Rational design of materials interface at nanoscale towards intelligent oil–water separation

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ARTICLE

Rational Materials Interface Design at Nanoscale towards Intelligent Oil-Water Separation

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Oil-water separation is critically important for the water treatment of oily wastewater or oil-spill accidents. The oil contamination in water not only induces severe water pollution but also threatens human beings' health and all living species in the ecological system. To address this challenge, different nanoscale fabrication methods have been applied in endowing biomimetic porous materials, which provides a promising solution for oily-water remediation. In this review, we present the state-of-the-art developments on the rational material interface design on special wettability for the intelligent separation immiscible/emulsified oil-water mixture. Mechanism understanding towards oil-water separation is firstly described, following with the summary of separation solutions for traditional oil-water mixture and special oil-water emulsion enabled by the self-amplified wettability due to nanostructures. Guided by the basic theory, rational interface design at nanoscale on various porous materials with special wettability towards superhydrophobicity-superoleophilicity, superhydrophilicity-superoleophobicity, and superhydrophilicity-underwater superoleophobicity is discussed in details. Although the above nanoscale fabrication strategies are able to address most of current challenges, intelligent superwetting materials developed to meet special oil-water separation demands and to further promote the separation efficiency are also reviewed for various special application demands. Finally, challenges and the future perspectives on the development of more efficient oil-water separation materials and devices by nanoscale control are provided. It is expected that the biomimetic porous materials with nanoscale interface engineering will overcome the current challenges of oil-water emulsion separation, realizing in practical applications in the near future with continuous efforts in this field.

1. Introduction

Oil leakage and oil spill accidents happening during oil exploitation and transportation^[1-5] has led to severe water and soil contamination, which threatens the health of human beings and other living species.^{[6-}

^{8]} In this regard, oil-water separation is urgently desirable to solve the above problems.^[9-11] Although the conventional oil contamination treatment techniques, such as in situ burning, centrifugation separation, filtration, and neutralization etc., are effective to solve the pollution issues, they normally face the drawbacks of low separation efficiency, time-consuming, high cost or even inducing a secondary pollution. More seriously, the incomplete separation often leads to oil remaining in water or water remaining in oil, which is still a potential risk for the living species.^[12-16] Therefore, it is highly desirable to develop reliable technologies based on rational materials design for highly efficient oil-water separation.

The unique superhydrophobic self-cleaning property of the lotus leaves is attributed to micro/nanoscale hierarchical architectures and the waxy nanocrystals on top of the papillae. Inspired by this, the nanoscale-implicated wettability concept has been widely used to fabricate superwetting surfaces for oily water remediation.^[17-22] The nanofabrication process normally can be divided into two steps: firstly,

some particles or polymers are used to create micro/nano architectures on its surface. Secondly, functional F-containing atom/molecules or CH₃-containing groups are self-assembled and grafted onto the rough surface to achieve low surface energy. Compared to the traditional separation techniques, the as-prepared bio-inspired materials by nanotechnologies with special wettability exhibit unique advantages in both the separation rate and efficiency. Due to the opposite affinities towards oil and water, both superhydrophobic-superoleophilic and superhydrophilic-superoleophobic materials are suitable for oil-water separation.^[23-29] Generally speaking, it is simple to fabricate superhydrophobic-superoleophilic materials for oil-water separation by allowing oil to permeate the as-prepared materials and blocking water outside simultaneously.^[30] However, it is a challenge to construct superhydrophilic-superoleophobic materials for oil-water separation because an oleophobic surface inherently exhibits hydrophobicity.^[31] To overcome this challenge, scientists have ingeniously developed the superhydrophilic-underwater superoleophobic materials to realize oil-water separation.^[32-35] Due to the underwater superoleophobicity, membranes can overcome the drawbacks of being easily fouled or even blocked by oil. Therefore, the separation efficiency is improved greatly. From the material perspective, porous materials with special wettability are ideal

candidates for oil-water separation due to the unique interconnected structures with micro/nano-sized pores, which can significantly accelerate the separation efficiency and rate.^[36-41] The oil-water separation can be realized based on filtration or absorption. For instance, two-dimensional (2D) membrane-like materials such as polymeric membranes, fabrics, and meshes are usually based on filtration, while three-dimensional (3D) porous materials such as foams, sponges and carbon-derived aerogels are normally based on absorption.

To further promote the oil-water separation efficiency and to meet special oil-water separation demands, intelligent superwetting materials with stimuli-responsive wettability, magnetism-assisted wettability and Janus-featured wettability, have been developed for the efficient separation of sundry oil-water-mixtures, such as simple oil-water-mixture, ternary phases of oil-water-oil-mixture and even oil-water emulsion.^[42,43] To be specific, biomimetic porous materials with some polymers or functional inorganic nanoparticles can switch between super-wetting and super-anti-wetting by applying an external stimulus such as the pH value, light illumination, temperature, and voltage, etc. This offers a significant advantage for oil-water mixture and emulsion separation by selectively allowing only water or oil to pass through.^[44-46] Besides, when endowing special wettable materials with magnetic nanoparticles, they can be remotely controlled by a magnet during the oil-absorption process, saving a large amount of human labour and time.^[47-49] Furthermore, Janus wettable surfaces, such as asymmetric and patterned membranes, exhibit unique unidirectional and non-uniform properties for oil-water separation and oil/water collection.^[50-54] Therefore, endowing these special wettable materials with intelligent functions is promising for efficient oil-water separation.^[55-59]

In this review, we summarize the latest development of materials interface engineering techniques at micro/nanoscale for oil-water separation (Figure 1). Firstly, a comprehensive mechanism towards oil-water mixture and emulsion separation is introduced. Secondly, nanoscale fabrication considerations on various porous materials with special wettability towards superhydrophobicity-superoleophilicity, superhydrophilicity-superoleophobicity, and superhydrophilicity-underwater superoleophobicity are described in detail. Thirdly, intelligent superwetting materials are also reviewed, which are developed to further promote the separation efficiency and to meet special oil-water separation demands such as oil-water emulsion remediation, switchable oil-water separation, remote controllable oil-absorption and oil/water collection, etc. Lastly, the challenges and an outlook in this field are briefly discussed.

Figure 1. Recent developments in the rational interface structure design of different porous materials with special wettability including superhydrophobicity-superoleophilicity (hydrophobicity-oleophilicity), superhydrophilicity-superoleophobicity (hydrophilicity-oleophobicity) and superhydrophilicity-underwater superoleophobicity (hydrophilicity-underwater oleophobicity) and emerging intelligent functions for special oil-water separation.

2. Basic considerations for oil-water separation

The surface wettability is one of the most important parameters when applying into oil-water separation, water collection, liquid manipulation, etc. In the past decades, extensive studies on the surfaces of biomaterials have promoted a comprehensive understanding of the mechanism behind superwetting surfaces.^[60-62] Inspired by these discoveries, four types of wetting behaviors, including Young's mode,^[63,64] Wenzel's mode,^[65,66] Cassie's mode,^[67,68] the intermediate state between the Wenzel and the Cassie modes,^[69,70] emerge to describe the relationship between surface roughness and surface wettability, which has been reviewed in recent review papers^[71-73] and will not be discussed in detail here. Based on Young's model, an ideally flat surface has limited hydrophobicity as the low-surface-energy alone will not be able to achieve superhydrophobicity in any known solids without micro/nano hierarchical structures. By creating rough surface with architectures at the micro/nanoscale, the Wenzel and Cassie models predict superhydrophobic contact angle can be easily realized. Among the two, Wenzel state is a wet-contact mode and displays high contact hysteresis, while Cassie state exhibits a high contact angle and low contact hysteresis. And the Lotus effect is considered as the special case of superhydrophobic Cassie state. Additionally, in practical situations, there often exists a transitional state between Wenzel's and Cassie's states, wherein surface water droplets can slide when the surface is tilted at a certain angle. Therefore, various biomimetic surfaces with special wettability could be achieved by adjusting surface architectures at micro/nano scales and the chemical composition.

Special wettable materials with superhydrophobic-superoleophilic, superhydrophilic-superoleophobic or superhydrophilic-underwater superoleophobic property are suitable for oil-water separation.^[74-77] Generally, oil-water-mixture or oil-water-emulsion separation mainly depends on the selective rejection of oil or water.^[78-81] Taking the superhydrophobic-superoleophilic membranes as an example, with a proper pore size larger than several tens micrometers, oil droplets quickly penetrate through the big pores of the membranes, while water droplets are rejected by the superhydrophobic surface and still remain above the surface, resulting in separation of layered oil-water-mixture (Figure 2a, above). On the other hand, by adjusting pore size to be smaller than or comparable to the diameter of emulsified droplets (usually smaller than 20 μm), oil-water emulsion (oil-in-water emulsion or water-in-oil emulsion) can also be separated by allowing oil to pass through the membrane and repelling water droplets (Figure 2b, above).^[82,83] Under this condition, polymer membranes with smaller pores have been successfully synthesized and widely used for this task. While for metal meshes and fabrics, their pore size should be less than tens of micrometers, which can be achieved by depositing a surface-active polymer or via growing inorganic nanoparticles on the surface. However, the separation efficiency of a membrane is largely decreased with reducing the pore size and it is a time-consuming process. In addition, when using polymer membranes for oil-water emulsion separation, it can be easily fouled and the pores will be blocked by oil, leading to a quick decline of permeation.^[84,85] Therefore, membranes with too small pores are ineffective and it is undesirable for practical oil-water separation.

Commercial porous materials such as fabrics and metal meshes usually possess large pore size larger than several tens of micrometers, which seems not to be applicable for oil-water-emulsion separation.

In order to overcome this limitation, a promising separation strategy based on a synergistic effect of demulsification, coalescence and rejection has emerged. Based on this novel strategy, emulsified oil-water droplets were firstly demulsified upon contacting membrane surface, and then coalesced to form normal oil-water-mixture. Followed by the rejection of water, oil-water emulsions are finally separated (Figure 2c, above). Likewise, in superhydrophilic-superoleophobic or superhydrophilic-under water superoleophobic condition, the mechanism of oil-water separation is similar to the superhydrophobic-superoleophilic situation, where water will pass through the membrane and oil droplets will remain above the surface by the rejection of oil, which exhibits opposite phenomenon (Figure 2a-c, below).

Until now, great progress has been made on superwetting porous materials with small or large pore size for simple oil-water-mixture separation. However, the field of stabilized oil-water emulsion separation is far from mature and has much less progress when compared to traditional oil-water-mixture separation. Most special wettability stimulated membranes with small pore size and compact structure have been successfully applied in emulsified oil-water-mixture separation, but separation efficiency is relatively low. Besides, though intelligent superwetting materials with large pore size exhibit superior efficiency in emulsion separation, the separation conditions are hard to be controlled. Therefore, how to realize emulsion separation in a more efficient and effective way is still a big challenge. Recent progress on the superwetting porous materials with various special wettabilities or intelligent functions for oil-water emulsion separation has been summarized in Table 1, and some typical works will be discussed in the following sections.

