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Interfacial design for detection of a few molecules

Ying Dong,^{af} Jing Li, ^(b)*^b Christoph Janiak ^(b)^c and Xiao-Yu Yang ^(b)*^{de}

Major advances in molecular detection are being driven by goals associated with the development of methods that are amenable to miniaturization and automation, and that have high sensitivity and low interference. The new detection methods are confronted by many interfacial issues, which when properly addressed can lead to improved performance. One interfacial property, special wettability, can facilitate precise delivery and local enrichment of molecules to sensing elements. This review summarizes applications of unique features of special wettability in molecular detection including (1) chemical and electrochemical reactions in anchored microdroplets on superwetting surfaces, (2) enrichment of analytes and active materials at low contact areas between droplets and superwetting surfaces, (3) complete opposite affinities of superwetting surfaces toward nonpolar/polar solutes and oil/ water phases, and (4) directional droplet transportation on asymmetric superwetting surfaces. The challenges and opportunities that exist in design and applications of special wettability in interfacial delivery and enrichment for detection of a few molecules are also discussed.

1. Introduction

Wettability is the propensity of a droplet or bubble to replace an immiscible liquid or air on the surface of a solid. Materials and

surfaces with special wettability engage in maximum or minimum areas of contact with the wetting phase, which greatly depends on surface interactions governing the affinity with the wetting/medium phases and on surface roughness. The famous

^a Department of Forensic Medicine, Tongji Medical College, Huazhong University of Science and Technology, 13 Hangkong Road, Wuhan 430030, China

- ^b Hubei Province Key Laboratory of Coal Conversion and New Carbon Materials, School of Chemistry and Chemical Engineering, Wuhan University of Science and
- Technology, 947 Peace Avenue, Wuhan 430081, China. E-mail: jli82@wust.edu.cn
- ^c Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, 40204 Düsseldorf, Germany
- ^d State Key Laboratory of Advanced Technology for Materials Synthesis and Processing & Shenzhen Research Institute & Joint Laboratory for Marine Advanced Materials in Pilot National Laboratory for Marine Science and Technology (Qingdao), Wuhan University of Technology, 122 Luoshi Road, Wuhan, 430070, China. E-mail: xyyang@whut.edu.cn
- e School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA. E-mail: xyyang@seas.harvard.edu

^f Shenzhen Huazhong University of Science and Technology Research Institute, 9 Yuexing Third Road, Nanshan District, Shenzhen 518000, China



Ying Dong

Ying Dong received her PhD in 2015 from Lanzhou Institute of Chemical Physics, Chinese Academy of Science. She is currently working as an associate professor at Huazhong University of Science and Technology. Her research interests mainly focus on the application of various functional materials in analytical chemistry.



Jing Li

Jing Li received his PhD from Huazhong University of Science and Technology. After a postdoctoral fellowship at FUNDP of Belgium, he worked as an associate professor at Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. He is currently working as an associate professor at Wuhan University of Science and Technology. His research interests are design of surfaces and interfaces for environmental chemistry. Cassie equation $(\cos \theta^* = f \cos \theta + f - 1)$ quantifies the relationships between surface chemistry and surface roughness,¹ where θ^* and θ are the respective apparent and intrinsic contact angles, and *f* is the area fraction of the solid in contact with a droplet.

Based on the results of their investigation of biological surfaces using scanning electron microscopy (SEM),^{2,3} Barthlott⁴ and Jiang⁵ designed model surfaces, such as lotus leaf-inspired superhydrophobic/superoleophilic surfaces⁶⁻¹⁰ and fish scale-inspired superhydrophilic/underwater superoleophobic surfaces.¹¹⁻¹⁵ The efforts demonstrated the importance of micro-/nanohierarchical structures in creating superwetting surfaces. Moreover, these surfaces have prominent advantages in various methods that are based upon interfacial properties, including separation, drag reduction, printing, catalysis, water harvesting, and anti-icing, -corrosion and -fouling.¹⁶⁻²⁰ Recently, superwettability has been utilized in numerous interfacial applications in molecular detection.

Sample pretreatment (*i.e.*, preparation and purification) is an essential part of any detection method. Because typical environmental, biological and food samples have low-content analytes intermingled within a complex matrix, sample pretreatment is required to separate and enrich analytes before measurements are made.²¹⁻²³ To date, adsorbent- and solventextraction-based sample pretreatment techniques have been widely exploited for matrix separation. These approaches include solid-phase extraction (SPE), solid-phase microextraction (SPME), liquid-liquid extraction (LLE), liquid-phase microextraction (LPME), liquid-membrane extraction (LME) and electromembrane extraction (EME). In general, following its migration and arrival at the interface between sample and extraction phases, the target analyte is transferred into the extraction phase based on its affinity. In some three-phase extraction systems, such as those presented in LME and EME, the analyte is finally released into the acceptor phase through the interface between extraction and acceptor phases.

Detection techniques, such as gas chromatography (GC), highperformance liquid chromatography (HPLC), mass spectrometry



Fig. 1 Summary of the uniqueness of special wettability in molecular detection.

(MS), and the combinations GC-MS and HPLC-MS, are commonly used to obtain accurate and sensitive measurements. In order to overcome limitations associated with these large-scale instrumental methods (e.g., expense and time-consumption), various in situ rapid detection techniques, based on colorimetric, fluorescence, surface-enhanced Raman spectroscopy (SERS) and electrochemical detection, have been developed.²⁴⁻²⁶ Rates of reactions involved in colorimetric and fluorescence analysis are normally controlled by the reactant concentration and diffusion, which can be accelerated by using solid catalysts. SERS analysis is primarily performed on substrates with precise delivery of analytes onto SERS hot spots. Moreover, signals arising from electrochemical analysis can be amplified by promoting electron transfer through interfaces between electrodes and electrolytes. Owing to the fact that many interfacial issues are involved in sample pretreatment and rapid detection techniques, interface optimization with a focus on controlling wettability provides many more opportunities to promote improvements in the selectivity and sensitivity of detection methods.

In this review, we summarize the critical progress that has been made in studies utilizing special wettability to reach major objectives in the field of molecular detection, including high sensitivity, low interference, miniaturization and automation



Christoph Janiak

Christoph Janiak is full professor for Bioinorganic Chemistry and catalysis at the University of Düsseldorf, with research interests in the synthesis and properties of metal and porous organic frameworks (MOFs, COFs), metal nanoparticles, ionic liquids, and catalysis. Until 2018 he was a visiting professor at Wuhan University of Technology in China.



Xiao-Yu Yang

Xiao-Yu Yang received his PhD from Jilin University (co-educated at FUNDP of Belgium). After a postdoctoral fellowship at the FUNDP, he worked as a "Chargé de Recherches" at the FNRS in Belgium. He is currently working as full professor at WHUT. His research is aimed at hierarchical assembly techniques and hierarchical structured materials for the applications in catalysis, energy, and environment.

