SUPPLEMENTARY INFORMATION: ENHANCING SPRAY RETENTION USING CLOAKED DROPLETS TO REDUCE PESTICIDE POLLUTION

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Viscous dissipation terms that model energy dissipation in the oil phase of cloaked droplets

Oil cloaked droplets undergo viscous dissipation during impact. In addition to the dissipation that occurs in the water – which can be accounted for using the coefficient of restitution, there are three additional modes of dissipation in the oil phase.

(A) Dissipation rate in the oil cap ($E\mu_I^{'}$)

The oil cap is the thin layer of oil on top of the droplet. We assume that the mechanism of viscous dissipation in the oil cap is similar to the mechanism of dissipation in the water phase. In the following expressions, μ_o and μ_w are the viscosities of oil and water, respectively. R_{max} is the maximum radius of the impacting droplet, h is the thickness of the water phase in the pancaked state, t is the thickness of the oil cloak and U_r is the retraction velocity of the contact line.

The rate of dissipation in water per unit volume scales approximately as $\mu_w(U_r/h)^2$. By replacing the viscosity of water with that of oil, dissipation per unit volume scales as $\mu_o(U_r/h)^2$. The total viscous dissipation rate in the oil cap is obtained by multiplying the above quantity with the volume of the oil cap $\sim R_{max}^2 t$.

$$E\mu_I^{'} \sim \mu_o\left(\frac{U_r}{h}\right)^2 R_{max}^2 t \sim \mu_o\left(\frac{U_r}{h}\right)^2 R_{max}^2 t \tag{S1}$$

(B) Dissipation rate in the oil film underneath the droplet ($E\mu_{II}^{'}$)

Shear continuity at oil-water interface gives rise to the following condition.

$$\mu_w\frac{U_r}{h} \sim \mu_o\frac{U_i}{t} \tag{S2}$$

Here, the rate of viscous dissipation in the oil film underneath the water droplet per unit volume is given by $\mu_o(U_i/t)^2$ where U_i is the velocity of the oil-water interface. Imposing the shear continuity and multiplying by the volume of the oil film underneath the water droplet, we can express the viscous dissipation rate in the oil film under the droplet as:

$$E\mu_{II}^{'} \sim \mu_o \left(\frac{U_i}{t}\right)^2 R_{max}^{\ 2} t = \frac{\mu_w^2}{\mu_o}\left(\frac{U_r}{h}\right)^2 R_{max}^{\ 2} t = \frac{\mu_w^2}{\mu_o} U_r^2 t \frac{R_{max}^{\ 2}}{h^2} \qquad \text{(S3)}$$

(C) Dissipation rate in the oil ridge ($E\mu_{III}^{'}$)

The bulk of the oil inside the wetting ridge retracts approximately at the same rate as the droplet's peripheral retraction rate (U_r). If h_{ridge} is the height of the ridge, then the dissipation rate per unit volume in the wetting ridge is given by $\mu_o (U_r/h_{ridge})^2$. Multiplying this by the volume of the wetting ridge we can express the total viscous dissipation rate in the ridge as:

$$E\mu_{III}^{'} \sim \mu_o \left(\frac{U_r}{h_{ridge}}\right)^2 R_{max}\, h_{ridge}^{\ 2} = \mu_o U_r^2 R_{max} \qquad \text{(S4)}$$

Relationships between *h*, *t* and R_{max}

For the experiments where the volume fraction of oil is 1%, the volume of water droplet is 100 times the sum of volume of oil cap, the oil film underneath the water droplets and in the volume of the wetting ridge (which is negligible). Thus, we can calculate that the thickness of the oil layers is much smaller than the height of the pancaked droplet.

$$R_{max}^{\ 2} h \sim 100 R_{max}^{\ 2} t \times 2$$
$$\frac{t}{h} \sim \frac{1}{200} \qquad \text{(S5)}$$

