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Condensation-assisted micro-patterning of low-surface-tension liquids on reactive oil-repellent surfaces†

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In this work, we reveal a reactive oil-repellent surface as a new platform for surface micro-patterning of low-surface-tension liquid precursors. Fluorescent molecules could be immobilized on the reactive oil-repellent surface by high-density and high-resolution patterning of microdroplets via a synergetic effect of droplet evaporation and condensation-enrichment. We envision that our proposed surface can broaden surface functionalization for analytical and biomedical applications.

Introduction

Spatially controlled functionalization of surfaces with desired chemistry and wettability plays an important role in a variety of analytical and biomedical applications ranging from sensor design and biochips to cell and drug screening. ¹⁻⁹ In this context, droplet spotting based wet chemistry methods, such as dip-pen lithography, ¹⁰,¹¹ contact printing, ¹²,¹³ and inkjet printing, ¹⁴,¹⁵ have attracted great interest, because they offer a couple of unique advantages and flexibilities including high-throughput sample treatment, controlled droplet size, broad selection of precursor solvents, versatile combination of chemical reactions, and ease of post-treatment. Based on these technologies, various applications have been derived from high-resolution surface chemical patterning. For example, large scale droplets or liquid arrays could be trapped on the patterned surface and thus serve as microreactors for the preparation of nanoparticles with controlled size and chemical components, and cell-encapsulated liquid or gel arrays in downstream biomedical applications. ¹⁶⁻¹⁸ While being effective, the patterning resolution of these technologies largely depends on both the volume of spotted liquid droplets which is restricted by instrumentation, and the spreading of the liquid on the targeted substrate. Previous work has shown that the spreading of aqueous droplets could be suppressed by using flat hydrophobic surfaces, on which aqueous droplets would evaporate and condense into higher concentrations of solutes. ¹⁹⁻²¹ Furthermore, the condensation process could be further promoted on a textured superhydrophobic surface on which the water droplet is in a nearly spherical shape with an equilibrium contact angle of around 150°. ²²⁻²⁶ However, this method often fails when low-surface-tension liquids such as organic solvents (e.g. acetone 25.2 mN m⁻¹, toluene 28.5 mN m⁻¹, tetrahydrofuran (THF) 26.4 mN m⁻¹, and 1,4-dioxane 33.0 mN m⁻¹) are involved.

There are a couple of studies on the controlled patterning and condensation of organic liquids for downstream applications. Levkin et al. reported the high-density patterning of microdroplet and nanoparticle arrays through the discontinuous dewetting of organic solutions on surface patterns with high surface energy contrast. ²⁶ Wong et al. described the smooth condensation procedure and the corresponding condensation-enrichment of organic droplets on the slippery liquid-infused porous surface (SLIPS), which allows for ultra-sensitive molecular detection. ²⁷ Although the condensation of organic liquids could be controlled on omniphobic surfaces for droplet patterning or condensation-assisted enrichment, the utilization of liquid condensation in surface micro-patterning and functionalization is still elusive as most omniphobic surfaces are unfortunately chemically inert or resistant to post chemical modification.

In this work, we reveal a reactive oil-repellent surface as a new platform for surface micro-patterning and functionalization via the condensation-enrichment approach of low-surface-tension liquid precursors. The reactive oil-repellent surface was fabricated by sequentially grafting “liquid-like” polydimethylsiloxane (PDMS) copolymer brushes with pendant reactive groups on flat substrates. ²⁸ PDMS based materials have been widely used in tuning surface oil repellency. ²⁹ As we have previously reported, the “liquid-like” feature offers surface low contact angle hysteresis (CAH) to a range of polar or nonpolar organic liquids, and the pendant reactive groups provide
inherent reactivity for post chemical functionalization. Our results indicate a synergetic effect of droplet evaporation and condensation-enrichment on both high-density micropatterning of organic droplets and surface functionalization. First, the organic precursor droplets deposited on the oil-repellent surface will retract and undergo a smooth shrinkage of the droplet profile during the evaporation due to the low CAH of the surface, allowing for high-density spotting of the organic liquid. Meanwhile, the concentrations of solutes in the precursor will increase accordingly resulting in a condensation-enrichment procedure, which allows the surface patterning of precursors of lower initial concentrations. Micropatterns were created and demonstrated via a chemical reaction between the surface tethered reactive moieties (NH₂) and fluorescein isothiocyanate (FITC), which is a widely used reagent for surface patterning.\textsuperscript{5,16,16,31} Our work indicates the great potential of spatially controlled functionalization on surfaces with superwettability, which may have technical implications in detection of metal ions and explosives.\textsuperscript{32,33}

