Supporting Information

Electric-Field Induced Selective Directed Transport of Diverse Droplets

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Section 1. Fabrication process of RIDE, the structures of AF-HN-HS and Pure-AF-HS, and the optical characterization of the two types of electrodes

Figure S1. Fabrication process of the RIDE patterns with an ITO substrate. (a) Glass cleaning. (b) Electrode deposition. (c) Photoresist deposition. (d) Photo lithography. (e) Electrode etching. (f) Photoresist removing. The structures of the dielectric layers: (g) AF-HN-HS and (h) Pure-AF-HS. The microscope images around the center of RIDE: (i) neighboring electrode angle 10° (standard sample) (j) neighboring electrode angle 5° (larger and more complex sample).
Section 2. Comparison of the droplet transport velocities between LIHS and PTFE-based slippery surface based on the equivalent voltage method

The thicknesses of PTFE film (~20 μm) and Pure-AF-HS (~4 μm) are different. To compare the transport velocities on these two types of surfaces, we need to ensure that the EHD forces are equal for the two cases. Assuming the change of contact angles are the same \( \Delta \cos \theta = \cos \theta_U - \cos \theta_0 \), given that a voltage of \( X \) volts is applied to the PTFE film, then the voltage of \( Y \) volts applied to the Pure-AF-HS film with an equivalent EHD force can then be determined.

(1) Young-Lippmann equation of the coplanar RIDE

Yi et al.\(^1\) proposed that when a droplet is at the center of RIDE and experienced by EWOD, the change of contact angle is given by:

\[
\Delta \cos \theta = \frac{\varepsilon_0 \varepsilon_d}{2 \gamma_{lg}} \left[ \frac{A_d}{A_{total}} \left( \frac{A_r}{A_d+A_r} \right)^2 + \frac{A_r}{A_{total}} \left( \frac{A_d}{A_d+A_r} \right)^2 \right] U^2 \tag{S1}
\]

In this equation, \( \varepsilon_d \) is the dielectric constant of the dielectric layer, \( \gamma_{lg} \) is the air-liquid surface tension, \( d \) is the dielectric layer thickness, \( A_d \) is the area of droplet covering the driving electrodes, \( A_r \) is the area of droplet covering the reference electrodes, \( A_{lg} \) is the area of droplet covering the gap area between the electrodes, \( A_{total} = A_r + A_d + A_{lg} \) is the total area. \( U \) is the applied voltage. For the two types of surfaces, because their static contact angles are close (PTFE-based slippery surface ~119.5° and LIHS ~119.0°), the parameters \( A_{total}, A_r, A_d, A_{lg}, \) and \( \gamma_{lg} \) are all approximately the same, the only difference lies in \( \varepsilon_d, d, \) and \( U \) (to be calculated). Under the same \( \Delta \cos \theta \) in the EWOD mechanism, the ratio of applied voltages to the two types of surfaces is then:

\[
\frac{U_Y}{U_X} = \sqrt{\frac{\varepsilon_{PTFE}}{\varepsilon_{AF}} \cdot \frac{d_{AF}}{d_{PTFE}}} \tag{S2}
\]

in which \( \varepsilon_{PTFE} \sim 2.55, \varepsilon_{AF} \sim 1.93, d_{PTFE} \sim 20 \mu m, \) and \( d_{AF} \sim 4 \mu m. \) For simplicity, In this case, the thickness of lubricant film is neglected. Then we obtained \( \frac{U_Y}{U_X} \approx 0.514. \) In the work of Tang et al.\(^2\), \( U_X = 900 \text{ V}_{rms}, \) therefore \( U_Y \approx 462.6 \text{ V}_{rms}. \)

(2) Approximate Young-Lippmann equation of the coplanar RIDE on slippery surface

In this case, the thickness of lubricant film is considered. McHale et al.\(^3\) proposed that the contact angle change by EWOD on parallel interdigitated electrodes with SLIPS is given by:

\[
\Delta \cos \theta = \frac{\varepsilon_r \varepsilon_f}{2 \gamma_{eff} d} U^2 \tag{S3}
\]

with \( \varepsilon_r \) the effective relative permittivity of the solid dielectric with the SLIPS coating, \( d \) the total dielectric thickness, \( \gamma_{eff} \) the effective interfacial tension given by:

\[
\gamma_{eff} = \begin{cases} 
\gamma_{lg} & \text{if } s_{ai} < 0 \\
\gamma_{fo} + \gamma_{og} s_{ai} & \text{if } s_{ai} \geq 0
\end{cases} \tag{S4}
\]
In this equation, $\gamma_{lg}$ is the air-liquid surface tension, $\gamma_{lo}$ is the liquid-oil (lubricant oil) surface tension, $\gamma_{og}$ is the oil-air surface tension, and $S^0_{oi} = \gamma_{lg} - (\gamma_{lo} + \gamma_{og})$ is the spreading coefficient. An approximate equation learned from Eq.(S1) and Eq.(S3) is given:

$$\Delta \cos \theta = \frac{\varepsilon_0 \varepsilon \varepsilon r}{2 \gamma_{eff}} \left( \frac{A_g}{A_d + A_r} \right)^2 + \frac{A_r}{A_{total} (A_d + A_r)} U^2$$

(S5)

the effective interfacial tension $\gamma_{eff}$ is given by Eq.(S4).