Table 1	Comparison of	performance	for various si	uperwetting	detection systems
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	Materials used for super- wetting coating	Structures	Wettability	Sensitivity	Detection range	Applications
Small analyte droplet	Oxides (SiO ₂), ²⁷ metals (Ag, Au) ³¹ and corresponding modifiers (alkyl, per- fluorinated modifiers)	Most particles, ²⁷ nanodendrites ³¹	Superhydrophilic microwell on super- hydrophobic surfaces	Main ^a µM level, ²⁹ optimum ^b nM level ³¹	$\begin{array}{l} \text{Main}^{a} \ 10^{-6} 10^{-3} \\ \text{M},^{29} \ \text{optimum}^{b} \\ 10^{-9} 10^{-6} \ \text{M}^{31} \end{array}$	Environment, wearable device
Low contact area	Oxides (SiO ₂ , ZnO, TiO ₂), ^{36,41} metals (Ag, Au), ⁶² CNT, ⁴⁹ polymeric spheres, ⁵⁵ AIEgens ⁵² and corresponding modifiers	Particles, ³⁶ array, ^{41,49} nanorods, ³⁹ aggregate, ⁶² flowerlike structures, ⁶⁵ nanocubes ⁶⁶	Superwetting patterns, ³⁶ superhydrophobic, ⁴¹ slippery liquid-infused surfaces ⁶²	Main ^c pM level, ⁴² optimum ^d aM level ^{41,62}	$\begin{array}{c} \text{Main}^c \ 10^{-12} 10^{-6} \\ \text{M}, ^{52} \ \text{optimum}^d \\ 10^{-16} 10^{-11} \ \text{M}^{36} \end{array}$	Medicine, environment, forensic science, food
Complete opposite affinity	Oxides (SiO ₂ , MO ₂), ⁷⁵ MOFs ⁷³ and corresponding modifiers; polymeric membranes (polytetra- fluoroethylene, polypropylene) ^{87,97}	Particles ⁷³ and nanosheets ⁷⁵ coated on fibers ⁷³ and membranes ^{87,97}	Superhydrophobic, ⁸⁷ underoil superhydrophobic, ⁹⁷ underwater superoleophobic ⁹⁷	Main ^e pM level ⁷⁵	Main ^e 10 ⁻¹² -10 ⁻⁹ M ⁷⁵	Medicine, environment, forensic science, public security
Directional droplet transportation	Oxides (SiO ₂ , TiO ₂), ¹¹⁵ magnetic particles, ¹⁰⁵ calix[4]resorcinarene, ¹⁰⁷ graphene ¹⁰⁹ and corres- ponding modifiers	Particles, ¹¹⁵ microcilia array, ¹⁰⁵ nanorods, ¹⁰⁸ nanosheets ¹⁰⁹	Hydrophilic, ¹⁰¹ superhydrophobic, ¹⁰⁵ slippery liquid-infused surfaces, ¹⁰⁹ super- wetting patterns ¹¹⁵	Main ^f pM level ¹¹⁵	$ \underset{M^{115}}{\text{Main}^{f}} 10^{-12} 10^{-7} \\ \text{M}^{115} $	Medicine, foren- sic science, food
"Main" repres	ents main detection range a	nd consitivity ^a Dotecti	on methods: colorimetri	a SEPS ^b Detection	n method, electro	chemical

"Main" represents main detection range and sensitivity. " Detection methods: colorimetric, SERS. " Detection method: electrochemical. ' Detection methods: fluorescence, electrochemical, SERS. ^d Detection methods: fluorescence, SERS. ^e Detection method: GC-MS. ^f Detection method: fluorescence.

(Fig. 1 and Table 1). The first topic discussed in Section 2 below addresses chemical reactions that proceed in microdroplets anchored on (super)-hydrophobic-(super)-hydrophilic patterns, which can be further accelerated by using catalysis or electrocatalysis. The second topic (Section 3) covers efforts that demonstrate how minimum contact area between microdroplets and superwetting surfaces enhances the enrichment effect through evaporation and provides a location for growth and self-assembly of active materials. Section 4 discusses how analyte migration in sample pretreatment can be effectively controlled by the completely opposite affinity of superwetting surfaces toward nonpolar/polar solutes and oil/water phases. The fourth part covered in Section 5 summarizes studies how directional droplet transportation can be manipulated by programming the surface energy and additional pressure via adjusting the external energy and geometric configuration. The final topic (Section 6) concerns potential opportunities and remaining challenges that exist in further developing applications of special wettability, especially by combining macroscopic wettability with microscopic design. The goal of this review is to provide insight into how interfacial issues play an important role in molecular detection by providing a promising approach toward the design of miniaturized and automated superwetting detection systems that possess high sensitivity and low interference.

2. Detection in microdroplets for miniaturization

Use of superhydrophobic surfaces with a stable air cushion that can completely support water droplets as detection platform requires only small amounts of analyte solutions (0.5–10 μ L). However, the droplets containing analytes readily roll off these

surfaces when exposed to even slight vibrations. As a result, most current studies aimed at creating (super)-hydrophilic micropatterns on superhydrophobic surfaces focus on developing methods to anchor the microdroplets. One approach takes advantage of the extreme water repellence of superhydrophobic walls that restricts spreading of the analyte droplets. To generate these types of superwetting patterns, superhydrophobic surfaces are first fabricated by using various nanomaterials and nanotechnologies to generate micro-/nanohierarchical structures. Then, by using plasma etching or UV irradiation, the low-surface-energy components at the patterns can be destroyed while forming hydrophilic regions that capture water. The superwetting micropatterns produced in this manner can be used for chemical and electrochemical detection.

Chemical reactions of analytes can take place in anchored microdroplets (Fig. 2(A)), and the rates of these processes are proportional to analyte concentrations. Moreover, the products formed in the reactions can be detected and quantitatively assessed based on their characteristic color and fluorescence. Xu et al. utilized colorimetric reactions in the small analyte droplets arrayed on superwetting patterns to detect important physiological markers such as glucose, calcium and proteins.²⁷ The superhydrophobic coating was prepared by using the following steps involving (1) the deposition of candle soot, (2) the coating of a silica shell, (3) the removal of the candle soot by calcination and (4) the surface modification with octadecyltrichlorosilane (OTS). UV irradiation through a photomask was then used to decompose the surface OTS in the patterned manner. The formed microwells strongly capture water microdroplets against gravity (Fig. 2(B)). Inspection of the detection platform can be made visually without the need for expensive and complicated instrumentation (like Fig. 2(C)).

