Generation of picoliter droplets by pyroelectrodynamic effect

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The droplet generation under the action of the pyroelectric field created by uniform heating or cooling of the monodomain lithium tantalate plate was studied. The droplets of dielectric and conductive liquid with the volume below picoliter have been deposited on glass substrate with good reproducibility. It was shown that the drying of the dispensed colloid droplets allowed producing the uniform circular and ring-like micron-size patterns of Ag nanoparticles on the substrate. The numerical simulation of attractive force induced by pyroelectric field which is applied to the drop allowed us to explain the obtained results.

Keywords: lithium tantalate, electrohydrodynamics, pyroelectric field, dispensing

Short title: Generation of droplets by pyroelectric field

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1. Introduction

Manipulating and dispensing of the micron size droplets of various liquids is important for biotechnology, combinatorial chemistry, and new kinds of bioassays [1-4]. One more application of the micron size droplets is surface patterning with solid nanoparticles (NPs) by their sedimentation from liquid phase at liquid-solid interfaces during evaporation of dispensed colloid droplets [5-7]. The NPs patterns with certain spatial distribution on the surface are used for surface enhancement of Raman scattering (SERS) and allow realizing single molecular recognizing and creating biological sensors [8].

Different dispensing methods have been developed in past decades. Inkjet printing is an example of a well- developed microfluidic technology based on thermal or acoustic pulse formation in ink-filled chamber leading to ejection of droplets through nozzle apertures. High-resolution electrohydrodynamic jet printing, which produces 10-20-pl-volume droplets, has been realized by applying voltage between the nozzle and a conducting substrate [9]. The capillary nozzles require complicated fabrication procedures and may be subject to cross contamination. Recently, the new method of electrohydrodynamic-based droplet generation called pyroelectrohydrodynamic shooting has been reported [10, 11]. It has been shown that the local pyroelectric field, appeared as a result of local heating of a lithium niobate plate using a hot tip or an infrared laser beam, allows dispensing droplets with typical volumes about nano- and picoliters and micron-scale radii. This technique does not require electrodes, high-voltage circuit connections, or special capillary nozzles.

In this paper, we have applied the pyroelectrohydrodynamic shooting method for dispensing micron size droplets of dielectric polydimethylsiloxane (PDMS) and of conductive colloid of silver NPs in water. The uniform heating and cooling of monodomain plate of congruent lithium tantalate (CLT) allowed us to dispense the droplets with volume down to femtolitre. The spatial distribution of pyroelectric field initiating attractive force applied to the drop was estimated.

2. Experimental

Experimental setup consisted of Z-cut plate of CLT single crystal (10x10x0.5 mm^3 sizes) with optically polished polar surfaces and drop reservoir placed under the plate (Fig. 1). Monodomain CLT plate was fixed on thermoelectric cooler (TEC), which allowed us to change uniformly the plate temperature with accuracy 0.1 °C. The drop reservoir represented an initial drop deposited on the basis or capillary filled with liquid (Fig. 1). 100-mμ-thick glass substrate fixed on a motorized 2D motion driver was placed between plate and drop reservoir for droplet patterning. The CCD camera Prosilica GX1050C (Allied Vision Technologies GmbH, Germany) with frame rate up to 120 fps was used for *in situ* recording of the droplet generation process.

Two kinds of liquids have been used in this work: dielectric PDMS and conductive colloid of silver NPs with concentrations 0.1 and 0.5 g/l produced by laser ablation of pure silver target in deionized water [12]. The initial drop with minimum volume 0.5 μl was placed on the glass basis by single channel microliter pipette.

3. Results and discussion

3.1. Droplets of dielectric liquid PDMS

The initial drop was placed on glass basis under the center of Z$^+$ surface of CLT plate. Initial 2-μl-volume drop represented the layer with thickness much less than the distance *h* between CLT plate and basis. It was found that the heating of the CLT plate above 3K led to noticeable change of the drop shape. Further heating stimulated formation of liquid cone similar to the Taylor cone [13] and growth of its top. The final cone height depended on the initial drop volume only (Fig. 2). For example for initial drop with 2-μl-volume, the height of the cone was about 0.4 mm. Thus, for *h* below 0.4 mm the cone growth led to formation of liquid bridge (contact between cone top and CLT plate surface) (Fig. 2b). For *h* above 0.4 mm, after termination of the cone growth the further temperature increase led to droplet generation representing appearance of the fine microjet on the cone top and to dispensing of the separate droplets onto the plate surface (Fig. 2a). The phase diagram of PDMS drop behavior during uniform heating of monodomain CLT plate for various distances *h* between basis and plate was obtained experimentally. The critical values of ΔT corresponding to droplet generation regime increased linearly with increasing of h (Fig. 3).