Figure 2. Design strategies for oil-water-mixture and oil-water emulsion separation. Membrane with large pore size for oil-water-mixture separation based on rejection of oil/water (a). Membranes with small pore size for oil-water-emulsion separation based on the rejection of oil/water (b). Membranes with large pore size for oil-water-emulsion separation based on synergistic effects of demulsification, coalescence and rejection of oil/water (c).

Table 1. Recent progresses on superwetting porous materials for oil-water-emulsion separation

Substrate	Modification materials	Modification method	Special wettability	Intelligent functions	Emulsion type	Permeation flux (L m ⁻² h ⁻¹)	Separation efficiency (%)	Ref.
PVDF Membranes	Poly(acrylic acid)	Phase separation	Superhydrophilicity-underwater superoleophobicity	\	Oil-in-water	570	\	86
	Ammonia	Phase separation	Superhydrophobicity- superoleophilicity	\	Water-in-oil	3415 ± 150	>99.95	87
	PVDF	Phase separation	Superamphiphobic/underwater superoleophobicity-underoil superhydrophobicity	Switchable wettability	Oil-in-water/ water-in-oil	9380 ± 874/ 8180 ± 755	>99.96	88
	Polyamide 6	Electrospinning	Hydrophilicity-underwater oleophobicity	\	Oil-in-water	890	>99	89
Polyurethane membrane	PSMA ^{a)}	Phase separation	Hydrophobicity-oleophilicity	Thermal-response	Water-in-oil	\	>99.9	90
	PDA ^{b)} , SiO ₂	Wet chemical reaction	Superhydrophilicity-underwater superoleophobicity	\	Oil-in-water	140	\	91
	Dopamine	Self-polymerization	Superhydrophilicity-underwater superoleophobicity	\	Oil-in-water	6605	\	92
	PMAAPS ^{c)}	ATRP ^{d)}	Superhydrophilic-underwater superoleophobicity	\	Oil-in-water	16084	>99.999	93
PAN ^{f)} membrane	PNIPAM ^{e)}	Polymerization	Switchable superhydrophilicity/superoleophobicity	Thermal-response	Oil-water- emulsion	\	>99.2	94
	PAN, SiO ₂	Electrospinning, electrospraying	Superhydrophilicity-underwater superoleophobicity	\	Oil-in-water	6290	>99.9	95
	Nano cellulose crystal	Coating, deposition	Hydrophilicity-underwater oleophobicity	\	Oil-water- emulsion	378	99.6	96
	Poly(sulfone)	Solution casting	Superhydrophobicity/ superoleophilicity	\	Oil-in-water	230	98.63	97
CNT membrane	SWCNT	Vacuum-filtering	Hydrophobic-superoleophilicity	\	Oil-in-water	100000	>99.95	98
	PDA, Au, pNIPAm-co- AAm ^{h)}	Wet chemical reaction	Superhydrophobic-superoleophilicity	Photothermal- response	Oil-in-water	35890	>99.99	99
Nylon membrane	PS ⁱ⁾ , PDMAEMA ^{j)}	Photografting, photopolymerization	Hydrophobic/oleophilic (one side) Hydrophilic/oleophilic (the other side)	Janus wettability	Oil-in-water/ water-in-oil	6780/ 8550	>99.98	100
	PAM ^{k)} , PDVB ^{l)}	Hydrothermal method	Superhydrophilic-underwater superoleophobicity	\	Oil-in-water	<12	>99	101
Ceramic membrane	CNT	Chemical vapor deposition	Superhydrophilic-underwater superoleophobicity	\	Oil-in-water	36	100	102
Polypropylene membranes	PDA, PEI ^{m)} , SiO ₂	Dip-coating	Superhydrophilic-underwater superoleophobicity	\	Oil-in-water	>1200	>99	103
Aerogel membranes	Agarose, chitosan	Crosslinking-drying	Hydrophilicity-underwater superoleophobicity	\	Oil-in-water	>600	>99	104

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Substrate	Modification materials	Modification method	Special wettability	Intelligent functions	Emulsion type	Permeation flux (L m ⁻² h ⁻¹)	Separation efficiency (%)	Ref.
Polypropylene membrane	PAA, CaCO ₃ PDMA ⁽ⁿ⁾	Grafting, dip-coating	Superhydrophilicity-underwater superoleophobicity	\	Oil-in-water	> 2000	> 99	105
Filter paper	PTMSPMA ^(o) , PDMAEMA	Polymerization	Superhydrophilic/superhydrophobicity	pH-response	Oil-in-water/water-in-oil	\	> 98	106
Fabric	Polyvinyl alcohol	Crosslinking	Superhydrophilicity-underwater superoleophobicity	\	Oil-in-water	63	> 99	107
	PDMS, PDMAEMA	Grafting	Superhydrophobicity/superoleophilicity	Janus wettability	Oil-in-water	1500	99.7	108
	PDMS, PDMAEMA	Grafting	Superhydrophobicity/superoleophilicity	Janus wettability	Oil-in-water	6700	99.97	109
	Ppy ^(p)	Electrochemical, polymerization	Underwater superoleophobicity-underoil superhydrophobicity	\	Oil-in-water/water-in-oil	300-500/720	99.9	110
Stainless steel mesh	Polyvinyl butyral	Electrospinning	Hydrophobicity-superoleophilicity	\	Water-in-oil	6110	99.5	111
	Fluorodecyl POSS ^(q) , PDMS	Dip-coating	Superhydrophilicity-superoleophobicity	Voltage-response	Oil-in-water/water-in-oil	200	≥99.9	112
	PDVB	Solothermal method	Superhydrophobicity/superoleophilicity	\	Water-in-oil	\	> 99.99	11
	SiO ₂ , fluoropolymer	Dip-coating	Superhydrophobic/superoleophilic	Patterned wettability	Water-in-oil	\	99.95	113
Copper mesh	PDA, PEPA ^(r)	Dip-coating	Superhydrophilic-underwater superoleophobicity	\	Oil-in-water	34096	> 99.6	114
	Cu(OH) ₂	Surface oxidation	Superhydrophilic-underwater superoleophobicity	\	Oil-in-water	\	\	115
	Cu(OH) ₂ , HS(CH ₂) ₁₀ COOH, HS(CH ₂) ₉ CH ₃	Grafting	Superhydrophobic/superhydrophilicity-underwater superoleophobicity	pH-response	Oil-in-water	\	\	116
	HS(CH ₂) ₉ CH ₃ , HS(CH ₂) ₁₀ COOH	In situ growth	Superhydrophobic-superoleophilic/superhydrophilicity-underwater superoleophobicity	pH-response	Oil-in-water/water-in-oil	3000-12000	> 99.9	117
RGO Sponge	GO	Freeze-drying	Hydrophobic/oleophilic (one side) Hydrophilic/oleophilic (the other side)	Janus wettability	Oil-in-water/water-in-oil	\	≥99.2	118
Melamine sponge	Hydrophobic polymer solution	Solvent-immersing	Superhydrophobic-superoleophilicity	\	Water-in-oil	156700	> 99.98	119
Cellular aerogels	PAN, SiO ₂	Electrospinning, freeze-drying	Superhydrophobic-superoleophilicity	\	Water-in-oil	1590	> 99.995	120
Cu foam	Cu nanoparticles, N-Dodecyl mercaptan	Electrodeposition, liquid phase reaction	Superhydrophobic-oleophilic	\	Water-in-oil	6560	> 99.89	121
Ti foam	Fluorine-containing electrolyte	Anodization	Superhydrophobic-superoleophilicity	\	Oil-in-water	\	> 99	122

Notes: a)-Poly(stearyl methacrylate), b)-Polydopamine, c)-Poly(3-(N-2-methacryloxyethyl)-N, N-dimethyl) ammonatropanesultone, d)-Atom transfer radical polymerization, e)-Poly(N-isopropylacrylamide), f)-Polyacrylonitrile, g)-Polyethylene-co-polyvinyl alcohol, h)-Poly(N-isopropylacrylamide-co-acrylamide), i)-Polystyrene, j)-Poly(N,N-dimethylaminoethyl methacrylate), k)-Polyacrylamide, l)-polydivinylbenzene, m)-Polyethylenimine, n)-Poly(dodecyl methacrylate), o)-Poly((trimethoxysilyl)propyl methacrylate), p)-Polypyrrole, q)-1H,1H,2H,2H-Heptadecafluorodecyl polyhedral oligomeric silsequioxane, r)-Polyethylenepolyaniline.

3. Special wettability stimulated porous materials for oil-water separation

Endowing different porous materials with special wettability, including superhydrophobicity-superoleophilicity, superhydrophilicity-superoleophobicity and superhydrophilicity-underwater superoleophobicity is desirable for oil-water separation. Therefore, different types of porous materials and the nanofabrication strategies on how to construct special wettability will be introduced in this section (Figure 3).

Figure 3. The latest efforts on the nanofabrication strategies of traditional porous materials such as 2D-membranes, textiles, meshes and 3D-sponges, foams, carbon-derived aerogels with special wettability from superhydrophobicity-superoleophilicity and superhydrophilicity-superoleophobicity to superhydrophilicity-underwater superoleophobicity.

3.1 Superhydrophobic-superoleophilic Materials

Superhydrophobic-superoleophilic materials are the most typical oil removing materials for oil-water separation through either oil filtration (2D-membranes, textiles, and metal meshes) or oil absorption (3D-sponges, foams, carbon and carbon-derived materials).^[123,124] Since surface roughness and surface chemical composition are the two key factors to construct special wettability, superhydrophobic-superoleophilic materials can be fabricated by two methods: 1) enhancing surface roughness by creating micro/nano architectures on the substrate; 2) modifying hydrophobic rough surface with low-surface-energy F-containing atom/molecules or CH₃-containing groups.^[125,126] Accordingly, different types of superhydrophobic-superoleophilic materials and their corresponding fabrication methods will be introduced below.

3.1.1 Construction of 2D-membranes, metal meshes, and fabrics with special wettability

As mentioned before, 2D metal meshes, fabrics and membranes can be applied to oil-water separation based on the filtration. These superhydrophobic-superoleophilic porous materials have been

successfully synthesized by modification via electrospinning technique, dip/spray-coating method, wet chemical reaction, chemical vapor deposition, phase separation and gas phase coating strategies etc.

