Investigation of Droplet Evaporation on Copper Substrate with Different Roughness

Xin Wang, Zeyu Liu, Li Wang, Yuying Yan*

Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, United Kingdom

Abstract

In the present study, we investigated the evaporation process and deposition pattern of saline droplet on a copper substrate with different roughness under 40°C ambient temperature. These four substrates are classified as smooth surface and rough surface based on their droplet contact angles. It has been found in this study that the evaporation pattern of droplets has a strong relationship to substrate roughness. The thickness boundary of the evaporation pattern on a smooth surface is larger than that on a rough surface and the particles are closer to boundary and the tendency more obvious on a smooth surface. The below factors contribute to the result. On the smooth surface, the contact angle of droplet increases as the roughness decreases. On the rough surface, the contact angle increases as the roughness increases. With contact angle decreasing, the evaporation rate at the boundary increases leading to the particles at the boundary more easily sedimentate. Moreover, the capillary flow is hindered by increasing the substrate roughness, while the Marangoni flow remains constant, resulting in more particles remain in the center of the droplet on the rough surface. To sum up, the deposition pattern of droplet has a strong relationship to substrate roughness. The coffee-ring formation is suppressed by increasing the substrate roughness on a copper substrate under 40°C temperature.

Keywords: Saline droplet evaporation, Surface roughness, Coffee ring, Marangoni flow, Capillary flow

*corresponding author: Yuying Yan
Email: yuying.yan@nottingham.ac.uk

1. INTRODUCTION

Droplet evaporation is one of the ubiquitous phenomena in nature. This phenomenon has long attracted much attention from academic researchers because of its rich fundamental phenomenon and the number of related applied aspects [1,2]. Furthermore, the distribution of sediment in the nature can be affected by the self-cleaning surface [3,4] and phase change of liquid [5] during the evaporation process. It is inspired by the nature that the droplet deposition pattern can be control by the surface with various wettability without extra chemicals. The coffee ring effect is one of sub-section of droplet evaporation, which is deposited by non-volatile solute of liquid after evaporation [6,7]. However, this effect is an unexpected result in adverse effect during the manufacturing process involving inkjet printing [8], spray cooling [9], substrate patterning [10], and DNA/RNA microarrays [11].

Therefore, many researchers have been carried out to understand and control the process of solute deposition in the presence of the coffee-ring effect (CRE). In 1996, Parisse et al. [12] revealed a theoretical model to predict the film thickness upon complete evaporation first time. Later, Deegan et al. [13] studied the mechanism of coffee-ring formation by observing the colloid droplet evaporation and his results show that uneven evaporation is the most important role of capillary flow on mass transport.

Thenceforth, there are many researchers studying unceasingly the mechanism of the CRE. The formation of CRE is a complex process and mainly relates to the contact line pinning and contact angle hysteresis [14]. Due to the relatively larger proportion of liquid-air interface at the contact line, the evaporation rate is higher there, as a result the flow rate there is also relatively higher [15]. For the evaporation of droplets containing colloidal suspension, the magnitude of Capillary flow affects the order of the particle deposition at the contact line. Marin et al.[16] observed that the capillary flow diverges at the end of the evaporation process, and the particle deposition also transforms from ordered to disordered. Meanwhile, the CRE is contributed by a number of other factors such as Marangoni flow [17,18], the geometry of the substrate and particle surface[19,20], the ratio of the thermal conductivities of the substrate and liquid[21]

Thus, the final arrangement of solute particles in the coffee ring can be controlled by different methods such as changing the PH value of dispersion[22], adding surfactant to solutions[23] and using the Nano-fluid[24,25]. The substrate plays one of the most important roles in the drying pattern of droplets. Additional, Zhang et al.[26]revealed that a high-purity vapor-deposited film is hard to be produced by changing the droplet composition, for example, by introducing polymers or changing the particle shape although these methods made a significant advance in controlling the coffee-ring effect during droplet evaporation.

Therefore, the role of the substrate with different morphology and deposition of particles has been studied by several researchers. A part of researchers focuses on the interaction between the droplet and different substrates. Wei Gong et al. [27] used a lattice Boltzmann approach to numerical study the water droplet wetting transitions on the biomimetic surface and clarified the mechanism of wetting transitions. Zu et al. [28] investigated the wetting behaviors of a single droplet on biomimetic microstructured surfaces with different roughness and the results of theoretical analysis can effectively predict the wetting transition. The contact angle hysteresis [29-31] is a factor affecting the pattern formation. The CAH increases with increasing the roughness of the substrate [32]. The droplet evaporates mainly in the pinning mode with a high contact angle hysteresis, whereas the contact line slips easily and the stage of constant contact angle is dominant with a small contact angle [33].

