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TOPICAL REVIEW — Soft matter and biological physics

Surface-tension-confined droplet microfluidics*

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This article is a concise overview about the developing microfluidic systems named surface-tension-confined droplet microfluidics (STORMs). Different from traditional complexed droplet microfluidics which generated and confined the droplets by three-dimensional (3D) poly(dimethylsiloxane)-based microchannels, STORM systems provide two-dimensional (2D) platforms for control of droplets. STORM devices utilize surface energy, with methods such as surface chemical modification and mechanical processing, to control the movement of fluid droplets. Various STORM devices have been readily prepared, with distinct advantages over conventional droplet microfluidics, which generated and confined the droplets by 3D poly(dimethylsiloxane)-based microchannels, such as significant reduction of energy consumption necessary for device operation, facile or even direct introduction of droplets onto patterned surface without external driving force such as a micropump, thus increased frequency or efficiency of droplets generation of specific STORM device, among others. Thus, STORM devices can be excellent alternatives for majority areas in droplet microfluidics and irreplaceable choices in certain fields by contrast. In this review, fabrication methods or strategies, manipulation methods or mechanisms, and main applications of STORM devices are introduced.

Keywords: surface-tension-confined, droplet, microfluidics, micropatterning, wettability

PACS: 92.20.cn, 79.60.Jv, 61.30.Hn, 05.70.Np **DOI:** 10.1088/1674-1056/27/2/029202

1. Introduction

Microfluidics is a technique that deals with the behavior, precise control and manipulation of fluids that are geometrically constrained to a small, typically sub-millimeter scale. Over the past decades, droplet microfluidic devices,[1,2] which largely rely on channel-based three-dimensional (3D) structured chip fabrication, have gained great interest in applications such as chemical reactions and synthesis,[3–5] single-cell analysis,[6,7] polymerase chain reaction (PCR),[8,9] and so forth. However, traditional droplet-based microfluidic manufacturing usually needs the devices to be equipped with 3D poly(dimethylsiloxane) (PDMS) channels produced by complexed methods and various steps, such as soft lithography and photolithography, combined with micro-electro-mechanical system (MEMS) design. This brings about a great many problems, such as difficulty in mass production, unsustainable long-term preservation, risks of cross-contamination, and expensive procedures. Additionally, external actuation such as heaters, micropumps, and microvalves will add more complexity and vulnerability on the ultimate devices.

To solve or avoid the arising problems, more and more researchers have endeavored to figure out two-dimensional (2D) droplet-based microfluidic systems which can be defined as surface-tension-confined droplet microfluidics (STORMs), on the basis of development of surface-tension-confined microfluidics (STCMs).[10] Surface tension is defined as the elastic tendency of a fluid surface which makes it acquire the least surface area possible. When surface tension applies to solids, the term surface energy is used in the dimension of energy per unit area. According to the principle of lowest energy, liquids will be confined to a specific area which has a higher surface energy than the background surface or move along a specific path on the surface with lower surface energy. Both of STCMs and STORMs have employed surface tension as the source of control over liquids while the distinct difference between them lies in the morphology of liquids controlled by surface tension, and the methods for manufacturing specific surfaces and droplet-forming accordingly. By exploiting surface tension, STORM devices confine and control the location and movement of microliters to femtoliters of droplets on the surface where hydrophobicity/hydrophilicity patterns[11] or micro- and nano-structures exist. Surface tension gradient,[12,13] capillary force,[14] vibration,[15] and so on, eliminate the need for auxiliary hardware such as a micropump for STORM devices, making the transportation of droplets more low-cost and eco-friendly. Without channels, drops of liquids can be readily deposited on the surface by micropipettes or sprayer nozzles, and after the experiments, the systems may be facilely refreshed and reusable.

During the past decades, STORM devices have been gaining increased attention in microfluidics research due to

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their easy accessibility, with numerous approaches developed, mainly including surface chemical modification and micromachining. Compared to STCM devices, they have also been widely applied in various fields including chemical reactions and biological assays, in a quantitative way due to the more accurate control over certain volumes of droplets by regulating the frequency of droplet formation.[16,17] In this review, we will primarily reveal recent advancement on the fabrication of STORM devices by different methods and their applications. The advantages, disadvantages, and limitations of the methods of fabricating STORM devices, current challenges, and future perspectives are discussed.

2. Heterogenous substrate preparation

During past decades, various methods have been developed for the preparation of specific substrates for STORMs, mainly including two types: (i) fabrication methods of hydrophilic/hydrophobic alternating patterns on substrates and (ii) fabrication methods of asymmetric structures on surfaces. The former can be summarized as the following seven methods: 1) photolithography, 2) selective photoirradiation onto photoresponsive substrates, 3) depositing hydrophobic materials onto hydrophilic substrates, 4) depositing hydrophilic materials onto hydrophobic substrates, 5) selective plasma treatment, 6) laser treatment, 7) mechanical method. With these fabrication techniques, hydrophilic patterns were surrounded by hydrophobic background, acting as the path or reservoir for liquid, and hydrophobic areas played a role of curbs that would prevent the undesired movement of liquid. Fabrication techniques of asymmetric structures categorized into six groups: i) molding combined with metal vapor deposition, ii) replication of biological surfaces, iii) oblique angle polymerization, iv) oblique reactive ion etching, v) polymer molding with a hierarchically-structured template, and vi) ferrofluid-molding.The asymmetric structures on surfaces can be exploited for the control of fluid movement. Such structures as inclined pillars and ratchets on surfaces have been confirmed as the key to realize the directional movement of fluid.

2.1. Fabrication of hydrophilic/hydrophobic alternating patterns

2.1.1. Photolithography

Photolithography is a popular method for the fabrication of microfluidic devices, where photoresist is the most primary source of specific patterns on substrate. There are mainly two kinds of photoresists that are usually used by researchers called negative resists, such as SU8, and positive resist, such as AZ photoresist. For example, Qun Fang' group[17–19] combined photolithography using AZ photoresist and wet etching technique to create a surface where the hydrophilic spots were surrounded with hydrophobic area. The silicon substrate was thermal oxidized to grow a layer of SiO_2 on the surface and then the layer of SiO_2 was silanized. The decorated surface was then spin-coated with AZ photoresist, covered with a specific photomask, exposed to UV light and developed. The exposed area (no photoresist) was later in touch with wet etching solution to remove the layer of silanized coating and expose the hydrophilic SiO_2 surface while the area protected by resist was then developed to remove the resist coating and expose the hydrophobic silanized layer. Shouichi Sakakihara *et al.*[20] also applied photolithography to the preparation of hydrophilic-in-hydrophobic micropatterned surface using AZP4903 photoresist. The hydrophobic background was prepared by spin-coating a hydrophobic polymer of carbon-fluorine diluted to 0.84 wt% with a solvent on a cleaned coverglass at 4000 rpm and baking the resulting glass for 1 h at 180 °C.

2.1.2. Selective photoirradiation onto photoresponsive substrates

The wettability of surface can be readily changed by chemical modification which can be easily achieved by photoinitiated photografting or photoirradiation onto a photoresponsive substrates. Such methods usually need a favor from masks which make a hydropathy property possible on the substrates. Neto *et al.*,[21] Kobaku *et al.*,[22] Li *et al.*,[23] and Pinar Beyazkilic *et al.*[24] respectively exploited the superhydrophobicity brought by the micro/nanoscale structures on surfaces of PS film, TiO_2 particles, silanized porous silicon plate and ormosil nanoparticles, and treated the superhydrophobic surface with UV light under the help of photomasks. For example, Li *et al.*[23] firstly dipped the silicon wafer into $HF/AgNO_3$ solution and HNO_3 solution in order to create a porous structure on the silicon substrate, then modified the porous surface by chemical vapor deposition (CVD) with 1H, 1H, 2H, 2H-perfluorodecyltrimethoxysilane (PFDTS) to make the surface superhydrophobic. Finally, the superhydrophobic substrate was covered by a photomask, and exposed under deep UV light. The exposed regions were superhydrophilic against the supurhydrophobic parts.

