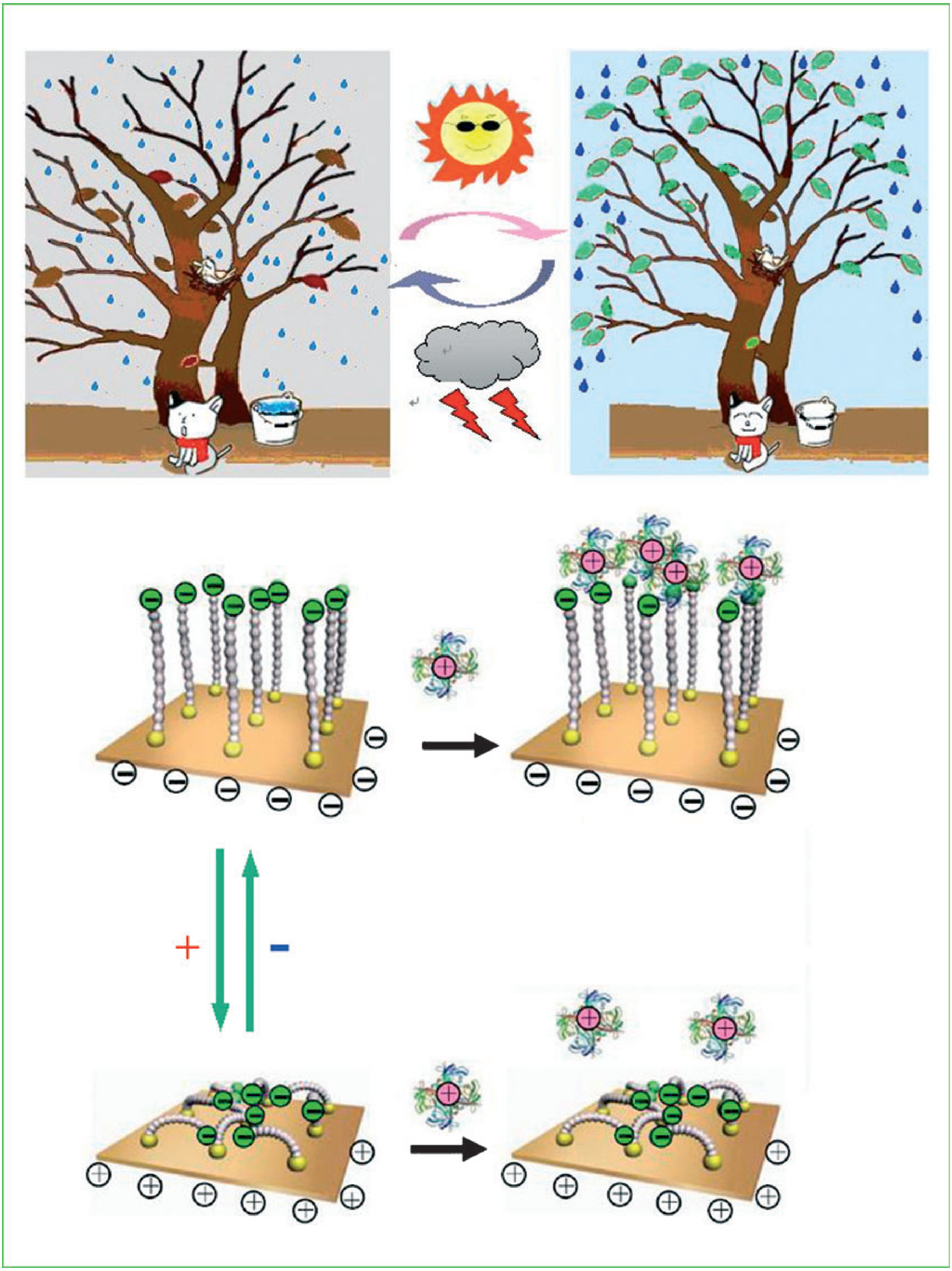

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Controlled Switchable Surface

Ying Liu, Li Mu, Baohong Liu, and Jilie Kong*[a]

Abstract: The macroscopic properties of a surface can be intelligently controlled by alternating the states of the modified molecules, such as polymers, metallic oxide, or self-assembled monolayers (SAMs). This article reviews various approaches to create a switchable surface and different types of external stimuli used to switch the surface properties. This area is of potential benefit for biomaterials, biosensors, information storage, microfluidic systems, adhesive materials, nanolithography, and so on.

Keywords: monolayers • surface chemistry • wettability

Introduction

To date, increasing attention has been placed on the development of controlled switchable surfaces, also known as "smart surfaces",[1] that can respond to environmental stimuli.[2] Reversible control of the surface properties has been achieved with various methods, including photoillumination,[3] potential effects,[4–6] thermal driving,[7] and surrounding media[8] treatment, whereby the emphasis is focused on the switchability and reversibility. Various surface properties, such as wettability,[9] adhesive features,[10] roughness,[11] biocompatibility,[12,13] and so forth have been demonstrated to switch reversibly on different kinds of specially designed surface. With the development of micro-electro-mechanical systems (MEMS) and nanotechniques, the controlled switchable surface has been employed for construction of smart devices that can be used for bioanalysis, microfluid devices, protein separation, and so on.[14–19]

To review the majority of work related to the controlled switchable surface, here we sum them up in three categories as shown in Table 1. The first one is based on the modification of solid substrates with certain photo-, electro-, and thermo-switchable polymer molecules. The reversible switching of morphologies for polymer molecules and, hence, the macroscopic properties for the modified surface respond to the change of the surrounding medium, that is, temperature or light. Secondly, self-assembled monolayers (SAM) also play an important role in this area. The switching of a SAM-modified surface between different states is normally based on the changes of the molecular components, molecular conformation, and the attachment of the SAM onto the substrate in response to the external stimuli. The third category involves metallic oxide thin films, which show distinct reversible changes in wettability triggered by photons.

