Supporting Information

Dynamic Control of Particle Deposition in Evaporating Droplets by an External Point-Source of Vapor

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1. Materials and Methods

Unless stated otherwise, each evaporation experiment was performed by depositing a 1-μL droplet of a 1-wt% water suspension of 2-μm monodisperse silica particles (Microparticles GmbH, SiO2-R-L1561) on a clean glass slide (VWR, 631-0113). A fresh particle suspension was prepared before each experiment in deionized (DI) water (resistivity > 18 MΩ.cm). To eliminate all source of contamination that could influence droplet spreading or pinning on the substrate, the slide was cleaned by sequentially sonicating it in acetone (Aldrich, > 99.8%), ethanol (Fisher, > 99.8%) and DI water for 5 minutes each. It was then immersed in a 1-M NaOH solution for 10 minutes, followed by a 5-minute sonication in DI water, and re-immersed in a 1-M HCl solution for 10 minutes, followed by sonication in DI water for 5 minutes for three consecutive times. The slide was finally dried by withdrawing it from the water bath while exposing its surface to ethanol vapor (Marangoni drying).[1] After drying, the slide was placed on a homemade inverted microscope equipped with a CMOS camera for imaging (Thorlabs, DCC1545M). A custom-made environmental chamber (Okolab) enclosed the

microscope to control temperature (T = 25 ± 0.2 °C) and relative humidity (RH = 45 ± 5%). The entire setup was mounted on a floated optical table in order to reduce vibrations. At the start of each experiment, the droplet was gently deposited on the slide with a graduated pipette using a disposable low-retention pipette tip (Brand, Z740080) and centered under the point source of vapor using the microscope stage. The point source consisted of a glass capillary (1.3 mm inner diameter) terminated with a blunt metal needle at one end. The needle was fixed to the capillary with a silicone-based sealant. The opposite end contained 10 μL of anhydrous ethanol (Aldrich, > 99.5%) held in place through capillary forces by sealing the open end with wax. Finally, the capillary was fixed to a three-axis motorized micrometric stage (Thorlabs, Z812B actuators with 0.2-µm minimum step) for fine positioning. To determine the distance between the needle and the substrate, a periscope together with a flip mirror allowed us to switch optical path so as to visualize the droplet's side view instead of its basal plane on the CMOS camera.

2. Calculation of the Sedimentation Velocity v_s

The sedimentation velocity of the 2-µm silica microparticles in water can be calculated using the following formula which takes into account the particle's gravitational force, drag force and buoyancy:

$$v_s = \frac{2}{9}\frac{(\rho_{Si} - \rho_w)ga^2}{\eta} = 2.1\ \mu m\ s^{-1}$$

where a and ρ_{Si} are the microparticles' radius and density, ρ_w and η are the density and viscosity of water, and g is the gravitational acceleration.

