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Liquid-liquid coffee-ring effect

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Abstract

The so-called coffee-ring effect (CRE) is extraordinarily common, problematic in industry and attractively puzzling for researchers, with the accepted rule that it requires two key-ingredients: solvent evaporation and contact line pinning. Here, we demonstrate that the CRE also occurs when the solvent of a pinned sessile drop transfers into another liquid, without involving any evaporation. We show that it shares all characteristic features of the evaporative CRE: solvent transfer-driven transport of solutes to the contact line, ring-shaped deposit, closely-packed particle organization at the contact line, and size-dependent particle sorting. We thus suggest expanding the definition of the coffee-ring effect to any pinned drop having its solvent transferring to an outer medium where the drop compounds cannot be dissolved.

Keywords: Colloids; Deposition; Sessile drop; Liquid-liquid interface; Drop drying

Introduction

A spilled drop of coffee usually dries by leaving most of its residue along the perimeter of its initial contour. The phenomenon that leads to the formation of such a ring-like pattern is usually called the coffee-ring effect (CRE). Since the seminal report by Deegan *et al.* in 1997, [1] there is a rich literature that reports and studies this familiar yet highly complex phenomenon. [2–9] It was shown that the CRE is a ubiquitous process that is not limited to coffee but includes virtually any fluid involving a drying pinned sessile drop containing non-volatile compounds, covering fluids as broad as rain, blood, inks, alcoholic beverages or paints, [10–12] and a plethora of deposited materials including particles, synthetic polymers, DNA or proteins. [13,14] For many industrial and biotechnological processes relying on the deposition of materials from liquid drops, the CRE is a major obstacle that leads to heterogenous depositions. This has triggered efforts to suppress or circumvent the CRE so that homogenous deposits rather than rings could be obtained. [6,15] Conversely, the CRE has been identified as a powerful tool for both guiding particle deposition [5,16] and realizing quick and cheap diagnosis. [11,17] Canceling or harnessing the CRE requires a fine understanding that is rendered difficult by its unsteady and multiscale character involving the formation of complex flow patterns, phase transition, and transport phenomena, as well as intricate and multiscale interactions inside the drop and at its interfaces. [18] This large amount of studies has rather exclusively considered the situation of liquid drops evaporating in a gas phase, leading to the generally admitted picture that at least two ingredients are essential for the CRE to occur: drop evaporation and contact line pinning. The combination of both leads to a radial evaporation-driven flow that transports all the non-volatile compounds toward the contact line where evaporation is stronger. Here we challenge this picture by considering a system without any evaporation nor external gas phase (e.g., air) involved. We created small sessile drops containing particles inside another partially miscible liquid, where liquid inside the drop could be dissolved but not the particles. Strikingly,

we observed that a “liquid-liquid coffee ring effect” (LLCR) occurred in such a situation. We analyzed the deposit morphology, the transport of particles during solvent dissolution as well as the way particles organized in the deposit, and compared these features to the signatures of conventional evaporative CRE in air. Marked similarities led us to reconsider and propose an expansion of the definition of the coffee-ring effect.

Results and discussion

Our system consisted of a sessile water drop deposited on glass immersed in large bath of anhydrous ether. Water is only partially miscible in anhydrous ether (around 1.5 wt% [19]) allowing both the creation of a stable liquid/liquid interface and its transfer to the outer phase (**Fig. 1A**). We will refer to this transfer as a solvent dissolution. The drop contained silica particles (560 nm in diameter), which were insoluble in both the drop solvent and the outer liquid phase. The sessile drops were obtained by emulsifying the particle suspension in ether, prior to letting the drops sediment to the bottom of a homemade closed chamber (**Fig. 1B**). Our chamber featured a removable glass substrate at its bottom, allowing *in situ* observations to follow the deposition process in time, as well as *ex situ* analyses to more precisely characterize the particle deposits. The produced droplets ranged in size from tens of micrometers to several hundreds of micrometers in diameter, which resulted in dissolution times ranging from tens of seconds for the smallest ones to tens of minutes for the biggest ones. Under our experimental conditions, the sedimentation time was always significantly smaller than the dissolution time, making most of the dissolution occurring once the drop became fixed on its substrate. After full dissolution, all deposits displayed in transmission optical microscopy a darker edge surrounding a lighter area (**Fig. 1C**). This overall morphology was strikingly similar to patterns typically obtained with the conventional coffee ring effect (CRE) in air (for instance, the patterns left by mm- to cm-sized drops of spilled coffee, **Fig. S1**). The deposit edge closely reproduced the

initial drop contour, except for the presence of a few small spikes at the locations the drop underwent partial depinning. This shows that drop components, here silica particles, accumulated at the contact line position upon solvent dissolution to the external liquid phase. Scanning electron microscopy (SEM) analyses revealed that the dark edges corresponded to tridimensional scythe-shaped deposits of closely packed particles that collected at the rim of the dissolving drops (**Fig. 1D**).

In situ observation of the dissolution process revealed that most of the drops followed a similar temporal evolution, with a decrease of the contact angle (**Fig. S2**) accompanied by the progressive accumulation of particles at their contour (**Movie S1, Fig. 2A**). The dissolution time t_{dis} decreased with drop radius R , with a characteristic dissolution speed R/t_{dis} being almost constant and equaled to $\sim 0.4 \mu\text{m}\cdot\text{s}^{-1}$ for all the drops studied (**Fig S3**). Tracking individual particle motion in a quasi-circular dissolving drop revealed that particles followed streamlines toward the contact line with a marked radial symmetry (**Fig. 2B**). Particles moved at almost constant velocity prior to accelerating when approaching the drop edge (**Fig. 2C**). The typical measured particle velocity U_{part} during the constant regime was around $0.7 \mu\text{m/s}$, a value comparable to the characteristic flow velocity R/t_{dis} due to solvent transfer to the outer phase (dashed line in **Fig 2C**). This shows that the transport of particles was directly driven by the solvent transfer to the outer phase and not affected by thermal variations that can significantly alter the particle transport speed in evaporative CRE. [18]

Upon accumulation at the contact line, the particles formed a ring of packed particles (**Figs. 1D, 3A**) where they organized (mainly in hexagonal lattices) close to the outer part of the ring (**Figs. 3B cyan box, 3C**) but formed disordered assemblies closer to the inner part of the ring (**Figs. 3B blue box, 3D**). Such order-to-disorder transition in the particle arrangement from the outside

to the inside of the pattern, a feature also commonly observed in CRE patterns formed in air, can be explained by the so-called rush-hour behaviour. [20] The first particles reaching the drop contour were packed at low velocities and had enough time to rearrange and form crystalline structures (**Fig. 3C**). In contrast, toward the end of the dissolution process, the acceleration of the particle did not leave enough time for particles to assemble into an efficient way leading to jamming and disordered packing (**Fig. 3D**). The transition between these two regimes should occur when the characteristic time for a new particle of radius R to reach the deposit ($t_{part} \sim d/U_{part}$ where d is the interparticle distance) becomes comparable to the characteristic diffusion time of packed particles in the deposit ($t_{diff} \sim (2R)^2/D$ where D is the diffusion coefficient). This corresponds to a critical particle speed $U_{part}^{crit} \sim dD/(2R)^2 \approx 9 \mu\text{m/s}$ which is significantly higher than the speed we typically tracked (**Fig. 2C**), explaining why most particles had enough time to organize and crystallize upon deposition.

