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Oil/Water Separation

Oil/Water Separation with Selective Superantiwetting/Superwetting Surface Materials

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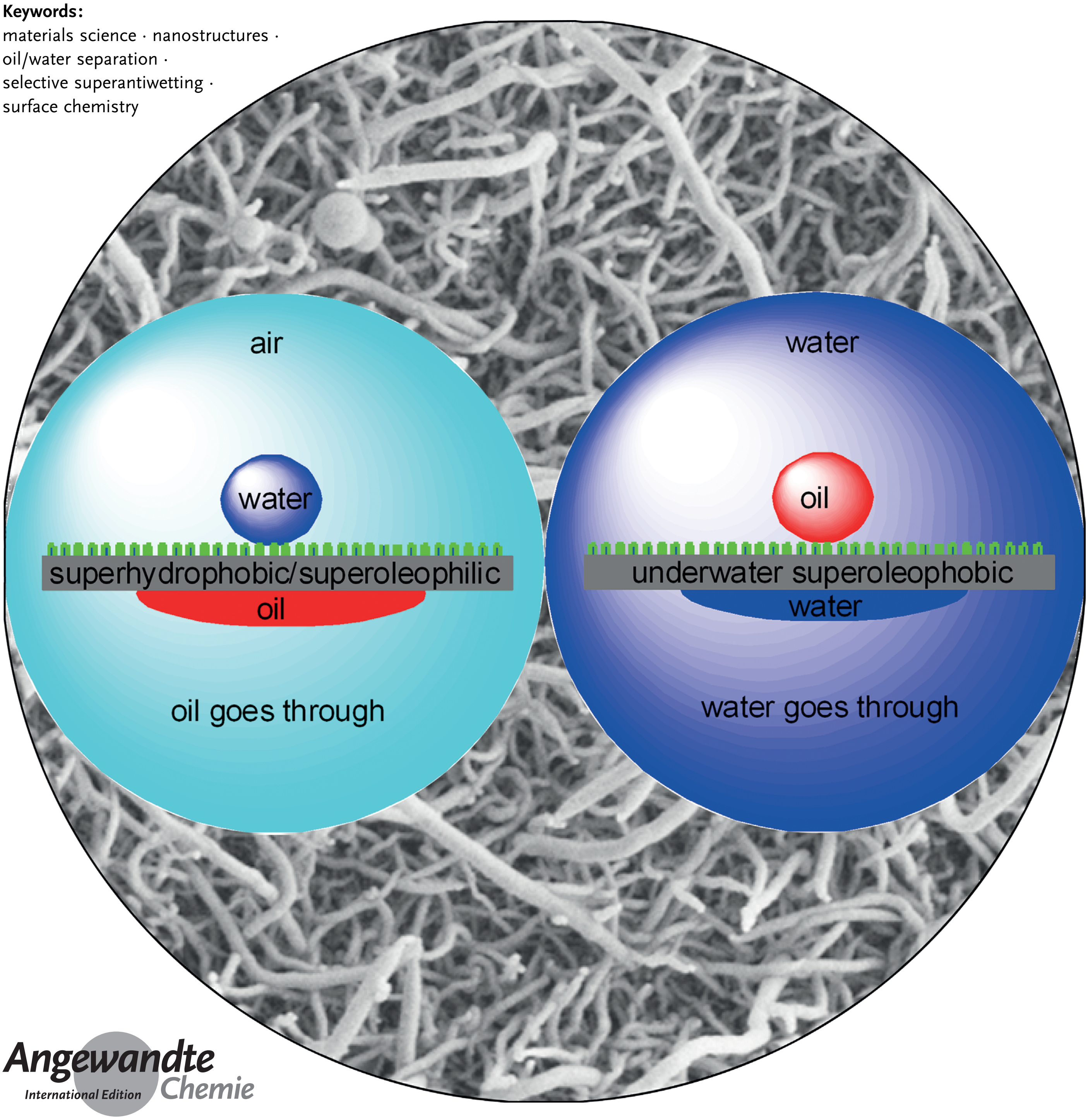

The separation of oil from oily water is an important pursuit because of increasing worldwide oil pollution. Separation by the use of materials with selective oil/water absorption is a relatively recent area of development, yet highly promising. Owing to their selective superantiwetting/superwetting properties towards water and oil, superhydrophobic/superoleophilic surfaces and underwater superoleophobic surfaces have been developed for the separation of oil/water-free mixtures and emulsions. In this Review, after a short introduction to oil/water separation, we describe the principles of materials with selective oil/water absorption and outline recent advances in oil/water separation with superwetting/superantiwetting materials, including their design, their fabrication, and models of experimental setups. Finally, we discuss the current state of this new field and point out the remaining problems and future challenges.

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1. Introduction

Oil pollution caused by the petrochemical, textile, and food industries as well as the frequent oil-pollution accidents during offshore oil production or marine transportation has become one of the most urgent global environmental problems.[1,2] For example, the explosion of the "Deepwater Horizon" oilrig belonging to BP in the year 2010 with the release of more than 210 million gallons of oil into the Gulf of Mexico was the most serious pollution incident of the last decade.[3] Oil-polluted water usually contains toxic chemicals, which may harm people's health or even have a disastrous impact on the ecosystem. Therefore, the development of methods for the collection and removal of large amounts of organic pollutants from water is attracting global attention.

Traditional techniques, such as gravity separation, skimming, and flotation, are useful for the separation of oil/water free mixtures, but suffer from the limits of low efficiency and high operation cost. Besides, they are not applicable to the separation of oil/water emulsions.[2] Although traditional hydrophobic/oleophilic absorbent materials and filtration membranes are frequently used in practical applications owing to their low cost and ready availability,[4–6] they still face two main limitations:[6–8] First, they absorb both water and oil during the separation process, thus displaying poor separation selectivity and efficiency, whereby separation efficiency is crucial to many applications. For example, a thin film of residual oil above water may damage an ecosystem. Also, the residual water in oil obtained in this way needs to be removed before the oil is used as a fuel, and in the area of analytical chemistry, the efficient separation of molecules is a key parameter in terms of the accuracy of chemical analysis and detection.[9] Second, they suffer from the problems of pore clogging and surface fouling by oil or grease, which normally lead to a remarkable reduction in absorption capacity and fluid flux. Moreover, these materials show poor recoverability for reuse and thus cause secondary contamination to the environment.[7] Furthermore, the safe handling of the oil-sorbent waste is challenging, as is the recovery of the absorbed oil.[10]

Consequently, the development of advanced oil/water-separation materials that can selectively absorb oil (or water) while completely repelling water (or oil) is highly desirable.[7,11] Because water and many oils are intrinsically immiscible, materials with extremely different affinities towards oils and water are believed to be promising for highly efficient oil/water separation.[12–14] To date, two different types of surface materials, superhydrophobic/superoleophilic (SHBOI) surfaces and underwater superoleophobic (UWSOB) surfaces, have been successfully designed, fabricated, and employed in oil/water separation on the basis of their selective oil/water adhesion.

