Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Field Emission From Micro Tubule Structure of CNt/Conducting Polymer Composites

Sang Min Cho [a] , Yongkeun Son [a] , Youngkwan Lee [b] , Jae-Hong Pack [c] & Ji-Beom Yoo [c]

[a] Department of Chemistry, and Advanced Materials and Process Research Center for IT, Sungkyunkwan University, Suwon, Korea

[b] Department of Chemical Engineering, Sungkyunkwan University, Suwon, Korea

[c] School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea

Version of record first published: 31 Aug 2012.

To cite this article: Sang Min Cho , Yongkeun Son , Youngkwan Lee , Jae-Hong Pack & Ji-Beom Yoo (2008): Field Emission From Micro Tubule Structure of CNt/Conducting Polymer Composites, Molecular Crystals and Liquid Crystals, 492:1, 147/[511]-154[518]

To link to this article: http://dx.doi.org/10.1080/15421400802332883

Mol. Cryst. Liq. Cryst., Vol. 492, pp. 147/[511]–154/[518], 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802332883

Taylor & Francis
Taylor & Francis Group

Field Emission From Micro Tubule Structure of CNT/Conducting Polymer Composites

Sang Min Cho[1], Yongkeun Son[1], Youngkwan Lee[2], Jae-Hong Pack[3], and Ji-Beom Yoo[3]
[1]Department of Chemistry, and Advanced Materials and Process Research Center for IT, Sungkyunkwan University, Suwon, Korea
[2]Department of Chemical Engineering, Sungkyunkwan University, Suwon, Korea
[3]School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea

A conductive polymer and multi-wall carbon nanotube composite was used in fabrication of field emission (FE) electrode array. The emission electrode was prepared by using a new template method adapting a microporous membrane filter as a template. Field emission characteristics were measured with and without removing the template. The measurement was done at atmosphere of 10^{-6} torr. The final emission cell provides the turn on of 0.6 V/μm and current density up to 650 μA/cm² at 1.2 V/μm.

Keywords: carbon nano tube; composite; conducting polymer; field emission; template

1. INTRODUCTION

The field emission display (FED) is expected to create a high marketing demand in the future because it has potential advantages i.e., active mode, view angle, power consumption, response time, resolution [1]. However, not many cases of using FED has been found because of problems in fabrication of metal emission electrode tips in array forms. Lots of research efforts have concentrated in developing an effective

Authors are grateful to acknowledge the financial support from KRF grant funded by the Korean government (MOST) (R01-2007-000-20679-0), and BK21 program through School of Chemical Materials Science.

Address correspondence to Yongkeun Son, Department of Chemistry, and Advanced Materials and Process Research Center for IT, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: ykson@skku.edu

emitter array with the various materials. Most cases, fabrication of metal cathode tips on silicon substrate by using procedures developed for micro-chip fabrications. Recently, research work has been focused to the usage of MWCNT (multi wall carbon nanotube) [8] or conducting polymers [2–7]. CNT (carbon nanotube) have been expected to show good conductivity and stability in this application, but fabrication process is not easy to accomplish [9]. Conducting polymers have been also expected to exhibit good emission property with simple fabrication but their emission was need to be improved more [10–11]. CNT-polymer composite could be a good material for the tip fabrication. A lot of research papers reported that CNT was used as a good reinforcing material for polymer composites [12]. However, two main strategies need to be solved are homogeneous dispersion of CNT in a polymer and good interface interaction between CNT and polymer [13–14]. Generally, it is very difficult to make homogeneous disperse of CNT in a polymer because of aggregation of CNTs due to the strong van der Waals attraction between them in the polymer matrix.

