Reversibly switchable wettability

Bingwei Xin and Jingcheng Hao*

Received 8th July 2009
First published as an Advance Article on the web 20th October 2009
DOI: 10.1039/b913622c

This *critical review* outlines the current state-of-the-art research on the reversibly switchable wettability of surface brought about by external stimuli and the exchange of counterions. Chemical composition and surface topography are the two key factors in the wettability of solid substrates. Applying external stimuli and exchanging counterions of ionic liquids and polyelectrolyte films are valuable approaches for rendering the change in surface chemistry and/or topography, and for driving the transition between hydrophilicity and hydrophobicity of surfaces. Through the combination of stimuli-responsive films and micro-/nanostructural surfaces, smart surfaces with reversible switching between superhydrophobicity and superhydrophilicity have been achieved. As an important advancement in reversibly switchable wettability, this review briefly introduces ionic liquids (ILs) as on–off systems to obtain reversibly switchable wettability and then discusses in more detail the methods to induce the reversibly switchable wettability of surfaces modified by ILs, additives, or thin films. In addition to reversibly switchable wettability mechanisms, open problems and potential solutions are discussed (157 references).

1. Introduction

Wettability of a solid surface is an important property, and it has been widely studied to fabricate superhydrophobic surfaces. Surface properties (hydrophobic or hydrophilic) are generally characterized by measuring the contact angle (CA) of a liquid droplet sitting on the surface. When water is used, a CA less than 90° is indicative of a hydrophilic surface, while a CA greater than 90° is hydrophobic. Two extreme cases, superhydrophobic surface (with CA larger than 150°) and superhydrophilic surface (with CA lower than 5°),[1,2] have attracted great attention because of their importance in both fundamental research and practical applications. Research on superhydrophobic surfaces focuses on their potential in functional coatings, drug delivery, and biomimetic materials.[3–7] It is well-known that surface wettability is governed by surface chemistry and morphology.[8–10] Chemical composition determines the surface free energy, and a lower surface energy leads to higher hydrophobicity. Generally, films terminated by nonpolar groups such as –CF_3 possess lower surface energy. Fluoroalkylsilane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, FAS) is one of the most conventional chemical modification agents[11–13]

Key Laboratory of Colloid and Interface Chemistry (Shandong University), Jinan, 250100, P.R. China. E-mail: jhao@sdu.edu.cn; Fax: +86-531-88366074

Bingwei Xin

Dr Bingwei Xin received her PhD from Zhejiang University in 2007. She is currently working a postdoctoral research with Professor Jingcheng Hao at Shandong University on the reversible wettability of solid surfaces. She has published 18 original articles.

Jingcheng Hao

Dr Jingcheng Hao received his PhD from the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (CAS) in 1995. From 1995, he studied postdoctoral research at the Lanzhou Institute, Nagoya University (Japan), Bayreuth University (Germany), and SUNY at Stony Brook (USA). In Dec. 2002, he jointed Shandong University. He is now a full-professor and director of Key Laboratory of Colloid and Interface Chemistry, Ministry of Education. His research focuses on Colloid and Interface Sciences including surfactants in solution and self-assembly at all scale in bulk solutions and at surfaces. He obtained the National Outstanding Youth Funds (2006), Changjiang Scholars (2007), and other scientific awards. He has published 170 articles including original papers, reviews and chapters of books.

used to construct superhydrophobic surfaces. On smooth surfaces, however, chemical modification has a certain limitation in improving surface wettability. Until now, the maximum CA can only reach about 120° for smooth CF_3-terminated surfaces.[14,15] According to theoretical considerations,[16] the surface roughness is a crucial factor in a superhydrophobic surface. At the same time, roughness is very important to surface hydrophilicity because of the 2D or 3D capillary effect,[17,18] that is, roughness will amplify the wetting behavior of substrates. Inspired by superhydrophobic living organisms in nature such as lotus leaves and water-strider legs,[19,20] increasing attention is given to studies on special surface roughness with micro- (or nano-) structures. Various elegant approaches have been proposed for the preparation of fine surface geometrical structures such as template synthesis,[21] phase separation,[22] electrochemical deposition,[23] electrohydrodynamics,[24] crystallization control,[25] chemical vapor deposition (CVD),[26] self-assembly,[12] and so on. By combining hierarchical micro/nanostructure with appropriate materials, a variety of surfaces with superhydrophobicity or superhydrophilicity have been synthesized[27] including polymer films,[28] aligned carbon nanotubes (ACNTs),[29] inorganic metal oxides films,[30,31] and so on.

Smart surfaces with reversibly switchable wettability, especially switching between superhydrophobicity and superhydrophilicity, are of great importance due to their numerous industrial applications such as in self-cleaning surfaces, microfluidic tools, tunable optical lenses, lab-on-chip systems, and so on.[4,9,32] Versatile approaches including appropriate external stimuli[1,33] and exchange of counterions[34,35] can dynamically trigger the reversible wettability conversion. External stimuli, such as light illumination, temperature, solvents, electrical potential, pH, and others, can change the surface conformation and/or morphology of stimuli-sensitive materials, which results in the change of surface wetting behavior. This method has been intensively studied, and many positive results have been obtained. Recently, the exchange of counterions of charged organic films and ionic liquid layers was found to be a novel and valuable strategy to achieve reversible wettability conversion because the nature of the counterions strongly influence surface behavior. Although currently it is only a burgeoning research field, its potential advantages and theoretical significance make it relevant in surface science applications. Nowadays, a variety of inorganic oxide films and organic materials are used as stimuli-sensitive materials. In general, inorganic oxides offer clear advantages over organic molecules in terms of structural and photochemical stability, low toxicity, and remarkably larger wettability changes.[36] However, compared with inorganic metal oxides, organic compounds are more varied, ranging from photo-sensitive materials and thermal-responsive films to pH-stimulated polymers. Furthermore, organic polymers can undergo conformational reorientation, such as from *trans* to *cis* isomer or from bending to stretching form when changed from one temperature to another, or from one solvent to another. Stimuli-responsive polymers, in some cases, have the potential advantage of being able to simultaneously control the surface energy and topography. Moreover, the sophisticated design of organic films provides a versatile platform for introducing appropriate chemical functionalities to satisfy various practical demands.[37]

In this critical article, the methods to produce reversibly switchable wettability of surfaces are reviewed in detail. In section 2, we describe the stimulating effect of various external stimuli on switchable wettability changes, particularly the reversible transformation between superhydrophobicity and superhydrophilicity through the amplifying effect of surface roughness and the reversible transition of surface chemistry and/or conformation. In section 3, reversible wettability *via* the exchanging counterions of ionic liquids and polyelectrolyte brushes is discussed. Surface free energy and geometrical structure play key roles in the wettability of solid substrates. The significant effect of micro- (or nano-) surface roughness of inorganic oxides or organic compounds is highlighted when fabricating superhydrophobic and superhydrophilic reversible-switched surfaces. Finally, we provide conclusions about this review and also provide an outlook on the future of this research. Considering the rapid developments in this topic, we would like to point out that the methods presented here approximately cover the period from 2003 to March 2009.

2. Reversible switching of surface wettability *via* external stimuli

2.1 Light illumination as external stimulus

Light is one of the most important external stimuli.[38] A variety of photo-responsive inorganic oxides and organic polymers undergo the transition from larger CAs to relatively lower CAs upon ultraviolet (UV) illumination, reverting to the original states with larger CAs after the UV-irradiated films are placed in the dark or exposed to visible (Vis) illumination. This alternating transition can repeat for several cycles under this environment.

Among the photo-sensitive inorganic oxides, TiO_2 and ZnO are the most studied semiconductors. TiO_2 films can remain under sunlight and natural rainfall due to their intrinsic photocatalytic and photo-stimulated properties, and they have been widely used as anti-fogging and self-cleaning materials. In 1997, Fujishima[18] found that the water CA of anatase TiO_2 polycrystalline films was 72 ± 1°, and the wetting behavior could be reversibly switched using UV irradiation. Subsequently, wettability conversion has been observed on both anatase and rutile TiO_2 surfaces in the form of polycrystals or single crystals.[39,40] Since then, research efforts have been devoted on the modulation of the wetting behavior of TiO_2.[36,41] Among these studies, coating with low-surface-energy compounds has received great attention. However, desired wettability-switching surfaces, have yet to be produced. For example, the CA of TiO_2 colloidal crystal films modified with FAS is only switched between 100 and 0°.[42]

Therefore, there is increasing attention on the introduction of fine surface roughness to TiO_2 films. For example, based on the flower-like Al_2O_3 gel film, a rough TiO_2 gel layer modified with FAS was prepared in 2000.[43] A combination of microstructure and chemical modification succeeded in obtaining superhydrophobic surfaces with CA larger than 150°. After exposure to UV light, the films would switch to

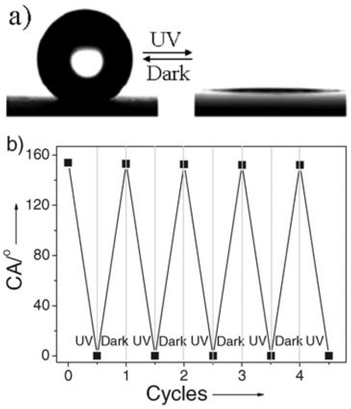


Fig. 1 (a) Photographs of a spherical water droplet with a CA of 154 ± 1.3° (left) and a flat water film with a CA of 0° (right) before and after the films were exposed to UV illumination, respectively.[44] (b) Cycles of reversible superhydrophobicity/superhydrophilicity transformation of the films by alternating between UV irradiation and storage in the dark.[44]

superhydrophilic with CA smaller than 5°. With the development of techniques in fabricating surface roughness, lotus leaf-like inorganic TiO_2 nanorod films with dual-scale hierarchical structures were fabricated and had their wettability modulated from 154 ± 1.3° to about 0° with several cycles before and after UV irradiation without any chemical modification (Fig. 1(a)).[44] Recently, superhydrophobic TiO_2 nano-strawberry rutile films were prepared on a large scale from aqueous solution *via* a seeded growth method at low temperature.[45]

To obtain a simple and reproducible method to roughen surfaces, Fujishima adopted a CF_4 plasma etching technique to produce TiO_2-based superhydrophobic surfaces.[46,47] For example, after coating with an octadodecyl phosphonic acid (ODP) monolayer, the discontinuous TiO_2 wedge-like micro-textural films were formed after etching for 30 s, which showed water CAs larger than 165°. After 1 h of UV illumination, the surfaces were converted to superhydrophilic ones with CA about 0°.