Geyer and Erica Ueda[25,26] from Levkin's group prepared a superhydrophilic porous poly (2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) (HEMA-EDMA) film on a glass substrate by UV-initiated free-radical polymerization and fabricated the superhydrophobic grid-like pattern on the superhydrophilic surface by UV-initiated photografting. Under the help of photomask, the size and shape of the superhydrophilic spots and superhydrophobic barriers can be precisely controlled. Based on the above results, Levkin's group[27–32] firstly applied a methodology named phototriggered thiol-yne reaction to successfully create superhydrophobic-superhydrophilic micropatterns. Firstly, they fabricated a nanoporous polymer layer of

poly (2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) (HEMA-EDMA) modified with alkyne groups by a standard esterification procedure. Then, the resulting alkyne porous polymer surface was wetted with thiol solution and irradiated with UV light at room temperature to accomplish the thiol-yne reaction. The surface hydropathy property could be determined by using thiols with different terminal groups, such as 3-mercaptopropionic acid for superhydrophilic modification and 1-dodecanethiol for superhydrophobic. What called for special attention was that the first thiol-yne reaction needed a photomask while the second step of modification did not require a photomask as a reactive alkyne pattern was created by the first step of irradiation through a photomask, which was an advantage of using a reactive surface for patterning (Fig. 1).

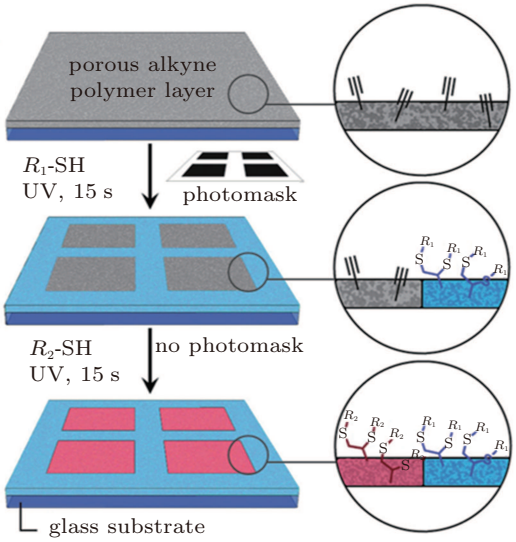


Fig. 1. (color online) Schematic representation of the thiol-yne photo-click reaction for creating superhydrophobic-superhydrophilic micropatterns using the alkyne-modified porous polymer layer as a substrate (from Ref. [29], Fig. 2(A)).

2.1.3. Depositing hydrophobic materials onto hydrophilic substrates

Kirsten A. Ganaja *et al.*[33] introduced wax printing method to the patterning of paper microzone plates. Hydrophilic arrays of microzones with a designed diameter of 6.00 mm and a line width of 0.30 mm were to be prepared on chromatography paper using a solid ink printer. The process where patterned solid wax was printed onto the surface of the paper and the hot plate melted the wax so that it penetrated the full thickness of the paper created complete hydrophobic barriers in paper that defined hydrophilic reaction zones. After following heating and cooling procedures, the final diameter of the microzones was 4.6 mm due to the limitations of resolutions and they could be filled with 1.0 μL of solution. Besides the above inkjet printing method, Du *et al.*[34] patterned the glass slide by microcontact printing which was developed by Xia *et al.*[35] In brief, polydimethylsiloxane (PDMS) stamps with defined patternings were attached onto the hydrophilic surface of glass slide which was treated with Piranha solution tightly and then the PDMS stamp was spin-coated with an octadecyltrichlor-osilane (OTS) solution. Thus, the OTS pattern was transferred from the PDMS stamps onto the glass slide and the regions that were treated with OTS became hydrophobic (Fig. 2).

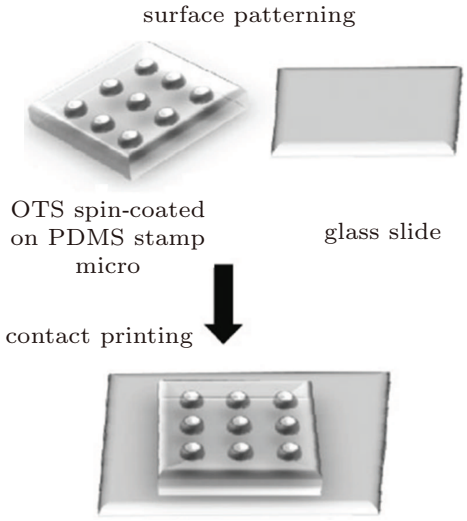


Fig. 2. Generating hydrophobic regions of OTS patterns on a hydrophilic glass by microcontact printing (from Ref. [34], Fig. 1(A)).

2.1.4. Depositing hydrophilic materials onto hydrophobic substrates

Alternatively, hydrophilic inks can also be printed onto hydrophobic surface. Li *et al.*[36] developed a simple method for creating superhydrophilic micropatterns on a superhydrophobic surface using a microcontact printer. The superhydrophilic area formation was based on printing an "ink", an ethanol solution of a phospholipid, onto a superhydrophobic porous polymer surface (Fig. 3). You *et al.*[37] combined photolithography and polydopamine coating after photoresist developing to successfully pattern hydrophilic polydopamine on nanostructured superhydrophobic anodized aluminum oxide surfaces. Briefly, positive photoresist was spin-coated on the superhydrophobic surface at a rate of 4000 rpm/s for 50 s. After UV exposure for 30 s under the photomask and the photoresist was developed, a 10-mg/mL dopamine solution was applied onto the substrate for 6 h to conduct a complete polymerization action, and then the residual photoresist was removed by acetone washing. Ultimately, a hydrophilic polydopamine 2D microchannel formed on the superhydrophobic AAO surface (Fig. 4). Besides, Wang *et al.*[38] patterned the superhydrophobic surface by inkjet printing with dopamine solution.

2.1.5. Selective plasma treatment

With the assistance of mask or stencil with cut-out patterns, hydrophilic patterns can be readily formed on the surface by plasma treatment.[39] Meldrum's group[40–42] applied

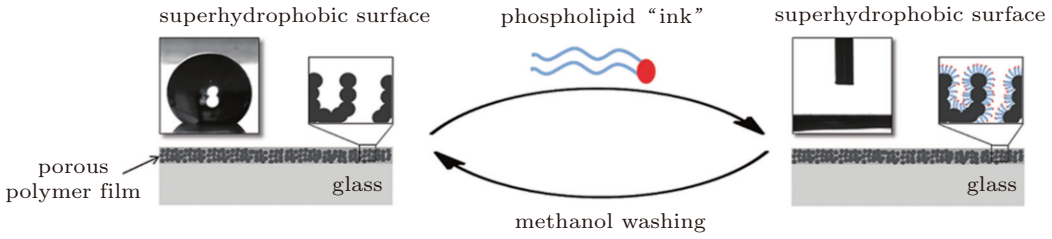


Fig. 3. (color online) Schematic representation of switching from superhydrophobicity to superhydrophilicity by applying an "ink" containing a phospholipid (from Ref. [36], Fig. 1(A)).

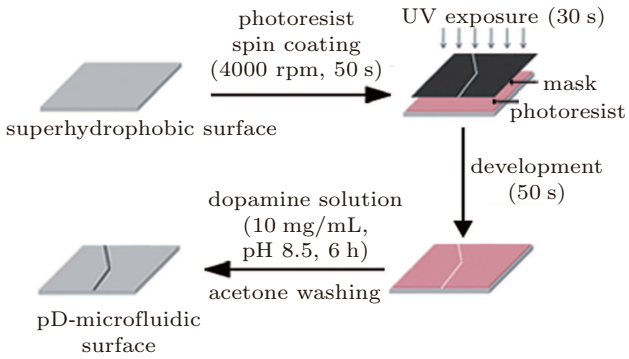


Fig. 4. (color online) Introduction of kinked pD micro-lines on superhydrophobic AAO surfaces (width = 60 mm) (from Ref. [37], Fig. 1(a)).

plasma treatment to surface modification to easily fabricate STORM devices. For example, Lin *et al.*[40] presented a simple and efficient method for single-cell analysis based on a hydrophilic/hydrophobic patterned surface. Such a patterned surface only relied on a technique called microscale Plasma Activated Templating (μPLAT) that employed an aluminum screen as the mask to expose designed areas to air plasma and thus increased the hydrophilicity of specified areas. A common microscope glass cover slip was used as the substrate and the aluminum stencil was set on it, and the assembly was then put in a plasma cleaner with 6.8-W RF-power for 10 seconds. Ultimately, the mask was removed, leaving an array of hydrophilic areas on the glass substrate (Fig. 5).

