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Suppression of the Coffee Ring Effect by Hydrosoluble Polymer Additives

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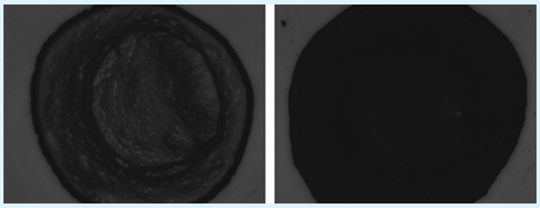
S *Supporting Information*



ABSTRACT: A simple and novel method has been demonstrated for avoiding coffee ring structure based on hydrosoluble polymer additives during droplet evaporation. The polymer additives lead to the motion of the contact line (CL) resulted from the viscosity and Marangoni effect. The viscosity provides a large resistance to the radially outward flow. It results in a small amount of spheres deposited at droplet edge, which do not facilitate the pinning of the CL. The Marangoni effect resulted from the variation of polymer concentration at droplet edge during droplet evaporation contributes to the motion of the CL. Thus, uniform and ordered macroscale SiO_2 microspheres deposition is achieved. What's more, the coffee ring effect can be eliminated by different hydrosoluble polymer. This method will be applicable to a wide of aqueous system and will be of great significance for extensive applications of droplet deposition in biochemical assays and material deposition.

KEYWORDS: *coffee ring, hydrosoluble polymer additives, dewetting, droplet deposition, the motion of contact line*

INTRODUCTION

Coffee ring phenomenon is commonly observed during evaporating droplet containing nonvolatile solutes resulted from a combination of capillary flow and pinning of the contact line (CL) and has attracted great research interest because of its broad practical applications in inkjet printing,[1−3] functional coating,[4] spot test analysis,[5,6] color filter,[7] chromatography,[8,9] etc. The physical mechanisms behind it are rather complex and have been extensively studied experimentally and theoretically.[10−12] The method for suppressing coffee ring effect presents one of the most fundamental issues and plays an utmost important role in high-resolution inkjet printing technique because of the usual non-uniformity of deposited structures. Recently, Yunker et al. reported that eliminating coffee ring effect has been achieved by means of anisotropic particle.[13] Moreover, under appropriate condition, suspensions of spheres could also produce uniform deposition by mixing with a small number of ellipsoids. This method provides a convenient way to control the deposition of particles without modification of particle or solvent chemistry. Shen et al. explored the minimum droplet size for forming a coffee ring structure by investigating the relationship between the time scales of liquid evaporation and the particle movement within the droplets.[14] Other methods for avoiding coffee ring formation are still limited including controlling the suspension formulation,[15−17] manipulating substrate temperature,[18−20] using electrowetting,[21] or depinning the CL.[22−24] Unfortunately, most methods mentioned above are complex due to the requirement of flammable and toxic organic solvent[15−17] and are restricted by thermal conductivity of the substrate,[18−20] conductive liquid,[21] or the nonuniform droplet deposition.[22−24] Therefore, the simple method for eliminating coffee ring phenomenon and obtaining homogeneous droplet deposition is highly desirable.

Coffee ring effect is also observed in polymer solutions and has been studied both theoretically and experimentally.[25−30] This problem is crucial to the inkjet printing technology in the fabrication of electronic devices and biomaterials. Typically, Lin and co-workers have reported the fabrication of complex ordered structures on the submicrometer and longer length scales based on controlled evaporative self-assembly of polymer droplets in confined geometries by learning from "coffee rings".[27] Doi et al. showed that the motion of the CL played an important role in polymer droplet dewetting.[30]

It is commonly believed that the coffee ring structure occurs via capillary flow because of droplet evaporation, and Marangoni flow due to surface tension gradient is engineered to ameliorate the coffee ring effect.[10−12] In this paper, we present suppressing coffee ring effect is developed based on hydrosoluble polymer additives by means of the motion of the CL, and ca. 22 mm^2 uniform and macroscale SiO_2 microspheres deposition is achieved on glass slides surface after droplet evaporation. The motion of the CL is attributed to the Marangoni effect induced by the inhomogeneity of the polymer concentration due to the fast evaporation of the droplet edge.[4,25−33] Otherwise, hydrosoluble polymer additives in-

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troduce viscosity increase of the droplet, which dramatically blocks capillary flow outward from the droplet centre. This leads to few suspended SiO_2 microspheres deposited on the droplet edge as evaporation proceeds, which is not beneficial to the pinning of the CL.[10−12,34−37] Thus, uniform SiO_2 microspheres are left with the motion of the CL during droplet evaporation. What's more, the coffee ring effect can be eliminated by different hydrosoluble polymer. This provides a convenient method to control the deposition of particles, without modification of particle or solvent chemistry, which will be of practical importance to directly writing photonic devices, sensor array, and high-resolution inkjet printing.