These results demonstrate the ability of dispensing the liquid droplets on the surface of CLT plate, but for practical application it is necessary to pattern separate droplets with controlled distances and periods on functional substrates. For these purpose, the dielectric substrate was placed between CLT plate and a drop reservoir. The direction and velocity of substrate motion was controlled.

Linear array of periodic droplets of PDMS was patterned on glass substrate using the PDMS drop deposited on the basis and capillary filled with PDMS. The minimum diameter of droplets dispensed from the drop placed on the basis was about 200 μm and was limited by the volume of initial drop equal to 0.5 μl. Using capillary with internal diameter 0.5 mm allowed us to decrease the diameter of the dispensed droplets down to 10 μm and volume about 300 femtolitre (Fig. 4). The linear array with period about 25 μm has been produced for the substrate velocity 0.1 mm/s.

3.2. Droplets of conductive liquid – colloid with Ag NPs

The pyroelectrohydrodynamic shooting method was used for creation of the silver NPs patterns on the glass substrate as a result of evaporation of dispensed droplets of water colloid. In order to reduce the evaporation rate of the initial drop of colloid, the dispensing was carried out by pyroelectric field arising after cooling of CLT plate from 320 to 300 K. The surface of preheated plate was discharged by metal plate to exclude the temperature hysteresis of pyroelectric field [14, 15]. The initial 0.5-μl-volume drop was placed on the glass basis under the center of Z^+ surface of the CLT plate. The distance between drop top and plate ranged from 0.5 to 1 mm. The drying of the sessile droplets on the glass substrate led to formation of self-assembled Ag NPs patterns with diameter ranged from 10 to 100 μm (Fig. 5).

The obtained patterns allowed us to estimate the sizes of dispensed droplets corresponding to pico- and femtolitre scale volumes. The spatial distribution of NPs depended significantly on the droplet drying time and the concentration of NPs in colloid. Using the colloid with concentration about 0.1 g/l allowed us to realize the uniform distribution of NPs. Increasing of the colloid concentration to 0.5 g/l led to formation of the ring-like structures due to coffee-ring effect [16] (Fig. 6).

3.3. Pyroelectric field

Due to pyroelectric effect, under the chosen temperature change ΔT in the range from 300K to 320K the uncompensated bound charges appear on the polar surfaces of CLT plate with density $\sigma = \gamma\Delta T$, where γ is the pyroelectric coefficient ($\gamma = 1.4–2.3 \cdot 10^{-4}$ C m^{-2} K^{-1} for CLT at 300 K). The pyroelectric field E_{pyr} initiated by these bound charges is the driving force of micro-size droplet dispensing. The slow bulk screening of bound charges within used temperature range allows us to use this charged plate as the source of the constant field. Due to the finite sizes of the plate, the E_{pyr} arises outside the plate volume and thus creates an attractive force applied to the initial liquid drop. The numerical simulation of the spatial distributions of the electric potential V and E_{pyr} was carried out using the finite-element method (Fig. 7).

Under the action of E_{pyr} the vapor-liquid interface of the initial drop charges due to redistribution of free charges and polarization of the liquid volume. Moreover, there is a volumetric distribution of charge [13]. It leads to change of the drop shape induced by Maxwell stresses. In our numerical simulation the action of the attractive force only on surface charges produced by initial drop polarization were taken into account.

The force applied to the drop top along Z direction normal to the plate is equal to $F_z = \sigma E_z = \varepsilon_0 \chi E^2_z$, where χ is the dielectric susceptibility of the liquid. The simulated dependences of F_z on the distance from the center of the surface of uniformly heated monodomain CLT 10x10x0.5 mm^3 plate for various heating temperatures ΔT are shown in Fig. . It is seen that increase of ΔT leads to stronger forces, thus allowing to dispense the droplets from the longer distances.