Like its evaporative counterpart, the liquid-liquid coffee-ring effect is not limited to a specific particle system. Particles of different sizes were successfully organized into rings with our solvent dissolution method. Interestingly, when different binary mixtures of particles were employed, the outmost periphery of the deposit was always composed of the smallest particles only, immediately followed by a front mainly composed by bigger particles aligned parallel to the contact line (**Fig. 4**). This is another reminiscent trait of the evaporative CRE, which is explained by the meniscus confinement near the contact line that excluded the bigger particles. [21,22] Toward the inner part of the deposit where confinement was weaker, both particles were more homogeneously distributed and crystallization was avoided due to the size heterogeneity. Systems with other solutes than particles were also explored such as, for instance, the dissolution of sessile water drops containing DNA into ether. Although significant depinning occurred in that system, most of DNA accumulated at the edges of the deposits indicating the

transport of DNA molecules toward the contact line by a liquid-liquid CRE (**Fig. S4**). It thus seems that the liquid-liquid coffee-ring effect is robust enough to occur with various suspension and solution compositions.

Conclusion

We studied the deposit left after the dissolution of a sessile drop containing insoluble particles into another partially miscible liquid. We evidenced similarities between this process and the CRE. First, the general appearance of a deposit perfectly matched that of a one produced during the conventional CRE: the perimeter appeared darker and was more concentrated in particles than the inside. Second, we observed the formation of a radial flow resulting from the pinning of the droplet and solvent diffusion to the external phase. This radial flow drove the particles' migration towards the meniscus of the droplet where they arranged into a ring-like deposit. Third, looking more closely at the deposit, we revealed that the particles assembly displayed some microstructural features characteristic of the CRE, namely the order-to-disorder transition, going from the outside to the inside of the ring, as well as the confinement-driven size-selective segregation in a mixture of particles. We conclude, considering these compelling evidence, that the dissolution of a sessile drop in another liquid should be rightfully considered as a CRE. As a consequence, we propose to generalize the definition of the coffee-ring effect, by including any type of fluid droplet pinned and immersed into another fluid that can undergo mass transfer. We also suggest the liquid-liquid coffee-ring effect (LLCR) to be exploitable for original applications such in-liquid printing [23] and patterning [24–26] or low-cost point-of-care diagnostic systems [11,27] that can be less sensitive to on-field ambient air conditions.

Acknowledgements

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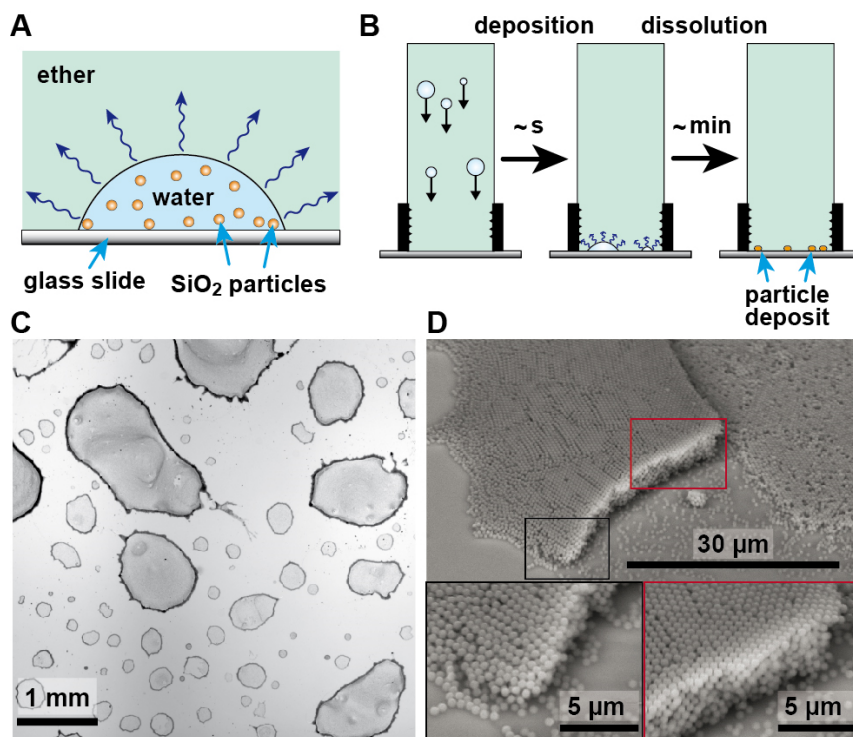


Figure 1. Pinned sessile drops of water containing particles dissolve in ether to form rings of packed particles. (A) Sessile drops on glass contain silica particles (diameter: 560 nm) at a concentration of 0.5 wt% and dissolve in ether. (B) Sessile drops are produced in a few seconds by emulsification in ether and sedimentation onto a glass substrate. (C) Transmission optical microscopy image of the particle deposits obtained after full drop dissolution. (D) Scanning electron microscopy (SEM) images with a 120° incident angle of a broken deposit to reveal its morphology and content.

