

Study of the Emission Characteristics of Single-Walled CNT and Carbon Nano-Fiber Pyrograf III

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Abstract: Field emission microscopy measurements from Single-Walled Carbon Nanotubes (SWCNTs) and Carbon Nano-Fibers Pyrograf III PR-1 (CNF) were performed. Details of the materials employed in the experiments are as follows: (a) Carbon Nano-Fibers Pyrograf III PR-1 (CNF), having an average fiber diameter that is ranging between (100-200) nm with a length of (30-100) μm . (b) Single walled Carbon Nanotubes were produced by high-pressure CO over Fe particle (HiPCO: High-Pressure Carbon Monoxide process), having an average diameter ranging between (1-4) nm with a length of (1-3) μm . The experiments were performed under vacuum pressure value of (10^{-7} mbar). The research work reported here includes the field electron emission current-voltage (I-V) characteristics and presented as Fowler-Nordheim (FN) plots and the spatial emission current distributions (electron emission images) obtained and analyzed in terms of electron source features. For both the SWCNT and the CNF a single spot pattern for the electron spatial; distributions were observed.

1. Introduction

It is known that Pyrograf-III can be uniformly dispersed in a polymer in order to provide maximum conductive network using mixing and compounding equipment [1]. Electron emission (FE) refers to the release of electrons from the surface of a material into vacuum [2], which is occurring when the electric field strength is at the scale of (10^9 V.m^{-1}) [3]. FE has a long history up to the derivation of the original Fowler-Nordheim (FN) equation in 1928. In early days of FE experiments, metal was used as field emitters. However, because of the active nature of materials the residual gases and ion bombardment during FE working limited the lifetime of metal field emitters, impeding the development of FE [4]. Since discovering of Carbon Nanotubes (CNTs) from 1991 to 1993 with both types Multi-Walled Carbon Nanotubes (MWCNTs) and Single Wall Carbon Nanotubes (SWCNTs) by Sumio Iijima [5] [6], it has a growing attentions due to their perfect properties that make it the best candidate to be the next generation of field emitters such as, low turn-on fields, high emission current, stable emission current, long lifetime, low energy spreading, and high brightness [7].



The history of Carbon Nano-Fibers (CNFs) goes back more than a century. In a patent published in 1889 [8], it is reported that Carbon filaments are grown from Carbon-containing gases using a metallic crucible as the catalyst [9]. Carbon nanofibers (CNFs), also known as Stacked-Cup Carbon Nanotubes (SCCNTs), is with in the class of materials termed Multi-Walled Carbon Nanotubes and are produced by the floating catalyst method. CNFs are discontinuous and highly graphitic, but there are differences in the structure as figure (1) shows.

(SCCNTs) or (CNFs) have a unique morphology in that graphene planes are canted from the fiber axis, resulting in exposed edge plane on the interior and exterior surfaces of the fiber; CNTs, on the other hand, typically resemble an assembly of concentric cylinders of graphene [10].

Fowler-Nordheim (FN) first derived a semiclassical theory of FE based on physical assumptions and mathematical approaches; the theory has been modified many times over years to describe Cold Field Emission (CFE) from bulk metal where it is known as Fowler-Nordheim (FN) equations.