For the two types of surfaces, because their static contact angles are close (PTFE-based slippery surface $\sim 119.5^\circ$ and LIHS $\sim 119.0^\circ$), the parameters $A_{total}, A_r, A_d, A_g,$ and $\gamma_{eff}$ are all approximately the same, the only difference lies in $\varepsilon_r, d,$ and $U$ (to be calculated). Under the same $\Delta \cos \theta$ in the EWOD mechanism, the ratio of applied voltages to the two types of surfaces is then:

$$\frac{U_Y}{U_X} = \sqrt{\frac{\varepsilon_{PTFE}}{\varepsilon_{AF}} \frac{d_{PTFE} \gamma_{oil}}{d_{AF} \gamma_{oil}}}$$

(S6)

in which $\varepsilon_{PTFE} \sim 2.55$, $\varepsilon_{AF} \sim 1.93$, $\varepsilon_{oil} \sim 2.2$, $d_{PTFE} \sim 20 \mu m$, $d_{AF} \sim 4 \mu m$, and $d_{oil} \sim 11 \mu m$ (the weight of oil was measured. The density of oil, $\sim 1.92 \times 10^3 \text{ kg/m}^3$, and the area of lubricant film on RIDE are known. Then $d_{oil}$ can be calculated, to be considered as the same in two cases). The real thickness of lubricant film under droplet cannot be measured, thus $d_{PTFE/ \gamma_{oil}} \approx d_{PTFE} + d_{oil} \approx 31 \mu m$ and $d_{AF/ \gamma_{oil}} \approx d_{AF} + d_{oil} \approx 15 \mu m$ are approximately given. According to the formula of capacitance, the effective relative permittivity of the SLIPS (and LIHS), $\varepsilon_r = \frac{\varepsilon_{dielec} \varepsilon \varepsilon r (d_{dielec} + d_{oil})}{\varepsilon_{dielec} d_{oil} + \varepsilon_{oil} d_{dielec}}$, can be calculated, thus $\varepsilon_{rPTFE} \approx 2.41$ and $\varepsilon_{rAF} \approx 2.12$ are calculated. Then we obtained $\frac{U_Y}{U_X} \approx 0.742$. In the work of Tang et al., $U_X = 900 \text{ V}_\text{rms}$, therefore $U_Y \approx 667.5 \text{ V}_\text{rms}$. As we all know, however, the real thickness of lubricant oil film covered by a droplet (especially under the influence of the electric field) must be smaller than the above ideal calculation (due to the infusing of the lubricant oil, the droplet gravity, etc.). Therefore, the actual situation is between the case (1) and the case (2) ($462.6 < U_Y < 667.5 \text{ V}_\text{rms}$).

(3) Young-Lippmann equation of parallel interdigitated electrodes

In L-DEP, the theoretical model of contact angle shift for RIDE is not yet available. We thus approximately used the model for parallel interdigitated electrodes. McHale et al.\(^9\) proposed that the contact angle change by L-DEP is given by:

$$\Delta \cos \theta = \frac{\varepsilon_0 (\varepsilon_t - \varepsilon_b)}{2 \gamma_{lg} \delta} U^2 \cdot C^2$$

(S7)

with $\varepsilon_t$ the dielectric constant of droplet, $\varepsilon_b$ the dielectric constant of bulk fluid ($\sim 1$ for air), $\delta = \frac{D_T}{\alpha}$ the penetration depth related to the electrode structure, and $D_T$ the “electrical period length”, defined as $D_T = 4d$ for parallel interdigitated
electrodes with both the electrode and the gap width \( d \). \( C = \left( \frac{4 \varepsilon_d^2 - \varepsilon_l^2}{4 \varepsilon_d^2 + \varepsilon_l^2} \right)^{\frac{2d}{\varepsilon_l}} \) is the voltage reduction factor which is the key parameter different between the two types of surfaces. In this case, the thickness of lubricant film is neglected. Under the same \( \Delta \cos \theta \) in the L-DEP mechanism, the ratio of applied voltages to the two types of surfaces is then:

\[
\frac{U_Y}{U_X} = \frac{C_X}{C_Y} = e^{-\frac{2 \pi (d_{\text{PTFE}} - d_{\text{AF}})}{d_T} \frac{\varepsilon_{\text{PTFE}} - \varepsilon_{\text{AF}}}{\varepsilon_{\text{PTFE}} + \varepsilon_{\text{AF}}} + \frac{4 \varepsilon_{\text{AF}} - \varepsilon_{\text{PTFE}}}{\varepsilon_{\text{PTFE}} + \varepsilon_{\text{AF}}} \frac{d_{\text{AF}}}{d_T}} \cdot \frac{1 + \frac{\varepsilon_{\text{PTFE}} - \varepsilon_{\text{AF}}}{\varepsilon_{\text{PTFE}} + \varepsilon_{\text{AF}}} e^{-\frac{4 \pi d_{\text{AF}}}{d_T}}}{1 + \frac{\varepsilon_{\text{PTFE}} - \varepsilon_{\text{AF}}}{\varepsilon_{\text{PTFE}} + \varepsilon_{\text{AF}}} e^{-\frac{4 \pi d_{\text{PTFE}}}{d_T}}} \tag{S8}
\]