SHBOI surfaces have aroused broad interest in recent years. They are also referred to as "oil-removing" materials, since they can effectively separate oil/water mixtures or emulsions by selective filtration or absorption.[2] For example, SHBOI polyester textiles,[15] metal meshes,[16] and polystyrene[17] were developed and successfully applied to oil/water separation either by the removal of oil through selective oil absorption or by membrane filtration. Alternatively, UWSOB materials show very high water affinity but extremely low oil adhesion; these properties also enable oil/water separation.[1] In Section 2, the theoretical background to wetting phenomena on solid surfaces, including special wetting states, is first introduced; then, in Sections 3 and 4, recent developments in SHBOI and UWSOB surfaces for highly efficient oil/water separation are discussed.

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2. Wetting on Solid Surfaces

According to the model developed by Thomas Young, a sessile drop placed on a flat surface normally forms the shape of a sphere sectioned by the surface, and the so-called contact angle (θ_{CA}) is a function of the interfacial energies between the solid–liquid (γ_{SL}), solid–vapor (γ_{SV}), and liquid–vapor (γ_{LV}) interfaces [Figure 1 a, Eq. (1)]:[18]

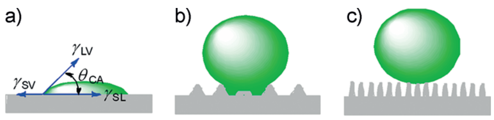


Figure 1. Schematic illustration of a droplet placed on a) a flat substrate and b, c) a rough substrate. Depending on the roughness of the surface, the droplet is either in the Wenzel regime (b) or the Cassie–Baxter regime (c).

$$\cos\theta_{CA} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

The surface is regarded as hydrophilic when $\theta_{CA} < 90°$; otherwise, the surface is hydrophobic. In contrast, two different models, the so-called Wenzel regime[19] (Figure 1 b) and the Cassie–Baxter regime[20] (Figure 1 c), were developed to explain wetting behavior on a rough surface. In the Wenzel model (Figure 1 b), the difference between the apparent angle θ_{CA} and the "true" contact angle θ_F of a flat surface made of the same component is described by Equation (2), in which R is the ratio of the actual surface area to the apparent area of the rough surface.[19]

$$\cos\theta_{CA} = R\cos\theta_F = R\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2)$$

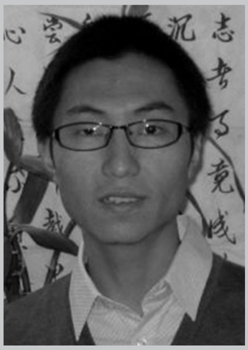
In this model, surface roughness promotes either wettability ($\theta_{CA} < 90°$) or nonwettability ($\theta_{CA} > 90°$), depending on the chemical properties of the surface. The highest θ_{CA} value reported so far for water on a flat substrate is around 120°;[21] however, it is possible to create surfaces with very high θ_{CA} values for water, even close to 180°,[22] through an appropriate combination of surface energy and surface roughness.[23–26] When the surface is textured with small protrusions that are surrounded by air and thus cannot be filled with a liquid, that is, air is trapped underneath a liquid droplet, the wetting phenomenon can be described by the Cassie–Baxter equation [Eq. (3)], in which Φ_S is the fraction of the surface that is in contact with the liquid.[20]

$$\cos\theta_{CA} = -1 + \Phi_s\left(1 + \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}\right) \quad (3)$$

The angle θ_{CA} under these conditions is much higher than that of a flat surface composed of the same material because the pores between the bumps are filled with air.[23–28] In such a case, the liquid touches only the highest asperities of the surface with a very limited contact area. Thus, the adhesion between the water droplets and the substrate surface is extremely low. As a consequence, the water droplets will immediately roll off the surface if it is only tilted slightly relative to the horizontal. Specifically, a surface displaying a water θ_{CA} value greater than about 150° as well as low contact-angle hysteresis is usually regarded as a superhydrophobic surface.[23,29–31]

According to the Young equation, a surface may display both hydrophobicity and oleophilicity at the same time if the surface tension of the solid substrate is between those of water and oil. If such a surface has appropriate roughness, it may show both superhydrophobicity and superoleophilicity simultaneously, as predicated by the Wenzel equation. In fact, experimental findings demonstrated that the interplay of appropriate surface roughness and surface chemistry can generate surfaces that display superhydrophobicity and superoleophilicity simultaneously.[11,15]

When an oil droplet is deposited on a substrate surface that is under water, the Young equation can be modified to give Equation (4), in which γ_O, γ_W, and γ_{OW} are the oil/air, water/air, and oil/water interface tensions, respectively, and θ_O, θ_W, and θ_{OW} are the contact angles of oil in air, water in air, and oil in water, respectively.[32,33] Underwater oleophobicity ($\theta_{OW} > 90°$) will be observed as long as Equation 5 is valid. Similar to the situation in air, a flat underwater oleophobic surface may show UWSOB properties if an appropriate surface roughness is introduced. It was demonstrated that a hydrophilic chemical composition and a hierarchical rough structure are the two most important parameters for the



Zonglin Chu completed his PhD in chemical engineering (applied chemistry) with Prof. Yujun Feng at the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences in 2011. After a year of postdoctoral research in multistep organic synthesis in the laboratory of organic chemistry at the ETH Zurich, he joined the research group of Prof. Stefan Seeger at the University of Zurich, where he is currently working on surfaces with special wettability. His research interests lie at the interface of organic synthesis, colloid and interface science, hydrogels, smart materials, and functional surfaces.

