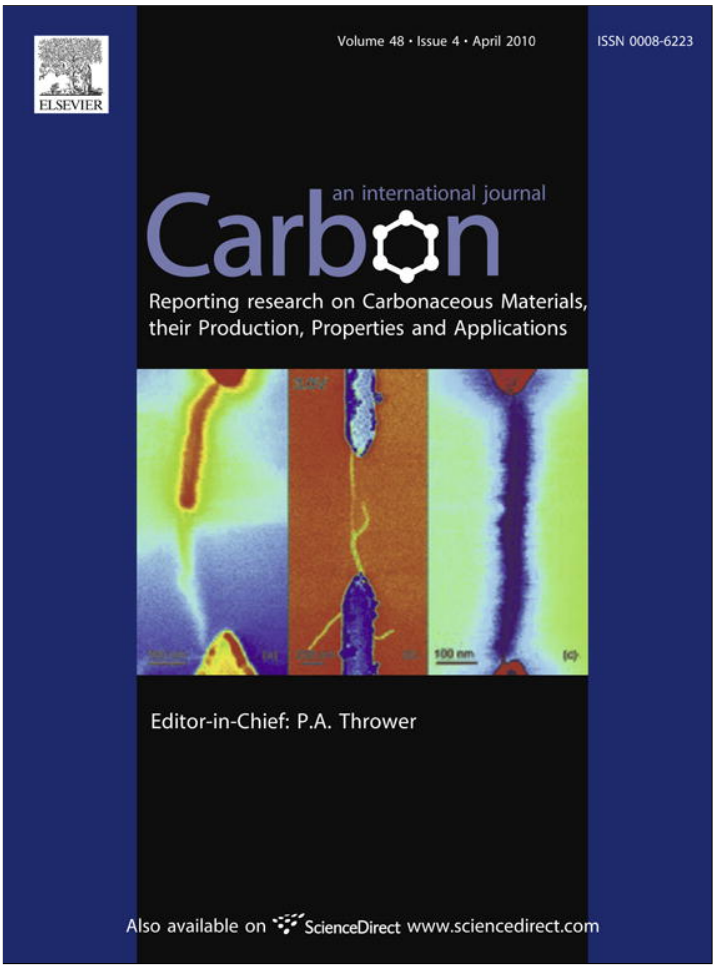

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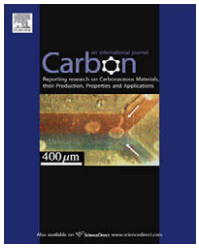

Multi-walled carbon nanotube/ribonucleic acid hybrid field emitters fabricated by spray deposition

Yang Doo Lee [a], *Jung-Wan Yu* [a], *Woo-Sung Cho* [a], *Yong Churl Kim* [b], *In Taek Han* [b], *Yun-Hi Lee* [c], *Byeong-Kwon Ju* [a,*]

[a] *Display and Nanosystem Lab., College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea*
[b] *Display Devices and Processing Lab., Samsung Advanced Institute of Technology, Giheung-gu, Yongin-si, Gyeonggi-do 446-712, Republic of Korea*
[c] *Department of Physics, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea*

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) are shown to disperse in water, and be functionalized using RNA so that MWCNT/RNA hybrids can be fabricated on substrates by spray method. The material has strong adhesion on glass substrates or metal wires. A liquid elastomer surface treatment is used to make the field emitter tips protrude from the cathode. Possible methods of realizing field emitter sources, including X-ray sources, are discussed. The MWCNT/RNA hybrids have a higher emission current density and more uniform emission image than the MWCNTs on their own, since the RNA coated MWCNTs attach more strongly to the substrate. A diode configuration field emission X-ray source using the MWCNT/RNA hybrids on tungsten wire tip was tested and found to provide clear X-ray images.