In another effort, Han *et al.* placed a vacuum tip beneath a robust and stretchable microwell patterned superwetting



Fig. 2 Detection in a microdroplet for miniaturization. (A) Schematic diagram of chemical reactions in the anchored microdroplet. (B) Photograph and cross-section SEM image of typical superhydrophobic–superhydrophilic pattern. (C) Color intensity *versus* Ca^{2+} concentration. (B) and (C) Reproduced with permission.^{27,29} Copyright 2017 and 2018 American Chemical Society. (D) Schematic diagram of catalytic reactions in superhydrophilic microwells. (E) Photograph and SEM images of Au nanoparticle-functionalized microwells. (F) SERS spectra of catalytic oxidation of *o*-phenylenediamine to form 2,3-diaminophenazine in the presence of H₂O₂. (E) and (F) Reproduced with permission.³⁰ Copyright 2015 American Chemical Society. (G) Schematic diagram of electrocatalytic reactions in superhydrophilic microwells. (H) Photograph and SEM images of the superhydrophilic microwells on a conductive substrate. (I) Cyclic voltammogram measured using an analyte droplet. (H and I) Reproduced with permission.³¹ Copyright 2018 American Chemical Society.

substrate to control the movement of microdroplets.²⁸ When the parent droplets move through the superhydrophilic microwells, small amounts of analyte solutions leave and deposit in the microwells due to the existence of a high surface adhesion force. Because the dispensed analyte solutions have volumes of only 0.05–1 μ L, the method can be applied to the detection of analytes that are available in only small quantities.

The ability to create superhydrophilic microwells facilitates the ingenious design of the droplet-based assays. For example, micro-/nanohierarchical structures with high affinities for water can be employed for physical immobilization and then diffusion-controlled release of indicators. In addition, chemical reactions between released reactants and analytes occurring in anchored microdroplets can be utilized to determine concentrations quantitatively. In one example, color indicators were immobilized in superhydrophilic spots on a flexible substrate for quantitative colorimetric assessment of heavy metals in wastewater and sweat, with respective detection ranges of 0.5– 9, 1–12 and 5–40 mg L⁻¹ for Cr(vi), Cu(ii) and Ni(ii). The corresponding limits of detection (LODs) for these metals were found to be 0.36, 1.28 and 2.39 mg L^{-1} .²⁹

Catalysis can be employed to accelerate reactions of analytes that form detectable products. In this regard, patterned areas in micro-/nanohierarchical structures can be functionalized by introducing catalysts for specific processes (Fig. 2(D)). For example, a droplet-based H₂O₂ sensor was created by depositing Au nanoparticles with peroxidase-like activity on a bare Cu substrate around superhydrophobic Cu/Ag surface (Fig. 2(E)).³⁰ The peroxidase-like activity of the Au array was demonstrated by observing a color change associated with catalytic oxidation of *o*-phenylenediamine to form 2,3-diaminophenazine in the presence of H₂O₂. Furthermore, the analyte solution was mixed with colloidal Au for SERS analysis (Fig. 2(F)). The SERS based assay showed that the rate of the catalytic reaction was closely related to H₂O₂ concentration. By using this superwetting platform, the LOD for H₂O₂ in 2 µL analyte solution was observed to be as low as 3 pmol.

When combined with conductive substrates and electrocatalysts, droplet-based electrochemical cell systems can be created to quantitatively determine analyte concentrations by the effects on interfacial electron transfer and consequent control of electrical potential and/or current (Fig. 2(G)). In one platform of this type, indium tin oxide (ITO) with a titanium layer and an Au film was used to construct superwetting patterns.^{31,32} As shown in Fig. 2(H) and (I), Au nanoparticles were electrochemically deposited to form micro-/ nanohierarchical structures, followed by surface modification with dodecanethiol and then plasma etching through a photomask. The superhydrophobic–superhydrophilic patterns fabricated in this way were used for electrochemical detection of cancer biomarkers such as miRNAs (LOD = 0.8 nM) and prostate-specific antigen (LOD = 1.0 pM), as well as foodborne microorganisms ssDNA (LOD = 30 aM).

In another study, an electrochemical 1,4-benzoquinone and H_2O_2 detection system was created containing orthogonally arranged Au bands, which served as working, counter, and pseudo-reference electrodes.³³ For this purpose, highly hydrophilic spots on the highly hydrophobic alkyne-functionalized porous polymeric film were formed by photopatterning. Due to opposite water affinities, individual microdroplets (about 20 nL) spontaneously deposited on the hydrophilic spots when the patterned substrate was exposed to an aqueous analyte solution. The electrochemical detection of 1,4-benzoquinone and H_2O_2 in the microdroplet system was found to have detection ranges of 0.5–25 and 1–50 mM, respectively.

Chan *et al.* exploited a system comprised of patterned graphene arrays for simultaneous capture and electrochemical measurements of H_2O_2 in sweat droplets.³⁴ To create this assay protocol, polyimide was transformed to graphite and graphene in a patterned manner by using lower and higher laser scribing, respectively. The patterned graphene containing more exposed edges has a higher hydrophilicity than layered graphite. When this patterned superwetting substrate is attached to human skin, the formed sweat droplets pass through the device under gravity or the force created by body movement to form a spot of sweat held on the superhydrophilic graphene patterns. This system, modified by using glucose oxidase on graphene and parallel metal electrode arrays, can be used for amperometric detection of H_2O_2 with a LOD of 6 μ M.

Superhydrophilic microwells can serve as miniaturized detection platforms, in which detection volumes of analyte solutions can be as low as dozens of nanoliters. The design of chemical and electrochemical reactions that are compatible with the microdroplet environment must take into account three aspects including the droplet, microwell and substrate. Traditional spectroscopic methods (e.g., colorimetric, fluorescence, and chemiluminescence) can be also made compatible with the microdroplet based assay system. Moreover, the kinetics of reactions occurring in microdroplets could be different from that in bulk media. The effect of droplet volume and its change caused by evaporation is also important. Functionalization of the superhydrophilic microwells can be carried out to optimize the solid-liquid interface, on which catalytic and electrocatalytic reactions occur. Conductive and/or flexible substrates with special wettability should be explored in the context of wearable and portable devices for point-of-care detection.

3. Enrichment at low contact area for high sensitivity

As demonstrated in studies by Garcia-Cordero *et al.*,³⁵ droplet evaporation caused by natural convection arising from Marangoni effect, can increase analyte concentrations, resulting in expedited assay reactions, reduced detection time, and increased sensitivities. Through evaporation of a whole droplet, analytes can be enriched at the contact region between microdroplet and superwetting substrate, leading to further enhanced sensitivity. Moreover, in the evaporation process, active materials can be also deposited in the contact region *via* self-assembly processes, which spontaneously form organized structures with interfacial properties that are different from those of individual components. Thus, the low contact areas at solid–water–air interfaces on superwetting surfaces could play an important role in analyte enrichment and self-assembly of active materials.

