

Improvements in Field Emission Properties of Carbon Nanotube Field Emitters

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This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contribution

This paper consists of several studies based on 3 refereed journal publications (Chapters 3 to 6). I am the main author of these works. My contributions to these works include design, production, measurement, data analysis and manuscript writing. The following is a list of publications included in this thesis.

1. **Liu, J. A.**, Chen, S., Mao, N., Cheraghi, E., Sun, Y., Wang, J., & Yeow, J. T. (2022). Computational simulation and phenomenological analysis of freestanding carbon nanotube coulomb explosion induced by field emission. *Journal of Materials Chemistry C*, 10(42), 15872-15882.

(This work is presented in Chapters 3 & 4)

2. **Liu, J. A.**, Wang, J., Cheraghi, E., Chen, S., Sun, Y., & Yeow, J. T. (2022). Improvement of field emission performances by DMSO and PEDOT: PSS treated freestanding CNT clusters. *Nanoscale*, 14(41), 15364-15372.

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(This work is presented in Chapter 6)

Abstract

With an increasing demand for better medical diagnostic systems, improving the efficiency and effectiveness of medical diagnostics has never been more crucial. Field electron emission (FE) based X-ray source which is a more responsive and controllable alternative to traditional thermionic-emission-based X-ray sources has stimulated much research interest. Among the materials for FE, carbon nanotube (CNT) is one of the most promising candidates due to exceptional properties such as a high aspect ratio and good electrical and thermal conductivities. CNT-based FE has been studied for many years, however, a significant challenge in the use of CNT has been the difficulty in achieving a uniform emission current over extended periods of time. Notably, rapid degradation of CNT emitters under high current load is one of the major concerns. Two main failure mechanisms proposed in the literature are melting and catastrophic explosion of CNTs due to the generation of Joule heat and the excessive Coulomb energy. Thus, to improve the reliability of CNT emitters in high-current applications, CNT's failure mechanisms need to be investigated and methods to improve CNT-based FE need to be developed.

The most destructive failure mechanism in FE is Coulomb explosion. To study this phenomenon, the underlying causes were investigated through experimental and theoretical analyses. Then, the explosion process was modeled and simulated from the perspective of computational chemistry based on the experimental results. In addition, to slow down melting of CNTs and stabilize emission current during FE, two methods were studied including chemical treatments and coating a metallic protective layer on CNTs. For the chemical treatment method, dimethyl sulfoxide (DMSO) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) solutions were used after CNT synthesis. Both treatments force CNTs to be

bundled into clusters and reduce the threshold electric field and significantly improve the lifetime of CNT emitters. On the other hand, the effects of three different metal shells (Au, W, and Ti) on the FE performance are investigated through long-term FE testing and characterization to gain insight into the underlying causes. Therefore, the findings in this thesis play an important role in the development of efficient, stable, and robust field emitters. As such, CNT-based FE technology can be reliably adopted in multiple fields.

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Table of Contents

List of Figures	xii
List of Tables	xvi
List of Abbreviations	xvii
Chapter 1 Introduction	1
1.1 Motivation.....	1
1.2 Objectives	4
1.3 Thesis Approach and Overview	4
Chapter 2 Background	7
2.1 Electron Emission	7
2.1.1 Thermionic Emission	9
2.1.2 Field Emission	10
2.1.3 Schottky Emission.....	14
2.2 Metal & Semiconductor based Field Emitters	15
2.2.1 Spindt-type Field Emitters	16
2.2.2 Silicon-based Field Emitters	17
2.3 CNTs based Field Emitter.....	19
2.3.1 CNT Point Emitter	21
2.3.2 CNT Film Emitter	22
2.3.3 Patterned CNT Emitter Array	23
2.3.4 Vertically Aligned CNT Field Emitter.....	24
2.4 Failure Mechanism of CNT-based FE	26
2.4.1 Joule Heat Generation during FE.....	26
2.4.2 FE-induced Coulomb Explosions	28

2.5 Improvement in CNT-based FE Performance.....	29
2.5.1 Gated VACNT for Improving FE Lifetime	30
2.5.2 Treated CNT-based Field Emitter for Improving FE Performance	32
2.5.3 Decorating, Coating & Doping Methods for Improving FE Performance.....	35
2.5.4 Advancement of CNT-based FE Properties Based on Synthesizing Methods.....	37
2.6 Chapter Summary	38
Chapter 3 Phenomenological Analysis of Freestanding CNT Coulomb Explosion Induced by Field Emission.....	40
3.1 Chapter Introduction	40
3.2 Materials and Methods.....	41
3.2.1 Cathode Design and Fabrication.....	41
3.2.2 Experimental Method.....	44
3.3 Results and Discussion	45
3.3.1 Coulomb explosion phenomenon.....	45
3.4 Chapter Summary	54
Chapter 4 Computational Simulation of FE-induced Coulomb Explosion on CNT Field Emitters	56
4.1 Chapter Introduction	56
4.2 Modeling and Simulation.....	56
4.2.1 Simulation Results	62
4.3 Analysis of CNT Coulomb Explosion	67
4.4 Chapter Summary	69
Chapter 5 Improvement of Field Emission Performances by DMSO and PEDOT: PSS Treated Freestanding CNT Clusters.....	71
5.1 Chapter Introduction	71
5.2 Experimental methods	73

5.2.1 Fabrication process	74
5.2.2 Measurement & Characterization Methods	75
5.3 Results and discussion	77
5.3.1 Morphology Comparison of CNT Bundles Before and After Treatments.....	77
5.3.2 Turn-on Electric Field Characterization.....	82
5.3.3 Long-term Stability & Lifetime Testing	84
5.3.4 Uniformity Testing.....	88
5.4 Chapter Summary	89
Chapter 6 Advancement of Field Emission Lifetime of Freestanding VACNTs by Coating Metallic Protective Layer	91
6.1 Chapter Introduction	91
6.2 Materials & Methods	92
6.2.1 Material Selection	92
6.2.2 Fabrication Methods	92
6.2.3 Measurement & Characterization Methods	94
6.3 Results and discussion	96
6.3.1 Morphology of Metal-coated CNT	96
6.3.2 Turn-on Electric Field Characterization.....	99
6.3.3 Lifetime & Stability Testing	101
6.4 Chapter Summary	106
Chapter 7 Summary	108
7.1 Conclusion	108
7.2 Future Work.....	110
References.....	112

List of Figures

Figure 2.1 Schematic diagram of (a) electrons near the metal surface, (b) thermionic emission, ...	8
Figure 2.2 a) The SEM image of the Spindt-type field emitter [60]. b) the schematic structure of the Spindt-type field emitter [58,59].	16
Figure 2.3 The fabrication process of a traditional Si-based field emitter [67].	18
Figure 2.4 (a) the structure of the CNT point emitter device using the electrophoresis method. (b) The SEM image of CNT point emitter [10].	22
Figure 2.5 SEM image of high-density CNT film emitter grown by the CVD process [95].	23
Figure 2.6 a) Top view SEM image of the as-grown honeycomb structure CNT mesh, while b) shows the image at 45° tilt. c) Cross-sectional SEM image of the VACNT array showing uniform, high-density, and vertically aligned CNTs. d) TEM image of multiwall CNTs with a diameter range of 5–15 nm. e) SEM image of CNT forest, the inset shows the zoom-in image. f) Simulation results of the electric field distribution along “edges” of the honeycomb-shaped VACNT array [102].	25
Figure 2.7 a) Dependency of the FE current density on the applied electric field J-E. Top-right inset shows the corresponding FN plot, left-top inset shows the emission image at a current density of 1 mA/cm ² . b) Stability tests of CNT mesh and CNT forest. The initial current density is 50 mA/cm ² [102].	26
Figure 2.8 (A-G) The real-time TEM images showing the evolution of a CNT during FE and the failure process. (H) The corresponding temperature distribution along the CNT’s axis. Note that all the images were taken without the presence of bias voltage [108].	27
Figure 2.9 (a)(b) The comparison between normal FE and coulomb explosion. (c) The explosion mark was recorded on PMMA thin film [109].	29
Figure 2.10 (a) SEM images of coaxial gated field emission cathode. (b) The cross-section view of the structure of ballasted coaxial gated field emitter [113].	31
Figure 2.11 (Color online) Field emission J-E curves for various weight fractions of MWCNT-PS composites [114].	32
Figure 2.12 The emission current stability over time, at a constant voltage bias of 600 V, for a 40 wt% SWCNT mat deposited on an SWCNT-P3OT composite substrate with 75 wt% nanotube loading (solid circles) and for the same mat deposited on n+Si (solid squares) [117].	33
Figure 2.13 SEM images of the MWCNTs before and after NH ₃ plasma treatment: (a) P-0.0 min, (b) P-0.5 min, (c) P-1.0 min, and (d) P-2.0 min. The insets show the corresponding top-view images [118].	34

Figure 2.14 (a) & (b) SEM image of CNTs grown on Si with Al decoration in different magnification [121].	35
Figure 2.15 (a) J-E plot for pristine CNT, In (50 nm)/CNT, and In (100 nm)/CNT films, indicates (~250%) enhanced current density for In coated CNT films. (b) F-N plot for pristine CNT, In(50 nm)/CNT, and In (100 nm)/CNT, shows slight variation in the field enhancement factor on In decoration in high field region [120].	36
Figure 2.16 a) low magnification and corresponding high magnification b) SEM micrographs, c) and d) TEM micrographs; of CHC, respectively (Fe NPs are shown by blue arrows). e) FE characteristics current density (J) as a function of applied electric field (E), f) F-N plot $\{\ln(J/E^2)\}$ versus $1/E$, g) Field emission current stability (i-t) plot and corresponding field emission image (inset); of CHC [125].	37
Figure 3.1 a) Schematic diagram of the cathode structure. b) SEM image of 4×4 CNT array.	41
Figure 3.2 a) Structural diagram of the experimental device includes the vacuum chamber and the high-speed camera connected with a microscope lens. b) the intergraded cathode and anode structure.	45
Figure 3.3 a) The 4×4 CNT array is directly observed through a high-speed camera connected with a microscope lens. a flashlight caused by the Coulomb explosion is captured by the high-speed camera. The instantaneous value of current was measured over 100 μ A. b) The dark mass leaves on the PMMA layer. c) The exposure trace on the PMMA layer. d) The exposure trace becomes darker and larger. e) A flashlight appears on the exposure trace. f) Scattered dark mass leaves on the PMMA layer.	46
Figure 3.4 Continuous screenshots of the first Coulomb explosion in the first approach occurs on a single CNT within 1 ms.	47
Figure 3.5 Continuous screenshots of the second Coulomb explosion in the first approach occurs on a single CNT within 1 ms.	48
Figure 3.6 a) b) c) d) The snapshot of three flashes continuously occurs on the same cathode. e) f) g) h) The enlargement process of exposure trace on PMMA without Coulomb explosion.	48
Figure 3.7 Screenshots of the three continuous Coulomb explosions in the second approach occurs on a single CNT within 2 ms.	49
Figure 3.8 FE IV curve of a) the first approach, b) the second approach.	50
Figure 3.9 a) b) c) d) SEM image of craters caused by the Coulomb explosion. e) f) The emission current of two explosions during FE in the first experiment.	51
Figure 3.10 SEM image of crater caused by Coulomb explosion in the second approach. a) the image of the whole 4×4 array. b), c) the image of the craters. d) the change of emission current in the second approach during Coulomb explosion, the highest peak is the time when three continuous explosions occur.	52

Figure 4.1 The structural diagram of the model consists of 190 carbon ions and 183 neutral carbon atoms.	59
Figure 4.2 The plot of a) Coulomb energy and total potential energy, b) Kinetic Energy, c) bond potential energy caused by bond stretching in each step, and d) average bond length in 100 steps.	63
Figure 4.3 The plot of a) Coulomb energy and total potential energy, b) bond potential energy of 180-ions' model in 100 steps (10 random atoms are deionized).	65
Figure 4.4 The potential energy and kinetic energy on each ion and atom at a) $t=0.05$ fs, b) $t=0.08$ fs and c) $t=0.1$ fs	66
Figure 5.1 Process flow of CNT cluster fabrication: a) Ni catalyst deposition on a spacer-integrated Si substrate, b) CNT synthesizing via PECVD method, c) chemical treatment by DMSO/ PEDOT: PSS, d) formed CNT clusters after drying process.	74
Figure 5.2 Experimental setup & cathode-anode connection diagram.	76
Figure 5.3 SEM image of a) untreated, b) DMSO treated, and c) PEDOT: PSS treated CNT cathode; Expanded image of d) untreated, e) DMSO treated, f) PEDOT: PSS treated CNT cathode.	78
Figure 5.4 The C 1s XPS spectra of CNT emitters. a) without treatment, b) with DMSO treatment, c) with PEDOT: PSS treatment.	79
Figure 5.5 XPS spectra of untreated CNT emitter (black), DMSO treated CNT emitter (red), and PEDOT: PSS treated CNT (blue)	80
Figure 5.6 Visible Raman spectra of untreated CNT emitter (black), DMSO treated CNT emitter (red), and PEDOT: PSS treated CNT (blue).	81
Figure 5.7 a) Field emission current density (J) versus applied field (E) characteristics of untreated CNTs, DMSO treated CNTs, and PEDOT: PSS treated CNTs. b) F-N plot corresponding to a), and typical liner fit to each set of data are shown by solid lines. (This turn-on electrical field includes the voltage assigned to the add-on serially connected resistor and the resistance of the Si substrate)	83
Figure 5.8 Long-term lifetime and stability testing current (I) versus time (t) of untreated CNTs, DMSO treated CNTs, and PEDOT: PSS treated CNTs.	85
Figure 5.9 SEM image of CNT structure after 80 hours of FE for a) untreated, b) DMSO treated, and c) PEDOT: PSS treated CNT cathode; Expanded image of d) untreated, e) DMSO treated, f) PEDOT: PSS treated CNT cathode.	87
Figure 5.10 Exposure trace on PMMA layer for a) untreated, b) DMSO treated and c) PEDOT: PSS treated CNT emitters.	89

Figure 6.1 Process flow of metal coated VACNT fabrication: a) Cr buffer pad patterning and deposition, b) Ni catalyst dots patterning and deposition, c) CNT synthesizing via PECVD method, d) metal shell coating via sputter.	94
Figure 6.2 Experimental setup & circuit connection diagram. Negative bias is added on CNT coated and the ITO-coated glass anode is connected to the ground. A 50 μ m PTFE spacer is added between the cathode and anode.	95
Figure 6.3 SEM image of a) freestanding VACNT array, b) bare VACNT, c) titanium coated, d) gold coated, and e) tungsten coated individual VACNT.	97
Figure 6.4 a) TEM image of the single VACNT tip. b) EELS analysis of Ni element on the VACNT tip. c) EELS analysis of tungsten element on the surface of the VACNT.	98
Figure 6.5 a) Field emission current density (J) versus applied field (E) characteristics of bare VACNTs and three types of metal coated VACNTs. b) F-N plot corresponding to a).....	99
Figure 6.6 Long-term lifetime and stability testing of bare VACNT, 5 nm & 10 nm titanium coated, gold coated, and tungsten coated low-density VACNT array.....	102
Figure 6.7 SEM image of VACNT structure after long-term FE testing. a) Bare VACNT array, b) expansion view of a crater on Cr pad, c) 10 nm tungsten coated VACNT array, d) 10 nm gold coated VACNT array, e) 5 nm titanium coated single VACNT, and f) 5nm tungsten coated single VACNT....	103
Figure 6.8 a) TEM image of 5 nm tungsten-coated VACNT after long-term testing. b) EELS analysis of tungsten on VACNTs after long-term testing.	106

List of Tables

Table 1: Summary of the duration time and current peak of each Coulomb explosion in three experiments.	54
Table 2 Summary of FE performance of untreated, DMSO treated and PEDOT: PSS treated CNT field emitters.	90
Table 3 Summary of FE performance of different metal-coated and noncoated CNT field emitters.	107

List of Abbreviations

1D one-dimensional

3D three-dimensional

AI artificial intelligence

ALD atomic layer deposition

CHC carbon hollow cylinder

CMP chemical mechanical polishing

CNT carbon nanotube

CT computational tomography

CVD chemical vapor deposition

DC direct current

DMSO dimethyl sulfoxide

DRIE deep reactive ion etching

EBL electron beam lithography

F-N Fowler-Nordheim

FE field emission

IPA isopropyl alcohol

ITO indium tin oxide

MIBK methyl isobutyl ketone

MWNT multi-walled carbon nanotube

PECVD plasma-enhanced chemical vapour deposition

PEDOT: PSS poly (3,4-ethylenedioxythiophene) polystyrene sulfonate

PMMA poly (methyl methacrylate)

RIE reactive ion etching

SEM scanning electron microscopy

SWNT single-walled carbon nanotube

TEM transmission electron microscopy

Chapter 1 Introduction

1.1 Motivation

The close attention to human health has led to a huge demand for advanced medical equipment, especially for diagnostic systems like computed tomography (CT) machines for medical imaging. Since the use of X-rays in medical imaging technology, more diseases, especially tumors, can be detected early in their malignant development and treated accordingly, allowing more patients to be treated quickly and effectively. Thus, the goal is to develop faster, and more accurate medical imaging devices with better control.

The conventional way to generate X-ray is based on thermionic emission. Although it is a reliable method, it requires operation at high temperatures. This limitation makes both the controllability and the response time of thermionic emission extremely restricted. Such disadvantages restrain the development of this technology for many medical applications that requires high speed and large area imaging. Therefore, field emission (FE), an alternative cold electron emission technology that can alleviate the limitation of thermionic emission, is attracting attention as an advanced technology that enables fast and accurate diagnosis.

Since FE was first introduced by R. W. Wood [1], with the advantages of fast response speed, low emission temperature, and high efficiency, it plays an important role in various applications, such as field emission display, X-ray guns, point electron source [2–4]. FE describes an electron extraction phenomenon by which electrons tunnel from the surface of materials into vacuum by applying a strong electrostatic field. The FE current density is mainly determined by the work function of the emission material and the strength of the electric field [5]. Many types of

FE devices including metal-based FE devices, semiconductor-based FE devices and carbon nanotube (CNT) based FE devices were studied and developed so far. In the early FE research, metal-based and semiconductor-based FE devices dominated most of the experiments, since metal and Si can be easily obtained, and most of them have good thermal and electric conductivity and are relatively easy to machine and process. However, the limitations of metal- and semiconductor-based FE devices, such as short lifetime (easy to melt with high temperature), unstable emission current, and low emission current, cannot satisfy most applications in modern medical fields.

CNT, a nano-scaled material, is widely studied as a field emitter since its FE performance was first reported in 1995 [6]. Most researchers considered that CNT is the most suitable field emitter for FE [7–10]. An excellent field emitter needs to meet many criteria, such as good electrical conductivity, high thermal conductivity, low work function, and sharp emission tips. CNTs exactly fulfill all the criteria [6,11–13]. When compared to metal- and semiconductor-based field emitters, CNT not only has good mechanical and electrical properties, but it also has good chemical stability, a naturally sharp tip, and a high aspect ratio. With these excellent characteristics, the CNT field emitter has shown great promise by providing stable emission current and long emission duration. However, this technology is still under development. Many types of CNT-based field emission devices were designed by different groups and were used for different applications [8,14–18]. Among these designs, freestanding vertically aligned CNT (VACNT) emitter array is reported to have the lowest turn-on electric field (lower than 1 V/ μm), most stable FE performance, and longest lifetime [19,20]. This type of CNT cathodes usually has a patterned CNT array by using microfabrication technology. The devices will be fabricated into a neatly arranged catalyst dot array, and CNTs would be selectively grown at the location of those dots array by plasma-enhanced chemical vapor deposition (PECVD) method to form the CNT

array. However, CNT field emission is still not sufficient for many practical applications, especially those requiring high emission currents exceeding hundreds of milliamperes. The main issue for the imperfect FE performance at high emission current can be attributed to two factors: (i) low lifetime; and (ii) poor emission current stability. Rapid degradation of CNTs due to the large amount of Joule heat generated under a high current load leads to a short working lifetime [21–23]. In addition, the stability of the emission current is poor due to the non-uniformity of the CNT cathode [24]. Hence, finding methods to extend the lifetime and increase the uniformity of CNT emitters have become the most critical issues to be solved.

The first motivation behind the work of this thesis is to resolve the challenge of CNT's quick degradation during FE process at high emission level, which includes understanding the CNT failure mechanism, in-depth analysis and finding solutions on how to avoid CNT failure. In our group's previous studies, Coulomb explosion is observed during the FE process, especially at high current density around the level of milliamperes per square centimeter. However, the detailed phenomena and causes of the occurrence of the Coulomb explosion have yet to be investigated. Thus, a deeper understanding and detailed analysis are needed to eradicate the occurrence of this devastating phenomenon. The second motivation is to develop CNT-based field emitters with better FE performance. So far, it has been over 25 years since the first report of CNT FE; however, there are only few available commercial products of CNT-based field emitters on the market. Ways to improve the FE performance includes fabricating a more uniform CNT cathode or controlling the emission current at the gate electrode. Although many studies achieved success in various degree in improving the FE lifetime of CNTs and stabilizing the emission current, many of the improvements require very complex fabrication processes, and the costs are also high. Hence,

developing simple and cost-effective methods to improve the FE performance including enhancing the FE lifetime and the stabilized emission current is highly desired.

1.2 Objectives

The overall goal of this study is to improve the FE performance of CNT emitters and allow CNT-based FE to be an alternative to conventional thermal emission that can be truly applied to many applications with its unique advantages. In order to achieve this goal, this thesis has three objectives.

1. Investigates the failure mechanisms of CNT FE, and gains insight into the main causes of its short lifetime and unstable emission current through experimental and analytical analyses and develop potential solutions to address the issues.
2. Based on the investigation of CNT's failure mechanisms, develop methods to eliminate CNT's emission failure, and slow down the degradation speed of CNTs.
3. Design new CNT cathodes to avoid the causes of a short lifetime and unstable field emission, and fundamentally slow down its degradation speed so as to improve its lifetime and stability of emission current.

1.3 Thesis Approach and Overview

This thesis details work performed to increase FE performance of CNT-based field emitters, including studying the failure mechanisms of CNT-based FE, finding reliable methods to increase the lifetime of CNT emitters during FE especially under high current density emission

(the level of 1 mA/cm^2), reducing the turn-on electric field and stabilizing the emission current density, and fabricating high-performance field emitters.

Chapter 2 begins by providing a literature review of electron emission theory and familiarize readers with the fundamental knowledge of FE. The differences between FE and thermionic emission are discussed. Then, CNTs, as one of the most suitable candidates for field emission are introduced. The basic physical and chemical properties and the classifications are summarized. The main challenges reported in the literature are also reviewed and followed by a discussion of the recent methods to improve performance, which will help readers to better understand the state-of-the-art development in the field.

The investigations of the failure mechanisms are presented in Chapters 3 and 4. In Chapter 3, one of the most crucial failure phenomena is studied from an experimental point of view. This experiment is based on using a high-speed camera to capture the Coulomb explosion phenomena which occur instantaneously and collect the current and voltage data as the explosions occur. Chapter 4 focuses on analyzing the Coulomb explosions using an analytical model. This model was formulated from the data collected during the experiments. By analyzing this model from the perspective of the change and distributions of Coulomb potential energy and other energies in the system, the detailed causes and the process of the Coulomb explosion are simulated, and potential solutions are proposed according to the simulation results.

Different methods to improve the CNT FE performance are provided in Chapters 5 and 6. In Chapter 5, two chemical treatment methods to improve the FE performance of VACNT using DMSO solution and PEDOT: PSS solution are presented respectively, and their different FE performances are characterized and compared. Both treatments force CNTs to be bundled into clusters, but the resulting structures are very different. After treatment, both methods reduced the

threshold electric field, and the FE efficiency and lifetime are also significantly improved. In addition, the uniformity of both treated CNT emitters is improved which enables more CNTs to contribute to the overall current emission. Chapter 6 presents a method to improve the FE lifetime of freestanding VACNTs by uniformly coating the surface of VACNTs with a thin metallic layer that has low work function, high melting point, or high electrical conductivity. The effects of three different metal shells on the FE performance are investigated. The FE performances of these VACNTs are evaluated by testing the turn-on electric field and long-term FE performance. Furthermore, characteristic methods are used before and after FE testing to observe the uniformity of metal shells, and the protection conditions of the VACNT from being melted by the Joule heat during FE. Finally, a conclusion and future work are presented in Chapter 7.

Chapter 2 Background

2.1 Electron Emission

When a small piece of metal is left at room temperature, the free electrons in the metal will undergo random motion due to thermal energy. However, the electrons can only move inside the metal because of the attraction of the positively charged nuclei which is also known as the surface potential barrier. This barrier cannot be overcome without external energy intervention. By applying energy to this metal, the electrons will gain sufficient energy exceeding the work function of the metal to break through the barrier and leave the metal surface. This phenomenon is called electron emission [25]. Electron emission is the ejection of an electron from the surface of a matter. It has been known for over a century, and it has extremely wide utility in various fields. Many modern industrial, scientific, and medical devices require a good electron source for operations, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron displays, and X-ray source. There are three main electron emission methods: (i) thermionic emission; (ii) Schottky emission; and (iii) FE. The mechanistic differences of three types of electron emission methods from the potential energy point of view are shown in Figure 2.1 [26].

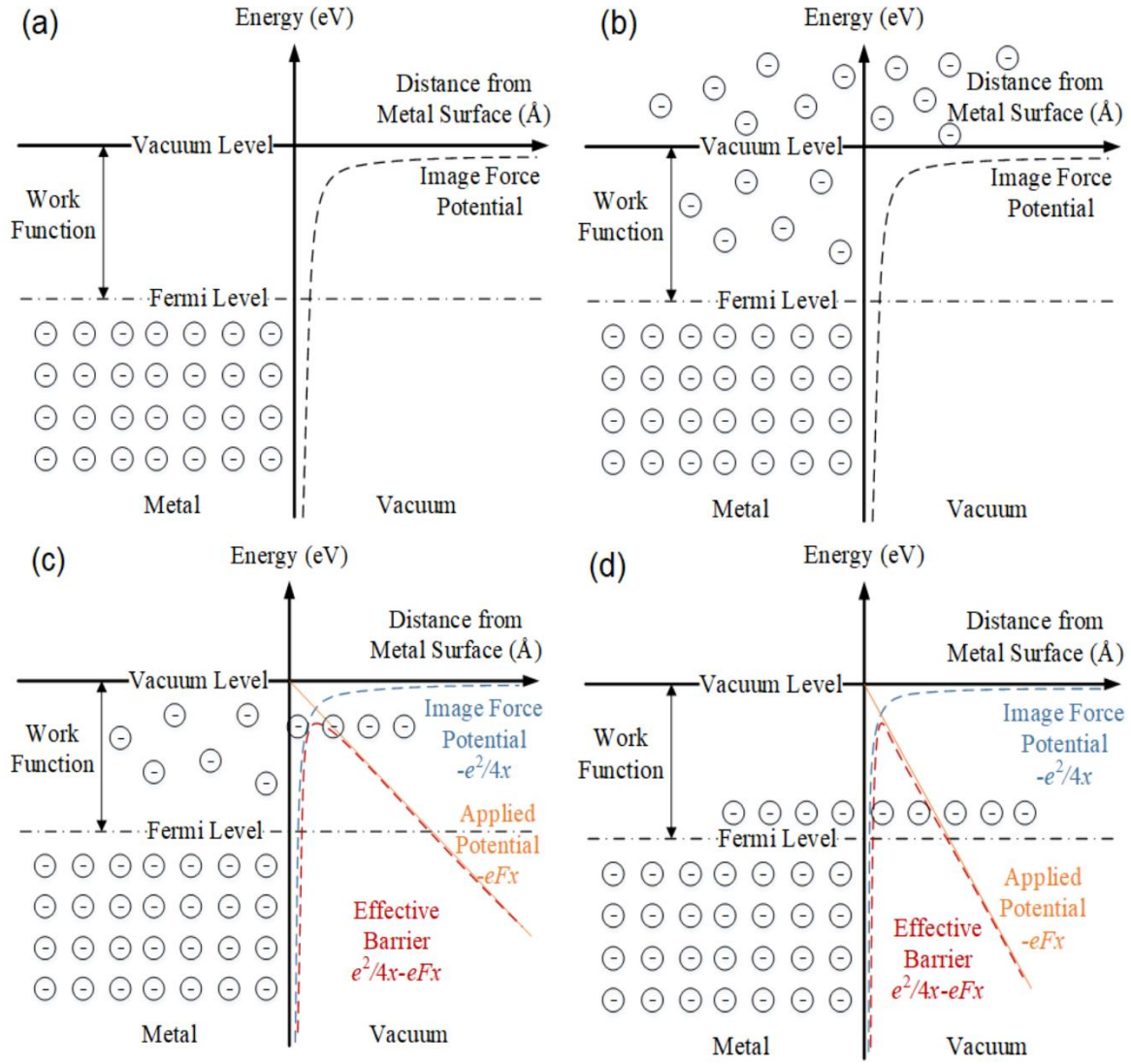


Figure 2.1 Schematic diagram of (a) electrons near the metal surface, (b) thermionic emission, (c) Schottky emission, and (d) FE. [26]

2.1.1 Thermionic Emission

Thermionic emission, a well-known electron emission method, is currently considered to be the most practical electron emission technology. The process of thermionic emission is regarded as a thermal-electric process by which electrons are extracted from the metal surface by heating the metal. At room temperature, as mentioned above, free electrons tend to be in the lowest energy state and do not have enough energy to escape from the metal surface. As the temperature of the metal increases, the kinetic energy of free electrons is increased. When the energy gained by the electrons in metal exceeds the work function of the material, the electrons will surmount the constraint of the surface potential barrier; thereby, escaping from the metal surface (Figure 2.1b) [26]. For thermionic emission, the emission current mainly depends on the temperature level and the escaping efficiency of the electrons from the potential barrier to vacuum. The emission current follows the Richardson–Dushman equation (2.1) [27].

$$J = \lambda_R A_0 T^2 e^{-\frac{\phi}{K_B T}} \quad (2.1)$$

where J is the emission current density, λ_R is the correction factor for the material which is typical of order 0.5, T is the temperature of the metal, ϕ is the work function of the metal, K_B is the Boltzmann constant, A_0 is a universal constant gained by equation (2.2).

$$A_0 = \frac{4\pi m K_B^2 e}{h^3} = 1.20173 \times 10^6 A \cdot m^{-2} \cdot K_B^{-2} \quad (2.2)$$

where m is the mass of the electron, e is the charge of the electron, and h is Planck's constant. Typically, in a thermionic-emission-based electron generator, a V-shape tungsten (W) filament is used as the cathode, by applying a voltage between the filament, the temperature will be raised to

emit electrons into the vacuum [26]. Thus, thermionic emission has been considered the simplest electron emission method, and it is also a mature and reliable technology, which is widely applied to various fields. However, the restriction of thermionic emission such as emission current fluctuation and slow responding speed limit its applications. The reason of these limitations is mainly due to the poor controllability of the thermal circuit. To achieve a more efficient, more controllable, and fast-responding electron generation method to keep up with the great demand of current scientific requirements, researchers are committed to developing a new electron emission technology such as FE [28].

2.1.2 Field Emission

FE is an alternative mechanism to thermionic emission for electron generation. It is an electron extraction phenomenon in which electrons tunnel from the surface of the material into the vacuum by applying a strong electrostatic field [29]. With the advantages of fast response, cold emission temperature, and high efficiency, FE is considered the most promising alternative to thermionic emission [30–33]. The phenomenon of FE was first discovered by R. W. Wood on a piece of platinum in 1897 [34], and the original theory of this phenomenon is derived from Schottky in 1923 [35]. The FE theory describes that strong external electrostatic field will distort the potential barrier. This potential barrier of emitting materials is not only determined by the work function of the materials but is also dependent on the local electric field at the emitting surface (Figure 2.1d). The stronger the electrostatic field, the more distortion is experienced by the potential barrier; thus, resulting in a higher possibility of tunnelling electrons [36]. As the electrostatic field increases to a certain level, which is known as the turn-on electric field, the electrons with the energy around the Fermi level will have a substantial probability to escape from

the metal surface and enter the vacuum condition. This phenomenon is also called the quantum tunneling effect [29].

Quantum tunneling theory was developed by Ralph H. Fowler and Lothar Wolfgang Nordheim in 1928 [29]. By 1930, the quantum tunneling theory was significantly improved with the derivation of the Fowler-Nordheim (F-N) equation (and F-N plot) which is the criterion to identify FE and also used to assess the FE performance [37]. In F-N theory, to simplify the model, the system is considered a one-dimensional (1D) structure along the direction of the external electric field. The emission current is mainly determined by the work function of the material and the strength of the electric field [7], which can be calculated by the F-N equation.

$$J = a(\beta E)^2 \exp\left(-\frac{b\phi^{3/2}}{\beta E}\right) \quad (2.3)$$

where J is the current density, E is the applied electric field, b is a constant that is originally equal to 2.1×10^8 in early FN papers. This constant was currently corrected to 6.8×10^7 in recent publications [38]. β here is the enhancement factor of the electric field, which is the ratio between local and applied electric fields. A large local electric field is essential for FE, thus, besides applying high voltage, a geometrically sharp tip or protrusion has a significant effect on intensifying the local electric field. a is the correct factor that follows the equation (2.4).

$$a = 6.2 \times 10^{-6} \frac{\mu^{1/2}}{(\mu + \phi)^{1/2} \phi^{1/2}} \quad (2.4)$$

where μ is the electron distribution parameter in Fermi-Dirac statistics. Through the F-N equation, it is found that the emission current has an exponential relationship with the local electric field and

work function. Thus, a meaningful influence of the emission current would occur by a small variation of the shape or the physical or chemical properties of materials. The F-N equation can be changed into another expression which is shown in the following equation (2.5).

$$\ln\left(\frac{J}{E^2}\right) = b - \frac{6.8 \times 10^7 \phi^{3/2}}{\beta E} \quad (2.5)$$

This equation shows that the $\ln\left(\frac{J}{E^2}\right)$ has an inverse linear relationship with $1/E$ which is also known as the F-N plot. Originally, F-N theory and F-N plot were usually applied to analyze the FE performance of metal blocks or crystal blocks. However, recently there are many other materials, such as carbon fiber materials, and metal oxides were also used to perform FE and applicable to F-N theory and F-N plot [26].

When compared to thermionic emission, FE has many advantages. For example, many-electron emission applications require current emission response to be instantaneous and controllable. To adjust the emission current of thermionic emission, the temperature of the metal is required to be carefully controlled, which limits its response speed [28]. However, FE can easily meet these criteria, the voltage input and emission current output providing a fast-responding current. Furthermore, by setting up a closed-loop control, the emission current can be made more uniform by fast adjustment of the input voltage bias. On the other hand, since FE generally utilize tiny emission tips, the emission area is much smaller than the thermionic emission, which can realize smaller emission pixels and higher resolution. In addition, by separately controlling each pixel via digital circuits, the multi-pixeled electron beam emission system can be achieved, which has great potential to provide significant improvement for modern imaging technology such as SEM and large-area X-ray [18,39]. For example, the current X-ray diagnosis system used in

medical imaging commonly applies a large area of the X-ray beam generated from a thermionic-emission-based X-ray source to target the organs of patients. The target organs are usually much smaller than the exposed area which increases unintended peripheral irradiation to surrounding healthy tissues. By introducing multi-pixel electron beam technology, controlling the emission status of each pixel to form the shape-varied electron beam, different shapes of the X-ray beam can be achieved. A user-defined X-ray profile, that greatly reduces the absorbed emission dose by only irradiating targeted organs or tissues, will have great implication for clinical medical imaging. Moreover, the multi-pixel X-ray beam has a high potential for replacing the traditional CT system, which scans by mechanically rotating the X-ray tube [30]. A phased array systems can be implemented, which would achieve a three-dimensional (3D) image by calculating the X-ray images from different angles, resulting in faster and more efficient diagnoses [40]. Thus, with these advantages, FE has attracted a great deal of interest from researchers.

However, although FE theory has been extensively studied for almost a century, the application of FE remains far and few, the reason is that state-of-the-art field emitters still do not provide the required stable emission current and long emission lifetime [26,41–44]. Because a high electric field is required to apply to field emitters, the strong electrostatic field generates high current density which would also produce a huge amount of Joule heat resulting in the raise of the temperature on emitters. On the other hand, a sharp-tip structure is usually applied to field emitters for increasing the field enhancement factor which is a more vulnerable structure under high temperatures and frequent chemical reaction conditions [38]. Under this condition, researchers aim to find a type of emitter with an easy machining property to form a sharp tip, good electric and thermal conductivity, high melting point, and high chemical stability. The reason for requiring field emitters to have good electrical and thermal conductivity is to enable a high emission current.

With these properties, the heat in the emitters would be quickly conducted and dissipated, reducing the damage on the emitters caused by Joule heat. On the other hand, during the FE process, because of the ion bombardment and Joule heat, many chemical reactions will occur frequently, thus, high melting point and chemical stability are also required to constrain field emitters [45,46].

2.1.3 Schottky Emission

Schottky effect, or Schottky emission, refers to electron emission that occurs under the influence of both electric field and temperature, which is a phenomenon in condensed matter physics named after Walter H. Schottky. When subjected to an electric field, the potential barrier becomes narrower, and the emitting electrons in metals gain higher energy levels due to increased temperature, assisting the quantum tunneling (Figure 2.1c). The current density of Schottky emission can be several orders of magnitude larger than the simple sum of thermal ionization and FE [47]. The model for Schottky emission can be described by a modified Richardson-Dushman equation (2.1) with the addition of a correction for the effect of the electric field strength on the material work function.

$$J = \lambda_R A_0 T^2 e^{-\frac{\phi - \Delta\phi}{k_B T}} \quad (2.6)$$

$$\Delta\phi = [eE/(4\pi\epsilon_0)]^{\frac{1}{2}} \quad (2.7)$$

where ϵ_0 is the vacuum permittivity. This equation is relatively accurate for electric field strengths below $100 \text{ V} \cdot \text{um}^{-1}$. As the electric field becomes larger, the FN equation would become more precise to describe the model. Therefore, Schottky emission can be divided into thermally assisted

FE and field-assisted thermionic emission, depending on the difference in operating electric field and temperature [26].