Yujun Feng earned his PhD in 1999 from Southwest Petroleum University (China) with Prof. Pingya Luo and then undertook postdoctoral research in France at the CNRS/Université de Pau and the Institut Français du Pétrole with Prof. Jeanne François and Dr. Guy Chauveteau, respectively. He was a team leader at the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences from 2004 until 2012, when he moved to Sichuan University as a professor. His research focuses on the fabrication of smart materials and their application in oil and gas production as well as crude-oil/water separation.

design of UWSOB surfaces.[11] Normally, a surface that is superhydrophilic in air displays superoleophobicity under water.[32,33]

$$\cos\theta_{OW} = \frac{\gamma_O \cos\theta_O - \gamma_W \cos\theta_W}{\gamma_{OW}} \quad (4)$$

$$\cos\theta_O < \frac{\gamma_W}{\gamma_O}\cos\theta_W \quad (5)$$

3. Oil/Water Separation with SHBOI Materials

3.1. SHBOI Meshes for the Separation of Oil/Water Mixtures

Metal meshes, such as stainless-steel meshes and copper meshes, are pore-structured semipermeable barriers made of connected metal strands. After surface functionalization to make them superhydrophobic/superoleophilic, meshes with a pore size of tens to hundreds of microns have frequently been used for separating oil/water mixtures.[7,16,34–39] The Jiang research group[16] pioneered research in the field of oil/water separation with SHBOI materials. In 2004, they described a facile, inexpensive spray-and-dry method for the preparation of a novel mesh with both superhydrophobicity and superoleophilicity.[16] Briefly, a homogeneous emulsion containing the low-surface-energy material polytetrafluoroethylene (PTFE), the adhesive polyvinyl acetate, the anionic surfactant sodium dodecyl benzene sulfonate, and water was spray-coated onto stainless-steel-mesh substrates. Subsequently, the substrates were dried to remove the water, the surfactant, and the adhesive while keeping the micro/nanostructure of the PTFE backbone. The contact angle θ_{CA} of water on such coated films is greater than 150°, whereas that of diesel oil is around 0°, owing to the nano/microscale hierarchical roughness combined with the hydrophobic chemical composition of the films. Because of this special wettability, the coating does not allow water but does allow diesel oil to spread and pass through the film. As a result, mixtures of water and oil can be effectively separated with such SHBOI mesh films.

Wang et al.[34] developed an electrospinning process for the creation of SHBOI mats with a bead-on-string morphology from thermoplastic polyurethane (TPU). First, TPU was dissolved in a mixture of *N*,*N*-dimethylformamide and tetrahydrofuran, and then the TPU solution was electrospun onto a copper-mesh substrate. The hydrophobic TPU electrospun film obtained in this way became superhydrophobic/superoleophilic upon treatment with hydrophobic silica nanoparticles, which were synthesized by heating nanosilica at reflux in toluene in the presence of hexadecyltrimethoxysilane. The resulting SHBOI TPU film was successfully used for the separation of an oil/water mixture.

Parkin and co-workers prepared SHBOI copper meshes by aerosol-assisted chemical vapor deposition of polymeric silicone elastomers.[38] The polymer coating rendered all meshes superhydrophobic, with $\theta_{CA} = 152–167°$, depending on the pore size of the mesh. Ultra-high-speed video capture was used to monitor the oil/water separation process (Figure 2a). Water droplets that impinged upon the coating were deformed while they were in contact with the surface, and then bounced and rolled off the surface easily. However, droplets of toluene wetted the coating and went through the coated mesh very quickly. The authors designed a dual-layered filtration system, which focused on directing the transportation of oil away from water with the highest efficiency (Figure 2b). In this system, water rolls over the surface of the top mesh and into a large beaker, whereas the oils spread out and falls through into a smaller beaker. The bottom mesh fixed inside the oil receptacle was used to minimize the spreading of the oil and prevent oil from

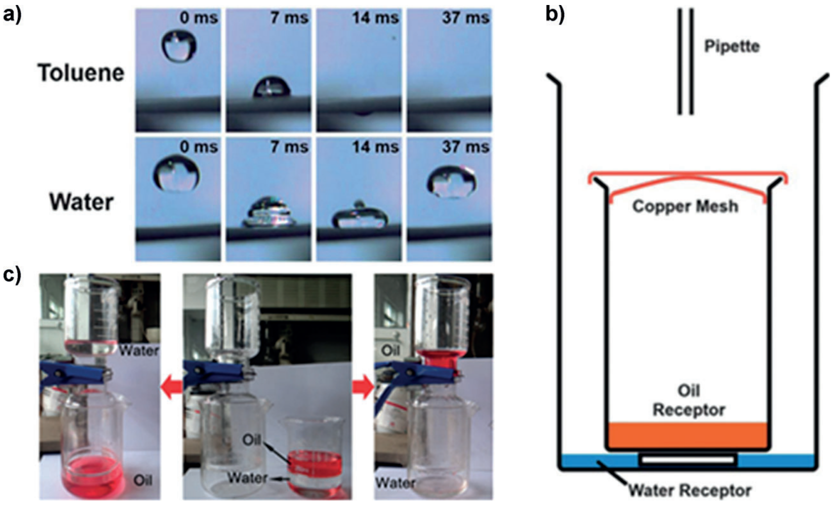


Figure 2. Examples of SHBOI copper meshes for oil/water separation.[38,39] a) Photographs showing the interaction of a SHBOI mesh with toluene and water. b) Schematic representation of the separation apparatus developed by Parkin and co-workers. c) Controlled oil/water separation with a pH-switchable surface. Parts (a) and (b) are reprinted from Ref. [38] with permission; part (c) is reprinted from Ref. [39] with permission.

Stefan Seeger completed his PhD in 1992 with Prof. Jürgen Wolfrum at the University of Heidelberg, where he subsequently led a research group for biophysical chemistry. He later carried out postdoctoral research with Prof. Klaus Mosbach at the University of Lund (Sweden). After completing his habilitation in Heidelberg in 1997, he was appointed professor for biochemistry and biosensor technology at the University of Regensburg/Germany. In 1999, he moved to the University of Zürich, where he holds the chair of Physical Chemistry, and has been the director of the Institute for Physical Chemistry.

spreading far enough on the top mesh to fall into the water receptacle. Experimental results showed that a SHBOI copper mesh in such a system is exceptionally efficient in separating organic solvents (e.g., hexane, petroleum ether, and toluene) from water.