1) Electrospinning method

Electrospinning is a versatile technique to create polymer-based membranes, which spontaneously exhibits high specific surface areas and 3D interconnected architectures with micro/nano pores. In this term, electrospun membranes exhibit promising potential in oil-water separation when endowed with special wettability, which can be fabricated by direct electrospinning or surface modification.^[127-129] In the first step, hydrophobic polymeric materials such as polystyrene (PS), poly(vinylidene fluoride) (PVDF), polydimethylsiloxane (PDMS) and fluorinated silane functionalized polymers have been widely used for direct electrospinning of hydrophobic membranes.^[130,131] Jiang et al. fabricated hydrophobic films by electrospinning of polystyrene/dimethylformamide (PS/DMF) solutions.^[132] By controlling PS concentration, surface micro/nano architectures were significantly enhanced (Figure 4a,b) and subsequently super water-repellency was realized. Cao et al. developed an intrinsic superhydrophobic-superoleophilic microfibrillar membrane with microporosity by electrospinning nanotechnology.^[133] Due to its high contrast wettability to oil and water, both immiscible oil-water mixtures and water-in-oil emulsions can be separated with high efficiency. In addition, an environment-friendly polymer, polyvinyl butyral, has been chosen to fabricate superhydrophobic-superoleophilic nanofibrous membranes by electrospinning because of its stability and hydrophobicity, and stainless steel wire meshes with different mesh numbers (12#, 20#, 30#, 40#) were used as collectors.^[111] The pore size of the nanofibrous membranes could be finely controlled by using different mesh numbers and all of the nanofibrous membranes showed highly hydrophobic and superoleophilic properties (Figure 4c). It was demonstrated that the nanofibrous membranes could selectively and rapidly separate oil from both a layered oil-water-mixture and water-in-oil emulsion, and the enlarged pore size could greatly improve the oil flux without obvious influence on the separation efficiency (Figure 4d-f and Table 1). The designed nanofibrous membranes with controllable pore sizes showed large oil flux, high separation efficiency, excellent durability, and recyclability for oil-water separation, which have made them great candidates in the management of oily water. Apart from solvent and polymer concentration, external additives such as micro/nano particles (ZnO, SiO₂, TiO₂, Fe₃O₄ etc.), nanotubes and ionic liquid also have a significant impact on surface wettability.^[134-137] Moreover, electrospinning followed by nano modification is more effective for fabricating superhydrophobic membranes with proper surface wettability and durable mechanical/chemical durability. In this term, superhydrophobicity can be obtained by combining electrospinning with some other modification techniques such as phase separation, wet chemical reaction and chemical vapor deposition, etc.^[138,139] Rutledge et al. constructed a superhydrophobic membrane by electrospinning and then coated with a thin layer of hydrophobic polymer by chemical vapor deposition.^[140] Though electrospinning

membrane has been used for oil-water separation, it suffers from low penetration speed, inadequate mechanical strength and integrity, which greatly limits practical applications.

Figure 4. SEM images of a film prepared by 25% (a) and 7% PS/DMF solution (b), respectively. And insets are the corresponding water droplets on the film. Digital images of water droplets stained with methylene blue and liquid paraffin droplets stained with oil red on the surface of nanofibrous membranes (c). Oil flux and separation efficiency of the five kinds of nanofibrous membranes for separation of a water-in-oil emulsion (d). Digital images of the water-in-oil emulsion before (e) and after separation (f), and the corresponding optical images of the water-in-oil emulsion before and after separation. (a,b) Reproduced with permission.^[132] Copyright 2004, Wiley-VCH. (c-f) Reproduced with permission.^[111] Copyright 2016, American Chemical Society.

2) Dip/spray-coating method

Dip-coating is one of the simplest approaches to decorate different substrates with either micro/nano-architectures or low-surface-energy components. Thus, dip-coating is suitable for one-step modification to achieve superhydrophobicity without further treatment.^[141,142] For example, Zhou et al. used a nanocomposite, which contained PDMS, fluorinated alkyl silane functionalized silica nanoparticles and fluoroalkylsilane, as a nanocoating material to endow fabrics with superhydrophobicity.^[143] When compared to the unmodified fabric (Figure 5a), the silica nanoparticles were uniformly dispersed on the fiber surface after dip-coating, which created architectures at the nanoscale and made fabric highly water-repellent (Figure 5b). Besides, Deng et al. successfully fabricated a superhydrophobic fabric via immersing in TiO₂-SiO₂@PDMS hybrids solution.^[144] The prepared superhydrophobic fabrics exhibited excellent resistance to strong acid attack (Figure 5c), and can be applied to a filter cloth for oil-water separation. Though nanoparticles can be easily dispersed in the polymer solution and directly coated on various substrates by one-step dip-coating method, the dispersed particles are unstable and tend to aggregate in a short time, limiting its large-scale production.

Considering no distinct micro/nano architectures on most pristine substrates, the dip-coating process combined with pre-treatment to

roughen smooth surface is more appealing to construct superhydrophobic interfaces.^[145,146] Among various pre-treatment approaches, chemical etching,^[147,148] in situ growth,^[149,150] and particle-coating^[151,152] are the mostly widely used techniques to endow surface with micro/nano architectures for suitable roughness. Lu et al. created a superhydrophobic-superoleophilic steel surface via first immersing it into a salt solution to etch micro/nano-sized structures on its surface, and then modifying it using a low-surface-energy material by dip-coating.^[153] Besides, Cheng et al. synthesized superhydrophobic-superoleophilic copper mesh by creating micro/nano architectures on its surface and then modifying with the hydrophobic/oleophilic components (Figure 5d).^[154] In addition, our group developed superhydrophobic fabric by a simple and fast dip-coating of organically modified silica aerogel (ormosil) thin film onto the fabrics first, followed by PDMS top-coating. The process has endowed the fabric with a rough surface and low surface energy at the same time (Figure 5e,f).^[155] By varying the grafted PDMS concentration, the surface exhibited repulsive and adhesive states, which are applicable for both oil-water-mixture separation and oil-in-water emulsion separation, respectively (Figure 5g,h).

Beyond dip-coating method, spray-coating is another effective and low-costing technique for making desirable substrates superhydrophobic.^[156,157] For example, Feng et al. sprayed the polytetra-fluoroethylene coating on a stainless steel, and the polytetra-fluoroethylene coated mesh exhibited superhydrophobicity-superoleophilicity due to the superhydrophobicity of polytetra-fluoroethylene coating for water rejection.^[158] As shown in Figure 6i, water droplets can maintain the original morphology above the surface, while oil droplet spread and permeated the mesh quickly. Though dip-coating and spray-coating are very efficient and cost-effective, adhesion between decorative micro/nano coatings and various substrates is generally low and it's easy to be destroyed by either chemical etching or mechanical actions.^[159-161] To enhance the durability, a robust coating can be realized by other more promising techniques, such as wet chemical reaction, chemical vapor deposition and so on.

Figure 5. SEM images of the unmodified (a) and modified (b) polyester fabrics and the right pictures are the corresponding optical images of water drops on the polyester fabrics, respectively. The optical image of an acid water droplet dyed with methyl blue on superhydrophobic-superoleophilic steel mesh (c). Schematic diagram

of fabrication process for the superhydrophobic-superoleophilic film (d). SEM images of PDMS-ormosil@fabric (e, f), inset of (e) is its corresponding low-magnification image and insets of (f) are static and dynamic behavior of the droplet on PDMS-ormosil@fabric. Schematic illustration of the continuous separation mechanism of the oil-water-mixture (g) and the surfactant-free oil-in-water emulsion separation (h). (i) Optical picture of water droplet on the coating mesh film with a high contact angle (top image), and process of oil spreading and permeating on the coating mesh film (bottom image). (a,b) Reproduced with permission.^[143] Copyright 2012, Wiley-VCH. (c) Reproduced with permission.^[144] Copyright 2012, Royal Society of Chemistry. (d) Reproduced with permission.^[154] Copyright 2016, Wiley-VCH. (e-h) Reproduced with permission.^[155] Copyright 2016, Royal Society of Chemistry. (i) Reproduced with permission.^[158] Copyright 2015, Royal Society of Chemistry.

3) Wet chemical reaction method

Wet chemical reaction includes various processes, such as in situ growth of both metal oxides and metallic nanomaterials, in situ polymerization, electrochemical deposition and atom transfer radical polymerization (ATRP).^[162-165] Both surface chemical composition and surface rough micro/nano architectures can be controlled by gradually growing or grafting reaction materials. The binding force between created micro/nanocoatings and substrates is largely enhanced due to the strong chemical bonding energy between each other, which is more favorable for practical application.^[166,167] For example, Wang et al. constructed a rough structure on fabrics and sponges via in situ growth of metal oxide/metallic nanocrystals and then followed by a coating of thiols.^[168] These as-prepared superhydrophobic-superoleophilic fabrics and sponges were successfully used for oil-water separation. Besides, hierarchically structured fabric surface can also be achieved by in situ growth of some other metal oxide particles, such as TiO₂ and ZnO via one-pot hydrothermal technology. And the remarkable superhydrophobicity was constructed with subsequent chemical modification of low-surface-energy components.^[169-171] Chang et al. grew the micro/nano-structured ZnO nanorods on the stainless-steel mesh film via a simple hydrothermal method.^[172] After the hydrothermal treatment, aligned ZnO nanorod arrays were formed radially and uniformly along every wire (Figure 6a). After post-modification with stearic acid, superhydrophobicity-superoleophilicity was achieved. When oil droplet (toluene, gasoline and diesel oil) was placed onto mesh surface, it spread and penetrated quickly, with the oil eventually dripping down, while water would stay on the mesh surface. Furthermore, we successfully fabricated TiO₂@fabric composites by a one-pot hydrothermal reaction and fluoroalkylsilane modification.^[173] After the treatment, micro-marigold flower-like hierarchical TiO₂ particles were uniformly coated on the fiber surface and the superhydrophobic TiO₂@fabric has been demonstrated highly efficient oil-water separation due to its extreme wettability contrast (superhydrophobicity/superoleophilicity).

The surface micro/nano structure will be unstable if the polymers are simply dissolved in a solution and then coated on the substrate surface without chemical actions. However, if the polymer chains are

cross-linked, the coating will be resistant to damages by either chemical or mechanical attack. In situ crosslinking has been proven an effective technique to enhance coating stability. In addition to copolymers, monomers can self-polymerize and form micro/nano particles with a catalyst on the surface of substrates. For example, Tang et al. fabricated a superhydrophobic-superoleophilic membrane by in situ polymerization of fluorinated polybenzoxazine functional layer on the membrane surface (Figure 6b).^[174] With the incorporation of SiO₂ nanoparticles on the surface again, water-repellency was largely enhanced and the water contact angle can reach 161°. Thus, layered oil-water-mixture can be separated efficiently (Figure 6c).

