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High-Resolution Electrohydrodynamic Printing of Silver Reactive Inks

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ABSTRACT

Nano-inkjet printing using an Electrohydrodynamic's (EHD) pulsed cone-jet approach has the potential to bring affordable additive manufacturing to the micro and nanoscale. Ink technology is a major limitation of current EHD techniques. Specifically, most EHD printing processes print either nanoparticles or polymers. The materials are structurally weak and often have poor electrical or mechanical properties. For example, printing nanoparticles effectively creates a cluster of nanoparticles that must be sintered to create a continuous material. To address these issues, we have been adapting reactive inks to work with an EHD pulsed cone-jet. Specifically, we demonstrate that silver micron-scale structures can be printed using an EHD pulsed cone-jet regime. These inks produce solid structures without sintering steps and with good electrical properties.[1,2] This work shows that reactive ink chemistries can be combined with EHD printing to produce fine-resolution features consisting of solid metal without an annealing step.

INTRODUCTION

Electrohydrodynamic (EHD) inkjet printing is a robust method of additive manufacturing that has been used to fabricate 3D geometries,[3,4] organic light-emitting diodes (OLED)[5] and quantum dots,[6] and devices.[7] Recently, this process has been brought to the nanoscale to fabricate structures from nanoparticles with 50 nm resolution.[8] This additive process is particularly attractive for micro/nano-scale device fabrication because it enables direct printing of a complete device with little cost and time. However printing nanoparticles results in structures with relatively poor mechanical and electrical properties as shown by the bending of Au nanoparticle wires in Galliker et al.[9]

In this work we demonstrate the ability to use a reactive silver ink[1] in the EHD cone-jet regime to fabricate solid structures instead of clusters of nanoparticles. The typical nanoparticle inks can use a wide variety of solvents as long as the nanoparticles are properly functionalized as well as maintain a low electrical conductivity after the nanoparticles are added. In contrast, reactive inks can be more sensitive to solvent properties and even after heavy dilutions, this fluid yields a high electrical conductivity (limiting the EHD regimes that can be accessed). We show that high conductivity (~10^{-2} S/m) self-reducing silver inks can be used to fabricate structures with features sizes down to 2 µm.

EXPERIMENTAL DETAILS

Thin-walled glass capillaries were pulled to inner diameters ranging from 1 to 2 µm using a four-step micropipette puller (*World Precision Instruments* PUL-1000). 10 nm of gold is deposited on each side of the nozzle using a (*Ted Pella*, 108 Auto Sputter Coater). The capillary tip and substrate are dipped in 0.1 wt% 1H,1H,2H,2H-per-fluorodecane-1-thiol (*Sigma Aldrich*) in dimethylformamide (*Sigma Aldrich*) for 12 minutes to form hydrophobic layers with a 3 minute anneal at 100˚C to drive off residual solvent afterwards. A nozzle is then loaded with

approximately 5 µL of fluid and positioned over a substrate. Using an eight-axis stage (*Newport* 8-axis Universal Controller/Driver) the location of the tip, with respect to the substrate, is found by measuring the resistance between the tip and the substrate as the capillary is moved closer (in increments of 40 nm). Once a resistance is measured, the tip is retracted a few microns. A voltage is applied between the pipette and substrate using an amplifier (Trek 10/10B-HS High Voltage Amplifier) that amplifies a waveform signal (Keysight 33510B Waveform Generator). To fabricate the printed structures, a slightly modified version of the Ag reactive ink detailed by Walker and Lewis in 2012 was used.[1] All chemicals were used as received. 2.00 g of silver nitrate ($C_2H_3AgO_2$ – anhydrous 99 %, *Alfa Aesar*) was dissolved in 5.00 mL of 35 wt % ammonium hydroxide (NH_4OH – ACS grade, *BDH Chemicals*). The solution was then stirred for 2 minutes on a vortex mixer. 0.40 mL of formic acid (CH_2O_2 – ACS reagent ≥ 96%, *Sigma Aldrich*) was added in two steps with a quick stir at the end of each step. The ink was then allowed to sit for 12 hours before being filtered through a 450 nm nylon filter and stored at 3 ˚C (refrigerator temperature) until use. For printing, the ink was diluted with 2,3-butanediol (BD, *Sigma Aldrich*) 1:200 Ag ink:BD by volume to improve the stability of the ink for inkjet printing.

