Aligning carbon nanotubes via aerosol jet printing for flexible electronics

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ALIGNING CARBON NANOTUBES VIA AEROSOL JET PRINTING FOR
FLEXIBLE ELECTRONICS

GOH GUO LIANG

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2019

ALIGNING CARBON NANOTUBES VIA AEROSOL JET PRINTING FOR
FLEXIBLE ELECTRONICS

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University in partial fulfillment of
the requirements for the degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Yeong Wai Yee

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 2 is published as **Goh, G. L.**, Agarwala, S., & Yeong, W. Y. (2019). Directed and on-demand alignment of Carbon nanotube: A Review toward 3D Printing of Electronics. *Advanced Materials Interfaces*, 6, 1801318.

The contributions of the co-authors are as follows:

- Prof. Yeong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Shweta and Prof. Yeong.

Chapter 4 is published as **Goh, G. L.**, Saengchairat N., Agarwala, S., Yeong, W. Y., Tuan T., (2019). Sessile Droplets Containing Carbon Nanotubes: A Study of Evaporation Dynamic and CNTs Alignment for Printed Electronics. *Nanoscale*, 11(22), 10603-10614. DOI: 10.1039/c9nr03261d

The contributions of the co-authors are as follows:

- Prof. Yeong suggested the research direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Prof. Shweta, Prof Tuan, and Saengchairat.
- I performed all the drops study, collected FESEM images, conducted Raman spectroscopy, and conducted data evaluation.
- Saengchairat helped me with the drop study.

- Prof. Tuan provided his lab equipment for the experiment.

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- Prof. Yeong suggested the research direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Prof. Shweta.
- I performed all the fabrication of the device, characterization of the device such as dimension measurement, FESEM, pH test, and conducted data evaluation.
- Dr. Tan helped with cell viability test.

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List of Publications

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- [2] **Goh, G. L.**, Saengchairat N., Agarwala, S., Yeong, W. Y., Tuan T., (2019). Sessile Droplets Containing Carbon Nanotubes: A Study of Evaporation Dynamic and CNTs Alignment for Printed Electronics. *Nanoscale*, 11(22), 10603-10614. DOI: 10.1039/c9nr03261d
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- [4] Agarwala, S., **Goh, G. L.**, Le. T. S. D., An J., Peh Z. K., Yeong, W. Y., & Kim Y. J. (2019). Wearable Bandage-Based Strain Sensor for Home Healthcare: Combining 3D Aerosol Jet Printing and Laser Sintering, *ACS Sensors*, 4 (1), 218-226.
- [5] Agarwala, S., **Goh, G. L.**, and Yeong, W. Y., (2018). Aerosol Jet Printed Strain Sensor: Simulation Studies Analyzing the Effect of Dimension and Design on Performance, *IEEE Access*, 6, 63080-63086. DOI: 10.1109/ACCESS.2018.2876647
- [6] **Goh, G. L.**, Agarwala, S., Tan, Y. J., & Yeong, W. Y. (2018). A low cost and flexible carbon nanotube pH sensor fabricated using aerosol jet technology for live cell applications. *Sensors and Actuators B: Chemical*, 260, 227-235.

- [7] **Goh, G. L.**, Agarwala, S., Goh, G. D., Tan, H. K. J., Zhao, L., Chuah, T. K., & Yeong, W. Y. (2018). Additively manufactured multi-material free-form structure with printed electronics. *The International Journal of Advanced Manufacturing Technology*, 94(1-4), 1309-1316.
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- [9] Agarwala, S., **Goh, G. L.**, Yap, Y. L., Goh, G. D., Yu, H., Yeong, W. Y., & Tran, T. (2017). Development of bendable strain sensor with embedded microchannels using 3D printing. *Sensors and Actuators A: Physical*, 263, 593-599.
- [10] **Goh, G. L.**, Ma, J., Chua, K. L. F., Agarwala, S., Yeong, W. Y., & Zhang, Y. P. (2016). Inkjet-printed patch antenna emitter for wireless communication application. *Virtual and Physical Prototyping*, 11(4), 289-294.
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- [3] Agarwala, S., **Goh, G. L.**, & Yeong, W. Y. (2017, April). Optimizing aerosol jet printing process of silver ink for printed electronics. In IOP Conference Series: Materials Science and Engineering (Vol. 191, No. 1, p. 012027). IOP Publishing.
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- [2] **Goh, G. L.**, Yeong, W. Y., Controlling morphology of CNT film and printing transparent CNTs twin-line for transparent electronics and motion sensing. (*Submitted*)

Abstract

The alignment of carbon nanotubes (CNT) is paramount in determining the performance of the CNTs electronics devices due to the higher electron mobilities. Apart from the microstructures of the materials, high print resolution is also essential for the fabrication of miniature electronic component design, which is vital for achieving high performance printed electronics devices. As such, this work aims at achieving alignment of CNTs and high print resolution using aerosol jet printing (AJP) technique with the intention of producing high-performance electronics. AJP is a droplet deposition technique, where the aerosols of ink are formed and mixed with carrier gas flow and aerodynamically focused by sheath flow to form a tiny beam of aerosols for high-resolution printing. This work aims at utilizing evaporation-driven self-assembly (EDSA) phenomenon (also known as coffee ring effect) to form aligned CNTs in the printed trace.

Sessile drop experiments, a fundamental representation of the AJP process, are conducted to understand the factors affecting the EDSA mechanism of CNTs during the evaporation process. Factors such as substrate temperatures, concentration, pH and drop size of CNTs suspensions have been studied and their effects on the evaporation dynamics and final deposition patterns are discussed. CNTs are found aligned along the liquid-air-substrate interface and the resulting microstructures are characterized by Raman spectroscopy and Herman orientation factor (f) to help understand the mechanism of EDSA process and optimize for achieving better CNTs alignment. Solvent evaporation time is found to be critical for good CNTs alignment with large

drop evaporating at low substrate temperature favoring the formation of highly aligned CNTs ($f > 0.9$). Subsequently, the process window of the AJP process for achieving good quality and high-resolution line traces is investigated. An analytical model for the AJP process, which can help explain and understand the process, is developed and presented. A tradeoff between the degree of alignment and the printed line width is observed. The lowest line width of preferentially aligned CNTs traces is approximately $16\text{ }\mu\text{m}$ with $f \approx 0.4$. It is found that the print speed and the number of print passes are the main factors affecting the electrical conductivity of the printed CNTs traces. The preferentially aligned CNTs twin-lines exhibit almost 200-1000 times better electrical resistance as compared to the randomly and homogeneously distributed CNTs traces. The resistance per unit length of the printed CNTs traces was found to be tunable from $160\text{ k}\Omega/\text{cm}$ to $1.1\text{ G}\Omega/\text{cm}$ using suitable print parameters. Lastly, functional CNTs-based flexible sensors such as optically transparent motion sensors and pH sensor are fabricated as a proof-of-concept.

These favorable findings ascertain the feasibility of fabricating preferentially aligned CNTs using aerosol jet printing and contributed to the scientific knowledge in the respect of having (i) determined the key factors and mechanisms of evaporation-driven self-assembly of CNTs, (ii) analyzed AJP process comprehensively from aerosol transportation to ink deposition, and (iii) determined the process windows for printing high-resolution preferentially aligned CNTs and correlating the microstructure to the process parameters.

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List of Abbreviations

AF – atomizer flow	FWHM – full-width half-maximum
AFM – atomic force microscopy	LC – liquid crystal
AJP – aerosol jet printing	LJ - Lennard-Jones
AM – additive manufacturing	MWNT – multi-walled CNTs
CNT – carbon nanotubes	NS – nozzle size
CVD – chemical vapor deposition	PCB – printed circuit board
DCE - 1,2-dichloroethane	PmPV - poly(m-phenylenevinylene-co- 2,5-diocetoxy-p-phenylenevinylene
DI - deionized	PS – print speed
DLVO - Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek	SAM – self-assembled monolayer
DMM – digital multimeter	SF – sheath flow
EDSA – evaporation-driven self- assembly	SMU – source-measuring unit
f – Herman’s orientation factor	ST – substrate temperature
FESEM – field emission scanning electron microscopy	STM – scanning tunneling microscopy
FFT – Fast Fourier transform	SWNT – single-walled CNTs
	UC – ultrasonic current
	XRD – X-ray diffraction

List of Symbols

Section 2.3

χ - magnetic susceptibility

E – Magnetic energy

H – *Magnetic field strength*

Ω - volume of the particle

ε - permittivity of the material

σ – conductivity of the material

E - magnitude of the electric field

L_x - depolarization factor

ω - angular frequency of the electric field

μ - viscosity of the medium

R_p - CNT radius

U - particle velocity

C - correction factor

σ, γ - surface tension of the medium

φ_p - orientation angle of quadrupole

φ - principal direction of the host interface

R_C - quadrupole distance from the center of the particle

k_I - elastic constant;

θ_0 - particular tilting angle

k_2 - phenomenological surface tension

T - temperature

c - CNTs concentration

I - intensity of the acoustic wave

D - diameter of the CNT

L - length of the CNT

θ - azimuth angle on a plane

Φ - angle from the normal axis of the plane

Y_R - related to the property of the fluid and the geometry of CNT

Aerosol generation and transport

d_a - aerosol diameter

M – mass of material

ρ - density of material

f - frequency of the acoustic radiation

v_a - velocity vector of the aerosol

F_{St} - Stokes force (steady viscous drag force)

F_{Ba} - Basset force (nonsteady viscous drag force)

F_{Vm} - virtual mass force (inertia of fluid surrounding particle added to particle)

F_{Ps} - pressure gradient force, F_{Gr} is the buoyancy force caused by gravity

F_{Ma} - Magnus lift force due to particle rotation

F_{Sa} - Saffman lift force on a particle with local shear flow

Aerosol evaporation

$\dot{m}$ – mass transfer

$Ch_{i,s}$ - concentration of vapor at the droplet surface

$C_{i,\infty}$ - the concentration of vapor in the bulk gas

$M_{w,i}$ - molecular weight of species i

$k_{c,i}$ - transfer coefficient

m_p - mass of droplet

C_p - droplet heat capacity

T_p droplet temperature

A_p - surface area of droplet

T_∞ - temperature of the continuous phase

ε_p - droplet emissivity,

σ - Stefan–Boltzmann constant ($5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$)

θ_R - radiation temperature

ΔH_V - difference between the latent heat of droplets and the bulk gas

Aerosol deposition

ρ_i - film density

A_c - area of film projected on the substrate

δ - film height

V_f - film velocity

l_i - length of the cell side i

S_d - source term

$\dot{M}_{vap}$ - ink solvent vaporization rate.

$T = -P\mathbf{I} + \mu[\nabla\mathbf{u} + (\nabla\mathbf{u})^T]$ is the stress tensor

$\mathbf{u}$ - velocity flow field

$\mathbf{n}$ - unit normal to the surface

$\mathbf{t}$ - unit tangent to the interface

$\delta(x - x)$ - three-dimensional delta function

$J(x)$ - local curvature of gas-liquid interface

$\bar{T}$ - mean film temperature

C_v - liquid specific heat

k - liquid film thermal conductivity

∇_S - surface gradient operator

$\dot{Q}_{imp}$ - energy source due to impinging aerosol

$\dot{Q}_s$ energy source due to droplets that splash

T_s - liquid-gas interface temperature

T_w substrate temperature

We - webber number

w_0 – velocity

E – evaporation number

S – scaled surface tension

D – density ratio

Ma – Marangoni number

P – Prandtl number

$\mathcal{W}$ - describes the thermal effects in the solid

d_s - typical thickness

k_s - thermal conductivity of the substrate

A – non-dimensional parameter of contact angle behavior

g – gravitational acceleration

ϕ - fraction of surface area that can be occupied by the colloid particles

Forces acting on particles-substrate-liquid system

F_C - resultant conservative force acting on the particles due to interaction with other colloidal particles

F_H - hydrodynamic force as a result of the solvent motion

F_B - total Brownian force

a - particle radius

ρ_∞ - bulk electrolyte concentration

κ - inverse Debye screening length

ψ_0 - potential at a particle at the particle surface

R - hydrodynamic resistance tensor

$\delta_D(\tau)$ - Dirac delta function

F_{VDW} – van der Waal's force

F_e – electrostatic force

k - Debye-Huckel parameter (which is the reciprocal of electrical double layers thickness

Ψ - surface potential of particle 1 or plate 2

θ - contact angle of the thin liquid film at the interface

f - coefficient of friction

F_a - total adhesive force

F_g - force due to the gravity

t - evaporation time

θ_e - equilibrium contact angle

φ - CNT concentration

$\lambda(\theta)$ - a parameter that describes the profile of the drop's local evaporation rate

D - diffusion coefficient of the water in the air

H -relative humidity

t_f - time taken for the solvent to evaporate from the drop

T_s - substrate temperature

V_{L0} - initial drop volume

D - diffusion constant for the vapor molecule in gas phase

k_B - Boltzmann's constant

T - temperature of vapor

$\beta = (2 + \cos \Theta)(1 - \cos \Theta)^2$, Θ is the contact angle

P_0 - vapor pressure of liquid with a planar surface

V_m - molecular volume in the liquid phase

x - saturation level of the vapor

f - polynomial function of contact angle

Chapter 5

N - number of droplets

d - diameter of each droplet, θ is the contact angle of the ink

L - length of the deposited drop

w - width of the deposited drop

r - radius of the cylindrical cap

$\dot{V}_{aerosol}$ - aerosol deposition rate

$\dot{V}_{atomizer}$ - atomizer flow rate

φ - volume fraction of aerosol

τ - lifespan of aerosol

Sh is the Sherwood number

ρ_c - density of carrier gas

ρ_d - density of the ink's solvent

D_v - diffusion coefficient

ω_∞ - moisture content at ambient condition

ω_s -moisture content at the surface of the aerosol

1. INTRODUCTION

1.1 Background

The demand for lightweight, adaptable, portable electronics with added functionalities has resulted in a paradigm shift in the field of electronics to explore flexible and stretchable electronics [1, 2]. The growing interest in the field of flexible and stretchable electronics has spurred the search for the new materials and fabrication methods to replace the conventional devices, which are often made by printed circuit board (PCB) method [3-5].

Carbon nanotubes (CNTs) are 1-dimensional nanomaterials, which are inherently flexible and possess excellent electrical conductivity and high electrons mobilities, are seen to be suitable materials for fabricating flexible high-speed electronics. CNTs are the carbon allotropes and their structures resemble hollow cylinders [6]. CNTs can be viewed as a graphene layer being rolled into cylinders forming walls of hexagonal carbon [6]. Each carbon atom is bonded to the adjacent carbon atoms by strong covalent bonds and possesses free-electron due to the hybridization of electron orbitals [6]. This explains the high mechanical strength and electrical conductivity of the CNTs. Due to the 1-dimensional structure of CNTs, they exhibit different mechanical and electrical properties in the direction parallel to the tube axis and perpendicular to the tube axis. For instances, the electron mobility of highly-ordered CNTs film is 10-43 times higher than its counterpart with random CNTs network and the amount of CNTs in nanocomposite can be an order lesser to produce a conducting percolation network when the CNTs were aligned [7-9]. Also, the strain sensitivity of well-organized CNTs composite film is 6 times higher compared to the random counterparts [10]. In terms of the mechanical property, the storage modulus of

aligned CNTs nanocomposite improved by approximately 40 % as compared to the random CNTs nanocomposite [11]. More importantly, the alignment and uniformity of 1-dimensional materials such as CNTs have a significant effect on the performance reproducibility [12]. Therefore, the ability to obtain aligned CNTs architectures is important for fundamental characterization and potential applications with enhanced performance.

This unique property of CNTs is useful for applications in the electronics, optoelectronics, mechanical reinforcement, heat transfer enhancement, and sensing. As such, researchers have been exploring various fabrication techniques to control the orientation of CNTs for electronics and structural devices. Various techniques have been employed to align the CNTs such as chemical vapor deposition (CVD) [13], electrospinning [14], spin coating [15] and dip coating [16]. However, these techniques have limitations, such as the choice of substrate materials and the ability to do patterning. For instance, polymeric substrates, which are often used in flexible electronics, cannot be used in CVD process due to high processing temperature, whereas freeform patterning of CNTs cannot be achieved by electrospinning (Figure 1), spin coating, and dip coating. Thus, alternative methods that allow controlled patterning of inks on low heat resistance polymeric substrate are required for fabricating of flexible and stretchable electronics.

Material-jetting is a class of additive manufacturing (AM) or 3D printing techniques which additively deposits inks on the substrates as per the digital formats [17]. Material-jetting AM techniques provide simple ways to pattern functional inks on-demand at considerably low temperature, thus allowing fabrication of flexible electronics on polymeric substrates. CNTs inks can be made into dispersions with suitable solvents to

form stable suspension solutions for printing. More importantly, CNTs could possibly be aligned with evaporation-driven self-assembly (EDSA) which is a naturally occurring phenomenon in the droplet-based AM process.

Figure 1 Images of (a) randomly aligned CNTs and (b) highly aligned CNTs made from electrospinning method. (Reproduced from Ref. [18] with permission from MDPI)

1.2 Motivation

The performance of printed CNTs devices (eg. speed of transistor) is determined by on the electron mobilities of CNTs, which depends on the alignment of CNTs and the dimensions of the devices [19]. In general, more aligned CNTs network and smaller component size can result in a device with an enhanced performance [20]. This can be done by using high-resolution printing techniques. However, existing work on inkjet printing of CNTs shows that the process can only achieve aligned CNTs with print resolution reported in the range of 100 μm to 1 mm, thus imposes limitation for the fabrication of high-performance miniature electronics. The low print resolution of inkjet printing is due to the fact that large nozzle diameter must be used to prevent clogging. In addition, the existing

inkjet printing technique lacks design freedom as it is limited to printing planar electronic design.

With the intention of achieving aligned CNTs with a high print resolution, the state-of-the-art aerosol jet printing (AJP) technique is chosen for this research because of its ability to achieve print resolutions of up to a few microns, thus allowing the realization of high-performance devices. Furthermore, AJP not only gives electronics designers the flexibility to fabricate electronics on a wide variety of substrate such as flexible substrates at low processing temperature but also the design freedom to print electronics on 3D structures to realize lightweight and multifunctional devices. With the capability of AJP to print fine resolution advanced electronics, improving the print resolution for aligned CNTs thin film is made possible. However, it has been found that the printed CNTs thin films via AJP are often randomly aligned.

Based on the current information available, there is a lack of explanations about the difference in the film morphology between inkjet printed and aerosol jet printed CNTs. This strongly suggests that the knowledge on EDSA of CNTs at such high print resolution is not well understood, thus indicating the need and potential for more in-depth research. A deeper and comprehensive understanding of EDSA phenomenon of CNTs by investigating the interplay among the competing factors such as solvent evaporation time, surface charge and particle diffusion, can help improve the alignment of CNTs fabricated by high-resolution AJP technique.

1.3 Aims and objectives

This research aims at achieving preferential alignment of CNTs via AJP technique utilizing evaporation-driven self-assembly. Through this research, the understanding of AJP process and EDSA phenomenon will improve the capability of fabricating aligned CNTs thin film for electronics. The objectives of this research are listed below:

1. To investigate the EDSA phenomenon of the evaporating CNTs drops. The mechanism of formation of CNTs thin film with respect to the particle-flow dynamics in the evaporation process will be studied.
2. To study the effect of various process parameters on the print resolution of the AJP. The process window of the AJP to fabricate high-resolution line traces will be discussed and an analytical model of the AJP process will be presented.
3. To obtain preferentially aligned CNTs fabricated by AJP process utilizing EDSA phenomenon. The degree of alignment of the AJ printed CNTs traces will be characterized. The measured electrical property of the AJ printed CNTs traces will be discussed.
4. To develop a process for direct printing CNTs with alignment for the fabrication of a functional flexible electronic device as a proof-of-concept.

1.4 Scope

The scope of this research is listed below:

1. Sessile drop experiment, as a fundamental representation of the AJP process, is carried out to investigate the effect of temperature, concentration, pH and drop size of CNTs suspension on the alignment of CNTs by the EDSA phenomenon.
2. Optimization of the process parameters such as the sheath gas flow rate, atomizer gas flow rate, print speed, substrate temperature and ultrasonic current for atomization is carried out. The dimensions and quality of the printed traces will be characterized to understand the basic phenomena that occur in the AJP process.
3. The degree of alignment of the CNTs fabricated in sessile drop experiment and AJP will be characterized with suitable techniques such as polarized Raman spectroscopy, field emission scanning electron microscopy (FESEM), and image analysis. A comparison of characterization techniques will be carried out to verify the results.
4. Electrical resistance of the printed CNTs traces will be measured and fabrication of functional CNTs-based flexible electronic devices will be presented.

The approach to achieve the objectives and scope of the research is summarized in Figure

2.

Figure 2 Research overview

1.5 Organization of Report

This thesis begins with the introduction which discusses the background, motivations, objectives, and scope of the research in Chapter 1. It is then followed by literature review which discusses the general information about CNTs, the mechanisms of different CNTs alignment techniques, the working principle of aerosol jet printing process and findings of prior work in Chapter 2. The materials and research methodology used in this research are described in Chapter 3. The characterization of the CNTs such as the particle size and zeta potential of the CNTs suspension is presented.

Chapter 4 describes the study of sessile drop experiments containing CNTs. The science behind the alignment of CNTs by evaporation-driven self-assembly (EDSA) process is explained using the hydrodynamic flow and the inter-particle forces experienced by the CNTs during the evaporation process. The interplay among factors such as the substrate temperature, concentration, pH and drop size of CNTs suspension on the evaporation dynamics and alignment of CNTs are highlighted. The characterization of the degree of alignment of CNTs using Raman spectroscopy, field-emission scanning electron microscopy (FESEM), and image analysis are also presented.

The investigation of the effect of the process parameters of AJP on the print resolution and quality is discussed in Chapter 5. An analytical model of AJP is developed to explain the AJP process. Experiments are conducted to validate the analytical model. Building from the understanding of EDSA in Chapter 4, Chapter 6 details the study on the alignment effect of CNTs of AJ printed CNTs traces by EDSA. The effect of the print

resolution on the degree of alignment quantified and electrical measurement is also conducted.

In Chapter 7, proof-of-concept applications of aerosol jet printed devices such as functional flexible CNTs-based pH sensor and optically transparent motion sensors are presented. Chapter 8 summarizes the research and possible future work.

2. LITERATURE REVIEW

2.1 Driving torques for CNTs alignment: theoretical background

The alignment of the CNTs requires a driving torque to change the orientation of the CNTs. The driving torque can be generated by applying external force fields or induced by condition and constraints of the surrounding medium and substance. For instance, the driving torque can be generated by applying a shear field, electric field, and magnetic field to the CNTs. Besides, the aligning torque on CNTs can also be induced by van der Waals interaction and a pinned end of CNTs by the tip adsorption to the substrates as shown in Figure 3a and Figure 3b. The torque is normally generated to minimize the misalignment angle between 2 adjacent nanotube axes or between the nanotube axis and the force field which is largely attributed to the geometric and electronic structures of the CNTs [21].

The one-dimensional structure of CNTs can be considered as a graphene sheet being rolled into a nano-cylinder. Therefore, CNTs possess similar electronic configuration as a graphene sheet that is the hexagonal carbon rings and valence free electrons due to the sp^2 hybridization of the carbon atom. As such, the electrons can flow freely along the wall of the nanotubes and also in the direction of the tube axis (Figure 3c)[22]. The movement of the electrons circling around the circumference of the nanotubes results in a large orbital magnetic moment and explains the anisotropic susceptibility of CNTs that is responsible for the magnetic-induced torque acting on the CNTs in the presence of magnetic field as shown in Figure 3c[23]. Thus, they are magnetically symmetric along the tube axis and possess molar susceptibilities parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to it [24]. For a diamagnetic CNTs with n carbon atoms, the magnetic energy in a magnetic field, the

magnetic energy can be expressed as equation (1) with $\chi_{\perp} < \chi_{\parallel} < 0$ [24]. As such, the nanotube is most stable when the tube axis is parallel to the magnetic field as the magnetic energy is minimized at $H(\theta) = 0$.

$$E(\theta, H) = -\left(\frac{nH^2}{2}\right)[\chi_{\perp} + (\chi_{\parallel} - \chi_{\perp})\cos^2\theta] \quad (1)$$

Besides, it is well-known that the van der Waals interaction between CNTs can be explained by the electromagnetic forces between them[25]. The electromagnetic force is formed by the temporary dipole as a result of the fluctuation of the electron density. It is discovered that the van der Waals potential of CNTs should go as C_3/R^3 with R representing the intermolecular distance[25]. The coefficient C_3 is evaluated at the imaginary frequencies and it is calculated from the dielectric constant of infinite nanotubes and frequency-dependent polarizabilities of the molecular fragments[26-29]. By calculating the minimization of surface free energy of 2 skewed CNTs, the van der Waals torque between them to make them align parallel to each other can be estimated[30].

Apart from the abovementioned, CNTs in the presence of an electric field can induce dielectrophoretic torque to make them align parallel to the electric field[31]. The polarizability of the elongated CNT is responsible for the formation of dipole across the CNT tube as shown in Figure 3d [32, 33]. The torque acting on the CNTs in an electric field can be estimated by using equation (2) [31].

$$T_{align} = \frac{1}{4}\Omega\epsilon_m \text{Re}[\alpha^*]E^2 \sin 2\theta \quad (2)$$

and,

$$\alpha^* = \frac{(\varepsilon_p^* - \varepsilon_m^*)^2}{[\varepsilon_m^* + (\varepsilon_p^* - \varepsilon_m^*)L_x](\varepsilon_p^* + \varepsilon_m^*)}$$

$$\varepsilon_{m,p}^* = \varepsilon_{m,p} - j \frac{\sigma_{m,p}}{\omega}$$

Where Ω is the volume of the particle, ε_m is the permittivity of the surrounding medium, ε_m^* and ε_p^* are complex numbers ($j^2 = -1$) expressed in terms of the electrical permittivities (ε) and conductivities (σ) of the medium (m), and particle (p); E is the magnitude of the electric field; L_x is the depolarization factor, ω is the angular frequency of the electric field ($\omega = 2\pi f$) and ‘ Re ’ represents the real part of the complex expression within brackets.

The aforementioned driving forces such as van der Waals’ interaction, dielectrophoretic torque, and magnetic-field-induced torque are closely related to the intrinsic property of the CNTs, that is the electron flow within the CNTs. Besides these forces, there are other external forces and torques that can affect CNTs alignment. For instance, the drag force and the Brownian motion of the particles in a flowing fluid. The former has a strong dependence on the geometric shape of the CNTs and the latter depends on the thermal energy of the medium[32].