Besides, atom transfer radical polymerization is a controlled radical polymerization technology that has been proven a useful tool for synthesis of functional macromolecules with controllable architectures on various substances.^[175,176] Generally, the hydroxyl group is often used to produce active sites for reacting with an initiator. Thus, cellulose fabric containing abundant hydroxyl groups is readily used to graft functional monomers. For example, Li et al. developed a highly hydrophobic silk by grafting acrylate fluoride monomers via ATRP route.^[177] For other substrates without abundant hydroxyl groups, they can be pre-treated easily by O₂ plasma sputtering or chemical modification to generate large quantities of hydroxyl groups. Xue et al. prepared a superhydrophobic-superoleophilic poly(ethylene terephthalate) fabric surface by surface initiated atom transfer radical polymerization of fluorinated methacrylates on sodium hydroxide solution etched poly(ethylene terephthalate) fabrics (Figure 6d).^[178] The obtained superhydrophobic fabric showed excellent chemical robustness and mechanical durability. Even after 2500 abrasion cycles, it still maintained highly superhydrophobicity and water droplet could stand sphere on the fabric surface (Figure 6e,f). In addition to hydroxyl group, an amino-containing dye intermediate (2-chloro-4,6-diamino-1,3,5-triazine) was also used to make more active sites for in situ polymerization.^[179] Besides the in situ growth, in situ polymerization and ATRP methods, cathodic electrodeposition is another common wet chemical reaction technique to achieve superhydrophobicity-superoleophilicity. Wang et al. constructed a micro/nano-structured copper mesh by electrodeposition method in an aqueous solution containing copper sulfate and sulfuric.^[180] After the long-chain fatty acid monolayer polymerized on the as-prepared surface-roughed copper mesh, a superhydrophobic copper mesh was obtained.

4) Chemical vapor deposition method

Chemical vapor deposition (CVD) has been demonstrated to be another facile technique to gradually construct hierarchical structures on substrates.^[181-183] Compared to simple dip/spray-coating method and wet chemical reaction technique, chemical vapor deposition is controllable and tends to form a more uniform coating with high density on the substrates. For example, Zhang's group developed a one-step technique to construct superhydrophobic-superoleophilic polyester textile via chemical vapor deposition of trichloromethylsilane for applications in oil-water separation and selective oil absorption.^[184] The uncoated polyester textile composed

of microfibers with the diameter from 15 to 20 μm exhibits a smooth surface (Figure 6g). After CVD, the textile displayed a rough surface with a dense layer of randomly grown silicone nanofilaments (Figure 6h), which resulted in super water-repellency. Besides, Crick et al. used aerosol assisted CVD technique to coat copper meshes with a hydrophobic silicone elastomer.^[185] When compared to the pristine copper meshes, the modified surfaces were made up of agglomerations of micro/nano polymer microparticles and exhibited superhydrophobicity-superoleophilicity. Likely, Zhou et al. also produced a superhydrophobic-superoleophilic fabric via a vapor phase deposition technique.^[186] Compared to pristine cotton, the modified fabric had outstanding superhydrophobic property for oil-water separation. As CVD has limited effect on surface roughness, pre-treatment via chemical etching or nanoparticle decoration is essential to enhance micro/nano architectures.^[187,188] From this view, Cortese et al. used O_2 plasma pre-treatment to introduce a dual-scale nanostructure on the textile surface, followed by conducting diamond like carbon coating on the cotton fabrics via CVD technique to achieve the low surface energy and rough surface simultaneously.^[189] With the special superhydrophobicity-superoleophilicity property, fabric could absorb oil from oil-water-mixture (Figure 6i). Although CVD method was usually conducted under high temperature and vacuum condition, this facile method may destroy the textile texture and accelerate the aging process.

Figure 6. SEM images of the as-prepared micro-structured ZnO nanorods on the stainless-steel mesh films (a) and the inset is the corresponding magnified image. Schematic diagram of in situ polymerization of fluorinated polybenzoxazine functional layer on the membrane surface (b). The process of oil-water separation using the as-prepared membranes (c). Schematic illustration of the fabrication of superhydrophobic fabrics by ATRP technique (d). Changes of contact angle and sliding angle with repeated abrasion cycles (e). Photograph of a water droplet on the superhydrophobic fabrics after 2500 cycles (f). SEM images of uncoated (g) and coated (h) polyester textiles. The process of oil removal from an oil-water-mixture (i). (a) Reproduced with permission.^[172] Copyright 2012, American Chemical Society. (b,c) Reproduced with permission.^[174] Copyright 2013, Royal Society of Chemistry. (d-f) Reproduced with permission.^[178] Copyright 2015, American Chemical Society. (g,h)

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5) Other methods

Beyond the modification methods mentioned above, other methods such as layer by layer assembling, candle-soot coating, incorporation, phase separation and gas phase coating strategies have also been developed to achieve special wettability.^[190-194]

Layer-by-layer assembling approach, usually with electrostatic interactions between each layer, can provide the flexibility to improve adhesion to the substrate and create a low surface tension coating at the air interface.^[195] For example, Lin et al. created a superhydrophobic surface firstly via a versatile electrostatic layer by layer self-assembly technique for constructing micro/nano surface structures, followed by a post-fluorinating modification.^[196] Compared to the pristine cotton, modified cotton fabrics grafted by a number of silica-nanoparticle multilayers and surface roughness was largely enhanced. Besides, candle-soot as a low-surface-energy material exhibits excellent durability towards chemical attack and in harsh environment, thus it has been utilized for constructing superhydrophobic surfaces. Li et al. used an overlapping deposition of candle-soot on the metal mesh to obtain a hydrophobic surface. Subsequently, superhydrophobic surfaces were successfully achieved with post-modification of hydrophobic silica nanoparticles.^[197] The obtained superhydrophobic candle-soot and silica coated meshes could maintain high separation efficiency above 98.5% for many types of organic oils and exhibited stable recyclability after tens cycles of separation. Recently, a facile and inexpensive one-step sonochemistry irradiation method appeared for the fabrication of SiO_2 nanoparticles functionalized with octadecyltrimethoxysilane and in situ incorporation onto cotton fabrics.^[198] The double sides of as-prepared fabrics showed both superhydrophobic and superoleophilic properties simultaneously with a high water contact angle of 159° and an oil contact angle of 0° , which was successfully used to separate oil-water-mixture. What's more, phase separation is also effective for enhancing micro/nano architectures. Xue et al. constructed a rough PDMS coating on the fabric surface via a phase-separation method.^[199] The phase-separated polydimethylsiloxane/polyvinyl chloride composites coating was rougher than original polydimethylsiloxane/polyvinyl chloride coating. In addition, Zimmermann et al. developed superhydrophobic textile fibers through a similar gas phase coating technique.^[200] All these new emerged methods are important implements to traditional techniques and make superwetting porous materials much easier to be obtained.

3.1.2 Construction of 3D-sponges, foams and aerogels with special wettability

Both sponges and foams are cheap and commercial porous materials with high absorption property to various liquids. When endowing them with superhydrophobicity-superoleophilicity, sponges and foams can be applied in oil-water separation based on selective oil absorption, which can also be fabricated by the nanoscale fabrication strategies mentioned above such as dip-coating, wet chemical reaction,

chemical vapor deposition, etc. Zhu et al. developed a robust superhydrophobic polyurethane (PU) sponge by immersion method, accompanied with the hydrolysis of methyltrichlorosilane on the surface (Figure 7a).^[201] After the treatment, hierarchically porous coatings covered the interconnected skeleton of the as-prepared sponge, which is responsible for robust superhydrophobicity (Figure 7b,c). Moreover, it can be used to absorb oil at the water surface, and oil can also be collected through a simple mechanical squeezing process (Figure 7d). Likely, Zhu et al. also fabricated a superhydrophobic PU sponge by a simple dip-coating method.^[202] The soft and elastic sponges could be deformed readily by an external force-mechanical squeezing, which is useful for oil absorption and collection (Figure 7e). In general, octadecylamine, PDMS and other low-surface-energy polymers and monomers have been coated on the surface of sponge to improve their water-repellency (Figure 7f).^[203,204] In addition to these polymers, hydrophobic carbon nanomaterials such as carbon nanotube (CNT), graphene also have been applied as coating materials for fabricating superhydrophobic sponges and foams. For example, Zhou et al. developed a graphene coated PU sponge via one-pot solvothermal technique.^[205] Because the functionalized PU sponge retained original structural integrity with high porosity, it was chemically robust and capable of separating oil up to 53,000 times of its own weight with high oil-water separation efficiency over 99.5% (Figure 7g). Besides, Chen et al. prepared an elastic carbon foam by carbonization of a polymer foam, as shown in Figure 7h.^[206] The as-prepared carbon foam exhibited lots of excellent characteristics including good elasticity and extremely high porosity for efficient oil-absorption (Figure 7i,j). Furthermore, Wu et al. developed a polymer-based graphene foams by self-assembly of graphene sheets on a 3D polymer skeleton.^[207] The obtained polymer-based graphene foams exhibited hydrophobicity, outstanding mechanical properties and excellent cycling performances, making them as ideal oil-water separators. In addition, Ding et al. created 3D hierarchical cellular aerogel sponges by combining electrospinning method and freeze-shaping technique.^[120] Significantly, all the cellular aerogel sponges exhibited prominent superoleophilicity with the extremely low oil contact angle approaching zero because of the oleophilicity of polybenzoxazine, which contained numerous benzene groups (Figure 7k). Besides, the cellular aerogel sponges with 0.5 wt% SiO₂ nanoparticles could effectively separate water-in-oil emulsions with high flux of 1590 L m⁻² h⁻¹ and stable recyclability (Figure 7l,m and Table 1). Unlike fabrics and meshes, superhydrophobic-superoleophilic sponges and foams displayed a 3D interconnected framework with huge space for oil absorption and storage, which are more favourable for oil-water separation.

Figure 7. Schematic illustration process of the fabrication of robust superhydrophobic PU sponges (a). SEM image of the sponges treated with methyltrichlorosilane (b). Optical image of a water column squirted on the superhydrophobic sponge (c). Photograph of collection of lubricating oil from the superhydrophobic sponge (d) and a piece of sponge deformed by tweezers (e). Schematic illustration of fabrication process of superhydrophobic melamine foam (SHD-MF) with hierarchical-dimension microstructures (f). Images of oil-water-mixture before and after absorption (g). Photos of a piece of MF and the derived carbon foam (h). SEM image of carbon foam (i) and inset is the cross-sectional image of one network fiber in the carbon foam. Removal process of benzene from the water surface using carbon foam (j). Photo images of droplets of dyed water and oil on a 3D hierarchical cellular aerogel sponges (k). Process of water-in-oil emulsions separation using the aerogels and the microscopic images of emulsions before and after separation (l). Changes of the separation flux and flux recovery after separation within 10 cycles (m). (a-d) Reproduced with permission.^[201] Copyright 2013, Royal Society of Chemistry. (e) Reproduced with permission.^[202] Copyright 2011, American Chemical Society. (f) Reproduced with permission.^[204] Copyright 2015, Royal Society of Chemistry. (g) Reproduced with permission.^[205] Copyright 2016, Elsevier. (h-j) Reproduced with permission.^[206] Copyright 2013, Royal Society of Chemistry. (k-m) Reproduced with permission.^[120] Copyright 2015, American Chemical Society.

