Tip-assisted electrohydrodynamic jet printing for high-resolution microdroplet deposition

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HIGHLIGHTS
• A novel method of tip-assisted electrohydrodynamic (EHD) printing for printing higher-viscosity solutions is proposed.
• High printing resolution can be obtained owing to tip-assisted enhancement effect of electric field intensity.
• Controllable micropatterns with sizes smaller than the nozzle inner diameter are realized by tip-assisted EHD technique.

ABSTRACT
The controlled patterning of microdroplets or microwires at precise positions plays an essential role in micro/nano device applications. In this context, we propose a novel and efficient method called tip-assisted electrohydrodynamic (EHD) printing that combines the tip-assisted electric field intensity enhancement effect and the high-resolution capability of EHD printing. The tip-assisted electric field enhancement effect is first systematically investigated by simulation analysis. Under optimized experimental conditions, we obtain microdroplet arrays and microwires down to sizes of 2.3 μm and controlled micropatterns composed of droplet arrays or microwires with sizes smaller than the inner diameter of nozzle by means of the tip-assisted technique. We find that with our designed tip-assisted nozzle, solutions with a high viscosity of ~2000 cps can be extracted from the nozzle, and the printing resolution can increase by nearly five times the current resolution. Our results demonstrate that tip-assisted EHD printing provides a potential and flexible method for precision and controlled manufacturing of micropatterns.

1. Introduction
Micro/nano-patterned structures composed of functional droplets and micro/nanowires play a key role across a broad range of applications such as flexible electronic devices [1–3], flexible displays [4,5], biosensing [6,7], and biological tissue engineering [8–10]. In order to fabricate controllable droplet arrays and patterned structures, researchers have developed several methods for preparing droplets and fabricating micro/nanowires. The typical techniques reported mainly include photolithography [11,12], template-assisted methods [13,14], and inkjet printing [15–17]. Among these methods, photolithography has been widely used owing to its higher manufacturing resolution of <100 nm [18]. However, its application is limited by the shortcomings of expensive equipment, its time-consuming nature and complicated chemical processing steps, and high cost of masks [19]. The template-assisted method in conjunction with traditional micro/nano methods...
such as inkjet printing offers high flexibility and is suitable for processing multiple materials [20-22], but the disadvantages of high cost, complex manufacturing process, and short service life restrict its development. Meanwhile, inkjet printing is a type of bottom-up direct fabrication method, wherein droplets are ejected through thermal or acoustic forces. Inkjet printing enables precisely positioned microdroplet arrangements with different functional materials, and it is inexpensive, mark-free, and lends itself to mass production [23-25]. With the abovementioned advantages, inkjet printing can overcome the drawbacks of photolithography, which also requires etching and stenciling processes [26]. However, inkjet printing still faces two major challenges: limited resolution and clogging [27,28]. When compared with the manufacturing resolution of photolithography, the conventional inkjet printing yields lower resolutions, with a minimum resolution of 20–20 μm [25,29,30]. Meanwhile, functional high-viscosity ink is difficult to print, and the use of finer nozzles to reduce the size of patterned structures can lead to nozzle clogging [23,31].

As one type of inkjet printing, electrohydrodynamic (EHD) printing affords unique advantages and numerous potential applications [32,33]. This method utilizes the application of an electric field (generated by a DC voltage) between the nozzle and the substrate instead of thermal or acoustic forces [34], and charged ink is induced as a jet or droplets onto the substrate. In particular, the electric field intensity has a significant impact on the resolution; the increased electric field intensity due to a higher working voltage or smaller nozzle–substrate gap distance allows for the ejection and deposition of smaller droplets and finer micro/nanowires [35]. In contrast to the conventional inkjet technique, uniform droplets or micro/nanowires with sizes significantly smaller than the inner diameters of the nozzles can be generated to realize the printing of high-viscosity functional inks [36]. Although EHD printing can effectively overcome the limitations of the nozzle diameter in achieving high-resolution results, the technique still requires a fine glass nozzle subsequent to gold-plated treatment to enhance its conductivity [25], which can be cumbersome in terms of nozzle fabrication. Further, the clogging problem still occurs when high-viscosity inks are printed by using a very fine nozzle. In this context, nozzle design plays an important role in improving the printing resolution and device performance, and it has been the focus of considerable research attention [37]. Various novel nozzle designs such as multi-nozzle [38], multi-hole nozzle [39], and coaxial nozzle [40,41] designs have been developed and utilized in printing applications. These novel nozzles can achieve efficient parallel manufacturing and realize the fabrication of nanoscale structures with the use of hundred micrometers nozzle.