Nowadays, TiO_2-based surfaces with reversible superhydrophobic and superhydrophilic transition are widely used in smart surfaces and other functional materials. However, some rough morphologies lead to severe light scattering due to their roughness being larger than the wavelength of the visible light. That is, by increasing the surface roughness, it is possible to induce the loss of the optical transparency and other desirable properties of the solid substrates. To overcome this disadvantage, reducing the level of surface roughness to a scale much smaller than the wavelength of visible light is a promising strategy.[48]

ZnO is another important photo-responsive inorganic oxide that possesses optical, electronic and acoustic properties. It shows a similar wetting behavior and conversion mechanism to the TiO_2 surface.[49,50] Based on flat ZnO substrates, the maximum water CA is only 109°. Considering the amplifying effect of surface roughness on superhydrophilicity/superhydrophobicity, efforts have been devoted to studying the micro-/nanostructural surfaces on a wide range, from nanoporous ZnO films,[51] aligned ZnO nanorod films[52] to nanocolumnar ZnO surfaces,[53] and to hierarchically structured ZnO film[54] and nanoprotrusions,[55] and so on. Correspondingly, many synthesized methods are adopted including electrochemical deposition, sol–gel method, chemical vapor deposition, pulsed laser deposition, and others. Combining certain microroughness with low-surface-energy materials, ZnO-based surfaces switch between superhydrophobicity and superhydrophilicity upon alternating UV irradiation and storage in the dark.

In addition, WO_3,[56] V_2O_5,[57] SnO_2,[58] and some metal alloys[59] are also found to be photo-sensitive, and reversible conversions between the two extreme cases (hydrophilicity/hydrophobicity) are observed under the amplifying effect of roughness. Significantly, α-Fe_2O_3 nanoflake films were observed for the first time to have reversible wetting behavior, which reversibly switched from CA about 160 to 0° stimulated by UV irradiation.[60] It is well-known that Fe_2O_3 is a cheap and extensive inorganic oxide, and its reversible wetting property will open up a new means to study wettability switching surfaces.

Besides UV illumination, X-rays have been observed to be an effective stimulus that can tune successfully the wettability of a variety of inorganic materials (ZnO, p-Si, Al_2O_3, $SrTiO_3$, TiN, ZnS, CuO, Ag_2O and Cr_2O_3).[61] The wettability can be reversed between on and off by exposure to X-rays.

Up to now, photo-responsive inorganic oxide surfaces (TiO_2, ZnO, WO_3, V_2O_5, SnO_2 and so on) readily show superhydrophobic/superhydrophilic transitions by combining appropriate roughness and chemical modification, and this reversible switching of wettability has aroused great interest in photo-related applications. However, the photo-driven wettability conversion requires several days, thereby restricting application in smart devices.

In addition to semiconductor inorganic oxides, some organic materials containing photochromic functional groups, such as azobenzenes,[62] spiropyrans,[63] dipyridylethylenes,[64] stilbenes,[65] and pyrimidines[66] also have the ability to undergo reversible transition of conformation triggered by UV/visible irradiation, leading to changes in their wetting properties.[67] Among these materials, azobenzene and its derivatives are particularly promising as photo-stimulated materials, and they have been widely investigated as such.[68] The azobenzene layers will transform from *trans* to *cis* isomers upon UV irradiation and this is reversed by visible irradiation (Fig. 2).[69] The *trans* isomer exhibits a higher water CA because of a smaller dipole moment and lower surface energy, while the *cis* form has a lower water CA due to its higher dipole moment and larger surface free energy. Consequently, the reversible *trans–cis* photoisomerization results in the wettability change of azobenzene-modified surfaces, and it should withstand repeated light-induced cycling. However, on flat surfaces, the change of water CA of azobenzene is less than 10° upon alternating UV and visible irradiation.[70] Such a small change encourages efforts to study the design of fine surface roughness and molecular compositions.

In 2005, Jiang *et al.*[69] obtained a rough silicon wafer with patterned square pillars through photolithography and the inductive coupling plasma etching technique, on which an electrostatic self-assembly azobenzene monolayer was prepared. It was found that the wetting behavior was related to the pillar spacing on the silicon. As shown in Fig. 3, the decrease of the

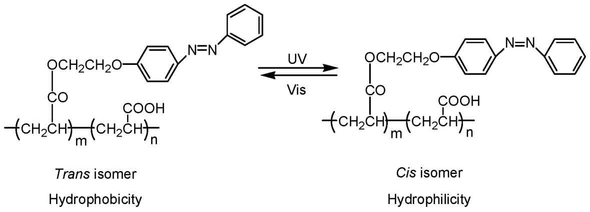


Fig. 2 The *trans* and *cis* structures of azobenzene upon UV and visible irradiation, as illustrated by Jiang.[69]

pillar spacings led to the increase of CA values under both *trans* and *cis* forms. As the spacing changed from flat (pillar spacing of ∞) to 40 μm, the water CA value rose from 78.3 ± 1.5 ° to 152.6 ± 1.9° under the *trans* state while the CA underwent a slight change in the *cis* form. However, the maximum change in CA was only about 66° between *trans* and *cis* isomers based on 40 μm spacing. Obviously, the conversion was limited between superhydrophobic and superhydrophilic states.

The unique wetting property of trifluoromethyl makes it a perfect group to decrease the surface free energy in organic molecules.[32] As shown in Fig. 4, when fluorine-containing azobenzene films are exposed to visible light, the molecules are in the *trans* form, and the $–CF_3$ groups are outside the monolayer, which makes the films exhibit hydrophobicity. However, fluorinated sites will disappear from the surface due to *trans*-to-*cis* isomer change upon UV irradiation, changing the films to the hydrophilic state.

By combining fluorine-containing azobenzene films with ideal surface roughness, Cho *et al.*[71] for the first time achieved superhydrophobic/superhydrophilic transition of organic molecules *via* UV/visible irradiation. Using 7-[(trifluoromethoxyphenylazo)phenoxy]pentanoic acid (CF3AZO) (Fig. 5)[71,72] as a photoswitchable agent, they fabricated nanoporous organic–inorganic hybrid multilayer films *via* the layer-by-layer (LBL) technique with poly(allylamine hydrochloride) (PAH) and SiO_2 nanoparticles as the polycation and polyanion, respectively. The number (*n*) of PAH/SiO_2 bilayer deposition cycles had a direct effect on surface wettability, as illustrated in Fig. 6. With the increase of the number of PAH/SiO_2 bilayers, the CA of multilayer films gradually increased from 76 ± 1° (flat, $n = 0$) to 152 ± 3° ($n = 9$) in the *trans* isomer. When the samples were irradiated with UV light, the CA slowly decreased from 71 ± 1° (flat, $n = 0$) to $<5 \pm 1°$ ($n = 9$); that is, with nine PAH/SiO_2 bilayers, the films could reversibly switch between superhydrophobicity and superhydrophilicity *via* alternating UV/Vis light illumination.

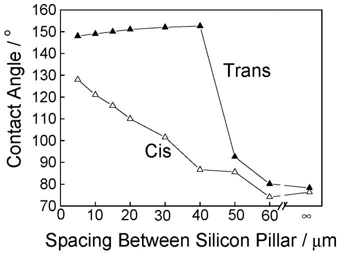


Fig. 3 The variation of water CA of a photo-responsive monolayer on a patterned substrate with pillar spacing. The spacing of ∞ represents a flat substrate.[69]

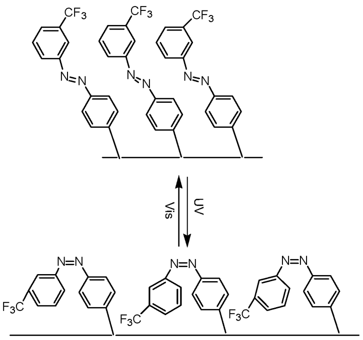


Fig. 4 Model of the structural change of a single-layer LB film of a fluorinated polymer accompanied by photoisomerization.[32]

Similarly, spiropyran is another type of photochromic organic molecule, and it possesses a light-switchable wetting property.[63,73] Its closed nonpolar form with hydrophobicity and its highly polar open type with hydrophilicity may be reversibly tuned upon UV and Vis irradiation (Fig. 7). Obviously, the surface wettability of films modified by spiropyrans can be switched and can be further amplified by introducing surface roughness.[74]

2.2 Temperature as external stimulus

Temperature can trigger change in chemical compositions and/or surface roughness of thermo-sensitive compounds, and hence it is considered a promising external stimulus to easily alter the surface wettability. Poly(*N*-isopropylacrylamide) (PNIPAAm) is an excellent thermal responsive polymer with a lower critical solution temperature (LCST) of about 32–33 °C.[75–78] Below the LCST, the intermolecular H-bonding between PNIPAAm chains and water molecules is predominant, which results in an extended brush structure displaying hydrophilicity. Above the LCST, intramolecular H-bonding in the PNIPAAm chains leads to a compact and collapsed conformation with hydrophobic property (Fig. 8).[1,79] Apparently, the reversible wettability conversion induced by the conformational change can be achieved in a narrow temperature range of about 10 °C and can repeat for many cycles.

