

Optimization of the fabrication process using nanostructured carbon for low-cost FED application

Z.Sun *, L.L.Wang, T.Chen, Z.J.Zhang, Z.Y.Cao, Y.W.Chen, L.K.Pan, T. Feng
Nanotech Center, East China Normal University & Nanoking Technology Co.
North Zhongshan Rd. 3663, Shanghai 200062, China
Phone: 86-21-62232054, E-mail: zsun@mail.ecnu.edu.cn

Abstract

Nanostructured carbon (nm-C), including carbon nanotubes and nanofibers (CNTs/CNFs) is promising for low-cost field emission display (FED) application. By modification of CNTs/CNFs, uniform CNTs/CNFs can be obtained and used for field emission cathode (FEC) on glass substrate. By screen-printing (SP) and electrophoretic deposition (EPD) process, large area FEC can be obtained. The FED properties are studied and compared. Both SP and EPD FEC show excellent field emission properties, such as low emission field and uniform emission, after optimization the fabrication process. While EPD FEC exhibits better luminescence image. By vacuum sealing, the low cost nm-C-FED prototypes based on EPD cathode have been demonstrated.

1. Objectives and Background

Nanostructured carbon (nm-C), including carbon nanotubes and nanofibers (CNTs/CNFs) possess the properties favorable for field emitters, such as high aspect ratio, extremely small diameter, high emission current, high mechanical strength, and high chemical stability [1-7]. The nm-C field emission display (nm-C-FED) has the potentials to be developed as a flat panel display for large screen TV applications [8-9], because the cathodes and anodes can be formed by low cost processes such as screen-printing (SP) [10-12] and electrophoretic deposition (EPD) methods [13-15]. SP eliminates sophisticated process steps (such as micron range lithography), and enables a lower investment in equipment and facilities [16-18]. EPD is based on the presence of small charged particles in a liquid, which, on the application of a DC electric field, will move to and deposit on an oppositely charged electrode. As another promising method for carbon powder

materials-based cold cathode fabrication, EPD has the advantages of short formation time, simple deposition apparatus, low cost, little restriction in the shape of the substrates and suitability for mass production.

In this paper, SP and EPD methods have been used to produce nm-C field emission cold cathodes. The comparison of emission properties and uniformity of the cathodes as-prepared will propose better method for FED.

2. Results

The CNTs/CNFs were synthesized by thermal CVD system on nickel plate in the H₂ ambient at the temperature of 600 °C, using acetylene (C₂H₂) as the carbon source. The as-grown CNTs/CNFs were scraped off from the nickel substrates and then milled into powder. The milled CNTs/CNFs powder was mixed with ethylcellulose and terpineol, and then sufficiently stirred in an agate bowl for about 1 hour to make the CNTs/CNFs homogeneously dispersed in the organic materials. After that, the CNTs/CNFs slurry was screen printed through a mesh on the glass substrate, which had already been coated with a silver conductive layer by SP process. After exposed to air at room temperature for about 20 min, the substrate was put into 200 °C sinter furnace to remove the organic binders in the paste. The CNTs/CNFs film cathode was finally formed after heated at 550 °C in hydrogen for 15 minutes.

The general scheme of the EPD process, used for the sample preparation, is shown in Fig. 1. The CNTs/CNFs powder, same as those used for SP, was placed into the vessel with the

mixture of acetone and ethanol which is used as a dispersion medium. $\text{Al}(\text{NO}_3)_3$ was added into the suspension to increase the deposition rate and improve the adhesion of the powder particles to the substrate. The solution was then ultrasonicated about 30 min to form a stable suspension. Glass plates with a silver film layer or with ITO coating were used as substrates and the counter-electrode was a Ni plate. Two electrodes were kept parallel at 10mm apart in the suspension. The deposition was carried out with applying a constant DC voltage in the range of 10-50 V. The negative potential was connected to the cathode substrate. The deposited CNTs/CNFs cathode was dried in air at room temperature.

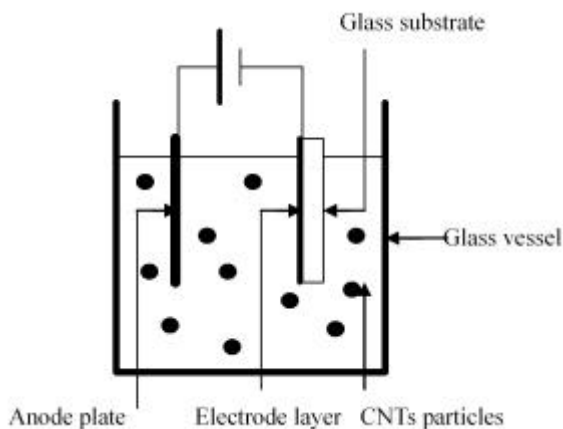


Fig.1 Scheme of the CNTs/CNFs powder electrophoretic deposited on the substrate.