3. Supporting Figures

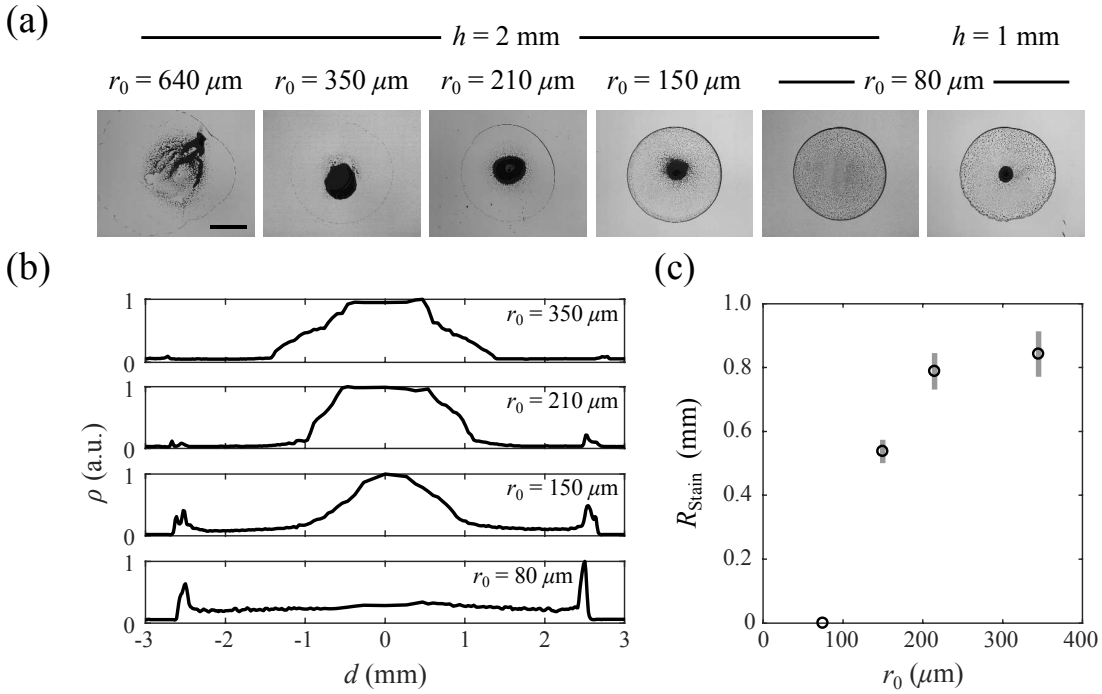


Figure S1: Effect of the point source's radius on the final deposition pattern. (a) Final deposits after evaporation for 1-μL water droplets of a 1-wt% water suspension of 2-μm monodisperse silica particles evaporating on a clean glass slide under needles of different inner diameters r_0 for h = 2 mm. The case for r_0 = 80 μm is also shown for h = 1 mm. The scale bar corresponds to 1 mm. (b) Histograms showing the density profile ρ (averaged along the angular coordinate) along one droplet's diameter (calculated as in Fig. 1) of the deposits in (a) for r_0 varying from 350 μm to 80 μm. The central spot decreases in size when r_0 is reduced and, at the same time, weakening of the Marangoni flows leads to an increase of the particles deposited towards the droplet edge. (c) Average radius (averaged along the angular coordinate at 0.05-rad intervals) of the central deposit for varying r_0. The gray bars show one standard deviation around the mean values and give information about the uniformity of the stain by measuring its

deviation from a perfectly circular spot: the uniformity increases for decreasing r_0. The experimental values are averaged over at least 5 different droplets.

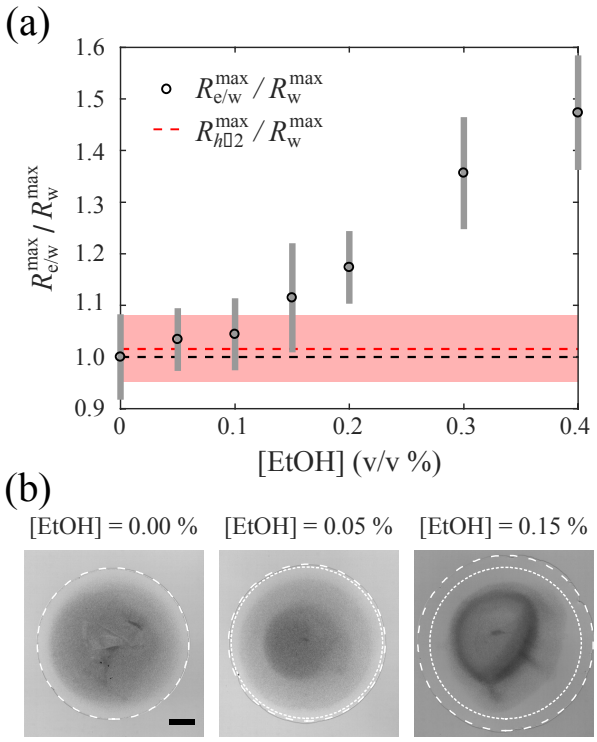
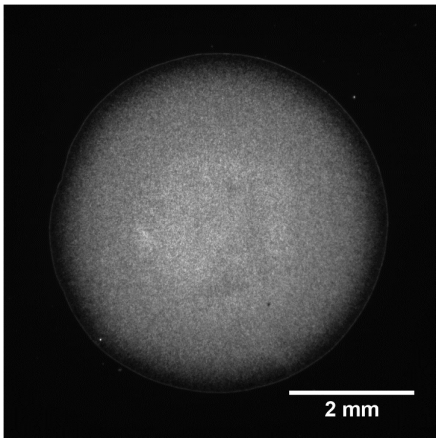


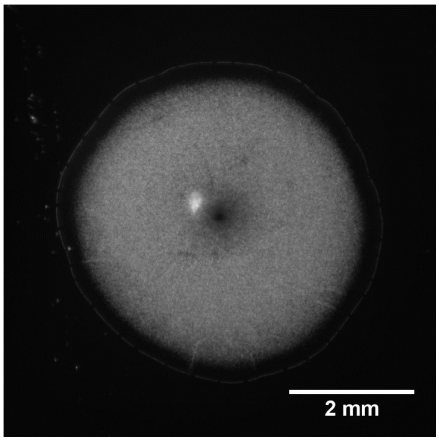
Figure S2: Spreading of water-ethanol binary mixtures during evaporation on a clean glass slide. (a) Average maximum radius $R_{e/w}^{max}$ during evaporation (circles) for 1-μL droplets of different water-ethanol binary mixtures. The droplets were let evaporate on a clean glass slide ($\theta \leq 5°$). All values are normalized to the average maximum radius R_w^{max} for pure water droplets (black dashed line). The experimental values are averaged over at least 3 different droplets. The bars show one standard deviation around the mean values. For reference, the red dashed line represents a typical maximum droplet spreading during evaporation in the presence of the point source of ethanol at a distance $h \leq 2$ mm with the red shaded area showing one standard deviation around the mean value. (b) Typical images of water-ethanol binary mixture droplets during evaporation taken at the time when they reached their maximum spreading radius (white