■ EXPERIMENTAL SECTION

Materials. The SiO_2 microspheres were prepared by the Stöber method as mentioned in reference[38,39] and the average diameter of SiO_2 microspheres used in our work were 972 nm measured by SEM with a calibrated length. The glass slides were cut into 20 mm × 20 mm pieces, were soaked in the mixture of 98% H_2SO_4/30% H_2O_2 (volumetric ratio 7:3) for 20 min under boiling (caution: strong oxide), and then were rinsed with Milli-Q water (18.2 MΩ cm^{-1}) and ethanol several times, at last were dried with N_2 stream. Polyethyleneoxide (PEO1, $M_w = 4 \times 10^6$), poly(vinylpyrrolidone) (PVP, $M_w = 5.5 \times 10^4$) and poly(vinyl alcohol) 98−99% hydrolyzed (PVA, $M_w = 3.1 \times 10^4$ to 5×10^4) were all purchased from Sigma Aldrich. Polyethyleneoxide (PEO2, $M_w = 3 \times 10^5$) was purchased from Alfa Aesar. All the above chemical reagents in our work were used as received.

Droplet Deposition. Prior to each deposition, the latex suspension is sonicated for 30 min. In our experiments, the volume of droplets is 2 μL, controlled by a micropipet, with different polymer concentration. Furthermore, micrometer-sized SiO_2 spheres in them are all 972 nm in diameter and 0.5 wt % in concentration. The weight fraction of 0.5 wt % is selected by taking into account subsequently easy quantification of the SiO_2 microspheres density, and SiO_2 microspheres are monolayer deposition after coffee ring effect is destroyed. The experiment is carried out on glass slides at the room temperature of 23−25 °C and humidity of 35−45%.

Characterization. SEM micrographs were examined using a JEOL JSM 6700F field-emission scanning electron microscope with an accelerating voltage of 5.0 kV. The samples were sputtered with a thin layer of Pt prior to imaging. Static emulsion droplet CAs were measured on a Krüss DSA100 (Krüss GmbH, Hamburg, Germany) drop shape analyzer at ambient temperature. The static CA was read by injecting 2 μL emulsion droplet. The average CA was obtained by measuring more than five different positions on the same sample. The optical microscope images were recorded using an Olympus fluorescence microscope (BX51). Viscosity data were recorded using a Julabo 536 10 Ubbelohde viscometer.

■ RESULTS AND DISCUSSION

In general, previous work on the physics of the coffee ring effect has been demonstrated with SiO_2 microspheres.[2,22,23] Here we also utilize such microspheres. It is important to note that coffee ring effect on hydrophilic glass slide surface can be easily eliminated based on adding hydrosoluble polymer additives to the aqueous phase and similar results are obtained for different hydrosoluble polymer. This will further make us have in-depth understanding on particle transfer during droplet evaporation and endow new method for solving coffee ring problem in aqueous system.

Figure 1 shows the optical microscope image of final deposition after droplet evaporation. We can see that markedly uneven coffee ring deposition of SiO_2 microspheres persists in Figure 1a and SiO_2 microspheres are primarily deposited at the original perimeter of the droplet in a manner similar to previous report.[10−12] In contrast, SiO_2 microspheres with polyethyleneoxide (PEO1, $M_w = 4 \times 10^6$) additives (1 g/L in concentration) are distributed much more uniformly (Figure 1b).

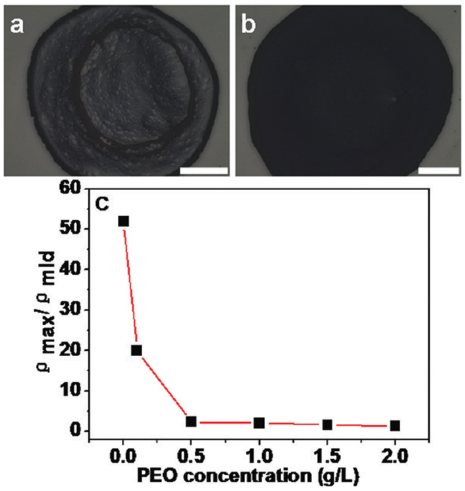

Figure 1. (a, b) Images of the final distribution of SiO_2 microspheres (a) without PEO1 and (b) with PEO1 additives (1 g/L in concentration) after evaporation. The scale bar is 1 mm. (c) The maximum local density, ρ_{max}, normalized by the density in the droplet centre, ρ_{mid}, plotted for different PEO1 concentration. Red lines guide the eye.