Since the volume of water pancake is the same as the volume of the impacting water droplet of radius *R*, we can drive the following relation:

$$\frac{4}{3}\pi R^3 \sim \pi R_{max}^{\ 2} h$$
$$\frac{h}{R_{max}} \sim \frac{4}{3}\left(\frac{R}{R_{max}}\right)^3 \qquad \text{(S6)}$$

From our experimental results shown in figure 3, we know that $R_{max}/R \approx 3$, Thus

$$\frac{h}{R_{max}} \sim 0.05 \quad \text{(S7)}$$

Comparing the magnitude of three viscous dissipation modes in the oil

Once again, the summation of all three viscous dissipation rate terms explained above - $E\mu_I{}'$, $E\mu_{II}{}'\ and\ E\mu_{III}{}'$, gives us the net viscous dissipation in the oil phase.

$$E_\mu{}' \sim E\mu_I{}' + E\mu_{II}{}' + E\mu_{III}{}' \quad \text{(S8)}$$

$$E_\mu{}' \sim \mu_o \left(\frac{U_r}{h}\right)^2 R_{max}^{\ 2} t + \frac{\mu_w^2}{\mu_o} U_r^2 t \frac{R_{max}^{\ 2}}{h^2} + \mu_o U_r^2 R_{max}$$

Comparing the magnitude of $E\mu_I\ and\ E\mu_{III}$:

$$\frac{E\mu_{III}{}'}{E\mu_I{}'} \sim \frac{\mu_o U_r^2 R_{max}}{\mu_o \left(\frac{U_r}{h}\right)^2 R_{max}^{\ 2} t} \sim \frac{h^2}{tR_{max}} \sim \frac{h}{t}\left(\frac{h}{R_{max}}\right) \sim 10 \gg 1 \quad \text{(S9)}$$

$$E\mu_{III}{}' \gg E\mu_I{}'$$

Comparing the magnitude of $E\mu_{II}\ and\ E\mu_{III}$:

$$\frac{E\mu_{III}{}'}{E\mu_{II}{}'} \sim \frac{\mu_o U_r^2 R_{max}}{\frac{\mu_w^2}{\mu_o} U_r^2 t \frac{R_{max}^{\ 2}}{h^2}} \sim \left(\frac{\mu_o}{\mu_w}\right)^2 \frac{h}{t}\left(\frac{h}{R_{max}}\right) \quad \text{(S10)}$$

$$\frac{\mu_o}{\mu_w} > 1\ or \gg 1$$

$$Thus\ E\mu_{III}{}' \gg E\mu_{II}{}'$$

Therefore, the viscous dissipation rate in the oil ridge ($E\mu_{III}{}'$) is the only relevant dissipation term and $E_\mu{}' \sim E\mu_{III}{}' \sim \mu_o U_r^2 R_{max}$. To obtain the scaling of the absolute viscous dissipation we multiply this dissipation rate by the time taken for the droplet to go from the maximum diameter to its final diameter.