1. Introduction

Carbon nanotubes (CNTs), possessing a cylindrical graphitic structure with nanometer-scales, are of enormous interest within the scientific field due to their unique electronic, chemical and physical properties. It is clear that CNTs have potential for many applications, including their use as nanoscale biochemical devices, energy storage devices, ceramic–matrix composites, and field emission tips [1–5]. Other areas of considerable interest are nanobioelectronic applications of CNTs with biomolecules [6]. CNTs are difficult to dissolve and disperse in aqueous solutions, such as water and organic solvents, because of their van der Waals forces and hydrophobic properties. Zheng et al. have reported that, by using sonication, single-stranded deoxyribonucleic acid (ssDNA) become soluble single-walled carbon nanotubes (SWCNTs) in water due to the π-stacking interaction between the base of the DNA and the sidewall of the CNTs [7]. Demonstrations of dissolved CNTs with ribonucleic acids (RNA) have also appeared in the literature [8,9]. Nucleic acid-wrapped CNTs have good potential for use in electronic applications, optical devices, and electrochemical detection or sensing equipments [10–15]. The CNTs are of considerable interest as field emitter materials because of their good emission stability and ability to operate at low-voltage. Recently, research groups have applied the CNT field emission backlighting unit to liquid crystal displays (LCD) [16,17] and CNT emitters are an attractive prospect for applications of X-ray sources, such as medical diagnosis and nondestructive inspection [18–20]. CNT emitters can also be fabricated through screen-printing, using CNT paste, including organic binders, and on metal catalyst coated substrates, by the use of a chemical vapor deposition (CVD) processes. However, the CVD method has the disadvantages of producing only limited cathode sizes and the need for high

* *Corresponding author:* Fax: +82 2 3290 3791.
E-mail address: bkju@korea.ac.kr (B.-K. Ju).
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temperatures for realizing good growth. Screen-printing has the advantage of offering a low-cost fabrication technology, and being capable of processing large areas whereas the paste consisting of CNTs, binder resins, and ceramic or metal particles remain problematic in causing damage to the CNTs during the heat treatment. The spray deposited CNTs can be made of large sized panels and without reference to the form of cathode, but the adhesion between the emitters and the substrate is poor. This study discusses the field emission of multi-walled carbon nanotubes (MWCNTs) and MWCNT/RNA hybrids, attached strongly on substrates by spray method. The RNA can be used to effectively dissolve the MWCNTs, and the nanotubes show good dispersion in the aqueous solution. The MWCNT/RNA hybrid film produced in this way is usable as the cold cathode in field emission displays and as the X-ray sources; clearly, the field emission properties for these applications need investigation.

2. Experimental

A CVD synthesized MWCNTs, purchased from Iljin Nanotech (CMP-310F), a *N*,*N*-dimethylformamide (DMF), purchased from Sigma–Aldrich, and RNA have been used to transfer the RNA from baker's yeast (Catalog Number 83853, Sigma–Aldrich). The MWCNTs (20 mg) is added to 100 mL of DMF, and sonicated for 2 h, and then centrifuging (Vision Scientific, VS-15000N) was carried out at 1800*g* for 15 min to remove some undissolved CNTs. Aqueous dispersion of the MWCNTs (20 mg) is prepared with RNA (7 mg) in 100 mL of deionized water. The MWCNT/RNA hybrids is sonicated using an ultra bath-type cleaner, under iced water, for 2 h, and centrifuged by the same method. The suspension is then sprayed onto a soda lime glass coated with indium tin oxide (ITO), using kapton tape (polyimide) as a shadowing mask with a size of 0.5 cm × 0.5 cm. The MWCNT/RNA hybrids is sprayed onto tungsten wire tip with diameter of 200 μm for the X-ray source and copper was used as the metal target (anode). These films were prepared by using an airbrush spray gun (www.airfactory.co.kr, model: SHINE 3). The solution of 5 mL was sprayed onto substrate under N_2 pressure through a nozzle size with a diameter of 0.3 mm. The distance between a nozzle and a substrate was maintained at 5 cm. The spray deposition of the samples is onto a hot plate at 160 °C. The ITO glass of the anode plate is printed with green phosphor, which is normally used in a cathode ray tube. A PDMS (polydimethylsiloxane, Sylgard™ 184 Silicone Elastomer, Dow Corning) has been used for the surface treatment to modify the surface morphology and field emission activation. A PDMS was prepared by the manufacturer's directions. A weight ratio of 10:1 of elastomer and curing agent was stirred thoroughly and then placed under vacuum for 1 h to remove entrapped air. The mixture was poured onto the sprayed films (MWCNTs and MWCNT/RNA hybrids on ITO glass) and cured in an oven at 70 °C for 2 h. After curing, the PDMS layer was peeled from the films [21]. The morphology of MWCNTs and MWCNT/RNA hybrids are characterized by scanning electron microscopy (SEM, Hitachi S-4300) and high-resolution transmission electron microscopy (HRTEM). The TEM images are obtained using the FEI Tecnai G2 F30 instrument at an acceleration voltage of 300 kV and the samples have been prepared by drop casting on holey carbon film supported by copper TEM grids. The field emission and the properties of the X-ray source are measured inside a vacuum chamber with diode-type configuration at a pressure of 5×10^{-6} Torr using a high voltage DC power supply.