Against this backdrop, here, we demonstrate a novel and effective tip-assisted EHD printing technique to enhance the local electric field intensity, thereby improving the print resolution for higher-viscosity inks without the requirement of very-small-inner-diameter nozzles and high working voltages (of the order of thousands of volts). In our study, the tip-assisted electric field enhancement effect is systematically investigated through simulation analysis and experimental verification. Under optimized experimental conditions, we first design the tip-assisted nozzle, and we demonstrate that two solutions with a high viscosity of ~2000 cps, polydimethylsiloxane (PDMS) and UV-curing glue, can be printed by this method. More importantly, customized droplet arrays or microwires patterns with sizes smaller than the inner diameter of the nozzle (down to 2.3 μm) can be directly printed. With the assistance of the tip, a more stable jet can be generated with the application of smaller starting and working voltages, and further, the problem of nozzle clogging is avoided, with the resulting printing resolution increasing by about five times the current resolution. Further, we apply our technique to fabricate microscale structures with the use of an 80-μm nozzle, with the ratio of the nozzle diameter to droplet diameter being 36:1. In effect, we believe that this work provides a promising strategy for printing higher-viscosity functional inks with higher resolution.

2. Materials and methods

2.1. Experimental system

The schematic of the tip-assisted EHD apparatus is illustrated in Fig. 1. The setup includes a high-voltage DC power source, high precision X-Y motion stage, three-dimensional (3D) mobile platform, motion controller, and CCD camera.

The high-voltage DC power source (Tianjin Dongwen High Voltage Power Supply Plant, China) generates an electric field between the nozzle and the substrate, and this field can eject functional inks from the nozzle when the electrostatic force is greater than the ink surface tension. The positive pole of the power source is connected to the nozzle and the negative pole is connected to the grounded silicon substrate. The silicon substrate is positioned on the X-Y-direction-aligned high-precision mobile platform controlled by the motion controller (Newport ESP301, USA). A CCD camera is used to observe the deposition process of droplets and lines.

2.2. Preparation of materials and substrate

In our study, the tip was made of tungsten wire with a diameter of 20 μm after its subjection to electrochemical corrosion. The corrosion solution was 2 mol/L NaOH, and the corrosion voltage was 10 V DC. The tungsten wire was connected to the positive electrode of the power source as the anode. The stainless nozzle had an inner diameter of 80 μm and outer diameter of 240 μm, and its outer wall was laser-cut to form a channel (depth = 70 μm, length = 4 mm, and width = 50 μm). The corrodcd tungsten wire filament adhered to the groove in the outer wall (see Supporting Information, Fig. S1). PDMS (Dow-Corning, Sylgard-184, USA, 1:1 curing agent weight ratio, viscosity: 3500 cps, density: 1.03 g/cm³) and UV-curing optical glue (Norland, NOA63, viscosity: 2000 cps, refractive index: 1.56) were used as experimental materials without dilution. Opaque silicon wafers (Suzhou Research Materials Microtech Co., Ltd., China, resistivity < 0.01) were prepared for use as substrates. The substrate was ultrasonically cleaned with acetone to remove organic impurities, and it was subsequently cleaned with deionized (DI) water before experiments.

2.3. Characterization

The printing results were characterized by use of an optical microscope (OM, KH-7700, HIROX, Japan) and an atomic force microscope (AFM, Dimension Icon, Bruker, USA) with an AFM probe (OTESP, Veeco Instruments, Inc.)