Supplementary figures

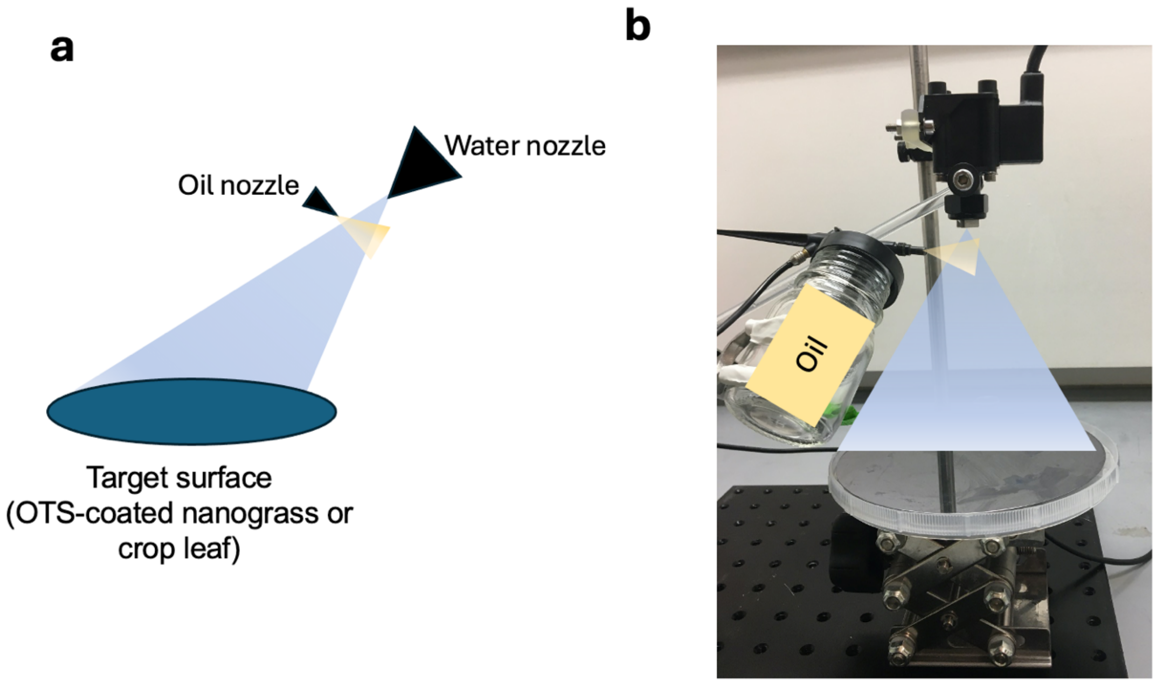

Figure S1: a) schematic side view and b) image front view of the prototype oil-cloak sprayer. The water nozzle sprayer was oriented such that the droplets impinged the surface at an angle of roughly 45 degrees, and the oil airbrush sprayer was oriented such that it was not directly above the surface, thus preventing any potential oil dripping from reaching the surface outside of cloaked droplets. The secondary airbrush sprayer containing the oil was operated at a pressure of 30psi, and the relative flow rates of oil and water were controlled to maintain a ~1% volumetric fraction of oil.