To quantify the behavior shown qualitatively in images a and b in Figure 1, we calculate and plot ρ_{max}/ρ_{mid}. Specifically, SEM image analysis enables counting of the number of particles, N, in an area set by ca. 13600 μm^2, which is the area of SEM image with the magnification of 1000. The areal particle density $\rho = N/A$ with $A = 13600\ \mu m^2$. ρ_{max} is the maximum value of ρ at the edge of droplet deposition and ρ_{mid} is the average value of ρ in the center of droplet deposition. The top and tilt view SEM image is providing two-dimensional and three-dimensional information, respectively. Figure 1c displays the values of ρ_{max}/ρ_{mid} evidently vary with different PEO1 concentration. For SiO_2 microspheres without PEO1 additives, the value of ρ_{max}/ρ_{mid} is ∼52, which means the density of SiO_2 microspheres is 52 times larger at droplet edge than that in droplet centre. This is in accordance with the droplet deposition in Figure 1a. Conversely, the value of ρ_{max}/ρ_{mid} can be down to 1.3 as PEO1 concentration increasing, which means coffee ring effect disappears. Concretely, as the PEO1 concentration in the droplet is 0.1 g/L, corresponding ρ_{max}/ρ_{mid} is ∼20. This indicates the coffee ring effect persists, but it can be evidently weakened by means of introducing a small amount of PEO1 additives. Then, the value of ρ_{max}/ρ_{mid} was 2.3, 2, 1.6, and 1.3 with further increasing the PEO1 concentration up to 0.5, 1, 1.5, and 2 g/L. This indicates that the coffee ring problem could be solved, which is in consistent with droplet deposition in Figure 1b. It is also noted droplet deposition changes little as the PEO1 concentration exceeding 0.5 g/L.

To explore the droplet deposition in detail, optical microscope images of the magnified edge and centre of droplet deposition are characterized in Figure 2 and Figure S1-2 (Supplementary Information). Clearly, we can see that SiO_2 microspheres exist highly concentrated along the original droplet edge in Figure 2a and Figure S3a in the Supporting Information, and distribute random and unevenly at droplet centre for droplets without PEO1 additives in Figure 2c and Figure S3b in the Supporting Information. Subsequently, the

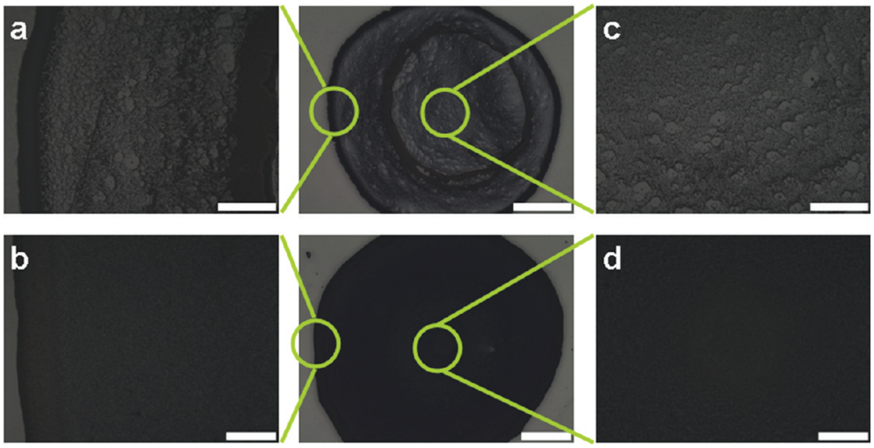

Figure 2. (a, b) Magnification optical microscope images of SiO_2 microspheres at droplet edge (a) without PEO1 and (b) with PEO1 additives. (c, d) Magnification optical microscope images of SiO_2 microspheres at droplet center (c) without PEO1 and (d) with PEO1 additives. The scale bar is 250 μm for a−d.