2.2 Metal & Semiconductor based Field Emitters

In early studies, silicon (Si), W, and molybdenum (Mo) emitters were commonly used for performing FE, since these metals possess high melting points and stable chemical properties that can withstand high temperatures and frequent chemical reactions during the FE process [48–52]. Through micromachining, these metal- & semiconductor-based field emitters would have tiny-tip structures, which allows them became suitable for performing FE in the vacuum. In later experiments, coating a layer of thin metal film (which is reported as a single-layer atom of metal thorium or sodium) on the surface of the metal emitter was frequently adopted, because the W and Mo emitters usually have a higher work function (about 4.5 eV). When coating a metal film with a lower work function (about 2.36 eV), it will reduce the work function of the emitters and increase the emission current [53–55]. These experiments gained improvement in the emission current of metal-based field emitters. However, the coated film was easily be destructed by ion bombardment during the FE process in a relatively short time. Therefore, the metal-emitter-based experiment still did not achieve a satisfying FE performance with stable and high emission current for a long operating time [56]. Since nanofiber, especially CNT, typically has a high aspect ratio, and originally own extremely sharp tips, was found in 1991, the research interest of metal field emitters was quickly turned to CNT field emitters [26].

2.2.1 Spindt-type Field Emitters

The first FE device was developed by K. R. Shoulders at Stanford Research Institute in 1961. Since then, researchers have been exploring different types of metal emitters for FE, and many have achieved significant results [57]. Some typical designs of field emitters and their fabrication methods are still widely used until now. In 1968, Spindt designed a type of thin-film FE device, which uses thin-film deposition and etching methods combined with electron-beam lithography (EBL) methods to fabricate a type of sharp, individual, vertically aligned and gated Mo field emitter cathode, which was called Spindt-type emitter [58,59]. The structure and the SEM image of the Spindt-type emitter are shown in Figure 2.2. For the Spindt-type emitter, EBL was applied to pattern the “hole” for alignment of each individual emitter. The Mo emitter arrays were deposited into the “hole” by sputtering, with sharp tips formed at the top. The tips are formed by a combination of angled evaporation of a sacrificial layer followed by vertical evaporation of the emitter material. Another Mo thin layer was also deposited which served as a gate layer controlling the emission current during the FE process.

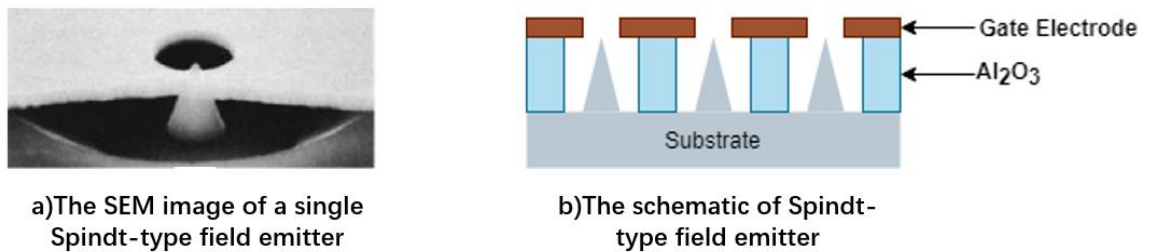


Figure 2.2 a) The SEM image of the Spindt-type field emitter [60]. b) the schematic structure of the Spindt-type field emitter [58,59].

Since the Spindt-type emitters have extremely sharp tips, the threshold voltage for FE is low. It is shown that this type of emitter can create a high electric field by applying a relatively low voltage on the gate around 200 V. A stable emission current of 20 $\mu\text{A}/\text{tip}$ was achieved from a 100-emitters array for over 4000 h FE with a gating frequency of 60 Hz [61]. In 1991, the Spindt-type emitters were further improved, and the emission current and lifetime were raised further. For this type of improved Spindt-type emitter, it was reported that an emission current of 50 $\mu\text{A}/\text{tip}$ was continuously tested for 8 years at a gate frequency of 60 Hz [60,62,63]. Compared to the thermionic emitter and some other common metal-based field emitter, there are great advantages for the Spindt-type emitter, which includes relatively high and more stable emission current. However, complex fabrication processes, high cost, and limited lifetime with applied direct current (DC) bias led to the end of the development of Spindt-type emitter. Thus, the interest in Spindt-type emitter only lasted until 2000, and there was only a little further research on this type of emitter.

2.2.2 Silicon-based Field Emitters

During the development of the Spindt-type emitter, there is another promising field emitter was found, which is the Si-based emitter. It is considered a potential alternative to the Spindt-type Mo-based emitter. In 1972, Tomas et al. fabricated a microdevice based on a Si field emitter with no integrated gate electrode, which was the first example of the Si-based emitter [64]. Later, in 1976, Smith et al. filed a patent for the fabrication of an integrated gate on the Si-based emitter [65]. Then, in 1986, Gray et al. patented a vacuum field-effect transistor, using gated micron-sized Si field emitters [66]. The use of Si emitters in cold cathode FE experiments continues to be of great interest to researchers, which is continued until recently. For the Si-based emitter, it has

unique fabrication methods and great FE performance. Unlike the Spindt-type emitter, where the deposited emitter passes through the porous gate layer into the "hole," the gate layer for a typical Si-based field emitter is deposited after the emitter tips are fabricated using anisotropic reactive ion etching (RIE) method [67]. The detailed fabrication process is shown in Figure 2.3. The process involved depositing a layer of patterned nitrides on a Si substrate to serve as a mask for subsequent Si etching, resulting in the formation of Si tips via wet etching or RIE, and the tips were sharpened by the oxidization method. An isolated SiO_2 layer was deposited as a spacer and isolation layer, followed by the deposition of a metal layer for the gate electrode. Finally, the nitride mask, Si posts, and oxidized layer were removed by etching method. Compared to Spindt-type emitters, although the fabricated method is different, the resulted structure is similar.

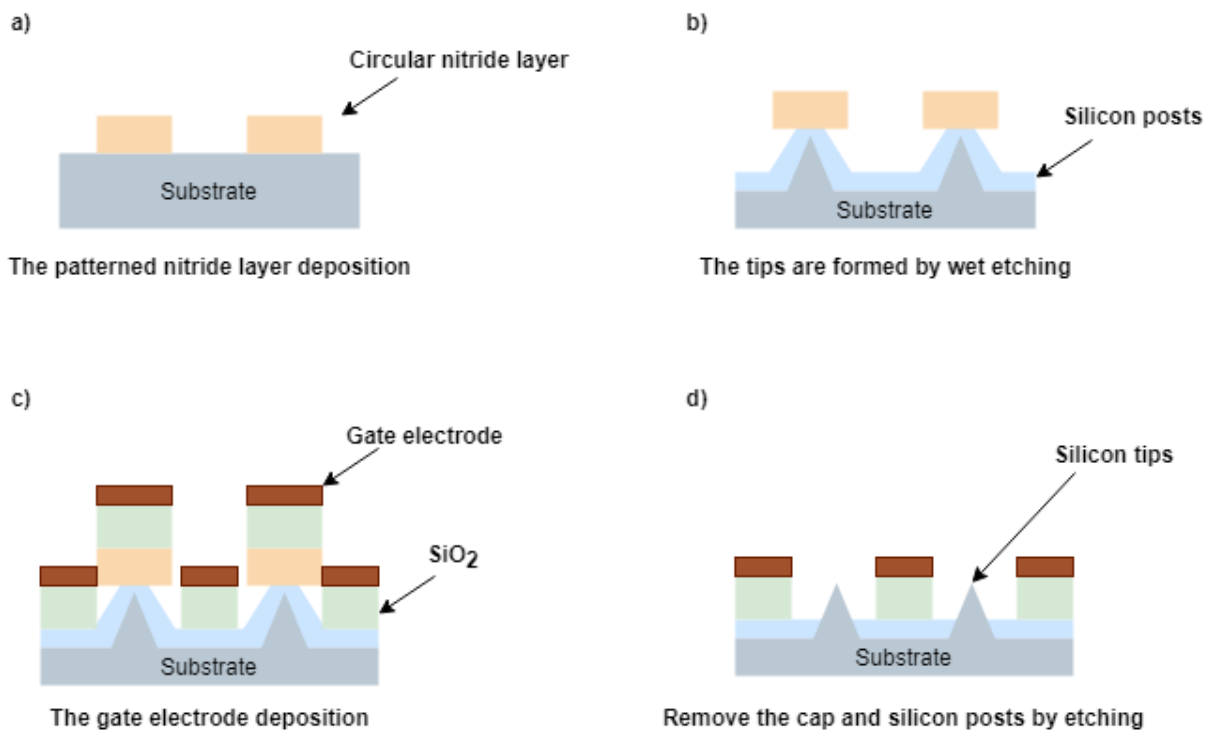


Figure 2.3 The fabrication process of a traditional Si-based field emitter [67].

Many studies reported on the FE performance of Si-based field emitters in the 1980s and 1990s. In 1989, D. Temple et al. using the isotropic RIE method to fabricate sharp tips, which generate an emission current of 1.1 mA, resulting in a higher emission current than the normal anisotropic RIE method (1.05 mA) at the same stop voltage of 96 V [46]. They also achieved a maximum emission current of 5 mA from an array of 18291 Si-based field emitter (in an area of $2.6 \times 10^{-3} \text{ cm}^2$) at a gate voltage of 75 V [67]. Until now silicon-based field emitters are still being studied by several groups. In 2016, Guerrero et al. presented a study on silicon field emitter arrays in which they observed current densities exceeding 100 A/cm² at gate voltages approximately 75 V. These results are the highest current densities reported for a semiconductor-based field emitter.

2.3 CNTs based Field Emitter

Until the early 21st century, the interest in research on Si-based emitters began to decline [68,69]. As a result, FE research shifted towards using CNTs as emitters. Researchers discovered that CNT emitters possess a high aspect ratio and excellent physical properties. The primary advantage of CNT emitters over metal and semiconductor emitters (i.e., Spindt-type and Si-based emitters) is that their high aspect ratio remains intact after undergoing chemical reactions, heat damage, and ion bombardment during continuous FE process. In contrast, Spindt-type emitter and Si-based emitter tips would be burned or damaged into a flattened surface during the FE process, which will decrease the enhancement factor and leads to FE failure [26]. These findings suggest that CNT emitters have promising potential for performing FE.

CNT was discovered using a high-resolution TEM by Sumio Iijima, a physicist at NEC laboratory in Tsukuba, Japan. It was synthesized from the carbon fiber produced by arc discharge in early 1991 [70]. Following the first CNT-based FE experiment in 1995, this naturally occurring 1D material was recognized as a highly promising candidate for FE applications [71]. The structure of CNTs can be considered closed cylindrical polyhedral containing numerous graphite planes and also composed of tubular carbon molecules with each carbon atom being SP_2 hybridized [72]. The honeycomb-shaped molecular structure formed by the carbon bonds provides CNTs with unique properties such as the sharpest tip found in nature, high electrical and thermal conductivity, high strength, and stable chemical properties [73,74]. As a result of these advantages, the FE threshold of CNT is relatively lower, typically in the order of 1-2 V/ μm and the emission current from CNT field emitters is more stable than metal emitter [75,76].

Commonly, there are two types of CNTs: single-wall CNTs (SWNTs) and multiple-wall CNTs (MWNTs). For SWNTs, the geometric structure can be regarded as curled single layer of graphene, which determines the excellent electronic and mechanical properties. The excellent properties of SWNTs make them highly promising candidates for many applications, such as high mobility transistors [77], infrared emitters [78], sensors, and catalyst carriers [79]. For MWNTs, their structures can be considered as consisting of multilayer SWNTs, which also offer good physical and chemical properties. However, their multi-layer structure leads to many defects between each graphene layer. In contrast, the single-layer structure of SWNTs results in fewer defects and more stable emission current during the FE process. However, due to the weak stiffness, the SWNTs cannot be independently and vertically grown on the substrate.

Several methods have been developed to synthesize SWNTs and MWNTs by the end of 20th century, including arc discharge, laser ablation, and chemical vapor deposition (CVD)

methods [80–82]. These methods all involve an external energy source applied on a carbon-rich surface, and thus, produce carbon atoms for synthesizing CNTs [83]. Among these methods, the CVD method is considered the most favorable method for synthesizing CNT due to its lower operating temperature and easy control of CNTs' length, thickness, and pattern. In contrast, arc discharge and laser ablation have limitations in achieving patterning on specific substrates [7,83].

In the 21st century, researchers focus more on using CNT emitters for FE than metal emitters. New fabrication technologies of CNT-based field emitters were developed, including PECVD, screen-printing, and electrophoretic deposition technology [84,85]. These techniques have been widely employed for the growth of both single and multiple-wall CNTs, with screen-printing and electrophoretic deposition methods being particularly suitable for MWNTs [86,87]. In order to achieve better FE performance, the design of the CNT-based cathode was varied. The types of design depend on the type, the spatial distribution, and the orientation of CNTs. Under this condition, the design of the CNT-based emitter is divided into three categories, which are CNT point emitter, CNT film emitter, and patterned CNT emitter array, each with distinct fabrication methods and FE performance [26].

2.3.1 CNT Point Emitter

Despite CNT point emitter is the least common one among all types of CNT emitters for FE, it is a valuable tool used for studying and understanding the FE principle. Usually, the fabrication method for a CNT point emitter is to mount a single CNT on a sharp metal tip (W, gold (Au), or Si), as shown in Figure 2.4. Various methods can be used to mount a CNT point emitter, such as the dielectrophoretic method [88], and direct growth by the PECVD method [89], or

manually attaching CNTs on metal tips [90]. The maximum emission current density of a single MWNT emitter has been reported to exceed 107 A/cm^2 [91]. However, in most applications, the CNT point emitter is not only vulnerable under ion bombardment during the FE process, but also cannot provide stable FE current density.

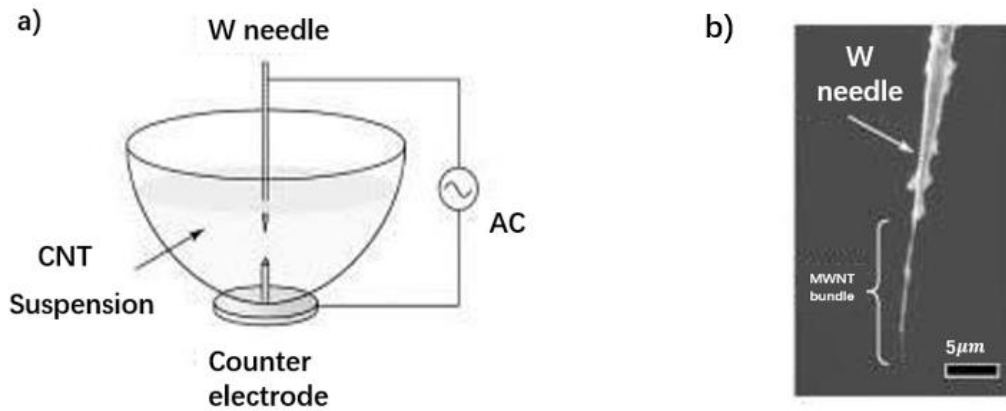


Figure 2.4 (a) the structure of the CNT point emitter device using the electrophoresis method. (b) The SEM image of CNT point emitter [10].

2.3.2 CNT Film Emitter

CNT film emitters are the most widely used types due to their relatively simple fabrication methods. The screen-printing method [87], electrophoresis method [92], and CVD method are the most common method for CNT film emitter [80]. Figure 2.5 shows the structure of CNT film emitter grown by the CVD methods. The potential application for CNT film emitter is vast because of their large emission area which meet the requirement of applications such as FE display, FE microscopy, and X-ray generation [9,91,93,94]. According to Calderon et al., the CNT film

emitters fabricated by the electrophoresis method have excellent FE performance, which provides a stable emission current at 3 mA under the applied gate voltage of 1800 V [24]. However, although the emission current of CNT film emitters is large and stable, the non-uniformity of emission current across the emission area limits their applicability in applications requiring uniform emission such as display technology. Also, the non-uniformity of CNTs' length results in only a small part of CNTs contributing to the overall emission current, leading to rapid degradation. Therefore, improving the uniformity of the emission current remains a critical challenge for CNT film emitters in high-current density and high-voltage FE applications.

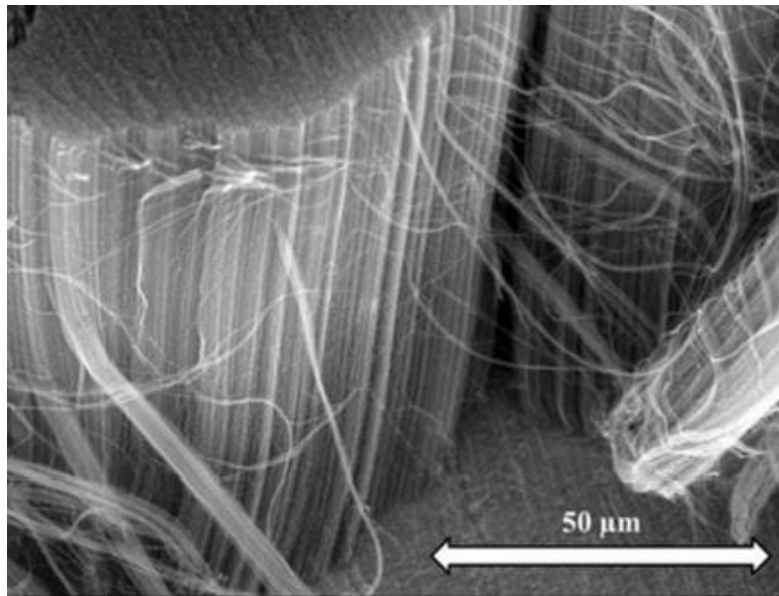


Figure 2.5 SEM image of high-density CNT film emitter grown by the CVD process [95].

2.3.3 Patterned CNT Emitter Array

To achieve both a large emission area and more uniform electron emission, the CNTs were patterned into array. Typically, the pattern is usually created through the selective growth of CNTs on a catalyst-patterned substrate using the CVD method [14,41,60], or by using laser ablation to

obtain a desired patterned CNT array [96]. Patterned CNT emitters have many advantages in applications which each pixel needs to be controlled separately, such as FE display and FE-based stationary CT, etc. For patterned CNT emitter, MWNT is better qualified, since MWNT is strong enough to vertically stand on the substrate [97]. In the early experiment, Ren et al. fabricated the patterned independent CNTs, with nickel dots as the catalyst, on a silicon substrate through PECVD methods [98]. In 2001, Sohn et al. used 800 °C thermal CVD to synthesis a well-aligned CNT array on Fe catalyst particles which deposited by pulsed laser on porous silicon and silicon substrate [99]. An emission current density of 80 A/cm² was achieved at an applied electric field of 3 V/μm, which was the best result obtained at that time for FE with CNTs.

2.3.4 Vertically Aligned CNT Field Emitter

CNTs can be classified not only by their distribution (e.g., point, film, patterned array) but also by their orientation, including VACNT and non-aligned types. Usually, VACNTs are grown via the PECVD method. Due to the high electric field during growth, the CNTs are directionally grown, resulting in a CNT array with consistent orientation. It is also reported that VACNTs can be grown by the thermal CVD method using Fe catalysts with strictly controlled specifications [17]. Because the increasing length of CNTs during the CVD process, the van der Waals forces between their outer walls interact with neighboring nanotubes to form a rigid bundle. This rigidity allows the nanotubes to continue growing along their original direction, without branching away. VACNTs have been shown to exhibit better FE performance compared to non-aligned CNTs [100], because VACNTs expose more emission tips that lead to a higher electric field enhancement factor resulting in a better FE performance [101]. Therefore, among all types of CNT-based field emitters, the VACNTs field emitters offer superior uniformity [102–104].

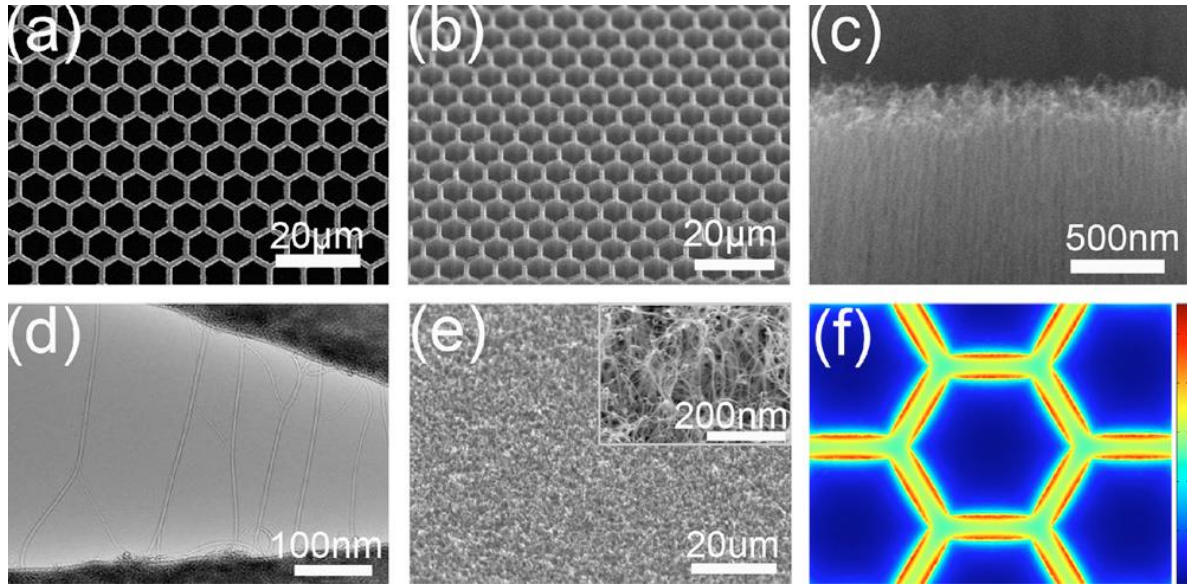


Figure 2.6 a) Top view SEM image of the as-grown honeycomb structure CNT mesh, while b) shows the image at 45° tilt. c) Cross-sectional SEM image of the VACNT array showing uniform, high-density, and vertically aligned CNTs. d) TEM image of multiwall CNTs with a diameter range of 5–15 nm. e) SEM image of CNT forest, the inset shows the zoom-in image. f) Simulation results of the electric field distribution along “edges” of the honeycomb-shaped VACNT array [102].

By patterning the catalyst before PECVD growth, VACNTs can be fabricated into films with different shapes or freestanding arrays [8]. Compared to the nonpatterned type, a patterned VACNT emitter array has many advantages, such as a more stable emission current and an addressable electron emission source (each pixel can be addressed from a single or a group of CNTs). Thus, there is an interest to study these types of CNT-based FE cathode. In 2010, Li et al. investigate FE performance from a patterned VACNT array. In this study, VACNTs were patterned by photolithography into a honeycomb-like mesh (Figure 2.6) [102]. Al (10 nm) and Fe

(1 nm) layers were deposited on the glass substrate as the catalysts. VACNTs were synthesized by thermal CVD method at 450 °C and 14 mbar with a flow rate of 200 SCCM of acetylene (C_2H_2). The lengths of the VACNTs were approximately 10 μm after 60 s grown time. With this structure, the FE performance was significantly enhanced (Figure 2.7). The turn-on electric field was measured around 2 V/ μm , and the emission current was reported to be stable during a long-term FE testing.

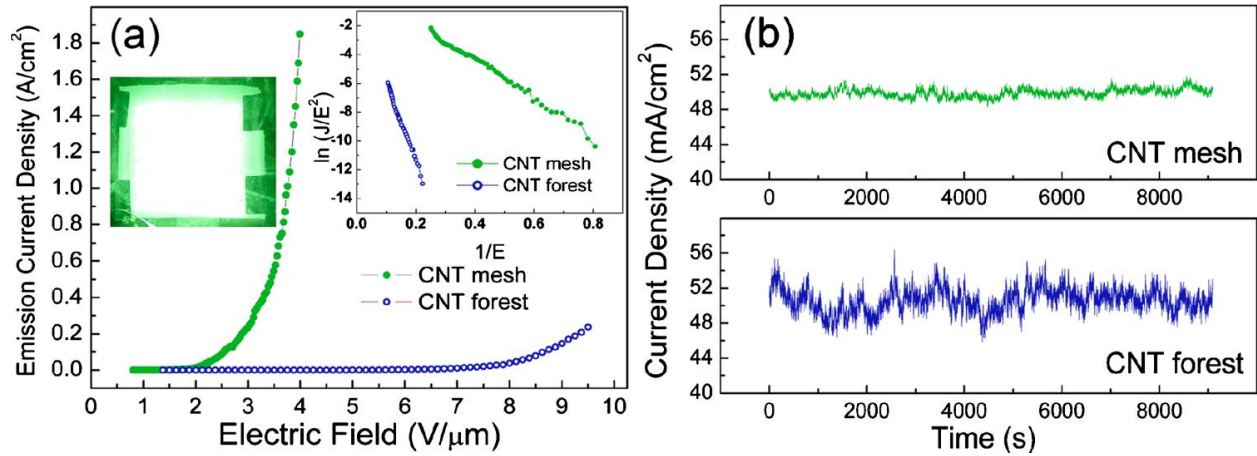


Figure 2.7 a) Dependency of the FE current density on the applied electric field J-E. Top-right inset shows the corresponding FN plot, left-top inset shows the emission image at a current density of 1 mA/cm². b) Stability tests of CNT mesh and CNT forest. The initial current density is 50 mA/cm² [102].

2.4 Failure Mechanism of CNT-based FE

2.4.1 Joule Heat Generation during FE

Many studies show that VACNT field emitters are able to provide stable but low emission current with a long-time duration [102–104]. However, few commercial applications use CNT for

FE, and most of the applications that exploit CNT-based FE are still in the research stage. The underlying reasons that prevent CNT-based FE from replacing conventional thermionic emission can be attributed to the low lifetime of CNT emitters during high current emission [21–23]. It has been reported that a large amount of Joule heat is generated and accumulated during the current emission process [105]. The Joule heat increases the temperature at the CNT emission tips and melts the CNTs, which leads to a FE failure [106,107].

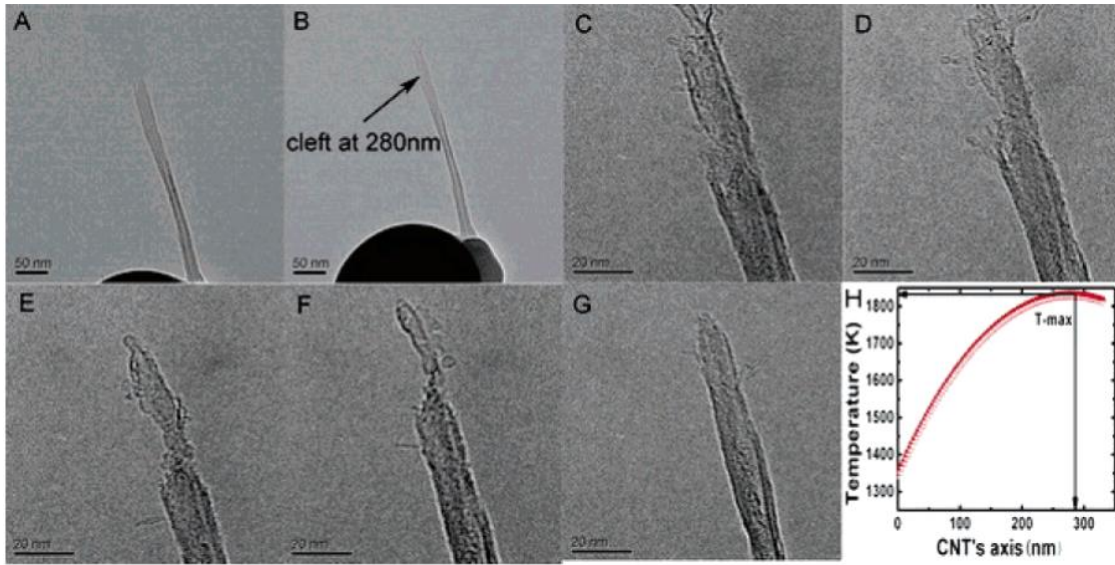


Figure 2.8 (A-G) The real-time TEM images showing the evolution of a CNT during FE and the failure process. (H) The corresponding temperature distribution along the CNT's axis. Note that all the images were taken without the presence of bias voltage [108].

In 2007, Wei et al. studied the failure mechanism of CNTs during the FE process in detail [108]. In this study, the whole process of CNTs' melting was clearly observed and recorded under TEM (Figure 2.8). With the gradual increase of the applied bias voltage, the increase of the emission current density raises the temperature, causing the heat to be collected at a certain point

of the CNT and leaving a cleft. Then, the cleft further expanded with an increase of the emission current and the assistance of electrostatic force, which eventually caused CNTs to degrade. Therefore, these results prove that the causes of CNTs' melting are attributed to the generation and the accumulation of Joule heat as well as the assistance of the electrostatic force.

2.4.2 FE-induced Coulomb Explosions

There is another phenomenon, Coulomb explosion, that induces the failure of CNT emitter during FE was recently reported [109]. The Coulomb explosion is a devastating and fatal phenomenon for FE that is caused by the solid bond of the CNTs being broken by the Coulomb repulsion of particles during FE process [110]. Similar to the Coulomb explosion induced by the electron beam exposure or chemical reaction, the mechanism of FE induced Coulomb explosion can be explained by the CNTs' ionization during the current emission process, and the rising of the charge increases the Coulomb repulsion energy to exceed the limit of bond energy between the carbon ions, which eventually inducing an explosion [109,111,112]. Also, the Coulomb explosion usually results a strong arcing between cathode and anode, which would destroy to the whole device. Compared with CNTs' melting, FE-induced Coulomb explosion would result a more detrimental damage.

It is reported by Li et al. that during the high current FE process, when the cathode is heated by Joule heating, the FE would be converted into a Schottky emission. With the assistance of Schottky effect, the emission current density would increase [109]. When the temperature reaches to the melting point of the substrate, light emission is observed, and due to the excessive electric charges overcoming the van der Waals forces between the carbon bonds of CNTs, an explosion

would occur. Then, the CNTs are torn apart into charged fragments. Furthermore, the fragments are accelerated by the high electrostatic field and crashed into the anode, and an electrical discharge is generated. By applying a camera that is assembled with a microscope lens and an indium tin oxide (ITO) anode covered with a layer of PMMA, the explosion was directly observed and traced. In Figure 2.9 (c), the light emission phenomena were observed recorded by camera and microscope, and the emitting electrons and the exploded CNT fragments can expose or leave a crater on PMMA thin film. The results show that the Coulomb explosion would seriously reduces the stability and lifetime of CNT-based FE. Therefore, to achieve a stable and reliable CNT-based FE, Coulomb explosion is required to be eliminated.

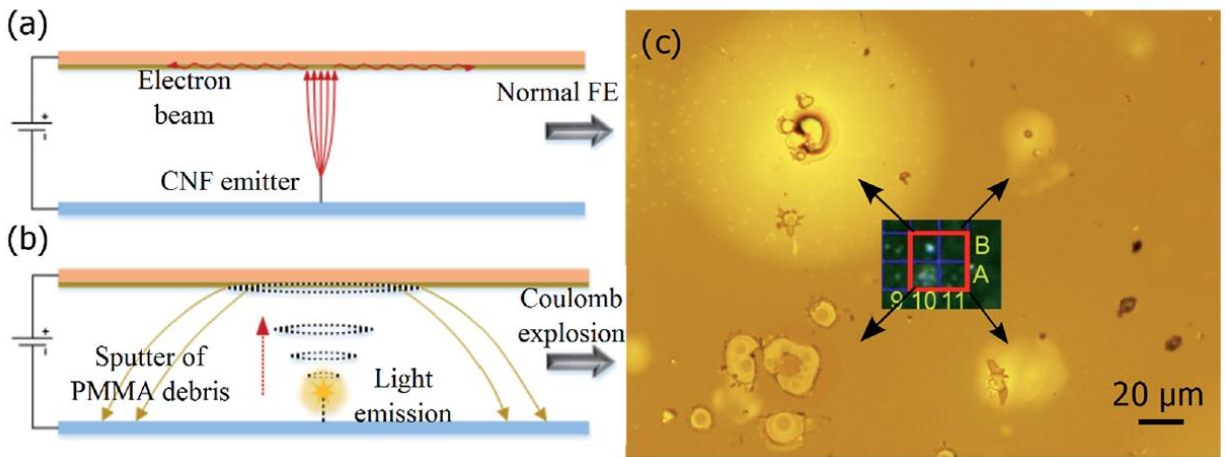


Figure 2.9 (a)(b) The comparison between normal FE and coulomb explosion. (c) The explosion mark was recorded on PMMA thin film [109].

2.5 Improvement in CNT-based FE Performance

To improve the performance of CNT field emitters, researchers have taken multifaceted approaches. Specifically, they have explored three distinct perspectives, each aimed at enhancing

the efficiency, reliability, and robustness of CNT-based field emitters. The approaches are (i) control the FE current density by adjusting the applied voltage, so that avoiding the overcurrent phenomenon on CNT emitters, (ii) modifying the physical and chemical properties of CNT to increase the FE lifetime or lower the work function of CNTs, and (iii) altering the FE electric field distribution by adjusting the CNTs' structure to increase the uniformity of emission current, thus, increasing the lifetime or reducing the screening effect to lower the turn-on electric field.

2.5.1 Gated VACNT for Improving FE Lifetime

To mitigate the degradation of VACNTs, numerous studies have investigated the implementation of an external control system to regulate the emission current density emitted by CNTs. By utilizing an output current detection, the impending melting of the CNT due to Joule heating can be predicted and provide feedback to halt the input voltage before the melting event occurs, allowing the CNT to cool down and prolong its lifetime. To realize this, a triode-gated structure is necessary. To this end, Sun et al. developed a type of coaxial gated VACNT array in 2013. This development greatly improved the lifetime of the CNT emitter during FE [113]. The fabrication process of this type of CNT-based emitter starts with patterning and depositing the chromium (Cr) into a circular pad array on a pre-deposited resistive layer, which serves as a buffer layer. The Ni catalyst dot is then patterned onto the buffer pads using EBL, followed by CNT synthesis via PECVD method. After the growth process, CNTs will independently and vertically grow on the pads along with the deposited catalyst dots. Then, SiO₂, that worked as the spacer for the coaxial cylindrical gate, was established by the atomic layer deposition (ALD) method and followed by the gate electrode deposition on the top of the oxide layer. The thickness of the ALD layer determines the gap between the gate electrode and the CNT field emitter. A support layer is

applied for subsequent chemical mechanical polishing (CMP), and the insulating layer is removed via RIE to expose the CNT emitter. The whole structure observed under SEM is shown in Figure 2.10. With this designed structure, a maximum 200 μA emission current was measured at a gate voltage of 400V.

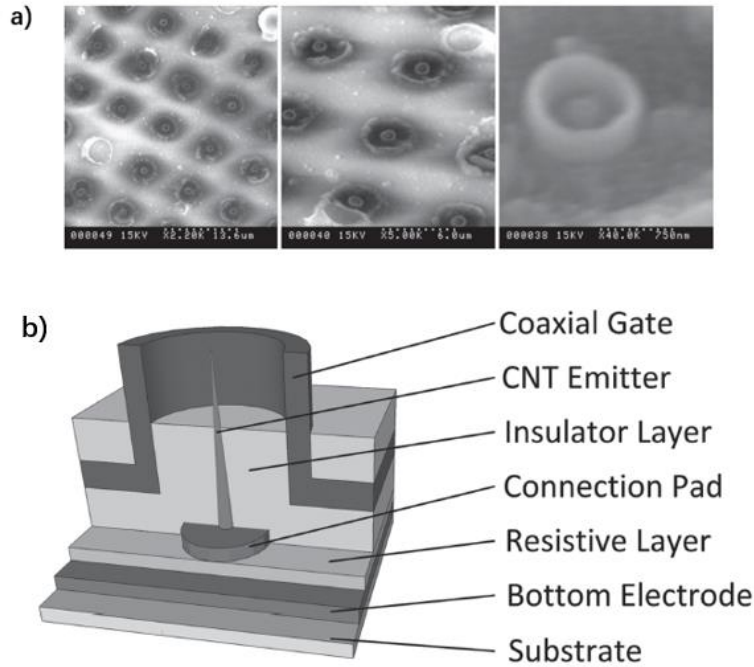


Figure 2.10 (a) SEM images of coaxial gated field emission cathode. (b) The cross-section view of the structure of ballasted coaxial gated field emitter [113].

Compared with VACNT field emitters without the gate electrode, the gated VACNT array has been found to exhibit greater stability and a longer lifetime. However, the sophisticated and challenging fabrication process of the coaxial gates makes mass production difficult. Also, the CNTs could be easily damaged during the ALD process, leading to a low success rate. Additionally, the insulation layer prevents the gate electrode higher than the tip of CNT, causing

that some of the electrons would be attracted and dispersed by sidewall electrode, resulting in a larger focal point. Therefore, the quest for a more stable and longer-lasting FE source remains ongoing.

2.5.2 Treated CNT-based Field Emitter for Improving FE Performance

Without the gate electrode or resistive components to control or limit the emission current density, bare CNTs/VACNTs field emitters are not applicable to many high-current applications. As a result, researchers are still actively exploring methods to further enhance the FE performance of CNT field emitters, particularly by directly improving the FE properties of CNTs through chemical treatments. In some recent studies, it was reported that after some specific treatments, the turn-on electric field, lifetime, and the emission stability of CNT emitters were significantly improved, such as adding polymer to form CNT-polymer composites [114], using microwave or plasma treatment [115,116],

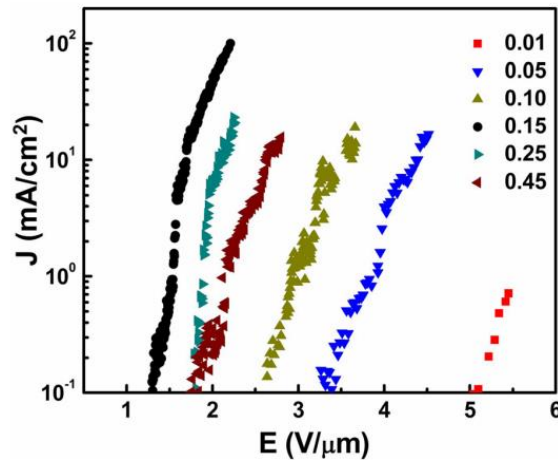


Figure 2.11 (Color online) Field emission J-E curves for various weight fractions of MWCNT-PS composites [114].