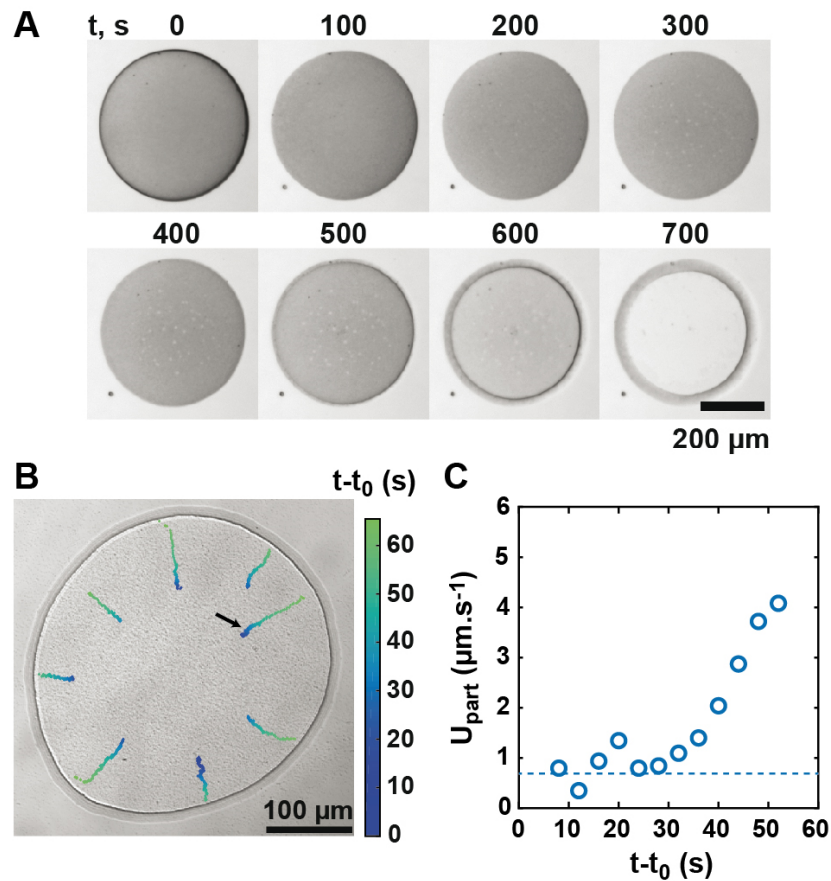


Figure 2. Radially symmetric solvent dissolution-driven transport of particles toward the contact line. A) *In situ*, timelapse transmission optical microscopy images of the dissolution of a single drop containing 0.5 wt% of 560 nm diameter silica particles. B) 8 individual particles tracked during solvent dissolution. Each position is marked by a disk with a color corresponding to $(t - t_0)$ where t represents the actual time and t_0 the time at the beginning of the tracking. (C) Speed of the particle indicated by a black arrow in (B), as a function of $t - t_0$. The dashed line indicates the ratio between the drop radius ($R = 185 \mu\text{m}$) and its full dissolution time ($t_{dis} = 260 \text{ s}$).

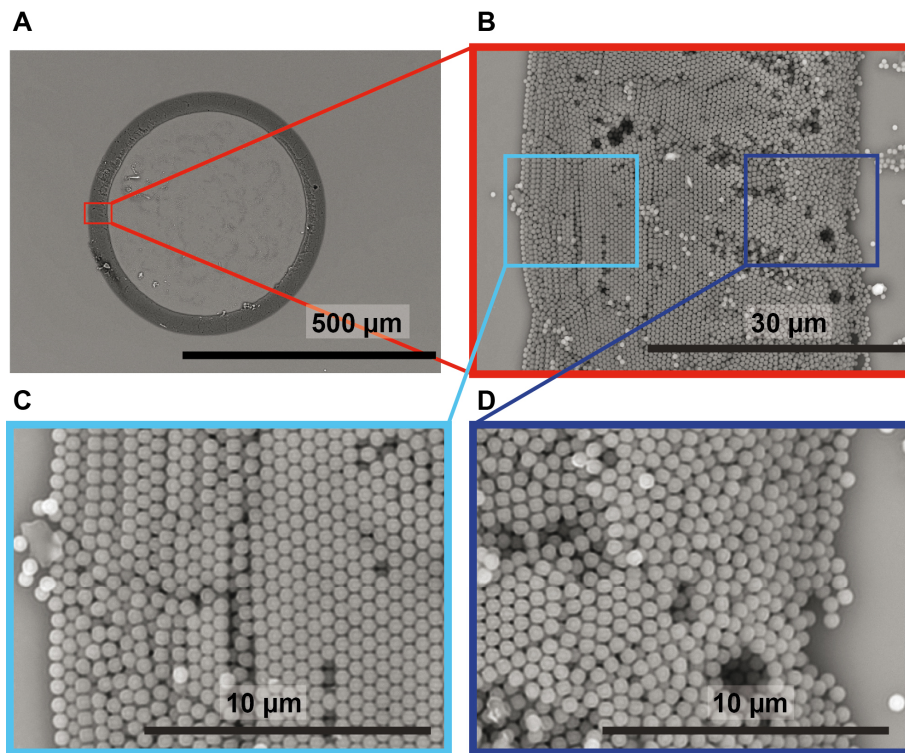


Figure 3. Order-to-disorder transition of particle packing from the outside to the inside of the deposit. SEM images of the same deposit at different magnifications: 180× (A), 3000× (B) and 10000× (C,D). The water drop initially contained 0.5 wt% of 560 nm diameter silica particles.

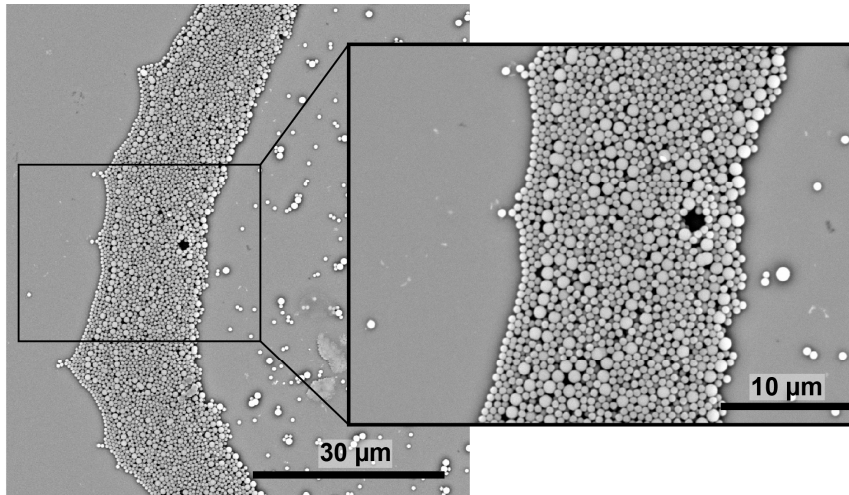
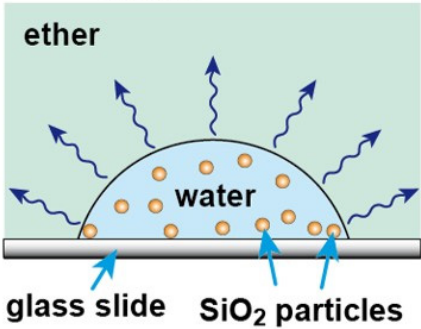


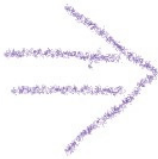
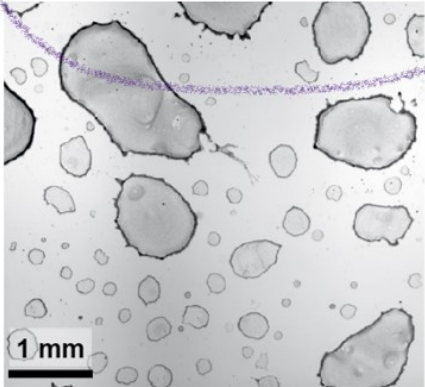
Figure 4. Size-selective segregation of particles upon deposition. SEM images of the same deposit obtained by the dissolution of water drops containing a mixture of 0.25wt% of 560 nm diameter silica particles and 0.25 wt% of 1 μm silica particles.