Figure 3. Schematic showing different types of CNTs alignment torque (a) van der Waals' torque, (b) torque induced by external force on a pinned end of a CNT, (c) magnetic-induced torque, and (d) dielectrophoresis-induced torque. (Reproduced from Ref [34] with the permission from John Wiley and Sons)

For CNTs suspended in a medium, the CNTs can experience various forces such as the drag force, the capillary force between the CNTs, and the pulling force by the surface tension of the medium. The drag force of a CNT in a medium depends on its geometry and the viscosity of the medium. In general, the drag force of a rod-like structure such as CNTs in the perpendicular, $\perp$ and parallel directions, $\parallel$ can be expressed as equation (3) and equation (4) respectively [35, 36].

$$F_{drag,\perp} = - \frac{4\pi\mu L}{\ln\left(\frac{L}{2R_p}\right) + C_{\perp}} U_{\perp} \quad (3)$$

$$F_{drag,||} = - \frac{2\pi\mu L}{\ln\left(\frac{L}{2R_p}\right) + C_{||}} U_{||} \quad (4)$$

Where L is the CNT length, μ is the viscosity of the medium, R_p is the CNT radius, U is the particle velocity, and C is the correction factor. The capillary force between the CNTs can be expressed as equation (5) [37].

$$F_{p-p} \sim - \frac{2\pi R_1 R_2 \gamma}{d} \quad (5)$$

Where R_1 and R_2 are particle radii, γ is the surface tension of the medium, and d is the distance between the CNTs. On the other hand, the capillary force ($-\nabla_x E$) and torque ($-\partial E / \partial \phi_p$) due to the surface tension at the interface of fluid can be derived from the capillary energy, $E = -\pi\gamma H_p R_p^2 \frac{1}{R_c(r)} \cos 2(\phi_p - \phi)$ of the elongated body, where H_p is the quadrupole amplitude, R_c is the quadrupole distance from the center of the particle, ϕ_p is the orientation angle of quadrupole and ϕ is the principal direction of the host interface[35]. This explains why the CNTs tend to be more stable at the solid-fluid interface[38]. This is also the fundamental driving force of the evaporation-driven self-assembly which the mechanism will be discussed in a later section.

For CNTs suspensions that exhibit 2D nematic phase, the governing equation (equation 6) that describes CNTs orientation can be derived from the free energy of the nanotubes, $G = \frac{1}{2} c k_1 \left(\frac{\partial \theta}{\partial x}\right)^2 + \frac{1}{2} c k_2 \sin^2(\theta - \theta_0) + k_b T \ln c$, where the first term is the elastic distortion energy due to the CNTs interaction and k_l is the elastic constant; the second term is the surface anchoring energy due to the substrate-CNTs interaction that

prefers a particular tilting angle, θ_0 and k_2 is the phenomenological surface tension constant, the third term is related to the thermal energy of temperature, T , and c is the CNTs concentration. Equation 6 can be expressed as[39],

$$\frac{\partial^2 \theta}{\partial x^2} - \frac{k_2}{2k_1} a \sin 2(\theta - \theta_0) = 0 \quad (6)$$

A driving torque can also be generated to align the CNTs when the acoustic wave is applied to a CNTs suspension. The aligning moment generated by the nonlinear radiation pressure acting on a straight CNT can be derived as equation 7[40].

$$M_\theta = \frac{IDL^2}{2} \sin \theta \left(Y_R \sqrt{\cos^2 \theta + \sin^2 \Phi \sin^2 \theta} \right) \quad (7)$$

Where I is the intensity of the acoustic wave, D is the diameter of the CNT, L is the length of the CNT, θ is the azimuth angle on a plane, Φ is the angle from the normal axis of the plane, Y_R is related to the property of the fluid and the geometry of CNT.

2.2 Existing CNTs alignment techniques

Various techniques have been used to achieve aligned CNTs. These techniques include the growth of aligned CNTs via chemical vapor deposition (CVD), and the post-growth alignment via applying a magnetic field and electric field, shearing, straining, fiber drawing/electrospinning, spin coating, liquid crystal, surface acoustic wave, and self-assembly as summarised in Table 1 to the best of authors' knowledge. Figure 4 shows

various in-situ and ex-situ CNTs alignment techniques and their respective resulting end products.

In brief, the CNTs alignment techniques can be categorized into in-situ alignment and ex-situ alignment. In-situ alignment refers to a class of technique which the alignment of CNTs is achieved during the growing process of CNTs (ie. CVD or direct spinning process). The resulting CNTs architectures of direct spinning process is normally CNTs rope, CNTs yarns, or CNTs fibers, whereas CVD process normally produces CNTs arrays that can be either random, horizontally aligned, or vertically aligned. These techniques normally produce large-scale and free-standing CNTs architectures that can be used for fibers in composite materials, conducting textile, and Bucky paper. However, these techniques lack design freedom and have high processing temperatures which make them difficult to be integrated with polymeric materials for the fabrication of flexible electronics, thus the need for post-growth or ex-situ CNTs alignment techniques. Among the ex-situ techniques, solution-processed CNTs has become the most popular processing method for electronics fabrication on flexible polymeric substrates due to the low processing temperature and the extra CNTs sorting and purification steps for improved reliability and performance of the fabricated devices. The dispersed CNTs in the solvent can be aligned by various methods such as electric field, magnetic field, acoustic wave, shear flow, and self-assembly. The advantages and disadvantages of each technique are discussed in Table 1.

Figure 4 Flowchart showing in-situ and ex-situ CNTs alignment techniques and their respective final CNTs architectures. (Reproduced from Ref [34] with permission from John Wiley and Sons)

Table 1 Various principle of CNTs alignment and techniques (Reproduced from Ref [34] with permission from John Wiley and Sons)

Principle of alignment (driving force)	Advantages	Disadvantage	During growth/Post-growth	Various processes	Forms of CNTs	Type of alignment	Herman's orientation factor ^{a)} / FWHM ^{b)}	Ref
Electrostatic and Van der Waal's interaction	<ul style="list-style-type: none"> •Large area coverage •CNTs patterning is possible (by patterning the catalyst or SAM) •Scalable 	<ul style="list-style-type: none"> •Only work with high CNTs density •Not applicable to composite materials 	During growth	thermal CVD	Pure forest CNTs	Vertically aligned	0.99	[41]
			Post-growth	Self-assembled monolayers (SAM)	Pure film CNTs	Vertically aligned	0.96	[42]
Magnetic field-induced alignment	<ul style="list-style-type: none"> •Non-contact •Remote action •Applicable to viscous liquids •Improve CNTs dispersion •Prevent agglomeration 	<ul style="list-style-type: none"> •Require very strong magnet (typically >10T) •CNTs must be filled with paramagnetic particles •Unable to control CNT separation 	During growth	CVD + magnetic field	Pure forest CNTs	3D aligned	0.61-0.89	[43, 44]
			Post-growth	Pure CNTs/CNTs composite dispersion + magnetic field	Thin films of SWNTs rope	aligned fiber rope	FWHM (25°-35°)	[45]
					SWNTs–epoxy composite	3D aligned	0.62-0.95	[46]
Electric field induced alignment	<ul style="list-style-type: none"> •Fast process (<1minute) •Applicable to viscous liquid 	<ul style="list-style-type: none"> •Electrode/terminal is required •Possible accumulation of CNTs on the electrode •Migration of CNTs can occur 	During growth	Plasma-enhanced CVD	Pure MWNTs	Vertically aligned	0.89	[47]
			Post-growth	Pure CNTs/CNTs composite dispersion + electric field	Pure SWNTs	3D aligned	0.89	[48]
					MWNTs composite	3D aligned	0.94	[49]

		•The effectiveness of alignment is dependent on frequency applied							
Strain-induced alignment	<ul style="list-style-type: none"> •simple procedure •Controllable degree of alignment by varying strain 	<ul style="list-style-type: none"> •stretching is inhomogeneous at film edge •the sample size is limited •time-consuming •require experience 	Post-growth	Stretching Pulling	Pure film	CNTs	In-plane	0.83	[50]
						CNTs composite	In-plane	0.67-0.87	[51, 52]
						CNTs sheets	In-plane	0.99	[53]
						CNTs yarns	Aligned yarns	0.99	[54]
Shear-induced alignment (in-plane shear)	•Controllable degree of alignment	<ul style="list-style-type: none"> •Can incur damage on materials •the degree of alignment depends on the film thickness •only work with low CNTs density 	Post-growth	Rubbing	Pure film	CNTs	In-plane	0.78	[55]
				Domino-pushing		CNTs Bucky paper	In-plane	0.77	[56]
				Doctor blade technique		CNTs/polymer composite	In-plane	0.70	[57]
				Cutting		CNTs composite	In-plane	0.72	[58]
Shear-induced alignment (extrusion-induced)	<ul style="list-style-type: none"> •fast and simple process •CNTs fiber are highly aligned 	<ul style="list-style-type: none"> •Tend to bend and twist CNTs •Formation of bent and twisted CNTs and agglomerate •Possible fiber formation 	During growth	Direct-spinning	Pure and fiber	SWNTs and MWNTs	aligned fiber rope	0.78	[59]
			Post-growth	Fiber spinning		CNTs/polymer composite	aligned fiber embedded in filament matrix	0.50-0.97	[60]
				Electrospinning		Pure CNTs or CNTs composite	aligned fiber embedded	0.25	[14]

						in filament matrix		
					Nano drawing	Pure CNTs	aligned fiber embedded in filament matrix	0.94 [61]
Shear-induced alignment (flow-induced)	•Simple	<ul style="list-style-type: none"> •Limited to low viscosity solutions •the degree of alignment depends on the type of substrates •limited to in-plane alignment 	During growth		thermal CVD	Pure CNTs	In-plane and vertically aligned	0.82 [62]
			Post-growth		Gas flow	Pure CNTs or CNTs composite	In-Plane	0.87 [63]
					Spin coating	Pure CNTs or CNTs composite	In-Plane	0.54 [15]
					Microfluidic	Pure CNTs	In-Plane	0.53 [64]
					Blown bubble-film	Pure CNTs	In-Plane	0.85 [12]
Self-assembly and Liquid crystal-induced	<ul style="list-style-type: none"> •the orientational behavior of carbon nanotubes can be preselected and determined •Can use various techniques such as mechanical, electrical and magnetic forces with a much lower field force 	<ul style="list-style-type: none"> •Have a strong tendency towards clustering and aggregation of single tubes into a network •Limited to solution 	Post-growth		Dip coating	Pure CNTs	In-plane	0.51 [16]
					Inkjet printing	Pure CNTs	In-plane alignment	0.65-0.91 [65]
					Langmuir-Blodgett technique	Pure CNTs	In-plane alignment	0.84 [66]

<ul style="list-style-type: none"> • Large area oriented-synthesis of CNTs thin film • Densely packed • Suitable for various substrates 										
Surface acoustic wave-induced		<ul style="list-style-type: none"> • the spacing of the CNTs can be controlled by adjusting the frequency of the SAW 	<ul style="list-style-type: none"> • highly dependent on the substrate-nanotube interaction • not suitable for CNTs with large curvature 	Post-growth	Drop-cast	Pure CNTs	In-plane alignment	0.68-0.83	[67], [40]	
Guided growth-induced alignment		<ul style="list-style-type: none"> • In-situ alignment 	<ul style="list-style-type: none"> • Low density CNTs 	During growth	<ul style="list-style-type: none"> • Lattice-guided • Nano-steps guided 	Pure CNTs	In-plane	Most CNTs fall within $\pm 5^\circ$	[68]	Angle deviation from the aligning angle

^{a)}Herman Orientation Factor: the value of 1 represents perfect alignment; the value of 0 represents random alignment. This Herman Orientation Factor is obtained by extracting the SEM images from the original article and then processed by using the image processing software, ImageJ.

^{b)}Full Width Half Maximum: smaller angle deviation suggests better alignment.

2.3 Self-assembly of aligned CNTs

Among the CNTs alignment techniques for solution-processed CNTs, self-assembly technique is the simplest fabrication method for achieving aligned CNTs as it relies on naturally occurring phenomenon. Sections below discuss different self-assembly techniques for aligning CNTs.

2.3.1 Liquid crystal-induced CNTs alignment

Liquid crystal (LC) are soft and ordered structure that can be used to alter the microstructure of materials. Many studies have shown that SWNT and MWNT can be aligned using LC by first creating a well-dispersed CNTs-LC solution. Different classes of LC such as thermotropic LC (display-type) [69-73] and lyotropic (amphiphilic molecule dispersed in water, e.g. surfactant encapsulated-CNTs) LC can be used for CNTs aligning purpose[74-77]. However, thermotropic LC could not be removed from the CNTs thin film once the alignment is done, whereas the surfactant in lyotropic CNTs-LC can be easily removed by rinsing with water. Generally, LC in nematic phase is normally used for CNTs alignment purpose[78]. The orientation of the LC can be altered by mechanical, electrical and magnetic forces and hence the CNTs alignment. Depending on how surfactant molecules are attached to the CNTs surfaces, the surfactant-coated CNTs will interact with the host LC solution to promote alignment in a preferential direction with respect to the LC director. CNTs concentration is an important criterion for the formation of lyotropic CNTs solution, typically ranges between 1-4 % [79]. One disadvantage of LC-induced CNTs alignment method is that it only works within the certain temperature range of LC's nematic phase.

An extensive review of carbon nanotube and liquid crystalline phase has been done by Zakri et al[80].

2.3.2 CNTs alignment by Evaporation-Driven Self-Assembly

Patterning of CNTs-LC into aligned CNTs thin films is essential to fabricate functional electronic devices. Various techniques have been used to pattern the CNTs-LC such as dip-coating[16] and inkjet printing (Figure 5) [65], just to name a few. These techniques basically use the principle of evaporation-driven self-assembly of the nanoparticle to control the adsorption of CNTs to the substrate. Generally, there are 2 modes of evaporation, which are (1) constant contact angle (shrinking or depinned contact) and (2) constant contact area (pinned contact) [81]. The mode of evaporation is affected by various factors such as rheology of suspension, surface roughness, the rate of evaporation and evaporation mechanism. However, it has been shown that a third mode (switching between mode 1 and 2) is also possible and it is generally believed that it is due to the existence of contact angle hysteresis on the surface [82]. The pinning of the liquid-substrate interface is due to the friction between the substrate surface and the CNTs suspension coupled with the higher evaporation at the interface. The accelerated evaporation rate at the interface causes a capillary flow (also known as convective transport) which brings CNTs to the interface forming CNTs aggregates at the liquid edge. This phenomenon is more commonly known as “coffee-ring” effect. Besides pushing the CNTs to the edge, the capillary flow also induces a torque on those CNTs are pinned on one end so that they align parallel to the interface. This phenomenon can also be attributed to the minimization of the surface energy of the CNTs because the CNTs is more thermodynamically stable along the triple-phase

junction line and causing the junction line to be pinned [75]. Due to the equilibrium of van der Waals' force, the CNTs will then stack next to one another [83]. In other words, the first CNT at the interface will act as the LC director to align the subsequent CNTs as the solvent evaporates. Combining the principles of self-assembly and LC-induced alignment, a thin film of highly aligned CNTs can be produced. For the case of inkjet printing, an additional force invoked by the incoming droplets in the printing direction would interfere with the radial capillary force resulting in a total velocity flow which can be resolved in radial direction and printing direction[83]. The effect of the resultant velocity flow is that CNTs would tend to align parallel to it resulting in CNTs being aligned in a preferential direction [83]. The CNTs spacing can be adjusted by varying the concentration of CNTs and surfactant in the suspension [65]. Self-assembly by dip coating is suitable for large-area fabrication, however, the process is very slow due to the fact the process depends on the evaporation rate instead of the pulling speed of the substrate [84]. One advantage of evaporation-driven self-assembly method is that non-lyotropic CNTs solution can also be used. This is because local CNTs concentration could exceed the critical concentration when CNTs are pushed toward the periphery via convective transport forming lyotropic CNTs solution locally [38]. Since the alignment is concentration-dependent, the CNTs concentration could recede well below the critical concentration in the middle region of the drying CNTs suspension due to the “coffee ring” effect forming randomly oriented CNTs. One way to overcome this issue is to use CNTs suspension with a concentration higher than the critical concentration. Other ways to pattern the CNTs-LC is by using a substrate patterned with different wettability (both hydrophilic and hydrophobic) for CNTs-LC or substrates placing in a wedge configuration [37, 85]. With self-assembled monolayer (SAM)

together with inkjet printing, it has been shown that aligned CNTs thin film can be produced using strong wettability boundary and coffee-stain effect [86]. It is interesting to note that SWNTs tend to align better than MWNTs since SWNTs bend more easily than MWNTs, thus their orientations at the outer edge can be easily adjusted to form a large area well-organized CNTs architectures [75].

Figure 5 Self-assembly method by (a) dip-coating method[16] and (b) inkjet printing method [65]. (Reproduced from Ref [34] with permission from John Wiley and Sons)

2.3.3 Sessile drop study of CNTs suspensions

Sessile drop experiment is a fundamental representation of these droplet-based 3D printing techniques and commonly used to understand the printing processes. Although many sessile drop studies have been conducted to investigate the particle arrangement and/or alignment of elongated particles at the coffee ring, the materials used in these works are either micro-sized elongated bead with low aspect ratio (<10)[87, 88] or straight nanotubes that are not flexible like CNTs[89]. CNTs are flexible materials with a high aspect ratio (~ 100) which displays different particle-flow dynamics and hence the particle arrangement. However, there are only a few studies focusing on the arrangement and orientation of CNTs in a sessile

drop[90-93]. Duggal et al. suspended the CNTs in pluronic solution and observed a crusting phenomenon in where CNTs assembled themselves at the free surface[91]. Li et al. found that lower concentrations of CNTs suspension lead to higher ordering of the network due to less entanglement[93]. They also reported that enhanced ordering of nanotube networks at an elevated temperature that only happens with single-walled CNTs but with multi-walled CNTs. Small et al. investigated the contact line dynamics of CNTs sessile drop on different hard surface substrates (like glass, copper, and silicon) and observed different deposition patterns[92]. Zhang et al. pointed out the critical concentration of CNTs suspension (around 0.2 w%) where the CNTs suspension is isotropic below 0.2w% concentration and single nematic liquid crystalline (LC) phase can be observed at a concentration of 3.8w% [90]. It has been found that nanotubes tend to align along the contact line and a transition of nanotubes orientation from parallel to perpendicular to the contact line have been observed further away from the contact line[93, 94]. The degree of alignment of the nanotubes is affected by the length and charge of the nanotubes along with the ionic strength, pH and temperature of the solvent[89].

2.3.4 Printing of aligned CNTs

Dinh et al. made use of this EDSA method to create aligned CNT twin-line using inkjet printing technique[83]. However, these existing techniques are limited by the resolution of the printed features, thus constricting the potential for achieving high-performance devices. For instance, the Beyer et al. achieved a homogenous and aligned CNT network by printing a line width of around 800 μm , whereas Dinh et al. showed that the minimum line width of a twin-line with aligned CNT network achievable using inkjet printing technique is around

130 μm . As such, alternative printing technique is required for achieving such aligned CNT with high print resolution. However, increasing print resolution is challenging because the time scale competition between solvent evaporation and CNT diffusion becomes prominent[95].

The motivation of this work is to explore a suitable technique for the fabrication of high resolution aligned CNT network for high-performance devices. In this work, the aerosol jet printing (AJP) technique is used to achieve high-resolution, self-assembled, aligned CNT twin-line based on coffee-ring effect printed on flexible material like polyimide substrate. Several studies have demonstrated print resolution of 10 μm is achievable by AJP process, making it a suitable tool for printing CNT at high resolution [96]. However, only a few studies have demonstrated printing CNT with AJP but none of them have studied how the process parameters such as nozzle size, print speed, gas flow rates, and substrate temperature affect the resulting CNT traces which is important at the stage of designing and fabrication of the electronics[97-101]. Besides, none of these studies show the possibility of printing aligned CNT network with AJP process. Besides, the evaluation of the degree of CNT alignment of such printed CNT trace is seldom reported.

2.4 Methods for CNTs alignment characterization

Normally, the alignment of the as-grown CNTs films or arrays can be evaluated visually by microscopy technique such as atomic force microscopy (AFM) [102], scanning electron microscopy (SEM) [103], scanning tunneling microscopy (STM)[104], and polarizing microscopy [105]. This technique is especially suitable for samples that have a very thin thickness and low CNTs density which cannot be inspected effectively using other laser-

based or X-ray-based technique. Transmission electron microscopy is not suitable because (i) the sample preparation steps could disturb the arrangement of CNTs in the sample and (ii) the small scanning area could not provide the correct information about the actual alignment of CNTs in the sample. The alignment of CNTs can then be further analyzed by using the Fast Fourier transform (FFT) method to evaluate the degree of alignment of the CNTs [9]. Herman orientation factor, f as shown in equation (8) is commonly used to quantify the degree of alignment of the CNTs [9].

$$f = \frac{3\langle \cos^2 \delta \rangle - 1}{2} \quad (8)$$

Where $\langle \cos^2 \delta \rangle$ can be derived from the result of FFT.

The aforementioned techniques are suitable for CNTs that are thoroughly exposed, however not suitable for evaluating the alignment of CNTs embedded inside matrix materials. The alignment of CNTs in composite materials can be evaluated by using Raman spectrometry [106] and XRD spectrometry [50]. For Raman spectrometry, a change in peak amplitude at 1590 cm^{-1} when the orientation of the CNTs sample is adjusted from 0° to 180° indicates there is a preferential alignment of CNTs in the sample. For XRD spectrometry, the alignment of CNTs can be evaluated by plotting the integrated x-ray intensity along the 2θ along the azimuth angle. Generally, 2 peaks can be observed from aligned CNTs and no peaks for the random counterparts. Full-width-half-maximum (FWHM) is normally used to evaluate the degree of alignment of the CNTs, normally, a small FWHM indicates the CNTs sample has a higher degree of alignment. Besides, a more recent study used X-ray computed tomography (CT) scan to inspect the 3D texture of the

CNTs film[107]. Also, the three-dimensional distribution of CNTs network can be inspected by electron tomography with which the orientation of the CNTs can be visualized[108, 109].

Readers are encouraged to read the textbook and review article by Ren et al.[110] and Iakoubovskii[111] respectively for more detailed information about the techniques for evaluating the alignment of CNTs.

2.5 Conventional fabrication method of flexible electronics

Flexible electronics are normally manufactured using additive manufacturing/ printing technology. These additive manufacturing techniques can be categorized into contact printing and non-contact printing techniques[112]. Contact printing techniques refers to a class of printing techniques that the printing tools are in contact with the substrate materials during the printing process, such as screen printing, flexographic printing, gravure printing and offset printing [113]. Non-contact printing techniques, on the other hand, refers to the printing techniques that the printing tools do not contact with the substrate materials, such as inkjet printing and aerosol jet printing. Contact printing techniques are commonly employed for mass production of flexible electronics due to their high throughputs [114]. However, some issues of these contact printing techniques are low resolution, high initial cost, and complex setups and preparations prior to printing which make them unsuitable and uneconomical for fabrication of customized electronic devices [112]. Inkjet printing technique, on the other hand, is a contactless digital printing process which does not require pre-manufactured master printing plates/tooling making it suitable for fabrication of customized devices. Nonetheless, inkjet printing technique often has problems such nozzle

clogging and limited choice of inks due to the strict requirement for ink's viscosity and surface tension [112]. In contrast, aerosol jet printing can achieve high printing resolution and allows for wide range of printing materials. As such, aerosol jet printing technique is explored in this research for the fabrication of flexible electronics.

2.6 Aerosol jet printing

The aerosol jet printer used in this project is developed by Optomec™. The aerosol jet printing process consists of three stages, which are (i) atomization, (ii) aerosol transportation, and (iii) aerosol deposition. The first stage involves the formation of aerosols of functional ink, which happens at the atomizers. The ink can either be atomized pneumatically or ultrasonically using pneumatic and ultrasonic atomizers respectively. Pneumatic atomizer creates atomized ink by passing a mixture of ink and air through a nozzle at high speed, whereas ultrasonic atomizer creates ink droplet through ultrasonic vibration using a transducer. Due to the fundamental difference in the way the ink droplet is created, the atomizers have different ink requirement in term of ink viscosity and create different ink droplet diameter. A larger droplet size means that larger particle size (nanoparticles, flakes, tubes, etc.) can be entrained in the droplet while the ink is being atomized. Table 2 summarizes the difference in ink requirement, droplet size, and recommended particle size for both pneumatic and ultrasonic atomizers.

Once the aerosol is created, it is then transported to the deposition head via the delivery tubing. At the deposition head, the sheath flow is then used to focus the aerosol ink and prevent clogging at the nozzle. Figure 6 shows the schematic of pneumatic and ultrasonic atomizers.

Table 2 Comparison between the pneumatic atomizer and ultrasonic atomizer

	Pneumatic atomizer	Ultrasonic atomizer
Ink viscosity	1-1000 cP	<10 cP
Droplet size	3-5 μm	$\sim 1 \mu\text{m}$
Particle size	<1 μm	<0.1 μm

Figure 6 Schematic of the aerosol jet printing process

AJP is rapidly becoming an alternative printing method for screen printing and inkjet printing. It is a 5-axis non-contact printing method with an acceptable range of substrate-to-nozzle standoff distance between 1-5 mm. This has made printing on non-planar surfaces possible with aerosol jet printing. Besides the flexibility and scalability of aerosol jet printing, a wide variety of materials such as organic and inorganic conductor,

organic and inorganic semiconductor, insulator and ceramic have been proven printable with aerosol jet printing.

In aerosol jet printing, there are several factors that affect the ink deposition/printing process. The factors involved are tabulated in Table 3.

Table 3 Factors involved in aerosol jet printing

Ink parameters	Printing parameters	Substrate parameters
Particle size	Atomizer flow	Surface roughness
Particle distribution	Sheath flow	Hydrophilicity
Viscosity	Exhaust flow (pneumatic atomizer)	Substrate temperature
Volatility	Ultrasonic current (ultrasonic atomizer)	
Ink temperature	Print speed	
	Nozzle diameter	
	Hatch spacing	

The key processing parameters involved in aerosol jet printing are atomizer flow (AF), sheath flow (SF), exhaust flow, ultrasonic current, print speed (PS), and nozzle diameter (NS). These factors affect the amount of ink that will be deposited on the substrate during printing, which eventually influences the printed line in terms of its quality and dimension (width). The atomizer flow controls the amount of aerosol ink that will be transported to the deposition head for printing (the higher the atomizer flow, the higher the amount of aerosol ink being transported). The maximum atomizer flow is limited by the aerosol jet printer at 50 sccm. The sheath flow focuses the atomizer flow onto the substrate,

in other words, the higher the sheath flow, the narrower the aerosol ink jet stream will get. However, there is an upper limit to the sheath flow as too high sheath flow will result in turbulent flow at the nozzle which might affect the print quality or clog the nozzle. For pneumatic atomizer, exhaust flow is used to densify the aerosol mist at the virtual impactor. For ultrasonic transducer, the ultrasonic current controls the amount of aerosol created in the ink reservoir. Both the print speed and nozzle diameter affect the feed rate of the ink onto the substrate. Generally, higher print speed and smaller nozzle diameter give a finer line width. However, the print speed should match the flow rate of the aerosol ink. For instance, too high print speed might result in discontinuous lines, whereas too low print speed might result in bulging in the printed lines.

The volume fraction of the aerosol, ϕ in the AF is typically about $\phi = 10^{-5}$ [115] and the diameter of the aerosol exiting the nozzle is about $5\text{ }\mu\text{m}$ [116]. At the deposition head, in the converging combination chamber at the deposition head, a cylindrical sheath gas flow (SF) surrounds the AF; which contains the aerosols and to help focus it. The system is designed such that the flow is laminar and the stoke numbers of the aerosols are small before the aerosol exits the nozzle. This is to ensure that the aerosol stream can follow tightly to the AF. Besides, the sheath gas is also used to prevent the clogging of the nozzle due to the impact of the liquid droplets and condensation of the solvents from the aerosols [116]. The aerosol jet diameter can also be controlled by changing the SF. The SF and AF together with the aerosols are strongly accelerated by the decreasing cross-section area of the channel. At the exit, the aerosols that gain sufficiently high momentum as a result of the acceleration

will no longer follow the gas flow path and impinge onto the substrate. Heating the substrate can accelerate the evaporation of the deposited solvents.