in which \( \varepsilon_{\text{PTFE}} \sim 2.55, \varepsilon_{\text{AF}} \sim 1.93, d_{\text{PTFE}} \sim 20 \mu m, \) and \( d_{\text{AF}} \sim 4 \mu m. \) For the 10° RIDE with a droplet located at 2.5 mm from the electrode center, we obtained \( D_T \sim 1.5437 \) mm. For 2 μL n-tetradecane droplet, \( \varepsilon_l \sim 2.0, \) then \( \frac{U_Y}{U_X} \approx 0.953; \) for 2 μL 1,2-propanediol droplet, \( \varepsilon_l \sim 27.5, \) then \( \frac{U_Y}{U_X} \approx 0.655. \) Given \( U_X = 900 \) Vrms in Tang et al.,\(^2\) the calculated \( U_Y \) is 857.6 Vrms for n-tetradecane and 589.2 Vrms for 1,2-propanediol. The L-DEP calculated root-mean-square voltages are higher than that calculated by EWOD (whether or not the lubricant oil film is considered), indicating that the electric field gradient is less sensitive to dielectric film thickness. Note that the estimation based on Eq. (S8) has assumed parallel interdigitated electrodes, which might be not suitable for RIDE because the electric field gradient distribution is different.

(4) Comparison of average velocities in the experiments

In experimental validation, we refer to the calculated voltage (462.6 Vrms) in the case (1). We placed a 2 μL 1,2-propanediol droplet on 10° RIDE covered by LIHS films (Pure-AF-HS ~ 4 μm). Using a lower voltage 400 Vrms 60 kHz (see Figure 2b of the main text), results show that the average radial inward velocity is \( 0.22 \pm 0.03 \) mm/s. Compared to transport velocity \( (\leq 0.04 \) mm/s) on PTFE-based slippery surface films (PTFE film ~ 20 μm), the LIHS films shows a significant advantage for faster droplet transport.

In addition, using the simplest linear approximation, a 20 μm thick substrate with a 900 Vrms voltage corresponds to a 4 μm substrate with a 180 Vrms voltage. When applying a 180 Vrms 60 kHz voltage to the 1,2-propanediol droplet on LIHS, its measured average radial inward velocity was \( 0.044 \pm 0.008 \) mm/s (Figure S2), which is still slightly higher than the velocity of PTFE-based slippery surface.
Figure S2. Transport of a 2 μL 1,2-propanediol droplet at 180 V$_{\text{rms}}$ 60 kHz voltage on 10° RIDE. The average velocity was 0.044 ± 0.008 mm/s.
Section 3. The effect of lubricant film

In fact, the lubricant film inherently experiences a loss of lubricant oil over long-term use. Therefore, the lubricant oil can be constantly replenished as needed, without significantly affecting practical applications. In our study, the effect of lubricant film, including the mass loss of lubricant oil (evaporation, cloaking and drainage) and the effect of lubricant oil on droplet (wetting ridge), are considered in the following.

(1) Evaporation of lubricant oil

In the field of lubricant-infused surfaces, which is closely linked to the stability and reliability of devices, the evaporation of lubricant oil must be taken into consideration. The lubricant oil used for the experiment is perfluoropolyethers (PFPE), Krytox GPL 103. One of the reasons for choosing Krytox GPL 103 is its low evaporation rate. As reported by Wong et al., the evaporation rate of Krytox GPL 103 was measured to be less than 0.05% per day.10

In our work, the time of all cases of droplet transport takes less than 3 mins (relatively, the cases of n-tetradecane and 10 mM NaCl solution spend long time due to weak L-DEP or the obstruction of EWOD. In fact, most cases last between 10s and 30s), thus the evaporation of lubricant oil can be neglected.

(2) Wetting ridge

Wetting ridge is a meniscus of lubricant that forms around a droplet due to capillarity. It plays a more significant role than the cloaking layer in depleting the lubricant.4, 5, 11 A 10 mM NaCl solution droplet placed on the LIHS with wetting ridge is shown in Figure S3. In general, the lubricant film is designed to reduce the friction and adhesion of the droplet to the surface, allowing it to transport easily. The wetting ridge, which forms around the droplet, can add some resistance to the droplet's motion due to the increased contact area with the surface. However, if the lubricant is able to maintain a low-friction interface between the droplet and the surface, the wetting ridge may not significantly obstruct the droplet's transport.

In our work, the values of wetting ridge height of 5 types of droplets, $h_{\text{ridge}}$, were measured (see Table S1). As a comparison, all droplets transported in air had a volume of 2 μL, and the values of droplet height of each 5 types of droplets, $h_{\text{drop}}$, were also measured (see Table S1). The average ratios between the droplet height and the wetting ridge height, $h_{\text{drop}}/h_{\text{ridge}}$, are calculated (see Table S1). The results show that each of droplets is ten times higher than the wetting ridge, meaning that the size of the droplet is significantly larger than that of the wetting ridge, resulting in a negligible obstruction effect from the wetting ridge on droplet transport.