Recently, some researchers [34-39] investigated the evaporation of the droplets on different morphology substrate. Pham et al. [34,35] mathematically studied drying of droplets of colloidal suspensions on rough substrates. Their mathematical model can describe several phenomena that were investigated experimentally and therefore, it is suggested that the pinning of droplets to a defect arises out of a competition between the capillary-pressure and disjoining-pressure gradients. In 2018, after investigating the evaporation and patterns of colloidal suspension droplets on glass substrates with different surface roughness, Zhang et al. [36] found that under room temperature, the coffee-ring phenomenon is more obvious than on smooth substrate, and the cross-section of the ring is wedge-shaped with its thickest part on the edge. Lohani et al. [37] investigated the factors affecting the pattern formation process, such as nanoscale roughness, topography, and skewness of roughness. Drops containing polystyrene colloidal particles are adopted in their experiment. Their results showed that with the increase of nanoscale roughness, the wetting property as well as Van de Waals interaction decreases. In 2011, Smith et al. [38] used microscopy and a modified cantilever deflection technique to investigate the crack formation and the evolution of stress in drying films of colloidal particles. They found that the cracking length scale was found to increase with decreasing substrate modulus. Darbha et al. [39] studied the deposition of latex colloids on a nanopatterned surface. They mainly focus on the effects of hydrodynamics and colloidal interactions in transport and deposition dynamics of a colloidal suspension in a parallel plate flow chamber. The results show that the impact of surface roughness on retention is more significant for smaller colloids and explains the differences in retention efficiency of mineral colloids in the environment as a function of particle size.

However, these experiments are carried out when the ambient temperature is near room temperature and the contact angle of a droplet is smaller than 90°. Currently, there are small amount of researches about the droplet evaporation under relatively high ambient temperature and the droplet with a large contact angle. Thus, we studied the evaporation and the deposition patterns of saline droplet on a copper substrate with different roughness and the ambient temperature is controlled at 40°C by a water bath. The Marangoni flow is induced under the high ambient temperature because of the temperature gradient. The Marangoni flow also affects the distribution of deposit. We aim to explore the effect of roughness on deposit pattern under 40 °C ambient temperature.

2. METHODOLOGY

2.1 Experimental Set Up

In the present study, a droplet of the saline solution was deposited by a micro-syringe on the copper substrate. The volume and concentration of the droplet is 0.2 μL and 1.75%, respectively. A high-speed camera(basler acA2040-90uc), which was mounted on the microscope, was placed vertical to the saline droplet and records the whole process of the droplet evaporation on substrates with different roughness (400pp, 1200pp, 0. 2 μm and original) per 1s. Besides, the gooseneck lamp is used to ensure that the high-speed camera has enough exposure. To achieve the substrates with different roughness, the copper substrate was polished by abrasive paper with the help of grinding and polishing equipment. The grits of abrasive paper is 400pp and 1200pp, respectively. Additionally, a high polish copper substrate was polished by the hemp wheel (0.2μm). The original substrate is without any polishing. The surface roughness was measured by Atomic force microscopy (AFM). In the whole experiment, the substrate temperature is set to 40℃, which is higher than normal temperature and controlled by a water bath and the relative humidity is 40%±5%. The date taker (Agilent 34970A) is used to measure the substrate temperature.

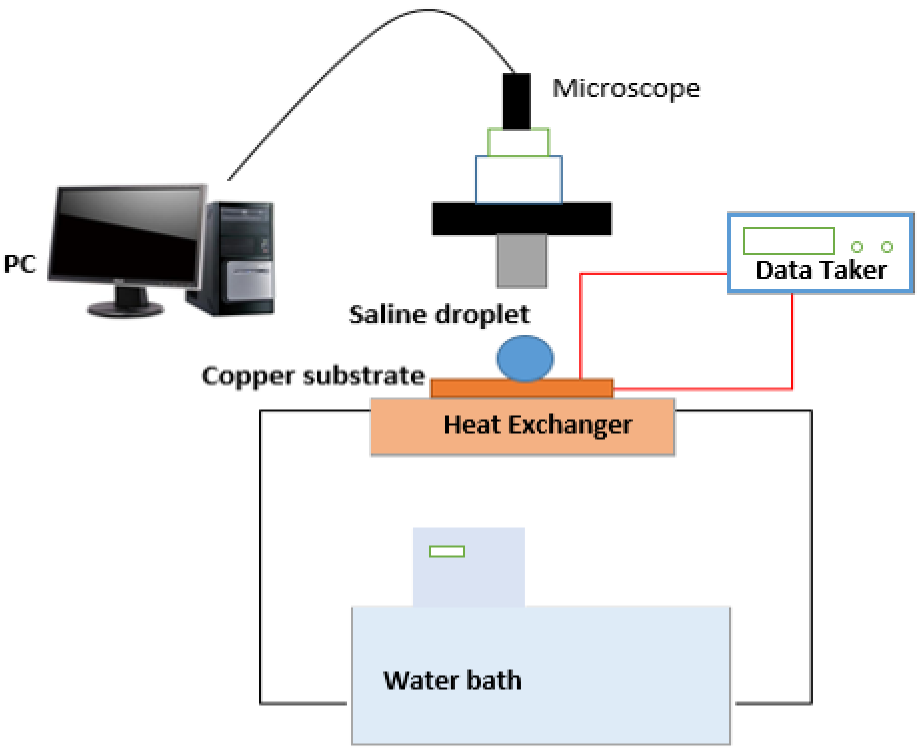


Figure 1. the set-up of the experiment

2.2 The Contact Angle

The Wenzel model can be used to present and verify the relationship between the roughness and contact angle, which is written as below:

$$\cos\theta^{*} = r\cos\theta$$

where θ^{*} is the apparent contact angle which corresponds to the stable equilibrium state, the roughness of the substrate is presented by r, and θ is the contact angle of the substrate also called young contact angle. When the roughness increases and θ is constant, the r will increases. Therefore, the apparent contact angle of the droplet is inversely proportional to substrate roughness when the θ^* smaller than 90°. When the θ^*larger than 90°, the apparent contact angle of a droplet in direct proportion to substrate roughness. To investigate the relationship between the substrate roughness and contact angle of the saline droplet. CA is measured for different surfaces, which was carried out via a contact angle meter (CAM200,KSV Instruments). Figure 2(a) – figure 2(d) show the results.

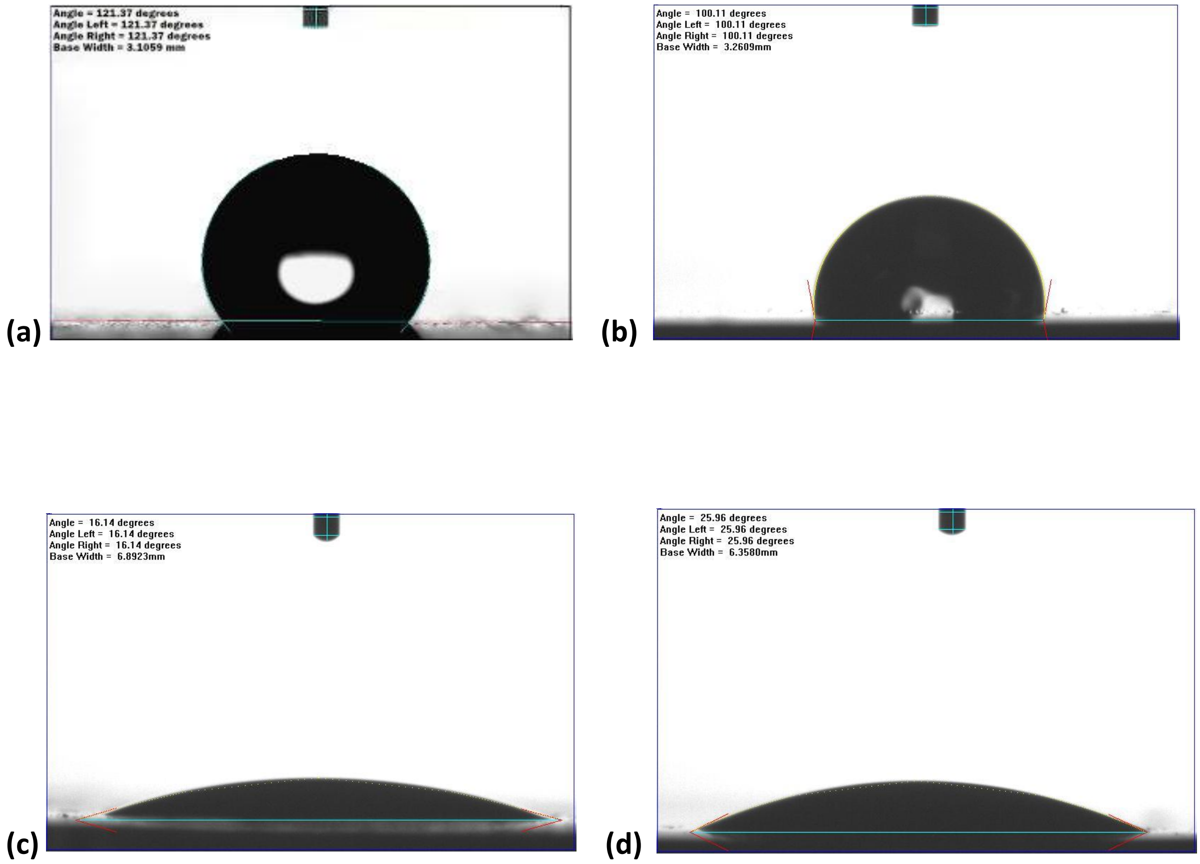


Figure 2. Surface contact angle of saline droplets on copper substrate (a) droplet on original surface (b) 400pp (c) 1200pp (d) high polishing surface(0, 2 μm)