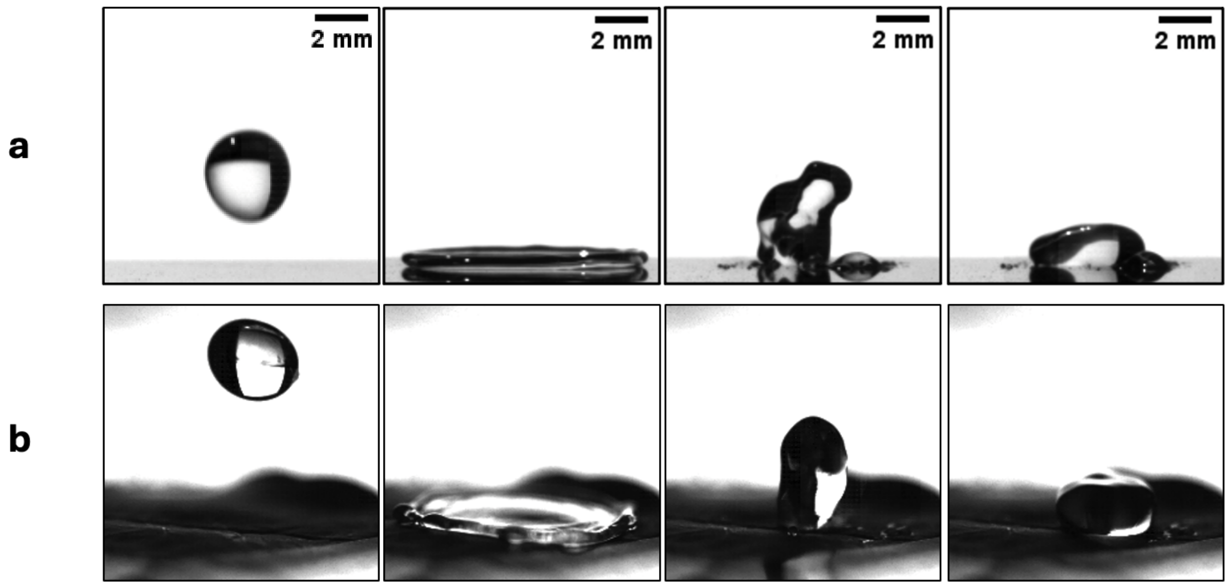

Figure S2: a) Impact of a droplet cloaked with 1% wt soybean oil at approximately 1.25 m/s on an engineered non-porous superhydrophobic OTS-nanograss surface. In b), all conditions are held constant except the droplet impacts the adaxial surface of a fresh kale leaf. The expansion and retraction dynamics match very well, with similar extents of extension, followed by the formation of an pinning oil ring. In both cases, this oil pinning ring breaks during retraction, resulting in contact line motion, but not enough to enable the droplet to rebound. These dynamics lie in direct contrast to the dynamics shown by Han et al, where no contact line retraction is observed[1]. We continue to use the superhydrophobic OTS-nanograss on account of its similar behavior to actual plant leaves.