3. Results and discussion

Fig. 1a shows the SEM image of the spray deposited MWCNTs on ITO glass and a SEM image of the MWCNT/RNA hybrids is shown in Fig. 1b. The images show that the functionalized CNTs change as a result in the morphology of the cathode. Further analyses of the structure and surface morphology of the MWCNT/RNA hybrids has been carried out using HRTEM and Fig. 2 shows the HRTEM images of MWCNTs and RNA coated MWCNT hybrids.

Fig. 2a and b presents MWCNTs and MWCNT/RNA hybrids with diameters ranging from 3 to 10 nm. The MWCNTs could be clearly distinguished from the RNA covered around the sidewall, as shown in Fig. 2b. The molecular modeling for the SWCNT/DNA hybrids reported that DNA can bind to SWCNTs through π-stacking interactions between the DNA and the SWCNT sidewall, resulting in DNA wrapping on the surface [7,22]. Aromatic groups in the nucleic acid base are

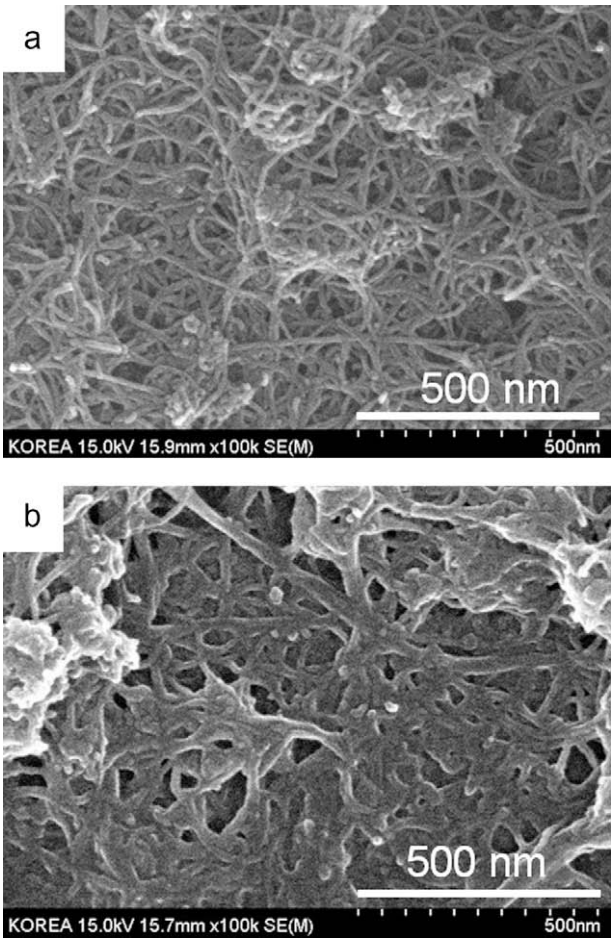

Fig. 1 – The SEM image of (a) MWCNTs and (b) MWCNT/RNA hybrids on ITO glass by spray method.

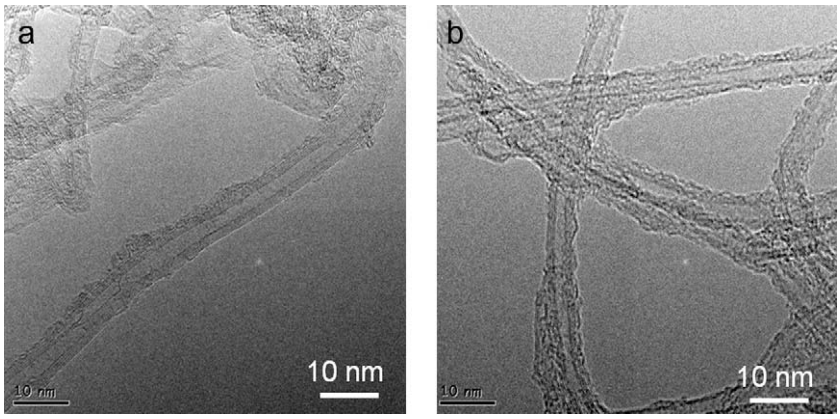

Fig. 2 – HRTEM images of (a) MWCNTs and (b) MWCNT/RNA hybrids.