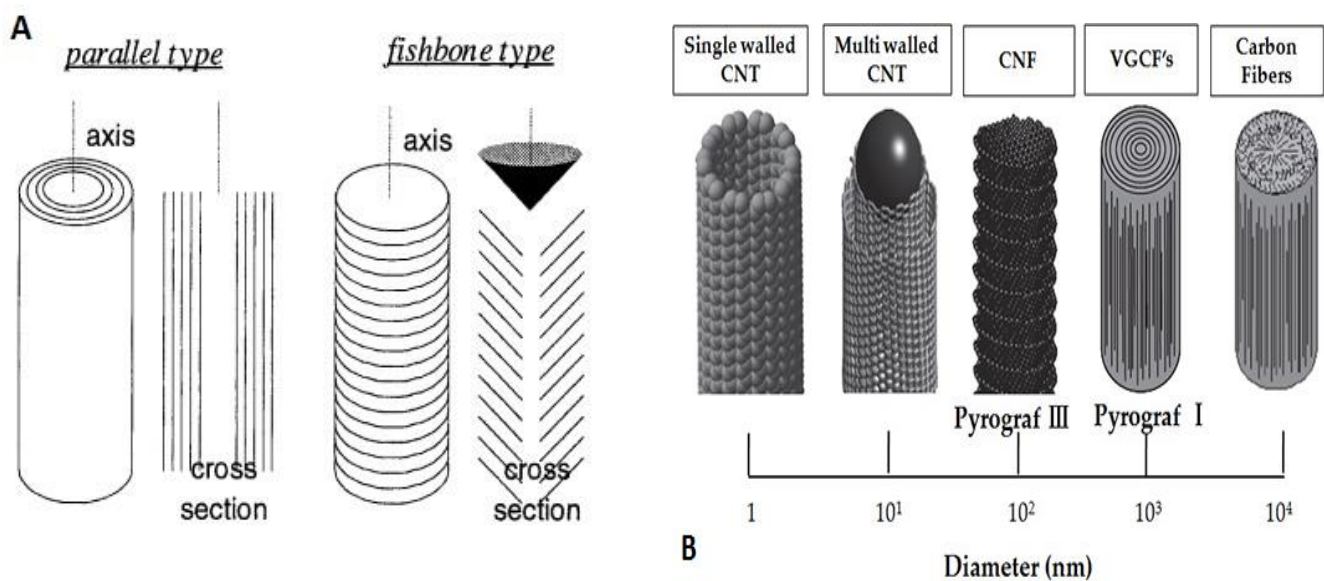


Figure 1(A) Simplified representation of the structure of parallel (left) and fishbone (right) Carbon Nanotubes. (B) Nano-Fibers sizes from Single wall Carbon Nanotubes to conventional Carbon Fibers.

The simplest of these is the so-called elementary FN-type equation

$$i = A_n \{ a \phi^{-1} (\beta_V V)^2 \} \exp \left(- \frac{b \phi^{\frac{3}{2}}}{\beta_V V} \right)$$

Where i is the current emission, ϕ local work function, V is the applied voltage, a and b are the first and second FN constants, as usually defined in Ref [11], β_V is the local voltage-to-surface field conversion factor at some specific reference point on the emitter surface, and A_n is the national emission area defined by considering the local emission current density at the reference point. This equation and related equations that use macroscopic field as an independent variables have often been used to describe CFE from Carbon Nanotubes (CNTs) including closed single walled (CNTs) of small apex radius, particularly in technological context [12].

2. Materials and Methods

The apparatus are used to create a prepared glass micro-point emitter where the CNTs inserted in it, so they would protrude at the tip. Figure (2) and (3) shows the produced sample.

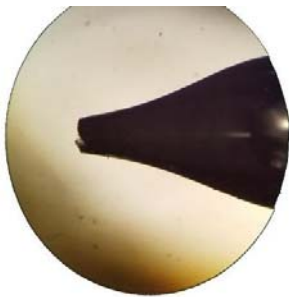


Figure 2: Optical micrograph of (SWCNT-15) tip at magnification 50x times.

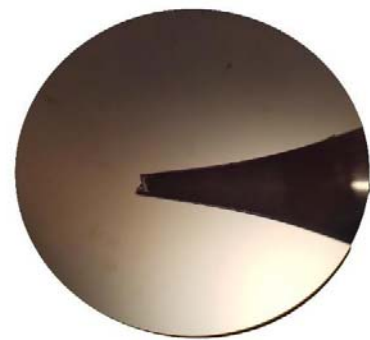


Figure 3: Optical micrograph of (CNF-25) tip at magnification 50x times.

This study uses two types of CNTs, (a) Single-Walled Carbon Nanotubes (SWCNTs) were produced by high-pressure CO over Fe particles (HiPCO: High-Pressure Carbon Monoxide process), having an average diameter ranging between (1-4) nm with length (1-3) μm [13].

(b) Carbon Nano-Fibers pyrograf III PR-1 (CNFs), having average fiber diameter that is ranging between (100-200) nm, with the length of (30-100) μm .