Generally, PNIPAAm films are easily grafted on both flat and rough substrates using the surface-initiated atom transfer radical polymerization (ATRP) technique.[80,81] On the flat surface modified by PNIPAAm, however, the wettability is only changed from 63 to 93° when the temperature is elevated from below to above the LCST. Surface roughness has been intensively investigated, and many achievements have been reported. Nanostructured PNIPAAm-grafted membranes were prepared on nanoporous aluminium oxide with nominal pore sizes.[82] As shown in Fig. 9, when the pore size was 200 nm, the PNIPAAm films exhibited superhydrophobicity

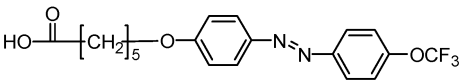


Fig. 5 Chemical structure of the 7-[(trifluoromethoxyphenylazo)-phenoxy]pentanoic acid (CF3AZO).[71,72]

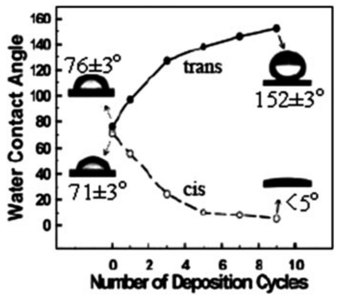


Fig. 6 The relationships between the number (*n*) of deposition cycles (*trans* and *cis*) and the water contact angles.[71]

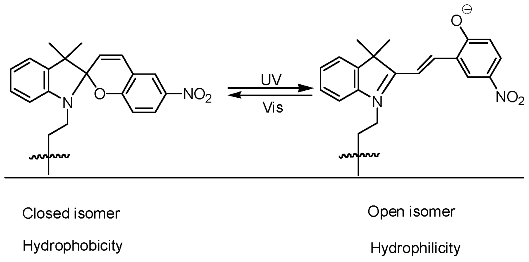


Fig. 7 Switching of surface-bound spiropyran between nonpolar (left) and polar (right) forms under UV and visible irradiation, respectively.[73]

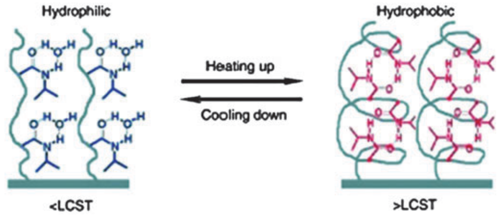


Fig. 8 The effect of temperature on the change in hydrogen bonding and corresponding conformation of PNIPAAm.[1,79]

at 40 °C, while the CA was about 40° at 22 °C. Obviously, the introduction of surface roughness remarkably improves the change in the range in wettability.

In order to improve further surface wetting behavior, PNIPAAm films were grafted on a well-controlled rough silicon surface *via* surface-initiated ATRP (Fig. 10).[79] As expected, the change of CA depended strongly on the spacing (*D*) on the silicon surface. Above 40 °C, the CA increased gradually from 93.2 ± 2° (flat substrate) to 149.3 ± 2.5° (*D* ≈ 6 μm). Below 25 °C, the films would change gradually in CA from 63° to about 0° with the decrease of spacing. The experimental results showed that the substrate with *D* ≈ 6 μm could achieve reversible switching between superhydrophilicity and superhydrophobicity in a narrow temperature range of about 10 °C. However, wetting behavior below *D* = 6 μm has not been reported.

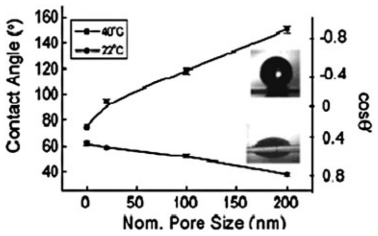


Fig. 9 Water CA data (sessile drop) measured at 22 and 40 °C for PNIPAAm grafted to aluminium oxide surfaces with varying nominal pore sizes.[82]

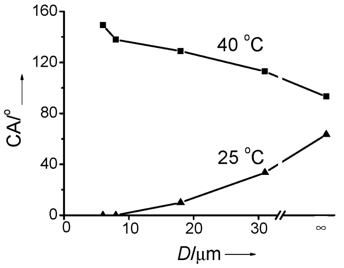


Fig. 10 The relationships between groove spacing (*D*) of rough surfaces and the water CAs at 25 and 40 °C.[79]

With the development of smart materials, dual-responsive surfaces with tunable wettability have been intensively studied. To date, temperature/pH[83] and temperature/light[84] dual-sensitive surfaces have been fabricated by the introduction of multi-responsive functional groups to films. For example, adding the pH-dependent component acrylic acid (AAc) to NIPAAm leads to temperature/pH dual-stimulated P(NIPAAm-*co*-AAc) copolymer thin films. These films are hydrophilic at low temperatures and hydrophobic at high temperatures when the pH is fixed, and hydrophobic at low pH and hydrophilic at high pH when the temperature is fixed. At 45 °C and with pH values of 2, both the PAAc and PNIPAAm components are at their most hydrophobic, and the water CA is 148.8°; however, the CA is 7.6° on the rough substrate at 21 °C and with a pH value of 11. This indicates that the wetting behavior is controlled simultaneously by temperature and pH. Using the same method and utilizing the azobenzene moiety to act as the photo-sensitive part, copolymerizing *N*,*N*-dimethylacrylamide with 4-phenylazophenyl acrylate will lead to temperature/light dual-responsive surfaces. Meanwhile, the poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) brush is an inherently pH- and temperature-responsive polymer with an LCST at around body temperature.[85]

PNIPAAm, as a well-known thermo-stimulated polymer, has been widely used in smart surfaces and bioapplications, such as in controlled drug delivery, solute separation, tissue culture substrates, *etc.*[76–78,86] However, its moderate cytotoxicity at 37 °C[87] has urged researchers to search for substitutes.[88–91] Copolymer P(MEO$_2$MA-*co*-OEGMA) composed of 2-(2-methoxyethoxy)ethyl methacrylate (MEO$_2$MA) and oligo(ethylene glycol) methacrylate (OEGMA) is found to be a perfect thermo-responsive material.[88,92] Owing to its non-toxic and non-immunogenic properties and its LCST in water, it is an ideal substitute for PNIPAAm. Interestingly, its LCST can be finely tuned anywhere between 26 and 90 °C depending on the OEGMA content.

As discussed above, with increasing temperature, the conventional temperature-driven wettability conversion is from hydrophilicity to hydrophobicity. However, hard foamy films with porous structure prepared by condensing organotriethoxysilanes exhibit a reverse process, that is, the superhydrophobic-to-superhydrophilic conversion will occur when the temperature is raised.[93]

2.3 Solvent and solute as external stimuli

Treated with different solvents, some materials, including heterogeneous (mixed) polymer brushes (HPBs), xerogels, and siloles with special structures, will change in molecular morphology and corresponding wetting property.

A combination of two moieties with different solubility in the same thin polymer coating leads to HPBs which exhibit different components as the topmost surface layer in different solvents.[94,95] For instance, in nonpolar solvents, the hydrophobic polymer chains are in extended configuration, while the hydrophilic chains are in collapsed states. As a result, the hydrophobic chains with lower surface energy become the topmost surface layer. In contrast, the reverse will occur in polar solvents. It is obvious that the intriguing property of dramatic surface reorganization results in the modulation of the surface wettability when exposed to different solvents.

Polystyrene (PS) is conventionally used as hydrophobic moiety in solvent-responsive HPBs, and many copolymers containing it have been prepared in special shapes.[95] For example, Y-shaped block copolymers composed of PS and hydrophilic poly(acrylic acid) (PAA) grafted to a silicon surface exhibit the desired solvent-responsive wetting property.[96] Upon exposure to toluene or cyclohexane, which are both good solvents for PS, the topmost surface layer becomes predominantly composed of PS arms, and the PAA arms collapse into cores. In this case, the CA value reaches 79 ± 3°. However, after treatment with water, which is a selective solvent for PAA, the CA will decrease to 52 ± 3° because PS is partially covered by PAA chains.

ABA-type triblock copolymer brushes, where the middle block has different physicochemical properties from the end blocks, are another kind of HPBs that have aroused great interest with regard to solvent-responsive surfaces. Taking PMA-*block*-PS-*block*-PMA (PMA: poly(methyl acrylate)) on Si/SiO_2 as an example,[97,98] when treated with dichloromethane (a good solvent for all the blocks), the films adopt an extended brush configuration, and hydrophilic PMA is at the topmost surface layer, displaying a CA of 69° (Fig. 11), however, when the films are exposed to cyclohexane (a good solvent for only the middle block, PS) they are in folded brush conformation, and they exhibit high hydrophobic property with CA = 90°. It is found that PS-*b*-PMA-*b*-PS films exhibit similar properties.

Like other cases, a suitable morphological texture of surfaces in solvent-sensitive materials is essential for superhydrophilicity/superhydrophobicity. In 2003, Minko *et al.*[94] fabricated two-level structured surfaces and successfully prepared a smart surface with reversible transformation between two extreme cases. The first level was a poly(tetrafluoroethylene) (PTFE) substrate with needle-like morphology of micrometer size prepared by ammonia plasma etching, on which PSF-COOH (PSF: pentafluorostyrene) and P2VP-COOH (P2VP: poly(2-vinylpyridine)) were attached by hydroxyl and amino groups. The second level was made up of nanoscopic demixed-polymer brushes. After treatment with toluene, the top of the films became predominantly composed of the hydrophobic PSF components, and the water CA was measured as 160°. Upon exposure to water (pH 3), the hydrophilic P2VP moieties became the outer layers, driving a drop of water to spread on the surface.

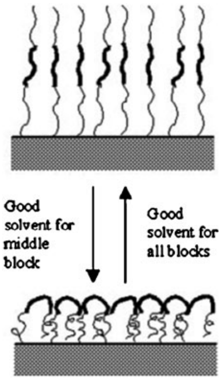


Fig. 11 Reversible response of triblock-copolymer brushes to different solvents.[97,98]

Interestingly, xerogels prepared from tris-urea-based gelators (Fig. 12) have been demonstrated to be modulated between hydrophobicity and hydrophilicity by applying a sol–gel process with different solvents.[99] The morphologies and surface characteristics of the tripodal gelators are strongly influenced by the nature of the gelling solvents. The reason is that the cooperation of hydrogen bonds, hydrophobic interactions, and azobenzene–azobenzene interaction aggregation ability results in two-dimensional self-assembly, driving the formation of different nanostructures in different solvents. In a polar solvent such as *n*-BuOH, the xerogels exhibit a regular flake-like structure with small CA (80.3°). When exposed to a nonpolar solvent such as xylene, the films present a cabbage-like topography with approaching superhydrophobicity (CA 146°). The reversible switching between the *n*-BuOH xerogel and the xylene one was reversed several times by alternately changing solvents.

Recently, a silole also revealed aggregation-induced wetting behavior due to change in the mode of solid-state molecular packing under different external conditions.[100] Exposed to ethanol vapor, 1,2,3,4,5-hexaphenylsilole (HPS) (Fig. 13) changed to nanostructures, on which water droplets could shrink with the contact angle of 136.3 ± 1.6°. However, after fuming with toluene vapor, the surface would return to its initial amorphous solid state with the CA returning to the original value of 97.0 ± 1.5°.