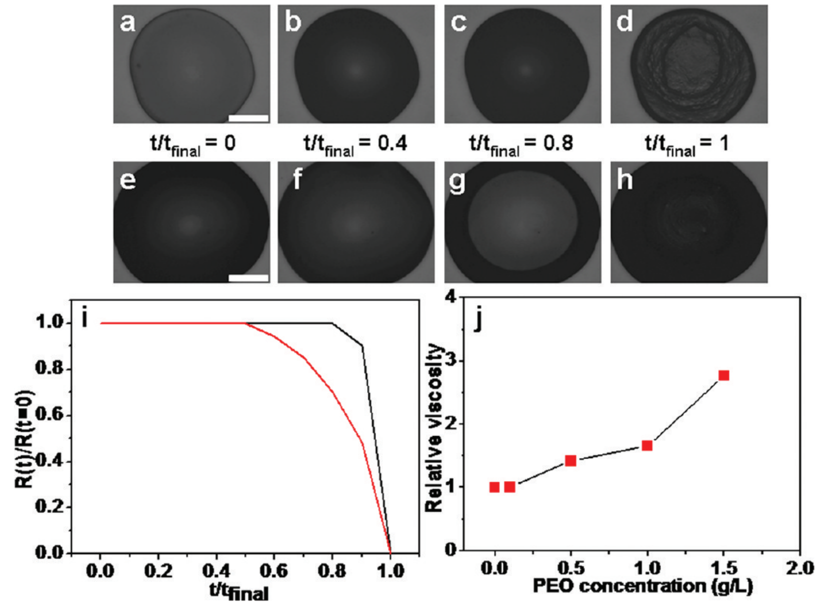

Figure 3. (a−h) Experimental optical microscope images at different times (t/t_{final}) during the evaporation of a droplet of SiO_2 microspheres suspension; shown are data for SiO_2 microspheres (a−d) without PEO1 and (e−h) with PEO1 additives. The scale bars is 1 mm. (i) The radius, R, of droplets of different suspensions is plotted versus time, t, for evaporating droplets. Suspensions of SiO_2 microspheres without PEO1 (black line) and with PEO1 additives (red line) are shown. To facilitate comparisons, the time is normalized by the time evaporation ends (t_{final}), and R is normalized by the value of R at t = 0 min. (j) Relative viscosity versus PEO1 concentration for SiO_2 microspheres suspension.

number of SiO_2 microspheres decreases at the droplet edge and increases at the droplet centre with increasing PEO1 concentration in Figure S1a, b in the Supporting Information. Finally, SiO_2 microspheres with PEO1 additives (1 g/L) are distributed much more uniformly both at droplet edge and at droplet centre. In this case, the coffee ring effect is destroyed. It should be mentioned the coffee ring effect can be also suppressed as the concentration of PEO1 is 1.5 g/L, as shown in Figure S1c in the Supporting Information. But, in this case, it is difficult to quantify the number of SiO_2 microspheres because of SiO_2 microspheres largely covered by PEO1 additives. The optical microscope images are basically in agreement with the values of $\rho_{\mathrm{max}}/\rho_{\mathrm{mid}}$ in Figure 1c. Moreover, it is found that SiO_2 microspheres with PEO1 (0.5 g/L in concentration) additives in Figure S1b in the Supporting Information distribute most uniform at the droplet edge and random at the droplet centre. However, the value (2.3) of its $\rho_{\mathrm{max}}/\rho_{\mathrm{mid}}$ is similar to that of $\rho_{\mathrm{max}}/\rho_{\mathrm{mid}}$ in higher concentration. Therefore, combination the data in Figure 1c and optical micrograph images in Figure 2 and Figure S1-2 in the Supporting Information indicate the coffee ring effect is eliminated with PEO1 (1 g/L in concentration) additives. Herein, it should be noted that coffee ring structure during SiO_2 microspheres deposition can be avoided via PEO1 additives, which is our focus. Meantime, it is interesting to note PEO1 droplet dewetting (1 g/L in concentration) without SiO_2 microspheres exists coffee ring structure shown in Figure S4 in the Supporting Information.