known to interact strongly with the plane of the graphite on the nanotube surfaces due to π–π stacking [7,23]. The improvement of nanotube solubility and dispersion using nucleic acids such as RNA and DNA could be caused by reduced van der Waals interactions, so the MWCNT/RNA hybrid solutions are found to be stable in water.

The adhesion properties between the spray deposited MWCNT/RNA hybrids and the ITO glass together with their field emission properties for X-ray sources are investigated. Fig. 3 shows photographs optical and SEM images of the PDMS layer separated from the cathode film, which have been sprayed with MWCNTs and MWCNT/RNA hybrids after the PDMS surface treatment process. Fig. 3a displays the detached PDMS from the spray deposited MWCNTs on ITO glass and the optical and SEM image of the bottom surface of the PDMS layer. Most of MWCNTs has been transferred to the PDMS because of the low adhesive force and this is confirmed in the photograph, the optical and the SEM image. The MWCNT/RNA hybrids on the ITO glass remains completely after the PDMS surface treatment, as shown in Fig. 3b. This SEM image show the morphology of the sprayed MWCNT/RNA hybrid film and A SEM image of Fig. 3b show the morphology of the sprayed MWCNT/RNA hybrid film and MWCNT/RNA was not observed in PDMS layer from optical image. The RNA coated MWCNTs are not observed on the PDMS layer during the detaching step and their morphological shapes are seen to appear only in the SEM images whereas the adhesion of the MWCNT/RNA hybrids on the glass substrate is larger than the MWCNTs. Adhesive strength test of MWCNT and MWCNT/RNA hybrid film on ITO glass substrate were prepared by Scotch Magic tape 810 (3M), as shown in Fig. S1 of Supporting Information (SI). As a result, MWCNT film completely stripped off from the surface of glass and MWCNT/RNA hybrid film was firmly adhered to the surface of glass after peel-off test. It is clear that the RNA can be play the role of enforcing CNTs adhesion onto the ITO glass sub-