Both tips prepared by employing a drawing technique using a glass puller, figure (4) shown the apparatus that are used to produce such tips, then the emitters are mounted in a standard Field Emission Microscopy (FEM) with an emitter-screen distance of ~ 10 mm [14], and current limiting resistor of (100 M Ω) is used. The system was evacuated to pressure $\sim 10^{-8}$ mbar after baking at $\sim 150^\circ\text{C}$ overnight.

The FEM applied voltage V is increased slowly until a “switch-on voltage” V_{sw} is reached, at which point the emission current suddenly “switch-on”, at V_{sw} the current increase rapidly from about a Nano-ampere to a much greater saturated value I_{sw} , by slowly decreasing the applied voltage to a lower value the emission current starts to be decreasing until limit reached, beyond which the emission current falls smoothly to zero as the applied voltage is decreased to the threshold value V_{TH} [15].

3. Results and Discussion

This section describes the results of experiments on the emission characteristics of the Carbon Nano-Fibers and Single-Walled Carbon Nanotubes. These results include the I-V characteristics, Fowler-Nordheim (FN) plot, and emission images. Emission current measurements are made using a pico-ammeter connected between the cathode and earth.

As the applied electric field is slowly applied, the emission is only observed after a threshold field is reached, and emission suddenly jumps to a constant saturated value I_{SAT} , further increasing the applied electric field the V_{MAX} will be reached, after that the tip explode, as the voltage slowly decreasing, the emission current fall to nearly zero, reaching the threshold value V_{TH} .

Figure (2) shows an optical image of the first tip to be discussed. As we increase the applied voltage slowly, “switch-on” phenomena has been occurring at applied voltage value $V_{\text{sw}} = 800$ V, with emission current value $I_{\text{sw}} = 4$ μA , then the applied voltage was reduced, the V_{SAT} remained constant to the saturated voltage value of $V_{\text{SAT}} = 400$ V, with emission current value $I_{\text{sw}} = 1.06$ μA , further voltage reduction, the emission current falls smoothly

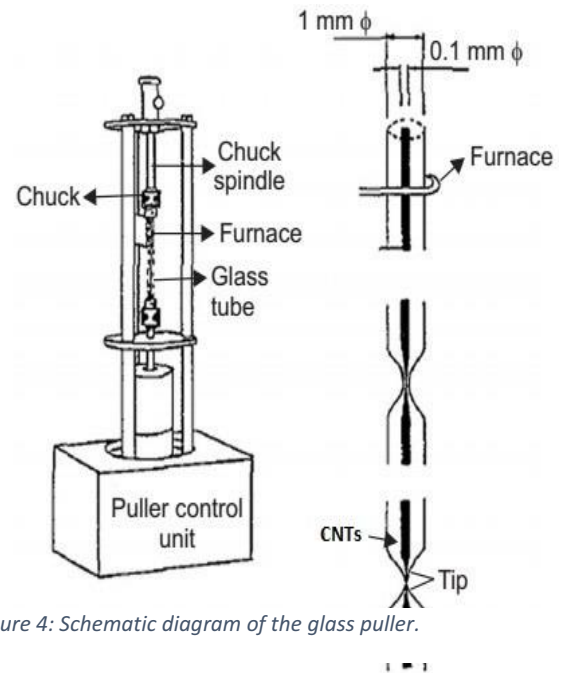


Figure 4: Schematic diagram of the glass puller.

to $I_{TH} = 7 \text{ pA}$ at applied voltage value (180 V). Figure (5) below shows the I-V behaviour during increasing and decreasing the applied voltage, and FN plot.

