Post-Treatment of Printed Carbon Nanotubes for Vertical Alignment

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Abstract

Fabrication of photosensitive carbon nanotubes paste and its post-treatment has been developed for high resolution with good electron emission uniformity. We report novel post-treatment techniques including rubber-rolling and multiple field emission cycling from which we could improve the field emission properties of printed carbon nanotubes. These techniques would be easily applicable to large area field emission display using paste of carbon nanotubes

1. Objectives and Background

Paste mixing of carbon nanotubes (CNTs) offers several advantages over competing direct deposition or other types of field emission cathodes in large-area and low-cost application. However, as-prepared CNTs in printed cathode layer show very poor electron emission characteristics because of their insufficient outcrop to the surface, random distribution and possible organic residues. Therefore, special post-treatment methods[1-3] have been proposed to modify surface properties of prepared CNTs.

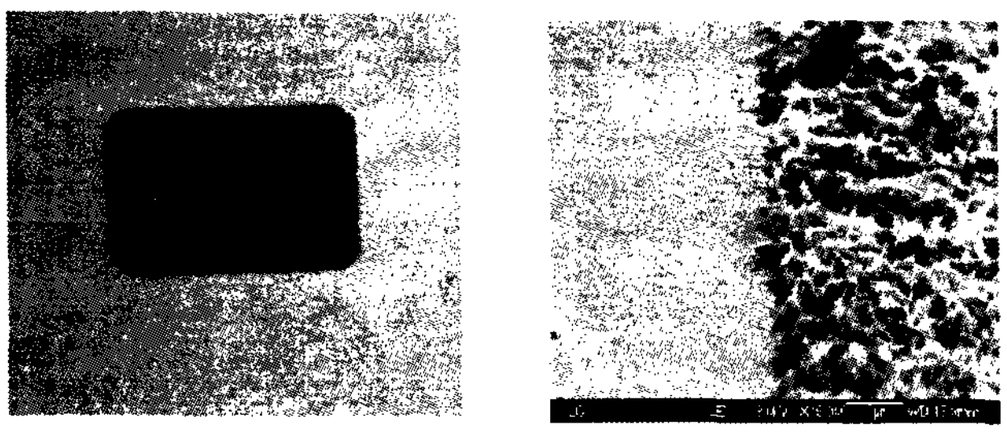
In this context, we have developed a non-destructive and cost-effective technique using soft rubber roller followed by multiple field emission cycles. Here we report the experimental results of these novel methods supported by analysis of scanning electron microscopy (SEM), emitted current-applied voltage (I-V) measurement and phosphor screen images for discussion.

2. Results

Arc discharged single-walled CNTs were used for paste mixing. The raw materials of CNT bundles were well dispersed in alcohols, butyl carbitol acetate (BCA) and/or α-terpienol using high-speed (30,000 rpm) homogenizer for 30 minutes. Photosensitive organic binders based on acrylate or cellulose were mixed with the prepared CNT/solvent solution, also added tin oxide, indium tin oxide and/or frit glass powders for conductive fillers and adhesion improvement, respectively. Intensive 3-roll milling was finally processed for the control of paste rheology.

The paste of well-dispersed CNTs was printed using a blade onto the Cr-patterned (100x150 μm^2 aperture, 120x160x3 pixels) PD200 glass (155x155 mm^2) through metal meshes with 20 μm in size, and subsequently dried at 120 °C for 20 min in conventional oven. For fine patterning of CNT pixels, back-side UV exposure[4] and organic solvent development technique was applied. After 2-step firing at 350 °C in air and 400 °C in N_2 each for 30 minutes, self-aligned 0.2 ~ 1.5 μm thick CNT patterns were formed. For the post-treatment of prepared CNT cathode, we have tested various methods such as adhesive-tape, soft rubber rolling, plasma treatment, and electron bombardment, etc. The key issues of

post-treatment of CNT paste are outcrop of CNTs to the surface, effective removal of contaminants from CNT surface, and following vertical alignment of CNTs. As for soft rubber rolling, rollers should be made of highly soft and elastic rubber so that the roller face could uniformly cover all over the CNT pixels. Through this method, we could make direct treatment on the CNT surfaces without destruction of pattern shape or particle generation. The optical and electron microscopic pictures of CNT pixels after rolling are shown in Fig. 1. It revealed that the photo-lithographically formed CNT pixels have good patterns with sharp edges and relatively uniform thickness, which is dependent on the UV exposing duration.