Compared to the metal (Cu, Ni, Ti, etc.) foams and polymer-derived foams/sponges, carbon-derived aerogels are another type of ideal candidates for oil-absorption owing to low-cost and their outstanding properties such as low density, high porosity, large surface area, good stability and excellent flexibility etc.^[208,209] To date, template method, pyrolysis and freeze-drying techniques have been utilized to achieve carbon-derived aerogels.

1) Template method

Using template technique to fabricate carbon-derived aerogels usually can be realized by firstly modification of self-supported porous templates with carbon nanomaterials, and then removing the template.^[210,211] In the first step, CVD is the most frequently combined modification method to deposit carbon materials such as graphene, CNT etc. onto the porous template. For example, Dong et al. developed a superhydrophobic-superoleophilic monolithic 3D hybrids via rational coating of graphene and carbon nanotubes onto the nickel foam, followed by removing the template by acid etching.^[212] Thus, a dense forest of CNT uniformly wrapped around the 3D graphene scaffold. Besides, Yu et al. fabricated a uniform carbonaceous nanofibers aerogels via using ultrathin Te nanowires as template.^[213] The prepared carbonaceous nanofiber aerogels exhibited extremely low density, high flexibility and they can sustain a large compression strain and almost recovered their original volume after releasing of the compression. The carbonaceous nanofiber aerogels also exhibited high adsorption rate and good cyclability for toxic metal ions and organic dyes (Figure 8a). Owing to the synergistic effects of flexibility and excellent adsorption performance, carbonaceous nanofiber aerogels could be used directly as compressible adsorbents for simple removal of dye pollutants and recovered by burning (Figure 8b).

2) Pyrolysis strategy

Since the template method often encounters many difficulties in prefabrication and removal of the previous templates and usually results in impurities, pyrolysis strategy is another widely used technique to form carbon-based aerogels.^[214,215] Sun et al. fabricated twisted carbon fibers aerogels by carbonization of economic raw cotton.^[216] The twisted carbon fibers aerogels could absorb a wide range of oils and exhibited excellent recyclability. Similarly, Yu et al. also fabricated ultralight, flexible and fire-resistant carbon nanofiber aerogels via a facile pyrolysis technique.^[217] The as-prepared carbon nanofiber aerogels showed excellent recyclability and selectivity for different types of organic solvents and oils due to hydrophobicity, high porosity and mechanical stability (Figure 8c). Besides, they also reported PDMS-coated carbonaceous nanofiber hydrogels and aerogels as oil removing materials by combining hydrothermal method and carbonization strategy.^[218] Moreover, the pyrolysis-induced carbon-derived aerogels can be divided into flexible and inflexible materials based on their elastic property. It should be noted that the flexible carbon-derived aerogel sponges can be reused by the direct squeezing method, combustion method or distillation method.

3) Freeze-drying technique

Besides the template and pyrolysis methods, freeze-drying is also frequently used to achieve carbon-derived aerogels.^[219,220] Generally, precursor solutions used for freeze-drying to form aerogel are usually prepared by dispersing graphene oxide (GO) or CNT in a suitable solvent. Then, to reduce the density and enhance absorption property, chemical reductants such as dopamine, metal nanoparticles, ethylenediamine and hydrazine are often employed to transform GO into graphene after freeze-drying.^[221,222] Gao et al. developed an all carbon ultra-light aerogel by freeze-drying a mixed solutions of CNTs

and giant graphene oxide sheets, and followed by chemical reduction with hydrazine vapor.^[223] Due to synergistic effect of hierarchical nanostructures and superhydrophobic properties, all carbon aerogels exhibited integrated properties of ultra-low density, super recyclable compressibility, and excellent conductivity. In addition to chemical reductants, thermal reduction strategy is also employed to transform GO to graphene. For example, He et al. developed three kinds of GO foams via using different freezing methods and then the corresponding RGO foams were prepared by thermal reduction.^[224]

On the other hand, reduction-assembly before freeze-drying is another popular method to construct carbon-derived sponges for oil-water separation. Li et al. developed compressive graphene aerogels through one-step reduction and then followed by freeze-drying.^[225] The aerogels displayed extremely low density, good compressibility and fire-resistance (Figure 8d,e). The aerogels were able to absorb different organic liquids due to its inherent high porosity with a hydrophobic nature. Besides, oil collection can be realized by the absorption-squeezing process. Furthermore, macroscopic graphene monoliths can be easily achieved by incorporating functional nanomaterials such as α -FeOOH nanorods and magnetic Fe₃O₄ nanoparticles into graphene sheets during the freeze-drying process.^[226-227] Such functional graphene-based aerogels all exhibited excellent capability for removal of pollutants, and thus could be used as promising adsorbents for wastewater treatment. In this condition, Cong et al. developed a macroscopic graphene/iron oxide aerogels by using metal-oxide nanoparticles as reductants, followed by freeze-drying.^[228] The aerogel exhibited high adsorption capacity towards different organic solvents and oils (Figure 8f). In addition, Bi et al. developed a superhydrophobic graphene sponge via hydrothermal treatment of GO suspension and followed by freeze-drying.^[229] The spongy graphene showed highly efficient absorption towards toxic solvents with higher efficiency than conventional absorbers. And it can be reused by heat treatment. Since doping graphene with substituent heteroatoms could effectively improve the electrical property, physical and chemical features, Zhao et al. developed a versatile ultralight 3D N-doped graphene framework with fire-resistant properties, exhibiting a very high capacity for the reversible absorption of oils and organic solvents.^[230] Therefore, freeze-drying is one of the most promising techniques to produce porous carbon-based aerogels with low density, high porosity and large surface area for oil-absorption because of low-cost, less time, facile manipulation and large-scale production.

Figure 8. Process of dye pollutant removal and being squeezed for reuse (a). Photograph of carbonaceous nanofiber aerogels in a hot flame for distilling the absorbed oil (b). Process of uptaking organic liquids by the carbonaceous nanofibers aerogels (c). Photograph of an ultra-light aerogel sitting on a green bristle grass (d). Image of an aerogel glowing on a flame with fire-resistance property (e). Adsorption capacities of the aerogels for a range of organic solvents and oils in terms of its weight gain (f). (a,b) Reproduced with permission.^[213] Copyright 2012, Wiley-VCH. (c) Reproduced with permission.^[217] Copyright 2013, Wiley-VCH. (d,e) Reproduced with permission.^[225] Copyright 2013, Royal Society of Chemistry. (f) Reproduced with permission.^[228] Copyright 2012, American Chemical Society.

3.2 Superhydrophilic-superoleophobic & superhydrophilic-underwater superoleophobic materials

Theoretically, superhydrophilic-superoleophobic porous materials are also applicable for oil-water separation based on water filtration or absorption. However, according to basic wetting theory, a superoleophobic surface generally exhibits superhydrophobicity because oils commonly exhibit lower surface free energy. Therefore, it is a challenge to achieve a surface with superhydrophilicity-superoleophobicity in normal environment.^[231,232] Researchers have found some of stimuli-responsive materials can simultaneously show hydrophilic and oleophobic properties based on an opposite adhesion to polar liquids (e.g., water) and non-polar liquids (e.g., hexadecane). Based on this mechanism, Zhang et al. fabricated a smart superhydrophilic-superoleophobic surface using poly(diallyldimethylammoniumchloride)-perfluorooctanoate/SiO₂ as functional coatings.^[31] Combination of fluorinated groups together with carboxyl and quaternary ammonium groups resulted in a superhydrophilic-superoleophobic property. Moreover, micro/nano surface roughness was largely realized by the incorporation of SiO₂ nanoparticles, which has led to enhanced wettability and anti-wettability. The poly(diallyldimethylammoniumchloride)-perfluorooctanoate/SiO₂ coated mesh showed water permeation and excellent oil repellent behaviors, indicating that the modified mesh could be applied in oil-water separation. It is interesting that the

meshes could be cleaned with water and dried to return to its original state. Besides, Kota et al. successfully fabricated intelligent membranes with both superhydrophilicity and superoleophobicity in air and underwater (Figure 9a,b).^[233] The prepared membranes can separate large quantities of different oil-water-mixtures with over 99.9% separation efficiency by the different capillary forces on the two phases. Likewise, the superhydrophilic-superoleophobic fabrics displayed a similar performance to oil-water emulsion. When an emulsion is placed onto the intelligent membranes, and water in the emulsion is in contact with the membrane, the surface starts to reconfigure. Within several minutes, the water passed through the membrane while the hexadecane-rich counterpart will be retained above the membrane surface. These superhydrophilic-superoleophobic porous materials are the ideal tools for the clean-up of oil spills, wastewater treatment and the separation of oil-water emulsions. Though this novel strategy is desirable for constructing superhydrophilic-superoleophobic surfaces, the achievements are still limited in practical applications.

Inspired by fish, which are known to be well protected from oil contamination underwater, porous materials with superhydrophilicity-underwater superoleophobicity are of great interest and seem to be more desirable for oil-water separation.^[86] Generally, rough fish scales are covered by a layer of mucus mainly consisting of a hydrophilic hydrogel. Due to this hydrophilic chemical composition on the surfaces and hierarchical micro/nanoscale structures, fish skin exhibits superhydrophilicity in air and superoleophobicity underwater with an oil contact angle of $156.4 \pm 3.0^\circ$. Another type of underwater superoleophobic organism, clams, can remain clean on the outside and internal surfaces of their shells, especially on the pallium-covered region. The inorganic CaCO₃ composition of their shells and their surface hierarchical structures are two key factors in determining their excellent underwater oil repellency.^[234] By the simulation of natural architectures at nanoscale and low-surface-energy compositions, researchers have developed numerous artificial superhydrophilic-underwater superoleophobic porous materials for both oil-water-mixture and oil-water emulsion separation.^[235]

Considering GO with a characteristic layered nanostructure, it is expected to be an ideal building block for construction of underwater superoleophobic films.^[236,237] For example, Dong et al. coated hydrophilic GO onto stainless steel meshes by immersing the meshes into GO aqueous solution.^[238] After repeating this process for several times, GO layers formed uniform nanostructures on the steel mesh and it showed excellent superhydrophilicity-underwater superoleophobicity. By taking advantage of this underwater opposite wettability, a series of oil-water-mixtures were successfully separated. Besides, hydrogel is another typical hydrophilic composition for designing superhydrophilic-underwater superoleophobic surface, due to their excellent water-absorbing and water-retaining capacities. Jin et al. developed a robust poly(acrylic acid)-grafted poly(vinylidene fluoride) hydrogel-coated copper mesh (Figure 9c,d) with unprecedented underwater anti-adhesion and self-cleaning property to crude oils under an aqueous environment, which could effectively separate a crude oil-water-mixture with extremely high

flux of about $50000 \text{ L m}^{-2} \text{ h}^{-1}$ and high separation efficiency of 97.1% (Figure 9e-g).^[239] It also displayed superior performance for oil-water emulsion separation due to ultralow oil-adhesion and oil-blocking property. Furthermore, Jiang et al. constructed a hydrogel-coated filter paper, which exhibited superior separation performance for both oil-water-mixtures and oil-in-water emulsion with high separation efficiency (>99%) in complex environment (Table 1).^[107] Beyond GO and hydrogel, some hydrophilic nanomaterials such as palygorskite, TiO_2 , $\text{Cu}(\text{OH})_2$ have also been used for constructing superhydrophilic-underwater superoleophobic materials with micro/nano architectures.^[240-243] Yu et al. also reported an outstanding superhydrophilic-underwater superoleophobic mesh for oil-water separation by growing pure silica zeolite crystals on the film.^[244] What's more, Zhang et al. used a one-step chemical oxidation of a smooth copper mesh to obtain a superhydrophilic-underwater superoleophobic $\text{Cu}(\text{OH})_2$ -covered mesh.^[115] Similarly, they all exhibited stable recyclability and high efficiencies for oil-water emulsion separation. Compared to conventional superhydrophilic-superoleophobic materials, superhydrophilic-underwater superoleophobic materials exhibit more promising potential in oil-water separation.