Figs. 2(a) and 2(b) show the original surface and 400pp surface respectively. They are classified as rough surface in the experiment, in which the surface contact angle is large than 90°. With the increase of the roughness from 400pp to original, the contact angle increases gradually from 100.11° to 121.37° , the increase of the roughness can reduce the wetting of droplet on rough surface and the hydrophobicity became stronger. Thus, the contact angle of droplet increase as the roughness increases on the rough surface. The other two figures Figs. 2(c) and (d) show the 1200pp and high polishing surface and they are classified as the smooth surface which surface contact angle is smaller than90°. With the increase of the roughness from 0, 2 μm to 1200pp, the contact angle decrease gradually from 25.96° to 16.14°, the increase of the roughness can promote the wetting of droplet on the smooth surface and enhance the hydrophilicity of the surface. Thus, the contact angle of droplet decreases as the roughness increases on the smooth surface. Therefore, the experimental results are follow the Wenzel model.

2.3 Marangoni Flow

By heating the substrate, the Marangoni flow occurs due to non-uniform evaporation flux along with the droplet interface. The thermal Marangoni number is used to characterize the Marangoni flow. The Thermal Marangoni number is the ratio of surface tension induced by a temperature gradient along the free surface to adhesive [40].

$$\mathrm{Ma}_T = -\frac{d\sigma_{lv}}{dT}\frac{l\Delta T}{\eta\alpha}$$

3. RESULTS AND DISCUSSION

3.1 Deposited Patterns on Difference Roughness Substrates. The top view of deposited patterns of saline droplets on the rough and smooth substrate are shown in figure 3. The resolution of figure is 96 dpi and the dimensions of figure is 2040x2046 pixels. The particle distribution is different between rough surface and smooth surface. The particle distribution of rough surface is much uniform than smooth surface. For the smooth surface, the particles are more close to boundary and tendency more obvious. Meanwhile, the tendency of high polishing surface is more obvious than the 1200pp surface. The width of the drying pattern decreases with the increase of the roughness on the rough surface, as shown in Fig 3(a)-3(b) (3.10mm, 3.26mm, respectively). As Figure3(c)-3(d) shown, the width decreases as the roughness decreases on the smooth surface (6.89mm, 6.35mm, respectively). The boundary thickness of the droplet decreases as the roughness decreases on the rough surface. On the contrary, the boundary thickness decreases as the roughness increases on the smooth surface. As shown in Fig. 3(a)-(d), the boundary thickness is 0.42mm, 0.4mm, 0.43mm and 0.6mm respectively.