3. Simulation results

To investigate the electrostatic properties of the tip-assisted EHD model, we established a 2D finite-element model of tip-assisted EHD printing using the commercial software package COMSOL Multiphysics 4.3a to simulate the electric field intensity distribution between the nozzle and the substrate. First, in the tipless version of the technique, the parameters of the nozzle inner diameter and outer diameter were set as 80 μm (Din) and 240 μm, respectively, and the gap distance between the nozzle and the substrate (Hgap) was set as 1 mm under the application of U0 = 600 V (DC). Fig. 2(a) depicts the electric field intensity and electric field line distribution between the nozzle and the substrate; we note from the figure that the maximum magnitude of the electric field intensity at the wall of the nozzle can be as high as 2.02 × 10⁶ V/m, and further, the electric field distribution between the nozzle and the substrate can be approximated as that of a uniform electric field.

For the abovementioned initial parameters (U0 = 600 V, Din = 80 μm, and Hgap = 1 mm), Fig. 2(b–d) show the variation in electric field intensity at the nozzle with working voltage U0 (with Din = 80 μm and Hgap =
1 mm); gap distance $H_{\text{gap}}$ (with $D_{\text{in}} = 80 \, \mu\text{m}$ and $U_0 = 600 \, \text{V}$); and nozzle inner diameter $D_{\text{in}}$ (with $U_0 = 600 \, \text{V}$ and $H_{\text{gap}} = 1 \, \text{mm}$), respectively. From the figures, we note that the electric field intensity ($E$) increases with increase in $U_0$ and decreases with increase in $D_{\text{in}}$ and $H_{\text{gap}}$.

In the tip-assisted mode, the tip diameter and tip length should be taken into consideration in the simulation. Consequently, with the same basic experimental parameters ($U_0 = 600 \, \text{V}$, $D_{\text{in}} = 80 \, \mu\text{m}$, and $H_{\text{gap}} = 1 \, \text{mm}$) as those utilized for the tipless mode, the tip diameter and tip length were set as 20 $\mu\text{m}$ and 0.2 mm, respectively. Ideally, the tip is inserted at the center of the nozzle, for which we can precisely obtain the distribution and change in the electric field intensity. However, in the study, the tip of the needle was not stably fixed at the center of the nozzle during the experiment. The tip is actually attached to the groove in the outer wall of the nozzle to ensure jet stability in the experiments. Therefore, the condition corresponding to the tip being attached to the outer wall of the nozzle was also considered in the simulation. As shown in Fig. 3(a) and (b), the electric field intensity distribution at the tip and the electric field line distribution under the condition of tip inserted in the center of the nozzle are identical to those under the condition of the tip attached to the outer wall of the nozzle. Even under these two different conditions, we note that the maximum magnitude of the electric field intensity at the apex of the tip is both as high as $7.1 \times 10^6 \, \text{V/m}$, which is 3.55 times that of the value obtained without the tip. Further, the electric field is uniformly distributed, as in the case of the tipless mode.

For the abovementioned initial simulation parameters ($U_0 = 600 \, \text{V}$, $D_{\text{in}} = 80 \, \mu\text{m}$, $H_{\text{gap}} = 1 \, \text{mm}$, $D_{\text{tip}} = 20 \, \mu\text{m}$, and $L_{\text{tip}} = 0.2 \, \text{mm}$), Fig. 3(c–f) illustrate the variation in the electric field intensity at the apex of the tip as a function of working voltage $U_0$, tip diameter $D_{\text{tip}}$, gap distance $H_{\text{gap}}$, and tip length $L_{\text{tip}}$, respectively. The simulation results show that the electric field intensity increases with increase in $U_0$ and decreases with increase in $H_{\text{gap}}$ and $D_{\text{tip}}$. Fig. 3(g) and (h) illustrate the variation in the electric field intensity at the apex of the tip and the nozzle, respectively, as a function of nozzle inner diameter $D_{\text{in}}$. Interestingly, there is no obvious change in the electric field intensity at the tip and nozzle with increase in $D_{\text{in}}$. As shown in Fig. 3(i), the ratio of $E_{\text{tip}}/E_{\text{nozzle}}$ can be about 7:1, which indicates that $E_{\text{tip}}$ plays a decisive role in the tip-assisted technique. Further, the change in electric field intensity caused
by an increase in $D_{in}$ exerts little influence on $E_{gap}$. As regards the tip length, when the tip extends out of the nozzle, the electric field intensity increases significantly and there is no subsequent obvious change because the volume charge density of the tip remains constant.

