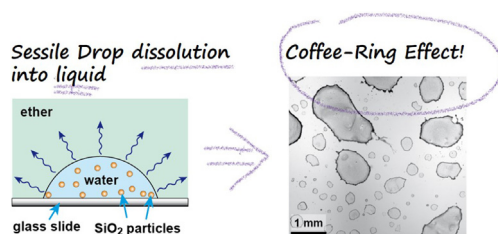


Liquid-liquid coffee-ring effect

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GRAPHICAL ABSTRACT



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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.

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1. 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 [2–11]. 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 rainwater, blood, inks, alcoholic beverages or paints [12–14], and a plethora of deposited materials including particles,

synthetic polymers, DNA or proteins [15,16]. For many industrial and biotechnological processes relying on the deposition of materials from liquid drops, the CRE is a major obstacle that leads to heterogeneous depositions. This has triggered efforts to suppress or circumvent the CRE so that homogenous deposits rather than rings could be obtained [6,10,11,17]. Conversely, the CRE has been identified as a powerful tool for both guiding particle deposition [5,18] and realizing quick and cheap diagnosis [13,19]. 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 [20,21]. 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

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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.

2. Materials and methods

2.1. 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 M Ω -cm). The diethyl ether was purchased from Sigma-Aldrich (Sigma-Aldrich, anhydrous, 99.7%).

2.2. 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.

2.3. 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 drops were allowed to sediment to the bottom of the cell.

2.4. Imaging

The time-lapses were imaged *in situ* with a bright-field inverted microscope (Zeiss, Observer D1) at a magnification of $2.5\times$ or $20\times$ and equipped with a sCMOS camera (Andor, Zyla). The acquisition started a few seconds after the cell was flipped. To analyze the dry deposits, the screw cap was removed and the ether was let to evaporate prior to imaging. Scanning electron microscopy was performed with a tabletop microscope (Hitachi, TM3000) with the *Analy* mode (15 kV), at magnifications ranging from $180\times$ to