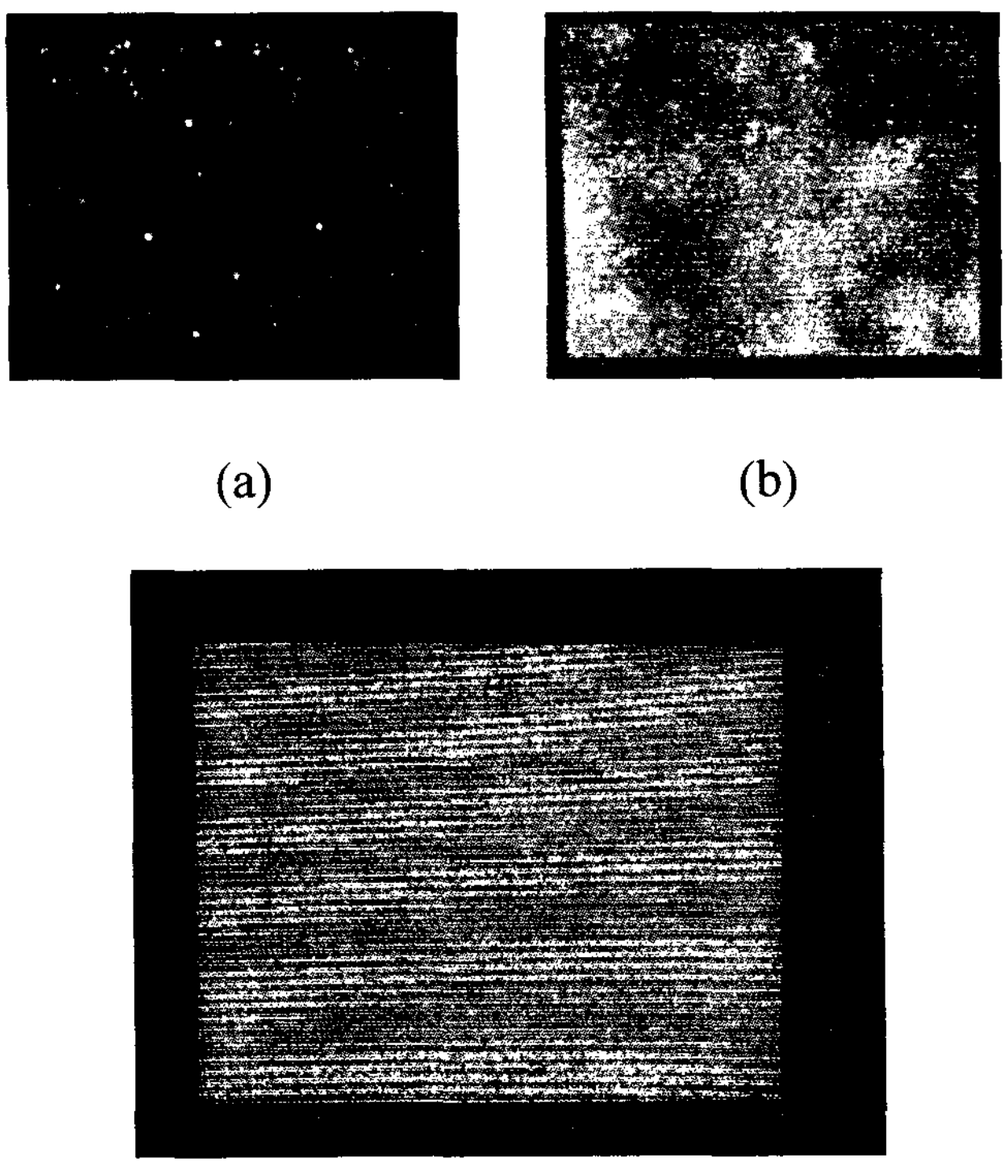


(a) (b)

Figure 1. (a) An optical microscopic view of photo-lithographically patterned CNT paste. (100x150 μm) (b) A magnified view of CNT pixel after rubber rolling.

Such photo-lithographic patterns of CNT paste have been realized to define a small pixel size as small as 5 μm. Thus our photo-sensitive CNT pastes are applicable to precise FED cathodes.