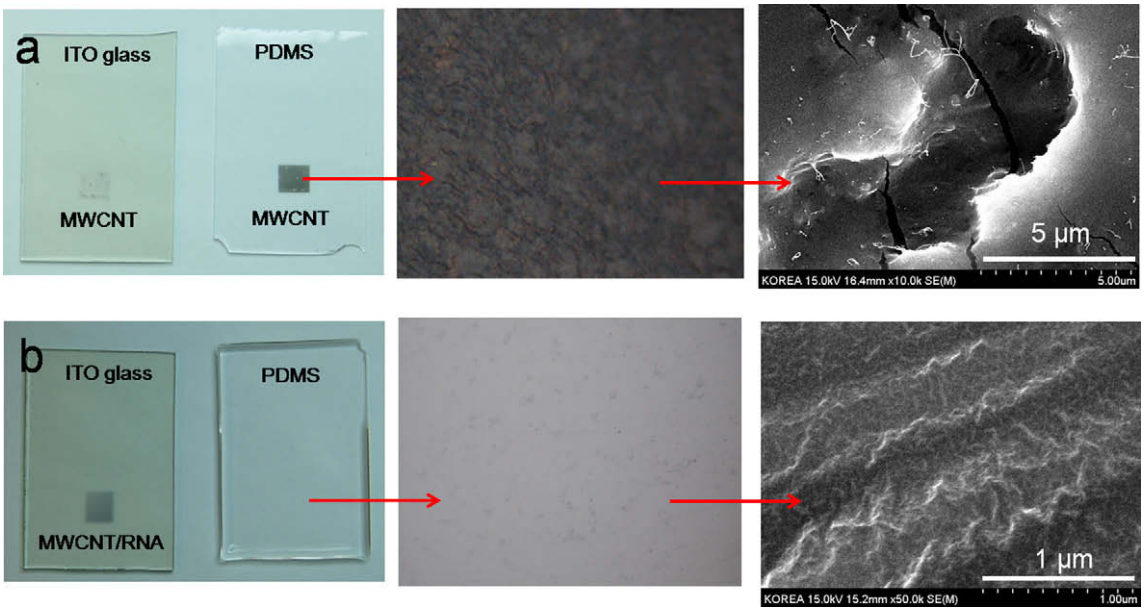

Fig. 3 – (a) Photographs show MWCNTs under the PDMS surface treatment process (left) and the optical and SEM image of the detached PDMS from the cathode (middle and right). (b) Photographs show MWCNT/RNA hybrids under the PDMS surface treatment process (left) and the optical and SEM image of the detached PDMS from the cathode (middle and right).

strate. It is found that high dispersion of the CNTs is assisted by the nucleic acid and the CNTs has a high surface free energy as well as good interaction between the nucleic acid molecules and the surface involving electrostatic forces [13,24]; hence the RNA coated MWCNTs strongly adheres to the glass substrate during the water evaporation.

Fig. 4 shows the field emission results of the spray deposited the MWCNTs, the MWCNT/RNA hybrids before and after the PDMS surface treatment. MWCNT/RNA hybrids after PDMS treatment is defined MWCNT/RNA–PDMS; note that the measurements have been performed using a green phosphor anode where the insulating spacer is kept at 400 μm between the cathode and anode. The turn-on fields, which produce emission current density of 10 $\mu A/cm^2$ are 3.8, 3.9, and 3.2 V/μm for MWCNTs, MWCNT/RNA hybrids, and MWCNT/RNA–PDMS, respectively, as shown in Fig. 4a. At an applied field of 5 V/μm, the current density of MWCNTs has been measured to be 1 mA/cm^2, while it could not be obtained after the PDMS treatment because of the poor adhesion to the substrate as shown in Fig. 3c. The current density of MWCNT/RNA hybrids was obtained 0.2 and 5.1 mA/cm^2 at 5 V/μm before and after the PDMS treatment, respectively. Fig. 4a and b shows SEM images of the spray deposited MWCNT/RNA hybrid emitters before and after the PDMS surface treatment process, respectively. Exposed MWCNT/RNA hybrid emitters at the cathode are removed from the surface after the PDMS process to achieved a high emission current density and shows a homogeneous image for the MWCNT/RNA–PDMS than the MWCNTs and the MWCNT/RNA hybrids cases as presented in Fig. 4d. Other samples such as MWCNT and MWCNT/RNA hybrids give emission images before the surface treatment mainly from the edges; and it appears from the phosphor images that these emissions move to the sides of the samples due to the surface treatment effects when kapton tape as the shadow mask detaches from the substrate after the spray coating process. The spray deposited CNTs need the surface treatment to activate the electron emission because of insufficient protrusions of the nanotubes to the surface. This surface treatment leads to changes in the morphology of the substrate and causes the buried CNTs to protrude over the surface. The MWCNT/RNA hybrid emitters are better at sticking to the glass substrate than the MWCNTs and it displays an improved field emission characteristic as shown by the phosphor images.

In addition, investigations of spray coated MWCNT/RNA hybrids on tungsten wire tip of 0.2 mm diameter as a diode-type field emission X-ray source are been performed. Fig. 5a shows a photograph of a simple X-ray system, which has been assembled with a copper target as the anode and MWCNT/RNA hybrid emitters on the tungsten wire tip after the PDMS treatment as the cathode. Fig. 5b shows SEM image of the sprayed MWCNT/RNA hybrid emitters on tungsten wire tip. The cathode is fixed at the tip holder as the cathode in a vacuum chamber kept at under 5×10^{-6} Torr pressure using a turbo pump. The target uses a copper rod with a diameter of 10 mm and the angle of the anode surface is approximately 10°. The distance between the target and the emitters is approximately 5 mm and X-rays are produced by bombarding the metal target to accelerate the field emission electrons from the cathode by applying an anode at a high voltage. X-ray images of the samples are recorded on X-ray film (KODAK Dental Intraoral E-Speed Film, size 31 × 41 mm) using