It is reported by Sameera et al. that the MWNT-polystyrene composites exhibit great improvement in FE performance [114]. The improvements in turn-on electric field with different weight fractions of the MWNT-polystyrene composites was compared and recorded (Figure 2.11). Meanwhile, another group (Stratakis et al.) reported an improvement in the FE performance of SWNT-poly(3-octylthiophene) composites [117]. The SWNTs-poly(3-octylthiophene) composites were formed by dispersing and sonication in solution, diluting in water, and drying. The turn-on electric field of different weight fractions was compared, and 0.75 weight fraction owned the lowest turn-on electric field. Moreover, the study performed lifetime testing, and reported 50 hours of stable emission at a high current density (Figure 2.12).

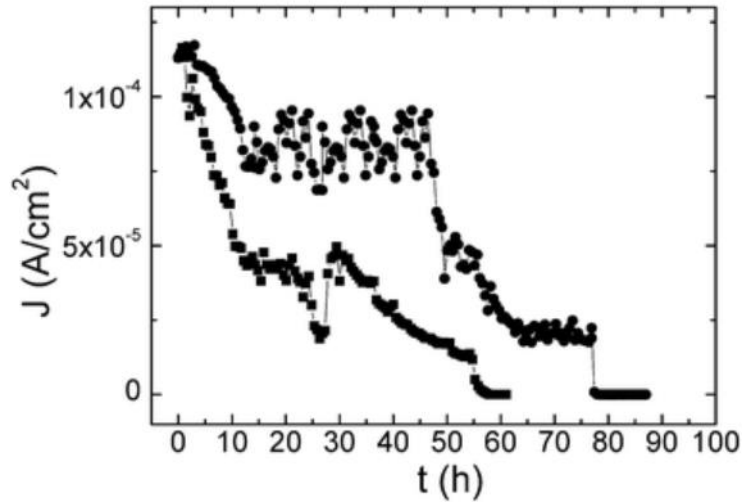


Figure 2.12 The emission current stability over time, at a constant voltage bias of 600 V, for a 40 wt% SWCNT mat deposited on an SWCNT-P3OT composite substrate with 75 wt% nanotube loading (solid circles) and for the same mat deposited on n+Si (solid squares) [117].

For other treatment methods without using composites, Kakade et al. treated CNTs with acid (oleum and 70% HNO_3) and with the assistance of a microwave [115]. This type of treated CNT presented remarkable improvements in FE current stability and emission uniformity. In addition, Chen et al. treated VACNT grown on Cu substrate with NH_3 DC plasma for different duration time and studied their different formed microstructure and FE properties [118]. After plasma treatment, the tip of the VACNT becomes sharper and the FE characteristics of VACNTs have been greatly improved. The SEM image of a treated sharper tip is shown in Figure 2.13. Among them, VACNTs treated with plasma for 1 min have the best performance, the field enhancement factor increases from 319 to 546, the turn-on electric field decreases from 11.93 to 8.84 $\text{V}/\mu\text{m}$, and the maximum emission current reaches 0.85 mA. On the other hand, it is also reported that longer time NH_3 plasma treatments (5 - 10 min) can change the morphology of VACNT by bundling the tips of CNTs together [119], which also lowers the turn-on electric field, increases the lifetime, and stabilizes the emission current.

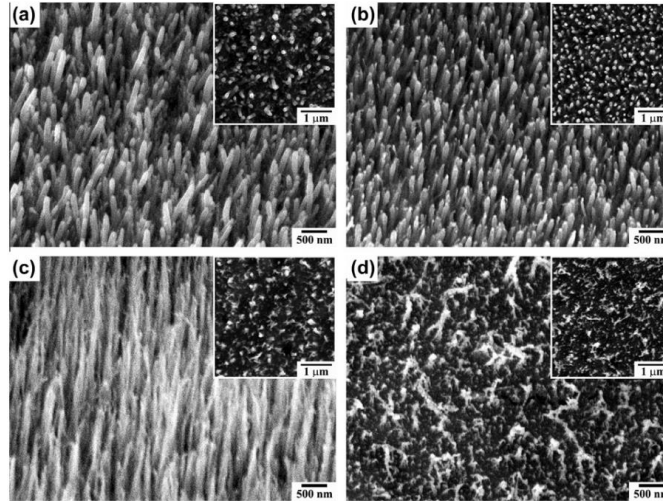


Figure 2.13 SEM images of the MWCNTs before and after NH_3 plasma treatment: (a) P-0.0 min, (b) P-0.5 min, (c) P-1.0 min, and (d) P-2.0 min. The insets show the corresponding top-view images [118].

2.5.3 Decorating, Coating & Doping Methods for Improving FE Performance.

Besides the above treatment methods, decorating, coating, and doping materials on CNTs are the other mainstream methods for improving the FE performance of CNT emitters. The improvements of FE performance are mainly attributed to the amplified density of states near the Fermi energy level and the reduction of work function of the emitting CNTs [120]. Sridhar et al. achieves ultra-low turn-on electric field by decorating CNTs with Al and Cu nanoparticles via electrophoretic deposition methods (Figure 2.14). The measured electric field was around $0.13 \text{ V}/\mu\text{m}$ [121]. In addition, the FE properties of VACNT arrays having a surface decorated with a Tantalum (Ta) layer were investigated by Wang et al. in 2013 [122]. VACNTs with Ta decorated exhibit better FE performance than undecorated type. A low turn-on electric field of $0.64 \text{ V}/\mu\text{m}$ at $10 \text{ mA}/\text{cm}^2$, a threshold field of $1.06 \text{ V}/\mu\text{m}$ at $1 \text{ mA}/\text{cm}^2$, and a maximum current density of $7.61 \text{ mA}/\text{cm}^2$ at $1.6 \text{ V}/\mu\text{m}$ were measured. The work function of CNTs with Ta decoration measured by UV photoelectron spectroscopy decreases from 4.74 eV to 4.15 eV with increasing the thickness Ta layer.

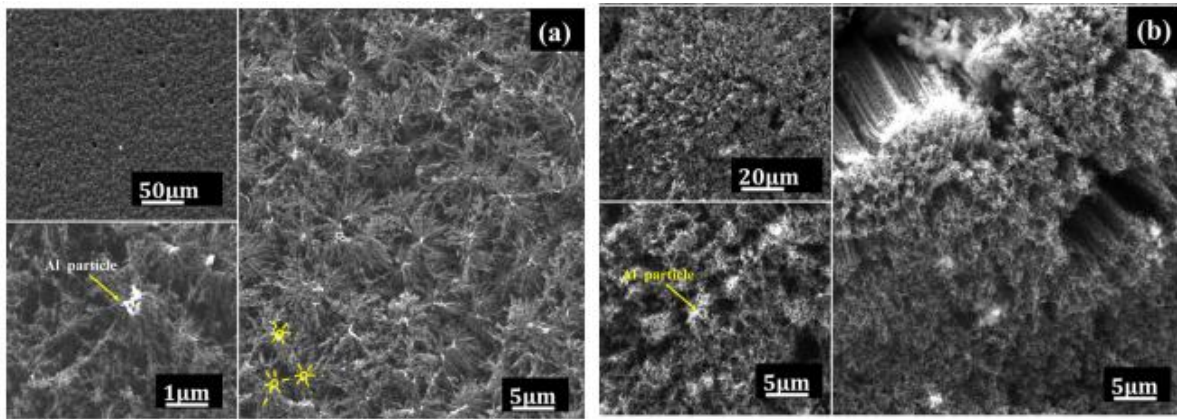


Figure 2.14 (a) & (b) SEM image of CNTs grown on Si with Al decoration in different magnification [121].

Meanwhile, Sreekanth et al. decorated indium on MWNT for improving the FE performance. The In-decorated CNT emitters present a 250% enhancement in FE current density, lower turn-on and threshold fields, and better temporal stability compared to the unmodified film Figure 2.15 [120]. Furthermore, Uh et al. coated titanium (Ti) on VACNTs to improve the FE current density and lower the turn-on electric field of CNT emitters[123]. These improvements were not only attributed to the low work function of the Ti but also lowering the resistance contact between CNTs and substrates. On the other hand, the FE properties of boron (B) and nitrogen (N₂) doped CNTs are studied by Sharma's group. The emission current density was significantly improved by this method, the current density (J) was 4 A/cm² at 368 V/μm for boron-doped CNTs and at 320 V/μm for nitrogen-doped CNTs grown on W tips, compared with the value of 1.5 A/cm² at 290 V/μm for undoped CNTs [124].

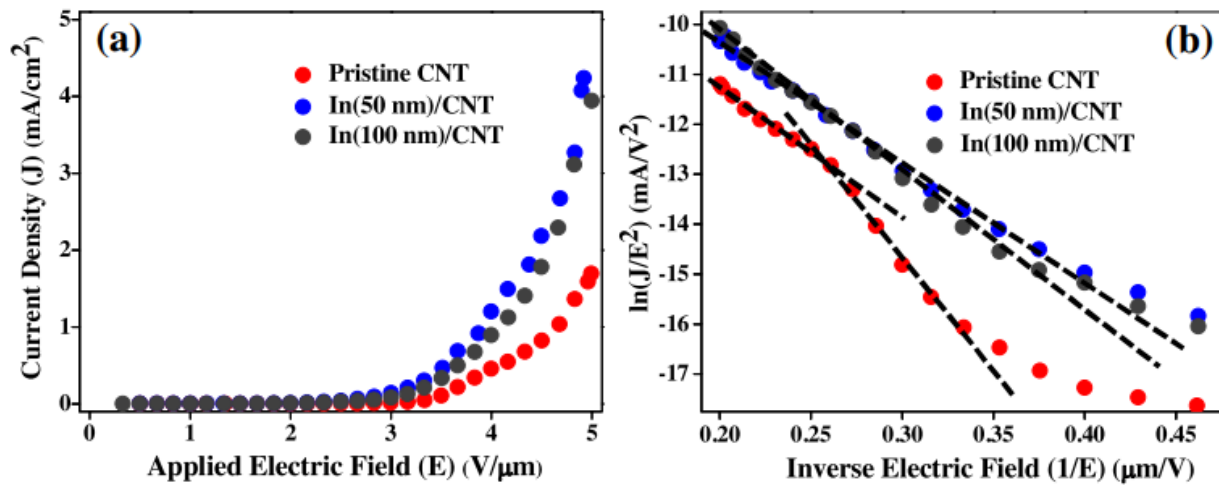


Figure 2.15 (a) J-E plot for pristine CNT, In (50 nm)/CNT, and In (100 nm)/CNT films, indicates (~250%) enhanced current density for In coated CNT films. (b) F-N plot for pristine CNT, In(50 nm)/CNT, and In (100 nm)/CNT, shows slight variation in the field enhancement factor on In decoration in high field region [120].

2.5.4 Advancement of CNT-based FE Properties Based on Synthesizing Methods

Recently, Tripathi et al. used one-pot synthesized aligned CNTs endowed with related Fe nanoparticles to form a carbon hollow cylinder (CHC) for FE process [125]. The resulting structure exhibited exceptional FE performance, such as the ultra-low turn-on field ($0.35 \text{ V}/\mu\text{m}$ at $10 \mu\text{A}/\text{cm}^2$), low threshold field ($0.41 \text{ V}/\mu\text{m}$ at $100 \mu\text{A}/\text{cm}^2$), and high FE current density ($7.71 \text{ mA}/\text{cm}^2$ at $0.78 \text{ V}/\mu\text{m}$) (Figure 2.16). The field enhancement factor was also increased, and highly stable current emission was maintained at $100 \mu\text{A}$ for 14 hours. On the other hand, Thapa et al. synthesizes VACNT pillar-based field-emitter arrays on stainless steel, which also has high FE performance. Low turn-on electric field ($1.57 \text{ V}/\text{mm}$), high field enhancement factor ($\beta=4977$), and high emission current density ($\sim 33 \text{ mA}/\text{cm}^2$ at a field of $4 \text{ V}/\text{mm}$) were measured [126].

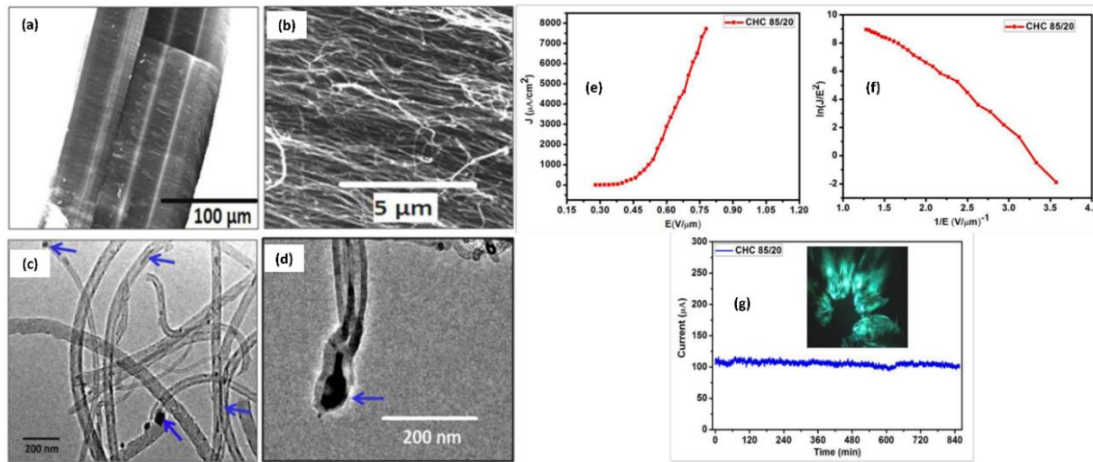


Figure 2.16 a) low magnification and corresponding high magnification b) SEM micrographs, c) and d) TEM micrographs; of CHC, respectively (Fe NPs are shown by blue arrows). e) FE characteristics current density (J) as a function of applied electric field (E), f) F-N plot $\{\ln(J/E^2)\}$ versus $1/E$, g) Field emission current stability ($i-t$) plot and corresponding field emission image (inset); of CHC [125].

2.6 Chapter Summary

In this chapter, a comprehensive review of the background knowledge was presented pertaining to electron emissions. It begins from the theory and mechanism of various types of electron emission to the development of field emitters based on metals, semiconductors, and, more recently, CNTs. Compared to thermionic emission, FE offers several advantages, including fast response speed, lower operating temperature, and better emission efficiency. These advantages have inspired many researchers to use FE to achieve better electron emission thus replacing thermionic emission. Since CNTs was discovered, many researchers have been engaged in FE research to investigate their potential as field emitters. Besides the SWNT and MWNT, CNT field emitters can also be classified into point emitter, film emitter and patterned emitter array, as well as VACNTs and nonaligned CNTs according to the emission area and the orientation of CNTs. Each type of CNT emitter has distinct advantages for different applications, for example, CNT film emitters are simpler to fabricate than individual CNT arrays but has higher turn-on electric field and worse uniformity, whereas VACNTs have better FE performance than non-aligned CNTs but more sophisticated synthesizing methods.

During the FE process, CNT emitters are susceptible to degradation. Because of the generation of Joule heat and the excessive Coulomb repulsive energy, CNTs are melted or exploded under large load of emission current density. Therefore, it is crucial to develop methods that allow CNT emitters to reliably perform FE at high emission current. So far, many approaches have been explored to improve the FE properties of CNTs, including the addition of a gate electrode for current control, chemical and plasma treatments, as well as decorating, coating, doping, and unique synthesizing methods. These approaches have achieved many successes in lowering the turn-on electric field, increasing lifetime, and stabilizing long-term emission current

density. Although various methods have been proposed to mitigate the degradation rate of CNTs, these techniques are often associated with inherent defects and limitations that limit their practical applications, particularly in enhancing the long-term stability and durability of CNTs under high current density emissions. Despite significant progress in the development of new strategies to address these limitations, achieving a sustainable and reliable performance of CNTs remains a major challenge in the field of nanoelectronics and materials science. Therefore, a method that completely prevents CNT failure is still necessary to be discovered.

Chapter 3 Phenomenological Analysis of Freestanding CNT

Coulomb Explosion Induced by Field Emission

3.1 Chapter Introduction

In order to reduce the risk of the Coulomb explosion during CNT FE, it is important to first understand its mechanism. At present, there has limited investigation been conducted on the phenomena of the Coulomb explosion induced by CNT FE. Li et al. observed some signs of the explosion based on a microscope camera [109]. However, the observation and recording of the whole explosion process are deficient to have a complete cognition of this phenomenon (the cause and mechanism). Hence, a more complete and detailed observation of this phenomenon is necessary to analyze its underlying mechanism, and more comprehensive studies on its cause of occurrence are required.

In this chapter, a significantly improved experimental methods is implemented to further investigate the cause of this phenomenon. In-situ observation of the CNT Coulomb explosion process is performed using a slow-motion high-speed microscope camera. PMMA thin film is coated on the FE anode used to sensitize the exposure of FE electrons and trace the atomic impact from the Coulomb explosion. The mechanism of the CNT Coulomb explosion during the FE process is studied further through the recorded explosion phenomenon.

3.2 Materials and Methods

3.2.1 Cathode Design and Fabrication

To clearly observe the explosion, individual freestanding CNTs are chosen to be grown on the cathode. There are two important design parameters of the freestanding CNT array, which include the number of CNTs and the distance between adjacent CNTs. These two parameters need to be carefully considered since the distance controls the field screening during FE which would cause the change in the field enhancement factor, and the viewport size of the camera (depending on the resolution of the camera and the magnification of the micro-lens) limits the size of the CNT array. Considering the Coulomb explosion is instantaneous, the frame rate is set to 3800 per second with a resolution of 350×350 pixels. 4×4 freestanding CNT array with a distance of $50 \mu\text{m}$ between adjacent CNTs and a length of $10 \mu\text{m}$ is chosen to be used in the experiment. With this experimental design, the Coulomb explosion effect on each CNT can be clearly observed.

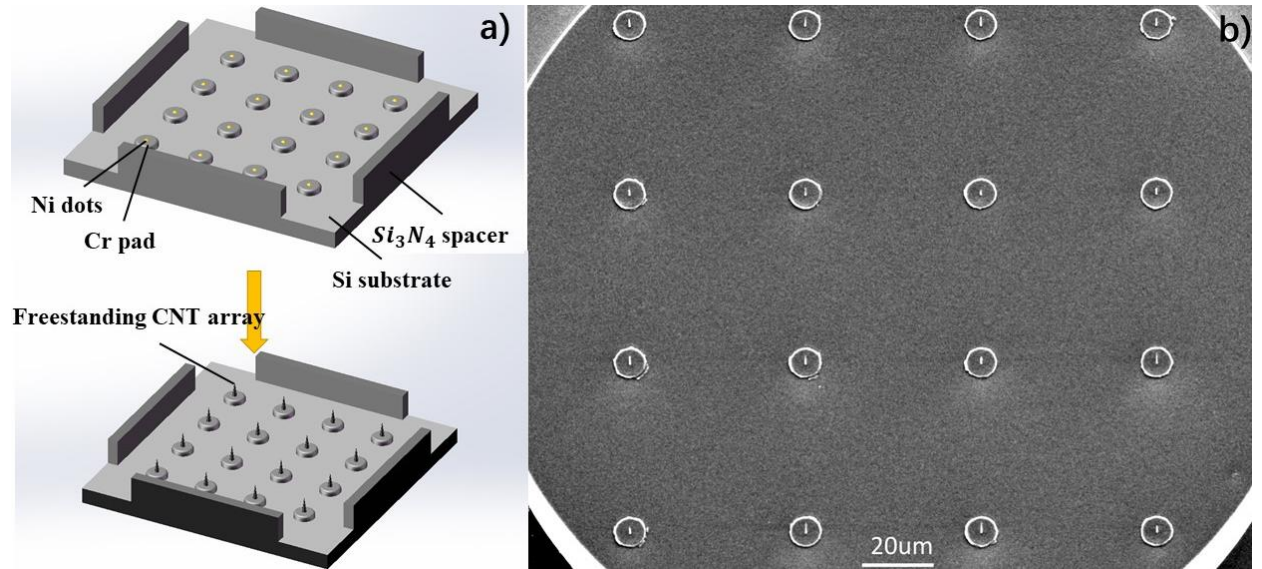
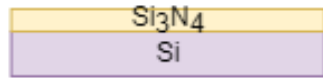


Figure 3.1 a) Schematic diagram of the cathode structure. b) SEM image of 4×4 CNT array.

The fabrication of the CNT array starts from the deposition of a Si_3N_4 insulation layer, followed by an etching process to form a 50 μm distance-fixed spacer structure. Then, circular Cr buffer pad arrays with a diameter of 6 μm are patterned and deposited on the Si substrate. The thickness of these contact pads is 200 nm, and the interval is 50 μm . These pads play two roles: 1) perform as the protection structure to prevent particles from diffusing into the substrate during FE; 2) regarded as the marker that localizes the position of CNT arrays in the camera lens. Secondly, 100 nm circular Ni dot arrays are patterned, aligned and deposited on the center of the Cr pad. The thickness of the Ni dots is 80 nm, which aims to grow CNTs with a length of around 10 μm , resulting in the structure shown in Figure 3.1. The CNTs are then synthesized by a PECVD (Black Magic, Aixtron, Germany) for 20 min. Acetylene (C_2H_2 , 50sccm) and ammonia (NH_3 , 200sccm) are used for the growth of CNTs. The SEM image of the fabricated 4×4 CNT array is shown in Figure 3.1 b. In order to fabricate different lengths of CNTs for comparison, different plasma power (60W and 75W), and different growing temperatures (800 °C and 850 °C) are applied to different cathodes during the PECVD process (**Error! Reference source not found.**). In the experiment, two different types of cathodes with different quality and uniformity are tested for the comparison study to investigate the possible causes of FE-induced Coulombic explosion. For the first type, a CNT array that applies 75 W plasma power and 850 °C growing temperature during PECVD is used as the cathode. The higher plasma power and higher temperature would provide a more rapid and intense chemical reaction, resulting in a more unstable and uneven growth environment, which leads to the nonuniformity of the CNT array and may also cause defects in CNTs. The purpose of using a longer, more non-uniform, and imperfect CNT array is to test if these factors would induce the Coulomb explosion easier. On the other hand, the second type of

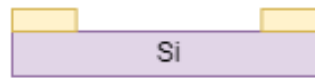
cathode applies 60 W plasma and 800 °C to grow CNTs, which are shorter and more uniform under SEM.

(I)



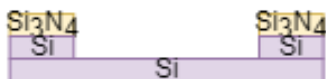
2000nm Si_3N_4 Deposition

(II)



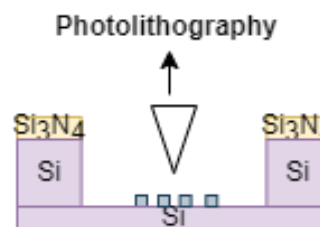
Si_3N_4 etching

(III)



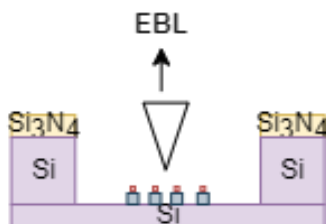
Si etching using DRIE

(IV)



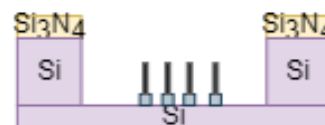
Cr buffer layer patterning & deposition

(V)



Ni catalyst dots patterning & deposition

(VI)



CNT grown by PECVD

3.2.2 Experimental Method

Figure 3.2 depicts a basic experimental setup for conducting the explosion test. In this setup, a slow-motion high-speed camera (Kron Technologies Inc., Chronos 1.4) is installed on the trinocular port of the microscope with a 20× lens. The lens is directly aligned with the vacuum chamber, thus, the FE device inside the vacuum chamber can be observed and recorded in detail with the desired magnification through the transparent observation window. Besides the fabricated CNT cathode, the FE device also consists of an ITO coated glass anode. As shown in Figure 3.2 a and b, the transparent ITO-coated glass allows the camera to directly observe the phenomenon that occurred on the CNT cathode during the Coulomb explosion. In addition, another transparent PMMA thin film (200 nm) is coated on the ITO glass anode that worked as the electron-beam resist to sensitize the electron emission during the FE. The integrated spacer fixes the distance between anode and cathode. The whole FE experiment is conducted in a vacuum environment of 8×10^{-9} Torr. During the FE process, a DMM-6500 (Keithley) amperemeter is series connected to the CNT cathode to continuously measure the FE current, and a positive bias voltage is applied on the ITO glass anode from 0 V to 2000 V. In addition, the high-speed camera focuses on the surface of PMMA thin film to capture the influence of Coulomb explosion on PMMA layer by the exposure of electron and the impact of the explosion. SEM is used for characterizing each CNTs before and after the Coulomb explosion.

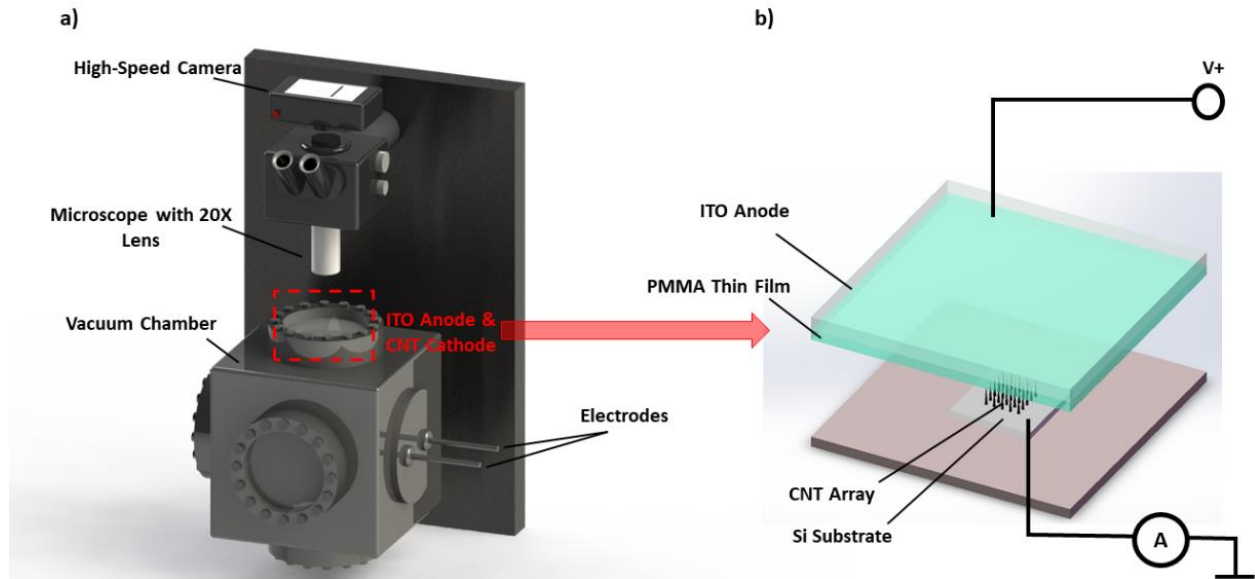


Figure 3.2 a) Structural diagram of the experimental device includes the vacuum chamber and the high-speed camera connected with a microscope lens. b) the intergraded cathode and anode structure.

3.3 Results and Discussion

3.3.1 Coulomb explosion phenomenon

The whole process of the Coulomb explosion is directly recorded by a high-speed camera and the recorded videos are played back slowly to observe the details of the moment when the explosion occurred. The videos show free-standing CNTs exploding independently at an instantaneous on 4×4 CNT arrays.

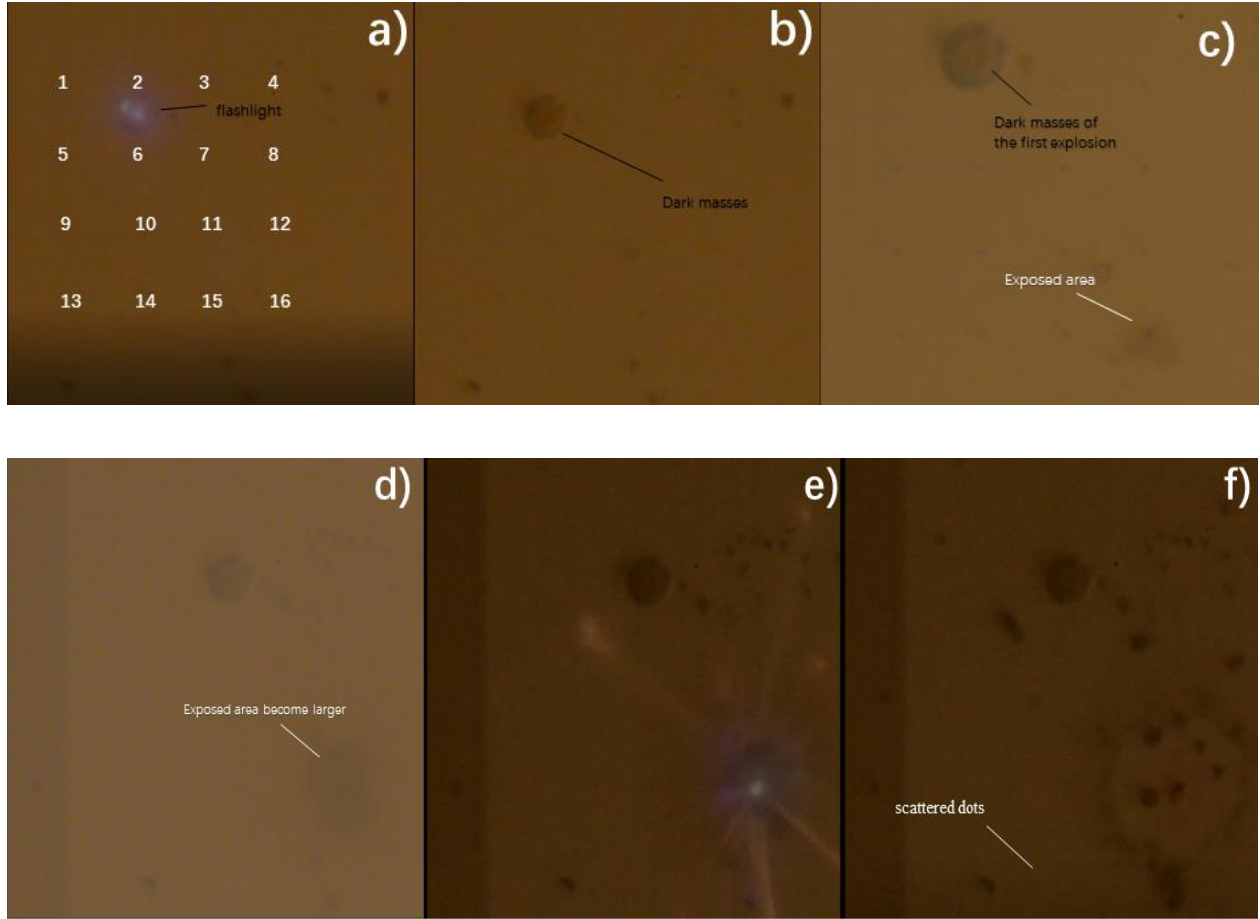


Figure 3.3 a) The 4×4 CNT array is directly observed through a high-speed camera connected with a microscope lens. a flashlight caused by the Coulomb explosion is captured by the high-speed camera. The instantaneous value of current was measured over $100 \mu\text{A}$. b) The dark mass leaves on the PMMA layer. c) The exposure trace on the PMMA layer. d) The exposure trace becomes darker and larger. e) A flashlight appears on the exposure trace. f) Scattered dark mass leaves on the PMMA layer.

For the first approach shown in Figure 3.3, the entire coulomb explosion process on a CNT array is captured by the camera during an experiment using the first type of cathode. In the process, when the bias voltage is gradually increased from 0 to 1450 V, a purple-spotted ultra-short light

flash occurred from a single CNT, subsequently, a dark masses form on the PMMA film corresponding to the location where the CNT explodes (Figure 3.4). After several minutes, the second CNT explodes (Figure 3.5). Different from the first explosions, the second explosion begins with a formation of a large black spot, which represents the exposure of PMMA by FE electrons from the corresponding CNT. Subsequently, as the spot becomes darker and larger, the purple light flash occurs also in an extremely short time, then, an explosive pattern of scattered dots forms on the PMMA film. This explosion of the second CNT in this experiment causes serious discharge, resulting in a violent fluctuation of emission current.

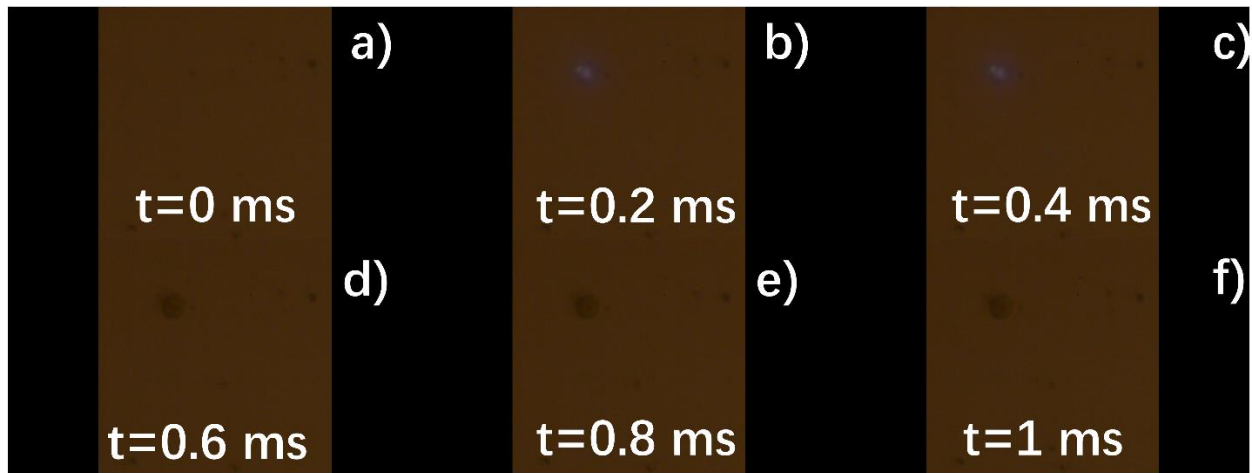


Figure 3.4 Continuous screenshots of the first Coulomb explosion in the first approach occurs on a single CNT within 1 ms.

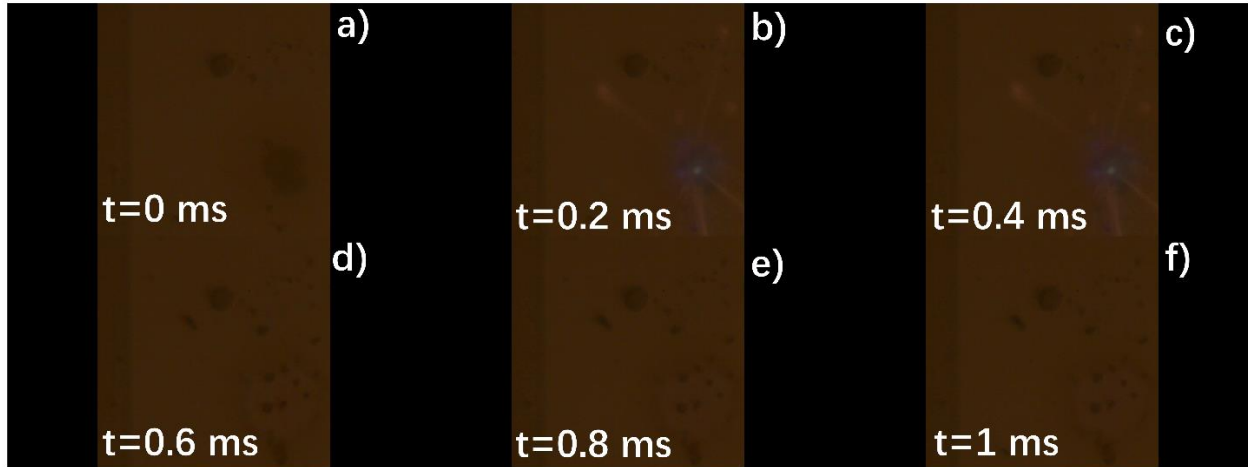


Figure 3.5 Continuous screenshots of the second Coulomb explosion in the first approach occurs on a single CNT within 1 ms.

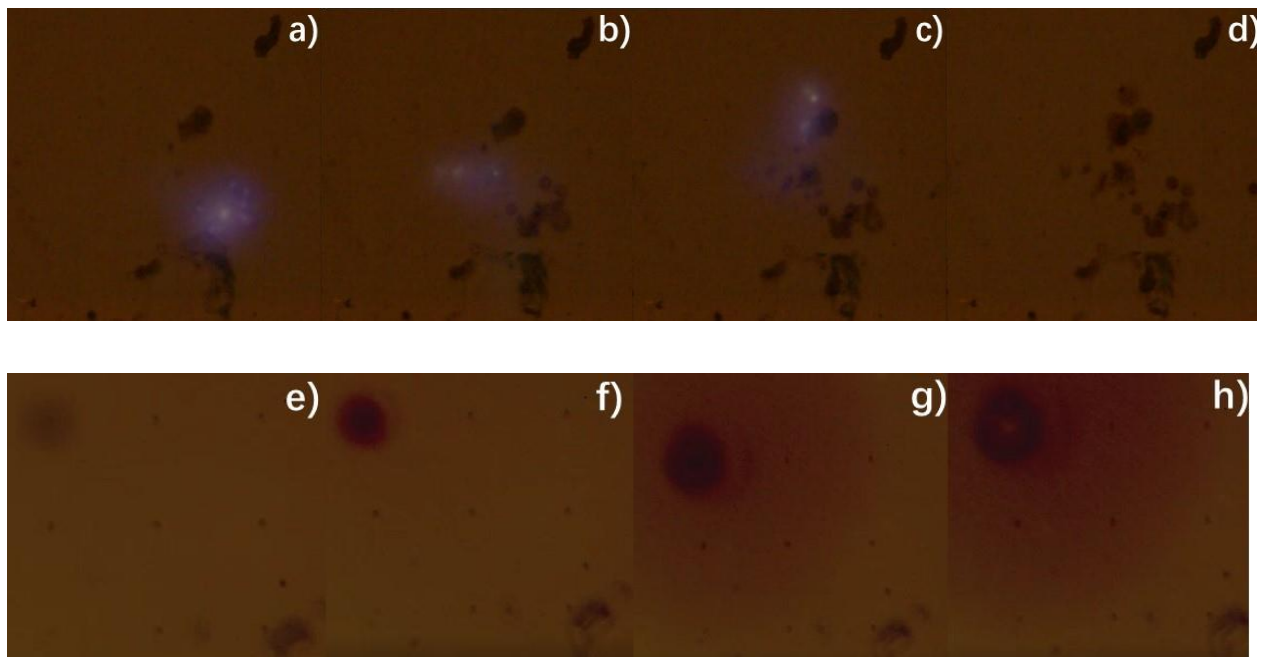


Figure 3.6 a) b) c) d) The snapshot of three flashes continuously occurs on the same cathode. e) f) g) h) The enlargement process of exposure trace on PMMA without Coulomb explosion.