It is worth noting that solute anion identity and concentration can also induce changes of wettability. Immersed in a variety of aqueous solutions with different concentrations of salts such as Na_3Citrate, NaH_2PO_4, Na_2SO_4, NaSCN and pure water, PNIPAAM-*c*-PNASI (poly(*N*-acryloxysuccinimide)) films[101]

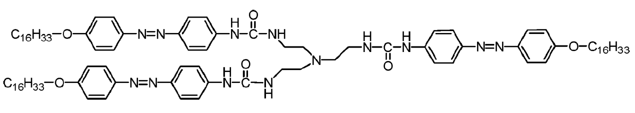


Fig. 12 Chemical structure of tris-urea-based gelator.[99]

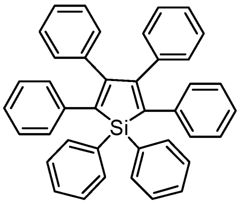


Fig. 13 Chemical structure of HPS.[100]

grafted on silica nanoparticles by covalent layer-by-layer assembly exhibit different degree swelling states, and hence trigger reversible switching between hydrophilicity and hydrophobicity.

2.4 Electrical potential as external stimulus

The best advantage of using electrical potential as an external stimulus is its ability to control the surface chemistry and/or morphology in a few seconds or less. Therefore, it is considered a simple, versatile, and effective external stimulus to switch smart surface wettability.[102,103]

The conformational reorientation of polyelectrolytes is a common phenomenon induced by electrical potential. Choi[104] found that a self-assembled monolayer (SAM) of (16-mercapto)-hexadecanoic acid (MHA) deposited on a gold surface could undergo the transition between straight and bent molecular conformations by applying an electrical potential. As shown in Fig. 14, the molecules revealed hydrophilicity in the straight forms due to the carboxylate anion on the topmost layer, while they displayed hydrophobicity in the bent states because of the exposure of the hydrophobic tails outwards. The two inverse situations rendered the change of surface wettability in the range of CA from 20 to 30°. However, in the process of conformational reorientation, sufficient space was required to ensure the bending of alkanethiol. Hence, the SAM must be prepared as a low-density form. Based on the same reason, low-density protein assembly monolayers with switchable property were prepared in 2004.[105]

Moreover, electrical potential may also induce the reduction–oxidation (redox) reaction of polyelectrolyte brushes or their electroactive counterions, which drives the chemical variation of the surface. Various conducting polymers have been studied in the electro-switchable redox transition.

PPy is widely used due to its unique optical, electrical and mechanical properties.[106] Oxidized PPy film shows hydrophobicity, while neutral PPy containing pyrrole moieties is usually slightly hydrophilic (Scheme 1).[107]

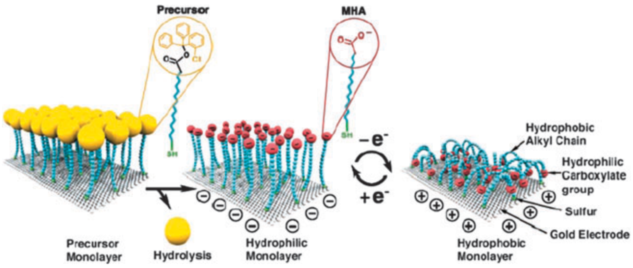
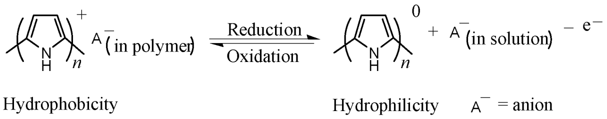


Fig. 14 Idealized representation of the transition between straight (hydrophilic) and bent (hydrophobic) molecular conformations.[104]



Scheme 1 The reversible switching process between the oxidized and neutral state of PPy.[107]

In general, the electrochemical process only produced electropolymerization, offering a compact structure. However, to obtain perfectly electro-responsive smart surfaces, an elegant method that combines a porous structural surface with perfluorinated dopant was designed. In 2005, Yan and co-workers[107] added tiny amounts of $FeCl_3$ to 0.1 M pyrrole electroplating solution to drive the chemical polymerization of pyrrole on Au-coated glass (Scheme 2).

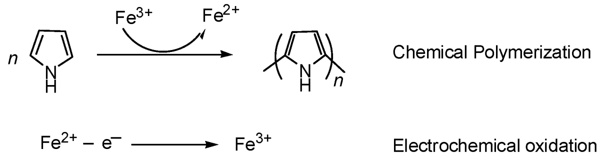
Experimental results showed that the coexistence of chemical-polymerization and electropolymerization processes played a key role to the formation of porous PPy films. When low-surface-energy perfluorooctane sulfonate (PFOS) was used as dopant, oxidized PPy films with fine roughness showed superhydrophobicity with water CA of 152 ± 2°, while neutral PPy films showed superhydrophilicity with CA of about 0°. The switching of the redox states could be cycled by adjusting the electrical potential.

Likewise, Ag^+-biphenyldithiol (BPDT) monolayers on an Au electrode can be converted to Ag^0-BPDT nanoclusters upon the application of alternating electrical potential, and corresponding wettability conversion can be repeated over many cycles.[108]

In addition, electro-active counter-anions can also induce the redox switching *via* the electrochemical process. Ferricyanide ($[Fe(CN)_6]^{3-}$) is a common anion in electrochemistry, and it easily undergoes the transition between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ upon application of electrical potential.[109] For example, based on polycationic poly[2-(methacryloyloxy)-ethyltrimethylammonium chloride (PMETAC), Huck[110] found that $[Fe(CN)_6]^{3-}$-coordinated brushes with CA = 41–44° would transform to $[Fe(CN)_6]^{4-}$-coordinated brushes with relatively hydrophilic CA of 26–27° using negative potential while reversible switching would occur upon application of positive potentials.

Much more noticeable is the fact that the use of molecular machines has attracted great attention.[111–113] The electrochemically-driven mechanical switching or shuttling of molecular components on surfaces is demonstrated to be a powerful approach towards controlling the hydrophilic/hydrophobic property of surfaces.

Electrowetting is another method to control surface wettability based on external electrical fields (Fig. 15).[114–116] The application of an external voltage across the solid/liquid interface will lead charges to build up both at the liquid side



Scheme 2 The process of catalytic chemical polymerization.[107]

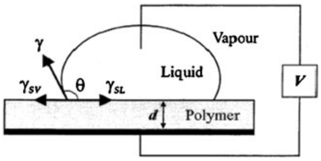


Fig. 15 Sessile drop setup for electrowetting measurements.[117]

and at the solid electrode, decreasing the solid/liquid interfacial tension. This results necessarily in a hydrophobicity-to-hydrophilicity change without changing the surface composition.[117]

Although studies on electrowetting have been done for many years, it is still difficult to achieve electrowetting on superhydrophobic surfaces. To achieve this aim, the exploration of fine surface roughness has been highlighted. In 2004, Krupenkin *et al.*[118] designed nanostructured silicon wafer surfaces, which underwent dynamic electrical control of the wetting behavior of liquids. By combining chemical modification and thin low-surface-energy polymer layers, switching of the surface wettability between superhydrophobic and superhydrophilic states based on electro-wetting was achieved for the first time. In addition, CNTs have been important materials in electrical and magnetic applications, and their electrochemical behavior has been increasingly investigated. In 2006, Hess *et al.*[119] studied the electrowetting of aligned CNT films using the sessile drop method by dispensing deionized water. The geometrical roughness of aligned CNTs induced the surfaces to exhibit superhydrophobic property with a static contact angle of 155° at zero external voltage. With the increase of the external voltage, the CA for deionized water was reduced to 98°. Presently, electro-wetting of ionic liquids is attracting much interest, and advances have been achieved[120–122] which aid in reversibly switchable wettability.

2.5 pH as external stimulus

Polymers containing acidic or basic functional groups such as amine and carboxyl groups usually exhibit pH-responsive wetting behavior because their morphologies and/or charges are dramatically influenced by the pH of solution.[123,124]

The carboxyl group at low pH can be protonated (–COOH) showing relatively hydrophobic property, while at high pH it occurs as carboxylate anion (–COO$^-$) with relatively hydrophilic property. As expected, the change in charges will render the alternation in molecular conformation.[125] Therefore, some compounds containing the carboxyl group have been widely used in smart surfaces.

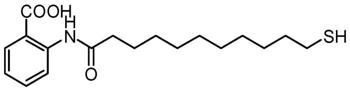


Fig. 16 Chemical structure of MUABA.[126]

Using the SAM of a dendron thiol as the underlying surface, Zhang *et al.* fabricated micro- and nano-scale rough gold substrates, on which 2-(11-mercaptoundecanamido)benzoic acid (MUABA) (Fig. 16)[126] or a mixed monolayer of $HS(CH_2)_9CH_3$ and $HS(CH_2)_{10}COOH$[127] were attached, respectively. Ideal wetting conversions achieved between the two extremes were attributed to the optimum roughness and the tuning of pH value. When the mixed polymer $HS(CH_2)_9CH_3$ and $HS(CH_2)_{10}COOH$ was used as a modifying agent on the rough surface, the wettability was strongly affected by its composition. As shown in Fig. 17, with χ_{COOH} = 0.2 or 0.6 (mole fraction of $HS(CH_2)_{10}COOH$ in the solution used for the modification of the substrate), the surface could not reversibly switch between superhydrophobicity and surperhydrophilicity. However, the mixed polymer containing 40% $HS(CH_2)_{10}COOH$ (χ_{COOH} = 0.4) did show a pH-responsive superhydrophobic–superhydrophilic property, and the CAs could be reversibly switched between 154° (pH 1) and about 0° (pH 13) by the alternation of the pH value.

On the other hand, the transition between –COOH and –COO$^-$ may or may not affect the formation of hydrogen bonding and drive the change in surface chemical composition. In 2006, the hydrogen-bonding-driven wettability change of poly(styrene-methyl methacrylate-acrylic acid) (poly(St-MMAAA)) crystal films in the presence of sodium dodecylbenzenesulfonate (SDBS) was reported.[128] At pH = 6.0, the carboxyl group was the in –COOH state, which would form hydrogen bonding with SO_3^- of SDBS. As illustrated in Fig. 18, in this case its hydrophobic tails spread outwards, triggering the rough crystal films to be superhydrophobic with water CA of 150.4 ± 0.8°. After treatment with $NH_3{\cdot}H_2O$ (pH = 12), deprotonation of –COOH to –COO$^-$ suppressed the hydrogen bonding. Hydrophilic groups of both –COO$^-$ and $-SO_3^-Na^+$ were exposed to the surface, inducing the surface to superhydrophilicity with CA of about 0°.