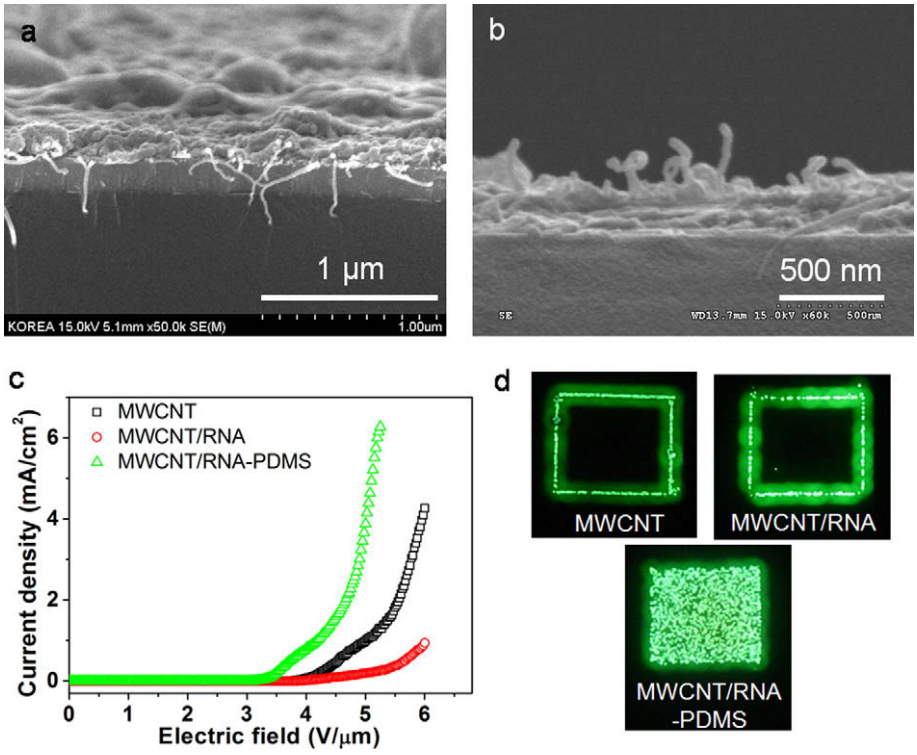

Fig. 4 – Cross-sectional SEM image of (a) MWCNT/RNA and (b) MWCNT/RNA–PDMS. (c) The emission current density plot of MWCNTs, MWCNT/RNA hybrids, and MWCNT/RNA–PDMS. (d) Photographs of emission images of MWCNTs, MWCNT/RNA hybrids, and MWCNT/RNA–PDMS.