Graphical Abstract

Sessile Drop dissolution
into liquid



Coffee-Ring Effect!



Supporting Information for:

Liquid-liquid coffee-ring effect

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This PDF file includes:

- Materials and Methods
- Figures S1 to S4
- Legend of Movie S1

Other Supplementary Materials for this manuscript include the following:

- Movie S1

Materials and Methods

Materials

We used silica particles (microParticles GmbH, diameters: 560 nm and 1 μm). The water used was dispensed by a Milli-Q system (Millipore, resistivity: 18.2 $\text{M}\Omega\cdot\text{cm}$). The diethyl ether was purchased from Sigma-Aldrich (Sigma-Aldrich, anhydrous, 99.7 %).

Observation cell

The observation cell was made from a modified 8 mL screw-top glass vial (Kimble, screw thread, Opticlear). The observation window of the cell consisted of a screw cap that was hollowed and glued onto a microscope slide with epoxy glue (Loctite, Hysol 3430). All cells were washed and rinsed successively with Milli-Q water, ethanol (Sigma-Aldrich, puris., absolute 99.8%), and acetone (Sigma-Aldrich, for HPLC 99.8%) prior to use.

Sample preparation

The particle solution was emulsified according to the following protocol. First, a 100 μL drop of silica particles dispersed in Milli-Q water at a concentration of 5 mg/mL was deposited on the glass slide, within the glued cut screw cap. Then, the glass vial was filled with diethyl ether, threaded with Teflon tape, and screwed onto the glass slide. The whole cell was vigorously shaken by hand for a few seconds to emulsify the suspension of silica particles. Finally, the cell was flipped window-side down, and the droplets were allowed to sediment to the bottom of the cell.

Imaging

The time-lapses were imaged *in situ* with a bright-field inverted microscope (Zeiss, Observer D1) with a magnification of 2.5 \times or 20 \times . The acquisition started a few seconds after the cell was flipped. The imaging of the ring patterns was performed on dry deposits, by unscrewing the screw cap and allowing the ether to evaporate, and with a bright-field inverted microscope (Zeiss, Observer D1) at a 2.5 \times magnification. Both were recorded with a sCMOS camera (Andor, Zyla). The scanning electron microscope imaging was performed with a tabletop microscope (Hitachi, TM3000) with the *Analy* mode (15 kV), at magnifications ranging from 180 \times to 10,000 \times . The incident angle used in the SEM was 90 $^\circ$, except when it is otherwise reported.

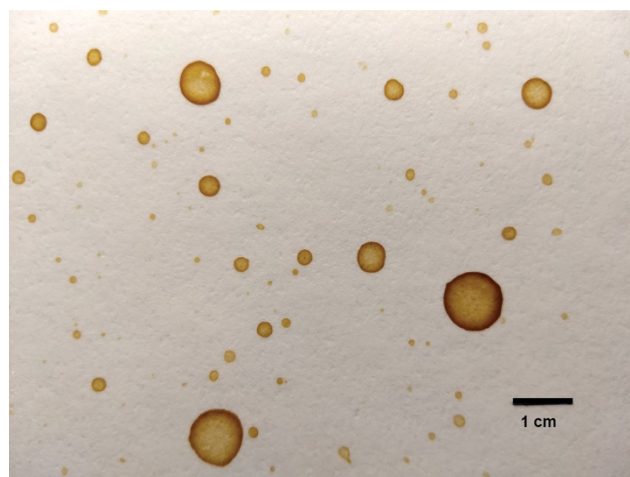


Figure S1. Coffee rings in air. Photograph of projected coffee droplets dried in air onto surface protection paper (Whatman Benchkote).

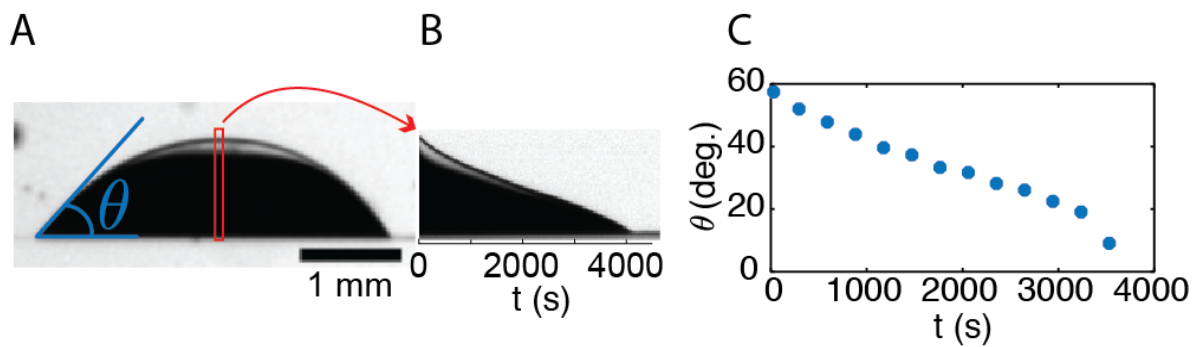


Figure S2. Droplet-dissolution driven change in height and contact angle.

(A) Side view of a sessile drop containing silica particles (diameter: 560 nm) at a concentration of 0.5 wt%. The red rectangle highlights the portion corresponding to the maximum height of the droplet and used in (B) to make a kymograph that shows the time-evolution of the maximum drop's height. The blue lines show the angle θ that the droplet makes with the interface. The time evolution of θ is shown in (C).

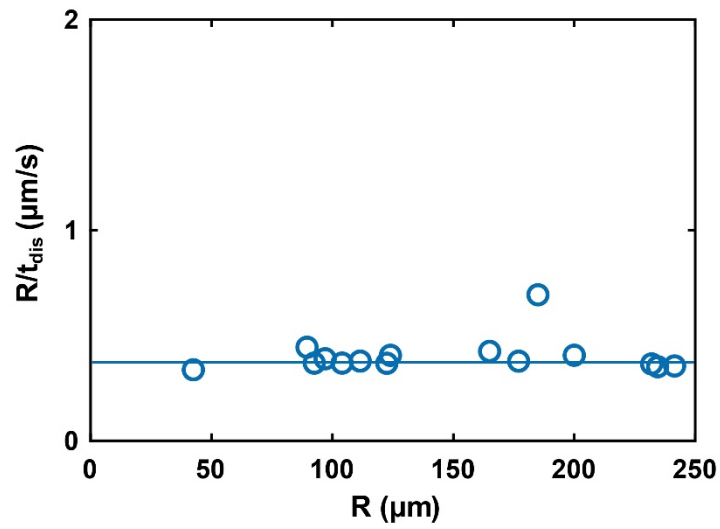


Figure S3. Characteristic velocity during the droplets' dissolution.