Superwetting patterns have been widely used to enrich analytes at the superhydrophilic spots as part of highly sensitive assay systems (Fig. 3(A)). For example, highly sensitive fluorescence detection of DNA and prostate-specific antigen was accomplished using the enrichment capability of the superwetting patterns.^{36,37} Using candle soot as the template and a photomask for UV etching of an OTS-modified nanodendritic SiO₂ coating, superhydrophilic microwells were prepared to capture analyte droplets (Fig. 3(B) and (C)). Upon complete evaporation of the microdroplet, the analytes were concentrated at the superhydrophilic zone with low contact area. Highly amplified fluorescence signals arise from the microwells experiencing this concentration phenomenon. As a result, the system can be utilized to measure DNA and prostate-specific antigen with respective LODs of 0.23 fM and 10 fg mL⁻¹. In contrast, on hydrophobic and hydrophilic glasses, DNA containing microdroplets form coffee-ring spots during evaporation (Fig. 3(C)), giving rise to nonuniform and relatively weak detection signals. Without the enrichment effect, the LOD associated with DNA on commercial hydrophilic glass is 1 µM.

Wu *et al.* utilized the self-cleaning property of TiO_2 to design a renewable superwetting platform for identification and quantitative detection of miRNA-141.³⁸ To construct this system, hydrothermally synthesized, OTS modified TiO_2 nanowires were etched by using photomasked UV irradiation to form superhydrophilic microwells that were photocatalytically active. A higher fluorescence intensity of miRNA-141 shows from the small microwell, indicating the occurrence of a condensingenrichment effect. On this platform, the linear range and LOD for detecting miRNA-141 were 0.1–50 nM and 88 pM, respectively. After UV irradiation, analyte-containing microwells do not display observable fluorescence signals and OTS-modified superhydrophobic walls become superhydrophilic. In this way, consistent results can be obtained by using the regenerated superwetting platform for several cycles.

Wang *et al.* devised a system in which the analyte glutathione (GSH) was deposited on superhydrophilic microwells of Ag–ZnO-OTS superwetting arrays on ITO electrode.³⁹ Taking



Fig. 3 Enrichment of analytes at low contact area for high sensitivity. (A) Schematic diagram of analyte enrichment on superwetting pattern. (B) and (C) Enrichment of analytes on superhydrophobic–superhydrophilic patterns and enhanced fluorescence intensity of single chain DNA. Inset in (C) shows the formation of coffee-ring spots on hydrophilic glass. Reproduced with permission.^{36,37} Copyright 2015 Wiley-VCH and 2018 Elsevier. (D) Schematic diagram of analyte enrichment on superhydrophobic surface. (E) and (F) Enrichment of analytes on superhydrophobic surfaces and enhanced Raman intensity of R6G. Reproduced with permission.⁴¹ Copyright 2011 Nature Publishing Group. (G) Schematic diagram of analyte enrichment of analytes via a partial Leidenfrost evaporation and enhanced fluorescence intensity of R6G. Reproduced with permission.⁴⁹ Copyright 2020 American Chemical Society.

advantage of the enrichment effect and specific Ag–GSH interaction, the electroanalysis of GSH was conducted by observing a decrease of AgCl peak current. The method has high sensitivity and a LOD of 11.25 pM. In another effort, Huang *et al.* prepared a superhydrophobic surface having a highly ordered tip-capped nanopore structure.⁴⁰ Superhydrophilic spots were obtained on this structure by sputtering Au nanoparticles through a mask, so that the enriched analytes from highly dilute solutions can be detected using SERS. This assay enabled sensitive detection of rhodamine 6G (R6G) and thiram with LODs of 10^{-10} and 10^{-7} M, respectively.

The contact area between patterned superwetting surfaces and microdroplets corresponds to the diameters of the superhydrophilic microwells (millimeter scale). In contrast, superhydrophobic surfaces can completely support water droplets with a smaller contact area, thus, they display a potentially more prominent condensing-enrichment effect (Fig. 3(D)), even though microdroplets readily roll off and the smaller enriched spots are harder to observe. For example, silicon micropillar arrays decorated with Ag nanoparticles were used as superhydrophobic SERS substrates.^{41,42} During the evaporation process, a supported droplet gradually shrinks while maintaining a low contact area rather than being pinned to the original contact point (Fig. 3(E)). When its quasi-spherical shape becomes unstable, the droplet collapses leading to deposition of the ultratrace analyte on a restricted region with a size of tens of micrometer. Due to the enrichment effect, ultratrace analytes such as R6G and DNA from extremely dilute solutions of attomolar concentrations (10^{-18} M) can be localized and detected (Fig. 3(F)).

Ling *et al.* utilized a Langmuir–Blodgett assembly of Ag nanocubes to construct a superhydrophobic SERS substrate, which exhibits an analyte concentrating factor of 14-fold, and a LOD of 100 aM for R6G in 1 μ L of analyte solution.⁴³ In addition, a pattern of micropillars with radial density gradient and nanotip array was fabricated. This superhydrophobic array promoted spontaneous movement of the droplet toward the pattern center. When used in a SERS detection system, the platform was utilized to measure R6G in an aqueous solution (10⁻⁹ M) with a much higher signal intensity than that in an ethanol solution (10⁻⁶ M). This observation demonstrates the

occurrence of an enrichment factor of at least 1000-fold.⁴⁴ Superhydrophobic filter paper with a dendritic Ag coating was also used as SERS substrate to detect nitenpyram as a typical pesticide with a LOD of 1 nM.⁴⁵

Although the mechanism of concentration of solutes on special wetting surfaces during evaporation is still unclear, some effort has been made to accumulate analytes on a smaller footprint to enhance sensitivity. Shiratori et al. found that on a superhydrophobic surface, the formed inorganic/organic (SiO₂/ polyvinylalcohol, PVA) containing spot was flatter and smaller than the coffee rings formed by most SiO₂ and the balloon structures constructed by most PVA.46 The small hydrophilic spot concentrated high-density caffeine from a trace analyte solution, and enabled highly sensitive detection of caffeine using colorimetric analysis. It was also found that the surface energy of SERS substrates has an impact on the concentration of substances at plasmonic nanogaps.47 In this system, the surface energy is precisely controlled by using plasma etching of a low-surface-energy modifier. The results show that after enrichment *via* evaporation, the plasmonic nanopillar array with partial wetting property exhibits better SERS performance than hydrophilic and superhydrophobic SERS substrates. It is proposed that analyte molecules are condensed outside of the hot spots or that the surface modifier blocks the hot spots.

Droplets on a hot surface are levitated by a thin vapor cushion produced by liquid evaporation, which is known as the Leidenfrost effect.48 Recently, the Leidenfrost effect was utilized to lower the contact area between a droplet and a special wetting substrate (Fig. 3(G)). To construct this type of hydrophobic SERS substrate, SERS-active nanoparticles were coated on superhydrophobic carbon nanotube (CNT)-decorated Si micropillar arrays in the absence of a low-surface-energy modifier.49 Under partial Leidenfrost-assisted evaporation conditions, elevating the temperature in the 80-160 °C region facilitates formation of the analyte droplet in the Cassie-Wenzel hybrid state, in which the droplet has low contact area with the substrate and enhanced interaction is present between dilute analyte molecules and the substrate. As a result, fast enrichment of the analytes occurs on a reduced footprint (10 µm diameter) which is significantly smaller than that caused by natural evaporation (Fig. 3(H) and (I)). This superwetting platform enabled SERS detection of a highly dilute R6G solution (10^{-9} M) with an enhancement factor exceeding 10^7 .