4. Conclusion

We demonstrated the application of pyroelectrohydrodynamic shooting method realized on uniformly heated monodomain CLT plate for dispensing of the dielectric and conductive liquids. The developed technique does not require high-voltage circuit and hot tip or an infrared laser beam for local heating. The phase diagram of the behavior of PDMS drop placed under the uniformly heating CLT plate at different distances from its surface was measured experimentally. It was found that the critical value of the temperature change corresponding to droplet generation regime increased linearly with increasing of the distance from the plate surface. It was shown that the drying of the dispensed colloid droplets allowed producing the uniform circular and ring-like micron-size patterns of Ag NPs on the substrate. The numerical simulation of the spatial distribution of pyroelectric field and attractive force applied to the initial drop allowed us to explain the obtained results. The developed technique can be used for production of active substrates for SERS and electrode patterns with controlled geometry for polarization reversal in ferroelectrics.

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Figure captions

Fig. 1. Scheme of experimental setup for investigation of droplets dispensing.

Fig. 2. The sequence of recording frames for PDMS: a) droplet generation, b) liquid bridge formation. Time interval between frames is 6.6 ms. The bar size is 500 μm.

Fig. 3. Phase diagram of the behavior of PDMS drop placed under the uniformly heated monodomain CLT plate.

Fig. 4. Optical microscope image of linear array of PDMS droplets with volume about 300 femtolitre patterned on glass substrate from the capillary filled with PDMS.

Fig. 5. The patterns of Ag NPs formed after drying of the sessile colloid droplets on the glass substrate. Optical microscopy in dark field mode.

Fig. 6. Ring-like pattern consisting of Ag NPs.

Fig. 7. Schematic view of YZ plate cross-section with the simulated distributions of (a) electric potential and (b) E_{pyr} generated by uniformly heated monodomain CLT 10x10x0.5 mm^3 plate for $\Delta T = 4$ K.

Fig. 8. Dependences of z-component of attractive force on the distance from the center of the surface of uniformly heated monodomain CLT 10x10x0.5 mm^3 plate for various ΔT.

Fig. 1.

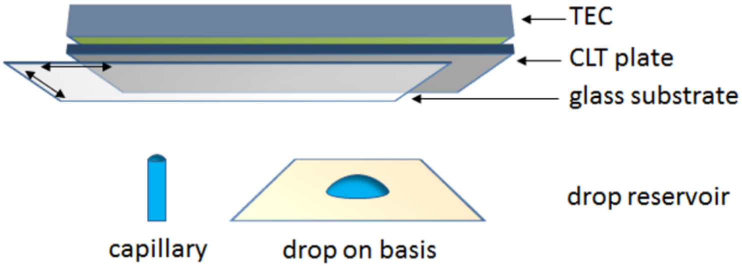

TEC
CLT plate
glass substrate
capillary
drop on basis
drop reservoir

Fig. 2.

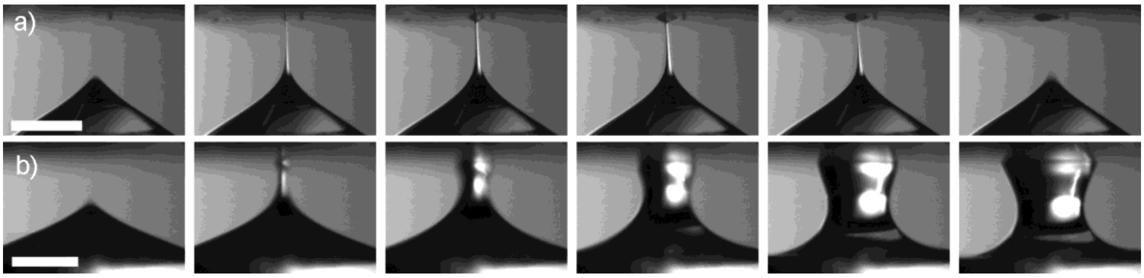
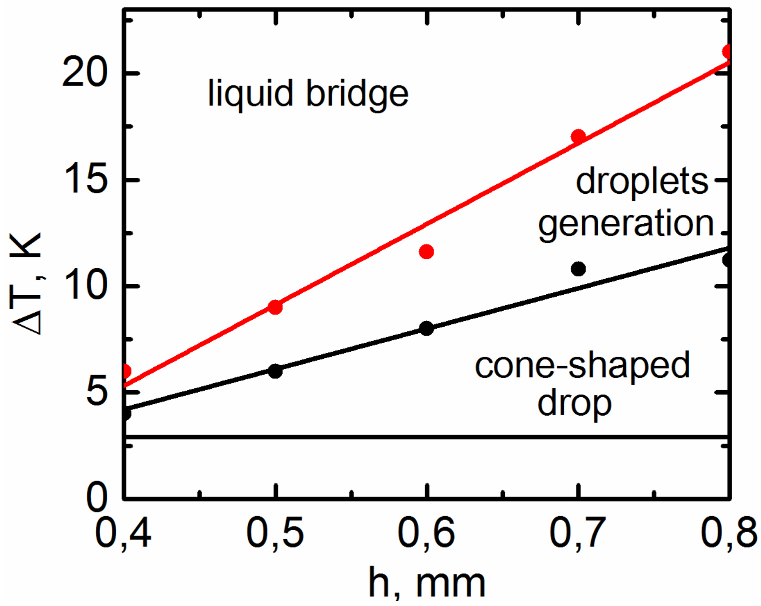


Fig. 3.