Switchable Surfaces Based on Polymers

Fabricating thin films with polymer molecules on a solid substrate is an effective way to tune a wide range of surface properties, for example, wettability, adhesion, and colloidal stabilization. Stimuli-responsive polymer layers can be designed by using a variety of approaches, including reversible photoisomerization reactions, reversible swelling/collapsing of water-soluble grafted polymers, and phase separation in mixed grafted brushes or diblock copolymers. These surfaces are capable of responding to very subtle changes in the surrounding environment such as temperature, light, and solvent quality. The macroscopic responses are caused by the reorganization of the internal or external surface structure of the grafted layers. These surfaces can be used as both sensing elements and as active elements responsive to environmental conditions. More and more attention has been paid to the promising applications of these polymer layers, such as environment responsive lithography, surface patterning, and templating for the fabrication of information storage devices.[20]

Surrounding media driven: Two different kinds of covalent attachment processes are reported to create a surface with a

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Table 1. Summary of typical reversible surface with different properties and applications.[a]

Type	Description	Driving force	Switchable properties	Applications	Ref.
polymer	PS-PAA, PSF-PVP (grafting to) PS-PMMA,PS-PVP (grafting from)	surrounding media	wettability, friction force	assembly of nanoparticles, proteins, charged chemical species, microfluidic devices, etc.	[23] [25] [28]
	PNIPAAm	temperature			[34]
	photochromic polymer [4′-(trifluoro methoxy-4,4′dibenzoazo)]	light			
SAM	reversible association (supermolecules, oligomer, etc.)	PH, light	wettability, conductance	protein chips, patterning surfaces, smart devices	[38] [55] [58]
	reversibly conformational transition (azobenzene derivants; alkanethiolate)	light, potential			
	reversible attachment (alkanethiolate)	potential			
metallic oxide	ZnO, TiO_2	light	wettability	self-cleaning materials	[68] [69]

[a] PS: polystyrene; PAA: poly(acrylic acid); PSF: poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene); PVP: poly(2-vinylpyridine); PMMA: poly(methylmethacrylate); PNIPAAm: poly(*N*-isopropylacrylamide).

reversibly switchable surface behavior of polymer films: normally called "grafting to" and "grafting from" methods.[21–27]

For "grafting to" processes, the pre-formed end-functionalized polymers react with a suitable substrate surface under appropriate conditions to form a tethered polymer brush. For the "grafting to" technique, two kinds of grafting processes reported in the literatures. Firstly, some block copolymers were grafted to a solid substrate[21] and the contact angle changing of the resulting polymer droplets was measured. Secondly, the fabrication of a two-component brush (mixed brush) has been reported in which two different and completely incompatible polymers are grafted to the same substrate. The mixed polymer brushes could be synthesized onto the surfaces resulting in many interesting reversible macroscopic phenomena.[22] Polymer chains of carboxyl-terminated poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) (PSF-COOH) and poly(2-vinylpyridine) (PVP-COOH) were attached to the poly(tetrafluoroethylene) (PTFE) substrate by end functional groups (Figure 1, adapted from reference [22a]). Hydroxyl and amino functional groups, introduced covalently by ammonia plasma treatment into the PTFE surface, were used to graft the mixed brush. This approach for the design and the fabrication of two-level structured surfaces leads to surfaces that are capable of reversible switching from hydrophilic to ultrahydrophobic states upon external stimuli (solvent selectivity). However, this kind of surface structure formed in mixed brushes under conditions of spatial constraints imposed by their chemical connection to a single grafting site has not been greatly explored due to synthetic limitations. To conquer this remaining problem, Tsukruk and co-workers have designed a novel type of Y-shaped molecules and attached them to a silicon surface to create a layer about 2 nm thick.[23] These Y-shaped molecules are composed of two dissimilar polymer chains (arms). One arm of each molecule is a hydrophobic polystyrene (PS) polymer, while the other is a hydrophilic polyacrylic acid (PAA) polymer chain. These two types of molecules (hydrophobic and hydrophilic) are attached to a single focal point that is capable of chemical grafting to a silicon surface. Taking into consideration that toluene is a good solvent for PS and a bad solvent for PAA, they treated the polymer brushes with toluene and found that the topmost surface layer is predominantly composed of PS arms which dissolve well in toluene, whereas the collapsed PAA arms, which do not dissolve well in toluene, constitute their "cores". The dynamics of switching the surface properties was studied by observing changes