Sensitivity is not only governed by the concentration of an analyte but also by the responses of active materials. Specifically, self-assembly of materials at the confined contact area facilitates formation of an organized structure during evaporation of a droplet, which can have enhanced responses over that of individual components. For example, conventional fluorophores usually display strong luminescence in dilute solutions but become weakly emissive or even completely non-fluorescent when they are part of aggregates owing to a phenomenon called aggregation-induced quenching (AIQ) effect. However, as a consequence of another photophysical process called aggregationinduced emission (AIE), AIEgens are non-emissive in their mono-molecular states but emit fluorescence upon aggregation which restricts intramolecular motion.^{50,51} Similar to the evaporation-induced self-assembly concept described above, the AIEgens can be aggregated at the low contact area to form fluorescent visualizers that emit light with intensity levels that are suitable for analysis and detection (Fig. 4(A)). For example, a solution of the quaternized tetraphenylethene salt, which is a water-soluble AIEgen, was introduced into well-defined superhydrophilic microwells and induced to undergo aggregation via a self-assembly process.52 Condensed fluorescence spots with uniform fluorescence signals were created with intensities that increase as the microwell diameter decreases (Fig. 4(B)). In contrast, uneven signal distribution was obtained when hydrophilic or hydrophobic substrates are employed, observations that are attributed to the formation of coffee ring structures. The AIEbased superwetting microchip was found to have a detection range for miRNA-141 from 10^{-12} to 10^{-6} M and a LOD of 1 pM (Fig. 4(C)).

Photonic crystals with photonic band-gap properties are periodic dielectric structures that control the transmission of a certain frequency of light.^{53,54} Therefore, organized periodic structures of photonic crystals are of great importance for bringing about a fluorescence enhancement effect (Fig. 4(D)). Hou *et al.* used this property to design highly sensitive assays for R6G, cocaine and the antibiotic tetracycline.^{55,56} For this purpose, droplets of a colloidal solution containing monodispersed latex spheres poly(styrene-methylmethacrylate-acrylic acid) were printed on a hydrophobic polydimethylsiloxane (PDMS) substrate. After complete evaporation of a droplet containing the spheres, hydrophilic photonic crystal spots with a highly ordered face-central-cubic structures are formed via a self-assembly process (Fig. 4(E)). By optimizing the band structure and introducing a molecularly imprinted polymer, this system was used for determinations of ultratrace R6G (LOD = 1.4×10^{-17} M), cocaine (LOD = 10^{-16} M) and tetracycline (LOD = 2×10^{-9} M). The photonic crystal microchip created in this manner displays a superior performance in contrast to systems comprised of the hydrophilic glass, hydrophobic PDMS and a conventional photonic crystal film (Fig. 4(F)).

In another system created using this strategy, Zhao *et al.* self-assembled monodispersed silica spheres with different diameters (220, 263, and 298 nm) on superhydrophilic microwells composed of a patterned superwetting substrate.⁵⁷ It was observed that the photonic crystal micropatterns formed by evaporation display blue, orange and red colors. By taking advantage of the enrichment effect of superwetting substrates and the fluorescence enhancement effect of photonic crystals, this system can detect the blood coagulation factor thrombin, a serine protease at concentrations as low as 5×10^{-12} M.

In SERS detection systems, rich fingerprint information about analytes is mainly a consequence of electromagnetic enhancements at the surfaces of Au, Ag and Cu nanoparticles. When two plasmonic nanoparticles are closely spaced, hot spots are generated by extremely high electromagnetic enhancements.^{58,59} Thus, the use of SERS substrates that enable coupling between plasmonic nanoparticles leads to highly sensitive detection. Importantly, self-assembly of



Fig. 4 Self-assembly of Materials at low contact area for high sensitivity. (A) Schematic diagram of self-assembly of AlEgens on superwetting pattern. (B and C) Self-assembly of AlEgens and enhanced fluorescence intensity of miRNA. Reproduced with permission.⁵² Copyright 2018 Elsevier. (D) Schematic diagram of self-assembly of photonic crystals on superhydrophobic surface. (E) and (F) Self-assembly of photonic crystals and enhanced fluorescence intensity of R6G. Reproduced with permission.⁵⁵ Copyright 2014 Wiley-VCH. (G) Schematic diagram of self-assembly of Au and Ag nanoparticles on SLIPSs. (H) and (I) Self-assembly of Au nanoparticles and enhanced SERS intensity of BSA. Reproduced with permission.⁶² Copyright 2016 National Academy of Sciences.

plasmonic nanoparticles at low contact areas of special wetting surfaces can enhance interactions in an organized structure and lead to a great increase of the SERS signal intensity (Fig. 4(G)). Crozier *et al.* employed this principle to create a superhydrophobic bull's-eye containing array of micro-pillars and radial microfins, which forms a hydrophobic gradient.⁶⁰ A water droplet is guided to the center of the bull's-eye during the evaporation process, enabling the delivery of active materials and analytes to this confined location. This concept was used to aggregate plasmonic nanoparticles densely in the central region, resulting in a considerable electromagnetic enhancement. This SERS based system was employed for ultrasensitive detection of R6G (LOD = 10^{-15} M).

Lu *et al.* utilized the evaporation-induced self-assembly process to confine Ag nanoparticles to the tops of hydrophobic Si nanopillar arrays.⁶¹ A high electromagnetic enhancement was obtained when the size of nanogaps between Ag nanoparticles on a single Si nanopillar was less than 10 nm. The resulting system was used for quantitative SERS analysis of R6G with a LOD of 10^{-11} M.

In addition to superhydrophobic surfaces, slippery liquidinfused porous surfaces (SLIPSs) have been developed for ultrasensitive SERS detection in common fluids.⁶² Importantly, the infused fluorinated lubricants in this system are immiscible with both aqueous and nonaqueous solutions. Consequently, they form smooth and stable interfaces that eliminate pinning of common liquids on substrate. The low contact area and small resistance for droplet movement in this system facilitates self-assembly of plasmonic nanoparticles and enables precise delivery of analytes during evaporation of common fluids (Fig. 4(H)). Various extracting solvents were used in the SLIP-SERS platform to detect analytes present in liquid, solid or air phases with LODs at the attomolar level (Fig. 4(I)). In addition, *in situ* electrochemical growth of SERS nanoparticles on conductive substrates can be utilized to create hot spots at low contact areas in sensitive SERS detection systems.^{63–65}

Low contact areas that exist between microdroplets and special wetting surfaces serve as locations in which large analyte mass per unit area exist. This feature can be used advantageously to enhance detection sensitivities of emerging analytical methods that are based on special wettability. As a result, much effort has gone into developing techniques that maintain low contact areas during evaporation of analyte droplets and gaining an understanding of the deposition