ΔT, K
0
5
10
15
20
0,4
0,5
0,6
0,7
0,8
h, mm
liquid bridge
droplets
generation
cone-shaped
drop

Fig. 4.

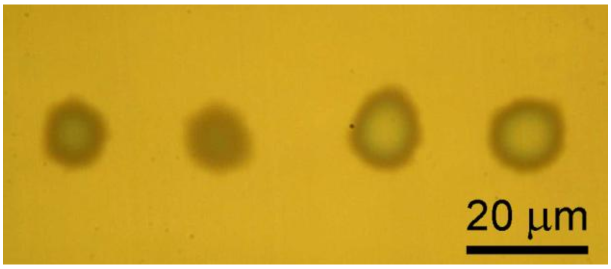


Fig. 5.

Fig. 6.

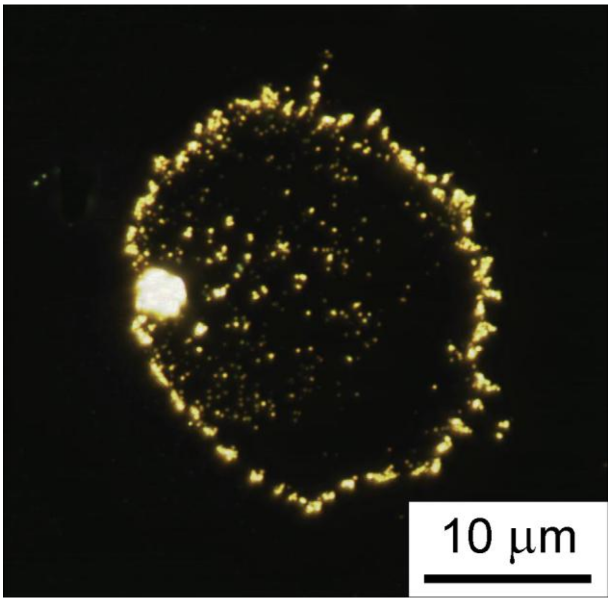


Fig. 7.

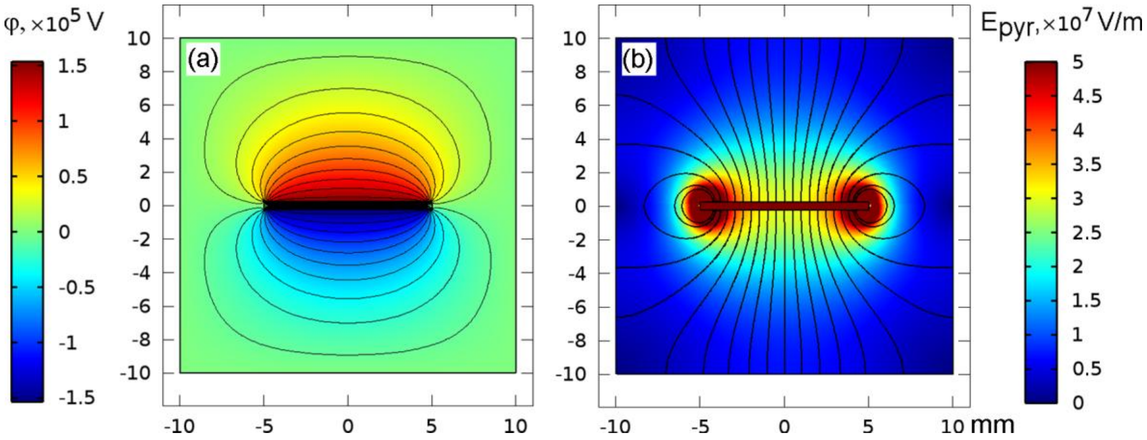

φ, ×10^5 V
1.5
1
0.5
0
-0.5
-1
-1.5
(a)
(b)
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-5
0
5
10
mm
E_pyr, ×10^7 V/m
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

Fig. 8.