The emission properties of the SP and EPD cathodes were tested in a diode arrangement with a distance of $170\ \mu\text{m}$ between anode and cathode. The anode was a glass substrate with ITO coating and phosphor layer on its top. Then the electrodes were installed into the vacuum chamber with residual gas pressure less than $10^{-5}\ \text{Pa}$. The field emission images of the cathodes have been taken using the digital camera in the process of the tests.

Fig. 2 shows scanning electron microscope (SEM) of CNTs/CNFs as grown and deposited uniformly on the entire glass substrate. The original CNTs/CNFs synthesized by CVD in Fig.

2a distributed randomly with 100-150 nm and 3-4 μm in diameter and length respectively. After SP process, the CNTs/CNFs are randomly distributed in the inorganic matrix, the morphology is similar except the density is lower, as shown in Fig. 2c. For CNTs/CNFs electrophoretic deposited on glass (Fig. 2b), the morphology was similar to that of as-grown one, while their length was shortened due to the milling process before CNTs/CNFs were added into the solution.

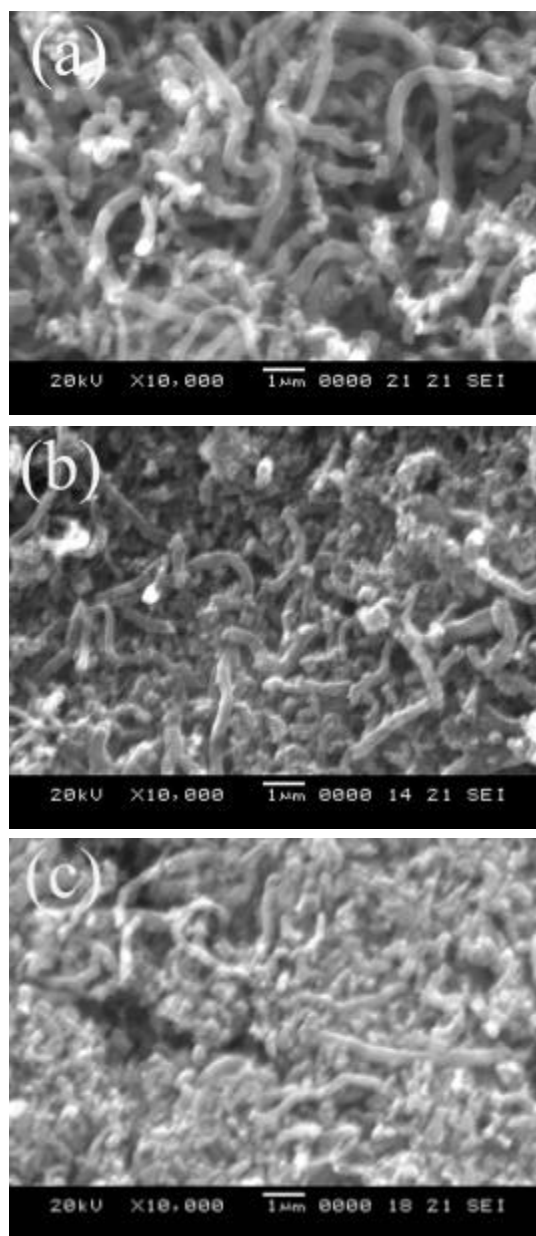


Fig. 2 The SEM images of (a) as-grown CNTs/CNFs (b) EPD CNTs/CNFs cathode (c) SP CNTs/CNFs cathode

The Raman spectra in Fig.3 further illustrates that as-grown CNTs/CNFs and CNTs/CNFs after EPD process possess the similar structure. The two peaks located at approximately 1350 cm^{-1} and 1597 cm^{-1} in the spectra respectively, showing the typical graphite structure features. The first-order Raman spectrum of CNTs/CNFs shows strong sharp peaks at $\sim 1597\text{ cm}^{-1}$ identified as the G peak of crystalline graphite arising from zone-center E_{2g} mode and $\sim 1350\text{ cm}^{-1}$ corresponding to the D-line associated with disorder-allowed zone-edge modes of graphite. The full width at half maximum (FWHM) of D peak and G peak decreases somewhat for the EPD CNTs/CNFs, showing the graphitization of CNTs/CNFs somewhat enhances. This means that the milling and EPD processes have not caused large changes on the structures of CNTs/CNFs but shortened their lengths, which is corresponding to the previous SEM results.