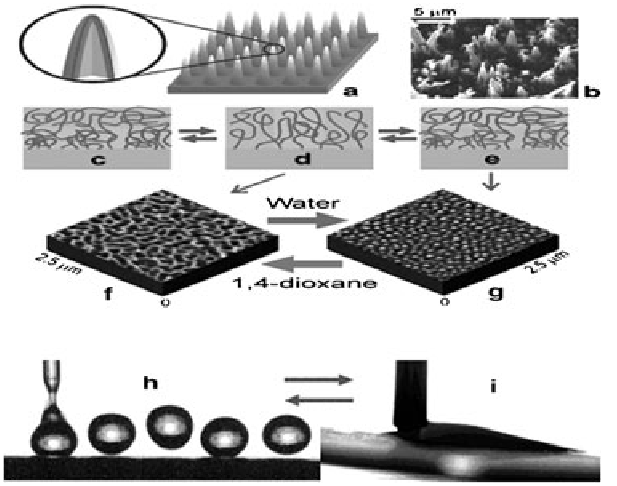

Figure 1. Illustration for the grafting-to process. a) Schematic representation of the PTFE surface (first level). b) SEM image of the covalently grafted mixed brush (second level). In selective solvents the preferred polymer occupies the top of the surface (c and e); in nonselective solvents, both polymers are present in the top layer (d). f) and g): AFM images of the different morphologies after exposure to water and 1,4-dioxane. h) After exposure of the sample to toluene. i) Exposure to acidic water. Adapted from reference [22a].

of the water contact angle, which is a classical measurement used to directly visualize the reversible wettability of solid substrates. This surface-structure switchable behavior can be considered as a promising way toward the patterning of solid substrates with adaptive nanowells, which could be used for trapping and adsorbing nanoscale objects.[24] Switching of the surface-wetting properties on the nanoscale is of potential interest in facilitating assembly of nanoparticles, proteins, and charged chemical species. On the other hand, the formation of surface-bound polymer monolayers by such a "grafting to" technique is mostly limited to low graft densities and low film thickness. To solve this problem, researchers have used the "grafting from" approach,[25–27] which has become more attractive for the preparation of thick, covalently tethered polymer brushes with a controlled and high grafting density.

For "grafting from" processes, the surface is generated by using tethered diblock copolymer brushes.[25] These brushes (composed of poly(methyl methacrylate) (PMMA) and PS polymers) exhibit a reversible change in water contact angle upon exposure to different solvents, presumably by means of self-organization of the polymers. These films are predicted to be good examples of responsive films that possess adaptable adhesion or wettability. The tethered diblock copolymers undergo reversible changes in water contact angles when the film is treated with different solvents (Figure 2[26c]).

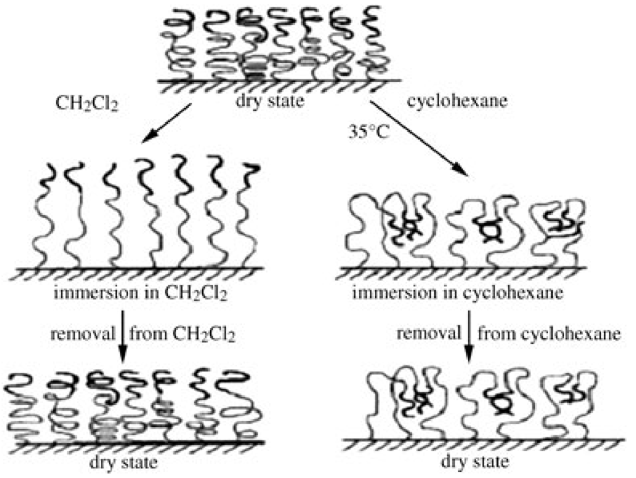

Figure 2. Illustration for the grafting-from process, reversible responses of tethered PS-b-PMMA brushes to different solvent treatments.[26c]

Initially, the film exhibits a contact angle characteristic of PMMA; following treatment with methylcyclohexane (a better solvent for PS than for PMMA), the contact angle increased to a characteristic value for PS. Subsequent treatment of the same sample with CH_2Cl_2 (a good solvent for PMMA and PS) reverses this change.[25] The ability to reversibly switch the properties of the solid substrates would allow a diverse range of applications.[26] Another illustrative example is the two-component polymer brushes (polystyrene and poly (2-vinylpyridine)) synthesized by Minko et al.[27] They also took advantage of the "grafting from" technique by grafting the polymer from the surface of Si-wafers. The brushes are sensitive to the surrounding medium, and their morphology and composition of the top of a brush can be switched upon exposure to different solvents. Thus the surface energetic states and roughness of the film can be precisely tuned.

Hence, these two kinds of processes are readily used as the effective methods to fabricate the smart surfaces with reversibly switchable macroscopic properties. Usually by treatment with different solvents, the surfaces can switch between hydrophilic and hydrophobic states.