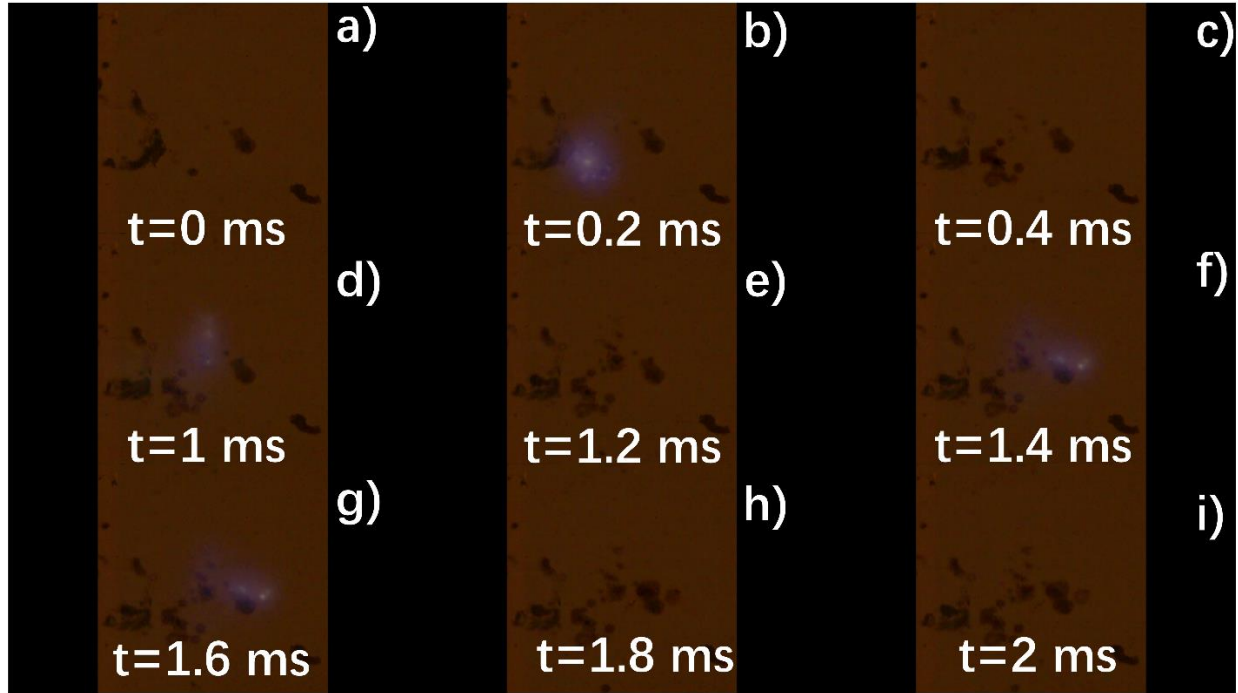


Figure 3.7 Screenshots of the three continuous Coulomb explosions in the second approach occurs on a single CNT within 2 ms.

In order to verify the repeatability of the explosion, the same experiment is conducted again (Figure 3.7). In this trial, three explosions also continuously occur along with the sparking light flash within 0.5 microseconds. After the light flashes in an instance, with the same condition as the last experiment, an integrated black pattern appears on PMMA at the location of the flashlight. Figure 3.6 a to d shows three flashes of light during the explosions and the black pattern after the explosions. Compare with the first experiment, the only difference is the explosion occurs at a lower applying voltage of 750V in a much longer time.

In addition, turn-on electric field tests were conducted to demonstrate the FE behaviour (Figure 3.8). For the first experiment, the turn-on electric field was around 10 V/ μm , and the emission current raised to 5 μA as the applied electric field increased to 17 V/ μm . The small FE

current in this experiment is due to the very small number of emitted CNTs, that only 16 CNTs emitting electrons at the same time. For the second experiment, the turn-on electric field was almost the same compared to the first trial, which demonstrates that the performance between these two FE tests were similar.

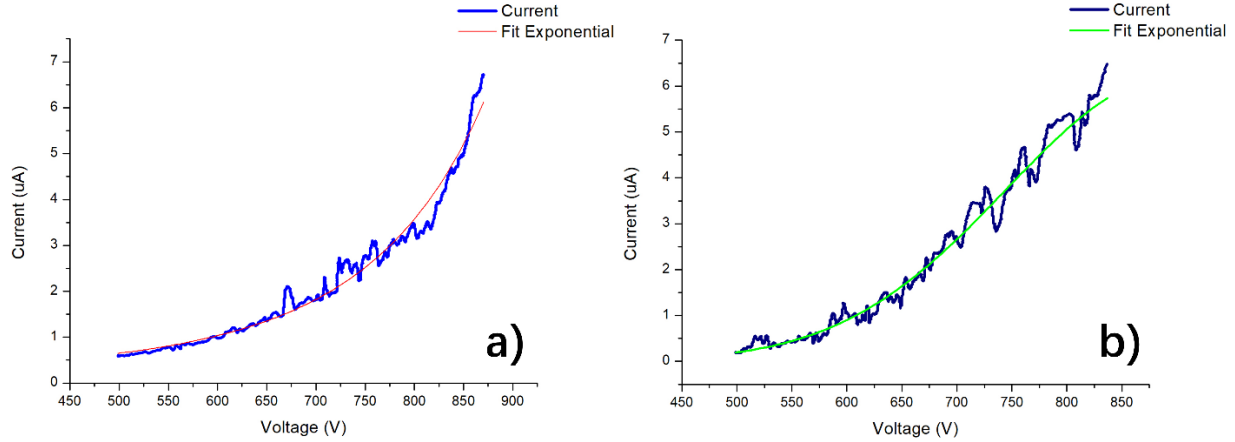


Figure 3.8 FE IV curve of a) the first approach, b) the second approach.

The third experiment is conducted using the second type of cathode for comparison. During the experiment, no signs of an explosion are observed. However, there is a clear electron exposure trace found on the PMMA layer during the FE. As shown in Figure 3.6 e to h, with the same bias voltage applied at 800 V and keep for around 10 min, the exposure trace becomes larger and darker. In the end, the middle of the dark spot becomes transparent which indicates that the PMMA layer has been ablated by electrons and some parts of the PMMA have been burned out. During the whole process, only one exposure trace is found that occurs directly above the longest CNT.

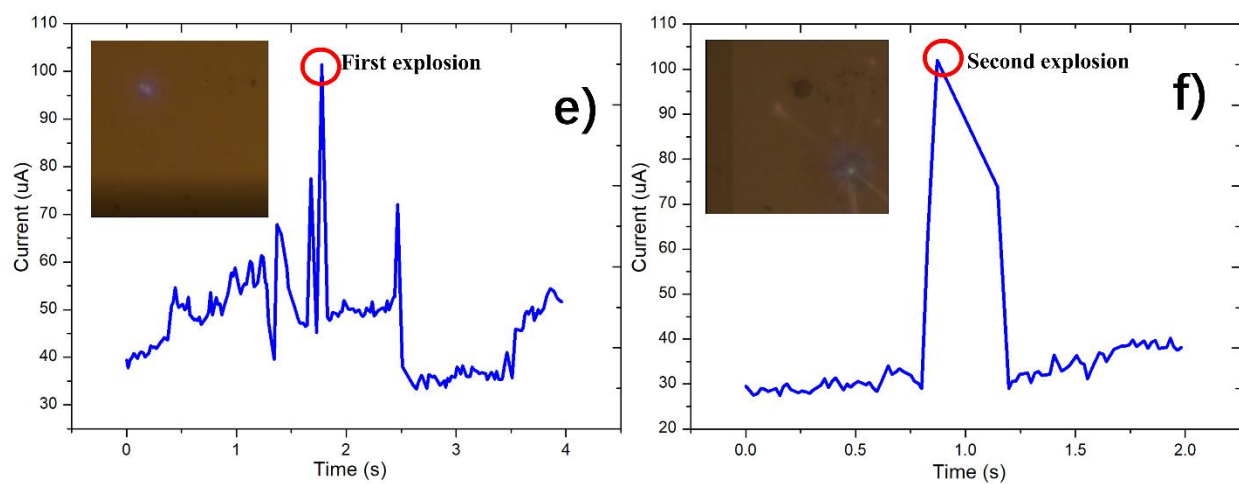
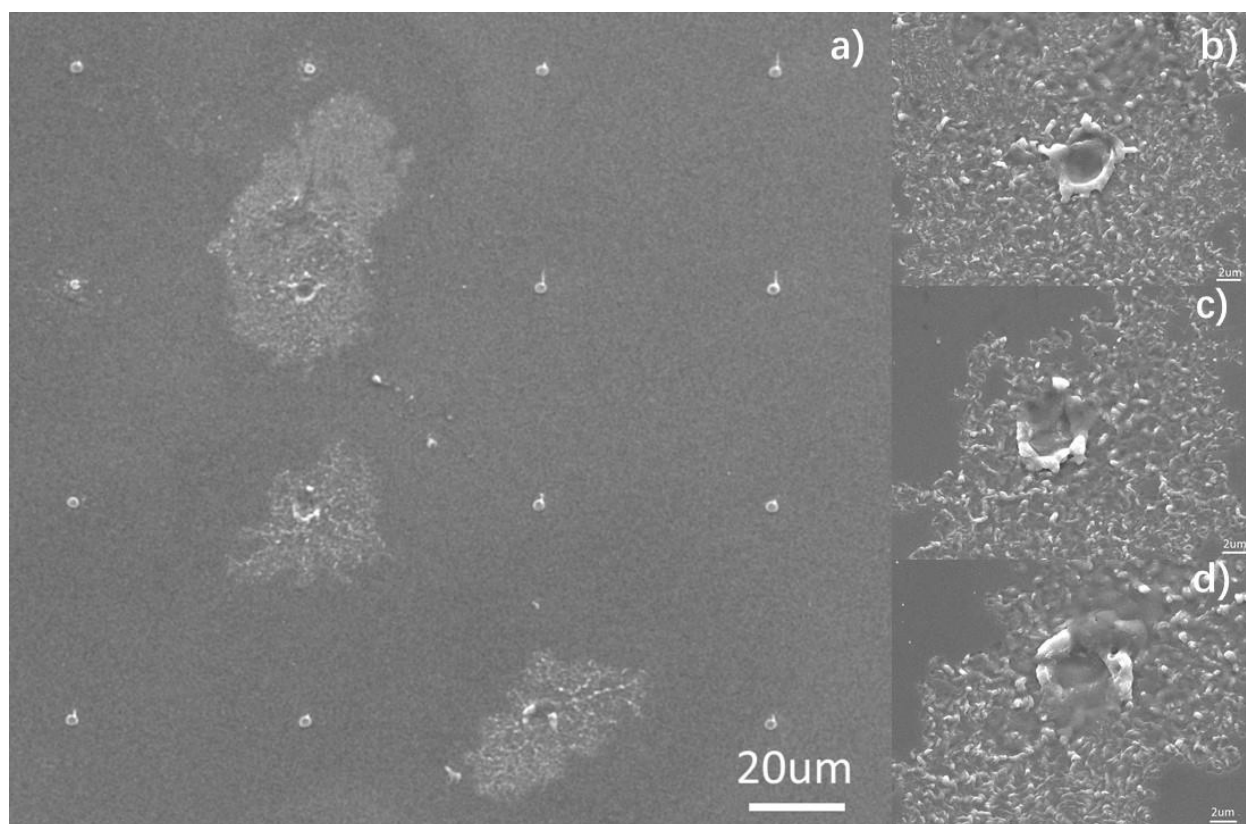


Figure 3.9 a) b) c) d) SEM image of craters caused by the Coulomb explosion. e) f) The emission current of two explosions during FE in the first experiment.

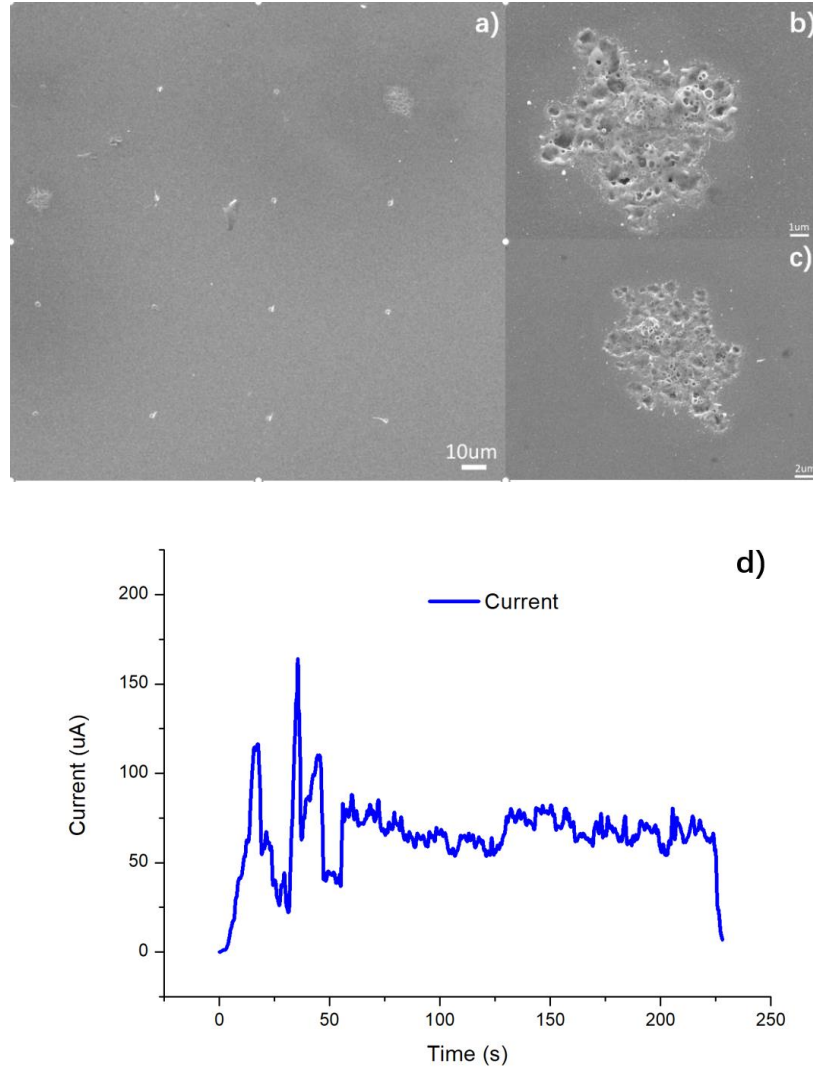


Figure 3.10 SEM image of crater caused by Coulomb explosion in the second approach. a) the image of the whole 4×4 array. b), c) the image of the craters. d) the change of emission current in the second approach during Coulomb explosion, the highest peak is the time when three continuous explosions occur.

After the experiments, SEM is used to view the explosion effects on CNTs and the surroundings. Figure 3.9 and Figure 3.10 shows the explosion effect on CNT emitters in experiment 1 and 2. After the explosion, the entire pad was destroyed, leaving an irregular crater.

The size of the crater depends on the scale of the explosion, and the largest crater is caused by the third explosion in the second approach with a diameter of 20-30 μm (Figure 3.9 b). Oppositely, the second explosion in the second approach that has the smallest dark dot leads to the smallest crater on the substrate (Figure 3.9 d).

Consider the Coulomb explosion would cause a very quick change of the emission current. The amperemeter is set to a fast and continuous current data acquisition mode. For the first approach, Figure 3.9 e and f show the change of the emission current during the Coulomb explosion for the first experiment. Two high peaks can be found in the collected current data, which are exactly the time the explosions occur. During the experiment, there are two explosions are captured at two different time points, in which the first explosions occur at the same time at $t=0.8\text{ s}$ in Figure 3.9 e, and the second explosion occurs at around $t=1.8\text{ s}$ in Figure 3.9 f. For the second approach, Figure 3.10 shows that the explosions also cause a sudden current rise and leave a large crater on the Si substrate. Also, the occurrence of a black pattern on the surface of PMMA was observed to coincide with a sudden increase in the emission current, providing evidence to support the notion that the formation of the black pattern is directly linked to Coulomb explosion. Thus, these results indicate the Coulomb explosions are usually accompanied by the sudden rise of emission current or arcing during the FE process, and that would cause the emission current to be unstable. It should be noted here that the peak value recorded by the amperemeter, which is over 1 mA, greatly exceeds the measurement range due to the current overload caused by the explosion, hence it is removed from the current plot to show the other details in the emission current. In addition, the arcing or the sudden rise of the emission current would cause the vacuum condition become worse (the pressure would increase from 8×10^{-9} to around 1×10^{-7} Torr).

Table 1: Summary of the duration time and current peak of each Coulomb explosion in three experiments.

		Duration	Current peak (μA)
Experiment 1	Explosion 1	<0.6ms	100
	Explosion 2	<0.6ms	100
Experiment 2	Explosion 1	<0.4ms	120
	Explosion 2	<0.3ms	160
	Explosion 3	<0.6ms	115
Experiment 3	No explosions occurred	N/A	N/A

3.4 Chapter Summary

During the FE process, a Coulomb explosion is the most common and detrimental cause of FE failure and the short lifetime of CNT emitters. To avoid the occurrence of the Coulomb explosion, this study focuses on the causes and phenomena of the explosion from the perspectives of experiments. In the experiment, the high-speed camera is applied to capture the instantaneous change of Coulomb explosion on the cathode and PMMA coated anode. The Coulomb explosion phenomena can be concluded into three phases. 1) The atoms at the emitter's tip have been ionized at the moment current starts to be emitted. 2) Atomic bonds be broken as a result of a large amount

of Coulomb potential energy converted into kinetic energy. 3) The CNT structure collapse due to the accumulated Coulomb potential energy converting into light flash and explosion shock. In addition, the emission current rises sharply at the time of the Coulomb explosion, from an average of 40 μA to over 1 mA instantaneously.

Chapter 4 Computational Simulation of FE-induced Coulomb Explosion on CNT Field Emitters

4.1 Chapter Introduction

To further investigate the deep cause of the Coulomb explosion induced by FE, modeling and simulation are conducted in this chapter. To achieve this, we conduct modeling and simulation based on the equations of computational chemistry to analyze the process of Coulomb explosion in CNT-based FE. Specifically, a computation of the potential energy, interaction force between the carbon atoms, and the distribution of the energy during the Coulomb explosion process was calculated to gain insights into its underlying mechanisms.

A comprehensive analysis of the Coulomb explosion process in CNT-based FE was presented, based on the results of the experiments and simulations. The analysis reveals that Coulomb explosion occurs when the emission current exceeds a critical threshold, leading to a sudden, explosive release of energy that causes the CNTs to break apart. Moreover, the formation of defects and the accumulation of charge in the CNTs can exacerbate the Coulomb explosion process. Furthermore, according to the analysis of the Coulomb explosion, several potential solutions to avoid its occurrence were proposed.

4.2 Modeling and Simulation

The Coulomb explosion is defined as a cold explosion caused by the excessive Coulomb energy accumulated in molecules. The Coulomb repulsive force compels atoms away from each other and stretches the bonds until they break [127]. As the bonds break, the Coulomb energy

would further repel atoms leading to the atoms irregularly spreading around and traveling away causing the imbalance of the whole structure. Subsequently, the structure would explode and collapse because of the unbalanced force [109]. Normally, a Coulomb explosion occurs when a highly charged cluster containing many ions move toward a neutral surface. As the cluster approaches closer, the ions in the cluster would have a great attraction to the electrons on the surface. As the electrons are captured by the cluster, the atoms on the surface are ionized and positively charged. These charges will lead to a formation of large Coulomb energy and results in an explosion. However, the Coulomb explosion caused by FE is different from the traditional Coulomb explosion described in the above case. During the FE, electrons are emitted from the surface of the material into the vacuum by applying a strong electrostatic field. The relationship between electric field and emission current can be described by Fowler and Nordheim equation that shows as follow (combined equation (2.3) & (2.4)). [128]

$$J = 6.2 \times 10^{-6} \frac{\mu^{\frac{1}{2}}}{(\mu + \varphi)^{\frac{1}{2}} \varphi^{\frac{1}{2}}} (\beta E)^2 \exp\left(-\frac{b\varphi^{\frac{3}{2}}}{\beta E}\right), \quad (4.1)$$

where J is the emission current density, E is the applied electric field, φ is the work function parameter, and β is the enhancement factor of the electric field, which is the ratio between local and applied electric fields. Thus, according to equation (4.1), the emission current is affected by three main parameters which are φ , β , and E . As the electron emits into the vacuum from the surface, the atoms on the surface are ionized and positively charged. However, to achieve an emission current, usually a high bias voltage is applied. The high bias voltage not only increases the emission current but also increases the drifting velocity of the electrons as described in equation (4.2).

$$V = \mu E \quad (4.2)$$

where μ is the electron mobility of the CNT and E is the external electric field. The higher drifting velocity would lead to a faster electron flow that allows electrons to replenish the holes on the surface in a shorter time. Generally, Coulomb energy is difficult to accumulate between atoms on the surface to induce the Coulomb explosion, unless huge Coulomb energy increases dramatically when the electrons have no time to replenish, which illustrates the case that a small drifting velocity with a large emission current density. The field emission of CNT, especially the long CNT, is likely to have this problem. The long CNTs have a great aspect ratio that provides a huge enhancement factor that described in equation (4.3) [129],

$$\beta = \frac{2h/R_a}{\ln\left(\frac{4h}{R_a}\right) - \alpha} \quad (4.3)$$

where h and R_a are the height and radius of the emitters, α is the factor related to the shape of the emitter. With a large enhancement factor, larger emission current can be generated by a lower applied voltage bias and lower drifting velocity. It leads to a sudden accumulation of large Coulomb potential energy on the emission tips of CNTs, this Coulomb potential energy provides the carbon bonds with an extremely large potential energy to stretch the bonds and exceed their maximum bond length, breaking the bonds before free electrons flow to the surface and neutralize those ionized atoms. Therefore, in order to verify whether the FE process can break the bonds between carbon atoms and lead to a Coulomb explosion due to a dramatic increase in Coulomb potential energy in an instant (a moment faster than the drifting speed of the electron), a simulation is created to calculate the time in which the bonds of carbon atoms are stretched to break when a

certain number of carbon atoms are ionized, and the changes in potential energy during the whole process of the chemical bonds being stretched.

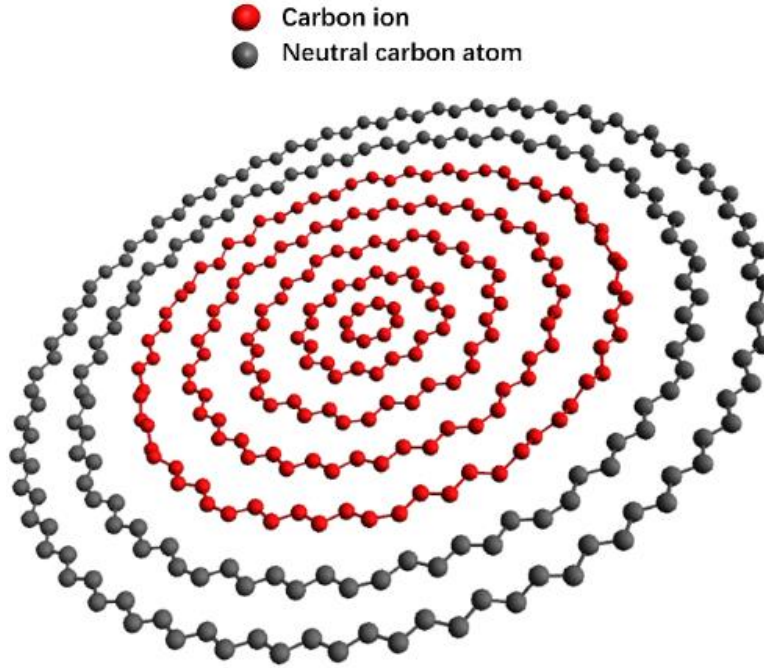


Figure 4.1 The structural diagram of the model consists of 190 carbon ions and 183 neutral carbon atoms.

The simulations begin by building a model of a freestanding multiwall CNT (MWNT) structure. By using equation (4.4), the number of charges at a certain moment can be calculated.

$$I = \mu E n A e \quad (4.4)$$

Here, the total charge is estimated to be 3×10^{-17} C by bringing in the information from experimental measurements that include the measured emission current, the electron mobility of the CNT, the applied voltage, and the length and the diameter of grown CNT. Also, due to the σ -

π orbital hybridization in CNT, only one electron is provided by each carbon atom has the free electron in the π orbital. Thus, it is assumed that there are 190 carbon atoms be ionized simultaneously when a Coulomb explosion occurs based on the experimentally determined total charge. These 190 atoms are assumed to be the outermost carbon atoms at the tip of CNTs since only the outermost layer of carbon atoms can directly emit electrons into the vacuum and the electric field intensity at the tip of the CNT is the largest, leading to most of the electrons are emitted from the tip.

To simplify the model, the 190 carbon ions are considered to stay in the same plane. On the other hand, in order to form a stable structure, 190 carbon ions are arranged into five annular structures consistent with the sectional shape of CNT. Considering the effect of neutral carbon atoms (the carbon atoms are not ionized in the boundary), especially the short-range atom interactions on the ions at the outer ring of these 190 carbon ions, an additional 183 neutral carbon atoms are also added to the model. They are arranged into two rings similar to the MWNT structure, wrapped in the outer layer of those carbon ions. To ensure a typical distance of 3.4 Å between each CNT layer and the initial bond length to be approximately 1.42 Å [130,131], 8 and 68 ions are placed at the innermost and outermost ionized layers respectively. The structure of the model is shown in Figure 4.1, which consists of 190 carbon ions (red ball) plus 183 neutral atoms (black ball). Noted that the modeled structure is the atomic structure of the middle segment of CNT, not the actual atomic arrangement structure at the tip of CNT.

The whole structure is optimized by Avogadro Molecular Editor using the UFF force field. It is assumed that no Joule heat generated during the FE process, thus, the temperature is fixed to 300 K throughout the whole process. Furthermore, assuming that the whole structure is in a vacuum for FE, thus, the pressure is fixed at 0 Torr. At time $t=0$, all the atoms in the system are

set to be stationary, and each of the 190 inner carbon atoms releases an electron and obtains a positive elementary charge ($1.602 \times 10^{-19}\text{C}$). To set the appropriate time interval, the drifting velocity is calculated to be $9 \times 10^{13} \text{ } \mu\text{m/s}$ by using the electron mobility of multi-wall CNT (75 to $30000 \text{ cm}^2/\text{V}\cdot\text{s}$) and the external electric field from the experiment ($30 \text{ V}/\mu\text{m}$) [132,133]. Hence, the time for electrons to move in the π -bonds of the CNT should be on the order of 0.001 fs to 1 fs. Therefore, the time step in the simulation is chosen to be 0.001 fs.

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is used to calculate the total potential energy of the interactions between atoms due to the stretching of the bonds. The total potential energy in this model is approximately equal to the sum of the Coulomb energy and bond potential energy (the van der Waals energy is neglected because it is relatively small). The Coulomb repulsive energy between atoms can be calculated according to the Coulomb law,

$$E_{Coulomb} = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_i q_j}{r} \quad (4.5)$$

where ϵ_0 is the Vacuum permittivity, and q is the particle charges. In addition, before the bond broken, the potential energy is dominated by the bond energy that caused by the stretching of the bonds which follows the equation below,

$$E_{bond} = K(r - r_0)^2 \quad (4.6)$$

where r_0 is the equilibrium bond distance which is the initial bond length of $1.42 \text{ } \text{\AA}$ and K is the bond force constant which is around $680 \text{ kcal}/(\text{mol}\cdot\text{\AA}^2)$ [134]. Finally, the bonds would be stretched to be broken when the bond length exceeds its limitation which is $1.803 \text{ } \text{\AA}$ for the carbon-

carbon bond [135]. In the simulation, the positions, velocities, and force in each direction of all ions are obtained via numerical solution through the equations above at each time step. Moreover, Coulomb energy, and bond potential energy of the whole system are also calculated for each time step.

4.2.1 Simulation Results

Figure 4.2 shows the changes in Coulomb energy (red), total potential energy (black), kinetic energy (green), bond potential energy (blue) and average bond length (pink) in 100 steps (0.1 fs). At the beginning of the simulation ($t=0$), the 190 carbon atoms in the outermost layer of CNT emit an electron at the same time which leads to an increase of the FE current as observed in the experiment. There is a huge Coulomb repulsive energy generated between these positively charged carbon ions. Among those ionized atoms, the dramatically increased Coulomb repulsive energy causes the atoms repel from each other and stretching the carbon bonds. The stretched carbon bond subsequently increases the bonds' potential energy until the bonds are pulled to break. After the carbon bonds are broken, the Coulomb repulsive force continually provides repulsive energy to force each atom to disperse rapidly.

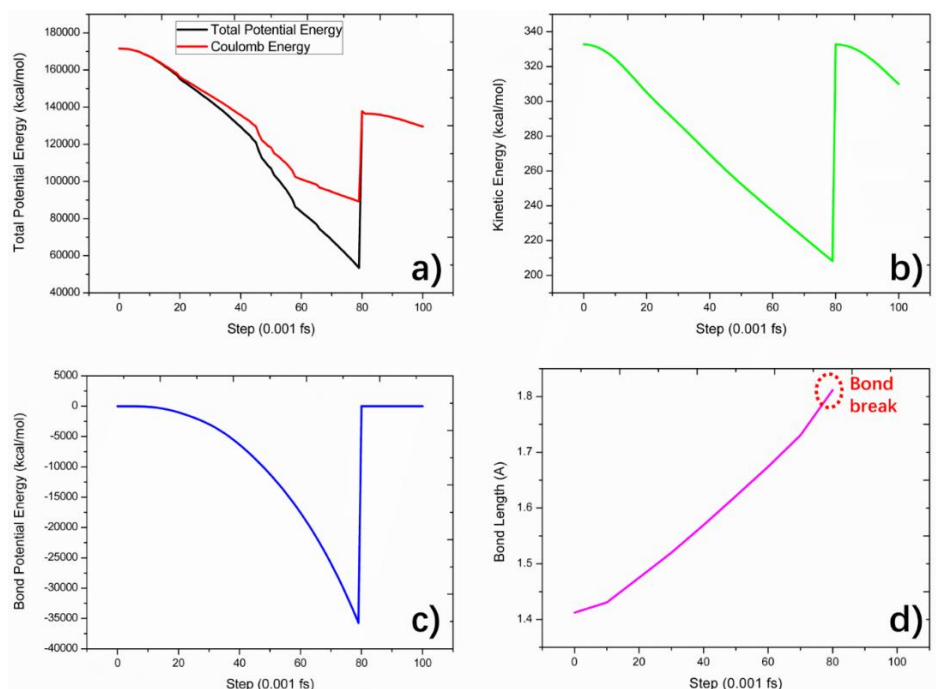


Figure 4.2 The plot of a) Coulomb energy and total potential energy, b) Kinetic Energy, c) bond potential energy caused by bond stretching in each step, and d) average bond length in 100 steps.

Figure 4.2 a, the total potential energy, which consists of Coulomb repulsive energy and bond potential energy almost equals to the Coulomb energy at the beginning, and it gradually becomes smaller than the Coulomb energy until the bonds are pulled to be broken. When $t=0$, the whole structure is in the equilibrium state, so the bond potential energy is zero. Since the bond energy is negatively enlarged as the bonds become lengthened, as a result the potential energy continuously decreases until it provides sufficient energy to shrink the bonds. However, before the contraction of bonds start, the bonds are broken, as their lengths exceed the maximum value which is $1.803 \text{ \AA}$ at 0.08 fs (Figure 4.2 d), and the maximum bond energy is calculated to be around $3.6 \times 10^4 \text{ kcal/mol}$ (considering different bond force constant for different type of CNTs this value would be changed). In addition, the bond breakage is verified by calculating whether the potential energy of the carbon bond is greater than the threshold energy required for breaking the bond,

which is 32600 kcal/mol in total. Thus, as shown in Figure 4.2 c, after around 0.075 fs, the bond potential energy exceeds this threshold value. Thus, this results again prove that the bonds are stretched to be broken at 0.08 fs. When the bonds break, the Coulomb energy and potential energy suddenly increases because of the loss of bond energy inhibition. So that the Coulomb energy originally used to overcome the bond contraction generated by the bond potential energy returns, and this part of the increased energy will contribute to the work of atoms repelling. Also, the increased potential energy would convert to kinetic energy and light causing the whole area to disintegrate quickly and generate a flash of light in an instance.

To further prove this hypothesis, an additional computational analysis was conducted in which the charges of ten carbon ions are randomly selected from those 190 ions. The charge of those selected ions are eliminated, while preserving their original positions within the CNT structure. This procedure was used to further assess the extent to which the Coulomb repulsion between charged carbon atoms plays a role in the occurrence of the Coulomb explosion. The results are shown in Figure 4.3. In this simulation, because of the smaller number of atoms are ionized, the bond between carbon atoms resisted longer times, where the bond was pull to be broken until step 89. Also, the initial value of total potential energy as well as the Coulomb energy was much smaller than that of the 1st simulation which is the result of removing the charges of the selected carbon atoms. As charges were partially removed, the number of charged atoms within the CNT decreased, leading to an increase in the average interatomic distance. And this results also applied to the bond potential energy. On the other hand, although there is obvious difference between these two calculations, the trend of the energy change during the testing was unchanged. This result provides empirical support for the hypothesis that Coulomb explosion is a possible failure mode

under high current density, regardless of the specific number or position of ionized atoms within the CNT structure.

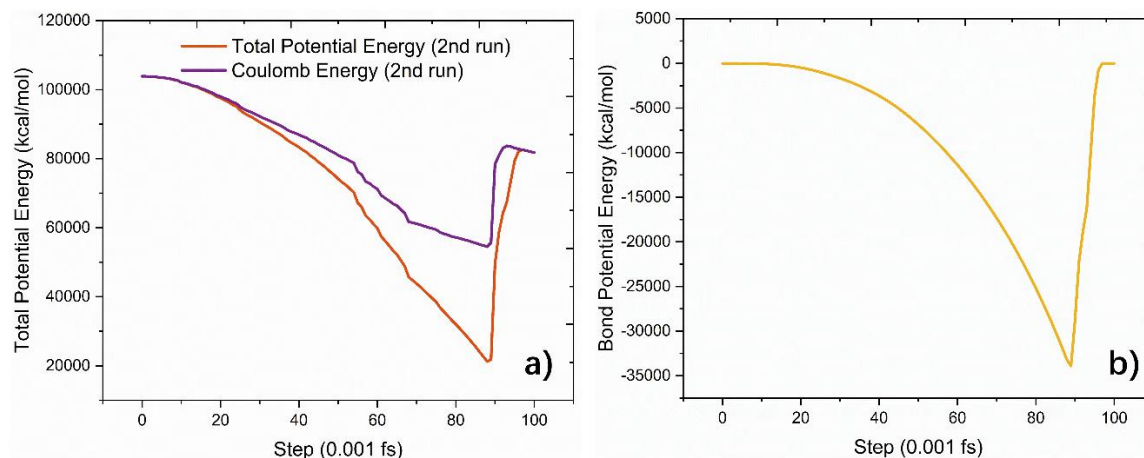


Figure 4.3 The plot of a) Coulomb energy and total potential energy, b) bond potential energy of 180-ions' model in 100 steps (10 random atoms are deionized).

The energy distribution includes potential energy and kinetic energy on each atom and ions in the sample at $t=0.05$, 0.08 and 0.1 fs are calculated and shown in Figure 4.4. In the beginning, most of the potential energy is accumulated at the center of the ionized region, The highest potential energy in the system at $t=0$ is approximately around 1200 kcal/mol at the most inner ring of ions, and it becomes smaller to around 800 kcal/mole at $t=0.05$ fs (Figure 4.4 a), which indicates the process of the bond energy negatively increases. At $t=0.08$ fs, as discussed above, the bonds are broken which causes the potential energy to quickly expand to the atoms on the outer rings (Figure 4.4 b). Finally, at $t= 0.1$ fs, the potential energy increases again with a more uniform distribution due to the rise of the Coulomb energy, and the release of the increased potential energy caused by the broken bonds at 0.08 fs. For the kinetic energy, from $t=0.05$ to $t=0.08$ fs, the kinetic energy decreases because the tightened carbon bonds inhibit the movement of atoms. However,

since the bond energy of the carbon atom is much less than the Coulomb energy of the ions, the bond energy is not sufficient to cause the bonds to contract, hence, the whole ring of the neutral atom will be pushed outward by the inner-layer ions instead of attracting them back. At $t=0.1\text{fs}$, the kinetic energy is released from the ions in inner rings to the outer rings.