Graph of the characteristic velocity R/t_{dis} plotted versus the radius R . Each single point corresponds to the dissolution of a drop of water containing silica particles (diameter: 560 nm) at a concentration of 0.5 wt%. The solid line corresponds to a mean value for $R/t_{dis} \sim 0.4 \mu\text{m/s}$.

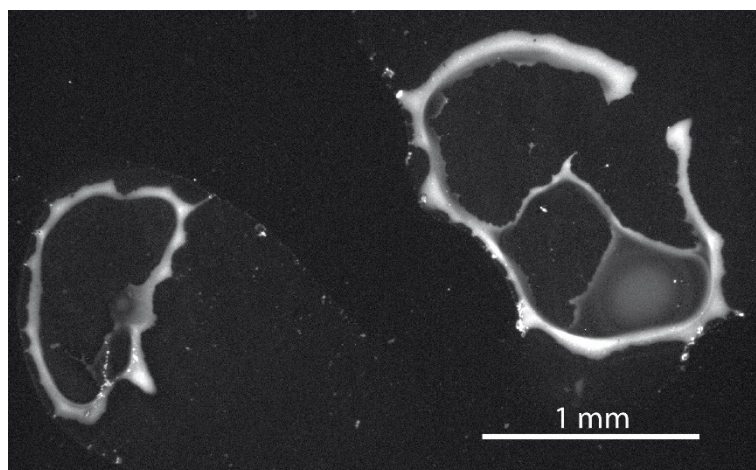
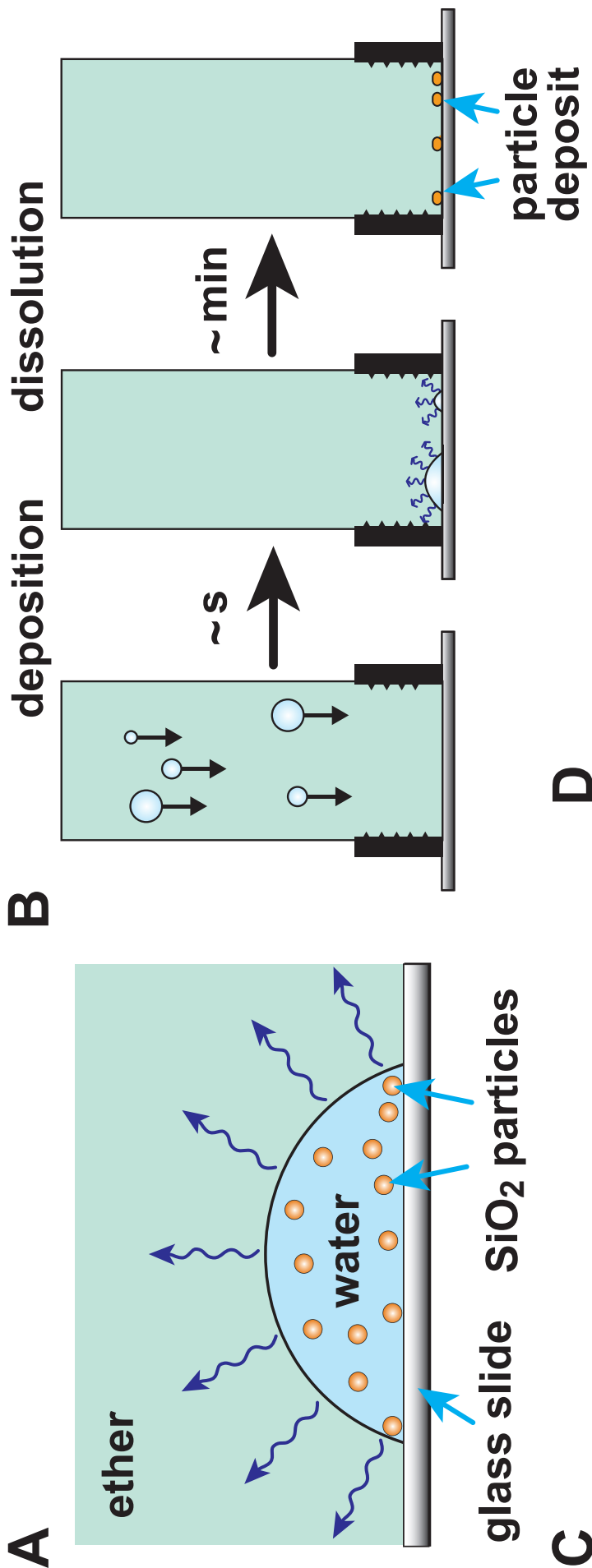


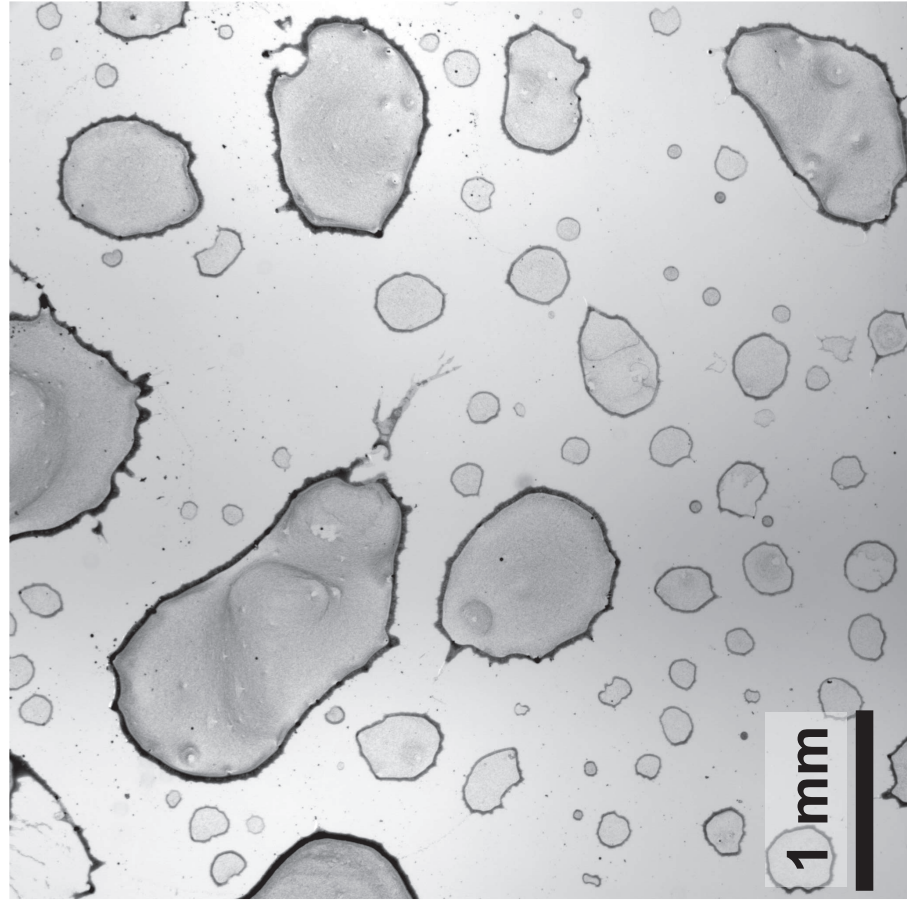
Figure S4. Representative fluorescence microscopy image of the deposits left by sessile water drops containing YOYO-1 labelled DNA after their dissolution in ether.