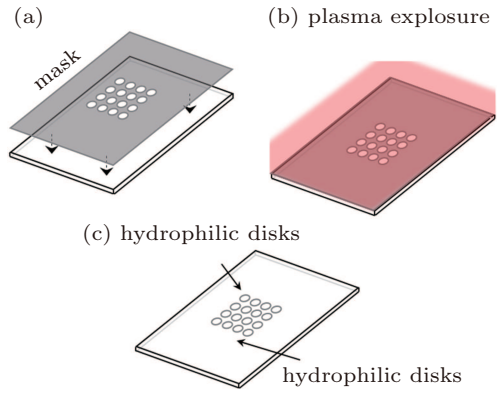


Fig. 5. (color online) Hydrophilic patterning process. (a) Adhere a stencil to a glass cover slip; (b) Expose to air plasma; (c) Remove the stencil, leaving a hydrophilic disk array on the surface (from Ref. [40], Fig. 1).

To create wettability micropatterned surface for surface-wettability-guided assembly (SWGA), Li *et al.*[43] explored a simple surface modification strategy combining a micropatterned polydimethylsiloxane (PDMS) stencil fabricated by conventional soft lithography with plasma treatment. The PDMS stencil was attached to a clean glass slide and treated with oxygen plasma, temporarily bonding together. The glass regions in contact with the PDMS stencil was coated with a nano-layer of PDMS oligomers which was hydrophobic while the areas exposed to plasma showed a hydrophilicity.

2.1.6. Laser treatment

Laser treatment can be employed as an effective method to control the wettability of surface. Schutzius *et al.*,[44] Yong *et al.*,[45] Bahador Farshchian *et al.*,[46] and Bachus *et al.*[47] demonstrated the strategy that utilized laser irradiation to fabricate the superhydrophillic/superhydrophobic binary patterned surface. For example, Bachus *et al.*[47] presented a facile method to form superhydrophilic regions on the superhydrophobic surface by laser micromachining. Laser micromachining relied on an Oxford Lasers and A Series Compact Micromachining System which was equipped with a 355-nm solid-state diode-pumped picosecond-pulsed laser. The integrated programs were created to mill circles on the superhydrophobic surface varying the size and spacing of the array, the circle diameter, laser power, pitch between laser passes, and the speed at which the stage moved when processing. Before the laser treatment, a glass substrate was applied with a commercial superhydrophobic fluorinated silica nanoparticle-based coating. Once the superhydrophobic-coated substrates was placed inside the enclosure of the laser micromachining system, with the system's software (Cimita), the substrate was brought into focus by adjusting the height of the laser optics (with mounted camera) and focusing using the on-screen optical image. The G-code machining routine was initiated and the milling process began after the substrate was in focus. Upon the completion of the program, the hydrophilic patterned surface was ready for directly use without any further processing.

2.1.7. Mechanical method

Micro-indentations can be introduced onto the superhydrophobic surfaces as fools for the fixing of liquid droplets based on the rose-petal effect. Neto *et al.*[48,49] firstly prepared superhydrophobic polystyrene surfaces via a phase-separation methodology which mimicked the effect of lotus leaves. The micro-indentations were fabricated using a microhardeness tester equipment with a sharp rigid Vickers diamond pyramid

indenter penetrating into the surface. Micro-milling can also be applied to fabricate hydrophilic patterns on the superhydrophobic surfaces. Yang *et al.*[50–52] proposed the micro-milling method for fabricating hydrophilic patterns such as micro-dots, lines, and circle grooves on the superhydrophobic surfaces. The superhydrophilic surfaces were fabricated by electrochemically etching the polished clean Al alloy plates at 600 mA·cm^{-2} for 8 min in the 0.1-mol·l^{-1} NaCl aqueous solutions, subsequently immersed in the 1-wt% ethanol solution with fluoroalkylsilane for 90 min to lower the surface energy. Micro-dots and groove patterns were milled on the superhydrophobic surfaces utilizing a milling system which was set up by mounting a motorized spindle on the Z axis of a three-axis motion platform. During the milling process, the spindle speed and the scanning rate were at constant values of 2×10^4 r·min^{-1} and 10 mm·min^{-1}, respectively.

2.2. Fabrication of asymmetric structures on surfaces

2.2.1. Molding combined with metal vapor deposition

The methods of molding generally included replica molding, soft lithography, and so on. Choi *et al.*[53] and Chen *et al.*[54] fabricated arrays of polymer nanopillars by simple replica molding followed by metal vapor deposition. Choi *et al.*[53] first fabricated an anodized aluminum oxide (AAO) mold as a reusable template and conducted surface modification of the AAO mold. Then polyurethane acrylate (PUA) was poured onto the AAO mold and a polyethylene terephthalate film was placed on the PUA layer as a substrate. After UV treatment, the polymer replica was detached from the AAO mold. To fabricate asymmetrically bent nanopillars, gold was thermally deposited onto one lateral side of the polymer nanopillars at an angle of 45°. Janus nanopillars were bent toward the Au-deposited side, and the curvature was regulated by controlling the thickness of the Au layer (Fig. 6).

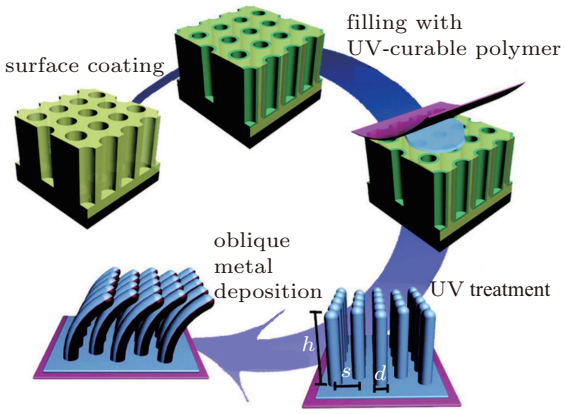


Fig. 6. (color online) Schematic illustration of the procedure for the fabrication of highly packed, uniformly bent polymeric Janus nanopillar arrays prepared from reusable AAO templates (from Ref. [53], Fig. 1).

Similarly, Chen *et al.*[54] also employed the replica molding method combined with metal deposition. The difference was that the polymer used was a shape memory polymer (SMP), which showed a property of recovery from deformation. After the epoxy-based SMP pillars was fabricated by replica molding, the SMP pillars were deformed completely by mechanical shearing and then gold or gold–palladium alloy was sputtered onto the deformed SMP pillars. The entire system was reheated at the temperature of 80 °C to access the partially deformed state (Fig. 7).

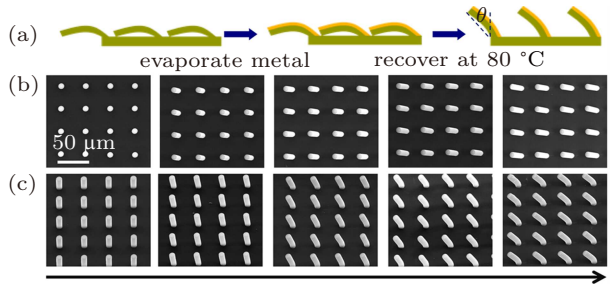


Fig. 7. (color online) Control of the tilting angle (θ) of SMP pillars coated with a thin layer of metal. (a) Schematics of metal coating. Top-view (b) and side-view (c) SEM images of SMP pillars tilted at different θ depending on the thickness of Au coating, which is increased by ~6.44 nm/increment from left (0 nm) to right (25.8 nm) (from Ref. [54], Fig. 1).