The experiment was repeated under the same condition and the results were as follows, the

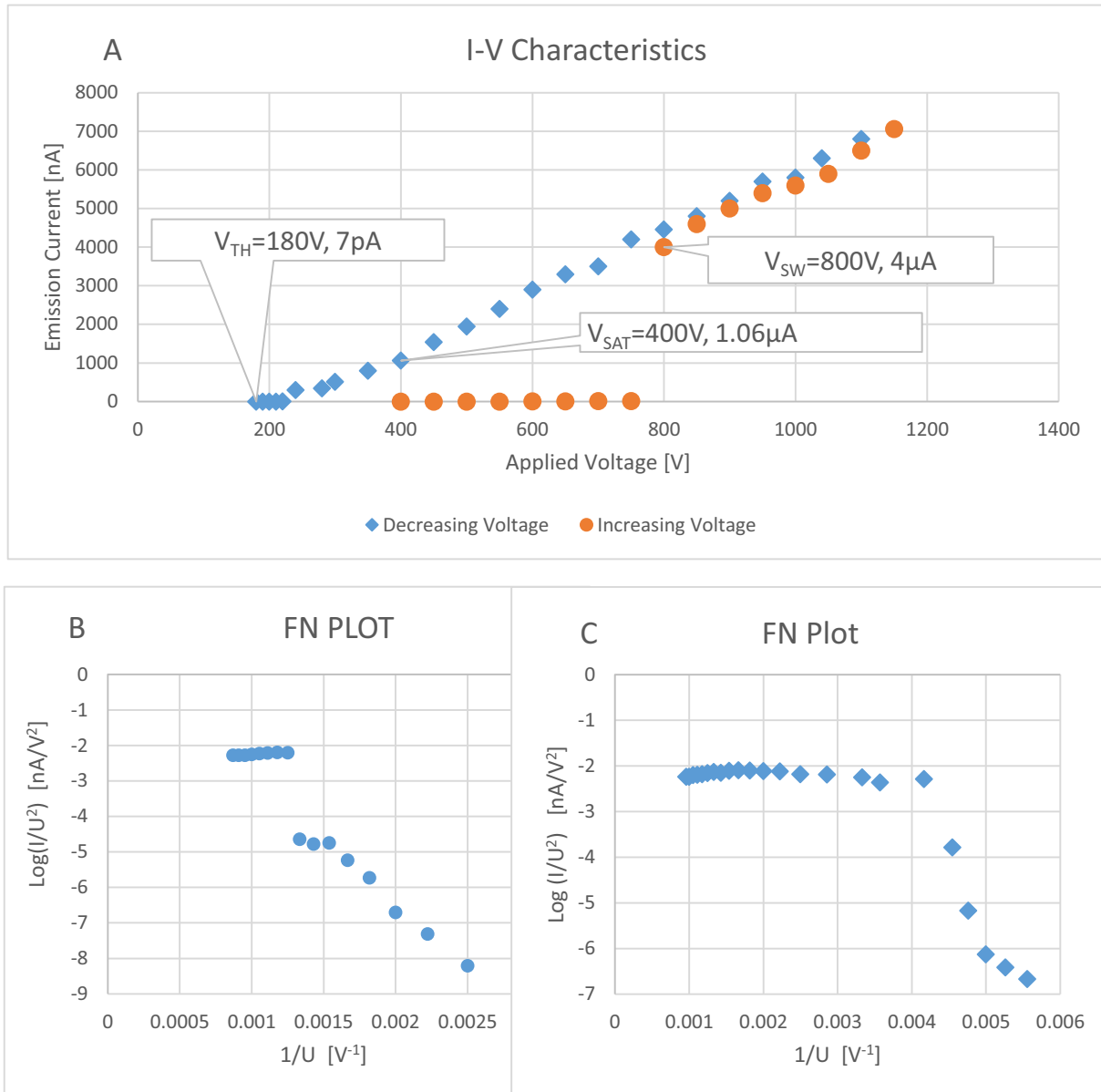


Figure 5. (A) I-V plot for increasing and decreasing voltage (B) FN plot for increasing voltage (C) FN plot for decreasing voltage.

electron emission is initiated at an applied voltage of (320 V) with emission current value (2 pA), and by continue increasing the applied voltage, a point was reached, at $V_{SW} = 650 \text{ V}$, where the emission current suddenly “switched-on” to a stable saturated value I_{SAT} , and by decreasing the applied voltage the saturated region extends down to value $V_{SAT} = 380 \text{ V}$, with emission current value ($1.06 \mu\text{A}$). Further voltage reduction causes the emission current to fall to nearly zero, reaching the threshold value $V_{TH} = 140 \text{ V}$, with emission

current value (3 pA). Figure (6) shows the I-V behavior and FN plot and, some field electron microscope images for the first cycle and second cycle.