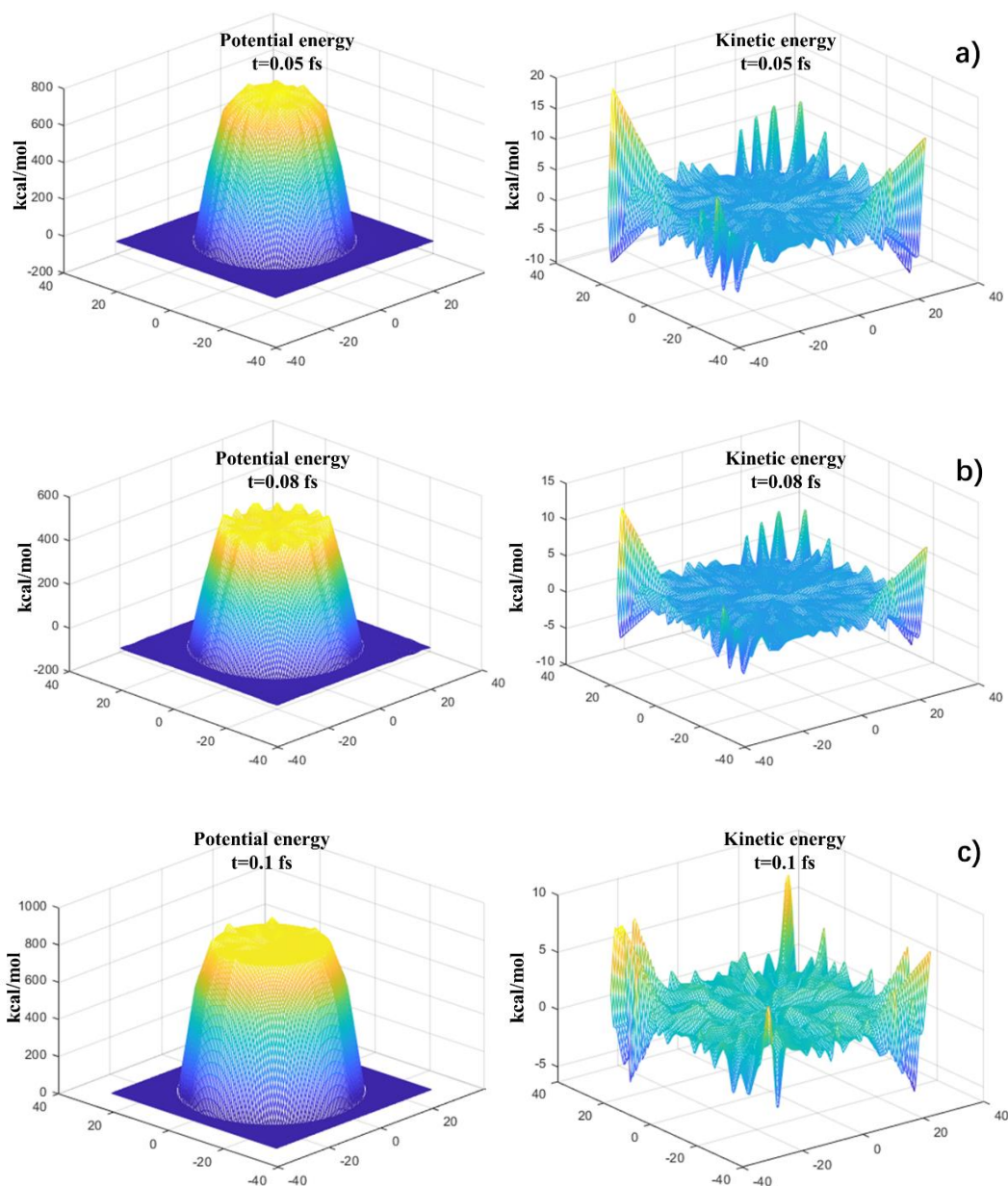


Figure 4.4 The potential energy and kinetic energy on each ion and atom at a) $t=0.05\text{ fs}$, b) $t=0.08\text{ fs}$ and c) $t=0.1\text{ fs}$

4.3 Analysis of CNT Coulomb Explosion

By analyzing the recorded videos, SEM images, and emission current, the entire process of Coulomb explosion induced by CNT FE can be described in three steps. The first step is achieving charges. In this step, with the rising of the emission current, the field electron emission begins, and electrons flow through the entire vertical CNT along the electric field, which leads to the charging and ionization of the carbon atoms on the tips of CNTs. It usually first happens on the longest CNT, that the longest CNTs require more time to drain the accumulated charges to the ground (electrons require more time to reach the ionized atoms on the tips), also the longest CNT first performs FE because of the space charge limit, and then evaporates and shortens, allowing the second long CNT start field emission. In the second step, after the charging of the carbon atoms, the Coulomb repulsion of the atom in that CNT rapidly rise. The Coulomb repulsion energy converts to the kinetic energy of atoms, causing the atoms to move far away from each other and stretching the bonds. Finally, when the bonds are pulled to be broken, the Coulomb repulsive energy would further compel the atoms to be scattered, which makes the atomic structure of the whole CNT unbalanced, resulting in the collapse of the whole structure. When the disintegration occurs on the CNTs, the flashlight occurs. In addition, with the impact of the CNT disintegration and the acceleration of Coulomb repulsion force and the strong electrostatic force, the charged carbon ions sputter along the strong electrostatic field on the anode forms the black patterns on PMMA film, and the impact of the explosion also forms the craters on the substrate. Different from our previous experiment conducted by Li et al., there is no obvious light emission occurs

before the Coulomb explosion because there is only little Joule heat generated during the FE process when a protective pad which also worked as the buffer layer made of Cr with good heat conduction is deposited under each CNT. Instead of the light emission, a flashlight is captured that flashes at the same time as the explosion in a very short time. This phenomenon can be verified from the above simulation results. From the simulation, it is known that at the moment of explosion, a large amount of potential energy is accumulated in the whole system. These energies are released at the moment of explosion, resulting in a large amount of light energy, kinetic energy, and heat energy. The kinetic energy and the external electric field force a large number of atoms to bombard the surrounding Si substrate and Cr pads at a very fast speed during diffusion, forming a huge crater.

Thus, the causes of the whole Coulomb explosion and the causes of these phenomena have all been studied. The way to avoid the occurrence of the Coulomb explosion is also important to be discussed. In the experiments, by using two different setups of cathodes, there have two very different results. Since a more uniform CNT array will get a more uniform field emission current, and because the current is small, the ionized carbon atoms are reduced, and not enough Coulomb potential energy can be accumulated in a short time, so the probability of Coulomb explosion will be greatly reduced. Also, the Coulomb explosion may be caused by the defect of CNT. In the synthesizing process of CNT in PECVD, there will be defects due to the ion irradiation damage or uneven electric field [136–139]. Because Ni is used as the catalyst for growing CNT, these defects mainly consist of Ni particles, especially at the tip of CNTs [140]. These Ni would also be ionized during FE, and Ni ions will form a Ni-C bond with the carbon ions during the FE process, resulting in the lengthening of atoms' distance ($\sim 1.65 \text{ \AA}$ for Ni-C bond), and so decreasing the Coulomb energy [141]. Therefore, when carbon ions are ionized, carbon ions near Ni atoms will receive

greater Coulomb force. Moreover, because the bond energy of c-c (3.61 eV) is greater than that of Ni-Ni (2.1 eV), the ionized Ni ion will be more likely to break the bonds under stretching force, resulting in more possible for occurring Coulomb explosion. Thus, growing more uniform and high-quality CNT with fewer defects could reduce the possibility of the occurrence of the Coulomb explosion. However, due to the demand of a large number of CNT for FE in applications that require high emission current, it is difficult to fabricate a uniform large array. Thus, the way to fabricate a very uniform and large number of CNT arrays still needs to be studied.

In addition, according to equations (1) (4) and (5), the higher applying voltage causes higher drifting velocity which would promote electrons replenishing holes faster, however, the higher applying voltage can also generate a larger current. Therefore, adding a resistance layer to a short circuit can reduce the current and make the Coulomb energy not easy to accumulate. There have been reported that extending the lifetime of CNT by depositing a ballast layer. However, this method will sacrifice the emission current. Here a possible solution without sacrificing current is proposed. Learn the current change trend before the Coulomb explosion through the machine learning method, predict whether the Coulomb explosion will occur with probability, reduce the emission current when the Coulomb explosion is about to occur, then, gradually increase the emission current after the longest CNT currently being field emission is burned short in the process of emission current.

4.4 Chapter Summary

The experimental data are substituted into the modeling and simulation to calculate and analyze the changing trend of the energy at each time point in the process of the Coulomb

explosion. The simulation results indicate that as 190 carbon atoms are ionized at the same time, the coulomb energy in the system can reach 1.7×10^5 kcal/mol in an instant, which causes the bonds to be broken in 0.08 fs leading to the Coulomb explosion. Therefore, an in-depth investigation of Coulomb explosion in CNTs has revealed that the primary cause of this failure phenomenon is the broken of CNT bonds. As a result, efforts have been directed towards developing strategies to protect CNTs from such failures under high field emission currents, or to enhance their fundamental properties to improve their resistance to degradation. Based on the analysis, several methods to avoid the Coulomb explosion are also proposed. Fabricating more uniform CNT cathode and higher quality CNTs, adding a resistive layer to limit emission current, or reducing the voltage before the explosion by the prediction through artificial intelligence (AI) machine learning can effectively reduce the probability of an explosion. By utilizing predictive modeling, it becomes possible to adjust the emission current with appropriate timing, hence, allowing sufficient cooling time before increasing the current once again. This effectively mitigate the detrimental effects of high current densities on the stability and longevity of CNTs. On the other hand, although the Coulomb explosion has a fatal impact on FE, it may have its usable value for other applications, such as surface treatment, etching, and ablation, or other applications that require ion or particle bombardment.

Chapter 5 Improvement of Field Emission Performances by DMSO and PEDOT: PSS Treated Freestanding CNT Clusters

5.1 Chapter Introduction

After the study of Chapter 4, the investigation of Coulomb explosion has highlighted the critical importance of protecting individual CNTs from excessive current density in order to improve their FE lifetime. Accordingly, developing effective strategies to mitigate the risk of CNT damage under high current conditions has become a key research focus in this thesis, with the aim of enhancing the longevity and stability of CNT-based devices and systems. As also mentioned in Chapter 2, it has been reported that only a small percentage of CNTs is contributing to the overall current emitted from an array of CNTs. Under this condition, most of the CNTs are dormant. As such, a large amount of current passes through those small numbers of CNTs, allowing Joule heat to accumulate and ultimately destroy the CNTs [106,107]. Therefore, in order to improve the lifetime of CNT emitters and the stability of FE, many studies have been focused on how to slow down or eliminate the degradation of CNTs. Most of the research is aimed at achieving uniform current distribution by using different methods to fabricate more uniform CNT films or arrays to avoid heat concentration on a few CNTs [142,143]. On the other hand, there are also other ways to reduce degradation, including limiting the maximum current through the CNT to a safe range [144], or cooling down the CNT so that the accumulated heat does not rise rapidly [145]. However, these methods are less effective when CNT emitters are used in applications that require continuous high-emission current. Hence, because of the low lifetime of CNT field emitters,

researchers gradually turned to find other carbon materials with better field emission properties, such as diamonds, or nanowalls [146–150]. These carbon-based field emitters have been measured to have lower turn-on voltages and more stable emission currents and longer lifetimes, especially after certain chemical treatments. However, these types of emitters usually have relatively more complex and costly fabrication processes. Therefore, researchers are still devoted to investigating methods for further improvements in the FE performance of CNT field emitters, which include reducing the turn-on electric field and improving the FE stability and lifetime of CNT emitters.

In some recent studies, it was reported that after some specific treatments, such as adding polymer to form CNT-polymer composites [114], using microwave-assisted acid treatment [115], doping [151], or synthesizing process [125], the turn-on electric field and the emission stability of CNT emitters are improved. Also, it was found that after vertically aligned CNT or other nanotubes or fibers were immersed in a solution or a droplet and dried, the tubes would be tilted and be self-assembled into a cluster ranging from a few microns to tens of microns, that is similar in shape to pyramid-like structures [152–158]. It is considered that this binding effect is the result of attractive capillary forces that are generated during the evaporative drying process [159]. During the evaporation process, the droplets pass through the tiny gaps between the nanotubes and bring them closer to each other. After the droplets evaporated, the Van der Waals forces take place and keep the entire bundle from unraveling and sticking tightly together [160,161]. By this means of binding the CNTs together, the properties of the emitters are greatly altered. In addition, due to the different solutions used for treating the structures, the resultant CNT clusters are different in shape and can be divided into two categories: (i) island-like structure (larger bundled area but less sharp tip); and (ii) pyramid-like structure (sharper tip but smaller bundled area) [152]. However, there are only a few studies on the FE performance of CNTs with such cluster structures formed after the treatment

of solution, and almost no studies comparing the FE performance of CNT clusters with different structures formed by different treatments [162].

In this chapter, two treatment methods are developed to improve the length-randomness of grown vertically aligned CNT forests and enhance the FE properties of CNTs. By treating the CNT forest with dimethyl sulfoxide (DMSO) and poly (3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT: PSS) solutions, the CNT would be bundled into clusters. CNTs after two different treatments form different cluster structures. Three types of CNT emitters: (i) untreated; (ii) DMSO treated; and (iii) PEDOT: PSS treated CNT emitters, are characterized in terms of turn-on electric field and long-term FE respectively to demonstrate and compare their FE performance. On the other hand, theoretical analyses are presented to illustrate the reasons for the occurrence of these different FE properties by analyzing their FE current curves, FE uniformity, and the observation of the post-FE structure.

5.2 Experimental methods

The details of the design and the structure of the CNT cathodes are described in Figure 5.1. The freestanding vertically aligned CNTs were synthesized by the plasma-enhanced chemical vapor deposition (PECVD) method on Si substrate with a pre-deposited Ni catalyst layer and Cr buffer layer. In addition, an integrated insulation spacer is deposited on the Si substrate to control the distance between the cathode and anode. The DMSO solution and PEDOT: PSS solution are prepared to treat the CNTs, and a comparison of the FE performance of the different self-assembled CNTs is presented.

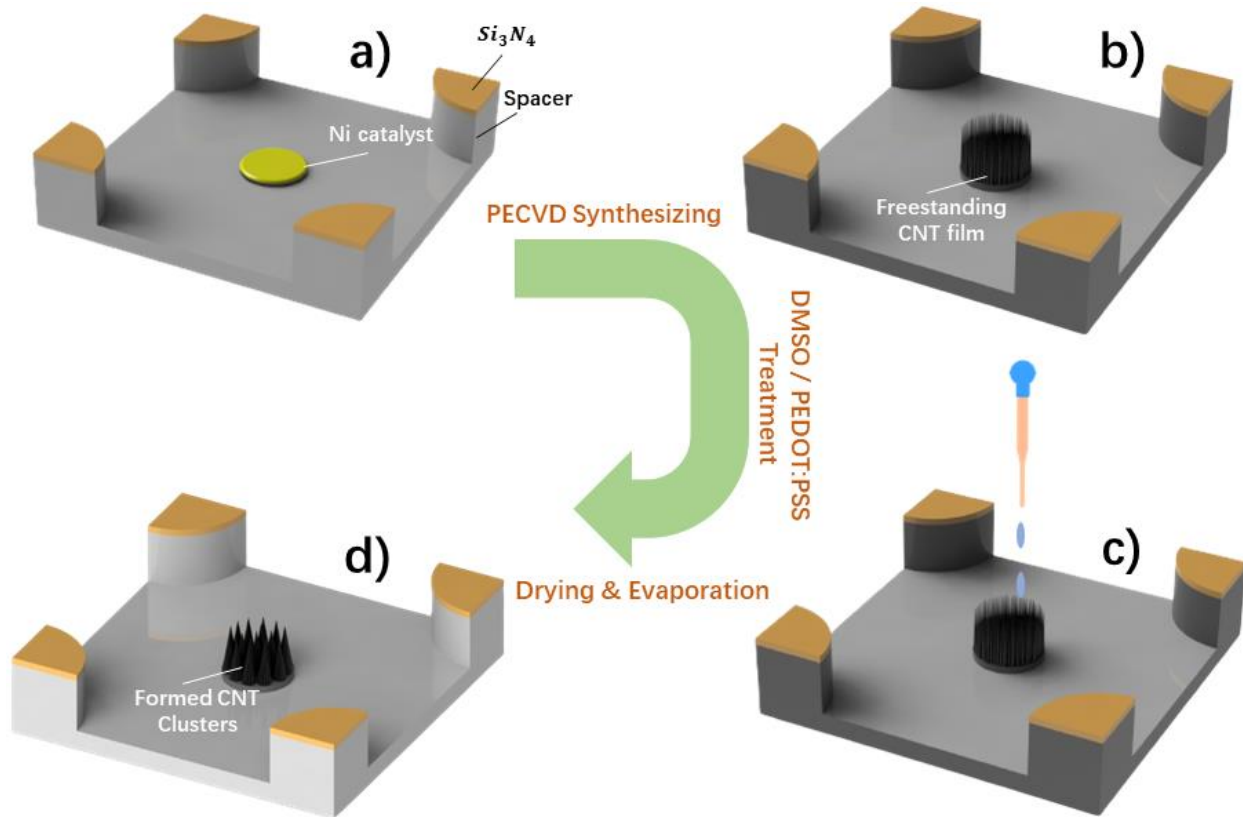


Figure 5.1 Process flow of CNT cluster fabrication: a) Ni catalyst deposition on a spacer-integrated Si substrate, b) CNT synthesizing via PECVD method, c) chemical treatment by DMSO/PEDOT: PSS, d) formed CNT clusters after drying process.

5.2.1 Fabrication process

The fabrication of the CNT array starts from the deposition of a Si_3N_4 insulation layer on a p-type Si substrate, followed by an etching process to form a 50 μm deep distance-fixed spacer structure. The resistance of the Si substrate is around 1 M Ω . The Cr buffer layer and the Ni catalyst layer are then patterned into a circle with a diameter of 1 mm and thicknesses of 10 nm and 40 nm, respectively, using a photolithography method. The CNTs are then synthesized by a PECVD system (Black Magic, Aixtron, Germany) for 20 min. Acetylene (C_2H_2 , 50sccm) and ammonia

(NH₃, 200sccm) are used for the growth of CNTs. After growing the CNTs, 100 μ L of DMSO and PEDOT: PSS solutions were separately dropped in the area of CNTs. For DMSO treatment the CNTs were immersed in the droplet and naturally dried. For PEDOT: PSS treatment, the CNTs were immersed in the solution for 15 min, then, the residual PEDOT: PSS solution was removed with DI water and dried at room temperature.

5.2.2 Measurement & Characterization Methods

For FE testing, a patterned ITO coated glass anode is added directly on top of the integrated spacer. The ITO pattern allows only the area on the glass anode where directly above the CNT region that grows on the cathode to be conductive and keeps the other regions insulated. A 200nm polymethyl methacrylate (PMMA) film is spin-coated on the ITO glass to test the FE uniformity of CNT emitters without and with two different treatments (Figure 5.2). A negative bias voltage of 0-500V and a positive bias voltage of 0-1000V was applied to the cathode and anode separately to reduce the risk of high voltage breakdown of the vacuum chamber. The applied bias and the emission currents were monitored using a Keithley DMM-6500 multimeter to evaluate the turn-on voltage, the I-V characteristic, and stability during the FE process. In addition, a 5 M Ω resistor is connected in series between the anode and the positive power source to protect the equipment (the add-on resistance would lower the emission current during the testing [163]). The FE tests were performed in a vacuum chamber at 10⁻⁹ Torr. In addition, the turn-on/threshold voltage is measured by slowly increasing the bias voltage from 0V until an emission current is generated. On the other hand, long-term FE testing is carried out to test the lifetime and stability of the CNT

cathode with and without solution treatment. The test starts with a 50uA initial emission current and is left running continuously for 80h.

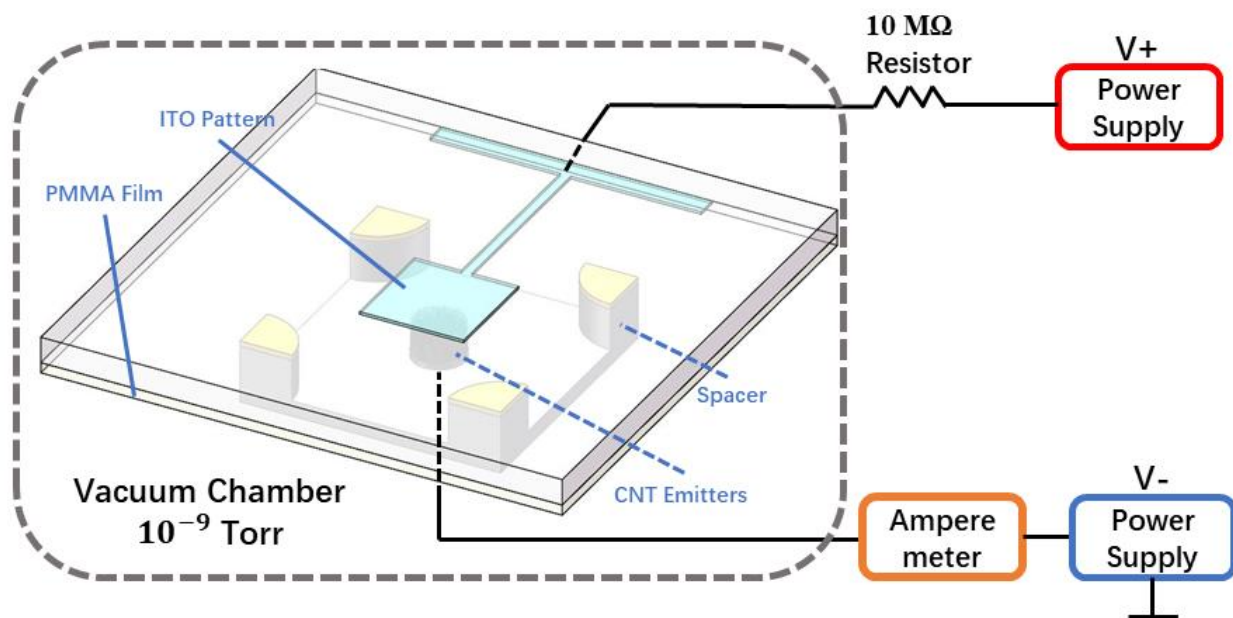


Figure 5.2 Experimental setup & cathode-anode connection diagram.

The morphology of the vertically aligned CNT films was characterized by scanning electron microscopy (SEM) (JEOL JSM-7200F) separately before and after the FE process. Raman spectroscopy with 785 nm of visible laser excitation and X-ray photoelectron spectroscopy (XPS; VJ ESCALAB 250) were used to characterize the chemical composition and chemical bond after the treatment of DMSO and PEDOT: PSS.

5.3 Results and discussion

5.3.1 Morphology Comparison of CNT Bundles Before and After Treatments

Figure 5.3 shows the SEM image with a 15° tilted angle from the top view. The structure of CNT film before and after solution treatment is observed. For the CNT cathode before the treatment, after the PECVD process, the Ni-coated area grows a full layer of vertically aligned CNTs, with a length of about 9 μm to 12 μm . The tip diameter is around 5 nm and the base diameter is around 200 nm. For PEDOT: PSS treated CNT cathode (Figure 5.3 c & f), after the treatment, the CNTs are gathered together into pyramid-like clusters with a slight bend. The clusters form a quite uniform size, the average diameter of these conical pyramid-like clusters is around 3 μm in size. On the other hand, after being treated with DMSO, the CNTs tilted and clustered together to form many conical island-like bundles (Figure 5.3 b & e). These islands form in random sizes, with the smallest ones being cones of about 1 micron in diameter and the largest ones reaching about 8 microns in diameter. In comparison, the micro-pattern formed by the PEDOT: PSS treatment will form sharper tips.

For both treatments, the main reason for this phenomenon is that the strong capillary forces force the liquid to force the CNTs close to each other after flowing through the narrow gaps between them, causing the CNTs to not only bind together but also bend. After the liquid is evaporated, the molecular forces between each of them keep the CNTs in close proximity without being separated. For PEDOT: PSS treatment, the mechanism for the bundling effect is different from DMSO treatment and Yan et al. proposed a possible theory [152]. After soaking CNT in PEDOT: PSS solution, a layer of solution will be coated around the periphery of CNT, resulting in CNT getting negative charges. With these negative charges, the Coulomb repulsion force pushes

CNTs closer and makes the micro-pattern different from the result of treatment with DMSO solution, forming sharper tips with a more uniform size of clusters. In addition, the CNTs in the center of each bundle remain perpendicular to the substrate, and so the formed clusters inherit both the tip diameter and the length of the longest CNT in the entire CNT cluster. The size of this tip is critical for FE, as it determines the FE enhancement factor of the entire CNT bundle as well as the turn-on/threshold voltage.

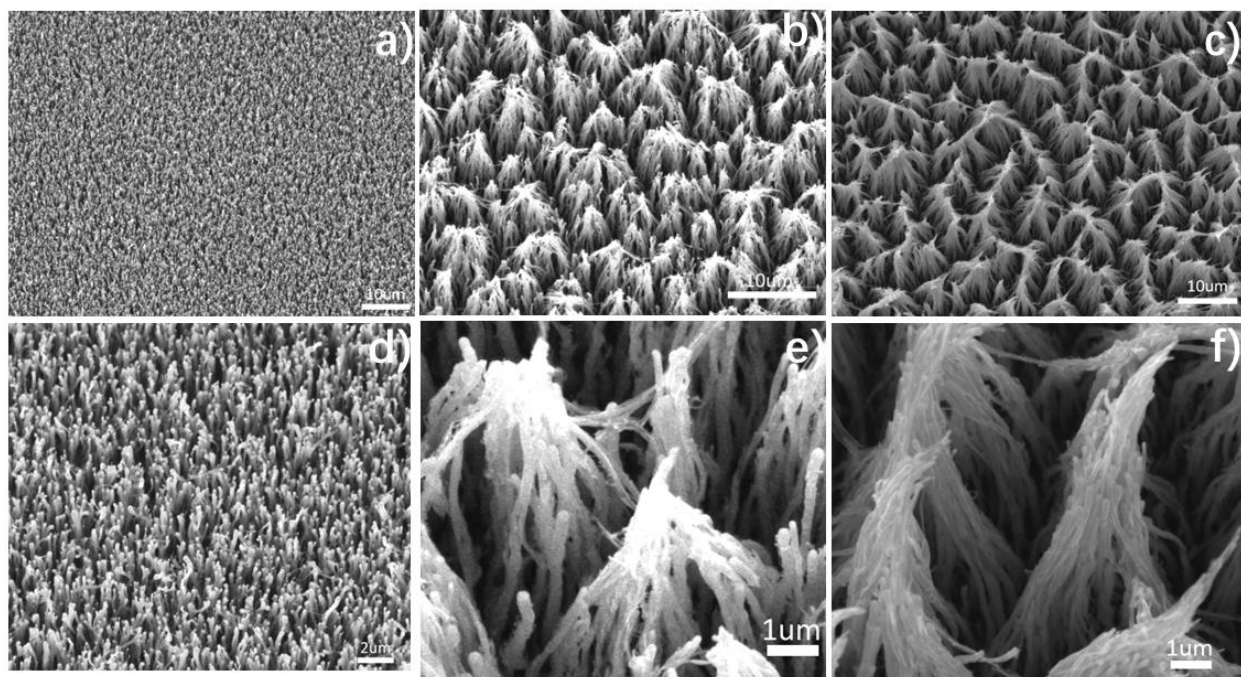


Figure 5.3 SEM image of a) untreated, b) DMSO treated, and c) PEDOT: PSS treated CNT cathode; Expanded image of d) untreated, e) DMSO treated, f) PEDOT: PSS treated CNT cathode.

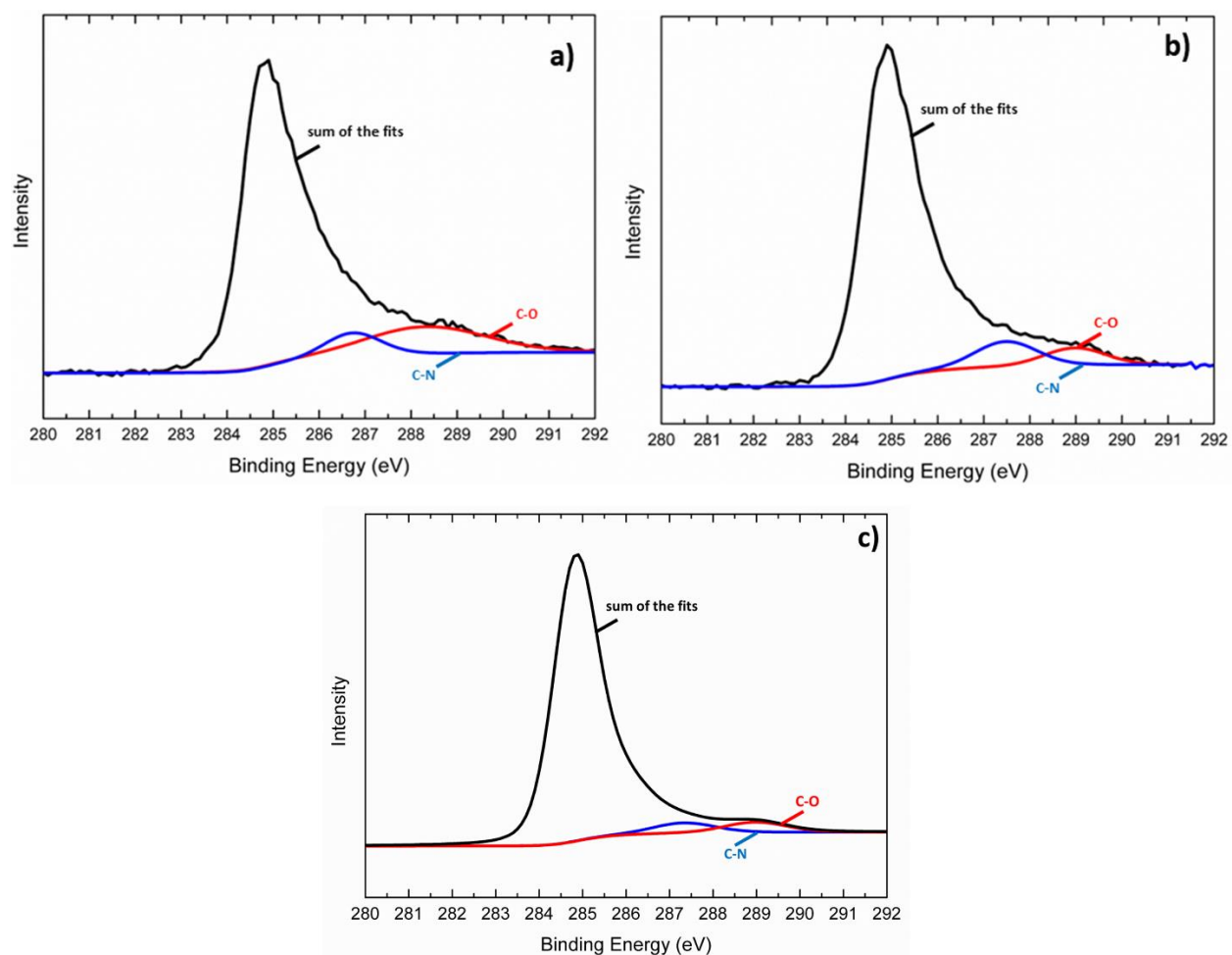


Figure 5.4 The C 1s XPS spectra of CNT emitters. a) without treatment, b) with DMSO treatment, c) with PEDOT: PSS treatment.

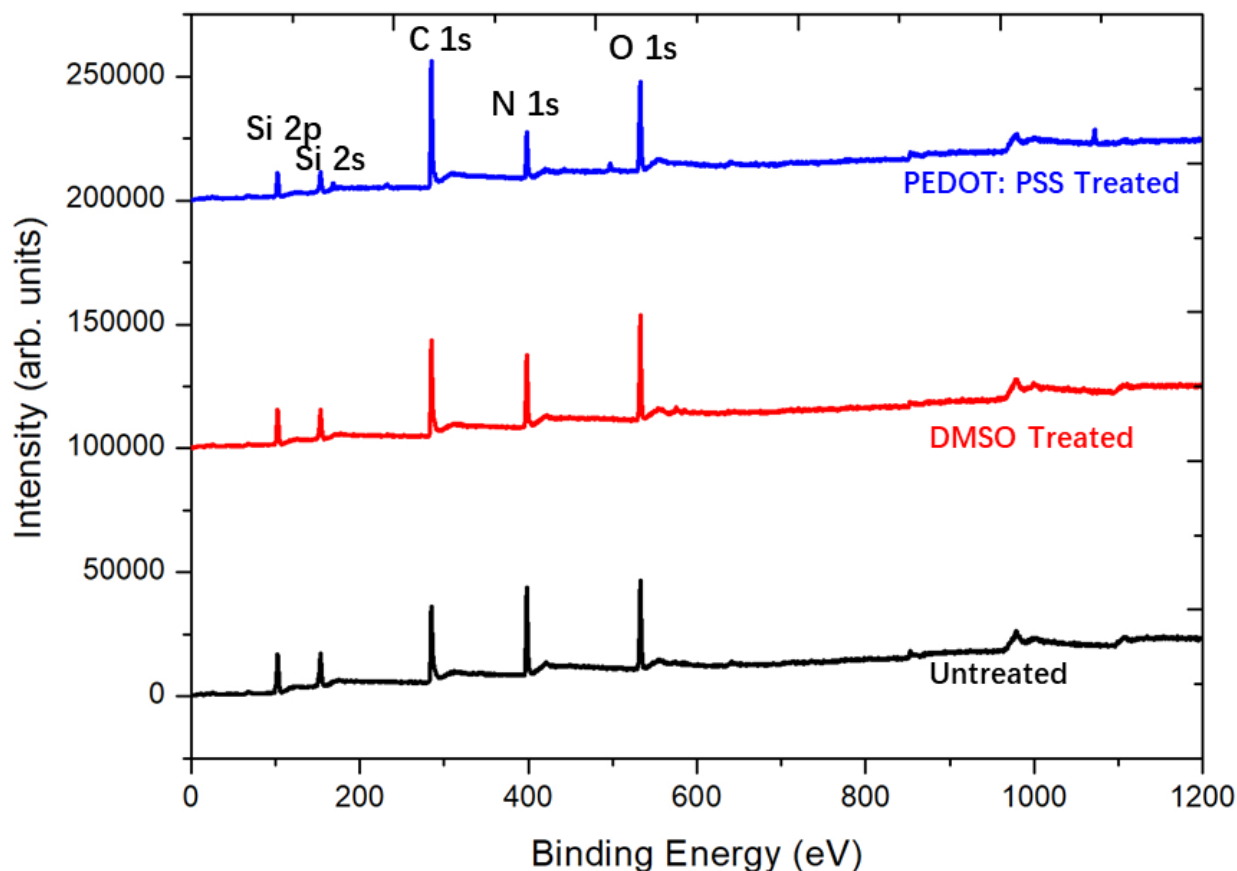


Figure 5.5 XPS spectra of untreated CNT emitter (black), DMSO treated CNT emitter (red), and PEDOT: PSS treated CNT (blue)

After the treatment, although the structure of the CNT emitter changed, the chemical composition and bonds remain unchanged based on the results of XPS (Figure 5.4 & Figure 5.5) and Raman spectroscopy (Figure 5.6). According to the XPS results, the major C1s peak for all three types of CNTs is around 284.7 eV. The peak values of C-O and C-N are around 288.3 and 286.6 eV for untreated one, and approximately 288.8 and 287.5 eV for DMSO and PEDOT: PSS treated samples, respectively. Both treatments resulted in a positive shift of C-O and C-N, which is mainly because residual DMSO and PEDOT: PSS solutions with higher oxidation states resulting in the higher binding energy of C-C, C-O, and C-N were detected when XPS was

performed [164,165]. Furthermore, according to Figure 5.5, the increase in the peak intensity of C1s after both treatments is also caused by residual DMSO and PEDOT:PSS, which are both carbon-based. In addition, the peak intensity of C1s is lower because DMSO is more volatile than PEDOT: PSS, resulting in less residue on CNTs. Conversely, the peak intensity of the detected N1s is lower due to the CNTs being covered by residual solutions.

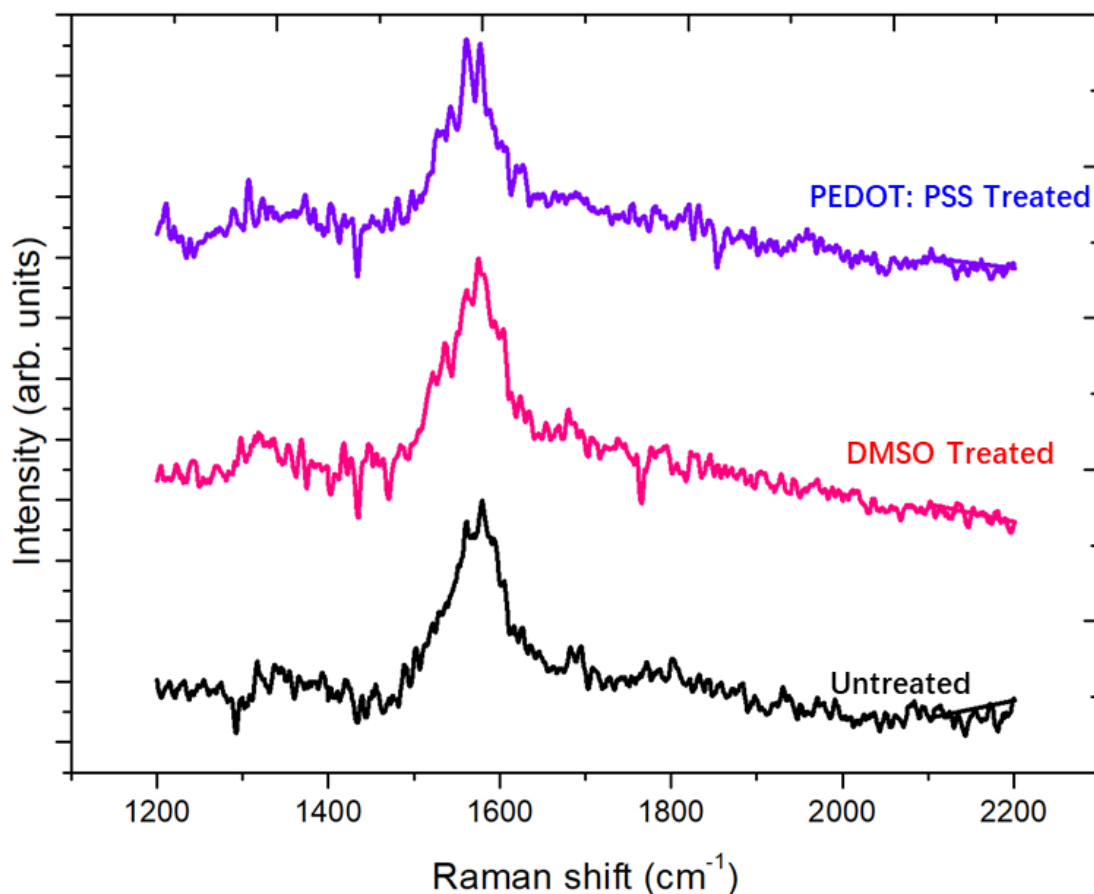


Figure 5.6 Visible Raman spectra of untreated CNT emitter (black), DMSO treated CNT emitter (red), and PEDOT: PSS treated CNT (blue)

5.3.2 Turn-on Electric Field Characterization

The current density versus applied electric field as the field emission characteristics of vertically aligned CNT before and after DMSO and PEDOT: PSS treatment is shown in Figure 5.7, where the turn-on fields for these different types of vertically aligned CNT cathodes are directly compared. During the FE testing, the applied field was controlled by the increase and decrease of applying bias. The distance between the cathode and anode is fixed to be 50 μm . In addition, in order to examine the turn-on electric field, the bias voltage was steadily and gradually increased from 0V to 1000V in 60 seconds, and the electric field required to reach the emission current of 20 $\mu\text{A}\cdot\text{cm}^{-2}$ for the first time is recorded as turn-on field. Therefore, as shown in Figure 5.7, for the bare CNT cathode without treatment, the turn-on field is around 12 V/ μm , and the current density increases to 7500 $\mu\text{A}\cdot\text{cm}^{-2}$ as the applied field reaches 15 V/ μm . After the treatment with DMSO and PEDOT: PSS solution, the turn-on fields become smaller compared to the cathode without treatment. For the DMSO-treated CNT emitters, the turn-on field is reduced by 30% with respect to the untreated cathode, where the turn-on field becomes around 8 V/ μm , and the current density reaches 12500 $\mu\text{A}\cdot\text{cm}^{-2}$ as the applied bias increases to 15 V/ μm . For the emitters after PEDOT: PSS treatment, the turn-on field is greatly reduced to 4 V/ μm . In addition, the current density rises much faster with increasing applied electric field than the untreated and DMSO-treated ones, in which the emission current density rapidly increases to around 25000 $\mu\text{A}\cdot\text{cm}^{-2}$ at the applied bias of 15 V/ μm .

