Switchable and Reversible Superhydrophobic Surfaces: Part Two

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Additional information is available at the end of the chapter

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Abstract

In this book chapter, most of the methods used in the literature to prepare switchable and reversible superhydrophobic surfaces are described. Inspired by Nature, it is possible to induce the Cassie-Baxter-Wenzel transition using different external stimuli such as light, temperature, pH, ion exchange, voltage, magnetic field, mechanic stress, plasma, ultrasonication, solvent, gas or guest. Such properties are extremely important for various applications but especially for controllable oil/water separation membranes, oil-absorbing materials, and water harvesting systems.

Keywords: superhydrophobic, reversible, switchable, bioinspiration, biomimetism

1. Reversible superhydrophobic surfaces: Part two

This section provides continuation of the description of the stimuli used in the literature to induce reversible changes in surface wettability.

1.1. Ion exchange

Since 2004, the researchers have shown that the presence of charged species such as quaternary ammonium groups are sensitive to ion exchange and lead to different surface wettabilities. In 2004, Choi et al. prepared self-assembled monolayers (SAM) with imidazolium groups on smooth Au and Si/SiO_2 substrates [1–3]. They studied the effect of a series of anions as shown in **Figure 1** and they found that the surface hydrophobicity increases like this: $Br^- > BF_4^- > PF_6^- > NO_3^- > ClO_4^- > TfO^- > Tf_2N^-$. Hence, Br^- ions led to the highest surface hydrophilicity and Tf_2N^- the highest hydrophobicity.

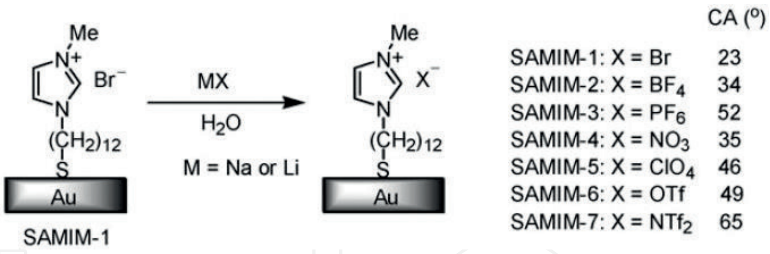

Figure 1. Grafting of monolayers on smooth gold substrates with imidazolium groups with sensitivity to ion exchange and surfaced hydrophobicity as a function of the ion-exchanged. Ref. [1], Copyright 2004. Reprinted with permission from American Chemical Society, USA.

The substituent has also an important influence on the surface wettability [3, 4]. For example, using a long substituent with 1-octyl-3-methylimidazolium ([omim]), θ_w was 68, 72, and 75° for Br⁻, BF_4^- et Tf_2N^-, respectively while with 1-benzyl-3-methylimidazolium ([bmim]) θ_w did not change because the anions are absent in [bmim] aggregation. Similarly, for compounds such as 1-alkyl-3-(3-triethoxysilylpropyl)imidazolium ([C1tespim]) (**Figure 1**), θ_w was 24, 30, and 42° for Cl⁻, BF_4^- et PF_6^-, respectively while with ([C4tespim]) θ_w did not change. Moreover, the cation nature has also an influence on the surface hydrophobicity [3].

In order to elaborate reversible superhydrophobic properties by ion exchange, gold micro and nanostructured substrates were performed by electroless etching process by immersing silicon substrates in aqueous solution of $HAuCl_4$ and HF (**Figure 2**). The surface was then modified by SAM using a thiol terminated by a quaternary ammonium. Then, the surface wettability could be reversely changed from superhydrophilic to superhydrophobic after exchanging Cl⁻ ions by perfluorooctanoate ($C_7F_{15}COO^-$ or PFO^-) ions [4].

Moreover, polymers with charged species such as polyelectrolytes were also used to change the surface wettability [5–15]. For example, [PVBIm][PF_6] ([1-(4-vinylbenzyle)-3-butylimidazolium hexafluorophosphate]) brushes were grafted on a silicon wafer by atom transfer radical polymerization (ATRP). The surface properties could be changed from hydrophobic (θ_w = 95°) to hydrophilic (θ_w = 41°) after exchanging PF_6^- ions by Cl⁻ ions. The wettability of polyelectrolyte

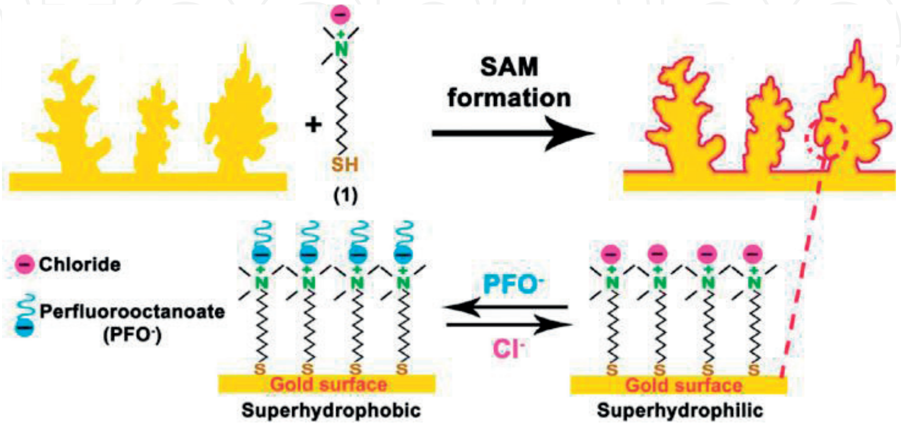

Figure 2. Grafting of ion-sensitive molecules on rough gold substrates. Ref. [4], Copyright 2016. Reprinted with permission from American Chemical Society, USA.

brushes could be modified with appropriate counter-ions [12–15] using poly(2-methacryl poly oxyethyl trimethylammonium chloride) (PMETAC) and poly(2-dimethylaminoethyl methacrylate chloride) (PDMAEMAC).

Superhydrophobic properties could be reached by grafting PMETAC on gold micro and nanostructured substrates by ATRP [16]. Then, reversible and switchable properties from superhydrophobic to superhydrophilic were obtained after exchanging Tf_2N^- ions by SCN^- ions. PMETAC were also grafted onto the surface of multiwalled carbon nanotubes [17]. Their surface properties could be reversely changed from superhydrophobic/highly oleophobic to superhydrophilic/superoleophobic after exchanging PFO^- ions by SCN^- ions. PMETAC was also grafted on cotton fabrics leading to similar properties [18]. Zhang et al. fabricated first silicone nanofilaments and modified them by P(METAC-*co*-trifluoroethyl methacrylate) to the obtained reversible surface [19].

Cho et al. developed a multifunctional polyelectrolyte membranes by electrospinning of P(METAC-*co*-[trimethoxysilyl]propylmethacrylate) (PMETAC-*co*-TSPM) [20]. Here, the presence of TSPM (sol-gel precursor) was used not only to form a polymer network *via* intramolecular interactions but also to anchor substrates (**Figure 3**). The membranes could reversely change from superhydrophobic/highly oleophobic to superhydrophilic/superoleophobic after exchanging Cl^- ions by heptadecafluorooctanesulfonic acid ($C_8F_{17}SO_3^-$ or HPS^-) ions. Moreover, the membranes were also highly efficient filter medium for removing multiple contaminants such as SO_2 form waster gas streams. Another strategy was to deposit polyelectrolyte multilayers poly(diallyldimethylammonium chloride (PDDA) and poly(sodium 4-styrenesulfonate) (PSS) on gold micro and nanostructured substrates [21]. The authors studied the influence of the exchanged ions and the highest properties were obtained by exchanging Cl^- ($\theta_w < 5°$) ions by PFO^- ($\theta_w = 164°$). The authors also deposited polyelectrolyte multilayers on micro and nanostructured aluminum substrates obtained by etching in HCl and immersion in boiling water [22, 23]. Using PFO^- ions, the substrates were superhydrophobic and superoleophobic. When the substrates were immersed in seawater, the PFO^- ions were exchanged by hydrophilic Cl^- or SO_4^{2-} making the substrates underwater superoleophobic.