Figure 9. Images of droplets of water (dyed blue) and rapeseed oil (dyed red) on superhydrophilic-superoleophobic stainless steel mesh (a) and polyester fabric (b), respectively. Insets of (a,b) are the corresponding SEM images. SEM images of a poly(acrylic acid)-grafted poly(vinylidene fluoride)-coated copper mesh (c,d). The mechanism of the poly(acrylic acid)-grafted poly(vinylidene fluoride) coating-membrane for underwater superanti-oil-adhesion (e). Separation flux and oil content in filtrate within 20 cycles for the crude oil-water-mixture separation (f). Self-cleaning processes of latex glove with and without PAAS-g-PVDF coating (g). (a,b) Reproduced

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4. Intelligent functions for on-demand oil-water separation

Compared to traditional strategies on the construction of special wettability, on-demand intelligent superwetting materials have become more appealing for improving separation efficiency and meeting special oil-water separation demands such as oil-water-emulsion remediation, switchable oil-water separation, remote controllable oil absorption and oil/water collection.

4.1 Stimuli-responsive wettability

Porous materials with stimuli-responsive wettability can switch between super-wetting and super-anti-wetting by applying an external stimulus (e.g., pH, light illumination, temperature and voltage etc.), which can be constructed by grafting some stimuli polymers or functional inorganic micro/nano particles, offering a significant advantage for selectively allowing oil or water to pass through alone.^[215,245-249] Therefore, porous materials with extreme wettability transition have been successfully developed for controllable oil-water separation in various situations, such as simple oil-water-mixture separation, continuous oil-in-water and water-in-oil emulsion separation, etc.

4.1.1 pH-responsive wettability

Among various external stimuli, pH-induced reversible special wettability is attractive because of its easy operation, rapid response and no need with special facilities. Most pH-responsive components have ionizable groups, such as sulfonates, carboxylic acids, pyridines and amines, etc., which are very sensitive to pH changes and can dramatically change their conformation quickly in response to minor changes of pH, leading to switchable affinity between oil/water and substrate interface.^[250-251] Weak polybases and weak polyacids are the most commonly used pH-responsive polymers for achieving switchable wetting properties. Weak polybases transform into polyelectrolytes at low pH with electrostatic repulsion forces between the molecular chains, while they transform into neutral polymers at high pH. A momentum along with the hydrophobic interaction is given to govern hydrophobic/hydrophilic characteristics of surfaces. At the same time, weak polyacids have a pH-responsive carboxyl group, consisting of a carbonyl and a hydroxyl group. The carboxyl groups can be protonated, and the surface exhibits hydrophobicity at low pH, while carboxyl groups dissociate into carboxylate anions with hydrophilicity at high pH.^[252] Therefore, by combining the pH-responsive polymers with rough surface structures, various smart pH-responsive surfaces with controllable wettability have been fabricated. For example, Zhang et al. constructed an intelligent surfaces by grafting a block copolymer made up of blocks of pH-responsive poly(2-vinylpyridine) and oleophilic/hydrophobic polydimethylsiloxane (P2VP-b-PDMS).^[253] On the one hand, the P2VP block could change its wettability and conformation via protonation and deprotonation upon pH changes, which provided

switchable access of oil by the block, resulting in the switchable oil wettability in the aqueous (Figure 10a). On the other hand, the PDMS block also had switching reversibility towards surface oil wettability. Moreover, a smart fiber membrane was achieved by depositing pH-responsive copolymer poly(methyl methacrylate)-block-poly(4-vinylpyridine) on stainless steel mesh via electrospinning (Figure 10b).^[254] The obtained mesh exhibited two switchable wettability states (superhydrophobicity-superoleophilicity/superhydrophilicity-underwater superoleophobicity) and it also could be used in separating water-oil or water-organic solvent mixtures (Figure 10c,d). Furthermore, Dang et al. fabricated smart 2D membranes (cotton fabric and filter paper) and 3D foam (PU foam) by a simple dip-coating of non-fluorinated random copolymer, poly(dodecyl methacrylate-co-3-trimethoxysilylpropyl methacrylate-co-2-dimethylaminoethyl methacrylate) (PDMA-co-PTMSPMA-co-PDMAEMA).^[106] The coated membranes and foams exhibited switchable superhydrophilicity/superhydrophobicity with different pH values (Figure 10e) and can be applied in different types of continuous oil-water emulsion separation with high separation efficiency (Table 1). At neutral and high pH values, PDMAEMA chains were not protonated and maintained their collapsed conformations. The dominantly exposed PDMA chains prohibited the coating from being wetted by water and kept their high affinity to oil, leading to superoleophilicity. Upon contacting with oil, the PDMA chains preferentially stretched out into the oil because of their oleophilic nature (Figure 10f, left). When the pH decreased to 2.0, the nanocoatings became hydrophilic and were wetted by the acidic water because of the protonated PDMAEMA chains, which exhibited an extended conformation due to the electrostatic repulsion of the protonated tertiary amine group and were dominantly exposed. The dominantly exposed PDMAEMA chains were hydrophilic and could trap water, and thus, an oil-water-solid composite interface could be formed (Figure 10f, right). In addition to block copolymers, monomers can also be utilized to fabricate pH-responsive wettability. For example, Cheng et al. developed a smart copper mesh with pH-responsive wettability by the grafting of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$ molecules.^[255] The smart wetting responsive ability was attributed to the synergistic effect of the surface chemistry variation and rough structures. The surface showed superoleophilicity in acidic water while superoleophobicity in basic water, which can be realized by changing the pH of the solution. The smart surface exhibited underwater superoleophilicity for its high affinity to oil under non-basic water (Figure 10g). When the pH increased to basic conditions, surface carboxylic acid groups were deprotonated, resulting in a strong hydrogen bonding between water and the deprotonated carboxylic acid (Figure 10h). Due to the reversible wettability, oil-water-mixture can be separated in a more controllable way. This strategy opens a new perspective in controlling the surface oil wettability and can be applied to other relevant applications such as antifouling, antipollution, and microfluidic devices, etc.

Figure 10. Schematic diagrams of the switchable oil wettability of the P2VPb-PDMS-grafted textile at different pH (a). Schematic diagram of the electrospun pH-responsive membrane fabrication process (b). Oil/water separation process: Oil passed through the membrane, whereas water remained in the upper glass apparatus (c); water passed through the membrane, while oil remained in the upper glass apparatus (d). Photographs of the acidic, neutral, and basic droplet on the coated fabric before and after 30 minutes (e). Mechanism of pH responsive coatings at different pH (f). Schematic illustration of the responsive oil wettability on the rough surface in non-basic water (g) and basic water (h). (a) Reproduced with permission.^[253] Copyright 2012, Nature Publishing Group. (b-d) Reproduced with permission.^[254] Copyright 2015, American Chemical Society. (e,f) Reproduced with permission.^[106] Copyright 2016, American Chemical Society. (g,h) Reproduced with permission.^[255] Copyright 2014, American Chemical Society.

4.1.2 Photo-responsive wettability

Photo-responsive wettability switching between superhydrophobicity and superhydrophilicity decorated by UV-sensitized semiconductors (ZnO, TiO₂ etc.) for effective controllable oil-water separation has also been widely studied.^[256-261] When the decorative ZnO or TiO₂ particles are exposed to UV illumination, electron-hole pairs are produced on the surface, forming high-surface-energy hydroxyl radicals. Thus, the wetting state can change from hydrophobicity to hydrophilicity due to the existence of hydrophilic hydroxyl groups. While storing in the dark for a period of time, the hydroxyl groups are removed easily by oxygen in the environment. As a result, the surfaces recover their original hydrophobic wettability. For example, Jiang et al. fabricated a ZnO nanorod arrays-coated stainless steel mesh with switchable superhydrophobicity-superhydrophilicity and underwater superoleophobicity for photo-induced oil-water separation.^[262] Herein, due to the excellent UV-sensitive property of ZnO, extreme wettability transition can be realized by UV irradiation and storage in the dark place (Figure 11a). Namely, after UV illumination, the superhydrophobic surface changed into superhydrophilicity owing to the lower intrusion pressure, while superoleophilicity displayed extreme underwater superoleophobicity with oil contact angle higher than 150°. Combining UV-induced superhydrophilicity and underwater superoleophobicity, they showed excellent controllability and high separation efficiency of different types of oil-water-mixtures. Especially, the underwater superoleophobicity of the ZnO-coated stainless steel mesh film can effectively prevent the mesh film from being polluted by oils, exhibiting good self-cleaning performance.

Besides, photo-induced wettability changes enable external manipulation of liquid droplet motion and further could facilitate demulsification. Kwon et al. demonstrated the wettability state of a dye-sensitized TiO₂ surface could be changed upon visible light illumination.^[263] By utilizing this photo-induced changeable surface wetting, liquid droplet motion on the surface can be manipulated (Figure 11b). After irradiation, surfactant-stabilized brine-in-oil emulsion gradually demulsified via interfacial coalescence of brine droplets under visible light illumination (Figure 11c). This novel strategy serves as an interesting example towards sunlight-driven oil-water separation technologies in the future.