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mechanisms of analytes having different polarities and interfacial properties. The occurrence of self-assembly processes during droplet evaporation leads to deposition of materials with organized structures that display distinctly different performances than those of the corresponding non-assembled components. To further enhance sensitivity, it is crucial to understand the self-assembly mechanism of functional materials in microdroplets. Moreover, methods that integrate analyte enrichment and self-assembly of active materials have the potential of offering greater detection sensitivities.⁶⁶

4. Complete opposite affinity for anti-interference

Methods that enhance detection sensitivities should eliminate interference arising from the complex matrix. For this purpose, sample pretreatment is generally performed to separate or enrich low-content analytes before measurements are made. SPME, which was first reported by Pawliszyn et al., is an attractive pretreatment technique owing to its remarkable ability to accomplish isolation and enrichment in a single step.^{67,68} In theory, SPME relies on the distribution coefficient of an analyte between the sample matrix and a coating adhered to an underlying substrate. The desired coatings used for SPME have large surface areas and good affinities toward analytes (Fig. 5(A)). These features play important roles in governing the selectivity, mass transfer, enrichment and reproducibility of this technique. Recently, superhydrophobic materials have been developed for high-performance SPME. Micro-/nanohierarchical rough structures and low-surface-energy components are prerequisites for creating superhydrophobic surfaces, which have large surface areas and consequently high adsorption capacities, and completely opposite affinities toward the aqueous sample matrix and nonpolar analytes.

Metal-organic frameworks (MOFs) with large surface areas, tunable porous structures and open frameworks linked by coordination bonds between metal cations and multidentate



Fig. 5 Completely opposite affinity for anti-interference. (A) Schematic diagram of SPME using superhydrophobic materials. (B) Contact angles and SEM images of the superhydrophobic fiber. (C) Extraction efficiencies of various extraction fibers. (B) and (C) Reproduced with permission.⁷⁵ Copyright 2020 Elsevier. (D) Schematic diagram of oil–water separation using superwetting membranes after liquid-phase extraction. (E) Photographs and contact angles of the superwetting membranes. (F) Separation fluxes and efficiencies of the superwetting membranes with different pore sizes. (E) and (F) Reproduced with permission.⁸⁷ Copyright 2018 American Chemical Society. (G) Schematic diagram of LME using superwetting membranes. (H) SEM images of the UWSO and UOSH membranes and photographs of unidirectional solute transfer through a Janus membrane. (I) Absorbance of analytes in the acceptor phase as a function of extraction time using a Janus membrane. (H) and (I) Reproduced with permission.⁹⁷ Copyright 2020 Elsevier.

organic ligands, have been tested as SPME coatings.^{69,70} However, the low stabilities of MOFs exposed to water greatly limit their practical applications to sample pretreatment.^{71,72} In a recent study to address this problem, the phenylsilanemodified MOF NH₂-UiO-66(Zr) was coated on the surface of steel wire using glue.⁷³ The hydrophobic modification effectively prevented water molecules from entering and deconstructing the MOF lattice. The prepared hydrophobic SPME fiber coating displayed high extraction efficiencies toward ultraviolet filters even after exposure to water steam at 100 °C for 21 h. Incorporation of this pretreatment techniques into a detection method of ultraviolet filters led to low LODs (0.6–2.1 ng L^{-1}), wide linear ranges (10–50 000 ng L^{-1}) and high recoveries (82–115.6%). In a similar manner, Wei et al. used PDMS to modify a ZIF-8/Mn_xO_v nanosheet composite material.^{74,75} The prepared SPME fiber coating possessed a micro-/nanohierarchical rough structure and exhibited a superhydrophobic property (Fig. 5(B)). Compared to PDMS, Mn_xO_y nanosheet and ZIF-8 fibers, the prepared superhydrophobic SPME fiber displayed superior extraction efficiencies toward nonpolar organic compounds such as benzene, toluene, ethylbenzene and xylene (Fig. 5(C)). This observation was attributed to the large surface area as well as strong hydrophobic interactions between the superhydrophobic extraction phase and hydrocarbon analytes. In addition, a superhydrophobic SPME fiber with silica aerogel coating, prepared using tetraethyl orthosilicate and methyltrimethoxysilane as coprecursors, displayed high performance in the extraction of chlorobenzenes with the LODs of 0.1–1.2 ng L^{-1} and recoveries of 88-115%.76

LLE is a traditional sample pretreatment technique used to isolate analytes from the complex matrix using extraction solvents. The efficiency of LLE strongly depends on the distribution coefficient of analytes between the oil and water phases. To improve extraction efficiencies, LPME has been developed in which a small volume of extraction solvent is used to isolate and enrich analytes from highly dilute samples. However, the analyte-containing extraction solvents are difficult to separate from the formed stable emulsions before measurements are made. Thus far, superwetting membranes have been found to have significant advantages in oil-water separation applications due to their completely opposite affinity toward water and oil.^{77–81} Superhydrophobic membranes selectively enable oil to pass through but block water whereas superhydrophilic membranes serve as water-removal materials.

Recently, multiple extreme wettability has been used as a principle guiding the development of high-efficiency on-demand oil-water separation systems.^{82–86} As a result, superwetting membranes serve as a potential alternative for rapid, selective and continuous removal of various extracting agents (Fig. 5(D)). For example, the nanosecond pulse laser technique was used to fabricate porous polytetrafluoroethylene (PTFE) membranes that have high affinities toward extracting agents and high repellence against aqueous solutions (Fig. 5(E)). The special wetting membrane prepared in this manner was used to perform continuous *in situ* removal of an extracting agent from a complex matrix.⁸⁷ In parallel with increase in pore sizes, separation fluxes

increase from 0.7 to 14 L cm⁻² h⁻¹ along with bringing about high removal efficiencies (>99.5%) of the extracting agents (Fig. 5(F)). Compared to use of traditional LLE, utilization of the superwetting extraction system leads to diminished operation time (about 4 min for 64 mL) and high recoveries (>99.4%).

On-demand liquid–liquid separation was realized using a membrane that has tunable wettabilities toward nonpolar, polar protic and aprotic liquids.⁸⁸ Owing to the tunable wetting property of the reconfigurable membrane, *in situ* operations including exaction and back exaction can take place between polar and nonpolar liquids. In the liquid–liquid separation system, concentrating phenol in the back extraction agent requires about 3 min, and it has a higher efficiency (about 82%) and recoverability (about 98%) than those using the traditional method. The content of nonpolar liquid in the back extraction agent using the superwetting membrane is about 30 ppm, which is much lower than that obtained employing a traditional back exaction (about 100 ppm).

In an interesting study, Liu *et al.* separated oil-in-water emulsions using Janus superwetting fabrics that have superhydrophobicity on one surface and superhydrophilicity on the other.⁸⁹ The continuous phase (aqueous solution) sufficiently wets the superhydrophilic side but is effectively obstructed by the superhydrophobic side. Due to presence of large pore sizes in the fabrics, small oil droplets in the emulsions enter the superhydrophilic side and gain contact with the superhydrophobic side. As a result, analyte-containing extracting agents can be rapidly collected by using the Janus superwetting membranes.