**Experimental**

**Materials**

Aminopropyl-terminated polydimethylsiloxane (H₂N-PDMS-NH₂) with a molecular weight of about 3000 was purchased from Gelest, Inc. Isophorone disiocyanate (IPDI), fluorescein isothiocyanate (FITC), pyrene, and 3-aminopropytriethoxysilane (APTES) were purchased from Sigma-Aldrich. All the solvents used were obtained from RCI Labscan and VWR. Silicon wafers were purchased from Turbo Co., Ltd. (China).

Prior to use, silicon wafers were cleaned with O₂ plasma for 20 min followed by immersion in a piranha cleaning solution for 1 h at 90 °C. (Caution: Piranha solution is extremely corrosive and should be handled carefully).

**Preparation of amino-functionalized surfaces**

The substrates were placed in individual vials and silanization was carried out in an APTES solution of anhydrous toluene of 1% (v/v) at 70 °C for 1 h.\textsuperscript{34,35} The samples were then rinsed individually with excess toluene and ethanol, followed by sonication in toluene and ethanol for 10 min, respectively.

**Preparation of reactive oil repellent surfaces**

IPDI toluene solution (0.5 mg mL\textsuperscript{-1}) and H₂N-PDMS-NH₂ THF solution (1 mg mL\textsuperscript{-1}) were used for film build-up. The aminofunctionalized substrates were first dipped in the IPDI solution for 30 minutes at room temperature, followed by rinsing in anhydrous toluene and rapid washing. The silicon wafer terminated with isocyanate groups was then dipped in the H₂N-PDMS-NH₂ solution for another 30 minutes at room temperature, followed by rinsing in excess pure THF. The process was repeated once for two-layer polymer grafting.

**Micropatterning on the reactive oil-repellent surface**

A biodot spotter (AD3200, XYZ3210 Dispense Platform, BIODOT INC, USA) was used to print FITC inks. Surface patterning was carried out by dotting FITC solution ($10^{-6}$ mol L\textsuperscript{-1}, acetone) onto the reactive oil-repellent surfaces using the micro-spotting metal pins (Arrayit, USA) at room temperature. Relative humidity in the spotting chamber was about 57–60%. The unreacted ink was subsequently washed with excess pure acetone and ethanol followed by sonication in ethanol for

![Fig. 1 Schematic diagram showing the fabrication process of the reactive oil repellent surface. The sequential grafting of IPDI and H₂N-PDMS-NH₂ was repeated twice to allow a two layer polymer coating on the amino-functionalized surface.](image-url)

![Fig. 2 Chemical analyses of the oil repellent surface. (a) X-ray photoelectron spectra. Inset indicates the peak fitting of the N 1s. (b) ToF-SIMS positive spectrum of PDMS copolymer films. PDMS characteristic peaks are indicated.](image-url)
2 min. The spotting process of droplets was recorded using a high-speed camera (Olympus).

**Characterization**

Time of flight secondary ion mass spectroscopy (ToF-SIMS) was performed using a TOF SIMS V (ION-TOF GmbH, Germany). Mass analysis was carried out using a time of flight mass analyzer, sputtering with a Bi\(^{3+}\) ion source. X-ray photoelectron spectroscopy (XPS) was performed with a Scanning Auger XPS PHI5802. Contact angle and contact angle hysteresis measurements were carried out using OCA20 equipment (Data Physics, Germany) under ambient conditions. For measuring the contact angle hysteresis, the surface was tilted with respect to the horizontal plane until the liquid droplet starts to slide along the surface. Then advancing (\(\theta_{\text{Adv}}\)) and receding (\(\theta_{\text{Rec}}\)) contact angles were measured using a single 10 \(\mu\)L droplet of liquids with tilt angles less than 10°.\(^{36,37}\) The fluorescence images were captured using a Nikon Eclipse Ni-E upright fluorescence microscope. The condensation-enrichment process of pyrene was achieved with an exposure time of 500 ms with a 10× objective lens. The brightness and contrast of the optical images were enhanced for clarity.