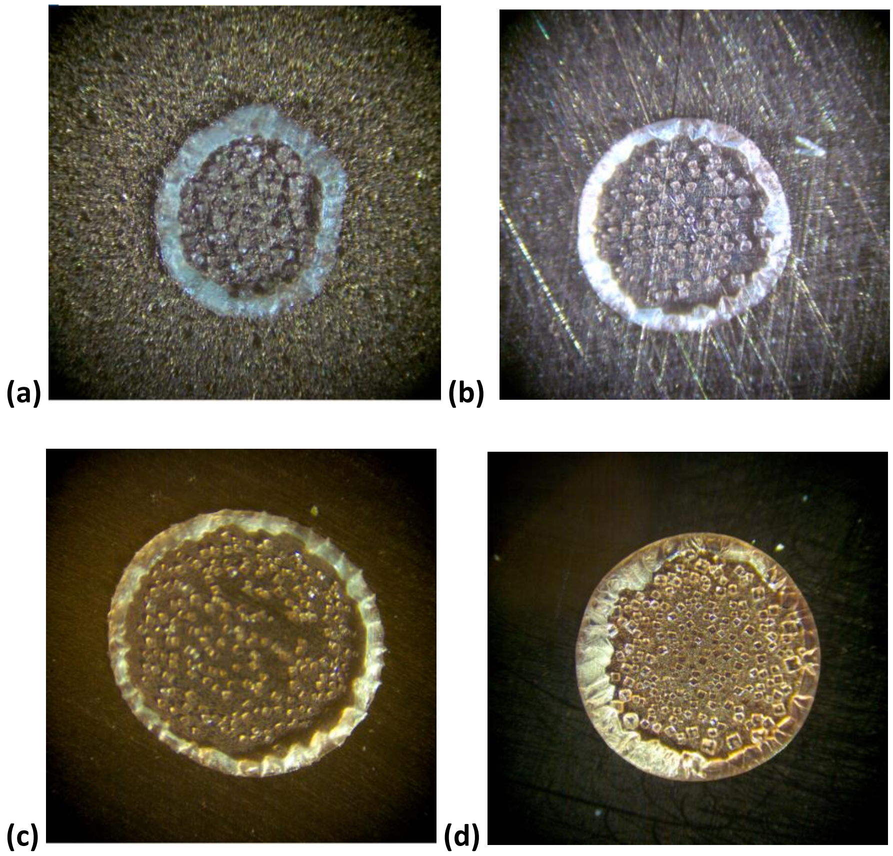


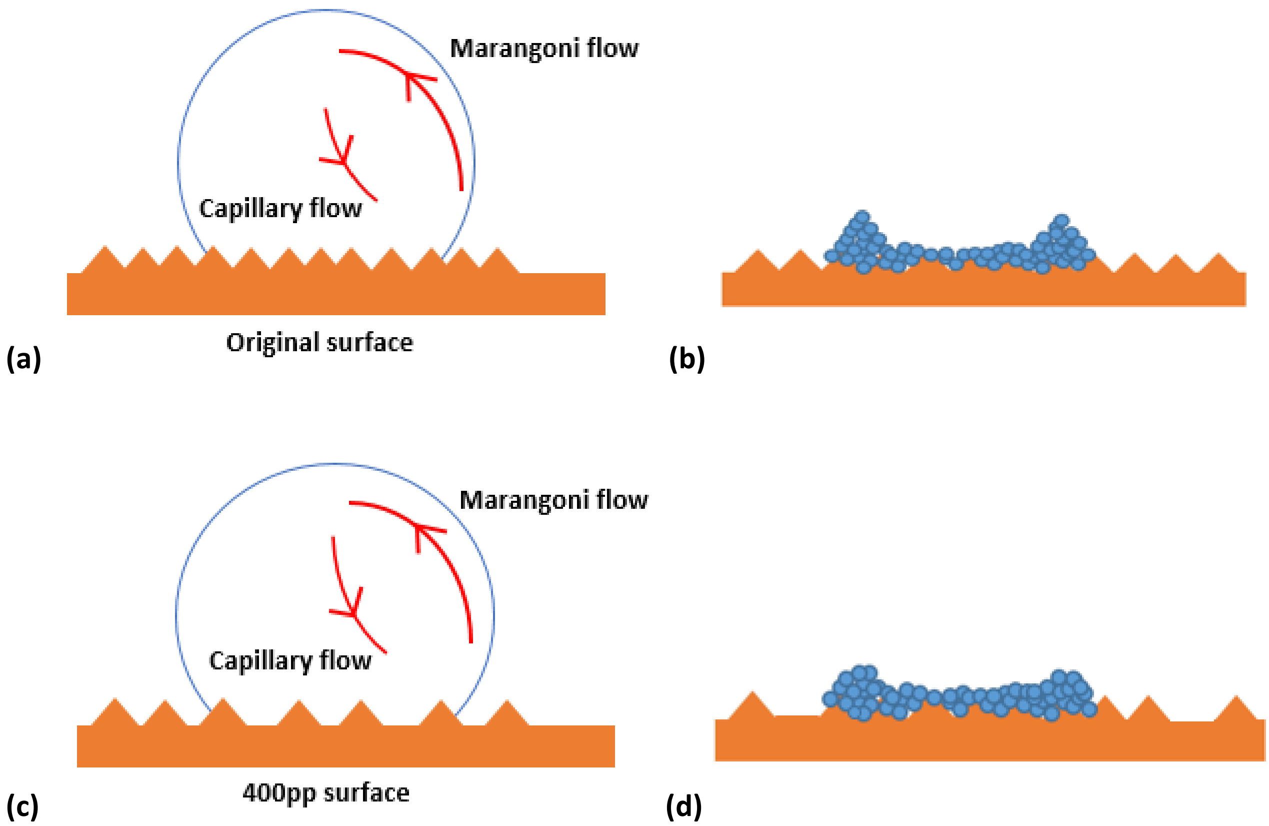
Figure 3: Evaporation patterns of saline droplet on copper substrates with different roughness (a) substrate without polishing (b) 400pp (c) 1200pp (d) high polishing (0.2 µm)

3.2 Evaporation Dynamics of Saline Droplet. The boundary thickness of the droplet on smooth surface is larger than the droplet on rough surface. Several factors contribute to this result. For droplet evaporation, the edge temperature of the droplet is the highest. Thus, the evaporation rate of the edge is faster than other parts, which results in more saline evaporating at the droplet edge than the center of droplet. Therefore, the saline moves from the center to the edge of the droplet to offset the losing part. When the whole process of evaporation completed, the concentration of the boundary is higher than the center of droplet due to the transported and deposited of the saline. However, the boundary thickness of the droplet not the thinnest part on the rough surface. Hence, there is less saline particle move to the edge of the droplet and distribute in the center of the droplet on the rough surface. Thus, the boundary evaporation rate of droplet increases as contact angle decreases, results in more particles transport to the edge.

Second, the Capillary flow is hindered by roughness of the substrate. This factor results in the particles hard transport to edge from the center of the droplet and remain at the center. It also can explain why the boundary thickness of droplet on the high polishing surface is larger than 1200pp surface, despite the boundary evaporation rate of droplet on the 1200pp surface is faster than that on the high polishing surface. Therefore, the capillary flow is weakened by increasing the roughness of substrate result in more particles remain in the center of droplet.

