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Review

Photoresponsive surfaces with controllable wettability

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Abstract

In this paper, current progress in the area of photoresponsive surfaces with controllable wettability is reviewed, including mainly surface conversion between wetting and anti-wetting, prepared from inorganic oxides (e.g., titanium dioxide, zinc oxide, and tungsten oxide) or/and photoactive organic molecules (e.g., azobenzene, and spiropyran), and movement of liquid droplets driven by molecular machines (e.g., molecular shuttles such as rotaxanes). Photoresponsive controllable wettability originates from a transition between the bistable states of photoresponsive materials. The exploration of the basic mechanisms provides a basis for the construction of novel smart responsive surfaces.

Keywords: Photoresponsive; Controllable wettability; Surface switch; Hydrophobicity; Hydrophilicity; Superhydrophobicity; Superhydrophilicity; Liquid motion

Contents

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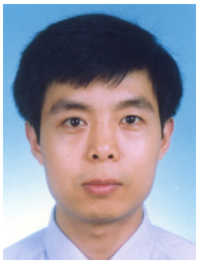

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1. Introduction

Light has been widely used as a predominant stimulus to control chemical reactions, special physical properties, and biological evolution by taking advantage of the non-contact mode, as well as utilizing the optimal, precisely controlled wavelength, direction, illuminated area, and intensity [1–13]. Under light illumination, photoresponsive materials can often reversibly change their molecular geometric and electronic structures in solutions, crystals, and gels; these changes then induce physical property changes such as those of polarity, fluorescence, refractive index, and magnetism. In the past decade, a series of photoresponsive chemical and physical properties have been extensively explored, including photoswitching of electrical conductivity and magnetism, photocontrollable micropatterning, photoresponsive biocatalysis, and cell adhesion. For example, Lehn and co-workers first proposed the idea of controlling electrical conductivity using photochromic compounds, because the electrical conductivity can be controlled if the π-conjugation length or π-overlaps between adjacent molecules are tunable [14,15]. Irie and coworkers incorporated diarylethenes into conductive polymers, through which a photoresponsive change in the π-conjugated system brought out a change in the conductivity [16]. At the same time, Irie and Matsuda also observed the photoswitching behavior of magnetism using diarylethene derivatives [17]. Recently, Einaga and coworkers realized the reversible photoswitching of magnetism successfully by combination of photochromic molecules with magnetic nanomaterials [18,19]. These studies may provide some useful candidates for high-density photo-recording media and optical switches in molecular devices. Moreover, light energy can be efficiently converted to mechanical energy. Ikada et al. have provided a relevant example: a liquid-crystal polymer film can be directly bent on a macroscopic scale under precisely irradiation of linearly polarized light [20]. In addition to the photoresponsive electrical, magnetic or mechanical properties, photoresponsive biological materials and behaviors have also been extensively investigated. For instance, Willner et al. chemically attached azobenzene compounds onto papain, which then exhibited reversible biocatalytic activity under photostimulation [21]. On an azobenzene-modified RGD peptide surface, Kessler et al. observed photoswitchable cell adhesion properties by changing the distance and orientation of RGD peptides with respect to the surface [22]. Therefore, these photoswitchable functions of films or surfaces are desirable for many promising applications. It is noteworthy that for the construction of smart devices, to graft photoactive molecules or to prepare photoactive coatings on surfaces is an important and useful route to endow smart devices with some unique photoresponsive physical properties, such as wettability, friction, biocompatibility, and optical properties.

Recently, the study of surfaces with controllable wettability has emerged as an exciting focus topic in surface science [23–27]. In Nature, superhydrophobic surfaces with water contact angles (CA) higher than 150° are observed in many plants and insects, such as lotus leaves [25,28], water strider legs [29], and cicada wings [30]. In particular, the discovery of the "lotus effect," originating from waxy materials and micro–nanobinary structures on the lotus leaf surface, promotes the extensive construction of novel bio-inspired superhydrophobic surfaces [25]. Accordingly, various intriguing methods have been developed to prepare super-hydrophobic surfaces and films by controlling the surface chemistry and surface roughness, for instance, the template extrusion method [31], the cast-coating method [32], the electrohydrodynamic technique [33], the layer-by-layer treatment [34], and a one-step immersion process [35]. Moreover, it was also found that, through the dewaxing treatment of lotus leaves, micro- and nanoscale binary structures are also important to obtain superhydrophilic surfaces with CA approaching 0° [36]. Now, increasing attention is being paid to the development of responsive smart surfaces that respond to external stimuli, e.g., light [37–40], temperature [41–43], electricity [44,45], pH [46], and solvent [47]. The first example of a surface that is switchable between superhydrophobicity and superhydrophilicity, a thermally responsive polymer surface, has accelerated the development of the field of controllable surface wettability [43]. By virtue of the above-mentioned unique advantages of photoresponsive materials, many exciting results on photoresponsive controllable surface wettability have been reported, which provide a guide for us to stride forward with even more elegant designs and intelligent control, beyond simple mimickry.

In this review, the scope has been limited to recent studies on photoinduced smart surfaces with controllable wettability. There are four sections, including background, switchable wettability on photoresponsive surfaces, light-driven movement of liquid droplets on photoresponsive surfaces, and conclusions.

2. Background

2.1. Basic theory of surface wettability

Surface wettability is one of the paramount properties of solid surfaces and is related closely to both fundamental scientific theory and practical applications. The wettability of a solid surface is commonly determined by CA measurements. For a liquid on a flat surface, the CA is considered to be the cooperative result of three different types of surface tension at the solid/liquid/gas interface, which is given by Young's equation [48]. Based on Young's equation, hydrophilicity refers to CA less than 90° on solid surfaces, while hydrophobicity refers to CA higher than 90°. This definition can reflect some characteristics of surface wettability. However, this definition contains more mathematical convenience rather than real physical and chemical meaning. The definition of hydrophilicity and hydrophobicity should be able to reflect the physical and chemical situation of solid/liquid/vapor at the interface in a more real sense. In recent years, from the viewpoint of water structure and reactivity at surfaces, Vogler defined hydrophobic surfaces (CA higher than 65°) and hydrophilic surfaces (CA less than 65°) based on the observation that there are two distinct kinds of water structure and reactivity, which was revealed by using a surface force apparatus and ancillary techniques [49]. Although this definition is different from the classical definition of 90°, and there remains a continuous debate in the literature, even with a convergence of experimental observations, it has aided the understanding of the intrinsic properties of surface wettability, including force interactions in water/solid/vapor, the function of surface roughness, and CA hysteresis, and explain some unusual surface wettability phenomena. For instance, a poly(vinyl alcohol) nanofiber film shows a CA of about 171°, while on a smooth poly(vinyl alcohol) surface, the CA is merely 72° [50]. On rough titanium dioxide nanostructured films, the CA is about 154°, while for the smooth surface, the CA is about 74° [51]. These phenomena make the traditional view of 90° as the dividing line seem simplistic, because, according to common sense, a hydrophilic surface should become more hydrophilic by introduction of surface roughness. However, this new definition makes the wetting properties of many organic/inorganic films, polymer surfaces, and biomaterial surfaces more easily understandable than before.