In contrast to the above strategies, Wang and Guo developed a superhydrophobic copper-mesh film with pH-responsive properties.[39] This mesh could be used to separate an oil-and-water mixture bidirectionally. First, a hierarchically structured copper-mesh film was fabricated by a facile electrochemical deposition technique and sputter-coated with a layer of gold. The surface was subsequently modified with a mixture of decane-1-thiol and 11-mercaptoundecanoic acid, which bears a thiol group at one end and a pH-sensitive carboxylic group at the other. The two thiols bonded to the gold surface through the formation of a thiol–gold complex. The protonation and deprotonation of the carboxylic groups could be controlled by changing the pH value of the aqueous medium, thus resulting in a pH-switchable surface that allowed the separation of oil/water mixtures in a bidirectional way. When a mixture of oil and a neutral or acidic aqueous solution was poured into the upper bottle shown in Figure 2c, the oil penetrated the mesh and flowed down into the lower bottle, whereas the water was retained above the mesh (Figure 2c, left). In contrast, if the mesh was prewetted with a basic aqueous solution (pH 12.5), the opposite separation process was observed (Figure 2c, right).

3.2. SHBOI Textiles for the Separation of Oil/Water Mixtures

Textiles are another type of materials that have frequently been used for oil/water separation. In contrast to metal meshes, textiles are flexible, inexpensive materials without a size limitation. Moreover, they usually possess better mechanical stability owing to their flexibility.

Seeger and Zhang[15] prepared the first superhydrophobic/superoleophilic textiles for oil/water separation by a facile, one-step chemical vapor deposition technique with trichloromethylsilane (Figure 3).[40–42] SEM observations revealed that the polyester fabric used as the substrate was uniformly coated with a dense layer of silicone nanofilaments (Figure 3a). Such a coating leads to a remarkable change in the wettability of surfaces.[15,40–43] The uncoated polyester textile could be wetted readily by both water and oils, whereas the coated textile showed superhydrophobicity and superoleophilicity simultaneously and could only be wetted by oils (Figure 3b). Because of their flexibility and superhydrophobicity/superoleophilicity, the reusable coated textiles exhibit excellent oil/water separation efficiency (Figure 3c). In subsequent studies,[44,45] a facile approach was developed for the preparation of mechanically more durable superhydrophobic polyester materials by dip-coating in a nanocomposite solution of polymerized tetraethoxysilane and hexadecyltriethoxysilane. The coated samples exhibited extreme superhydrophobicity/superoleophilicity with excellent mechanical and chemical stability, which can be ascribed to the tight binding of the nanocomposite to the polyester fibers and the inherent stability of silicone. The coated samples could quickly absorb petrol, diesel, and crude oil, and showed very high selectivity in oil/water separation. Furthermore, this simple approach can be readily scaled up for the production of large samples, which makes it more promising for practical oil separation.

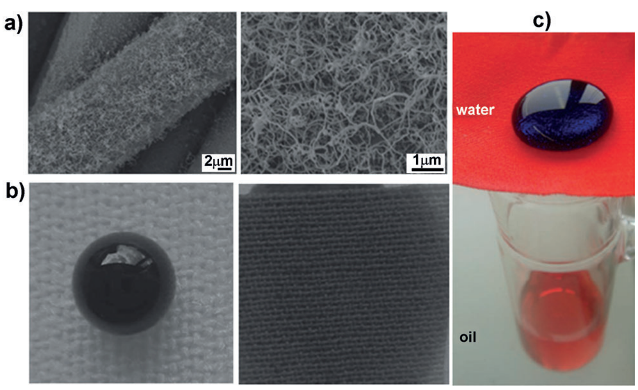


Figure 3. Polyester textiles coated with SHBOI silicone nanofilaments for oil/water separation. a) SEM images of a coated sample. b) A water (left) and an oil droplet (right) were deposited on the coating. c) Experimental setup for oil/water separation. The water was colored with methylene blue. Reprinted from Ref. [15] with permission.

By incorporating polyaniline and a fluorinated alkyl silane through a facile vapor phase deposition process, a cotton fabric was functionalized with simultaneous superhydrophobicity and superoleophilicity by Men and co-workers.[46] The resulting material was used for effective oil/water separation with a separation efficiency as high as 97.8%. Moreover, the coated sample retained high separation efficiency under extreme environmental conditions, that is, when exposed high temperature, high humidity, high mechanical stress, or harsh acids or bases. This material with its advantages of scalable fabrication, high separation efficiency, stable recyclability, and excellent durability has great potential for industrial applications.

Guo and Liang deposited polyaniline nanofibers on the surface of fabrics to generate a rough structure similar to the micromorphology of a lotus leaf.[47] After further modification with octadecane-1-thiol, SHBOI fabrics that can be applied successfully and effectively to the separation of oil/water mixtures were obtained. Moreover, the coated fabrics showed robust superhydrophobic properties and stability towards many corrosive solutions (acids, bases, and salt solutions), hot water, and mechanical abrasion. It was demonstrated that this approach can also be applied to other porous materials. In another study,[48] the same research group coated fabric and sponge substrates with various types of inorganic nanoparticles, then modified the surface with 1*H*,2*H*,3*H*,4*H*-perfluorodecanethiol, and finally obtained SHBOI materials that could be used to separate oil/water mixtures.

