

# Recent Advances in Superhydrophobic Papers for Oil/Water Separation: A Mini-Review

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**ABSTRACT:** The separation of oceanic spilled oils and industrial oily wastewaters becomes a great challenge, and it is highly desirable to develop efficient materials for oil/water separation. As abundant sustainable resources, superhydrophobic papers (SPs) have drawn much attention because of low-cost and efficient oil/water separation. Herein, this mini-review summarizes recent advances of SPs in terms of design, preparation, and properties. On the basis of the many excellent properties of SPs (i.e., self-cleaning, durability, chemical corrosion resistance, and reusability), the oil/water separation performances (i.e., separation efficiency, permeation flux, and recyclability) of SPs as well as the corresponding mechanisms are discussed. The efficient oil/water separation property and recyclability of SPs make them promising candidates in the field of oily wastewater treatment.



## INTRODUCTION

Oceanic oil spill incidents and the discharge of oily wastewaters have caused long-term significant threats to the environment and human health.<sup>1</sup> To address this issue, traditional methods have been reported to remove oils from oily wastewaters, including in situ burning, bioremediation, centrifugation, coagulation, flotation, and chemical dispersion.<sup>1a–d</sup> Unfortunately, these methods suffer from complex operations, high cost, low separation efficiency, and secondary pollution.<sup>1b–d</sup> Therefore, efficient and energy-saving methods are highly desired for the separation of oily wastewaters.

Due to excellent liquid repellency, superhydrophobic materials have been utilized in the applications of oil/water separation,<sup>1c</sup> anti-icing,<sup>2</sup> self-cleaning,<sup>3</sup> anticorrosion,<sup>4</sup> and antibacterial activity.<sup>5</sup> Various substrate materials have been developed to obtain surface superhydrophobicity, such as papers, metals, polymers, ceramics, wood, and glass. Among them, papers have drawn much attention because of abundant sustainable resources,<sup>6</sup> light weight,<sup>1c</sup> low cost,<sup>1a,5</sup> flexibility,<sup>5</sup> and environmental friendliness.<sup>6,7</sup> For example, SPs show much better resistance to highly acidic or alkaline solutions when compared with metals (i.e., stainless steel and copper grid) and polymer (i.e., polyester) fabrics.<sup>1e</sup> Also, SPs with proper pore sizes have good performances for the separation of oil/water emulsions rather than other materials (i.e., metal meshes and glass fiber membranes).<sup>1e,7b</sup> Generally, the paper material is a type of cellulosic material, consisting of porous structures, microtextures, and rich hydrophilic functional groups. Thus, superhydrophobic papers (SPs) can be easily achieved via the decoration of nanomaterials and chemical

modification. The rational design endows SPs with many excellent properties, including self-cleaning,<sup>1c</sup> mechanical and thermal durability,<sup>5</sup> chemical resistance (i.e., acid, base, and saline solutions),<sup>1c–e</sup> and reusability.<sup>1a,4</sup>

Recently, SPs have been used in the field of oil/water separation because oil can easily wet and penetrate SPs with low surface tension.<sup>8</sup> For example, He et al. prepared durable TiO<sub>2</sub>/polydopamine (PDA)-based SPs and found that the TiO<sub>2</sub>/PDA-based SPs can maintain the separation efficiency of an oil/water mixture (or water-in-oil emulsions) above 94.3% (or 93.7%) after 15 cyclic separation processes.<sup>1c</sup> Yang et al. designed recyclable, magnetic, and fire-retardant SPs, and the SPs showed a separation selectivity above 99.0% and a good recycling ability for >10 times.<sup>4</sup> Li et al. reported that a durable and sustainable superhydrophobic/superoleophilic paper can be prepared by layer-by-layer assembly and polydimethylsiloxane (PDMS) modification, and the SPs exhibited good separation efficiencies of >99% for oil/water mixtures even after 30 cycles.<sup>9</sup> Herein, we summarize recent advances of SPs in terms of design, preparation, and properties. Then, the oil/water separation application of SPs as well as corresponding mechanisms is discussed. Due to the excellent separation properties of oil/water mixtures (or emulsions), the low-cost,