However, most smart membranes with large pore size at micrometer scale are not applicable for the separation of emulsified oil-water-mixtures. Taking advantages of single-walled carbon nanotube (SWCNT) ultrathin network film with a unique micro/nano structure in thickness and pore size, smart membranes with photo-responsive wettability for oil-water emulsion separation have been widely investigated.^[98] Jiang et al. reported a facile approach to construct photo-responsive Au nanorods decorated ultrathin SWCNT network membranes with light-modulated pore sizes for switchable ultrafast separation of oil-water nano-emulsions (35890 L m⁻² h⁻¹).^[99] It is remarkable that the permeation flux can be simply adjusted by light illumination density during separation process (Table 1). Furthermore, Gao et al. developed an ultrathin film made up of an SWCNT network and TiO₂ nanocomposites, which possesses photo-induced superhydrophilic and underwater superoleophobic properties. The film can be used in both surfactant-free emulsion separation and surfactant stabilized oil-in-water emulsion separation with a high flux.^[264] The as-prepared TiO₂-containing membrane above all possesses outstanding self-cleaning performance resulting from the excellent photocatalytic property of TiO₂, which has practical significance in recyclability and saving solvents. What's more, in addition to photo-responsive filtration for oil-water separation, a novel strategy based on oil-absorption and oil-desorption process was reported recently. Zhu et al. prepared robust and superhydrophobic melamine-formaldehyde sponge by modifying with light-responsive spiropyran methacrylate derivative via radical copolymerization (Figure 11d,e).^[265] Interestingly, superhydrophobic melamine-formaldehyde sponge exhibited excellent absorption capacity for both light oil and heavy oil (Figure 11f,g). Meanwhile, the absorbed oil can be effectively desorbed under UV light irradiation (Figure 11h).

Figure 11. Photo-induced surface wettability of the aligned ZnO nanorod arrays-coated mesh films (a). Process of manipulating droplet

motion on dye-sensitized TiO₂ surface under light irradiation (b). Schematic illustration of demulsification of brine-oil emulsion via interfacial coalescence of brine droplets on dye-sensitized TiO₂ surface upon visible light illumination (c). Photo image (d) and SEM image (e) of light-responsive superhydrophobic superhydrophobic melamine-formaldehyde sponge. Removal process of toluene floating on water (f) and chloroform sinking at the bottom (g). Process of oil desorption under UV irradiation (h). (a) Reproduced with permission.^[262] Copyright 2012, Royal Society of Chemistry. (b,c) Reproduced with permission.^[263] Copyright 2017, Nature Publishing Group. (d-h) Reproduced with permission.^[265] Copyright 2016, Wiley-VCH.

4.1.3 Thermal-responsive wettability

Similar to photo-responsive wettability, thermal-response has been also utilized to control the surface wettability in recent years.^[266-268] Poly(N-isopropylacrylamide) (PNIPAAm) is an excellent thermal responsive polymer with a relative low critical solution temperature about 32-33 °C. When below the low critical solution temperature, the intermolecular H-bonding between the PNIPAAm chains and water molecules is predominant, which results in an extended brush structure displaying hydrophilicity. Above the low critical solution temperature, intermolecular H-bonding in the PNIPAAm chains leads to a compact and collapsed conformation with hydrophobicity (Figure 12a).^[269] Therefore, PNIPAAm and PNIPAAm-containing polymers can be grafted or coated on the rough substrates to realize controllable wettability. For example, Zhou et al. modified metal mesh with poly(2,2,3,4,4,4-hexafluorobutyl methacrylate)-block-poly(N-isopropylacrylamide) through a simple dip-coating method.^[270] After coating, their average diameter increased from 36 μm (Figure 12b) to about 39 μm (Figure 12c). Compared to pristine mesh, the modified one showed controllable wettability under different temperatures, which can be used for switchable oil-water separation (Figure 12d). Besides, Jiang et al. reported an underwater thermal-responsive surface that can switch between superoleophobicity and superoleophilicity by grafting heptadecafluorodecyltrimethoxysilane and PNIPAAm.^[271] The heptadecafluorodecyltrimethoxysilane acted as the oleophilic component in aqueous environment, while PNIPAAm could conceal or expose oleophilic component by inherently thermoresponsive conformational change. Therefore, it is a big breakthrough on the fabrication of underwater temperature-responsive surfaces with switchable underwater wettability and exhibits great potential for special oil-water separation. Moreover, copolymers such as (methyl methacrylate)-block-poly(N-isopropylacrylamide),^[272] poly(N-isopropylacrylamide)-block-polystyrene,^[273] and poly(N-isopropylacrylamide-co-1-adamantan-1-ylmethyl acrylate)^[274] also have been used for fabricating smart thermal-responsive surfaces.

4.1.4 Voltage-responsive wettability

Applying voltage is an electrowetting stimulus to control the surface chemistry, which is the re-arrangement of charges and dipoles between a liquid and a solid, resulting in a reduction in the interfacial energy and an increase in surface wettability. This approach has been successfully applied in surface wettability control without changes in

the surface composition and structure.^[112,252,275,276] In order to achieve the selective permeation of oil or water, the hydrostatic pressure can be overcome by applying an electric field. The conducting materials such as polyaniline, polypyrrole etc. are widely used to decorate porous materials with potential-induced switchable wettability. For example, Zhang et al. coated a potential-responsive polyaniline coating on stainless steel mesh through emulsion polymerization (Figure 12e).^[277] After modification, different surface wettability to water appeared by changing applied voltage (Figure 12f), which could be used for controllable oil-water separation. Besides, Lin et al. modified 3D copper foam with voltage-sensitive N-dodecyltrimethoxysilane polymer to realize the reversible wettability between superhydrophobicity and superhydrophilicity.^[278] Such electricity-induced switchable wettability showed rapid response and wide-range variation, which was considered to be more applicable in controllable water permeation and oil-water emulsion separation. Considering electricity can generate heat, Yu et al. pioneered a strategy to clean-up of the viscous crude-oil spill by applying a voltage to superhydrophobic graphene modified sponge (Figure 12g, left).^[279] When graphene modified sponge contacted the viscous crude oil on a water surface, the oil was absorbed selectively into the pores at a low oil-sorption speed because of the hydrophobic property of graphene. After applying a voltage to the graphene modified sponge, current flew through the graphene coating and Joule heat was generated, quickly heating up the superhydrophobic graphene modified sponge (Figure 12g, middle). Then the hot graphene modified sponge can heat up the surrounding crude oil and thus the oil viscosity decreases, which then increased the diffusion of the crude oil into the graphene modified sponge (Figure 12g, right). After cutting off the applied voltage, the absorbed oil localized in the pores of graphene modified sponge was still hot and remains of low viscosity, which also facilitated the subsequent oil-recovery and transportation processes. Compared to non-heated graphene modified sponge (Figure 12h), the oil sorption time was reduced by 94.6% and also the oil-recovery speed was increased to a certain extent (Figure 12i). This novel strategy offers an alternative way for viscous oil remediation, which has contributed to the fabrication technologies of advanced absorbers to deal with the oil spills and oil accidents.

Figure 12. The effect of temperature on the changes in hydrogen bonding and corresponding conformation of PNIPAAm for surface wettability (a). SEM of uncoated stainless steel mesh (b) and coated mesh (c), inset of (c) is its corresponding magnified image. Schematic illustration of the switchable oil-water separation at different temperatures (d). SEM image of hierarchical-structured polyaniline mesh (e). The contact angle of water and oil change by different applied voltages on the mesh (f). Schematic illustration of Joule-heated graphene modified sponge used to clean-up a viscous crude-

oil spill (g). Continuously collecting the viscous crude oil from the surface of sea water by in situ pumping through graphene modified sponge under applied voltages of 0 (h) and 17 V (i), respectively. (a) Reproduced with permission.^[269] Copyright 2010, Royal Society of Chemistry. (b-d) Reproduced with permission.^[270] Copyright 2015, American Chemical Society. (e,f) Reproduced with permission.^[277] Copyright 2016, Wiley-VCH. (g-i) Reproduced with permission.^[279] Copyright 2017, Nature Publishing Group.

4.1.5 Magnetism-responsive wettability

Endowing sponges, foams and other 3D self-supporting porous superhydrophobic materials with magnetic property can greatly facilitate and control the water-remediation process.^[280-282] In particular, 3D porous superhydrophobic materials with magnetic property can be remotely driven by a magnet during the adsorption process. In this way, the 3D superhydrophobic materials could be easily guided to absorb oil spills. For example, Calcagnile et al. coated polyurethane foams with superparamagnetic iron oxide nanoparticles and sub-micrometer polytetrafluoroethylene particles.^[283] The functionalized foams exhibited both excellent water repellency and magnetic responsivity and they could float freely on water due to their ultra-light weight (Figure 13a,b). Hence, they can absorb the floating oil from the polluted regions by simply moving them around oil-polluted region using a magnet control. The materials have exhibited much high oil adsorption capability, up to hundreds or thousands times of their own weight (Figure 13c). Besides, Du et al. devised 3D magnetic melamine foams with a well-defined rough surface morphology (Figure 13d,e) that are remotely controllable by magnetism. The materials have displayed substantially enhanced oil/water selectivity (Figure 13f,g).^[284] Likewise, various 3D porous superhydrophobic materials with magnetism such as CNT sponges, MWCNT/PDMS nanocomposites, and polyurethane/iron oxide foams have also been demonstrated effective for controllable water-remediation.^[285,286] More importantly, 3D porous superhydrophobic materials with magnetism can be simply collected by the magnet after using, avoiding secondary pollution.^[287-290] For example, Gui et al. successfully synthesized a magnetic carbon nanotube sponge with porous structures consisting of interconnected CNTs with rich Fe encapsulation.^[291] The magnetic carbon nanotube sponge exhibited high mass adsorption capacity for diesel oil. In addition, they can be guided by magnetic force for water reclamation and desorption by simple heat treatment (Figure 13h). Though magnetic materials exhibit desirable property for controllable oil adsorption, the 3D self-supporting porous superhydrophobic materials would undergo several tens or even several hundred times weight gain when a large quantity of oil was adsorbed. This will cause a potential problem in collection of the used adsorbent by a magnetism.

Figure 13. Mixed oil (a) and water drop (b) are phase separated, and the oil is immediately absorbed while water remains on the superhydrophobic foam surface. Subsequent removal of the oil by the magnetically driven the superhydrophobic foam (c1-c4) and photograph showing the variation of the weight of the foam with time (c5). SEM (d) and TEM (e) images of superhydrophobic magnetic melamine foam. Inset of d is the corresponding SAED patterns. On-water (f) and underwater adsorption (g) of organic solvents by superhydrophobic magnetic melamine foam, respectively. Clean-up process of oil (dyed blue) by the magnetic carbon nanotube sponge using a magnet (h). (a,c) Reproduced with permission.^[283] Copyright 2012, American Chemical Society. (d-g) Reproduced with permission.^[284] Copyright 2016, Royal Society of Chemistry. (h) Reproduced with permission.^[291] Copyright 2013, American Chemical Society.

Besides modifying porous materials with single intelligent function, combination of binary or ternary intelligent functions has also emerged for oil-water-mixture and emulsion separation with customized configuration. Though some achievements have been made in external stimuli-induced such as pH, light, thermal, voltage etc. switchable surface wettability, they may cause damages on the inherent structures of the substrate and shorten their life-time. What's more, gas, salts and stress etc. have been used as external stimuli to control surface wettability, but they are rarely reported for oil-water-separation.^[290-294] Therefore, more attention should be paid on these more environmental-friendly, less-toxic and cost-effective external-responsive technologies for on-demand oil-water separation.