In fact, solid surfaces are usually not perfectly flat but are somewhat rough, so the effect of surface roughness has to be considered for surface wettability. The basic idea is to account for this through r, termed the surface roughness factor, which is the ratio of the actual to the projected area. Wenzel's equation [52] and Cassie's equation [53] are two main theories that bear on the relationship between the apparent CA and surface roughness (defined as r) on solid surfaces. In Wenzel's model, it is assumed that the liquid can enter completely and contact the concave regions on the solid surface, with the equation:

$$\cos\theta_{\mathrm{r}} = r\cos\theta \tag{1}$$

where θ_{r} is the apparent CA on a rough surface.

If air can be trapped by the liquid to give a composite surface, the latter belongs to Cassie's case, and thus the apparent CA is described in a modified equation:

$$\cos\theta_{\mathrm{r}} = rf_1\cos\theta - f_2 \tag{2}$$

where f_1 and f_2 are the area fractions of the projecting solid and vapor on the surface, respectively, and $f_1 + f_2 = 1$. From these two theories, it can be found that surface roughness can enhance surface wettability on solid surfaces, either hydrophobic or hydrophilic. This finding guides us to tune the surface wettability by controlling surface geometrical structures independently of the chemical composition.

Moreover, the surface roughness has been reported to strongly affect the CA hysteresis [54–56] and dynamic wettability [57]. The sliding angle is defined as the critical angle at which a water droplet begins to slide on a tilted surface. This depends on the difference between the advancing and receding angles and acts as a monitor of CA hysteresis. Our recent studies revealed that hierarchical microstructures and nanostructures can improve the hydrophobicity and also yield a small sliding angle [25]. The theoretical analysis proposed by Marmur also provides the well consistent result that the hierarchical structure may decrease the concrete contact between the water droplet and the solid surface and the triple phase contact line (water/solid/air), and lead to a small sliding angle [58]. Therefore, independent of the chemical composition, the fabrication of surface microstructure and nanostructure plays also an important role in controlling surface wettability.

2.2. *Photoresponsive materials*

Photoresponsive materials have been widely studied, involving everything from inorganic nanomaterials to small organic molecules and photoactive polymers. Herein, we focus on those that are endowed with two basic features under light stimulus: one is the switching of bistable states, and the other is the change of surface free energy. For inorganic complexes, some oxides exhibit photoinduced hydrophilicity, e.g., titanium dioxide, zinc oxide, tungsten oxide, and tin oxide. This phenomenon is different from photocatalysis but conforms to a similar mechanism that involves photogenerated electrons and holes and absorbed water [59–61].

For organic complexes, there are several kinds of derivative compounds based on their photoactive groups (Fig. 1), such as azobenzenes, spiropyrans, and cinnamates. Under photoirradiation, the chemical configuration of these groups changes between two states, with which the molecular polarity and surface free energy change accordingly, leading to a transition of surface wettability. Although surface microstructures and nanostructures are important in fabricating surfaces with unique wettability, the change of surface chemical composition is the essential key to realize responsive surface switching with controllable wettability.

3. Switchable wettability on photoresponsive surfaces

3.1. *Inorganic-oxide-based photoresponsive surfaces*

Inorganic oxides always occupy a paramount position in many industrial applications because of their intrinsic advantages, such as good chemical and mechanical stability, low cost, and outstanding photo/electro-properties. Recently, the photoinduced changes of surface chemical states of inorganic oxide materials make it possible to create an intelligent surface with controllable wettability. Among the various oxide materials, research on the photoresponsive behavior of titanium dioxide, a typical photoresponsive material, attracts much attention worldwide, and many scientists have been inspired to devote much energy to the study of the photoresponsive wettability of inorganic oxides. Herein, we would like to start our review with titanium dioxide.

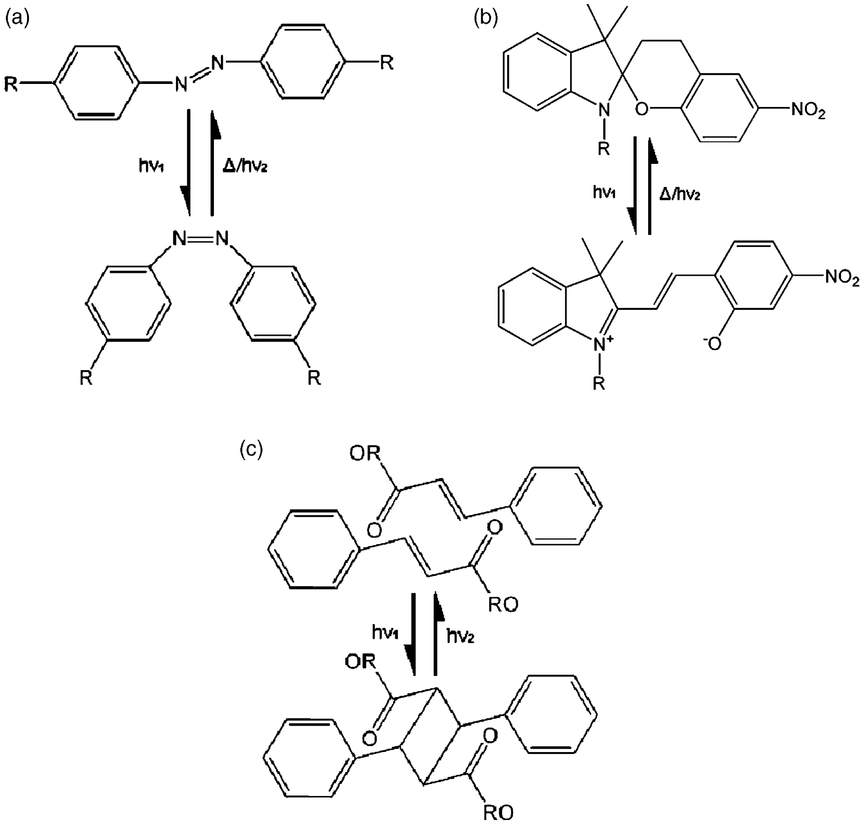

Fig. 1. Schematic illustration of light-induced isomerization and photochemical reactions. (a) *Trans–cis* photoisomerization of azobenzene groups. (b) Photoinduced reversible photochemical cleavage of the C–O bond in spiropyran groups. (c) Photodimerization of the cinnamic acid group.