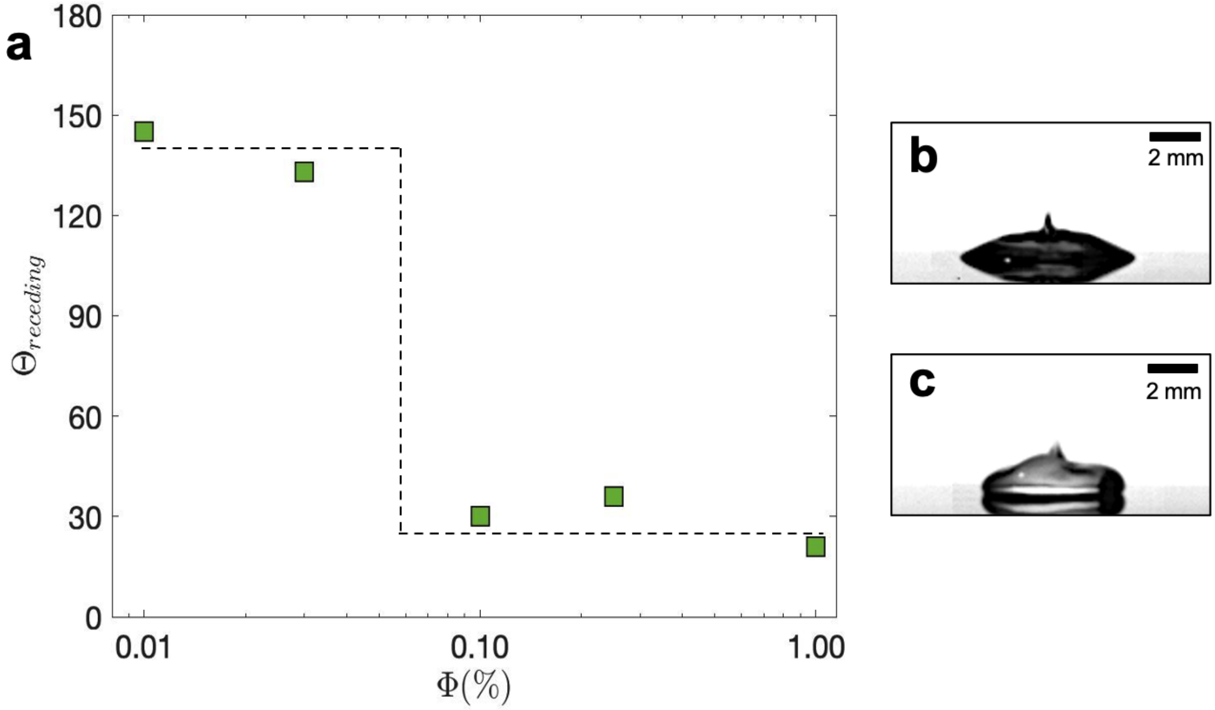

Figure S3: (a) Average dynamic contact angle measured during the retraction phase for water droplets cloaked in 10cSt Silicone oil at the low oil volume fractions shown in Figure 4. The increase in retraction contact angle at 0.04% oil fraction accompanies the increase in restitution coefficient observed in Figure 4, indicating that at sufficiently low oil fractions, the oil can no longer pin the contact line and suppress droplet rebound. **(b)** and **(c)** are snapshots taken during the retraction of oil cloaked droplets with 0.10% and 0.04% oil by volume, respectively, demonstrating the markedly different contact angle.

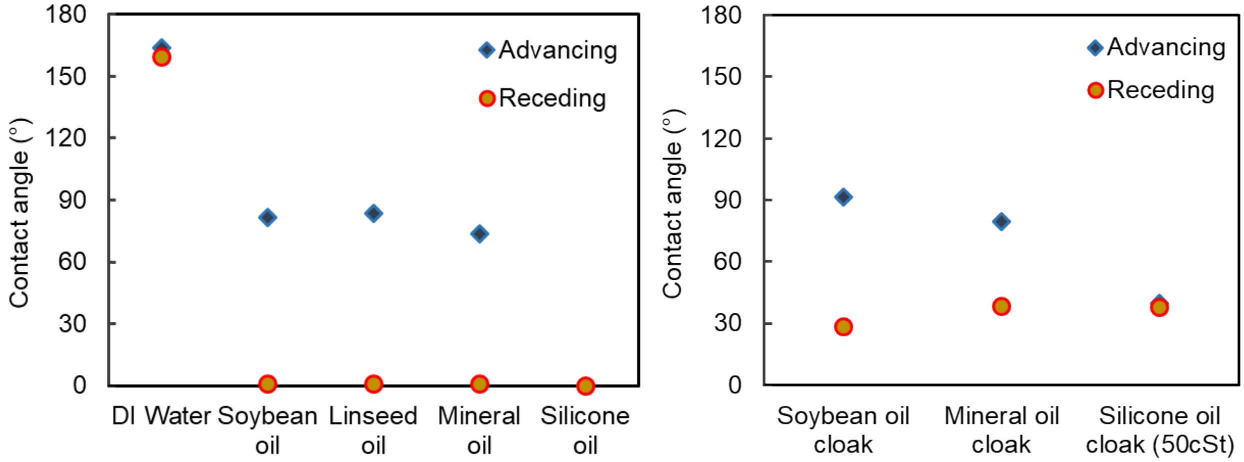

Figure S4: Advancing and receding contact angles of water and representative cloaking oils on minimally pinning superhydrophobic surfaces coated with octadecyltrichlorosilane. Measurements were obtained by gently placing a droplet on the surface and dispensing fluid into or withdrawing fluid from the droplet to measure advancing and receding angles, respectively. These measurements were performed for **(a)** homogenous liquid drops composed of only oil or only water and **(b)** oil-cloaked water droplets (1% oil by volume).