2.7 AJP-related work

AJP process has been widely researched and utilized as fabrication tool for devices such as solar cells [117, 118], strain gauges [119], pH sensor [101], antenna [120], circuit [121], battery [122], molded interconnect device [123], and metamaterials [124] etc. Many studies have shown that AJP is suitable for processing a wide variety of nanomaterials with different shapes such as 0-dimensional nanoparticle (silver, silica, and iron) [125, 126], 1-dimensional nanowires (silver) [127] or nanotubes (CNTs) [101], and 2-dimensional nanoparticles or nanoflakes (silver, graphene, and MXenes) [96, 128, 129], just to name a few.

In addition, many studies have been carried out to understand and investigate the AJP process. For example, there are articles that described the modeling of AJP process [116, 130] and investigated the stability of round jet in AJP [131], ink deposition rate of AJP [132], annular drying of AJP [133], sessile drop deformation due to impinging jet of AJP [134], drop size effect on print quality [135], the expansion of the beam exiting from the nozzle and its influence on the standoff distance between the nozzle and the substrate [136] and controlling the morphology of deposited particle such as the width-to-thickness ratio [137]. However, none of these studies explicitly used AJP for aligning CNTs during the fabrication process. Thus, this work attempts to investigate the feasibility of using AJP for achieving aligned CNTs during the printing process.

2.8 Physics of AJP process and particles' interactions

The proposed methodology involves aligning CNTs orientation by controlled patterning of CNTs suspension using AJP technique. It involves processes such as aerosol generation, transportation and deposition, solvent evaporation of aqueous CNTs ink, and external forces acting on the CNTs while in its liquid phase. This is a complex study as the proposed methodology consists of various stages which are interdependent. Therefore, it is essential to discuss the fundamental physics of each stage in order to better understand the entire process. As such, the following section aims at discussing the essential factors and governing equation for each stage in the process.

2.8.1 Modeling of the aerosol jet printing process

Aerosol generation

Aerosol of CNTs suspension is formed at the ultrasonic atomizer of the printer. In the ultrasonic atomizer, an ultrasonic transducer is used to transmit ultrasound to the CNTs suspension. During the process, the surface acoustic wave is transmitted to the CNTs suspension and capillary wave is formed at the air-liquid interface of the CNTs suspension [138]. With sufficient power input, destabilization occurs at the interface when the acoustic stress overcomes the capillary stress and hence forming the aerosols [138]. The aerosol diameter, d_a can be estimated using equation (9) [139, 140]:

$$d_a = 0.34 \left(\frac{8\pi\gamma}{\rho f^2} \right)^{1/3} \quad (9)$$

where γ is the surface tension of the CNTs suspension, ρ is the density of the CNTs suspension, and f is the frequency of the acoustic radiation.

From equation (9), it is clear that the diameter of aerosols is dependent on the property of the liquid suspension. For fixed frequency atomization process, the aerosol diameter is tunable to encapsulate longer CNTs by formulating CNTs suspension with higher surface tension and lower density [141]. Besides, the deposition of CNTs suspension's aerosols exiting the nozzle requires a sufficiently high Stoke number, which depends on the significantly on the aerosol diameter. As such, equation (9) gives an idea how the property of the ink can be tuned for achieving good quality ink deposition.

Aerosol transport

Once the aerosol is formed, the motions of the aerosol are determined by the forces acting on each of the aerosols which are governed by Newton's second law of motion as shown below:

$$\frac{4}{3}\pi\left(\frac{d_a}{2}\right)^3\rho_a\frac{dv_a}{dt}=\Sigma F \quad (10)$$

where d_a is the diameter of the aerosol, ρ_a is the density of the aerosol, v_a is the velocity vector of the aerosol, and ΣF is the sum of forces acting on the aerosol. Generally, the forces involve in fluid-particle interaction aerosol are listed in the equation below [142]:

$$\Sigma F = F_{St} + F_{Ba} + F_{Vm} + F_{Ps} + F_{Gr} + F_{Ma} + F_{Sa} \quad (11)$$

where F_{St} is Stokes force (steady viscous drag force), F_{Ba} is Basset force (nonsteady viscous drag force), F_{Vm} is the virtual mass force (inertia of fluid surrounding particle added to particle), F_{Ps} is the pressure gradient force, F_{Gr} is the buoyancy force caused by gravity, F_{Ma} is the Magnus lift force due to particle rotation, and F_{Sa} is the Saffman lift force on a particle with local shear flow [142]. The equation and explanation of each force can be found in the Appendix A [142]. For aerosol jet printing process (with a typical aerosol diameter of 1-5 μm), however, most of the forces may be ignored except for Stokes and Saffman forces as they are not appreciable as compared to these 2 forces [143-145]. Hence, the equation can be reduced as shown below:

$$\Sigma F = F_{St} + F_{Sa} \quad (12)$$

In essence, understanding the existence of these forces in the aerosol delivery process gives insight into certain issues about AJP and allows better engineering control of the process. For example, the accumulation of the inks in the aerosol delivery tube maybe caused by the settling of the larger drops on the inner tube, which can be possibly solved by controlling the diameter of the aerosol for longer printing time.

Aerosol evaporation

As the aerosol leaves the atomizer, it exits the atomizer and is transported to the nozzle at a velocity. During the transportation, the aerosol mixes with the nitrogen gas carrier and exposes into the ambient after passing through the nozzle. Depending on the ambient condition and aerosol size, the aerosol undergoes physical changes as depicted in

Figure 7 [146].

Figure 7 Evolution of aerosol at different conditions (a) increasing temperature and (b) decreasing initial droplet size. (Reproduced from Ref [146] with permission from Elsevier)

The cloud of aerosol with mass (m) and density (ρ) produced by the ultrasonic atomizer can be modeled with a multi-component droplet system of equations as shown below [147]:

$$m = \sum_i m_i \quad (13)$$

$$\rho = \left(\sum_i \frac{m_i}{m \rho_i} \right)^{-1} \quad (14)$$

where the subscript i refers to aerosol species i .

The aerosol evaporation can be described by the mass transfer and heat transfer from the aerosol in using equations as shown below [148]:

Mass transfer:

$$\dot{m}_i = -A_p M_{w,i} k_{c,i} (C h_{i,s} - C_{i,\infty}) \quad (15)$$

where $Ch_{i,s}$ is the concentration of vapor at the droplet surface, and $C_{i,\infty}$ is the concentration of vapor in the bulk gas. $M_{w,i}$ is the molecular weight of species i . The transfer coefficient $k_{c,i}$ is calculated from the Sherwood correlation which can be found from [148].

Heat transfer:

$$\dot{Q}_{i,s} = m_p C_p \frac{dT_p}{dt} = A_p \varepsilon_p \sigma (\theta_R^4 - T_p^4) + h A_p (T_\infty - T_p) - \Delta H_V \dot{m}_i \quad (16)$$

where m_p is the mass of droplet, C_p is the droplet heat capacity, T_p is the droplet temperature, A_p is the surface area of droplet, T_∞ is the temperature of the continuous phase, ε_p is droplet emissivity, σ is Stefan–Boltzmann constant ($5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$), θ_R radiation temperature, and ΔH_V is the difference between the latent heat of droplets and the bulk gas. Understanding the evaporation process of the aerosols at the delivery stage gives insight into how the process impacts the print quality which will be discussed in Chapter 5.

Aerosol deposition

After the focused aerosol beam exits the nozzles and travels through the ambient, the aerosol will then reach the target substrate and undergo processes of aerosol impingement and thin film formation. This section aims at providing readers an overview of for thin film formation, thus only fundamental governing equations and the effect of dominant factors are discussed. A detailed explanation of the modeling of the process can be found in [149]. In general, the analysis can be dissected into 2 parts, which are the modeling of liquid film formation and the modeling of aerosol/spray interaction.

Modeling of film formation

The liquid film model is based on the physics of the printed ink film flow over the substrates. To analyze the thin film, the thin film is assumed to be made up of many ink film cells. Each of the ink film cells can be depicted in Figure 8a [150]. The continuity, momentum, and energy equations are applied to each of these ink film cells.

The continuity equation for each cell is shown below:

$$\rho_i A_c \frac{\partial \delta}{\partial t} + \rho_i \oint (V_f \cdot \hat{n})_i \delta_i dl_i = S_d - \dot{M}_{vap} \quad (17)$$

where ρ_i is the film density, A_c is the area of film projected on the substrate, δ is the film height, V_f is the film velocity, l_i is the length of the cell side i , S_d is the source term, and $\dot{M}_{vap}$ is the ink solvent vaporization rate. The source term, S_d is the rate of the mass of aerosol that impinges upon the film or secondary droplets that leave the film due to splashing effect. The formula of S_d for each condition can be found in Appendix B.

The momentum equation for each cell is shown below:

$$\rho_i A_c \frac{\partial (\delta v_f)}{\partial t} + \int_{L_1}^{L_2} \int_0^S v_f (v_f \cdot \hat{n}) d\hat{x}_3 d\hat{x}_1 = \oint (P \hat{n}) \delta_i dl_i + \rho_i A_c \delta_i g + M_{tang} + (\tau_s + \tau) A_c \quad (18)$$

where P is the dynamic pressure, g is gravitational acceleration, τ_s and τ represents the substrate shear and shear at the liquid-gas interface.

The first term in the equation is the time derivative of the film momentum. The second term represents the convective momentum of the film, the third term represents the dynamic pressure, P which can also be described as $P_\infty + p_d$, P_∞ is the ambient pressure and p_d is the

dynamic pressure as a result of aerosol impingement. The formula of p_d for each condition can be found in Appendix B. The fourth term is the gravitational force acting on each cell, the fifth term, which is M_{tang} , represents the tangential momentum contribution to the film as a result of aerosol impingement and splashing of secondary droplets. The last term is the viscous shear force acting on the film cell.

Surface tension acts only at the free surface of the printed liquid thin film, thus it does not appear in the momentum equation, but rather enters through the boundary conditions. The normal stress balance at a free surface must be balanced by the curvature force associated with the surface tension:

$$\mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} = \sigma(\nabla \cdot \mathbf{n}) \quad (19)$$

where $\mathbf{T} = -P\mathbf{I} + \mu[\nabla\mathbf{u} + (\nabla\mathbf{u})^T]$ is the stress tensor, $\mathbf{u}$ is the velocity flow field, and $\mathbf{n}$ is the unit normal to the surface.

The tangential stress at the free surface must balance the local surface tension gradient:

$$\mathbf{n} \cdot \mathbf{T} \cdot \mathbf{t} = \nabla\sigma \cdot \mathbf{t} \quad (20)$$

where $\mathbf{t}$ is the unit tangent to the interface.

The surface tension force density can be described by the following integral [149]:

$$\int \sigma \mathbf{n} J(x) \delta(x - x) dS(s) \quad (21)$$

Where $\delta(x - x)$ is a three-dimensional delta function, $J(x)$ is the local curvature of gas-liquid interface. The integral is to be integrated over the air-liquid interface.

The energy equation that is used to calculate the mean film temperature, $\bar{T}$ is shown below:

$$\rho C_v \frac{\partial(\bar{T}\delta)}{\partial t} + [v_f \cdot \nabla_s] \left(\bar{T} + \frac{T_s - T_w}{6} \right) = k \left(\frac{T_s - \bar{T}}{\delta/4} - \frac{\bar{T} - T_w}{\delta/4} \right) + \dot{Q}_{imp} - \dot{Q}_s \quad (22)$$

where C_v is the liquid specific heat, k is the liquid film thermal conductivity, ∇_s is the surface gradient operator, $\dot{Q}_{imp}$ is the energy source due to impinging aerosol, $\dot{Q}_s$ is energy source due to droplets that splash, T_s is the liquid-gas interface temperature, T_w is the substrate temperature.

The convective heat transfer equation can be applied at the interface to calculate the liquid-gas interface temperature, T_s of the film. The convective heat transfer equation is shown below:

$$\dot{Q} = k \frac{T_s - [2\bar{T} - (T_w + T_s)/2]}{\delta/2} + \dot{M}_{vap} \Delta H_V = h(T_\infty - T_s) \quad (23)$$

Figure 8 Modeling of thin liquid film, (a) sign notation of a single cell, (b) schematic of all boundary conditions on single-cell (c) aerosol impingement mechanism (d) sign convention for aerosol impingement. (Reproduced from Ref [150] with permission from Elsevier)

Modeling of aerosol/film interaction

There are many modes of aerosol impact depending on the situations under which the impact happens. Figure 8c shows the possible scenarios of the aerosol impact such as stick, rebound, spread, and splash. The outcome of the collision depends on the properties of the aerosol, of the impact surface, and of the fluid which the drop traverses before impact. It has been found that the mode of aerosol impact depends on the Weber number, We . The formula for Weber number is shown below:

$$We = \frac{\rho w_0^2 d_0}{\sigma} \quad (24)$$

where ρ is the density of the fluid, w_0 is its velocity, d_0 is the droplet diameter, σ is the surface tension. Table 4 summarizes the criteria for each mode. The knowledge on aerosol impingement allows better understanding of the aerosol deposition onto the substrate in AJP process and could help explain some of the print artefacts such as the satellites of ink around the printed traces.

Table 4 Criteria for a different mode of aerosol impingement [150].

Mode of aerosol impingement	Criteria
Stick	$We < 5$
Rebound	$5 < We < 10$
Spread	$10 < We < 18.0^2 d_d \left(\frac{\rho}{\sigma}\right)^{1/2} v^{1/4} f^{3/4}$
Splash	$18.0^2 d_d \left(\frac{\rho}{\sigma}\right)^{1/2} v^{1/4} f^{3/4} < We$

2.8.2 Modeling solvent evaporation of liquid thin film

In order to model the solvent evaporation of liquid thin film, it is very important to first determine the evaporation mechanism of the liquid thin film. In general, there are two evaporation mechanisms, which are pinned contact and moving contact evaporations. Basically, a pinned contact evaporation mechanism assumes the film edge/contact line of the evaporating liquid thin film pinned or remained stationary while the contact angle varies during the process. On the other hand, moving contact evaporation mechanism assumes the film edge/contact line moves inwards with the contact angle remains constant during the evaporation process.

The evolution of film of liquid can be modeled using the governing equations (i.e. continuity, momentum, and energy equation) with suitable boundary conditions and assumptions. Since the printed film is very thin, lubrication approximation is employed and the final equation is obtained as equation below [151]:

$$\begin{aligned} & \frac{\partial h}{\partial t} + EJ + \frac{S}{J} \left[rh^3 \left(h_{rrr} + \frac{1}{r} h_{rr} - \frac{1}{r^2} h_r \right) \right] - \frac{E^2}{rD} [\sigma h^3 J J_r]_r \\ & + \frac{\mu_a}{rP} [rh^2 [(h + w)J]_r]_r + \frac{A}{r} \left[rh^3 \left(\left(\frac{b}{h} \right)^3 - \left(\frac{b}{h} \right)^2 \right) \right]_r + \frac{G}{r} [rh^3 h_r]_r = 0 \end{aligned} \quad (25)$$

The consecutive terms describe viscous dissipation, evaporation, capillary effects, vapor recoil, the Marangoni effect, disjoining pressure, and gravity respectively. The non-dimensional parameters in the equation above can be described as follow:

$$E = \frac{k\Delta T}{\rho v L}, S = \frac{\sigma_0 d_0}{3\rho v^2}, D = \frac{3\rho_v N}{2\rho}, Ma = \frac{\gamma\Delta T d_0 c_p}{2vk}, P = \frac{v\rho c_p}{k} \quad (26)$$

are the evaporation number, scaled surface tension, density ratio, and Marangoni and Prandtl numbers respectively. Also,

$$\mathcal{W} = \frac{k d_s}{k_s d_0}, A = \frac{\Omega d_0}{3v^2 \rho \mathcal{N} b}, G = -\frac{d_0^3 g}{3v^2} \quad (27)$$

where $\mathcal{W}$ describes the thermal effects in the solid: d_s is the typical thickness and k_s is the thermal conductivity of the substrate. The non-dimensional parameter A represents the contact angle behavior, where $\Omega = \sigma_0(1 - \cos\theta)$, $\mathcal{N} = (n - m)/((n - 1)(m + 1))$ and $b = d_{equil}/d_0$, d_{equil} is the equilibrium film thickness. Finally, g is the gravitational acceleration.

Assuming the solvent evaporates at a constant rate, the internal flow in the cylindrical drop is similar to the spherical droplet. Hence, the resulting internal flow velocity components can be described in Cartesian coordinate as follow [152]:

$$u = v_x(\alpha, \beta) = \frac{\cosh \alpha \cos \beta + 1}{\cosh \alpha + \cos \beta} v_\alpha + \frac{\sinh \alpha \sin \beta}{\cosh \alpha + \cos \beta} v_\beta \quad (28a)$$

$$w = v_y(\alpha, \beta) = -\frac{\sinh \alpha \sin \beta}{\cosh \alpha + \cos \beta} v_\alpha + \frac{\cosh \alpha \cos \beta + 1}{\cosh \alpha + \cos \beta} v_\beta \quad (28b)$$

where the velocity components in a bipolar coordinate system are:

$$v_a(\alpha, \beta) = -\frac{2}{\pi} (\cosh \alpha + \cos \beta) \times \int_0^\infty \frac{\cosh x \beta \sin \lambda \alpha}{\sinh \lambda \theta_c(t)} \times \left(\int_0^\infty \frac{(u_{ns} + J/\rho) \cos \lambda a'}{\cosh a' + \cos \theta_c(t)} da' \right) d\lambda \quad (29a)$$

$$v_{\beta}(\alpha, \beta) = \frac{2}{\pi} (\cosh \alpha + \cos \beta) \times \int_0^{\infty} \frac{\sinh x \beta \cos \lambda \alpha}{\sinh \lambda \theta_c(t)} \times \left(\int_0^{\infty} \frac{(u_{ns} + J/\rho) \cos \lambda a'}{\cosh a' + \cos \theta_c(t)} da' \right) d\lambda \quad (29b)$$

where J is the local evaporation flux, and $\theta_c(t)$ is the contact angle at time t , ρ is the liquid density, and $u_{ns}(t)$ is the normal component of the surface velocity at time t given by:

$$u_{ns}(t) = \frac{J_0}{\rho} \frac{\theta_c(t)}{\sin \theta_c(t) - \theta_c(t) \cos \theta_c(t)} \left(\cos \theta_c(t) - \sqrt{1 - \left(\frac{x}{2}\right)^2 \sin^2 \theta_c(t)} \right) \quad (30)$$

and J can be described as the equation below [153]:

$$J(R, r, t) = \frac{2}{\pi} \frac{D(n_s - n_{\infty})}{\rho \sqrt{R^2(t) - r^2}} \sqrt{1 + \left(\frac{\partial h}{\partial r}\right)^2} \quad (31)$$

where D is the diffusion coefficient, n_s and n_{∞} are vapor mass density at the interface and ambient respectively.

Factors such as loss of solvent, internal fluid flow and adsorption of insoluble molecules to the surface (i.e. CNTs) can result in the change in the concentration of the insoluble molecules in the thin liquid film. The concentration of the solute is governed by a two-dimensional convection-diffusion equation as shown below:

$$\frac{\partial C}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} (rCu) - \frac{\partial}{\partial z} (Cw) + D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + D \frac{\partial^2 C}{\partial z^2} - F\delta(z) \quad (32)$$

where C is the insoluble colloid, u and w are the radial and axial velocity respectively, $\delta(z)$ is the delta function. The function, F describes the mass loss of the colloid due to the binding

between molecules and surface. Using conservation of colloid mass, the rate of colloid mass loss is defined as the sum of the rate for reversible and irreversible adsorption.

$$F = k_a C \phi - \frac{k_d M_r}{\sqrt{\phi}} + k_s C \phi \quad (33)$$

where variable ϕ defines the fraction of surface area that can be occupied by the colloid particles, and it is described by:

$$\phi = 1 - \frac{Ma}{m} \quad (34)$$

where M is the total adsorbed mass per unit area, a is the area occupied by a single colloid and m is the mass of a single colloid.

A typical analytical solution of the evolution of the shape of the liquid film for both pinned and moving contact line is shown in Figure 9.

Figure 9 Evolution of the shape of liquid film for pinned contact (left) and moving contact line (right). (Reproduced from Ref[153] with permission from Elsevier)

Besides, the typical analytical solution of the evolution of solute adsorbed on the substrate is depicted in Figure 10.

Figure 10 Evolution of particle adsorbed on the substrate for pinned contact (left) and moving contact line (right). (Reproduced from Ref[153] with permission from Elsevier)

The internal flow at any instant t as a result of the convection current depends on the Marangoni number, and the effect is shown in Figure 11 [154]:

Figure 11 Convection flow in the thin liquid film. (Reproduced from Ref[154] with permission from ACS publications)

Understanding the evaporation process of the evaporating drop allows the prediction of the hydrodynamic flow that is formed inside the drop, thus allowing a better control of the final deposition pattern of the ink.

2.8.3 Modeling of forces acting on suspending particles

This section discusses the particle dynamic modeling for colloid suspension. The motion and trajectory of the particles in the suspension depend on the forces acting on them. Basically, the modeling of particle dynamic can be implemented in 2 different domains, which are the motion of the particles of (1) suspending particle further from the substrate and (2) particle adsorbed on the substrate.

Forces acting on suspending particle

For a suspension of colloidal particles with moving particles in the carrier liquid/solvent, the motion of each particle can be described by the force equation.

$$m \frac{du_p}{dt} = F_C + F_H + F_B \quad (35)$$

where m is the mass of a single particle, u_p is the velocity of the particle, F_C is the resultant conservative force acting on the particles due to interaction with other colloidal particles, F_H is the hydrodynamic force as a result of the solvent motion, F_B is the total Brownian force.

The conservative force acting on each particle, F_C can be described by the summation of interparticle forces and any external forces. The interparticle forces can be approximated as pairwise 2-body interactions with 2 bodies separated with a distance, r . Each conservative forces can be related to the potential energy associated with the interaction between the 2 particles and can be obtained from:

$$F_c(r) = - \frac{dU(r)}{dr} \quad (36)$$

According to the classic DLVO theory, the overall potential of a particle is the summation of the electrostatic component, U_{el} and the attractive and repulsive dispersion interaction, U_{cc} .

The potential energy as a result of the electrostatic charges on the particle surface can be described by:

$$U_{el}(r) = \frac{64\pi kT \rho_{\infty} a \psi_0^2}{\kappa^2} e^{-\kappa(r-2a)} \quad (37)$$

where k and T are Stefan-Boltzmann constant and temperature of the particle respectively, a is the particle radius, ρ_{∞} is the bulk electrolyte concentration, κ is the inverse Debye screening length and ψ_0 is the potential at a particle at the particle surface.

The potential energy due to the attractive and repulsion can be described by:

$$U_{cc}(r) = \frac{A_{cc}}{6} \left[\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \log \left(\frac{r^2 - 4a^2}{r^2} \right) \right] + \frac{A_{cc}}{37800} \frac{\sigma^6}{r} \left[\frac{r^2 - 14ar + 54a^2}{(r - 2a)^7} + \frac{r^2 + 4ar + 54a^2}{(r + 2a)^7} - 2 \frac{r^2 - 30a^2}{r^7} \right] \quad (38)$$

where Hamaker constant is described by $A_{cc} = 4\pi^2 \epsilon \rho_1 \rho_2 \sigma^6$, ϵ and σ are parameters of Lennard-Jones (LJ) particles, ρ_1 and ρ_2 are the number densities of constituent LJ particles in colloid particle 1 and 2.

The hydrodynamic force, F_H is described by:

$$F_H = R u_p \quad (39)$$

where R is known as the hydrodynamic resistance tensor which describes the effect of the velocity of any particle on the hydrodynamic force experience by any other particle in the system.

The Brownian force can be described by the equation below:

$$\langle F_B(t)F_B(t + \tau) \rangle = 2k_B T R \delta_D(\tau) \quad (40)$$

where $\delta_D(\tau)$ is the Dirac delta function.

The motion of each particle is governed by equation (35). Hence, the overall motion of the particles can be determined by solving equation (35) and equation (18). A comprehensive analysis of the forces acting on the colloidal particle in suspension can be found in [155]. In general, there are 3 competing mechanisms to form the thin film, which are the radial flow driven by evaporation, DLVO attractive force, and Marangoni recirculation as shown in Figure 12 [156].

Figure 12 Three competing mechanisms for film formation of the insoluble particle. (Reproduced from Ref[156] with permission from Elsevier)

Forces acting on particles near the substrate

At the substrate surface, the interaction between the substrate and the particles become dominant and cannot be ignored from the analysis viewpoint. Hence, it is vital to understand the governing forces such as the drag force, van der Waal's force, electrostatic force and the surface tension force acting between the particles and the substrate.

The drag force, F_D exerted on the particles due to the internal convective flow can be described as [157]:

$$F_D = 6\pi R\eta v \quad (41)$$

where R is the particle radius and η is the dynamic viscosity of the liquid.

The van der Waal's force between particles and the substrate is described as the following equation [157]:

$$F_{VDW} = -\frac{A_{132}R}{6z^2} \left(1 + \frac{a^2}{R_z}\right) \left(\frac{1}{1 + 14(z/\lambda_{ret})}\right) \quad (42)$$

where a is the deformation-induced contract radius, λ_{ret} is the characteristic wavelength of interaction, z is the particle-surface closest-separation distance and A_{132} is the Hamaker constant of particle 1 on a substrate 2 in a medium 3, and it can be approximated as equation below:

$$A_{132} \cong (\sqrt[4]{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (43)$$

where A_{ii} is the interaction constant of 2 bodies of materials i .

The electrostatic force between particles and substrate can be expressed as [157]:

$$F_e = \frac{2\pi\epsilon kR}{1 - \exp(-2kz)} [2\Psi_2 \exp(-kz) + (\Psi_2^2 + \Psi_1^2) \exp(-2kz)] \quad (44)$$

where ϵ is the permittivity of the medium, k is the Debye-Huckel parameter (which is the reciprocal of electrical double layers thickness), and Ψ is the surface potential of particle 1 or plate 2.

At the liquid-air-solid interface, surface tension force exerts a force on the particles trapped at the edge of the thin liquid film. If a particle is surrounded by a liquid layer, the surface tension force can be expressed as:

$$F_{ST} = 2\pi R\sigma \cos \theta \quad (45)$$

where σ is the surface tension of the liquid and θ is the contact angle of the thin liquid film at the interface.

When a particle moves on the substrate under external force, the coefficient of friction (f) is given by [157]:

$$f = F_D/F_a \quad (46)$$

where F_a is the total adhesive force, which is given by [157]:

$$F_a = F_g + F_e + F_{VDW} + F_{ST} \quad (47)$$

where F_g is the force due to the gravity.

A comprehensive analysis of the forces acting on the colloidal particle in suspension can be found in [157]. Weaker total adhesive force implies weaker particle-substrate interaction, thus higher chance of the particles being carried along with the hydrodynamics flow. Understanding the governing forces on the CNTs particle in the suspension can give better

insight of the interaction between the flow, particles and substrates, thus their effects on the final deposition pattern.