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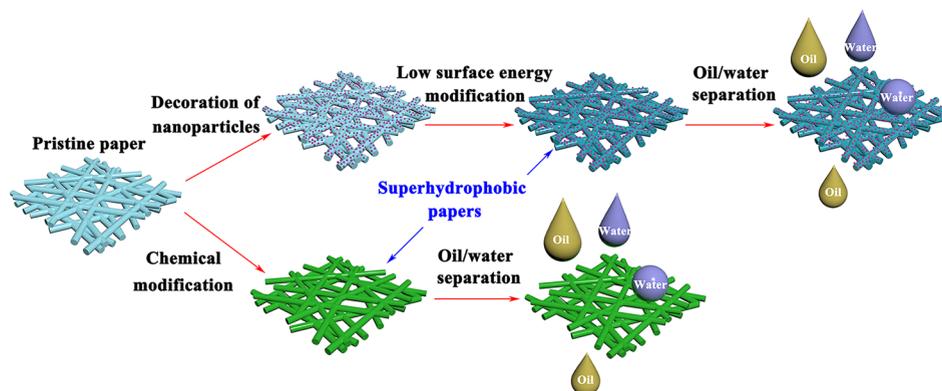


Figure 1. Schematic overview of preparation and oil/water separation of SPs.

Table 1. Preparation and a Comparison of SPs for Oil/Water Separation

preparation methods	decorated materials	absorbed materials	separation efficiency (%)	permeation flux ( $L m^{-2} h^{-1}$ )	cycles (times)	ref
vacuum filtration	HAP, $Fe_3O_4$ , PDMS	chloroform, 50% (v/v)	99.6	2924.3	10	4
	HAP, $TiO_2$ , SA	oil/water mixtures	>99.4		10	10b
	HAP, ZnO, PFDS	oil/water emulsions		66–185	10	10a
drop-coating	$SiO_2$ , PS	<i>n</i> -hexane, 50% (v/v)	79			18
spray-coating	EP, PDMS, $SiO_2$ , $Fe_3O_4$	oil/water mixtures	>98	41.5–129	30	13c
	CNFs, ODA	oil/water mixtures	>98		10	13a
	$SiO_2$	DCE/water emulsion	>99.9	>600		13b
ATRP	cellulose, PFOEMA	oil/water mixtures	>95		10	14a
	C18-FP-g-SAN	oil/water mixtures	>98.5		10	14b
solution casting	$SiO_2$ , LLDPE	petroleum ether, 50% (v/v)	99.9		10	19
layer-by-layer assembly	PDMS, Cu-MOFs	oil/water mixtures	>98	4.24–55.8	30	5
	ZnO	oil/water mixtures	>99	14.2–132.7	30	9
in situ growth	PDA, Ag, <i>n</i> -DM	oil/water mixtures	>97	24–95.3	30	20
self-assembly	PPP	oil/water mixtures	>97		2	15
phase separation	$SiO_2$ , PS	crude oil/water mixture	99			11
dip-coating	$SiO_2$ , TMCS	oil/water mixtures	>82			16
colloidal deposition	PTFE, PS	oil/water mixtures	>99		30	12
wire rod coating	$TiO_2$ , KH550, PDMS	dichloromethane/water mixture	>98		10	21
freeze-drying	CNF, MTMS	chloroform, 50% (v/v)	>96.8		10	22
	SA	oil/water emulsions	>98.5		10	1a
immersion	$Cu(OH)_2$	diesel oil/water mixture	>99	1452.7	100	17g
	OTS, MTS	diesel oil, 50% (v/v)	>97		4	17e
	$SiO_2$ , PS	diesel oil, 50% (v/v)	98.2			8
	$SiO_2$ , PDMS	chloroform emulsion	93.4		5	17b
	$TiO_2$ , EP	diesel/water mixture	98.2		5	17c
	BTCA, SHP	oil/water emulsions		25.8–4920		7b
	SA	chloroform, 30% (v/v)	>95		10	17a
$Cu(OH)_2$ , SA	oil/water emulsions		>5500	5	17d	
$TiO_2$ , FDTS	oil/water emulsions	>93.7		15	1c	
$SiO_2$ , PDMS	soybean oil/water mixture	93.8		>10000	10	17f

