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COMMUNICATION

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

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Carbon nanotubes (CNTs) are 1-dimensional (1D) and flexible nanomaterials with high electric conductivity and also high aspect ratio. These features make CNTs highly suitable materials for fabrication of flexible electronics. CNTs can also be made into dispersion which can be used as the feedstock material for droplet-based 3D printing technologies, e.g., inkjet printing and aerosol jet printing to fabricate printed electronics. These printing technologies involve several physical processes including deposition of ink droplets on the flexible polymeric substrates such as polyimide, evaporation of the solvent and formation of thin films of CNTs, all of which are not thoroughly investigated. Besides, alignment of the CNTs in the resulting thin films dictates their electrical performance. In this work, we examine the effect of substrate temperature and CNTs concentration on the evaporation dynamic and also the alignment in the deposition patterns. Evaporation-driven self-assembly of CNTs and their preferential alignment are observed. Image analysis and Raman spectroscopy are utilised to evaluate the degree of alignment of the CNTs network. It is found that contact line dynamic depends greatly on the CNTs concentration. Besides, the substrate temperature plays a significant role in determining the order of the CNTs in the drying deposition pattern. Our findings show the possibility of controlling film morphology and the degree of alignment of CNTs for printed electronics in the printing process.

Keywords: Carbon nanotubes, 3D printing, printed electronics, nanomaterials, Sessile drop evaporation

Introduction

Evaporating the solvent from a suspension consisting of insoluble solutes such as micro- and nano-particles, polymers and biomolecules, can lead to laying down electrical circuits with desired assemblies for various applications in biology, chemistry, material engineering and more recently electronics.¹ The fabrication of printed electronics via 3D printing or additive manufacturing techniques such as inkjet printing and aerosol jet printing process involves deposition functional inks on to a substrate and formation of the patterned thin films.²⁻⁶ Various kinds of nanoparticle suspensions (metal, semiconductor, dielectric materials) such as silver nanoparticle,^{7, 8} graphene pallets,⁹ carbon nanotubes,¹⁰ and poly(methyl methacrylate) (PMMA)¹¹ have been demonstrated for fabricating different devices. For instance, nanomaterials such as carbon nanotubes, metal oxide, reduced graphene oxide have been processed using 3D printing techniques for applications such as wireless power transmission module, transistor and counterfeit coin recognition respectively.¹²⁻¹⁴ Sessile drop experiment is a fundamental representation of these droplet-based 3D printing techniques and commonly used to understand the printing processes. Earlier research on the evaporation of sessile drops have investigated the effects of surface roughness,¹⁵ hydrophobicity,^{16, 17} atmospheric condition,^{18, 19} and textured surfaces.^{20, 21} This has paved the way to further investigate the evaporation dynamics of liquid containing nanomaterials for printed electronic applications. Another important factor in achieving good printed circuit using liquid suspension inks is the effect of drying. The drying pattern of the colloidal suspensions depends on various factors such as the hydrodynamic flow

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(convective, capillary & Marangoni flows), pinning and depinning of contact line (substrate-liquid-air interface), nature of the substrate, particle geometry, interparticle interaction, particle-substrate interaction, composition and concentration of the suspensions, temperature and external field.^{22, 23} A homogeneous film is achieved when Marangoni flow is present; diffusion of the particle overpowers the convective flow; the contact line does not pin and particle-substrate interaction is strong. Absence of the above factors results in coffee ring effect.^{22, 24-26} Understanding these factors allows the researchers to design the film morphology (homogeneous/coffee ring effect) for different design requirements.^{27, 28}

The study of the arrangement of particles at the ring of the thin film is another important aspect of sessile drops experiment. The self-assembly of the particles at the air-liquid-solid interface, also known as three-phase contact line, has been well studied and the arrangement of the particles at the coffee ring depends on the geometric shape of the particles (sphere, ellipsoid, rod or long tube).²⁹ Evaporation-driven assembly is widely used because it is simple, inexpensive and a range of materials with various shapes such as micro- and nanospheres, ellipsoids, rod-like structures, and pallets can be used. Generally, several variants of such process are possible, namely (i) drop-based evaporation (sessile and pendant drops), (ii) evaporation with confinement such as a wedge, parallel plate and cylindrical confinement, and (iii) vertical deposition.³⁰ The arrangement of the particles in the assemblies has a strong dependence on the shape of the particles. Numerous kind of particle arrangements such as hexagonal packing, nematic/3D, tetragonal packing, and nematic/smectic with polyhedral, bipyramid, nanocubes, and nanorods, respectively, have been reported.³¹ For spherical particles, the particles were found to be organized in a sequential square and hexagonal manners near the contact line and transition to disorder particle organization further away from the contact line.³² For elongated particles like nanotubes, 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.^{33, 34} 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.³⁵