The photoinduced superhydrophilicity of titanium dioxide was first reported by the Fujishima group [23]. On titanium dioxide surfaces, the water CA is about $72 \pm 1^\circ$. According to Vogler's definition of hydrophobic surfaces, this surface should belong to the weakly hydrophobic state. After the sample is exposed to ultraviolet (UV) irradiation, water droplets spread over the surface immediately, and the water CA reaches about $0 \pm 1^\circ$, producing a superhydrophilic state with an unstable three-phase boundary. After dark storage for a long period, the surface can revert to the original state. Thus, a transition between hydrophobicity and superhydrophilicity is realized under light stimulus, and accordingly, the three-phase boundary changes from a stable case to an unstable one. By use of this unique phenomenon, several commercial products have been designed and produced, such as antifogging, self-cleaning titanium dioxide-coated glass.

In contrast to the superhydrophilicity of titanium dioxide, Nature has selected the superhydrophobic surface to realize the self-cleaning phenomenon, e.g., lotus leaves. Inspired by Nature, Nakajima et al. prepared superhydrophobic films with titanium oxide photocatalysts by modification with fluoroalkyl silane [62]. This film provides the first example of a film that simultaneously satisfies the requirements of transparency, superhydrophobicity, and long lifetime. Recently, Zhang et al. combined the antireflective property with the superhydrophobic property in a core-shell-like titanium dioxide/silicon dioxide particle coating [63], which improves the practicability of superhydrophobic surfaces at a large extent. By means of UV irradiation though a photomask, Tadanaga et al. developed a superhydrophobic–superhydrophilic micropatterned coating film, which consists of three layers, a flowerlike alumina gel film, a thin titanium dioxide gel layer, and a fluoroalkyl silane layer [64]. This study may extend the practical applications of hydrophobic–hydrophilic patterns.

While the self-cleaning effect of high wettability attracts most of the attention, the reversible wettability switching of inorganic-oxide films is emerging as a new highlight. The Fujishima group further investigated the controllable wettability of zinc oxide and titanium dioxide films prepared by the spray pyrolysis method [60]. Photoinduced reversible wettability conversion on both films was observed by alternating UV irradiation and dark storage. Before UV illumination, the zinc oxide and titanium dioxide films exhibited water CAs of 109° and 54°, respectively; after UV illumination, both surfaces became superhydrophilic, with CAs less than 10°; dark storage reconverted the superhydrophilic surfaces to their original states. The alternation of oxygen atoms and adsorbed water molecules on the surface is thought to make a major contribution to these similar phenomena.

An important question is whether other oxide semiconductors also show this fascinating photoinduced hydrophilicity. By examining both hydrophilicity and photocatalytic properties, Hashimoto and co-workers provided the initial answer that this effect was indeed observed in several oxide semiconductors [60,61]. These findings pave the way towards the construction of photoresponsive surfaces that switch between superhydrophobicity and superhydrophilicity, by use of inorganic oxides.

Surface geometric morphology also plays an important role in controlling surface wettability, in addition to the intrinsic chemical properties. Mother Nature has produced many plants and insects with elegant and unique wettability [27]. One of the best-known examples is the lotus leaf, on which microscale and nanoscale hierarchical structures and waxy materials cooperate in harmony to produce a superhydrophobic surface. Inspired from this, we introduced surface microstructure into a surface where changes of polarity and chemical composition could be induced by light irradiation. We selected zinc oxide, an excellent photosensitive oxide semiconductor, to fulfill this strategy. On a flat zinc oxide substrate, the CA can decrease from 109° to 10° through UV illumination; after long-term dark storage, the initial hydrophobic surface can be recovered. Interestingly, on microscale and nanoscale hierarchically structured zinc oxide films (Fig. 2a) prepared via CVD [39], both the hydrophilicity via UV illumination and the hydrophobicity under dark storage are amplified by the roughness. On the hierarchically structured surface, as shown in Fig. 2c, the CA can reach 163.4° under dark storage, while, via UV illumination, the CA becomes about 0° owing to the cooperation between surface 2D and 3D capillary effects [65,66], suggesting that a photoresponsive switching between superhydrophobic and superhydrophilic has been realized. Similar remarkable surface wettability alternations were also reported on aligned zinc oxide nanorod films prepared via a solution approach [67], a vapor–solid process [68], and solution-dipping template methods [69,70]. Zhang et al. also fabricated superhydrophobic and superhydrophilic micropatterns by light lithography using the UV-induced wettability conversion of a zinc oxide nanocolumnar film [71]. Recently, a reversible wettability transition on nanoporous titanium dioxide films, prepared by Li and co-workers via the anodic oxidation procedure [72], was achieved but was limited in the range from hydrophobicity to hydrophilicity. Further, by increasing the surface roughness, a reversible photoinduced surface switching between superhydrophobic and superhydrophilic states was realized on flower-like nanostructured titanium dioxide films prepared by hydrothermal (Fig. 2b) [51] and photoelectrochemical etching methods [40].

Many unique functions are of importance in fabricating intelligent surfaces, smart windows, and microfluidic switches. It will be highly desirable to combine excellent properties with a superwettability switch on the same film. For example, an aligned tin oxide nanorod film (Fig. 3a), prepared by a crystal-seed-based hydrothermal method, exhibits switchable superhydrophobicity and superhydrophilicity [73]. The CA changes from 154.1° to 0° when exposed to UV-irradiation (inset in Fig. 3a), and the wettability converts to its initial superhydrophobic state by storing the films in the dark for a certain time. Tin oxide is a wide band-gap semiconductor that is important for its excellent transparency and conductivity. However, transparency and superhydrophobicity are competing properties in the preparation of transparent superhydrophobic films. Nanorod structures are essential in increasing the surface roughness and forming a superhydrophobic film, but their formation decreases the transparency of the film. In this case, a film with this type of smart wettability shows 60% transmittance in the visible region and semiconducting properties. Although the transparency and conductivity need to be improved further (Fig. 3b), this study does indeed demonstrate an embryonic combined functional switchable surface.