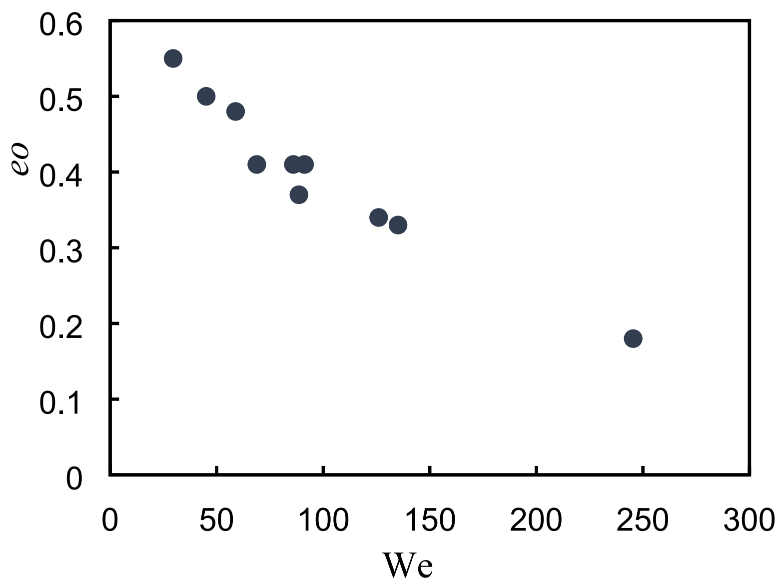

Figure S5: Measured coefficient of restitution (e_o) as a function of the incoming droplet Weber number (We) for control DI water droplets.

Figure S6: Representative methodology for measuring the leaf coverage in Figure 1i. **(a)** Image of a cabbage leaf after 3.0 seconds of control DI water spray. **(b)** the total leaf area is calculated via manual annotation in ImageJ. **(c)** the leaf surface visibly covered by water droplets, here shown in white, is measured via manual annotation in ImageJ.

Supplementary Movie captions:

https://www.dropbox.com/scl/fo/aaqmlc9xfcpuu2odbwvcl/AO2TnyQF-Hp1bWkprHXMaDU?rlkey=7t8yxcwynykxpc6iuk0m292r5&dl=0

Supplementary Movies 1 and 2: Demonstrates the effectiveness of oil cloaking: **(SM 1)** Water sprayed using a commercial agricultural nozzle onto a cabbage leaf for ~3 seconds **(SM 2)** Water drops cloaked with soybean oil (~1 wt% oil) sprayed onto a cabbage leaf for ~1 second.

Supplementary Movies 3-6: Compares single droplet impacts on superhydrophobic surfaces of oil cloaked and control DI water droplets released from 8cm height and having ~1.25 m/s velocity at impact. DI water droplet impact from a side **(SM3)** and top down **(SM4)** view impacting on a OTS coated minimally pinning superhydrophobic surface. Soybean oil cloaked (1% oil by volume) droplet impact from a side **(SM5)** and top down view **(SM6)** onto the same surface.

Supplementary Movies 7 and 8: Compares droplet impacts of DI water and cloaked droplets at high impact velocities, released from 20cm height and having ~2.0 m/s velocity at impact. Satellite droplets of a splashing DI water droplet scatter off the surface (**SM7**). In contrast nearly all the satellite droplets in the oil cloaked case (1% of soybean oil by volume) stick to the surface **(SM8)**

Supplementary Movies 9-13: Illustrates the effect of volume fraction of oil per droplet. Soybean oil cloaked droplet impact for oil volume fractions (Φ) of **(SM9)** 1%, **(SM10)** 0.4%, **(SM11)** 0.1%, **(SM12)** 0.04%, **(SM13)** 0.01%. As the amount of oil becomes <0.1%, we see that the droplet doesn't pin during the retraction phase, there is no visible oil left behind on the surface and droplet retention begins to fail. All experiments are performed by releasing droplets from 8cm height, yielding roughly 1.25 m/s impact speed.

Supplementary Movies 14 and 15: Demonstrates the effectiveness of the prototype oil cloaking nozzle on a minimally pinning surface. **(SM14)** Almost all the DI water sprayed using a commercial agricultural nozzle onto a minimally pinning surface bounces off. **(SM15)** In contrast, cloaked water drops (soybean oil ~1 wt% oil), stick effectively.

Supplementary Movie 16: Demonstrates how extremely high viscosities result in rebound of the droplet. This video shows a droplet cloaked in ~1 wt% 500cP Silicone oil at an impact speed of ~1.25 m/s.

REFERENCES

1. Han, X. *et al.* Slippery damper of an overlay for arresting and manipulating droplets on nonwetting surfaces. *Nat Commun* **12**, 3154 (2021).