2.9 Summary

Many methods have been developed to achieve CNTs alignment for structural components and functional electronics. Evaporative driven self-assembly (EDSA) of CNTs is seen to be the simplest way to produce aligned CNTs for thin-film electronics. Among all the existing techniques for achieving aligned CNTs architectures, only additive manufacturing techniques such as inkjet printing process allow the design freedom to pattern the CNTs yet able to achieve aligned CNTs architectures. Besides, it also allows the fabrication process of the CNTs-based electronic to be done at much lower processing temperature for flexible polymeric substrates which typically have low melting temperatures. However, inkjet printing is limited in terms of the print resolution which typically falls within the range of 50-100 μm [112]. Also, inkjet printing technique only allows printing of flat design which gives less design freedom for electronics fabrication. Thus, AJP process, which the ink deposition and evaporation process resemble inkjet printing process and the ability to print much higher print resolution ($\sim 10 \mu\text{m}$), is seen to be the potential tool for achieving multifunctional structures with aligned CNTs network. A comparison between inkjet printing and AJP processes are illustrated in Figure 13.

Figure 13 Time evolution of EDSA mechanism of (a) inkjet printing and (b) aerosol jet printing

However, existing knowledge on the EDSA and AJP is still lacking in a few ways:

- (i) the understanding of EDSA of CNTs ink (specifically for AJP process),
- (ii) the understanding of the AJP process. (eg. the role of aerosol evaporation),
- (iii) the process window for achieving the evaporation-driven self-assembled CNTs traces, and
- (iv) the effect of print resolution on the alignment of CNTs.

Thus, this warrants the need for more studies to investigate the evaporation-driven self-assembled CNTs via aerosol jet printing which will be discussed in detail in Section 3.1 Research methodology.

3. RESEARCH METHODOLOGY, MATERIALS, AND METHODS

3.1 Research methodology

3.1.1 Understanding the EDSA process on CNTs alignment via sessile drop experiments

Evaporative driven self-assembly (EDSA) of CNTs is seen to be the simplest way to produce aligned CNTs for thin-film electronics. This is because it does not require any additional tooling and preparations as it relies purely on natural fluid convection. Besides, this technique can be potentially applied to aerosol jet printing of CNTs ink. However, the effect of the change in properties of the ink such as CNTs concentration and pH of the CNTs ink, and process condition such as substrate temperature on the CNTs alignment of drying thin film is still not well studied. Besides, the understanding of the CNTs alignment by EDSA at such a micrometer scale is not well established. As such, a thorough study is needed to fully understand the effect of these factors on the CNTs alignment by EDSA for the aerosol jet printing process. The study will serve as a baseline for this research to achieve CNTs alignment by EDSA.

3.1.2 Investigating the process window of the AJP process for achieving self-assembled CNTs

AJP process is a complex process where many process parameters are involved in the printing process. The process parameters such as sheath gas flow rate, atomizer flow rate, ultrasonic atomization current, print speed, nozzle size, and substrate temperature have effects on the dimensions of the printed line width. One issue with AJP process is that the current predictive analytical model with AJP is not accurate and fail to explain the effect of

certain process parameters such as the print speed and substrate temperature. Besides, the role of aerosol evaporation in the transportation stage is often neglected. In this project, a predictive analytical model is proposed and validated with experimental results. The effect of each process parameter mentioned earlier is investigated to understand their influence on the printed CNTs traces. The role of aerosol evaporation in AJP is also discussed. Besides, the process window of the AJP process for obtaining self-assembled preferentially aligned CNTs traces is investigated. A novel way of fabricating high resolution preferentially aligned CNTs traces with AJP process utilizing EDSA technique is then implemented to fabricate electronic devices.

3.1.3 Proof-of-concept: AJP printing of functional electronic devices

As proof-of-concept applications, an optically transparent motion sensor based on CNTs twin lines and a pH sensor are fabricated. The studies from the earlier chapters are critical toward the AJ printing of the preferentially aligned CNTs for electronics devices. The pH sensor is fabricated via a two-step AJP strategy with silver and CNTs. The sensor fabrication process involves the patterning of pH-responsive CNTs ink on a flexible polyimide substrate for wearables. The printed CNTs-based pH sensor is then tested with different pH buffer solutions and mechanical tests such as bending and cyclic loading tests are conducted to test for the device reliability.

3.2 Materials preparation

In this study, Kapton polyimide substrate was used. In order to remove contaminants, the substrates were clean with soapy water and then sonicated in an ethanol bath for 5 mins. The cleaned substrates were then dried with an air gun.

The CNTs ink used in this work is NINK single-walled CNTs aqueous dispersion purchased from Nanolab[®] as shown in Figure 14. This ink contains carboxyl (COOH) functionalized carbon nanotubes in an aqueous suspension with the minimum concentration of additives to impart long term stability and printability to the ink. The NINK has a concentration of 2 g/L with measured average CNTs length of $1.3 \pm 0.6 \mu\text{m}$ as shown in Figure 14c. This allows the CNT to be atomized together with the solvent of the ink (typical aerosol diameter is 1-5 μm), thus allowing the deposition of CNT in AJP process. Different concentrations (0.07 w%, 0.02 w%, 0.007 w%) of CNTs suspensions were prepared by diluting the NINK 1100 ink with of deionized (DI) water. The preparation of the diluted CNTs ink can be found in Appendix C.

Figure 14 (a) Nanolab SWNT suspension and (b) CNTs ink in an ultrasonic atomizer glass vial (c) Plot of CNT length distribution

3.3 Micro- & nanostructures characterization using field-emission scanning electron microscopy (FESEM)

Field-emission scanning electron microscopy (FESEM) was heavily used in this project for characterizing the CNTs length, CNTs alignment of the thin film, and the width of the

printed self-assembled CNTs traces. Before scanning the samples, the non-conductive samples were pasted on the stub with carbon tape before being coated with platinum using a sputtering system for 90 seconds at 10 mA. The microstructure study was conducted using field emission scanning electron microscopy (FESEM, JSM7600, JEOL). The scanning voltage was set to around 2.0 kV and current to 7 mA to obtain good image quality. FESEM images were taken in GB-H mode. Multiple microscopy images were taken for a sample to ensure experimental reliability and repeatability.

In order to measure the CNTs length, the CNTs ink was first diluted with DI water to achieve a concentration of 0.0007 w%. The diluted CNTs suspension is then drop cast and left dried on a polyimide substrate. The dried sample is then scanned using FESEM and 25 FESEM images of the drop cast CNTs thin film were taken randomly and 260 CNTs with entire length visible (not obstructed/covered) were measured and analyzed using ImageJ image processing software to provide statistically meaningful CNTs length distribution. Calibration is done using the scale bar on the FESEM images.

3.4 Contact angle characterization

The contact angle of the ink on the polyimide substrate was measured by a custom-built setup with a diffused light background and a high-speed camera. Drop volume of 0.2 μL was used for the drop study. The ink is dispensed manually onto the substrate using a micropipette. The contact angle measurement was done using ImageJ software's plugin (dropsnake analysis). A minimum of 5 measurements was taken to obtain a statistically meaningful result. The drop volume is measured using image analysis method with proper calibration.

3.5 CNTs alignment characterization

In this research, qualitative and quantitative analysis of the alignment of CNTs has been used. The qualitative analysis is done by evaluating the alignment of the CNTs using FESEM images. The relative degree of alignment of CNTs across different conditions can be made by comparing the FESEM images. However, this evaluation method is thought to be subjective. As such, quantitative analysis is done to complement the qualitative analysis. The two commonly used quantitative analysis method is by calculating the Herman orientation factor, f and using Raman spectroscopy to characterize the degree of alignment of the CNTs.

The determination of the degree of alignment of the CNTs network via Herman orientation factor was first done using ImageJ image processing software's plugin, OrientationJ [158]. At least 8 FESEM images of the CNTs films for each condition were analyzed by OrientationJ orientation analysis tool to determine the orientation of the CNTs network. The gradient computation that was used in the analysis is "Finite Difference" method with a local window of 6 pixels. With OrientationJ analysis, orientation distribution of CNTs was obtained. The degree of alignment of the CNTs is determined by calculating Herman's orientation factor, f from the angular distribution result obtained using OrientationJ. $f = 1$ indicates the CNT network is perfectly aligned, whereas $f = 0$ indicates randomly oriented CNT network. The workflow of determining CNTs alignment degree via an image processing technique is summarized in Figure 15.

Figure 15 Determination of CNTs alignment via image processing technique, microscopic images of (i) aligned CNTs and (ii) random CNTs (insets show the orientation distribution analysis of the microscopic images)(Reproduced from Ref [9] with permission from The Royal Society of Chemistry.)

In this research, Raman spectroscopy is done using Renishaw® inVia Reflex Raman microscope. The system comprises a 50 mW laser source with a wavelength of 633 nm. The laser power was fixed at 50% and a line grating of 1800 lines/mm. The Raman spectrum was obtained by averaging the 5 measurements taken from each condition. The degree of alignment was quantified by the relative intensities of the peaks within the spectrum and across different spectra.

3.6 Measurement of the ink flow rate of AJP process

The ink flow rate of the AJP process is done by measuring the mass of the accumulated liquid ink, m in a weighing boat. The liquid ink is accumulated for a period of 4 minutes to obtain sufficient weight for accurate measurement by the weighing scale. The weighing scale used in this project is an ANP analytical balance. The ink flow rate is then calculated by dividing the measured mass of the ink with the density of the ink and the deposition time, t as shown in equation (48).

$$\dot{M} = \frac{m}{t} \quad (48)$$

3.7 Characterization of printed line width

The printed features were observed with an Olympus CKX41 optical microscope and JEOL JSM-7600F.

3.8 Electrical property characterization

The electrical resistance measurement of the printed CNTs traces was done using Keithley S4200 parametric analyzer equipped with 2 source-measuring units (SMU). The parametric analyzer is connected to a manual probe station when measuring the samples. The probe station consists of tungsten probe tips and controlled air-bearing stage with micrometer positioner which allows precise probe placement for accurate measurements. The electrical resistance is calculated from the measured voltage, V and current, I during the test which is as shown in equation 49.

$$R = \frac{V}{I} \quad (49)$$

The resistance per unit length (Ω/cm) is measured by keeping the probe 1 cm apart during measurements.

3.9 Zeta potential measurement

The zeta potential of the CNTs in the suspension solution was done using Malvern Nano ZSP that can measure particle size of 0.3 nm to 10 microns. A disposable folded capillary cell (DTS1070) was used for the zeta potential measurement. A multipurpose auto-titrator (MPT-2) was used to adjust the pH of the CNTs suspension solution. 0.5 M of hydrochloric (HCl) acid and 0.1 M of sodium hydroxide (NaOH) solution were used for the pH titration. A glass electrode pH probe was used for the pH measurement. Three zeta potential measurement was taken for each pH condition for statistically meaningful results.

3.10 Nano-liter drop dispenser

An HP D300e digital dispenser was used to precisely control the volume of the drop size for deposition pattern study. A C8 dispensing cassette was used for dispensing drop volumes ranging from 0.35 nL to 15nL.

3.11 Aerosol jet printing (AJP) process

The aerosol jet printer used in this project is AJ5X[®] developed by Optomec[®]. The ultrasonic atomizer is selected to print the CNTs due to its advantage to keep the CNTs well-dispersed during the printing process. The actual image of the aerosol jet printer setup is shown in Figure 16.

Figure 16 Setup of the aerosol jet printer with ultrasonic atomizer configuration

Here, the key process parameters that were studied are atomizer current, atomizer, sheath flow, substrate temperature, and print speed. Each of these parameters was studied independently by keeping other process parameters constant. For all the conditions, the atomizer temperature was kept at 28 °C. As aerosol jet printing technique deposit ink continuously, line feature has been identified as the most fundamental features of this printing technique. A benchmark design has been designed using AutoCAD and the toolpath of the design is generated using VMTools extension in AutoCAD. To ensure the repeatability and reproducibility of the experiment, the benchmark design is designed with three lines of length of 1 cm each so that various characterizations can be done on 3 different printed traces for a statistically meaningful result.

4. SESSILE DROPLETS CONTAINING CARBON NANOTUBES: A STUDY OF EVAPORATION DYNAMIC AND CNTS ALIGNMENT FOR PRINTED ELECTRONICS

4.1 Scope of experiment

The motivation of this research is to investigate how the polyimide substrate affects the evaporation of CNTs sessile drop. Besides, the effects of CNTs concentration, substrate temperature, pH of the solutions, and drop size on the contact line dynamic are also investigated. Image analysis and polarised Raman spectrometry are used to provide a quantitative analysis of the CNTs orientation/arrangement of CNTs thin film formed from CNTs sessile drops. Figures in this chapter are reproduced from Ref [159] with permission from The Royal Society of Chemistry.

4.2 Evaporation rate of sessile drops

The average surface roughness, R_a of the polyimide substrate was found to be $0.60\ \mu\text{m}$. The evaporation dynamics of the sessile drops with CNTs concentrations of 0.2 w%, 0.07 w%, 0.02 w%, and 0.007 w% on different substrate temperatures of $30\ ^\circ\text{C}$, $50\ ^\circ\text{C}$, $70\ ^\circ\text{C}$ and $110\ ^\circ\text{C}$ were studied. The evaporation at lower substrate temperature such as $20\ ^\circ\text{C}$ or lower is not considered in this study because the evaporation at low temperature is mainly driven by the vapor concentration gradient, not so much by the temperature of the liquid drop. Figure 17a, Figure 17b, Figure 17c, and Figure 17d illustrate the influence of substrate temperature on the average volume evolution of sessile drop with an initial volume of approximately $0.3\text{-}0.4\ \mu\text{L}$. The evaporation time (t) of the drop volume on substrate temperatures of $30\ ^\circ\text{C}$, $50\ ^\circ\text{C}$, $70\ ^\circ\text{C}$ and $110\ ^\circ\text{C}$ was observed to be approximately 230 s,

55 s, 25 s, and 9 s respectively. The decrease in the evaporation time is caused by the increased heat transfer due to the higher substrate temperatures. It is observed that the drops exhibit an almost linear evaporation rate for every condition. The evaporation rate of each condition is estimated by calculating the gradient of the linear fitted line. The calculated R^2 value for each condition is at least 0.9 which shows the high linearity of the evaporation of the drops. Figure 17e shows the evaporation rate of the sessile drops at various substrate temperatures. It is found that the concentration of CNTs in the sessile drops does not exhibit a substantial effect of the evaporation rate. The average evaporation rates (comprising all concentrations) are approximately 0.0013 $\mu\text{L/s}$, 0.0054 $\mu\text{L/s}$, 0.0129 $\mu\text{L/s}$, 0.0405 $\mu\text{L/s}$ for substrate temperature of 30 °C, 50 °C, 70 °C and 110 °C respectively. Figure 17f shows the influence of the substrate temperature on the contact angle of the sessile drops. The average contact angle (comprising all concentrations) for a substrate temperature of 30 °C, 50 °C, 70 °C and 110 °C are calculated to be 72°, 74°, 65°, and 53° respectively. It is noticed that the contact angle remains almost constant at a lower substrate temperature (30 and 50 °C), however, the contact angle decreases when the substrate is heated to a higher temperature (from 50-110 °C). Petke et al. have shown that the contact angle of water sessile drop on various polymeric substrates is constant up to 90 °C and decreases significantly at a temperature higher than 90 °C[160]. Bernardin et al. also showed a similar result using aluminum substrate and found that the critical temperature for the decrease in contact angle is around 120 °C[161]. Adamson developed a temperature-dependence model and showed that the decrease in contact angle at higher temperature is due to the change in surface free energy on the substrate[162]. Besides, the decrease in the surface tension of the liquid with increasing temperature also contributes to the decrease in contact angle[163]. The effect of

particle concentration on the contact angle in this work, however, is not noticeable. Khaleduzzaman et al. have reviewed several works on the influence of particle concentration on the contact angle and found out several contradictory results, indicating a lack of understanding on this issue [163]. As such, a more in-depth study is required to

further examine the influence of the CNTs concentration on the contact angle of the ink. *Figure 17. Graphs showing the evolution of drop volume drying at surface temperatures of (a) 30 ° C, (b) 50 ° C, (c) 70 ° C, (d) 110 ° C (sample size, $n \geq 3$). Plots showing the (e) evaporation rates and (f) contact angles at different substrate temperatures (sample size, $n \geq 6$).*

4.3 Contact line dynamics of the sessile drop

The evaporation mode of the CNTs sessile drops is further analyzed using Figure 18. Figure 18 shows the normalized contact radius and the contact angle of the sessile drops at various substrate temperatures. It is found that lower CNTs concentration inks such as 0.007 w% and 0.02 w% show depinned evaporation mode, whereas higher concentration ink such as 0.07 w% and 0.2 w% show pinned evaporation mode throughout the evaporation process. The pinned mode is also called constant contact radius (CCR) mode. The difference in the evaporation mode at different CNTs concentrations will be discussed in a later section. For 0.007 w% CNTs concentration, the drop depins at a critical contact angle of approximately 50° at both substrate temperature of 30°C and 50°C . For 0.02 w% CNTs concentration, on the other hand, the drop depins at a critical contact angle of approximately 38° at both substrate temperature of 30°C and 50°C . At higher substrate temperature, the evaporation mode of both 0.007 w% and 0.02 w% CNTs concentration turn from depinned into pinned evaporation mode. The depinning of the contact line can be elucidated by the unbalanced Young's force, $F = \sigma (\cos\theta - \cos\theta_e)$ is closely related to the surface tension of the liquid, σ and the deviation from the equilibrium contact angle, θ_e [164]. The change in evaporation mode of the CNTs drops at elevated temperature is due to decrease in the surface tension of the liquid which reduces the unbalanced Young's force and makes the drop more stable at lower contact angle [164]. Besides, the lower critical contact angle of the 0.02 w% CNTs ink compared to the diluted 0.007 w% ink is due to higher surfactant concentration and lower surface tension. This reduces the unbalanced Young's force and lowers the critical contact angle.

Figure 18. Graphs showing the evolution of normalized contact line and contact angle for drops drying at substrate temperatures of (a) 30 °C, (b) 50 °C, (c) 70 °C, (d) 110 °C.

4.4 Deposition pattern of dried CNTs film

Figure 19 shows the influence of CNTs concentration on the contact line dynamics and the final patterns of the thin film. The pinning and depinning phenomena can be explained by aggregate-induced pinning[92]. The CNTs aggregate at the ring can stop the contact line from moving. Based on the final patterns of the CNTs thin film, the coffee ring effect is noticed across all samples. The coffee ring effect happens when the contact line is pinned by the aggregates and the particles are carried to the contact line via the hydrodynamic flow, mainly the radial capillary flow, due to the solvent evaporation. It is observed that there are no residual or excess CNTs within the rings of the 0.007 w% and 0.02 w% CNTs ink drops. The result suggests that the depinning phenomenon for 0.007 w% and 0.02 w% CNTs drops is due to the lack of aggregate-induced pinning as all the CNTs particles have been deposited at the contact line. In contrast, excess or residual CNTs is observed in the final deposition pattern of 0.07 w% and 0.2 w% CNTs drops. This signifies that there are enough CNTs for aggregate-induced pinning to occur at higher concentration CNTs drops. The aggregate-induced pinning can be confirmed by comparing the results with several published studies, where pure water droplets exhibit depinning contact line on different polymeric substrates[165-167]. Interestingly, crusting is observed for CNTs drops with a concentration of 0.2 w% where a thin film of CNTs is formed by assembling themselves at the free surface.

Figure 19. Figure showing the evolution of the sessile drops of different concentrations from $\phi=0.007$ w%, $\phi=0.02$ w%, $\phi=0.07$ w%, and $\phi=0.2$ w% (from left to right) at substrate temperature of 30 °C. Depinned contact line is observed for low concentration CNT drops, whereas pinned contact line is observed for higher concentration CNT drops.

The coffee ring formation is governed by convective resulting from the evaporation of the solvent from the surface of a sessile drop. The local evaporation rate can be expressed as equation 50 based on Deegan's approximation[168].

$$J(r, t) = J_0(\theta) \left(1 - \left(\frac{r}{R}\right)^2\right)^{-\lambda(\theta)} \quad (50)$$

where r is the radial position from the center of the drop, R is the radius of the drop, θ is the contact angle, and $\lambda(\theta)$ is a parameter that describes the profile of the drop's local

evaporation rate. It is normally expressed as $\lambda(\theta) = \frac{1}{2} - \frac{\theta}{\pi}$. The evaporation is uniform across the drop surface when the contact angle is 90° and $\lambda=0$, whereas the evaporation is highest at the edge when the contact angle is small and $\lambda \approx 0.5$. J_0 is a function of contact angle and can be approximated as equation 51[169].

$$J_0(\theta) = \frac{Dc_v(1-H)}{R} (0.27^2\theta + 1.30) \left(0.6381 - 0.2239 \left(\theta - \frac{\pi}{4} \right)^2 \right) \quad (51)$$

where D is the diffusion coefficient of the water in the air and H is the relative humidity. Combining equation 50 and equation 51 together with the mass balance equation, the height-average radial velocity, $\bar{u}_r$ can be derived as equation 52[170].

$$\bar{u}_r(r, t) = \frac{1}{4} \frac{1}{(t_f - t)} \frac{R^2}{r} \left[\left(1 - \left(\frac{r}{R} \right)^2 \right)^{\lambda(\theta)} - \left(1 - \left(\frac{r}{R} \right)^2 \right) \right] \quad (52)$$

where t_f is the time taken for the solvent to evaporate from the drop. It can be seen that the radial velocity is a reciprocal function with an asymptote at $t = t_f$. It implies that the radial flow velocity is accelerated throughout the evaporation process and reaches the highest speed when the drop is fully evaporated [171]. This phenomenon can be inferred from the drop with concentration $\phi=0.07$ w% and $\phi=0.2$ w% (Figure 19) that there is no CNT near the rings as they are pushed towards the contact line by the strong radial flow at the final stage of evaporation. Also, equation 52 suggests that the evaporation rate of a sessile drop is highest at the contact line, resulting in a convective transport which carries the particles radially from the middle of the drops towards the contact line[172]. However, equation 52 does not take into consideration the shear stress at the drop surface. With a heated substrate,

the movement of the particles relies on the competition between the outward radial flow and the recirculation flow due to the temperature-induced Marangoni stress. At higher temperature, it has been reported that the Marangoni flow can bring the particle at the edge of the drop back to the apex of the drop which can then hinder the formation of coffee ring effect [172]. However, the Marangoni flow is dependent on the shape of the particles [173]. It has been found that needle-like particles show the slowest interfacial velocity when compared to the sphere-shaped and disc-shaped particles [173]. This also explains the formation of coffee ring effect at high substrate temperatures (110 °C) in this study, as the high aspect ratio CNTs can impede the Marangoni flow.

4.5 Microstructure of the deposited CNTs films

Figure 20a shows the SEM image at the contact line of the drop indicating three regions based on the arrangement of the CNTs. These regions are namely, aligned region (Figure 20b), transition region (Figure 20c), and randomly oriented region (Figure 20d). This phenomenon was observed for all samples fabricated with different CNTs concentrations and substrate temperatures. It was observed that the CNTs aligned orderly along the contact line/edge in region b which is near to the contact line. In region c, which is the transition region, the CNTs appeared to be aligned in the direction both parallel and perpendicular to the contact line. In region d, the CNTs are randomly oriented. Figure 20e is an illustration of the CNTs orientation and movement as a result of the convective flow transport.

At the start of the experiment when the ink drop is cast on the substrate, the CNTs are homogeneously distributed and randomly oriented. As the solvent evaporates, a radial flow is developed and the CNTs are brought to the contact line by the flow. The CNTs tend

to align themselves along the flow direction due to the shear force acting on their 1-dimensional structure[174, 175]. As the CNTs reach the contact line, the surface tension at the substrate-liquid-air interface will realign the CNTs along the contact line. As more CNTs are pushed towards the liquid boundary, the local CNTs concentration at the contact increases and the local viscosity of the suspension also increases which slows down the flow and dampens the particle motions due to other factors like temperature[172, 176]. This makes the hydrodynamic force of the radial flow on the CNTs more dominant. Besides, the local CNTs suspension at the contact line can exhibit nematic liquid crystal property when it reaches a critical concentration [65]. Also, the initial velocity at the contact line as a result of the radial convective flow is low [177]. These factors allow the van der Waals interaction between the CNTs to be sufficiently strong and have time to align themselves along the contact line as shown in Figure 20b. The transition region is where the radially aligned CNTs (perpendicular to contact line) and the nematic CNTs meet during the formation of the thin film. Figure 20c shows how the CNTs are brought to the contact line and reorient themselves to align along the contact line. Figure 20d shows randomly oriented CNTs. The random nature of CNTs has been found to result from several factors (Figure 20d). First, the decrease in local CNTs concentration deters the formation of the nematic phase, as most CNTs get deposited at the contact line (as in the case of $\phi=0.007$ w% and $\phi=0.02$ w%). Second, reduced viscosity (due to lower CNTs concentration and higher convective flow velocity (towards the end of the evaporation process) [177] results in less damping and fast-moving particles which suppress the van der Waals interaction between the CNTs. The overall result is less alignment of CNTs. The 5th sector of the drop in Figure 20e shows the

final stage of drop evaporation and the 3 regions of different CNTs alignment corresponds to Figure 20b, Figure 20c and Figure 20d respectively.

Figure 20. (a) Image showing three distinct arrangements of the CNT namely, (b) highly aligned region, (c) transition region, (d) randomly oriented region. (e) Schematic showing the mechanism of the CNT alignment due to the hydrodynamic flow on solvent evaporation.

4.6 Alignment of CNTs

With the intention of investigating the influence of substrate temperature and CNTs concentration on the degree of alignment of CNTs at the ring, FESEM images were taken near the contact line of the drops (Figure 21). It is found that the CNTs near the contact line are highly aligned in the direction parallel to the liquid-air interface for all the CNTs concentration at substrate temperature of 30 °C. At substrate temperature of 70 °C, most CNTs are aligned to the contact line but there is noticeable misalignment at certain regions.

Figure 21. FESEM images showing the morphology of the CNT thin film at the coffee ring for different substrates temperatures and CNT concentrations. The contact line is in the horizontal direction. The direction of alignment is in the same direction as the contact line.

At substrate temperature of 110 °C, most of the CNTs are randomly aligned. However, there is no noticeable difference across the drops of different CNTs concentrations that are dried at the same substrate temperatures.