Another example is a photoinduced dual-responsive tungsten oxide nanofilm, which combines wettability conversion and photochromism (Fig. 4) [74]. The rough tungsten oxide films, prepared by a simple electrochemical deposition process, exhibit a pebble beach-like morphology that is made up of many nanoprotuberances with diameters in the range of 40–350 nm (Fig. 4a). The as-prepared film is superhydrophobic, with a CA of about 151.3°. Upon UV irradiation, the CA decreases to

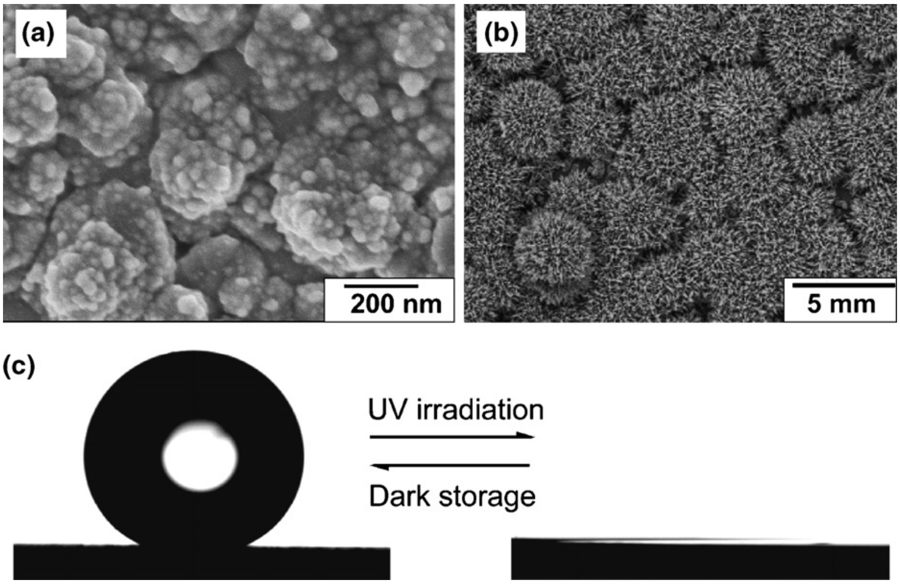

Fig. 2. (a) SEM image of micro- and nanoscale hierarchically structured zinc oxide films at high magnifications. (b) Flower-like nanostructured titanium dioxide film. (c) Photographs of water droplet shape on the zinc oxide/titanium dioxide nanorod films before (left) and after (right) UV illumination.

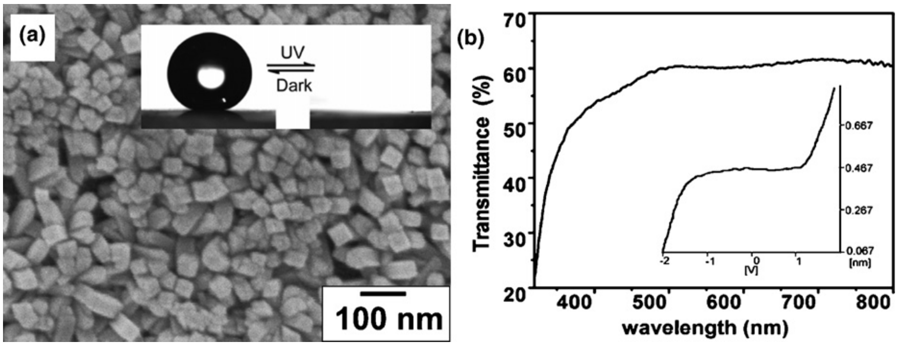

Fig. 3. (a) SEM image of a tin oxide nanorod film. (b) Transmission spectrum of the as-prepared film in the visible region (insert is an *I–V* curve of the as-prepared film).

less than 5° (inset in Fig. 4a). Long-term dark storage of these irradiated films caused them to recover their original superhydrophobicity. As an excellent photochromic material [75–78], tungsten oxide also exhibits photochromic behavior during the wettability conversion. Interestingly, after UV irradiation, an as-prepared film turned from the original brown to a yellowish-green (Fig. 4b); when this film was placed in the dark, it recovered the brown color. Further experiments confirmed that the switching process involved reversible changes in tungsten valent states, oxygen vacancies, oxygen gas, and adsorbed water molecules [79–81]. The adsorbed water molecules link the photoresponsive wettability switch and the photochromism.

Briefly concluding, it has been found that these inorganic-oxide-based photoresponsive wettability transitions conform to a similar mechanism. The photoinduced redox processes of the oxide, the generation and annihilation of oxygen vacancies, the absorption of water molecules, and the presence of environmental gases have strong influences on the switching process. These studies suggest that those semiconductor oxides with photoresponsive redox properties have a promising future as potential responsive and/or multifunctional surface switches in new technological applications such as smart functional windows, microfluidic devices, and bioanalysis.

3.2. *Organic-compound-based photoresponsive surfaces*

In comparison with inorganic materials, organic materials have many advantages in terms of the number of adaptable species, the capability of chemical modification, and reaction diversity. Here, the favored photoresponsive organic materials are those materials that have a reversible photoinduced transformation between two states. During the photoinduced transformation, various physical and chemical properties change, such as the surface energy, absorption spectra, refractive index, dielectric constant, oxidation/reduction potential, and geometrical structure. These organic materials have not only been widely used for the design of photoswitchable devices and data storage, but also provide an abundant source for the fabrication of photoresponsive surfaces with controllable wettability. The immobilization of organic molecules onto a substrate determines whether a uniform responsive surface can be successfully fabricated and whether the surface is stable, and accordingly, many ingenious strategies have been developed to modify solid surfaces, such as aggressive ion beam techniques [82], self-assembly processes [83,84], the chemical attachment of long-chain molecules to a surface [85], and the cross-linking of a random copolymer film [86]. In the following, we will discuss recent contributions on organic photoresponsive surfaces with controllable wettability; these are classified by the types of organic functional groups.

Azobenzene is a typical photoresponsive organic material that undergoes a reversible conformational transition between *cis* and *trans* isomers under UV and visible irradiation. The transition between *trans* and *cis* isomers causes a change in dipole moment, resulting in a change of surface wettability. By using a chemisorption self-assembly technique, Brittain et al.