3.3. Three-Dimensional SHBOI Materials for the Separation of Oil/Water Mixtures

Superhydrophobic 3D porous materials are considered as promising high-capacity absorbents owing to their well-developed pores and larger surface area as compared to that of their 2D counterparts. Therefore, commercially available 3D porous materials, such as polyurethane foam sponges, were used as substrates for the fabrication of superhydrophobic absorbents for water/oil separation. The resulting materials were shown to be efficient in selectively collecting oils from oily water.[49–53] For example, Liu and co-workers[49] recently developed a bioinspired foam with self-cleaning properties and oil/water-separation ability. By mimicking lotus leaves and porous self-cleaning materials in nature, they prepared polyurethane foams with simultaneous superhydrophobicity and superoleophilicity by chromic etching and subsequent surface modification with a fluoroalkyl silane. Such superhydrophobic foams also exhibit superantiwetting towards corrosive liquids and can float on water because of their low density and superrepellency. In a straightforward experimental setup developed for the separation of crude oil from water with the SHBOI polyurethane foams, a piece of coated foam was fixed in a glass tube. When a mixture of crude oil and water was poured into the glass tube above the coating, the crude oil penetrated through the foam and flowed into the beaker below owing to the superoleophilicity, whereas water was gradually collected above the filter because of the superhydrophobicity. Since the crude oil has a higher density than that of water and thus forms the bottom layer of the mixture, it can penetrate the foam. No water was detected in the collected crude oil, a result indicative of very high separation efficiency. The multifunctional foam was also effective in the separation of a variety of mixtures of water with an organic solvent, including gasoline, crude oil, hexane, and petroleum ether, thus implying that it is a good candidate for the treatment of industrial oil-polluted water and the cleaning up of oil spills. Furthermore, the oily compounds absorbed by the foam can be readily collected by a simple squeezing process and cleaned by the use of water or ethanol, thus avoiding secondary environmental pollution.

Pan and co-workers fabricated a robust superhydrophobic polyurethane sponge as a reusable oil absorbent by coating a polysiloxane layer derived from methyltrichlorosilane onto the surface of the sponge by a one-step solution-immersion method (Figure 4).[51] SEM measurements revealed that pores with diameters of a few hundred nanometers to a few microns constitute the hierarchical roughness required for superhydrophobicity (Figure 4b). The contact angles of the as-coated sponges were measured to be approximately 157°, whereas droplets of lubricating oil quickly spread into the pores of the sponges (Figure 4c). When such sponges were placed on the surface of oil/water mixtures, the oil was absorbed by the sponges in a few seconds. The oil-absorption capacity of the coated sponges for various oils was 10–25 times their own weight, depending on the density and viscosity of the oil. The absorbed oils were readily collected through a simple mechanical squeezing process by taking advantage of the elasticity of the sponge (Figure 4d), and the sponges could be cleaned with solvents and dried for reuse for oil/water separation. No water was detected in the collected oils by FTIR spectroscopy, thus implying high separation efficiency. The superhydrophobic sponges could be reused for more than 300 cycles and exhibited excellent elasticity, high mechanical durability, and good chemical stability.

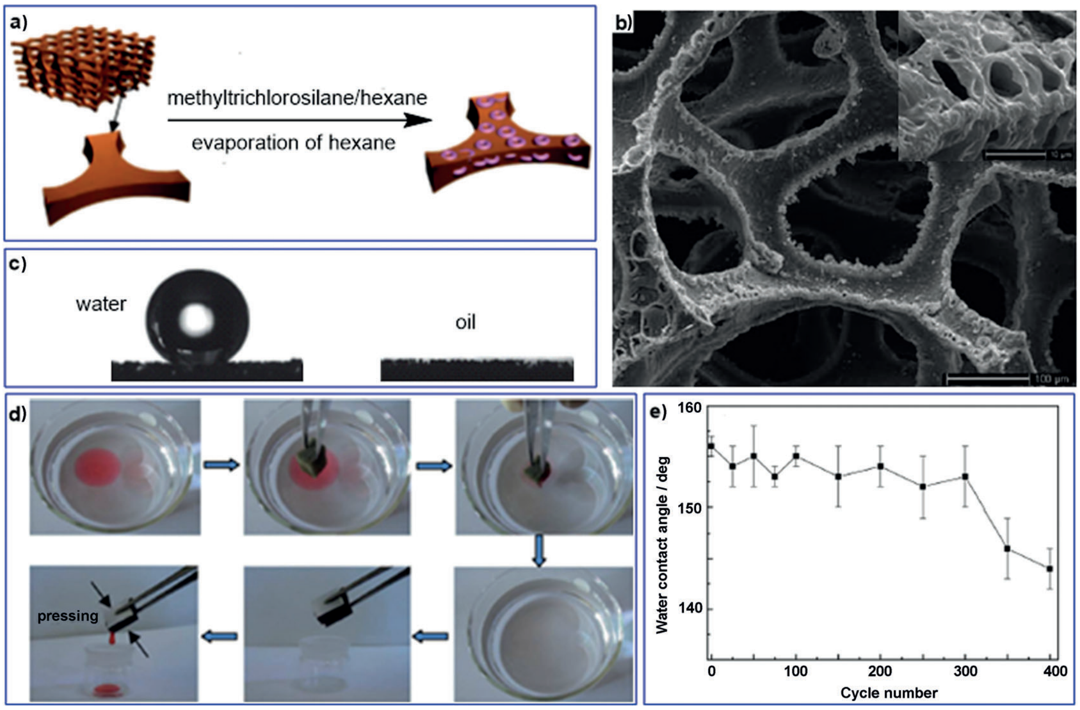


Figure 4. Reusable superhydrophobic polyurethane sponges for oil absorption.[51] a) Fabrication. b) SEM image of the coated sponge. c) A water and an oil droplet were deposited on the coated sponge. d) Removal of lubricating oil (dyed red) from the surface of water with a piece of the superhydrophobic sponge. e) Variation of the water contact angle on the superhydrophobic sponge in repeated absorption/collection processes. Reprinted from Ref. [51] with permission.

Similarly, Guo and co-workers[52] fabricated 3D SHBOI sponges for oil/water separation from thio-functionalized nanocrystals, including those composed of VIII and IB metals or metal-oxide nanoparticles of Fe, Co, Ni, Cu, and Ag. One of the most important advantages of this fabrication technique is that VIII and IB nanocrystals can strongly interact with O, N, and S ligands. In this way, not only is the stability of the nanocoating on the textile substrate improved, but it can also be readily modified with alkyl thiols.

Magnetically driven floating polyurethane foams for the removal of oil contamination from water were prepared by functionalizing the foams with colloidal superparamagentic iron oxide nanoparticles and submicrometer polytetrafluoroethylene particles.[53] Foams, which are inherently hydrophobic and oleophobic, were transformed into SHBOI materials by the deposition of polytetrafluoroethylene particles by a solvent-free, electrostatic technique. The combined functionalization of the foams with colloidal iron oxide nanoparticles increased the speed of oil absorption remarkably as a result of the hierarchical roughness. Besides their oil-removal capabilities, the functionalized foams also exhibit magnetic response. These SHBOI foams float on water owing to their low density. When they are simply moved around on oily water by the use of a magnet, they can absorb the floating oils, thereby purifying the water underneath. It was proposed that this low-cost process could readily be scaled up for cleaning up large-area oil spills in water.

3.4. Other SHBOI Materials for the Separation of Oil/Water Mixtures

SHBOI gels with a spongelike porous structure are another type of material developed for oil/water separation.[9,54,55] Besides SHBOI polymeric[56,57] and ceramic[6] membranes, carbon-nanoparticle networks[58] and calcium carbonate powders[59] can also be used for effective oil/water separation.

3.5. SHBOI Materials for the Separation of Oil/Water Emulsions

The SHBOI materials discussed above can be used for the separation of oil/water free mixtures but are not able to separate oil/water emulsions. An emulsion is a mixture of two or more liquids that are normally immiscible in which one liquid is very finely dispersed in a continuous phase of the other liquid(s). Porous filters, which only allow materials with a size smaller than that of the pores to pass through owing to the so-called "size-sieving" effect, are applicable for the separation of emulsions. Emulsions usually have a droplet size of tens of microns and thus cannot be separated by the aforementioned materials because of their very large pore size: hundreds of micrometers. Therefore, filters with a pore size as small as possible are needed to separate oil/water emulsions by the "size-sieving" effect. However, a reduction in pore size results in a decrease in the filtration rate, since the rate is directly proportional to the square of the pore size according to permeation theory.[60] The other very important parameter is the thickness of the filter, since it is inversely proportional to the filtration rate. Therefore, an ideal filter is expected to have an active separation layer that is as thin as possible and a sufficient pore size.[61]

For the separation of oil from emulsions, Jin and co-workers[62] fabricated a SHBOI poly(vinylidene fluoride) (PVDF) membrane by an inert-solvent-induced phase-inversion process (Figure 5 a). A modified phase-inversion process was employed in which ammonia was added as an inert solvent to the polymer solution. In contrast to common phase-inversion techniques, the added ammonia can induce localized microphase separation and thereby the formation PVDF clusters, which function as growth points and grow gradually into spherical particles in the following phase-inversion process. The obtained membrane displayed both superhydrophobicity and superoleophilicity (Figure 5 b,c) because it was uniformly textured with spherical nanoparticles (Figure 5 e–g). It was demonstrated that such a membrane can effectively

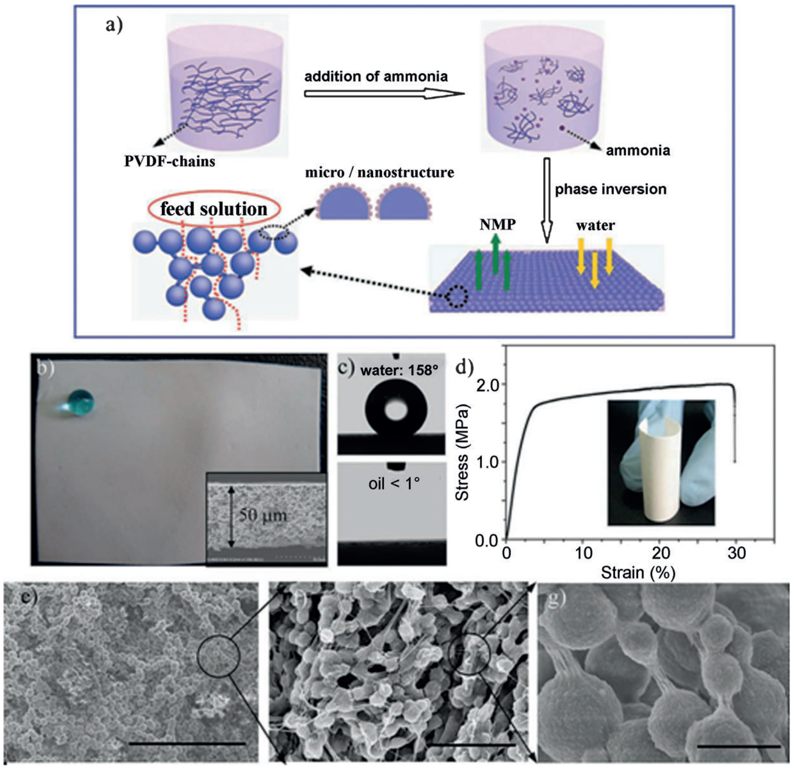


Figure 5. a) Fabrication of a SHBOI poly(vinylidene fluoride) (PVDF) membrane.[62] b) Photograph of an as-prepared PVDF membrane with a water droplet on it. The inset is a cross-section SEM image of the membrane. c) Photographs of a water droplet on the membrane with a contact angle of 158° and an oil droplet on the membrane with a contact angle of about 0°. d) Stress–strain curve of the membrane. The inset is a photograph of the bent membrane. e–g) SEM images of the membrane at different magnifications. Scale bars: 50 (e), 5 (f), and 1 μm (g). Reprinted from Ref. [62] with permission.

separate both micrometer- and nanometer-sized surfactant-free and surfactant-stabilized water-in-oil emulsions; the efficiency of the separation, which was solely driven by gravity, was very high (oil purity in the filtrate > 99.95 wt %).

In a subsequent study,[63] the same authors fabricated ultrathin films of single-walled carbon nanotubes for the ultrafast separation of oil/water emulsions. The films had a thickness of several tens of nanometers and could effectively separate not only water-in-oil emulsions with micrometer-sized droplets, but also emulsions with nanometer-sized droplets, as well as both surfactant-free and surfactant-stabilized emulsions, with fluxes of up to 100000 $L m^{-2} h^{-1} bar^{-1}$ and very high separation efficiency (oil purity in the filtrate > 99.95 wt %).

In general, SHBOI materials can be fouled by the adsorbed oils, particularly high-density crude oil. The fouling results in a clear decrease in hydrophobicity and thereby a rapid decrease in separation efficiency, thus causing secondary pollution, although some materials can be cleaned with organic solvents and reused several times. SHBOI materials are hardly applicable to the separation of water-rich oil/water mixtures or oil-in-water emulsions, in which water acts as a barrier layer to prevent oil permeation. To overcome the disadvantages of SHBOI materials, UWSOB surfaces have been developed as alternatives for efficient oil/water separation.[8,11,64–67]

4. Oil/Water Separation with UWSOB Materials

4.1. UWSOB Materials for the Separation of Oil/Water Mixtures

As discussed in Section 2, UWSOB surfaces, which are also applicable to oil/water separation, can be designed on the basis of a combination of appropriate surface energy and surface roughness.[11,64] Feng and co-workers[11] developed a novel UWSOB polyacrylamide-hydrogel-coated mesh which can selectively and effectively separate water from oil/water mixtures with gasoline, diesel, vegetable oil, and crude oil as the oil component owing to its selective absorption of water. This surface material shows a very low affinity for oil droplets and thus prevents fouling of the coated mesh by oils, which enables high recyclability of the material for repeated separation processes. As this novel water-removing material overcomes the disadvantages of ready fouling and poor recyclability that are usually encountered with SHBOI materials, it shows great potential for industrial oily-water treatment and the cleaning up of oil spills.

Recently, a self-cleaning UWSOB mesh that can be used for oil/water separation was prepared by the layer-by-layer deposition of sodium silicate and TiO_2 nanoparticles on a stainless-steel mesh.[64] The TiO_2 nanoparticles enable the convenient removal of contaminants from the mesh by ultraviolet illumination and thus the facile recovery of the separation ability of the contaminated mesh.

Smart surfaces that are able to switch between superoleophilicity and superoleophobicity in aqueous media were fabricated by using commonly used materials, such as textiles and polyurethane sponges, as substrates.[65] The smart coatings were formed by grafting a block copolymer comprising blocks of pH-responsive poly(2-vinylpyridine) (PVP) and oleophilic/hydrophobic polydimethylsiloxane onto the substrates. The PVP block possesses the ability to alter its wettability and its conformation through protonation and deprotonation in response to the pH value of the aqueous medium, thus resulting in switchable oil wettability under water. The authors demonstrated that such materials can be used for highly controllable oil/water separation (Figure 6). In brief, 1,2-dichloroethane colored with Oil Red O was deposited on the bottom of a beaker containing water at pH 6.5; subsequently, a piece of the functionalized sponge was lowered into the water and moved towards the oil droplets (Figure 6a). When the oil came into contact with the sponge, it was quickly soaked up by the sponge (Figure 6b). Finally, the captured oil was released by decreasing the pH value of the water to 2.0 (Figure 6c).

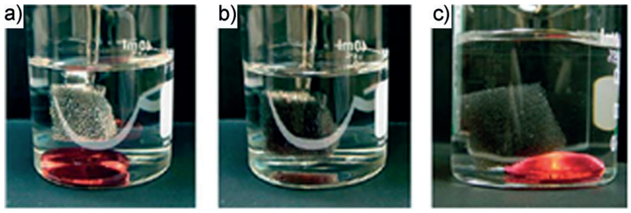


Figure 6. Oil/water separation using a sponge with switchable superoleophilicity/superoleophobicity.[65] a, b) Snapshots showing the absorption of an oil droplet (dyed with Oil Red O) by the functionalized sponge in water at pH 6.5. c) Release of the captured oil from the same sponge upon compression at pH 2.0. Adapted from Ref. [65] with permission.

4.2. UWSOB Materials for the Separation of Oil/Water Emulsions

UWSOB materials with the ability to separate oil/water emulsions were also developed recently.[2,8,66,67] For example, UWSOB hybrid membranes that can be used for effective oil/water separation were fabricated by depositing a $CaCO_3$-based mineral coating on poly(acrylic acid)-grafted polypropylene microfiltration membranes.[2] Under the drive of external pressure or even just by the force of gravity, the hybrid membranes could separate various oil/water mixtures and emulsions with high separation efficiency and high water flux. Furthermore, the UWSOB membranes showed a high oil-breakthrough pressure (> 140 kPa) and low oil fouling, thus exhibiting potential for practical oil/water separation.

Tuteja and co-workers fabricated membranes with hygro-responsive surfaces that are both superhydrophilic and superoleophobic in air and under water.[66] The membranes can separate a variety of oil/water mixtures with separation efficiency higher than 99.9 % by utilizing the difference in the capillary forces acting on the two phases. These membranes have the following advantages:

1) The water flux through the steel mesh is extremely high at around 43000 $L m^{-2} h^{-1}$, which is 1000 times that of a typical industrial ultrafiltration membrane.[68]

2) They are highly energy efficient, since they are solely driven by gravity.
3) The method can be applied not only to metal meshes but also to other substrates, such as textiles.

For these reasons, the separation method is expected to have numerous applications, including wastewater treatment, the cleaning up of oil spills, and fuel purification, as well as the separation of commercially relevant emulsions.

Very recently, a novel UWSOB poly(acrylic acid)-grafted PVDF filtration membrane was fabricated by an approach based on salt-induced phase inversion.[8] The hierarchical micro/nanoscale roughness created on the membrane surface in this way (Figure 7) imparted it with the property of underwater superoleophobicity. The membrane could effectively separate both surfactant-free and surfactant-stabilized oil-in-water emulsions under either gravity or a small applied pressure (< 0.3 bar) with a flux 1–2 orders of magnitude higher than that of its commercial counterparts. Such UWSOB membranes show excellent antifouling properties and can be recycled readily for long-term reuse. The efficient energy- and cost-effective preparation process and the outstanding oil/water separation performance highlight the potential of these membranes for practical applications.

Most of the techniques described herein for oil/water separation make use of polymeric coatings, which display disadvantages in practical applications, especially in terms of long-term preservation for repeated use, stability under severe conditions, and antifouling ability. To address these challenges, Jin and co-workers[67] developed a novel all-inorganic membrane with superhydrophilicity and underwater ultralow adhesive superoleophobicity for oil/water separation. The obtained membrane, which was composed of a $Cu(OH)_2$ nanowire-haired copper mesh, effectively separated both oil/water free mixtures and oil-in-water emulsions with extremely high separation efficiency (residual oil in the filtrate after only one separation was lower than 30 ppm) solely under the force of gravity. More importantly, the membrane possessed excellent antifouling properties and a high separation capacity: It could separate 10 L of an oil/water mixture continuously without a decrease in flux. The low cost and readily scalability of the preparation process as well as the excellent capacity of the material for oil/water separation indicate its great potential for practical applications.