Temperature driven: Reversibly switching a surface from being hydrophilic to hydrophobic with a change in temperature has been aroused paramount interest.[27–30] Polymers with photoswitchable groups allow the investigation of thin films or microstructures for reversible changes in optical, geometric, or mechanical properties. One typical example is poly(*N*-isopropylacrylamide) (PNIPAAm), which has a lower critical solution temperature (LCST) of about 32–33 °C.[28] The polymer chains can hydrate to form expanded structures in water when the solution temperature is below its LCST, but become compact structures by dehydration when heated up above the LCST. Thus the PNIPAAm surface exhibits large wettability changes in aqueous media in response to small changes in temperature. The reversible superhydrophilic/superhydrophobic properties of the surface were evaluated by dynamic measurement of the contact angle (Figure 3[28]). It is expected that this kind of smart polymer film can be used to realize several desirable applications, one of which is controlled cell attachment/detachment.[29] Okano et al. have prepared terminally grafted surfaces by using end-functionalized PIPAAm with a carboxyl-end group and studied the effect of graft conformation on the dynamics of grafted PIPAAm molecules by means of aqueous, dynamic contact-angle measurements. Endothelial cells and hepatocytes are attached and proliferate on a PNIPAAm grafted surface. At 37 °C, above the LCST of PNIPAAm, the cultured cells were easily detached from these surfaces.[29] Another interesting practical application was

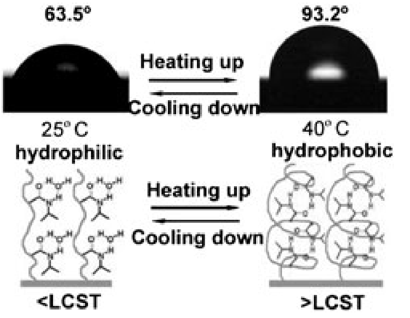

Figure 3. Thermally responsive wettability for a flat PNIPAAm-modified surface.[28a]

demonstrated by Huber and co-workers.[30] By carrying out some extended research work on this switchable surface, they produced some intriguing results on microfluidic devices (Figure 4[30]). The films were formed on a silicon chip, made from a type of plastic with a network of tiny gold wires (only four nanometers thick) to supply heating. The chip-based film formed a switchable surface, which attracts water at room temperature and repulses water when the chip was heated, by means of the gold wires, from room temperature to body temperature, that is, the hydrophilic or hydrophobic state of the film can be readily switched by programmed on-chip heating. Each tiny gold wire on the chip can be heated or cooled separately on demand, and thus it was employed to capture or release proteins at specific sites on command in less than 1 s. This surface has been shown to perform very crude separation of large proteins and small proteins.[30] The temperature-sensitive characteristics that produce remarkable and rapid changes of surface properties make this technology applicable to actuators, modulators, sensors, and switches.[31a,b] In addition, temperature-responsive properties of PNIPAAm have also been utilized in a variety of applications, including controlled drug delivery[31c] and solute separation.[31d] Recently the research on polypeptides, also named protein-based polymer, has become an important and intriguing field.[32] For instance, in response to external stimuli, such as changes in temperature or ionic strength, polypeptides such as ELP (elastin-like polypeptide) undergo a switchable and reversible hydrophilic–hydrophobic phase transition at the LCST.

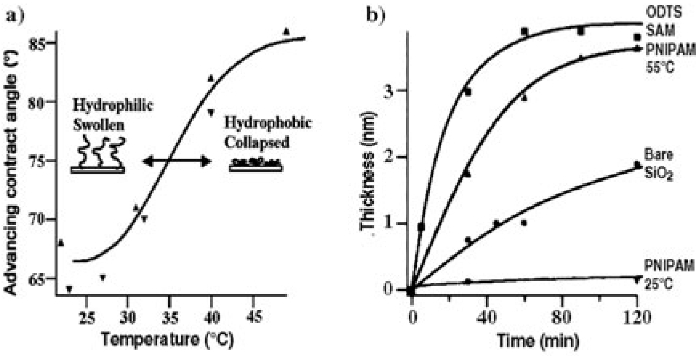

Figure 4. a) Contact angle measurements for water obtained on an azo-initiated PNIPAM film as a function of temperature. b) Ellipsometry results showing the adsorption of HSA from a solution on PNIPAM-coated surfaces relative to other model surfaces.[29a]

Light-driven: An attractive way for creating a smart surface is utilizing derived polymer molecules that have side chains functionalized with azobenzene chromophore.[33] The *trans–cis* isomerization of azobenzene is a well-known photochemical phenomenon. The photocontrollable wetting behavior on this kind of surface with the azo polymer has been extensively studied.[34–36] Transitions between the states (*trans*/*cis*) can be triggered by illumination with light of two different wavelengths. The *cis* and *trans* states differ in their dipole moment, which in turn has also an impact on the corresponding wetting behavior. The formation of water microdroplets on a patterned monolayer can thus be controlled by light. Completely reversible writing and erasing of patterns is carried out as shown in Figure 5.[34] Further more, Jiang et al.[35] transferred a monolayer of a polymer with an azobenzene chromophore in the side chains onto a solid substrate by the Langmuir–Blodgett (LB) technique. The reversible processes of photoisomerization of the LB films induced by light is shown in Figure 6.[35] Films of the polymer

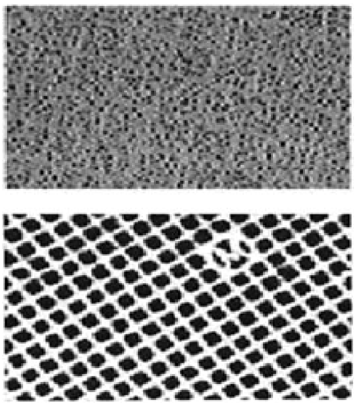

Figure 5. A *cis–trans* pattern written in the monolayer by illumination with UV light and a mask.[34]