For evaluation of electron emission properties of CNT paste and post-treatment effect, I-V measurements were carried out with diode structure in vacuum chamber (5 x 10^{-6} Torr). The anode and cathode was spaced at 500 μm with glass spacers. Phosphor coated ITO glass was used as anode. Figure 2 shows the emission images demonstrated from three different CNT cathodes; (a) without surface treatment, (b) with rubber-roll treatment, and (c) with rubber-roll treatment followed by multiple field emission cycles.



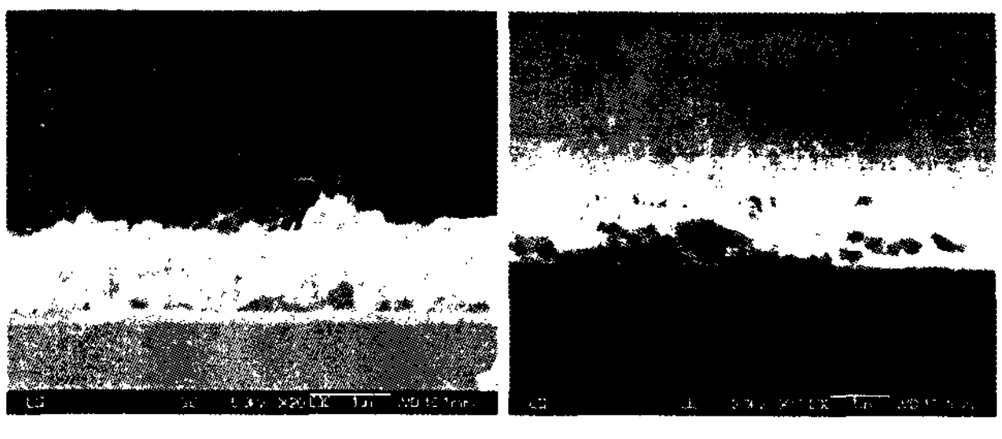
(a) (b)

(c)

Figure 2. Phosphor screen images from three different samples. (a) Before rolling. (b) After rolling. (c) After rolling + multiple I-V cycles.

The emission images in Fig. 2 were all obtained at an applied anode voltage of 2 KV (4 $V \cdot \mu m^{-1}$). Multiple field emission cycles were simply applied by repetition of I-V measurements from 0 V to 1.65-1.70 KV. The

emission image in Figure 2 (c) was captured after thirteen I-V cycles. The rubber-rolled one exhibited good emission patterns over the nearly full emitter area except for a little non-uniformity, whereas few pixels emitted electrons in the untreated samples. Though the rubber-rolled cathode had a remarkably enhanced emission image compared with the untreated one, it is worth noting that the majority of the CNTs in the rubber-rolled layer are not oriented to the vertical direction as shown in Fig. 3 (a). Therefore it may be a reasonable assumption that the main role of the rubber-rolling process is not acting on the CNT alignment but removal of contaminants from the CNT surfaces.



(a) (b)

Figure 3. SEM images show the morphology changes of pasted CNTs (a) before, and (b) after multiple field emission cycles.

With repetition of field emission cycles, the more emission uniformity was enhanced as shown in Fig. 2 (c). The dramatic changes in surface morphology after emission cycles were apparently observed from SEM micrographs shown in Fig. 3 (b). Without emission cycles, the morphology of the CNTs had curved ends and totally random orientations, but on the other hand, by multiple field emission cycles, the CNTs were irreversibly deformed to orient themselves parallel to the field direction and enhanced emission image with good uniformity was obtained from them. We believe this morphological change caused by high voltage and emission current became permanent after multiple cycles of field emission. From the sample in Fig. 3 (b), we extracted a continuous stable emission current density of about 2 $mA \cdot cm^{-2}$ at the field strength of 3.6 $V \cdot \mu m^{-1}$. Under this emission condition, the current fluctuation was negligible and only 2 % of current decrease was detected after 12 hours of continuous measurement.

The improvement of emission properties is also apparent from the I-V curves shown in Fig. 4 (a), which were obtained from our field emission cycles. The field emission threshold was about 2.5 $V \cdot \mu m^{-1}$ for the first measurement. In the successive cycles, the threshold fields were decreased gradually to the value of 1.9 $V \cdot \mu m^{-1}$ for the final 13th cycle.