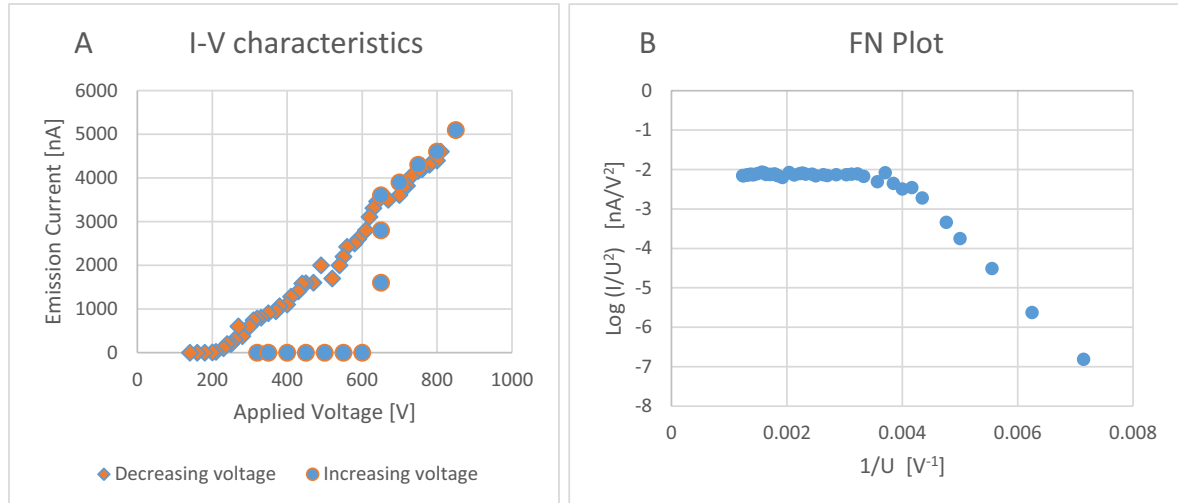


Figure 6. Second Cycle of test (A) I-V plot for decreasing and increasing voltage. (B) FN plot for decreasing voltage.

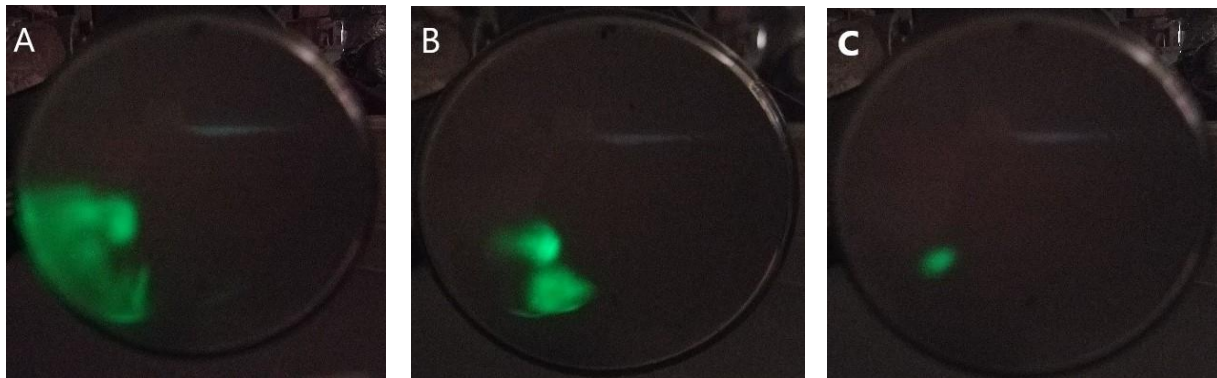


Figure 7. Emission images for first cycle at: (A) $V_{SW}=800 \text{ V}$, $4 \mu\text{A}$. (B) $V_{SAT}=400 \text{ V}$, $1.06 \mu\text{A}$. (C) $V \text{ (Before switch-on)}=650 \text{ V}$, 7.6 nA .