1.2. Magnetic field

Environment protection against oil leakage during oil tankers sinking is a major global problem. Finding new materials to separate oil/water mixtures is hence extremely important [24–26]. Athanassiou et al. reported the formation of a novel composite material based on polyurethane (PU) foams functionalized with colloidal superparamagnetic iron oxide (spinel-cubic γ-Fe_2O_3/Fe_3O_4) nanoparticles and submicrometer PTFE particles [27]. The resulting foams could efficiently separate oil from water. The combination of the functionalization of the PTFE-treated foam surfaces with colloidal iron oxide nanoparticles significantly increased the speed of oil absorption. The foams were also magnetically responsive because they could be magnetically actuated. Durable and magnetic PU sponges were also reported by CVD of tetraethoxysilane (TEOS) to bind Fe_3O_4 nanoparticles [28]. The sponges exhibited fast magnetic responsivity with a saturation magnetization of 22.73 emu/g and can be easily manipulated with a magnet. The sponges were also superhydrophobic and superoleophilic, quickly absorbed floating oils on the water surface and also displayed high mechanical properties.

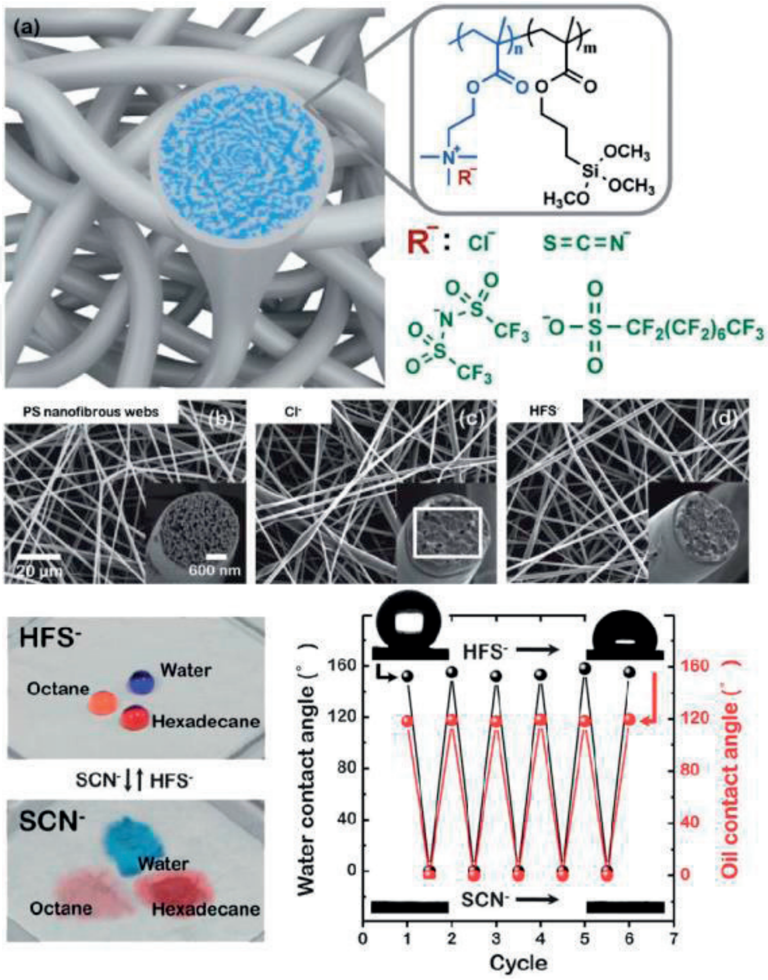

Figure 3. Membranes sensitivity to ion exchange prepared by electrospinning of PMETAC-co-TSPM. The resulting membranes could switch from superhydrophobic/highly oleophobic to superhydrophilic/superoleophobic by changing the counter-ions. Ref. [20], copyright 2012. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

Other materials were also used in the literature [29–35]. Inspired by marine mussel adhesive, Jiang et al. used dopamine to link Fe_3O_4 nanoparticles on electrospun PVDF [29]. After fluorination, the materials displayed oil adsorption properties and could move towards a magnet. Using magnetically responsive mesh substrates, micro-robots were fabricated (**Figure 4**) [30]. The meshes could float and move on air/water and oil/water interfaces and could be guided by a magnetic field.

Zhang et al. reported superamphiphobic elastic and magnetic silicone sponges with excellent thermal stability [31]. Their sponges were prepared by hydrolytic condensation of methyltrimethoxysilane, dimethoxydimethylsilane in the presence of $Fe_3O_4@SiO_2$ nanoparticles and finally fluorinated. Superhydrophobic and magnetic quartz fibers were also reported by loading in cobalt and modification with PDMS [32].

Another potential application of magnetically responsive materials is the control of liquid moving using a magnet [36]. Randomly oriented hierarchical arrays with control geometries (diameter, height, and density) could be prepared by the mouldless self-assembly of solutions

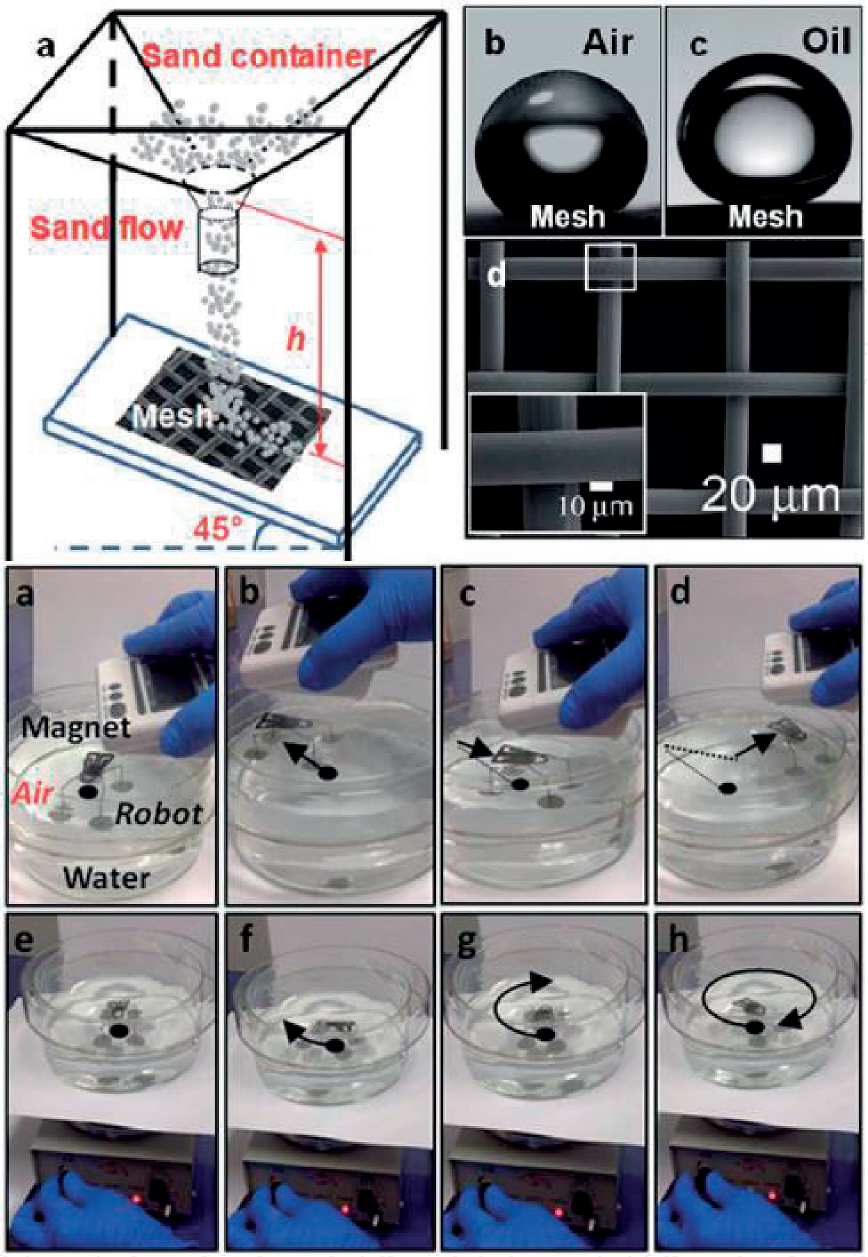

Figure 4. Fabrication of micro-robots using magnetically responsive mesh substrates and Fe_3O_4 nanoparticles. Ref. [30], Copyright 2015. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

comprising procured polymers and magnetic particles under a magnetic field. With their actuating and superhydrophobic properties, these flexible films enabled active, fast, precise, and reversible manipulation of droplets with the use of a magnet.