(3) Cloaking effect

In the field of lubricant-infused surfaces, the lubricant oil mass loss caused by cloaking cannot be ignored. "Cloaking" refers to the phenomenon where high-surface-energy working droplets draw in and encapsulate low-surface-energy lubricants. Although the lubricant film prevents contact line pinning (immobility of the three-phase contact line), it can still cause adverse
effects like encapsulating condensate droplets with lubricant, resulting in a thin layer of lubricant coating the condensate liquid.\textsuperscript{4, 6} Many studies have been conducted on the cloaking, with most of them indicating that the spreading coefficient of lubricant over the droplet, \( S_{ot}^g = \gamma_{tg} - (\gamma_{to} + \gamma_{og}) \), is the determining factor for whether cloaking occurs (mentioned in (2) of Section 2): when \( S_{ot}^g > 0 \), the working droplet will be cloaked by the lubricant oil. Instead, \( S_{ot}^g < 0 \) is desired to prevent the cloaking from happening.\textsuperscript{4-8}

In our work, the surface tension between Krytox and 10 mM NaCl solution, \( n \)-tetradecane, 1,2-propanediol, cyclopentanone, and propylene carbonate, respectively, has been measured (see Table S2. Also, the surface tensions of five liquids and Krytox are shown) by an optical contact angle meter (OCA Pro 15, Dataphysics, Germany). The values of \( S_{ot}^g \) of five cases are calculated, and only the result of 10 mM NaCl solution is positive (see Table S2). This indicates that only the 10 mM NaCl solution droplet will be cloaked in theory. According to the traditional cloaking theory, the thickness of cloaking film can be calculated:\textsuperscript{5, 12}

\[
d_{cloak} = \left( \frac{A_H R}{12 \pi \gamma_{tg}} \right)^{1/3} \tag{S9}
\]

In this equation, \( A_H \) is Hamaker constant (estimated to be \( 2 \times 10^{-20} \) J for air-solution-Krytox interface),\textsuperscript{4, 7} \( R \) is the radius of curvature of the droplet (measured to be \( \sim 0.8 \) mm), \( \gamma_{tg} \sim 18.95 \) mN/m is the oil-air surface tension. Hence, \( d_{cloak} \) can be calculated to be approximately 26 nm, indicating the mass loss resulting from the cloaking effect during the transport of 10 mM NaCl solution droplet.

<table>
<thead>
<tr>
<th>Type of droplets</th>
<th>( h_{drop} ) (mm)</th>
<th>( h_{ridge} ) (mm)</th>
<th>( h_{drop} / h_{ridge} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM NaCl solution</td>
<td>( \sim 0.074 )</td>
<td>( \sim 1.21 )</td>
<td>( \sim 16.3 )</td>
</tr>
<tr>
<td>( n )-Tetradecane</td>
<td>( \sim 0.066 )</td>
<td>( \sim 0.80 )</td>
<td>( \sim 12.1 )</td>
</tr>
<tr>
<td>1,2-Propanediol</td>
<td>( \sim 0.053 )</td>
<td>( \sim 1.03 )</td>
<td>( \sim 19.4 )</td>
</tr>
<tr>
<td>Cyclopentanone</td>
<td>( \sim 0.071 )</td>
<td>( \sim 0.90 )</td>
<td>( \sim 12.7 )</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>( \sim 0.057 )</td>
<td>( \sim 1.00 )</td>
<td>( \sim 17.4 )</td>
</tr>
</tbody>
</table>

Moreover, Chen \textit{et al.} point out that if the theoretical value of \( d_{cloak} \) was used as the average thickness of the entire cloaking layer to estimate the total volume of the cloaking layer, it is likely that there would be a significant overestimation.\textsuperscript{4} Recent studies have suggested that the size of the droplet can also affect the effectiveness of cloaking. When compared to the size of the wetting ridge, larger volume droplet are more difficult to be cloaked.\textsuperscript{13, 14} In other words, the Eq. (S9) does not consider the impact of the actual volume or height of the working droplet (e.g. a large droplet with high height, \( R \), may cause
a significant overestimation of the value of calculation), but only considers the radius of curvature. According to the spreading coefficient (negative value) of 10 mM NaCl solution, the size effect of the above case is considered. From the above data and (2) in Section 3, the average ratio between the droplet height and the wetting ridge height, $h_{\text{drop}} / h_{\text{ridge}} \approx 16.3$, indicating that the 10 mM NaCl solution droplet is considerably large in size compared to the wetting ridge (the optical image is shown in Figure 3). Meanwhile, this ratio value suggests that the lubricant oil may hardly cloak the droplet, allowing us to neglect the mass loss resulting from the cloaking during each droplet transport.

(4) Drainage

In the field of SLIPS, drainage of the lubricant film caused by droplet movement is a common occurrence. After continuous droplet movements, the shear stresses between the droplet and the lubricant film act against capillarity and cause oil to be drained away, resulting in a loss of oil (shear-driven drainage) and the destroy of the stability of lubricant film.$^{4, 15-17}$ Additionally, the lubricant may also flows out of the substrate resulting in a mass loss of oil.$^{15}$

In Movie S2, five cases of droplet transportation are shown. We can observe that after the droplet slides on the lubricant film surface, a trail is left behind due to the thinner lubricant film in that region. However, in the experiments, we also observed that after tens of seconds, the trail is refilled by the surrounding lubricant due to the lubricant's relatively low viscosity ($v \sim 80$ cSt) and the self-healing properties of the lubricant film.$^{4}$ As for the overflow of lubricant oil caused by drainage, it was not observed in all experiments, thanks to the strong capillary and affinity of Pure-AF-HS for Krytox. Moreover, it is worth mentioning that the droplet does not leave the transport platform with the lubricant oil (of course, in future applications, the droplet may leave the platform to achieve new purposes). Hence, the oil drained by the droplet movements can refill the trail rather than lost as the wetting ridge or cloaking layer in our experiments.