**Results and discussion**

**Fabrication of substrates with reactive oil-repellent coatings**

The PDMS copolymer films were grafted onto flat silicon wafers or glass slides via the sequential layer-by-layer reaction. As illustrated in Fig. 1, the initial amino-functionalized surface was immersed in the solutions of \(\text{H}_2\text{N-PDMS-NH}_2\) and IPDI.

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**Fig. 3** Evaporation induced retraction process of the organic drop. (a) Images of the drop sliding down the tilted reactive oil-repellent surface, exhibiting oleophobic behavior. (b) Time-sequence images of the evaporating 5 \(\mu\)L droplets (scale bar = 2000 \(\mu\)m). (c) Variation of the instantaneous contact angle of the droplet with respect to time. (d) Variation of the instantaneous volume of the droplet with respect to time.
alternatively to graft the polymer brushes. The sequential grafting was repeated twice to allow a two layer polymer coating with a thickness of around 5 nm (Fig. S1†). The thickness of the polymer coating could be further increased by adjusting the cycles of the polymer grafting. The “liquid-like” PDMS backbone in the copolymer chains affords the surface excellent oil repellency (Table S1†), and the pendant amino groups provide the capability of post chemical functionalization.28

Fig. 2 shows the characterization of the PDMS copolymer films by XPS and ToF-SIMS measurements. The peaks of oxygen (O 1s at 532.9 eV), carbon (C 1s at 285.5 eV), and silicon (Si 2s and Si 2p) were all detected from XPS measurements (Fig. 2a). The peak fitting in N (1s) indicated the presence of the characteristic free amine at 401.0 eV and amide bond at 399.9 eV, as expected. As seen in the ToF-SIMS spectrum (Fig. 2b), the positive ion spectrum was dominated by the PDMS-characteristic fragments at m/z 73 (SiC3H9O+), 133 (Si2C5H15O+), 147 (Si2C5H15O3+), and 207 (Si3C5H15O3+), which indicated the existence of polysiloxane chains. In addition, the obvious peaks at m/z 30 (CH3N+) and 26 (CN−) (Fig. S2†) reinforce the identification of amino units on the copolymer films.

Droplet evaporation and condensation on the oil-repellent surface

A couple of organic solvents were used as probes in the test of droplet evaporation on the as-prepared oil-repellent surface. Fig. 3 shows the time-sequence images of the evaporation of 5 μL probe droplets on the reactive oil repellent surface and the variation of the droplet volume and contact angle with respect to time. All the probe droplets underwent similar procedures of condensation and profile shrinkage during the evaporation. Among them, acetone and tetrahydrofuran (THF) have the fastest evaporation rate, and the evaporation time of 1,4-dioxane is much longer than others. The contact angle measurements indicated that there are two stages of liquid condensation during the evaporation (Fig. 3b, S3 and Movie S1†). At the first stage, the contact angles remained constant, indicating smooth retraction and homogeneous volume shrinkage with extremely low hysteresis. And in the second step, the contact angles dropped sharply, but the droplet volume decreased slower than before, resulting in the collapse of the liquid profile at a smaller volume – the retraction of the contact line cannot match the volume decrease of the droplet.36 There might be two reasons ascribed to such a phenomenon, the inhomogeneity of the polymer coating on the substrate,39,40 and the condensation and adsorption of water from the atmosphere during the droplet evaporation. In the first step of smooth droplet retraction, the droplet is of a larger size and the inhomogeneity of the substrate could be neglected (Fig. S1 and S4†). In the second step of droplet collapse, the droplet became smaller, and the surface defects at the microscale might be amplified. The inhomogeneity of the surface coating would increase local hysteresis at the contact line and therefore retard the retraction of the contact line.41

The condensation and profile shrinkage of the organic droplets on the reactive oil-repellent surface during the evaporation procedure indicate the possibility of surface patterning with high resolution, high density microdroplet arrays of low-surface-tension liquids. The large change in the droplet volume also indicates the potential of the evaporation induced condensation-enrichment effect which allows surface modification with precursors with lower initial concentrations of solutes (Fig. 3c and d).

