Suppressing the Ring Stain Effect with Superhydrophilic/ Superhydrophobic Patterned Surfaces

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ABSTRACT: The ring stain phenomenon is a critical hindrance to the distribution of the solute during drying for biochemical assays and materials deposition. Herein, we developed a substrate, characterized with hydrophilic spots surrounded by hydrophobic areas, to suppress the ring stain effect, and fabricated four kinds of patterned surfaces to investigate the relationship between the surface free energy and ring-suppressing performance. We found that during the evaporation process, a drop was constrained on the hydrophilic spot with a pinned contact line, and the ring stain effect was suppressed significantly. The suppressing performance of the ring stain effect increases with surface free energy differences between the hydrophilic and hydrophobic regions.

1. INTRODUCTION

Ring-like deposits are commonly observed along the perimeter of evaporating drops, known as the “coffee ring” phenomenon, which is undesirable in many cases, including DNA chips,1,2 painting, and printing.3,4 In 1997, Deegan and co-workers’ first proposed that an outward capillary flow in a drying drop of liquid carried dissolved solids to the periphery, forming ring-like deposits, and two conditions are necessary for forming the capillary flow: contact line pinning and evaporation from the edge of the drop.

Since then, efforts for suppressing the ring stain effect were mainly focused on three strategies based on physical chemistry: (i) attenuating the pinning of the contact line, (ii) disturbing the outward direction of the capillary flow, and (iii) preventing the nonvolatile solutes to be transported to the edge of droplet.6 In short, it can be concluded that all these methods took control of the drying process by transition of the liquid property, transition of substrate property, interactions at solid−liquid or liquid−gas interfaces, and altering environmental conditions. The details are as follows:

If a droplet was pure ethanol instead of water, the drying process behaved in the manner with a constantly decreasing contact radius at an essentially constant contact angle.7 Jin et al.8 significantly reduced the coffee ring and improved the film uniformity by controlling the amount of ethanol added in the MnO2 droplet. Addition of surfactants or zwitterionic detergents9 and heating of the liquid were the methods based on the Marangoni flow effect,10 which needed to change the properties of solutes sometimes. The coffee ring effect suppression could also be demonstrated by addition of a hydrosoluble polymer,11 or a biocompatible, surfactant-like polymer (PEG)13 into the relative droplets.

Shimobayashi et al.14 found that sweet coffee drops above a threshold sugar concentration left a uniform rather than the ring-like pattern.

For altering environmental conditions including humidity, temperature, and acoustic or electric fields,15,16 complicated devices were needed to control the drying process. Eales and Routh17 showed that ring-shaped deposits could be removed through careful selection of the atmospheric conditions, and humidity cycling had potential for controlling the film shape of the volatile droplet. Deegan et al.18 restricted evaporation from the edge of drop by covering the drop with a lid that had only a small hole over the center of the drop. Yen et al.19 invented a methodology of laser-induced differential evaporation to remove the coffee ring effect.

In order to investigate the transition from the coffee ring deposition to the uniform coverage in drying pinned sessile droplets, Crivoi and Duan10,21 developed a Monte Carlo model to comprehend the relationship between ring stain inhibitions and interactions at solid−liquid and liquid−gas interfaces, while Xu et al.22 developed a discrete element model to comprehend the interparticulate activities. In the field of

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biochip and nanostructuring, Askounis et al.23 observed smoother ring stains with some nanostructuring when DNA self-assembly was indicative of the importance of DNA length. Nanosheets,24 nanorods,25 or their hybridization could also break the formation of coffee rings and deposit uniform films after drying. Yunker et al.26 carried the ellipsoids to the air−water interface by the outward flow that caused the coffee ring effect for spheres, but strong long-ranged interparticle attractions between ellipsoids led to the formation of loosely packed or arrested structures on the air−water interface.