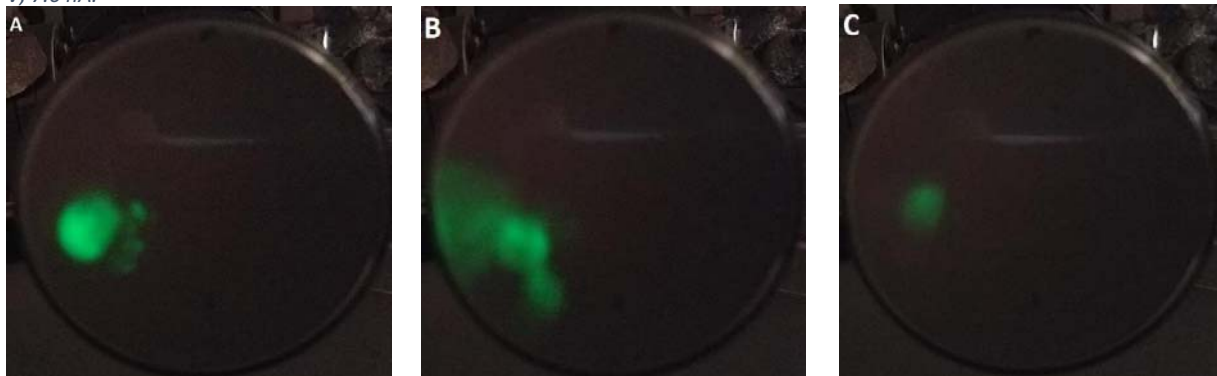


Figure 8. Emission images for second cycle at: (A) $V_{SW}=650 \text{ V}$, $1.6 \mu\text{A}$. (B) $V_{SAT}=380 \text{ V}$, $1.06 \mu\text{A}$. (C) $V \text{ (Before switch-on)}=590 \text{ V}$, 7.6 nA .

The second type of CNTs have been tested under the same conditions and the results were as follows, as the applied voltage increased slowly, the emission current initiated at applied voltage value (200 V), with emission current value (20 pA), then the emission current suddenly “switched-on” at $V_{SW} = 1100$ V, $I_{SW} = 1.2$ μ A, then as we reduce the applied voltage, the saturation region extends down to $V_{SAT} = 400$ V, with emission current value of (1.09 μ A), further reduction, the emission current falls down to (10 pA) at applied voltage value (150 V). Figure (9) shows the I-V behavior during increasing and decreasing cycle, as well as FN plot.