In this study, we tried to fabricate a field emissive tip array with MWCNT and conducting polymer utilizing a method of template synthesis. This method allowed us a simple procedure of fabricating MWCNT-Polymer composite tubule array on an ITO base. This microtubule structures were then observed with images obtained from SEM (scanning electron microscope). Finally, the emission property was determined with home made field emission apparatus at a vacuum condition of 10^{-6} torr.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

All ACS chemicals used in this work are ACS grade otherwise described. These chemicals were purchased from Sigma-Aldrich Korea Ltd. and used without further purification. The templates for fabricating conducting polymer emitters were polycarbonate membranes holding pores of 5 μm size diameter in 10 μm thick (Millipore Corp.). Transparent indium-tin oxide (ITO) glass electrode (Samsung Corning, Korea) was used as a supporting electrode after several cleaning steps. The polymer coating was done by employing a vacuum spin coater (Headway). Vacuum oven (VO-20X, Jeio Tech, Korea) was used for drying purposes. SEM images was obtained by using JSM 6700F (JEOL). For FE measurements, an ammeter (KEITHLEY 2001) and a voltage source (FUG HCN 700-3500) were used.

2.2. Fabrication and Characterization of Conducting Polymer Composite Emitters

First of all we made 1% CNT dispersion in water after acid treatment following the reported procedure [15–18]. This liquid dispersion was dropped on the rough side of the membrane template. In this process CNT was getting into the 5 μm pore of the template and finally CNT-template was formed. The CNT-template was put on top of our home-made conducting polymer glue composite coated on the ITO electrode [11]. As in Figure 1 the glue was got into the pores of the CNT-template. In other words, the glue was spin-coated onto an ITO glass then a piece of membrane template with include MWCNT was carefully placed on top of it before the composite was dried out completely. While the membrane was staying on the composite glue, the basic tubule structure was formed by the capillary action into the template. This structure was completely dried out in vacuum oven for 24 hours. Methylene chloride (MC) was used to remove the membrane to investigate the shape of tubule structure and to determine emission properties. Finally, the field emission current was measured using the field emission cell in Figure 1(d). A piece of stainless steel was used as an anode and kept 500 μm away from the cathode by using glass spacers. This measurement was carried out in a vacuum chamber at 10^{-6} torr.

3. RESULTS AND DISCUSSION

After following the acid treatment process, the MWCNT was dispersed well in aqueous condition. The CNT-template was formed by the addition a drop of 1% CNT dispersion on the template. Complete dry left the trace of CNTs on the rough side surface as well as pore inside. The home made PEDOT/PVA conductive glue was coated on a piece of ITO electrode. The CNT-template was placed onto the conductive glue carefully. In this way the glue was forming into tubular shape containing CNTs in itself. SEM images in Figure 2 show the formation of the CNT-polymer tubule structure in pores of the template. The image (a) shows as made tubule without removing the template. The inset shows the inside wall of the composite tubule having CNT fiber structures. The image (b) is the one obtained after removing the template., The inset shows the spike shape of CNT structures are appeared at the top of an individual tubule. And (c) shows entangled CNT structure in a piece of broken composite tubule. By using this new method the CNT-Polymer composite tubules which have sharp emitting tips on top could be constructed.