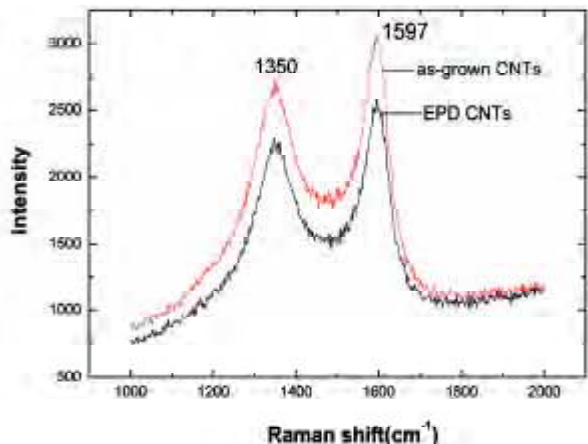


Fig.3 Raman spectra of CNTs

Fig.4 shows the comparison of field emission properties between EPD and SP cathodes. As shown in Fig. 4a, similar good emission properties such as low turn-on electric field ($\sim 1.3\text{ V}/\mu\text{m}$) and large current density ($\sim 200\text{ }\mu\text{A}/\text{cm}^2$) at the field of $4.0\text{ V}/\mu\text{m}$ are obtained for

both cathodes. Figs. 4b and 4c illustrate that emission sites are located on most area of the cathodes. The good uniformity of field emission has been achieved for both of EPD and SP cathodes. While EPD cathode exhibits better emission sites distribution and better luminescence image than SP one, which may results from the purification of CNTs/CNFs during EPD process.

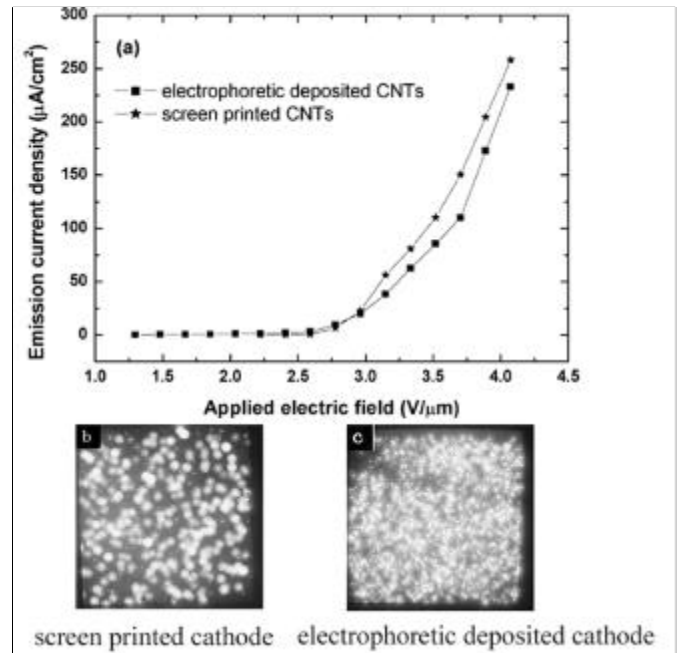


Fig.4 Field emission properties of the sample produced by EPD and SP: (a) E-J curve of CNTs/CNFs cathodes image taken after the first switch-on of the cathode. (b) The luminescence image on anode from the CNTs/CNFs cathodes by SP ($J=125.35\text{ }\mu\text{A}/\text{cm}^2$, $E=3.52\text{ V}/\mu\text{m}$) (c) image of cathode by EPD ($J=147.87\text{ }\mu\text{A}/\text{cm}^2$, $E=3.52\text{ V}/\mu\text{m}$)

The results indicate that EPD method might be a good way for CNTs/CNFs to fabricate field emission cold cathode, which can produce good emission properties and uniform luminescence images. The results were reproducible in several series of the experiment.