In addition, various pH-sensitive mixed polymers containing the carboxyl group have been reported, such as a PAA/PAMAM (poly(amidoamine)) dendrimer,[129] PAA star polymer/PAH (poly(allylamine hydrochloride)) multilayer film,[130] PAA/PVP micropatterned surface,[131,132] PVP/DEN-COOH (carboxyl-terminated polyether dendrimer) multilayer film,[133] and so on. All these materials allow the reversible inversion of surface topography and/or charge with the adjustment of pH, and wetting property is tuned correspondingly.

Another class of acidic compounds, orthophosphoric acids ($ROPO_3H_2$), displays the analogous property to carboxylic acids. Orthophosphoric acids are diacids with pK_{a1} ranging from 1 to 2, and pK_{a2} to about 6–7, and present three chemical states with change of pH (Fig. 19).[134–136] When pH > 8, polymethacryloyl ethylene phosphate (PMEP) brushes are fully deprotonated, and the electrostatic repulsion between charged polymer chains leads to a swelled form with high hydrophilicity, whereas the PMEP brushes are fully protonated

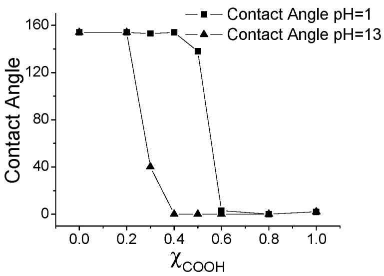


Fig. 17 Contact angle as a function of χ_{COOH} on a rough surface of $HS(CH_2)_9CH_3$ and $HS(CH_2)_{10}COOH$.[127]

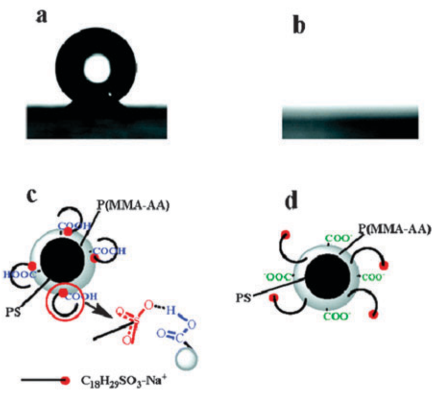


Fig. 18 (a and b) Photographs of a water droplet shape on the films assembled from suspensions with pH of 6.0 and 12, respectively; (c and d) corresponding schematic arrangement of groups in poly(St-MMAAA) (conformation of proposed hydrogen bonding is indicated by the arrow).[128]

and in collapsed states with relatively hydrophobic property when pH < 2.

The reversibly switchable wettability of DNA surfaces has also been investigated. DNA molecules modified by fluoride-containing hydrophobic groups were immobilized onto a rough gold surface, and a SAM of DNA was formed.[137] As the pH value changed, the enthalpy-driven transformation of the SAM of DNA took place. At low pH, the DNA molecules adopted the folded structure, in which the terminal hydrophobic groups were concealed in the SAM of DNA motors, and the hydrophilic backbones of the DNA strands were exposed on the surface (Fig. 20). Therefore, the surface is hydrophilic, and the CA is 8.8 ± 3.4°. At high pH, the destruction of non-classical intramolecular base pairs converted the DNA to stretched single-stranded structures, which indicated superhydrophobicity.

In general, the pH is usually adjusted by dilute HCl, NaOH, or phosphate buffer solutions. However, a variety of ammonia-responsive surfaces has been developed. For example, polyaniline (PANI)-coated fabrics[138] and $In(OH)_3$ films with micro- and nano-structures[139] can show altered surface structures and surface free energy in an ammonia atmosphere. Further, by adopting appropriate methods, reversibility to the original state can be achieved, and the wettability switch between superhydrophobicity and superhydrophilicity shows excellent reproducibility.

In addition to the above-discussed external stimuli, mechanical force can act as an external stimuli to drive the transition between superhydrophobicity and superhydrophilicity.[33] Mechanical extension and relaxation will change the density[140] and/or structure[141] of elastic surfaces, which induce necessarily the change of surface wettability. However, utilization of mechanical force to induce transition of wetting property has some limitations, for example, requiring materials with uniform stress–strain properties or use of large water droplets (at least 27 μL cm^{-2}).

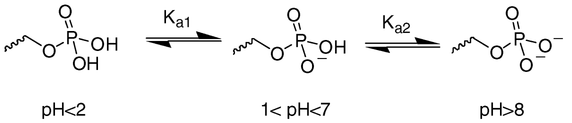


Fig. 19 Schematic of the association–dissociation equilibria of $ROPO_3H_2$ upon contact with solutions of different pH.[136]

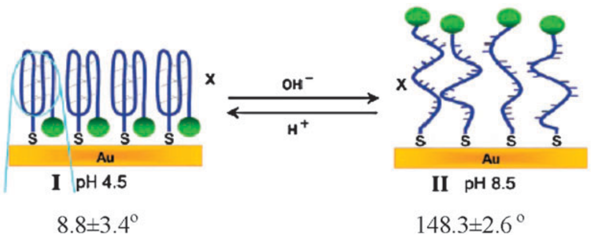


Fig. 20 Intelligent reversibly switchable surface driven by DNA nanodevices and the CA value in different states (circles indicate fluoride-containing hydrophobic groups).[137]

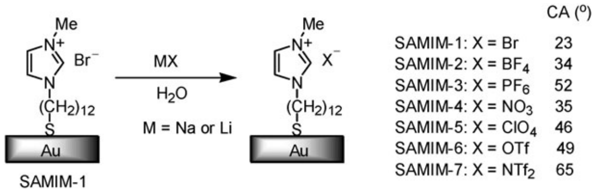
3. Reversible switching of surface wettability *via* counterion exchange

From 2004, researchers have demonstrated that the wettability of ionic liquids and polyelectrolyte brushes can be tuned by exchanging appropriate counterions. Compared with the utilization of external stimuli, however, the change in CAs rendered by this approach is very limited, and the transformation between superhydrophilicity and superhydrophobicity remains a challenge.

3.1 Exchanging the counterions in ionic liquids

In recent years, room-temperature ionic liquids (RTILs) have attracted great attention due to their unique characteristics, such as negligible vapor pressure, relatively high ionic conductivity, good chemical and thermal stability, non-flammability, and wide electrochemical potential window.[142–145] RTILs can be designed to the desired structures for specific applications through the variation of cations and anions. Hence, they are often referred to as "designer liquids." For example, the exchange of anions greatly alters the wettability of ILs. Conventionally, the RTILs with anions such as Cl^-, Br^- and BF_4^- show hydrophilicity, and those with PF_6^- and Tf_2N^- possess hydrophobicity. The solubility of RTILs in water follows the order of $Tf_2N^- > PF_6^- > BF_4^- > I^- > Cl^-$. In surface chemistry, the facile tunability of physicochemical properties of ionic liquids excellently satisfies the demand of surface modification to modulate surface wetting behavior.

In 2004, Choi *et al.*[35,146] prepared imidazolium ion-terminated self-assembled monolayers (SAMIMs) on Au and Si/SiO_2 surfaces *via* covalent bonding of alkanethiols or siloxanes, respectively. Subsequently, Lu[147] modified the negatively charged polyimide films using ionic liquids based on electrostatic self-assembly rather than by a covalent approach. To reveal the effect of anions on surface wettability, Choi screened a series of anions including Br^-, BF_4^-, PF_6^-, Tf_2N^-, OTf^-, ClO_4^- and NO_3^- (Scheme 3). As shown in Scheme 3, the SAMIM-1 with Br^- had a relatively hydrophilic property (water CA about 23 ± 1°), and the SAMIM-7 with Tf_2N^- exhibited the highest contact angle (CA 65 ± 1°), while other



Scheme 3 The process of the exchange of anions and the CA values of SAMIMs with different anions.[35]

SAMIMs bearing different anions revealed intermediate CA values. The effect of anions on hydrophobicity of the imidazolium-based ionic liquids was in the following order: $Tf_2N^- > PF_6^- > OTf^- > ClO_4^- > NO_3^- > BF_4^- > Br^-$. This is in agreement with the trend of solubility of RTILs. This was the first time that the reversible wettability conversions of surfaces were modified using ionic liquids. Lu extended imidazolium-based ionic liquids to ammonium-based ILs and achieved similar results. Direct immersion in an aqueous solution containing the indicated anion will achieve the exchange of counterion. For example, by immersion in a solution of $NaBF_4$ or $NaPF_6$ for several hours, Br^- of imidazolium salts can easily be exchanged with BF_4^- or PF_6^-. Facile exchange of counterion on SAMIM surfaces makes it a potential approach for manipulating surface wetting behavior.

The tunable property of ionic liquids can also be extended to control the properties of CNT-based materials. Thus single-walled carbon nanotubes (SWNTs)[148] and multi-walled carbon nanotubes (MWCNTs)[149] have had their wetting behavior tailored *via* modification with ionic liquids.

To combine the advantages of ionic liquids and polymers, polyelectrolyte-functionalized ILs (PFILs) (Fig. 21(a))[150] and poly(ionic liquid) brushes (Fig. 21(b))[151] were prepared on flat silicon substrates, in which the facile tunable wettability of ILs was retained. For example, $[PVBIm][PF_6]$ ([1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate]) brushes were grafted from the surface of a silicon wafer *via* a surface-initiated ATRP technique, and showed a rather hydrophobic behavior (CA = 95°). Immersion in 0.2 M NaCl aqueous solution for 1 h, leading to PF_6^- exchange with Cl^- promoted a drastic change in the wetting properties of the substrate (CA = 41°).