Superhydrophilic or superhydrophobic27,28 surfaces could be used to suppress ring deposition because on these two kinds of surfaces, a water drop has a moving contact line, but it is difficult to define the area for solute distribution. Maran-Mirabal et al.29 used a hydrophilic/hydrophobic mosaic surface to suppress ring deposition and found that the solute was concentrated on the hydrophilic zone while the capillary flow was reversed on the hydrophobic zone. Das et al.30 showed a suppression of ring deposits when a droplet, deposited on a glass substrate coated with a thin layer of silicone oil, was evaporated. Ji et al.31 presented a suppressed coffee ring system via a combination of a magnetically functionalized membrane and reciprocating magnetic field for highly reliable and ultrasensitive SERS detection. However, very little attention has been paid to a patterned substrate. Herein, we developed a substrate, characterized with hydrophilic spots surrounded by hydrophobic areas, to suppress the ring stain effect and fabricated four kinds of patterned surfaces to investigate the relationship between the surface free energy and ring-suppressing performance.

2. RESULTS AND DISCUSSION

According to Young’s equation,32 when a drop is placed on a homogeneous surface, there is a three-phase equilibrium at the edge of drop

$$\gamma_l \cos \theta = \gamma_{sg} - \gamma_{sl}$$

(1)

where $\gamma_l$, $\gamma_{sg}$, and $\gamma_{sl}$ denote the interfacial tensions of the liquid/gas, the solid/liquid, and the solid/gas interface, respectively. On a hydrophilic surface ($\theta < 90^\circ$), $\gamma_{sg} > \gamma_{sl}$, an aqueous solution will spread, while on a hydrophobic surface ($\theta < 90^\circ$), $\gamma_{sg} > \gamma_{sl}$, aqueous solution will bead up. So, when a drop is placed on the interface between hydrophilic and hydrophobic regions, the drop will have a tendency to leave the hydrophobic region and stay in the hydrophilic region. The driving force for the solution to move and remain depends on the difference of $(\gamma_{gs} - \gamma_{ls})$ between the hydrophilic and hydrophobic region: the larger difference of $(\gamma_{gs} - \gamma_{ls})$, the greater the driving force. In another perspective, the driving force could prevent water molecules escaping from liquid to air, which results in a slower evaporation at the edge of the drop and suppressed capillary flow. So, a substrate with hydrophilic spots surrounded by a hydrophobic area may be good for suppressing the ring stain effect.

To illustrate the abovementioned designation, four kinds of patterned surfaces were fabricated by removing fluoroalkylsilane (FAS) locally by O2 plasma from the hydrophobic or superhydrophobic surface: hydrophilic (CA 35 ± 2°)/hydrophobic (CA 105 ± 2°), hydrophilic (CA 35 ± 2°)/superhydrophobic (CA 150 ± 2°), superhydrophilic (CA 3 ± 1°)/hydrophobic (CA 105 ± 2°), and superhydrophilic (CA 3 ± 1°)/hydrophobic (CA 105 ± 2°).
± 1°)/superhydrophobic (CA 150 ± 2°) surfaces. Drops of 1 μL aqueous solution with different amounts of fluorescein isothiocyanate (FITC) (0.2, 0.4, 0.6, 0.8, and 1.0 ng) were spotted on hydrophilic (or superhydrophilic) spots of patterned surfaces and then were observed by a fluorescence microscope after being dried (Figure 1a–e). It is obvious that spots on patterned surfaces have higher uniformity compared to those on the homogeneous hydrophilic surface (CA 35 ± 2°), demonstrating that the ring-like stain was significantly suppressed on a hydrophilic/hydrophobic patterned surface. To assess the uniformity of FITC deposition, the percentage standard deviation (PSD) values of pixel fluorescence intensities within the spots were calculated (Figure 1f). Based on the analysis of PSD values, we can conclude that the ring stain effect can be suppressed most significantly on a superhydrophilic/superhydrophobic patterned surface, next came hydrophilic/superhydrophobic, the third rank is given to superhydrophilic/hydrophobic, and then hydrophilic/hydrophobic patterned surfaces. In our experiment, when the FITC concentration was 0.25 ng/mm², the PSD values on the abovementioned four kinds of patterned surfaces are 9, 12, 18, and 22%, respectively. It can be also noticed that the uniformity of drops on superhydrophilic spots is slightly better than that on hydrophilic ones and is much better on spots with superhydrophobic surroundings than that on spots with hydrophobic surroundings.