Herman's orientation factor. The degree of alignment of the CNTs at the coffee ring is characterized using image analysis software, ImageJ. The angular distribution of the CNTs can then be obtained using an ImageJ plugin, OrientationJ with suitable processing parameters mentioned in the experimental section. Herman orientation factor, f , is used to evaluate the degree of alignment based on the angular distribution, δ obtained using OrientationJ[34]. The Herman orientation factor, f can be expressed as, $f = 3\langle \cos^2 \delta - 1 \rangle / 2$. In general, $f = 1$ indicates the CNTs are perfectly aligned to the principle axis, $f = 0$ implies random distribution, and $f = -0.5$ signifies perpendicular orientation to the principal axis. It should be noted that the principal axis is defined parallel to the contact line and the images are processed in such a way that the principal axis is set to $\theta=0^\circ$ or in the horizontal

Figure 22. A plot showing Herman orientation factor (f) that describes the degree of alignment of the CNTs for different substrate temperatures and CNT concentrations. ($f = 1$ represents high degree of alignment whereas $f=0$ represents random CNT orientation.)

direction. Based on the analysis (Figure 22), it is found that the f values of all concentrations that are dried at substrate temperature of 30 °C fall within 0.7-0.9 suggesting the CNTs are closely aligned to the principle axis which is the contact line. This value is comparable to existing CNT alignment technique using EDSA as discussed in Table 1. At substrate temperature of 70 °C, it is found that the f values of all concentrations fall within 0.6-0.7 thus indicating more misalignment/randomness in the orientation of the CNTs network. At substrate temperature of 110 °C, it is noticed that the f values are reduced to 0.1-0.6 which suggests the CNTs network is mostly random in nature with slight preferential alignment along the contact line. The results thus imply that the degree of alignment of the CNTs decreases with increasing temperature.

Raman spectroscopy. Raman spectroscopy is conducted to confirm the results obtained by image analysis. Raman spectroscopy with a polarised laser was used to characterize the aligned CNTs samples by evaluating the relative strength of the peaks in the Raman spectra of the aligned samples. Figure 23 shows the Raman spectra of the CNTs at the contact line under different conditions. In general, 4 peaks are observed in the Raman spectra at wavenumbers of 216 cm^{-1} , 1326 cm^{-1} , 1575 cm^{-1} , and 2622 cm^{-1} , which correspond to radial breathing mode (RBM), disorder-induced mode (D band), tangential mode (G band), and G' mode [106]. It has been shown that the CNTs absorb/emit most of the light when it is oriented parallel to the direction of light polarization, $\theta=0^\circ$, whereas the absorption/emission of light is greatly suppressed when it is perpendicular to the direction of the light polarization, $\theta=90^\circ$ as shown in Figure 23a [106, 178, 179]. This anisotropic optical property of CNTs to the polarised light allows the characterization of the degree of

alignment of CNTs in a sample. It has been shown the relative intensity of the G band to D band (I_G/I_D) depends on the CNTs orientation, which can be used to characterize the degree of alignment of the CNTs network[180, 181]. Figure 23b illustrates the Raman spectra of the CNT network at the contact line formed from the 0.2 w% CNTs concentration at different substrate temperatures. It is noticed that the I_G/I_D ratio decreases from 4.87 to 1.78 when the temperature is increased from 30 °C to 110 °C. Comparing the FESEM images and Herman orientation factor to the I_G/I_D ratio, it is found that I_G/I_D ratio of 4.5 or higher indicates a good degree of alignment ($f > 0.7$). Figure 23c shows that the I_G/I_D ratio for all the CNTs concentration at 30 °C is higher than 4.5, indicating a high degree of alignment. The CNTs concentration of 0.007 w% is omitted from Figure 23c because the CNTs concentration is too low to give any measurable signal. Another way to characterize the degree of alignment of CNTs using Raman spectroscopy is by comparing the relative peak of G band, I_{G0}/I_{G90} at different sample orientation ($\theta=0^\circ$ & $\theta=90^\circ$)[182]. Figure 23d, Figure 23e, and Figure 23f show the Raman spectra of 0.2 w% CNTs concentration that are dried at substrate temperatures of 30 °C, 70 °C and 110 °C respectively. It is found that the I_{G0}/I_{G90} ratio for substrate temperatures of 30 °C, 70 °C and 110 °C are 1.75, 1.62, and 1.16 respectively. High I_{G0}/I_{G90} ratio implies higher degree of CNTs ordering as there are more CNTs aligned in 0° polarization than 90° polarization, whereas low ratio signifies that the CNTs are oriented randomly as the amount of CNTs that are aligned in 0° and 90° are about the same.

Figure 23. (a) Schematic showing the CNTs orientation and the direction of light polarization. Raman spectra showing (b) the effect of temperature on 0.2 w% CNTs concentration with $\theta=0^\circ$ light polarization, (c) effect of CNTs concentrations on drops drying at substrate temperature of 30 °C, the ratio of I_{G0}/I_{G90} for substrate temperature of (d) 30 °C, (e) 70 °C, and (f) 110 °C. The Raman spectra are offset for clarity.

Table 5 is used to compare the result of the image analysis and Raman spectroscopy.

The comparison is made among 3 indicators, namely the Herman orientation factor (f), the relative intensity of G band to D band (I_G/I_D), and the relative intensity at different

orientations (I_{G0}/I_{G90}). Based on the results, it can be observed that all the indicators show decreasing trends as the substrate temperature increases. Comparing these values to the FESEM images in Figure 21, it is easy to correlate them with the degree of alignment of the CNTs at the contact line. This comparison also helps to validate and cross-check the correctness of these indicators to the degree of alignment of the CNTs. The diminishing degree of alignment with the increasing substrate temperature can be attributed to (i) the shortening of evaporation time and (ii) the increase in the motion of the CNTs particles. It is shown in Figure 17 that the time taken for the drops to completely evaporate reduces from 230 s to 9 s when the temperature is elevated from 30 °C to 110 °C. This, in turn, reduces the time for the CNTs to rearrange themselves through inter-particle forces which may lead to less orderly aligned CNTs network at the contact line. Moreover, the temperature of the drop will increase at elevated temperatures values and result in the decrease in viscosity of the CNTs suspension and thus increase the Brownian motion of the CNTs[183, 184]. The compounding effect will result in a more violent, agitated and less dampened motion of the CNTs particles. This also reduces the chance of achieving a good degree of alignment of CNTs at elevated temperature.

Table 5. Comparison of different indicators for characterizing the degree of alignment of CNT.

Substrate temperature (°C)	Herman orientation factor, f	I_G/I_D	I_{G0}/I_{G90}	Trend
30	0.93	4.87	1.75	decreasing
70	0.67	3.35	1.62	
110	0.17	1.78	1.16	

4.8 Effect of drop size

Previous sessile drops study on substrate temperature shows inversely proportional correlation between the substrate temperature and the degree of alignment of CNTs. The misalignment of CNTs at elevated temperature could be a result of the increase in Brownian motion of CNTs or the decrease in self-ordering time. This section attempts to study the impact of self-ordering time on the alignment of CNTs independently by excluding the temperature effect. The reduce in self-ordering time is achieved by using smaller drop sizes. Figure 24 shows the final dimension of the drops with volumes 2 nL, 5 nL, 10 nL, 15 nL, and 200 nL respectively. It can be seen that the drop diameters reduce with decreasing drop volumes. The evaporation time of a 200 nL CNTs drop is approximately 300 s, whereas the evaporation time for drops with volumes of 2 nL, 5 nL, 10 nL, and 15 nL are very difficult to measure (typically less than a few seconds). However, it can still be deduced by using the evaporation model of sessile drop derived by Butt. et al. as shown in equation 53 [185]. It can be seen that the evaporation time, τ is shorter for smaller drops.

$$\tau = \frac{1}{4} \left(\frac{2}{\pi} \right)^{\frac{2}{3}} \frac{V_{L0}^{2/3} k_B T \beta^{1/3}}{D P_0 V_m x f} \quad (53)$$

where V_{L0} is the initial drop volume, D is the diffusion constant for the vapor molecule in gas phase, k_B is the Boltzmann's constant, T is the temperature of vapor, $\beta = (2 + \cos \Theta)(1 - \cos \Theta)^2$, Θ is the contact angle, P_0 is vapor pressure of liquid with a planar surface, V_m is molecular volume in the liquid phase, x is the saturation of the vapor ($x=0$ indicates perfectly saturated vapor, $x < 1$), f is a polynomial function of contact angle.

Figure 24 Images of the dimensions of the final drop deposition pattern of drop volumes (a) 200 nL, (b) 15 nL, (c) 10 nL, (d) 5 nL, and (e) 2 nL respectively.

Figure 25 shows the FESEM images of the CNTs alignment of different drop volumes. It can be observed that misalignment is more prominent for smaller drops. Figure 26 shows Herman's orientation factor of the FESEM images of different drop sizes. Despite the misalignment, preferential alignment is still observed at smaller drop sizes. However, Figure 26 suggests that the degree of alignment of CNTs decreases with decreasing drop sizes. This result suggests that the competition of relative time scales among the evaporation time, CNTs translational diffusion, and CNTs rotational diffusion. Based on the optical and FESEM images, it is found that "coffee ring" effects are formed in all the drops suggesting that the time scale of translational diffusion is shorter than the evaporation time. However, the time scale for CNTs rotational diffusion is significantly longer than the evaporation time of the smaller drops (2 nL, 5 nL, 10 nL, and 15 nL). This has resulted in good CNTs alignment in larger drop size, and CNTs misalignment in smaller drop sizes.

Figure 25 FESEM images showing the CNTs alignment at the contact line of drop volumes (a) 200 nL, (b) 15 nL, (c) 10 nL, (d) 5 nL, and (e) 2 nL respectively.

Figure 26 The effect of drop size on the degree of alignment of CNTs

4.7 Effect of pH

The formation of “coffee ring” effect is vital for achieving aligned CNTs network as aligning CNTs through EDSA requires sufficient CNTs concentration at the contact line to form a nematic LC phase of CNTs solution. This relies on the radial/outward moving

convective flow to bring the CNTs to the contact line due to the evaporation of the solvent. However, the formation of the “coffee ring” effect does not rely on the convective flow only, it also depends on the surface charge of CNTs in the suspension solution. The surface charge will affect the stability of CNTs in the suspension solution, thereby affecting the final deposition pattern. The surface charge of the CNTs can be tuned by the pH of the suspension solution. This is because carboxyl groups in the CNTs adsorb the H^+ or OH^- ions from the aqueous suspension resulting in a net charge on the surface of the SWNTs. The charge density on the SWNTs is dependent on the pH of the dispersion as this affects the extent of ionization and adsorption. Figure 27 shows the effect of the pH on the deposition pattern of the CNTs drops. It can be observed that the “coffee ring” effect is strong at pH ranging from pH 4 to pH 10, however, the effect diminishes at low pH values (pH 1.5 and pH 2.5).

Figure 27 Optical images showing the deposition pattern of the CNTs drops with different pH values.

The surface charge of micro- or nano-size particles in a suspension solution is normally characterized by the zeta potential. Zeta potential is the potential difference between the liquid dispersant and the stationary layer of liquid stuck to the particle's interface. Generally, a high zeta potential (omitting the polarity of voltage) indicates a solution with good stability, whereas a low zeta potential suggests that the solution is susceptible to aggregation and sedimentation. Figure 28 shows the graph of zeta potential against pH of the CNTs suspension solution and the polyimide substrate. The pH of the suspension can affect the surface charge of the CNT and the surface charge of the substrate. Figure below shows the effect of the pH on the zeta potential (surface charge) of the CNT and the polyimide substrate. It can be observed that at $\text{pH} < 4$, the zeta potential of the CNT and polyimide substrate have different polarity, indicating they have opposite surface charge. This means that the CNT will experience greater attractive force towards the substrate. The greater CNT-substrate attractive force overcome the hydrodynamic drag force thus resulting in a more homogeneous deposition pattern. On the other hand, at $\text{pH} > 4$, the substrate and CNT have similar surface charge, leading to weaker CNT-substrate interaction, thus favoring the formation of coffee ring. It can be seen in Figure 28 that there is a trend of increasing zeta potential (omitting the sign) with increasing pH value of the suspension solution. The results suggest a minimum pH of approximately pH 4.0 is required for the formation of coffee ring. The formation of coffee ring is vital for the CNT alignment because the phenomenon increases the CNTs concentration at the liquid-air-substrate interface to a level exceeding the critical concentration for the highly-ordered nematic liquid crystal phase.

This study reveals the importance of pH of the CNTs suspension solutions in determining the final deposition pattern, allowing designers to control the film morphology to achieve either “coffee ring” effect or homogeneous film.

Figure 28 Graph of zeta potential vs pH of CNTs suspension solution (Dashed line represents the trend line). The data for the zeta potential of polyimide substrate is extracted from reference[186].

4.9 Summary

Sessile drops experiment was conducted to investigate the influence of substrate temperatures and CNTs concentration on the evaporation dynamics of the CNTs inks. It is observed that the CNTs concentration has a much more significant influence on determining the contact line dynamic of the sessile drop. At concentrations of 0.007 w% and 0.02 w%, the drops show depinning contact line, whereas an opposite pinning effect is observed for CNTs drops with concentrations of 0.07 w% and 0.2 w%. The depinning of the contact line at low CNTs concentration can be attributed to the lack of aggregates-induced pinning.

Besides, it is also found that increasing the substrate temperature helps in promoting the pinning of the contact line of the evaporating drops. The pinning phenomenon at elevated temperature is due to the decrease in unbalanced Young's force at the contact line. Coffee ring effect is observed on the deposition patterns due to the evaporative-driven self-assembly. In addition, it is also found that the substrate temperature has a substantial effect on the degree of alignment of the CNTs network at the contact line. At a low substrate temperature (30 °C), the CNTs show a high degree of alignment at the contact line, however, the misalignment increases with increasing substrate temperature. In short, it is found that the evaporation dynamics of the CNTs depends on the concentration of the dispersion, whereas the degree of alignment of CNTs at the coffee ring depends greatly on the substrate temperature. In addition, drop size, which closely affects the evaporation time, is found to be an important factor affecting the degree of alignment of CNTs in the coffee ring. Besides, pH of suspension solution can be adjusted to control the deposition pattern.

5. ANALYTICAL MODELLING APPROACH: INVESTIGATION OF DEPOSITION AND EVAPORATION OF MATERIALS IN AEROSOL JET PRINTING

5.1 Scope of experiment

There are several limitations to Binder's analytical model [116], as it does not consider (i) effect of printing speed, (ii) the wetting property of the substrate, (iii) the deposition rate of the aerosol, and (iv) the aerosols beam expansion. As such, the model is only applicable in cases where the print speed is high and the deposition rate is low as depicted in Figure 29 (scenario i, ii and iii). Figure 29 shows the formation of liquid drops on the substrate by aerosol jet printing at (a) increasing deposition rate of aerosols and (b) decreasing print speed. Under different aerosol flow rate and print speed, there exists four possible scenarios namely, (i) the impinged liquid droplets does not coalesce, which happens when the amount aerosol deposited is too low, (ii) the impinged liquid droplets coalesce and the interface boundary is pinned, (iii) the impinged liquid droplets coalesce and contact angle does not exceed the critical contact angle, and (iv) the contact angle exceeds the critical contact angle and spreading occurs.

The scope of this chapter is to present a simple analytical model that can be used to address some of the limitations of Binder's analytical model by taking into consideration the effect of print speed, the wetting behavior of the substrate, and the aerosol flow rate. The model presented in this chapter will be useful to describe scenario (iv) as shown in Figure 29. Besides, the dominant role of the aerosol transportation stage in ensuring good

quality printing, whose investigation is often neglected, is also demonstrated. The work compares the actual printed line width with the model and discusses the validity of the model under different circumstances.

Figure 29 Image showing different possible scenarios for the formation of liquid drops under (a) increasing aerosol flow rate and (b) decreasing print speed. Depicted scenarios are: (i) the impinged liquid droplets do not coalesce, (ii) the impinged liquid droplets coalesce and the interface boundary is pinned, (iii) the impinged liquid droplets coalesce and contact angle does not exceed critical contact angle, and (iv) the contact angle exceeds the critical contact angle and spreading occurs, and (c) the corresponding deposition patterns for each scenario.

5.2 Theory and modeling

The model used for this research is adopted from the inkjet printing drops deposition model developed by Stringer *et al.* [187]. This model is adopted here because it is based upon the mass conservation law and can be used to explain many phenomena that cannot be explained by Binder's model. The deposition of drops mainly involves two stages namely, impact-driven and surface energy-driven stage. The model neglects both the effects of the kinetic energy of the drops and the gravitational force, thus assuming the formation of a cylindrical cap with a contact angle, θ to minimize the energy stage of the drop. The model is developed based on the volume conservation of the incoming drops to form a cylindrical cap liquid drop, and its analytical solution can be expressed as follows in equation 54.

$$\frac{\pi d^3}{6} N = \left(r^2 \theta - \frac{wr \cos \theta}{2} \right) L \quad (54)$$

where N is the number of droplets, d is the diameter of each droplet, θ is the contact angle of the ink, L is the length of the deposited drop, and w is the width of the deposited drop and r is the radius of the cylindrical cap, where $r = \frac{w}{2 \sin \theta}$. The first term in equation 54 is the total volume of the incoming drops and the second term represents the volume of the cylindrical cap of the liquid drop.

By the same token, the model is adopted and applied to aerosol jet printing's ink deposition process. Figure 30 shows the diagram of the model for predicting the line width, w via aerosol jet printing process. It is difficult to quantify the number of drops being

generated by atomizer at any instant, hence the number of drops is computed over period Δt . The change is reflected in the model by dividing equation 54 by Δt , as follows:

$$\frac{\pi d^3 N}{6 \Delta t} = \left(r^2 \theta - \frac{wr \cos \theta}{2} \right) \frac{L}{\Delta t} \quad (55)$$

It is to be noted that the first term in equation 55 represents the deposition rate or the aerosol volumetric flow rate, $\dot{V}_{aerosol}$ and the term $\frac{L}{\Delta t}$ represents the print speed, v . By simply rearranging the terms in equation 55, the line width predicted by the model can be expressed as follows in equation 56.

$$w = \sqrt{\frac{4\dot{V}_{aerosol}}{v \left(\frac{\theta}{\sin^2 \theta} - \frac{\cos \theta}{\sin \theta} \right)}} \quad (56)$$

Equation 56 describes the relationship between the line width with other parameters such as print speed, wetting behavior of the substrate, and the deposition rate of aerosols, and provides a simple solution. In addition, equation 56 can be rearranged as equation 57 to predict the aerosol deposition rate, $\dot{V}_{aerosol}$ in terms of the measured printed line width, print speed and contact angle of the ink on the substrate.

$$\dot{V}_{aerosol} = \frac{vw^2}{4} \left(\frac{\theta}{\sin^2 \theta} - \frac{\cos \theta}{\sin \theta} \right) \quad (57)$$

However, it is important to emphasize that the model is only valid with the assumptions that (i) printed lines are stable and form a cylindrical cap, (ii) printed liquid bead do not bleed into trenches due to the gas flow, and (iii) all the aerosol coalesce and form single liquid drop. Also, one should not confuse $\dot{V}_{aerosol}$ with the volumetric flow rate

of the carrier gas from the atomizer, $\dot{V}_{atomizer}$. The volume fraction of the aerosols can be expressed in terms of $\dot{V}_{aerosol}$ and $\dot{V}_{atomizer}$ as equation 58.

$$\varphi = \frac{\dot{V}_{aerosol}}{\dot{V}_{atomizer}} \quad (58)$$

Figure 30 Schematic showing the aerosol aerodynamic focusing and deposition in the aerosol jet printing process.

5.3 Experimental details for model validations

To validate our model, Optomec 5X aerosol jet printer with a nozzle size of 200 μm is used. Polyimide substrates with a thickness of 150 μm were employed. The substrate is first cleaned with alcohol in an ultrasonic bath. The distance between the nozzle and the substrate is kept around 5 mm. The volumetric flow rate of the carrier gas is kept at 40 sccm to ensure sufficient aerosol flow rate for good printability. The ultrasonic current is set to 0.5 A for

good atomization of the ink. The length of the aerosol delivery tube length is 60 cm unless otherwise stated. The ink used in this project is a homogeneous dispersion of single-walled carbon nanotube ink purchased from Nanolab[®]. The ink has a concentration of 0.2 w% and an average tube length of approximately 1.5 μm . The printing platform is kept at 25 °C to minimize the loss of solvent due to the evaporation of aerosol and the deposited liquid drops. The contact angle measurement is done using an in-house built setup with a magnifying lens and a slow-motion camera. The printed lines are left dried and the line widths were measured using an Olympus CKX41 optical microscope. At least 10 measurements are taken for each experimental condition to ensure the results are statistically significant.

5.4 Results and discussion

The calculated line width and the measured printed line width for different sheath flow, $\dot{V}_{sheath}$ are compared in Figure 31a. The calculated line width is obtained by fitting suitable values to the $\dot{V}_{aerosol}$ so that the calculated values match the experimental data. The contact angle of the CNTs ink was measured to be around 58°. Here, it is observed that by fitting $\dot{V}_{aerosol} = 390 \times 10^{-5}$ sccm, 138×10^{-5} sccm, and 12×10^{-5} sccm, the calculated line widths match relatively well with the experimental data for $\dot{V}_{sheath} = 10$ sccm, 20 sccm, and 30 sccm respectively for low print speed regime, <5 mm/s. For the case of $\dot{V}_{sheath} = 10$ sccm, the calculated line widths match quite closely for print speed between 1-5 mm/s when the fitted value for $\dot{V}_{aerosol} = 390 \times 10^{-5}$ sccm. The deviation of the experimental data from the calculated line width can be explained by the high $\dot{V}_{aerosol}$, which results in more ink being deposited on the substrate; thus making the deposited drop easier to be deformed/spread outward by the high gas flow as suggested by Feng [134]. This leads to a wider line width.

For the case of $\dot{V}_{sheath} = 20$ sccm, the calculated line widths match the entire range of the experimental data with the fitted value for $\dot{V}_{aerosol} = 138 \times 10^{-5}$ sccm. However, it is observed that the measured line width from the experimental data is almost constant at $\dot{V}_{sheath} = 30$ sccm. The model is only able to match the experimental data at low print speed regime (1-3 mm/s) when the fitted value for $\dot{V}_{aerosol} = 12 \times 10^{-5}$ sccm. The deviation of the experimental data from the model can be explained by the insufficient aerosol flow that results in no outward spreading of ink (case i, ii, and iii in Figure 29). In this case, the proposed model is not applicable to predict the line width and the Binder's model should be applied instead.

The model presented is not only able to explain the trend of the printed line width quite well but is also able to predict the aerosol deposition rate. Based on the fitting values of $\dot{V}_{aerosol}$ for different $\dot{V}_{sheath}$ conditions, it can be seen that the aerosol deposition rate decreases from 390×10^{-5} sccm to 12×10^{-5} sccm when the $\dot{V}_{sheath}$ increases from 10 to 30 sccm. Interestingly, the atomizer flow rate is kept constant at 40 sccm for all the experiments. This seems counter-intuitive as one would normally think that the aerosol deposition rate should remain the same if the atomizer flow rate remains constant. However, the results show the volume fraction of the aerosols reduces when the $\dot{V}_{sheath}$ increases. For instance, the estimated aerosols volume fraction for $\dot{V}_{sheath} = 10$ sccm is $\varphi = 9 \times 10^{-5}$; the estimated aerosols volume fraction for $\dot{V}_{sheath} = 20$ sccm is $\varphi = 3.45 \times 10^{-5}$; the estimated aerosols volume fraction for $\dot{V}_{sheath} = 30$ sccm is $\varphi = 0.3 \times 10^{-5}$. The estimated volume fractions are close to the volume fraction suggested by Chen and Yeh [115] and Gu *et al.* [132], thus confirming the validity of the method to estimate aerosol flow rate and volume fraction.

This could possibly be used as an alternative to estimate the deposition rate of the ink done by Gu *et al.* [132]. The reduction in the volume fraction of the aerosols indicates the loss of solvent during the printing process. The increase in the $\dot{V}_{sheath}$ enhances the evaporation of the solvent in the aerosols resulting in the changes in the line width of the printed lines. There are two possible explanations for the enhanced evaporation due to the increase in $\dot{V}_{sheath}$. Firstly, when a higher $\dot{V}_{sheath}$ is used a higher pressure is needed to drive the same amount of $\dot{V}_{atomizer}$ through the nozzle. The increase in atomizer flow field pressure will marginally reduce the enthalpy of vaporization of the solvent (water in this case) [188]. According to Holyst *et al.*, the simplified form of the rate of change of the radius of the aerosols, which directly link to the evaporation of aerosol, can be expressed as $\dot{a} = -\frac{\rho D c_p}{a q_{eff} \rho_L} [T_\infty - T_L(t)]$, where ρ is the density of the gaseous environment, D is the diffusivity of the solvent, a is the radius of aerosol, q_{eff} is the enthalpy of vaporization, ρ_L is the density of the solvent/ink, and $T_\infty - T_L(t)$ is the temperature difference between the liquid and the gaseous environment [189]. Here, it is obvious that the reduction of the enthalpy of vaporization of the solvent due to the increase in pressure enhances the evaporation of aerosols. Second, higher $\dot{V}_{sheath}$ provides a higher capacity for the absorption of moisture content from the enwrapped atomizer flow. This removes the moisture content in the atomizer flow and enhances the evaporation of aerosols. Both effects contribute to the reduction of the line width with the increase in $\dot{V}_{sheath}$.

The optical images of the printed CNTs lines obtained at different conditions are shown in Figure 31b. It can be seen that the coffee ring effect (twin lines) occurred in all the experimental conditions. The coffee ring effect can be used as an indication of the

deposited ink forming a straight and continuous liquid pool of ink, which further confirms the validity of the experimental conditions to be used to verify our analytical model. It is observed that very clean and straight edges for almost all printed lines, thus indicating that the over-spraying issue did not occur. This also suggests that almost all the aerosols have sufficiently high stoke numbers during the deposition stage of the AJP process.

Figure 31 (a) A comparison of our model with the experimental data using a 200 μm nozzle. Dashed lines represent the calculated line width (model) and solid dots represent experimental data. (b) Optical images of the printed carbon nanotube trace with different printing conditions (scale bar represents 500 μm)

5.5 Analysis of the effect of the sheath on mass deposition rate in AJP

To confirm the prediction of the model that the ink deposition rate of the ink is affected by the sheath flow, an additional experiment is conducted using UT Dots silver nanoparticle inks to show that the phenomenon is solely due to the process. Another reason for choosing UT Dots silver nanoparticle ink is because of 2 reasons. The first reason is its high density that allows taking mass measurements with a smaller amount of ink and shorter time, the second reason is the lower condensation rate on the tubing that allows experiments to be carried out without clogging issue. Figure 32 shows the effect of sheath flow on the mass deposition rate at different atomizer flow rates. It is found that the ink deposition rate decreases with increasing sheath flow at all atomizer flow rates. This result suggests that the sheath flow influences the evaporation of the aerosols before the aerosols of ink are deposited on to the substrates which confirm the explanation provided in the earlier section.

Figure 32 Effect of sheath flow on the ink deposition rate at different atomizer flow.

5.6 Analysis of the role of evaporation in AJP

In the previous section, the role of aerosol evaporation in AJP process has been discussed. Here, the lifespan of the aerosols, from generation to transportation and finally deposition is investigated to study how it affects the print quality. The lifespan of the aerosols can be sectioned into (i) non-combined flow (atomizer flow only) and (ii) combined flow (atomizer flow and sheath flow). The division of the lifespan is important because the aerosols experience very different gaseous environments in these two sections. For instance, the saturation of moisture in non-combined flow happens very quickly as the moisture cannot escape, whereas the saturation of moisture in the combined flow happens rather slowly as the moisture can escape into the sheath flow. Furthermore, depending on the design of the setup, the aerosols will have a different amount of residence time at different sections. All these factors result in different evaporation rate of the aerosols in the atomizer flow.