Condensation-enrichment effect on the reactive oil repellent surface

The condensation-enrichment effect on the reactive oil-repellent surface was therefore demonstrated by taking a pyrene–acetic acid solution as a test probe. The fluorescent dye, pyrene, cannot react with the pendant amino groups on the copolymer coating. The evaporation and condensation process of a diluted pyrene (10−6 M)–acetone drop was therefore performed on the as-prepared surface and recorded under a fluorescence microscope, at 25 °C and 60% relative humidity. As shown in Fig. 4a and b, in the beginning, the fluorescence signal of the droplet was undetectable due to the low initial concentration of pyrene. With evaporation and droplet condensation, the concentration of pyrene increased gradually, and the fluorescence signal was therefore amplified from the smaller droplet. The evolution of the droplet’s fluorescence profile during the condensation process is shown in Fig. 4c. The improved fluorescence intensity demonstrates the condensation-enrichment effect of the reactive oil-repellent surface which implies the surface patterning of organic
precursors with low initial solute concentrations. And the smaller volume of the condensing droplet also indicates the potential of high-density and high-resolution patterning of low-surface-tension liquids which is rarely achieved on other surfaces.

To demonstrate the condensation-assisted surface patterning, FITC molecules were used as the labelling probe in droplets of acetone solution. The isothiocyanate group in the FITC molecule can rapidly react with the pendant amino group on the substrate under mild conditions. The change in fluorescence intensities can help to evaluate the extent of the surface patterning reaction. Based on our results, we expect the retraction of the droplet and the condensation of FITC molecules in the droplet during evaporation. And the reaction between FITC and the free amino groups on the polymer coating would be triggered when the concentration of FITC reached a certain level (Fig. 5a).

We try to estimate the condensation-enrichment assisted surface reaction based on the classic collision theory that increasing the concentration of the reactants increases the rate of reaction. As the reaction occurs on the surface, the reaction rate is given by:

\[
\text{Rate} = \frac{kN_{\text{FITC}} \sin^3 \theta}{r (2 - 3 \cos \theta + \cos^3 \theta)}
\]

where \(N_{\text{FITC}}\) is the amount of FITC, \(\theta\) is the contact angle, \(k\) is the rate constant, and \(r\) is the radius of the droplet sphere (Fig. S5†).

Based on the Arrhenius equation, \(k\) was simply assumed as a constant in all measurements. The \(N_{\text{FITC}}\) was kept constant in the process of droplet shrinkage. The droplet evaporation was assumed in a constant contact angle mode before the unchanged state of the contact area. According to eqn (1), when \(r\) decreases, the rate of the reaction on the surface would increase. During the droplet evaporation, the droplet condensation would increase the concentration and induce more effective molecular collisions at the liquid–solid interface, and thus results in a higher reaction rate and a larger number of immobilized molecules.

The estimation fits quite well with our experiment. FITC–acetone solutions of different concentrations were added dropwise onto the reactive oil-repellent surface for condensation-assisted surface patterning. After wash, fluorescence intensities from the immobilized FITC probes were measured, which increased along with the shrinking pathway of the droplet (Fig. 5c). Particularly, at higher initial FITC concentrations (10\(^{-5}\)–10\(^{-7}\) M), the immobilized FITC molecules were washed thoroughly.

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**Fig. 5** (a) and (b) Schematic diagram showing the condensation-assisted reaction on the reactive oil-repellent surface. (c) Fluorescence intensity variation of reacted oil-repellent surfaces after dropping a 2 μL drop of FITC acetone solutions at different concentrations (scale bar = 100 μm, exposure time: 2 s). The unreacted fluorescent molecules were washed thoroughly.

**Fig. 6** Surface patterning on the reactive oil-repellent surface with low surface tension liquid drops. (a) Schematic representation of the process of surface patterning. (b) Images of spotting the drops of FITC solution (10\(^{-6}\) M, in acetone) onto the reactive oil-repellent surface (top) and amino surface (bottom, scale bar = 500 μm). The inset fluorescence images showing the patterned surface after wash (scale bar = 100 μm, exposure time: 2 s).
and $10^{-6}$ M), fluorescence signals could be detected at the edge of the droplet which means that the surface immobilization happened in the early stage of the droplet evaporation. Yet more FITC molecules will be immobilized in the region close to the center, indicating the effect of condensation-enrichment during the evaporation and condensation of the droplet. At a lower initial concentration ($10^{-7}$ M), minimal fluorescence signals were detected at the edge of the droplet which means that the reaction rate is too low in the beginning. While the immobilization of FITC molecules will be triggered until the FITC concentration reaches a certain value. At the test concentrations, no contact line pinning was observed during the process of condensation.

**Condensation-assisted patterning in droplet spotting**

The droplet spotting of high-density arrays of organic solvents is usually difficult to achieve because of the easily spreading nature of those low-surface-tension liquids. However, a number of functional molecules can only be dissolved in organic solvents and many chemical reactions rely on organic solvents. Therefore, developing a strategy of patterning high-resolution, high-density organic liquid arrays would be critically useful for surface functionalization and downstream applications. We here demonstrated that the reactive oil-repellent surface can provide a platform for surface patterning of organic droplet arrays. Fig. 6a shows the surface patterning process using a droplet spotter. A single acetone microdrop was spotted onto the reactive oil-repellent surface by using a metal pin with a diameter of approximately 150 μm. The spotting procedure was recorded with a high-speed camera. The condensation-enrichment effect occurs in the spotted droplet when the reactive oil-repellent surface was used as the substrate (Fig. 6b). As determined using the fluorescence microscope, the diameter of the spotted dot is around 70 μm when the initial FITC concentration of $10^{-6}$ M was used. For comparison, the amino-silane functionalized surface was used which is reactive to FITC but not oil-repellent – the acetone droplet would spread on the surface and evaporate rapidly. It could be clearly observed that the non-oil-repellent surface is incapable of inducing droplet retraction and condensation. The fluorescence signal was undetectable on the surface after the droplet evaporation because the FITC distributed in a larger area during the spreading of the drop and thus cannot reach the critical concentration as addressed previously.

Moreover, we also performed high-density chemical patterning on the reactive oil-repellent surface. Three kinds of patterning surfaces with dot pitches of 150, 300, and 450 μm were prepared. Compared to the pendant amino groups, the FITC molecule has a planar structure and distinct polarity and affinity to organic solvents, which would change the surface wettability after labelling (Fig. 7a). Briefly, the ethanol droplet could slide fast and smoothly on an inclined surface with low FITC patterning density, while it would slide slowly or even be pinned in the area where FITC patterning densities were high (Fig. 7b–c). The CAH measurement showed that the surfaces could maintain the oil-repellency to a few organic solvents after patterning. However, the CAH of ethanol is quite sensitive to the patterning density (Fig. 7d). The dependence

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Fig. 7  (a) Schematic showing the surface labelling of FITC patterns with different densities on the reactive oil-repellent surface. (b) Sliding of a 10 μL ethanol droplet on the patterned surfaces corresponding to different densities. (c) Fluorescence images of patterned microarrays on reactive oil-repellent surfaces with different densities (dot pitches are 150, 300, 450 μm corresponding to high, medium, low densities. scale bar = 200 μm). (d) CAH of the patterned substrates. Multiple organic liquids were selected as probes.
of CAH on surface patterning allows us to control droplet sliding on a tilted substrate.44

Conclusions

In summary, we revealed the use of reactive oil-repellent surfaces for surface micro-patterning of low-surface-tension liquid precursors. As a demonstration, fluorescent molecules were immobilized on the reactive oil-repellent surface by the high-density and high-resolution patterning of microdroplet arrays which was rarely achieved on other surfaces. Our results indicate a synergetic effect of the oil-repellent surface and condensation-enrichment on both high-density micro-patterning of organic droplets and surface functionalization. Our method demonstrated a simple approach to spatially control the surface chemistry and wettability which could be employed in many analytical applications. Considering the convenient coating process, our reactive oil-repellent surface holds great potential for sophisticated surfaces.45

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Notes and references