Legend of Movie S1.

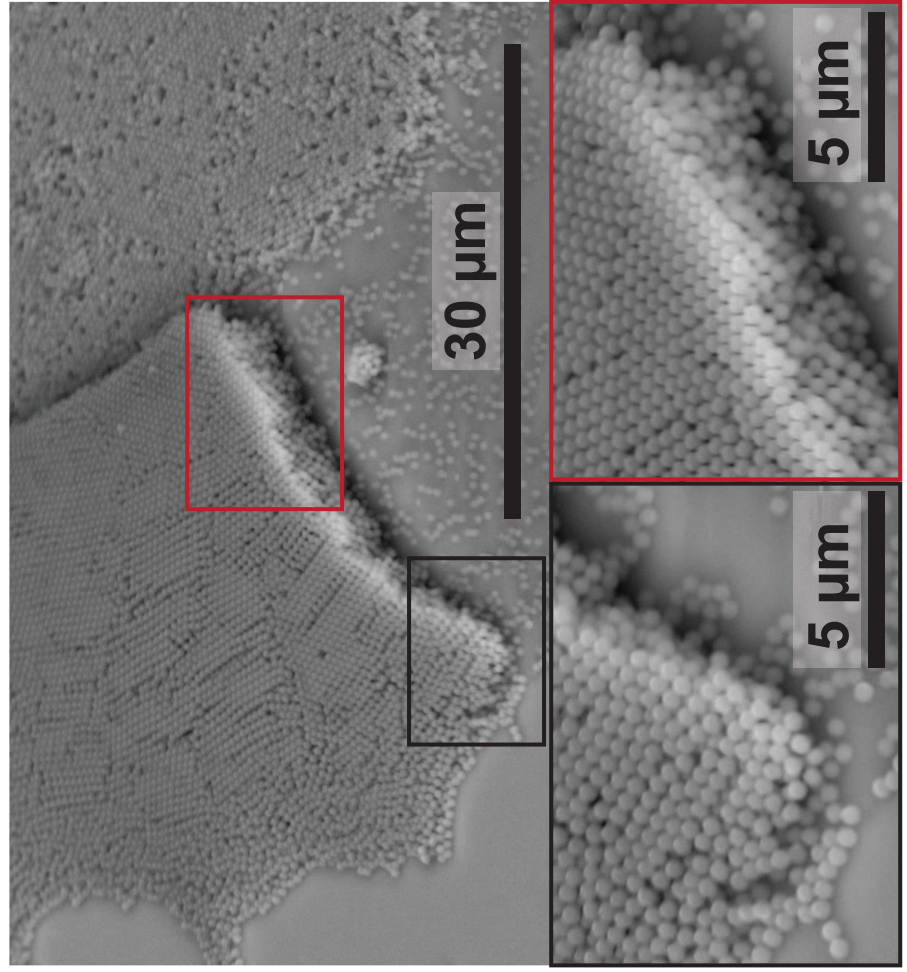
Bottom-view transmission optical microscopy movie showing the dissolution of a water drop containing silica particles (diameter: 560 nm) at a concentration of 0.5 wt%. The movie is accelerated 100 times and has a size 530 μm \times 530 μm .