It was noteworthy that PSD values of drops on all kinds of surfaces decreased significantly with the increasing of FITC concentration, implying that the ring stain effect was closely related to the initial solute concentration. The higher the concentration, the less ring deposition is.

For further explanation of this ring-suppressing performance, the droplets containing PS microsphere solutions (1 μL, 19% wt) were dried on the hydrophilic anodic aluminum oxide (AAO) surface and the superhydrophilic/superhydrophobic patterned surface. The SEM images of the residues on the edge of the ring showed that the PS microspheres uniformly dispersed on the patterned surface, while those close packed on the hydrophilic surface (Figure 2).

Figure 2. SEM images of the residues on the edge of the ring formed on the (a) superhydrophilic/superhydrophobic patterned surface and (b) hydrophilic AAO surface.

According to Deegan and co-workers’ theory, an outward capillary flow carried the solute to the edge of the drop, forming ring-like deposits. To detect whether the capillary flow in drops was altered on our hydrophilic/hydrophobic patterned surface, drops of an aqueous solution containing CdTe quantum dots were spotted on superhydrophilic/superhydrophobic patterned surfaces (CA 3/150°), and a hydrophilic surface (CA 35 ± 2°) was used as a control. The images of the drying process were captured with a camera from above down with a perpendicular angle to the surface in order to observe the residue dispersing process of a spotted droplet, especially to take the images of the droplet edge. By recording fluorescence microscopy images of spotted drops during drying, we observed that fluorescence intensity kept invariant as time was prolonged on the superhydrophilic/superhydrophobic patterned surface (Figure 3a). However, on the control surface, the fluorescence intensity at the edge increased with the evaporating time and decreased at the center of the drop simultaneously (Figure 3b), showing that quantum dots were carried to the edge by an outward capillary flow. In other words, the outward direction of the capillary flow was suppressed on the hydrophilic/hydrophobic patterned surface.

There are two necessary factors for the outward capillary flow: a pinned contact line and larger evaporation rate at the edge of the drop. Based on the video of the drying profile of the spotted drop on the superhydrophilic/superhydrophobic patterned surface (Figure 4), we found that the drop was constrained on the hydrophilic spot with a pinned contact line. So, we presumed that alteration of capillary flow direction inside the drop on a hydrophilic/hydrophobic patterned surface may be caused by the changing evaporation rate at the edge of the drop as proposed previously. In our case, water contact angles for the four kinds of patterned surfaces are 3/150, 35/150, 3/105, and 35°/105°, and the differences of cosθ were 1.865, 1.685, 1.258, and 1.078 respectively. As shown in Figure 1, the efficiency of ring stain suppressing decreased in the same sequential order. As well known, the water contact angle depends on the solid surface free energy, so the efficiency of ring stain suppressing increases with the difference of the surface free energy between hydrophilic and hydrophobic surfaces, and the superhydrophilic/superhydrophobic patterned surface is the best one.

3. CONCLUSIONS

In summary, our experimental results reveal that the ring deposits can be suppressed significantly on hydrophilic/hydrophobic patterned surfaces. The improvement of uniformity of spots depends on surface free energy differences between the hydrophilic and hydrophobic regions. Our results provide ways to better control the distribution of the solute during drying, which is important for biochemical assays and materials deposition.

4. EXPERIMENT SECTION

4.1. Materials. Annealed aluminum foils (99.99% purity) with a thickness of 100 μm from XinJiang JoinWorld Corporation (China) were used as the substrate material. All chemicals, unless otherwise specified, were obtained from China National Pharmaceutical Group Corporation and were analytically pure and used without further purification. Fluorescein isothiocyanate (FITC) was purchased from Fluka (Switzerland). Fluoroalkylsilane (FAS) was obtained from Sigma-Aldrich (St.Quentin Fallavier, France). Ultrapure water (18.2 MΩ) was prepared with a Millipore water purification system. PS microsphere solutions (1 μL, 19%wt) and 20 nm-sized CdTe nanoparticles were presented by ICCAS.