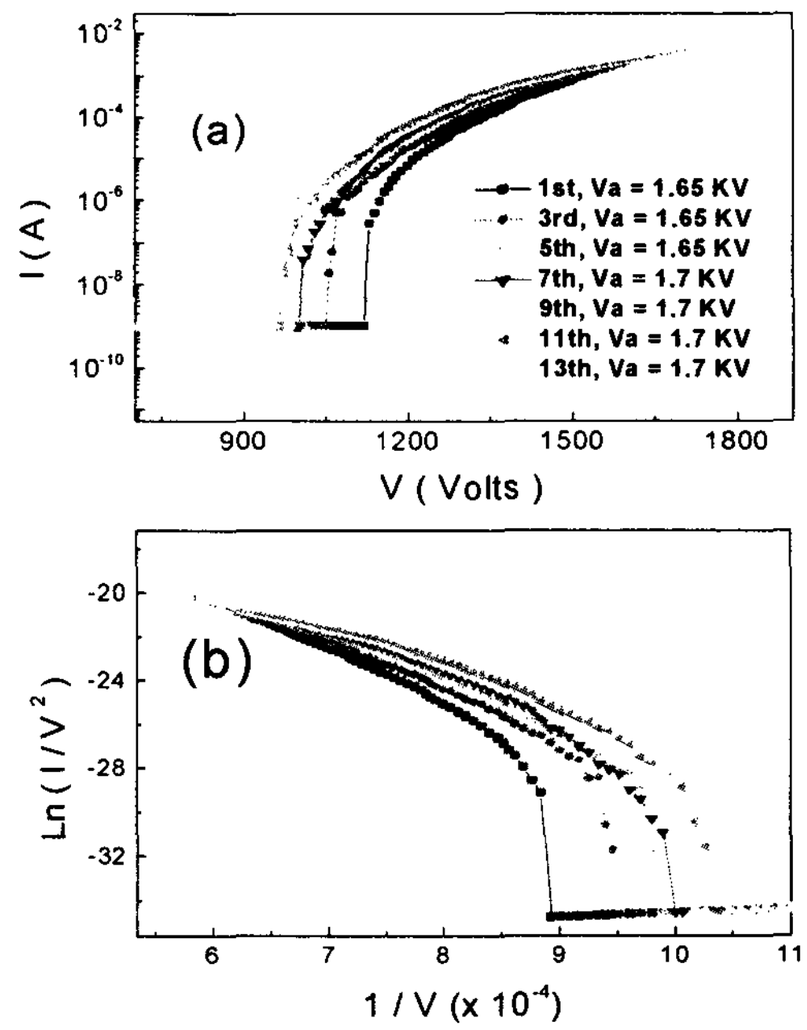


Fig. 4. (a) The measured I-V curves for multiple field emission cycles.
(b) Corresponding Fowler-Nordheim plots.

This behavior could be interpreted as the irreversible vertical alignment of CNTs by electric field, as well as the heat generation by field emission current.[5] From the corresponding Fowler-Nordheim (F-N) plots [Fig. 4 (b)], we evaluated the field enhancement factor (β) of each line using F-N equation.[6] It was revealed that the average β values were monotonically increased (from 1366 to 2120) with field emission repetition, which again confirmed the gradual vertical alignment of CNTs by multiple I-V cycles. Precisely, it was also interesting point that the main change of the F-N slopes took place in the low voltage region, whereas they conversed in the high voltage region of the graph. In the initial cycles, the flexing and vertical alignment of curved CNTs was accelerated with voltage increase to the final vertical orientation. However, after the bias voltage to the anode was turned down to 0 V, the CNTs were almost reversibly restored to their original curved states. Within subsequent cycles, the preferential vertical alignment of CNTs became gradually permanent little by little. This gradual effect appeared as a trend of β value increase in repetition of I-V measurements. Because the relatively low field (3.3 ~ 3.4 $V \cdot \mu m^{-1}$) was applied to our field emission cycles, we believe, even under low field strength, the multiple field emission process induces the irreversible vertical alignment of the pasted CNTs.

3. Impact

Photo-sensitive CNT paste was formulated for a precise pixel definition, which is easily applicable to large size FED. We have developed cost-effective post-treatment techniques using soft rubber roller followed by multiple field emission cycles. By this simple method, a dramatic enhancement of emission current and uniformity was obtained from printed CNTs.

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5. References

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