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Ultra near-field electrohydrodynamic cone-jet breakup of self-reducing silver inks

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ABSTRACT

Ultra near-field electrohydrodynamic (UNF-EHD) jetting of highly conductive self-reducing silver inks is investigated and compared to a theoretical cone-jet breakup model. While models connecting spray angle to fluid properties exist for large substrate-nozzle gap and inks with high ionic conductivity, little is known about the validity of these models when operating under UNF conditions. Using a pulsed cone-jet approach, data on the effects of nozzle height, applied voltage, and waveform (pulse length, pulse frequency, number of pulses/bursts, and delay between bursts) on spot size were collected showing high conductivity inks have a feature resolution very dependent on substrate-nozzle gap.

1. Introduction

Electrohydrodynamic (EHD) jetting is a robust, electric-field driven technique with numerous uses including thin film deposition [1], nanoparticle synthesis [2], and processing living organism suspensions [3]. In this process, liquid is dispensed from a capillary under application of a large electric field. Depending on fluid properties, applied electric field strength, and capillary shape, various flow regimes [4–6] can be accessed to create individual droplets from nm to mm in diameter [7], long fibers [8,9], or atomize fluids [10,11]. Of the numerous fluid properties that impact flow regime, fluid conductivity is closely tied to both the accessibility of different regimes [12] along with the stability of the jet [13]. Specifically, studies have shown that Coulombic repulsion and jet destabilization increases as fluid conductivity increases, with complete jet destabilization occurring as fluid conductivity exceeds approximately 10^{-3} S/m [14,15].

To avoid jet destabilization and improve feature resolution, most EHD inks consist of polymers [16] or colloidal nanoparticle solutions [6,14] dispersed in a non-polar solvent. While the nanoparticle inks have their utility fabricating plasmonic structures [17] or ultra-fine electrical interconnects [18], the net result of these dispersions is a cluster of particles that require additional thermal annealing to improve their mechanical and electrical properties [19]. Some of these inks can be susceptible to oxidation [20]; however, low temperature Ag nanoparticle inks [21] have been developed without significant oxidative issues [22]. Replacing particle-based inks with self-reducing reactive inks has the potential to eliminate the annealing step while also improving material properties. These inks are often easier to synthesize than nanoparticle-based inks [23] and low temperature reactive inks have been developed for Ag [23], Cu [24], and Al [25,26] that can deposit reasonably pure metals at temperature below 150 °C and with electrical properties close to those of bulk materials.

The limited research on EHD printed reactive inks largely focuses on very dilute reactive inks with very low conductivity (10^{-8} S/m–10^{-6} S/m) [27] and no information exists on the behavior of concentrated reactive inks where the high concentration of polar reactants and ionic species increases the conductivity of the ink to the point that Coulombic repulsion causes early jet destabilization [13]. In this study, the relationships between substrate-to-nozzle separation distance in the ultra-near field (UNF), applied voltage, electric field strength, and spot size were determined to show that an existing model for electrospray cone-jet breakup [13] accurately predicts the plume angle for reactive inks even in the ultra near-field condition. Our results verify that Coulombic fission occurs almost immediately as the fluid exits the nozzle with spray angle increasing with increasing electric field strength. This is in sharp contrast to the nano-drip EHD regime accessible to low-conductivity fluids, where droplet size is nearly independent of small changes in nozzle heights [6]. While neither the micro-drip or nano-drip regime could be accessed for the self-reducing silver ink used in this study, we do show that fluids with a high electrical conductivity can still be used to deposit fine features consisting of self-reducing ink even as it sprays with a 40° cone angle.

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Overall, this work demonstrates the ability to use a self-reducing, reactive silver ink [23] in the EHD cone-jet regime to deposit spots down to 5 µm in outer diameter. A Coulombic repulsion model for jet breakup was validated to explain relationships between fluid properties, applied voltage, nozzle height, and observed outer spray diameter.

2. Experimental methods

2.1. Ink synthesis

The room temperature, self-reducing silver reactive ink detailed by Walker et al. was used as a starting point for the reactive ink used in this study [23]. In this study, silver nitrate was used instead of silver acetate to increase the reduction temperature of the ink and reduce nozzle clogging without having to overly dilute the ink. 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 min on a vortex mixer. 0.40 mL of formic acid (CH_2O_2; ≥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 h before being filtered through a 450 nm nylon filter and stored in the dark at 3 °C until use. For printing, the ink was diluted with 2,3-butanediol (BD, $C_4H_{10}O_2$, 98%, *Alfa Aesar*) at a volumetric ratio of 1:200 base Ag ink:BD (0.11 wt% Ag) to improve the stability of the ink for inkjet printing. An ink dilution, coupled with a hydrophobic layer at the capillary tip (discussed below), greatly reduces clogging, allowing for prints lasting on the order of hours even with the nozzle held 2 µm above a 72 °C heated substrate. Fluid conductivity was measured after ink preparation with a conductivity probe (SevenExcellence, *Mettler Toledo*).