To study the residence time of the aerosols in each section, the dimensions (inner diameter and length) of each component of AJP that the aerosols pass through is measured. The components include the aerosol delivery tube, the deposition head, and the nozzle. The measurement can be found in Appendix C and Appendix D. The calculation of residence time of the aerosols also depends on the atomizer flow rate. In this study, the atomizer flow rate is set to 40 sccm. Here, a simple way is proposed to estimate the residence time by assuming the aerosols travel through each section with the same speed as the gas flow and no evaporation occurred. The residence time, Δt_{res} can be estimated using equation 59.

$$\Delta t_{res} = \frac{L_{channel}}{v_{flow}} = \frac{A_{channel} \times L_{channel}}{\dot{V}_{flow}} \quad (59)$$

Figure 33a shows the sectioning of the AJP process into a non-combined flow and combined flow. Figure 33b shows the two main factors affecting the residence time of the aerosols in the non-combined flow, which are the aerosol delivery tube length and the carrier gas/atomizer flow (AF). From the results, it is clear that the residence time of the aerosols increases as the tube length increases and the AF decreases. Figure 33c shows the effect of the combined flow rate on the residence time of the aerosols. A detailed calculation of the residence time for each flow can be found in Appendix E.

Figure 33 (a) Schematic of the deposition head of AJP showing non-combined flow and combined flow, (b) Graph showing the calculated residence time of aerosols in the non-combined flow, and (c) graph showing the calculated residence time of aerosols in the combined flow.

As the moisture content in each flow is not known, the evaporation rate of the aerosols in each flow could not be determined. However, based on the results, it can be deduced that the aerosols spent most of the time in the aerosol delivery tube (>1 s), whereas only a fraction

of time was spent in the combined flow (<100ms). In order to understand the impact of the residence time of the aerosols, the theoretical lifespan of the aerosol that is freely suspended in a moisture-free environment is calculated. The lifespan of such aerosol can be estimated using equation 60 [190].

$$\tau = \frac{D_0^2}{\lambda} \quad (60)$$

where $\lambda = \frac{4Sh\rho_c D_v}{\rho_d} (\omega_s - \omega_\infty)$, Sh is the Sherwood number, ρ_c is the density of carrier gas, ρ_d is the density of the ink's solvent, D_v is the diffusion coefficient, ω_∞ is the moisture content at ambient condition, ω_s is moisture content at the surface of the aerosol.

the lifespan of aerosol with a diameter of 10 μm is computed to be around 1.75 s, whereas that of the diameter of 5 μm is approximately 0.44 s. A detailed calculation of the lifespan of aerosols can be found in Appendix F. Considering the experiment values of 60 cm and of 40 sccm for tube length and atomizer flow respectively, the calculated residence time of the aerosols within the system is around 1.424s. This is shorter than the lifespan of an aerosol with a diameter of 10 μm (1.75 s). It means the aerosol with a diameter of 10 μm would still have time to be deposited onto the substrate before the solvent evaporates completely. Although the calculated residence time is longer than the lifespan of the aerosol with a diameter of 5 μm (0.44 s), it does not mean that the aerosol will disappear before exiting the nozzle as the moisture content in the aerosol delivery tube is very different from the assumed moisture-free environment (theoretical lifespan). This means that the actual lifespan of the 5 μm drop can be much longer than the theoretical 0.44 s. It is noted that the current analysis only provides a general idea of the importance of the balance between the

residence time and the lifespan of the aerosols during the AJP process. An accurate estimation of the aerosols' residence time and lifespan require complicated numerical modeling of the system that takes into consideration of many factors such as the evaporation and aerosol-fluid interaction which is beyond the scope of this research.

Figure 34 (a) Effect of tube length (in cm) on the printed line width and (b) Optical images showing the line morphology of the printed CNT traces.

The effect of the residence time in the non-combined flow has also been investigated. The residence time is varied by using aerosols delivery tubes with different lengths. Figure 34a shows the results when using tubes of lengths of 80 cm and 90 cm. it can be observed

that the line widths reduce as the tube length increases. This suggests that the $\dot{V}_{aerosol}$ reduces as the tube length increases. This is because the aerosols experience a longer residence time in the aerosol delivery stage giving the solvent more time to evaporate and hence resulting in aerosols lower volumes. The effect can be confirmed by using a longer delivery tube of 130 cm as shown in Figure 34b. The optical image shows that the printed line has fuzzy edges and only a very fade line is visible. This phenomenon is more commonly known as the over-spraying of ink. This is because most of the solvent in the aerosols would have evaporated before exiting the nozzle making the aerosol having very small stoke numbers. Only a small portion of the aerosols with sufficiently large stoke number can impinge on the substrate. Although not measured directly, the effect of the stoke number (aerosol's diameter) can be clearly seen in Figure 34b which overspray issue for the tube length of 130 cm is significant. Thus, this study shows the significance of aerosol residence time in AJP process and how it affects the print quality.

5.7 Summary

The aerosol jet printing (AJP) process parameters are analyzed analytically and validated experimentally. A simple AJP model (adopted from the inkjet printing process) is proposed that takes into consideration of print speed which is lacking in existing AJP analytical model. The model also provides new insight on how sheath flow affects the volumetric flow rate of inks at constant atomizer flow condition. Besides, the volumetric flow rate can be estimated with the model. Lastly, the evaporation of aerosols in the aerosol transportation stage, which is less studied, is investigated by using different tube length for aerosol

delivery. This study allows a better understanding of the AJP process for achieving good quality lines for electronics fabrication.

6. HIGH-RESOLUTION AEROSOL JET PRINTING OF ALIGNED CARBON NANOTUBE TRACES ON FLEXIBLE SUBSTRATES VIA COFFEE RING EFFECT

6.1 Scope of experiment

The aim of this work is to study the effect of print resolution on the EDSA of CNT which has not been extensively investigated. Besides, the alignment of the CNT on the printed twin-line is analyzed by using image processing software. In addition, the mechanism that drives the alignment of CNT is also discussed. In short, preferentially aligned CNT traces have been demonstrated here using AJP, achieving resolution higher than inkjet printing techniques reported in previous work. This study helps to understand the process parameters of AJP and the underlying mechanism of the EDSA process of printed CNT traces, thus identifying the essential factors for achieving high-resolution aligned CNT traces for printed electronics. Figures in this chapter are reproduced from Ref [191] with permission from ACS publications.

6.2 Aerosol jet deposition and evaporation-driven self-assembly concept

It is important to understand the process in the aerosol jet printing process to exploit it for obtaining the desired functionality. The nanoparticle ink undergoes atomization by the ultrasonic atomizer and the aerosols are then delivered to the deposition head and exits

through the nozzle as shown in Figure 35a and Figure 35b. As the aerosols exit the nozzle, they are impinged on the substrate and start to coalesce into larger drops, thus creating continuous thin lines. The surface tension of the ink, surface energy and roughness of the substrate and the printing parameters are crucial factors affecting the wetting area of the ink on the substrate and hence the print resolution. The wetting area of the deposited ink eventually decides the contact line (liquid-air-substrate interface) on the substrate, thus the final deposition pattern. In this work, it has been found in Chapter 4 that the contact line of the SWNT ink is pinned on the polyimide substrate during evaporation. As the solvent evaporates, the contact area of the ink remains constant and the contact angle at the pin contact reduces. Due to the higher evaporation rate at the contact line, a peripheral transport flow (also known as the capillary flow) will be induced in the deposited ink moving the SWNT towards the deposited ink's periphery. After complete evaporation of the solvent, a dry deposit of SWNT is mainly formed at the periphery of the contact line (Figure 35c). A twin-line conductive trace is created due to this phenomenon, also commonly known as evaporation driven self-assembly (EDSA) (Figure 35d). Only some of the SWNT will remain in between the twin lines due to the stronger electrostatic force between SWNT and the substrate. The electrostatic force pins the SWNT to the substrate which resists the hydrodynamic force caused by the capillary/periphery transport flow. Nonetheless, most of the SWNT is observed to have accumulated at the contact line's periphery after all the solvent evaporated as shown in Figure 36a.

Figure 35 Schematic of aerosol jet printing process (atomization, aerosol transportation, and ink deposition), (b) Zoomed in schematic of aerosol jet deposition from the nozzle and evaporation process at the substrate, (c & d) Schematics depicting the coffee ring effect of deposition pattern (side and top views) and timeline showing the formation of the conductive twin-line carbon nanotube trace by evaporation driven self-assembly (coffee ring effect).

6.3 Macroscopic line morphology of aerosol jet printed SWNTs

Figure 36 depicts the FESEM micrographs of aerosol jet printed line morphology. The printed features can be categorized into stable and unstable lines. For stable lines, the droplets from the nozzle will impinge on the substrate and the contact lines pin on the substrate to form printed traces that have straight edges. Good quality continuous twin lines are formed when there is a sufficient amount of SWNTs at the edges to form continuous traces (Figure 36a). On the other hand, sparse and discontinuous twin lines (Figure 36b) are formed due to insufficient SWNTs. For unstable lines, the printed traces are discontinuous or bulged due to the moving contact line (Figure 36c and Figure 36d). Figure 36c depicts

broken printed traces due to the unpinning of the contact line. The unpinning of the contact line could be due to several reasons such as the inhomogeneity of surface and surface energy of the substrate. Figure 36d shows the printed SWNTs traces with the bulging issue as a result of excess ink flow. The line instability can be explained by the pressure difference in

Figure 36 FESEM images showing aerosol printed CNTs traces with (a) good quality continuous twin lines, (b) sparse & discontinuous twin lines, (c) broken lines due to drop coalescence, and (d) bulging issue.

the flow which forces the excess ink to accumulate. The instability of the printed lines can be avoided by proper cleaning of the substrate and selection of printing parameters. It has been found that the optimized aerosol formation parameters are SF = 40 sccm, AF = 40 sccm, and UC = 0.6 A for stable uniform lines without bulging for SWNT inks. In order to better characterize the printed SWNTs trace, the scope of this study is limited to studying on the good quality and continuous twin line SWNTs trace.

The CNTs traces were printed with various aerosol jet deposition parameters such as print speed (PS), nozzle size (NS), and substrate temperature (ST), and characterized by measuring their line widths and coffee ring width. Other aerosol formation parameters are

kept at sheath flow (SF) = 40 sccm, atomizer flow (AF) = 40 sccm, and ultrasonic current (UC) = 0.6 A for the tests. The measurement of the line width and the coffee ring width is depicted in Figure 37a. Figure 37b, Figure 37c, and Figure 37d show the trend of the line dimensions in terms of the line width and the coffee ring width with respect to the print speed, the nozzle size and, the substrate temperature (PS, NS, and ST) respectively. In all cases, it has been found that the coffee ring width shows a very similar trend with the line width of the SWNT trace. Similar observations have been reported by Dinh et. al when printing multi-walled carbon nanotube using inkjet printing technique [83]. The coffee ring width depends very much on the amount of the SWNT available in the deposited liquid. In other words, the coffee ring width is proportional to the amount of ink being deposited which is closely related to the printed line width. For simplicity, the term “line dimensions” will be used to refer to both printed line width and coffee ring width for the rest of the discussion unless otherwise stated.

Effect of print speed. Figure 37b depicts that the line widths decrease with increasing print speed (1 mm/s, 3 mm/s, 5 mm/s) while keeping the other printing parameters such as nozzle size (150 μm) and substrate temperature (25 $^{\circ}\text{C}$) constant. This trend is similar to the inkjet printing technique when the drop spacing parameter is varied [83]. The decreasing line dimensions are due to the reduction in the amount of SWNT received per unit area as the print speed increases, hence smaller line widths and lesser SWNT accumulated at the periphery.

Effect of nozzle size. Figure 37c shows the effect of the nozzle size (150 μm , 200 μm , 300 μm) on the trend of the line dimensions while keeping the print speed (5 mm/s)

and substrate temperature (25 °C) constant. It is observed that the smaller line dimensions can be obtained by using a smaller nozzle. For instance, a line width of approximately 70 μm can be obtained by using a nozzle with a diameter of 150 μm . The influence of the nozzle size on the line dimensions can be explained by the direct correlation between the nozzle size and the ink flow. A nozzle with a larger diameter can have higher ink flow rate and hence the larger line dimensions.

Effect of substrate temperature. The effect of the substrate temperature (25 °C, 40 °C, 60 °C) on the line dimensions were studied (Figure 37d) while keeping the print speed (5 mm/s) and nozzle size (150 μm) constant. It is noticed that the line dimensions decrease as the substrate temperature increases. The anomaly at 40°C could be due to printing error such as fluctuation of flow pressure during the printing process or poor cleaning of the substrate's surface. It should be pointed out that the line width is affected by the contact angle, which is temperature dependent. Substrate temperature will change the surface energy of the substrate and surface tension of the ink, thereby changing the contact angle of the ink [159]. In theory, high substrate temperature will result in a lower contact angle, thus wider line width. However, the opposite trend is observed in the aerosol jet printing of CNT ink. Von de Berg et al. explained that this is due to the reduction in spreading of the ink and the loss in the solvent in the aerosols in the transportation stage due to the higher evaporation rate because of the higher substrate temperature [192]. As a result, lines with thinner line width is formed. It is arguable that the coffee ring width should remain constant as the amount of SWNTs in the aerosol remained unchanged. However, it is clearly seen in Figure 37d that the coffee ring width does not hold constant but decreases

with an increase in the substrate temperature. This is can be explained by the faster drying rate of the deposited ink and therefore the SWNTs do not have sufficient time to move towards the periphery at higher substrate temperature.

Discussion. In short, the line dimensions of the SWNTs traces can be controlled by using appropriate printing parameters. Printed traces with a line width ranging from 43.5-108.9 μm and a coffee ring width of 3.4-11.8 μm have been achieved. The effect of the printing parameters on the line dimensions is closely related to the amount of ink deposited on the substrate per unit area. The variation in the line width can be explained by the conservation of volume of the deposited ink. The volume of the deposited ink pool can be expressed as $\dot{V}_{ink} = A_c \times v$ (depicted in Figure 35b), where $\dot{V}_{ink}$ is the volumetric flow rate of the ink, A_c is the cross-sectional area of the ink pool and v is the print speed. By assuming

cylindrical ink pool geometry, the line width, w can be derived as $w = \sqrt{\frac{4A_c}{\frac{\theta}{\sin^2\theta} \frac{\cos\theta}{\sin\theta}}}$, θ is the

contact angle of the ink. Combining the two equations, it can be deduced that $w \propto \sqrt{\frac{\dot{V}_{ink}}{v}}$.

Each of the process parameters including nozzle size, print speed, and substrate temperature can be directly or indirectly related to the two parameters, namely the $\dot{V}_{ink}$ and v as discussed earlier. This explains the larger line width when using a larger nozzle, lower substrate temperature and lower print speed, whereas small line width can be obtained with a small nozzle, high substrate temperature, and high print speed. In this study, the line width achieved $43.5 \pm 0.7 \mu\text{m}$ (ST: 60 °C, NS: 150 μm , PS: 5 mm/s) in Figure 37d, while the width of the coffee ring was $3.4 \pm 0.2 \mu\text{m}$ (NS: 150 μm , ST: 25 °C, PS: 5 mm/s) in Figure 37b. It should be noted that these are not the optimized line dimensions (minimum) as this

Figure 37 Figures showing (a) the measurement of the line width and coffee ring width, and the effect of the (b) print speed, (c) nozzle size and (d) substrate temperature on the line width and the coffee ring width. All measurements are made with sample size, $n \geq 10$. (The error bars represent the standard error)

study is intended to study the effect of each printing parameter on the trend of the line widths only. Theoretically, the dimensions of the printed lines could potentially be further reduced by using a smaller nozzle, higher substrate temperature, higher print speed, and tuning the flow-related parameters such as sheath flow and atomizer flow.

Process windows of AJP. To further understand the effect of gas flow-related aerosol jet printing parameters on the limit of the aerosol jet printing process for achieving CNTs twin line, the CNTs ink is printed with a 150 μm nozzle and print speed of 1 mm/s at varying atomizer flow (AF) and sheath flow (SF). The atomizer flow is set to 25, 30, 35, 40 sccm, whereas the sheath flow is set to 10, 30, 50, 100, and 150 sccm. The sheath flow is essentially an annular flow of nitrogen gas encompassing the atomizer flow, which is

used to control the diameter of the aerosol jet. Atomizer flow, on the other hand, contains the aerosols of CNTs ink which is carried by nitrogen gas. Figure 38 depicts the interaction between the sheath flow and atomizer flow on the deposited CNTs traces and the process window for achieving CNTs twin line. It is observed that there are 5 types of line morphology, namely straight CNTs twin line, bulged CNTs twin line, straight homogeneous CNTs line, bulged homogeneous CNTs line, and fuzzy CNTs line. Straight CNTs twin lines are obtained at moderate atomizer flow rate (AF: 30-35 sccm) and low sheath flow rate (SF < 50 sccm). Bulged CNTs twin lines normally occur at a high atomizer flow rate (AF > 40 sccm) due to excessive ink flow that causes the ink to bleed outward. Homogeneous CNTs traces are normally formed at high sheath flow (SF $\approx$ 150 sccm) and it is observed that bulging issue could still occur at a higher atomizer flow rate. The shift of line morphology from CNTs twin line to homogenous CNTs trace is a result of the time scale competition between the solvent evaporation and the CNTs translational diffusion. [89, 95] At higher sheath flow, the deposited width of the CNTs traces are smaller which results in much faster solvent evaporation. As a result, the CNTs do not have sufficient time to be carried by the convective flow to form CNTs twin line at the contact lines. The smallest line width in this experiment is around $16.4 \pm 1.6 \mu\text{m}$ with SF=100 sccm and AF=30 sccm (Appendix G). Fuzzy CNTs traces obtained at low atomizer flow (AF: 25 sccm) could be due to the accelerated evaporation of droplets at higher sheath flow (SF: 30-100 sccm). The enhanced evaporation reduces the size of the aerosols resulting in more droplets with low stoke number that do not impinge on the substrate.

Figure 38 Optical images showing the process window of the aerosol jet printing process parameters (sheath flow and atomizer flow) for achieving different line morphology of CNTs traces.

In brief, the effects of each process parameters such as nozzle size, substrate temperature and print speed on the line morphology of the printed CNTs traces are studied and each case is explained by the volume conservation model of the deposited ink. The gas flow-related parameters such as the sheath flow and atomizer flow are also studied and the process window for achieving CNTs twin line was determined. The study helps designer and manufacturers to understand and decide suitable process parameters for desired line dimensions. Also, it has been demonstrated in this study that CNTs traces with coffee ring effect is achievable at a much better print resolution as compared to previous work using inkjet printing.

6.4 Micro- and nanoscopic line morphology of aerosol jet printed SWNTs

The self-ordering and alignment of SWNTs at the coffee ring is discussed through field-emission scanning electron microscopy (FESEM) analysis. Same samples as the ones used in section 6.3 were used.

Figure 39a is the edge of the printed traces, which can be divided into three different regions, namely (i) the not printed region, (ii) the coffee ring region, and (iii) the region in between the coffee ring/ edges of the printed line. A densely packed network of SWNTs is observed in region (ii), whereas region (iii) are sparsely distributed and do not form a continuous network of SWNTs. Since obtaining a continuous network of SWNTs is important to form conductive tracks for electronics devices, therefore this study will focus on the line morphology at the edge of the printed trace or the coffee ring. The coffee ring of SWNT trace is formed by the capillary/peripheral flow which pushes the SWNTs towards the edges of the deposited ink as explained earlier. The pinning of the contact line during evaporation causes a clear boundary at the edges (Figure 39a).

It is evident from the FESEM micrographs (Figure 39b, Figure 39c, and Figure 39d) that the SWNTs at the edges tend to align preferentially in the direction parallel to the boundary or the contact line. The mechanism of the alignment of SWNTs at the edges can be explained by using EDSA and multi-body interaction between the elongated beads (SWNTs in this case) as proposed by Dinh et al for inkjet printing technique [83]. A detailed schematic of Figure 39e depicts the process and sequence of the SWNTs movement in the drying ink pool.

Figure 39 Images (a), (b), (c), & (d) are FESEM micrographs showing the SWNTs are preferentially aligned in the direction parallel to the coffee ring's periphery. (e) Schematic showing the mechanism of the CNTs alignment due to the evaporative-driven self-assembly.

EDSA mechanism in AJP. The mechanism of SWNTs alignment can be split into five stages. In stage 1, the aerosols of SWNTs ink is deposited on the substrate and distributed randomly in the liquid pool of SWNTs ink. During the deposition process, an axial flow (f_{axial}) is induced in the ink pool from the nozzle end to the start point (ie. opposite to the print direction) due to the hydrodynamic pressure difference. During the deposition process, an axial flow (f_{axial}) is induced in the ink pool from the nozzle end to the start point (ie. opposite to the print direction) due to the gradient in Laplace pressure, $P = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$, where σ is the surface tension of the ink, R_1 and R_2 are the principal radii of

curvature of a point on the liquid/air interface of the ink. The incoming aerosols of ink has much greater curvature than the preexisting bead of ink on the substrate, resulting in a gradient in Laplace pressure that drives the ink towards the start point of the printed line [193]. Similarly, a capillary/peripheral flow ($f_{\text{peripheral}}$) is induced in order to compensate for the enhanced evaporation at the contact line. Both f_{axial} and $f_{\text{peripheral}}$ flows will result in flow velocity of v_{axial} and $v_{\text{peripheral}}$ respectively at any point in the deposited ink. The resultant flow velocity vector at any point in the deposited ink can be represented as v_{total} . In stage 2, SWNTs will tend to align with the v_{total} due to the shear flow [75]. Besides aligning to the flow direction, the SWNTs will also move in the direction of the flow until they reach the liquid-air-solid interface (the edge/boundary of the deposited ink). This phenomenon is observed on the aerosol jet printed trace as shown in Figure 40. Figure 40a depicts the direction of the capillary/peripheral flow relative to the self-assembled SWNTs at the contact line. Figure 40b shows the color-mapped orientation of the SWNTs in near the contact line, while Figure 40c shows the orientation distribution of the SWNTs. Both Figure 40b and Figure 40c suggest that the SWNTs preferentially aligned themselves perpendicular to the liquid-air-substrate interface, suggesting that the capillary/peripheral flow is dominant in the aerosol jet printed liquid SWNT ink. The existence of the dominant capillary/peripheral flow, which carries the SWNTs to the contact line, has further confirmed the mechanism of the evaporation-driven self-assembly of CNTs in the AJP process. In stage 3, one of the ends of the SWNTs has reached and pinned at the contact line/boundary of the deposited ink. At this point, the SWNT is partially exposed in the air and the surface tension of the solvent will act on the SWNT. The SWNT will be pulled towards and aligned to the boundary so that the surface energy can be minimized as

explained by Lu et al [38]. This process continues until the contact line is completely filled with the SWNTs (stage 4). The subsequent SWNTs at close proximity to the boundary will experience additional van der Waals' force of attraction by other SWNTs that have been accumulated at the boundary. Once the SWNTs have one of its ends pinned to the boundary (stage 5), the van der Waals' force will produce a torque to turn and align the SWNTs to the boundary.

Figure 40 FESEM images of (a) SWNT near the coffee ring, (b) the orientation of the SWNT preferentially aligned to the peripheral flow with color mapping, (c) graph showing the orientation distribution of the SWNT with peaks observed at $\pm 90^\circ$ (in the direction of the peripheral flow).

Characterization of CNTs alignment in printed traces. The alignment of the CNTs network at the twin-line is investigated using ImageJ image processing software. Figure 41a shows the color mapped orientation distribution of the CNTs at the printed CNTs twin-line.

It is obvious that most of the colors appear within the angular range of $\pm 45^\circ$ which indicates the preferential alignment of CNTs along the liquid drop's periphery. A graphical representation of a typical orientation distribution of the CNTs at the twin-line shown as Figure 41b provides a more objective and quantitative of the orientation distribution of the CNTs. An orientation distribution graph with a peak indicates that there is a preferential orientation/alignment of the CNTs. FWHM is used to determine the degree of alignment of the CNTs network. A larger FWHM value indicates a low degree of alignment, whereas a smaller FWHM value indicates a high degree of alignment. Based on our results, it is observed that the FWHM of the orientation distribution graphs averages 55° with a standard error of $\pm 3.59^\circ$. The orientation distribution analysis of the other samples can be found in Appendix H. This result indicates that the CNTs are preferentially aligned along the twin-line although not perfect. The misalignment of the CNTs could be due to the disturbances from the impinging aerosol jet flow, non-uniform adsorption of CNTs to the substrate and unpredicted hydrodynamic flow due to the non-uniform evaporation. Besides, several studies have shown that the orientation of nanotubes depends on the time scale of rotational diffusion, translational diffusion, and solvent evaporation [89, 95]. The solvent evaporation depends significantly on the amount of ink (in this case directly related to line width), whereas the rotational and translational diffusions depend on the temperature. The misalignment of the CNTs, in this case, could also be due to CNTs do not have sufficient time to reorient given the short evaporation time at high print resolution (small line width). This suggests that there could be a tradeoff between the degree of alignment and line width.

Figure 41 Orientation distribution analysis of CNTs network of the twin-line using. (a) visual with a color map on the right and (b) graphical representation of the CNTs orientational distribution showing peaks at 0° (parallel to the contact line).

Effect of line width on CNTs alignments. To further understand how the gas flow-related process parameters such as the SF and AF affect the arrangement of the CNTs, image analysis is performed to characterize the CNTs twin line at the contact lines. Herman's orientation factor (f), which can be expressed as $f = 3\langle \cos^2 \delta - 1 \rangle / 2$, is used to evaluate the degree of alignment of the CNTs, where δ is the orientation angle of the CNT with respect to the axis of interest [34]. In general, $f = 1$ indicates the CNTs are perfectly aligned to the principal axis, $f = 0$ implies random distribution, and $f = -0.5$ signifies perpendicular orientation to the principal axis. It should be noted that the principal axis is defined parallel to the contact line and the images are processed in such a way that the principal axis is set to $\theta = 0^\circ$ or in the horizontal direction. Figure 42 shows Herman's orientation factors of the CNTs twin line obtained at different atomizer flow and sheath flow conditions. It has been observed that the f values of the AJP printed CNT traces fall within the range of 0.4 to 0.6, which is relatively lower than the baseline of $f = 0.7-0.9$ as obtained in Chapter 4. Figure 42a shows a decreasing trend of Herman's orientation factor with decreasing atomizer flow, whereas Figure 42b shows a decreasing trend of Herman's

orientation factor with increasing sheath flow. ANOVA tests reveal that the results for both atomizer flow and sheath flow are significant with $p = 0.00275$ ($n \geq 10$) and $p = 0.00734$ ($n \geq 13$) respectively, suggesting both have an effect on the degree of CNT alignment as shown in Appendix I and Appendix J. The trends can be explained by the time scale competition between the solvent evaporation and the CNTs rotational diffusion. At low atomizer flow and high sheath flow, smaller line width is obtained which results in shorter evaporation time due to lesser deposited inks. As a result, the CNTs do not have sufficient time to realign themselves along the contact line before the completion of solvent evaporation. As such, smaller line width will result in less aligned CNTs, whereas larger line width can result in more aligned CNTs. In general, the process-structure correlation can be expressed as follow:

High atomizer flow and low sheath flow $\rightarrow$ larger line width $\rightarrow$ more aligned CNT, and the converse is also true.