Carbon nanotubes (CNTs), a 1-dimensional nanomaterial, has gained popularity in printed electronics due to their good electrical conductivity and mechanical properties. Compared with graphene or reduced graphene oxide,³⁶⁻³⁹ which are also frequently used for flexible electronics, CNTs comes in various diameters, lengths, chirality and chemical functionalization which can be harnessed and tailored for specific applications.^{40, 41} Also, CNTs are superior than its counterparts in terms of optical response and structural rigidity.⁴² In addition, CNTs can be used in composite materials for applications such as metamaterials, reinforcement, electrodes for energy storage, and electromagnetic wave absorption etc.⁴³⁻⁵⁰ Many studies have shown that aligning CNTs orientation in a desired orientation can bring advantages such as improved electrical

and thermal conductivities and enhanced mechanical property.⁵¹ 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)^{29, 31} or straight nanotubes that are not flexible like CNTs.³⁵ CNTs are flexible materials with high aspect ratio (~100) which displays different particle-flow dynamics and hence the particle arrangement. However, there are only few studies focusing on the arrangement and orientation of CNTs in a sessile drop.^{34, 52-54} Duggal et al. suspended the CNTs in pluronic solution and observed a crusting phenomenon in where CNTs assembled themselves at the free surface.⁵³ Li et al. found that lower concentrations of CNTs suspension leads to higher ordering of the network due to less entanglement.³⁴ 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 dynamic of CNTs sessile drop on different hard surface substrates (like glass, copper, and silicon) and observed different deposition patterns.⁵⁴ 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 phase can be observed at a concentration of 3.8w%.⁵² However, these studies did not investigate the effect on a polymeric substrate like polyimide, which is often used for fabricating printed flexible electronics. Moreover, the interplay between the CNTs concentration and the substrate temperature on the evaporation dynamic of sessile drop and the arrangement of CNTs or orientation are not well understood. In addition, these studies describe the CNTs alignment/arrangement in a qualitative manner.

In the present work, we investigate how the polyimide substrate affects the evaporation of CNTs sessile drop. Besides, the effect of CNTs concentration and substrate temperature on the contact line dynamic is also investigated. Image analysis and polarised Raman spectrometry are used to provide quantitative analysis of the CNTs orientation/arrangement of CNTs thin film formed from CNTs sessile drops.

Experiment methods

Preparation of CNTs inks. The CNTs ink used in this work is an aqueous single-walled CNTs suspension with a concentration of 0.2 w% (NINK 1100) purchased from Nanolab[®]. The ink contained carboxyl (COOH) functionalized SWNT dispersed in water solvent with a minimum amount of additive added to ensure long term stability. The CNTs in the ink has an average length of 1300 μm with a standard deviation of 615 μm . The CNTs have an average diameter of 1.5 nm according to the data sheet provided by Nanolab[®]. Different concentrations (0.07 w%, 0.02 w%, 0.007 w%) of CNTs suspensions were prepared by diluting the NINK 1100 ink with deionised (DI) water. The density of the CNTs can be estimated by the number of wall and the diameter of the CNTs as reported by Laurent et al.⁵⁵ The estimated density of the single-walled CNTs in the NINK 1100 is

found to be approximately 2.0 g cm^{-3} . However, it should be noted that water molecules can enter the interior of the hollow CNTs structure making the density higher than dry CNTs.^{56, 57} The density of the solvent (in this case is water) is roughly 1 g cm^{-3} at room temperature.