4.2 Janus-featured wettability

In addition to stimuli-responsive wettability, Janus-featured wettability is also widely investigated for both oil-water-mixture and oil-water emulsion separation with high efficiencies.

4.2.1 Asymmetric membranes with heterogeneous wettability

Asymmetric membranes with opposing wettability (superhydrophobic/superhydrophilic or superoleophilic/superoleophobic) on each side exhibit directional transport behaviors for oil and water. On the one hand, asymmetric membrane with oleophobic/oleophilic wettability on each side has been used to selectively filter oil from oil-water-mixtures due to its combined effect of directional oil transport and prevention of water penetration. In detail, when oil-water-mixture contact on the oleophobic side, oil will be gradually pulled through to the oleophilic side, while water will be repelled above the surface.^[110,295] For example, Wang et al. fabricated a superamphiphobic/oleophilic fibrous membrane via a layered electrospinning technique.^[296] By taking advantage of combined effect of highly water-repellent and directional oil-transport ability, oil-water-mixture could be effectively separated. Besides, since the superoleophobic surface is also superhydrophobic, undesirable adhesion and blocking by water is avoided. Thus, asymmetric membranes with oleophobicity/oleophilicity are more efficient and cost-effective in oil-water separation when compared to the ones with homogenous wettability.

On the other hand, asymmetric membranes with hydrophobicity/hydrophilicity on each side can also be used for oil-water separation. When the oil-water-mixture contact the hydrophilic side, water will spread on the hydrophilic side but cannot penetrate through the whole membrane, while oil can easily go through the membranes. Thus, oil-water-mixture separation is realized.^[297,298] Moreover, inspired by its special property of repelling water by the hydrophobic side, oil-water-emulsion can be separated under the synergistic effects of demulsification, coalescence and rejection of water. Taking oil-in-water emulsion as an example, when emulsion contacts on the hydrophilic side, water will spread on the hydrophilic surface but repelled by superhydrophobic side, while oil droplets will gradually coalesce and penetrate through the membranes. In this regard, Wang et al. reported a novel Janus fabric for separating emulsified oil, which was composed of oppositely hydrophilic (PDMAEMA) and superhydrophobic (PDMS) surface.^[108] Though the fabric with large filter pore sizes, the emulsion oil droplets will be demulsified upon contacting the hydrophilic side and then the coalesced oil droplets would penetrate through the fabric, while water could wet the hydrophilic side but is prevented from penetrating through by the hydrophobic PDMS layer (Figure 14a,b). The prepared asymmetric membranes exhibited high separation efficiency towards both oil-water-mixture and oil-water-emulsion (Table 1). Besides, by combining membranes with small pore size and asymmetric wettability, both oil-in-water emulsion and water-in-oil emulsion can be separated with ultra-high permeation flux and separation efficiency when compared to the ones with single function. Hu et al. developed bilayer membranes by depositing a thin layer of polydopamine-coated SWCNT onto its surface.^[299] By modulating the applied pressure across the membrane, surfactant-stabilized water-in-oil and oil-in-water emulsions can be easily separated. Furthermore, Gu et al. constructed an asymmetric hydrophobic/hydrophilic polymer/CNT membranes, by respectively grafting hydrophobic polymer (PS) and

hydrophilic polymer (PDMAEMA) on different sides of CNT membranes.^[100] When the superhydrophobic PS side contacted with the feeding emulsions, only continuous oil could pass through the membrane (Figure 14c, left). When the hydrophilic (PDMAEMA) side was in contact with the feed emulsions, the membrane only allowed continuous water phase to pass through (Figure 14c, right). Therefore, the obtained asymmetric polymer/CNT membrane has been applied in oil-water emulsion separation with good recyclability (Table 1).

Moreover, asymmetric membranes can be applied in oil/water collection from oil-water-mixture due to its directional liquid transport property.^[300,301] For example, Tian et al. developed a Janus membranes by depositing a thin hydrophobic layer on a hydrophilic cotton membrane, and exposed the hydrophobic side to the dispersed water drops in the oil (Figure 14d).^[302] The water droplets permeated the membrane but the oil could not. Similarly, oil droplets could be collected by exposing hydrophilic side to the dispersed oil droplets. Besides, Cao et al. fabricated a hydrophobic/hydrophilic integrated system combining hydrophobic dodecanethiol modified copper mesh and hydrophilic commercial cotton absorbent.^[303] When fog contacted the hydrophobic side, it condensed, and then they were absorbed by the hydrophilic side. Besides, the hydrophobic mesh could prevent the surface from being wetted by water, which is undesirable due to water evaporation (Figure 14e). Thus, it was more efficient and effective to collect water from atmosphere. This asymmetric system offers an ideal design of smart interface for oil-water emulsion separation and oil/water collection.

Figure 14. The emulsified oil-water-mixture before (a) and after separation (b). Schematic illustration of the hydrophobic/hydrophilic membrane for separating oil-in-water emulsions with the PDMAEMA side toward the feed emulsions (c, left) and with the polystyrene side toward the feed emulsions (c, right) for separating water-in-oil emulsions. Scheme illustration of the construction of “Janus trapper” for water droplet collection from oil (d). The schematic diagram (e, left) and the cross-section diagram (e, right) of the continuous fog harvesting process. (a,b) Reproduced with permission.^[108] Copyright 2016, Wiley-VCH. (c) Reproduced with permission.^[100] Copyright 2014, American Chemical Society. (d) Reproduced with permission.^[302] Copyright 2014, Wiley-VCH. (e) Reproduced with permission.^[303] Copyright 2015, Wiley-VCH.

4.2.2 Patterned surfaces with heterogeneous wettability

Inspired by certain beetle species in the Namib Desert, which collect water from fog on their backs by way of wettability micro/nano patterns (i.e., hydrophilic wax-free bumps surrounded by hydrophobic waxy background), a large number of patterned porous materials with hydrophobic-hydrophilic contrast emerged to realize water collection.^[304–306] For example, Bai et al. successfully fabricated a surface with star-shaped wettability patterns for fog collection.^[307] On the surfaces with star-shaped wettability patterns, fog droplets can be directionally collected toward more wettable regions. When a water droplet grew to a critical size, it would roll off the surface (Figure 15a). Besides, Zeng et al. prepared hydrophilic bumps-superhydrophobic/superoleophilic stainless steel mesh by firstly assembling hydrophilic silica micro particles on the as-cleaned stainless steel mesh surface, followed by further modification with a fluoropolymer/SiO₂ nanoparticle solution (Figure 15b).^[113] Attributed to the steep surface energy gradient, the superhydrophilic bumps, made up of hydrophilic silica micro particles, were able to capture emulsified water droplets and collect water from the emulsion, while oil portion permeated the mesh freely. The hydrophilic bumps-superhydrophobic/superoleophilic stainless steel mesh exhibited high efficiency for water-in-oil emulsion separation over 99.95% (Table 1), which shows great application potential for oil-water emulsion separation and oil purification.

Figure 15. Schematic illustration of the fabrication process of bioinspired surfaces with star-shaped wettability patterns (a) and preparation of superhydrophilic bumps-superhydrophobic/superoleophilic stainless steel mesh (b). (a) Reproduced with permission.^[307] Copyright 2014, Wiley-VCH. (b) Reproduced with permission.^[113] Copyright 2017, American Chemical Society.

5. Conclusions and outlook

In this review, we provide a comprehensive review on the state-of-the-art developments of oil-water separation based on the rational material interface wettability control, covering from traditional superhydrophobic-superoleophilic materials, superoleophobic-superhydrophilic materials to superhydrophilic-underwater superoleophobic materials. Among the reported nanofabrication routes, electrospinning, dip/spray-coating, wet chemical reaction and chemical vapor deposition are the main strategies used to construct superwetting materials due to the ease process and rational surface control of the nanostructures. The incorporation of certain nano features on the surface, including particles, nanofibers, and nanopores has clearly improved the surface properties and thus the separation performance. Besides, special wettable porous materials with intelligent functions, such as stimuli-responsive, and Janus-featured wettability etc., have been demonstrated to meet the on-demand oil-water separation and further improve the separation efficiency. All these biomimetic materials with intelligent interface have exhibited superior advantages for oil-water separation, especially for the more stubborn oil-water-emulsion separation, when comparing to traditional oil-water separation materials.

Although great progress has been made on the special wettable materials for oil-water separation, there still exist some crucial issues and challenges required to be solved. Firstly, in the past decades, porous materials with special wettability have been demonstrated with high performance in low viscosity solvents or oils uptake. However, crude oil spills always have a high-viscosity and penetrate the membrane with low speed. Therefore, fabrication of advanced functional devices/materials for the rapid and efficient separation of high-viscous oil-water mixtures should be taken into consideration. Secondly, commonly superhydrophobic or superoleophobic fabrics often contain expensive and toxic fluorine-containing groups, which is harmful to human beings and the environment after disposal. Consequently, novel nanofabrication technologies for new materials creation are highly desirable for construction of fluorine-free and environmentally friendly superhydrophobic or superoleophobic fabrics. Thirdly, the materials science and surface chemistry are the two key factors to construct superwetting surfaces for oil/water separation. However, most surface coatings can be easily damaged by external influences such as mechanical force (abrasion, washing) and chemical contamination (strong acid/alkaline etching, harsh weathering), which limits its widely practical applications. Thus, nanoscale fabrications have the advantages on synthesis of robust and durable rough micro/nano architectures with self-healing ability by atom/molecule manipulation. Last but not the least, most of traditional fabrication strategies for special wettable materials are not suitable for large-scale production, which is undesirable to meet industrial demands. The novel nanofabrication techniques such as direct inkjet printing or 3D printing displays promising prospects for mass production to cope with the oil spill accidents and oily wastewater from industries. In summary, compared to the conventional fabrication methods, the nanoscale fabrication strategies exhibit much higher efficiency for oil-water separation and pioneer the future-direction of technologies.

In light of the fruitful progress in this field, we believe that the rational design of artificial superwetting materials at nanoscale will provide us unprecedented chances to overcome the current challenges for oil-water separation. Besides, by continuous efforts put on the fundamental research, large-scale production and industrialization of the special wettable materials will be realized for water-remediation in the near future. In addition, by taking full advantages of intelligent functions, the smart interfacial materials will exhibit higher efficiencies for on-demand oil-water separation and facilitate oil/water collection processes. Furthermore, beyond the application in oily-water remediation, these special wettable materials also show a great interest in other research fields, such as energy storage and conversion, liquid transportation and delivery, and bio-engineering, and so on. Overall, the continuous research effort is highly demanded to address globally serious water pollution arising from oil spills and organic pollutants, and the design of intelligent materials interface proves particularly useful for oil-water separation with significant environmental implications.

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ARTICLE

Oil-water separation is critically important for the water treatment of oily wastewater or oil-spill accidents. In this review, we present the state-of-the-art developments on the rational material design at nanoscale on special wettability for separation of immiscible/emulsified oil-water mixture.