Yang *et al.*[55] fabricated surfaces with slanted micro-pillars arrays by using the soft lithography replication technique combined with oblique metal deposition. Firstly, the straight micro-pillar arrays were fabricated by pouring the PDMS polymer (mixture of PDMS base with the cyclic hydride curing agent in a 10:1 ratio by weight) over the silicon mold made from conventional photolithography using a mask aligner machine, degassing the polymer in a vacuum oven and curing the samples at 100 °C for 30 minutes. Then, to deflect the pillars, they used an electron-beam evaporator to obliquely deposit a thick silver layer (~500 nm) on one side of the micro-pillars. The bending angle of the micro-pillars could be varied by tuning the deposition incidence angle and the metal film deposition rate. BinAi *et al.*[56] fabricated a novel half-cone nanoshell array via a simple and efficient colloidal lithography and shadow metal deposition technique. Ordered polystyrene sphere monolayers were first prepared on a glass substrate coated by a photoresin film, following by a reactive ion etching to completely etch away the microspheres and construct the photoresin film into a periodic cone array. Secondly, a shadow deposition of Ag with an angle of 40° was conducted to coat one half of the photoresinnanocones and the inter-cone surface with a 100-nm layer of silver. The as-prepared sample was then immersed in ethanol to remove the photoresin completely. Finally, the half-cone nanoshell arrays were formed.

2.2.2. Replication of biological surfaces

In recent years, the biomimetic and bioinspired synthesis of nanostructures have been gaining increased attention due to its desirable properties for applications involving control of the

liquid. Among various well-developed methods, direct replication of biological surface is one of the simplest methods for the fabrication of asymmetric structures, such as leaves of the arid climate plant species eremopyrum orientale, which has a hierarchical surface structure. Gürsoy *et al.*[57] employed soft lithography combined with surface chemical functionalization to successfully fabricate the gradient multi-length-scale surface structure comprising macroscale grooves, microscale tilted cones, and nanoscale platelets. Firstly, leaves were rinsed with water to completely remove dirt and debris on surface before the polyvinylsiloxane base and cure mixture were applied to the substrate, and immediately pressed down by a glass slide for 10 min to fully cure. After the negative molds of these surfaces had hardened, the molds were carefully peeled away from the natural substrate surface and cleaned for the preparation of positive replicas. Positive replicas were prepared by pouring the epoxy resin which was consisted of a 5:2 ratio of resin to hardener over the negative mold. The mixture was cured for 36 h in a desiccator after its trapped air bubbles were removed under vacuum. Finally, after the negative molds were peeled away, hydrophobic surface nanocoatings consisting of 1H, 1H, 2H, 2H-perfluorooctyl acrylate were applied onto the surface of positive molds by initiated chemical vapor deposition (iCVD) (Fig. 8).

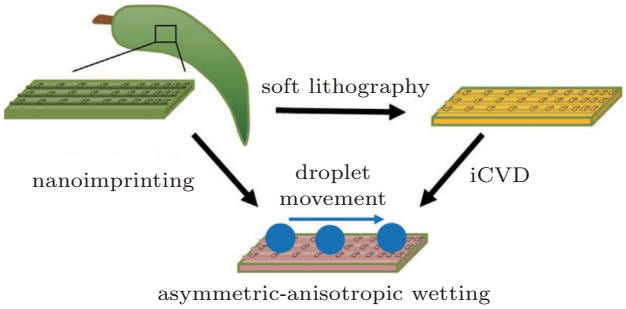


Fig. 8. (color online) Replication of eremopyrum orientale plant leaf surface (from Ref. [57]).

2.2.3. Oblique angle polymerization

Anisotropic textured polymer surface can be an excellent tool for the control of liquid movement. Malvadkar *et al.*[15] fabricated nanofilms consisting of arrays of poly (p-xylylene) (PPX) nanorods via a bottom-up vapor-phase technique called oblique angle polymerization (OAP). The key of this method was the generation of a diradical vapor flux by vaporization at 175 °C and pyrolysis of a p-cyclophane precursor, dichloro-[2,2]-paracyclophane (PDS) at 690 °C. Then, the flux was directed at a controlled shallow angle 10° onto a silicon substrate, leading to a selective growth of slanted PPX nanorods (Fig. 9).

Sekeroglu and Demirel[58] also adopted the same method to fabricate the textured nano-PPX surface as a fluidic platform, and used a rubber strip to apply constant pressure along the nano-rod direction to deform the nano-PPX surface due to its flexibility. The tilt angles of nano-rods on pristine and deformed surface were directly demonstrated by cross sectional electron images (Fig. 10).

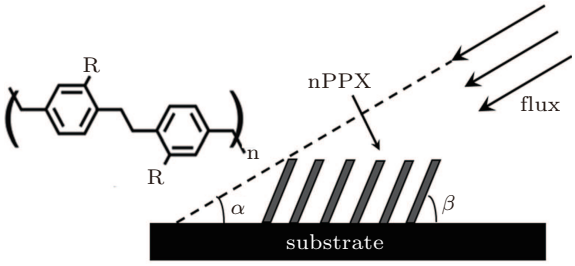


Fig. 9. Schematic diagram of PPX nanofilm deposition by OAP (from Ref. [15], Fig. 1(a)).

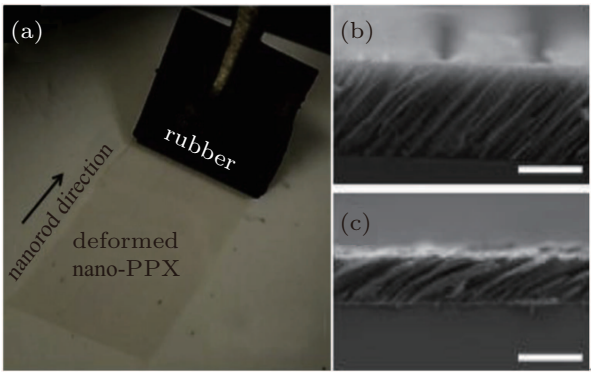


Fig. 10. (a) Nano-PPX surface is deformed by a rubber strip along the nano-rod direction (scale: 1 mm). (b) Cross sectional SEM of nano-PPX before (scale: 10 mm) and (c) after (scale: 5 mm) deformation are shown (from Ref. [58], Figs. 1(a)–1(c)).

2.2.4. Oblique reactive ion etching

Agapov *et al.*[59] fabricated arrays of nano-structured and micro-structured tilted pillars by reactive ion etching (RIE) of masked substrate at a tilt angle relative to the carrier wafer. In brief, nanoscale diameter pillars fabricated based on a method called metal dewetting. The substrate coated with a layer of platinum was dewetted to form circular metal islands under 850 °C in an atmosphere of H_2 and Ar. Such islands were employed as a mask on the substrate. The masked substrate was etched at an angle of 70° relative to the carrier wafer and thus formed nano-structured tilted silicon pillars. Different from the nanostructure patterning method, the micro-structured tilted pillars were fabricated by combining photolithography and oblique RIE. Finally, the tilted arrays were functionalized with a monolayer self-assembled silane (Fig. 11).

2.2.5. Polymer molding with a hierarchically structured template

To fabricate hierarchical structures on surfaces, Jang *et al.*[60] utilized a polymer molding process assisted with a template containing ratchet-like microscale structures and

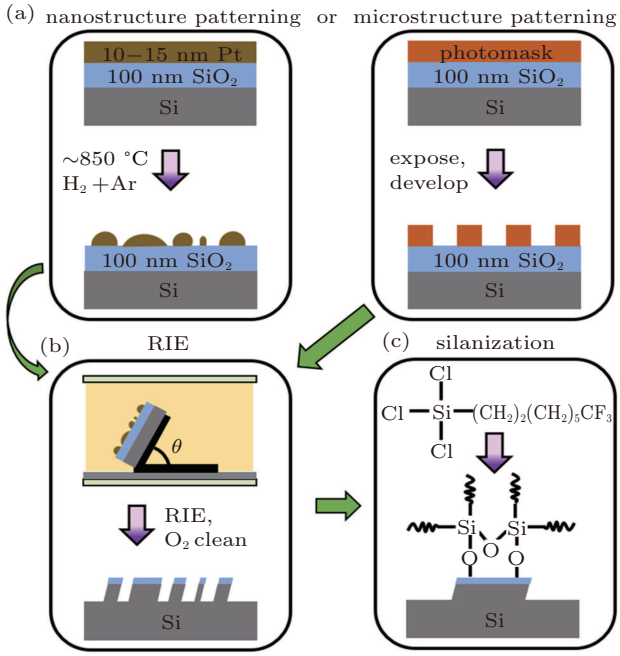


Fig. 11. (color online) (a) Fabrication sequence used in the present study to create tilted arrays. Nano-structures were masked using a dewet film of platinum. The dewet film consists of circular metal islands that serve as an etch mask. Microstructures were masked with either a positive or negative resist and patterned with photolithography. (b) Reactive ion etching (RIE) of each masked substrate tilted at a 70◦ angle relative to the carrier wafer resulted in tilted arrays of the masked features. (c) The tilted arrays were then functionalized with a self-assembled monolayer of a silane (from Ref. [59], Fig. 1).

nanoscale spheres on top of them. An ultra-thin layer coating was applied onto the template to protect the template from the repeated molding process to fabricate the functional surfaces. Through the one-step polymer molding, a variety of polymers with a hierarchical structure were simply fabricated for unidirectional droplet movement (Fig. 12).