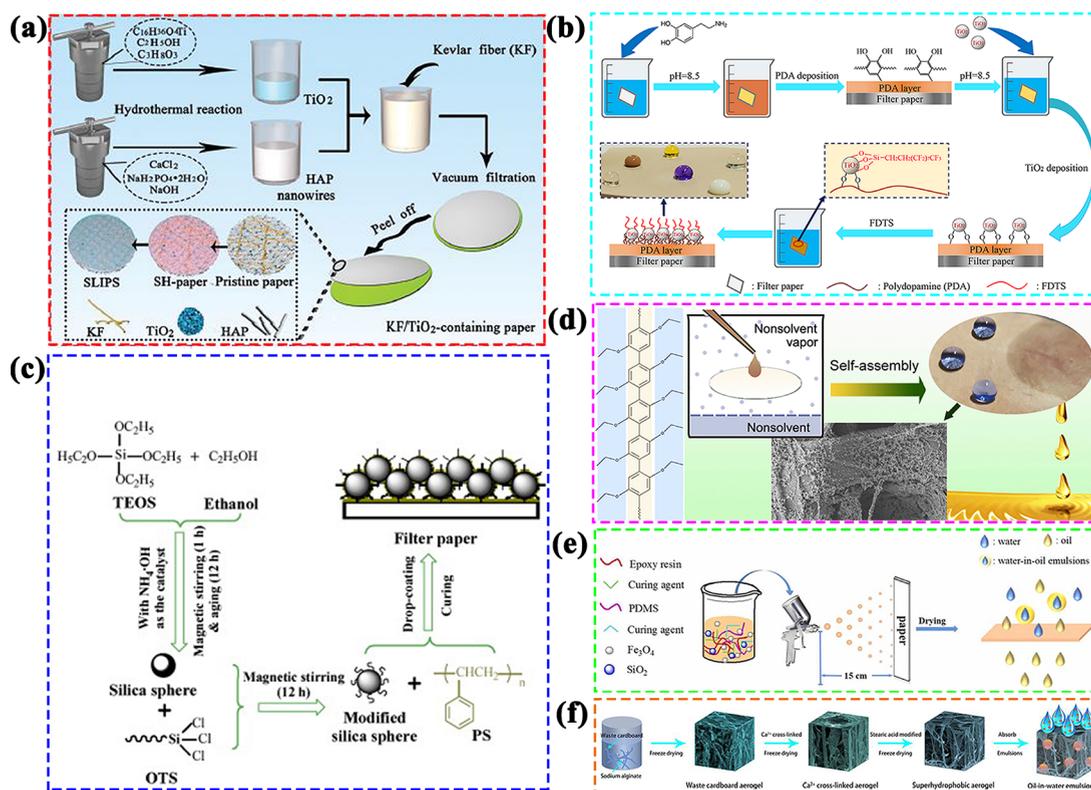
sustainable, and recyclable SPs become promising candidates for the treatment of oily wastewaters.

## DESIGN AND PREPARATION OF SUPERHYDROPHOBIC PAPERS

To achieve surface superhydrophobicity, porous and microtextured pristine papers usually need to be modified to meet two necessary requirements of superhydrophobic surfaces (i.e., hierarchical structures and low surface energy). Generally, SPs can be rationally designed via two main strategies: (1) modifying cellulosic fibers with low surface energy materials (i.e., fluoroalkylsilane and stearic acid) to form nanostructured

roughness on the microtextured fibers of pristine papers, and (2) decorating pristine papers with nanomaterials, followed by low surface energy modification (see Figure 1). Many preparation approaches can be used to achieve these two main strategies for SPs, including vacuum filtration,<sup>4,10</sup> phase separation,<sup>11</sup> colloidal deposition,<sup>12</sup> spray-coating,<sup>13</sup> atom transfer radical polymerization (ATRP),<sup>14</sup> layer-by-layer assembly,<sup>5,9</sup> self-assembly,<sup>15</sup> dip-coating,<sup>16</sup> immersion,<sup>1c,7b,8,17</sup> (see Table 1), etc.