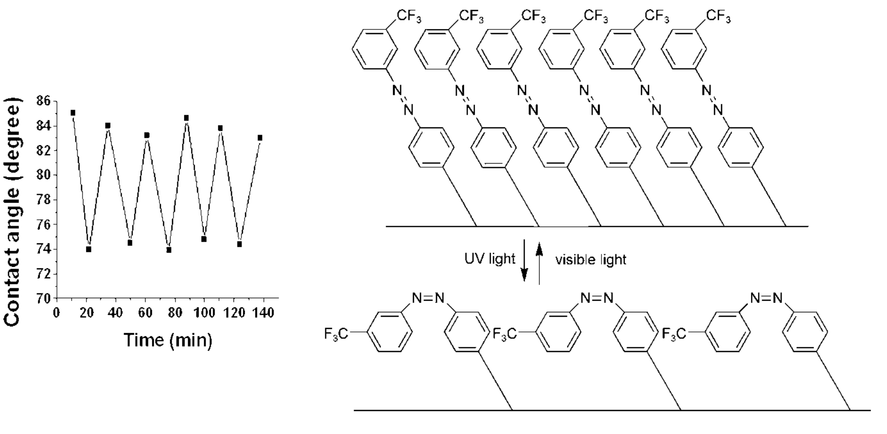

Figure 6. The corresponding interfaces differ in wetting behavior. Left: Reversible wettability for an 11-layer LB film on glass. Over several cycles of irradiation the value of the contact angles gradually decreased. Right: Model of the structural change of a single-layer LB film of the polymer as a result of photoisomerization. Adapted from reference [35].

showed the reversible change of morphological and friction force responses under alternate UV (365 ± 10 nm) and visible (436 ± 10 nm) irradiation. The films also undergo reversible wettability changes with UV and visible light irradiation, which can be directly confirmed by contact angle measurement. Another effective kind of film named as Langmuir–Blodgett–Kuhn (LBK) film can also be used to generate multiplayer assemblies of polymers containing photochromic azo units. The *trans–cis* photoisomerization of the azo molecules alternates them between a highly oriented *trans* configuration and a bent *cis* configuration, thus creates a smart switch upon irradiation.[37a,b] Frank et al. have utilized the layer-by-layer adsorption technique for deposition of polyionic films containing photoactive azobenzene groups on solid substrates. UV light irradiation was responsible for reversible changes in the optical thickness of the films.[37c]

Switchable Surfaces Based on SAMs

Employing special SAMs as switchable surfaces is an interesting subject. The approach is to assemble ordered monolayers followed by switching of the SAM properties by means of an external stimulus, such as light, electrochemical potential, the change of pH, and so on. Lots of efforts have been made to exploit this field and many exciting results have been achieved.[38–42,48–50,54–58] Several typical examples will be discussed in the following section.

Dissociation and re-association of assembled molecules: The dissociation and re-association of the components of the molecules that assemble in the SAM triggered by external stimulation bring remarkable changes for the properties of the resulting SAM.

Many SAMs are made up of supermolecules, among which the most highly investigated classes are the complexes known as pseudorotaxanes. Pseudorotaxanes are supermolecules that are composed of wheel- and axlelike components, and these components are free to dissociate from each other. The reversible association of various pseudorotaxanes is controlled by light and can subsequently behave with machinelike motion.[38–41] Besides, pH can also act on reversible formation of pseudorotaxanes.[42] Figure 7[42] depicts a SAM assembled with pseudorotaxanes containing cucurbituril (CB, a macrocyclic cage compound comprising six glycoluril units)[43,44] threaded onto a molecular string with a 1,2-dithiolane group[45] as an anchoring point toward a gold surface. The pseudorotaxane molecules in the SAM deform under alkaline conditions, while they reform under acidic conditions. Consequently, the obtained pseudorotaxane SAM may behave as an “ion gate” when the SAM is formed on the surface of an electrode. Depending on the presence or absence of the threaded CB, it may block or allow the access of electroactive species to the electrode surface. In other words, the conductance of the pseudorotaxane SAM may be switched under the control of pH. These switching processes are reversible and have been repeated up to three cycles with a ~10–20% decrease in the amount of CB molecules rethreading on molecule string in each cycle.

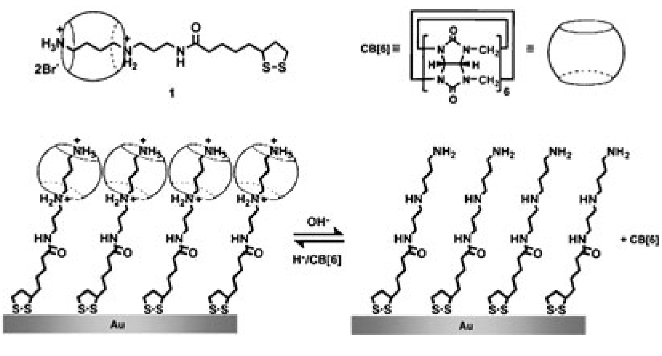

Figure 7. Schematic diagram of a SAM of a pseudorotaxane on Au and the dethreading and rethreading of CB molecules.[42]

Like pseudorotaxanes, certain oligomer molecules can also perform similar switching process taking advantage of their cleaving and reformation, and hence giving switchable wettability.[46] Under irradiation with UV light at 280 and 240 nm, a SAM of long-chain thymine-terminated thiols gives a contact angle change of 26°, which is much larger than that given by SAM of azobenzenes or spyropyrans, and other polymers, which give a rather small contact angle changes of 9° or so.[47] After eight cycles the magnitude of this change reduced to 14°.