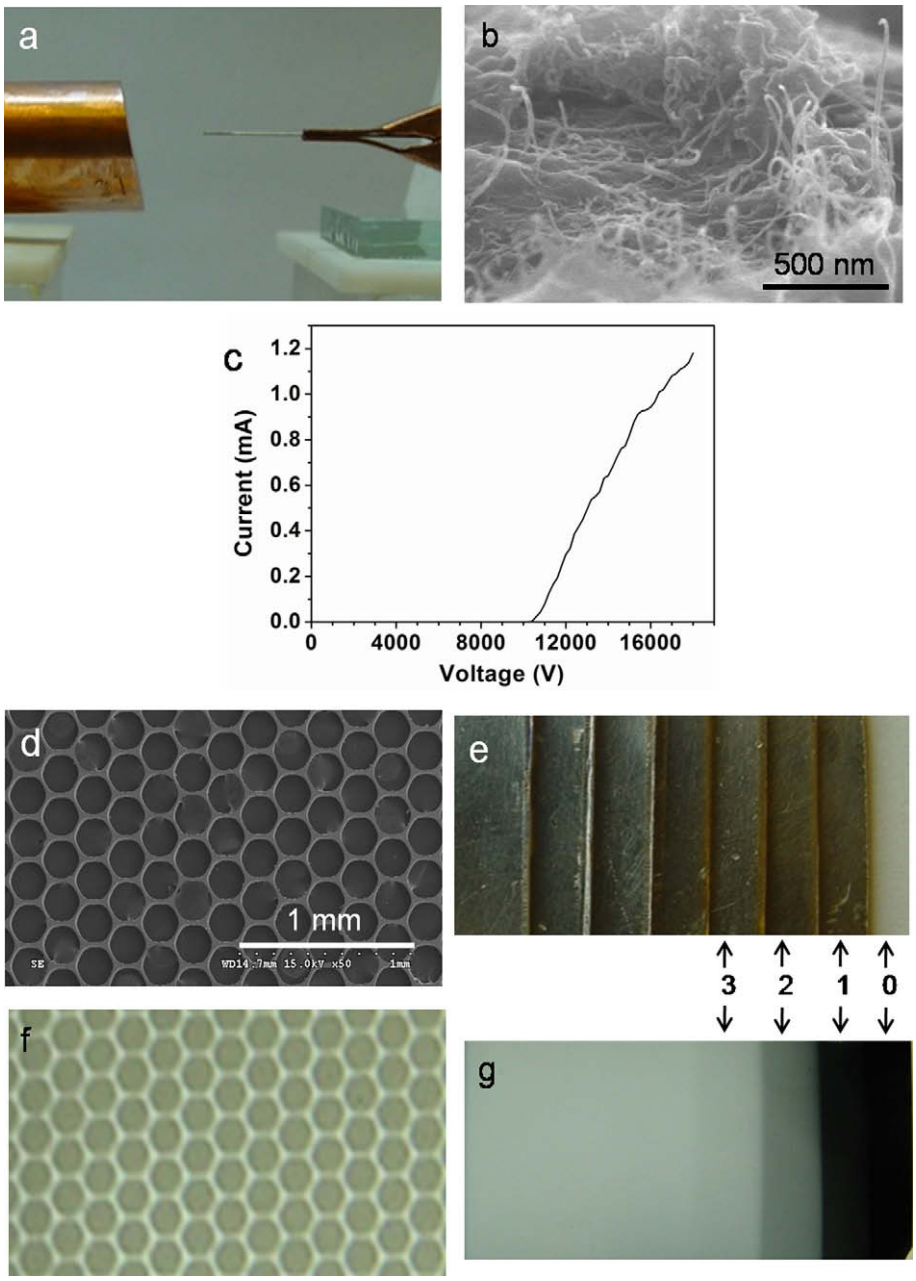

Fig. 5 – (a) Photograph of assembled the anode (copper target) and cathode (sprayed MWCNT/RNA hybrids on tungsten wire tip after PDMS treatment). Field emission current measured under DC mode at the 5 mm anode–cathode distance. (b) SEM image of MWCNT/RNA hybrid emitters on tungsten wire tip. (c) Plot of emission current versus applied voltage. Samples show (d) SEM image of SUS 304 and (e) photograph of step-wedge with aluminum plates (seven layers) corresponding to X-ray images of (f) metal mesh and (g) aluminum plates with seven layers at applied 18 kV, respectively.

dental developers and fixers. Fig. 5c shows the plot of emission current versus the applied voltage at the cathode and the emission current of 1.18 mA at 18 kV. Fig. 5f and g shows X-ray images of the samples obtained from the cathode within 20 s of exposure time at 18 kV. These samples are stainless steel mesh (Fig. 5d) and seven layers with 1 mm thickness of aluminum plate (Fig. 5e). As shown the Fig. 5f and g, the X-ray images are obtained using metal mesh (SEM image) and aluminum plates (photographic image), respectively. The X-ray is transmitted in three layers in the step-wedge of the aluminum. Compared to the MWCNT emitters (see Fig. S2 in SI), X-ray transmission image was obtained relatively good resolution in the MWCNT/RNA hybrid emitters. From these images, it is clear that this X-ray radiography is able to illustrate the spatial resolution and the interior structure without destroying the sample.

4. Conclusions

The paper has presented that dispersed MWCNT in water using RNA can improve the performance of the field emitters.

The MWCNT/RNA hybrids have been morphologically characterized by SEM and TEM and the images clearly show the RNA coated MWCNT structures. It has been found that spray deposited MWCNT/RNA hybrids have stronger adhesion than MWCNTs onto glass or metal substrates after PDMS surface treatments. These composite emitters improve the field emission properties more than MWCNTs and demonstrate the field emission X-ray sources can be applied to high-resolution X-ray radiography. The MWCNT/RNA hybrids are also potentially good candidates for electrochemical sensing applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2009.11.035.

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