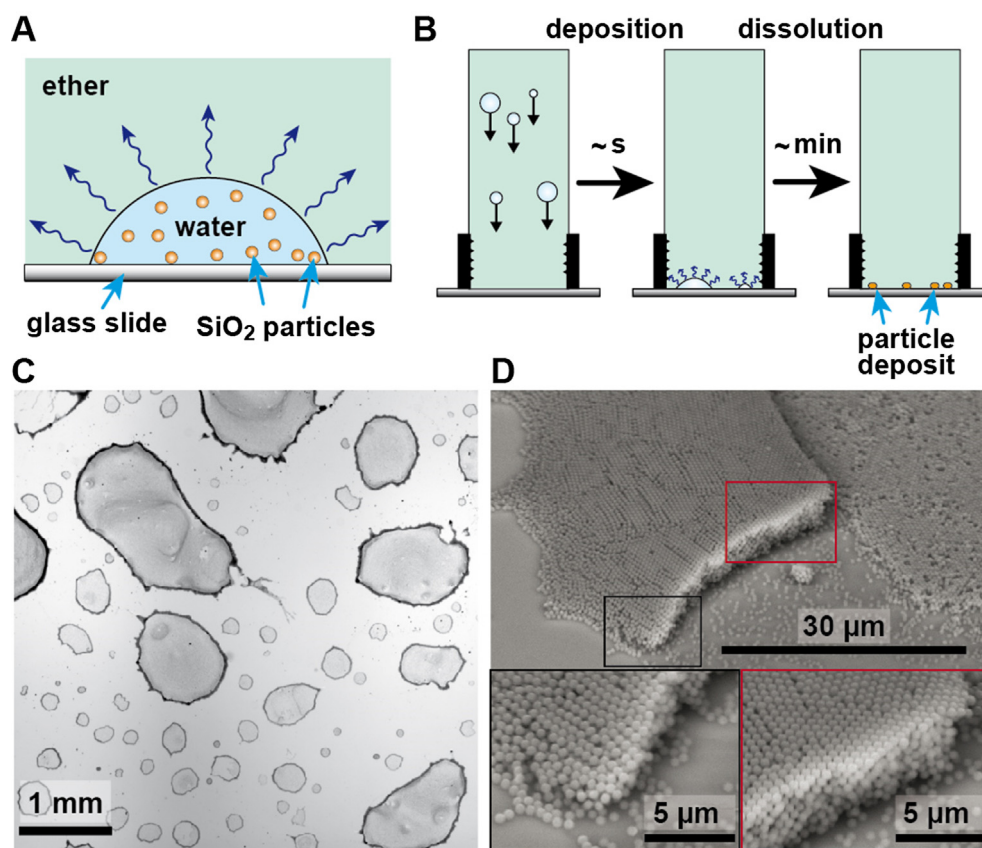


Fig. 1. Pinned sessile drops of water containing particles dissolve in ether to form rings of packed particles. (A) Sessile drops on glass contain silica particles (diameter: 560 nm) at a concentration of 0.5 wt% and dissolve in ether. (B) Sessile drops are produced in a few seconds by emulsification 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.

$10,000 \times$. The incident angle used in the SEM was 90° , except when it is otherwise reported.

3. 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% [22]) 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 drops 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} , defined as the time needed for the liquid of a given drop to fully transfer to the outer phase, 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

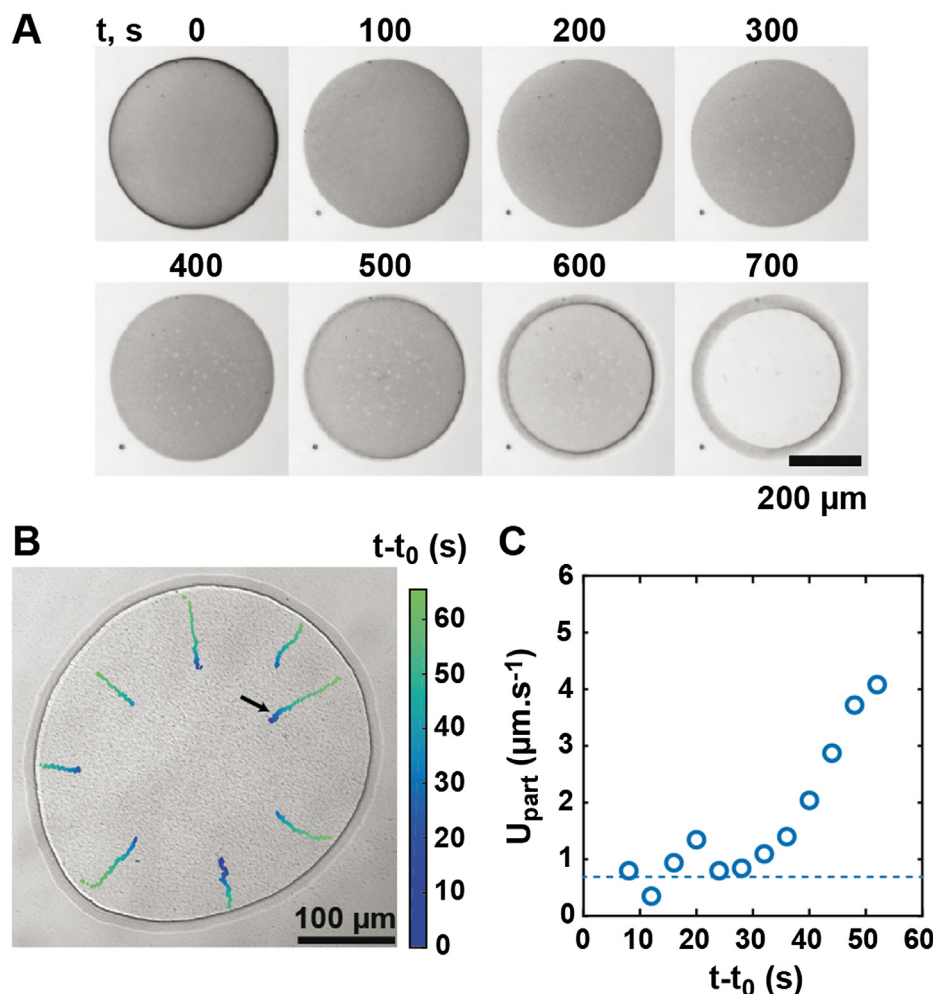


Fig. 2. Radially symmetric solvent dissolution-driven transport of particles toward the contact line. (A) *In situ*, timelapse transmission optical microscopy images of the dissolution of a single drop containing 0.5 wt% of 560 nm diameter silica particles. (B) 8 individual particles tracked during solvent 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 ($t_{dis} = 260 \text{ s}$).