Conformational transition: A spectacular approach to switching SAM properties involves reversible conformational transitions of the assembled molecules in the SAM, which can be driven by changes of environmental factors.

Light-driven photochromism of azobenzene resulting from the photoisomerization of azobenzene molecules has been known for years, and on this basis the controlling surface properties have been extensively studied.[48–50] For example, a liquid droplet several millimeters in diameter placed on a substrate surface modified with an azobenzene derivate, *O*-carboxymethylated calixresorcinarene (CRA-CM, Figure 8, left[50]) may be driven to move by asymmetrical photoirradiation. The driving force is attributed to the gradient in surface free energy formed by the photoisomerization of the azobenzene units on the surface. The CRA-CM SAM exposed to UV irradiation (360 nm) results in polar *cis*-azobenzene groups at the terminal positions, leading to an increase in the surface free energy and hydrophilic nature, while photoirradiation with blue light (436 nm) causes the *cis*-to-*trans* isomerization, making the surface hydrophobic. Furthermore, the various motions of a liquid droplet can be achieved and manipulated by varying the direction and steepness of the gradient in light intensity (Figure 8, right[50]).

Taking advantage of the photosensitive monolayered azobenzene, some promising photosensitive devices have been explored, such as optical channel wave-guides, writing/erasing optical memories, and optical image recording. For instance, a nematic liquid crystalline (LC) cell has been con-

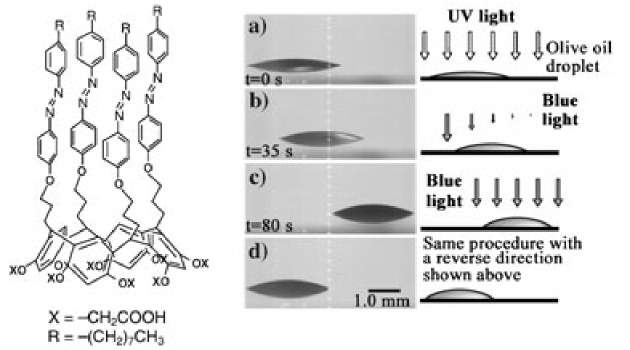

Figure 8. Left: Photochromic azobenzene units as tethers on a macrocyclic amphiphile (CRA-CM). Right: The light-driven motion of an olive oil droplet on a silica plate modified with CRA-CM. Movement of the droplet on a *cis*-rich surface in the direction of higher surface energy moved induced by asymmetric irradiation with 436 nm light perpendicular to the surface (a to c). The contact angles changed from 18° (a) to 25° (c). The moving direction of the droplet could be controlled by varying the direction of the photoirradiation (d). Adapted from reference [50].

structed with azobenzene SAM-modified quartz plates by putting the LC between two modified plates.[51,52] The reversible photoisomerization of azobenzene molecules by alternate exposure to UV and visible light regulates the alignment of a nematic LC between homeotropic and planar modes, and results in great changes of the transmittance through the cell. After 1000 cycles, the transmission through the UV-exposed cell and a crossed polarizer began to decrease and completely disappeared after about 2600 cycles; this behavior may be caused by the degradation of azobenzene units, which reduces the number of effective command molecular units.

Electrical potential stimulation is another convenient method widely used for controlling the surface properties.[53] Construction of low-density ionizable alkanethiolate SAMs (LD-SAM) on gold opens a new way to create reversible surfaces that undergo reversible conformational transitions stimulated by the applied electrical potential.[54,55] In order to ensure there is sufficient space for the conformational transition of alkanethiols, several approaches are employed to control the alkanethiols' density. One solution involves assembling synthetic capped alkanethiolates on gold surface, followed by dissociating the cap, that is, the bulky globular groups.[54] Considering the complexity of the design and synthesis of the globular groups, another alternative method[55] was introduced that generates the LD-SAM on a gold surface by assembling a pre-formed inclusive complex (IC), for example, a cyclodextrin (CD, which can readily form IC with various organic molecules) wrapped alkanethiolate, followed by unwrapping the CD from the anchored IC with suitable solvent. The thus-prepared LD-SAM shows reversible conformational reorientation behavior under negative and positive potential; this then induces observable changes in wettability, which was proved by means of contact angle measurements. Furthermore, an LD-SAM prepared in this way has been employed successfully for controlled assembly of two kinds of fluorescent-labeled avidin with different isoelectric points (Figure 9[55]).