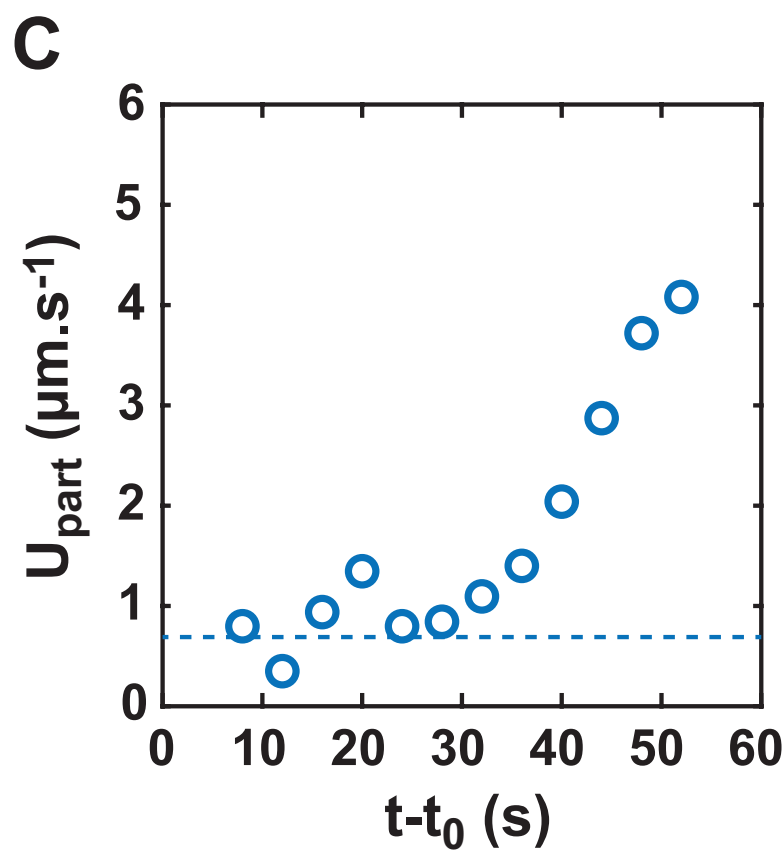
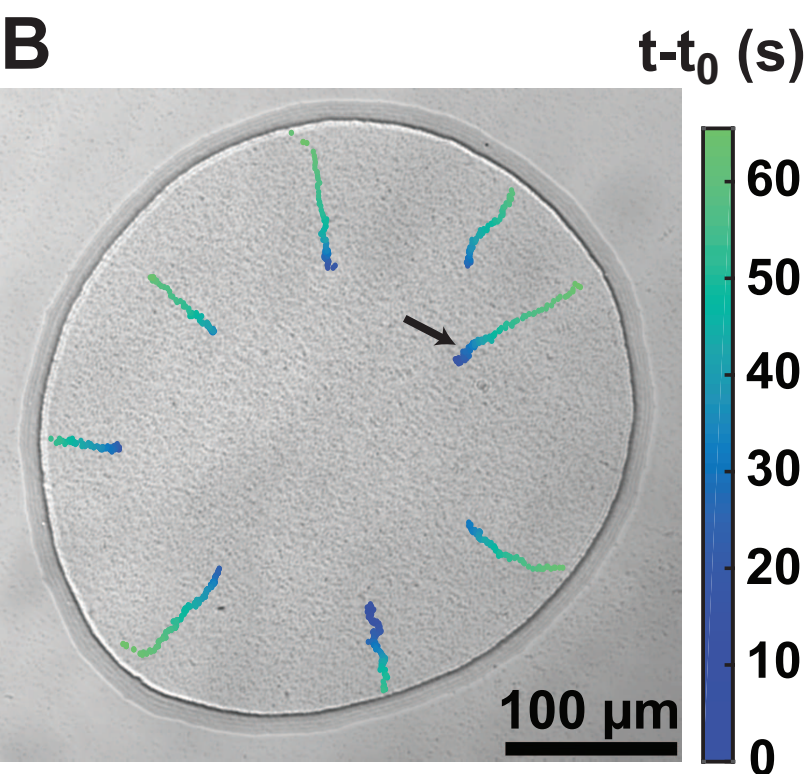
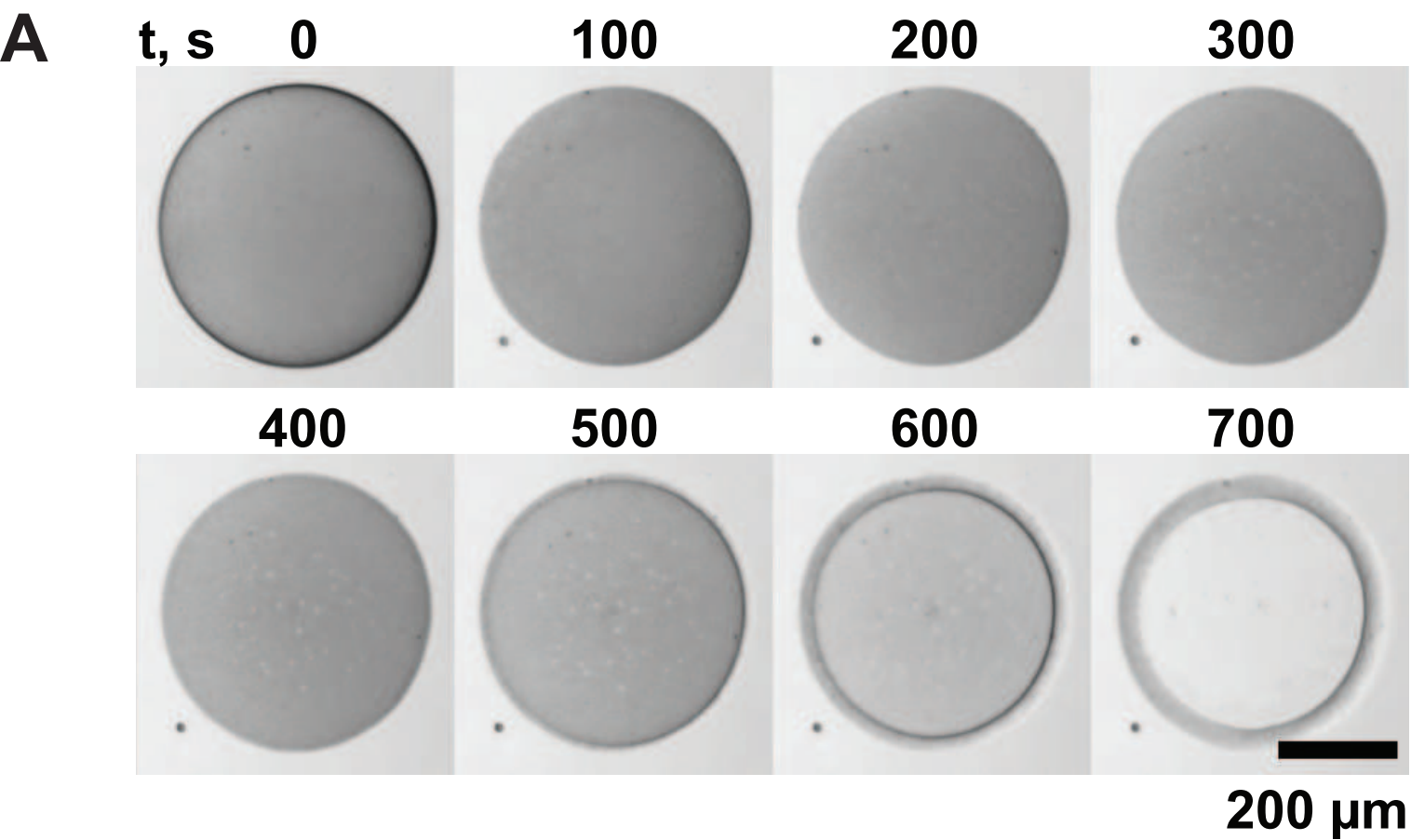