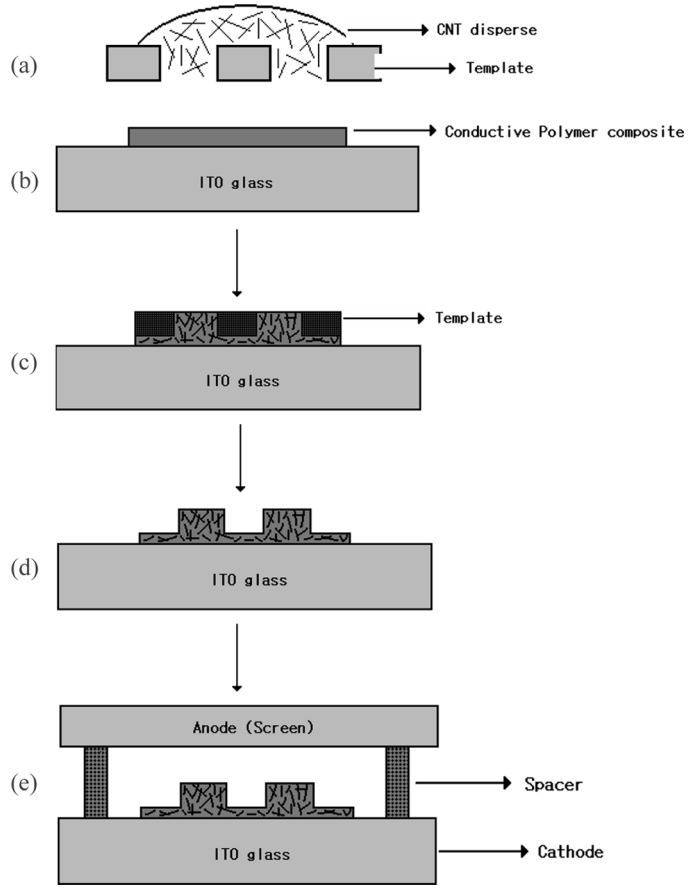

FIGURE 1 Schematic diagram of experimental procedure includes fabrication of micro tubule structures and emission measurement. (a) CNT dispersion on template; (b) Glue cast on the ITO glass; (c) the CNT-template was put on (b); (d) after dissolving the template; (e) cell structure for FE measurements.

Measurement of field emission current from the tubule array without removing the template membrane is in Figure 3. The emission starts at 0.7 V/μm and then the emission current density increases up to 0.05 μA/cm^2 at 1.4 V/μm. The linear line from Fowler-Nordheim plot as in inset confirms this is a field emission. And this emitting behavior is clean and smooth. But the current density is smaller than what was expected. Removing of the template was tried to improve the emission property of the same electrode. Figure 4 shows the measured

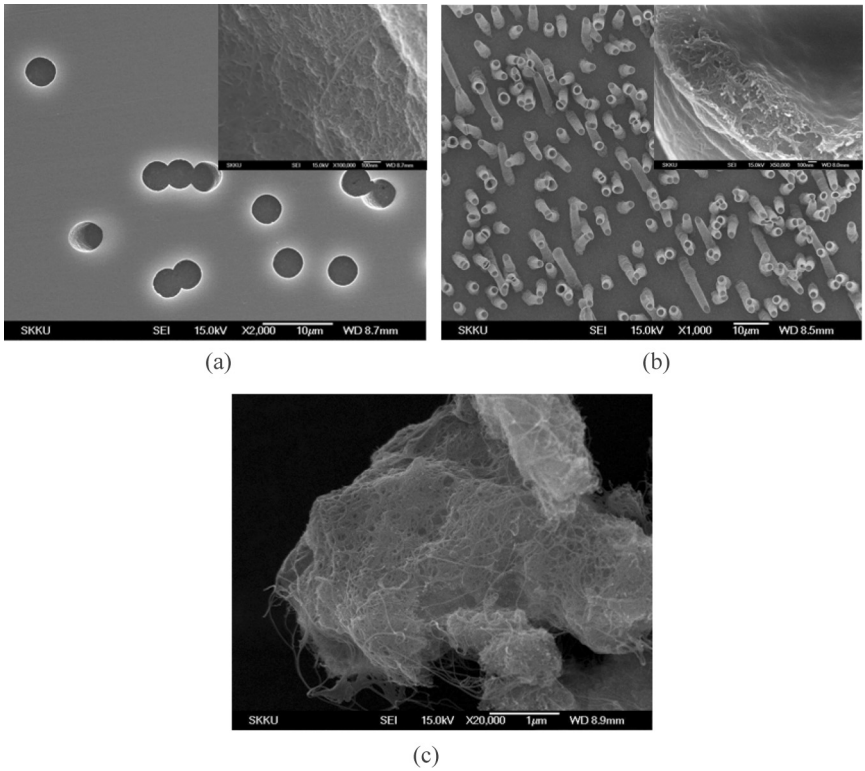

FIGURE 2 SEM images of MWCNT-Polymer electrodes: (a) before membrane exclusion, fine fiber structure of CNT was shown at the inside wall of the tubule; (b) after membrane exclusion, CNT appears like spikes on the top of the tubule; (c) SEM image of a piece of broken tubule, CNT appears like threads entangled in the PEDOT/PVA glue.