Besides the SHBOI and UWSOB surfaces discussed herein, oleophilic surface materials with an array of conical needle structures[69] and underwater superoleophilic surfaces[1] have also been reported to be applicable to oil/water separation.

5. Summary and Outlook

Theoretically, SHBOI surfaces can be generated by incorporating appropriate surface roughness with hydrophobic functionalities, whereas UWSOB surfaces can be developed by incorporating surface roughness with hydrophilic functionalities. Theoretical predictions have guided the development of SHBOI and UWSOB surfaces by the variation of surface roughness and surface energy on various substrates, such as metal meshes, textiles, foams, sponges, and polymeric membranes. Proof-of-concept experimental setups were developed that highlighted the special wettability of these surface materials, and laboratory-scale separations of oil/water mixtures and emulsions were carried out successfully.

However, challenges in this field remain. In most reported studies, the model oil used in the separation experiments was a pure oily liquid or gasoline, which is very different from the oil pollutant in the true situation of an offshore oil-pollution accident. In such a case, the viscosity and high density of the oil would weaken the separation ability and efficiency of the surfaces substantially. The fouling of the separating materials by these heavy oils can also be a serious problem, since it can easily destroy the pore structure of the substrate as well as the nanotexture of the coating. Finally, and perhaps most importantly, practical applications are hindered by the fragility of the nanoscale roughness features that are necessary for special wettability. Therefore, future studies in this field may aim towards the fabrication of mechanically stable superfunc-

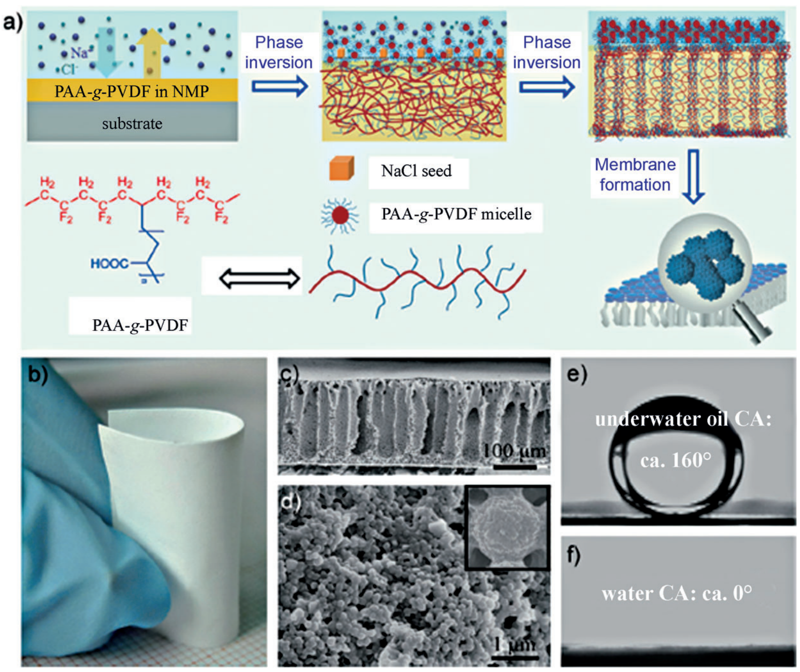


Figure 7. Oil/water separation with a poly(acrylic acid)-grafted PVDF membrane.[8] a) Formation of a superhydrophilic UWSOB PAA-*g*-PVDF membrane by a salt-induced phase-inversion process. b) Photograph of an as-prepared PAA-g-PVDF membrane. c) Cross-section and d) top-view SEM images of the membrane. e, f) Photographs of an underwater oil droplet (e) and a water droplet (f) on the membrane. The PAA-*g*-PVDF membrane was prepared by using PAA-*g*-PVDF with a graft ratio of 2.5 wt% at a salt concentration of 35%. Reprinted from Ref. [8] with permission.

tional surfaces with fast, large-scale separation ability: Materials that are not only applicable to the separation of oil/water mixtures and emulsions in the laboratory but are also able to remove true oil pollutants from seawater, particularly those containing heavy oils.

From a fundamental point of view, it is less well known how water and oil interact dynamically with a SHBOI or UWSOB surface during the separation process. For example, when it comes into contact with oil, a SHBOI surface is transformed into an oil-fused surface and may partly or even completely lose its superhydrophobicity, depending on the surface energy of the adsorbed oil film. Clearly, the surface tension of the oil plays an important role in the separation efficiency of both SHBOI and UWSOB surfaces. Therefore, the following interesting questions may be raised: Is it possible to separate oils such as glycerol ($\gamma = 63.0\,\mathrm{mN\,m^{-1}}$) and diiodomethane ($\gamma = 50.9\,\mathrm{mN\,m^{-1}}$), whose surface tension is slightly lower than that of water ($\gamma = 72.3\,\mathrm{mN\,m^{-1}}$)? What is the behavior of surfactants during the separation process? Unfortunately, it is less documented so far. We take the view that there must be a critical oil surface tension above which the corresponding oil cannot be separated from oil/water mixtures. The presence of surfactants in the aqueous medium probably lowers the separation efficiency and affects the critical oil surface tension required for effective separation.

Owing to their extremely high separation efficiency, superantiwetting/superwetting materials may find application in other areas, for example, for drying water-rich solvents, which could be of great interest to organic chemists. In an organic-chemistry laboratory, a crude product is usually purified by extraction with solvents. The extract then needs to be dried, for example over anhydrous $MgSO_4$, to remove the residual water and then filtered to get rid of the salt. SHBOI or UWSOB materials may simplify this process. Furthermore, these novel materials may open an opportunity for the separation of hydrocarbon vapors from water vapor owing to their extremely different affinity towards water and oil. In particular, if SHBOI materials can effectively adsorb hydrocarbon vapors from the air, many explosion hazards might be avoided by the simple placement of such materials in the environment.

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