Figure 42 Graphs showing Herman's orientation factor that indicate the degree of alignment of CNTs at the contact line for different process parameters. (Error bars represent $\pm$ standard error)

In short, the proposed mechanism of EDSA is confirmed and supported by the SWNTs orientation analysis. This study shows the possibility of using AJP to achieve preferentially aligned CNTs traces utilizing naturally occurring EDSA technique. Besides, it helps researchers to understand the process and challenge to align CNTs using AJP which could motivate more research in this field. A strong correlation between the line width (controlled by sheath flow) and the degree of alignment of CNTs is observed.

6.5 Effect of print passes

Printing multiple passes of ink is a print strategy that is often used in electronic printing to improve the mechanical and electrical performance of the printed devices. In order to investigate the effect of print passes, the CNTs twin lines are printed with 1 pass and 5 passes to compare the line thickness and coffee ring width. Figure 43a shows the optical images of the CNTs twin lines with 1 print pass and 5 print passes. Based on the images, an increase in the line width and the coffee ring width is observed. Figure 43b shows the 3D reconstructed profile of the printed twin lines of 1 print pass and 5 print passes taken using a confocal microscope. Figure 43c shows the cross-section of the printed twin lines revealing the line thickness, line width, and coffee ring width of the printed CNTs traces. It can be observed in Figure 43c that the average line thickness of the printed film for 1 print pass and 5 print passes are $3.49 \pm 0.20 \mu\text{m}$ and $3.45 \pm 0.5 \mu\text{m}$ respectively. The result reveals the print pass does not have a significant effect on the line thickness of the printed traces, however, it has a great effect on the line width and coffee ring width. The increase in line width and coffee ring width is due to the different pinning positions of the contact line (moving outwards) for each print pass which result in the accumulation of CNTs/formation

Figure 43 (a)Optical images showing the macroscopic line morphology of the printed lines with 1 print pass and 5 print passes, (b) 3D reconstruction images showing the profiles of the printed lines of 1 print pass and 5 print passes, (c) graphs showing the line thickness and the difference in the coffee ring width of printed line with 1 print pass and 5 print passes.

of the coffee ring at different positions. It is deduced that the outward movement of the pinning position of the contact line for subsequent print passes is due to the hydrophobic

nature of the deposited CNTs which makes the ink either to pin inwards or outwards on the more hydrophilic polyimide substrate [194]. However, pinning the contact line outwards is more stable as the energy can be minimized which explains the outward motion of the contact line over multiple print passes. This finding allows the flexibility to design the desired coffee ring width for the preferentially aligned CNTs twin line by controlling the number of print passes.

6.6 Summary

The alignment of CNTs is vital for the fabrication of the high-speed electronic device and it is achievable by utilizing evaporation-driven self-assembly. This CNTs alignment technique inevitably forms twin-line traces of CNTs, also known as coffee ring effect. In this project, an attempt is made to investigate printing twin-line carbon nanotube using aerosol jet printing technique based on evaporation-driven self-assembly. Proper experiments have been conducted and the process window of aerosol jet printing to achieve stable and straight twin-lines was determined. It was found that the coffee ring width and line width are more or less proportional to each other in most of the conditions. Both of them increase with increasing nozzle size, whereas decrease with decreasing print speed and substrate temperature. The effects of each process parameters are then explained by the ink volume conservation model which allows a better understanding of the AJP process. These findings are useful for controlling and optimizing the process parameters of the AJP process for various functional inks. It is found possible to obtain tunable width of CNTs twin line in the range of 43.5-108.9 μm and conductive tracks (coffee ring width) in the range of 4.3-11.8 nm which is significantly lower than the previous work [83]. The smallest

CNTs twin line obtained in this experiment is found to be approximately 16 μm using suitable sheath/atomizer flow ratio. The high print resolution of CNTs traces using AJP means that this printing technique can be potentially used for the fabrication of high-speed CNTs-based electronic devices. It is found out that the carbon nanotube in the twin-line formed by evaporation-driven self-assembly preferentially aligned along the printed edges of the thin film via image analysis with angular distribution showing FWHM averages 55° with a standard error of $\pm 3.59^\circ$. A mechanism model of the self-assembled CNTs for AJP process is proposed. It is found that it is challenging to achieve perfectly aligned CNTs utilizing AJP process as many competing factors such as the hydrodynamic flow of solvent, evaporation time of solvent, rotational diffusion, translational diffusion and adsorption of CNTs must be considered. A comparison of result of current work with prior art on EDSA CNT alignment is shown in Table 6. The analysis shows that the degree of alignment of AJP printed CNT traces is lower than the baseline f value as obtained in Chapter 4, suggesting room for improvement. A strong correlation between the line width (controlled by sheath flow) and the degree of alignment of CNTs is observed. Our study also reveals an outward movement of the contact line over multiple print passes which could be utilized to control the line width and coffee ring width of the printed features. The electrically conducting, high resolution, and aligned aerosol jet printed CNTs twin-line can be potentially used for fabricating transparent electrodes for flexible electronics due to the minimal light obstruction of the CNTs twin-line architecture and microchannels for lab-on-a-chip applications.

Table 6 Comparison of Herman's orientation factor of current work with existing work on EDSA CNT alignment.

	Herman's orientation factor, f	References
Prior art on EDSA CNT alignment	0.65-0.91	[65]
EDSA CNT alignment in this work (Chapter 4)	0.72-0.93	
AJP printed CNT twin-line (Chapter 6)	0.41-0.60	

7. APPLICATIONS OF AEROSOL JET PRINTED CNTs-BASED DEVICES

7.1 Improved optical transparency and electrical conductivity of printed CNTs devices

In section 4.7 , the effect of pH on the deposition pattern is discussed. In this chapter, the knowledge on controlling deposition pattern by adjusting the pH of suspension solution is applied to obtain homogeneously distributed CNTs traces and CNTs twin-lines by using aerosol jet printing. The homogeneously distributed CNTs traces and CNTs twin-lines are obtained by adding the same amount of 0.2 M HCL and NaOH solutions respectively to the CNTs suspension solution to ensure the same ionic concentration for comparison. The pH of the two CNTs suspension solutions is measured to be pH 2.9 and pH 8.5 respectively. In this experiment, the homogeneously distributed CNTs traces and the CNTs twin-lines are printed with the same aerosol jet printing process parameters to ensure both inks can be printed with the same atomization rate and ink deposition rate for better comparison.

To ensure the pH of the inks do not affect the surface tension (thus atomization rate), contact angle measurement of the inks on the polyimide substrate is conducted to check if there is a change in surface tension due to the pH change. Based on the result (Figure 44), it is observed that there is no noticeable difference in the contact angle of the inks. ANOVA analysis (n=10) reveals the $p=0.371$, indicating no statistical difference in the contact angle due to the pH change at $p < 0.05$. Hence, it is safe to conclude that the surface tension of the inks is not affected by the pH of the ink solutions.

Figure 44 Graph showing the contact angle and pH of different types of inks

7.1.1 Physical property of CNTs twin lines & homogeneous lines

Figure 45a and Figure 45b show the optical images of homogeneously distributed CNTs traces and CNTs twin-lines respectively printed by using the same process parameters. Both printed traces are straight and continuous CNTs traces, which are vital for the fabrication of electronics. The homogeneous CNTs traces are formed due to the lower zeta potential of the pH 2.9 CNTs suspension solution. This means the CNTs particles have lower surface charges and interparticle repulsive forces favoring CNTs coagulation and enhancing substrate-particle interaction. The CNTs twin-lines, on the other hand, are formed due to the higher zeta potential of the pH 8.5 CNTs suspension solution. The stronger surface

charges of the CNTs in the pH 8.5 suspension solution can result in more stable colloidal suspension, which allows the CNTs to assemble at the contact line by the natural-occurring capillary flow due to the evaporation of the solvent.

Figure 45 Optical images showing (a) homogeneous CNTs traces and (b) CNTs twin-lines

7.1.3 Effect of film morphology on electrical conductivity

Figure 46 depicts the difference in electrical conductivity of homogeneously distributed CNTs traces and CNTs twin-lines printed with 4 layers (print passes). FESEM images (Figure 46 a & b) reveal that the homogeneously distributed CNTs traces contains gaps and pores throughout the printed traces, whereas the CNTs twin-lines have densely packed CNTs accumulated at the contact lines. Orientation analysis of CNTs using image analysis technique suggests that CNTs at CNTs twin-lines are preferentially aligned with Herman's orientation factor, $f \approx 0.58$, whereas homogeneously distributed CNTs traces have more randomly distributed CNTs with $f \approx 0.25$ as shown in Figure 46c. Figure 46d shows the CNTs twin-lines exhibit lower resistances ranging from few hundreds to almost 1000 times as compared to its homogeneous counterpart depending on the printing condition (sheath

Figure 46 FESEM images of (a) homogeneous CNTs traces and (b) CNTs twin-line, (b) Graph showing the Herman's orientation factor of CNTs twin-line and homogeneous CNTs traces, (d) Graph showing the electrical resistance of the homogeneous CNTs traces and CNTs twin-lines with different sheath flows, (e) Schematic illustrating the difference in the electron transport paths for homogeneous CNTs traces and CNTs twin-line.

flow). The effect of the sheath flow on the electrical conductivity will be discussed in the following section. Figure 46e illustrates the difference in electron transport path between homogeneous trace and twin-line trace. Homogeneous trace results in CNTs of lower network percolation that tend to have longer and fewer electron transport paths due to the gaps, which causes high resistance. In contrary, twin-lines are densely packed and have higher network percolation which can result in more and shorter electron transport paths, hence the low resistance. In short, the combined effect of the more aligned and densely packed CNTs could possibly explain the better conductivity of the CNTs twin-lines as compared to the homogeneously distributed CNTs traces. Besides, this study also shows the advantage of printing CNTs twin-lines over homogeneous CNTs traces by achieving better electrical conductivity using lesser materials, thus saving material cost.

7.1.4 Effect of process parameter on electrical conductivity

The investigation of the electrical property of the aerosol jet printed CNTs trace is essential when designing and fabricating the CNTs-based electronic devices. The electrical property of the printed twin line SWNT trace is evaluated by measuring the resistance per unit length (Ω/cm) of a single CNTs trace (one of the twin lines). The printed twin line is first cut at both of ends to ensure that they are not electrically connected. The probes are set 1 cm apart for measuring the resistance per unit length (Ω/cm). Figure 46d shows the electrical resistance (per centimeter) of the homogeneous and twin-line CNTs traces printed with the same atomizer flow rate but different sheath flow rate. By mass conservation, the same atomizer flow rate suggests that the amount of deposited CNTs should be the same even when the sheath flow

rate is varied. The sheath flow, on the other hand, determines the diameter of the aerosol jet, hence the printed line width. Higher sheath flow normally results in a smaller line width. Interestingly, homogeneous CNTs traces and CNTs twin-lines show different trends on electrical resistance when the sheath flow is varied. The homogeneously distributed CNTs traces show decreasing electrical resistance with increasing sheath flow. The higher sheath flow can result in smaller line width, thus CNTs can be packed more densely which lowers the resistance despite the decrease in deposited materials due to the enhanced aerosols evaporation of sheath flow as discussed in chapter 5. In contrast, CNTs twin-lines exhibit increasing resistance with sheath flow. The increase in resistance can be explained by the reduction in the degree of alignment of the CNTs as discussed in Section 6.4 and the decrease in deposited CNTs due to the increasing sheath flow. Higher sheath flow can result in smaller line width, thus faster evaporation time of the solvent. Faster evaporation time of the printed trace will result in CNTs with less degree of alignment, thus higher resistance with higher sheath flow. The high electrical resistance of CNT at high sheath flow can be explained by the longer electron transport paths due to the lower degree of CNT alignment, whereas low electrical resistance of CNT at low sheath flow can be attributed to the shorter electron transport paths as a result of the higher degree of CNT alignment as depicted in Figure 47. In other words, there is a tradeoff between the print resolution and the degree of alignment of the CNTs, thus the electrical conductivity of the printed CNTs twin-lines. This result also shows the importance of the degree of alignment of CNTs in determining the electrical property of the CNTs twin-lines.

Figure 47 Schematic depicting the correlation between the electron transport paths and the degree of alignment. (Red and yellow lines represent the electron transport paths)

Process parameters such as print speed and number of print layers can determine the electrical property of the printed CNTs twin-lines because the amount of deposited CNTs is directly affected by them. Figure 48a and Figure 48b show the effect of the process

Figure 48 Graphs showing the effect of (a) print speed and (b) print layers on the electrical resistance of the printed CNTs twin-lines.

parameters such as print speed and print layers respectively on the electrical resistance of the printed CNTs twin-lines. It is observed that the electrical resistance (per centimeter) of the CNTs twin-lines increases with increasing print speed and decreasing number of print layers. Interestingly, the electrical resistance of the CNTs twin-lines exhibits high exponential correlation with the print speed and print layers which are indicated by the R^2 value of the fitted exponential equations of 0.9865 and 0.9609 respectively. This suggests that the electrical resistance of the aerosol jet printed CNTs twin-lines follows a power law. This finding is useful for predicting the electrical property of the CNTs twin-lines for various applications.

7.1.2 Effect of print layers on optical transparency of printed device with CNTs traces

Figure 49a shows the optically transparent CNTs twin-lines printed on polyimide substrate with silver electrodes and connecting wires. Figure 49b shows the effect of print layers on the line morphology of both homogeneous traces and twin-line traces with line pitch of 150 μm printed with the same process parameters (NS: 300 μm , SF: 70 sccm, AF: 30 sccm, PS: 4 mm/s). It can be observed that the CNTs traces with higher print passes appear to have darker shade of grey, suggesting lower optical transmission. The darker shade of CNTs traces with more print passes is due to the higher light absorption by the denser and thicker CNTs network. Figure 49c shows the schematic of light transmission for homogeneous line and CNTs twin-line. It can be seen that CNTs twin-line has higher area for light transmission which can give better optical transparency. Figure 49d shows the percentage of light transmission region for both homogeneous line and twin-line analyzed using image analysis method. The result shows that the traces with twin-line morphology have

approximately 20% more light transmissible region as compared to the homogeneous line morphology for the print pattern as shown in Figure 49d. This result suggests that the CNTs twin-lines can exhibit better optical transparency as compared to the homogeneously distributed CNTs traces with a similar amount of deposited CNTs due to the reduce in area covered by CNT compared to the homogeneous line which covers the entire drop footprint of similar sizes. It should be pointed out that current analysis only shows the potential of the CNT twin-line morphology to be used as transparent electronics over the homogeneous line morphology. The actual optical transmission, however, have not been studied.

Figure 49 (a) Optical image showing the optically transparent CNTs twin-lines printed on polyimide substrate, (b) Optical micrographs showing the effect of print layers on the optical transparency of the printed traces, (c) Schematic showing the light transmission through homogeneous and twin line morphology, and (d) Graphs showing the light transmissible region as a result of print layers for both homogeneous CNTs traces and CNTs twin-lines

7.1.5 Optically transparent motion sensor

As a proof-of-concept, CNTs twin-lines is printed on a 75 μm -thick flexible and transparent polyimide film to form an optically transparent motion sensor. Figure 50a shows the flexibility of the motion sensor which can be conveniently pasted on a glove to detect the motion of fingers. Figure 50b shows the cyclic loading and the sensing capability of the motion sensor for detecting the finger's motion. In the test, the finger is flexed and hold for 5 seconds and unflexed for another 10 seconds, and the cycles repeat. The flexing motion creates a bending radius of approximately 5 mm which induces a stretch on the CNTs twin-line, hence increasing the electrical resistance. The electrical resistance of the CNTs twin-lines increases sharply from 6.8 $\text{M}\Omega$ to almost an insulator ($>10 \text{ G}\Omega$) due to the flexing motion. The flexing and unflexing motions cause the CNTs network to break and reconnect, giving it motion sensing capability. It can be seen that the motion sensor can be repeatedly flexed and unflexed for 20 cycles without any observable damages. Figure 50c shows the enlarged version of Figure 50b. It is noticed that the sensor is able to return to the initial resistance of approximately 6.8 $\text{M}\Omega$ after each flexing cycle. Unlike flexing which the sensor gives an immediate response, it is observed that the electrical resistance does not returns to the initial resistance immediately when unflexed. A relaxation time of approximately $4.14 \pm 1.08 \text{ s}$ is observed. This is probably because the CNTs in the CNTs network requires a certain amount of time to rearrange and reconnect themselves to form a complete circuit. Nonetheless, it shows the potential of the CNTs twin-lines to be used in motion-sensing applications and transparent electronics.

Figure 50 (a) Optical images showing the flexibility of the printed motion sensor, (b) Graph showing the changes in resistance when the motion sensor is repeated flexed and unflexed, (c) Graph showing the relaxation time of the motion sensor (blue region indicates the sensor is flexed, red region indicates the sensor is unflexed).

7.1.6 Summary

The electrical and optical property of the homogeneously distributed CNTs traces and CNTs twin-lines are compared and investigated. It has been shown that CNTs twin-lines exhibit enhanced electrical and optical property as compared to its homogeneous counterpart. For instance, the electrical resistance of CNTs twin-lines is found to be 200-1000 times lower than the homogeneous CNTs. The alignment of the CNTs plays a role in determining the electrical property of the CNTs twin-lines. CNTs twin-lines appears to be more optically transparent than the homogeneous CNTs traces, showing its potential for transparent electronics. Besides, the printed CNTs twin-lines are found to have an exponential correlation with the process parameters. Lastly, a motion sensor is fabricated as a proof-of-

concept to show its usefulness for motion sensing applications. The advantage of aligning nanotubes by printing twin-line morphology is that lesser materials is used compared to the homogeneous line morphology. This offers added advantage such as improvement in optical transparency of the printed pattern by depositing much lesser materials yet achieving same level of or even better conductivity as homogeneous pattern.

7.2 Flexible CNTs-based pH sensor

7.2.1 Development of pH sensor

Detection and control of pH are important for many environmental, biological and chemical processes that impact human lives [195]. Water and food quality is judged by the change in the pH value. The pH level in a chronic wound bed is a key indicative parameter for assessment of the healing progress [196]. Many kinds of pH sensors exist such as potentiometric [197, 198], capacitive [199], chemiresistive [200], luminescence [201, 202], optical [203], and shape/mass [204, 205]. Different pH-sensitive materials such as metal oxides for solid-state electrodes [206]; epitaxial graphene for solution-gated electrode [199]; gold-coated polymer for dimension-changing materials [207]; polymers that change their optical properties [203] have been employed and tested. Commonly, pH sensing is done by using glass electrodes [208] and ion-selective field-effect transistor (ISFET) [209]. However, these pH sensing techniques require a reference electrode, which in turn restricts the miniaturization of the device; and also suffer from leakage of electrolyte [208, 209]. Chemiresistive pH sensors are the most popular amongst all as they have the simplest design and are thus easy to fabricate. Chemiresistive sensors are two-terminal microsensors, which work without a reference electrode and can detect many analytes like NO_x, O₂, NH₃, SO₂,

O₃, hydrocarbons, or CO₂ [210]. For pH sensing, carbon nanotubes (CNTs) are the most suitable material due to their good mechanical reliability, high surface-to-volume ratio, ease of chemical functionalization, and tunable electrical properties [211]. CNTs-based pH sensors are explored through unpatterned CNTs sheet [212] and by drop casting [213] method. However, unpatterned CNTs films increase the overall sensor dimensions and drop casting processes are not reproducible [214], thus making patterning of CNTs films an important research area.

Printing techniques have been widely explored for patterning of materials especially CNTs. Conventionally, CNTs-based electronics are fabricated using screen printing [215, 216], and gravure printing [217, 218] through the use of homogeneous paste-like ink. Transfer-printing [219], inkjet printing [220] and photolithography [221] have also been widely researched for printed electronics applications. However, most of these printing techniques are limited to flat surfaces and provide moderate-resolution [222]. New age printed electronic applications put additional demands on design architectures and printing parameters, and need to be met through new technique [112, 223]. Aerosol jet printing is an additive manufacturing (AM) technique, which has recently gained interest. It's 5-axis and non-contact capability with substrate-to-nozzle standoff distance between 1-5mm provides freedom to fabricate novel designs and explore complicated designs on arbitrary surfaces [224]. Aerosol jet offers high resolution and conformal printing [225].

Herein, the fabrication of flexible pH sensor based on CNTs material is reported. Some research has been done to print nanoparticle inks via aerosol jet printing [118, 226-228], but the study of CNTs printability via the same technique is not well-explored [229,

230]. The pH sensor reported here consists of a miniaturized serpentine sensing element with an effective sensing area as small as $500\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ printed on a polyimide substrate. The effect of various aerosol jet process parameters is investigated and optimized for the printing of the sensing element. Both qualitative and quantitative analysis have been carried out to investigate the process window for controlled, repeatable and good quality line trace. The sensor is tested in different pH conditions and its response is discussed. Lastly, an *in vitro* biocompatibility test of the fabricated pH sensor is conducted to check its suitability for live cell applications. (Figures in this chapter are reproduced from Ref [101] with permission from Elsevier.)

7.2.2 Fabrication of pH sensor

The substrate used is Kapton[®] polyimide film with a thickness of $150\text{ }\mu\text{m}$. The substrate is cleaned by sonicating in ethanol bath for 10 min. For the fabrication of the pH sensor, the silver electrode (PRELECT TPS[®], Clariant[™]) is first printed on the polyimide film. The serpentine CNTs sensing element is then printed on top of the silver electrode. The printed pH sensor is then sintered $200\text{ }^{\circ}\text{C}$ for 2 h. Finally, the connecting wires are attached to the pH sensor by using conductive epoxy. In order to investigate the printing parameters, a benchmark coupon with three lines of length of 2 cm is used. To precisely study the effect of each parameter on printing, only one parameter is varied at any given time. For this work, the range of variation for each parameter is AF 20-35 sccm and SF 10-40 sccm, Other working parameters are kept constant with nozzle size = $150\text{ }\mu\text{m}$, substrate temperature = $40\text{ }^{\circ}\text{C}$, print speed = 10 mm/s and ultrasonic current = 0.6 A.

7.2.3 Experimental section

The pH sensor is tested with pH buffer (Sigma Aldrich) of pH 4, 7, and 10. The sensor is connected to a Fluke digital multimeter (DMM) via crocodile clips to measure its change in resistance. First, a few drops of pH 10 buffer are first added to the CNTs sensing element to ensure the sensing element is fully covered with the pH buffer. The response of the pH sensor is then recorded by the DMM. Once the sensor readout reaches steady state, the pH buffer is then removed with Kimwipes®. The sensor is then cleaned with DI water and the DI water is removed before adding new pH buffer for testing. Similar steps are repeated for the subsequent tests for pH 4 and 7. In the experiment, it is found that the pH sensor response is not consistent in the first few cycles (1-3) but gradually become stable after several cycles. A similar observation is also reported by Li et. al, which the pH sensor becomes stable after approximately 10 cycles [231]. This can be explained by the removal of the loosely bonded CNTs from the sensing element due to the test cycles [231]. The pH sensor becomes stable when the sensing element is left with strongly bonded CNTs. The results presented in Section 7.2.5 excludes the inconsistent result for the first few cycles (1-3).

A resistivity coupon is designed to evaluate the electrical property of the printed CNTs film. The resistivity coupon has a straight line of length (L) 1 cm and width (W) 1 mm with two contact pads at both ends for the probes. The resistance (R) of the printed CNTs film is measured using a digital multimeter. The sheet resistance, R_s is calculated by $R \times W/L$. The effect of print passes (10, 20 and 30 passes) on the conductivity of the printed CNTs film is also investigated. Scanning electron microscopy (Joel JSM-5600LV) is used

to evaluate the surface morphology and film thickness. The contact angle measurements (Attension Theta optical tensiometer) are done to determine the wettability of CNTs ink on the polyimide surface. The surface roughness of substrate and printed films are also measured using Keyence VK-X series 3D laser scanning confocal microscope. Optical images are taken using an Olympus CKX41 microscope. All physical measurements are performed at least five times to achieve statistically significant results.

Murine myoblasts C2C12 was cultured and expanded before the experiment. The cells were cultured in the cell culture media of high-glucose DMEM supplemented with 10% FBS and 1% antibiotic-antimycotic, incubated under 5% CO₂ at 37 °C. For the experiment, the C2C12 cells were seeded at a density of 5×10⁴ cells per well in a 24-well plate and cultured for 1 day before gently placing the 1×1 cm² pH sensor (n=3) onto the cells. The polyimide surface faces the cells, mimicking the wearing of the device on the skin. The cells were maintained in an incubator and the medium (2mL in each well) was changed every two days. The cells were observed on day 0, 1, 3 and 7 under an inverted microscope (Zeiss Axio Vert. A1). The viability of the cells was imaged using the live/dead cell viability kit (Molecular Probes) after 7 days of culture. Briefly, the cells together with the sensors were rinsed twice with DPBS and incubated in a DPBS solution containing 5 µmol/L propidium iodide and 2 µmol/L calcein acetoxymethyl ester for 20 min at 25 °C before examining via an inverted fluorescent microscope (Zeiss Axio Vert. A1). The percentage of live cells (reported as the cell viability) was computed from the fluorescence readings.

7.2.5 Results and discussion

The pH sensor is basically made up of CNTs-based sensing element which connects two silver electrodes. The fabrication process of the pH sensor is schematically illustrated in Figure 51a with detailed descriptions presented in the experimental section. Figure 51b shows the printing parameters of the aerosol jet printer that will affect the line resolution and overall printability. Figure 51c shows the design of the pH sensors.

Figure 51 Schematic showing the (a) fabrication of the CNTs based sensor, (b) parameters affecting the printing process and (c) design and dimensions of the sensor.

The printability of the CNTs ink on the polyimide substrate depends on the surface tension of the ink, the surface free energy and the surface roughness of the polyimide substrate. The

average surface roughness (R_a) of the polyimide substrate is measured to be $0.60\text{ }\mu\text{m}$. The average contact angle of the CNTs ink on the polyimide substrate's surface is measured to be 47.6° , which signifies the hydrophilic nature of the ink.

Table 7 summarizes the results and shows the process window for aerosol printing of CNTs. Green, yellow, red and blue cells indicate good, discontinuous, bulging and no printing of lines respectively. The corresponding features can be seen in Figure 52a. The bulging phenomenon occurs due to excessive ink being deposited causing the ink to spread outward. On the contrary, there is insufficient ink being deposited at the atomizer flow (AF) of 20 sccm causing discontinuous lines.

Table 7 Parameters of aerosol jet printer affecting the line width of the printed tracks

Atomizer flow (sccm) Sheath flow (sccm)	Line Width (μm)			
	20	25	30	35
10	33.14	65.19	135.15	206.8
20		37.556	67.55	106.816
30		25.578	55.12	101.85
40			35.46	100.22

Based on the result, the smallest printed line width that can be obtained using $150\text{ }\mu\text{m}$ is approximately $20\text{ }\mu\text{m}$ with optimum process parameters of AF=25 sccm, SF=30 sccm, PS=10 mm/s, and UC=0.6 A. Although the results obtained here pertain to printing CNTs ink, this study can serve as a guideline for printing other inks. Figure 52b shows a fully

printed pH on the polyimide substrate. Figure 52c shows the magnified optical image of the printed CNTs sensing element. The film thicknesses for both silver and CNTs are 1.2 μm approximately. In order to evaluate the effect of print passes on the performance of the pH sensor, 3 pH sensors with different print passes (10, 20 and 30 print passes) are fabricated as shown in Figure 52b. The fabricated sensor is highly flexible and can be bent and twisted in any way, without losing its functionality (Figure 52d).

