Supplemental Information: Fabrication and characterization of a scalable surface textured with pico-liter oil drops by Jalali, White, Marti and Sheng

S1. Measurement of Surface Tensions
The pendant drop method is used to measure the surface tension between air and crude oil as well as air and 5% (v/v) crude in hexadecane. The surface tension measurements over time are shown in Fig. S1. The 5% crude-hexadecane mixture is measured for 8 hours when the surface tension has reached its equilibrium at about 24.5 mN/m, whilst the surface tension of crude is only measured for three hours due to the drop detaching from the needle at the end of experiment. Upon detachment, the surface tension of crude-air is approximately 21.75 mN/m that is much lower than that of 5% crude-hexadecane mixture. However, the two systems have similar initial surface tensions; the surface tension of 5% crude hexadecane mixture starts at 26.5 mN/m in comparison to that of crude at 27 mN/m. As time evolves, the surface tension of both liquids reduces exponentially. This trend can be attributed to the adsorption of oleophilic particles within crude onto interface that reduces surface energy. The decay rate decreases with the particle

![Graph](a)

![Image](b)

![Image](c)

![Image](d)

**Fig. S1** In (a) the surface tension of a crude – air and 5% crude in hexadecane – air surface using the pendant drop method is plotted versus time. In (b) and (c) 5 μl sessile drops of crude oil and hexadecane, respectively, are shown on OTS-coated printing substrate. The surface is clearly oleophilic with comparable apparent contact angles for crude and hexadecane drops. For comparison (d) showcases a water drop over the same substrate showing hydrophobic characteristics.
concentration, i.e. 5% crude-hexadecane mixture has higher equilibrium surface energy than 100% crude. Although the decay rates and equilibrium surface tensions differ substantially with respect to the volume concentration of crude, the surface tensions within the printing time scale (e.g. < 10 min) remain largely the same. (i.e. 25.5 mN/m for crude and 26.25 mN/m for mixture). Therefore the difference in surface tensions for the crude and crude-hexadecane mixtures within the time scale of printing vary only about 1%, and the changes in surface tension are less likely to cause spontaneous contact-line pinning. Additionally, macro sessile drops over the printing substrate (e.g. OTS treated glass) of crude and hexadecane show similar contact angles. This observation provides comforts in our assertion that contact line pinning is less likely resulted from intrinsic material properties.

**S2. Model for Self-pinning Drops by Particles at Contact Line**

**S2.1 Brief description on model.**

When a particle is adsorbed at the contact line (in Fig. 9a and 2), a capillary force will be exerted on the liquid film to counteract the spreading of the drop (or the contact line). When the number of particles is sufficiently large, the capillary force is large enough to pin the contact line completely. This self-pinning by particles can be best elucidated graphically as Fig. 9a and described mathematically as

\[
\cos^2 \theta = \frac{S}{\pi \sigma_{LV} \phi_L},
\]  

where \( \phi_L = \frac{rN_L}{\pi R} \) is termed as the line packing fraction, a dimensionless number indicating the fraction of the contact line with equivalent radius of \( R \) occupied by solid particles of mean radius of \( r \). Here \( N_L \) is the total number of particles at the contact line, \( S \) is the initial spreading coefficient, and \( \sigma_{LV} \) is the equilibrium surface tension between liquid and vapor. With a fixed line packing fraction, \( \phi_L^* \), relation S1 predicts a maximum apparent contact angle, \( \theta^* \). If the apparent contact angle of a drop exceeds \( \theta^* \), the contact line will move; if the angle is less than \( \theta^* \), the drop will be pinned.

**S2.2 Relate line packing fraction, \( \phi_L \), at contact line to volume packing fraction, \( \phi_V \)**

The relation (Eqn. S1) can be rewritten in terms of volume packing fraction, \( \phi_V \), a dimensionless quantity representing the fraction of the total volume occupied by particles. One can define the volume packing fraction as

\[
\phi_V = \frac{4\pi r^3 N_V}{V},
\]  

(S2)
where $V$ is the volume of the drop, and $N_V$ is the number of particles contained within the drop. Assuming a spherical cap of a pico-liter drop with contact line radius of $R$, the apparent contact angle, $\theta$, is related implicitly to droplet volume, $V$, as the following 

$$V = \frac{\pi R^3(2-3 \cos \theta + \cos^2 \theta)}{\sin^3 \theta}$$

(S3)

To relate $\phi_L$ to $\phi_V$ we must relate $N_L$ to $N_V$. We utilize the relation that the number concentration (i.e. number of particles per unit volume), $n_V = \frac{N_V}{V}$, is simply as

$$n_V = n_L^3,$$

where $n_L$ is the number concentration per unit length and can be approximated as $n_L = \frac{N_L}{2\pi R}$. Hence, we obtain $N_V$ in terms of $N_L$ as $\left(\frac{N_V}{V}\right) = \left(\frac{N_L}{2\pi R}\right)^3$. Recalling that $\phi_L = r N_L / \pi R$, the above relation can be expressed in terms of $\phi_L$,

$$\left(\frac{N_V}{V}\right) = \frac{1}{8} \left(\frac{\phi_L}{r}\right)^3 \quad \text{or} \quad \frac{r^3 N_V}{V} = \frac{1}{8} \phi_L^3.$$