2.2.6. Ferrofluid-molding

Huang *et al.*[61] took advantages of the ferrofluid-molding strategy to successfully generate microcone structures with different inclination angle by regulating the direction of external magnetic field applied to the ferrofluid. In a nutshell, 3 μL of water-based ferrofluid containing 10-nm magnetic nanoparticles was firstly divided into microdroplets owing to magnetic hydrodynamic instability and arrays of droplets formed a hexagonal pattern under the control of magnetic disks. Then the ferrofluid droplets could follow the direction of the external magnetic field and be slanted as the external magnetic field was tilted. A nickle layer was further deposited onto the microscale surface to decrease the nanoscale structures on the surface of trichomes which would influence the wetting property. The resulted slanted ferrofluid droplets were then treated as the master of the mother mold to fabricate microcone-shaped polydimethylsiloxane (Fig. 13).

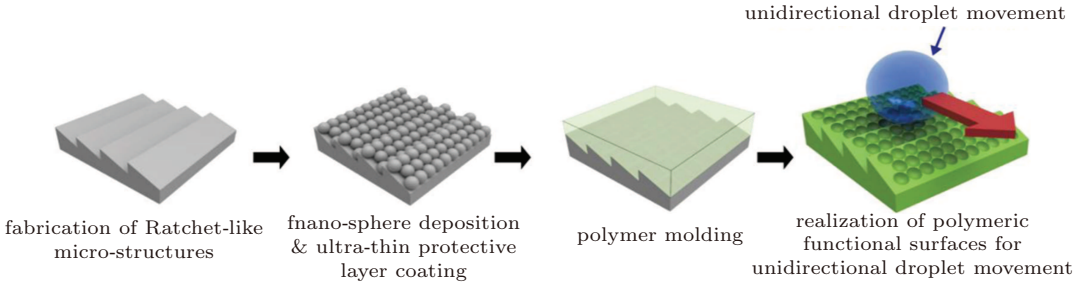


Fig. 12. (color online) Schematic diagram of the one-step molding process for fabricating the polymer functional surfaces to enable unidirectional droplet movement. Fabrication of the polymer functional surfaces is based on a simple molding process using a variety of polymers with a hierarchically structured template, which consists of ratchet-like microstructures, nanospheres, and an ultrathin protective layer (from Ref. [60], Fig. 1).

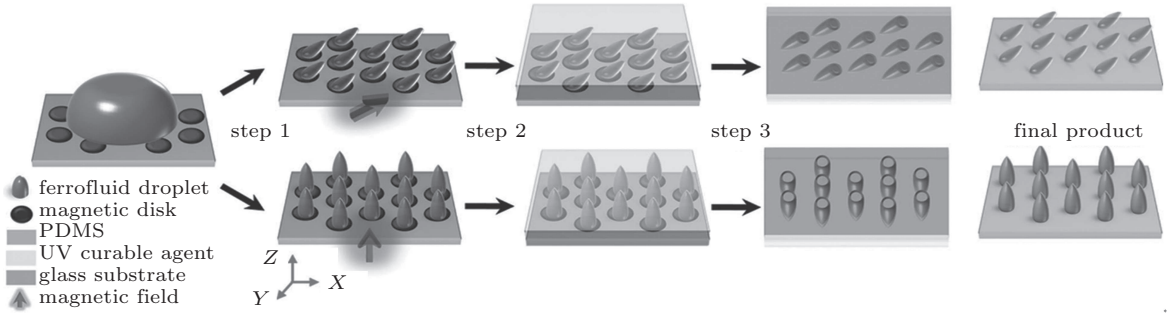


Fig. 13. Schematic illustration of the fabrication process generating cone-shaped PDMS structures based on the ferrofluid-molding method. The magnetic field was applied in the out-of-plane direction (z-axis) (from Ref. [61], Fig. 2).

3. Surface-tension-confined droplet generation and manipulation

With the aid of hydrophilic/hydrophobic alternating patterned surfaces, arrays of droplets could be generated facilely without complex extra devices due to surface tension from micropatterned surfaces. In most cases, micropipettes were used as the tools for depositing droplets onto hydrophilic areas and droplet volumes could also be conveniently regulated

by choosing corresponding types of pipettes. To realize manipulation of generated droplets, substrates with nano- and micro-structures and was employed due to unbalanced surface tension from asymmetric surface structures. Extra energy sources, such as magnetism, could also be applied to accomplish flexible control over generated droplets on patterned surfaces. By tilting the formed platform, gravity of generated droplets would be a superexcellent driving force for the manipulation of droplets.

3.1. Surface-tension-confined droplet generation

Traditional droplet microfluidics generally generated droplets by step-emulsion method, while in STORMs, arrays of droplets confined in hydrophilic areas can be generated mainly through two ways, dewetting and dispensing. The only difference between the two ways is whether hydrophobic areas and hydrophilic areas were both coated with aqueous solution or not during the process of droplet generation. To realize dewetting of patterned surfaces, substrates can be dip-coated or coated with aqueous solution first and tilted to remove extra solution occupying hydrophobic areas, and so on. Tools like micropipettes or an automatic robot system can be employed to dispense certain volumes of droplets onto arrays of hydrophilic patterns surrounding by hydrophobic background. Information about relative reports are summarized as follow in detail.

3.1.1. Dewetting

With generated hydrophilic/hydrophobic alternative patterns on the substrates, arrays of droplets can be formed through methods, such as dip-coating,[22,27,29,46] sliding,[23,26,31,32] rolling,[28,30,47,62,63] and so forth. For example, Bruchmann *et al.*[27] first fabricated a hydrophilic/hydrophobic patterned substrate and then immersed the substrate into water, thus arrays of microdroplets were generated on the hydrophilic areas while the hydrophobic areas remained dry due to the effect of discontinuous dewetting (Fig. 14).

Ueda *et al.*[26] developed a one-step for facile formation of arrays of microdroplets with defined geometry and volume. As aqueous solution was sliding along the superhydrophilic/superhydrophobic alternative patterned surface, arrays of completely separated droplets were instantly generated due to the extreme wettability contrast of superhydrophilic spots on a superhydrophobic background. This method is similar to a method called "rolling droplet",[30] which needs to tilt the substrate slightly so as to make the large droplet of an aqueous solution applied to the surface roll off the surface with an array of separated droplets formed spontaneously. In addition, some researchers also adopted a method of adding mineral oil to occupy the hydrophobic areas which were covered by aqueous solution in the former step due to mineral oil's higher density than water.[20,40]

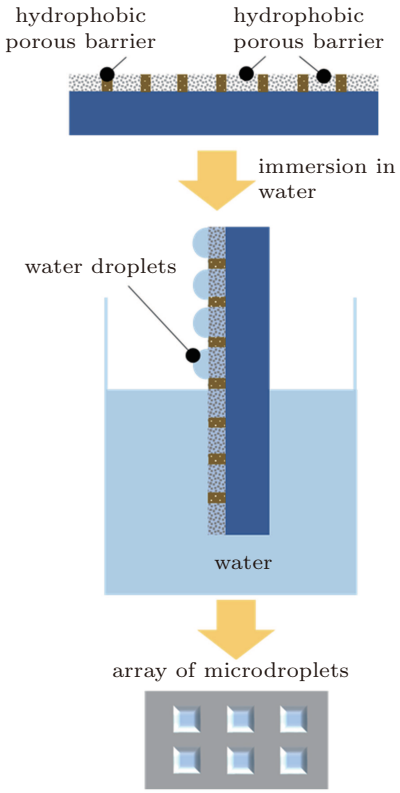


Fig. 14. (color online) When the hydrophilic–hydrophobic patterned substrate is immersed in water, an array of microdroplets is formed on the hydrophilic areas while the hydrophobic areas remain dry (effect of discontinuous dewetting). Different geometries of microdroplet arrays are shown (from Ref. [27], Fig. 1 (step 1)).