(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

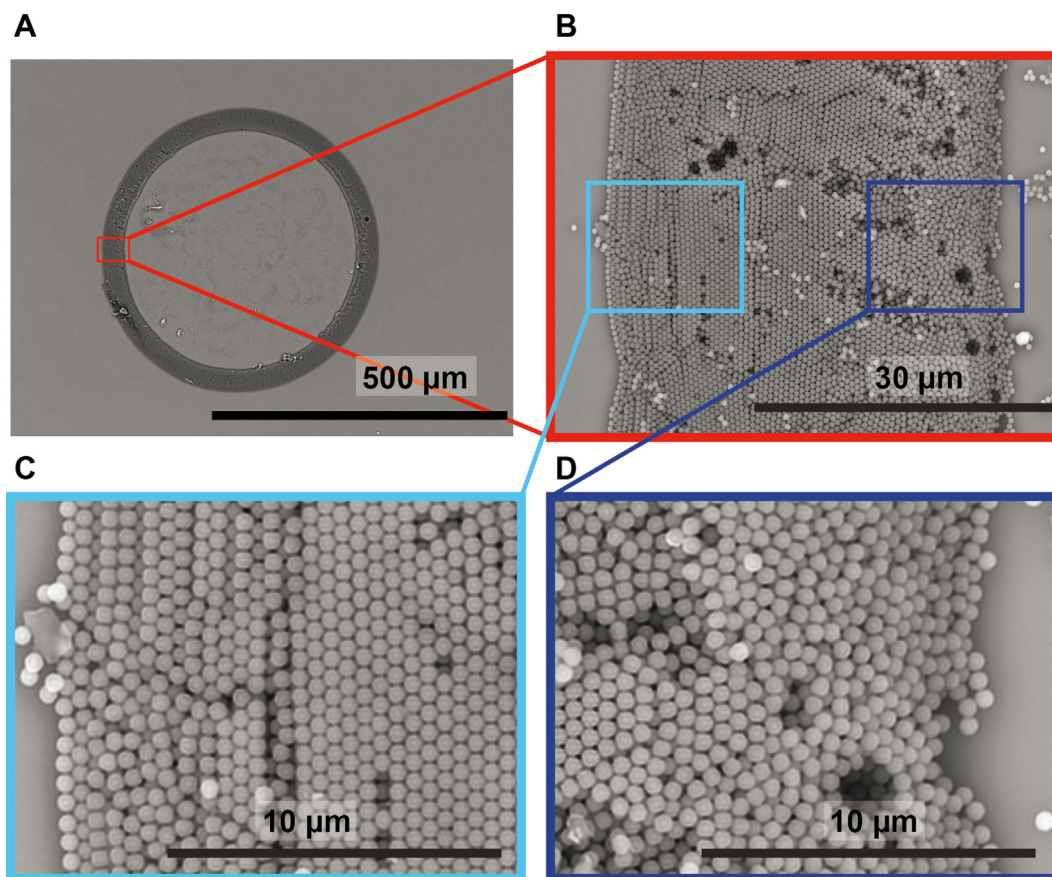


Fig. 3. Order-to-disorder transition of particle packing from the outside to the inside of the deposit. SEM images of the same deposit at different magnifications: $180\times$ (A), $3000\times$ (B) and $10000\times$ (C,D). The water drop initially contained 0.5 wt% of 560 nm diameter silica particles.

