Field Emission Properties of *Ex-situ* and *In-situ* Iron Catalyst-Grown Carbon Nanotubes

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***Abstract*— Carbon Nanotubes (CNTs) are grown using *ex-situ* and *in-situ* iron catalyst sources, and their respective Field Emission (FE) properties are investigated. At similar CNT heights (~16 µm), it is found that *in-situ* catalyst-grown CNT film shows better FE properties than *ex-situ* catalyst-grown CNT film. At the same time, it is found that *in-situ* CNTs show enlarged tips, forming "thumbtack"-shaped CNT tips. From the simulation study, enlarged CNT tip emits higher FE current, possibly due to the larger emission area. The obtained results demonstrated that *in-situ* catalyst-grown CNTs show better FE properties than *ex-situ* catalyst-grown CNTs.**

I. Introduction

It has been widely reported that Carbon Nanotubes (CNTs) show outstanding Field Emission (FE) properties [1], [2]. To grow CNTs, Chemical Vapor Deposition (CVD) technique can be used, where hydrocarbon vapor is diffused onto the catalyst clusters (Fe, Ni, Co, etc.) in high temperatures [3]. For iron (Fe) catalyst, CVD process can be carried out on a pre-deposited Fe layer (*ex-situ* catalyst) [4]; or using ferrocene/hydrocarbon pyrolysis process, where Fe particles are fed simultaneously with the hydrocarbon source (*in-situ* catalyst) [5]. Despite numerous studies reported on the FE properties of CNTs grown by *ex-situ* and *in-situ* catalyst sources, there are limited studies on FE comparison between CNTs grown by these two catalyst sources. Therefore, comparative studies on the FE properties of *in-situ* and *ex-situ* catalyst-grown CNTs are called for.

In this study, the FE properties of *ex-situ* and *in-situ* Fe catalyst-grown CNTs are investigated. From the obtained FE measurement, it is found that *in-situ* catalyst-grown CNTs show higher FE current density as compared to *ex-situ* catalyst-grown CNTs. From the Transmission Electron Microscopy (TEM) images and the electric field simulation, the mechanism of high FE current from *in-situ* catalyst-grown CNTs is speculated.

II. Experimental Method

A. CNT growth

Highly n-doped Silicon (Si) substrates (Thickness: 300 µm, Resistivity: 0.018 Ω.cm) are used for all sample preparations. For CNT growth using *ex-situ* catalyst source, the substrate preparation is carried out by sequentially depositing a combination of 8-nm-thick Al, 2-nm-thick Al_2O_3, and 2-nm-thick Fe, respectively serving as barrier, adhesion, and catalytic layers, on Si substrates. In the CVD process, the Fe catalyst is first pre-treated in the reactor with H_2 gas at 700 °C for 3 minutes followed by CNTs growth at 700 °C with H_2 and C_2H_2 flow rates of 700 and 200 sccm. For CVD process using *in-situ* catalyst source, bare Si substrate is first inserted into the reactor. Then, continuous injection of ferrocene/xylene solution is carried out into the reactor at 820 °C under continuous Argon gas flow. The growth temperatures and the growth durations are carefully tuned to achieve CNT heights of ~ 16 µm for both processes.

B. Characterization Techniques

The morphologies of CNTs are characterized by Scanning Electron Microscope (SEM, JEOL JSM-IT100) and Transmission Electron Microscope (TEM, Phillips Tecnai 20). The field emission characteristics of the CNT films are measured using a planar-anode measurement system under high vacuum condition (10^{-6} Torr). The measurement is carried out using 20 Hz pulsed voltage source with duty cycle of ~50%. The cathode-anode distance and the effective emission area is estimated to be 25 µm and 0.75 mm^2, respectively.

III. Results And Discussion

Figure 1 shows the SEM images of *ex-situ* and *in-situ* catalyst-grown CNT films. Generally, CNTs show high degree of vertical alignment for both catalyst sources. The heights of *ex-situ* and *in-situ* catalyst-grown CNT films are similar, estimated at 16.3 and 15.8 µm, respectively.

Research supported by Office of Space Technology and Industry (OSTIn), Singapore.

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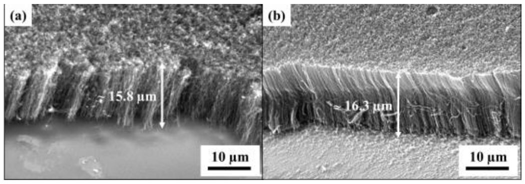

Figure 1: SEM images of (a) *ex-situ*, and (b) *in-situ* catalyst-grown CNTs

The FE properties of *ex-situ* and *in-situ* catalyst-grown CNTs are shown in Figure 2. *In-situ* catalyst-grown CNTs requires lower electric field (5.2 V/µm) than *ex-situ* catalyst-grown CNTs to achieve FE current density level of ~ 3 mA/cm^2. From the Fowler Nordheim (FN) plots, it is calculated that *in-situ* catalyst-grown CNTs show higher field enhancement factor (β) of 9314 as compared to 8150 from *ex-situ* catalyst-grown CNTs.