For the particle distribution, the particles can be easily transported to the edge on the 1200pp and high polishing surface because of the relatively faster evaporation rate and stronger capillary flow than the 400pp surface and original surface. Meanwhile, the uniform distribution of 400pp and the original surface due to the height of the droplet on the rough surface is larger than that on the smooth surface. The Marangoni flow also affects the particles to remain in the center of the droplet. Thus, more particles keep at the central region and then attenuation on the rough substrate.

On the rough surface, as can be observed in the comparison between fig. 3(a) and 3(b), the boundary thickness on the original surface is larger than that on the 400pp surface, despite that the Capillary flow is more suppressed by its rough substrate. That could be a result of contact line moving speed. As can be seen in Fig. (2), the contact angle of the droplet placed on the original substrate is larger than that on the 400pp substrate, thus with the evaporation ongoing, assuming the evaporation mode remains constant contact angle (CCA) mode, the contact line moves slower than that on 400pp substrate. Since the sediment is precipitated mainly on the ring area where the evaporation rate is the highest, it is fair to think that is the reason for a thicker coffee-ring being observed [41].



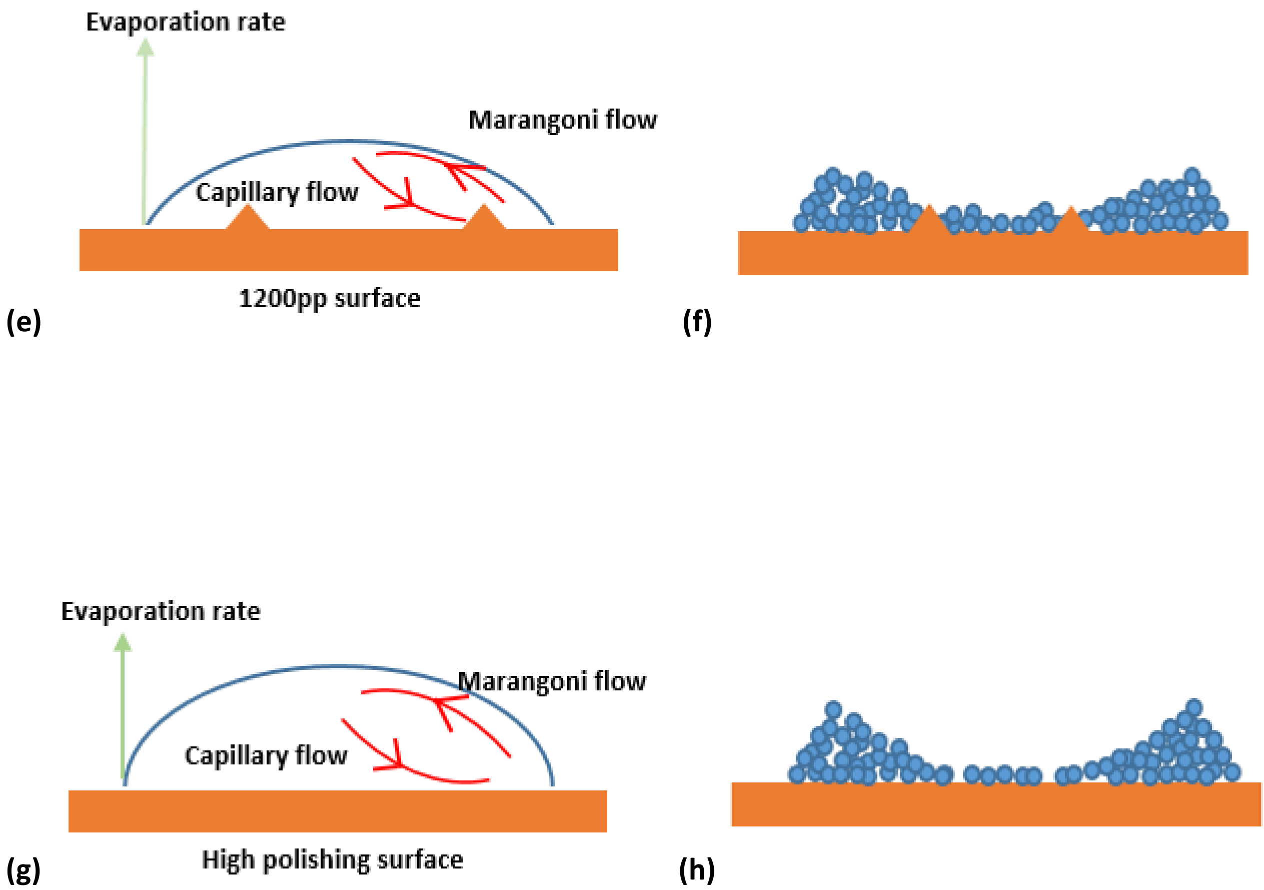


Figure 4. the evaporation patterns on a different roughness substrate. (a)(b) On the original substrate, the contact angle is the largest, there are more particles transported to the edge than that on the 400pp surface due to evaporation mode. A lot of particles remain at the center because of weakened capillary flow while Marangoni flow remains constant; (c)(d) On the 400pp surface, a few particles move to the edge and a large number remain at the center; (e)(f) on the 1200pp surface, more particles move to the edge than that on the rough surface and few particles in the center; (g)(h) on the high polishing surface, most of the particles move to the edge because of stronger capillary flow and high evaporation rate at the edge.