Moreover, using superparamagnetic droplets on a magnetic superhydrophobic film, it was also shown to switch from superhydrophobic (low adhesion) to parahydrophobic (high adhesion) properties after magnetization/demagnetization [37]. It is also possible to control the speed, the shape, and the self-assembly of magnetic droplets on the superhydrophobic surface by modulating the magnetic field (**Figure 5**) [38, 39].

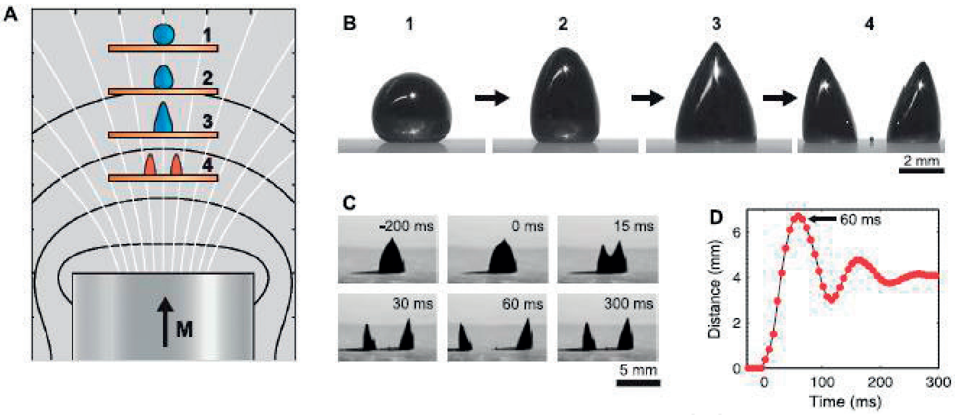

Figure 5. Modification of the speed, the shape and the self-assembly of magnetic droplets on the superhydrophobic surface by modulating the magnetic field. Ref. [38], Copyright 2013. Reprinted with permission from The American Association for the Advancement of Science, United Kingdom.

1.3. Mechanical stress

Most of the time, reversible switchable wettability is governed by the change in the surface chemistry (surface energy). However, the use of mechanical strains is a very interesting way to control the surface wettability by modifying the surface roughness. In 2004, Zhang et al. showed that the hydrophobicity of PTFE can reversely change from 108 to 165° as the material is extended to 190% [40]. This was attributed to an increase in the distance between the fibrous PTFE crystals. They also described a novel method to reversibly change the wettability (from superhydrophilic to superhydrophobic) of a polyamide film with a triangular net-like structure upon biaxial extension and unloading [41]. The average side-length of the triangular structures was around 200 μm before extension and the surface was superhydrophobic, and 450 μm and superhydrophilic after extension. The phenomena could be repeated around 20 times because the film had a good elasticity.

Using a flexible PDMS with micropillar arrays, it was reported the feasibility to drastic change the surface wettability by simple modification of the substrate curvature (**Figure 6**) [42, 43]. When the substrate was not incurved it was parahydrophobic (high water adhesion) while it became superhydrophobic after curvature become the curvature could induce air injection into the pillar arrays. This easy and reversible process could be used in microfluidic devices [42–45].

To obtain micro and nanostructures on PDMS, Singh et al. deposited Ag nanorods arrays using oblique angle deposition on prestretched PDMS (**Figure 7**) [46]. The substrates displayed both microbuckles/wrinkles and nanorods. Superhydrophobic properties with θ_w = 154.8° under 30% prestretching, which is due to optimal amplitude and periodicity of the wrinkles. The substrates also displayed anisotropic wetting and water droplets could move only along the direction parallel to the wrinkles. Reversible contact angles from 154.8 to 126.2° were also reported by simple stretching/relaxation cycles because the stretching changes the dimensions of the microstructures. Yang et al. also reported the properties of PDMS elastomers with microscale ripples and SiO_2 nanoparticles, allowing to reach anisotropic superhydrophobic properties [47]. The surface properties were dependent on the ripple amplitude and periodicity and also on the surface chemistry. Here, the sliding angle could also reversibly be tuned with external strains and with fast response.

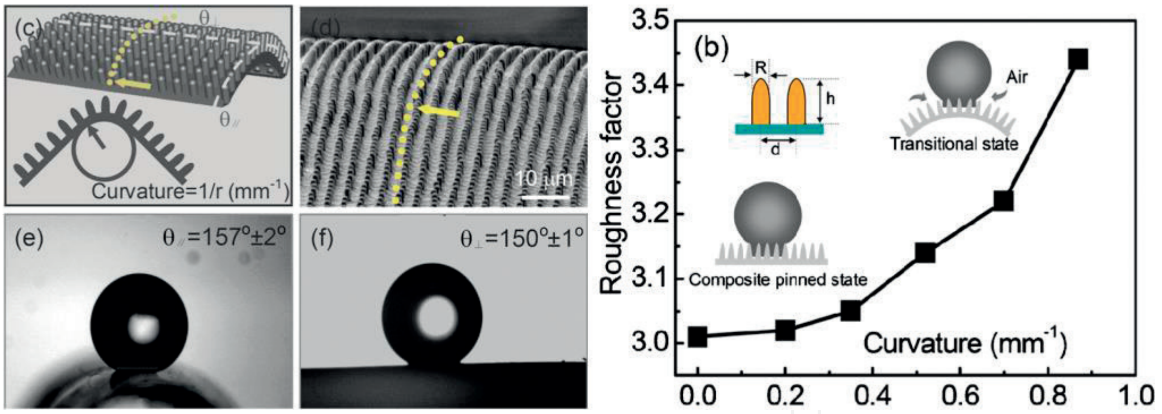

Figure 6. Change in the water adhesion by inducing flexion on a flexible micro-patterned substrate. Ref. [43], Copyright 2011. Reprinted with permission from AIP Publishing LLC, USA.

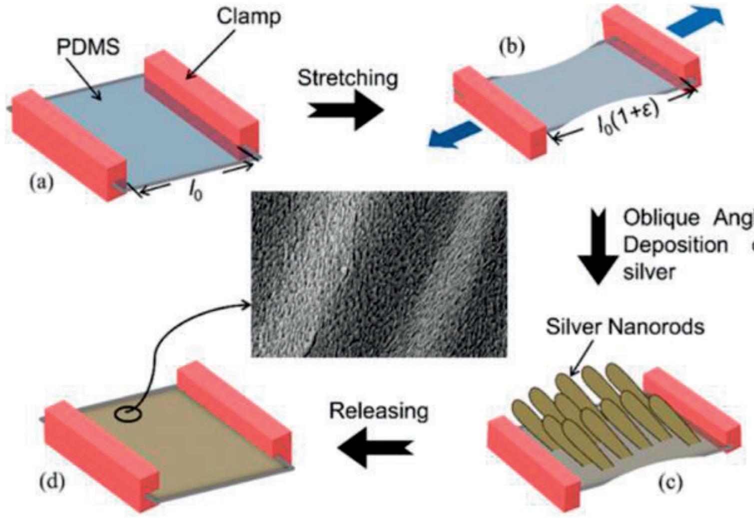

Figure 7. Preparation of microwrinkles of PDMS by pre-stretching following by oblique angle deposition of Ag nanorod. Ref. [46], Copyright 2015. Reprinted with permission from American Chemical Society, USA.

Self-healing superhydrophobic textiles with mechanical responsivity were also reported [48]. To induce this property, polydopamine nanocapsules with trapped hydrophobic agents were coated on the textiles. The nanocapsules could be released using different mechanical stresses, such as stretching, compression, friction, and even mechanical washing, and lead to self-healing properties.

1.4. Plasma

In a plasma chamber, highly ionized species are created by applying an electric field between two electrodes. When the plasma interacts with a substrate, different effects can be produced such as the surface cleaning, the formation of chemical groups, and/or the formation of surface structures. These effects are highly dependent on the plasma parameters such as the used gas, the pressure or the power and also on the substrate nature. For example, if a hydrophobic monolayer is used to prepare a superhydrophobic surface, the plasma treatment can remove the monolayer and leads to superhydrophobic properties [49–52].

However, to obtain reversible properties, it is often necessary to have again the hydrophobic monolayer and/or to storage in the dark.

Otherwise, following the used gas, the plasma treatment can also change the surface chemistry. For example, meshes substrates were coated by CVD with the nanocrystalline diamond film [53]. After H_2 plasma, the surface diamond termination changed with hydrogen atom leading to superhydrophobic properties. Moreover, the surface properties were reversible by annealing in air at 500°C.

1.5. Ultrasound

Very recently, full reversibility between the Cassie-Baxter and Wenzel states were reported through acoustic pressure [54]. Ultrasonication is used both for the nucleation of bubbles directly on superhydrophobic surfaces. Oppositely, the collapse of an entrapped air film was promoted to reversibly manipulate the material surface properties and the interaction with the environment.

1.6. Guest

It is known that specific interactions between "guest" and "host" molecules can be extremely strong. This is the case, for example, between crown ethers and ions. Li et al. used this strategy to develop superhydrophobic surfaces with specific sensitivity [55]. They grafted by click chemistry calix[4]azacrown (C4AC) on micro/nanostructured silicon substrates. Different organic ion pairs were selected (**Figure 8**): 1-butyl-3-methylimidazolium (C_4mim) with different counter ions (Cl^-, Br^- and PF_6^-). Reversible surfaces from superhydrophobic to superhydrophilic were observed but only in the presence of [C_4mim]Cl because [C_4mim]Cl interacts with C4AC cavities and cone resulting in 1,3-alternate conversion. Calix[4]arene lipoic acid (C4LA) was also grafted on the gold substrate [56]. The substrate had specific interaction with guest molecules, resulting in a high decrease of surface hydrophobicity. The interaction was specific with methomyl (a carbamate pesticide) but not with four other tested carbamate pesticides. With the aim to remove metal ions from the environment, responsive mesh was prepared by coating with poly(acrylic acid) hydrogel [57]. The resulting mesh was superhydrophilic and underwater superoleophobic. The mesh could complex Hg^+ ions by complexation with the COO^- groups of poly(acrylic acid) leading to an increase in water contact angle and a decrease in underwater oil contact angle.

Metal-organic frameworks (MOFs), also known as porous coordination polymers, were also used in the literature. In order to prepare hydrophobic MOFs, Planas et al. used an *ortho*-carborane functionalized with pyridylmethyl alcohol groups at the C-positions as a hydrophobic linker to Zn-1,4-benzenedicarboxylate [58]. Moreover, the substrate could change from highly hydrophobic to superhydrophilic by immersion in NaOH/DMF. In order to obtain fluorescent and hydrophobic MOFS, pyrene was incorporated in the structure [59]. The resulting materials displayed super-absorbency and could remove oils from oil/water mixture. They could also C_{60} as guest offering great promise for application in sensors.

In order to develop biosensors with switchable wettability, different strategies were used in order to bind biological molecules. For that, a tricomponent copolymer containing

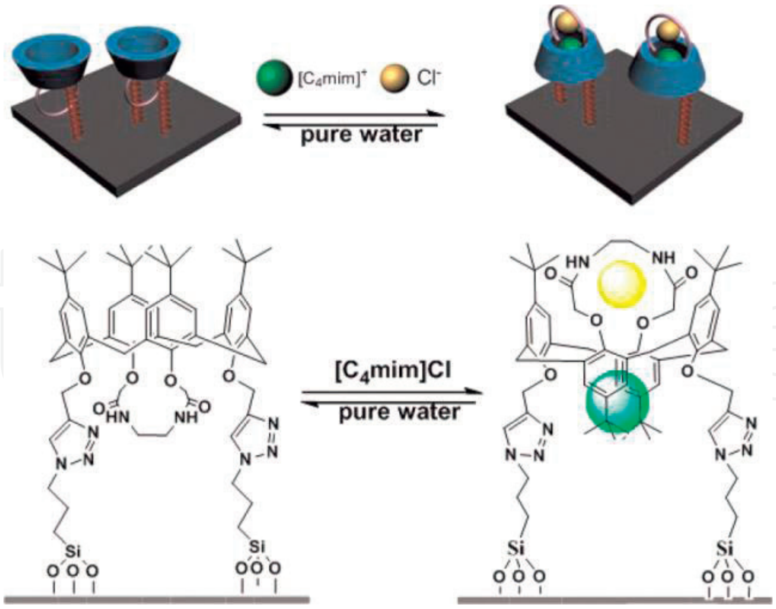

Figure 8. Preparation of guest-responsive surface using calix[4]azacrown derivatives. Ref. [55], Copyright 2012. Reprinted with permission from American Chemical Society, USA.

phenylthiourea and phenylboronic acid was designed [60]. As a strong hydrogen-bonding donor, phenylthiourea was used to combine with the phosphate units and phenylboronic acid to combine with the pentose rings. The copolymer was grafted on structured silicon substrates. The substrates could switch from superhydrophobic to superhydrophilic after immersion in adenosine diphosphate (ADP) aqueous solution. Using copolymers with phenylboronic acid units, biosensors that can bind sugars such as glucose were also reported in the literature [61].

1.7. Solvent and gas

When structured polymer materials are immersed into a solvent such as water, the interactions between the polymer chains and in contact with the solvent can highly varied leading to possible changes in surface morphology and wettability. Mixed polymer brushes with hydrophobic and hydrophilic blocks were used and fixed to a substrate. After exposure to different solvents, the organization of these chains can be highly affected as shown in **Figure 9** [62, 63]. As a consequence, the surface energy and as a consequence θ_w vary [64, 65].

To verify this hypothesis, molecules in Y-shape composed of hydrophobic polystyrene PS and hydrophilic poly(acrylic acid) (PAA) were grafted on a substrate [66, 67]. When the substrate was immersed in toluene, a good solvent for PS, the layer at the extreme surface was mainly composed of PS brushes and reversely the orientation of the polymers chains could highly vary as a function of the affinity with the solvent. PAA-block-PS was also grafted on multiwall carbon nanotubes. The surface could reversely switch from superhydrophobic to parahydrophobic by immersion in water and heating [68].

In order to reach superhydrophobic properties, Minko et al. grafted carboxyl-terminated poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) (PSF-COOH) and carboxyl-terminated poly(2-vinylpyridine) (PVP-COOH) on flat and rough (with needle-like structures) PTFE substrates functionalized with hydroxyl and amino groups (**Figure 10**) [69, 70]. After exposure to toluene,

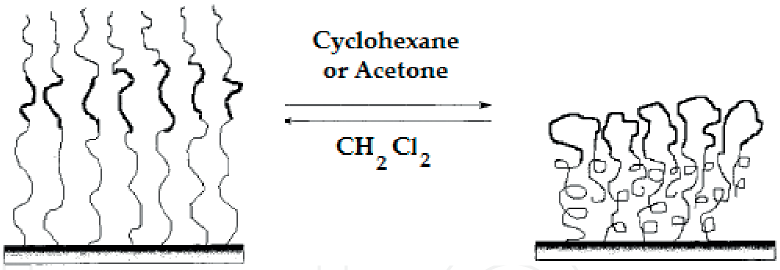

Figure 9. Changing in the organization of mixed polymer brushes with hydrophobic and hydrophilic blocks after exposure to different solvents. Ref. [63], Copyright 2002. Reprinted with permission from American Chemical Society, USA.

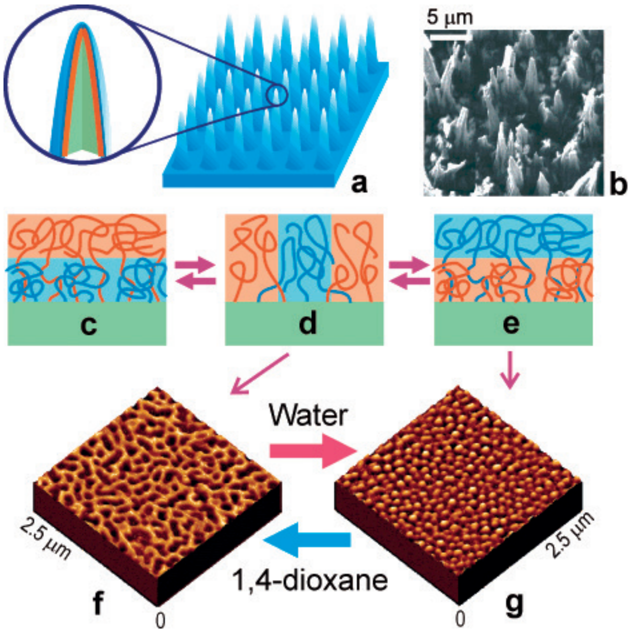

Figure 10. Change in the surface topography and organization of needle-like PTFE nanostructures grafted with PSF-COOH and PVP-COOH after exposure to different solvents. Ref. [70], Copyright 2003. Reprinted with permission from American Chemical Society, USA.

the top layer was mainly composed of hydrophobic PSF while after exposure to water the surface topography changed: PSF formed round domains inside the hydrophilic PVP matrix. As a consequence, on flat substrates, θ_w varies from 118 to 25° while on rough substrates θ_w varies from 160 to 0°.

Ji et al. developed an asymmetric free-standing film layer-by-layer (LbL) assembly using polyethyleneimine (PEI) and PAA [71]. After coating with Teflon on one side, the free-standing film was superhydrophobic on one side and hydrophilic on the other side. As a function of the humidity, the free-standing film could be in a control manner bended and unbended (**Figure 11**). In a similar manner, Sun et al. developed films that could reversely induce wrinkles in the presence of humidity by depositing hydrophobic SiO_2 nanoparticles on multilayer assembly of poly(allylamine hydrochloride) (PAH) and PAA [72]. Aizenberg et al. also reported a very innovative strategy by embedding nanoarrays in a hydrogel [73]. When the material was exposed to water, the orientation of the nanostructures changes leading to different surface hydrophobicity.

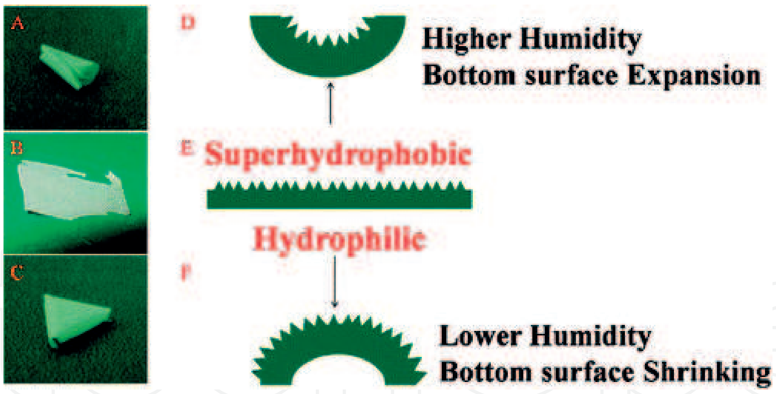

Figure 11. Control in the bending of free-standing films prepared by LbL of PEI and PAA as a function of humidity. Ref. [71], Copyright 2010. Reprinted with permission from American Chemical Society, USA.

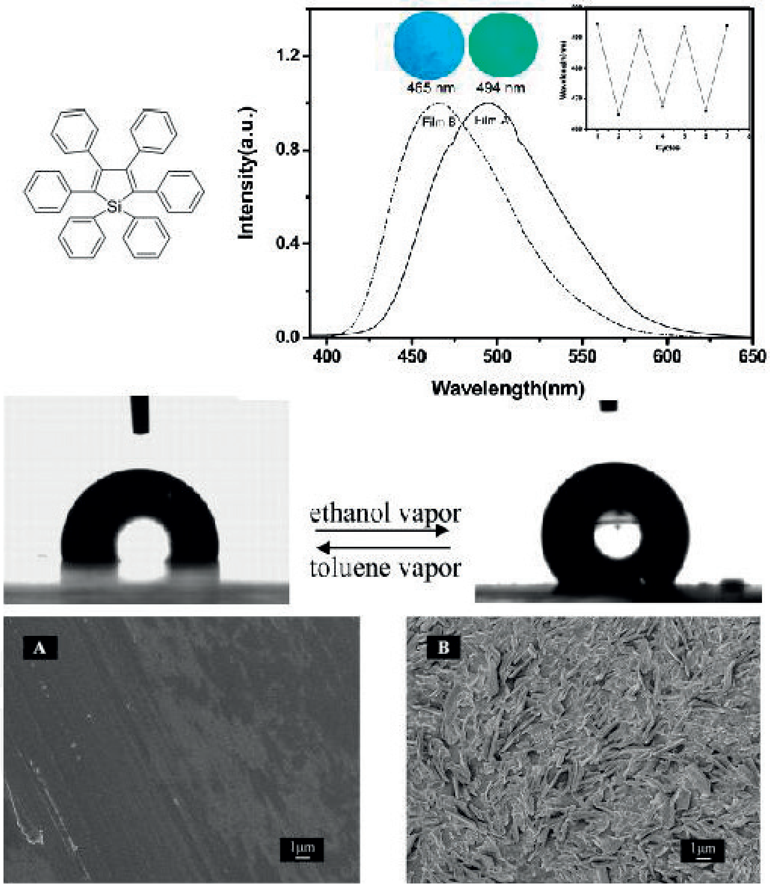

Figure 12. Reversible control in the surface structuration, hydrophobicity, and luminescence properties of 1,2,3, 4,5-hexaphenylsilole films after exposure to ethanol vapor and toluene vapor, respectively. Ref. [74], Copyright 2008. Reprinted with permission from American Chemical Society, USA.

Tang et al. reported that 1,2,3,4,5-hexaphenylsilole is a unique solvent-sensitive material with switchable luminescence properties (**Figure 12**) [74]. When this material is spin-coated on a substrate, the resulting material is smooth, slightly hydrophobic ($\theta_w = 97.0°$) and displayed a green light luminescence. After exposure to ethanol vapor, the substrate became nanostructured, highly hydrophobic (θ_w = 136.3°) and displayed a blue light luminescence. Moreover, the surface properties could be reversely switched using toluene vapor.

Inorganic materials can also be used to obtain solvent-sensitive but, here, it is often possible when interactions of the substrates with the solvent induce changes in the surface chemistry [75–77]. This is the case of titanate nanostructures in water. The authors reported a change in the surface hydrophobicity due to physically adsorbed water molecules [75]. Moreover, the surface was reversible by simple heating. Otherwise, the immersion of inorganic materials can also lead to the removal of the hydrophobic treatment and as a consequence highly decreases the surface hydrophobicity [78, 79].

Different materials sensitive to gases were also reported in the literature [80–86]. 19-25 Jiang et al. developed superhydrophobic indium hydroxide (InOH)$_3$) with microcubes and nanorods using a hydrothermal process in the presence of $InCl_3$ and urea (**Figure 13**) [80]. The surface could switch from superhydrophobic to superhydrophilic in the presence of ammonia ($NH_3{\cdot}H_2O$). Indeed, $In(OH)_3$ being acidic, the ammonia molecules would anchor to the surface and form an ammonia layer on the surface of $In(OH)_3$. Moreover, the bonds created between $In(OH)_3$ and $NH_3.H_2O$ being weak, they can be easily broken by heating leading again to superhydrophobic properties. $In(OH)_3$-PDMS sponges with NH_3 sensitivity were also prepared in the presence of polydopamine [81]. In a similar manner, CO_2 is an acid gas; it can react at the surface of a material if amine groups are present. This strategy was used by Yuan et al. [83]. They electrospun PMMA-*co*-poly(*N*,*N*-dimethylaminoethyl methacrylate), a copolymer with amine groups. The resulting materials could switch from highly hydrophobic and underwater oleophobic to highly hydrophilic and underwater oleophilic in the presence of CO_2. Moreover,

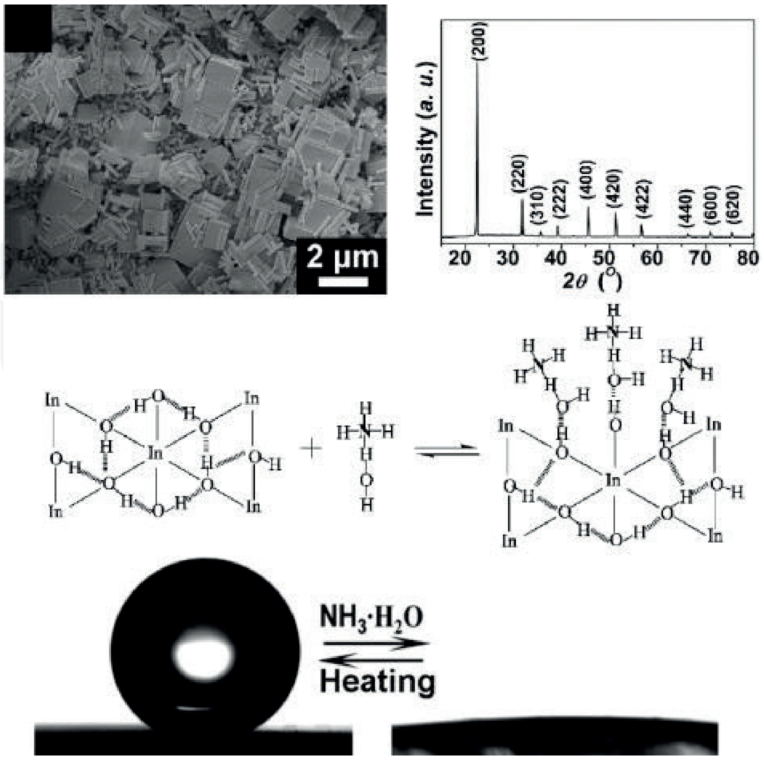

Figure 13. Influence of $NH_3{\cdot}H_2O$ on the surface hydrophobicity of $In(OH)_3$ with microcubes and nanorods. Ref. [80], Copyright 2008. Reprinted with permission from American Chemical Society, USA.

the properties were reversible in the presence of N_2. A very interesting work was reported by Wang et al. using the allochroic material (a material that can changes color) crystal violet lactone (CVL) [84]. To obtain superhydrophobic properties, palygorskite@polysiloxane was modified with CVL. The resulting materials could change from blue (CVL^+: the carboxylate group of CVL) to discolored (CVL) in the presence of different gas vapor such as acetone.

A palladium-based superhydrophobic substrate was reported by Pd coating on vertically aligned Si nanowires [85]. The resulting substrates could reversely switch from superhydrophobic to parahydrophobic (high adhesion) properties in the presence of H_2 or air, respectively. Here, the changes are due to a change in the surface energy due to the formation of β-phase Pd hydride (PdH_x). Moreover, the substrates could potentiate the therapeutic efficiency of 3D stem cell spheroids. ZnO nanowires could also be reversely switched from superhydrophobic to superhydrophilic in the presence of O_2 and H_2, respectively, but at high temperature (300°C) [86]. Using a model based on density functional theory, the authors showed that oxygen-related defects are responsible for the wettability switching.

1.8. Chemical reactions

Different grafting strategies can also be envisaged to prepare the surface with reversible wettability [87–89]. For example, nanofibers of poly(3,4-ethylenedioxythiophene) (PEDOT) functionalized with azido groups (N_3) were prepared by electropolymerization [87]. Then, dithiolane groups were introduced by reaction with lipoic acid also called thioctic acid. Then, various thiols were introduced to modify the surface properties. Both the surface morphology and the surface hydrophobicity were affected by the post-treatment with the used thiol. Interestingly, the use of fluorinated thiols highly changed the surface morphology and porosity leading to superhydrophobic properties and highly oleophobic properties. Moreover, the surface hydrophobicity and oleophobicity were reversible by reaction with dithiothreitol (DTT) to form the dithiolane groups again (**Figure 14**).

The boronic ester chemistry was also used to reversely change the surface properties [88]. This time, nanostructured PEDOT films functionalized with protected 1,2-diol were prepared by electropolymerization. After deprotection, the surface could easily react with different boronic acids containing different aromatic groups as shown in **Figure 15**. Similarly, both the surface morphology and the surface hydrophobicity were affected by the use of boronic acid post-treatment. The highest properties were obtained with the pyrene group for which the surface was parahydrophobic (extremely high water adhesion) with $\theta_w = 135°$.

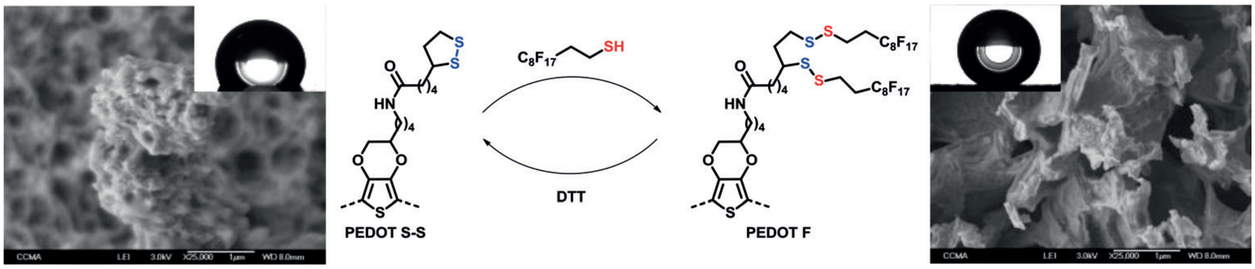

Figure 14. Reversible wetting properties by reaction of hydrophobic thiols on dithiolane and DTT [87].

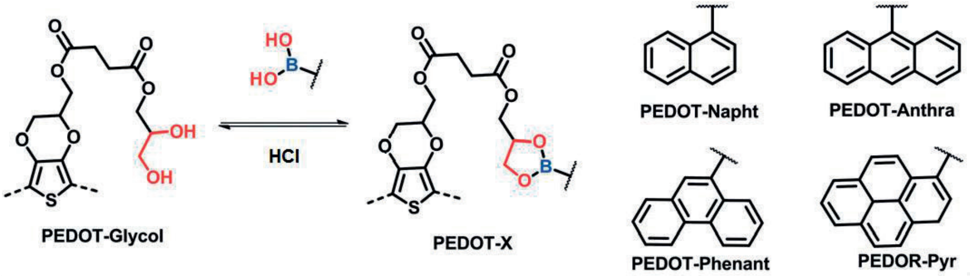

Figure 15. Reversible wetting properties by reaction of hydrophobic boronic acids on 1,2-diols and HCl [88].

1.9. Dual sensitivity

Temperature and pH: Switchable surfaces by temperature and pH were prepared using thermosensitive polymers functionalized by pH-sensitive groups such as carboxylic acids (COOH) or amines. For example, a copolymer of poly(*N*-isopropylacrylamide) (PNIPAAm: sensitive to temperature) and polyacrylic acid (PAA: sensitive to pH) was grafted on micro and nanostructured silicon substrates (**Figure 16**) [90, 91]. The resulting surface could switch from superhydrophobic (low adhesion) at high temperature (45°C) and/or low pH (2) to parahydrophobic (high adhesion) at low temperature (20°C) and/or high pH (11).

Different polymers with amino or pyridinium groups were also used to induce pH sensitivity [92–96]. Hybrid responsive nanoparticles were prepared by grafting on a SiO_2 core mixed block copolymers of PS and poly(4-vinylpyridine) (P4VP) [92, 93]. PS is a thermosensitive polymer

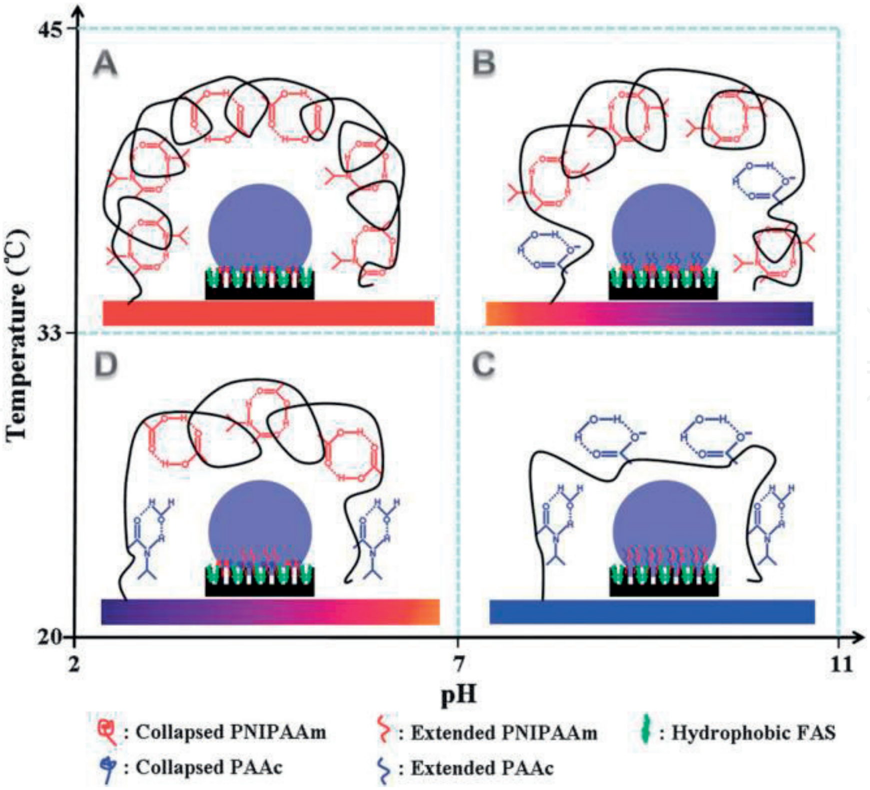

Figure 16. Temperature and pH-switchable surfaces using PNIPAAm and PAA copolymers. Ref. [90], Copyright 2012. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

with a Tg of 100°C while P4VP is sensitive to pH. The surface was superhydrophobic at high pH (6) and at a temperature (> 100°C) while θ_w decreased with the temperature and pH. The authors also observed that the surface roughness changed with the temperature and pH. Wang et al. modified stainless steel meshes with a hydrogel copolymer of 2-(dimethylamino)ethyl methacrylate and methacrylic acid (two monomers sensitive to pH) [95]. Using oil/water mixtures, the meshes could let water pass through with a separation efficiency of 98.35% but only at both high temperature (55°C) and low pH (7), or both low temperature (25°C) and high pH (13). Poly-L-lysine, as both pH and the thermosensitive peptide, was also tested on a micro and nanostructured silicon substrate [96]. The surface was superhydrophobic at both high temperature (60°C) and high pH (11.5), and became superhydrophilic as the temperature and/or the pH decrease.

Solvent and pH: To prepare polymer particles responsive to solvent and pH, copolymers were prepared using a hydrophilic moiety (PAA) and hydrophobic ones (poly(2,3,4,5,6-pentafluorostyrene) [97]. The polymer films produced by annealing in the air led to superhydrophobic properties while by annealing in water led to highly hydrophilic properties (**Figure 17**). This was due to the reorientation of the PAA groups in water. Moreover, due to the presence of COOH groups, the pH could also modify the surface charge between negative and neutral, which can also modify the surface hydrophobicity.

Voltage and pH: Switchable surfaces by voltage and pH were prepared using conducting polymers for their sensitivity to voltage. First, polyaniline was used for its sensitivity also to pH [98, 99]. To form superhydrophobic micro and nanostructured polyaniline with urchin-like and core-shell structures, polystyrene microspheres were used as seed (hard template) for the growth of polyaniline nanofibers [98]. The surface could switch from superhydrophobic to superhydrophilic depending on the voltage and the pH. Similar properties were also reported on polyaniline-polyacrylonitrile coaxial nanofibers prepared by electrospinning [99].

Switchable surface from superhydrophobic properties to highly hydrophilic were obtained by electro-copolymerization of PEDOT monomers with both pH-sensitive groups (COOH)

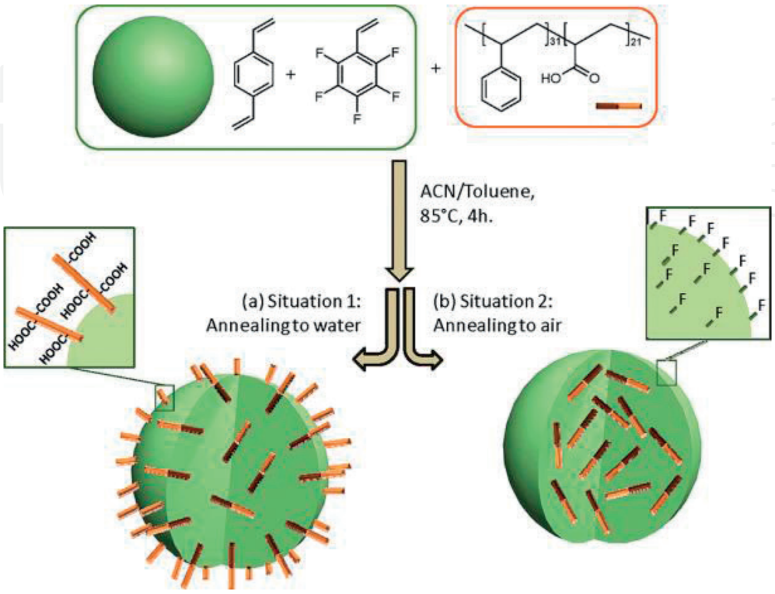

Figure 17. Solvent and pH-switchable surfaces using poly(2,3,4,5,6-pentafluorostyrene) and PAA copolymers. Ref. [97], Copyright 2010. Reprinted with permission from American Chemical Society, USA.

and fluorinated chains [100]. The authors studied the influence of the percentage of each monomer, the doping state and also the pH on both the surface hydrophobicity (**Figure 18**). The surface morphology changed with the percentage of each monomer. The highest wettability changes were observed for a mol% of EDOT-COOH between 12.5 and 25%.

Voltage and Ion Exchange: Switchable surfaces by voltage and ion exchange were prepared using conducting polymers for their sensitivity to voltage while the sensitivity to ion exchange could be obtained by introducing functional groups such as ammonium, imidazolium or sulfonate groups. For example, multiresponsive surfaces were obtained by grafting an imidazolium substituent on PEDOT polymers [101, 102]. Smooth polymer films were prepared by spin-coating and observed sensitivity to ion exchange, oxidative doping, temperature, and pH. Their surface hydrophobicity could be modified from 40 to 70–72° by exchanging the counter-anion of the imidazolium moiety with fluorinated bis(trifluoromethane)sulfonamide or nonafluoro-1-butanesulfonate anions. The surface properties could be also enhanced from 24 to 107° by depositing the polymer on ZnO nanowire arrays. The surface properties of PEDOT:PSS were also studied by the authors [103].

In order to reach superhydrophobic properties, PEDOT copolymers with both ion exchange functional groups and fluorinated chains were prepared by electro-copolymerization (**Figure 19**) [104, 106]. The authors studied the influence of the percentage of each monomer, the doping state and also the counter-ions of ion exchange functional groups on both the surface hydrophobicity (**Figure 19**) [104]. Surprisingly, using 25 mol% of EDOT-Py$^+$, the surface could switch from superhydrophobic to hydrophilic by reduction (dedoping using a different voltage) and again

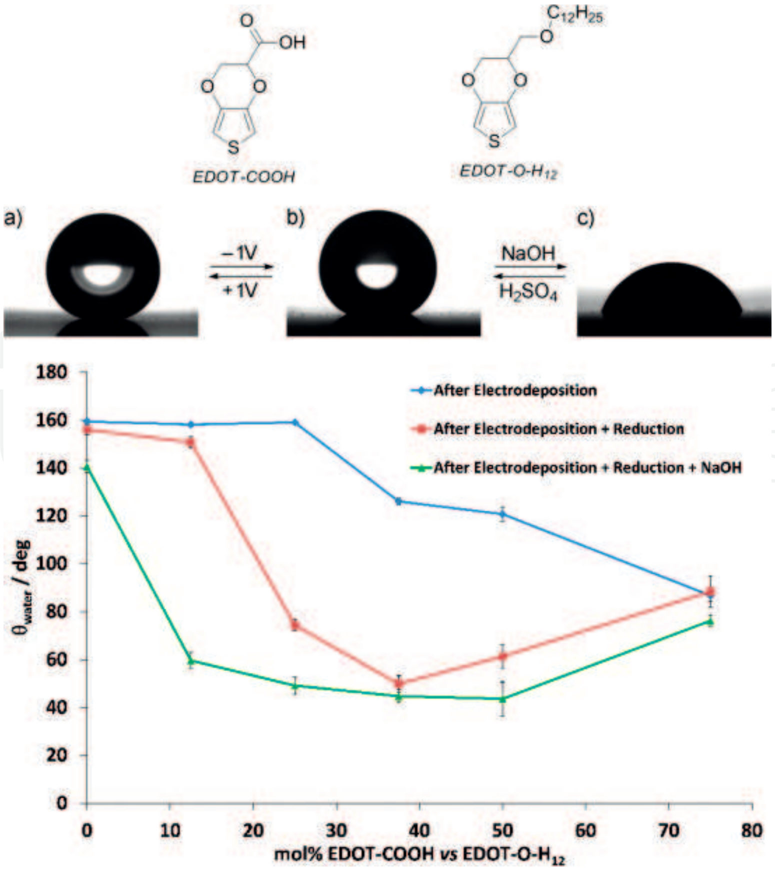

Figure 18. Voltage and pH-switchable surfaces using PEDOT-COOH and PEDOT-O-H_{12} copolymers [101].

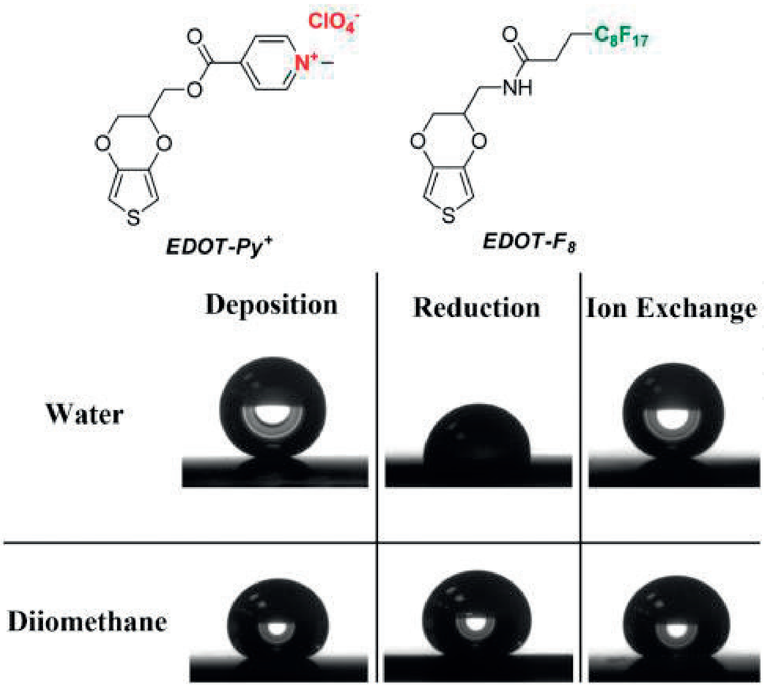

Figure 19. Voltage and ion exchange-switchable surfaces using PEDOT-Py$^+$ and PEDOT-F$_8$ copolymers [104].

superhydrophobic properties by ions exchange with hydrophobic bis(trifluoromethanesulfonyl) imide (Tf$_2$N$^-$) ions while the superoleophobic properties remained unchanged. Hence, it was possible to obtain both superoleophobic and hydrophilic properties, which is extremely rare in the literature [105]. Moreover, superoleophobic properties were also prepared with poly(3,4-ethylenedioxypyrrole) PEDOP copolymers with ion exchange functional groups and fluorinated chains [106].

Light and ion exchange: Switchable surfaces by light and ion exchange were reported by SAM of an imidazolium moiety (sensitive to ion exchange) terminated with a fluorinated chain on nanostructured ZnO (sensitive to light) films [107]. The authors studied the influence of ZnO morphology, the counter-ions (I$^-$, BF$_4^-$, PF$_6^-$, Tf$_2$N$^-$) of imidazolium groups and the light on the surface hydrophobicity. Superhydrophobic properties were obtained with ZnO nanoparticles and hydrophobic PF$_6^-$ or Tf$_2$N$^-$ ions. Moreover, the surface could reversely switch from superhydrophobic to hydrophilic by UV irradiation and dark storage.

Mechanic stress and magnetic field: Liu et al. developed flexible conical arrays coated with magnetic nanoparticles for fog harvesting systems [108]. Under an external magnetic field, static fog water could be spontaneously and continuously captured and directionally transported from the tip to the base of the spine through periodic vibration of the flexible conical spines driven by the magnetic field and the Laplace pressure difference arising from the conical shape of the flexible spines (**Figure 20**). Magnetically sensitive superomniphobic surfaces were also reported by fabricating flexible micronail caps [109]. The micronail caps could reversely bend using an external magnetic field, which changed the surface properties from superomniphobic to superomniphilic.

Multiresponsivity: Switchable surfaces with responsivity to both light, heat, and pH was prepared by modifying TiO$_2$ (sensitive to light) nanoparticles with a copolymer of poly(*N*-isopropylacrylamide) (PNIPAAm: sensitive to temperature) and polyacrylic acid (PAA: sensitive to pH) [110].

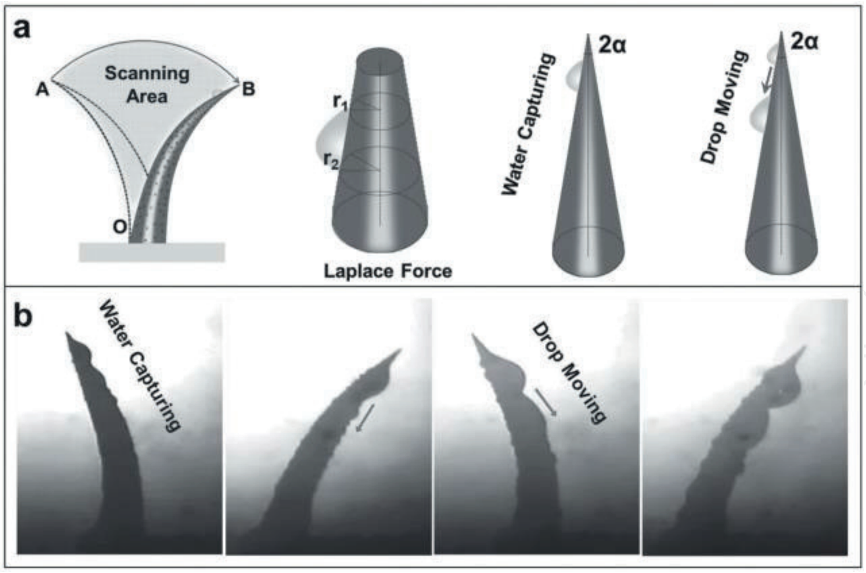

Figure 20. Switchable surfaces with mechanic stress and magnetic field by creating flexible magnetic conical arrays [108].

The resulting polymer surfaces displayed reversible wettability from superhydrophobic to superhydrophilic by UV and heat treatment at 150°C or immersion in solution of pH 12 and 2. Multiresponsive surfaces to heat, pH, and sugars was also reported by using a copolymer of PNIPAAm (sensitive to temperature) and poly(acrylamidophenylboronic acid (sensitive to both sugars and pH) [111]. The surface could switch from superhydrophobic to superhydrophilic by cooling at T = 20°C, exposure to glucose or immersion at high pH (10.1).

2. Conclusion

In this book chapter, most of the articles dedicated to switchable and reversible superhydrophobic surfaces were reviewed. If superhydrophobic properties are highly present in Nature, the preparation of reversible superhydrophobic properties has become one of the most studied domains. Indeed, if robust superhydrophobic surfaces can be obtained if the surface structures are able to stabilize the Cassie-Baxter state, it is possible to induce the Cassie-Baxter-Wenzel transition. In the literature, various techniques were developed to control the surface wettability using extern stimuli such as light, temperature, pH, ion exchange, voltage, magnetic field, mechanic stress, plasma, ultrasonication, solvent, gas or guest. Such properties are extremely important for various applications but especially for controllable oil/water separation membranes, oil-absorbing materials, and water harvesting systems.

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