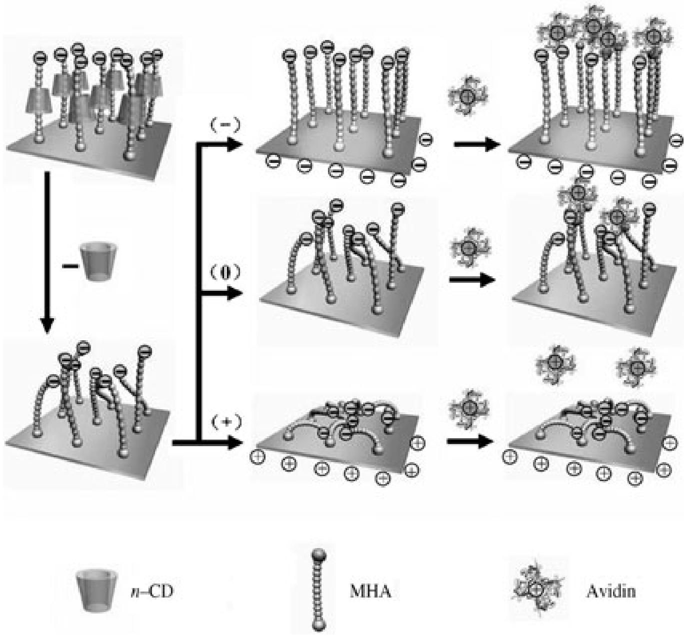

Figure 9. The idealized illustration for the preparation of LD-SAMs, and the conformational transition for anchored 16-mercaptohexadecanoic acid (MHA) molecules at applied potentials and the subsequent protein assembly at negative (−) and positive (+) potential, and the open circuit state (0).[55]

In addition to the above-mentioned LD-SAM investigations, correlative works involving other strategies have also been reported. For example, the SAM formed with alkanethiol molecules terminated with methoxytri(ethylene glycol) has also proved to be reversible by reorienting the terminal methoxy group to make its oxygen atom either exposed or buried when external electrostatic field was applied, thus being hydrophilic or hydrophobic.[56] Static energy minimization and Monte Carlo simulations have been carried out to provide information on the strength of the field.

Switchable attachment: As attachment of molecules onto a substrate is the foundation for the preparation of property-controlled surfaces, to control the switchable attachment process is an essential way to manipulate the functional surface.

Competition between reductive electrochemical desorption of a hydrophobic SAM[57] and its re-formation from alkanethiol in solution has been demonstrated.[58] Consequently, contact angle measurement of an aqueous solution revealed that a hydrophobic monolayer built up with alkanethiol became hydrophilic when the applied potentials change from neutral to negative states. As shown in Figure 10[58] the aqueous electrolyte forms a hemispherical drop on the hydrophobic monolayer of $CH_3(CH_2)_2S$ (Figure 10b) at neutral potentials, while at negative potential it spreads spontaneously over the area of the triangle and is bounded by the hydrophobic SAM of $CH_3(CH_2)_{15}S$ (Figure 10c). Subsequently, when the neutral potential is applied, the hydrophobic monolayer of $CH_3(CH_2)_2S$ reforms,

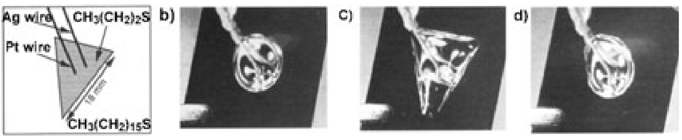

Figure 10. Potential-dependent wetting of an aqueous solution of electrolyte containing $CH_3(CH_2)_2SH$ on a gold film patterned with self-assembled monolayers of $CH_3(CH_2)_2S$ and $CH_3(CH_2)_{15}S$. a) Schematic diagram of the patterned surface. Photographs of liquid at b) $E=0$ V, c) $E=-1.4$ V, and d) $E=0$ V.[58]

and the drop of aqueous electrolyte retracts toward the center of the triangle (Figure 10d). Because the change in wettability is dependent on the distribution of the organic molecules in the monolayer, this method can be useful for patterning surfaces with areas of SAMs that have contrasting properties under electrical potential.

Other work relating to the switchable assembly of SAMs with practical applications have also been carried out. For example, the change of pH between 8.7 and 3 controls the reversible attachment of an pentamidine monolayer onto a gold surface functionalized with mercaptoalkanoic acid; this method has been successfully used for selective adsorption of phosphate biomolecules.[59,60] In addition a completely reversibly adsorption and desorption of avidin from a hydrophobic thiol-functionalized surface was achieved and has been employed for constructing micromachine silicon channels, in which fluid flow was controlled by the reversibly switchable wettability of the surface.

Undoubtedly, the controlled reversible SAM may lead to various important applications, such as controlling protein adsorption/release in a functionalized capillary or microfluidic channel, design and microengineering of intelligent protein chips for bioseparation, or data storage; for some of these applications primary development has already been achieved. Interesting areas for future work would be to explore and extend alternative stimuli and the switchable surface properties to achieve more types of response.