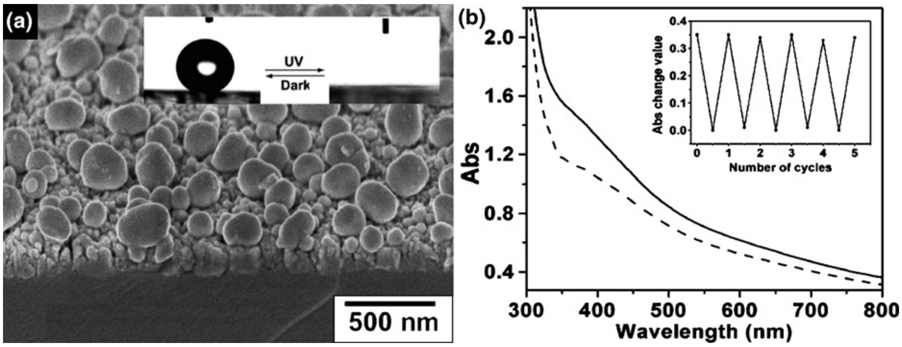

Fig. 4. (a) SEM images of tungsten oxide nanofilm. The inset shows a photoresponsive switch between superhydrophobicity and superhydrophilicity. (b) Absorption spectra of the as-prepared film before (solid line) and after (dashed line) irradiation with 365 ± 10 nm UV light. The inset shows the good reversibility.

prepared an azobenzene monolayer surface on a flat substrate, on which a small CA change (less than 10°) was observed via UV irradiation [87]. Bardeau and co-workers prepared an azobenzene-functional monolayer by covalent grafting onto a smooth silicon surface, and a CA transition from 67° to 62° was induced after UV irradiation. This transition from weak hydrophobicity to weak hydrophilicity was attributed to the *trans–cis* isomerization of the azobenzene units [88]. Feng et al. fabricated an azobenzene-tailored polymer film by the Langmuir–Blodgett technique, and the CA change by UV irradiation was about 11° [37]. The trans isomer, with a small dipole moment, has a low surface free energy, and the cis isomer, with a large dipole moment, possesses a high surface free energy. Thus, the isomerization of azobenzene from *trans* to *cis* results in the wettability change from a greater CA to a smaller CA. However, these studies rely upon a smooth substrate, without taking account of the effect of surface geometric structures. Recently, Jiang et al. fabricated a photo-switched azobenzene polyelectrolyte monolayer through simple electrostatic self-assembly (Fig. 5a) [89]. On the flat silicon substrate, the CA of the monolayer changed reversibly between 78.3 ± 1.5° and 76.4 ± 1.3° during the alternation of visible (494 nm) and UV (365 nm) irradiation. Interestingly, when the monolayers are transferred onto rough substrates, CA varies with the change of spacing between the aligned silicon columns on the substrate (Fig. 5b), and a greatly amplified effect is observed, so that a very limited CA change of about 2° is expanded to a large extent (about 66°), from superhydrophobicity to hydrophobicity. This result confirms that the surface roughness can be an effective tool for the amplification of the CA switching range on organic photoresponsive surfaces. Moreover, Ge et al. reported an inverse opal (Fig. 5c) with photoresponsive wettability, prepared by coating with a photoresponsive azobenzene monolayer [90]. The surface undergoes reversible changes in wettability without much influence on the photonic stop bands. The monolayer of azobenzene acts as a smart surface with photocontrollable properties. The ordered monodisperse air spheres throughout the inverse opal contribute to both structural color and the amplification of stimulus-induced CA switching. This case provides a new model for the construction of responsive wettable surfaces with unique functions.

For spiropyran molecules, the reversible photochemical cleavage of the C–O bond in the ring, which is the typical photochemical reaction in the spiropyran complex, can lead to a reversible transition between the closed nonpolar form and the open polar form [91]. Hence, spiropyran-based responsive surfaces have also attracted much attention in the exploration of stimuli-responsive surface wettability. Rosario et al. used a photoresponsive spiropyran monolayer to coat a silicon nanowire surface (Fig. 6) [92], on which the light-induced CA change, going from UV irradiation (366 nm) to visible irradiation (450–550 nm), increased to 23° from 12° on the flat surface. Importantly, under visible irradiation, a superhydrophobic surface appears on the coated nanowire substrate, and the CA hysteresis is reduced. These results provide an example of the lotus effect amplifying photoresponsive CA switching.

Very recently, Athanasiou and co-workers prepared a nanopatterned spiropyran-doped polymer surface and observed the impact of surface roughness on surface wettability by alternation of UV and green laser irradiation (Fig. 7) [93,94]. On the nanopatterned grating surface, the CA changes were amplified, and either surface hydrophobicity or hydrophilicity was enhanced on an optimized pattern size. Belfort et al. grafted spiropyran-containing responsive polymers onto synthetic membranes by photograft-induced polymerization,

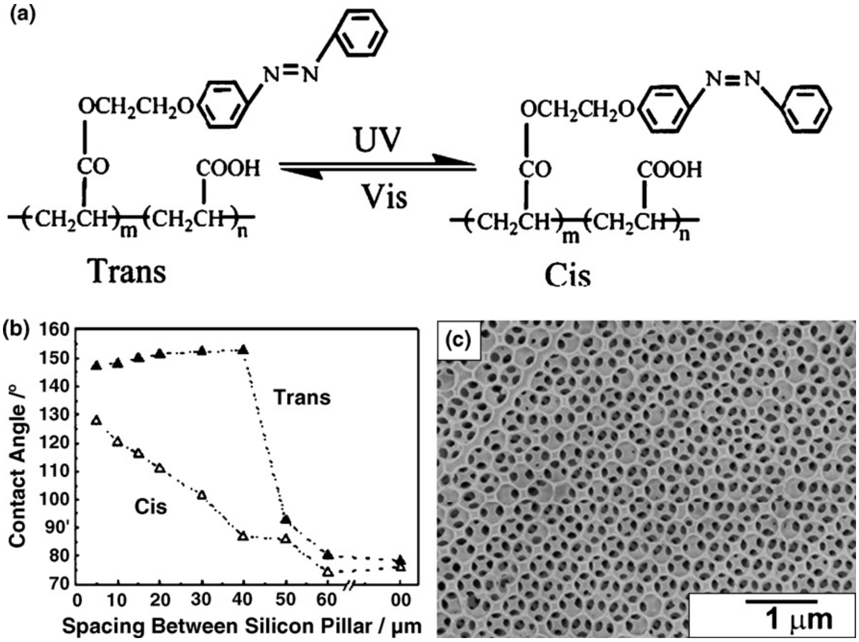

Fig. 5. (a) *Trans* and *cis* structures of azobenzene upon UV and visible irradiation. (b) Variation of water CA of a photoresponsive monolayer on a patterned substrate with pillar spacing. (c) Typical SEM image of inverse opals.