In order to investigate the electric field enhancement effect due to the tip, we compared the tip-assisted and tipless modes based on the following parameters: working voltage $U_0$; nozzle inner diameter $D_{in}$; and gap distance $H_{gap}$. The initial simulation parameters were as follows: $U_0 = 600$ V, $D_{in} = 80$ μm, $H_{gap} = 1$ mm, $D_{tip} = 20$ μm, and $L_{tip} = 0.2$ mm. As shown in Fig. 4, the electric field intensity with the use of the tip-assisted technique is always higher than that of the tipless one, which proves that the tip significantly contributes to the electric field enhancement effect.

### 4. Results and discussion

#### 4.1. Experiment of tip-assisted electric field intensity enhancement effect

Based on the above simulation results, we note that there is a linear relationship between the working voltage and electric field intensity; the working voltage forms one of the key factors affecting the printing resolution and printed micropatterns in our experiments. With increase in the applied voltage, the jet exhibits four modes of operation: dripping, microdripping, cone-jet, and multi-jet modes [42]. Fig. 5(a–e) illustrate the tip-assisted-EHD-printed PDMS droplets obtained with different working voltages of 400 V, 450 V, 500 V, 550 V and 600 V. When the working voltage is $<400$ V, the generated electrical force is unable to form a jet. With increase in the working voltage, the electrical...
force overcomes the surface tension, and a stable jet is generated. We note that the droplet diameter decreases from 8.34 μm to 2.27 μm while the droplet height (from the substrate) decreases from 155.37 nm to 37.57 nm. Fig. 5(f) and (g) show the AFM-scanned profiles corresponding to the printed droplets with an average aspect ratio of 0.019 and the relationship between the droplet diameter and working voltage, respectively. These results indicate that the working voltage significantly influences the jet morphology, which in turn affects the printing resolution and droplet size. Meanwhile, the droplet diameter–working voltage curve exhibits a trend similar to that of the simulation results. In tipless-mode operation, because the electrical force applied to the solution is weaker than the surface tension, charged droplets cannot be generated in the working voltage range from 400 V to 700 V. In this regard, Fig. S2 shows the optical microscope (OM) images of PDMS droplets generated with working voltages of 1000 V, 1100 V, 1200 V, and 1300 V in the tipless mode. We observe that the droplet diameter decreases from 43.7 μm to 10.8 μm. In comparison with the tipless technique, the experimental results of the tip-assisted mode show that the printing resolution can be improved by about 5 times and that the working voltage can be reduced by about 50%, which means that smaller high-viscosity droplets can be generated with lower starting and working voltages along with a large electric field intensity with the assistance of the tip. Meanwhile, a lower working voltage can guarantee stability of jet flow and reduce the generation of satellite droplets.

4.2. Influence of deposition time on droplet diameter

During printing operation in the continuous jet mode, droplets and lines are formed differently due to the difference in the moving speed of the platform driven by the DC power source. The lines consist of droplets that converge under low movement speeds of the platform [25]. Here, we remark that because of the continuous jet, the droplets deposited on the substrate are formed as the result of the accumulation of multiple small droplets, and thus, the effect of the deposition time on the droplet diameter becomes an important consideration. Fig. 6(a–d) and (e–h) depicts the deposition of UV-curing glue and PDMS droplets, respectively, for various deposition times. In this phase of the study, the
working voltage was maintained constant at 550 V, and the deposition time was varied as 100 ms, 200 ms, 500 ms, and 1000 ms. From these figures, we note that in the case where the flow rate of the solution is constant, an increasing deposition time leads to greater accumulation of multiple small droplets, which results in larger droplet diameters. We observe that the average droplet sizes range from 2.85 μm to 4.09 μm for the UV-curing solution and 4.12 μm to 6.86 μm for the PDMS solution. Further, the average droplet height ranges from 160.17 nm to 184.36 nm for the UV-curing solution and 79.87 nm to 110.28 nm for the PDMS solution. Fig. 6(k) and (l) depict the relationship between the sizes (diameters and heights, respectively) of the two high-viscosity solutions, and it can be observed that the diameter and height of the droplets increase over longer deposition times. In addition, due to the difference in surface tension and viscosity between the two materials considered, we note that the UV-curing solution forms smaller droplets than the PDMS solution and affords a greater droplet height than the PDMS solution for the same deposition time, which corresponds to a greater average aspect ratio of 0.053 for the UV-curing solution when compared with the average aspect ratio of 0.017 for the PDMS solution. Meanwhile, the PDMS droplets generate fewer satellite droplets around the main droplet because of the higher surface tension and viscosity of PDMS relative to the UV-curing glue.