<table>
<thead>
<tr>
<th>Liquid Type</th>
<th>$\gamma_{lg}$ or $\gamma_{og}$ (mN/m)</th>
<th>$\gamma_{lo}$ (mN/m)</th>
<th>$S_{ot}^\theta$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM NaCl solution (l)</td>
<td>72.76</td>
<td>43.33</td>
<td>10.48</td>
</tr>
<tr>
<td>$n$-Tetradecane (l)</td>
<td>23.79</td>
<td>12.85</td>
<td>-8.01</td>
</tr>
<tr>
<td>1,2-Propanediol (l)</td>
<td>35.98</td>
<td>26.94</td>
<td>-9.91</td>
</tr>
<tr>
<td>Cyclopentanone (l)</td>
<td>28.52</td>
<td>17.52</td>
<td>-7.95</td>
</tr>
<tr>
<td>Propylene carbonate (l)</td>
<td>40.77</td>
<td>29.04</td>
<td>-7.22</td>
</tr>
<tr>
<td>Krytox GPL 103 (o)</td>
<td>18.95</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure S3. A 2 μL 10 mM NaCl solution droplet was placed on the LHIS. Under the effect of lubricant oil (Krytox GPL 103), the wetting ridge forms around the droplet.
Section 4. The feature of droplet transport velocity

On the RIDE platform, there is an interesting feature in the velocity of droplet transport. From start to the end, the velocity of radial inward TCL of droplet gradually increases at the beginning and then accelerates significantly in the later stage, and this acceleration is in a phased manner (see the blue line in Figure S4 and the NO.5 of Movie S2). Taking 1,2-propanediol droplet for example, the velocity data with interesting feature in these ranges of displacement in Figure S4, about 0 – 0.6 mm, about 0.6 – 1.0 mm, about 1.0 – 1.6 mm and about 1.6 – 2.5 mm, are clear to be observed. At about 0 – 0.6 mm, the velocity is relatively uniform. At about 0.6 – 1.0 mm, the velocity suddenly increases and then decreases. At about 1.6 – 2.5 mm, the velocity suddenly increases and then becomes uniform. At about 1.6 – 2.5 mm, the velocity increases continuously until the droplet reaches the end. The root cause of these features is the structure of RIDE: when the droplet is at the starting position, it covers a relatively small number of electrodes, and as the droplet transports radially inward, the number of electrodes covered by the droplet will increase, finally reaching the center of RIDE. As we all know, interdigitated electrodes will form an energy barrier that obstructs droplet lateral spreading when the interdigitated electrodes are applied voltage. However, during droplet transport, the droplet can overcome the energy barrier and continue to transport radially inward. With the decrease of radial distance, the gap of electrode also decreases continuously. The droplet shows a slight stuttering phenomenon (sudden instability of TCL occurs) at the distance of about 1.0 mm. But after completely overcoming this energy barrier and covering more new electrodes, the droplet gains more sources of radial inward driving force, resulting in a more significant increase in droplet velocity (see the top view of droplet transport in the NO.7 of Movie S2). When the droplet is close to the center of RIDE, the instantaneous velocity even > 120 × 10^{-2} mm/s. It should be noted that in the main text, we used the average velocity of the entire transport process instead of the maximum or instantaneous velocity.

In addition, we prepared a droplet transport platform with a smaller thickness of LIHS (Pure-AF-HS ~ 0.5 μm instead of 4 μm, Krytox layer ~ 10 μm instead of 11 μm) and conducted droplet transport experiments (droplet: 2 μL 1,2-propanediol; external voltage: 500V_{rms} of 1 kHz). On the new LIHS, the velocity of droplet was significantly improved with an average velocity of ~ 68.2 × 10^{-2} mm/s (see the red line in Figure S4 and the NO.7 of Movie S2) compared to the main experiment (velocity ~ 31.1 × 10^{-2} mm/s. LIHS: Pure-AF-HS ~ 4 μm, Krytox layer ~ 11 μm) . When the droplet is close to the center of RIDE, the instantaneous velocity even > 600 × 10^{-2} mm/s. The phased manner feature of velocity is clearer than the feature of normal LIHS case (about 0 – 1.0 mm, about 1.0 – 1.7 mm, and about 1.7 – 2.5 mm). However, in this case where the velocity is particularly high, the phenomenon of the sudden instability of TCL is not as obvious.
Figure S4. The displacement diagram of the change over time of the transport of 2 μL 1,2-propanediol droplet (external voltage: 500Vrms of 1 kHz). Blue line: normal LIHS with ~ 4 μm Pure-AF-HS and ~ 11 μm Krytox film. Red line: Thinner LIHS with ~ 0.5 μm Pure-AF-HS and ~ 10 μm Krytox film.
Section 5. Frequency-dependent droplet shape modification

Under EWOD mechanism, the response of a droplet to an external electric field applied to the RIDE can not only lead to contact angle shift, but also an electric force induced shape modification around TCL.18 Using a high-speed camera mounted on the eyepiece of an optical microscope, the TCL outlines of three types of 2 μL droplets on RIDE (covered by lubricant-free AF-HS) were characterized, namely, a 10 mM NaCl solution (conductive polar) droplet, a 1,2-propanediol (non-insulating polar) droplet, and an n-tetradecane (insulating non-polar) droplet. The TCL images with and without a voltage are compared in Figure S5. A voltage of 500 V_{rms} (or V_{DC}) at various frequencies (DC, 10 Hz, 100 Hz, 1 kHz, 10 kHz, and 100 kHz) were applied.

We combined the two microscopic images with and without a voltage in order to illustrate the effect of the voltage on TCL shape. The “overlay” and “difference” of the two images are shown as the left and right part in each picture in Figure S5. For the “overlay” picture, the dark-color area on the right represents the droplet region without a voltage. The grey-color area in the middle represents the radial inward shift of TCL with a voltage. The light-color area on the left represents substrate without a droplet. For the “difference” picture, the light-color area denotes the change of droplet TCL before and after a voltage bias.

The experiments for characterization of droplet shape modification in this section are lubricant-free due to three reasons. (1) The characterization in this case is mainly due to droplet shape change, and the droplet centroid transport is suppressed due to TCL pinning and high CAH. Droplet oscillation can be better observed in the lubricant-free case because the lubricant penetrating into the substrate can effectively enhance viscous energy dissipation and suppress droplet oscillation.19 (2) The droplet outline can be more clearly observed in the lubricant-free case because the optical scattering between the droplet and lubricant can interfere the observation of TCL change (e.g. see Figure 2c of the main text). (3) The TCL at electrode gaps can form a “reverse crescent” shape more easily in the lubricant-free case due to pinning effect due to the balance of Laplace force, radial inward driving force, and the pinning resistance force. The TCL shape modification is more difficult to be observed on surfaces with lubricants (see Figure S5b and Figure 2c of the main text). The “reverse crescent” shape at electrode gaps and the protruding shape around the electrodes indicate that the forces experienced by a droplet are along the electrode lines, consistent with simulation results by Tang et al.2 When the EHD force is smaller than a certain value, the TCL cannot move due to the surface resistance of Pure-AF-HS (Figure S5c, f ≥ 10 kHz). In summary, although the droplet TCL shape is different between the lubricant-free Pure-AF-HS and LIHS, the EHD force during droplet transport can be indirectly characterized.

Experimental results show frequency-dependent TCL shape modification. For a conductive polar droplet (10 mM NaCl solution) on AF-HN-HS, the shift of TCL and droplet transport velocity show a decrease with increasing frequency (Figure
The three types of non-insulating polar droplets (e.g., 1,2-propanediol) on Pure-AF-HS show a more significant outline modification (Figure S5b). At 10 Hz, 100 Hz, and 1 kHz, radial inward protrusion was observed at the TCL. Note that the droplets strongly oscillate at low frequencies, and the results shown in Figure S5b (ii) and Figure S5b (iii) are snapshots with most significant shape modifications, implying a strong EHD force. At $f = 1$ kHz, TCL oscillation becomes insignificant, showing a stable sharp-angled contour (Figure S5b (iv)). At $f = 10$ kHz, the TCL angles become less sharp than the 1 kHz case (Figure S5b (v)). At $f = 100$ kHz, the TCL protruding parts become blunt, with less displacement and transport velocity (Figure S5b (vi)). The study on deformed TCL shape reveals the magnitude of EHD force experienced by the droplet. Specifically, the shape change of TCL is more significant in 1,2-propanediol than 10 mM NaCl solution, which is possibly related to the surface tension. The effect of surface tension tends to pull the TCL into a spherical shape. A smaller surface tension of 1,2-propanediol (35.98 mN/m) than 10 mM NaCl solution (72.76 mN/m) thus leads to a less smooth TCL outline for 1,2-propanediol.

For the case of insulating non-polar droplets (e.g., n-tetradecane) on Pure-AF-HS, the TCL shape modification is insignificant (Figure S5c). Given its small surface tension (23.79 mN/m), the reason for the TCL shape can be attributed to the small L-DEP force experienced by the droplet ($\epsilon_d \approx 2$). The TCL displacement at 10 kHz and 100 kHz is almost negligible accompanied by a small transport velocity (Figure S5c (v2) and Figure S5c (vi2)).

Finally for the case of a DC voltage, TCL modification was observed for all three types of droplets, but their transport velocity is not high. On the one hand, some droplets contain free charges preventing radial inward transport. On the other hand, the DC voltage induced EHD force is damped by static friction while the AC voltage induced EHD force is damped by (typically smaller) dynamic friction. Additionally, a DC voltage is also prone to charge trapping into the surface, affecting the TCL spread. Therefore, the TCL outline in DC is not a good judgement for the EHD force and transport velocity.

In summary, the displacement and shape modification of a TCL is frequency dependent. In relative low frequency regimes, radial inward movement of TCL is obvious (note the radial outward end of TCL might also move radially outward). The interplay between the EHD force and surface tension might result in multi-angular shape of TCL. As frequency increases, the radial inward movement of TCL is suppressed and its shape becomes more smooth and spherical. By monitoring the change in TCL, the EHD force and the droplet transport velocity can be indirectly reflected under an AC voltage, which is not the case for a DC voltage.
Figure S5. TCL shape modification with and without an applied voltage for a 2 μL (a) 10 mM NaCl solution, (b) 1,2-propanediol, and (c) n-tetradecane droplet on AF-HS platform. The 10° RIDE was applied with a 500 Vrms (or VDC) voltage at various frequencies (DC, 10 Hz, 100 Hz, 1 kHz, 10 kHz, and 100 kHz). The shapes of radial inward TCLs were characterized by a microscope. The left (1) and right (2) parts in the same picture were the “overlay” and “difference” of microscopic images processed in Photoshop between droplets with and without a voltage, respectively. The average velocities of droplets at corresponding frequencies were shown under each image.
Section 6. Tangential effect of gradient electric fields on liquids

Studying in parallel interdigitated electrodes system, McHale et al. believed that L-DEP force could shape the liquid-vapor (or liquid-liquid) interface, suggesting L-DEP force could help to obtain static undulations surface (“wrinkles”), which can be used to create voltage programmable amplitude phase gratings. If the liquid is in the very thin film scale, the free charges would accumulate along the edges of each parallel interdigitated electrode line, leading to a shape of the liquid-vapor interface of the liquid film follows the near field shape (higher harmonics). Therefore, in this section, the liquid film which can be shaped by electric field was used to confirm the electric fields simulation of RIDE experimentally. In short, the insulating photoresist OrmoStamp (Micro Resist Technology GmbH, Germany) liquid was spin-coated on Pure-AF-HS (10° RIDE), got UV curing in AC electric field and then got characterization to obtain its 3D data. In this experiment, a 4 μm thick AF-HS is one of the conditions of droplet transport, making the electric field that shaped the photoresist topography equal to the electric field that drove droplet transport.

In order to ensure the photoresist could be steadily spun on the 4 μm thick Pure-AF-HS (extremely hydrophobic), the Pure-AF-HS was treated with reactive ion etching (15 W for 2 min. Ion: oxygen) by reactive ion etcher (ME-6A, Institute of Microelectronics, Chinese Academy of Sciences). The larger CAH (CAH ~ 78.1°, advance contact angle ~ 113.4°, recede contact angle ~ 35.3°) showing more hydrophilic of the Pure-AF-HS after treating. ~ 5 mL photoresist liquid OrmoStamp (viscosity ~ 0.41 Pa·s, dielectric constant ~ 6.821) was placed on the Pure-AF-HS and spin-coated (5000 rpm for 65 s) using big spin coater (AC300-CTM, LEBO science, China). With 10° RIDE connecting to external power supply and applying AC voltage (500 Vrms 10 kHz. In AC electric field, the L-DEP effect lead to the topography shaping), the sample with photoresist film was placed into an UV curing device (UV-30-DC, HOURS, China) for UV curing for 15 min at the same time. After voltage off and UV off, the sample was thermally cured on an electric hot plate at 85 °C for 50 min and UV cured for 25 min at last. The topography of radial “wrinkles” was easy to observe through the naked eye (Figure S6a) and characterized by 3D surface metrology system (DCM8, Leica, Germany) (Figure S6b-c).

The 3D topography results show: (1) the photoresist molecules will gather along the two edges of each long electrode line, forming a “channel” (uplifted on the left and right side but depressed in the middle); (2) in the radial direction from outside to inside (i.e., RIDE center), the aggregation degree of photoresist molecules will first decrease, then increase, and finally decrease; (3) the electrode gap area which is far from the RIDE center gets a pattern protruding towards the electrode center (like a lying wave crest or a ripple of lake).

The comparison of the 3D topography result and the electric field simulation result (Figure. 1j) shows that they are qualitatively consistent with each other.

(1) In the direction of the circular reference line centered at the RIDE center (or tangential. It’s called “tangential” in the
following), there are an increasing electric field gradient from the center line of the electrode gap to the edge line of the electrode line, and an increasing electric field gradient from the center line of the electrode line to the edge line of the electrode line. The above each tangential electric field gradient is stronger than the radial electric field gradient at the same reference scale. And the tangential electric field gradient is confirmed due to the photoresist molecules gathering along two edge lines of electrode line (Figure S6c), revealing the strong L-DEP tangential effect induced by two edge lines of electrode line could form and bound the satellite droplets at low-frequency AC electric field (Movie S1).

(2) The simulation of electric field gradient (Figure 1j) shows that the electric field gradient would be larger when the liquid is closer to RIDE center, which also means the centripetal force would be stronger. The 3D topography results (Figure S6b-c) shows that the photoresist molecules far away from the RIDE center mainly gather along the edge line of the electrode line, while the photoresist molecules closer to the RIDE circular area are less (like a “yellow ring area”), suggesting the photoresist molecules of the “yellow ring area” have transported centripetally (means the “first decrease” of aggregation degree), and gathered to the edge of RIDE circular area (means “then increase” of aggregation degree). In addition, lack of center-neared simulation, most of the photoresist molecules of the RIDE circular area had transport to outer area, i.e., the edge of RIDE circular area (means “finally decrease” of aggregation degree), while just a small number of photoresist molecules of the RIDE center stay to form a small “hill”.

(3) The simulation of electric field gradient (Figure 1j) shows that the electrode gap area which is far from the RIDE center get more weak electric field gradient in radial direction leads its photoresist molecules to transport mainly toward the edge line of electrode line (tangentially) instead of radially inward, while the radial inward transport of photoresist molecules that further from the edge line of electrode line (e.g., the area around the center line of the electrode gap) is more obvious. Therefore, the radial inward transport distance of photoresist molecules at the center line of the electrode gap furthest from the edge of the electrode line is the longest, and the radial inward transport distance decreases in the direction of the electrode gap, resulting in a convex horizontal shape toward the RIDE center.

In summary, the experimental and the simulation results confirm each other, which is helpful for us to have a deeper understanding of the physical mechanism of droplet transport. Moreover, the above simulation result also explains the “wrinkles” of lubricant oil film when the external voltage is applied.
Figure S6. After curing, the topography of photoresist film shaped by AC electric field was characterized. (a) The radial “wrinkles” was easy to observe through the naked eye. The characterization using 3D surface metrology system was showed: (b) the whole view and (c) enlarged view of a part of cross section.
Section 7. Characterization of heating effect during droplet transport at different frequencies

In order to study the Joule heating and heat dissipation during various droplet transport, we characterized the temperature field for 2 μL droplet transport of 10 mM NaCl solution, 1,2-propanediol, and n-tetradecane by an Midwave Infrared Thermal Camera (FLIR A6700, Teledyne FLIR, US) at 500 Vrms AC voltage with frequencies $f = 1$ kHz, 100 kHz, and 400 kHz (Figure S7–S9). The slender electrode line connecting the RIDE center and radiating electrode is named the electrode main line. By controlling the position and orientation of the RIDE, the position and orientation of the electrode main line can be determined, which then affects the distance between the droplet and the main line of electrodes, and the observation of temperature field. Two experimental phenomena can be summarized as follows.

(1) As the frequency increases, the heating phenomenon of the electrode main line became more obvious, while the surrounding long electrodes did not show any significant heating phenomenon. This may be related to the design of the electrode pattern (from the overall design, as the connection part between the central radial electrode and the input electrode, the slender electrode main line actually has a resistance that cannot be ignored, and because the partial voltage of the RC circuit over the resistance increases with the increase of frequency, the electrode main line has a great probability of producing Joule heat).

(2) As the frequency increases, the temperature of the droplet also increases. This may be mainly affected by the heat conduction effect of the central electrode (especially the electrode main line), as the droplet does not seem to have an obvious heating phenomenon when moving away from the electrode main line. This heat transfer phenomenon causes a temperature difference between the radial inward and outward ends of the droplet, which may also affect droplet transport.

The results of temperature field characterization support a preliminary inference about the influence of high-frequency electric fields on droplet transport: when the input energy remains constant, as the frequency of the electric field increases, energy is increasingly dissipated in the heat loss between the electrode and the droplet. This heat loss indirectly reduces the energy used to drive droplet transport, thereby affecting its efficiency.
Figure S7. Temperature field characterization for a 2 μL 10 mM NaCl solution droplet driven radially inward by a 500 Vrms voltage at various frequencies. The main line of electrodes was placed horizontally on the side nearby and oriented 45° from the view (temperature range: 15.0 °C − 30.0 °C; OFF: no voltage; ON: voltage applied). (a) At \( f = 1 \) kHz, the droplet was placed on the right side and the change of temperature was negligible. (b) At \( f = 100 \) kHz, the droplet was placed on the right side and the rising temperature of the electrode main line was moderate. (c) At \( f = 400 \) kHz, the droplet was placed on the right side and the rising temperature of the electrode main line was strong. (d) At \( f = 400 \) kHz, the droplet was placed on the electrode main line and heated by the electrodes.

Figure S8. Temperature field characterization for a 2 μL 1,2-propanediol droplet driven radially inward by a 500 Vrms voltage at various frequencies. In (a-c), the electrode main line was placed horizontally on the side nearby and oriented perpendicular to the view. And in (d), the electrode main line was placed horizontally on the side nearby and oriented 60° from the view. The droplet was placed on the right side in the beginning (temperature range: 15.0 °C − 30.0 °C; OFF: no voltage; ON: voltage applied; 10 s: droplet transport at the 10th second). (a) At \( f = 1 \) kHz, the change of temperature was negligible. (b) At \( f = 100 \) kHz, the electrode main line and the droplet were both heated. (c) At \( f = 400 \) kHz, the electrode main line and the radial inward part of the droplet were both strongly heated, especially at the 10th second. (d) At \( f = 400 \) kHz, the droplet was placed farther away from the electrode main line than the droplet in (a-c), resulting in less heating.
Figure S9. Temperature field characterization for a 2 µL n-tetradecane droplet driven radially inward by a 500 Vrms voltage at various frequencies. The electrode main line was placed horizontally on the side nearby and oriented perpendicular to the view. The droplet was placed on the right side in the beginning (temperature range: 15.0°C – 30.0°C; OFF: no voltage; ON: voltage applied). (a) At $f = 1$ kHz, the change of temperature is negligible. (b) At $f = 100$ kHz, the electrode main line and the droplet were both heated. (c) At $f = 400$ kHz, the electrode main line and the radial inward part of the droplet were both strongly heated.
Section 8. List of physical properties of diverse liquids

Table S3. List of liquid parameters

<table>
<thead>
<tr>
<th>Liquid type</th>
<th>Conductivity (μS/cm)</th>
<th>Permittivity</th>
<th>Surface Tension (mN/m)</th>
<th>Density (10^3 kg/m³)</th>
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<tr>
<td>10 mM NaCl solution</td>
<td>118.5</td>
<td>80.1</td>
<td>72.76</td>
<td>1.001</td>
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<tr>
<td>n-Tetradecane</td>
<td>0</td>
<td>2.0</td>
<td>23.79</td>
<td>0.763</td>
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<tr>
<td>1,2-Propanediol</td>
<td>0.004</td>
<td>27.5</td>
<td>35.98</td>
<td>1.040</td>
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<tr>
<td>Cyclopentanone</td>
<td>0.55</td>
<td>13.6</td>
<td>28.52</td>
<td>0.951</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>0.046</td>
<td>66.1</td>
<td>40.77</td>
<td>1.189</td>
</tr>
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<td>Glycerol</td>
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<td>61.15</td>
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<td>Krytox GPL 103</td>
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<td>2.2</td>
<td>18.95</td>
<td>1.920</td>
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REFERENCES


(20) McHale, G.; Brown, C. V.; Newton, M. I.; Wells, G. G.; Sampara, N. Developing Interface Localized Liquid Dielectrophoresis