The full packaged nm-C-FED prototype was fabricated by vacuum sealing process. The whole process was carried below 500°C . After sealing, the getter inside of the device was excited and

high vacuum ($>10^{-6}$ Torr) was obtained. The examples of the high brightness nm-C FED prototypes based on EPD cathode are shown in Fig.5. A yellow color image of ECNU and Chinese characters can be clearly seen in Fig.5a. Figure 5b and 5c shows green dots and blue lines image arrays FEDs, respectively. The image of the prototypes looks uniform and bright. The brightness of the FED is in the range of 600-1000 cd/m^2 when field was applied in the range of 2.5 $\text{V}/\mu\text{m}$ to 4.0 $\text{V}/\mu\text{m}$. The result shows that the EPD cathode used for ϵ -FED exhibits excellent field emission properties.



Fig. 5: Field emission display prototypes: (a) yellow; (b) blue; (c) green

3. Impact

The emission characteristics of the cathodes fabricated by the EPD method compare favorably to those by SP method. The EPD process affords large area, high throughput, low cost, low nm-C consumption, and ambient deposition condition. Compared to arc-grown CNTs based FED [19], nm-C-FED prototypes based on EPD cathode show excellent field emission properties, such as low emission field, stable emission field, high emission current density, high brightness and uniform emission, but have lower cost. It is believed that field emission flat light source and display modular will be developed as products using this low cost process in the near future.

4. Acknowledgements

This work is supported by Shanghai Nanotechnology Foundation (0452NM048) and National Nature Science Foundation of China (60477003).

5. References

- [1] J. X. Guo, Z. Sun, B. K. Tay, X. W. Sun, *Appl. Surf. Sci.* **214**, 351 (2003).
- [2] Z. Sun, S. M. Huang, Y. F. Lu, J. S. Chen, Y. J. Li, B. K. Tay, S. P. Lau, G. Y. Chen, Y. Sun, *Appl. Phys. Lett.* **78**, 2009 (2001).
- [3] Z. Sun, J. S. Chen, Y. J. Li, B. K. Tay, S. P. Lau, G. Y. Chen, Y. Sun, *Appl. Surf. Sci.* **173**, 282 (2001).
- [4] Y. J. Li, Z. Sun, S. P. Lau, G. Y. Chen, B. K. Tay, J. S. Chen, X. Z. Ding, X. Shi, *Appl. Phys. Lett.* **79**, 1670 (2001).
- [5] Z. Sun, B. K. Tay, S. P. Lau, ASID'02, Singapore, Sept. 2-4, 2002.
- [6] Z. Sun, Y. W. Chen, P. S. Guo, APNF2004 "SINCS", Shanghai, Dec. 9-12, 2004.
- [7] J. M. Bonard, J. P. Salvetat, T. Stöckli, W. A. de Heer, L. Forró, A. Châ telain, *Appl. Phys. Lett.* **73**, 918 (1998).
- [8] Q. H. Wang, T. D. Corrigan, J. Y. Dai, R. P. H. Chang, A. R. Krauss, *Appl. Phys. Lett.* **70**, 3308 (1997).
- [9] W. Taylor, 14th IV MC, 77 (2001).
- [10] R. Tuck, *Inform Display* **16**, 146 (2000).
- [11] W. A. de Heer, A. Chatelain, D. Vgarte, *Science* **270**, 1179 (1995).
- [12] J. T. Li, W. Lei, X. B. Zhang, X. D. Zhou, Q. L. Wang, Y. N. Zhang, B. P. Wang, *Appl. Surf. Sci.* **220**, 96 (2003).
- [13] Y. Nakayama, S. Akita, *Synthetic. Metals.* **117**, 207 (2001).
- [14] S. J. Oh, J. Zhang, Y. Chang, H. Shimoda, O. Zhou, *Appl. Phys. Lett.* **84**, 3738 (2004).
- [15] C.Y. Hsiao, T. F. Chan, S. H. Lee, K. Cheng, Y. A. Li, J. L. Tsai, J. S. Fang, C. C. Kuo, SID'05 Digest, 411 (2005).
- [16] S. Iton, M. Tanak, *Processing of the IEEE* **90**, 514 (2002).
- [17] W. B. Choi, N. S. Lee, W. K. Yi, SID'2000 DIGEST[C], U. S, Long Beach, New York, 320 (2000).
- [18] J. W. Nam, Y. S. Jo, M. J. Yoon, IVMC'2001, Davis, California, USA, 57 (2001).
- [19] Y. S. Shi, C. C. Zhu, Q. K. Wang, *Diam. Relat. Mater.* **12**, 1449 (2003).