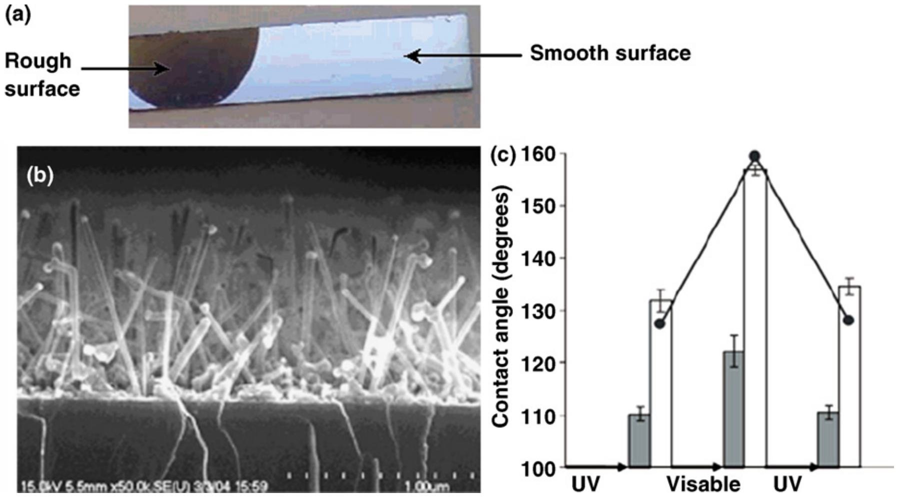

Fig. 6. (a) Silicon sample having smooth and rough (nanowire) areas, treated with a photoresponsive coating. (b) Cross-sectional SEM image of Si nanowire surface in the rough area. (c) Advancing CA changes on the smooth (gray bars) and rough (white bars) photoresponsive surfaces after UV and visible light irradiation.

leading to an optically reversible switching of wettability and protein adsorption [95].

Aside from macroscopic switchable wettability on non-curved surfaces, recently Smirnov et al. modified the surface of nanoporous alumina membranes using mixtures of spiropyran and hydrophobic molecules [96]. As shown in Fig. 8, the freshly modified membrane with the apolar spiropyran form is not wetted by an aqueous solution, while after UV exposure, the polar merocyanine form occupies the surface, outside and in the nanopores, allowing water or ions to enter the pores and cross the menbrane. Thus, the membrane acts as a photosensitive valve that not only switches the transport of water and ions across the membrane, but also switches the ion conductance.

Moreover, a reversible photodimerization reaction has also been used in an attempt to perform a wettability conversion. Roston et al. reported a wettability change on thin coatings of photoresponsive, pyrimidine-terminated molecules attached to solid substrates when irradiated with UV light at 280 and 240 nm [97,98]. The thymine-terminated self-assembled monolayers on gold gave the largest reversible photoinduced contact angle change (26°), originating from a photodimerization that induces a change in surface charge from ionized monomer to nonionized dimer, as shown in Fig. 9. In comparison to thymine, uracil self-assembled monolayers photodimerize but do not photocleave, and there is an irreversible CA change.

By virtue of the photoresponsive characteristics of malachite green carbinol base, Sasaki et al. proposed an alternative means to construct a photoresponsive surface by preparing a composite film made up of malachite green carbinol base and fluoride on silicon dioxide particles [99]. Upon exposure to UV light, the malachite green carbinol base changes into a less hydrophobic conformation when the hydroxide anion is detached (Fig. 10). As a result, on the composite surface, where silicon dioxide particles can tune the surface roughness, light induces a surface wettability transition from superhydrophobic to hydrophilic.

Very recently, Uchida et al. reported a new photoinduced reversible surface switch on a diarylethene microcrystalline surface [100]. As shown in Fig. 11a, the photoisomerization of a

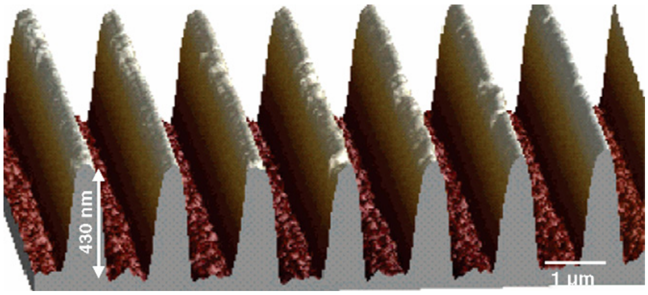

Fig. 7. Atomic force microscopy image of a nanoimprinted grating formed on the surface of a 5% SP–95% P(EMA)-*co*-P(MA) sample. The *x* and *z* axes are presented on different scales.

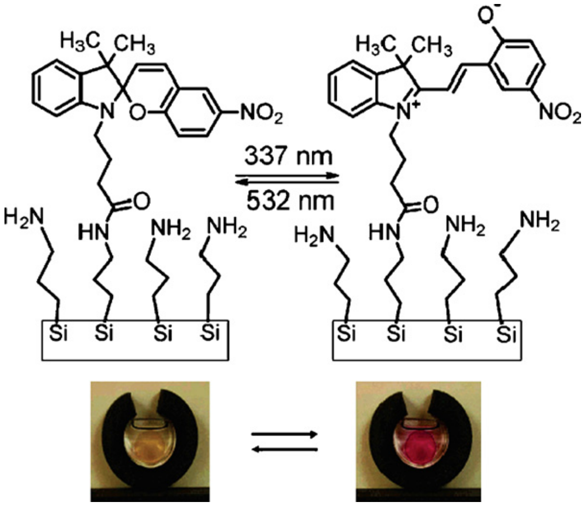

Fig. 8. Top: schematic diagram of the conversion between the immobilized spiropyran and merocyanine forms under UV and visible irradiation; bottom: corresponding membrane transition between hydrophobic spiropyran (transparent) and hydrophilic merocyanine (red) forms.