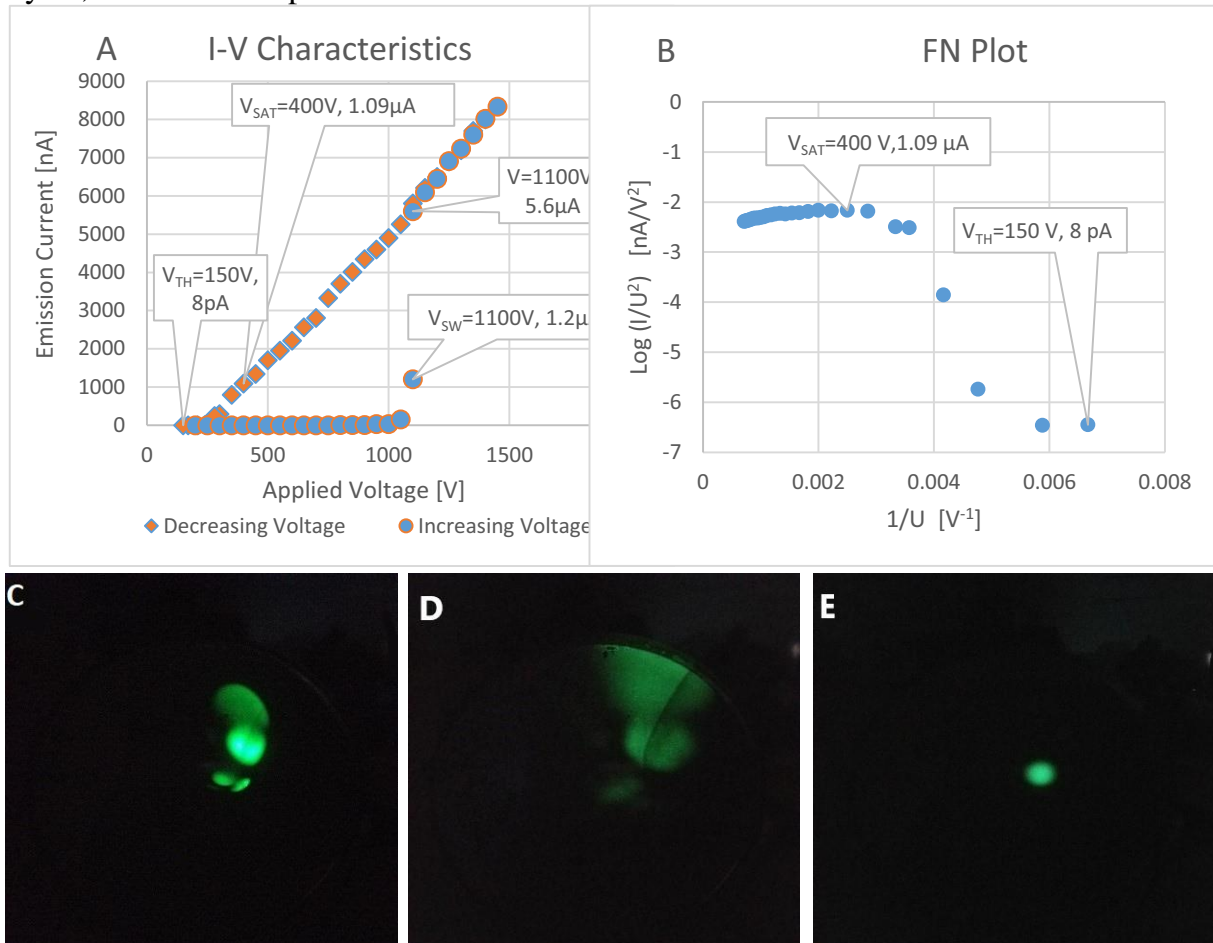


Figure 9. CNF-25 (A) I-V Plot for increasing and decreasing applied voltage. (B) FN plot for decreasing applied voltage. (C) Emission image at $V_{SW} = 1100$ V, $I_{SW} = 1.2$ μ A. (D) Emission image at $V_{SAT} = 400$ V, $I_{SAT} = 1.09$ μ A. (E) Emission image at V (Before switch-on) = 850 V, 7.2 nA.

As we did for the first type of CNTs, we did the same for the second type, the test has been repeated for another cycle of increasing and decreasing the applied voltage, under the same conditions, and the results were as follows, as we increase the applied voltage the emission current start from (20 pA) at applied voltage value (350 V), then the current emission suddenly “switch-on” to (3.6 μ A) at applied voltage value (750 V), we continue increasing the applied voltage until we reached (1900 V), and the emission current was (12.3 μ A), we

began decreasing the applied voltage, and the saturation region extends down to (1.09 μA), at applied voltage value (350 V), further decreasing the applied voltage resulting to vanish the emission current at $V_{\text{TH}}=140\text{ V}$, $I_{\text{TH}}=10\text{ pA}$. Figure (10) shows the I-V characteristics, FN plot, and some emission images at specific applied voltage value.