The possible formation mechanism of the uniform droplet deposition without coffee ring effect is explained as follows. For SiO_2 microspheres without PEO1 additives during the drying process, the CL of droplet remains pinned in all suspensions, and fluid (carrying microspheres) flows outward from the

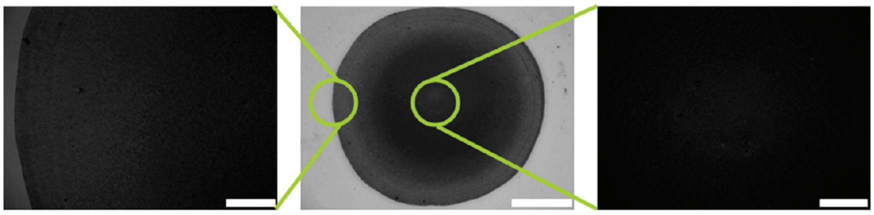

Figure 4. Optical microscope images of SiO_2 microspheres deposition with PEO2 additives. The scale bar is 1 mm in the middle optical microscope image and 250 μm in the left and right optical microscope images.

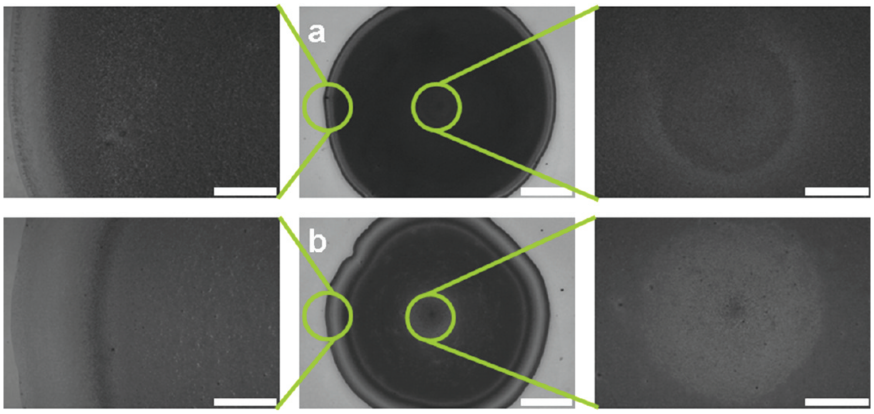

Figure 5. Optical microscope images of SiO_2 microspheres deposition with (a) PVA and (b) PVP additives. The scale bar is 1 mm in a and b, and 250 μm in the others optical microscope images.

droplet centre to replenish the edges.[10−12] SiO_2 microspheres are efficiently transported to the edge, leaving a ring after evaporation is complete. However, for SiO_2 microspheres with PEO1 additives, their mobility is markedly reduced, and the viscosity produced by the addition of PEO1 provides a large resistance to the radially outward flow. This leads to a small amount of spheres deposited at droplet edge, which do not facilitate the pinning of the CL. At the same time, the Marangoni effect resulted from the variation of PEO1 concentration contributes to the motion of the CL according to literature report.[4,25−37] Hence, SiO_2 microspheres with PEO1 additives are left with the CL moving toward the droplet centre during droplet evaporation and are much more uniformly deposited on the glass surface than SiO_2 microspheres without PEO1 additives after droplet evaporation is complete. As a result, both the viscosity and Marangoni effect play a crucial role on the motion of the CL in the present case, which will be investigated in the following section.

To confirm that the motion of CL is responsible for the uniform deposition of SiO_2 microspheres, typical optical micrograph sequence of droplet evaporation and droplet viscosity are characterized. The optical microscope images are measured with a frame rate of one frame per minute. In this case, the time at which evaporation finishes, t_{final}, is readily identified as the time when the droplet radius shrinks to zero. Figure 3a−d and S5a-f clearly reveals that for droplet without PEO1 additives the motion of the CL begins at the time of $t/t_{\mathrm{final}} > 0.8$, that is to say the CL remains pinned until the final stage of evaporation, which has been reported in the literature.[10−12] The SiO_2 microspheres are carried to the droplet edge and coffee ring structure appears. Whereas, for droplet with PEO1 additives the motion of the CL starts at the time of $t/t_{\mathrm{final}} > 0.4$ in Figure 3e−h and Figure S5g-l in the Supporting Information, which is obviously earlier than that of droplet without PEO1 additives. This behavior is attributed to the viscosity and Marangoni effect[4,25−37] and in accordance with our front conjecture and has been shown in Figure 3i. Concretely, it demonstrates the CL is pinned for the vast majority of the evaporation time period in all samples until $t = 0.8t_{\mathrm{final}}$ for suspensions of SiO_2 microspheres without PEO1 additives. Nonetheless, for suspensions of SiO_2 microspheres with PEO1 additives, the CL becomes depinned around $t = 0.5t_{\mathrm{final}}$. Additionally, the relative viscosity versus PEO1 concentration is shown in Figure 3j, the values are 1.01, 1.42, 1.66, and 2.77 corresponding the PEO1 concentration of 0.1, 0.5, 1, and 1.5 g/L.