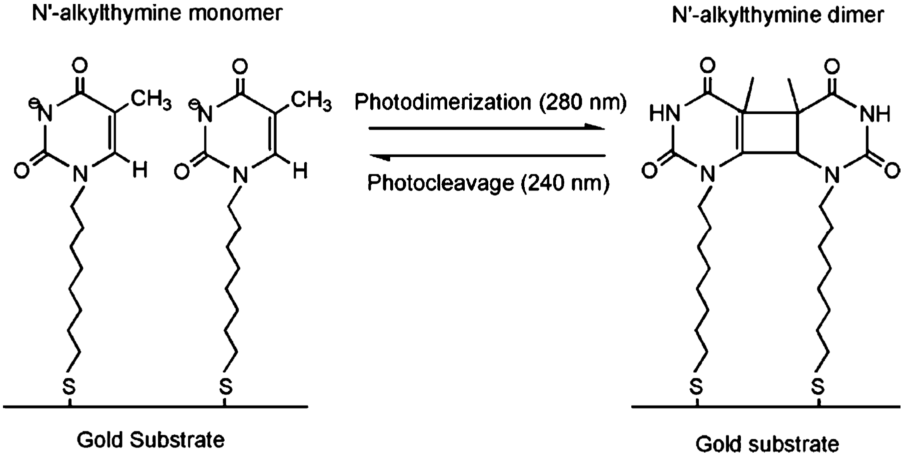

Fig. 9. Reversible photodimerization with contact angle and ionization change.

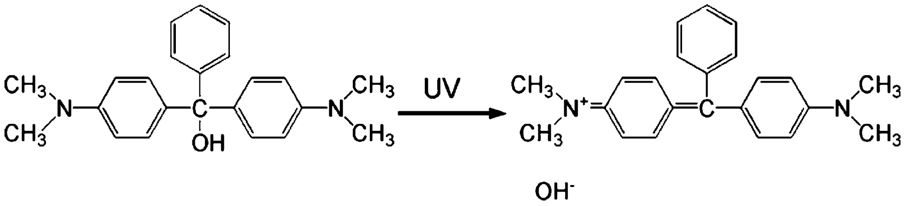

Fig. 10. Schematic of the photoisomerization of malachite green carbinol base.

diarylethene molecule between open-ring and closed-ring isomers is the origin of the switchable wettability. Upon irradiation of UV light, microfibrils form on the surface, leading to a superhydrophobic surface (CA 163°). Then, upon irradiation with visible light, the surface recovers its flatness and also returns to the initial CA of about 120° (Fig. 11b). In contrast to the previous organic wettability switches that rely on the change of surface polarity and chemical composition, here the reversible conversion of surface geometrical structure leads to the switchable wettability. This study develops a new function of diarylethene derivative films but also provides a new candidate for materials with photoresponsive reversible surface water repellency.

Comparing those inorganic-based photoresponsive surfaces with organic-based surfaces, until now, the latter have not exhibited a super-wettability switch between superhydrophobicity and superhydrophilicity like the former. It is well known that organic materials have distinct advantages in tailoring chemical compositions; hence, the combination of suitable chemical composition and photoresponsive organic units would light up the further exploration of photoresponsive wettability switches.

4. Light-driven movement of a liquid drop on photoresponsive surfaces

An interesting surface phenomenon is the movement of a liquid droplet on a solid surface caused by a surface energy gradient [101–107], which is important for industrial applications

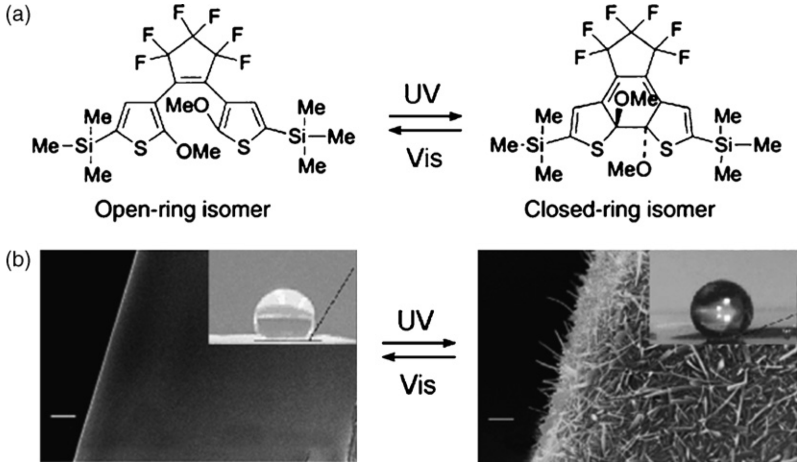

Fig. 11. (a) Reversible formation of open-ring and closed-ring isomers of diarylethene. (b) Reversible changes of surface morphology (scale bar: 10 μm) and CA under alternation of UV and visible irradiation.

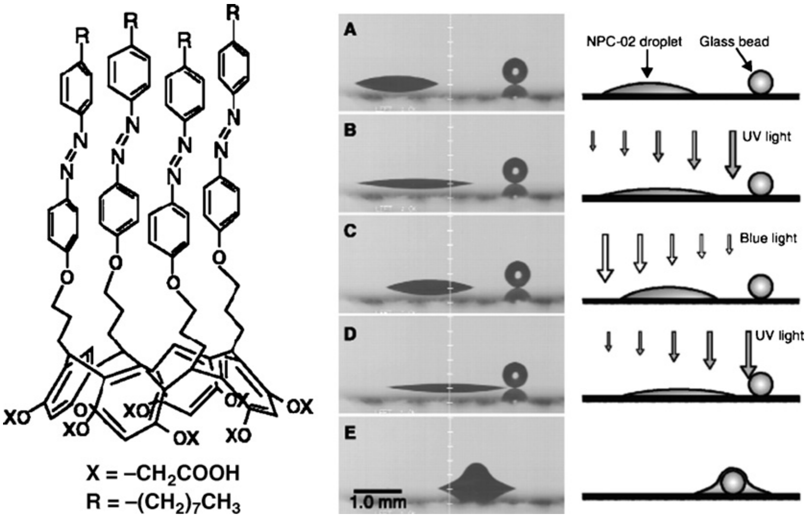

Fig. 12. Left: schematic diagram of a macrocyclic amphiphile tethering photochromic azobenzene units (CRA-CM). Right: lateral photographs of the light-driven motion of an olive oil droplet on a silica plate modified with CRA-CM. The olive oil droplet on a cis-rich surface moved in the direction of higher surface energy by asymmetrical irradiation with 436-nm light perpendicular to the surface. (A–C) The sessile contact angles were changed from 18° (A) to 25° (C). (D) The direction of movement of the droplet was controllable by varying the direction of the photoirradiation.

and laboratory research. For example, during the design and operation of microfluidic and DNA analysis devices, when a small volume of a liquid cannot be delivered using a mechanism based on scaled-down macroscopic pumps, or when chemical reactions on a tiny scale without a reaction vessels need to be performed by mixing individual drops containing different reactants, external-responsive surfaces may become candidates to overcome the problem of liquid transport. Recently, several photoresponsive surfaces have proven to be capable of moving droplets of liquids across surfaces [3,105,107].