RESULTS AND DISCUSSION

The ammonia and metal salt content result in a high-conductivity solution, even at high solvent dilutions. A liquid conductivity of approximately 10^{-13}-10^{-3} S/m is required to access dripping regimes.[4] However, it has been shown that using short bursts, the cone-jet regime can be used to deposit droplets smaller than the nozzle using low conductivity fluids.[10,11] When a liquid with a conductivity ~10^{-1} S/m is used, cone-jet breakup occurs meaning that at some distance, L_j away from the capillary tip, a deviation from a "perfect" cone-jet will occur.[12] Within the liquid plume (for substrate-nozzle separations > L_j), spot sizes of the deposited materials will increase linearly, whereas for a perfect cone-jet, spot sizes would be relatively independent of height. As seen in Figure 1, for large substrate-nozzle separations (10 µm), the spot size is very sensitive to voltage, but as the nozzle is moved closer, the spot size is much more constant across an array of voltages.

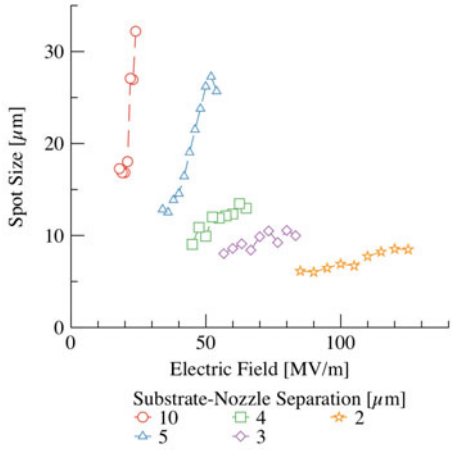

Figure 1. Printed spots with a 1.29 μm inner diameter nozzle using 200:1 2,3-butanediol to silver ink. Notice how the closer the nozzle is to the substrate, the smaller the effect of increasing voltage has on droplet spot size.

Viscosity and vapor pressure are the most important parameters to consider when choosing a solvent to decrease the metal loading. In theory, surface tension is also important but lowering the threshold for liquid ejection is not particularly important for our application, and liquid wicking up the capillary is avoided through a thiol coating. For EHD printing in the nanodrip regime, very low vapor pressure solvents (<150 Pa) can be used at room temperature since the falling droplets are much smaller than 1 μm in diameter. Similar vapor pressures are required for our setup, however with a pulsed cone-jet approach it is necessary to use a heated substrate to drive off the solvent. 2,3-butanediol is the chosen solvent, with a vapor pressure of 27 Pa and viscosity of 47 mPa·s. A high viscosity is chosen in order to slow the flow rate within the capillary, to lessen the amount of material deposited per burst. In principle, this could also be achieved by applying a back pressure within the nozzle.

Continuous silver lines are printed without the use of a hydrophobic coating. If a decreased line width was desired, a coating could be used and it would be necessary to print lines using an array/offset methodology, and backfilling any gaps to avoid discontinuous lines. The printing methodology for both spots and pillars seen in Figure 2-3 is a repeated sequence of 10 50 μs bursts, followed by a 2s wait time to allow drying on a heated substrate of 72˚C. Ten bursts is chosen since it produces an observable amount of material under an SEM. Figure 2, demonstrates the importance of substrate-nozzle separation. At first, printing is initiated at 3 μm away, yielding a very large initial spot size (>10 μm). As the material builds up in z, the nozzle is moved as well to show the much finer feature resolution achieved with <1 μm between the nozzle and material. Figure 3 is printed maintaining a separataion of <1 μm, by moving the nozzle upwards during printing.