4.3. Fabrication of various micro/nano-patterned structures

The above experimental results suggest that by suitably utilizing the optimized process parameters, controllable droplet arrays and microwires can be deposited to achieve complex patterns in conjunction with programming the motion of the mobile platform. More importantly, patterned structures with sizes smaller than the nozzle inner diameter can be obtained via tip-assisted EHD printing. In the next phase of the study, under the application of a working voltage of 550 V and deposition time of 100 ms, droplets were deposited in various micropatterns at specific positions on a silicon substrate with the use of the two high-viscosity solutions. For the UV-curing solution, the first patterned structure to be printed was the crisscross (or “plus”) pattern, whose details are shown in Fig. 7(a–c). In this case, the size of the design pattern was 50 μm. From the 2D AFM scan images of the patterned droplet arrays, we estimated the average droplet diameter and height to be 2.39 μm and 135.1 nm, respectively, with the average aspect ratio being 0.056. Further, due to the longer accumulation time resulting from the initial delay in the controller reading the programmed motion trajectory, the feature size of the droplet at the starting position was larger than that of subsequent droplets. The droplets at the starting position exhibited a larger droplet diameter of 3.64 μm and greater height of 193.7 nm. Fig. 7(d–f) depict the details of grid droplet arrays wherein the distance between adjacent droplets was 20 μm. Further, the average diameter and height of the droplet array patterns were 3.32 μm and 178.3 nm, respectively, with the aspect ratio being 0.054. The final patterned structure was the graphic “SIA,” whose details are shown in Fig. 7(g–i), wherein the designed pattern was 36 μm in length and 30 μm in width. The average diameter and height of the droplet array patterns were 2.61 μm and 151.9 nm, respectively, with the aspect ratio being 0.058. Thus, it was demonstrated that with stable experimental parameters, the droplets can maintain a stable aspect ratio along the horizontal and vertical directions, with the feature size of the droplets remaining unchanged.

Next, for printing the PDMS solution in the three patterned microstructures mentioned previously, we set the working voltage to be the same as that for the UV-curing solution (550 V), as shown in Fig. S3. In this case, for the crisscross pattern, the average diameter and height of the droplet array patterns were 3.34 μm and 34.1 nm, respectively. Further, the grid droplet arrays exhibited an average diameter of 4.2 μm and average height of 81.9 nm, and the average diameter and height of the droplet array patterned as the graphic “SIA” were 4.91 μm and 46.7 nm, respectively. Upon comparing the results for the two different

![Fig. 6. Effect of deposition time on droplet diameter at working voltage of 550 V. (a–d) Atomic force microscope (AFM) images of UV-curing solution for deposition times of 100 ms, 200 ms, 500 ms, and 1000 ms, respectively. (e–h) AFM images of polydimethylsiloxane (PDMS) solution for deposition times of 100 ms, 200 ms, 500 ms, and 1000 ms, respectively. (i) AFM-scanned profiles corresponding to cross-sections in (a) to (d); (j) AFM-scanned profiles corresponding to cross-sections in (e) to (h). (k) Diameters of UV-curing and PDMS droplets for various deposition times. (l) Droplet heights of UV-curing and PDMS solutions for various deposition times.](image-url)
solutions deposited on silicon substrates, we observed that the UV-curing droplet has a smaller diameter and greater height than the corresponding parameters of the PDMS solution for the same experimental parameters.