3.1.2. Dispensing

In most cases, researchers generally chosen tools like traditional pipettes to manually deposit certain volumes of droplets onto hydrophilic areas one by one if the sizes of target regions were not too small, such as 0.5-mm diameter.[18,21,41,43] This method is simple but limited to the size of hydrophilic areas and the measuring range of pipettes, thus leading to the development of automatic robot system.[16,17,19,33] For example, Qun Fang's group[17,19] had developed a sequential operation droplet array (SODA) system, and a surface-assisted multi-factor fluid segmentation (SAMFS) system which was created based on the combination of robotic liquid handling and surface-assisted droplet generation techniques. With assistance of above systems, various liquids flowed out from a capillary probe and were segmented into individual droplets with volumes from 1.2 nL–150 nL, left on the hydrophilic areas (Fig. 15).

As techniques of bioprinting were developed fast, Sun *et al.*[16] had developed a double-inkjet printing method to generate a novel picoliter droplet-in-oil array on a uniform hydrophobic silicon chip which did not need a process of patterning. The volumes of droplets could be regulated flexibly by changing the jet frequencies, ranging from 124 pL–496 pL.

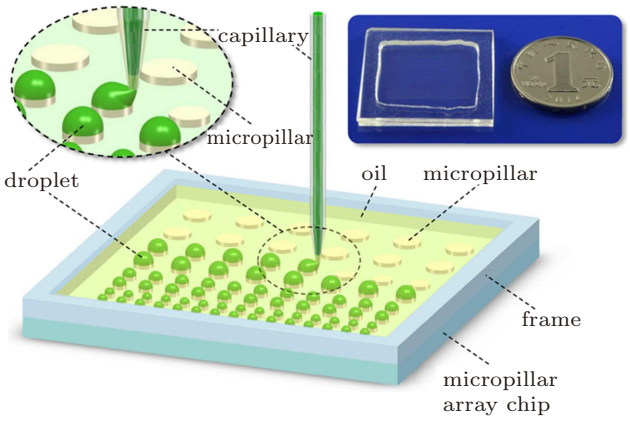


Fig. 15. (color online) Schematic diagram of the micropillar array chip. The insets show an enlarged image of the droplet during the generation process and a photograph of a micropillar array chip with different micropillar sizes (from Ref. [17], Fig. 1(a)).

3.2. Surface-tension-confined droplet manipulation

Different from traditional complexed channel-baseddroplet microfluidic chips whose driving force of generated droplet movement generally relies on external facilities, STORM systems realized manipulation over generated droplets in a friendlier and cost-saving way with assistance from capillary force, gravity, surface energy gradient, and so forth by designing corresponding surface patterns or structures. To illustrate mechanisms of manipulation over droplets on substrates in detail, relative contents are summarized and presented as follows.

3.2.1. Wettability from hydrophilic patterns

It has been summarized as follow that the most common method applied in STORM devices for droplet movement or confinement was to employ wettability or capillary force generated by (super)hydrophilic materials.[18–38,40,42,43,46,49] Generally, capillary force and surface wettability are related phenomena happening at the interfaces of solid, liquid, and air phases, and are highly dependent upon the interaction between liquids and solid surfaces. On the hydrophilic surface, liquids can move more easily than on the hydrophobic surface due to capillary force, which can also be explained by the better wettability of hydrophilic surface. In most cases, hydrophilic patterns were fabricated by depositing hydrophilic materials on a hydrophobic surface. When droplets were deposited on the surface, hydrophilic materials acted as a path or reservoir for droplet movement or confinement while the hydrophobic background played a role of fencing which would prevent droplets from moving out of control. For example, when droplets of 50% v/v glycerol–water mixture was introduced onto a hydrophilic 2D channel (width: 1 mm) fabricated by selective UV irradiation assisted with a mask, it spread instantly at a speed of 3 mm/s∼4 mm/s due to the capillary force from the hydrophilic paper. The liquid was confined within the hydrophilic channel with the hydrophobic areas acting as a virtual wall.[64]

3.2.2. Unbalanced capillary force from asymmetric structures

To flexibly control the movement of liquids on the surface, various micro/nanoscale topographic structures were fabricated via molding combined with metal deposition and other methods.[54,55,60,61,65,66] The mechanism of liquid movement on asymmetrically patterned substrates was studied by Chamakos *et al.*[67] As presented in above articles, a droplet on such a (super-)hydrophobic surface patterned with micro/nanoscale rods or pillars behaved like a "liquid sphere" which could easily move in direction which was generally decided by the direction of slanted or bended rods and pillars. It has been proved that the direction that a liquid droplet tends to move in was basically influenced by the unbalanced capillary retention force at the contact line and in cases where the capillary effect was weakened, the anisotropic friction behavior fades. The spacing between the rods or pillars and the hydropathy property could also affect the state of liquids placed on the substrate. Compared to capillary-force-driven STORMs, this kind of STORMs was fabricated by more complex methods, thus it could realize a more automatic control of liquids, which would be a promising orientation of future research.

3.2.3. Surface energy gradient

It has been confirmed that substrates with surface energy gradient could be fabricated by selective illumination of UV light with the irradiation time changed.[12] Wettability of the hydrophobic substrate could be changed from $>150^\circ$ to $<5^\circ$ after illumination under a UV light for about 60 min. Theoretically, surfaces with various kinds of wettability patterns could be designed effectively to improve water collection efficiency by integrating both surface energy gradient and Laplace pressure gradient. While in another paper, topographic wettability gradient arising from surface energy gradient could also be employed for the control of droplets motion.[13] The nonuniform spacing between pillars created the uneven energy barrier which made surface energy gradient on the substrate and determined the direction of droplet movement. The droplet could migrate either with or against the wettability gradient, depending on the pillar height and surface tension gradient. The droplet under a large pillar height and surface tension, meaning a larger antiwetting pressure, tended to generate a Cassie state for self-motion following the wettability gradient. A comparatively small antiwetting force due to a small pillar height and surface tension of the droplet leaded to a Wenzel state after impact. Meanwhile, the nonuniform spacing between pillars dominated the coexistence of the Cassie and Wenzel states in which depinning and pinning existed on either side of the droplet, respectively, and the coexistence of

Cassie and Wenzel states caused the droplet to migrate against the wettability gradient.

3.2.4. Gravity

By tilting the platform of STCMs at a certain angle, droplet movement could be controlled through gravity.[37,38,50,52,57,68,69] This method was simple and usually involved existence of hydrophilic patterns on hydrophobic substrates. Kong *et al.*[69] developed an open microfluidic system consisting of hydrophilic/hydrophobic alternative plastic sheets and a two-axis tilting platform which was powered stepper motors. Employing gravity, they realized multiple droplet operation such as one-direction transport of droplets, merging and mixing of various droplets, transport of droplets of different sizes, and so on. Taking the transport of a single droplet for example, a droplet was initially positioned on the left hydrophilic symbol printed on the superhydrophobic surface of a plastic sheet. The stage was tilted clockwise and then anti-clockwise to return to its default horizontal position (depicted by red block arrows). This rapid tilting action enabled the droplet to move to the right hydrophilic symbol. Time-lapsed images of an actual droplet showed how the droplet was transported from the left symbol to the right symbol by the tilting action of the stage.

3.2.5. Vibration

With the assistance of vibration, a liquid droplet could display a directional movement on the asymmetrically structured surface.[15,58,59] As shown in the Fig. 16, two half-pipes, one coated with PPX nanofilm and the other uncoated, were glued to a base which provided low-amplitude about 85-Hz random vertical vibration. A water droplet was placed on the surface of PPX-coated half-pipe and translated along the pipe under the vibration while the droplet on the surface of the other half-pipe merely vibrated randomly.[15] Agapov *et al.*[58] also applied water droplets onto vibrating chips with a nanostructured ratchet, finding that the droplets moved preferentially in the direction of the feature tilt while the opposite directionality was observed in the case of microstrutured ratchets.