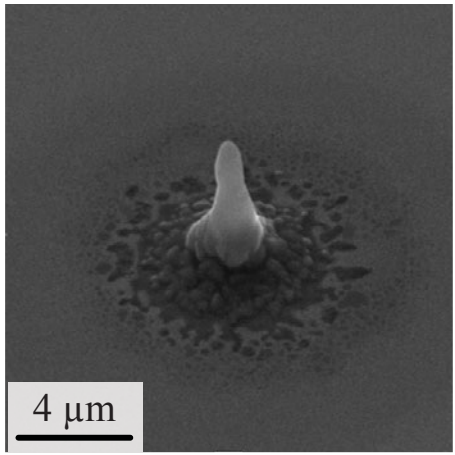

Figure 2. Printed pillar with a 1.29 μm inner diameter nozzle using 200:1 2,3-butanediol to silver ink at a substrate temperature of 72˚C. Notice the large spot size of the base, when the capillary is held at a constant height. As material is built up, the electric field strength felt at the capillary tip increases, and the separation between the top of the structure and nozzle decreases. This results in a finer resolution at the top of the structure.

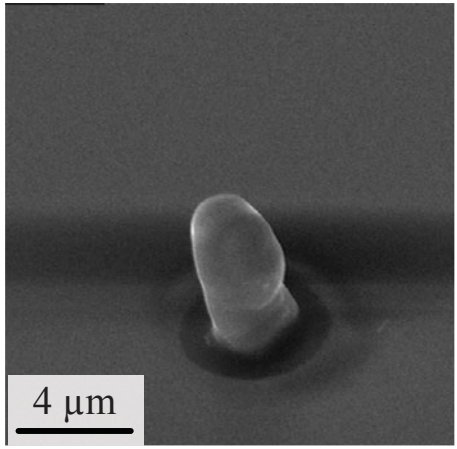

Figure 3. Printed pillar under same conditions as Figure 2, except the nozzle begins closer to the substrate and is brought upwards during printing. Notice the small base in comparison to Figure 2, because a small separation between the tip of the nozzle and top of the printing structure is maintained.

Pulsed cone-jet exhibits behavior of decreasing spot sizes with increasing frequencies, due to relaxation of the liquid meniscus.[10,11] From Figure 4, it is evident that this trend is not explicitly seen in our inks. Higher frequencies show larger spot sizes, but this is likely due to the

fact that each pulse does not dry before the subsequent one, creating the illusion of a larger spot size. An increased substrate temperature would be necessary to improve the printing speed, and eliminated the need for a wait time between bursts, but this would increase the risk of clogging.

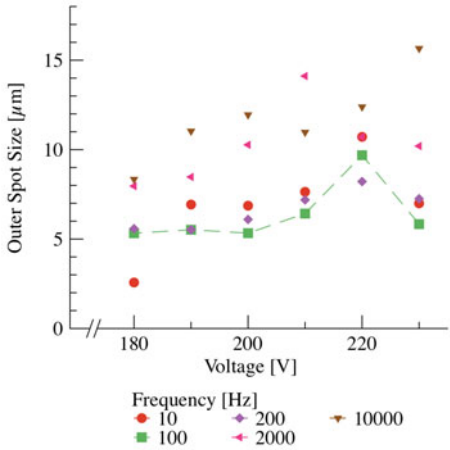

Figure 4. Printed spots with a 2.40 μm inner diameter nozzle using 200:1 2,3-butanediol to silver ink at a substrate temperature of 72˚C. A 100 Hz frequency was chosen for experiments since it produced the smallest spot size, in general (denoted by the dashed line). The irregularity, and lack of trend for larger frequencies could be due to the fact that this is approaching the limit that would be close to applying a continuous pulse.

CONCLUSIONS

We have demonstrated that high electrical conductivity, self-reducing silver inks can be used to fabricate high-resolution features using an EHD printing platform. This printing process results in solid, continuous structures without an annealing step. Substrate-nozzle separation has a significant effect on the variation of spot size with increasing electric field. When the capillary tip is brought within 3 μm of the substrates, 20-30 MV/m can be traversed corresponding to less than a 20% increase in spot size. Future work will involve developing a model relating substrate-nozzle separation and voltage to spot size for highly conductive fluids.

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