Sessile drop experiment equipment setup. The evaporation mechanism of the CNTs sessile drop on the polyimide substrate was measured by a custom-built setup. The setup was fitted with a diffused light background and a high-speed camera (SA, Photron Inc., Japan) with a 5x zoom lens (MP-E 65mm f/2.8 1-5x Macro, Canon, Japan). Prior to the experiment, the polyimide substrate is first cleaned with soap water and sonicated in an ethanol bath to remove oil and dirt from the substrate's surface. The surface roughness of the polyimide substrate was then evaluated using 3D laser confocal microscope (VK-X1000, Keyence, Japan). The polyimide substrate is first attached to a glass slide to ensure that it is flat. A custom-built platform heater with a temperature control feedback loop is used to adjust the substrate's temperature (T_s). Sessile drops with an expected volume of $0.5 \mu\text{L}$ is manually placed on the substrate by using a micro-pipette. The contact angle (θ), contact radius (r), and volume (v) of the sessile drop are measured using an ImageJ.⁵⁸ Each experiment is repeated at least 6 times for a statistically meaningful result.

Optical microscopy. The optical images of the dried sessile drop patterns are taken using an Olympus CKX41 microscope.

Field emission scanning electron microscopy (FESEM). The characterization of the CNTs particle arrangement and orientation is done by Jeol field-emission scanning electron microscopy in GB-low mode. Due to the low electrical conductivity of the polyimide substrate, the samples are first coated with platinum for 90s to ensure good electrical conductivity of the samples. The scanning voltage is set to around 2.0 kV and current to 7 mA to obtain good image quality. At least 10 FESEM images were taken for each experimental condition.

Raman spectrometry. The degree of the CNTs alignment in the sessile drop deposit was characterized by 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 is obtained by averaging the 5 measurements taken from each condition.

Image analysis for particle orientation/arrangement. The characterization of the alignment of the CNTs network is done using ImageJ image processing software's plugin, OrientationJ. At least 8 FESEM images of the CNTs network at the coffee ring of the sessile drop for each condition are analyzed by OrientationJ orientation analysis tool to determine the orientation of the CNTs network. The gradient computation that is used in the analysis is "Finite Difference" method with a local window of 6 pixels. The degree of alignment of the CNTs is

determined by calculating Herman's orientation factor from the angular distribution result obtained using OrientationJ.

Results and discussion

The average surface roughness, R_a of the polyimide substrate is 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 °C, 50 °C, 70 °C and 110 °C are studied. Figure 1a, 1b, 1c, and 1d illustrate the influence of substrate temperature on the 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 °C, 50 °C, 70 °C and 110 °C are 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 1e 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 1f 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.⁵⁹ 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.⁶⁰ 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.⁶¹ Besides, the decrease in the surface tension of the liquid with increasing temperature also contributes to the decrease in contact angle.⁶² 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 lack of understanding on this issue.⁶² 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.

The evaporation mode of the CNTs sessile drops is further analyzed using figure 2. Figure 2 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, also known as constant contact angle (CCA) 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 .⁶³ 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.⁶³

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 3 shows the influence of CNTs concentration on the contact line dynamics and the final patterns of the thin film. The pinning and depinning phenomena

Figure 1. 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, $n \geq 6$).

Figure 2. 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.

can be explained by aggregate-induced pinning.⁵⁴ The CNTs aggregates at the ring can stop the contact line from moving. Based on the final patterns of the CNTs thin film, coffee ring

effect is noticed across all samples. The coffee ring 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 is 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 is 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.⁶⁴⁻⁶⁶ 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.

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 1 based on Deegan's approximation.⁶⁷

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

where r is the radial position from the centre 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 2.^{67, 68}

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

where D is the diffusion coefficient of the water in the air and H is the relative humidity. Combining equation 1 & 2 together with the mass balance equation, the height-average radial velocity, $\bar{u}_r$, can be derived as equation 3.^{67, 69}

$$\bar{u}_r(r, t) = \frac{1}{4} \frac{1}{(t_f - t)} \frac{R^2}{r} \left[\left(1 - \left(\frac{r}{R}\right)^2\right)^{\lambda(\theta)} - \left(1 - \left(\frac{r}{R}\right)^2\right) \right] \quad (3)$$

where t_f is the time taken for the solvent to evaporate from the drop. It can be seen that the radial velocity is reciprocal function with asymptote at $t = t_f$. It implies that the radial flow velocity is accelerated throughout the evaporation process and reaches highest speed when the drop is fully evaporated⁷⁰. This phenomenon can be inferred from the drop with concentration $\phi=0.07$ w% and $\phi=0.2$ w% (figure 3) that there is no CNTs near the rings as they are pushed towards the contact line by the strong radial flow at the final stage of evaporation. Also,

Figure 3. 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 CNTs drops, whereas pinned contact line is observed for higher concentration CNTs drops.

equation 1 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.⁷¹ However, equation 1 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.⁷¹ However, the Marangoni flow is dependent on the shape of the particles.⁷² It has been found that needle-like particles show the slowest interfacial velocity when compared to the sphere-shaped and disc-shaped particles.⁷² 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. Figure 4a 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 4b), transition region (figure 4c), and randomly oriented region (figure 4d). 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 4e 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 casted 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 align themselves along the flow direction due to the shear force acting on their 1-dimensional structure.^{73, 74} 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.^{71, 75} 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.²⁸ Also, the initial velocity at the contact line as a result of the radial convective flow is low.⁷⁶ 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 4b. The transition region is where the radially aligned CNTs (perpendicular to contact line) and the nematic CNTs meet during the formation of thin film. Figure 4c shows how the CNTs are brought to the contact line and reorient themselves to align along the contact line. Figure 4d shows randomly oriented CNTs which corresponds to region d. The random nature of CNTs has been found to result from several factors (Figure 4d). First, the decrease in local CNTs concentration deters the formation of 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))⁷⁶ results in less damping and fast-moving

Figure 4. (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.

Figure 5. 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.

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 4e shows the final stage of drop evaporation and the 3 regions of different CNTs alignment corresponds to figure 4b, 4c and 4d respectively.

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 are taken near the contact line of the drops (figure 5). 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. 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.

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.⁵¹ The Herman orientation factor, f can be expressed as, $f = 3(\cos^2\delta - 1)/2$. 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 principle axis. It should be noted that the principle axis is defined parallel to the contact line and the images are processed in such a way that the principle axis is set to $\theta=0^\circ$ or in the horizontal direction. Based on the analysis (figure 6), 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. 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 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 7 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.⁷⁷ 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 7a⁷⁷⁻⁷⁹. This anisotropic optical property of CNTs to the polarised light also 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.^{80, 81} Similar technique has been utilized for characterizing the level of graphitization of carbonaceous materials.^{82, 83} Figure 7b illustrates the Raman spectra of the CNTs 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, we found I_G/I_D ratio of 4.5 or higher indicates good degree of alignment ($f>0.7$). Figure 7c shows that the I_G/I_D ratio for all the CNTs concentration at 30 °C are higher than 4.5, indicating high degree of alignment. The CNTs concentration of 0.007 w% is omitted from figure 7c 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 orientations ($\theta=0^\circ$ & $\theta=90^\circ$).⁸⁴ Figure 7d, 7e, and 7f show the Raman spectra of 0.2 w% CNTs concentration that are dried at substrate temperature 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.

Table 1 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

Figure 6. 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.)

Figure 7. (a) Schematic showing the CNT orientation and the direction of light polarization. Raman spectra showing (b) the effect of temperature on 0.2 w% CNT concentration with $\theta=0^\circ$ light polarization, (c) effect of CNT 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.

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 5, 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 1 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.^{85, 86} The compounding effect will result in a more violent,

Table 1. 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	<div style="display: flex; align-items: center;"> <div style="flex: 1; text-align: center;">↓</div> <div>decreasing</div> </div>
70	0.67	3.35	1.62	
110	0.17	1.78	1.16	

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.

Conclusions

In summary, sessile drops experiment was conducted to investigate the influence of substrate temperatures and CNTs concentration in suspension solutions on the resulting evaporation dynamic and deposition patterns of CNTs. It is observed that the CNTs concentration exerts a significant influence on determining the contact line dynamic during the evaporation process. At low CNTs concentrations, eg., 0.007 w% and 0.02 w%, the drops show depinning contact line, whereas an opposite pinning effect is observed for CNTs drops with higher concentration, eg., 0.07 w% and 0.2 w%. The depinning of contact line at low CNTs concentrations can be attributed to the lack of aggregates-induced pinning. 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 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. Moreover, it is found that the substrate temperature has 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 high degree of alignment at the contact line, the misalignment, however, increases with increasing substrate temperature. To conclude, we found that the evaporation dynamics of CNTs depends on the concentration of the dispersion, whereas the degree of alignment of deposited CNTs depends greatly on the substrate temperature.

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Conflicts of interest

There are no conflicts to declare.

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