4. CONCLUSIONS

In the present research, the evaporation of saline droplets on four different roughness substrate under 40 ° temperature have been studied. We found that the boundary thickness of the evaporation pattern on smooth surface is larger than that on a rough surface and the particles are more close to boundary and tendency more obvious on a smooth surface. These factors contribute to this result:

(1) On the smooth surface, the contact angle decreases and hydrophilicity enhances with increase of the roughness. On the rough surface, the contact angle increases and the hydrophobicity stronger with the increase of roughness. With contact angle decreasing, the evaporation rate at the boundary increases leading to the particles at the boundary more easily sedimentate.

(2) The capillary flow is hindered by increasing the substrate roughness. On the rough surface, most of the particles remain in the center of droplet due to the weakened capillary flow while Marangoni flow remains constant. However, the boundary thickness on the original surface is larger than that on the 400pp due to their evaporation motion.

To sum up, the coffee ring effect is suppressed by increasing substrate roughness. The smooth substrate helps to produce a ring shape.

Acknowledgement:

This work is supported by European Union project H2020 - MSCA - RISE 778104.

REFERENCES

[1] Larson R G. Re-shaping the coffee ring. *Angewandte Chemie International Edition*, 2012, 51, 2546-2548.
[2] Hong M M, Jing C H. Ordered patterns superlattices honeycomb structures and coffee rings. *Chemical Society Reviews*, 2011, 40, 5457–71.
[3] Yong C J, Bharat B. Mechanically Durable Carbon Nanotube−Composite Hierarchical Structures with Superhydrophobicity, Self-Cleaning, and Low-Drag. *American Chemical Society Nano*, 2009, 3, 4155-63.
[4] Ming J L, Shu T W, Zhi X W, Yan L S, Lei J. Bioinspired Design of a Superoleophobic and Low Adhesive Water/Solid Interface. *Advanced Materials*, 2009, 21, 665-559.
[5]Taylor R A, Phelan P E, Otanicar T, Adrian R J, Prasher R S. Vapor generation in a nanoparticle liquid suspension using a focused, continuous laser. *Applied Physics Letters*, 2009, 95, 161907.
[6] Hu H, Larson R G. Evaporation of a sessile droplet on a substrate. *The Journal of Physical Chemistry B*, 2002, 106, 1334–1344.
[7] Deegan R D, Bakajin O, Dupont T F, Huber G, Nagel S R, Witten T A. Capillary flow as the cause of ring stains from dried liquid drops. *Nature,* 1997, 389, 827–829.
[8] Soltman D, Subramanian V. Inkjet-printed line morphologies and temperature control of the coffee ring effect. *Langmuir,* 2008, 24, 2224− 2231.
[9] Bhattacharya P, Samanta A N, Chakraborty S. Sprayevaporative cooling to achieve ultra-fast cooling in runout table. *International Journal of Thermal Sciences*, 2009, 48, 1741−1747.
[10] Zeng H, Kristiansen K, Wang P, Bergli J, Israelachvili J. Surface-induced patterns from evaporating droplets of aqueous carbon nanotube dispersions. *Langmuir,* 2011, 27, 7163−7167.
[11] Pirrung M C. How ot make a DNA chip. *Angewandte Chemie International Edition*, 2002, 41, 1276-89.
[12] Parisse F, Allain C. Shape changes of colloidal suspension droplets during drying. *Journal of Physics*, 1996, II(6), 1111–1119.
[13] Deegan R D, Bakajin O, Dupont T F, Huber G, Nagel S R, and Witten A T. Capillary flow as the cause of ring stains from dried liquid drops. *Nature*, 1997, 389, 827-29.
[14] Dileep M, Huseyin Burak E. A review on suppression and utilization of the coffee-ring effect, *Advances in Colloid and Interface Science*, 2018, 252, 38-54.
[15] Parisse F, Allain C. Drying of colloidal suspension droplets: experimental study and profile renormalization. *Langmuir*, 1997, 13, 3598–602.
[16] Marín A G, Gelderblom H, Lohse D, Snoeijer J H. Order-to-disorder transition in ring-shaped colloidal stains. *Physical Review Letters*, 2011, 107, 085502.
[17] Davis S H. Thermocapillary instabilities. *Annual Review of Fluid Mechanics*, 1987, 19, 403.
[18] Hua H, Ronald G L, Marangoni effect Reverses Coffee-ring Depositions. *The Journal of Physical Chemistry B*, 2006, 110, 7090-7094.
[19]Bhardwaj R, Fang X, Somasundaran P, Attinger D. Self-assembly of colloidal particles from evaporating droplets: role of DLVO interactions and proposition of a phase diagram. *Langmuir,* 2010, 26, 7833–42.
[20] Yunker P J, Lohr M A, Still T, Borodin A, Durian D J, Yodh A G. Effects of particle shape on growth dynamics at edges of evaporating drops of colloidal suspensions. *Physical Review Letter*, 2013, 110, 035501.
[21] Ristenpart W D, Kim P G, Domingues C, Wan J, Stone H A. Influence of substrate conductivity on circulation reversal in evaporating drops. *Physical Review Letter*, 2007, 99, 234502.