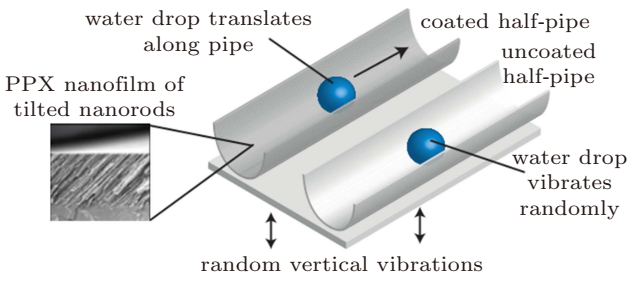


Fig. 16. (color online) Schematic of experimental set-up. Two half-pipes, one coated with PPX nanofilm and the other uncoated, were glued to a base. Low-amplitude ~85 Hz random vibration of the base caused translational droplet motion on the coated half-pipe, but not on the uncoated pipe (from Ref. [15], Fig. 3(a)).

3.2.6. Magnetism

Through adding magnetic beads or particles into liquids or surface structures such as pillars and ratchets, droplets motion on the substrates could be easily controlled by applying a magnetic field onto the STORM systems.[41,70–72] The magnetic beads added into the liquids should be compatible with the chemicals used and the microfluidic platforms in order to promise the normal reaction conducted on the platforms. Shi *et al.*[41] exploited commercially available magnetic beads with a variety of affinity options to accomplish nucleic acid extraction via external magnetic field. Furthermore, Almeida *et al.*[72] introduced super-paramagnetic particles with bound DNA into microliter-sized droplets covered with mineral oil on a hydrophobic glass surface by using magnetic force to conduct the pyrosequencing experiments. This magnetic bead-based method eliminated the need for fabricating structures for on-chip columns required for each purification reaction and reduced the complexity of fabrication. On the other hand, magnetizable particles could be added into the micro-pillars or micro-walls by simple molding methods to realize directional control of droplets on the structured surface.[70,71] Utilizing this method, switchable wettability and droplet shedding-off properties could be available through the effect of the external magnet.

4. Applications of STORMs

Since STORM devices have been developed fast during past decade, the applications of STORMs have involved a great many fields including single cell isolation and analysis, high-throughput synthesis and screening, real-time polymerase chain reaction (RT-PCR), and so forth. These applications are summarized and classified as follow according to the encapsulated target number in one droplet.

4.1. Single cell/molecule/particle encapsulation and analysis

Cell encapsulation generally takes place in 3D microchannels employing techniques called droplet microfluidics, where external pumps or complex channel design are in necessary. With hydrophilic/hydrophobic alternative patterns on the surface, STORMs can encapsulate cells individually and randomly with droplets adhering to hydrophilic areas readily. This strategy can be used for applications such as single cell/molecule/particle isolation and analysis.[17,19,20,23,40,42,62,73] Well-defined microdropets generation is of great significance to the high-resolution patterning and matrix distribution for chemical reactions and biological assays. Li *et al.*[23] had achieved single human breast cancer cell (MCF7) array by sliding a 10-μL droplet of cell culture medium (concentration: 10^7 mL^{-1}) on a patterned superhydrophilic/superhygrophobic substrate. This droplet-splitting

method was facile, sample-effective, and low-cost compared to traditional droplet microfluidics.

Sakakihara *et al.*[20] had developed a femtoliter droplet array as a platform involving many microreactors for the enzyme assay, greatly improving the detection sensitivity down to the single-molecule level. The formation and volume control of the droplet were readily realized with assistance from patterned surface. Access to individual droplets was achieved by a commercially available micropipette and a pressure controller connected to the micropipette. Single β-galactosidase (β-gal) molecules were enclosed and the catalytic activity of β-gal were measured in the droplet array very easily by mixing fluorescein-di-β-galactopyranoside (FDG) solution with low concentration of β-gal and using it as the aqueous phase of the droplet array formation procedure. The reaction was monitored by the increase in fluorescence during the process where β-gal hydrolyzed the fluorogenic substrate FDG into fluorescein. To realize precise control of the droplet volume so as to realize quantitative single-molecule measurement of catalytic activity, the above-mentioned micropipette combined with a pressure controller was applied.

Digital polymerase reaction (d-PCR) could also be conducted on a STORM platform. For example, Liu *et al.*[17] had developed a facile SAMFS approachfor generating a two-dimensional droplet array with tunable droplet volumes, for multivolume d-PCR. The throughput of droplet generation was high up to 50 droplet/s and the droplet volume adjusting range was from 0.25 nL to 350 nL. To test the performance of the multivolume digital PCR system, a serial of dilutions of synthetic PIK3CA plasmid DNA with final concentrations ranging from 1.1×10^2 copies/mL to 1.1×10^6 copies/mL was used to perform d-PCR assay. During the process of DNA replication, DNA concentration in droplets increased, and the positive and negative signals were captured with the in situ real-time fluorescence detector. For each concentration, there were corresponding droplets with volumes ranging from 1.2 nL to 150 nL. By counting the number of positive droplets in each set of individual volumes, the concentrations of DNA template were calculated using a Matlab program based on the Possion distribution. Self-consistent results of experiments indicated the reliability of the system for gene quantification. Measurement of HER2 gene expression in different breast cancer cells was conducted to demonstrate the potential of this multivolume digital PCR system in medical diagnosis. The result was compared with that obtained using the conventional quantitative real-time PCR, indicating the better precision of the multivolume digital PCR method over the quantitative real-time PCR method (Fig. 17).

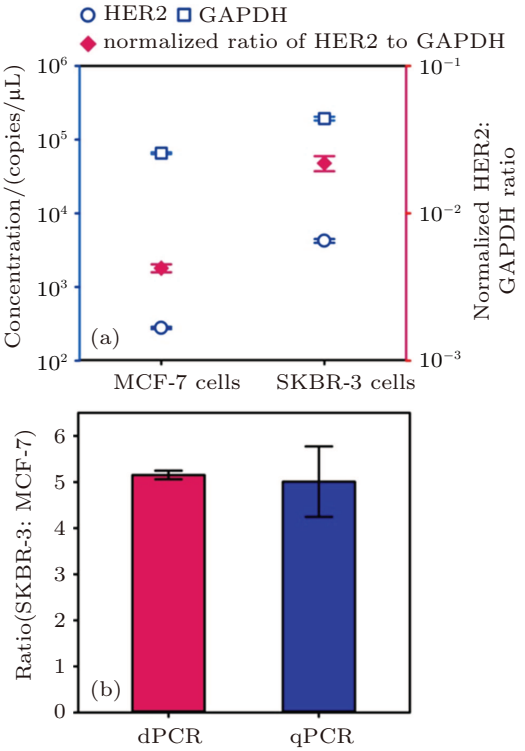


Fig. 17. (color online) (a) HER2 gene expression levels in MCF-7 and SKBR-3cells by multivolume digital PCR. The normalized ratio of HER2 to GAPDH in gene expression is represented by the red diamonds. (b) Ratios of HER2 gene expression between SKBR-3 and MCF-7 cells measured by the present multivolume digital PCR and conventional quantitative real-time PCR, respectively (from Ref. [17], Fig. 5).

4.2. High-throughput synthesis and screening

High-throughput micro-droplets on STORMs can behigh-efficient micro-reactors for synthesis of multiphasic particles,[22] real-time SERS monitoring,[74] combinatorial drug screening,[49] and cell screening.[21,24,26,30,31,48,63]

To realize precise control over the geometry and chemistry of multiphasic particles, Kobaku *et al.*[22] had developed a simple methodology involving the fabrication of a nonwettable surface patterned with monodisperse, wettable domains of different sizes and shapes. With assistance of such a surface, multiphasic particles were obtained after polymer solutions were dip-coated onto the patterned surface and then self-assembled within the wettable domains. Furthermore, multiphasic assemblies with precisely controlled geometry and composition could be fabricated through multiple, layered depositions of polymers within the patterned domains (Fig. 18). It was worth mentioning that the templates could be readily reused over 20 times for fabricating a new batch of particles, enabling a rapid, inexpensive, and easily reproducible method for high-throughput manufacturing of multiphasic particles.