The photoactivity of azobenzene resulting from the photoisomerization of azobenzene molecules has been known for years, and on this basis, the switchable surface wettability has been extensively studied, as mentioned above [37,87–89]. Ichimura et al. have shown another very important aspect of azobenzene molecules, that is, the photo-driven macro-

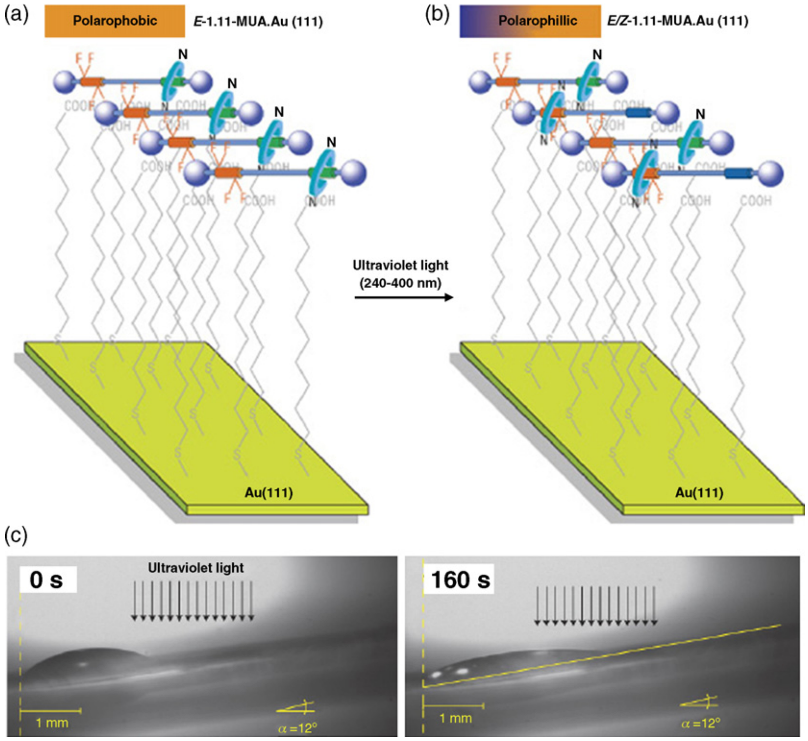

Fig. 13. A photoresponsive surface based on switchable fluorinated molecular shuttles. (a) Light-switchable rotaxanes with the fluoroalkane region exposed (E-1) were physisorbed onto a SAM of 11-MUA on Au(1 1 1) to create a polarophobic surface, E-1.11-MUA.Au(1 1 1). (b) Illumination with 240–400 nm light isomerizes some of the E olefins to Z, which encapsulates the fluoroalkane units, leaving a more polarophilic surface, E/Z-1.11-MUA.Au(1 1 1). (c) Lateral photographs of light-driven transport of a 1.25 μl diiodomethane drop on a E-1.11-MUA.Au(1 1 1) substrate on mica up a 12° incline.

scopic movement of a liquid droplet on a photoresponsive solid surface [3]. They assembled a photoresponsive monolayer surface using an azobenzene derivative, O-carboxymethylated calixresorcinarene (CRACM, left in Fig. 12). Asymmetrical photoirradiation can cause a gradient in surface free energy because of the photoisomerizaiton of surface azobenzenes, and if a liquid droplet several millimeters in diameter is placed on the modified surface, it will be forced to undergo directional motion. The modified surface under UV irradiation (360 nm) results in polar *cis*-azobenzene groups at the terminal positions, increasing the surface free energy and hydrophilic nature, while photoirradiation with blue light (436 nm) causes *cis*-to-*trans* isomerization, making the surface hydrophobic. An imbalance in contact angles was generated on both edges of the droplet, and the resultant gradient of surface free energy was the driving force of liquid motion. Thus, the motion of a liquid droplet can be manipulated precisely by varying the direction and steepness of the gradient in light intensity (Fig. 12, right).

Leigh and co-workers recently realized a macroscopic transfer of a liquid droplet using rotaxane-based photoresponsive molecular shuttles [107]. In the rotaxanes, the macrocycle is translocated from one position on the thread to a second site through biased Brownian motion in response to an external trigger (Fig. 13). They designed and synthesized a molecule shuttle that could expose or conceal a fluoroalkane segment in response to photoisomerization of the fumaramide station (the right green part of shuttle which has a high binding affinity for the ring) to maleamide (which has a low binding affinity for the ring). The biased Brownian motion associated with an E-1 to Z-1 transformation produces a rotaxane-terminated surface with switchable wettability. As light irradiation fuels chemical reactions, the nanometer positional changes take place in individual molecules by biased Brownian motion. The collective effect of nanometer motion of a molecular shuttle monolayer causes a surface energy gradient that can produce power enough to move a microliter droplet of diiodomethane up a 12° incline (Fig. 13c).

The controlled manipulation of small volumes of liquid is always a challenge in microfluidics. Here, liquid transport using photoresponsive surfaces may provide a useful way for delivering analytes in lab-on-a-chip environments, or for performing chemical reactions without reaction containers by bringing individual drops containing different reactants together. However, until now, only a few kinds of organic liquids can be manipulated on these photoresponsive surfaces, so novel photoresponsive surfaces should be explored and constructed to realize the facile manipulation of either water or organic liquids.

5. Conclusions and outlook

Reversible photoresponsive surfaces with controllable wettability have attracted enormous attention in recent years due to their importance in surface science and intelligent micro- and nano-devices. In this article, we have reviewed some recent progress on photoinduced surface wettability switches with different types of molecules, such as inorganic oxides and organic polymers and SAMs, and the photoinduced movement of a liquid droplet on photoresponsive surfaces driven by molecular machines. The research on photoresponsive surfaces with controllable wettability has just started, and numerous challenges remain in its development. These challenges include designing new photoresponsive materials that have improved stability and sensitivity, developing new smart windows, putting these entities in complex devices that can be used in microfluidic valves, and endowing photoresponsive biological activity and biocompatibility. Analogously, advances in nanomaterials and nanotechnology will produce new opportunities to develop photoresponsive surfaces and will facilitate the understanding of how smart solid surfaces interact with liquids. Finally, we note that many significant advances in this area will expand from the photoresponsive solid phase to the photoresponsive liquid phase. We believe this area will hold a great promise in designing and developing bioanalytical methods, environmental cleanup, microfluidic devices, biochips, smart windows, controllable drug release, and intelligent devices.

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