The speed of the moving platform plays an important role in determining the linear deposition results; microdroplets can be fused into lines at slow platform speeds. A slower movement rate results in greater accumulation of the jet deposited on the substrate, which eventually leads to increase in the width of the deposited lines. In our study, with suitable experimental parameters, the UV-curing microwires were deposited on the substrate with a working voltage of 550 V and platform speed of 20 μm/s. Linear patterned structures including crisscross and gridline patterns and the graphic “SIA” were formed with the use of the tip-assisted technique. Fig. 8(a–c) show the 2D AFM-scanned images, 3D AFM topography images, and AFM-scanned profile of the crisscross pattern with a set programming pattern size (length = 50 μm and width = 50 μm), respectively. The average width and height of the microwires were 2.31 μm and 55.7 nm, respectively. At each corner of the pattern, owing to acceleration and deceleration caused by change in the direction of the platform, a slower movement speed was generated and led to the fusion of a greater number of multiple small droplets, which eventually led to the formation of wider microwires; this phenomenon was observed for the other patterned structures as well. The next micropattern to be fabricated was the gridline, whose details are shown in Fig. 8(d–f); the pattern had a designed minimum grid size of 10 μm. The width and height of the gridline were 2.1 μm and 54.2 nm, respectively. The final micropattern to be fabricated was the graphic “SIA” with a designed size of 36 μm in length and 30 μm in width, whose details are shown in Fig. 8(g–i). The average width and height of the “SIA” pattern were 2.25 μm and 55.57 nm, respectively.

Next, we used PDMS solution to deposit the abovementioned patterns with the same pattern size as those of the UV-curing solution, and these results are shown in Fig. S4. The fabricated crisscross structure exhibited an average width of 2.49 μm and height of 9.6 nm. Due to the high viscosity of the printing solution, when microdroplets were fused into lines, droplets with diameters larger than the line width were also generated, particularly at the corners of the patterns. The width and height of the patterned gridline were 2.29 μm and 2.2 nm, respectively. As regards the patterned graphic “SIA,” the average width and height of the micro/nanowires were 2.09 μm and 13.6 nm, respectively. The size of the micropattern consisting of droplet arrays or microwires was less than the inner diameter of the nozzle (80 μm), which indicates that the tip-assisted EHD printing technique can be used to create high-precision micropatterns with high-density solutions.

5. Conclusion

In this work, we proposed a novel tip-assisted EHD printing method for the extraction and patterning of microdroplets or microwires. Compared with conventional EHD printing, this method overcomes the problems of the complex processing of finer glass nozzles for smaller patterns and the clogging problem encountered when printing high-viscosity solutions with finer nozzles. We first investigated the tip-assisted electric field intensity enhancement effect through simulation analysis. The effects of working parameters such as the working voltage, nozzle inner diameter, and gap distance on electric field intensity were
simulated in the tip-assisted and tipless modes. Subsequently, we experimentally examined the working voltage as a linear function of the electric field intensity to prove that electric field intensity enhancement effect can improve the printing resolution. Under optimal conditions, solutions with a high viscosity of $\sim 2000$ cps can be directly printed. A feature size of droplet or line of the size of 2.3 μm can be obtained by means of tip-assisted technique and the ratio of the nozzle diameter to the droplet diameter can be as large as 35:1. More importantly, high-density microdroplets and microwires can be patterned with sizes smaller than the printing nozzle inner diameter, which demonstrates that our proposed tip-assisted EHD printing technique offers the advantage of high-precision, highly controllable printing of high-viscosity solutions. In our method, the starting and working voltages can be decreased by use of the tip, which also improves the stability of the jet, thereby guaranteeing uniformity of the printed patterns. In conclusion, our tip-assisted EHD printing method can find potential application in the fabrication of microstructures, microlens self-assembly, and soft templates.

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Credit author statement
The authors contributed equally to this work.

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References