Combining a droplet-guiding-track-engraved superhydrophobic substrate covered with hierarchical SERS-active Ag dendrites and a SERS microscope, Shin *et al.*[74] presented a novel droplet-based SERS sensor for high-throughput real-time SERS monitoring. When successive analyte droplets moved along the guiding track and stopped at a laser spot

for Raman excitation, the static droplets on the surface covered with Ag-dendritic structures showed a completely spherical shape, which enabled stable SERS measurements to be obtained. It was well-known that Ag dendritic substrates composed of randomly oriented nanoparticles, branches, and leaves were effective SERS substrates due to the huge amount of micro-/nano-scale structures of sharp edges and nanoscale junctions, thus providing tremendous SERS hot spots. To give an evaluation of the SERS performance of the droplet-based real-time SERS sensor, a 10-μL droplet containing 10^{-3} M R6G was used as a probing molecule to carry out SERS measurements.

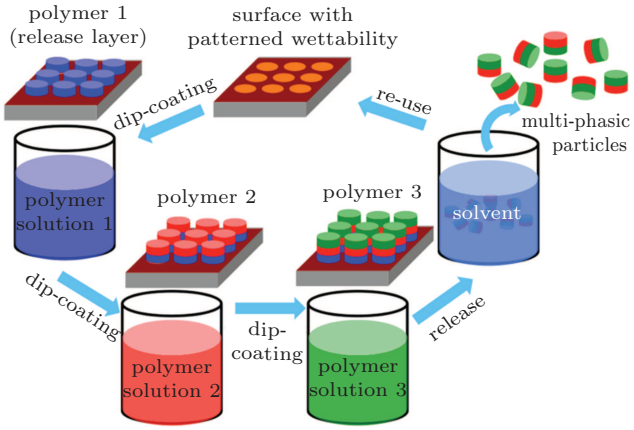


Fig. 18. (color online) A schematic illustrating the WETS technique for fabricating multiphasic particles (from Ref. [22], Fig. 1).

Employing a novel hanging spherical drop system, Neto *et al.*[49] generated independent spheroid bodies in a high-throughput manner in order to mimic in vivo tumour models on the lab-on-chip scale. To validate this system for drug screening purposes, the toxicity of the anti-cancer drug doxorubicin in cell spheroids was tested and compared to cells in 2D culture. Different from common STCMs, this system was face down with formed droplets containing cells hanging downwards. The platform was fixed into the lids polystyrene petri dishes, and the bottom part was filled with cell culture media. After 48 h of seeding time, drug-screening was conducted by adding the anti-cancer drug, doxorubicin (DOX). Different amounts of Dox were introduced into the droplets to assess the dose-dependent response of the formed tumour spheroids to this anticancer drug. The viability of the cells in the spheroids was measured after 24 hours by a live/dead cells assay.

High-throughput (HT) screening of live cells has been gaining increased attention in biological ad medical research, with numerous methods developed including droplet microfluidics, which largely depended on the complicated chip design, and digital microfluidics, which relied on electrowetting on dielectric (EWOD). By patterning superhydrophilic spots on a superhydrophobic background, simpler platforms were developed for facile formation of arrays of microdroplets and for cell screening applications.[24,26,30,31,63] For example, Popova *et al.*[31] had developed a superhydrophilic-superhydrophobic micropatterned platform via thiol-yne click chemistry to form a microdrplet array for HT cell screening. The process of cell screening can be summarized as four steps: 1) cells were seeded on the droplet-array (DA) slide by spreading a cell suspension

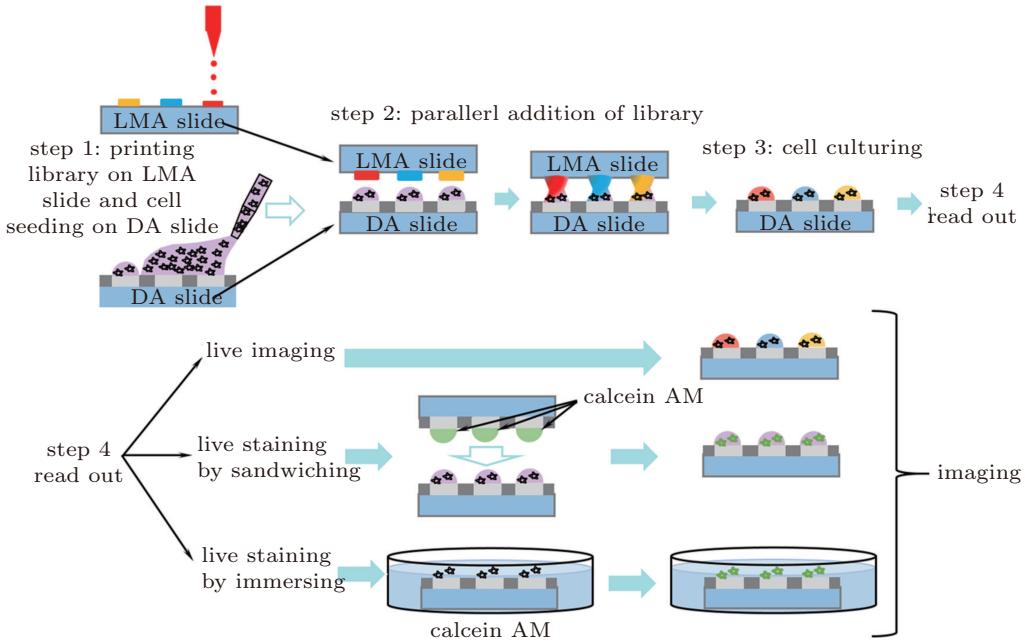


Fig. 19. (color online) Schematic illustration of a workflow of cell-based screening using DA sandwich chip. LMA slide is prepared by printing of substances of interest on a glass slide (step 1); DA slide is prepared by seeding cells using the effect of discontinuous dewetting (step 1). For parallel addition of library into individual droplets LMA slide is aligned and sandwiched with DA slide containing cells (step 2). After substances are transferred into droplets LMA slide is removed and DA slide is placed into cell culturing incubator (step 3). As a read-out cells can be either directly subjected to live imaging (step 4, upper panel) or after live staining by sandwiching DA slide containing cells with identical DA slide containing CalceinAM solution (Fig. 1(c), step 4, middle panel) or by immersing DA slide containing cells into CalceinAM solution (step 4, lower panel) (from Ref. [31], Fig. 1).

on the patterned surface due to the effect of discontinuous dewetting, and a library-microarray (LMA) slide was prepared by printing drugs or transfection mixtures onto a simple glass slide using a noncontact ultralow volume dispenser in the geometry corresponding to the geometry of the DA slide, 2) simultaneous addition of substances into each individual droplet is performed by precise alignment and sandwiching of the DA slide containing cells with the LMA slide containing the compounds of interest, 3) after library transfer, the LMA slide was removed and the DA slide containing the cells was placed in a cell-culture incubator, 4) live cells and stained cells were read out imaging (Fig. 19).

5. Conclusion and perspectives

STORM devices have several advantages over traditional droplet microfluidic systems, such as simple fabrication, low cost, high energy efficiency, and vast applications. Compared to droplet microfluidic systems, part of STORM devices were fabricated with same methods such as photolithography while steps were less than the former due to the unnecessary 3D-channels. Relatively speaking, though most of methods for the fabrication of STORM devices are simple, some methods for fabrication of asymmetric structures are complicated, which will largely limit its mass production and widespread applications. So far, the current challenge for the development of STORMs is the preservation of volatile droplets of liquids with volumes 10^{-15} L$\sim 10^{-9}$ L which need to be preserved for hours under certain temperature, such as applications on PCR and cell culturing. Though several methods have been developed such as double-inkjet method and robot droplet-forming system, this challenge still calls for simpler methods, with no complexed and precise control systems, making relative applications easier to be promoted. With the development of structured surface fabrication strategies, the applications of STORM devices are increasingly developed, including chemical reactions such as synthesis of microparticles, biological detection such as cell screening and d-PCR. It is believed that STORMs would show its potential in future on family diagnosis and biological research on a higher stage. It is expected that higher throughput, higher precision, lower cost, and less steps for fabrication would be the direction for the development of STORMs. During recent years, STORMs also began to perform well in the manipulation of organic solvents such as oil. Applications such as spill-oil collection and oil-repellent and self-cleaning coatings would be developed based on the advancing STORMs.

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