In some cases, the effect of anions in ILs is determined by the size of the oppositely charged ions. For longer-substituent ionic liquids such as 1-octyl-3-methylimidazolium ([omim]) salts, the water CA values were *ca.* 68, 72, and 75° for Br^-, BF_4^- and Tf_2N^-, respectively. However, for shorter-substituent cations such as 1-benzyl-3-methylimidazolium ([Bmim]) salts with Br^-, BF_4^- or Tf_2N^-, the water CAs maintained a constant value of *ca.* 56°. Lu *et al.*[147] explained that the anions in the assembled layers were present for [omim] salts and absent for [Bmim] salts due to the different aggregation behavior of the cations of the ILs. In addition, based on 1-alkyl-3-(3-triethoxysilylpropyl)imidazolium salt ($[C_1tespim]$) surfaces (Fig. 22), the water CAs of SAMs with anions Cl^-, BF_4^-, and PF_6^- on Si/SiO_2 were 24, 30 and 42°, respectively, whereas the water CAs of $[C_4tespim]X$ was almost invarient (CA about 51°). The reason was that anions were embedded in the butyl chains in the latter and were not exposed to the outermost layers.[146]

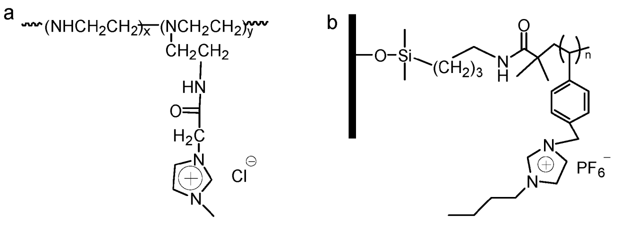


Fig. 21 (a) Chemical structure of PFIL[150] and (b) $[PVBIm][PF_6]$.[151]

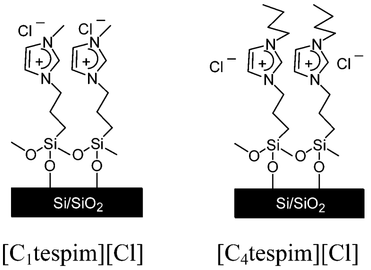
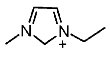
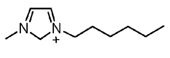
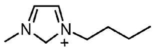
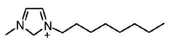
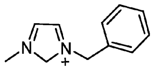
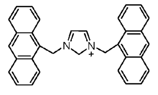


Fig. 22 Chemical structure of $[C_ntespim][Cl]$.[146]

Like anions, the change of cations in ionic liquids also has the ability to modulate surface wettability. As shown in Table 1, water CAs of $[C_2mim][Br]$, $[C_4mim][Br]$, $[C_6mim][Br]$ and $[C_8mim][Br]$ tends to increase, indicating that the hydrophobicity increases with the increase of chain length of substituents for a given anion. The order is quite consistent with the surface tension (γ) and solubility in water of the RTILs.[152,153]

Using ILs to modify surfaces provides a new strategy for reversible switching between hydrophobicity and hydrophilicity. However, the maximum contact angle can only reach up to 95°, and the highest change of CA is less than 45°. No switching between superhydrophobicity and superhydrophilicity *via* the exchange of counterions of ionic liquids has been reported yet. The amplifying effect of roughness has not been introduced to substrates modified with ILs.

Table 1 The effect of cations of ionic liquids on surface wettability (CA for water)[ab]

$[C_nmim]$	CA/°	$[C_nmim]$	CA/°
	27		63
	35		68
	56		80

[a] The anion of these imidazolium-based cations is Cl^- or Br^-. [b] CA values are from ref. 147.

3.2 Exchanging counterions in polyelectrolyte brushes

As discussed in sections 2.4 and 2.5, the crucial advantage of polyelectrolyte brushes as tunable surfaces is that their morphologies and/or chemistry may be readily controlled *via* light irradiation,[70] solvent,[98] electrochemical potential,[104] or pH.[134] However, a novel route to tailor their surface characteristics has recently emerged based on the nature of the counterions in them.[34,154] Huck's group[34,155] has demonstrated that the wettability of polyelectrolyte brushes can be tuned by choosing appropriate counterions. Using PMETAC[155] and PDMAEMAC[156] polycations bearing quaternary ammonium groups (QA^+), the effect of opposite-charged ions (Tf_2N^-, ClO_4^-, SCN^-, Cl^-, PO_4^{3-}) on the wettability of polyelectrolyte brushes has been investigated. Different surrounding opposite-charged ions exhibited different interactions with the cation groups. Taking the cationic PMETAC brush as an example, compared with hydrated Cl^-, ClO_4^- is more poorly hydrated, larger, and more polarizable (Table 2). Moreover, it interacts very strongly with QA^+ through ion pairing and promotes a drastic increase in the hydrophobicity of substrate with CA 79°. Perfluorinated Tf_2N^- always shows the highest hydrophobicity, giving a CA of 90°. Among the anions tested, polyphosphate (pp) displays the lowest CA at 15° when coordinated with Q-PMETA. As expected, with the exchange of anions, conformational transitions synchronously occur, affecting the wetting behavior as well.[34] The hydrophobic character follows the trend $Tf_2N^- > ClO_4^- > SCN^- > I^- > Br^- > Cl^- > PO_4^{3-} >$ pp, which is consistent with the wetting order in ionic liquids as advanced by Choi.[35]

Likewise, the effect of dopant on PPy films has been reported. Fluoro-surfactant dopants such as perfluoroalkyethyl sulfite[106,107] is rendered hydrophobic (water CA $>90°$ when the concentration of dopant is 0.01 mol L^{-1}). However, displacing fluorinated dopant by TS^- (tosylate), DS^- (dodecyl sulfonate), Cl^- or ClO_4^- in PPy films leads to a decrease of CA to 80 ± 5, 69.1 ± 5.9, 52.8 ± 3.2 and 51°, respectively.[157]

Exchanging counterions may be easily achieved using chemical and electrochemical means. One chemical method involves immersing the target anion directly in aqueous solution for several hours.[34] The electrochemical method is another convenient and promising strategy. For example, using $LiClO_4$, NH_4PF_6 and Tf_2NLi as electrolytes,[156] the change in anions can be easily carried out in a short time. On the other hand, electrical potential will drive the translation between reduced and oxidized states of polyelectrolyte or counterions, as discussed in section 2.4.

Table 2 The effect of anions based on Q-PMETA and Q-PDMAEMA polycations on the surface wettability (CA for water)

	CA/°	
Anions	Q-PMETA[a]	Q-PDMAEMA[b]
pp	15	—
PO_4^{3-}	19	—
Cl^-	35	—
SCN^-	65	—
NO_3^-	—	52
ClO_4^-	79	73
PF_6^-	—	87
Tf_2N^-	90	93

[a] Values are from ref. 34 and 156. [b] Values are from ref. 156.

The use of counterion exchanging in reversible switching wettability opens up a new method in surface science. However, as the case for ionic liquids, the highest contact angle is merely 90°, and the change of CA is 75°, which cannot meet the demand of smart devices.

4. Conclusion and outlook

In this article, we have given an overview of the recent achievements in the methods for reversibly switchable wettability, especially the reversible switching between superhydrophobic and superhydrophilic transformations. Applying external stimuli is a facile approach towards successful responsive switching for both inorganic oxides and organic materials showing ideal roughness and it has been widely used in the fabrication of smart devices. On the other hand, the exchange of counterions is a novel strategy, and the effect of counterions on the wetting behavior is highlighted.

Future research should be focused on the design, synthesis and application of new types of materials with promising wetting conversions between superhydrophilicity and superhydrophobicity. Ionic liquids hold the most potential for this purpose. Their facile tunability of properties, chemical and thermal stability, and conductivity allow them to be extensively applied in surface science. It will be necessary to explore further their reversible wetting bahavior and produce them as on–off systems. It is well-known that fluorinated compounds possess low-surface-energy, and they are promising hydrophobic materials. We believe that fluorinated long-chain ionic liquids can be ideal superhydrophobic materials and can achieve responsive switching between superhydrophilicity and superhydrophobicity by introducing fine surface roughness.

Abbreviations

CA	contact angle
FAS	$CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$
CVD	chemical vapor deposition
ACNT	aligned carbon nanotube
UV	ultraviolet
Vis	visible
ODP	octadodecylphosphonic acid
CF3AZO	7-[(trifluoromethoxyphenylazo)-phenoxy]pentanoic acid
LBL	layer-by-layer
PAH	poly(allylamine hydrochloride)
PNIPAAm	poly(*N*-isopropylacrylamide)
LCST	lower critical solution temperature
ATRP	atom transfer radical polymerization
PAA	poly(acrylic acid)
MEO_2MA	2-(2-methoxyethoxy)ethyl methacrylate
OEGMA	oligo(ethylene glycol)methacrylate
PDMAEMA	poly(2-(dimethylamino)ethyl methacrylate)
HPB	heterogeneous polymer brushes
PS	polystyrene

PMA	poly(methyl acrylate)
PTFE	poly(tetrafluoroethylene)
PSF	pentafluorostyrene
P2VP	poly(2-vinylpyridine)
HPS	hexaphenylsilole
PNIPAM	poly(*N*-isopropylacrylamide)
PNASI	poly(*N*-acryloxysuccinimide))
MHA	(16-mercapto)hexadecanoic acid
PANI	polyaniline
PPy	polypyrrole
PFOS	perfluorooctanesulfonate
BPDT	biphenyldithiol
PMETAC	poly[2-(methacryloyloxy)-ethyltrimethyl-ammonium chloride
SAM	self-assembled monolayer
MUABA	2-(11-mercaptoundecanamido)benzoic acid
poly(St-MMAAA)	poly-(styrene-methyl methacrylate-acrylic acid)
SDBS	sodium dodecylbenzenesulfonate
PAMAM	poly(amidoamine)
PAH	poly(allylamine hydrochloride)
DEN-COOH	carboxyl-terminated polyether dendrimer
PMEP	polymethacryloyl ethylene phosphate
RTIL	room-temperature ionic liquid
[PVBIm][PF$_6$]	[1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate]
QA$^+$	quaternary ammonium groups
TS$^-$	tosylate
DS$^-$	dodecyl sulfonate

Acknowledgements

Financial support from the National Basica Research Program of China ("973" Program, 2009CB930103) and the NSFC (Grant No. 20625307).