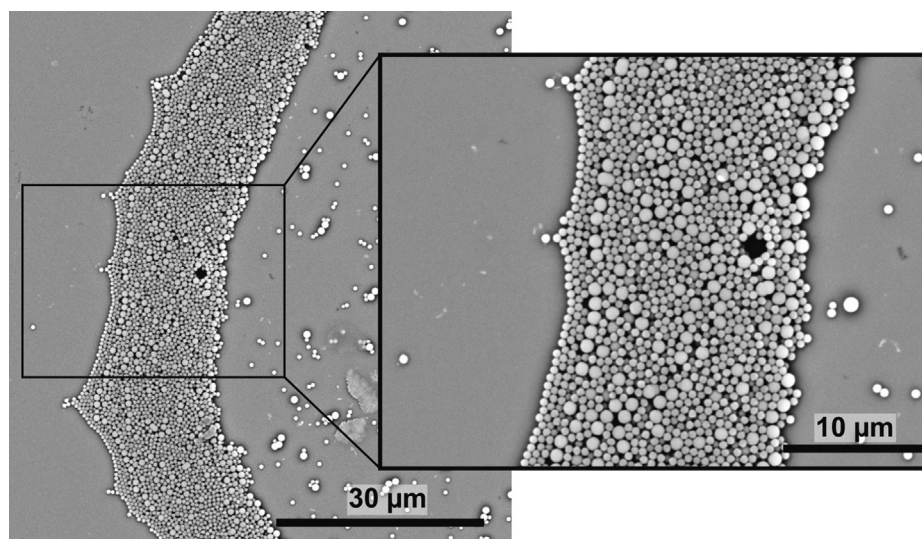


Fig. 4. Size-selective segregation of particles upon deposition. SEM images of the same deposit obtained by the dissolution of water drops containing a mixture of 0.25 wt% of 560 nm diameter silica particles and 0.25 wt% of $1 \mu\text{m}$ silica particles.

variations that can significantly alter the particle transport speed in evaporative CRE [20].

Upon accumulation at the contact line, the particles formed a ring of packed particles (Fig. 1D, Fig. 3A) where they organized (mainly in hexagonal lattices) close to the outer part of the ring (Fig. 3B light blue box, C) but formed disordered assemblies closer to the inner part of the ring (Fig. 3B dark blue box, D). 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 [23]. 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 increase in particles velocity resulted in insufficient 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_{part} 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 ($t_{diff} \sim (2R_{part})^2/D$ where D is the diffusion coefficient). This corresponds to a critical particle speed $U_{part}^{crit} \sim dD/(2R_{part})^2 \approx 9 \mu\text{m/s}$ 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 [24,25]. 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 deoxyribonucleic acid (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.

4. Conclusion

Denoting the accumulation of non-volatile solutes at the edge of a drying and pinned sessile drop, the coffee-ring effect (CRE) is both a scientific puzzle for the researchers due to its multiscale and unsteady character and an obstacle in industry as it works against the formation of homogenous deposits. The past 20 years of studies has been vastly dedicated to understand, control or circumvent the CRE [1], and mostly considering the scenario where drops dry in an outer gas phase. Here, we studied the deposit left after the dissolution of a sessile drop containing insoluble particles into another partially miscible liquid instead of a gas phase, and found that it recapitulated all the characteristic traits of a conventional evaporative CRE. We showed in particular that the combination of drop pinning and solvent diffusion to the external phase resulted in a radial flow that transported the particles towards the contact line where they arranged into a ring-like deposit. Such deposits showed a characteristic order-to-disorder transition going

from the outside to the inside of the ring, as well as a confinement-driven size-selective segregation in the case of mixtures of particles. We thus conclude 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 drop 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 as in-liquid printing [26] and patterning [27–29] or low-cost point-of-care diagnostic systems [13,30] that can be less sensitive to on-field ambient air conditions.

CRedit authorship contribution statement

Vincent Poulichet: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft. **Mathieu Morel:** Investigation, Formal analysis, Writing - review & editing. **Sergii Rudiuk:** Investigation, Formal analysis, Writing - review & editing. **Damien Baigl:** Supervision, Funding acquisition, Conceptualization, Methodology, Formal analysis, Writing - original draft.

Declaration of Competing Interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2020.03.094>.

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