dashed outer circles) for different initial ethanol concentrations ([EtOH] = 0 v/v%, [EtOH] = 0.05 v/v% and [EtOH] = 0.15 v/v%): Droplet spreading increases with ethanol concentration. The inner circle represents the maximum spreading radius for [EtOH] = 0 v/v% shown as reference. The scale bar corresponds to 1 mm.

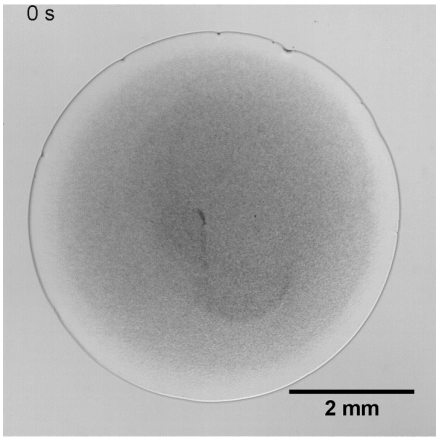
4. Supporting Movies



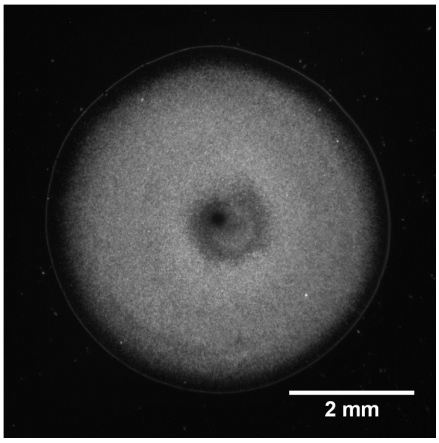
Supporting Movie 1: Movie of the evaporation process of the droplet corresponding to the final deposit in Fig. 1(b) showing the standard coffee ring effect. The video was recorded under a dark-field microscope. At the end a bright-field image of the final stain is shown.



Supporting Movie 2: Movie of the evaporation process of the droplet corresponding to the final deposit in Fig. 1(c) showing the formation of a deposit at the center due to the presence of an ethanol vapor point-source. The video was recorded under a dark-field microscope. At the end a bright-field image of the final stain is shown.



Supporting Movie 3: Movie of the evaporation process of a water-ethanol binary mixture droplet for [EtOH] = 0.05 v/v% on a clean glass slide. The presence of ethanol in the droplet initially drives flows that counteract the coffee-ring effect and start to accumulate the suspended particles at the center of the droplet. Because of the reduction in ethanol content over time due to evaporation, these flows are outperformed by outwards capillary flows at time 52 s. The movie was recorded under a bright-field illumination to highlight the edge of the droplet.



Supporting Movie 4: Movie of the evaporation process of a droplet in the presence of an ethanol vapor point-source showing the formation of a radial jet at time 14 s. The video was recorded under a dark-field microscope.

5. Supporting Table

Panel	r_0 (μm)	h (mm)	V_S (mm s^{-1})	Protocol
Fig. 4(a)	210	2	2	Start 1.5 mm away from the center and wait 3.5 s; move to the other end of the line and wait 3.5 s; repeat until the end of the droplet's lifetime.
Fig. 4(b)	80	0.65	2.6	Wait 20 s before approaching the needle to the droplet; stay 25 s on the first spot (0.5 mm from the center) and then 15 s on the second; finally move needle away.
Fig. 4(c)	80	0.75	2	Hold the needle on the first spot (1 mm away from the center) for 30 s; then move to the other outer spot and hold for 30 s; move to the middle spot and hold for 20 s; finally move needle away.
Fig. 4(d)	80	0.65	2.6	Wait 20 s before approaching the needle to the droplet; stay 25 s on the first spot and then 15 s each on the second and third spot; finally move needle away.
Fig. 4(e)	80	0.6	0.25	Trace cross twice; finally move needle away.
Fig. 4(f)	80	0.6	0.1	Wait 90 s before approaching the needle to the droplet; trace letters once, waiting 5s at the beginning of each letter.

Supporting Table 1: Detailed experimental protocol for the vapor point source's displacement in Fig. 4.

6. Supporting Reference

(1) Leenaars, A. F. M.; Huethorst, J. A. M.; van Oekel, J. J. Marangoni Drying: A New Extremely Clean Drying Process. *Langmuir* **1990**, *6*, 1701–1703. □