current density obtained as a function of electrical field strength. Field emission turns on at 0.6 V/μm which is a little bit lower compared that the one in Figure 3. In this structure the current density increases rapidly and reaches up to 650 μA/cm^2 at 1.2 V/μm. The inset shows linear plot of Fowler-Nordheim also. There is a dramatic increase in emission current density compared the one in Figure 3. Our previous result show that the Pt sputtered tubule gave about 150 μA/cm^2 [11]. Recently Ju et al. reported that PEDOT nanowire fabricated with nanoporous template produces 4 V/μm turn on and maximum current density of 100 μA/cm^2 at 4.5 V/μm [10]. This value is less than one sixth of the one we obtained even the pore density is not high. We presume the superior results definitely came from the effect of CNT.

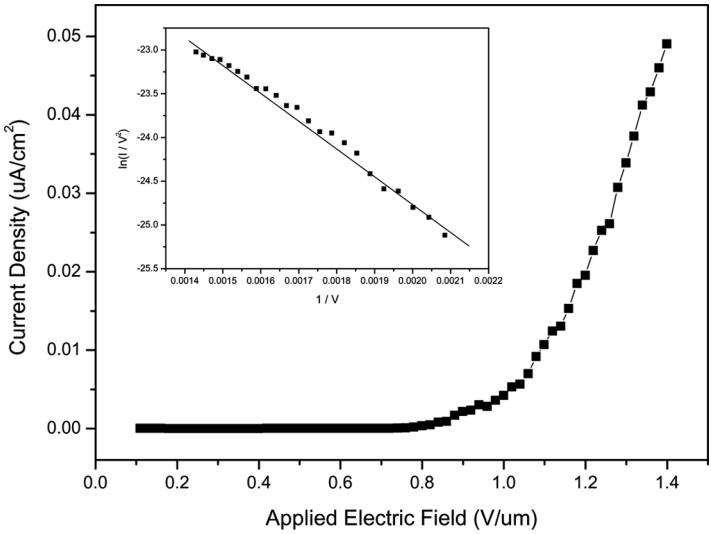

FIGURE 3 Field emission from the CNT/polymer composite tubule structure without removing the template. The linear plot in inset implies the emission follows the F-N mechanism.

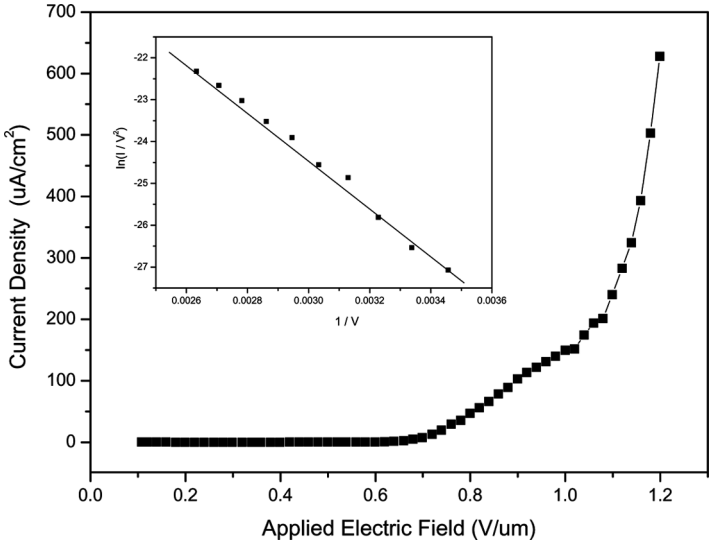

FIGURE 4 Field emission from the CNT/polymer composite tubule structure after removing the template. The linear plot in inset implies the emission follows the F-N mechanism.

There are two main reasons for CNT effect. The first one is conductivity effect of the conducting polymer glue in which the CNT was dispersed. The second one is the shape effect of the emission tip as in Figure 2(b). The spike shape of CNT at the top of microtubule increase the aspect ratio effect. Nevertheless the figure is much smaller that that of metals ($>1\,\mathrm{mA/cm^2}$) [19]. The polycarobonate template used in this study has pore density of $10^5 \sim 10^8\,\mathrm{pores/cm^2}$. This value is quite low compared to the that of typical alumnium oxside template (usually; $10^9 \sim 10^{11}\,\mathrm{pores/cm^2}$). This comparison leads us to use high pore density template to increase the emission current up to $\sim$mA level.

