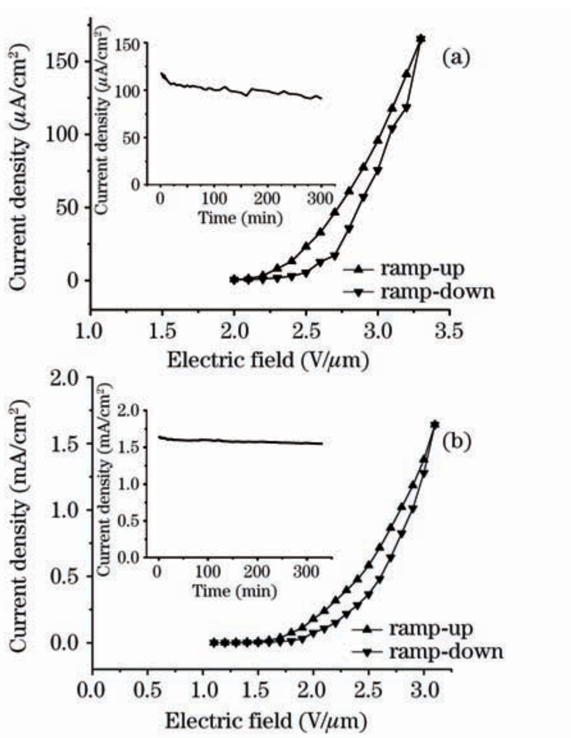

Fig. 5. Field emission curves obtained before and after treatment. (a) Untreated; (b) after hard hairbrush and electrical treatment. The insets show the typical fluctuations of field emitting density at 3.1 V/μm for 300 min.

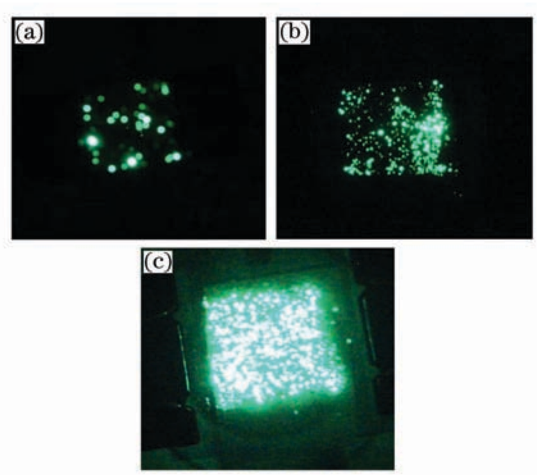

Fig. 6. Field emission images of printed CNT films at 3.1 V/μm before and after treatment. (a) Untreated; (b) after hard hairbrush treatment; (c) after hard hairbrush and electrical treatment.

hard hairbrush and electrical treatment.

In conclusion, the field emission capability and stability of screen-printed CNTs can be improved effectively with hard hairbrush and electrical treatment. The treated cathode film showed an increased turn-on field and an improved field emission current density. As an evidence, the emission current density at an applied field of 3.1 V/μm increased from 0.1177 to 1.642 mA/cm^2 after hard hairbrush and electrical treatment. Moreover, hard hairbrush and electrical treatment improved the emission uniformity and the stability of CNT cathode films obviously. The improved field emission characteristics are attributed not only to the produce active CNT emitters, but also to the generation of a high density of structural defects and the lower resistance contact to the topside CNT emitters. Therefore, the combination method of hard hairbrush and electrical treatment can enhance the field emission characteristics of the screen-printed CNT films in terms of emission characteristics, emission uniformity, and emission stability, which are essential to the commercial CNT field emission display (FED).

References

1. S. Iijima, Nature **354,** 56 (1991).
2. W. A. de Heer, A. Châtelain, and D. Ugarte, Science **270,** 1179 (1995).
3. P. G. Collins, A. Zettl, H. Bando, A. Thess, and R. E. Smalley, Science **278,** 100 (1997).
4. D. N. Davydov, P. A. Sattari, D. AlMawlawi, A. Osika, T. L. Haslett, and M. Moskovits, J. Appl. Phys. **86,** 3983 (1999).
5. T. Yoshitake, Y. Shimakawa, S. Kuroshima, H. Kimura, T. Ichihashi, Y. Kubo, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasaka, and S. Iijima, Physica B **323,** 124 (2002).
6. S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, Science **283,** 512 (1999).
7. W. Zhu, C. Bower, O. Zhou, G. Kochanski, and S. Jin, Appl. Phys. Lett. **75,** 873 (1999).
8. X. H. Liang, S. Z. Deng, N. S. Xu, J. Chen, N. Y. Huang, and J. C. She, Appl. Phys. Lett. **88,** 111501 (2006).
9. T. Chen, Z. Sun, P. Guo, L. Wang, and S. Huang, Acta Opt. Sin. (in Chinese) **26,** 777 (2006).
10. Y. S. Shi, C.-C. Zhu, Q. Wang, and L. Xin, Diamond Related Mater. **12,** 1449 (2003).
11. T. J. Vink, M. Gillies, J. C. Kriege, and H. W. J. J. van de Laar, Appl. Phys. Lett. **83,** 3552 (2003).
12. Y. C. Kim, K. H. Sohn, Y. M. Cho, and E. H. Yoo, Appl. Phys. Lett. **84,** 5350 (2004).
13. D.-H. Kim, C.-D. Kim, and H. R. Lee, Carbon **42,** 1807 (2004).
14. K. F. Chen, K. C. Chen, Y. C. Jiang, L. Y. Jiang, Y. Y. Chang, M. C. Hsiao, and L. H. Chan, Appl. Phys. Lett. **88,** 193127 (2006).
15. W. S. Kim, J. Lee, T. W. Jeong, J. N. Heo, B. Y. Kong, Y. W. Jin, J. M. Kim, S. H. Cho, J. H. Park, and D. H. Choe, Appl. Phys. Lett. **87,** 163112 (2005).
16. P. C. Eklund, J. M. Holden, and R. A. Jishi, Carbon **33,** 959 (1995).
17. C. Y. Zhi, X. D. Bai, and E. G. Wang, Appl. Phys. Lett. **80,** 3590 (2002).
18. Y. Saito, K. Hamaguchi, R. Mizushima, S. Uemura, T. Nagasako, J. Yotani, and T. Shimojo, Appl. Surf. Sci. **146,** 305 (1999).
19. Y. Chen, D. T. Shaw, and L. Guo, Appl. Phys. Lett. **76,** 2469 (2000).
20. C. A. Spindt, I. Brodie, L. Humphrey, and E. R. Westerberg, J. Appl. Phys. **47,** 5248 (1976).