Quantification of the spatiotemporal evaporation profile of the suspensions provides a further step towards understanding why SiO_2 microspheres are deposited uniformly. To this end, we measure droplet mass of different suspensions (20 μL in volume) during evaporation (see Figure S6 in the Supporting Information). (Note, large-volume droplets are utilized in this experiment to improve the accuracy of the evaporation rate measurement). The droplet mass decreases linearly in time, and the mass rate-of-change of 7.0 μg/s is the same for droplets of microspheres suspension and for droplets of water absent colloid. The evaporation behavior is also consistent with steady-state vapour-diffusion-limited evaporation of a spherical-cap-shaped droplet with a pinned CL.[10−12] In sharp contrast, the entire droplet evaporation time for droplet with PEO1 additives is longer than that without PEO1 additives and its mass rate-of-change is 6.0 μg/s. This indicates that the dewetting of the droplet is evidently prevented by hydrosoluble polymer additives. We believe that the retardation of dewetting is caused by an increase in local viscosity of the polymer caused by the polymer−filler attraction or surface roughness.[40] The contact angle was also measured by placing a 2 μL droplet on a glass slide. The PEO1 additives do not have distinct effect on the contact angle of the droplet in Figure S7 in the Supporting Information.

Finally, to demonstrate the versatile property of this method, we show that the addition of the same polymer with different molecular weight or different polymer to SiO_2 microspheres suspension can also destroy the coffee ring effect. To observe this effect, we evaporate the droplet of suspension containing polyethyleneoxide (PEO2, $M_w = 3 \times 10^5$), poly(vinyl alcohol) (98−99% hydrolyzed) (PVA, $M_w = 3.1 \times 10^4$ to 5×10^4), and poly(vinylpyrrolidone) (PVP, $M_w = 5.5 \times 10^4$), respectively.

Evaporative deposits are characterized by optical microscope images. First, we evaporate suspension containing low molecular weight PEO2. After evaporation, the coffee ring effect is inhibited with PEO2 additives (1.81 in viscosity and 3 g/L in concentration) (Figure 4 and Figure S8 in the Supporting Information). Meanwhile, we evaporate suspension containing PVA or PVP along with the same spheres at the same weight fractions used previously. When the relative viscosity is very small, the suspension exhibits a clear coffee ring effect. However, the coffee ring is diminished, and it eventually disappears with PVA (1.20 in viscosity and 5 g/L in concentration) or PVP (1.21 in viscosity and 10 g/L in concentration) additives (Figure 5 and Figure S9 in the Supporting Information). Thus, uniform deposition can potentially be made with existing suspensions, simply by adding hydrosoluble polymer additives. In the present case, we think that the polymers in droplet may get attached on SiO_2 microspheres via physisorption and through hydrogen bond because of the presence of the ——OH groups on the SiO_2 microspheres or form smaller aggregates.[41] The coffee ring problem is solved based on viscosity and Marangoni effect due to the introduction of hydrosoluble polymer additives. Furthermore, the relative viscosity is different for suppressing coffee ring effect with different polymer. We believe the viscosity difference for solving coffee ring problem is probably due to different interaction of polymer−SiO_2 microspheres, polymer−substrate, or between polymer chain structure during droplet evaporation.[41,42]

■ CONCLUSIONS

In conclusion, we have demonstrated a facile and novel approach for avoiding coffee ring structure based on hydrosoluble polymer additives during droplet evaporation. The uniform SiO_2 microspheres deposition is achieved depending on the motion of the CL aroused from viscosity and Marangoni effect due to the introduction of hydrosoluble polymer additives. The viscosity prevents the suspended SiO_2 microspheres from reaching the droplet edge, which does not facilitate the pinning of the CL. The Marangoni effect is derived from the change of polymer concentration at droplet edge and contributes to the motion of the CL. This method would offer a new way to solve coffee ring problem and is applicable to a wide range of aqueous system, and would be further extended to control droplet deposition for practical application in biochemical assays, material deposition, and high resolution printing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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