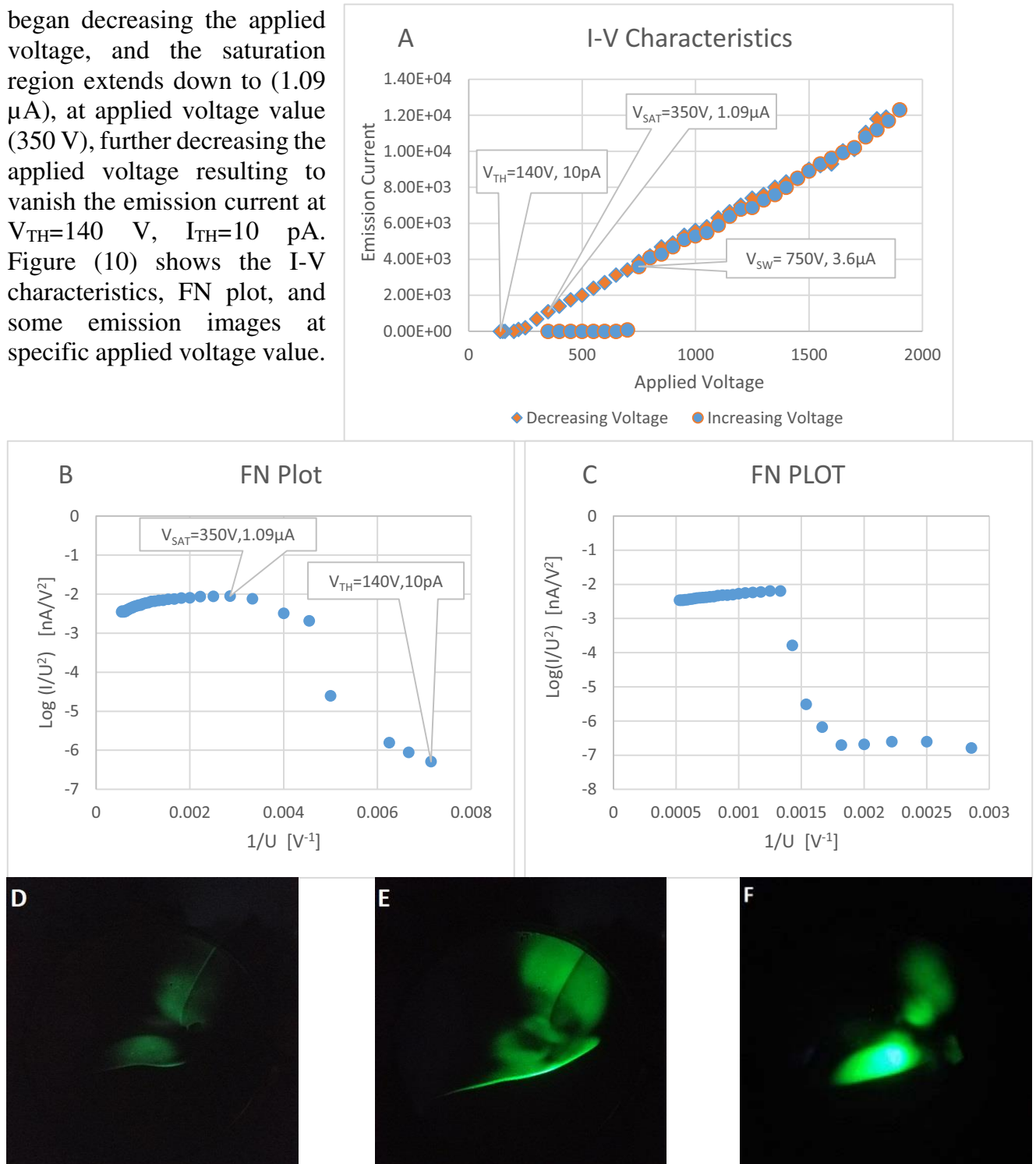


Figure 10. CNFs, second cycle: (A) I-V plot for increasing and decreasing applied voltage. (B) FN Plot for decreasing voltage. (C) FN Plot for increasing voltage. (D) Emission image at $V_{\text{SAT}}=350\text{ V}$, $I_{\text{SAT}}=1.09\text{ }\mu\text{A}$. (E) Emission image at $V_{\text{SW}}=750\text{ V}$, $I_{\text{SW}}=3.6\text{ }\mu\text{A}$. (F) Emission image at $V=1700\text{ V}$, $I=10.1\text{ }\mu\text{A}$.

4. Conclusions

Both types of the CNT emitters have been prepared by employing a drawing technique using glass puller, and the I-V characteristics and FN plot has been investigated, also the emission images have been studied, and it can be concluded by comparing their characteristics that SWCNTs have the lower V_{sw} than CNFs Pyrograf III PR-1 and larger emission current value at same applied voltage, the possible reason for this result is that the amount of field penetration in SWCNTs is larger than CNFs, which effects on the effective work function value. And the charge distribution on the tip apex [16].

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