In LME and EME, analytes migrate from the donor phase into the extracting phase (oil phase) and then are released into the acceptor phase (aqueous solution). These features provide advantages to aqueous detection methods such as HPLC and electroanalysis. In LME and EME processes, analytes in a complex matrix diffuse to the oil phase. At the interface of the donor and oil phases, analytes migrate into the oil phase based on their distribution coefficients (LME) or being driven by an electrical potential (EME). By migration through the oil phase, the extracted analytes arrive at the interface of the oil and acceptor phases and then are released into the aqueous solution. In general, organic solvents can directly act as free liquid membranes⁹⁰⁻⁹² or they can be immobilized on highly stable porous membranes.⁹³⁻⁹⁶ The latter system, called a supported liquid membrane (SLM), functions as a selective barrier. Thus, the wettability of the porous membrane has a great impact on analyte transfer.

Dong *et al.* utilized an underoil superhydrophobic (UOSH) polypropylene (PP) membrane and an underwater superoleophobic (UWSO) PP membrane with polydopamine and SiO₂ coating to form a Janus superwetting membrane (Fig. 5(G)).⁹⁷ In both LME and EME processes, migration of analytes successfully occurred through the Janus membrane from the UOSH side to the UWSO side, resulting in an increase in concentration of analytes in the acceptor phase, but was completely hindered in the reverse direction (Fig. 5(H) and (I)). It was suggested that the unidirectional transfer through what

essentially is a solute transfer "diode" is a consequence of the higher affinity of the UWSO surface toward solutes in water than that of the UOSH surface.

During sample pretreatment by using the extraction techniques, analytes selectively migrate from the complex matrix to other phases across various interfaces such as liquid-solid and oil-water interfaces. Extreme wettability can play an important role in improving extraction efficiencies because it enables advantage to be taken of the completely opposite affinity of superwetting surfaces toward nonpolar/polar solutes and oil/ water phases. In SPME, the factors governing adsorption of analytes with different polarities on superhydrophobic surfaces, especially the effect of the stable air cushion, are still unclear. In LPME, separation of small volume of extracting agents used as the dispersion phase from stable emulsions remains challenging. Finally, in LME and EME, the effect of membrane wettability on migration of analytes across SLM requires further systematic study.

5. Directional droplet transportation for automation

Wettability is related to the surface tension of droplet and its interaction with a solid surface. A directional force toward the curvature center is generated on a curved liquid surface, which can be calculated by using the Laplace equation, $\Delta P = 2\gamma/R$, where ΔP is the additional pressure, and γ and R are the surface tension of liquid and the radius of curvature, respectively. Based on this relationship, a smaller curvature radius leads to a larger additional pressure. For a spherical droplet on a homogeneous surface, the resultant force including the additional pressure and solid-liquid interaction is zero. Thus, by programming partial surface chemistry using an external energy source such as electric, magnetic and light fields, the droplet is exposed to an asymmetrical solid-liquid interaction which leads to directional droplet transportation. In addition, an asymmetric droplet on a surface with a geometric gradient spontaneously moves because of a Laplace pressure difference. The ability to manipulate directional movement of droplets on open surfaces has great interest in the area of automatic detection systems.

Electrowetting has been used to modulate directional droplet transportation. Exerting a potential (about 100 V) across a dielectric layer can charge a sessile water droplet to wet the substrate.^{98,99} The wetting behavior is described by the Young–Lippmann equation,¹⁰⁰ $\cos \theta_w = \cos \theta + \varepsilon_i \varepsilon_0 V^2/(2\gamma t)$, where θ and θ_w are the contact angles before and after exerting the potential, respectively, ε_i and ε_0 represent the dielectric permittivities of the insulator and vacuum, respectively, V is the applied potential, and t indicates the insulator thickness. When a droplet is placed on an array of hydrophobic electrodes and a potential is applied to an adjacent electrode, an asymmetrical solid–liquid interaction is generated and makes the droplet move. To reduce the potential, additives or injecting a charge can be added to the droplets.

In a study related to this phenomenon, Kim *et al.* placed a droplet containing a cationic surfactant on a hydrophilic conductive substrate and manipulated the droplet using electro-dewetting.¹⁰¹ Under an electric field, the cationic surfactant molecules migrate toward or away from the hydrophilic substrate, which causes the droplet to dewet or rewet (Fig. 6(A)). Compared to direct control by using an electric field, in this system the solid–liquid interaction was regulated by field-induced attachment and detachment of the cationic surfactant, at 0.015 times the critical micelle concentration, toward the substrate in the presence of only a ± 2.5 V applied potential. Using this platform technology, an open device in air was created to automatically perform droplet generation, transportation, splitting, and merging (Fig. 6(B)).

The use of magnetic actuation has special advantages such as no need for contact, non-destructive nature and compatibility with current biomedical techniques. The strategy for magnet-actuated droplet transportation involves adding magnetic components into droplets and then promoting structural deformation by applying a magnetic field. For this purpose, magnetic particles or ferrofluids are typically employed to endow the droplets with superparamagnetism and ability to undergo directional motion under an external magnetic field.^{102,103} To avoid trapping the particles on textured surfaces, paramagnetic salts are added to the water droplets to enable "particle-free" magnetic actuation.¹⁰⁴ A low surface friction (<2 µN) on superhydrophobic surfaces is required for reproducible droplet actuation. The cancer drug doxorubicin was successfully detected using an analytical system created by combining "particle-free" magnetic actuation with online fluorescence detection.

Without incorporating magnetic components, droplets can be directionally manipulated on magnetocontrollable superwetting surfaces.^{105,106} Liu *et al.* prepared a superhydrophobic magnetic microcilia array surface that has a structure that is switchable in response to an external magnetic field (Fig. 6(C)). When a magnet is close to the surface of the magnetoresponsive array, a tiny concave region is formed in which water droplets pool.¹⁰⁵ Water droplets on the concave region move in the same direction as the magnet is moved. The magnetocontrollable superwetting surface can be used for nondestructive droplet transportation and droplet reactions (Fig. 6(D)).