4.2. Fabrication of Hydrophilic/Hydrophobic Patterned Surfaces. Superhydrophilic anodic aluminum oxide (AAO) membranes with a contact angle (CA) less than 3° and hydrophilic surfaces (CA = 35 ± 2°) were prepared via an
anodic oxidation method by anodizing for 120 and 30 min under a constant current of 5 mA/cm². After modification by FAS, superhydrophobic AAO (155 ± 2°) and hydrophobic surfaces (105 ± 2°) could be obtained, respectively. Fabrication of patterns was carried out by locally removing FAS from hydrophobic AAO with a low pressure plasma cleaner (PlasmaPrep2, Diener Electronic, Germany). After the treatment by O₂ plasma with a mask, hydrophilic or superhydrophilic spots with a diameter of 1 mm were fabricated on the superhydrophobic surfaces (Figure 5a).

Fabrication of hydrophilic/hydrophobic patterns was carried out by locally removing FAS from hydrophobic AAO by O₂ plasma. After the treatment by O₂ plasma with a mask, hydrophilic spots with a diameter of 1 mm were fabricated on the hydrophobic surface (Figure 5b).

In order to fabricate superhydrophilic/hydrophobic patterns, a hydrophobic surface (105 ± 2°) was first obtained by removing FAS from superhydrophobic AAO treated with 40 W of O₂ plasma for 15 s, and then the superhydrophilic/hydrophobic patterns were obtained by locally removing FAS with a mask. After the treatment by O₂ plasma, superhydrophilic spots with a diameter of 1 mm were fabricated on the hydrophobic surface (Figure 5c).

Figure 3. Fluorescence microscopy images of the edge of drying drops containing 20 nm-sized CdTe nanoparticles on (a) superhydrophilic/superhydrophobic patterned and (b) hydrophilic surfaces.

Figure 4. Evaporation behavior and model of a water drop on the superhydrophilic/superhydrophobic patterned surface.
Under different powers and treating times of O₂ plasma to remove FAS from superhydrophobic AAO, it is found that the higher the power is, the shorter the treating time required for the complete removal of FAS. Thus, under a certain power, the surfaces with different wettability can be obtained by controlling the treating time, and only when the surface become superhydrophilic and the contact angle is close to 0 ° can it be indicated that FAS is completely removed (Figure 6).

To indicate the capillary flow behavior inside the drop during evaporation,

1 μL of an aqueous solution containing 0.312 μg CdTe quantum dots (20 nm sized, emission wavelength 631 nm) was placed on superhydrophilic spots of the superhydrophilic/superhydrophobic patterned surface, and a hydrophilic surface with a water contact angle of about 35° was used as the control substrate. The fluorescence microscopy images of the capillary flow near the contact line of the droplet at different times were recorded by a digital camera (Cannon, EOS-350D).

![Figure 6](https://pubs.acs.org/doi/10.1021/acsomega.0c01568)

**Figure 6.** Contact angle change of FAS-modified AAO surfaces with treating time by O₂ plasma.

The FAS-modified superhydrophobic AAO surfaces were treated with O₂ plasma for 10, 20, 30, and 40 s at 60 W of power; PES analysis showed that the signals of F, Si, and C elements still existed for a short treating time (<20 s), which indicated that FAS was not removed from AAO completely, while the signals of F, Si, and C elements disappeared for a longer treating time (>40 s), which indicated that FAS was removed from AAO completely (Supporting information).

4.3. Characterization. The water contact angle measurements were carried out with 2 μL water droplets at 22 °C by a commercial contact angle meter (OCA-20, Dataphysics, Germany). The drying profile of the spotted droplet was observed with a CCD in the abovementioned system to record side views of the droplet.

An FITC solution of 1 μL was spotted on the patterned AAO substrate with a syringe pump then dried at 22 °C with relative humidity of 40%. Spot quality analysis was carried out by analyzing fluorescence microscopy images recorded by a fluorescence microscope (Motic, AE30) equipped with a digital camera (Cannon, EOS-350D). For fluorescence imaging, a 100 W high-pressure mercury lamp was used as the excitation source. The pixel intensities of resulting images were recorded by a fluorescence microscope (Motic, AE30) equipped with a digital camera (Cannon, EOS-350D). For fluorescence imaging, a 100 W high-pressure mercury lamp was used as the excitation source. The pixel intensities of resulting images were recorded by a digital camera (Cannon, EOS-350D).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01568.

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