Substrate-Versatile Direct-Write Printing of Carbon Nanotube-Based Flexible Conductors, Circuits, and Sensors

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Manufacturing of printed electronics relies on the deposition of conductive liquid inks, typically onto polymeric or paper substrates. Among available conductive fillers for use in electronic inks, carbon nanotubes (CNTs) have high conductivity, low density, processability at low temperatures, and intrinsic mechanical flexibility. However, the electrical conductivity of printed CNT structures has been limited by CNT quality and concentration, and by the need for nonconductive modifiers to make the ink stable and extrudable. This study introduces a polymer-free, printable aqueous CNT ink, and, via an ambient direct-write printing process, presents the relationships between printing resolution, ink rheology, and ink-substrate interactions. A model is constructed to predict printed feature sizes on impermeable substrates based on Wenzel wetting. Printed lines have conductivity up to 10 000 S m⁻¹. The lines are flexible, with <5% change in DC resistance after 1000 bending cycles, and <3% change in DC resistance with a bending radius down to 1 mm. Demonstrations focus on i) conformality, via printing CNTs onto stickers that can be applied to curved surfaces, ii) interactivity using a CNT-based button printed onto folded paper structure, and iii) capacitive sensing of liquid wicking into the substrate itself. Facile integration of surface mount components on printed circuits is enabled by the intrinsic adhesion of the wet ink.

1. Introduction

Materials that combine mechanical strength, flexibility, and electrical conductivity are key to advances in flexible electronics, robotics, and medical devices. Mainstream approaches to scalable fabrication of electronics in non-wafer formats, such as for flexible displays, smart/RFID labels, and active clothing involve printing of liquid inks with conductive fillers. Typical ink fillers include metal nanoparticles and nanowires, carbon nanotubes (CNTs), graphene (or graphene oxide) sheets, and conductive polymers. The inks are selected for applications based on requirements for conductivity, flexibility, optical transparency, durability, and substrate compatibility.

For these uses, CNTs have advantages including high conductivity, low density, processability at low temperatures, and intrinsic mechanical flexibility. However, high concentration CNT dispersions are difficult to formulate due to the low dispersibility limit of pure CNTs in almost all liquids, and the need for stabilizers and rheological modifiers, such as polyvinyl alcohol, to create a printable ink. The use of these modifiers inherently limits conductivity and requires post-processing by methods such as rinsing with alcohols, acid washing, or hot pressing.

CNTs in solution percolate rheologically, or reach a semi-dilute interaction state, at low concentrations, often promoted by depletion-causing surfactants. The formation of this continuous, interacting CNT network influences solution viscosity, processability, and the electrical performance of the final product. High ink concentrations can even generate fluid yield stress behavior. As such, inkjet printing of CNTs has been possible only using dilute CNT dispersions, requiring several layers to generate conductive features. Conversely, a yield stress is beneficial for extrusion-based printing and screenprinting, as well as embedded extrusion printing into a soft matrix. The presence of the yield stress improves feature retention, resolution, and smoothness.

By comparison, printed metal nanoparticles typically have excellent conductivity, yet their low material yield strain (e.g., <0.5% for gold, silver) restricts flexibility of printed metal features. Meanwhile, the use of thinner metal layers to improve flexibility reduces conductivity, mechanical strength, and fatigue resistance. Alternative approaches use more complex manufacturing of wrinkled or pre-folded structures to allow macroscopic flexibility beyond the intrinsic fracture limit of the metal. Similarly, promising inks made from nanowires, typically silver, show improved flexibility, though the metals remain inherently soft. Metal particles are also prone to oxidation and sedimentation within ink suspensions, requiring protective and stabilizing additives, which in turn must be
removed after printing, for example, by sintering at high temperatures. Sintering in turn restricts printing to thermally compatible substrates, and can cause cracking of the metal. For the most stable (i.e., non-oxidizing) metals such as silver and gold, material cost is also of concern.

Moreover, scalable manufacturing of printed electronics demands compatibility with flexible, low-cost substrates. Polymeric films are widely used in roll-to-roll printing of electronics due to their good mechanical properties, and resistance to oxygen and water penetration. Polyimide and polyethylene terephthalate are predominantly used when high temperatures are required during processing such as for sintering of metal inks. Circuitry on paper has also been widely developed, such as for microfluidic diagnostics and electrokinetic particle transport, disposable RFID tags, actuators, and sensors for electrochemistry. Paper is readily modified, and clay and other coatings are commonly used to control ink sorption and fixation, as well as to adjust paper gloss and brightness and to promote adhesion of high-surface tension inks.

Here, we describe the production and use of an aqueous CNT-based ink in a direct-write extrusion technique, producing conductive, flexible traces on a variety of impermeable (polymer) and porous (paper) substrates. In Section 2.1, we describe a series of aqueous CNT inks having CNT volume fractions up to 2.4% and exhibiting shear thinning, yield stress rheological behavior. In Section 2.2 we relate process parameters (deposition rate) to feature size and conductivity during extrusion-based printing. In Section 2.3 we demonstrate the use of process control and percolation behavior to generate CNT traces with conductivity spanning 7 orders of magnitude, including low-concentration traces with a linear density less than 10⁻³ mg CNT m⁻¹. In Section 2.4 we demonstrate CNT printing onto six flexible substrates—glossy paper, hydrophobic paper, vinyl ethylene laminating film, Kapton film, a viscose filter, polyethylene terephthalate, and chromatography paper—and introduce a model to predict the width of features on the impermeable substrates based on the effective Wenzel contact angle. In Section 2.5 we demonstrate printing of 2D structures with an integrated light-emitting diode, using the ink itself for mechanical adhesion and electrical contact to the circuit. Also, we create an interactive CNT paper button that illuminates an LED, utilizing the low contact resistance of the printed CNTs. Last, we combine a printed CNT capacitive sensor and CNT circuitry on chromatography paper to measure wicking fluid within the substrate itself.

2. Results and Discussion

2.1. Formulation and Rheology of Aqueous CNT Ink

To begin this study, a variety of CNT inks were produced with volume fractions of 0.02% < φ < 2.4% CNT stabilized by sodium deoxycholate and Dowfax surfactants, which are known to be highly effective at suspending non-bundled CNTs at relatively high concentrations. Ink preparation involved sonication of CNTs in the water-surfactant mixture, followed by repeated addition of CNTs to increase concentration. Dispersions were centrifuged to remove bundles and impurities. In some cases, CNT concentration was further increased by dialysis as described by Maillaud, et al. CNTs were used from multiple sources for different inks, but uniformly had high aspect ratios, λ = L_CNT/ d_CNT = 500 – 4500, as measured previously, or reported by the manufacturer. The ink consistency ranges from liquid-like to paste-like, depending on the concentration. More details can be found in Section 4. The rheology of the CNT inks is tailored not by using polymeric fillers, as has been done before to achieve printability, but by using higher concentration and higher aspect ratio CNTs to create a fluid with a measurable yield stress. The absence of polymeric fillers or other rheological modifiers enables as-printed features to have high conductivity, without requiring post-processing. In addition, we believe that the yield stress contributes to shelf stability of the inks, and we have observed that inks printed up to 2 years after initial preparation showed consistent properties after printing, and no phase separation (e.g., no water layer below the solution, or hardened CNT layer on top).

At all concentrations used here, the CNT ink is shear-thinning. Above a threshold CNT concentration of φ = 0.5%, a yield stress develops and increases with concentration, as shown in Figure 1a,b, ranging from 0.05 to 150 Pa with a strong power-law dependence, σ̇ ~ φ³⁰, likely due to the long length of the CNTs. The presence of a yield stress in the CNT suspensions is attributed to the inter-tube interaction of CNTs and the formation of nematic liquid crystalline domains (as shown schematically in Figure 1c), which is a feature of concentrated CNT solutions in various solvents as well as CNT suspensions with dispersing agents. This is correlated with higher CNT concentration and length, which are predictors of higher conductivity. To verify this hypothesis, inks were imaged using transmission polarized light microscopy in Figure 1d. The opacity of inks increases with CNT concentration, and at higher concentrations (i.e., φ > 0.3%), the inks become visibly birefringent. An isotropic-to-nematic transition can be expected near φ = 3.34/λ = 0.1 – 0.7% using the Onsager transition for rigid rods. By comparison to this percolation threshold, isotropic conductive fillers like carbon black typically percolate electrically at 3–15%wt solution, while they do not exhibit liquid crystalline behavior.

Upon shearing deformation at large strains, γ > 40%, mimicking the flow condition of extrusion printing, the CNT inks yield (Figure 1e). All inks restructure quickly and demonstrate no aging, having the storage modulus, G′, stable over time (Figure 1f). Videos taken using transmission polarized light microscopy show similar absence of long-time change, with no visible change in liquid crystalline structure (e.g., coarsening) over time after shearing (Section S1 and Video S1, Supporting Information). Additional rheological measurements showing small amplitude oscillatory shear tests of our CNT inks, and loss modulus data for the large strain amplitude sweep, are included in Section S1.2, Supporting Information. Ink formulation to achieve the yield stress imparted by liquid crystalline behavior is key to its suitability for direct-write extrusion printing. In extrusion-based printing processes, higher yield stresses enable feature retention at smaller scales and allow greater feature complexity. The measured attributes of our CNT inks are also beneficial for printing by allowing extrusion through small nozzles at practical, low pressures.
followed by rapid recovery of full strength of the ink, imparting robustness to the printed structures.[15]

2.2. Direct-Write Extrusion of CNT Ink

Direct-write extrusion of the CNT inks is performed using a modified 3D printer. Briefly, a custom syringe displacement extruder was constructed using a micrometer linear actuator (Thorlabs) and 3D printed components to hold the syringe. The syringe was affixed to the upper rail of a desktop printer (MakerGear M2). The extruder enabled control of the ink volume dispense rate, ranging here from 0.2 to 9 μL s⁻¹. A stainless steel blunt-tipped needle (diameter = 0.12–0.60 mm) is used as the nozzle, and the ink is extruded with a small (0.1 mm) gap between the nozzle tip and the substrate, which in Figure 2 is a roughened polyimide/Kapton film (see Experimental Section for more details). After extrusion, the solvent evaporates over 1–10 min, leaving solid CNTs.

During printing, ink is extruded using the 2D motion stage to control the nozzle in a digitally prescribed path, as depicted in Figure 2a,b. The concentration of CNTs in the printed features is independently controlled by adjusting the 2D nozzle motion speed, \( v_{\text{nozzle}} \), and the average dispense speed of the ink, \( \nu_{\text{ink}} = 4Q_{\text{ink}} / \pi D_{0}^{2} \). Here, \( Q_{\text{ink}} \) is the volumetric flow rate of the ink through the nozzle and \( D_{0} \) is the inner diameter of the nozzle. The non-dimensional ink deposition rate, \( \nu \), is therefore defined in Equation (1) as:

\[
\nu = \frac{\nu_{\text{ink}}}{v_{\text{nozzle}}} \tag{1}
\]

Similar process parameters have been used before to understand dimensional control in hydrogels,[44] while \( \nu \) is defined here to best parameterize the influences of the printing process on geometry and electrical conductivity. A higher deposition rate increases the amount of ink deposited per linear distance, which also systematically increases the printed trace width, \( w \), normalized as \( w / D_{0} \). This scaling is examined by optical microscopy of printed features, and is plotted in Figure 2c,d. As the deposition rate increases, the resulting conductivity, \( \sigma \), systematically increases as well. To adopt units commonly reported in the textile literature, we calculate the linear density of deposited CNT material in units of tex (mass per length along the axis of the printing trajectory), as in Equation (2).

\[
\rho A_{c} = \frac{Q_{\text{ink}}}{v_{\text{nozzle}}} = \frac{cv\pi D_{0}^{2}}{4} \tag{2}
\]

Here, the mass density of printed CNTs is \( \rho \) and \( A_{c} \) is the cross-sectional area normal to the direction of printing. While neither property can be reliably measured at these size and mass scales, their product is readily calculated from input process parameters. We further note that we consider only the density and concentration from CNTs, not from residual surfactant. The initial mass concentration of CNTs in the liquid ink is \( c^{0} \). The DC linear conductivity, \( \sigma A_{c} \), is defined as
σ = \frac{4Q_{\text{ink}}}{\pi D_0^2 R} \quad (3)

where \( R \) is the resistance measured by a four-terminal electrical probe, and \( L \) is the length of this line trace that the resistance is measured across (see Section 4 for details). In this case, linear conductivity, \( \sigma A_c \), increases proportionally to linear density, \( \rho A_c \) (Figure 2e) as would be expected for fully percolated (dense) conductive rod-like particles.\(^{[45]}\) In addition, even at the lowest deposition rates, corresponding to the highest \( v_{\text{nozzle}} \) and shear forces applied on the ink between the nozzle and substrate (\( \gamma > 100 \text{ s}^{-1} \)), alignment of CNTs is not observed. Thus, changes in conductivity are attributed to changes in linear density of the printed CNT traces alone (see Figure S3 and Section S1.3, Supporting Information for details on CNT alignment).

### 2.3. Control of Conductivity During Printing

After printing a CNT feature, the water takes up to 20 min to evaporate, depending on the total liquid volume and \( v \), ultimately removing 95–98% of initial ink volume and leaving a layer of CNTs densified by capillary forces.\(^{[46]}\) The conductivity of the printed, dry CNTs may be described by network percolation theory. While the high CNT aspect ratio contributes to a beneficial high yield stress in the liquid ink, it also enables formation of a conductive network at a low CNT loading,\(^{[42]}\) and thereby enables printed features to span a very wide range (\( \approx 10^8 \)-fold) of DC conductivity simply by control of the printing process parameters described above.

To show the percolation scaling, using inks with \( \phi = 0.02\% \), 0.7\%, and 1\%, straight lines were printed onto a porous chromatography paper and the conductivity was measured as shown in Figure 3a. By representing both density and conductivity as products of the cross-sectional area, \( A_c \), percolation scaling laws can be applied to our data without need to measure \( A_c \) (which is challenging on substrates, for example, papers, with roughness greater than the thickness of the printed film). Percolation occurs at a linear density of \( (\rho A_c)_{\text{perc}} \approx 1.0 \times 10^{-4} \text{ mg m}^{-1} \). Above this value, the conductivity \( \sigma A_c \) increases quadratically with the linear density \( (\rho A_c) \), in which the incorporation of additional CNTs increases both the connectivity and the density of the CNT network. At \( \rho A_c = 1 \text{ mg m}^{-1} \), the scaling transitioned to a linear relationship \( \sigma A_c \approx (\rho A_c)^1 \), indicating a change in

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**Figure 2.** a) CNT ink is dispensed at an average speed \( v_{\text{ink}} \) from a nozzle of inner diameter \( D_0 \) moving at a speed \( v_{\text{nozzle}} \) over a dry substrate. b) Photographs of the experimental 3D printer writing cursive text onto a Kapton film. (c,d) As \( v_{\text{ink}}/v_{\text{nozzle}} \) is increased, the resulting denser deposition of CNTs controllably increases both the dimensionless line width, \( w/D_0 \), and (e) the electrical conductivity of the printed line.

\[
\sigma = \frac{L}{R}
\]

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**Figure 3.** a) The linear conductivity of printed CNT traces is controlled by the material deposited per area, and varies over a range of \( 10^8 \) due to percolation effects. b) Printed lines with CNT inks at different loading show enhanced opacity and increasing line edge smoothness with higher concentration of CNTs and higher \( v_{\text{nozzle}}/v_{\text{ink}} \).
electron transport, after which conductivity increases due to the increase of conductive mass alone. We observe that above this transition, the specific conductivity, \( \sigma = \sigma_0 / \rho_0 \), is approximately constant. Finally, a lower bound for the conductivity of the CNTs in the network is estimated using the constant of proportionality between \( \sigma_0 \) and \( \rho_0 \) in Figure 3a, predicting \( \sigma_{CNT} \geq 3 \, 000 \, \text{S} \, \text{m}^{-1} \) (see Section S1.4, Supporting Information for full details). This indicates that there remains a large margin of possible improvement in conductivity up to the scale demonstrated for fully-dense and aligned CNT fibers, which is 10.9 \, \text{MS} \, \text{m}^{-1}.\(^{[47]} \) and the expected conductivity of an individual CNT, which is around 100 \, \text{MS} \, \text{m}^{-1}.\(^{[48]} \) However, the much lower conductivity of our printed CNT material is expected because of residual surfactant, the higher density of CNT–CNT contacts due to their lower alignment and lower surface area of contact, and the absence of doping, which cumulatively contribute to higher CNT–CNT contact resistance (compared to aligned fibers) as well as lower carrier density within CNTs\(^{[49–51]} \) in the sparse isotropically-conductive network.

From these distinctive scaling laws, additional insights into the structure and nature of conductivity in printed CNTs can be made. First, the conductivity of the CNT network is dominated by bulk resistance rather than contact resistance,\(^{[45]} \) which is an indicator that the stabilizers in the CNT ink are not unduly preventing CNT network formation. Second, the conductivity indicates 3D percolation, showing that the CNT network retains a 3D, foam-like structure.\(^{[42,45]} \) This is likely enabled by the mechanical percolation within the ink resulting in a jammed microstructure and preventing full densification. Third, as the data for our three inks overlaps, there is again no evidence of large-scale alignment, which would have increased the percolation threshold concentration, and offset the data sets accordingly.\(^{[42]} \) These comparisons are also described in more detail in Section S1.4, Supporting Information.

Microscopic comparison of lines printed with three CNT inks at two deposition rates show key differences in morphology and detail in Section S1.4, Supporting Information. The Bond number, \( Bo = \rho g h^2 / \gamma \), as depicted in Figure 4c and Figure S8, Supporting Information. The Bond number, \( Bo = \rho g h^2 / \gamma \), evaluates the relative influence of gravity and capillary forces on maintaining the droplet shape, where \( g \) is the acceleration due to gravity, \( \rho \) is the density of the liquid ink, and \( \gamma \) is the surface tension. When the deposition rate is small, surface tension causes a contraction of the line into a hemicylindrical trace, according to

\[
\frac{w}{D_0 \tan \theta^*} = \left( \pi \nu \right)^{1/2}
\]

which we refer to as the “2D droplet model”. This is shown by a schematic inset in Figure 4c. When the deposition rate is large, gravity causes the fluid to spread laterally, as

\[
\frac{w}{D_0 \tan \theta^*} = \frac{h}{D_0 \tan \theta (\pi)^{1/2}} + \frac{\pi v D_0}{4 \, h \, \tan (\pi \nu / \rho g)}
\]

which we refer to as the “2D puddle model”. Here, \( h \) is set by the balance of gravity and surface tension, as

\[
h = \sqrt{\frac{2 \gamma (1 - \cos \theta)}{\rho g}}
\]

2.4. Ink-Substrate Interactions for Impermeable Substrates

A wide variety of substrates are useful for printed and flexible electronics, and substrate selection depends on requirements for durability, abrasion resistance, and tolerance to temperature, humidity, and/or chemical exposure.\(^{[3]} \) To understand the influence of the substrate on conductivity, feature size, and mechanical flexibility, we print CNTs onto a selection of substrates (Figure 4a,b): glossy paper, hydrophobic paper (glassine), Kapton film, vinyl ethylene-coated film, a viscose filter, polyethylene terephthalate (PET), and chromatography paper. The interaction between the ink and substrate is captured by the contact angle, \( \theta \), which represents the balance of interfacial energies between liquid ink, solid substrate, and vapor from the ink at the three phase contact line. However, differing surface morphology and texture of the selected substrates has a confounding effect with the contact angle in governing the overall ink-substrate interaction. The texture is captured by the surface roughness, \( r \), which is defined as the ratio of the true area of the surface solid compared to the normally projected area. In order to condense the menagerie of substrates to a single material parameter, we use Wenzel’s law to assemble both terms into an apparent contact angle, \( \theta^* \), where \( \cos (\theta^*) = \rho \cos \theta \). This expression predicts that roughness amplifies the effect of native surface wetting properties.\(^{[53]} \) In Figure 4, we show representative images of lines printed under identical conditions on each substrate including nozzle size (0.6 mm inner diameter), extrusion speed, and printing speed (\( \nu = 0.5 \)). We also list values of \( \cos (\theta^*) \) in increasing order from left to right, which transition from \( \cos (\theta^*) < 1 \) for impermeable substrates in Figure 4a to \( \cos (\theta^*) > 1 \) for porous paper in Figure 4b. When \( \cos (\theta^*) > 1 \), hemi-wicking\(^{[54]} \) causes increased lateral flow along the paper, contributing to spreading that is ultimately limited by the deposited fluid volume rather than the contact angle. Values of \( r \) and \( \theta \) for each substrate are tabulated in Section S1.8, Supporting Information.

From this concept of printing, a quasi-static equilibrium model was constructed to predict the width of lines based on the wetting parameter, \( \cos (\theta^*) \), and the dimensionless deposition rate, \( \nu \), as depicted in Figure 4c and Figure S8, Supporting Information. The Bond number, \( Bo = \rho g h^2 / \gamma \), evaluates the relative influence of gravity and capillary forces on maintaining the droplet shape, where \( g \) is the acceleration due to gravity, \( \rho \) is the density of the liquid ink, and \( \gamma \) is the surface tension. When the deposition rate is small, surface tension causes a contraction of the line into a hemicylindrical trace, according to
These models are compared to data in Figure 4c. Unreduced data is included in Figure S9, Supporting Information. First, we observe that all data within our printable range is within the range of the droplet model due to the small volumes and small dimensions typical for printing. The droplet model adequately predicts the scaling of the printed line widths for all tested substrates and nozzle sizes, with best agreement for intermediate values $0.05 < v < 1$. In the case of higher deposition rate, deviations from the model are attributed to more complex effects and solvent evaporation. Further details can be found in Section S1.8, Supporting Information. We note that the model is generalized to capture the influence of printing our CNT ink onto different non-wicking substrates and to classify or rank these substrates. In addition, the model assumes no specific mechanism of ink application, nor specific details of the CNT ink rheology, but only the deposited volume of ink, the surface tension of the solvent, and the ink contact angle with the substrate. Given this baseline, it should apply more widely to printing of other liquid inks, and maskless printing methods such as inkjet printing that deposit similar relative volumes of ink. This would require further study to understand the influence of wetting across different printing processes.

For a dimensionless deposition rate of $0.5 < v < 50$ on impermeable substrates, the substrate influences the width of printed lines, but does not influence the conductivity (Figure S4, Supporting Information). To understand this more, we compared the morphology of CNT lines on different substrates. In Figure 4e, optical height maps show the surface texture of the hydrophobic paper and chromatography paper before and after printing.
CNTs. The bare substrates vary in structure and roughness, showing larger voids in the hydrophobic paper and extended cellulose fibers in the chromatography paper. CNT lines printed on both substrates have similar final texture, suggesting that the finer-scale morphology of the printed CNTs is insensitive to the substrate, and hence the conductivity is also insensitive to the substrate. This is similar to results obtained in screenprinting, for which printed layers beyond a critical thickness are no longer influenced by micron-level roughness of the substrate.[55]

As a further exploration, we studied the dynamics of the printing process from extrusion to the fully dried state by monitoring the resistance of the printed trace over time. This is particularly important because even bare CNTs are well-known to have humidity-sensitive resistance.[56–58] Our results showed approximately linear drying rates for each substrate, as is expected for small volumes,[59,60] and drying times of 1–20 min for different substrates and volumes, as shown in Figure S10, Supporting Information.

Though not analyzed in detail here, we also observed the influence of the substrate on feature fidelity. In particular, we observed that less rough substrates had better feature fidelity. This was evaluated by low edge tortuosity of printed features, defined as the perimeter length of the line edge normalized by the line length, as shown in Figure S12, Supporting Information. In contrast, rougher substrates increase feature fidelity in inkjet printing when drop impact, contact angle hysteresis, and retraction of the fluid meniscus are also involved.[61]

In addition, de-wetting of ink from the substrate increases the variation of the width along a line at large scales, impacting feature fidelity, and ultimately limiting minimum feature size. The low wettability of viscose filter paper caused lines to become discontinuous at larger scales on viscose filter compared to the more strongly wetting glossy paper, limiting the minimum width of printed lines (Figure 4f, Figure S11a,b, Supporting Information). Similarly, because line edges were smooth when printing onto Kapton film, printed designs could be spaced close together without shorting between them, for instance enabling printing of spiral patterns with a fine gap (see also Figure S4g, Supporting Information).

2.5. Application of Printed CNTs to Flexible Conductors, Circuits, and Sensors

In the following sections, the fundamental ink formulation and printing process controls introduced above are applied to create functional artifacts on various substrates.

2.5.1. Conformal and Extensible Circuit Elements

Conductive traces are useful for delivering power to elements within a circuit, and flexible circuits must do this effectively during bending and twisting deformations. CNTs are known

Figure 5. a) A CNT trace was printed to spell “mechano synthesis” with b) a blue surface mount diode (1 mm in length) manually placed between words c) to illuminate when powered. d) The conductivity of printed traces is constant within 3% when bent at a radius of >1 mm, which is shown by sustained illumination of the diode when wrapping the printed artifact around containers with radii of e) 35, f) 13, g) 1.5, and h) 2.7 mm. Scale bars in (e–h) are all 10 mm.
to be piezoresistive when subjected to in-plane strain, and so here we focused on bending deformations, which generate lower material strains and can be applied to a larger variety of substrates. To this end, a CNT trace was printed onto a polyethylene terephthalate film with the name of one of our research laboratories, “mechano synthesis,” using $v = 0.07$. A gap between words held a blue surface-mount light-emitting diode (LED), which was manually placed onto wet ink immediately after printing so it adhered upon drying, as shown in Figure 5a–c. Using the relationships between material deposition rate and conductivity measured above, the words were designed to have a total resistance of $450 \pm 15 \, \Omega$, allowing the 20 mA LED to be powered by a 9V battery.

We measured the relationship between the bending radius of the substrate and resistance for printed traces with linear density of 0.2–9 mg m$^{-1}$ and radii of curvature from 0.02 mm (sharp fold) to 35 mm, corresponding to compressive strains of 1 to 0.002, respectively. Compared to the resistance of traces measured on a flat substrate (of $20 - 1200 \, \Omega$, depending on the linear density), bending the substrate to a radius of >1 mm show a change in resistance within 3% (Figure 5d). In addition, the conductivity of lines with the highest CNT linear density (9 mg m$^{-1}$) are less sensitive to bend radius even for lower bending radii. To demonstrate this consistent resistance, a sticker with printed CNT text and a LED was wrapped onto various objects including a glass vial and a fine rod, with radii of curvature of 35 and 1.5 mm, respectively (Figure 5e–h). The LED remained illuminated, suggesting compatibility of printed CNTs to conformal electronics that can be printed in a planar configuration and then applied to 3D surfaces.

2.5.2. Interactive Touch Sensor

Based on the percolation results of Section 2.3, we judged that printed CNT networks have low contact resistance, which is useful for fabrication of electrical contacts. To understand this further, the contact resistance between printed CNT traces was measured to determine the dependence on CNT linear density and on applied pressure in a single cycle. As shown in Figure 6a, the contact resistance decreases with greater applied pressure for all paper substrates. For the more compressible chromatography paper, the change is more gradual than for the stiffer glossy paper. In addition, the contact resistance is proportionally larger for lower density CNT prints (Figure 6b. Here, CNT linear density was varied by changing the CNT volume fraction in the ink, $\phi$, while the dimensionless ink deposition rate, $v$, was kept constant so the line width, and contact area, remained constant. Measurements are further described in Section S1.12, Supporting Information, along with contact behavior over several cycles of applied pressure, which shows no noticeable hysteresis.

Next, we built an interactive CNT-based button activated by contact between two printed CNT traces, inspired by children’s

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**Figure 6.** a) Contact resistance between two separately printed CNT traces when put in planar contact is measured for CNTs printed onto papers as a function of applied pressure at the contact point. Here, contact resistance is normalized by $R_m$, the resistance of the CNT trace for 1 mm of length. b) The contact resistance normalized by CNT network resistance decreases with printed linear density, indicating improved contact. c) During printing onto glossy paper, the LED, indicated by the arrow, is placed by the printer at a designed 2 mm break in the printed line, making physical and electrical contact with the still-liquid ink. d) The overall CNT circuit connected a power source, LED, and button that close the circuit to illuminate the power source. e) The LED was protected with an adhesive overlayer to prevent detachment and f) the button is made by a folded paper section holding a discontinuous line segment. g) This blue LED is used to illuminated an image of a (SpaceX Dragon) rocket blasting off when the button was pressed through an overlaid illustrated page. Photograph used in Figure 6g courtesy of NASA.
books with interactive elements enabled by embedded electronics. The touch sensor is connected to activate an LED in the circuit, after the user presses the button. During printing, the LED was put in place using the printer nozzle to fill a small, 2 mm break in the printed line, which is shown in Figure 6c and Video S2, Supporting Information. The CNT button uses an additional CNT line printed onto a folded section of paper. When digital (finger) pressure is applied to the button, it closes the circuit to illuminate the LED (Figure 6d–f). When pressure is removed, the folded paper relaxes, breaking the contact and opening the circuit. This button structure is used to create an interactive scene that was illuminated by pressing a location indicated on the page (Figure 6g).

2.5.3. A Capacitive Fluid Sensor

Last, we demonstrate the ability to sense fluid motion, leveraging the printing of CNTs onto porous substrates that can imbibe liquid. As such, a device for sensing fluid wicking speed in situ or in papyrus was fabricated onto chromatography paper by printing a three-part device including i) a CNT interdigitated capacitive sensor and with circuit elements to ii) indicate the sensor is receiving power by lighting a red LED, and iii) amplify the measured signal using a bipolar junction transistor (Figure 7a–c). Printing used \( v = 0.07 \) to maintain a high-quality printing range with well-prescribed line thickness; the printing process is shown in Video S3, Supporting Information. The

![Diagram of a capacitive fluid sensor](image)

**Figure 7.** a–c) A device for sensing fluid wicking speed is fabricated by printing a six-line interdigitated capacitive sensor with a two-sided circuit on a sheet of chromatography paper and d) directly incorporating circuit elements to amplify the measured signal. e) The two faces of the circuit are connected by conductive vias. f) A second version of the circuit uses a two-line capacitive sensor connected by wires to the main circuit. g) The height of wicking fluid is verified by video analysis, and h) measured by sensor output. After calibration, i) the wicking speed is measured within 12% (1 mm of height) for two different fluids (distilled water, isopropyl alcohol).
The capacitive sensor uses two parallel CNT lines that are on a separate sheet tethered by wire to the base circuit. For both circuits, the height of wicking fluid is measured by recording the sensor output and is verified by video analysis. The wicking followed Washburn’s Law, in which the fluid height $h \propto \sqrt{t}$ for all tests. After calibration, the fluid position and wicking speed are measured by the sensor within 12% (1.0 mm of height) for distilled water and isopropyl alcohol. The printed circuits are reusable once dry.

The capacitive sensor can also be used to interrogate droplet impact. We test this capability by adding droplets of distilled water of different volumes from 0.2 to 2 $\mu$L, which result in a sharp increase in capacitance within 50 ms of impact, followed by a steady decrease back to the baseline as the droplet spreads and dries (Figure S18a, Supporting Information). Both the initial spike and the total area under the response curve vary systematically with the total volume over the entire tested range (Figure S18b, Supporting Information). The sensor can also register addition of sequential droplets, and remains sensitive to the total volume of liquid deposited, whether that volume is added all at once together or as sequential droplets (Figure S18c,d, Supporting Information). Such a sensor could be adapted to measure the influence of droplet impact on various porous substrates, such as face masks or granular beds.

2.6. Benchmarking the Conductivity and Flexibility Achieved by Direct-Write CNT Printing

An Ashby-style plot, Figure 8, is used to compare the specific conductivity and the flexibility of the lines printed in this work to other materials. Available materials used for producing conductive traces include printable colloidal or nanoparticle metals,[66,67] metal[68] and carbon nanomaterial[68,69] foams, bulk carbon nanomaterial-based inks,[10,35,70–72] and conductive polymers including PEDOT and PEDOT:PSS composites[73–78] filled thermoplastic polyurethanes,[79] and zwitterionic polymers.[30] Also compared here are CNT-based fibers made by various spinning processes.[80] Here we only consider homogeneous conducting materials and CNT-based composites.

While the change in resistance with bending angle, and change in resistance after cyclic bending, presented here, are both typical measurements of flexibility and durability, the fine details of the measurements (e.g., bending radius, thickness of substrates and printed features, adhesion) are highly nonstandard and rarely reported in prior literature. In order to compare the flexibility of our printed ink with a spectrum of other printable inks, we compare the elastic compliance, or the inverse of the Young’s modulus, $D = 1/E$. This compliance, in addition to the thickness of printed wires and substrates, adhesion, and printed geometry, strongly influences the mechanical behavior of flexible printed electronics. A benchmark flexibility is denoted as that of the substrate. When the compliance, $D$, of a print is too small/rigid, $D_{\text{print}} < D_{\text{substrate}}$, the printed material will stiffen the entire printed artifact and suffer the brunt of applied mechanical loads, reducing compliance and leading to failures of substrate adhesion.

Here, our printed CNTs exhibit an attractive combination of conductivity and compliance. The specific conductivity and compliance of several printed/printable materials is compared.
in Figure 8. Vertical bars indicate compliance of two typical substrates for printed electronics: Kapton\(^{[34,35]}\) and paper.\(^{[31]}\) Bulk metals and metal features obtained by printing typically have excellent conductivity but low compliance compared to the substrates, while conductive polymers are generally extremely compliant (and sometimes extensible as well) but have significantly lower conductivity.

In comparison to other materials, CNT traces have a high maximum specific conductivity of \(\sigma/\rho = 1.4 \times 10^2 \text{ S m}^{-1}\) kg\(^{-1}\) and have a larger elastic compliance than the typical flexible substrates. Our printed CNT lines have a tensile modulus of 1.4 ± 0.7 GPa, an ultimate tensile strength of 38 ± 19 MPa, and a solid yield strain of 4.2 ± 2.1%, and exhibit brittle failure. Details of the mechanical characterization are included in Section S1.7 and Figure S7, Supporting Information, but, in brief, we used tensile measurements of printed CNT wires that had been carefully removed from non-porous substrates. Metal foams/aerogels have similar flexibility and slightly lower conductivity, while spun CNT fibers have similar conductivity and much lower compliance. Other printed CNTs are typically more rigid due to the use of polymeric additives such as poly(vinyl alcohol) and thermoplastics to enhance printability, with significant loss of conductivity. We note that much of the published literature data for many conductive printed inks fell below the lower bound of the plotted data, with printed CNT inks ranging down to \(\sigma/\rho < 10^{-11} \text{ S m}^{-1}\) kg\(^{-1}\). In addition, data was projected for low-density CNTs, for which mechanical properties were extrapolated from other measurements, increasing the range of possible compliance as CNT mass is reduced.

CNT lines show stable resistance over repeated folding cycles, as shown in Figure S13a and in Section S1.11, Supporting Information. On both impermeable and permeable substrates, lines made with a linear density of \(\rho A = 2.7\) mg m\(^{-1}\) have a mean percent change in resistance under 2%. This behavior continues for sparser prints with \(\rho A = 0.2\) mg m\(^{-1}\) on impermeable substrates; however, resistance changes by over 30% for lines printed onto porous substrates with the more sparse linear density of \(\rho A = 0.2\) mg m\(^{-1}\). While the influence of bending to line conductivity is important for consistent performance of flexible electronics, extension is also relevant. CNTs have much larger strain-to-failure than metals, but are also known to be piezoresistive when large in-plane strain is applied.\(^{[62]}\) Optimal stretchability requires not just a stretchable printed feature but also a substrate capable of extension, and often patterned substrate designs are used to most effectively allow macroscopic strain without damaging printed features, for example, by using cleverly designed, non-affine deformations.\(^{[20–22,34]}\)

Because minor flexion does not affect the printed CNT conductivity, we adapt the kirigami design work of Morikawa et al.\(^{[34]}\) to design and create an ultrastretchable PET substrate capable of folding and macroscale extension, with our design and measurements shown in Figure S15, Supporting Information. Using the equations presented by Morikawa et al., we tuned the simple kirigami pattern to employ only planar bending of the substrate, minimizing in-plane extension of the CNT network itself while achieving high macroscale strain. CNTs deposited on this substrate show DC conductivity with under 5% change for a single cycle deformation up to 830% (maximum) strain of the base substrate, or similarly under 5% change for 100 cycles up to 400% strain each, and under 1% change in resistance for 100 cycles at 200% strain. This extensibility can help one-time integration into devices (e.g., for thermoforming) and for repeated cycles of moderately large (<500%) strain.

3. Conclusions
We have described the development and application of a series of aqueous, surfactant-stabilized CNT inks for use in direct-write printing of electronically functional features and devices. We showed in detail how the properties of the ink determine the electrical conductivity of printed features, and the related processing capabilities (feature size, production speed) required for manufacturing success. While the extrusion-based methods presented herein are best suited to localized deposition, the ink could readily be adapted to production-scale methods, such as gravure and screenprinting, that can readily handle and benefit from the rheological properties of yield-stress fluids. Moreover, the ability to process and deposit CNTs from aqueous inks can be beneficial to the development of low-cost and wearable sensors, RFID tags, disposables, and morphable structures.

4. Experimental Section

Materials and Preparation of Carbon Nanotube-based Aqueous Ink: Carbon nanotube (CNT) inks were prepared to concentrations between 2.4 and 7.6 mg mL\(^{-1}\) of CNTs with sodium deoxycholate (DOC) surfactant to stabilize the suspensions with 2 wt% (20mg DOC g\(^{-1}\) solvent) for each suspension. The CNTs were tip sonicated for up to 10 h in water (10 mL) with DOC (0.2 g), adding more CNTs over time (24-76 mg) until the desired concentration was reached. The CNTs used (EC1.5, Mejio, Japan for 2.4 and 5.1 mg mL\(^{-1}\)) have a mean diameter of 1.5 nm and initial length of 9.4 μm.\(^{[34]}\) For the lowest concentration ink, 0.06 mg mL\(^{-1}\), a low-concentration ink was prepared and then centrifuged for long times, keeping the supernatant. For the highest concentration inks, 7.6 and 18 mg mL\(^{-1}\), Tuball (Coat E) (20 mL) was dialyzed in 5–10%wt Dowfax and dialysis tubing was placed in the reservoir and stirred for several days to concentrate the ink, using the method introduced by Maillaud et al.\(^{[33]}\) The final CNT concentration in each ink was determined using the absorbance (550 nm) of serial dilutions of the CNT ink compared to standards of known concentration with the same surfactant concentration, using Beer’s Law. Four commercial CNT inks using single-walled CNTs were printed “as-is” alongside the in-house created CNT inks for comparison: CG300 (SWeNT), Coat E (OCSiAl), and Invisicon 3500 and 3400 (Nano-C). For the inks that were prepared, CNT concentration, \(c_s\) was converted into volume fraction, \(\phi\) by dividing by the CNT mass density, \(\rho_{CNT}\), using

\[
P_{CNT} = \frac{4000}{A_s(d + \delta_{vdw}^n)} \left( n d - 2\delta_{vdw} \sum_{i=1}^{n-1} i \right)
\]

where \(A_s = 1315 \text{ m}^2 \text{ g}^{-1}\), \(\delta_{vdw} = 0.34 \text{ nm}\), \(n\) is the number of walls of the CNT, and \(d\) is the diameter.\(^{[34]}\)

Rheological Measurements: Rheological behavior of the inks was measured with a stress-controlled shear rheometer (DHR-3, TA Instruments) using a cone-and-plate fixture (20 mm diameter, 4° cone angle; TA Instruments) with adhesive sandpaper having 10 μm roughness (Trizact A10; 3M) applied to prevent slip of the fluid sample. The shear viscosity was measured by decreasing the shear rate from...
the maximum to the minimum value to allow the sample to equilibrate. Small amplitude oscillatory shear tests were performed with strain control at \( \dot{\gamma} = 1\% \) strain. Strain amplitude tests were performed at \( \omega = 1\) rad s\(^{-1}\) and the subsequent recovery test was performed at \( \omega = 1\) rad s\(^{-1}\) and \( \dot{\gamma} = 10\% \) strain to obtain a measurable signal while remaining within the regime of small (linear) deformation.

2D Printing of CNT Inks: A 3D printer (MakerGear M2, MakerGear) used a custom syringe displacement system based on a micrometer-resolution single-axis translation stage (PT1, Thorlabs) to print the CNT inks at room temperature. The printer used a 1 mL capacity syringe and sterile blunt-tipped metal needles (Sanants and Nordson). The orifice size of the needles ranged from 0.12 to 0.60 mm inner diameter (30 to 20 gauge). The lateral speed of the printhead ranged from 10 to 3 000 mm min\(^{-1}\), and the extrusion flow rate ranged from 0.2 to 9 \( \mu L \) s\(^{-1}\). After printing, samples were left to fully dry in ambient conditions for 20 minutes before further characterization. Substrates used here include regenerated cellulose (10410214, Whatman), chromatography paper (3MM, Whatman), glossy paper (Xerox digital color), hydrophobic paper (glassine, Cole Palmer), Kapton film (Major, 1 ml thickness), polyethylene terephthalate (IVict) and laminating film with heat-sensitive coating (TVH Supplies). Kapton film was roughened with sandpaper (P2000) before printing to promote ink adhesion.

Characterization: Measurements of printed line width were made using an optical microscope (Zeiss SmartZoom 5). Surface roughness was measured using a laser scanning confocal microscope (Keyence VK-X2500) and averaged over an area for each substrate. The conductivity of CNT prints was measured using an LCR meter with 4 terminal Kelvin (VK-X250) and averaged over an area for each substrate. The conductivity of CNT prints was measured using an LCR meter with 4 terminal Kelvin (VK-X250) and averaged over an area for each substrate. The conductivity of CNT prints was measured using an LCR meter with 4 terminal Kelvin (VK-X250) and averaged over an area for each substrate. The conductivity of CNT prints was measured using an LCR meter with 4 terminal Kelvin (VK-X250) and averaged over an area for each substrate. The conductivity of CNT prints was measured using an LCR meter with 4 terminal Kelvin (VK-X250) and averaged over an area for each substrate.

Functional Artifacts: Integrated circuit elements included LEDs that were 20 mA surface-mount units from a reel (Chanzon 0603 SMD LEDs, 1.6 mm × 0.8 mm), a J3Y transistor, and standard 101 and 102 SMD resistors. These were attached manually or using the printer nozzle, using the same wet CNT ink for mechanical adhesion and electrical connection.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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[1] Printed Electronics: Global Markets to 2022, Tech. Rep., 2018.
[2] A. Kamyshny, S. Magdassi, Chem. Soc. Rev. 2019, 48, 1712.
[3] S. Azoubel, S. Magdassi, ACS Appl. Mater. Interfaces 2014, 6, 9265.
[4] B. Zhou, Y. Li, D. Zhang, G. Zheng, K. Dai, L. Mi, C. Liu, C. Shen, Compos. Commun. 2019, 15, 80.
[5] B. Vigolo, C. Coulon, M. Maugey, C. Zakri, P. Poulin, Science 2005, 309, 920.
[6] W. Bauhofer, J. Z. Kovacs, Compos. Sci. Technol. 2009, 69, 1486.
[7] Y. F. Liu, M. H. Tsai, Y. F. Pai, W. S. Hwang, Appl. Phys. A: Mater. Sci. Process. 2013, 111, 509.
[8] S. Azoubel, S. Shemesh, S. Magdassi, Nanotechnology 2012, 23, https://doi.org/10.1088/0957-4484/23/34/340403.
[9] B. G. Compton, J. A. Lewis, Adv. Mater. 2014, 26, 5930.
[10] G. Postiglione, G. Natale, G. Griffin, M. Levi, S. Turri, Compos. Part A 2015, 76, 110.
[11] J. N. Rodriguez, C. Zhu, E. B. Duoss, T. S. Wilson, C. M. Spadaccini, J. P. Lewicki, Sci. Rep. 2016, 2016, 27933.
[12] V. H. Mouser, F. P. Melchels, J. Visser, W. J. Dhert, D. Gawliotta, J. Malda, Biofabrication 2016, 8, 035003.
[13] A. M’Bariki, L. Bocquet, A. Stevenson, Sci. Rep. 2017, 7, 6017.
[14] Y. Weng, M. Li, M. J. Tan, S. Qian, Constr. Build. Mater. 2018, 163, 600.
[15] E.-J. Courtial, C. Perrinet, A. Colly, D. Mariot, J.-M. Frances, R. Fulchiron, C. Marquette, Addit. Manuf. 2019, 28, 50.
[16] S. S. L. Chan, R. M. Pennings, L. Edwards, G. V. Franks, Addit. Manuf. 2020, 35, 101335.
[17] C. Xu, N. Willenbacher, J. Coat. Technol. Res. 2018, 15, 1401.
[18] G. J. Donley, W. W. Hyde, S. A. Rogers, F. Nettesheim, Rheol. Acta 2019, 58, 361.
[19] Y. Jin, W. Chai, Y. Huang, Mater. Sci. Eng. C 2017, 80, 313.
[20] D. H. Kim, J. A. Rogers, Adv. Mater. 2008, 20, 4887.
[21] D.-H. Kim, J.-H. Ahn, W. M. Choi, S.-H. Kim, T.-H. Kim, J. Song, Y. Y. Huang, Z. Liu, C. Lu, J. A. Rogers, Science 2008, 320, 507.
[22] Y. Sun, J. A. Rogers, J. Mater. Chem. 2007, 17, 832.
[23] A. C. Siegel, S. T. Phillips, M. D. Dickey, N. Lu, Z. Suo, G. M. Whitesides, Adv. Funct. Mater. 2010, 20, 28.
[24] B. Weigl, G. Domingo, P. LaBarre, J. Gerlach, Lab Chip 2008, 8, 1999.
[25] S. S. Das, S. Kar, S. Dawn, P. Saha, S. Chakraborty, Phys. Rev. Appl. 2019, 12, 054017.
[26] L. Yang, R. Zhang, D. Staiculescu, C. P. Wong, M. M. Tentzeris, IEEE Antennas Wireless Propag. Lett. 2009, 8, 653.
[27] M. Weng, P. Zhou, L. Chen, L. Zhang, W. Zhang, Z. Huang, C. Liu, S. Fan, Adv. Funct. Mater. 2016, 26, 7244.
D. E. Tristant, A. S. Zubair, P. Puech, F. Neumayer, S. Moyano, A. W. K. Ma, F. Chinesta, T. Tuladhar, M. R. Mackley, B. N. Altay, J. Jourdan, V. S. Turkani, H. Dietsch, D. Maddipatla, E. Svanholm, Ph.D thesis, Karlstad University, Karlstad 2007.

Z. Lei, P. Wu, Nat. Commun. 2019, 10, 3429.

W. Wenseleers, I. L. Vlasov, E. Coovaerts, E. D. Obraztsova, A. S. Lobach, A. Bouwen, Adv. Funct. Mater. 2004, 14, 1105.

R. Haggennmueller, S. S. Rahatekar, J. A. Fagan, J. Chun, M. L. Becker, R. R. Naik, T. Krauss, L. Carlson, J. F. Kadla, P. C. Trulove, D. F. Fox, H. C. DeLong, Z. Fang, S. O. Kelley, J. W. Gilrnn, Langmuir 2008, 24, 5070.

L. Maillaud, R. J. Headrick, V. Jamali, J. Maillaud, D. E. Tsentalovich, W. Neri, E. A. Bengio, F. Mirri, O. Kleinerman, Y. Talmon, P. Poulin, M. Pasquali, Ind. Eng. Chem. Res. 2018, 57, 3554.

D. E. Tsentalovich, A. W. K. Ma, J. A. Lee, N. Behabtu, E. A. Bengio, A. Choi, J. Hao, Y. Luo, R. J. Headrick, M. J. Green, Y. Talmon, M. Pasquali, Macromolecules 2016, 49, 681.

J. H. Kim, S. Lee, M. Wajahat, H. Jeong, W. S. Chang, H. J. Jeong, J.-R. Yang, J. T. Kim, S. K. Seol, ACS Nano 2016, 10, 8879.

E. K. Hobbie, Rheol. Acta 2010, 49, 323.

F. Mirri, A. W. K. Ma, T. T. Hsu, N. Behabtu, S. L. Eichmann, C. C. Young, D. E. Tsentalovich, M. Pasquali, ACS Nano 2012, 6, 9737.

V. A. Davis, A. N. G. Parra-Vasquez, M. J. Green, P. K. Rai, N. Behabtu, V. Prieto, R. D. Booker, J. Schmidt, E. Kesselman, W. Zhou, H. Fan, W. W. Adams, R. H. Hauge, J. E. Fischer, Y. Cohen, Y. Talmon, R. E. Smalley, M. Pasquali, Nat. Nanotechnol. 2009, 4, 830.

N. Behabtu, C. C. Young, D. E. Tsentalovich, O. Kleinerman, X. Wang, A. W. Ma, E. A. Bengio, R. F. Ter Waarbeek, J. J. De Jong, R. E. Hoogerwerf, S. B. Fairchild, J. B. Fergusson, B. Maruyama, J. Kono, Y. Talmon, Y. Cohen, M. J. Otto, M. Pasquali, Science 2013, 339, 182.

S. Zhang, S. Kumar, Small 2008, 4, 1270.

G. Ao, D. Nepal, M. Aono, V. A. Davis, ACS Nano 2011, 5, 1450.

R. M. Mutiso, Ph.D. Thesis, University of Pennsylvania, Philadelphia, PA 2013.

J. Ruhammer, M. Zens, F. Goldschmidtboeing, A. Seifert, P. Woisia, Sci. Technol. Adv. Mater. 2015, 16, 015003.

H. Yuk, X. Zhao, Adv. Mater. 2018, 30, 1704028.

P. Keblinski, F. Cleri, Phys. Rev. B 2004, 69, 180101(R).

M. De Volder, S. J. Park, S. H. Tawfick, D. O. Vidaud, A. J. Hart, J. Micromech. Microeng. 2010, 21, 12.

L. W. Taylor, O. S. Dewey, R. J. Headrick, N. Komatsu, N. M. Peraca, G. Wehmeyer, J. Kono, M. Pasquali, Carbon 2021, 171, 689.

P. L. McCuen, J. Y. Park, MRS Bull. 2004, 29, 272.

A. Zubair, D. Tristant, C. Nie, D. E. Tsentalovich, R. J. Headrick, M. Pasquali, J. Kono, V. Meunier, E. Flahaut, M. Monthoux, I. C. Gerber, P. Puech, Phys. Rev. Mater. 2017, 1, 064002.

D. Tristant, A. Zubair, P. Puech, F. Neumayer, S. Moyano, R. J. Headrick, D. E. Tsvan tolivich, C. C. Young, I. C. Gerber, M. Pasquali, J. Kono, J. Leotin, Nanoscale 2016, 8, 19668.

B. Dan, G. C. Irvin, M. Pasquali, ACS Nano 2009, 3, 835.

A. W. K. Ma, F. Chinesta, T. Tuladhar, M. R. Mackley, Rheol. Acta 2008, 47, 447.

R. N. Wenzel, Ind. Eng. Chem. 1936, 28, 988.

J. Bico, U. Thiele, D. Quéré, Colloids Surf. A 2002, 206, 41.

B. R. Altay, J. Jourdan, V. S. Turkan, H. Dietsch, D. Maddipatla, A. Pekarovicova, P. D. Fleming, M. Atashbar, ACS Appl. Energy Mater. 2018, 1, 7164.

D. Jung, M. Han, G. S. Lee, Mater. Lett. 2014, 122, 281.

A. Quellmalz, A. D. Smith, K. Elgammal, X. Fan, A. Delin, M. Östling, M. Lemme, K. B. Gylfason, F. Niklaus, ACS Appl. Mater. Interfaces 2018, 10, 41738.
[94] H. Kizil, M. O. Pehlivaner, L. Trabzon, *Adv. Mater. Res.* **2014**, 970, 132.

[95] K. S. Johansson, in (Ed: K. L. Mittal), *Contact Angle, Wettability and Adhesion*, CRC Press, Utrecht, The Netherlands **2006**, p. 339.

[96] V. A. Lubarda, K. A. Talke, *Langmuir* **2011**, 27, 10705.

[97] N. Savva, S. Kalliadasis, *J. Eng. Math.* **2012**, 73, 3.

[98] G. McHale, M. I. Newton, N. J. Shirtcliffe, *Journal of Physics Condensed Matter* **2009**, 21, https://doi.org/10.1088/0953-8984/21/46/464122.

[99] D. C. Thomas, S. D. Christian, *J. Colloid Interface Sci.* **1980**, 78, 466.

[100] A. Buganza Tepole, A. K. Gosain, E. Kuhl, *International Journal of Non-Linear Mechanics* **2012**, 47, 938.

[101] C. E. Owens, A. J. Hart, *Lab Chip* **2018**, 18, 890.