Light-responsive smart surfaces, including those of inorganic semiconductors and azobenzene dyes, have been widely explored. Inorganic semiconductors have photo-induced superhydrophilicity and can recover their original superhydrophobicity in the dark. The photo-switching wettability of azobenzene dyes is caused by the selective transformation between *cis*- and *trans*-configurations using different photoirradiation wavelengths. Light controllable solid–liquid interaction has been explored in the context of directional droplet transportation. Ichimura *et al.* manipulated droplet motion on a flat surface modified with a calix[4]resorcinarene derivative containing photochromic azobenzene units.¹⁰⁷ Photoirradiation with blue light induced *cis*-to-*trans* photoisomerization of the surface azobenzenes creating a surface energy gradient which promotes



Fig. 6 Directional droplet transportation for automation. (A) Schematic diagram of directional droplet transportation by electric field. (B) Photographs of droplet transportation, splitting, and merging *via* ionic-surfactant-mediated electro-dewetting. Reproduced with permission.¹⁰¹ Copyright 2019 Nature Publishing Group. (C) Schematic diagram of directional droplet transportation by magnetic field. (D) SEM images of magnetocontrollable superwetting surfaces and photographs of droplet transportation and merging using the magnetic actuation. Reproduced with permission.¹⁰⁵ Copyright 2019 Wiley-VCH. (E) Schematic diagram of directional droplet transportation by light field. (F) SEM images of a photocontrolled graphene film and photographs of droplet transportation along programmed wettability pathways. Reproduced with permission.¹⁰⁹ Copyright 2018 the American Association for the Advancement of Science. (G) Schematic diagram of directional droplet transportation by geometric shape. (H) Photographs of water droplet on superhydrophobic coating and superhydrophilic microspine and the transportation of an analyte droplet along geometric-gradient microchannels. Reproduced with permission.¹¹⁵ Copyright 2020 American Chemical Society.

directional droplet motion. Monteleone *et al.* designed a surface energy gradient system that involves irradiating adjacent regions of TiO_2 nanorod-based surfaces to manipulate the motion of water droplets.¹⁰⁸

Compared to electric and magnetic actuation, irradiationbased actuation generally takes longer time (at least 30 min irradiation). Recently, the photothermal effect of materials has been used to change the wettability of substrates (Fig. 6(E)). For example, a reversible transition between a rough and a slippery state of a paraffin-infused porous graphene film was performed by utilizing the photothermal effect of graphene.¹⁰⁹ Under nearinfrared light irradiation through a mask, infused paraffin melts to form corresponding patterns, that serve as programmable flow pathways for slippery droplets (Fig. 6(F)). This type of programmable droplet transportation system was employed as the basis for a microfluidic microreactor for blood group diagnosis.

Inspection of natural systems such as cactus spine, *Nepenthes alata* and spider silk, suggests that substrates with

asymmetrical geometric shapes (e.g., wedge and conical structures) can govern the directional motion behavior of droplets without the need of external energy.^{110–114} For example, it has been shown that the drought-tolerant capability of Cactaceae species can be ascribed to its possession of an efficient fog collection system comprised of well-distributed clusters of conical spines and trichomes on the cactus stem. According to the Laplace equation, the pressure on the region near the spine's tip with a small curvature radius is larger than that at the base where a larger curvature radius exists. With the Laplace pressure difference serving as the driving force, the droplets move from the tip to the base side along the cactus spine. Based on a consideration of the fog collection mechanism of the cactus spine, Chen et al. developed a superwetting microspine chip that enabled an analyte droplet to spontaneously and directionally move.¹¹⁵ A superhydrophilic microspine with geometric-gradient microchannels and microwells was constructed on a superhydrophobic surface (Fig. 6(G) and (H)). Driven by the Laplace pressure difference, the analyte droplet is spontaneously transported along the geometric-gradient microchannel and then becomes anchored in the microwell. This directional transformation was used as part of an assay of the prostate-specific antigen following the antigen-antibody immunoreaction conducted on the detection zone. Highly sensitive (LOD = 10^{-12} g mL⁻¹) and reproducible detection of this cancer biomarker was achieved.

Besides the geometric gradient, a rewritable surface charge density gradient is created by impact of droplets on the superamphiphobic surface which stimulates droplet propulsion without the need for an extra energy input.¹¹⁶ The occurrence of directional droplet transportation is attributed to an asymmetrical solid–liquid induced electrostatic attraction. A surface charge printing system of this type enables high-velocity, longdistance and no mass-loss transportation of liquid droplets that have low surface tension and/or high viscosity.

6. Conclusions and perspectives

Special wettability has been demonstrated to have remarkable advantages in applications to various interfacial systems including those relevant to the field of molecular detection. In the above review, we discussed some highly desirable features of analysis platforms that have been developed on the basis of special wettability, such as miniaturization, sensitivity, anti-interference and automation. Owing to issues of small analyte droplet sizes, low contact areas, completely opposite affinities and directional surface tension, wettingrelated detection platforms have a wide range of promising applications, even though critical challenges remain.

Superhydrophobic surfaces and patterns have been developed mainly in the context of miniaturized detection platforms, selective separation of analytes or extracting agents and directional droplet transportation. Recently, special wettability has being subdivided into multiple extreme wetting states, in which water (or polar liquid), oil (or nonpolar liquid) and air act as medium and wetting phases, respectively. It is believed that multiple superwetting surfaces can be flexibly designed for use in high-performance chemical/biological sensing. Generally, surfaces for these purposes require micro-/nanohierarchical structures and more sensitive surface chemistry, which can be readily destroyed and contaminated. Thus, the stability and antifouling properties of special wetting surfaces need to receive attention as part of programs aimed at developing continuous and repeatable sensing systems.

Low contact areas in superwetting systems can support formation of small analyte droplets, and serve as sites where analytes are enriched and self-assembly occurs to form active materials. As a result, studies that focus on various materials and nanotechnologies used to functionalize and optimize solidliquid interface are important. Low-surface-energy modifiers, usually employed to prepare superhydrophobic surfaces, could make a great impact on the performance of functional materials. In the absence of low-surface-energy modifiers, intrinsic hydrophobicity of functional materials can be taken advantage to construct superhydrophobic detection platforms that have enhanced sensitivities associated with the functionality of each building block. Furthermore, mechanisms for interfacialreactions, -electron transfer, -analyte enrichment, and -selfassembly need to be more comprehensively addressed.

The use of interfacial materials that have special wettability can facilitate sample pretreatment processes, enhance the recovery of analytes and diminish interference from components of the complex matrix. In ideal circumstances, it is good that the acceptor phase used in sample pretreatment well matches the droplet-based detection platform. For example, the acceptor phase in LME and EME can be applicable for the testing in water droplets. Nevertheless, interferents remain in the acceptor phase even after sample pretreatment. To date, development of most droplet-based testing systems has focused on high sensitivity rather than selectivity. The introduction of sensing elements with specific recognition capabilities and the integration of multiple testing methods for use on single detection spots can boost the versatility and reliability of assay platforms.

Analyte droplets can be effectively manipulated to move directionally under external stimuli such as electric, magnetic and light fields, and geometric configuration. Combining this ability with sample pretreatment and droplet-based analysis, will lead to highly useful integrated detection systems and devices. To achieve commercialization, several long-term goals need to be met including applicability to high-throughput testing of practical samples, low-cost and feasible preparation processes, and highly stable and accurate detection performance. To accelerate robust innovative growth in this research field, global collaborative efforts especially between members of the wetting and analytical chemistry communities will be required. We hope that this review will motivate researchers to address interfacial issues and applications of superwetting in molecular detection.

Conflicts of interest

There are no conflicts to declare.

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