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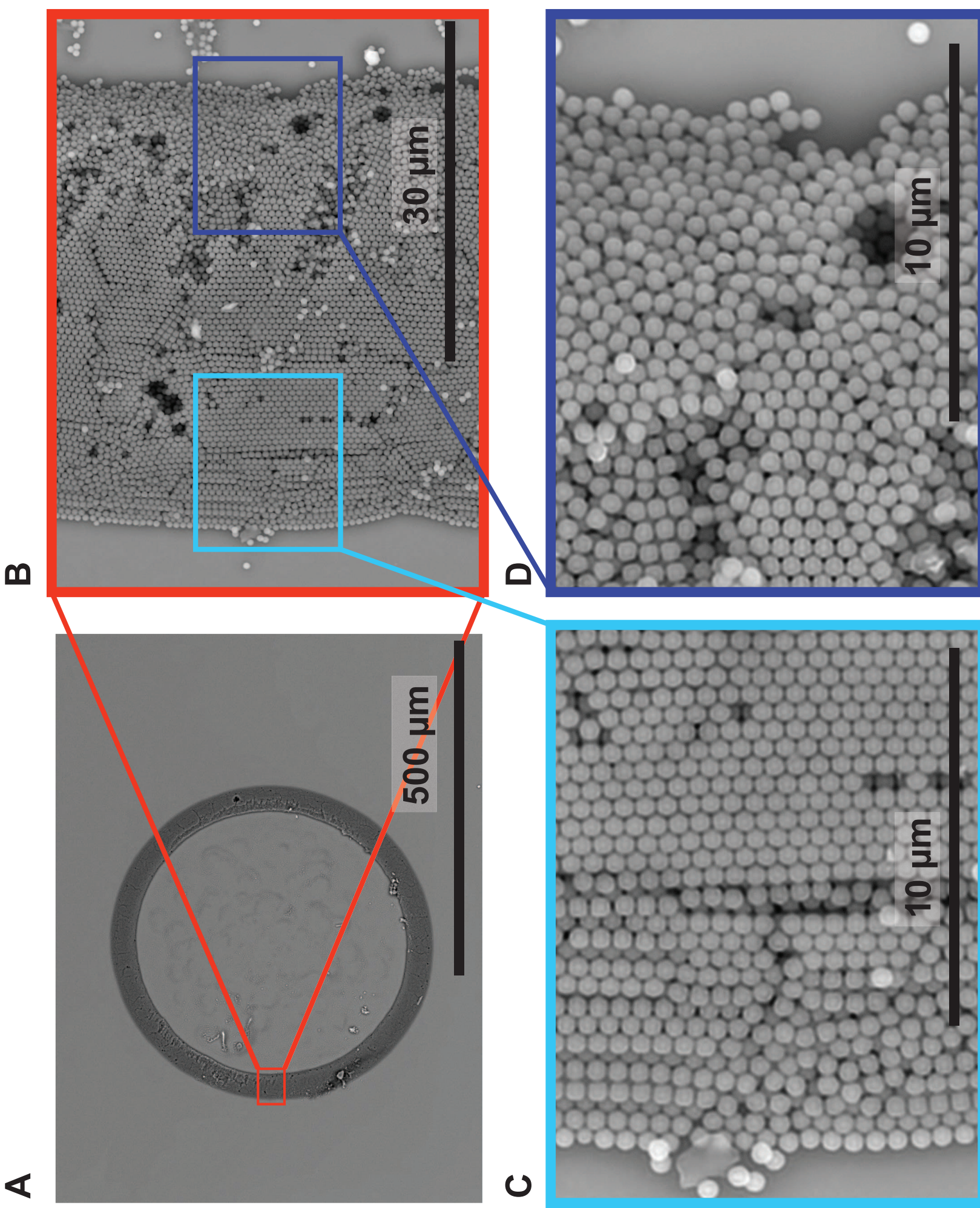


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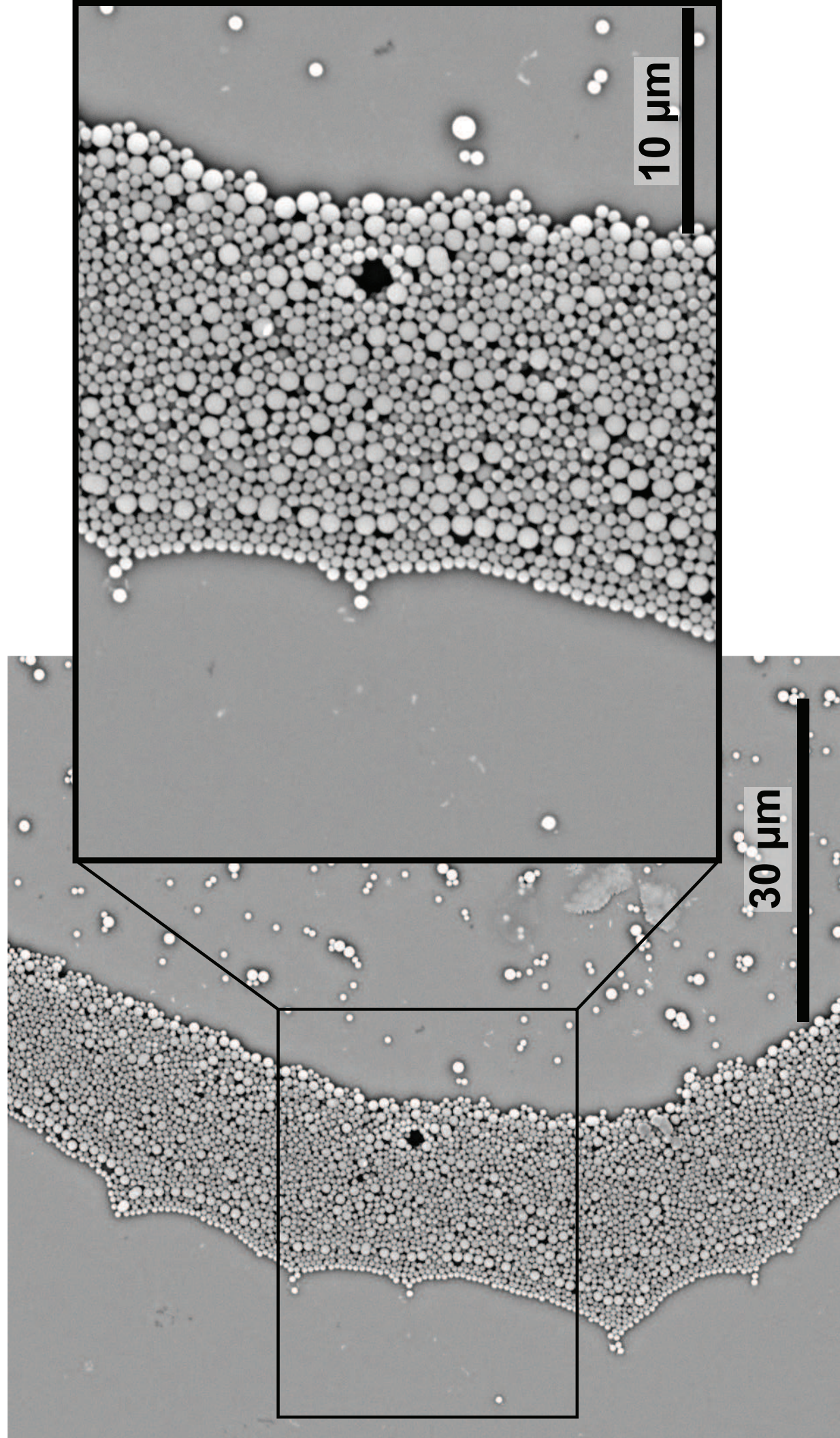




5: Figure



5: Figure



7:Supplementary Material

[Click here to download 7:Supplementary Material: Movie S1.avi](#)

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: