Supporting Information

Inkjet Printing Micro/nanopatterned Surface to Serve as Microreactor Arrays

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Figure S1. The advancing contact angles (ACA), equilibrium contact angles (CA), receding contact angles (RCA) for the (a) plasma-treated, (b) untreated, (c) ATPS-treated, (d) PFOS-treated, and (e) OTS-treated substrates.

The advancing contact angle (ACA), equilibrium contact angle (CA), and receding contact angle (RCA) on the plasma-treated substrate are $41.2^\circ \pm 3.2^\circ$, $33.5^\circ \pm 4.8^\circ$, and $18.0^\circ \pm 5.7^\circ$, respectively. The ACA, CA, and RCA on the untreated substrate are $60.7^\circ \pm 2.6^\circ$, $55.4^\circ \pm 3.4^\circ$, and $26.6^\circ \pm 3.8^\circ$, respectively. The ACA, CA, and RCA on the ATPS-treated substrate are $78.2^\circ \pm 2.5^\circ$, $68.7^\circ \pm 3.0^\circ$, and $39.3^\circ \pm 3.8^\circ$, respectively. The ACA, CA, and RCA on the PFOS-treated substrate are $90.0^\circ \pm 2.4^\circ$, $88.1^\circ \pm 2.9^\circ$, and $78.2^\circ \pm 2.3^\circ$, respectively. The ACA, CA, and RCA on the OTS-treated substrate are $100.3^\circ \pm 2.4^\circ$, $98.4^\circ \pm 1.3^\circ$, and $93.3^\circ \pm 1.9^\circ$, respectively. Although the volume of the droplets for measuring CA is larger than that of the printed droplets, the influence of droplet size on the contact angle could be negligible. It has been established that there exists a capillary length, denoted $\kappa^{-1}$, beyond which the shape of the drop will be flattened by gravity $^1$. For small droplets of radius less than $\kappa^{-1}$, gravity is negligible and the capillary force is the only factor to come into play. For large droplets of radius exceeding $\kappa^{-1}$, gravitational effect dominates. The capillary length can be calculated by $\kappa^{-1} = \sqrt{\gamma / \rho g}$ $^1$. For H$_2$O, the calculated capillary length is $\sim$2.7 mm and the critical volume is $\sim$80 µL. The CA values were measured from droplets with a volume of 2 µL, which is far smaller than the critical value. Therefore, the CA values should be the same as the printing droplets with a smaller volume (10 pL).
Figure S2. Calculated $D_0 \cdot V^{-1/3}$ for printed droplets on the substrates with different equilibrium contact angles. The initial contact diameter ($D_0$) of the droplets gradually decreases with increasing equilibrium contact angle.

Figure S3. Optical microscope images of the printed droplets on (a) PFOS- and (b) plasma-treated substrates.

Because the CA of the plasma-treated substrate is much lower than that of the PFOS-treated substrate, the printed droplets are easier to spread on the plasma-treated surface (Figure S1). The initial size of the droplets printed on PFOS-treated substrate is much smaller than that on the plasma-treated substrate (Figure S2, S3).
Figure S4. Time sequence of optical captures displaying that the diameter of the droplets does not change until the end of the process. The initial concentration of the particle is 0.3 wt%.

The TCLs of the droplets on the plasma-treated substrate are fixed and the diameter of the droplets does not change until the end of the process where a sharp decrease in diameter is seen shortly before fully drying. Ring-shape depositions are formed after drying. Ring-shape depositions are formed after evaporation due to the outwards capillary flow.

Figure S5. Deposition morphology on (a) plasma and (b) PFOS-treated substrates. The initial concentration is 3 wt%.

On the plasma-treated substrate, the nanoparticles are prone to deposit on the edge of the droplets (Figure S5a). In contrast, densely packed assemblies are formed after the droplets evaporation on the PFOS-treated substrate (Figure S5b).
**Force analysis of the particles during evaporation procedure.**

The competition between capillary force and attractive force determines the sliding or pinning of the three-phase contact line (TCL) of an evaporating particle-laden droplet. For an evaporating droplet, the TCL recedes on the substrate when the contact angle reduces to the receding contact angle ($\theta_R$). While receding, the TCL moves inwards and encounters the particles within the droplet. The liquid surface deforms along the particle surface, which generates forces induced by Laplace pressure ($F_p$) and surface tension ($F_s$) exerted on the particle (Figure S6a)\(^1\).

![Figure S6.](image)

**Figure S6.** (a) Schematic representation of meniscus deformation along the particle surface at the receding contact angle ($\theta_R$). The deformed liquid surface generates forces exerted on the particle, which are induced by Laplace pressure ($F_p$) and surface tension ($F_s$), respectively. (b) Scheme for the competition of capillary force from TCL and attractive force from substrate to a particle.

As illustrated in Figure S6a, the liquid surface deforms and generates a new meniscus along the particle surface. $F_p$ directs to the particle center and can be calculated as follows:

$$F_p = \int \frac{2\gamma}{R} ds = 2\pi\gamma R \cos^2 \beta \quad (1)$$

$F_s$ is the force along the air-liquid-particle contact line. Their resultant force ($F_S$) also directs to the particle center and can be calculated as:

$$F_S = \oint \gamma d\ell = 2\pi\gamma R \cos \beta \cos (\beta + \alpha) \quad (2)$$

Where, $\gamma$ denotes the surface tension of the liquid; $R$ signifies the radius of the particle and $\alpha$ refers to the contact angle of liquid on particle.

Both $F_p$ and $F_s$ reach the maximum value as $\beta$ approaches to zero, i.e. the liquid surface
wraps up the semisphere. Therefore, the maximum resultant force \( F \) is

\[
F = 2\pi \gamma R (1 + \cos \alpha)
\]  

(3)

The horizontal component force \( (F_h) \) acts as a driving force to push the particle moving inwards, denoted as the capillary force \( (F_{cap}) \). The vertical component force \( (F_v) \) induces an attraction force \( (F_{att} = fF_v) \) between the particle and substrate, which prevents the movement of the particle.

Therefore, we obtain

\[
F_{cap} = F_h = 2\pi \gamma R (1 + \cos \alpha) \sin \theta_R
\]

(4)

\[
F_{att} = fF_v = 2f\pi \gamma R (1 + \cos \alpha) \cos \theta_R
\]

(5)

Where, \( f \) denotes the attraction coefficient between the particle and substrate. For the elastic contact, \( f \) is 0.2~0.5.

According to Equation S4 and S5, \( F_{cap} \) and \( F_{att} \) mainly depend on the liquid surface tension \( (\gamma) \), the radius of particle \( (R) \), the wettability of particle \( (\alpha) \) and the receding contact angle of substrate \( (\theta_R) \). A substrate with higher \( \theta_R \) tenders larger driving force and lower attractive force for the sliding behavior of the TCL, which is favorable for the movement of the particle together with the sliding TCL.

![Figure S7](image)

**Figure S7.** (a) The adhesive force between the suspension and the substrate as a function of the \( \theta_R \) of the substrate (with particle concentration of 3 wt%). (b) The adhesive force between the suspension and the substrate as a function of the particle concentration.

On substrate with \( \theta_R \) of \( \sim 0^\circ \), the adhesive force between the suspension and the substrate impedes the TCL to recede and induces a ring deposition. When the \( \theta_R \) of
substrate increases from ~ 0°, 18.0° ± 5.7°, 39.3° ± 4.9°, 67.2° ± 3.6° to 78.2° ± 2.3°, the adhesive force between the suspension and the substrate decreases from 992.8 ± 74, 668.3 ± 98, 472.8 ± 72, 397.8 ± 46 to 181.7 ± 21 μN. Along with the increase of particle concentration, the adhesive force between the suspension and the substrate increases.

References