Substituting the above relation to Eqn. S1, we relate the $\phi_V$ with $\phi_L$ as

$$\phi_V = \frac{\pi}{6} \phi_L^3.$$  

(S4)

Hence, the relation between apparent contact angle and line packing fraction can be obtained by substituting Eqn. S4 into Eqn. S1 as the following form

$$\cos^2 \theta = \left(\frac{S}{\sigma_{LV}}\right) \left(6\pi^2 \phi_V\right)^{-\frac{1}{3}}$$

(S5)

or the more intuitive form:

$$\cos^6 \theta = \frac{1}{6\pi^2 \phi_V} \left(\frac{S}{\sigma_{LV}}\right)^3.$$  

(S6)

The relation (Eqn 6) show a power law dependency between the apparent contact angle, $\theta$, and volume packing fraction, $\phi_V$.

**S2.3 Model for crude-hexadecane binary system**

Since direct measurement of $\phi_V$ is difficult, we resort to using a crude-hexadecane binary system to vary the volume packing fraction, $\phi_V$, by changing the volume concentration of crude in crude-hexadecane mixture. The resultant, $\phi_{V,\chi}$, is

$$\phi_{V,\chi} = \frac{\phi_{V,1} v_{\text{crude}}}{v_{\text{hexadecane}} + v_{\text{crude}}} = \chi \cdot \phi_{V,1},$$

(S7)

where $\chi$ is the volume concentration of crude in mixture, $\chi = \frac{v_{\text{crude}}}{v_{\text{hexadecane}} + v_{\text{crude}}}$, assuming simple volume addition to the mixture. Therefore, the model (Eqn. S6) can be expressed in terms of $\chi$ as
\[
\cos^6 \theta_x = \frac{1}{\chi} \cdot \frac{1}{6\pi^2 \phi_{V,1}} \left( \frac{S_x}{\sigma_{LV,\chi}} \right)^3 , \tag{S8}
\]

Justified in the main text and section S1 above, the ratio between spreading coefficient, \( S_x \), and surface tension, \( \sigma_{LV,\chi} \), remains constant for mixtures at different concentration, i.e. \( S_x / \sigma_{LV,\chi} = \text{const} \). Thus the model for apparent contact angle with respect to \( \chi \) is

\[
\cos^6 \theta_x = \frac{1}{\chi} \cos^6 \theta_1 . \tag{S9}
\]

Note that the volume of a printed oil drop with a contact angle \( \theta \) and a contact radius \( R \) can be approximated as \( V = \pi R^3 (2 - 3 \cos \theta + \cos^3 \theta) / \sin^3 \theta \).

**S3. Particle Size Distribution by Dynamic Light Scattering**

The mean particle size distribution of crude-hexadecane mixture was averaged over five independent samples at \( \chi = 0.01, 0.05, 0.1, 0.3 \) and 0.5. The measurements are obtained using dynamic light scattering (DLS) method. Two peaks corresponding to particles at 4 nm and ~1 \( \mu m \) are observed. The results show that crude does contain nano-scale and micron-scale particles, while Hexadecane does not.

**S4. Compute local curvatures of AFM measurement.**

Due to the non-axisymmetric base of the printed drops like squares, conventional means of topology characterization using cross-sectional profiles are inadequate. Instead, we characterize the 2D surface, \( z(x, y) \), directly by calculating the distribution of local principal radii of curvature, \( R_1(x, y) \) and \( R_2(x, y) \), or mean curvature, \( H(x, y) = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \), where \( x \) and \( y \) are the lateral positions. Recall that since both the Young-Laplace equation for a larger sessile drop and Kelvin
equation for micro/nano-colloidal particle contain the geometric term of \( H \) (or \( 1/r_{eq} \), where \( r_{eq} \) is the equivalent radius of curvature), the proposed quantification is justified.

To estimate the local \( H \), we must first approximate the local principal radii, \( R_1 \) and \( R_2 \). We apply least square fit of a second order polynomial surface, \( z(x, y; x, y) = k_{11}r_x^2 + k_{12}r_xr_y + k_{22}r_y^2 + k_1r_x + k_2r_y + k_0 \) over a local surface centered around the position, \((x, y)\), with an extent of \((\Delta_x, \Delta_y)\), where \( r_x \) and \( r_y \) are distance originated from \((x, y)\), i.e. \( r_x \leq \Delta_x \) and \( r_y \leq \Delta_y \). Note that the coefficients, \( k_{11}, k_{22} \) and \( k_{12} \), represent the curvatures of a convex surface in the \( x \), \( y \) and diagonal direction respectively. The principal curvature, \( \kappa_1 \) (or \( 1/R_1 \)) and \( \kappa_2 \) (or \( 1/R_2 \)), are then obtained by applying a coordinate transformation that rotates about z-axis allowing \( k_{12} \) to vanish. It yields the following relationship.