References

1 X. Feng and L. Jiang, *Adv. Mater.*, 2006, **18**, 3063.
2 G. Kumar and K. N. Prabhu, *Adv. Colloid Interface Sci.*, 2007, **133**, 61.
3 T. Sun, L. Feng, X. Gao and L. Jiang, *Acc. Chem. Res.*, 2005, **38**, 644.
4 F. Shi, Y. Song, J. Niu, X. Xia, Z. Wang and X. Zhang, *Chem. Mater.*, 2006, **18**, 1365.
5 Y. Liu, L. Mu, B. Liu and J. Kong, *Chem.–Eur. J.*, 2005, **11**, 2622.
6 D. Öner and T. J. McCarthy, *Langmuir*, 2000, **16**, 7777.
7 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Adv. Mater.*, 1998, **10**, 135.
8 M. Calliea and D. Quéré, *Soft Matter*, 2005, **1**, 55.
9 T. P. Russell, *Science*, 2002, **297**, 964.
10 G. de Crevoisier, P. Fabre, J. M. Corpart and L. Leibler, *Science*, 1999, **285**, 1246.
11 A. Nakajima, A. Fujishima, K. Hashimoto and T. Watanabe, *Adv. Mater.*, 1999, **11**, 1365.
12 J. Genzer and K. Efimenko, *Science*, 2000, **290**, 2130.
13 D. Schondelmaier, S. Cramm, R. Klingeler, J. Morenzin, Ch. Zilkens and W. Eberhardt, *Langmuir*, 2002, **18**, 6242.
14 S. R. Coulson, I. Woodward, J. P. S. Badyal, S. A. Brewer and C. Willis, *J. Phys. Chem. B*, 2000, **104**, 8836.
15 T. Nishino, M. Meguro, K. Nakamae, M. Matsushita and Y. Ueda, *Langmuir*, 1999, **15**, 4321.
16 R. N. Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.
17 J. Bico, U. Thiele and D. Quéré, *Colloids Surf., A*, 2002, **206**, 41.
18 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Nature*, 1997, **388**, 431.
19 X. Gao and L. Jiang, *Nature*, 2004, **432**, 36.
20 F. Xia and L. Jiang, *Adv. Mater.*, 2008, **20**, 2842.
21 M. Sun, C. Luo, L. Xu, H. Ji, Q. Ouyang, D. Yu and Y. Chen, *Langmuir*, 2005, **21**, 8978.
22 J. Han, D. Lee, C. Ryu and K. Cho, *J. Am. Chem. Soc.*, 2004, **126**, 4796.
23 F. Shi, Z. Wang and X. Zhang, *Adv. Mater.*, 2005, **17**, 1005.
24 L. Jiang, Y. Zhao and J. Zhai, *Angew. Chem., Int. Ed.*, 2004, **43**, 4338.
25 H. Y. Erbil, A. L. Demirel, Y. Avci and O. Mert, *Science*, 2003, **299**, 1377.
26 K. K. S. Lau, J. Bico, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratung, W. I. Milne, G. H. McKinley and K. K. Gleason, *Nano Lett.*, 2003, **3**, 1701.
27 L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang and D. Zhu, *Adv. Mater.*, 2002, **14**, 1857.
28 J. A. Crowe and J. Genzer, *J. Am. Chem. Soc.*, 2005, **127**, 17610.
29 H. Li, X. Wang, Y. Song, Y. Liu, Q. Li, L. Jiang and D. Zhu, *Angew. Chem., Int. Ed.*, 2001, **40**, 1743.
30 F. Shi, X. Chen, L. Wang, J. Niu, J. Yu, Z. Wang and X. Zhang, *Chem. Mater.*, 2005, **17**, 6177.
31 S. Bliznakov, Y. Liu, N. Dimitrov, J. Garnica and R. Sedev, *Langmuir*, 2009, **25**, 4760.
32 C. Feng, Y. Zhang, J. Jin, Y. Song, L. Xie, G. Qu, L. Jiang and D. Zhu, *Langmuir*, 2001, **17**, 4593.
33 S. L. Gras, T. Mahmud, G. Rosengarten, A. Mitchell and K. Kalantar-zadeh, *ChemPhysChem*, 2007, **8**, 2036.
34 O. Azzaroni, A. A. Brown and W. T. S. Huck, *Adv. Mater.*, 2007, **19**, 151.
35 B. S. Lee, Y. S. Chi, J. K. Lee, I. S. Choi, C. E. Song, S. K. Namgoong and S. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 480.
36 G. Caputo, C. Nobile, T. Kipp, L. Blasi, V. Grillo, E. Carlino, L. Manna, R. Cingolani, P. D. Cozzoli and A. Athanassiou, *J. Phys. Chem. C*, 2008, **112**, 701.
37 Z. Lin, T. Kerle, T. P. Russell, E. Schaffer and U. Steiner, *Macromolecules*, 2002, **35**, 6255.
38 S. Wang, Y. Song and L. Jiang, *J. Photochem. Photobiol., C*, 2007, **8**, 18.
39 N. Sakai, R. Wang, A. Fujishima, T. Watanabe and K. Hashimoto, *Langmuir*, 1998, **14**, 5918.
40 N. Stevens, C. I. Priest, R. Sedev and J. Ralston, *Langmuir*, 2003, **19**, 3272.
41 N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 2003, **107**, 1028.
42 Z. Gu, A. Fujishima and O. Sato, *Angew. Chem., Int. Ed.*, 2002, **41**, 2067.
43 K. Tadanaga, J. Morinaga, A. Matsuda and T. Minami, *Chem. Mater.*, 2000, **12**, 590.
44 X. Feng, J. Zhai and L. Jiang, *Angew. Chem., Int. Ed.*, 2005, **44**, 5115.
45 W. Sun, S. Zhou, P. Chen and L. Peng, *Chem. Commun.*, 2008, 603.
46 X. Zhang, M. Jin, Z. Liu, S. Nishimo, H. Saito, T. Murakami and A. Fujishima, *Langmuir*, 2006, **22**, 9477.
47 X. Zhang, M. Jin, Z. Liu, D. A. Tryk, S. Nishimoto, T. Murakami and A. Fujishima, *J. Phys. Chem. C*, 2007, **111**, 14521.
48 X. Zhang, H. Kono, Z. Liu, S. Nishimoto, D. A. Tryk, T. Murakami, H. Sakai, M. Abe and A. Fujishima, *Chem. Commun.*, 2007, 4949.
49 R. D. Sun, A. Nakajima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 2001, **105**, 1984.
50 M. Miyauchi, A. Shimai and Y. Tsuru, *J. Phys. Chem. B*, 2005, **109**, 13307.
51 M. Li, J. Zhai, H. Liu, Y. Song, L. Jiang and D. Zhu, *J. Phys. Chem. B*, 2003, **107**, 9954.
52 X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang and D. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 62.

