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Switchable and Reversible Superhydrophobic Surfaces: Part One

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Abstract

In this 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. Introduction

Superhydrophobic surfaces are characterized by a water apparent contact angle (θ_w) above 150° and ultra-low water adhesion or hysteresis (H). The obtaining of superhydrophobic surfaces is crucial in a theoretical point of view and also for various applications such as in self-cleaning windows and textiles, antifingerprint or antireflective properties for optical instruments and mobile phones, liquid transportation, separation membrane, cell and antibacterial adhesion. In Nature, many plants and animals have superhydrophobic properties [1]. These surface properties are extremely important for example to survive against predators or in hostile or arid environments. One can cite the famous Lotus leaves with their self-cleaning properties and also other plants and animals able to slide on the water surface, to see in fogging environments, to walk on vertical substrates, to breath underwater or to swim very rapidly (**Figure 1**) [2–14].

For practical applications, it is often necessary to have “robust” superhydrophobic properties, which is possible combining appropriate surface structures and low surface energy materials.

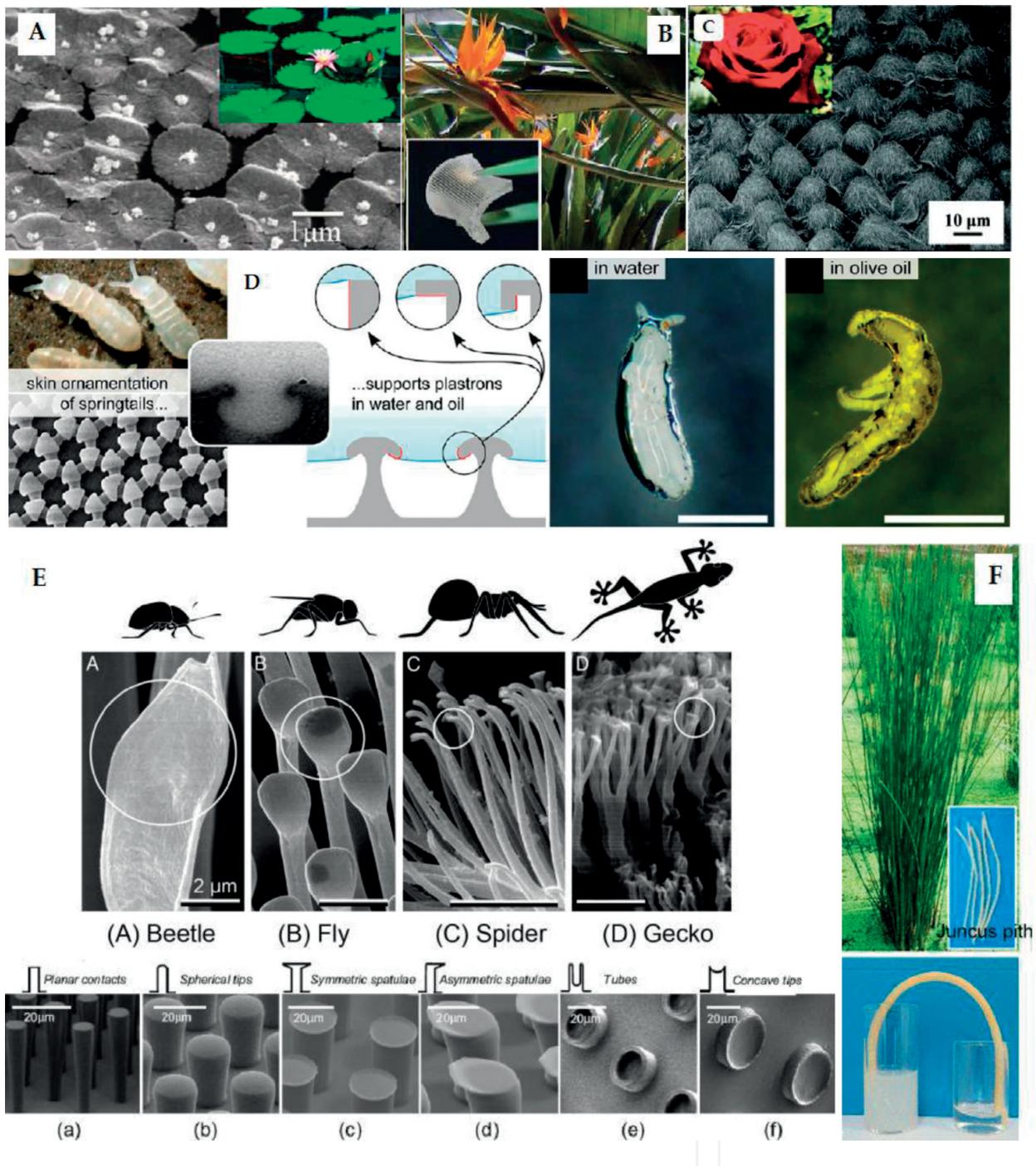


Figure 1. Various species with special wettability properties. A (golden Candoak leaves) Ref. [4], Copyright 2011. Reprinted with permission from American Chemical Society, USA. B (*Strelitzia reginae* leaves) Ref. [5], Copyright 2012. Reprinted with permission from American Chemical Society, USA. C (rose petals) Ref. [9], Copyright 2008. Reprinted with permission from American Chemical Society, USA. D (springtails) Ref. [8], Copyright 2013. Reprinted with permission from American Chemical Society, USA. E (insect and animal foot) Ref. [13], Copyright 2009. Reprinted with permission from American Chemical Society, USA. F (*Juncus pith*) Ref. [14], Copyright 2017. Reprinted with permission from American Chemical Society, USA.

Indeed, robust superhydrophobic surfaces are obtained if the surface is able to stabilize the Cassie-Baxter state. Using an external pressure, it is possible to induce the Cassie-Baxter–Wenzel transition but the transition is irreversible. Hence, in order to induce reversible Cassie-Baxter–Wenzel transition, external stimuli are often used. In this chapter, most of the methods

used in the literature to obtain switchable and reversible superhydrophobic surfaces are summarized. Indeed, different external stimuli can be used such as the light, temperature, magnetic field, mechanical stress or ion exchange. Such materials are extremely used for applications in controllable oil/water separation membranes and water harvesting. One of the main applications is membranes with controllable wettability for oil/water separation. This application is extremely important to find solutions to the spill of oil tankers. Another application is their use in car or building windows in order to see clearly even when it is raining. Water is also not wanted in building materials because it has a high thermal conductivity. Methods to remove quickly water are highly expected. Water harvesting is another important application and systems able to control water wettability are extremely promising especially in hot and arid environments.

2. Theoretical part

Both the surface energy (γ_{SV}) and the presence of surface roughness are key parameters to reach superhydrophobic properties. As reported by Young, the contact angles of a “smooth” substrate are governed by three surface tensions following the reaction: $\cos \theta^Y = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$ where γ_{SV} , γ_{SL} and γ_{LV} are the surface tensions at the solid-vapor, solid-liquid and liquid-vapor interfaces, respectively [15]. However, the presence of surface roughness is fundamental to reach contact angles above 150° , as reported by Wenzel and Cassie-Baxter [16, 17] (**Figure 2**). These two equations take into account the effect of surface roughness, contrary to the Young equation but are also related to the Young equation. When the water droplet follows the Wenzel regime, it penetrates inside all the surface roughness leading to a full solid-liquid interface but amplified by the roughness parameter following the equation: $\cos \theta = r \cos \theta^Y$ (r is the roughness parameter) [16]. Hence, the adhesion of water droplet is important because the roughness parameter increases the solid-liquid interface. Moreover, it is possible to reach contact angle above 150° but only using intrinsically hydrophobic materials ($\theta^Y > 90^\circ$). However, it is now admitted possible to obtain superhydrophobic and even superoleophobic properties using intrinsically hydrophilic and oleophilic materials, respectively. This is possible only if air is present inside the surface roughness, as reported by Cassie-Baxter [17]. The Cassie-Baxter equation has to be applied when there is air trapped inside the surface roughness between the water droplet and the surface. The Cassie-Baxter equation is $\cos \theta = r_f \cos \theta^Y + f - 1$ where r_f is the roughness ratio of the substrate wetted by the liquid, f the solid fraction and $(1 - f)$ the air fraction. Moreover,

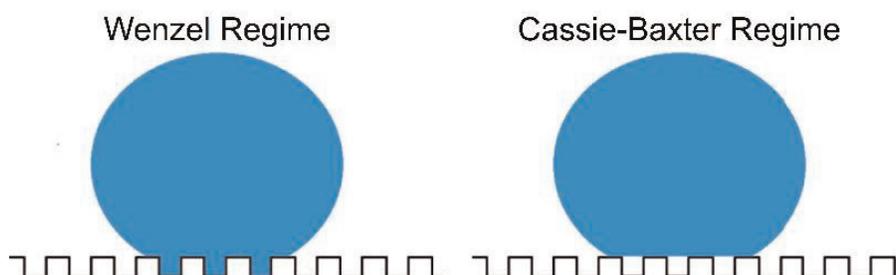


Figure 2. Schematic representation of a water droplet following the Wenzel and Cassie-Baxter equations.

with the Cassie-Baxter, it is possible to obtain superhydrophobic properties with ultra-low adhesion if the air fraction between the water droplet and the surface is extremely important.

The Wenzel and Cassie-Baxter are two extreme states, and it is possible to induce the Cassie-Baxter-to-Wenzel wetting transition by applying an external pressure. Indeed, the Cassie-Baxter equation is a metastable state, and it is possible to switch from the Cassie-Baxter to the Wenzel state by supplying a sufficient energy. “Robust” superhydrophobic surfaces are surfaces that can repel water even if a high pressure is applied [18, 19]. This is the case of the lotus leaves, which remain superhydrophobic even during rainfalls. It was also shown that the presence of re-entrant surface structures often to increase the surface robustness [20–23]. However, the Cassie-Baxter-to-Wenzel wetting transition by applying an external pressure is irreversible because the dewetting forces are too strong [24, 25]. In this review, by supplying other energies to the system, it will be shown how it is possible to obtain reversible Cassie-Baxter-to-Wenzel wetting transition with the possibility to obtain, for example, reversible superhydrophobic-to-superhydrophilic properties. Indeed, it is possible to obtain reversible superhydrophobic properties if this energy modifies the surface energy (γ_{SV}) and/or the surface roughness. Most of the external stimuli used in the literature to obtain reversible superhydrophobic properties will be reviewed.

3. Reversible superhydrophobic surfaces

The surface energy and surface morphology are two main key parameters governing surface wettability. External stimuli are very interesting approaches to induce a change in surface energy and/or surface morphology and lead to a transition from hydrophobic/superhydrophobic to hydrophilic/superhydrophilic. The stimuli used in the literature will be described in order to induce reversible changes in surface wettability (**Figure 3**).

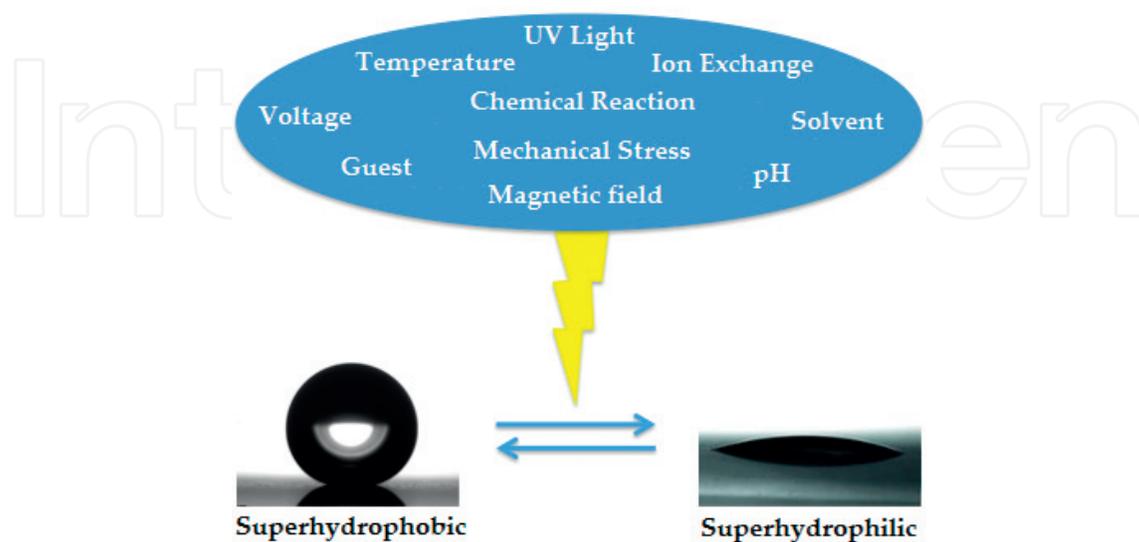


Figure 3. Schematic representation of reversible changes in the surface wettability using external stimuli.

3.1. UV light

Light is one of the major external stimuli used in the literature because of the easiness of utilization and high changes in surface wettability [26]. Various photosensitive inorganic oxides and organic polymers can undergo transitions from hydrophobic/superhydrophobic to hydrophilic/superhydrophilic after UV light irradiation and come back to the original state after storing in dark or exposing to visible light (VIS). This transition is often reversible during many cycles.

3.1.1. Inorganic materials

Among the photosensitive inorganic oxides, TiO_2 and ZnO are the most studied semiconductors. TiO_2 films are now largely used as steamtight and self-cleaning windows for their intrinsic photocatalytic properties and photo-induced hydrophilicity. Indeed, as shown in **Figure 4**, the presence of UV irradiation induces the formation of photoexcited electrons, which can reduce O_2 to generate superoxide radicals ($^{\bullet}\text{O}_2^-$) or hydroperoxyl radicals (HO_2^{\bullet}). These reactive oxygen species are able to convert organic pollutants into CO_2 and water and as a consequence clean the surface [27, 28].

In 1997, Watanabe et al. [29, 30] showed that the water contact angle (θ_w) of polycrystalline anatase TiO_2 was $72 \pm 1^\circ$ and that their wettability properties could reversely change after UV light irradiation. Indeed, as shown in **Figure 4**, the surface of TiO_2 consists of oxygen bridges and UV irradiation creates oxygen vacancies converting Ti^{4+} into Ti^{3+} . These defects can then react with water forming hydrophilic groups at the surface and as a consequence increase the surface hydrophilicity. Then, the wettability conversion was observed on both polycrystalline/monocrystalline anatase and rutile [31, 32]. Many works were dedicated to the modulation of the wettability of TiO_2 films [33, 34]. Among these works, low surface energy coatings were used to enhance the surface hydrophobicity. For example, the contact angle of colloidal crystal of TiO_2 films modified by fluoroalkylsilanes (FAS) was 100° [35]. Then, as observed in Nature, a huge attention was dedicated to the increase in surface roughness of TiO_2 films in order to obtain superhydrophobic properties ($\theta_w > 150^\circ$ and low water adhesion). For example, based on Al_2O_3

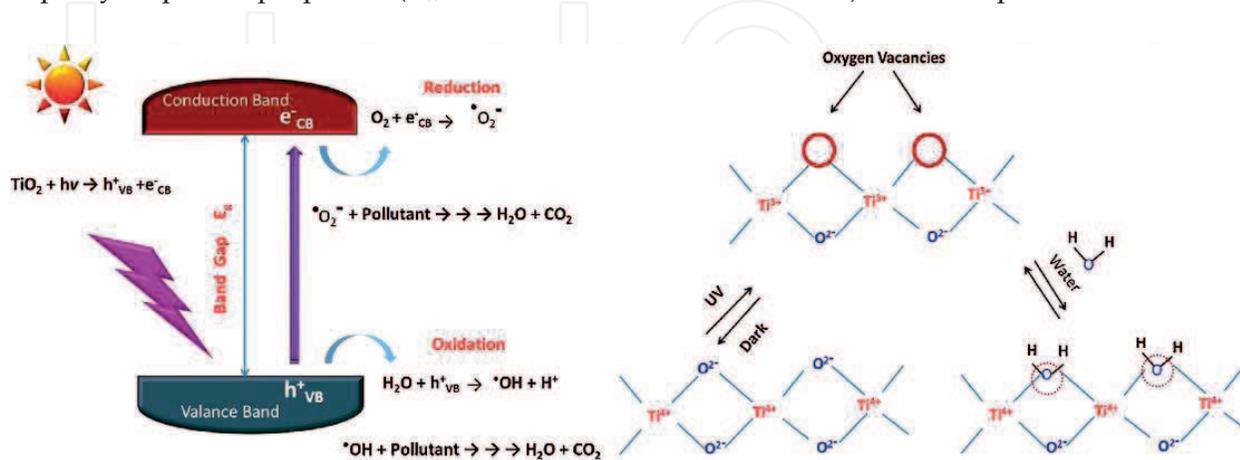


Figure 4. Left: Schematic representation of photocatalytic processes; right: schematic representation of photo-induced hydrophilicity, occurred during UV light irradiation of TiO_2 .

colloids with flower-like morphology, rough colloidal TiO₂ films modified by fluoroalkylsilanes (FAS) was prepared in 2000 [36]. The combination of surface microstructures with low surface energy materials allowed reaching superhydrophobic properties with $\theta_w > 150^\circ$. After exposure to UV light irradiation, the films became superhydrophilic with $\theta_w < 5^\circ$.

Then, with the development of fabrication techniques, many processes were employed to obtain rough surface with various surface morphology [37–54]. TiO₂ nanorods with hierarchical dual-scale roughness were obtained using a hydrothermal process in the presence of TiO₃ and NaCl. The surfaces displayed superhydrophobic properties with $\theta_w = 154 \pm 1.3^\circ$ without using low surface energy materials and superhydrophilic properties with $\theta_w \approx 0^\circ$ after UV light irradiation. Moreover, after dark storage, the surface properties could reversely change from superhydrophobic to superhydrophilic during different cycles [37].

Vertically aligned TiO₂ nanotubes were also reported by anodization of Ti substrates in the presence of F⁻ [38–40]. The tube diameter and length were 175 nm and 3.3 μm , while the density of TiO₂ the nanotubes was 2.3×10^7 tubes mm^{-2} . After modification with a fluoroalkylsilane, the substrates displayed superhydrophobic properties with low water adhesion before UV irradiation and parahydrophobic with high water adhesion after UV irradiation. Moreover, the substrates could reversely switch from non-sticky to sticky by UV irradiation and heat annealing. Other authors also report the possible switching from highly hydrophobic and superhydrophilic using N-doped TiO₂ nanotubes but without low surface energy materials (**Figure 5**) [39]. Superhydrophobic TiO₂ surfaces with nanostrawberry-like morphology were also reported using a seeding growth process [41].

Now, TiO₂-based superhydrophobic surfaces with reversibility are largely used for the conception of smart surfaces and other functional materials. However, some rough morphologies lead to a severe dispersion of the light if their roughness is higher than the wavelength of the light and as a consequence to a loss in transparency. Hence, a promising strategy is the use of surfaces with low surface roughness [42]. In order to obtain an easy and reproducible method, Fujishima et al.

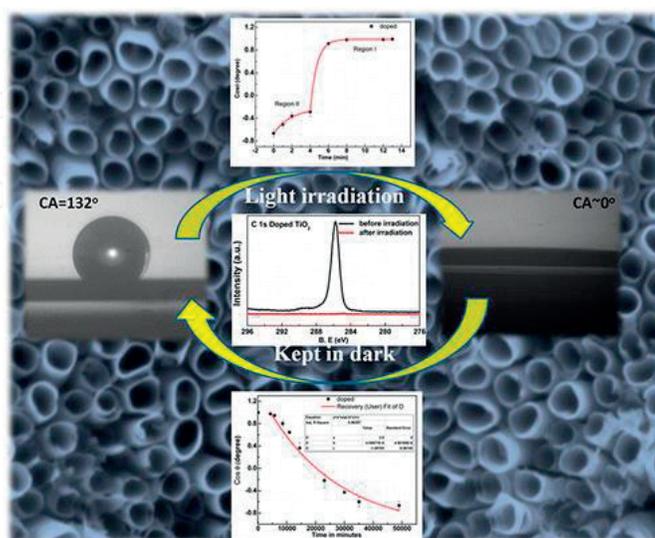


Figure 5. TiO₂ nanotubes with reversible wetting properties upon UV light irradiation and dark storage. Ref. [39], copyright 2013. Reprinted with permission from American Chemical Society, USA.

used a CF_4 plasma etching to reach microstructured TiO_2 -based superhydrophobic properties [43, 44] after coating with octadecylphosphonic acid (ODP). After an etching time of 30s, surfaces with $\theta_w > 165^\circ$ were obtained with reversible conversion by UV irradiation. Ti substrates with switchable and reversible wettability from underwater superoleophobic to superoleophilic were also obtained by femtosecond laser treatment. The substrates are excellent candidates for separating oil/water mixtures [45]. TiO_2 nanoparticles were also deposited on microstructured surfaces in order to enhance the surface properties [45–54]. For example, Franssila et al. used substrates with microscale overhang pillars before depositing TiO_2 nanoparticles by atomic layer deposition [46, 47]. Depending on the UV irradiation time, the surfaces could switch from superhydrophobic to parahydrophobic (1 min), hydrophilic (5 min) or superhydrophilic (10 min). TiO_2 nanoparticles were also deposited on pre-patterned substrates such as paper, membranes or sponges in order to induce different special wettabilities [51–54].

ZnO is another extremely important photosensitive semiconductor for its intrinsic optical, electronic and acoustic properties, reacting similarly to TiO_2 [55, 56]. Here, also many works were dedicated to induce ZnO structures with high roughness [57–79]. Jiang et al. reported the obtaining of ZnO nanorod arrays using hydrothermal processes (**Figure 6**). Their diameter and length were 50–150 nm and 1.2 μm , respectively. The surfaces displayed switchable and reversible properties from superhydrophobic ($\theta_w = 161.2^\circ$) to superhydrophilic by alternating UV light irradiation and dark storage [57]. These kinds of materials could also be used as memristors controllable with the illumination direction [60].

Another application is the preparation of controllable membranes for oil/water separation with specific wetting properties. For example, Jiang et al. developed switchable and reversible superhydrophobic-superhydrophilic and underwater superoleophobic properties by growth of ZnO nanorods on stainless steel meshes (**Figure 7**). More precisely, the meshes were both superhydrophobic and underwater superoleophilic but became both superhydrophilic and underwater superoleophobic after UV light irradiation [61].

ZnO nanorods were also reported using other processes, including chemical vapor deposition (CVD) [62], spray [63, 64] or electrodeposition [65, 66]. Otherwise, ZnO nanostructures of various shapes, including nanosheets, nanowires or nanoflowers, can be easily produced [67–77]. For example, nanoflower structures were obtained just by adding NH_3 during the hydrothermal process in order to form $\text{Zn}(\text{NH}_3)_4^{2+}$ complexes before the formation of ZnO structures [76]. ZnO nanowires were also reported by annealing Zn films at 500°C [70]. Otherwise, the growth of ZnO can also be induced on pre-structured surfaces. For example, a smooth ZnO film was added to Si nanospikes to reach reversible wettability and photocatalytic behavior [78, 79].

Various other oxides, including WO_3 , V_2O_5 , SnO_2 , CuO , Fe_2O_3 , In_2O_3 , SiC and GaN , were used to reversibly change the surface wettability from superhydrophobic to superhydrophilic by alternating UV light irradiation and dark storage or heat treatment [80–92]. For example, Wang et al. showed that the protein adsorption and cell adhesion on GaN nanowires can be modulated by UV irradiation because the surface wettability changes from superhydrophobic to superhydrophilic. It was also sometimes necessary to add a hydrophobic molecule to enhance the surface hydrophobicity and the UV treatment is often able to remove this molecule [93–97]. For example, Bi_2O_3 hyperbranched dendritic structures were superhydrophobic but only after immersion in stearic acid solution [96]. Then, the UV irradiation was able to remove stearic acid

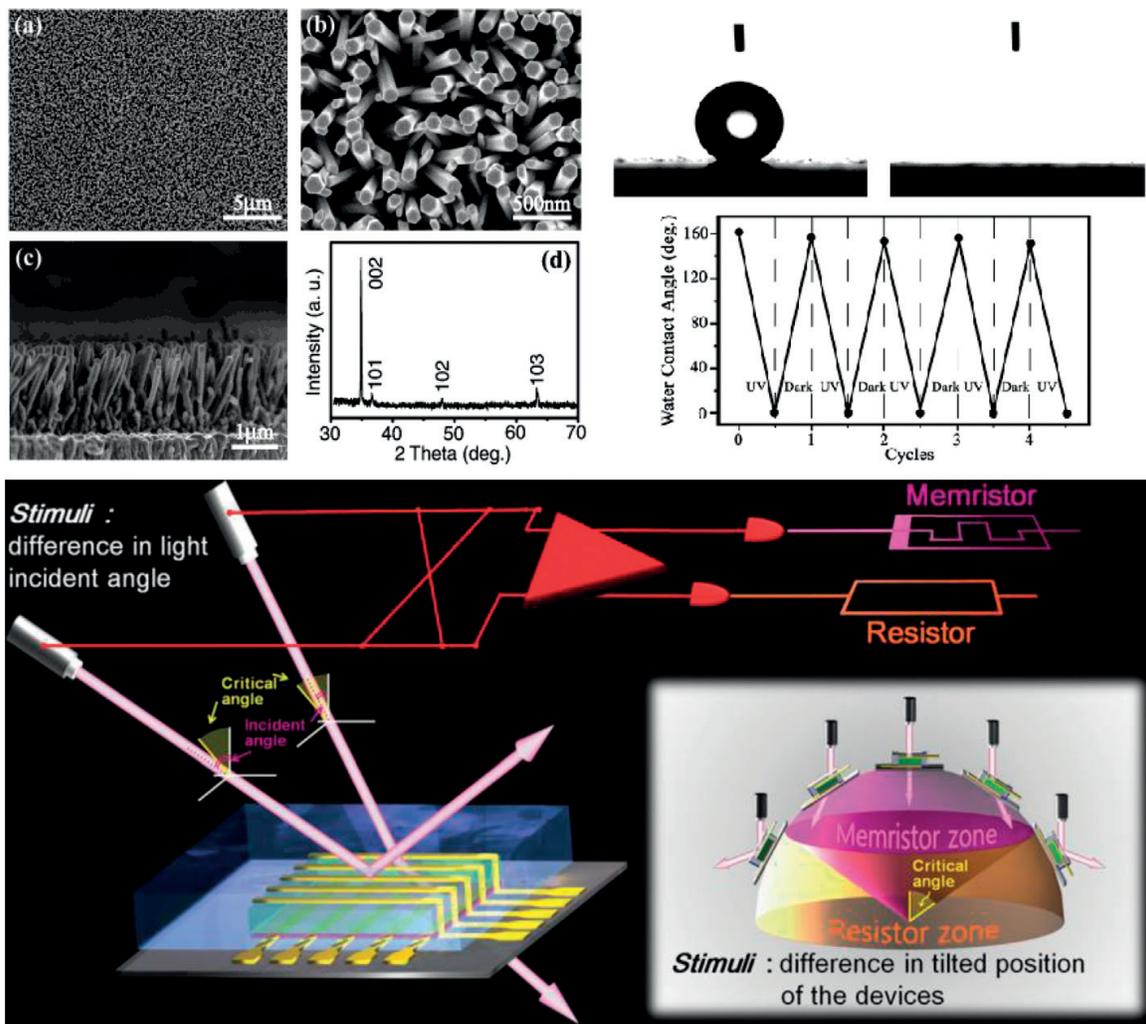


Figure 6. ZnO nanorod arrays with reversible wetting properties upon UV light irradiation and dark storage. The panels a-d represent FE-SEM top-images at low and high magnifications, cross-sectional view and XRD pattern of the ZnO nanorod films. The materials were used as controllable memristors. Ref. [57, 96], Copyright 2004. Reprinted with permission from American Chemical Society, USA [60].

and the surface became superhydrophilic. However, to obtain superhydrophobic properties again, it was necessary to add stearic acid again.

Similarly, carbon-based materials, including carbon nanotubes and graphene films, were also found to change from superhydrophobic to superhydrophilic by UV light irradiation and dark storage [98–101]. Here, the authors proposed that UV irradiation allows to change the absorbed O_2 molecules into hydrophilic groups such as hydroxyl ones [98]. Moreover, various inorganic oxides (such ZnO, p-Si, Al_2O_3 , $SrTiO_3$, Sn, ZnS, CuO, Ag_2O and Cr_2O_3) were found to be also sensitive to X-ray with reversible wettability [102].

3.1.2. Nanocomposites

In order to enhance the stability of the light-sensitive materials, nanocomposites are often performed [103–114]. For example, superhydrophobic TiO_2 /polystyrene (PS) nanocomposites were prepared in the literature. The material wettability could be reversely switch from

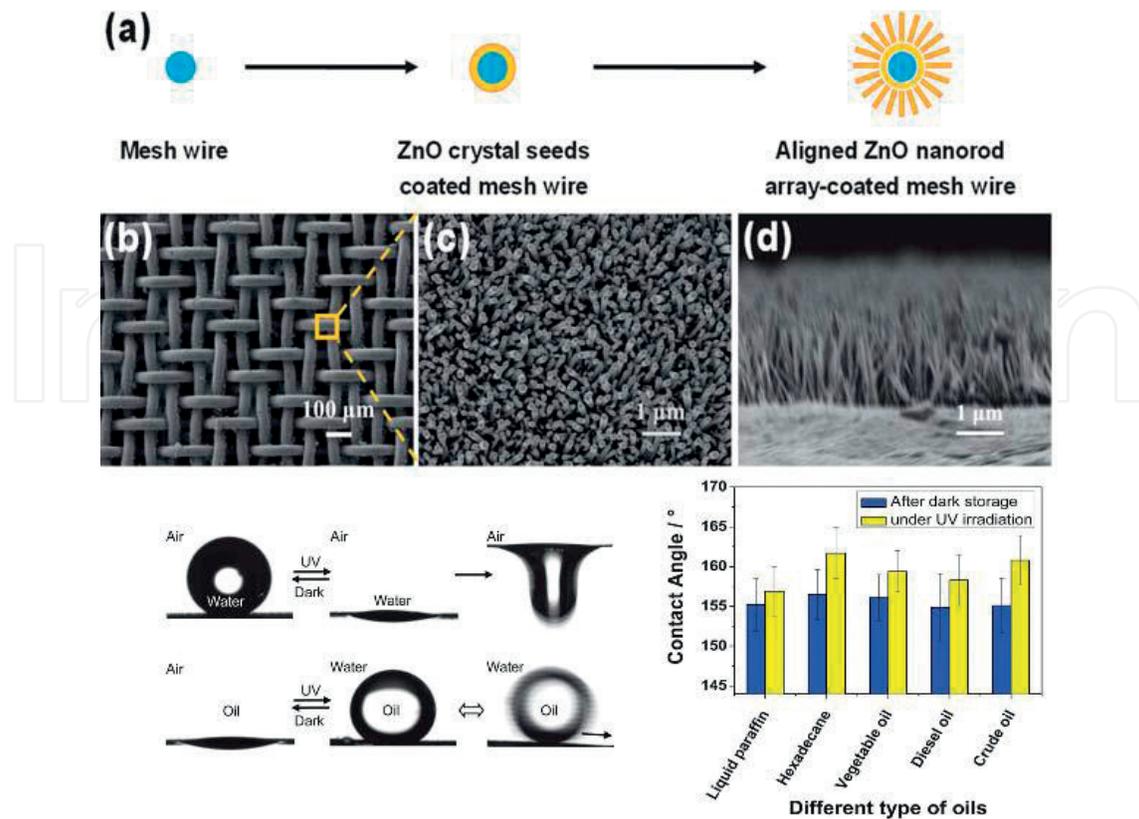


Figure 7. ZnO nanorod arrays grown on stainless steel meshes (Panel A). The Panels b-d represent SEM top view, local enlarged view and side view of the aligned ZnO nanorod array-coated stainless steel mesh film. The resulting meshes could switch from superhydrophobic and underwater superoleophilic to superhydrophilic and underwater superoleophobic upon UV light irradiation. Ref. [61], Copyright 2012. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

superhydrophobic to superhydrophilic by alternating UV light illumination and heat treatment [103, 104]. Using Ag-TiO₂/poly(methyl methacrylate) (PMMA) nanocomposites, it was also possible to switch from superhydrophobic (low adhesion) to parahydrophobic (high adhesion) after UV irradiation [105]. Moreover, the materials displayed anticorrosive properties. ZnO/polyurethane (PU) nanocomposites were also sprayed on stainless steel meshes [110]. The resulting meshes displayed superhydrophobic and superhydrophilic/underwater superoleophobic properties by alternating UV treatment and heat treatment. These meshes could be used to separate oil/water mixtures. Chen et al. also used TiO₂ – SiO₂/polydimethylsiloxane (PDMS) to coat polyester-cotton fabrics [111]. The resulting fabrics were wash-resistant, resistant to strong acids and could be used to separate oil/water mixtures. Moreover, the photocatalytic properties of TiO₂ were also useful to treat dye waste water. Fluorinated compounds or polymers can also be used in order to enhance the superhydrophobic properties [112–114]. For example, TiO₂/poly(vinylidene fluoride) (PVDF) displayed both extremely high $\theta_w = 160.1^\circ$ and low sliding angle (5.5°), and anticorrosive properties [112].

3.1.3. Photochromic organic groups

Organic chemicals containing photochromic functional groups such as azobenzenes [115], diarylethenes, spiropyran [116], bipyridyl ethylenes [117], stilbenes [118] or pyrimidines [119] can follow a reversible transition by UV/vis light, which can lead to differences of wettability.

the first to show the possibility reversibly switch from superhydrophobic to superhydrophilic during the *trans/cis* transition [124, 125]. Using a layer-by-layer strategy alternating poly (allylamine hydrochloride) (PAH) and SiO₂ nanoparticles to obtain rough surfaces, the azobenzene substituents were grafted during the last step. Even if the UV irradiation induced a small θ_w difference (5°) for the smooth substrate, the increase in roughness induces a huge θ_w difference up to 147° for nine deposition cycles. Similar results were obtained using core-shell Fe₃O₄@SiO₂ nanoparticles [126]. The surface hydrophobicity could be easily controlled with the UV or visible light illumination time (**Figure 10**). These materials could also be used to selectively induce water permeation inside membranes.

Other works showed the possibility to modify cotton and paper substrates with these kinds of photosensitive polymers [127–129]. Using polyhedral oligomeric silsesquioxane (POSS) and fluorinated azobenzene, Gao et al. reported the possibility to obtain cotton fabrics with switchable from superhydrophobic/superoleophobic to highly hydrophobic/oleophobic [128, 129]. Indeed, many works were dedicated to the switching from superhydrophobic (low adhesion) to parahydrophobic (high adhesion) after UV irradiation. In order to achieve these properties, many strategies were employed in the literature [130–135]. For example, Xu et al. used an organotellurium-mediated controlled radical polymerization (TERP) in order to achieve polymers

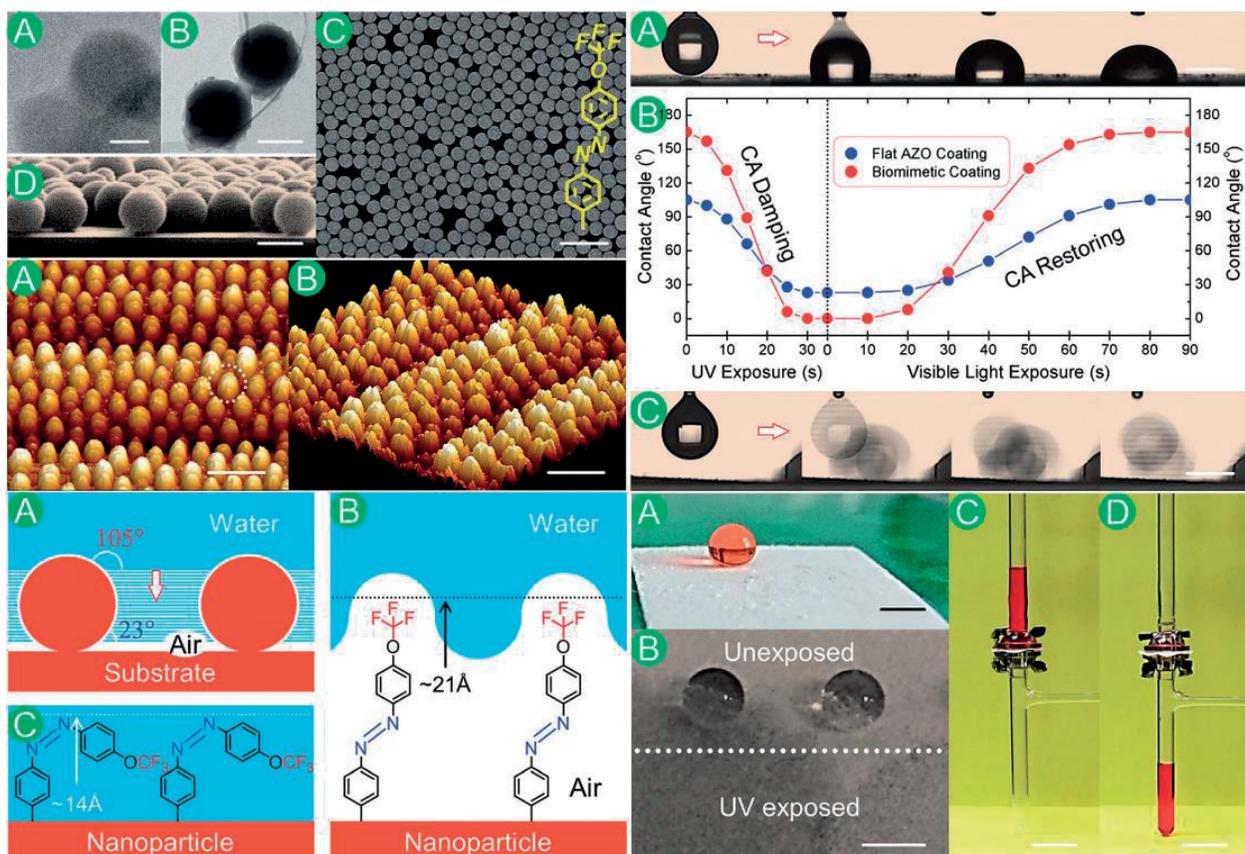


Figure 10. Preparation of light-induced water permeation membranes by grafting azobenzene with CF₃ groups on Fe₃O₄@SiO₂ nanoparticles. Ref. [126], Copyright 2014. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

with micro/nanostructures [130–132]. Hu et al. used SiO_2 nanoparticles and polydopamine in order to graft the azobenzene moieties on SiO_2 nanoparticles [131]. By contrast, other groups deposited azobenzene-based materials on pre-structured surfaces [133–135]. For example, Rhe et al. deposited the azobenzene moieties on Si nanograss obtained by etching Si substrates with C_4F_8 , SF_6 and O_2 . The surfaces could switch from low adhesion to completely sticky after UV irradiation [133]. Yu et al. used micro and nanostructures substrates obtained by photolithography and etching before depositing the azobenzene moieties [134]. The authors measured an adhesion force of $60.6 \pm 12.3 \mu\text{N}$ and $80.8 \pm 4.9 \mu\text{N}$ before and after UV illumination, respectively. Liu et al. used anodized aluminum substrates with a “building blocks” morphology. After coating with a PDMS polymer grafted with azobenzene moieties, the substrates displayed switchable wettability from superhydrophobic (low adhesion: $6.2 \mu\text{N}$ for the *trans* isomer) to parahydrophobic (high adhesion: $44.8 \mu\text{N}$ for the *cis* isomer) properties after UV irradiation [135].

Diarylethene derivatives were found to be another excellent choice for light-sensitive switchable wettability (**Figure 11**). In this case, the light induces a change in the chemical structure from open-ring isomer to closed ring isomer. Uchida et al. reported the unique behavior of this molecule. Upon UV light irradiation, the film became superhydrophobic with $\theta_w = 163^\circ$ due to the formation of microfibrils of diameter around $1 \mu\text{m}$ [136, 137]. Upon visible light irradiation, the surface again became flat with $\theta_w = 120^\circ$. The chemical structure of the diarylethene can also be changed in order to modify the microcrystalline structures. For example, the surface morphology could be modified by sulfonation of the thiophene rings [138].

Different substituents were also introduced to change the material crystallinity [139–141]. The authors demonstrated that in order to obtain superhydrophobic properties with $\theta_w > 170^\circ$, it is preferable to form densely submicrometer sized needle-shaped crystals [139]. For that, it is important that the eutectic temperature of the two isomers of the diarylethene is above that the temperature of formation. Otherwise, large crystals are formed (**Figure 12**).

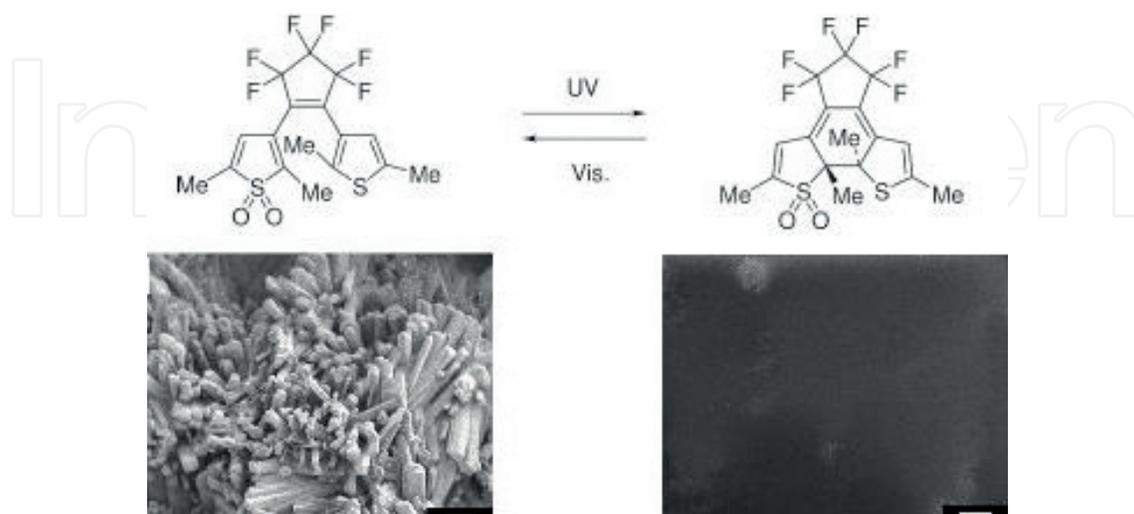


Figure 11. Reversible change of diarylethene from smooth open-ring isomer to microfibrils of closed ring isomer upon UV light irradiation. Ref. [138], Copyright 2011. Reprinted with permission from American Chemical Society, USA.

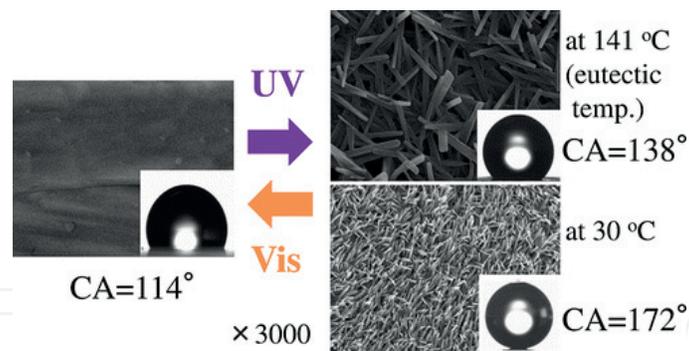


Figure 12. Influence of the eutectic temperature of the diarylethene-type molecule of the parameters of the formed crystals. Ref. [139], Copyright 2012. Reprinted with permission from American Chemical Society, USA.

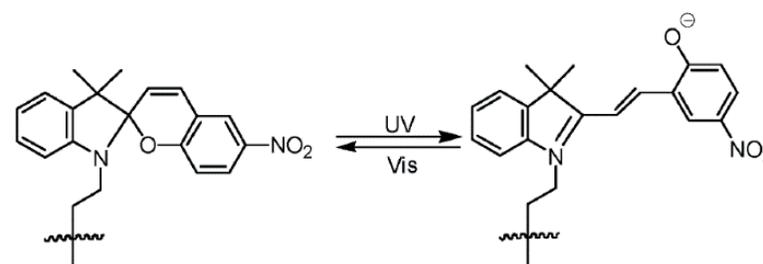


Figure 13. Reversible change in the form of spiropyran upon UV light and visible light irradiation. Ref. [142], Copyright 2002. Reprinted with permission from American Chemical Society, USA.

Spiropyran is another kind of photochromic organic moiety with wetting properties sensitive to light. Its closed form is apolar and hydrophobic, whereas its open form is polar and hydrophilic (**Figure 13**). These two forms can be reversely switched by UV and visible light irradiation [142–144].

In order to obtain superhydrophobic, spiropyran-based molecules can be deposited on rough surface [145–148]. For example, the deposition on Si nanograss gave rise to superhydrophobic properties. Moreover, the authors observed a change from superhydrophobic (low adhesion) to parahydrophobic (high adhesion) properties upon UV light irradiation [145]. Smirnov et al. also reported the possible control of water into a nanoporous aluminum membrane containing a spiropyran moiety using light [147]. Here, the photosensitive membrane acts as a burst valve, allowing the transport of water and ions across the membrane. Lu et al. also reported the formation of melamine-formaldehyde sponge with spiropyran moiety for oil recovery. The sponge was able to control oil absorption and desorption under light illumination [148].

Coumarin was also used in the literature to change the surface wettability. Here, the UV light induces the dimerization of coumarin as shown in **Figure 14**. Hampp et al. deposited a self-assembled monolayer (SAM) with coumarin moieties [149]. They observed a change of θ_w from 70 to 55°. Xu et al. grafted coumarin on SiO₂ nanoparticles [150]. The authors observed in a change of the surface morphology from random nanoparticle aggregates to rings accompanied with a change of θ_w from 102 to 163°.

3.2. Temperature

The reversibility of surface wettability by thermal treatment has given rise to a huge interest during the last years [151, 152]. Poly(*N*-isopropylacrylamide) (PNIPAAm) has been extensively used as an example polymer with thermal response, which has a low critical solution temperature (LCST) of around 32–33°C [151]. On smooth substrate, the θ_w of modified PNNIPAAm can be changed from hydrophilic to hydrophobic when the temperature is over LCST, resulting from competition between intra- and intermolecular interactions, as shown in **Figure 15**.

By grafting the polymer on rough silicon surface obtained by etching, the surface wettability could be changed from superhydrophilic to superhydrophobic with $\theta_w = 149.3^\circ$ when the

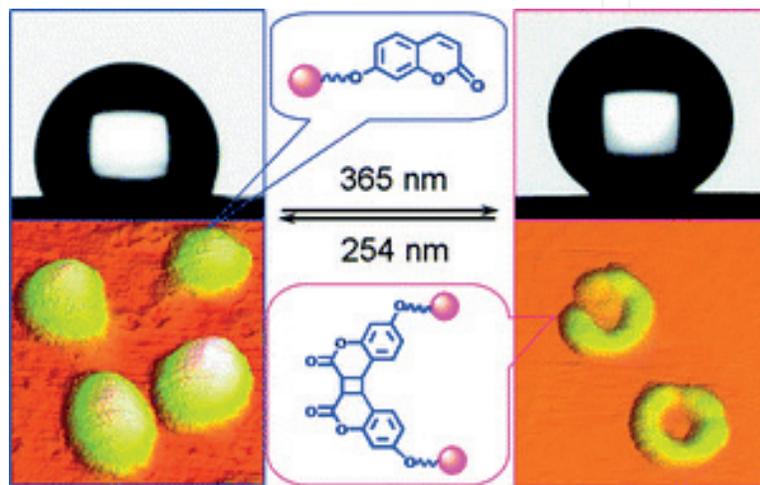


Figure 14. Reversible change of coumarin from aggregates of monomers to rings of dimers upon UV light and visible light irradiation. Ref. [150], Copyright 2012. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

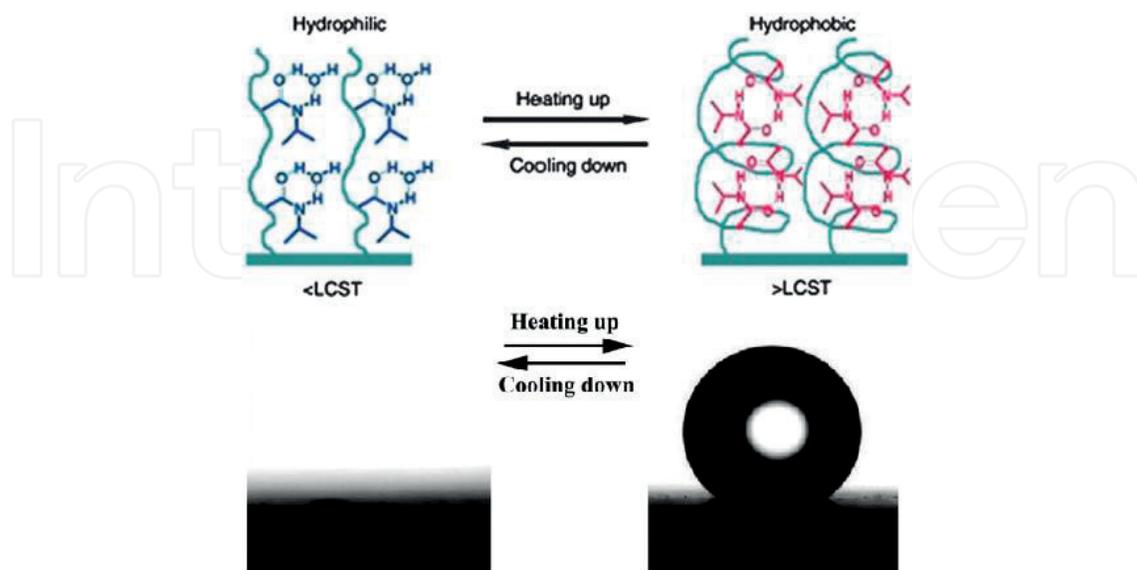


Figure 15. Influence of heating on the intra- and intermolecular interactions in PNNIPAAm and the resulting surface hydrophobicity [151].

temperature changed from 25 to 40°C. Other works also reported this possibility using different strategies [153–156].

PNIPAAm/PS and PNIPAAm/poly(*L*-lactide) (PLLA) nanocomposites were also produced by electrospinning [157, 158]. Depending on the concentration of the constituents, the surface morphology could be changed from beads to long nanofibers. At high concentration of PNIPAAm, the surface could change from superhydrophilic to superhydrophobic when the temperature changed from 20 to 50°C. It was also shown that the response time to switch is depending on the size of the fibers [159]. When the diameter of the fiber was small (around 380–1500 nm), the response time was 4–5 s [160]. Other nanocomposites were also reported with this technique. PNIPAAm/PS blends were used to obtain densely packed nanocupules using an anodized aluminum oxide (AAO) template (**Figure 16**) [161]. Here, the surface could switch by changing the temperature from parahydrophobic (high adhesion) to superhydrophobic (low adhesion) with a difference in adhesion force of around 20 μN.

PNIPAAm was also polymerized on an elastic polyurethane (PU) microfibrous membrane by free radical polymerization [162]. The membrane could be used for controllable oil/water separation. At 25°C, the membrane was underwater superoleophobic, while at 45°C the membrane was underwater superoleophilic (**Figure 17**).

Xin et al. reported the preparation of PNIPAAm-cotton fabrics able to collect different amount of water from fog [163]. At room temperature, the cotton showed a water uptake of 340%, while at 40°C the uptake was only 24%. Such materials are extremely interesting for water harvesting systems. Microfluidic thermosensitive valves were also prepared [164, 165]. After coating with PNIPAAm, the valve was hydrophilic at room temperature and allowed the flow (opening status), while at 70°C, the valve was superhydrophobic and stopped the water flow

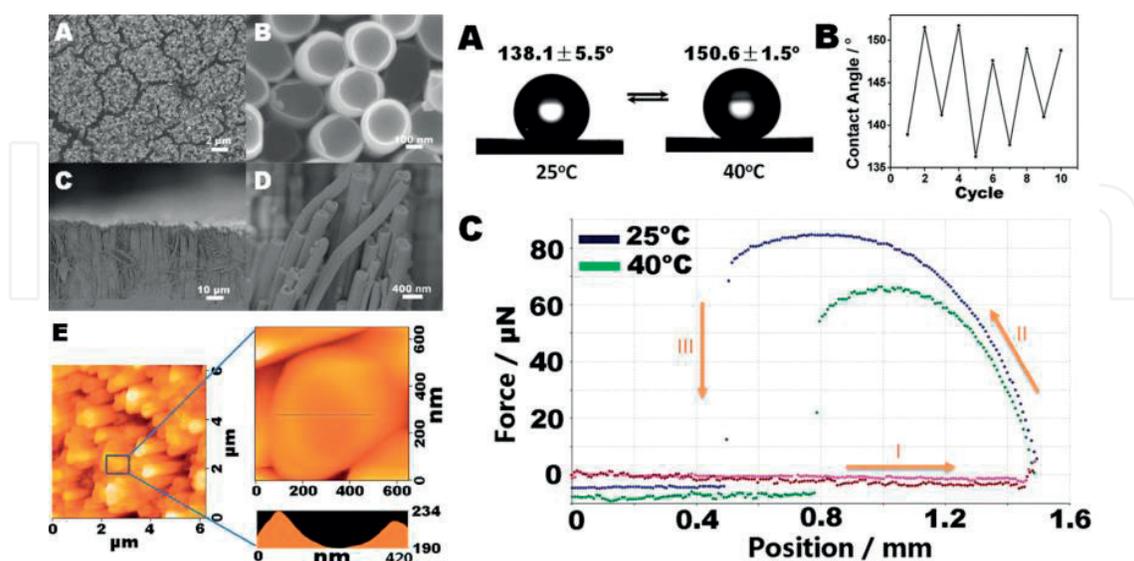


Figure 16. Densely packed PNIPAAm/PS blends nanocupules with reversible change from superhydrophobic (low adhesion) to parahydrophobic (high adhesion) by heating and cooling. Ref. [161], Copyright 2014. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

(closing status). Using a similar idea, an “ON-OFF” switchable enzymatic biofuel cell was reported [166]. Here, gold nanoparticles protected glucose oxidase and laccase were entrapped into PNIPAAm chains. At room temperature, the fuels and the mediator could access to the catalytic centers of enzymes (“ON” state), while at 50°C the process of reactant transmission was blocked (“OFF” state).

Poly(ϵ -caprolactone) (PCL) was also tested as a thermosensitive polymer with a transition from crystalline phase to amorphous phase (**Figure 18**) [167]. Jiang et al. showed that PCL₁₀₀₀₀ is an ideal material. For a smooth surface, θ_w of PCL₁₀₀₀₀ was 88.1°C at room temperature because the polymer chains are frozen by crystallization. However, at 60°C, θ_w was 60.8°C because water can induce the reorientation of the hydrophobic/hydrophilic groups. Moreover, by depositing this polymer rough substrate composed of arrays of square pillars (10 $\mu\text{m} \times 10 \mu\text{m}$ in width, 30 μm in height), a change from superhydrophobic to superhydrophilic was observed after heat treatment. The highest properties were obtained groove spacing of 40 μm .

SiO₂ and carbon nanotube/PCL nanocomposites were also used in the literature [168, 169]. For example, using carbon nanotubes, it was reported the possibility to switch from hydrophobic to hydrophilic or from superhydrophobic (low water adhesion) to parahydrophobic (high water adhesion), dependent on PCL concentration.

Liquid crystalline polymers also showed thermosensitivity when the temperature induces a reversible change from liquid crystalline to isotrope. After grafting liquid crystalline segments (butyl-oxy biphenylcarbonitrile) on a smooth PDMS elastomer, the authors observed a change of θ_w from 92.4 to 89.3° due to a change of the polymer from smectic A to isotrope [170]. The same polymer was also used to cover rough substrates composed of arrays of square pillars (10 $\mu\text{m} \times 10 \mu\text{m}$ in width,

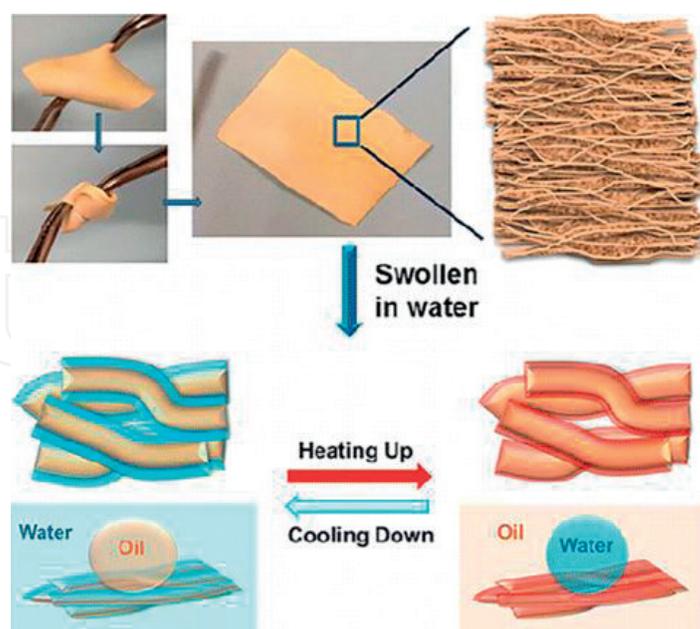


Figure 17. PU membrane grafted with PNIPAAm to induce reversible change from underwater superoleophobic to underwater oleophilic by heating and cooling. Ref. [162], Copyright 2016. Reprinted with permission from American Chemical Society, USA.

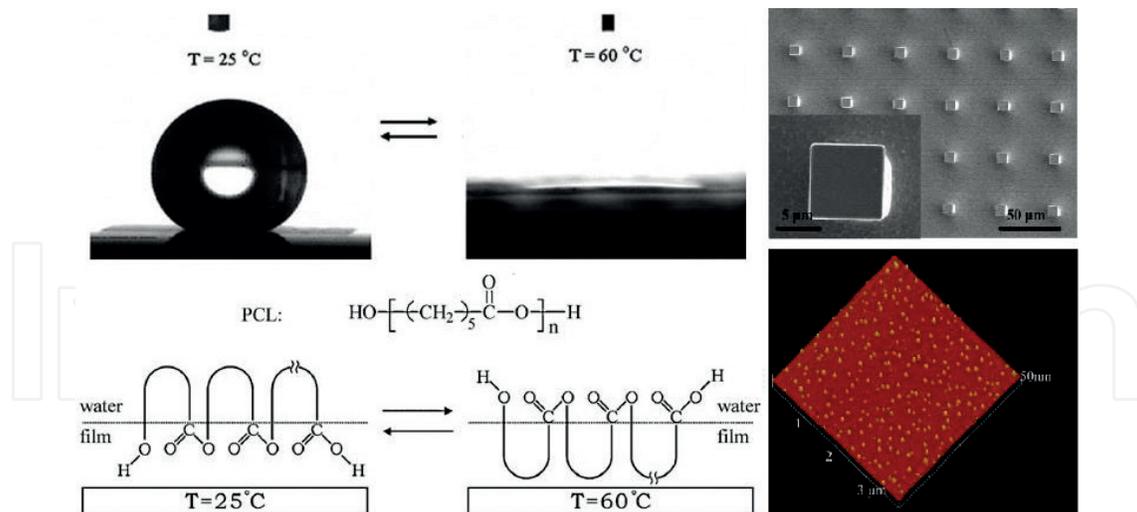


Figure 18. Influence of heating on the phase transition from crystalline to amorphous of PCL₁₀₀₀₀ and the resulting surface hydrophobicity. Ref. [167], Copyright 2008. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

30 μm in height). A huge influence of the groove spacing was observed. Interestingly, a change from superhydrophobic (low water adhesion) to parahydrophobic (high water adhesion) was observed for a groove spacing of 15 μm. Liquid crystalline elastomers were also prepared using a side-on liquid crystalline monomer 4''-acryloyloxybutyl 2,5-di(4'-butyloxybenzoyloxy)benzoate [171]. Here, a change from nematic to isotrope was observed at a temperature up to 70°C depending on the used polymer. By depositing the polymer on a smooth substrate, a change in θ_w of only 3° was observed, while by depositing rough substrates composed of arrays of cylindrical pillars (3 μm in diameter, 6 μm in height, 1.5 μm in spacing), a change from 127 to 86° was measured.

Various inorganic materials also showed thermal response. Shirtcliffe et al. studied the wettability of porous SiO₂ foams obtained by sol-gel from methyltriethoxysilane (MTEOS) [172, 173]. The resulting materials displayed switchable wettability from superhydrophobic to superhydrophilic (Cassie-Baxter-to-Wenzel transition) when they are heated at 400°C. To become hydrophilic, the surface must become more polar. The authors think that this could occur by the formation of new groups or by a change in the relative abundances of apolar methyl groups and polar silica species. Sol-gel foams were also prepared using varying proportions of phenyltriethoxysilane (PhTEOS) and TEOS. The temperatures at which switching occurred were increased when larger fractions of PhTEOS and reversely. SiO₂ suspensions, made from SiO₂ nanoparticles hydrophobically modified with chlorotrimethylsilane and PDMS vinyl terminated, were deposited by spraying [174]. The resulting substrate could reversely switch from superhydrophobic to hydrophobic after cooling at very low temperature (−15°C). Here, the authors attributed this possibility to water vapor condensation on the surface. When the subfreezing film was placed in ambient environment, the humidity in the air condensed to the subfreezing surfaces and increased the surface hydrophilicity. Otherwise, inorganic materials could also be coated using a hydrophobic material in order to achieve superhydrophobic properties [175–179]. Here, the heat treatment could induce the desorption

of the hydrophobic material and switch the surface from superhydrophobic to superhydrophilic. However, these kind of materials are reversible but only after surface remodification with the hydrophobic material.

3.3. pH

Materials containing functional acid or basic groups such as amines or carboxylic acids can be used to induce switchable properties by pH changing [180, 181]. For example, at low pH, the COOH group is protonated, while at high, pH it is deprotonated (COO^-) with a much higher hydrophilicity [182]. Zhang et al. modified rough gold substrates with micro/nanostructures by self-assembly of different thiols. They used the dendron thiol 2-(11-mercaptoundecanamido)benzoic acid (MUABA) [183] or mixed solution of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$ [184].

Depending on the surface roughness and the pH, it was possible to obtain switchable surface from superhydrophobic to superhydrophilic. Using mixed solution of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$, the wetting properties were highly dependent on the percentage of each constituent [185, 186]. Using 40 mol% of $\text{HS}(\text{CH}_2)_{10}\text{COOH}$, the surface could change from superhydrophobic ($\theta_w = 154^\circ$) to superhydrophilic ($\theta_w \approx 0^\circ$) as the pH increases.

Mixed solution of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$ was also used on rough mesh substrates [187–191]. $\text{Cu}(\text{OH})_2$ nanoneedles were grown on copper meshes by anodization in KOH solution or by immersion in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NaOH (**Figure 19**) [187–189]. After surface modification with mixed solution of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$, the best properties were obtained with 60 mol% of $\text{HS}(\text{CH}_2)_{10}\text{COOH}$. The best properties were also obtained for a mesh pore size of 58 μm . Indeed, the authors showed that the pressure that the meshes can support is depending on the mesh geometry and pore size, formation of surface structures on the meshes (nanoneedles) and the surface energy, which here changes with the pH [187–190]. For acidic and neutral water, the meshes were superhydrophobic and underwater superoleophilic. For basic water, the meshes were superhydrophilic and underwater superoleophobic. Here, both the immiscible oil/water mixture and oil-in-water emulsions could be separated on-demand through changing the water pH and with high efficiency and high flux. pH-responsive fabrics were also reported after growth of Ag structures and surface modification with mixed solution of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$ [192].

The change of wettability of DNA nanodevices was also studied [193]. DNA molecules modified with fluorinated hydrophobic groups were fixed to gold substrates by SAM. The conformation of the DNA molecules on the substrate could change with the pH. The substrate was superhydrophilic at low pH and superhydrophobic at high pH.

Various polymers with pH-sensitive groups were also used in the literature. Polymers with carboxylic groups were reported [194–199]. In 2006, Jiang et al. deposited colloidal crystal films made of poly-(styrene-methyl methacrylate-acrylic acid) via a batch emulsion polymerization in the presence of sodium dodecylbenzenesulfonate (SDBS) (**Figure 20**) [194]. At pH 6, the carboxylic groups are in the protonated state (COOH), which could do hydrogen bonds with the SO_3^- groups of SDBS. As a consequence, the hydrophobic tails of the SDBS

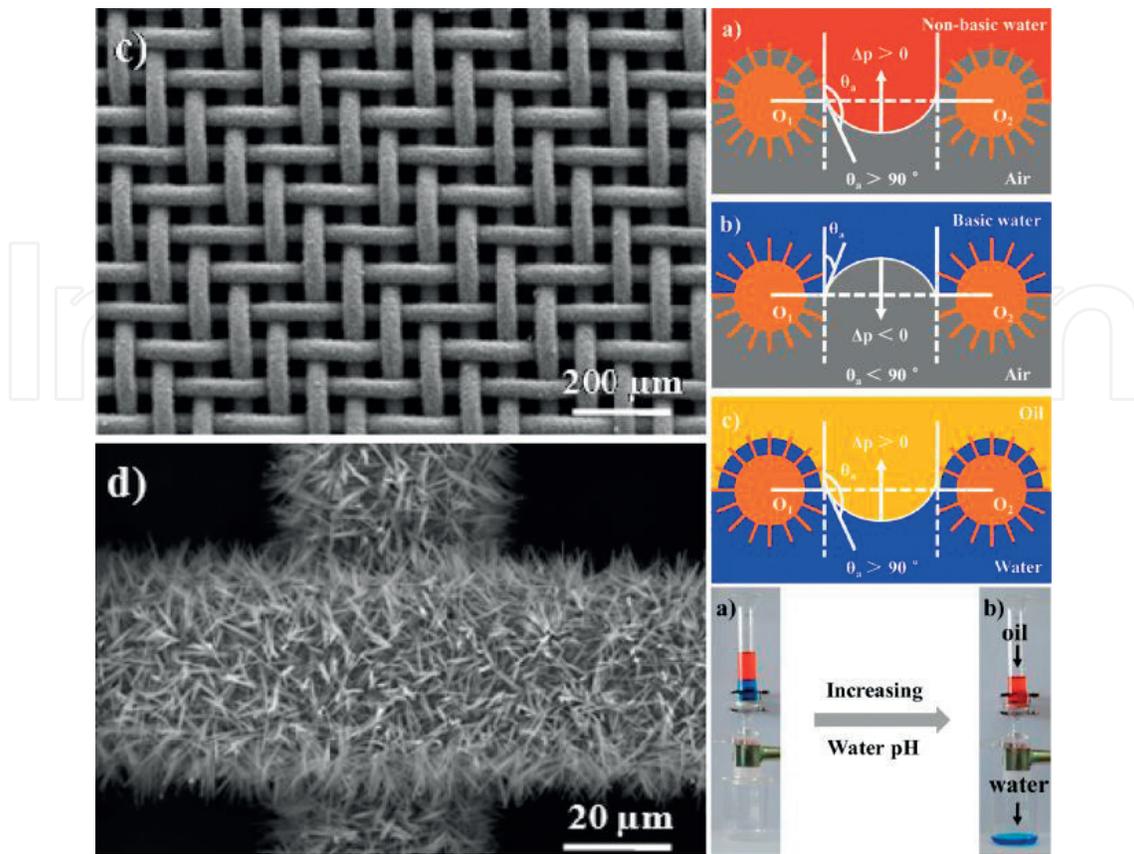


Figure 19. $\text{Cu}(\text{OH})_2$ nanoneedles grown on copper steel meshes. The resulting meshes could switch from superhydrophobic and underwater superoleophobic to superhydrophilic and underwater superoleophobic by changing the pH. Ref. [188], Copyright 2015. Reprinted with permission from American Chemical Society, USA.

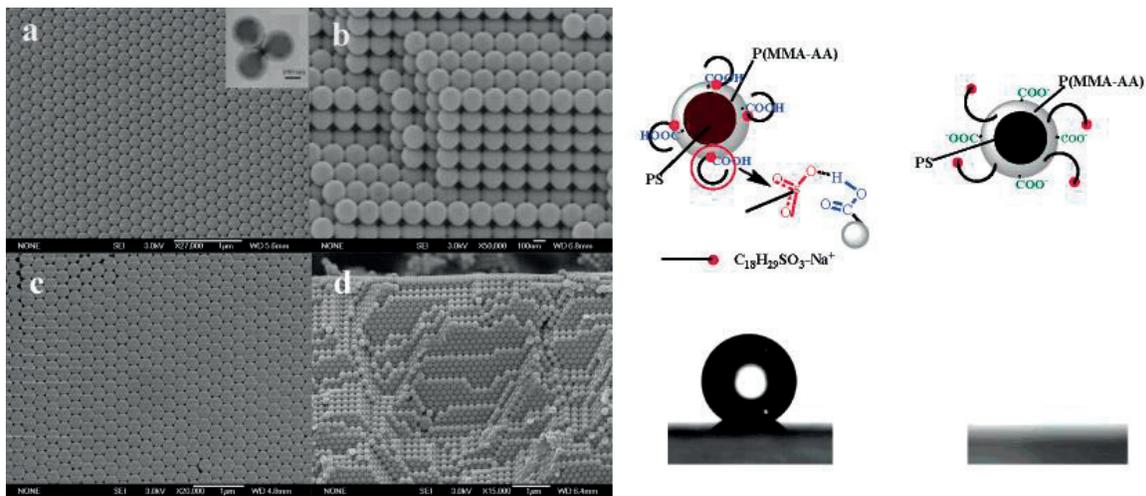


Figure 20. Reversible change from superhydrophobic to superhydrophilic of colloidal crystals (Panels A–D) made of polymers with COOH groups as a function of the pH (Figure on the right). Ref. [194], Copyright 2006. Reprinted with permission from American Chemical Society, USA.

are spread toward air and the surface was superhydrophobic ($\theta_w = 150.4^\circ$). At high pH (pH = 12), the COOH groups are deprotonated (COO^-) suppressing the hydrogen bonds. Here, the surface was superhydrophilic due to the presence of both COO^- and SO_3^- .

Orthophosphoric acids (ROPO_3H_2) were also studied. These acids are diacids with a pK_{a1} between 1 and 2 and a pK_{a2} between 6 and 7 (**Figure 21**). Three different acids are present dependent on the pH [200–202]. Poly(methacryloyl ethylene phosphate) (PMEP) brushes were used. At $\text{pH} > 8$, the phosphate groups are deprotonated and the electrostatic repulsions between the charged polymer chains led to a swollen state with high hydrophobicity, while at $\text{pH} < 2$, the brushes are protonated and in a collapsed state.

In order to induce basicity, amino groups were also highly used in the literature using different strategies [203–205]. Liu et al. used a triblock copolymer: one block with a hydrophobic group, one block with a pH-sensitive amino group and another one with a functional group for grafting on SiO_2 nanoparticles [203]. The material could be dip-coated on different substrates such as cotton fabric, filter paper and PU foam and could be used for pH-responsive oil/water separation membranes. Among the basic groups, pyridine was also reported. Wang et al. reported the grafting of block copolymer brushes of poly(4-vinylpyridine-*block*-dimethylsiloxane) (P4PV-*b*-PDMS) on SiO_2 nanoparticles [206]. After casting the suspension particles on non-woven cellulose textiles and PU sponges, the resulting materials displayed superhydrophobic and underwater superoleophilic properties at pH 6.5, and superhydrophilic and underwater superoleophobic properties at pH 2.0. Such materials could also be used for controlling the separation of oil/water mixtures by changing the pH. Graphene foams with switchable oil wettability were also reported by grafting block copolymer brushes of poly(2-vinylpyridine-*block*-hexadecyl acrylate) (P2PV-*b*-PHA) [207]. By contrast, other authors chose to graft the polymer directly on substrates [208, 209].

Luo et al. also reported the fabrication of fiber membrane by electrospinning of the block copolymer poly(4-vinylpyridine-*block*-methyl methacrylate) (P4PV-*b*-PMMA) on stainless steel meshes (**Figure 22**) [210]. Using oil/water mixtures, oils can selectively pass through the membrane at pH 3, while at pH 7, water pass selectively. Finally, other authors used block copolymers with both acid and amino groups [211, 212]. For example, Zhou et al. showed that using these kind of polymers it is possible to control the slip length of fluids by changing the pH.

3.4. Voltage

The best advantage of using electrical sensitivity as external stimulus is the rapidity of implementation [213, 214]. Among the most used materials, conducting polymers are extremely interesting because they can exist in different doping states. The neutral dedoped state is uncharged, while the doped states are charged (**Figure 23**). Moreover, in their doped states, conducting polymers incorporated doping agents (most of the time counter-anions) in order to neutralize the charges present inside the polymer backbone.

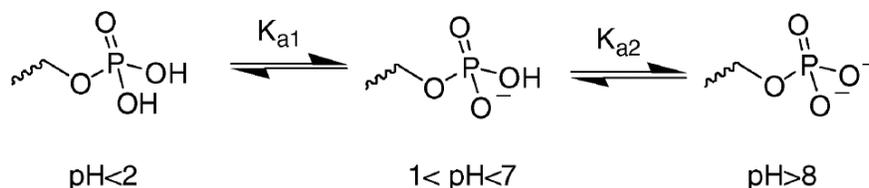


Figure 21. Different species present using orthophosphoric acids as a function of the pH. Ref. [202], Copyright 2005. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

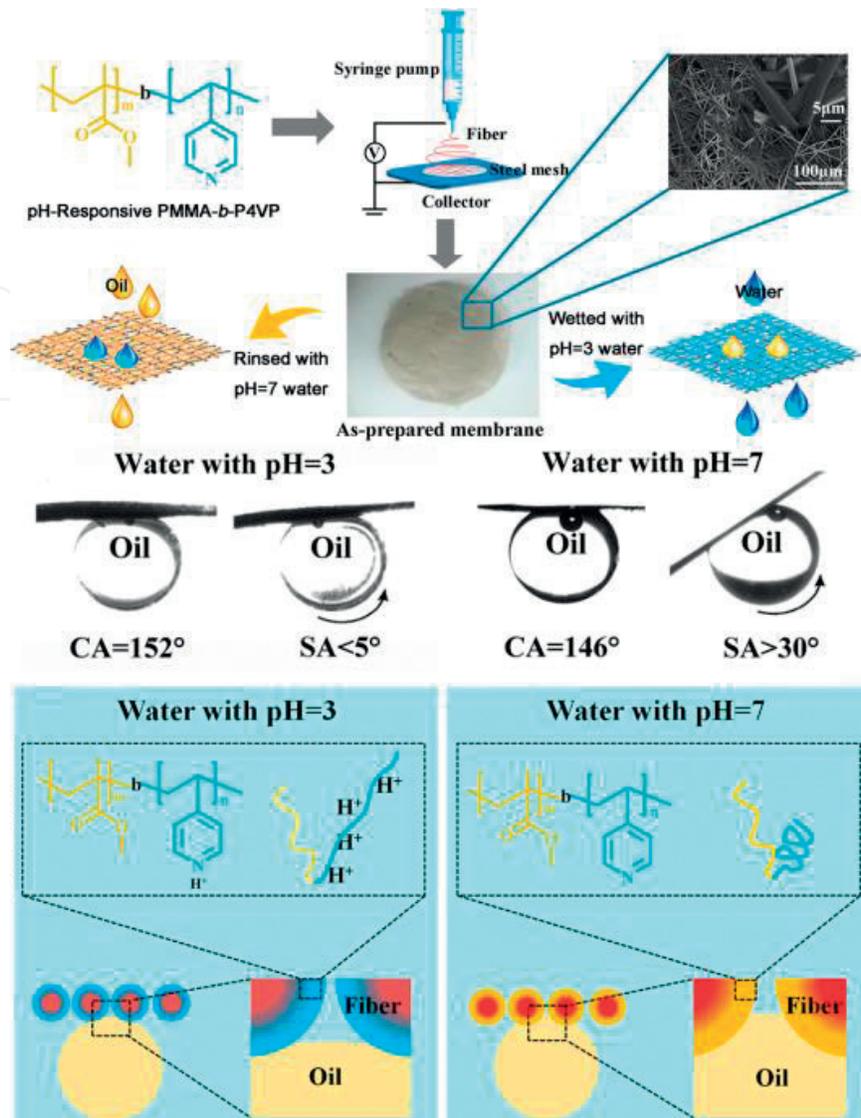


Figure 22. Preparation of pH-induced oil permeation membranes by electrospinning of P4PV-b-PMMA. Ref. [210], Copyright 2015. Reprinted with permission from American Chemical Society, USA.

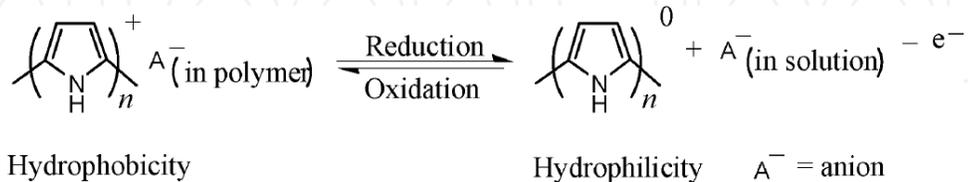


Figure 23. Reversible change in the doping state of conducting polymers by oxidation and reduction [163].

For example, smooth poly(3-alkylthiophene) films prepared by spin coating were studied (**Figure 24**) [215]. In their doping state, different anions (Cl^- , NO_3^- , PO_4^{3-} , CO_3^{2-} and SO_4^{2-}) were introduced. The authors observed that all the anions induced a decrease of θ_w . The highest decrease (from 105.9 to 76.7°) was observed with SO_4^{2-} anions. In order to enhance the wettability difference between the reduced and the oxidized state, the authors also deposited micro-patterned substrates. Then, they observed a much higher decrease from 147.4 to 62.2°.

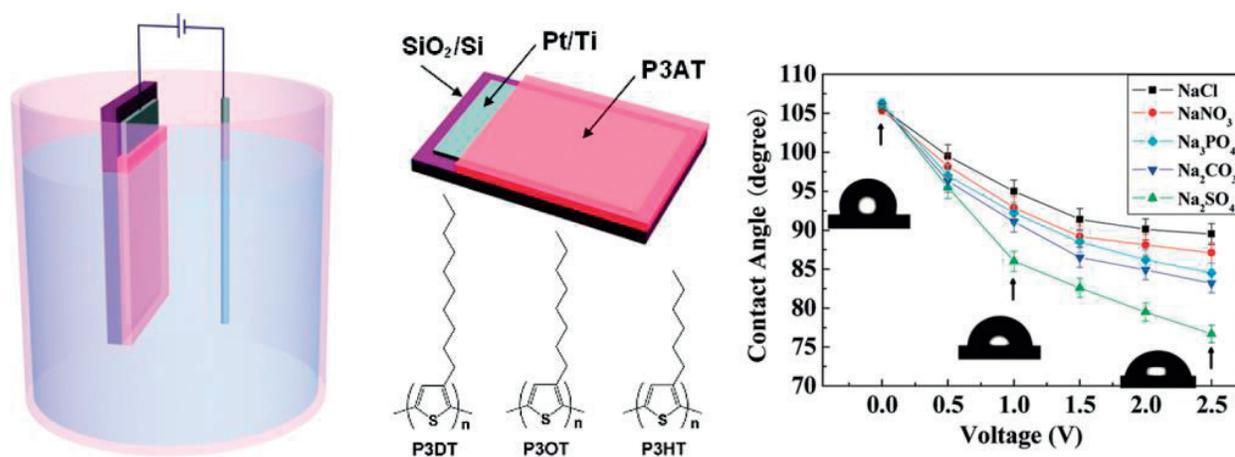


Figure 24. Influence of doping anions in the surface hydrophobicity of smooth poly(3-alkylthiophene). Ref. [215], Copyright 2009. Reprinted with permission from American Chemical Society, USA.

Otherwise, various other techniques can be used to prepare structured conducting polymer films. Among them, using an electrochemical cell, the electropolymerization allows in one step having polymerization, deposition of conducting polymer film and obtaining of structured films. The surface structures are highly dependent on electrochemical parameters (deposition method, time, solvent, electrolyte...) and on the monomer used [216–222]. For example, superhydrophobic rough polypyrrole films were reported by electropolymerization of pyrrole by galvanostatic deposition (constant current of 0.25 mA cm^{-2}) in the presence of highly hydrophobic perfluorooctanesulfonate ($\text{C}_8\text{F}_{17}\text{SO}_3^-$) doping ions and also FeCl_3 in order to induce by polymerization and electropolymerization [162]. Here, the surface structures consisted in sub-micron particles ($1\text{--}3 \text{ }\mu\text{m}$) forming a porous film. The surface could easily and reversibly switch from superhydrophobic to superhydrophilic by oxidation/reduction using different voltages. Moreover, Chang et al. reported a faster electrical process (3 s) and also eliminated the need to immerse the substrate within an electrolyte [165]. Jiang et al. also reported that the oil adhesion can also be controlled during the doping/dedoping process [222].

Other monomers were also studied [223–228]. Yan et al. reported the use of aniline to produce helical polyaniline fibers in aqueous electrolyte and in the presence of perfluorooctanesulfonic acid by galvanostatic deposition (constant current of 0.2 mA cm^{-2}) [223]. Polyaniline is an interesting polymer because different chemical forms can be produced also depending on the pH. In the presence of tetraethylammonium perfluorooctanesulfonate, the authors reported the possible switching from superhydrophobic (emeraldine salt form) to superhydrophilic (leucoemeraldine base form) by changing the voltage. Poly(3,4-ethylenedioxythiophene) (PEDOT) was also used (Figure 25) [224]. Here, two different fluorinated electrolytes were chosen: tetrabutylammonium nonafluorobutanesulfonate ($\text{Bu}_4\text{NC}_4\text{F}_9\text{SO}_3$) and tetrabutylammonium heptafluorooctanesulfonate ($\text{Bu}_4\text{NC}_8\text{F}_{17}\text{SO}_3$). Their electropolymerization was performed in acetonitrile and at constant potential. Porous films were obtained and the surface morphology was highly dependent on the electrolyte. Superhydrophobic properties were obtained with $\text{Bu}_4\text{NC}_8\text{F}_{17}\text{SO}_3$ and using a deposition charge (Q_s) of 300 mC cm^{-2} [226, 227]. Lu prepared first a porous PEDOT film on which a second was electrodeposited by cyclic

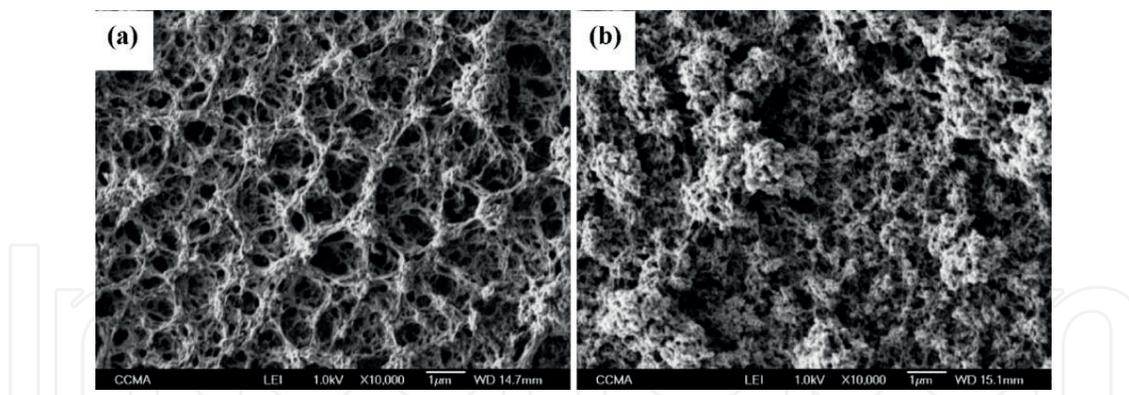


Figure 25. Rough PEDOT substrates obtained in the presence of (a) $\text{Bu}_4\text{NC}_4\text{F}_9\text{SO}_3$ and (b) $\text{Bu}_4\text{NC}_8\text{F}_{17}\text{SO}_3$ [224].

voltammetry. Using poly(3-methylthiophene), a switchable and reversible surface from superhydrophobic to superhydrophilic was obtained after doping/dedoping in the presence of ClO_4^- anions [170]. By contrast, using poly(3-hexylthiophene), the surface could switch from superhydrophobic to parahydrophobic (high water adhesion) [227]. The surfaces could also induce switchable cell adsorption [228].

Advincula created first polystyrene colloidal crystals in hexagonal packing, on which a polythiophene film with short alkyl chains was electrodeposited by cyclic voltammetry [229]. The surface could switch from superhydrophobic to highly hydrophilic. Here also, the protein and bacterial cell adsorption could also be switched at the same time [230].

Otherwise, different strategies were employed to create nanostructured conducting polymers in solution. For that, polyaniline is a choice material due to the presence of amine groups that allow to induce self-assembly by hydrogen bonds [231–237]. Jiang et al. reported the polymerization *in-situ* on fabrics in the presence of perfluorosebacic acid ($\text{HOOC-C}_8\text{F}_{16}\text{-COOH}$) and FeCl_3 , as dopant and oxidant, respectively [232]. Nanoparticles were formed on the fabrics. The resulting fabrics could switch from superhydrophobic to superhydrophilic by doping/dedoping while the dedoping could be performed in the presence of NH_3 gas. Fabrics with switchable wettability from superoleophobic to superoleophilic were also reported using perfluorooctanoic acid [233, 234]. In order to prepare membranes with selective responsivity for oil/water separation, stainless steel meshes were coated with root-like polyaniline nanofibers fabricated by emulsion polymerization [235]. The meshes could switch from superhydrophobic to superhydrophilic at different voltages.

Metal ions and organic molecules sensitive to redox reactions can also be used to switch the surface wettability by voltage [238, 239]. For example, Ag^+ –biphenyldithiol (BPDT) SAMS could be converted to Ag^0 -BPDT by applying a difference potential [238]. Ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$) could also be converted into $[\text{Fe}(\text{CN})_6]^{4-}$ [240]. Huck et al. showed that polycationic [2-(methacryloyloxy)-trimethylammonium chloride] (PMETAC) brushes coordinated to $[\text{Fe}(\text{CN})_6]^{3-}$ had $\theta_w = 41\text{--}44^\circ$ while the brushes coordinated to $[\text{Fe}(\text{CN})_6]^{4-}$ had $\theta_w = 26\text{--}27^\circ$ [241].

The reorientation of polyelectrolyte conformation is another phenomenon induced by electric potential [242, 243]. Choi et al. observed that a SAM of (16-mercapto)hexadecanoic acid

(MHA) deposited on a gold substrate could undergo a transition from a straight conformation to a curved one by applying an electric potential. The molecules in the straight conformation are hydrophilic due to the presence of carboxylate ions and that in the curved conformation are hydrophobic due to the presence of the hydrophobic chains.

Electrowetting is another method allowing the control of the surface wettability by applying an external electric field. In this process, a water droplet is placed on a superhydrophobic surface coated with an insulating layer. The applying of the electric field induces an accumulation of charges and decreases the solid-liquid interface (γ_{SL}) and as a consequence the surface hydrophobicity, as shown in **Figure 26** [244, 245].

In 2004, Krupenkin et al. studied the electrowetting of superhydrophobic substrates prepared by modifying nanostructured silicon substrates with a low surface energy material [246]. After electrowetting, they could change the surface wettability from superhydrophobic to superhydrophilic. Vertically aligned superhydrophobic carbon nanofibers and ZnO nanorods

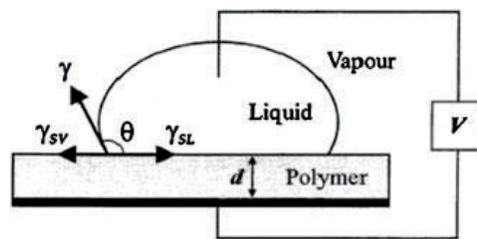


Figure 26. Schematic representation of electrowetting experiment. Ref. [244], Copyright 2003. Reprinted with permission from American Chemical Society, USA.

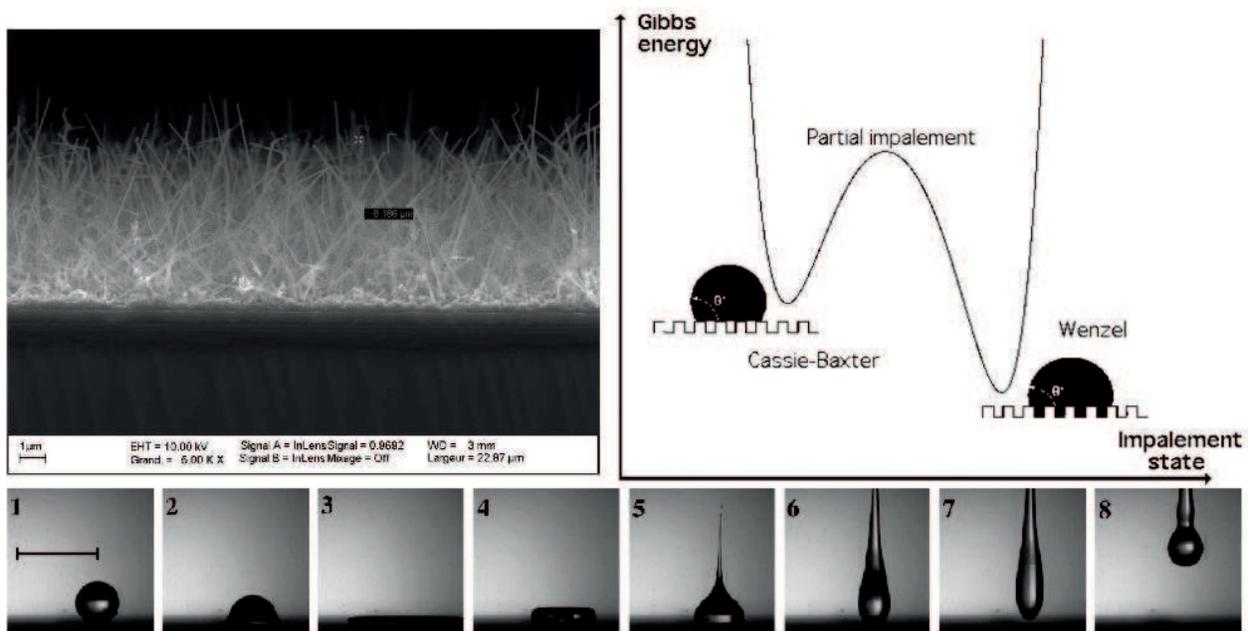


Figure 27. Relationship between the resistance to drop impact impalement and electrowetting impalement using silicon nanowires with double nanotextures. Ref. [254], Copyright 2008. Reprinted with permission from American Chemical Society, USA.

were also highly used in the literature to induce a switch from superhydrophobic to hydrophilic or superhydrophilic [247–251]. Boukherroub et al. reported the possible obtaining of reversible electrowetting on silicon nanowires with double nanotextures (length of 10 and 30 μm) [252–255]. They found a relationship between the resistance to drop impact impalement and electrowetting impalement (**Figure 27**) [254]. The thresholds for drop impact and electrowetting irreversibility increase and the contact angle hysteresis decrease when the length and the density of nanowires increase. Other mechanisms for reversible electrowetting were also reported in the literature [256, 257]. Otherwise, electrowetting could also be used to control protein adsorption or for accelerating reaction by mixing liquid droplets [258, 259].

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