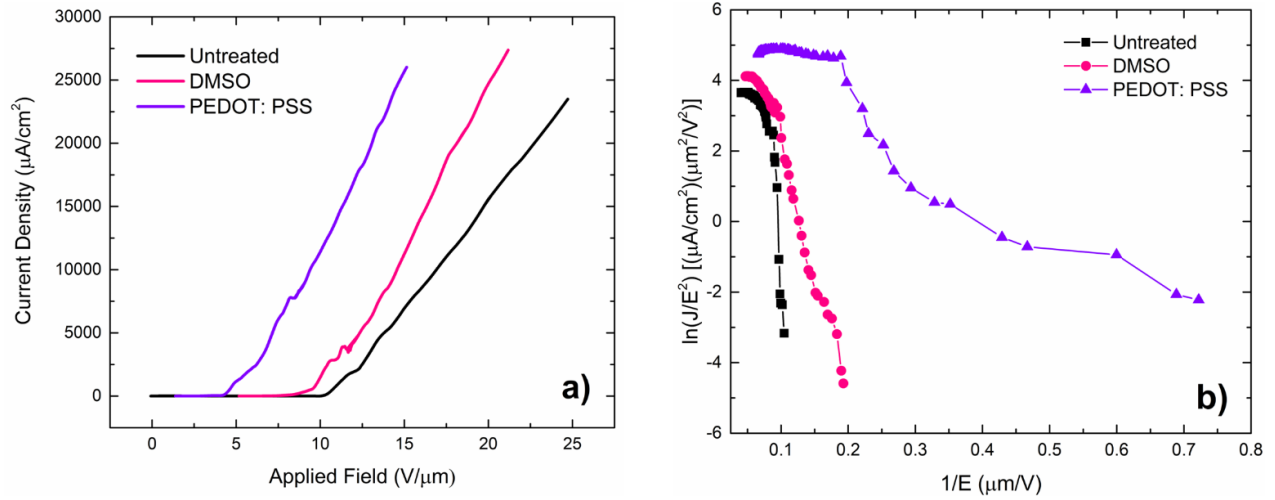


Figure 5.7 a) Field emission current density (J) versus applied field (E) characteristics of untreated CNTs, DMSO treated CNTs, and PEDOT: PSS treated CNTs. b) F-N plot corresponding to a), and typical liner fit to each set of data are shown by solid lines. (This turn-on electrical field includes the voltage assigned to the add-on serially connected resistor and the resistance of the Si substrate)

Theoretically, the difference in FE turn-on field between the treated and untreated CNT emitters is mainly caused by the change of the enhancement factor β of the CNT field emitters (equation (4.1)). The larger β will cause the turn-on field to become smaller and the FE efficiency will also be greatly improved (equation (4.3)). For the same length, the smaller the emitting radius, the stronger the resulting electric field strength. In addition, considering the screening effect, in the case of a uniform array of vertically aligned nanotubes, the electric potential formed near the tip of each nanotube is shielded by the neighboring CNTs [166], and the overall turn-on field becomes smaller because the CNT becomes sparser after being treated with the solution. Thus, for DMSO-treated CNT emitters, although the diameter of the island-like cluster tip R_a becomes larger after DMSO treatment, the shielding effect becomes smaller because of the larger cluster-to-cluster spacing, leading to a smaller turn-on field and better FE efficiency than the untreated one. On the other hand, compared to the DMSO-treated CNT emitters, after being treated with

PEDOT: PSS solution the CNT clusters are sharper and more uniform, leading to the lowest turn-on field and most efficient FE performance among these three types of emitters.

5.3.3 Long-term Stability & Lifetime Testing

To further compare the FE performance of the three types of CNT emitters, long-term testing is conducted to evaluate the stability and lifetime of each type with the same sample size and distance between the electrodes. The variation of the current during the test is shown in Figure 5.8. At the beginning of the test, the applied bias was gradually increased until the emission current reaches 50 μA for each emitter and was kept constant for the test. This set current allows the CNT emitters to have a large enough starting current at which the CNTs are expected to start to be burned slowly due to Joule heating, but not high enough to cause arcing that would terminate the FE process due to the high instantaneous current on a single CNT. For untreated CNT emitters, after about 5 hours of continuous current emitting, there was a significant drop in current from 50 μA to 45 μA and followed by a slower continuous drop for the next 40 hours to around 70% of the initial emission current (35 μA). The current is much more stable after 45h because the melting of CNTs is slowed down due to less heat accumulation at this current level. Although there is occasionally a small rebound in current, it drops again in a few hours and becomes lower than before the rebound. For the emitters after DMSO treatment, the long-term FE performance varies greatly. The current was overall stable with a slight upward trend and started to increase to about 54 μA after about 15 hours. After a period of stable emission current (from 15 hours to 25 hours), the current decrease back to the value before the increase and keep on cycling with such a tendency during the whole testing. On the other hand, CNT emitters treated with PEDOT: PSS also exhibit

different long-term FE performances. Compared to the other two CNT emitters, the FE lifetime and long-term stability of the PEDOT: PSS-treated emitter is the best. The current starts to increase about 20 minutes after the start of emission, decreases only slightly after 5 hours, and stabilizes after 10 hours. There is almost no decrease throughout the whole 80 hours of long-term emission, and the emission current is more stable than the other two types of emitters.

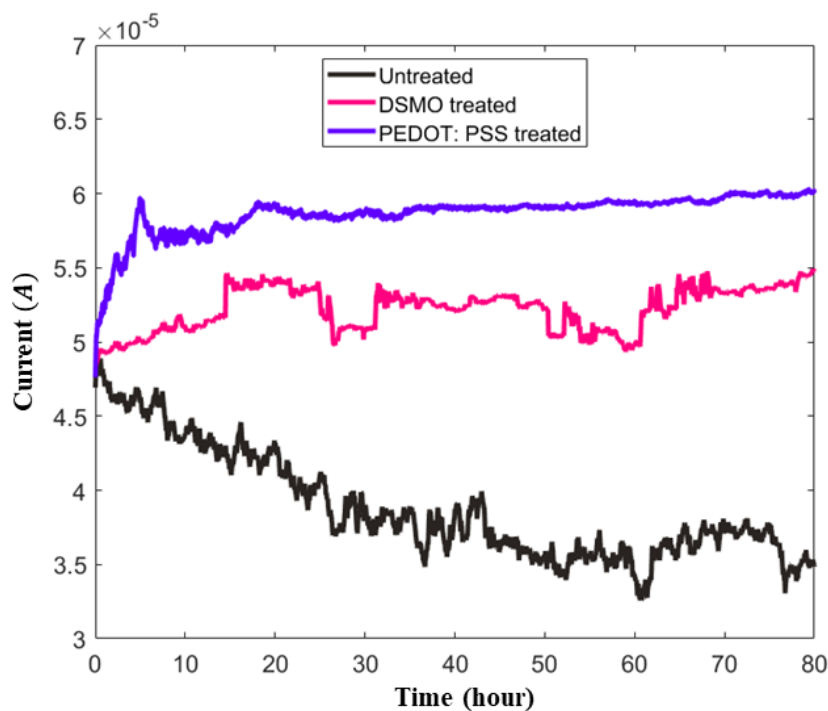


Figure 5.8 Long-term lifetime and stability testing current (I) versus time (t) of untreated CNTs, DMSO treated CNTs, and PEDOT: PSS treated CNTs.

The results of the long-term FE testing indicate that the treatment of CNT emitter by DMSO and PEDOT: PSS solutions result in a significant improvement in the lifetime of the CNT emitter, and different solution treatment has a different influence on the performance. To investigate the cause of such a large difference in the lifetime of CNT emitters that are treated by

different methods, these different emitters are observed under SEM after 80 hours of the FE process to be compared with the before-testing morphology (Figure 5.9). For the untreated CNT emitters, the continuous drop in emission current is due to the continuous burning of the CNT emitter throughout the FE process. The structure change after 80 hours of FE is shown in Figure 5.9 a & d that most of the CNTs fell down due to burnt roots. For the emitters treated by DMSO solution, because the formation of the island-like structures is equivalent to connecting a range of CNTs in parallel, the newly synthesized emitters would have smaller resistance, which reduces the generation of Joule heat and avoids the burning of CNTs. In addition, compared to the structure of untreated one, CNT emitters treated with DMSO have only a few damaged areas that scattered due to the burning of the upper aggregation point by Joule heating, but most of the area remains the same as before the emission, with the entire cluster upright on the substrate (Figure 5.9 b and e). Moreover, the cause of the field emission current fluctuating continuously in the case of long-term field emission can be explained as follow: i) the longest CNT clusters would first start to emit the current, and at the beginning of the emission, due to the generation of Joule heat, the thermionic emission will assist the emission that leads to the Schottky emission, resulting in the rise of current; ii) the residual degassed elements chemically react with the CNT, that the reactions are assisted by the generation of Joule heat [167,168]. After a period of FE, the CNT in the cluster would start to be evaporated by the Joule heat at the locations with the largest defects, which causes the decrease of emission current. As soon as these longer clusters are burned, those shorter CNT clusters will start FE, so that the current rises again. For emitters after PEDOT: PSS treatment, like the DMSO-treated one, the cluster structure has a lower resistance than individual freestanding CNTs, hence, a longer lifetime is observed. Moreover, the structure after 80 hours of FE is also similar to that of the DMSO-treated emitter which only small areas are burned during FE, and most of the clusters

remain. In addition, as shown in Figure 5.9 c and f, after long-term testing, the sharp tips of the clusters are burned, leaving blunt tips that are reconsolidated from melted CNTs. Although the tips of the clusters seem to be cut off, there still exists the longest CNTs in each cluster, allowing the FE to continue without any significant current degradation. Hence, although the turn-on electric field is not significantly improved and is still much higher than many reported ultralow turn-on field emitters, these two treatments methods greatly extend the lifetime of CNT emitters, which is longer than the lifetime of those field emitters with lower turn-on electric field. emitters [114,115,125,146–150,169,170]. Therefore, this simple and cost-saving treatment gives CNT emitters an advantage over other types of CNT emitters as well as other carbon material-based ones.

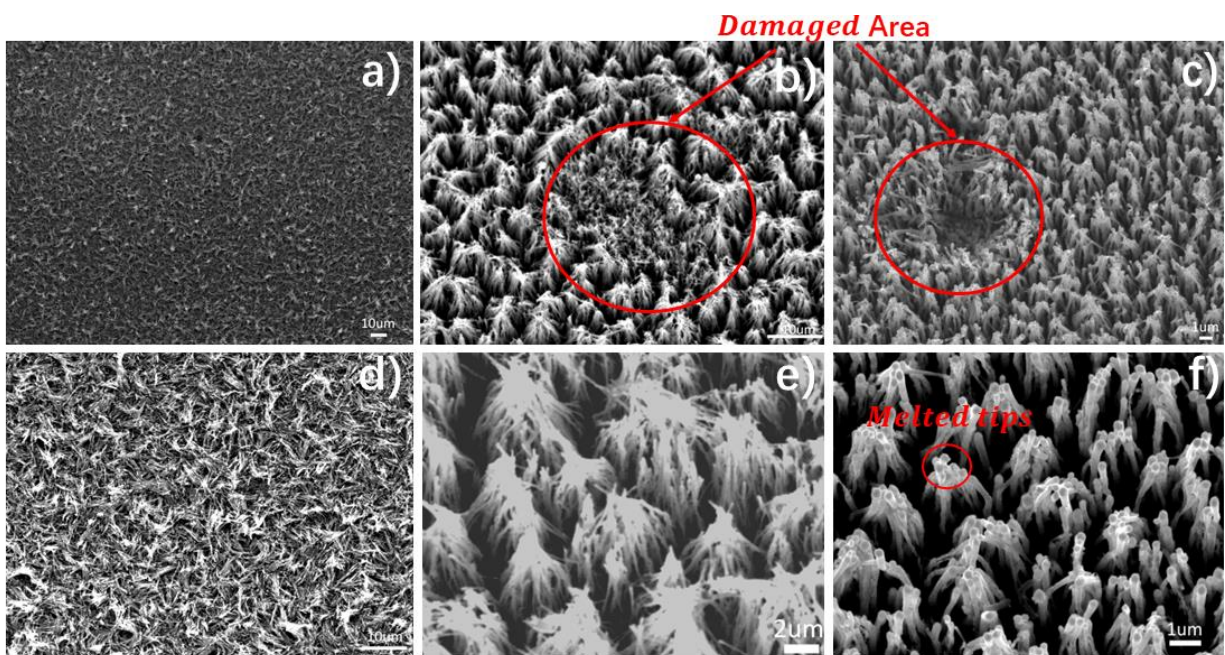


Figure 5.9 SEM image of CNT structure after 80 hours of FE for a) untreated, b) DMSO treated, and c) PEDOT: PSS treated CNT cathode; Expanded image of d) untreated, e) DMSO treated, f) PEDOT: PSS treated CNT cathode.

5.3.4 Uniformity Testing

As a positive electron-beam lithography resist, PMMA film is sensitive to electron exposure. The exposed area can be developed by (methyl isobutyl ketone (MIBK): isopropyl alcohol (IPA) solution) to reveal the electron exposure pattern [107]. During the FE process, the electrons emitted from CNT emitters would expose the PMMA and leave a trace after the PMMA film is developed. From these exposed traces, it can be inferred which areas of the CNT array were emitting electrons and the number of active CNTs over a period of time. This test was performed after increasing the emission current from 0 to 55 μ A and keeping the voltage constant for 5 minutes. For untreated CNT emitter, only a few areas are exposed by electrons which means only a small portion of CNTs was active during the 5-minute FE process (Figure 5.10 a). This result further explains the short emission lifetime of untreated CNTs due to the large amount of current that traveled through the few emitting CNTs which resulted in degrading the CNTs. After treatment with DMSO (Figure 5.10 b), it is shown that the areas with electron exposure on PMMA film were significantly increased. The larger exposed area represents that more CNTs were emitting simultaneously during testing, which allows DMSO-treated CNT to have a longer lifetime. The current from each emitter is reduced as the total current is contributed by more emitters, thus, slowing down the degradation process which, in turn, increases the emitter's lifetime. Lastly, it was determined that PEDOT: PSS treated CNT emitters further improve the emission uniformity with an even larger exposed area on the PMMA film. which led to a lower current from each CNT cluster. As the result, the emission current is distributed more evenly among the emitters and so the PEDOT: PSS treated CNT emitters have the longest lifetime and most stable emission current among these three types.

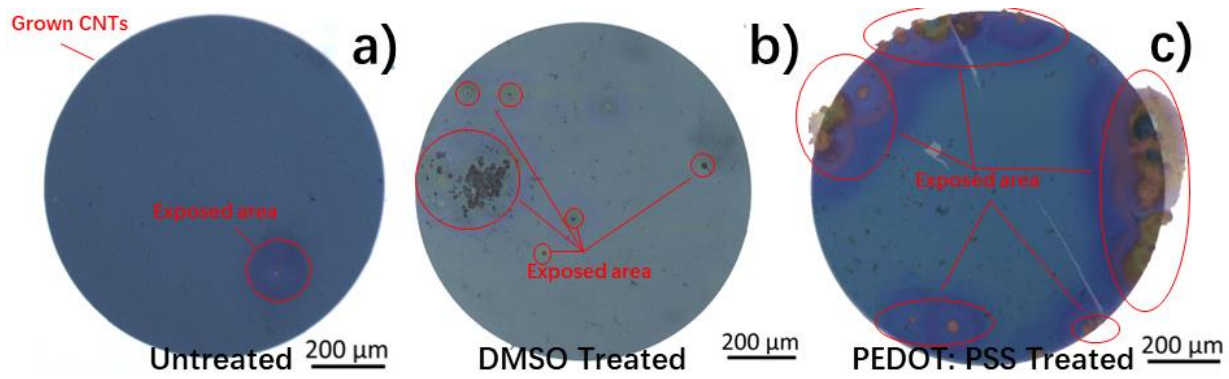


Figure 5.10 Exposure trace on PMMA layer for a) untreated, b) DMSO treated and c) PEDOT: PSS treated CNT emitters.

5.4 Chapter Summary

In this chapter, the FE performance of untreated, DMSO, and PEDOT: PSS treated CNT emitters are investigated and compared. With the treatments, vertically aligned CNT are bundled into many clusters and improve the FE performance. The FE performance for different types of treated or untreated CNT field emitters is summarised in Table 2. According to the SEM observation, the CNT emitters treated by PEDOT: PSS has sharper tips of cluster and better uniformity in terms of cluster size than that of the DMSO treatment. There are three main improvements in FE performance after the treatments: (i) both treatments reduce the emission turn-on electric fields and increase the FE efficiency by lowering the screening effect; (ii) the treatments increase the number of CNTs that are simultaneously contributing to the overall current and thereby improving the emission uniformity, and reducing current emission required per CNTs; (iii) both treatments significantly improve the long-term FE performance of CNT emitters as the results of the improved emission uniformity and the reduction of Joule heat generation. These two

treatment methods solve the fatal problem of the short FE lifetime of CNT to a certain extent by slowing down the degradation speed of CNT during the FE process.

Table 2 Summary of FE performance of untreated, DMSO treated, and PEDOT: PSS treated CNT field emitters.

	Turn-on electric field (V/ μm)	Current degradation during 80 hours	Current stability	Uniformity
Untreated	12	12	poor	poor
DMSO treated	8	No degradation	poor	better
PEDOT: PSS treated	4	Current increased by 10 μA	good	best

Chapter 6 Advancement of Field Emission Lifetime of Freestanding VACNTs by Coating Metallic Protective Layer

6.1 Chapter Introduction

Before the emergence of the CNT field emitters, researchers experimented with applying a metallic layer on vertically aligned Si field emitter array to improve FE properties [171]. This kind of Si emitters with a metallic shell around the surface shows better FE uniformity and stability than bare Si emitters. In addition, after CNT-based field emitters were investigated, many studies used metal-particle-doped CNTs or directly depositing metal layers on CNT films to improve FE properties [120,121,123,172,173]. However, there remains a lack of detailed study on coating metal shells on low-density freestanding VACNT arrays for improving the FE performance, especially in terms of increasing their lifetime. Therefore, finding a feasible, and stable method to improve the FE performance of low-density freestanding VACNTs is required.

In this study, a method that uniformly coats a metallic layer on freestanding VACNT array is proposed to improve FE performance. VACNT array coated with different types of metal shells with various thicknesses are designed and fabricated to investigate the improvement of FE performance by comparing the results of uncoated CNTs with each type of coated CNTs. Three metals, Ti, W, and Au are selected as metallic shells. The VACNTs coated with these metals were characterized in terms of their turn-on electric field, long-term lifetime and stability. The investigation on the role of metal coatings and their thickness on FE properties were comprehensively performed and the structural changes of VACNT were observed.

6.2 Materials & Methods

6.2.1 Material Selection

Generally, the four most critical features for a good field emitter are i) the size of the emission tips; ii) the electrical conductivity; iii) the melting point and thermal conductivity, and iv) the work function. Since VACNTs already possess an extremely good aspect ratio, the improvement can be made by adjusting the electrical conductivity, melting point, thermal conductivity, or the work function of emitters by coating a metallic layer. Increasing the electrical conductivity and work function could directly increase the emission current. Raising the melting point of emitters would reduce the risk of emitting tip degradation. Similarly, increasing the thermal conductivity so that heat can be conducted to the substrate more effectively which will, in turn, eliminate the heat accumulated at the emitter tips and reduce the change of emitter meltdown. Thus, W with the highest melting point and lower work function than CNT is selected as a potential candidate for a metal shell that can enhance the FE performance. In addition, Au and Ti were selected for comparison purposes. Au has good electrical and thermal conductivity but a higher work function, while Ti has a lower work function but poorer electrical and thermal conductivity. In addition, considering the smaller surface energy of Au, 2 nm of Ti was deposited between CNTs and the Au shells to obtain better adhesion between the two materials.

6.2.2 Fabrication Methods

The cathode consists of a 7 mm × 7 mm Si substrate on which a VACNT array is grown at the center. The freestanding array was synthesized by plasma-enhanced chemical vapor deposition

(PECVD) method on p-type <100> Si substrate. Ni and Cr are deposited as catalyst and buffer layer. The array is composed of 2,000 uniformly distributed VACNTs within a circle of 1 mm diameter. The distance between each VACNT was 20 μm . The detailed fabrication process is summarized into four steps (Figure 6.1). First, a circular array of Cr buffer pads is deposited on the Si substrate with a thickness of 150 nm. Subsequently, Ni catalyst dots aligned with Cr pads were patterned by electron-beam lithography and deposited by an electron-beam evaporator on the Cr buffer layer (the diameter of Ni dots is 100 nm, and the thicknesses are 80 nm). Then, VACNTs were synthesized by a PECVD system (Black Magic, Aixtron, Germany). Acetylene and ammonia were used for the growth of VACNTs. After these process, freestanding VACNT array with an average length of 10 μm were fabricated. In order to have good bonding strength between metal coatings and VACNTs, the processing parameters are controlled to limit the carbon accumulation during PECVD process, resulting in low surface roughness of CNTs. The growth time, heating power and plasma power were set to be 20 min, 550 W and 70 W respectively, After the growth of VACNTs, a metallic layer was deposited on the outer surface of VACNTs via a sputtering method (AJA ATC Orion Series) with different thicknesses for comparison. To ensure the uniformity of the deposited metals, deposition rate was precisely controlled for different metals (6.0 nm/min for Ti, 47 nm/min for Au, and 11.6 nm/min for W).

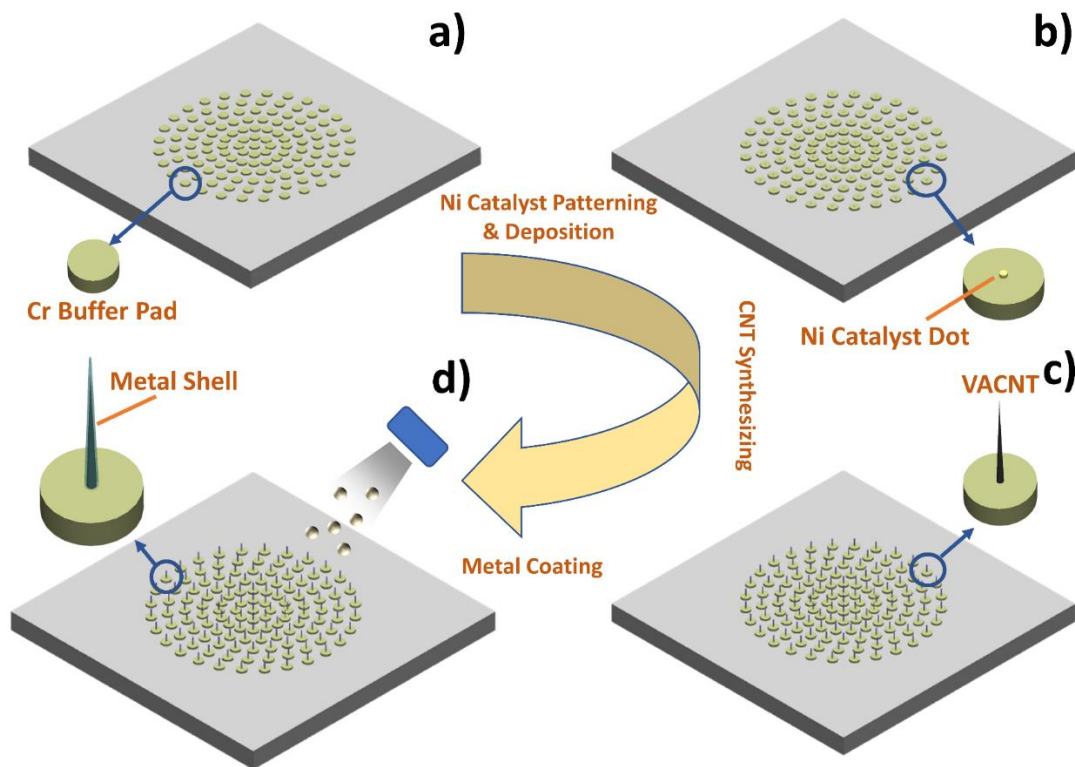


Figure 6.1 Process flow of metal coated VACNT fabrication: a) Cr buffer pad patterning and deposition, b) Ni catalyst dots patterning and deposition, c) CNT synthesizing via PECVD method, d) metal shell coating via sputter.

6.2.3 Measurement & Characterization Methods

A patterned ITO coated glass is applied as the anode. By using a 50 μm polytetrafluoroethylene (PTFE) film as a spacer between CNT cathode and ITO anode, the distance between the two electrodes was firmly fixed during FE. In order to reduce the risk of electric arcing between electrodes, the ITO pattern only allows the region directly above the VACNT area to be conductive while keeping other areas insulated (Figure 6.2). The CNT cathode was connected to a negative power supply (DC, 0-5000 V) and the ITO coated anode was grounded. In addition, two Keithley DMM-65000 multimeters were used to collect the emission current and applied voltage data at a

high frequency to record the fast and random fluctuation of the emission current during FE process. Furthermore, to protect the equipment, a resistance of 5 M Ω was connected in series between the cathode and the negative power supply (the add-on resistance has limited effect on the turn-on electrical field during the testing [163]). The entire FE testing was performed in a vacuum chamber at 10⁻⁹ Torr. The degassing process was performed by running the testing continuously for 20 min with an applied bias that was just below the turn-on voltage before the actual FE tests. To test the turn-on electric field, the bias voltage applied on the cathode was gradually increased from 0 until the emission current reached 50 μ A. In this test, the current density is calculated by dividing the measured current by the area of the anode. Since the anode is a circle with a diameter of 1 mm, the test terminated current (50 μ A) was 6.3 mA/cm². In addition, the lifetime and stability testing were carried out through long-term FE testing that started at the initial emission current density of 6.5 mA·cm⁻² and stopped until the emission current dropped below 4 mA·cm⁻² or over 48 hours.

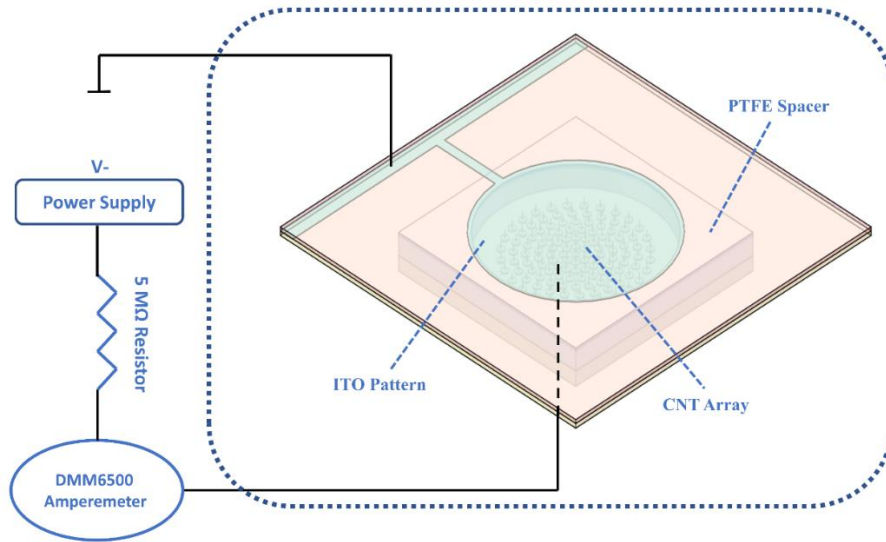


Figure 6.2 Experimental setup & circuit connection diagram. Negative bias is added on CNT coated and the ITO-coated glass anode is connected to the ground. A 50 μ m PTFE spacer is added between the cathode and anode.

The morphology of the VACNT arrays was characterized by scanning electron microscopy (SEM) (JEOL JSM-7200F) before and after the FE process. In addition, electron energy loss spectroscopy (EELS) was used to detect the content of the coated metals and their distribution on the CNTs. High-resolution transmission electron microscopy (TEM) (Talos 200X) was used to observe the thickness and uniformity of different metal coats on VACNTs.

6.3 Results and discussion

6.3.1 Morphology of Metal-coated CNT

Figure 6.3 shows the SEM image of different types of metal-coated VACNT and bare VACNT with a 15° tilted angle from the top view. The VACNTs were vertically grown at the center of the Cr pads where Ni dots were deposited after the PECVD process (Figure 6.3a). The average tip diameter is around 50 nm, and the average base diameter is around 350 nm. The formation of the tapered structure is mainly due to the plasma etching effect that reduced the size of Ni catalyst during the PECVD process [174]. For VACNT without a coated metal shell (Figure 6.3b), some distortions were found on VACNTs, and there was no other material with significant contrast was observed on the surface of CNTs. For Ti-coated CNTs as well as Au- and W-coated CNTs, distinct "scale-like" coverages of the CNT surfaces can be observed, uniformly covering the entire profile of the CNTs and with higher contrast between the shells and the substrate than for bare CNTs.

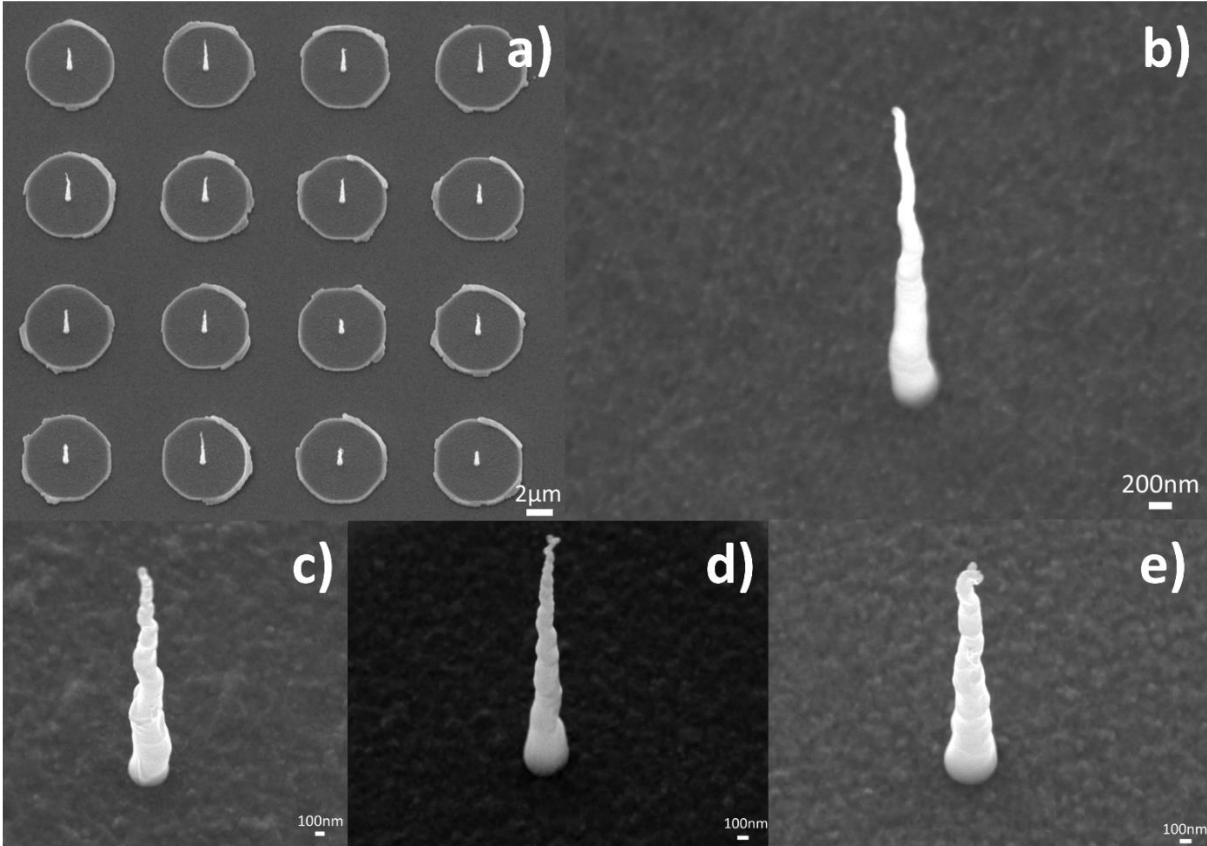


Figure 6.3 SEM image of a) freestanding VACNT array, b) bare VACNT, c) titanium coated, d) gold coated, and e) tungsten coated individual VACNT.

For metal-coated VACNT, the cause of the "scale-like" coverages is mainly due to the uneven thickness along the length of the CNT. The CNT can be seen as a cone structure with some bent sections. Since the metal material is sputtered from a source at the top of the CNT tips with some angles to the surface of the CNT, the lower surface of the bent portion on the surface cannot be covered by the sputtered material, so the scale-like laminar metal cover is formed. Also, because the density of the metal coating is greater than that of carbon, it has a higher contrast with respect

to the substrate. In addition, since the density of W and Au are larger than Ti, the contrast is more pronounced, and the scale-like coverings can be more clearly observed.

Figure 6.4 shows the TEM image and EELS results that focused on a single 5 nm W-coated VACNT tip. Uniform thickness of W coatings was found at the tip portion of the VACNT (Figure 6.4c), with only a slightly larger thickness on the top of the tip than on the side (5 nm on the side and 7 nm on the tip). In addition, according to the EELS results, the Ni catalyst dot is topped by the CNT grown along the electric field to the very tip during the PECVD process (Figure 6.4b).

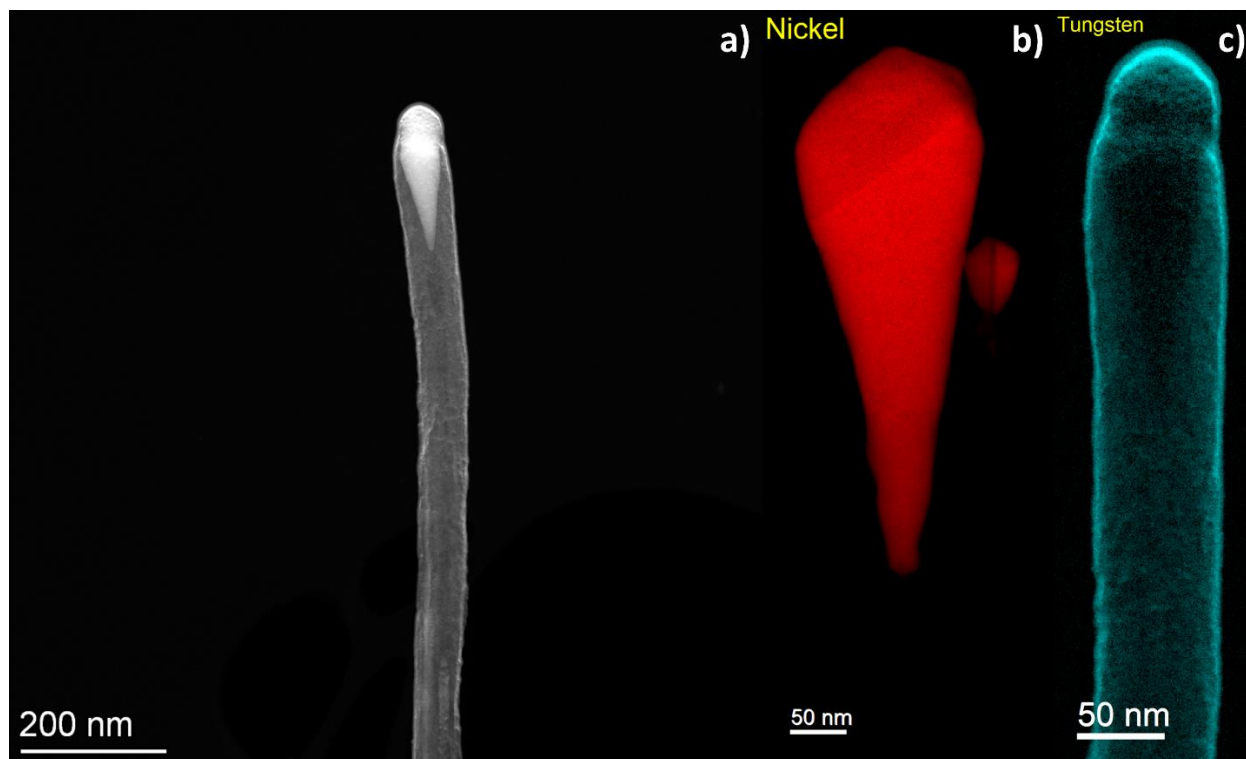


Figure 6.4 a) TEM image of the single VACNT tip. b) EELS analysis of Ni element on the VACNT tip. c) EELS analysis of tungsten element on the surface of the VACNT.