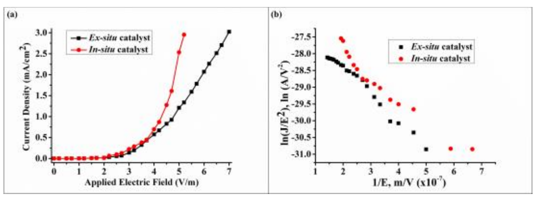

Figure 2: (a) FE measurements, and (b) FN plots of *ex-situ* and *in-situ* catalyst-grown CNT films

For further investigation, we have performed TEM analysis on both *ex-situ* and *in-situ* catalyst-grown CNTs, as shown in Figure 3. It is shown that *ex-situ* catalyst-grown CNTs have smaller diameter (~ 50 nm) as compared to *in-situ* catalyst-grown CNTs (~ 14 nm). At similar CNT heights of ~ 16 µm, smaller diameter of *in-situ* catalyst-grown CNTs gives higher CNT aspect ratio, which yields higher β value [6], as agreed with the calculated β values in this study. Besides the higher aspect ratio, it is found that *in-situ* catalyst-grown CNTs show an interesting morphological shape. As shown in Figure 3(a), *in-situ* catalyst-grown CNTs show enlarged, "thumbtack"-shaped CNT tips. The enlarged CNT tips can be postulated as a contributing factor to the superior FE properties of *in-situ* catalyst-grown CNTs over *ex-situ* catalyst-grown CNTs.

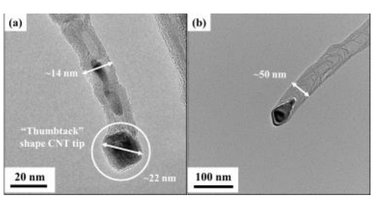

Figure 3: TEM images of (a) *in-situ*, and (b) *ex-situ* catalyst-grown CNTs

To postulate the effect of enlarged CNT tip on its FE properties, we have performed we have simulated the FE properties of the CNTs using CST STUDIO SUITE®. Based TEM images (Figure 3), we have built two simplified models to approximate the morphological structure as shown in Figure 4. From the simulation results, it is found that CNT model in Figure 4(b) delivers higher FE current of 2.8 x 10^{-5} A as compared to 1.57 x 10^{-5} A emitter from the CNT model in Figure 4(a), despite lower electric field on the tip. Therefore, the contributing factor for the high FE current by the CNTs with enlarged tips can be the larger emission area, which results in higher electron emission. In the case of *in-situ* catalyst-grown CNTs, the enlarged tip diameter is estimated to be 22 nm, which is smaller than the tip of the *ex-situ* catalyst-grown CNTs (~50 nm). Therefore, it can be expected that the electric field on *in-situ* catalyst-grown CNTs is higher than *ex-situ* catalyst-grown CNTs. Nevertheless, the mechanism of better FE properties from *in-situ* catalyst-grown CNTs is not fully understood and requires further investigations.

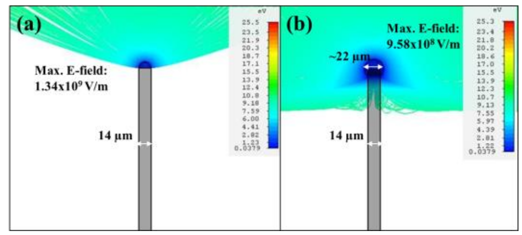

Figure 4: Electron trajectory of CNTs with (a) equal diameter; and (b) enlarged diameter, with the CNT body

IV. Conclusion

In this study, we have demonstrated that *in-situ* catalyst-grown CNT film shows better Field Emission (FE) properties than *ex-situ* catalyst-grown CNT film. From the Transmission Electron Microscope (TEM) images and the electric field simulation, it can be speculated that the enlarged tip of the *in-situ* catalyst-grown CNTs contributes to the superior FE properties of *in-situ* catalyst-grown CNTs over *ex-situ* catalyst-grown CNTs. The obtained results from this study provides a novel insight to the synthesis of high FE CNTs, which gives promising potential to the realization of CNTs in various FE applications.

Acknowledgment

This work has been partially supported by the Office for Space Technology and Industry (OSTIn), Singapore, under the project S14-1126-NRF OSTIn-SRP.

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