Figure 52 (a) Optical image showing printability of ink for good, discontinuous and bulging line quality. Photo of the (b) fabricated CNTs based sensor with different print passes, (c) thickness and the dimension of CNTs sensing element and (d) folded sensor showing its flexibility.

As it is difficult to formulate dispersion at high CNTs concentration, hence the CNTs inks are usually very dilute [220]. As such, multiple print passes are required to

ensure sufficient connectivity and percolation path for the current to flow [230]. Thus, it is vital to evaluate the effect of print passes on the electrical conductivity of the printed film. As observed from the SEM images, the printed film with 10 passes contains many nanovoids (Figure 53a) and is not homogenous. On the other hand, 20 passes of printing lead to more uniform film formation with no gaps (Figure 53b). The SEM image in the inset clearly depicts a closely woven network of CNTs resulting in a continuous film. The presence of nanovoids is detrimental to the electrical performance of the film as they result in increased resistance [214]. When compared to inkjet printing, which requires 200 print passes to print homogenous tracks, aerosol jet requires much less print passes to achieve the same results [214]. The change in the film thickness with the number of print passes was quantified (Figure 53c). It was found that the film thickness increases almost linearly with the number of passes. The average film thickness of the printed film for 10, 20 and 30 print passes are measured to be approximately 0.45 μm , 0.90 μm , and 1.30 μm respectively. The purpose of having higher print passes is not only to ensure homogeneous film, but also to improve the electrical conductivity of the CNTs film. However, the sheet resistance shows the opposite trend and decreases with increasing print passes (Figure 53d). It is to be noted that thicker films tend to peel off when folded or stretched. Therefore, there is always a tradeoff between electrical conductivity, thickness, and flexibility.

The sensor was fully characterized and measured for various responses. The change in resistance value with pH is plotted in Figure 54a. It is observed that the resistance of the sensor increases with the pH. In order to confirm that the change in resistance is solely due to the change in conductivity of the sensor, the pH sensor is tested open circuit (without the

CNTs sensing element) in the pH buffer solutions. The measured resistance value of the as-printed sensor with 10, 20, and 30 print passes was 40, 20, and 7.7 k Ω respectively. The

Figure 53. SEM image showing the top view of the CNTs film with (a) 10 and (b) 20 print passes. Inset displays the magnified SEM image of CNTs network in the film. Variation of (a) film thickness and (b) sheet resistance with the number of print passes.

aerosol jet printed pH sensor has resistance comparable to the ones reported in the literature [214, 232]. The sensitivity of the fabricated pH sensor is found to decrease with increasing print passes and is calculated to be 59.17, 4.48, and 4.29 k Ω /pH for 10, 20, and 30 passes respectively. Besides, it is observed that the linearity (represented by the R^2 value of the trend line) of the pH response also increases with the number of print passes. Ideally, R^2 value of 1 represents perfectly linear response and R^2 value calculated for 10, 20, and 30 print passes are 0.93, 0.87, and 0.88 respectively. The decreases in sensitivity can be

explained by the decrease in the effective surface area of the sensing element for the ion exchange as the film thickness increases. Comparing to the other CNTs-based pH sensor as reported by Li *et. al*, which has sensitivity in the range of hundreds Ω/pH , the pH sensor reported here shows much higher sensitivity due to the higher surface area of the sensing element [231]. The high surface area is achieved by printing a larger sensing element and is also enhanced by the serpentine design, thus allowing more ion exchange.

Normalized resistance is used to compare the response of the deviation of the fabricated sensor as shown in Figure 54b. The normalized resistance is calculated by dividing the measured resistance with the respective resistances at pH 7. However, it is also noticed that the pH sensor with higher print passes has a smaller standard deviation in the measured resistance. The normalized standard deviation in the measured resistance is 0.27, 0.09, and 0.04 for pH sensor for 10, 20 and 30 print passes respectively. By comparing the magnitude of the error bars, it can be observed that the pH sensor with more print passes give more reproducible results. The deviation in the resistance of the pH sensor can be explained by the redistribution and the change in the alignment of the CNTs network due to the hydrodynamic flow and surface tension when immersed in the buffer solution [5, 231]. As the redistribution mostly happens at the outermost surface of the CNTs film, the effect of the change in resistance on the CNTs with higher print passes has a lesser effect, hence the smaller deviation.

The response time of a pH sensor is an indicator to show how fast the pH sensor is able to reach the equilibrium resistance value (Figure 54c). It is defined as the time required for the pH sensor to reach 95% of the equilibrium resistance value. It is also observed that

the response time of the sensor is faster in acidic condition (~ 20 s) when compared to basic condition (~ 44 s). Moreover, the response time of the sensor at pH 7 is different and depends on the previous pH conditions. The response time of the pH sensor when changed from pH 10 to pH 7 is around 1-2 s, whereas it takes 30 s to change from pH 4 to 7. The slower response time at basic condition can be explained by the slower protonation/deprotonation process due to the lower concentration of hydrogen ions at the basic condition. Consequently, it takes a longer time for the CNTs to reach a stable resistance [231]. The different response time at pH 7 (faster for decreasing pH and slower for increasing pH) is mainly due to the hysteresis effect.

Sensor fabricated with 30 print passes showed good reliability hence subsequent tests are conducted using it. Figure 54c shows the change in resistance of the sensor against time with different pH buffers. It can be observed that the pH sensor is highly repeatable for 6 consecutive cycles. During the cyclic test, the electrical resistance is computed to be $48\text{ k}\Omega$ at pH 10 with a standard deviation of $0.55\text{ k}\Omega$ but drops to $22\text{ k}\Omega$ at pH 4 with a standard deviation of $0.08\text{ k}\Omega$.

Interestingly, some hysteresis is observed for the fabricated sensor. The steady-state value for at each pH is replotted in Figure 54d for better visualization of the hysteresis effect. The pH sensor gives a higher resistance output ($45.10 \pm 0.19\text{ k}\Omega$) when the pH is decreased from 10 to 7. However, a lower resistance output ($41.28 \pm 0.44\text{ k}\Omega$) is recorded when pH changes from 4 to 7. The net hysteresis is calculated as a difference between the initial resistance and final resistance at pH 7 [233]. For the loop (pH 7 $\rightarrow$ pH 4 $\rightarrow$ pH 7 $\rightarrow$ pH 10 $\rightarrow$ pH 7), the net hysteresis is found to be approximately $3.82\text{ k}\Omega$, which is about 14.7%

with respect to the resistance range of the fabricated sensor. The resistance range is calculated by the difference between the resistances at pH 10 and 4. The hysteresis effect observed could be due to the memory effect of the insulating layer (polyimide substrate) as explained by Mousse *et. al.* [234]. A buried site/gel layer is formed due to the attack of hydroxide ion giving rise to a slow and reversible reaction [235]. For the buried site, hydroxide ions take much longer time than hydrogen ions to diffuse through the insulating layers due to their larger ionic size [234]. This also explains slower response time of the pH sensor at the basic condition.

Figure 54 (a) Sensitivity response of the fabricated sensor (dotted lines represent the trend lines), (b) normalized resistance at different pH valves, (c) Repeatability and (d) hysteresis of the CNTs-based pH sensor.

Figure 55a shows the bending cyclic test for the flexible pH sensor. The sensor is flexed at a bending radius of 5 mm for 1000 cycles and remains fully functional with almost no variation in the resistance. The initial and final resistance of the sensor is measured to be 6.08 and 6.09 k Ω respectively after 1000 cycles. The mean resistance for the cyclic test is calculated to be 6.11 k Ω with a standard deviation of 0.016 k Ω and coefficient of variance of approximately 0.26%. The maximum resistance experienced by the pH sensor during the 1000 cycles is measured to be 6.14 k Ω , which deviates around 0.99% from the initial resistance. Thus, the CNTs film can bend and flex without much variation in its resistance, which manifests its suitability for flexible electronics (Figure 55b and Figure 55c).

Figure 55 (a) Cyclic bending test for the sensor. (f) The sensor attached to a glove showing repeated flexing and releasing mechanism.

In vitro biocompatibility of the pH sensor was studied and the results are shown in Figure 56. The sensor was placed directly onto murine myoblasts C2C12. The cells continue to grow on the culture well, as well as surround and under the pH sensor, from day 0 till day 7 as shown in Figure 56a. The cell viability of the construct was examined using the live/dead assay after 7 days of culturing. On the 7th day of culture, layers of cells (whitish in color) were clearly observed to grow on the edges of the top surface of the sensor (white arrow in Figure 56c). Live/dead images captured by a fluorescence microscope revealed that all the tested samples (n=3) show cell viability of more than 95%. The cells that started to grow on those top edges were mostly alive (Figure 56b), even on the silver ink (Figure 56d). The results show that the pH sensors fabricated were biocompatible.

Figure 56 Images depicting the biocompatibility test carried out on the pH sensor, (a) C2C12 cells continue to grow up to day 7 with the pH sensor placed onto the cells. (b-d) Cells growing on the top surface of the sensor. In (a), (b), and (d) live (green)/dead (red) assay indicate that more than 95% of the cells were alive. Note that polyimide and silver ink presented red autofluorescence.

7.2.4 Summary

Aerosol jet printing is an AM technique for printed electronics which is suitable for a wide variety of substrates and inks. The fine resolution printing of the aerosol jet printer opens a new possibility of designing and fabricating new high-performance devices such as sensors and transistors. With suitable dispersion, different particle type such as nanoparticles, flakes, and nanotube can be printed. This work presents a comprehensive analysis of the fabrication of aerosol jet printed electronics, from the optimization of process parameters to the characterization and testing of the printed device. Here, homogeneous and continuous carbon nanotube line trace with a line width of 25 μm is printed with the optimum parameters. Optical microscope and SEM are used to check the line quality and morphology. A flexible CNTs-based pH sensor is printed and successfully tested with different pH buffers. The fabricated pH sensors show high sensitivity and reliability, good response time, high mechanical stability. Besides, the *in vitro* biocompatibility test confirms the suitability of wearing the fabricated pH sensor on human skin.

8. CONCLUSIONS & FUTURE WORKS

In this research, evaporation-driven self-assembly (EDSA) of the carbon nanotubes (CNTs) in evaporating drops is explored in terms of the evaporation dynamics and alignment of CNTs for the first time. Secondly, the aerosol jet printing (AJP) process is studied to understand the physics governing the process. Thirdly, the feasibility of printing aligned CNTs using AJP process is studied. Lastly, the electrical property of the AJ printed CNTs traces is studied and proof-of-concept flexible electronics is presented.

The key contributions of the research are elaborated in the following sections.

8.1 Evaporation-driven self-assembly of carbon nanotubes in evaporating drops

In order to understand the underlying physics governing the alignment of CNTs in EDSA process, sessile drops experiments investigating the effects of substrate temperature, CNTs concentration, pH and drop volume involving flexible substrate and CNTs suspensions solution have been carried out for the first time. The results reveal that the evaporation dynamic of the drops depends significantly on the CNTs concentration. It is found that the pH of CNTs suspensions determines the final deposition patterns (homogeneous film or “coffee ring” effect) and the threshold of zeta potential deciding the deposition pattern have been determined. The results also show that the alignment of CNTs requires the formation of the “coffee ring” effect. The degree of alignment of the CNTs depends strongly on the self-ordering time which is affected by the substrate temperature and the drop volume. It should be pointed out that the degree of alignment of CNTs formed by EDSA in sessile drops experiment is characterized, evaluated and compared for the first-time using image

analysis technique and Raman spectroscopy. Through the experiments, the criteria for achieving good CNTs alignment via EDSA process have been identified. Potentially, this knowledge is transferable to any technology for aligning 1-dimensional nanomaterials using EDSA.

8.2 Analytical investigation of aerosol jet printing process

A simple analytical model for aerosol jet printing was proposed and validated experimentally. With this model, it is possible to explain the effect of the print speed and estimate the deposition rate of the aerosols during printing. In addition, the effect of the sheath gas flow rate on the deposition rate of the aerosols can be explained. The result shows the residence time of the aerosols in the printing system has a significant effect on the print quality in the AJP process. These findings affirm the need for in-depth analysis of AJP process from aerosol generation to transportation of aerosols, and finally to the deposition of aerosols. Furthermore, it is anticipated that this analysis will lead to a better understanding of the physics of AJP process, which in turn stimulate more in-depth research on AJP process.

8.3 Formation of carbon nanotubes twin lines using aerosol jet printing

8.3.1 Identified process windows of AJP for achieving CNTs twin lines

Previous work on AJ printing of CNTs is predominantly on printing homogeneous CNTs film with random CNTs network. In this study, the AJP capability in fabricating aligned CNTs is demonstrated. The results have shown the formation of CNTs twin lines with resolutions that have not been achieved before by using other AM techniques. A processing window of AJP parameters has been identified using macrostructural analysis. The smallest

width of the CNTs twin line obtained in this experiment is found to be approximately 16 μm , which is much smaller compared to the more commonly used inkjet printing technique.

8.3.2 Characterized the microstructure of the CNTs twin lines

Microstructural analysis of CNTs showed that the radial convective flow is responsible for the formation of the CNTs twin lines. The CNTs at the twin line exhibit preferential alignment along the contact line. The degree of alignment of the CNTs depends on the time scale competition between solvent evaporation, translational diffusion and rotational diffusion which is dependent on the printed line width resulting from different process parameters.

8.3.3 Improved electrical property and proof-of-concept applications

The electrical property of the AJ printed CNTs twin line is measured for the first time. A test method for measuring the electrical resistance of the CNTs twin lines is proposed. It has been demonstrated that the AJ printed CNTs twin line shows higher network percolation as compared to the homogeneously distributed CNTs trace, resulting in better electrical conductivity. The electrical resistance of the CNTs twin line is found to be dependent on the print parameters like the sheath flow, atomizer flow, print speed, and the number of print layers. Using suitable process parameters, an optically transparent flexible motion sensor has been demonstrated. Besides, a CNTs-based pH sensor is fabricated, and it shows high sensitivity and reliability, good response time, high mechanical stability.

The favorable results summarized above make aerosol jet printing of CNTs traces a potential novel approach for fabricating high resolution and high-performance electronics on various substrates, especially 3-dimensional and flexible surfaces.

Future work

The following future research directions are recommended.

i. Sessile drop study

- a. To study the effect of drop impingement and spreading on the final deposition pattern
- b. To investigate the effect of different substrate and solvents with different surface tension.

ii. Resistivity measurement of printed CNT traces

Resistivity measurement of the CNTs traces requires the measurement of film thickness. Accurate measurement of film thickness of CNTs traces remains a challenge due to the limitation of the optical confocal microscopy and surface profilometer. Other measurement techniques such as atomic force microscopy (AFM) could be explored for measuring the film thickness of CNTs traces.

iii. Optical transparency measurement of the printed CNT electrodes

Optical transparency measurement of the printed CNT electrodes can be done using spectrophotometer. With optical transparency and resistivity measurement, a correlation between the 2 parameters can be found which could be useful for the design and fabrication of transparent electronics.

iv. Computational fluid dynamic analysis for evaporation-driven self-assembly of CNTs in AJP process.

Most research on AJP process does not consider the effect of the sheath flow-induced hydrodynamic flow in the evaporating drops deposited on the substrate. A

CFD analysis could be useful to determine the effect of the sheath flow-induced hydrodynamic flow and how it may affect the self-assembly of CNTs.

v. To improve the alignment of CNT in the CNT network of printed traces

To explore printing the CNT traces in a cool environment so that the evaporation time can be lengthened in hope for better CNT alignment.

vi. To characterize the effect of alignment of the resistivity of the printed traces

Current result in this research only shows the effect of process parameters on the resistance of the printed traces. The effects may be attributed to both the CNT alignment and CNT packing density. Future work may involve devising new experiment method to eliminate the effect of CNT packing density so that the effect of CNT alignment can be characterized.

vii. Explore new applications.

Possible applications of this research work would be the fabrication of optically transparent triboelectric nanogenerator and microchannels for lab-on-a-chip applications.

viii. Explore printing other 1D or 2D materials

Knowledge learned from this research could be potentially applied to other 1D nanomaterials such as silver nanowires to achieve preferential alignment or 2D nanomaterials such as graphene to achieve transparent traces.

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Appendix A

List of formulae and equations [142]:

$$\mathbf{F}_{\text{St}} = 6\pi a\mu_f(\mathbf{v} - \mathbf{v}_p),$$

$$\mathbf{F}_{\text{Ba}} = 6a^2\sqrt{\pi\mu_f\rho_f} \int_0^t \left(\frac{d\mathbf{v}/dt - d\mathbf{v}_p/dt}{\sqrt{t-\tau}} \right) d\tau.$$

$$\varepsilon_{\text{Ba}} = \frac{|\mathbf{F}_{\text{Ba}}|}{|\mathbf{F}_{\text{St}}|} = \sqrt{\frac{18}{\pi} \frac{\rho_f}{\rho_p} \frac{\tau_\mu}{t}}$$

$$\tau_\mu = 2a^2\rho_p/9\mu_f.$$

$$\frac{|\mathbf{F}_{\text{Ba}}|}{|\mathbf{F}_{\text{St}}|} \cong \text{Re}_p^{1/2} \ll 1$$

$$\text{Re}_p \equiv \frac{2a\rho_f|\mathbf{v} - \mathbf{v}_p|}{\mu_f}.$$

$$\mathbf{F}_{\text{Vm}} = -c_M \frac{\rho_f}{\rho_p} m \left(\frac{d\mathbf{v}}{dt} - \frac{d\mathbf{v}_p}{dt} \right),$$

$$\mathbf{F}_{\text{Ma}} = -\frac{3}{4} m \frac{\rho_f}{\rho_p} \left(\frac{1}{2} \omega - \Omega \right) \times (\mathbf{v}_p - \mathbf{v}),$$

$$\varepsilon_{\text{Ma}} = \frac{|\mathbf{F}_{\text{Ma}}|}{|\mathbf{F}_{\text{St}}|} = \frac{a^2\rho_f|(1/2)\omega - \Omega|}{6\mu_f}.$$

$$\varepsilon_{\text{Ma}} \cong \frac{a^2\rho_f U}{6\mu_f R}.$$

$$\mathbf{F}_{\text{Sa}} = 6.46a^2(u - u_p) \sqrt{\rho_f \mu_f \left| \frac{\partial u}{\partial y} \right|} \text{sign}\left(\frac{\partial u}{\partial y}\right) \mathbf{e}_y,$$

$$\varepsilon_{\text{Sa}} = \frac{|\mathbf{F}_{\text{Sa}}|}{|\mathbf{F}_{\text{St}}|} \approx 0.3 \frac{a}{R} \sqrt{\text{Re}_c}, \quad \text{Re}_c = \frac{2RU\rho_f}{\mu_f}.$$

$$\varepsilon_{\text{Sa}} = \frac{|\mathbf{F}_{\text{Sa}}|}{|\mathbf{F}_{\text{St}}|} = \frac{6.46a}{6\pi} \sqrt{\frac{\rho_f}{\mu_f} \left| \frac{\partial(u - u_p)}{\partial y} \right|},$$

$$\varepsilon_{\text{Sa}} = \frac{|\mathbf{F}_{\text{Sa}}|}{|\mathbf{F}_{\text{St}}|} = \frac{6.46}{12\pi} \sqrt{\text{Re}_p}, \quad \text{Re}_p = \frac{2a\rho_f|\mathbf{v} - \mathbf{v}_p|}{\mu_f}.$$

Appendix B

A summary of the source term for the various impingement regimes identified in the spray–film interaction model [see equations (1) and (2)]

Impingement regime	Source term S_d	Nomenclature
Stick	$\frac{\pi}{6} \rho_l \sum_{k=1}^{N_{drop}} (N_k d_{d_k}^3)$	d_{d_k} —diameter of incident drop N_{drop} —number of incident drops or parcels N_k —number of particles in the incident parcel
Rebound	0	—
Spread	$\frac{\pi}{6} \rho_l \sum_{k=1}^{N_{drop}} (N_k d_{d_k}^3)$	Similar to stick
Splash	$\frac{\pi}{6} \rho_l \sum_{k=1}^{N_{drop}} \left[1 - \left(\frac{m_s}{m_d} \right)_k \right] N_k d_{d_k}^3$	$(m_s/m_d)_k$ —mass fraction splashed
Dynamic pressure, p_d		
Stick	$\rho_l \sum_{k=1}^{N_{drop}} V_{n_{d_k}}^2 \frac{A_{d_k}}{A_{wall}}$	$V_{n_{d_k}}$ —normal velocity component of incident drop N_{drop} —number of incident drops or parcels
Rebound	$\rho_l \sum_{k=1}^{N_{drop}} (1 + e_k^2) V_{n_{d_k}}^2$	e_k —coefficient of restitution for the k -th drop
Spread	$\rho_l \sum_{k=1}^{N_{drop}} V_{n_{d_k}}^2 \frac{A_{d_k}}{A_{wall}}$	Similar to stick
Splash	$\rho_l \sum_{k=1}^{N_{drop}} V_{n_{d_k}}^2 + \rho_l \sum_{j=1}^{N_{splash}} V_{n_j}^2$	V_{n_j} —normal velocity component of the j -th secondary droplet N_{splash} —number of secondary droplets
Tangential momentum, M_{tang}		
Stick	$\frac{\pi}{6} \rho_l \sum_{k=1}^{N_{drop}} (N_k d_{d_k}^3 V_{\tau_{d_k}})$	$V_{\tau_{d_k}}$ —tangential velocity component of incident drop N_{drop} —number of incident drops or parcels N_k —number of particles in the incident parcel
Rebound	$\frac{\pi}{6} \rho_l \sum_{k=1}^{N_{drop}} N_k d_{d_k}^3 \left(\frac{2}{7} V_{\tau_{d_k}} \right)$	—
Spread	$\frac{\pi}{6} \rho_l \sum_{k=1}^{N_{drop}} (N_k d_{d_k}^3 V_{\tau_{d_k}})$	Similar to stick
Splash	$\frac{\pi}{6} \rho_l \sum_{k=1}^{N_{drop}} (N_k d_{d_k}^3 V_{\tau_{d_k}})$ $+ \frac{\pi}{6} \rho_l \sum_{j=1}^{N_{splash}} (N_j d_j^3 V_{\tau_j})$	V_{τ_j} —tangential velocity component of j -th secondary droplet N_{splash} —number of secondary droplets or parcel N_j —number of particles in the j -th parcel resulting from splashing

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Appendix C

Details of CNTs ink dilution

Concentration (w%)	Amount of DI water added (g)	Amount of CNTs ink (g)
0.07	6.500	3.500
0.02	9.000	1.000
0.007	9.650	0.350
0.0007	9.965	0.035

Appendix D

Cross-section of AJP's deposition head with dimensions of channels for aerosols flow.

Appendix E

Calculation of aerosol residence time.

Sample calculation for residence time:

Atomizer Flow rate	40 sccm				
Sheath flow rate	40 sccm				
Sections	Channel length (cm)	diameter (cm)	Average area (cm ²)	Average velocity(cm/min)	residence time (s)
delivery tube	60	0.140	0.01539	2598	1.3854
dh1	1.06	0.177	0.02466	1621	0.0390
dh2	0.33	0.038	0.00113	70540	0.0003
dh3	0.25	0.144	0.01617	4946	0.0030
nozzle	2.45	0.100	0.00785	10185	0.0144
				Total time	1.4422
				Total mix time	0.0177
				Total non mix time	1.4245

Highlighted in yellow are the variables that can be changed

Non-combined flow		
Atomizer flow rate	Tube length	Residence time,s
20	60	2.84
20	80	3.77
20	100	4.69
20	120	5.62
30	60	1.89
30	80	2.51
30	100	3.13
30	120	3.74
40	60	1.42
40	80	1.88
40	100	2.34
40	120	2.81
50	60	1.13
50	80	1.50
50	100	1.87
50	120	2.24

Combined flow	
Combined flow rate	Residence time, ms
20	70.7
40	35.3
60	23.6
80	17.7
100	14.1

Appendix F

Calculation of the lifetime of aerosols of different diameters.

$$\text{Life time, } \tau_m = \frac{D_o^2}{\lambda}$$

$$\lambda = \frac{4Sh\rho_v D_v}{\rho_d} (\omega_{A,s} - \omega_{A,\infty})$$

Calculation for 10 µm diameter aerosol

Diffusion coefficient	0.282 cm ² /s
Sherwood number	2
Density of N2	0.00125 g/cm ³
Density of water	0.997 g/cm ³
Saturated vapor pressure	3.17 kPa
air pressure	101 kPa
molar mass of water	18 g/mol
molar mass of nitrogen gas	28 g/mol
omega	0.02017
lambda	5.707E-05 cm ² /s
Diameter	0.01 cm
Life time	1.75 s

Calculation for 5 µm diameter aerosol

Diffusion coefficient	0.282 cm ² /s
Sherwood number	2
Density of N2	0.00125 g/cm ³
Density of water	0.997 g/cm ³
Saturated vapor pressure	3.17 kPa
air pressure	101 kPa
molar mass of water	18 g/mol
molar mass of nitrogen gas	28 g/mol
omega	0.02017
lambda	5.7067E-05 cm ² /s
Diameter	0.005 cm
Life time	0.44 s

Appendix G

Optical image showing the minimum line width of CNT twin line obtainable by aerosol jet printing process. Inset shows the measurement of the line widths. (NS: 150 μm , SH: 100 sccm, UA: 30 sccm, SP: 1mm/s, ST: 25 $^{\circ}\text{C}$)

Appendix H

Microstructural analysis (orientation distribution analysis) of CNTs at contact lines of different samples.

(a) Enlarged image of Figure 39b in the manuscript, (b & c) CNT alignment analysis showing the angular distribution of CNT for different samples. Both samples show preferentially aligned CNT at the contact lines.

Appendix I

ANOVA test to analyze the effect of atomizer flow on Herman's orientation factor

Summary of Data						
	<i>Treatments</i>					
	1	2	3	4	5	Total
N	14	13	10	13		50
ΣX	5.7133	7.1552	5.9593	7.6613		26.489
Mean	0.4081	0.5504	0.5959	0.5893		0.53
ΣX^2	3.1012	3.9668	3.562	4.559		15.189
Std.Dev.	0.2433	0.0488	0.0345	0.0605		0.1536
Result Details						
<i>Source</i>	<i>SS</i>	<i>df</i>	<i>MS</i>			
Between-treatments	0.3027	3	0.1009	<i>F</i> = 5.44143		
Within-treatments	0.853	46	0.0185			
Total	1.1557	49				

The *f*-ratio value is 5.44143. The *p*-value is .00275. The result is significant at $p < .05$.

Appendix J

ANOVA test to analyze the effect of sheath flow on Herman's orientation factor

	Treatments					
	1.00	2.00	3.00	4.00	5.00	Total
N	13.00	17.00	20.00			50.00
ΣX	7.66	9.81	9.60			27.07
Mean	0.59	0.58	0.48			0.54
ΣX^2	4.56	5.78	4.99			15.33
Std.Dev.	0.06	0.09	0.14			0.12
Result Details						
Source	SS	df	MS			
Between-treatments	0.13	2.00	0.06	$F = 5.46574$		
Within-treatments	0.54	47.00	0.01			
Total	0.67	49.00				

The f -ratio value is 5.46574. The p -value is .007342. The result is significant at $p < .05$.