\[
\begin{align*}
\kappa_1 &= k_{11} \cos^2 \theta - k_{12} \cos \theta \sin \theta + k_{22} \sin^2 \theta \\
\kappa_2 &= k_{11} \sin^2 \theta + k_{12} \cos \theta \sin \theta + k_{22} \cos^2 \theta
\end{align*}
\]

where \( \tan(2\theta) = (k_{22} - k_{11})/k_{12}^2 \). The mean curvature is estimated as \( H = (\kappa_1 + \kappa_2)/2 \) or equivalently as \( H = (k_{11} + k_{22})/2 \). To ensure robust approximation and prevent spurious value of \( H \) from measurement uncertainties, coefficients of each polynomial surface are estimated over a sufficiently large window \((\Delta_x, \Delta_y) \geq 2\mu m\) for all prints with different features).

Figure S3 elucidates the characterization procedure using the distribution of local mean radius of curvature, \( r_{eq}(x, y) = \frac{1}{H} \) (or local mean curvature, \( H \)). The height profile of a fresh oil drop with a circular base (CIR50) is shown in Fig. S3a and the corresponding distribution of \( r_{eq} \) in Fig. S3b. The window for estimating \( r_{eq} \) is 3 \( \mu m \) in both directions. It is observed that the example drop has the apex height of 4.6 \( \mu m \) and a mean diameter of 56 \( \mu m \), slightly larger than that of the feature in the stamp. Although the drop retains a general circular base (Fig. S3a), the elongation in AFM scanning direction (positive \( x \)) are clearly observed. In addition, striations caused by AFM probes can also be observed in \( r_{eq} \) (Fig. S3b) but less pronounced in profile (Fig. S3A). More than 80% of the center portion of the drop has constant mean radius of curvature, \( r_{eq} = 182.8 \pm 8.9 \mu m \), while along the periphery (~20%), \( r_{eq} \) increases rapidly above 400 \( \mu m \) and transits to negative values. This trend is consistent regardless of the size and base shape (substantiated in §3.2) and suggests the oleophilic contact angle. Although due to the large measurement error near the periphery, the estimation of the contact angle and \( r_{eq} \) in this region is expected to be inaccurate, but it should provide us with qualitative information on drop shape. This trend can be further
elucidated with radial profile in Fig. S3c (red line), which is averaged over the azimuthal direction at the interval of 5° and superimposed with that of a best fit sphere. Note that the radial profile of drop agrees well within an error of 0.46μm or 0.5% with the profile of a sphere of an estimated radius, \( R_{sp} = 96.7\mu m \). Recall that the \( r_{eq} \) of drop is \( r_{eq} = \sim 1.89R_{sp} \) in our measurement, while the \( r_{eq} \) of a sphere must maintain twice of \( R_{sp} \) in principle.

**Fig. S3** Characterization of drop shape with mean radius of curvature, \( H \). (a) surface profile of a 50μm crude oil drop, \( z(x,y) \). (b) 2D distribution of mean radius of curvature, \( r_{eq}(x,y) \), using local best fit of 2nd order polynomial convex surface. (c) Red line: Radial profile of oil drop averaged over the azimuthal direction, Symbol: Radial profile of the best-fit sphere. Inset: Schematics of method used for estimating mean radius of curvatures.
### S5 Properties of printable oils

| Printing material               | Density, \( \rho \, (kg/m^3) \) | Surface tension, \( \sigma \, (mN/m) \) | Viscosity, \( \mu \, (cP) \) | Oh at 50um, \( \mu f / (\rho ad_f)^{1/2} \) | Data Spec. Source |
|--------------------------------|----------------------------------|------------------------------------------|----------------------------|----------------------------------|-------------------|
| Fresh crude                    | 856.2                            | 26.1                                     | 10.1                       | 0.30                             | Ref. 3            |
| 10% Weathered crude            | 877                              | 28                                       | 23.7                       | 0.68                             | Ref. 3            |
| Hexadecane                     | 770                              | 27.5                                     | 3.4                        | 0.10                             | Refs. 4,5        |
| 80% glycerol water             | 1200                             | 63.1                                     | 60.1                       | 0.98                             | Refs. 6,7        |
| Olive oil                      | 920                              | 32                                       | 84                         | 2.19                             | Refs. 7,8        |
| 5W30                           | 860                              | 60                                       | 64                         | 1.26                             | Refs. 9,10       |
| 10W40                          | 865                              | 99                                       | 94                         | 1.44                             | Refs. 9,10       |
| Vacuum oil                     | 890                              | 33                                       | 126                        | 3.28                             | Refs. 11         |

**Table S1** | Material properties of selected oils in current experiment. Crude is Louisiana sweet used to emulate the Deep Horizon Spilled oil. The weathered crude is obtained by baking the fresh crude at 90°C until 10% of initial mass is lost.
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