4. CONCLUDING REMARKS

We have fabricated field emissive electrode with array type microtubule from MWCNT-Polymer composite. A new template method was developed in this experiment using CNT disperse separately. The final emission cell provides the turn on of $0.6\,\mathrm{V/\mu m}$ and current density up to $650\,\mu\mathrm{A/cm^2}$ at $1.2\,\mathrm{V/\mu m}$. This leaves us the possibility one can produce applicable current density ($\sim$mA) with this type of cell by using higher pore density template.

REFERENCES

[1] Spindt, C. A., Brodie, I., Humphrey, L., & Westerberg, E. R. (1976). *J. Appl. Phys.*, *47*, 5248.
[2] Qian, D., Dickey , E. C., Andrews, R ., & Rantell, T. (2000). *Appl. Phys. Lett.*, *20*, 76.
[3] Alexandrou, I., Kymakis, E., & Amaratunga, G. A. J. (2002). *Appl. Phys. Lett.*, *8*, 80.
[4] Hill, D. E., Lin, Y., Rao, A. M., Allard, L. F., & Sun, Y. P. (2002). *Macromolecules*, *35*, 9466.
[5] Wang, H., Dai, J., & Yarlagadda, T. (2005). *Langmuir*, *9*, 21.
[6] Joo, J., Park , S. K., Seo, D. S., Lee, S. J., Kim, H. S., Ryu, K. S., Lee, T. J., Seo, S. H., & Lee, C. J. (2005). *Adv. Funct. Mater.*, *15*, 1465.
[7] Peng, C., Snook, G. A., Fray, D. J., Shaffer, M. S. P., & Chen, G. Z. (2006). *Chem. Commun.*, 4629.
[8] Ulmen, B., Kayastha, V. K., Coninck, A. D., Wang, J., & Yap, Y. K. (2006). *Diamond & Related Materials*, *15*, 212.
[9] Kim, J. M., Choi, W. B., Lee, N. S., & Jung, J. E. (2000). *Dia. Rel. Mater.*, *9*, 1184.
[10] Kim, B. H., Kim, M. S., Park, K. T., Lee, J. K., Park, D. H., & Joo, J. (2003). *Appl. Phys. Lett.*, *3*, 83.
[11] Kim, K. H., Son, Y., Lee, Y., Jeon, S. Y., Pack, J. H., & Yoo, J. B. (2007). *Mol. Cryst. Liq. Cryst.*, *472*, 77.
[12] Coleman, J. N., Khan, U., Blau, W. J., & Gun'ko, Y. K. (2006). *Carbon*, *44*, 1624.
[13] Wang, M., Pramoda, K. P., & Goh, S. H. (2005). *Polymer*, *46*, 11510.
[14] Zhang, X., Liu, T., Sreekumar, T. V., Kumar, S., Moore, V. C., Hauge, R. H., & Smalley, R. E. (2003). *Nano Lett.*, *3*, 1285.

[15] Kim, B., & Sigmund, W. M. (2004). *Langmuir*, *20*, 8239.
[16] Jiang, K., Eitan, A., Schadler, L. S., Ajayan, P. M., & Siegel, R. W. (2003). *Nano Lett.*, *3*, 3.
[17] Zeng, Y. L., Huang, Y. F., Jiang, J. H., Zhang, X. B., Tang, C. R., Shen, G. L., & Yu, R. Q. (2007). *Elect. Comm.*, *9*, 185.
[18] Mawhinney, D. B., Naumenko, V., Kuznetsova, A., Yates, J. T., & Jr. (2000). *J. Am. Chem. Soc.*, *122*, 2383.
[19] Joo, J., Lee, S. J., Park, D. H., Kim, Y. S., Lee, Y., Lee, C. J., & Lee, S. R. (2006). *Nanotechnology*, *17*, 3506.