6.3.2 Turn-on Electric Field Characterization

The current density versus the applied electric field during the FE turn-on testing is shown in Figure 6.5. The plots directly compare the turn-on electric field of VACNTs coated with three different metal shells and same thickness. The corresponding electric field is recorded as the turn-on electric field when the emission current first reaches $100 \mu\text{A}\cdot\text{cm}^{-2}$. The applied bias voltage was slowly increased until the current density reached $6.5 \text{ mA}\cdot\text{cm}^{-2}$ to prevent the VACNT being exploded. For the bare VACNT without coatings, the turn-on electric field is around $6 \text{ V}/\mu\text{m}$, and the emission current density increases to $6.5 \text{ mA}\cdot\text{cm}^{-2}$ as the applied electric field increases to $14 \text{ V}/\mu\text{m}$. The turn-on electric field of Ti-coated emitter is lowered to be around $4.5 \text{ V}/\mu\text{m}$, and this type of VACNT requires $12 \text{ V}/\mu\text{m}$ to reach the current density of $6.5 \text{ mA}\cdot\text{cm}^{-2}$. For W and Au coated VACNT, the obtained turn-on electric fields are larger than that of the bare CNT which are around $7 \text{ V}/\mu\text{m}$ and $8 \text{ V}/\mu\text{m}$ respectively, to reach the desired current density, the electric field needs to be $15 \text{ V}/\mu\text{m}$ for W coated sample, and $17 \text{ V}/\mu\text{m}$ for Au coated emitter.

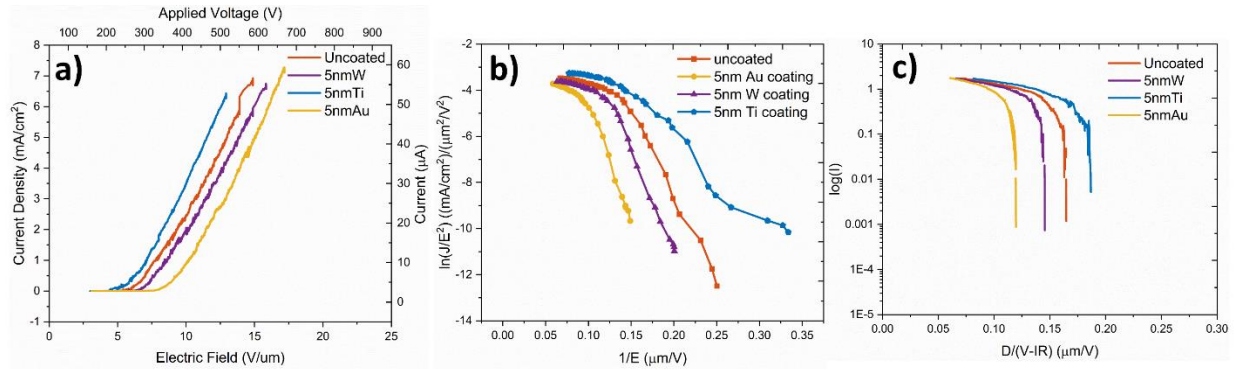


Figure 6.5 a) Field emission current density (J) versus applied field (E) characteristics of bare VACNTs and three types of metal coated VACNTs. b) F-N plot corresponding to a).

Theoretically, the difference in FE turn-on field between different types of emitters is mainly due to the various enhancement factor β and the work function of the material which based on the Fowler-Nordheim equation. The screening effect is ignored here because the distance between each CNTs is enough larger. In the case of metal-coated VACNT field emitters, the enhancement factor would become smaller as the tip diameter is increased by coating thicker metal shells [55]. Therefore, in order to obtain a better turn-on field voltage, all three metals are only deposited on the CNT surface with a thickness of 5 nm. Because the work function of the Ti bulk (~ 4.3 eV) is much smaller than the CNT (~ 4.8 eV), and thinner film generally leads to a lower work function ($\Delta \phi \sim 0.1$ eV) [175], thus, a slight decrease in turn-on electric field was observed for Ti coated VACNT, which was also reported in other study [123]. Moreover, Au has the highest work function among the three selected metals (~ 5.3 eV for the bulk), which leads to the largest turn-on electric field. In addition, although W has a similar work function with CNT, due to decrease of the enhancement factor after coating, W-coated sample was tested to have higher turn-on electric field than bare VACNT. These results of work function and field enhancement factor difference are also proved by the difference in slopes of Millikan-Lauritsen shown in Figure 6.5c (Here using Distance between cathode and anode dividing by the applied voltage on the gap replace to $1/E$ to show precise results on the difference of work function and enhancement factor). In addition, the variation of the slope of Ti coated sample may be because of the degassing as the emission current increases, resulting in the fluctuation of the emission current at low electric field region. Therefore, the metal coatings on the CNT surface have some effect on the turn-on electric field of the FE. However, the work function of these metal-coated VACNT do not differ much from each other, so that the variation of the turn-on electric field is not significant.

6.3.3 Lifetime & Stability Testing

The lifetime is another critical FE characteristic for field emitters. Very often, it may be considered to be more important than the turn-on electric field. Therefore, to further study the FE performance of metal-coated CNT emitters, long-term FE testing was conducted to evaluate the effect of three types of metal coatings and different coating thickness on lifetime as well as the long-term stability. Overall, as shown in Figure 6.6, regardless of the type of coating and coating thickness, with a constant electric field, the current density decreases as the CNT degrades, which affect the total lifetime of the cathode. Since these three types of metal shells have different properties, which is expected to result in different degradation speed. Here, because of the large difference in lifetimes, the results are divided into two groups to show better details. The samples with relatively small improvements in a lifetime are plotted in Figure 6.6a, and the coated VACNTs with significant improvements in FE lifetime are plotted together (Figure 6.6b). For the uncoated VACNT (orange line), the quick degradation speed led to a short lifetime which only lasted around 1 hour before the current density decreased from 6.5 to $4 \text{ mA} \cdot \text{cm}^{-2}$. For the VACNT that was coated with 5 nm and 10 nm Ti, the total lifetime of FE increased to 3 hours and 8 hours respectively. In addition, except for one surge of current density at approximately 5.8 hours, which was caused by an electric discharge between the cathode and the anode, the overall long-term stability of the VACNT coated with 10 nm Ti is better than that of the uncoated one, and the one coated with 5 nm Ti.

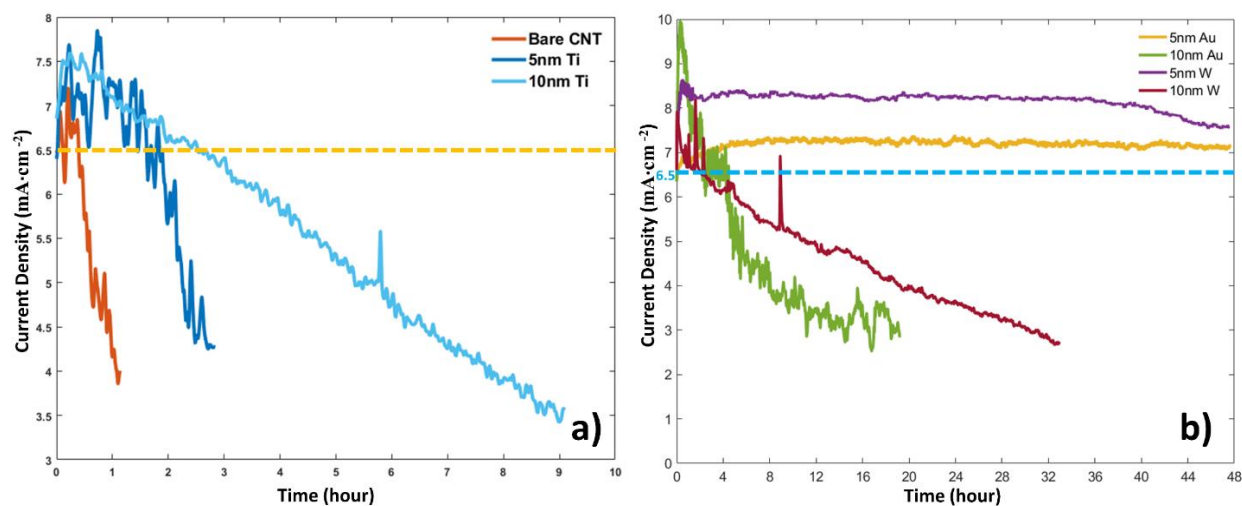


Figure 6.6 Long-term lifetime and stability testing of bare VACNT, 5 nm & 10 nm titanium coated, gold coated, and tungsten coated low-density VACNT array.

On the other hand, the lifetime was greatly improved for the VACNT coated with 5 nm W and 5 nm Au. Between these two types, the one with 5 nm W had a rapid increase in current density at the beginning of the test, which increased from $6.5 \text{ mA} \cdot \text{cm}^{-2}$ to around $8.6 \text{ mA} \cdot \text{cm}^{-2}$ within an hour. Then, the current density slightly dropped to around $8.2 \text{ mA} \cdot \text{cm}^{-2}$ and remained almost stable. After 35 hours, the current density tended to decrease slowly until the test was completed in 48 hours. For the type coated with 5 nm Au, compared to the one with 5 nm Ti, the current density only increased slightly at the beginning from 6.5 to $7 \text{ mA} \cdot \text{cm}^{-2}$ and stabilized afterwards until the end of test. However, with thicker coatings of W and Au, the lifetime and stability were not further improved and become worse than 5 nm coated samples, which shows an opposite trend from Ti coating. For the VACNT with 10 nm W, similar to the 5nm W sample, the current density has a substantial rise to $8 \text{ mA} \cdot \text{cm}^{-2}$ at the beginning of the testing. But after that, the current density kept decaying at a faster rate from 8 to $4 \text{ mA} \cdot \text{cm}^{-2}$ within 20 hours, which shows many sudden rises in

current density, that is similar to the one that occurred in the test of the 10 nm Ti sample as the result of electric discharge phenomenon. The VACNT coated with 10 nm Au showed a shorter lifetime and poor current density stability. The current density increased from $6.5 \text{ mA}\cdot\text{cm}^{-2}$ to $10 \text{ mA}\cdot\text{cm}^{-2}$ within half an hour at the beginning of the test, and then it decreased continuously until $2 \text{ mA}\cdot\text{cm}^{-2}$ with large fluctuations throughout. Overall, the 5 nm Au- and 5 nm W-coated emitter have better improvements in stability and lifetime. Although the total lifetime of metal-coated VACNT was shorter in the tests compared to other available reports (such as Shimoi et al. reported an over 1300 h of stable FE at $35 \text{ mA}\cdot\text{cm}^{-2}$) [16], these test results proved that the metal coating method is a promising option for improving the lifetime of CNT-based FE. With this method, other emitters with good FE performance can be further enhanced.

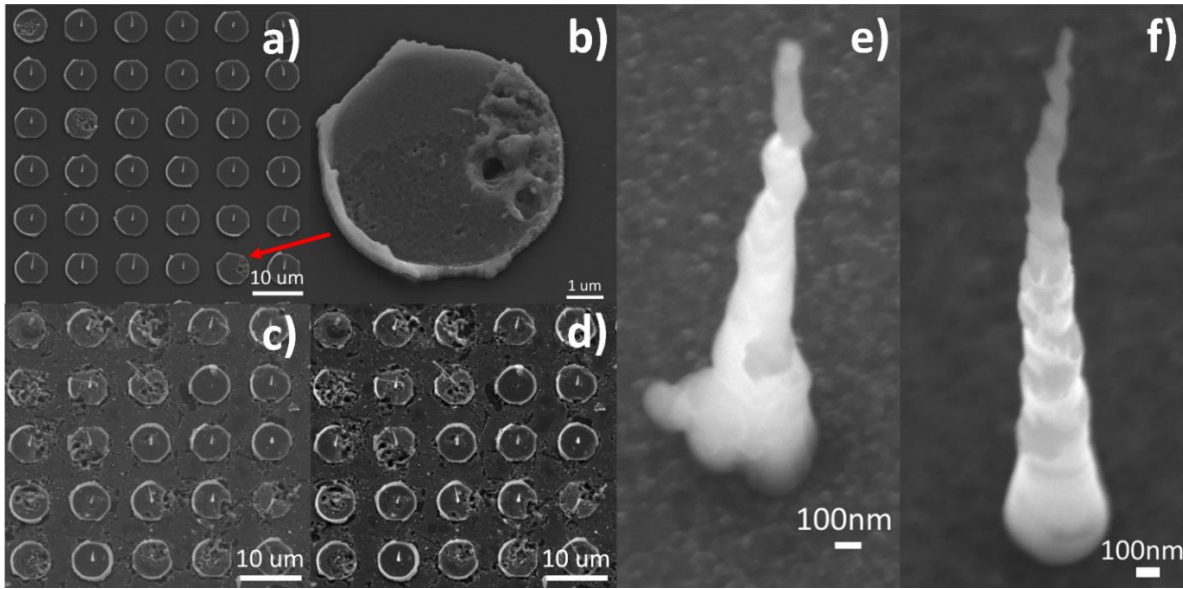


Figure 6.7 SEM image of VACNT structure after long-term FE testing. a) Bare VACNT array, b) expansion view of a crater on Cr pad, c) 10 nm tungsten coated VACNT array, d) 10 nm gold coated VACNT array, e) 5 nm titanium coated single VACNT, and f) 5 nm tungsten coated single VACNT.

The results of the long-term testing of different types of VACNTs emitters coated with and without metal shells indicate that both coating thickness and type of coating contribute to the improvement of the FE lifetime to different degrees. To investigate the cause of these differences, SEM was used to observe the change in the structure of VACNTs after the long-term FE testing (Figure 6.7). For the VACNTs without a coated metal shell after the lifetime test, most of the VACNTs remained in their original position, but the length of the CNT became shorter, that is mainly caused by the generation of Joule heat evaporates the emitting tips of VACNTs or burns the CNTs and causes defects. Therefore, the continuous depletion of CNTs' length led to a continuous decrease in current density at the same applied electric field. Furthermore, there were many craters found on the Cr pads (Figure 6.7b). The possible cause of these craters may attribute to peeling off phenomenon or the thermal runaway of VACNTs occur during the FE process resulting in the strong arcing between cathode and anode, which was demonstrated by several spikes in current density during the tests [24]. Also, Coulomb explosion is another possible explanation for the formation of the craters because of the accumulation of the excessive Coulomb repulsive energy at high emission current density [176].

For the VACNTs coated with 5 nm and 10 nm Ti, the improvement of the lifetime is because of the better uniformity in current density, and the thicker Ti shell resulting in better uniformity [123]. In addition, as shown in Figure 6.7e, the Ti shell at the top of the VACNT was melted, but the CNT inside was not damaged. Furthermore, it is shown that the shell at the bottom of the VACNT formed an irregular pile-up, which might be due to the melted Ti from the tip of the VACNT recondensed at the bottom. The phenomenon of the Ti shell protecting the VACNT can be attributed to faster heat dissipation from the tip of emitter to the substrate, as the contact area

between the emitter and substrate are expanded by coatings, thus, avoiding the burnout of CNTs, and improves the lifetime of coated VACNTs. On the other hand, for 5 nm Au and W coated samples, the improvement of the lifetime is also because of the improvement of uniformity [123]. The rise in current density at the beginning of the test is due to the generation of Joule heat, which makes the thermionic emission help the FE to increase the efficiency of the current emission. Because of the high melting point of W and the good thermal conductivity of Au, the Joule heat does not melt these metal coats quickly, which causes the current rise at the beginning, and as the metal coating slowly melts, the current density will fall back after several hours. In addition, like the Ti-coated one, the CNTs are protected by the outer metal shell, and the shell would act like a sacrificial layer during the FE process to protect CNT being directly damaged by the generation of Joule heat (Figure 6.7f).

The TEM image and the EELS results (Figure 6.8) further proves the role of metal coatings in improvement of FE lifetime. The results exhibit that the W coating at the tip of the CNT was partially sacrificed while the CNT remained almost intact. Furthermore, for the 5 nm Au and W coated VACNTs, the contact resistance between emitters and the substrate is greatly reduced and so lowers the Joule heat generated during FE, thus show significant improvement in the lifetime. As the coating thickness increased to 10 nm, the surface roughness generally increases, which leads to more fluctuations in emission current and less stability. Also, since W or Au have larger material density, as a thicker layer covers the surface of the CNT, the degassing elements would be trapped inside the metal shells and cannot be exhausted smoothly during the degassing process, causing the elements such as hydrogen and oxygen to expand during the FE heating process, hence, destroying the CNT (Figure 6.7c&d).

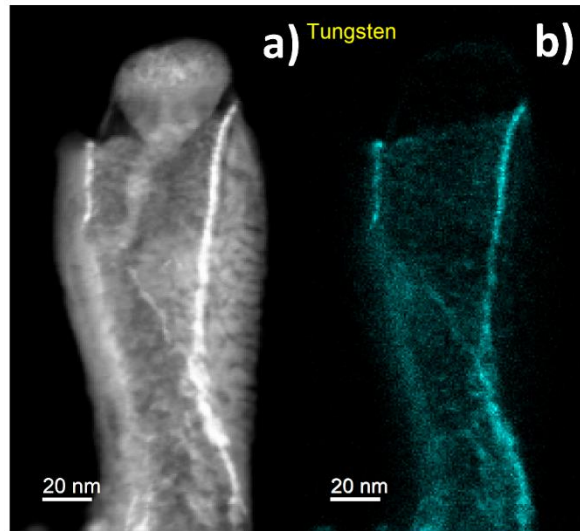


Figure 6.8 a) TEM image of 5 nm tungsten-coated VACNT after long-term testing. b) EELS analysis of tungsten on VACNTs after long-term testing.

6.4 Chapter Summary

In this chapter, a metal coating method to improve the FE performance of VACNT was proposed. The FE performance of VACNTs coated with three types of metals and two different thickness are investigated and directly compared. Through the sputtering method, the metals can be uniformly deposited on the surface of VACNT, forming a thin even layer of metallic shells. According to the testing results, coating metals on the surface of VACNT has only a small influence on the turn-on electric field and it is mainly attributed to the small change in work function. Among all the tested samples, the 5nm Ti coating had a small reduction in the turn-on electric field, while VACNTs coated with Au and W have a slightly higher turn-on electric field. Furthermore, for long-term testing, 5 nm W- and Au-coated VACNT show significant

improvement in lifetime and stability of the emission current density. In addition, the 10 nm Ti, Au, and W coatings resulted in some improvements, but the 5 nm Ti coating only shows little improvement in lifetime and stability. A summary of the FE performances improvement of each coated-CNT is shown in Table 3. Therefore, it is proved that the FE performance of VACNTs can be adjusted by coating a metal layer, and the thin-film W and Au-coated VACNTs are expected to be one of the potential candidates for FE at high current density.

Table 3 Summary of FE performance of different metal-coated and noncoated CNT field emitters.

Metal-coated	Work Function (eV)	Thickness (nm)	Turn-on electric field (V/ μ m)	Current stability	Lifetime (Hours)
Uncoated	4.6	5	6	poor	1
Titanium-coated	4.3	5	5	poor	3
		10	N/A	poor	8
Gold-coated	5.2	5	6	good	> 48
		10	N/A	poor	10
Tungsten-coated	4.5	5	7	good	> 48
		10	N/A	good	20

Chapter 7 Summary

7.1 Conclusion

The conclusion in this chapter is intended to provide a broader summary in the context of the overall goal: achieving reliable and long-term FE as a fast, precise, and controllable electron beam emission system to replace traditional thermionic emission. To achieve this goal, major challenges, such as melting and coulomb explosion of CNT emitters, need to be addressed. The findings and the methods presented in this thesis can be summarized below.

- Coulomb explosion is a highly destructive failure phenomenon that can occur during FE process. This phenomenon usually occurs in less than 0.5 ms with a sudden release of energy, and it is usually accompanied by a flash of light, cause a strong electric arcing between the cathode and anode and leaving a large crater on the cathode. The Coulomb explosion is mainly induced by excessive Coulomb energy accumulated on the tips of CNTs because of the ionization of carbon atoms during FE. A simulation is conducted based on experimental results to verify the mechanism of the FE-induced Coulomb explosion. The Coulomb energy, bond energy, and kinetic energy in a CNT model at each time point are calculated. Through this study, the causes of FE-induced Coulomb explosions are thoroughly understood, and the potential solutions to avoid Coulomb explosions are given, which are critical to optimizing the design of the longer lifetime CNT cathode.
- CNTs' melting issue due to the generation of Joule heat is another major destructive phenomenon during the FE process. Chemical treatments using DMSO and

PEDOT: PSS solutions are two promising methods to slow down the CNT's degradation caused by the CNT's melting problem. After treatment, both methods reduced the turn-on electric field due to the reduction in screening effects, whereas the PEDOT: PSS treatment greatly reduced the threshold field to far lower than that of the DMSO treatment. In addition, the FE efficiency and lifetime of treated CNT emitters are significantly improved. For both treated emitters, there is only little degradation of emission current after 80 hours of continuous FE at around 50 μ A. In addition, the uniformity of both treated CNT emitters is enhanced which enables more CNTs to contribute to the overall current emission. This, in turn, lowers the current emitted by individual CNTs and thereby increases the lifetime of the emitters.

- Another method presented in this thesis to protect CNTs from being melted is the metal coating method. By sputtering a thin metallic layer on the surface of VACNTs, the lifetime is extended, and long-term current emission becomes more stable. To compare different types of metal coatings, Ti, Au, and W are selected because of their desired properties including lower work function, good electrical and thermal conductivity, and high melting points. Where, the 5 nm tungsten and Au coatings have the longest FE lifetime and best current density stability, which shows negligible degradation during continuous 48-hour FE testing at a current density over 7.6 mA $\cdot$ cm⁻². In addition, the 10 nm Ti, Au, and W coatings also provide great improvements in lifetime and emission current stability. Furthermore, it was observed that the metal shells are uniformly distributed on the surface of VACNTs, and they can effectively protect the VACNT from being melted by the

Joule heat during FE. Therefore, metal-coated VACNTs have proven potential for high-current-density FE applications.

Thus, this thesis which presents the investigations of CNTs' failure mechanism during FE, and different methods to improve FE performance, especially by lowering the turn-on electric field and increasing the emitter lifetime, plays an important role in the development of efficient, stable, and robust field emitters. As such, CNT-based FE technology can be reliably adopted in multiple fields.

7.2 Future Work

The three main objectives presented in this thesis could lead to further research and assist the commercialization of CNT field emitters in industrial applications. The future work of this thesis can be divided into three directions: i) avoiding Coulomb explosions that occur during FE to increase the lifetime of CNT-based FE, ii) applying the treatment methods on the CNT array to form addressable electron beam emission source, and further decrease the screening effect, and iii) applying the chemical treatment and coating methods on other types of field emitters to enhance their FE performance.

In Chapters 4 and 5, the detailed phenomenon and cause of the Coulomb explosions are investigated. However, the methods to avoid the occurrence of the Coulomb explosion, especially under high emission current were not yet reported or verified. Possible solutions to avoid Coulomb explosion occurring on CNT under high emission current of FE are proposed, such as fabricating more uniform CNT cathodes and higher quality CNTs, adding resistive layers to limit emission

currents, or avoiding reaching the explosion voltage by predicting the pre-explosive voltage using AI machine learning. However, the actual possibilities and difficulties of implementation have not been tested. Therefore, finding methods to eliminate the Coulomb explosion that happened during FE is still required to be investigated. Furthermore, the simulation of FE-induced Coulomb explosion can also be further studied. The simulation in Chapter 4 is only for proving the explosion phenomenon observed during the FE experiments. For the simulations such as using FE-induced Coulomb explosion to assist surface treatment or other related applications, the model needs to be scaled up and the bonding between atoms and atoms needs to be considered more precisely to achieve a more accurate simulation.

For the chemical treatment methods presented in Chapter 5, VACNT forest was used as the FE cathode, however, the CNT array emitter is a more competitive field emitter than the CNT forest due to the formation of an addressable electron emission source. Thus, further investigations can be conducted on applying these treatment methods to CNT arrays, more work is needed to fabricate better FE cathodes, such as determining the size of the clusters formed by the two treatments and the change in cluster size caused by changing the treatment time or the angle of the solution drops on the CNT, thus ensuring that there is only one cluster per pixel in the array and reducing the screening effect. On the other hand, the chemical treatment and metal coating methods presented in Chapters 5 and 6 can be applied not only to the VACNTs field emitters used in the experiments described in this thesis but also to other types of CNT field emitters or other field emitters with different advantages in terms of FE properties to further improve their FE performance.

References

- [1] B.R. W, A NEW FORM OF CATHODE DISCHARGE AND THE PRODUCTION OF X-RAYS, TOGETHER WITH SOME NOTES ON DIFFRACTION. PRELIMINARY COMM UNICATIO¹, (n.d.).
- [2] J. Zhang, G. Yang, Y. Cheng, Cite as, Appl. Phys. Lett. 86 (2005) 184104. <https://doi.org/10.1063/1.1923750>.
- [3] W.B. Choi, D.S. Chung, J.H. Kang, Cite as, Appl. Phys. Lett. 75 (1999) 3129. <https://doi.org/10.1063/1.125253>.
- [4] N. de Jonge, M. Allieux, J.T. Oostveen, K.B.K. Teo, W.I. Milne, Optical Performance of Carbon-Nanotube Electron Sources, (n.d.). <https://doi.org/10.1103/PhysRevLett.94.186807>.
- [5] * Schottky, ' Z F Physik, ; § O W Richardson, J Millikan and Lauritsen, Proc. Nat. Ac. Sci. 14 (1923) 33. <https://royalsocietypublishing.org/> (accessed March 2, 2022).
- [6] W.A. de Heer, A. Châtelain, D. Ugarte, A Carbon Nanotube Field-Emission Electron Source, Science (1979). 270 (1995) 1179–1180. <https://doi.org/10.1126/SCIENCE.270.5239.1179>.
- [7] J.M. Bonard, J.P. Salvetat, T. Stöckli, W.A. de Heer, L. Forró, A. Chatelain, Field emission from single-wall carbon nanotube films, Appl Phys Lett. 73 (1998) 918. <https://doi.org/10.1063/1.122037>.
- [8] J.I. Sohn, S. Lee, Y.H. Song, S.Y. Choi, K.I. Cho, K.S. Nam, Patterned selective growth of carbon nanotubes and large field emission from vertically well-aligned carbon nanotube field emitter arrays, Appl Phys Lett. 78 (2001) 901. <https://doi.org/10.1063/1.1335846>.
- [9] K.A. Dean, B.R. Chalamala, Field emission microscopy of carbon nanotube caps, J Appl Phys. 85 (1999) 3832. <https://doi.org/10.1063/1.369753>.
- [10] A. Chatri, Carbon nanotube field emitters, n.d. https://www.rug.nl/research/zernike/education/topmasternanoscience/ns190_2015_rahimi.pdf (accessed November 28, 2022).
- [11] M.S. Dresselhaus, G. Dresselhaus, Science of Fullerenes and Carbon Nanotubes, Elsevier. (1996).

- [12] M. Meyyappan, ed., Carbon Nanotubes : Science and Applications, (2004).
<https://doi.org/10.1201/9780203494936>.
- [13] Y. Sun, D.H. Shin, K.N. Yun, Field emission behavior of carbon nanotube field emitters after high temperature thermal annealing, *AIP Adv.* 4 (2014) 77110. <https://doi.org/10.1063/1.4889896>.
- [14] V. Semet, V.T. Binh, P. Vincent, D. Guillot, K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, P. Legagneux, D. Pribat, Field electron emission from individual carbon nanotubes of a vertically aligned array, *Appl Phys Lett.* 81 (2002) 343. <https://doi.org/10.1063/1.1489084>.
- [15] K.Y. Chun, H.S. Lee, C.J. Lee, Nitrogen doping effects on the structure behavior and the field emission performance of double-walled carbon nanotubes, *Carbon N Y.* 47 (2009) 169–177.
<https://doi.org/10.1016/J.CARBON.2008.09.047>.
- [16] N. Shimoi, Y. Sato, K. Tohji, Highly Crystalline Single-Walled Carbon Nanotube Field Emitters: Energy-Loss-Free High Current Output and Long Durability with High Power, *ACS Appl Electron Mater.* 1 (2019) 163–171.
https://doi.org/10.1021/ACSAELM.8B00008/ASSET/IMAGES/LARGE/EL-2018-00008J_0004.JPEG.
- [17] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, Self-oriented regular arrays of carbon nanotubes and their field emission properties, *Science* (1979). 283 (1999) 512–514. <https://doi.org/10.1126/SCIENCE.283.5401.512/ASSET/FB7C5F12-EB39-418A-8A42-5E444EEECBCA/ASSETS/GRAPHIC/SE0397183004.JPEG>.
- [18] J. Zhang, G. Yang, S. Chang, J.P. Lu, O. Zhou, Hadamard multiplexing radiography based on carbon nanotube field emission multi-pixel x-ray technology, *Medical Imaging 2008: Physics of Medical Imaging.* 6913 (2008) 628–635. <https://doi.org/10.1117/12.770860>.
- [19] S.H. Jo, Y. Tu, Z.P. Huang, D.L. Carnahan, D.Z. Wang, Z.F. Ren, Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties, *Appl Phys Lett.* 82 (2003) 3520. <https://doi.org/10.1063/1.1576310>.
- [20] Y.J. Hung, Y.J. Huang, H.C. Chang, K.Y. Lee, S.L. Lee, Patterned growth of carbon nanotubes over vertically aligned silicon nanowire bundles for achieving uniform field emission, *Nanoscale Res Lett.* 9 (2014) 1–7. <https://doi.org/10.1186/1556-276X-9-540/FIGURES/8>.

- [21] D.-H. Kim, H.-S. Yang, H.-D. Kang, H.-R. Lee, Novel emission degradation behavior of patterned carbon nanotubes by field emission, *Chem Phys Lett.* 368 (2003). www.elsevier.com/locate/cplett (accessed May 25, 2022).
- [22] J.-M. Bonard, C. Klinke, K.A. Dean, B.F. Coll, Degradation and failure of carbon nanotube field emitters, *Phys Rev B.* 67 (2003). <https://doi.org/10.1103/PhysRevB.67.115406>.
- [23] J.H. Lee, S.H. Lee, W.S. Kim, H.J. Lee, J.N. Heo, T.W. Jeong, C.W. Baik, S.H. Park, S. Yu, J.B. Park, Y.W. Jin, J.M. Kim, H.J. Lee, J.W. Moon, M.A. Yoo, J.W. Nam, S.H. Cho, J.S. Ha, T.I. Yoon, J.H. Park, D.H. Choe, Current degradation mechanism of single wall carbon nanotube emitters during field emission, *Appl Phys Lett.* 89 (2006). <https://doi.org/10.1063/1.2416250>.
- [24] X. Calderón-Colón, H. Geng, B. Gao, L. An, G. Cao, O. Zhou, A carbon nanotube field emission cathode with high current density and long-term stability, *Nanotechnology.* 20 (2009). <https://doi.org/10.1088/0957-4484/20/32/325707>.
- [25] T. Awan, A. Bashir, A. Tehseen, *Chemistry of Nanomaterials: Fundamentals and Applications*, (2020). https://books.google.com/books?hl=zh-CN&lr=&id=1ZjhDwAAQBAJ&oi=fnd&pg=PP1&dq=Chemistry+of+Nanomaterials:+Fundamentals+and+Applications+chapter+7&ots=dUuERfJfw_&sig=B5DYk-Pee329sG9M6BOVbhv1kZM (accessed November 29, 2022).
- [26] Y. Li, Y. Sun, J.T.W. Yeow, Nanotube field electron emission: Principles, development, and applications, *Nanotechnology.* 26 (2015). <https://doi.org/10.1088/0957-4484/26/24/242001>.
- [27] XIII. The electrical conductivity imparted to a vacuum by hot conductors, *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character.* 201 (1903) 497–549. <https://doi.org/10.1098/RSTA.1903.0023>.
- [28] E.L. Murphy, R.H. Good, Thermionic Emission, Field Emission, and the Transition Region, *Physical Review.* 102 (1956) 1464. <https://doi.org/10.1103/PhysRev.102.1464>.
- [29] R.H. Fowler, Lothar Nordheim, Electron emission in intense electric fields, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character.* 119 (1928) 173–181. <https://doi.org/10.1098/RSPA.1928.0091>.
- [30] Z. Liu, G. Yang, Y.Z. Lee, D. Bordelon, J. Lu, O. Zhou, Carbon nanotube based microfocus field emission x-ray source for microcomputed tomography, *Appl Phys Lett.* 89 (2006). <https://doi.org/10.1063/1.2345829>.

- [31] Y. Cheng, J. Zhang, Y.Z. Lee, B. Gao, S. Dike, W. Lin, J.P. Lu, O. Zhou, Dynamic radiography using a carbon-nanotube-based field-emission x-ray source, *Review of Scientific Instruments*. 75 (2004) 3264–3267. <https://doi.org/10.1063/1.1791313>.
- [32] T. Nagatani, S. Saito, M. Sato, M. Yamada, Development of an Ultra High Resolution Scanning Electron Microscope by Means of a Field Emission Source and In-Lens System, *Scanning Microsc.* 1 (1987). <https://digitalcommons.usu.edu/microscopy/vol1/iss3/3> (accessed November 25, 2022).
- [33] N. Brodusch, H. Demers, R. Gauvin, *Field Emission Scanning Electron Microscopy*, (2018). <https://doi.org/10.1007/978-981-10-4433-5>.
- [34] K. Junker, K.H. status solidi (a), undefined 1974, Experimental examination of the field-enhanced thermal emission of holes in CdS, *Wiley Online Library*. 21 (1974) 451–456. <https://doi.org/10.1002/pssa.2210210208>.
- [35] *Field Emission in Vacuum Microelectronics*, *Field Emission in Vacuum Microelectronics*. (2005). <https://doi.org/10.1007/B139052>.
- [36] T.I. Awan, A. Bashir, A. Tehseen, S. Bibi, *Electrons in nanostructures*, *Chemistry of Nanomaterials*. (2020) 179–206. <https://doi.org/10.1016/B978-0-12-818908-5.00007-X>.
- [37] R.A. Millikan, C.C. Lauritsen, Dependence of Electron Emission from metals upon Field Strengths and Temperatures, *Nippon Sugaku-Buturigakkwaishi*. 3 (1929) 225–227. <https://doi.org/10.11429/SUBUTSUKAISHI1927.3.225>.
- [38] B.T. E Stern, B.S. Gossling, R.H. Fowler, Further studies in the emission of electrons from cold metals, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*. 124 (1929) 699–723. <https://doi.org/10.1098/RSPA.1929.0147>.
- [39] S. Wang, X. Calderon, R. Peng, E.C. Schreiber, O. Zhou, S. Chang, A carbon nanotube field emission multipixel x-ray array source for microradiotherapy application, *Appl Phys Lett*. 98 (2011). <https://doi.org/10.1063/1.3595268>.
- [40] *CT scanning systems and methods using multi-pixel x-ray sources*, (2008).
- [41] L.T. Williams, V.S. Kumsomboone, W.J. Ready, M.L.R. Walker, Lifetime and failure mechanisms of an arrayed carbon nanotube field emission cathode, *IEEE Trans Electron Devices*. 57 (2010) 3163–3168. <https://doi.org/10.1109/TED.2010.2069563>.

- [42] K.S. Yeong, J.T.L. Thong, Life cycle of a tungsten cold field emitter, *J Appl Phys.* 99 (2006) 104903. <https://doi.org/10.1063/1.2197267>.
- [43] B.R. Johnson, A.I. Akinwande, D. Murphy, Characterization of lateral thin-film-edge field emitter arrays, *Undefined.* (1996) 663–667. <https://doi.org/10.1109/IVMC.1996.601922>.
- [44] A. Oowada, M. Takeuchi, Y. Sakai, Y. Gotoh, M. Naeao, H. Tsuji, J. Ishikawa, S. Sakai, T. Kimoto, Extension of lifetime of silicon field emitter arrays in oxygen ambient by carbon negative ion implantation, *Technical Digest of the 20th International Vacuum Nanoelectronics Conference, IVNC 07.* (2007) 225–226. <https://doi.org/10.1109/IVNC.2007.4481006>.
- [45] W. Dyke, W.D.-A. in *electronics and electron physics*, undefined 1956, *Field emission*, Elsevier. (n.d.). <https://www.sciencedirect.com/science/article/pii/S0065253908612263> (accessed November 25, 2022).
- [46] R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, *Physical Properties of Carbon Nanotubes.* (1998). <https://doi.org/10.1142/P080>.
- [47] S. Coulombe, J.L. Meunier, Thermo-field emission: a comparative study, *J Phys D Appl Phys.* 30 (1997) 776. <https://doi.org/10.1088/0022-3727/30/5/009>.
- [48] W.B. Choi, J. Liu, M.T. McClure, Field emission from diamond coated molybdenum field emitters, *Citation: Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing.* 14 (1996) 2050. <https://doi.org/10.1116/1.588984>.
- [49] N. Zhu, J. Chen, Design, Fabrication and Characterization of Molybdenum Field Emitter Arrays (Mo-FEAs), *Micromachines (Basel).* 8 (2017). <https://doi.org/10.3390/MI8050162>.
- [50] C.A. Spindt, I. Brodie, MOLYBDENUM FIELD-EMITTER ARRAYS, *Technical Digest - International Electron Devices Meeting, IEDM.* (1996) 289–292. <https://doi.org/10.1109/IEDM.1996.553586>.
- [51] K. Kasuya, S. Katagiri, T. Ohshima, S. Kokubo, Stabilization of a tungsten $\langle 310 \rangle$ cold field emitter, *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena.* 28 (2010) L55–L60. <https://doi.org/10.1116/1.3488988>.
- [52] J. Liu, V. v. Zhirnov, A.F. Myers, G.J. Wojak, W.B. Choi, J.J. Hren, S.D. Wolter, M.T. McClure, B.R. Stoner, J.T. Glass, Field emission characteristics of diamond coated silicon field emitters,

- Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures. 13 (1995) 422–426. <https://doi.org/10.1116/1.587961>.
- [53] L.A. Dubridge, W.W. Roehr, L.A. Dubridge, W.W. Roehr, The Thermionic and Photoelectric Work Functions of Molybdenum, *PhRv.* 42 (1932) 52–57.
<https://doi.org/10.1103/PHYSREV.42.52>.
 - [54] E.W. Müller, Work Function of Tungsten Single Crystal Planes Measured by the Field Emission Microscope, *Undefined.* 26 (1955) 732–737. <https://doi.org/10.1063/1.1722081>.
 - [55] Jenkins, R.O., Field emission of electrons, *Reports on Progress in Physics.* 9 (1942) 177.
<https://doi.org/10.1088/0034-4885/9/1/315>.
 - [56] F.S. Baker, A.R. Osborn, J. Williams, The carbon-fibre field emitter, *J Phys D Appl Phys.* 7 (1974) 2105. <https://doi.org/10.1088/0022-3727/7/15/315>.
 - [57] K.S.-A. in *Computers*, undefined 1961, Microelectronics using electron-beam-activated machining techniques, Elsevier. (n.d.).
<https://www.sciencedirect.com/science/article/pii/S0065245808601424> (accessed November 28, 2022).
 - [58] C.A. Spindt, A Thin-Film Field-Emission Cathode, *J Appl Phys.* 39 (2003) 3504.
<https://doi.org/10.1063/1.1656810>.
 - [59] Spindt C, Shoulders K, Heynick L, A Thin-Film Field-Emission Cathode, U.S. Patent . No. 3,755,704 (1973).
 - [60] C.A. Spindt, C.E. Holland, R.D. Stowell, Field emission cathode array development for high-current-density applications, *Applications of Surface Science.* 16 (1983) 268–276.
[https://doi.org/10.1016/0378-5963\(83\)90073-9](https://doi.org/10.1016/0378-5963(83)90073-9).
 - [61] C.A. Spindt, I. Brodie, L. Humphrey, E.R. Westerberg, Physical properties of thin-film field emission cathodes with molybdenum cones, *J Appl Phys.* 47 (2008) 5248.
<https://doi.org/10.1063/1.322600>.
 - [62] G.N.A. van Veen, Space-charge effects in Spindt-type field emission cathodes, *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena.* 12 (1998) 655. <https://doi.org/10.1116/1.587407>.