53 X. Zhang, O. Sato and A. Fujishima, *Langmuir*, 2004, **20**, 6065.
54 H. Liu, L. Feng, J. Zhai, L. Jiang and D. Zhu, *Langmuir*, 2004, **20**, 5659.
55 E. L. Papadopoulou, M. Barberoglou, V. Zorba, A. Manousaki, A. Pagkozidis, E. Stratakis and C. Fotakis, *J. Phys. Chem. C*, 2009, **113**, 2891.
56 S. Wang, X. Feng, J. Yao and L. Jiang, *Angew. Chem., Int. Ed.*, 2006, **45**, 1264.
57 H. S. Lim, D. Kwak, D. Y. Lee, S. G. Lee and K. Cho, *J. Am. Chem. Soc.*, 2007, **129**, 4128.
58 W. Zhu, X. Feng, L. Feng and L. Jiang, *Chem. Commun.*, 2006, 2753.
59 A. M. Kietzig, S. G. Hatzikiriakos and P. Englezos, *Langmuir*, 2009, **25**, 4821.
60 B. Yan, J. Tao, C. Pang, Z. Zheng, Z. Shen, C. Huan and T. Yu, *Langmuir*, 2008, **24**, 10569.
61 Y. Kwon, B. M. Weon, K. H. Won, J. H. Je, Y. Hwu and G. Margaritono, *Langmuir*, 2009, **25**, 1927.
62 N. Delorme, J. F. Bardeau, A. Bulou and F. Poncin-Epaillard, *Langmuir*, 2005, **21**, 12278.
63 R. Rosario, D. Gust, M. Hayes, F. Jahnke, J. Springer and A. A. Garcia, *Langmuir*, 2002, **18**, 8062.
64 C. G. F. Cooper, J. C. MacDonald, E. Soto and W. G. McGimpsey, *J. Am. Chem. Soc.*, 2004, **126**, 1032.
65 P. F. Driscoll, N. Purohit, N. Wanichacheva, C. R. Lambert and W. G. McGimpsey, *Langmuir*, 2007, **23**, 13181.
66 S. Abbott, J. Ralston, G. Reynolds and R. Hayes, *Langmuir*, 1999, **15**, 8923.
67 K. Ichimura, S. K. Oh and M. Nakagawa, *Science*, 2000, **288**, 1624.
68 S. K. Oh, M. Nakagawa and K. Ichimura, *J. Mater. Chem.*, 2002, **12**, 2262.
69 W. Jiang, G. Wang, Y. He, X. Wang, Y. An, Y. Song and L. Jiang, *Chem. Commun.*, 2005, 3550.
70 L. M. Siewierski, W. J. Brittain, S. Petrash and M. D. Foster, *Langmuir*, 1996, **12**, 5838.
71 H. S. Lim, J. T. Han, D. Kwak, M. Jin and K. Cho, *J. Am. Chem. Soc.*, 2006, **128**, 14458.
72 D. Prescher, T. Thiele, R. Ruhmann and G. Schulz, *J. Fluorine Chem.*, 1995, **74**, 185.
73 R. Rosario, D. Gust, A. A. Garcia, M. Hayes, J. L. Taraci, T. Clement, J. W. Dailey and S. T. Picraux, *J. Phys. Chem. B*, 2004, **108**, 12640.
74 A. Athanassiou, M. I. Lygeraki, D. Pisignano, K. Lakiotaki, M. Varda, E. Mele, C. Fotakis, R. Cingolani and S. H. Anastasiadis, *Langmuir*, 2006, **22**, 2329.
75 L. Liang, X. Feng, J. Liu, P. C. Rieke and G. E. Fryxell, *Macromolecules*, 1998, **31**, 7845.
76 H. Yim, M. S. Kent, S. Mendez, S. S. Balamurugan, S. Balamurugan, G. P. Lopez and S. Satija, *Macromolecules*, 2004, **37**, 1994.
77 H. Yim, M. S. Kent, D. L. Huber, S. Satija, J. Majewski and G. S. Smith, *Macromolecules*, 2003, **36**, 5244.
78 S. Kidoaki, S. Ohya, Y. Nakayama and T. Matsuda, *Langmuir*, 2001, **17**, 2402.
79 T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang and D. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 357.
80 D. M. Jones, J. R. Smith, W. T. S. Huck and C. Alexander, *Adv. Mater.*, 2002, **14**, 1130.
81 L. Liang, P. C. Rieke, G. E. Fryxell, J. Liu, M. H. Engelhard and K. L. Alford, *J. Phys. Chem. B*, 2000, **104**, 11667.
82 Q. Fu, G. V. R. Rao, S. B. Basame, D. J. Keller, K. Artyushkova, J. E. Fulghum and G. P. Lopez, *J. Am. Chem. Soc.*, 2004, **126**, 8904.
83 F. Xia, L. Feng, S. Wang, T. Sun, W. Song, W. Jiang and L. Jiang, *Adv. Mater.*, 2006, **18**, 432.
84 W. Yuan, G. Jiang, J. Wang, G. Wang, Y. Song and L. Jiang, *Macromolecules*, 2006, **39**, 1300.
85 M. Zhang, L. Liu, C. Wu, G. Fu, H. Zhao and B. He, *Polymer*, 2007, **48**, 1989.
86 T. Sun, H. Liu, W. Song, X. Wang, L. Jiang, L. Li and D. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 4663.
87 H. Vihola, A. Laukkanen, L. Valtola, H. Tehnhu and J. Hirnoven, *Biomaterials*, 2005, **26**, 3055.
88 J. F. Lutz, O. Akdemir and A. Hoth, *J. Am. Chem. Soc.*, 2006, **128**, 13046.
89 L. Wan, H. Lei, Y. Ding, L. Fu, J. Li and Z. Xu, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 92.
90 S. Inoue, H. Kakikawa, N. Nakadan, S. Imabayashi and M. Watanabe, *Langmuir*, 2009, **25**, 2837.
91 J. Zhang, L. Xue and Y. Han, *Langmuir*, 2005, **21**, 5.
92 A. M. Jonas, K. Glinel, R. Oren, B. Nysten and W. T. S. Huck, *Macromolecules*, 2007, **40**, 4403.
93 N. J. Shirtcliffe, G. McHale, M. I. Newton, C. C. Perry and P. Roach, *Chem. Commun.*, 2005, 3135.
94 S. Minko, M. Müller, M. Motornov, M. Nitschke, K. Grundke and M. Stamm, *J. Am. Chem. Soc.*, 2003, **125**, 3896.
95 J. Draper, I. Luzinov, S. Minko, I. Tokarev and M. Stamm, *Langmuir*, 2004, **20**, 4064.
96 D. Julthongpiput, Y. Lin, J. Teng, E. R. Zubarev and V. V. Tsukruk, *Langmuir*, 2003, **19**, 7832.
97 S. G. Boyes, W. J. Brittain, X. Wang and S. Z. D. Cheng, *Macromolecules*, 2002, **35**, 4960.
98 G. K. Jennings and E. L. Brantley, *Adv. Mater.*, 2004, **16**, 1983.
99 Y. Zhou, T. Yi, T. Li, Z. Zhou, F. Li, W. Huang and C. Huang, *Chem. Mater.*, 2006, **18**, 2974.
100 L. Heng, Y. Dong, J. Zhai, B. Tang and L. Jiang, *Langmuir*, 2008, **24**, 2157.
101 K. Liao, H. Fu, A. Wan, J. Batteas and D. E. Bergbreiter, *Langmuir*, 2009, **25**, 26.
102 I. Choi and Y. S. Chi, *Angew. Chem., Int. Ed.*, 2006, **45**, 4894.
103 X. Wang, E. Katz and I. Willner, *Electrochem. Commun.*, 2003, **5**, 814.
104 J. Lahann, S. Mitragotri, T. N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai and R. Langer, *Science*, 2003, **299**, 371.
105 Y. Liu, L. Mu, B. Liu, S. Zhang, P. Yang and J. Kong, *Chem. Commun.*, 2004, 1194.
106 D. Mecerreyes, V. Alvaro, I. Cantero, M. Bengoetxea, P. A. Calvo, H. Grande, J. Rodriguez and J. A. Pomposo, *Adv. Mater.*, 2002, **14**, 749.
107 L. Xu, W. Chen, A. Mulchandani and Y. Yan, *Angew. Chem., Int. Ed.*, 2005, **44**, 6009.
108 M. Riskin, B. Basnar, V. I. Chegel, E. Katz, I. Willner, F. Shi and X. Zhang, *J. Am. Chem. Soc.*, 2006, **128**, 1253.
109 X. Wang, Z. Gershman, A. B. Kharitonov, E. Katz and I. Willner, *Langmuir*, 2003, **19**, 5413.
110 E. Spruijt, E. Y. Choi and W. T. S. Huck, *Langmuir*, 2008, **24**, 11253.
111 X. Wang, A. B. Kharitonov, E. Katz and I. Willner, *Chem. Commun.*, 2003, 1542.
112 E. Katz, O. Lioubashevsky and I. Willner, *J. Am. Chem. Soc.*, 2004, **126**, 15520.
113 B. C. Bunker, D. L. Huber, J. G. Kushmerick, T. Dunbar, M. Kelly, C. Matzke, J. Cao, J. O. Jeppesen, J. Perkins, A. H. Flood and J. F. Stoddart, *Langmuir*, 2007, **23**, 31.
114 J. Isaksson, C. Tengstedt, M. Fahlman, N. Robinson and M. Berggren, *Adv. Mater.*, 2004, **16**, 316.
115 R. A. Hayes and B. J. Feenstra, *Nature*, 2003, **425**, 383.
116 T. B. Jones, *Langmuir*, 2002, **18**, 4437.
117 A. Quinn, R. Sedev and J. Ralston, *J. Phys. Chem. B*, 2003, **107**, 1163.
118 T. N. Krupenkin, J. A. Taylor, T. M. Schneider and S. Yang, *Langmuir*, 2004, **20**, 3824.
119 L. Zhu, J. Xu, Y. Xiu, Y. Sun, D. W. Hess and C. P. Wong, *J. Phys. Chem. B*, 2006, **110**, 15945.
120 S. Millefiorini, A. H. Tkaczyk, R. Sedev, J. Efthimiadis and J. Ralston, *J. Am. Chem. Soc.*, 2006, **128**, 3098.
121 H. L. Ricks-Laskoski and A. W. Snow, *J. Am. Chem. Soc.*, 2006, **128**, 12402.
122 Y. Wang, W. Jiang, T. Yan and G. A. Voth, *Acc. Chem. Res.*, 2007, **40**, 1193.
123 A. J. Khopade and F. Caruso, *Langmuir*, 2002, **18**, 7669.
124 S. R. Holmes-Farley, C. D. Bain and G. M. Whitesides, *Langmuir*, 1988, **4**, 921.
125 M. D. Wilson and G. M. Whitesides, *J. Am. Chem. Soc.*, 1988, **110**, 8718.
126 Y. Jiang, Z. Wang, X. Yu, F. Shi, H. Xu and X. Zhang, *Langmuir*, 2005, **21**, 1986.

127 X. Yu, Z. Q. Wang, Y. G. Jiang, F. Shi and X. Zhang, *Adv. Mater.*, 2005, **17**, 1289.
128 J. Wang, J. Hu, Y. Wen, Y. Song and L. Jiang, *Chem. Mater.*, 2006, **18**, 4984.
129 B. Y. Kim and M. L. Bruening, *Langmuir*, 2003, **19**, 94.
130 L. A. Connal, Q. Li, J. F. Quinn, E. Tjipto, F. Caruso and G. Qiao, *Macromolecules*, 2008, **41**, 2620.
131 A. Synytska, M. S. Diez and L. Lonov, *Langmuir*, 2007, **23**, 5205.
132 Y. Fu, S. L. Bai, S. Cui, D. Qiu, Z. Wang and X. Zhang, *Macromolecules*, 2002, **35**, 9451.
133 H. Zhang, Y. Fu, D. Wang, L. Wang, Z. Wang and X. Zhang, *Langmuir*, 2003, **19**, 8497.
134 F. Zhou, W. Shu, M. E. Welland and W. T. S. Huck, *J. Am. Chem. Soc.*, 2006, **128**, 5326.
135 X. Dai, F. Zhou, N. Khan, W. T. S. Huck and C. F. Kaminski, *Langmuir*, 2008, **24**, 13182.
136 F. Zhou and W. T. S. Huck, *Chem. Commun.*, 2005, 5999.
137 S. Wang, H. Liu, D. Liu, X. Ma, X. Fang and L. Jiang, *Angew. Chem., Int. Ed.*, 2007, **46**, 3915.
138 Y. Zhu, J. Li, H. He, M. Wan and L. Jiang, *Macromol. Rapid Commun.*, 2007, **28**, 2230.
139 W. Zhu, J. Zhai, Z. Sun and L. Jiang, *J. Phys. Chem. C*, 2008, **112**, 8338.
140 J. Genzer and K. Efimenko, *Science*, 2000, **290**, 2130.
141 J. Zhang, X. Lu, W. Huang and Y. Han, *Macromol. Rapid Commun.*, 2005, **26**, 477.
142 T. Welton, *Chem. Rev.*, 1999, **99**, 2071.
143 J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667.
144 C. C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel and R. Haag, *Angew. Chem., Int. Ed.*, 2002, **41**, 3964.
145 J. S. Wilkes, *Green Chem.*, 2002, **4**, 73.
146 Y. S. Chi, J. K. Lee, S. G. Lee and I. S. Choi, *Langmuir*, 2004, **20**, 3024.
147 Y. Zhao, M. Li and Q. Lu, *Langmuir*, 2008, **24**, 3937.
148 Y. Zhang, Y. Shen, J. Yuan, D. Han, Z. Wang, Q. Zhang and L. Niu, *Angew. Chem., Int. Ed.*, 2006, **45**, 5867.
149 M. J. Park, J. K. Lee, B. S. Lee, Y. W. Lee, I. S. Choi and S. G. Lee, *Chem. Mater.*, 2006, **18**, 1546.
150 Y. Shen, Y. Zhang, Q. Zhang, L. Niu, T. You and A. Ivaska, *Chem. Commun.*, 2005, 4193.
151 X. He, W. Yang and X. Pei, *Macromolecules*, 2008, **41**, 4615.
152 G. Law and P. P. Watson, *Langmuir*, 2001, **17**, 6138.
153 P. J. Carvalho, M. G. Freire, I. M. Marrucho, A. J. Queimada and J. A. P. Coutinho, *J. Chem. Eng. Data*, 2008, **53**, 1346.
154 L. Wang, Y. Lin, B. Peng and Z. Su, *Chem. Commun.*, 2008, 5972.
155 O. Azzaroni, S. Moya, T. Farhan, A. A. Brown and W. T. S. Huck, *Macromolecules*, 2005, **38**, 10192.
156 F. Zhou, H. Y. Hu, B. Yu, V. L. Osborne, W. T. S. Huck and W. M. Liu, *Anal. Chem.*, 2007, **79**, 176.
157 A. Azioune, M. M. Chehimi, B. Miksa, T. Basinska and S. Slomkowski, *Langmuir*, 2002, **18**, 1150.