Switchable Surfaces Based on Metal Oxides

Metal oxide semiconductors (TiO_2 and ZnO): Much attention in the development of surface science and technology has been paid to the progress in understanding the physical and chemical properties of semiconductor surfaces. Among the various semiconductor materials, titanium dioxide (TiO_2) and zinc oxide (ZnO) are the classical compounds employed to create a smart reversible substrate owing to their unique chemical properties. Photoinduced surface wettability conversion before and after UV illumination has been observed.[62]

TiO_2 has been studied far more than other semiconductor photocatalysts owing to its strong oxidizing power, chemical inertness, and nontoxicity.[63–65] Since photoinduced water-splitting on TiO_2 electrodes[66] was discovered, a lot of effort has been made to research TiO_2 materials, which have been widely adopted as potential substances for solar energy conversion and environmental purification. Recent investigations reveal that a UV-light-illuminated TiO_2 single-crystal surfaces exhibit a 0±1° contact angle for both water and oil (Figure 11[67]), indicative of a highly amphiphilic surface against its native hydrophobic surface with a water-contact angle of 72°±1° (Figure 11[67]); long-term storage in dark resulted in reconversion of the surface's hydrophobic nature.[67,68] This result has found application in the preparation of TiO_2-coated glass that is antifogging (Figure 12[68])

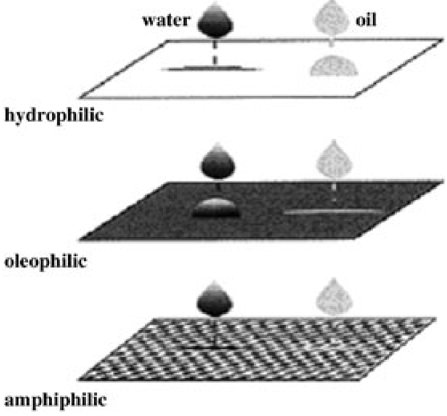

Figure 11. A schematic diagram depicting hydrophilic, oleophilic, and amphiphilic surfaces with distinct wettabilities for oil and water. Adapted from reference [67].

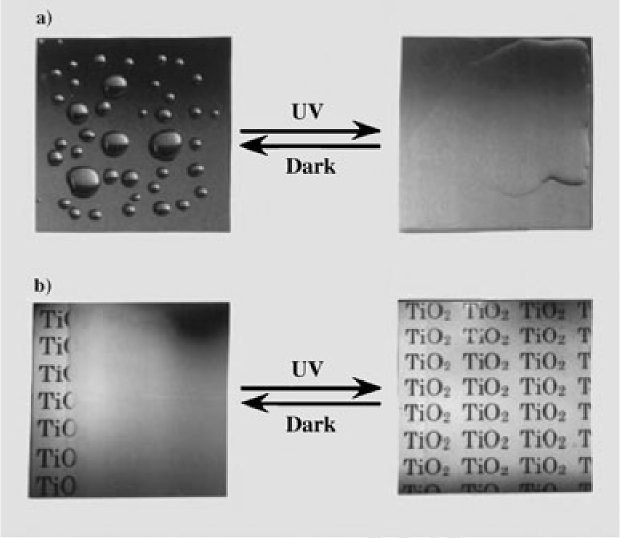

Figure 12. a) Effect of ultraviolet radiation. Left: A hydrophobic surface before ultraviolet irradiation. Right: A highly hydrophilic surface after ultraviolet irradiation. b) Illustration of antifogging surfaces. Left: A hydrophobic TiO_2-coated glass was exposed to water vapour; a fog formed (small water droplets) and obscured the text on paper placed behind the glass. Right: An antifogging surface was created on the glass by ultraviolet irradiation. The formation of water droplets was prevented by the high hydrophilicity, making the text clearly visible. Reproduced with permission from *Nature* **1997**, *388*, 431–432. Copyright 1997 Nature Publishing Group.

and self-cleaning; the self-cleaning property, in particular, provides prospects for practical applications.[68]

Additionally, ZnO thin films can even show a reversible switching from super-hydrophobic to super-hydrophilic by alternation from UV illumination to dark storage. This phenomenon can be attributed to the surface free energy and surface roughness, which are two main factors dominating the surface wettability.[69]

The switchable transition of surface wettability is a completely new concept for ZnO and TiO_2 thin films on solid substrates. Research in this area will have important implications for the further understanding of the wettability conversion phenomenon, also the creation of self-cleaning materials, and will promote the industrial applications for this kind of semiconductor in the future.

Conclusion

We have reviewed reversibly switchable surfaces that are generated by using versatile kinds of methods, including photoirradiation, electric field, thermal treatment, solvent inducement, and so on, with different types of molecules, such as polymers, SAMs, and metallic oxide. The controllable conversion of surface properties is normally attributed to the morphological changes of the molecules mentioned above. It is very challenging to tune a wide range of surface properties to meet the particular industrial demand, for example, wettability, adhesive properties, conductance, permeability, roughness, and biocompatibility. For polymers, changing the surrounding media, temperature, and irradiation with light are normal ways to control the wettability of solid surfaces (hydrophilic to hydrophobic). As for SAMs, controlling components of the molecules in monolayer, molecular conformation, and growth of the SAM can lead to switching of the surface properties. The driving forces also usually include pH, light, electrical potential, and so on. For metallic oxide films, photoirradiation is the main strategy for establishing smart surfaces that undergo a conformational transition and in turn show reversible macroscopic properties. The switching of surface properties driven by external stimuli is of potential interest, because the resulting interfaces can facilitate the assembly of inorganic nanoparticles, proteins, living cells, drug molecules, and so on. All the above-mentioned intelligent switchable surfaces hold a great promise in designing bioanalytical methods, environmental cleanup, microfluidic devices, biochips, sensor devices, controllable drug release, and smart materials devices.

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