[22] Kosmulski, M. The pH-dependent surface charging and the points of zero charge. *Journal of Colloid Interface Science*, 2002, 253 (1), 77−87.
[23] Zang D, Tarafdar S, Tarasevich Y Y, Choudhury M D, Dutta T. Evaporation of a droplet: from physics to applications. *Physics Report*, 2019, 804, 1–56.
[24] Mampallil D, Eral H B, van den Ende D, Mugele F. Control of evaporating complex fluids through electrowetting. *The Royal Society of Chemistry*, 2012, 8, 10614–10617.
[25] Chon C H, Paik S, Tipton J B , Kihm K D. Effect of nanoparticle sizes and number densities on the evaporation and dryout characteristics for strongly pinned nanofluid droplets. *Langmuir,* 2007, 23, 2953–2960.
[26] Yong J Z, Xu B C, Feng G L, Lei L, Jun D, Teng L. Enhanced Coffee-Ring Effect via Substrate Roughness in Evaporation of Colloidal Droplets. *Advances in Condensed Matter Physics*, 2018.
[27] Wei G, Yu Y Y, Sheng C, Donald G. Numerical Study of Wetting Transitions on Biomimetic Surface Using a Lattice Boltzmann Approach with Large Density Ratio. *Journal of Bionic Engineering*, 2017,14(3),486-496.
[28]Ying Q Z, Yu Y Y, Jian Q L, Zhi W H. Wetting behaviors of a single droplet onbiomimetic micro structured surfaces. *Journal of Bionic Engineering*, 2010, 7(2), 191-198.
[29] Bormashenko E, Musin A, Zinigrad M. Evaporation of droplets on strongly and weakly pinning surfaces and dynamic of triple line. *Colloids and Surface* A, 2011, 385, 235–40.
[30] Pittoni P G, Chang C C, Yu T S, Lin S Y. Evaporation of water drops on polymer surfaces: pinning, depinning and dynamics of the triple line. *Colloids and Surface A*, 2013, 432,89–98.
[31] Li Y F, Sheng Y J, Tsao H K. Evaporation stains: Suppressing the coffee-ring effect by contact angle hysteresis. *Langmuir*, 2013, 29 (25), 7802–7811.
[32]Eral H B, Mannetje D J C M, Oh J M. Contact angle hysteresis: a review of fundamentals and applications. *Colloid Polymer Science*, 2013, 291, 247–60.
[33]Kovalchuk N M, Trybala A, Starov V M. Evaporation of sessile droplet. *Current Opinion in Colloid & Interface Science*, 2014, 19, 336-342.
[34] Pham T, Kumar S. Imbibition and evaporation of droplets of colloidal suspensions on permeable substrates. *Physical Review Fluids*, 2019, 4, 034004.
[35] Pham T, Kumar S. Drying of droplets of colloidal suspensions on rough substrates. *Langmuir*,2017, 33, 10061–10076.
[36] Zhang Y, Qian Y, Liu Z, Li Z, Zang D. Surface wringkling and cracking dynamics in the drying of colloidal droplets. *The European Physical Journal E*, 2014, 37.
[37] Lohani D, Sarkar S. Nanoscale Topographical Fluctuations: A Key Factor for Evaporative Colloidal Self-Assembly. *Langmuir*, 2018, 34(43), 12751-12758.
[38] Smith M I, Sharp J S. Effect of substrate constraint on crack pattern formation in thin flims of colloidal polystyrene particles. *Langmuir*, 2011, 27, 8009-8017.
[39] Darbha K G, Fischer C, Michler A, Luetzenkirchen J, Schäfer T, Heberling F, Schild D. Deposition of latex colloids at rough mineral surfaces: an analogue study using nanopatterned surfaces. *Langmuir,* 2012, 28, 6606–6617.
[40] Du Y Z, Sujata T, Yu R Y, Moutushi D C, Tapati D. Evaporation of a Droplet: From physics to application. *Physics Reports*, 2019, 804, 1-56.
[41] Xue M C, Rui Y M, Jin T L, Chong L H, Wei G, Luk B L, Shuai C L, Shu H Y, Zuan K W. Evaporation of Droplets on Superhydrophobic Surfaces: Surface Roughness and Small Droplet Size Effects. *Physical Review Letters*, 2012, 109, 116101.