2.2. Jetting process

Thin walled 750 µm inner diameter (ID) glass capillaries (TW100F-4, *World Precision Instrument)* were pulled to IDs ranging from 1 to 2 µm using a four-step micropipette puller (PUL-1000, *World Precision Instruments*). Approximately 10 nm of gold was deposited using a DC sputter coater (108 Auto Sputter Coater, *Ted Pella*). A n-type single-sided silicon wafer substrate was used with a 50.8 mm diameter, ⟨100⟩ orientation, 0.001–0.005 Ω-cm resistivity, and 280 µm thickness (ID 2270, *University Wafer*). The capillary tip and substrate were dipped in 0.1 wt% 1H,1H,2H,2H-per-fluorodecane-1-thiol ($C_{10}H_5F_{17}S$, 97%, *Sigma Aldrich*) in dimethylformamide (C_3H_7NO, ≥99.8%, *Sigma Aldrich*) for 12 min to form hydrophobic layers with a 3 min anneal at 100 °C to drive off residual solvent [15]. A nozzle is then loaded with approximately 5 µL of the diluted reactive ink using a stainless steel dispensing needle (6710A38, *McMasterCarr*) and positioned over a substrate. No fluid delivery system was used during loading or printing to increase the flow rate or apply a specific pressure. To avoid damaging the tip prior to printing, the approximate substrate nozzle separation was determined using an optical microscope. The actual nozzle height was determined at the end of the print by incrementally moving the substrate upwards towards the nozzle (40 nm/increment) while monitoring the electrical resistance between the nozzle and the substrate. The nozzle height was set to 0 µm once the resistance dropped below 10,000 Ω. To ensure that any x/y movements were accurate, it is necessary to take into account that the substrate will not be perfectly flat. An optical displacement sensor (ZW-Series, *Omron*) was used to measure the height at four different locations on the substrate, all spaced 5 mm apart. From these measurements dz/dx and dz/dy were calculated such that for any movement in x/y, the nozzle height would be adjusted to account for the slope of the substrate.

A pulsed, square-wave voltage signal was applied between the pipette and substrate using a signal generator (33510B Waveform Generator, *Keysight*) connected to a high-speed, high-voltage amplifier (10/10B-HS High Voltage Amplifier, *Trek*). The rise and fall times of the output amplifier waveform were measured using an oscilloscope (DSO-X 3024A, *Agilent Technologies*). A schematic of the waveform used in this study is shown in Fig. 1 that consisted of a burst of pulsed square waves with a wait time between each set of pulses. For each substrate-nozzle separation tested, 100 V was chosen as the starting voltage, and it was increased in increments of 10 V. This allowed all tests to begin at approximately the turn-on voltage. The nozzle was held stationary while the substrate position was controlled using a *Newport* 8-axis Universal Controller/Driver connected to a custom 3-axis stage (xyz) setup. An image of the EHD setup is annotated in Figure S1.

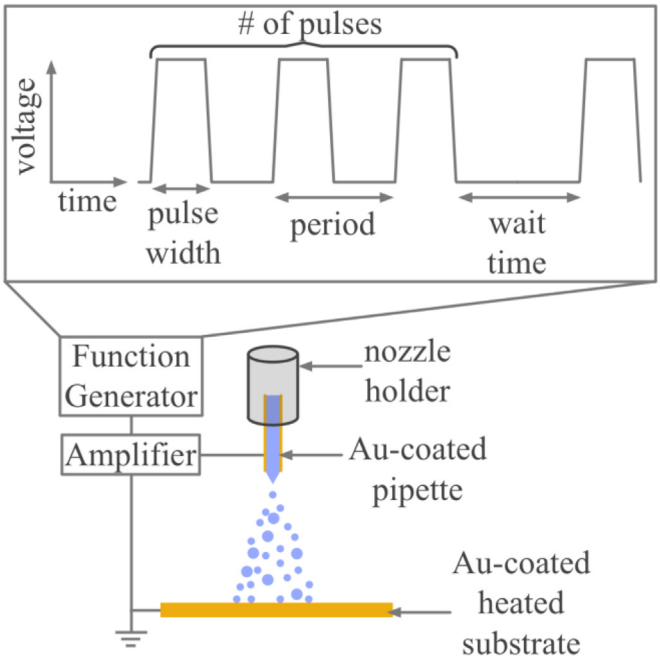

Fig. 1. Schematic of the experimental setup using a pulsed voltage to emit a spray of droplets. The input waveform consisted of a number of pulses followed by a wait time. The amount of pulses/burst was selected such that an observable amount of material was deposited. A wait time was used to ensure that adequate drying time was provided to ensure accurate spot size measurements.

The substrate was kept at 72 °C to ensure that solvent evaporation occurred before subsequent bursts were deposited and allow for faster deposition times. Additionally, the nozzle was regularly purged approximately every 5 min for 10 msec at 1000 V with a nozzle height of 200 µm.

2.3. Characterization

Morphology was characterized using an Amray 1910 Field Emission Scanning Electron Microscope (FESEM) at 20 kV accelerating voltage and a working distance of 5 mm for top-down images. An Apollo XPP Energy Dispersion Spectrometer (EDS) operating at 20 kV was used to collect spectra of a printed dot.

3. Results and discussion

As liquid conductivity increases, the EHD nano-drip, micro-drip, and dripping regimes associated with low flow rates and low electric field strengths are no longer accessible [14,16,17]. In this work, we modified the self-reducing silver reactive ink developed by Walker et al. to work with ultra near-field EHD jetting to deposit solid silver 2D dots with diameters down to 5 µm despite cone-jet breakup. Specifically, the silver acetate was replaced with silver nitrate and the dilution levels were increased to 200:1 (2,3-butanediol:base silver ink). These changes keep the reactive silver ink from reducing and clogging the 1 µm nozzles used in this study. Even when diluted 200:1, the ammonia and