- [63] C.A. Spindt, C.E. Holland, A. Rosengreen, I. Brodie, Field-Emitter Arrays for Vacuum Microelectronics, *IEEE Trans Electron Devices*. 38 (1991) 2355–2363.
<https://doi.org/10.1109/16.88525>.
- [64] R.N. Thomas, H.C. Nathanson, Photosensitive field emission from silicon point arrays, *Appl Phys Lett*. 21 (2003) 384. <https://doi.org/10.1063/1.1654423>.
- [65] D. Smith, JS Judge, Micro-structure field emission electron source, US Patent . 3, 970,887 (1976).
<https://patents.google.com/patent/US3970887A/en> (accessed November 28, 2022).
- [66] Gray H, Campisi G, Greene R, Int. Electron Devices Meeting (1986 Los Angeles, CA), IEEE. 32 (1986) 776–779.
https://scholar.google.com/scholar_lookup?hl=en&publication_year=1986&pages=776-779&author=H.+Grayauthor=G.+Campisiauthor=R.+Greene&title=International+Electron+Devices+Meeting (accessed November 28, 2022).
- [67] D. Temple, W.D. Palmer, L.N. Yadon, J.E. Mancusi, D. Vellenga, G.E. McGuire, Silicon field emitter cathodes: Fabrication, performance, and applications, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 16 (1998) 1980. <https://doi.org/10.1116/1.581207>.
- [68] S.A. Guerrero, A.I. Akinwande, Improved field emitter arrays with high-aspect-ratio current limiters and self-aligned gates, *Technical Digest - 2014 27th International Vacuum Nanoelectronics Conference, IVNC 2014*. (2014) 25–26.
<https://doi.org/10.1109/IVNC.2014.6894742>.
- [69] M.E. Swanwick, P.D. Keathley, A. Fallahi, P.R. Kroger, G. Laurent, J. Moses, F.X. Kärtner, L.F. Velásquez-García, Nanostructured ultrafast silicon-tip optical field-emitter arrays, *Nano Lett*. 14 (2014) 5035–5043. https://doi.org/10.1021/NL501589J/SUPPL_FILE/NL501589J_SI_001.PDF.
- [70] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 1991 354:6348. 354 (1991) 56–58.
<https://doi.org/10.1038/354056a0>.
- [71] A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tománek, P. Nordlander, D.T. Colbert, R.E. Smalley, Unraveling Nanotubes: Field Emission from an Atomic Wire, *Science* (1979). 269 (1995) 1550–1553. <https://doi.org/10.1126/SCIENCE.269.5230.1550>.
- [72] P.R. Unwin, A.G. Güell, G. Zhang, Nanoscale Electrochemistry of sp² Carbon Materials: From Graphite and Graphene to Carbon Nanotubes, *Acc Chem Res*. 49 (2016) 2041–2048.

- https://doi.org/10.1021/ACS.ACCOUNTS.6B00301/ASSET/IMAGES/LARGE/AR-2016-003014_0003.JPEG.
- [73] O. Zhou, H. Shimoda, B. Gao, S. Oh, L. Fleming, G. Yue, Materials science of carbon nanotubes: Fabrication, integration, and properties of macroscopic structures of carbon nanotubes, *Acc Chem Res.* 35 (2002) 1045–1053.
<https://doi.org/10.1021/AR010162F/ASSET/IMAGES/LARGE/AR010162FF00010.JPEG>.
- [74] A. Jorio, R. Saito, J.H. Hafner, C.M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, M.S. Dresselhaus, Structural (n, m) Determination of Isolated Single-Wall Carbon Nanotubes by Resonant Raman Scattering, *Phys Rev Lett.* 86 (2001) 1118.
<https://doi.org/10.1103/PhysRevLett.86.1118>.
- [75] Y. Sun, D.H. Shin, K.N. Yun, Y.M. Hwang, Y. Song, G. Leti, S.G. Jeon, J. il Kim, Y. Saito, C.J. Lee, Field emission behavior of carbon nanotube field emitters after high temperature thermal annealing, *AIP Adv.* 4 (2014) 077110. <https://doi.org/10.1063/1.4889896>.
- [76] D.N. Futaba, H. Kimura, B. Zhao, T. Yamada, H. Kurachi, S. Uemura, K. Hata, Carbon nanotube loop arrays for low-operational power, high uniformity field emission with long-term stability, *Carbon N Y.* 50 (2012) 2796–2803. <https://doi.org/10.1016/J.CARBON.2012.02.043>.
- [77] S.J. Tans, A.R.M. Verschueren, C. Dekker, Room-temperature transistor based on a single carbon nanotube, *Nature* 1998 393:6680. 393 (1998) 49–52. <https://doi.org/10.1038/29954>.
- [78] F. Xia, M. Steiner, Y.M. Lin, P. Avouris, A microcavity-controlled, current-driven, on-chip nanotube emitter at infrared wavelengths, *Nature Nanotechnology* 2008 3:10. 3 (2008) 609–613.
<https://doi.org/10.1038/nnano.2008.241>.
- [79] M.F. Yu, B.S. Files, S. Arepalli, R.S. Ruoff, Tensile Loading of Ropes of Single Wall Carbon Nanotubes and their Mechanical Properties, *Phys Rev Lett.* 84 (2000) 5552.
<https://doi.org/10.1103/PhysRevLett.84.5552>.
- [80] A.M. Cassell, J.A. Raymakers, J. Kong, H. Dai, Large Scale CVD Synthesis of Single-Walled Carbon Nanotubes, *Journal of Physical Chemistry B.* 103 (1999) 6484–6492.
<https://doi.org/10.1021/JP990957S/ASSET/IMAGES/LARGE/JP990957SF00011.JPEG>.
- [81] N. Arora, N.N. Sharma, Arc discharge synthesis of carbon nanotubes: Comprehensive review, *Diam Relat Mater.* 50 (2014) 135–150. <https://doi.org/10.1016/J.DIAMOND.2014.10.001>.

- [82] Y. Zhang, H. Gu, S. Iijima, Single-wall carbon nanotubes synthesized by laser ablation in a nitrogen atmosphere, *Appl Phys Lett.* 73 (1998) 3827. <https://doi.org/10.1063/1.122907>.
- [83] R. Purohit, K. Purohit, S. Rana, R.S. Rana, V. Patel, Carbon Nanotubes and Their Growth Methods, *Procedia Materials Science.* 6 (2014) 716–728. <https://doi.org/10.1016/J.MSPRO.2014.07.088>.
- [84] B. Gao, G.Z. Yue, Q. Qiu, Y. Cheng, H. Shimoda, L. Fleming, O. Zhou, Fabrication and Electron Field Emission Properties of Carbon Nanotube Films by Electrophoretic Deposition**, *Adv. Mater.* 13 (2001). <https://doi.org/10.1002/1521-4095>.
- [85] S.J. Oh, J. Zhang, Y. Cheng, H. Shimoda, O. Zhou, Liquid-phase fabrication of patterned carbon nanotube field emission cathodes, *Appl Phys Lett.* 84 (2004) 3738. <https://doi.org/10.1063/1.1737074>.
- [86] H. Furuta, H. Koji, T. Komukai, A. Hatta, Long lifetime emission from screen printing carbon nanotubes over 45,000 h at 1.27 mA/cm² with 10% duty ratio, *Diam Relat Mater.* 35 (2013) 29–35. <https://doi.org/10.1016/J.DIAMOND.2013.03.003>.
- [87] Y.S. Shi, C.C. Zhu, W. Qikun, L. Xin, Large area screen-printing cathode of CNT for FED, *Diam Relat Mater.* 12 (2003) 1449–1452. [https://doi.org/10.1016/S0925-9635\(03\)00170-5](https://doi.org/10.1016/S0925-9635(03)00170-5).
- [88] S. il Jung, J.S. Choi, H.C. Shim, S. Kim, S.H. Jo, C.J. Lee, Fabrication of probe-typed carbon nanotube point emitters, *Appl Phys Lett.* 89 (2006) 233108. <https://doi.org/10.1063/1.2402222>.
- [89] G. Zhao, J. Zhang, Q. Zhang, H. Zhang, O. Zhou, L.C. Qin, J. Tang, Fabrication and characterization of single carbon nanotube emitters as point electron sources, *Appl Phys Lett.* 89 (2006) 193113. <https://doi.org/10.1063/1.2387961>.
- [90] G. Chen, D.H. Shin, S. Roth, C.J. Lee, Field emission characteristics of point emitters fabricated by a multiwalled carbon nanotube yarn, *Nanotechnology.* 20 (2009) 315201. <https://doi.org/10.1088/0957-4484/20/31/315201>.
- [91] J.M. Bonard, J.P. Salvetat, T. Stöckli, L. Forró, A. Châtelain, Field emission from carbon nanotubes: perspectives for applications and clues to the emission mechanism, *Applied Physics A* 1999 69:3. 69 (1999) 245–254. <https://doi.org/10.1007/S003390050998>.
- [92] W.B. Choi, Y.W. Jin, H.Y. Kim, S.J. Lee, M.J. Yun, J.H. Kang, Y.S. Choi, N.S. Park, N.S. Lee, J.M. Kim, Electrophoresis deposition of carbon nanotubes for triode-type field emission display, *Appl Phys Lett.* 78 (2001) 1547. <https://doi.org/10.1063/1.1349870>.

- [93] W.B. Choi, D.S. Chung, J.H. Kang, H.Y. Kim, Y.W. Jin, I.T. Han, Y.H. Lee, J.E. Jung, N.S. Lee, G.S. Park, J.M. Kim, Fully sealed, high-brightness carbon-nanotube field-emission display, *Appl Phys Lett.* 75 (1999) 3129. <https://doi.org/10.1063/1.125253>.
- [94] J.W. Jeong, J.W. Kim, J.T. Kang, S. Choi, S. Ahn, Y.H. Song, A vacuum-sealed compact x-ray tube based on focused carbon nanotube field-emission electrons, *Nanotechnology.* 24 (2013) 085201. <https://doi.org/10.1088/0957-4484/24/8/085201>.
- [95] A. Szabó, P. Andričević, Z. Pápa, T. Gyulavári, K. Németh, E. Horvath, L. Forró, K. Hernadi, Growth of CNT forests on titanium based layers, detailed study of catalysts, *Front Chem.* 6 (2018) 593. <https://doi.org/10.3389/FCHEM.2018.00593/BIBTEX>.
- [96] J. Zhao, Z. Li, M.T. Cole, A. Wang, X. Guo, X. Liu, W. Lyu, H. Teng, Y. Qv, G. Liu, K. Chen, S. Zhou, J. Xiao, Y. Li, C. Li, Q. Dai, Nanocone-shaped carbon nanotubes field-emitter array fabricated by laser ablation, *Nanomaterials.* 11 (2021) 3244. <https://doi.org/10.3390/NANO11123244/S1>.
- [97] M. Meyyappan, A review of plasma enhanced chemical vapour deposition of carbon nanotubes, *J Phys D Appl Phys.* 42 (2009) 213001. <https://doi.org/10.1088/0022-3727/42/21/213001>.
- [98] Z.F. Ren, Z.P. Huang, D.Z. Wang, J.G. Wen, J.W. Xu, J.H. Wang, L.E. Calvet, J. Chen, J.F. Klemic, M.A. Reed, Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot, *Appl Phys Lett.* 75 (1999) 1086. <https://doi.org/10.1063/1.124605>.
- [99] J.I. Sohn, S. Lee, Y.H. Song, S.Y. Choi, K.I. Cho, K.S. Nam, Patterned selective growth of carbon nanotubes and large field emission from vertically well-aligned carbon nanotube field emitter arrays, *Appl Phys Lett.* 78 (2001) 901. <https://doi.org/10.1063/1.1335846>.
- [100] M. Sveningsson, R.-E. Morjan, O.A. Nerushev, Y. Sato, J. Bäckström, E.E.B. Campbell, F. Rohmund, Raman spectroscopy and field-emission properties of CVD-grown carbon-nanotube films, *Appl. Phys. A.* 73 (2001) 409–418. <https://doi.org/10.1007/s003390100923>.
- [101] K.B.K. Teo, S.-B. Lee, M. Chhowalla, V. Semet, V.T. Binh, O. Groening, M. Castignolles, A. Loiseau, G. Pirio, P. Legagneux, D. Pribat, D.G. Hasko, H. Ahmed, G.A.J. Amaratunga, W.I. Milne, Plasma enhanced chemical vapour deposition carbon nanotubes/nanofibres-how uniform do they grow?, *INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY Nanotechnology.* 14 (2003) 204–211.

- [102] C. Li, Y. Zhang, M. Mann, D. Hasko, W. Lei, B. Wang, D. Chu, D. Pribat, G.A.J. Amaratunga, W.I. Milne, High emission current density, vertically aligned carbon nanotube mesh, field emitter array, *Appl Phys Lett.* 97 (2010) 113107. <https://doi.org/10.1063/1.3490651>.
- [103] M. Chhowalla, C. Ducati, N.L. Rupesinghe, K.B.K. Teo, G.A.J. Amaratunga, Field emission from short and stubby vertically aligned carbon nanotubes, *Appl Phys Lett.* 79 (2001) 2079–2081. <https://doi.org/10.1063/1.1406557>.
- [104] S. Neupane, M. Lastres, M. Chiarella, W. Li, Q. Su, G. Du, Synthesis and field emission properties of vertically aligned carbon nanotube arrays on copper, *Carbon N Y.* 50 (2012) 2641–2650. <https://doi.org/10.1016/J.CARBON.2012.02.024>.
- [105] M. Cahay, W. Zhu, S. Fairchild, P.T. Murray, T.C. Back, G.J. Gruen, Multiscale model of heat dissipation mechanisms during field emission from carbon nanotube fibers, *Appl Phys Lett.* 108 (2016) 033110. <https://doi.org/10.1063/1.4940390>.
- [106] F.F. Dall’agnol, D. den Engelsen, Field emission from non-uniform carbon nanotube arrays, *Nanoscale Res Lett.* 8 (2013) 1–6. <https://doi.org/10.1186/1556-276X-8-319>.
- [107] Y. Li, Y. Sun, D.A. Jaffray, J.T.W. Yeow, A novel field emission microscopy method to study field emission characteristics of freestanding carbon nanotube arrays, *Nanotechnology.* 28 (2017). <https://doi.org/10.1088/1361-6528/aa613e>.
- [108] W. Wei, Y. Liu, Y. Wei, K. Jiang, L.M. Peng, S. Fan, Tip cooling effect and failure mechanism of field-emitting carbon nanotubes, *Nano Lett.* 7 (2007) 64–68. https://doi.org/10.1021/NL061982U/SUPPL_FILE/NL061982USI20061127_010008.PDF.
- [109] Y. Li, Y. Sun, D.A. Jaffray, J.T.W. Yeow, Coulomb explosion of vertically aligned carbon nanofibre induced by field electron emission †, *RSC Adv.* 7 (2017). <https://doi.org/10.1039/c7ra07474c>.
- [110] U. Saalman, C. Siedschlag, J.M. Rost, TOPICAL REVIEW Mechanisms of cluster ionization in strong laser pulses, *J. Phys. B: At. Mol. Opt. Phys.* 39 (2006) 39–77. <https://doi.org/10.1088/0953-4075/39/4/R01>.
- [111] X. Wei, D.-M. Tang, Q. Chen, Y. Bando, D. Golberg, Local Coulomb Explosion of Boron Nitride Nanotubes under Electron Beam Irradiation, *ACS Nano.* 7 (2013). <https://doi.org/10.1021/nn400423y>.

- [112] P. Sharma, R.K. Vatsa, Nanoclusters Under Extreme Ionization Conditions, *Materials Under Extreme Conditions*. (2017) 575–613. <https://doi.org/10.1016/B978-0-12-801300-7.00016-4>.
- [113] Y. Sun, J.T.W. Yeow, D.A. Jaffray, Design and fabrication of carbon nanotube field-emission cathode with coaxial gate and ballast resistor., *Small*. 9 (2013) 3385–3389. <https://doi.org/10.1002/SMLL.201300553>.
- [114] I. Sameera, R. Bhatia, V. Prasad, R. Menon, High emission currents and low threshold fields in multi-wall carbon nanotube-polymer composites in the vertical configuration, *J Appl Phys*. 111 (2012) 044307. <https://doi.org/10.1063/1.3685754>.
- [115] B.A. Kakade, V.K. Pillai, D.J. Late, P.G. Chavan, F.J. Sheini, M.A. More, D.S. Joag, High current density, low threshold field emission from functionalized carbon nanotube bucky paper, *Appl Phys Lett*. 97 (2010) 073102. <https://doi.org/10.1063/1.3479049>.
- [116] C.Y. Zhi, X.D. Bai, E.G. Wang, Enhanced field emission from carbon nanotubes by hydrogen plasma treatment, *Appl Phys Lett*. 81 (2002) 1690. <https://doi.org/10.1063/1.1503175>.
- [117] E. Stratakis, E. Kymakis, E. Spanakis, P. Tzanetakis, E. Koudoumas, Polymer - nanotube composite mats with improved field emission performance and stability, *Physical Chemistry Chemical Physics*. 11 (2009) 703–709. <https://doi.org/10.1039/B813198H>.
- [118] G. Chen, S. Neupane, W. Li, L. Chen, J. Zhang, An increase in the field emission from vertically aligned multiwalled carbon nanotubes caused by NH₃ plasma treatment, *Carbon N Y*. 52 (2013) 468–475. <https://doi.org/10.1016/J.CARBON.2012.09.058>.
- [119] M.M.H. Raza, S.M. Aalam, M. Sadiq, M. Sarvar, M. Zulfequar, S. Husain, J. Ali, Time-dependent resonating plasma treatment of carbon nanotubes for enhancing the electron field emission properties, *Journal of Materials Science: Materials in Electronics*. 33 (2022) 1211–1227. <https://doi.org/10.1007/S10854-021-07413-0/TABLES/4>.
- [120] M. Sreekanth, S. Ghosh, P. Biswas, S. Kumar, P. Srivastava, Improved field emission from indium decorated multi-walled carbon nanotubes, *Appl Surf Sci*. 383 (2016) 84–89. <https://doi.org/10.1016/j.apsusc.2016.04.170>.
- [121] S. Sridhar, C. Tiwary, S. Vinod, J. Jaime Taha-Tijerina, S. Sridhar, K. Kalaga, B. Sirota, A.H. C Hart, S. Ozden, R. Kumar Sinha, R. Vajtai, W. Choi, K. Kordá, P.M. Ajayan, Field Emission with Ultralow Turn On Voltage from Metal Decorated Carbon Nanotubes, 8 (2014) 7763–7770. <https://doi.org/10.1021/nn500921s>.

- [122] Z. Wang, Y. Zuo, Y. Li, X. Han, X. Guo, J. Wang, B. Cao, L. Xi, D. Xue, Improved field emission properties of carbon nanotubes decorated with Ta layer, *Carbon N Y.* 73 (2014) 114–124.
<https://doi.org/10.1016/J.CARBON.2014.02.046>.
- [123] H.S. Uh, S. Park, B. Kim, Enhanced field emission properties from titanium-coated carbon nanotubes, *Diam Relat Mater.* 19 (2010) 586–589.
<https://doi.org/10.1016/J.DIAMOND.2009.11.021>.
- [124] R.B. Sharma, D.J. Late, D.S. Joag, A. Govindaraj, C.N.R. Rao, Field emission properties of boron and nitrogen doped carbon nanotubes, *Chem Phys Lett.* 428 (2006) 102–108.
<https://doi.org/10.1016/J.CPLETT.2006.06.089>.
- [125] P. Tripathi, B.K. Gupta, A. Bhatnagar, C.R.P. Patel, P.K. Banker, D.J. Late, M.A. More, N.P. Lalla, D.M. Phase, R.J. Choudhary, M.A. Shaz, P.M. Ajayan, O.N. Srivastava, Highly efficient field emission properties of radially aligned carbon nanotubes, *J Mater Chem C Mater.* 6 (2018) 6584–6590. <https://doi.org/10.1039/c8tc00814k>.
- [126] A. Thapa, Y.R. Poudel, R. Guo, K.L. Jungjohann, X. Wang, W. Li, Direct synthesis of micropillars of vertically aligned carbon nanotubes on stainless-steel and their excellent field emission properties, *Carbon N Y.* 171 (2021) 188–200.
<https://doi.org/10.1016/J.CARBON.2020.08.081>.
- [127] E. Pomplun, & G. Sutmann, E. Pomplun{, G. Sutmann{, Is Coulomb explosion a damaging mechanism for 125 IUdR?, *Int J Radiat Biol.* 80 (2004) 855–860.
<https://doi.org/10.1080/09553000400017614>.
- [128] B.T. E Stern, B.S. Gossling, R.H. Fowler, Further studies in the emission of electrons from cold metals, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character.*, 124 (1929) 699–723. <https://royalsocietypublishing.org/> (accessed February 16, 2022).
- [129] D. Biswas, A universal formula for the field enhancement factor, *Phys Plasmas.* 25 (2018).
<https://doi.org/10.1063/1.5025694>.
- [130] A.M. Popov, I. v. Lebedeva, A.A. Knizhnik, Y.E. Lozovik, B. v. Potapkin, N.A. Poklonski, Andrei.I. Siahlo, S.A. Vyrko, AA stacking, tribological and electronic properties of double-layer graphene with krypton spacer, *Journal of Chemical Physics.* 139 (2013).
<https://doi.org/10.1063/1.4824298>.

- [131] M.F. Budyka, T.S. Zyubina, A.G. Ryabenko, S.H. Lin, A.M. Mebel, Bond lengths and diameters of armchair single wall carbon nanotubes, *Chem Phys Lett.* 407 (2005) 266–271.
<https://doi.org/10.1016/J.CPLETT.2005.03.088>.
- [132] M.A. Grado-Caffaro, M. Grado-Caffaro, Theoretical evaluation of electron mobility in multi-walled carbon nanotubes, n.d. <http://www.elsevier.de/ijleo>.
- [133] G. Pennington, A. Akturk, N. Goldsman, Electron Mobility of a Semiconducting Carbon Nanotube, n.d.
- [134] M. Kaukonen, A. Gulans, P. Havu, E. Kauppinen, Lennard-Jones parameters for small diameter carbon nanotubes and water for molecular mechanics simulations from van der Waals density functional calculations, *J Comput Chem.* 33 (2012) 652–658. <https://doi.org/10.1002/jcc.22884>.
- [135] Y. Ishigaki, T. Shimajiri, T. Takeda, R. Katoono, T. Suzuki, Longest C–C Single Bond among Neutral Hydrocarbons with a Bond Length beyond 1.8 Å, *Chem.* 4 (2018) 795–806.
<https://doi.org/10.1016/J.CHEMP.2018.01.011>.
- [136] S. Kyung, Y. Lee, C. Kim, J. Lee, G. Yeom, Deposition of carbon nanotubes by capillary-type atmospheric pressure PECVD, *Thin Solid Films.* 506–507 (2006) 268–273.
<https://doi.org/10.1016/J.TSF.2005.08.325>.
- [137] Y. Wang, S. Xu, G. Li, Thin film transistors using PECVD-grown carbon nanotubes, *Nanotechnology.* 21 (2010) 205202. <https://doi.org/10.1088/0957-4484/21/20/205202>.
- [138] L.-G. Tien, C.-H. Tsai, F.-Y. Li, M.-H. Lee, Band-gap modification of defective carbon nanotubes under a transverse electric field, *Phys Rev B.* 72 (2005).
<https://doi.org/10.1103/PhysRevB.72.245417>.
- [139] T. Mizutani, H. Ohnaka, Y. Okigawa, A study of preferential growth of carbon nanotubes with semiconducting behavior grown by plasma-enhanced chemical vapor deposition ARTICLES YOU MAY BE INTERESTED IN, *J. Appl. Phys.* 106 (2009) 73705. <https://doi.org/10.1063/1.3234389>.
- [140] Y. Abdi, J. Koohsorkhi, J. Derakhshandeh, S. Mohajerzadeh, H. Hoseinzadegan, M.D. Robertson, J.C. Bennett, X. Wu, H. Radamson, PECVD-grown carbon nanotubes on silicon substrates with a nickel-seeded tip-growth structure, *Materials Science and Engineering C.* 26 (2006) 1219–1223.
<https://doi.org/10.1016/J.MSEC.2005.09.012>.
- [141] L. Sha, P. Gao, T. Wu, Y. Chen, Chemical Ni–C Bonding in Ni–Carbon Nanotube Composite by a Microwave Welding Method and Its Induced High-Frequency Radar Frequency Electromagnetic

- Wave Absorption, *ACS Appl. Mater. Interfaces*. 9 (2017) 44.
<https://doi.org/10.1021/acsami.7b07136>.
- [142] X.H. Liang, S.Z. Deng, N.S. Xu, Cite as, *Appl. Phys. Lett.* 88 (2006) 111501.
<https://doi.org/10.1063/1.2180439>.
- [143] Z. Chen, Q. Zhang, P. Lan, B. Zhu, T. Yu, G. Cao, D. den Engelsen, Ultrahigh-current field emission from sandwich-grown well-aligned uniform multi-walled carbon nanotube arrays with high adherence strength, *Nanotechnology*. 18 (2007) 265702. <https://doi.org/10.1088/0957-4484/18/26/265702>.
- [144] Y. Sun, J.T.W. Yeow, D.A. Jaffray, Design and Fabrication of Carbon Nanotube Field-Emission Cathode with Coaxial Gate and Ballast Resistor, (2013). <https://doi.org/10.1002/sml.201300553>.
- [145] Y. Zhang, Y. Tan, L. Wang, B. Li, Y. Ke, M. Liao, N. Xu, J. Chen, S. Deng, Electron emission and structure stability of carbon nanotube cold cathode driven by millisecond pulsed voltage, *Vacuum*. 172 (2020) 109071. <https://doi.org/10.1016/j.vacuum.2019.109071>.
- [146] K. Jothiramalingam Sankaran, M. Ficek, S. Kunuku, K. Panda, C.-J. Yeh, J. Young Park, M. Sawczak, P. Piotr Michałowski, K.-C. Leou, R. Bogdanowicz, I.-N. Lin, K. Haenen, Self-organized multi-layered graphene-boron-doped diamond hybrid nanowalls for high-performance electron emission devices, *Nanoscale*. 10 (2018) 1345. <https://doi.org/10.1039/c7nr06774g>.
- [147] L. Huang, S. Harajiri, S. Wang, X. Wu, K. Teii, Enhanced Field Emission from Ultrananocrystalline Diamond-Decorated Carbon Nanowalls Prepared by a Self-Assembly Seeding Technique, *ACS Appl Mater Interfaces*. 14 (2022) 4389–4398.
<https://doi.org/10.1021/acsami.1c17279>.
- [148] K. Panda, J.J. Hyeok, J.Y. Park, K.J. Sankaran, S. Balakrishnan, I.N. Lin, Nanoscale investigation of enhanced electron field emission for silver ion implanted/post-annealed ultrananocrystalline diamond films, *Sci Rep*. 7 (2017). <https://doi.org/10.1038/s41598-017-16395-1>.
- [149] K.J. Sankaran, K. Panda, P.Y. Hsieh, P. Pobedinskas, J.Y. Park, M.K. van Bael, N.H. Tai, I.N. Lin, K. Haenen, Low temperature synthesis of lithium-doped nanocrystalline diamond films with enhanced field electron emission properties, *Nanomaterials*. 8 (2018).
<https://doi.org/10.3390/nano8090653>.
- [150] Y. Zheng, Y. Liu, L. Wang, J. Liu, J. Wei, L. Chen, K. An, X. Zhang, H. Ye, H. Zhou, H. Tao, Y. Yin, X. Ouyang, C. Li, Vertically Aligned Boron-Doped Diamond Hollow Nanoneedle Arrays for

- Enhanced Field Emission, *ACS Appl Nano Mater.* 5 (2022) 100878–10889.
<https://doi.org/10.1021/acsanm.2c02180>.
- [151] W. Huang, W. Qian, H. Luo, M. Dong, H. Shao, Y. Chen, X. Liu, C. Dong, Field emission enhancement from directly grown N-doped carbon nanotubes on stainless steel substrates, *Vacuum*. 198 (2022). <https://doi.org/10.1016/j.vacuum.2022.110900>.
- [152] X. bin Yan, B.K. Tay, Y. Yang, W.Y.K. Po, Fabrication of three-dimensional ZnO - Carbon Nanotube (CNT) hybrids using self-assembled CNT micropatterns as framework, *Journal of Physical Chemistry C*. 111 (2007) 17254–17259. <https://doi.org/10.1021/jp076064e>.
- [153] N. Chakrapani, B. Wei, A. Carrillo, P.M. Ajayan, R.S. Kane, Capillarity-driven assembly of two-dimensional cellular carbon nanotube foams, *PNAS March*. 23 (2004).
www.pnas.org/cgi/doi/10.1073/pnas.0400734101 (accessed May 25, 2022).
- [154] M.A. Correa-Duarte, N. Wagner, J. Rojas-Chapana, C. Morsczech, M. Thie, M. Giersig, Fabrication and Biocompatibility of Carbon Nanotube-Based 3D Networks as Scaffolds for Cell Seeding and Growth, *Nano Letters*. 4 (2004) 2233–2236. <https://doi.org/10.1021/nl048574f>.
- [155] C. v Nguyen, L. Delzeit, A.M. Cassell, J. Li, J. Han, M. Meyyappan, Preparation of Nucleic Acid Functionalized Carbon Nanotube Arrays, *Nano Letters*. 2 (2002) 1079–1081.
<https://doi.org/10.1021/nl025689f>.
- [156] K.K.S. Lau, J. Bico, K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, G.H. McKinley, K.K. Gleason, Superhydrophobic Carbon Nanotube Forests, *Nano Lett.* 3 (2003) 1701–1705.
<https://doi.org/10.1021/nl034704t>.
- [157] X. Zhou, J. Luo, J. Zhang, X. Wu, X. Tao, M. Zhu, Fabrication of self-assembly CNT flexible film and its piezoresistive sensing behaviors, *Nanotechnol Rev.* 11 (2022) 2050–2060.
<https://doi.org/10.1515/NTREV-2022-0121>.
- [158] R. Liu, Z. Liu, Self-pumping ultra-thin film evaporation on CNT-embedded silicon nitride nanopore membrane, *Nano Res.* 15 (2022) 1725–1729. <https://doi.org/10.1007/S12274-021-3851-8>.
- [159] J.-G. Fan, D. Dyer, | G Zhang, Y.-P. Zhao, Nanocarpet Effect: Pattern Formation during the Wetting of Vertically Aligned Nanorod Arrays, *Nano Lett.* 4 (2004) 2133–2138.
<https://doi.org/10.1021/nl048776b>.

- [160] Y.-P. Zhao, J.-G. Fan, Cite as, Appl. Phys. Lett. 88 (2006) 103123.
<https://doi.org/10.1063/1.2183735>.
- [161] H. Liu, S. Li, J. Zhai, H. Li, Q. Zheng, L. Jiang, D. Zhu, H. Liu, S. Li, J. Zhai, H. Li, L. Jiang, D. Zhu, Q. Zheng, Self-Assembly of Large-Scale Micropatterns on Aligned Carbon Nanotube Films, Angewandte Chemie International Edition. 43 (2004) 1146–1149.
<https://doi.org/10.1002/ANIE.200351988>.
- [162] H. Busta, Z. Tolt, J. Montgomery, A. Feinerman, Field emission from teepee-shaped carbon nanotube bundles, Citation: Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing. 23 (2005) 676. <https://doi.org/10.1116/1.1885009>.
- [163] J.W. Luginsland, A. Valfells, Y.Y. Lau, Effects of a series resistor on electron emission from a field emitter, Appl Phys Lett. 69 (1998) 2770. <https://doi.org/10.1063/1.117670>.
- [164] F.P. Du, N.N. Cao, Y.F. Zhang, P. Fu, Y.G. Wu, Z.D. Lin, R. Shi, A. Amini, C. Cheng, PEDOT:PSS/graphene quantum dots films with enhanced thermoelectric properties via strong interfacial interaction and phase separation, Scientific Reports 2018 8:1. 8 (2018) 1–12.
<https://doi.org/10.1038/s41598-018-24632-4>.
- [165] T.G. Avval, C. v Cushman, S. Bahr, Dimethyl sulfoxide by near-ambient pressure XPS, Surf. Sci. Spectra. 26 (2019) 14020. <https://doi.org/10.1116/1.5053099>.
- [166] Elets'kii A V, Physics-Uspekhi Carbon nanotube-based electron field emitters, Physics-Uspekhi. 53 (2010) 863. <https://doi.org/10.3367/UFNr.0180.201009a.0897>.
- [167] D.H. Kim, H.S. Yang, H.D. Kang, H.R. Lee, Novel emission degradation behavior of patterned carbon nanotubes by field emission, Chem Phys Lett. 368 (2003) 439–444.
[https://doi.org/10.1016/S0009-2614\(02\)01868-7](https://doi.org/10.1016/S0009-2614(02)01868-7).
- [168] S. Lee, D.Y. Jeon, Effect of degassed elements on the degradation behavior of carbon nanotube cathodes in sealed field emission-backlight units, Appl Phys Lett. 88 (2006) 063502.
<https://doi.org/10.1063/1.2167791>.
- [169] H. Murakami, M. Hirakawa, C. Tanaka, H. Yamakawa, Field emission from well-aligned, patterned, carbon nanotube emitters, Appl Phys Lett. 76 (2000) 1776.
<https://doi.org/10.1063/1.126164>.
- [170] S. Sridhar, C. Tiwary, S. Vinod, J.J. Taha-Tijerina, S. Sridhar, K. Kalaga, B. Sirota, A.H.C. Hart, S. Ozden, R.K. Sinha, Harsh, R. Vajtai, W. Choi, K. Kordás, P.M. Ajayan, Field emission with

- ultralow turn on voltage from metal decorated carbon nanotubes, *ACS Nano*. 8 (2014) 7763–7770. https://doi.org/10.1021/NN500921S/SUPPL_FILE/NN500921S_SI_001.PDF.
- [171] B. Günther, F. Kaldasch, G. Müller, Uniformity and stability of field emission from bare and metal coated Si tip arrays, Citation: *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing*. 21 (2003) 427. <https://doi.org/10.1116/1.1527642>.
- [172] L. Chen, Y. Mi, H. Ni, Enhanced field emission from carbon nanotubes by electroplating of silver nanoparticles ARTICLES YOU MAY BE INTERESTED IN, *J. Vac. Sci. Technol. B*. 29 (2011) 41003. <https://doi.org/10.1116/1.3610841>.
- [173] M.M.H. Raza, S.M. Aalam, M. Sadiq, M. Sarvar, M. Zulfequar, S. Husain, J. Ali, Study the electron field emission properties of silver nanoparticles decorated carbon nanotubes-based cold-cathode field emitters via post-plasma treatment, *Journal of Materials Science: Materials in Electronics*. 33 (2022) 7191–7211. <https://doi.org/10.1007/S10854-022-07900-Y/TABLES/7>.
- [174] L.H. Chen, J.F. AuBuchon, A. Gapin, C. Daraio, P. Bandaru, S. Jin, D.W. Kim, I.K. Yoo, C.M. Wang, Control of carbon nanotube morphology by change of applied bias field during growth, *Appl Phys Lett*. 85 (2004) 5373. <https://doi.org/10.1063/1.1830081>.
- [175] H. Hornauer, J. Vancea, G. Reiss, H. Hoffmann, Thickness dependence of the work function in double-layer metallic films, *Zeitschrift Für Physik B Condensed Matter*. 77 (1989) 399–407. <https://doi.org/10.1007/BF01453789>.
- [176] J.A. Liu, S. Chen, N. Mao, E. Cheraghi, Y. Sun, J. Wang, J.T.W. Yeow, Computational simulation and phenomenological analysis of freestanding carbon nanotube coulomb explosion induced by field emission, *J Mater Chem C Mater*. 10 (2022) 15872–15882. <https://doi.org/10.1039/D2TC02275C>.