As for the chemical modification of cellulosic fibers, low surface energy materials need to be elaborately chosen to react with the surface functional groups of cellulosic fibers of papers.



**Figure 2.** Preparation methods of SPs: (a) vacuum filtration, (b) immersion, (c) drop-coating, (d) self-assembly, (e) spray-coating, and (f) freeze-drying. (a) Adapted with permission from ref 10b. Copyright 2019 The Royal Society of Chemistry and the Centre National de la Recherche Scientifique. (b) Adapted with permission from ref 1c. Copyright 2022 American Chemical Society. (c) Adapted with permission from ref 18. Copyright 2012 Elsevier. (d) Adapted with permission from ref 15. Copyright 2018 Elsevier. (e) Adapted with permission from ref 13c. Copyright 2022 Elsevier. (f) Adapted with permission from ref 1a. Copyright 2021 American Chemical Society.

For example, Zhang et al. reported that a superhydrophobic poly(styrene-*co*-acrylonitrile) grafted filter paper can be prepared by combining octadecanoyl chain bonding and polymer grafting via surface-initiated atom transfer radical polymerization (ATRP).<sup>14b</sup> Yun et al. developed a facile and eco-friendly approach to prepare SPs by immersing the pristine paper in an ethanol solution of stearic acid.<sup>17a</sup> These studies obtained SPs by simply modifying both inner and outer cellulosic fibers with low surface energy materials (i.e., stearic acid). However, the control of reaction conditions between cellulosic fibers and low surface energy materials is very important, which greatly influences the homogeneous coverage of low surface energy materials on SPs.

The introduction of nanoparticles to the cellulosic fibers of pristine papers is an alternative strategy to obtain SPs. To achieve superhydrophobicity, inorganic nanomaterials (i.e., TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, Cu(OH)<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, and hydroxyapatite nanowires) have been used to decorate cellulosic fibers, followed by low surface energy modification. For example, Li et al. introduced hydroxyapatite nanowires (or TiO<sub>2</sub> nanoparticles) to Kevlar fiber-reinforced papers via a vacuum filtration method and lowered the surface energy by a chemical modification of stearic acid (Figure 2a).<sup>10b</sup> He et al. achieved SPs by immersing polydopamine-decorated filter papers in the TiO<sub>2</sub> nanoparticle suspension under magnetic stirring and modifying with a 0.5 wt % perfluorodecyltrichlorosilane (FDTS) solution (Figure 2b).<sup>1c</sup> Zhang et al. prepared SPs by drop-coating a tetrahydrofuran (THF) mixture solution of polystyrene (PS) and silica particles on filter paper (Figure 2c).<sup>18</sup> Bai et al. used a nonsolvent vapor self-assembly method

to prepare poly-*p*-phenylene micro/nanostructures decorated SPs for oil/water separation (Figure 2d).<sup>15</sup> Li et al. obtained robust and magnetic SPs by spray-coating a suspension consisting of epoxy resin, PDMS, Fe<sub>3</sub>O<sub>4</sub>, and SiO<sub>2</sub> (Figure 2e).<sup>13c</sup> Shi et al. fabricated superhydrophobic waste cardboards by combining Ca<sup>2+</sup> cross-links via freeze-drying and post-modification with stearic acid (Figure 2f).<sup>1a</sup> In short, the introduction of nanomaterials to porous microtextured cellulosic fibers can enhance the roughness and hierarchical structures of pristine papers and thus form micro/nanostructured roughness. When modifying with low surface energy materials, SPs finally can be obtained.

## PROPERTIES OF SUPERHYDROPHOBIC PAPERS

Except for surface superhydrophobicity, other properties are also very important for a reliable use of SPs in practical applications, including thermal stability, chemical resistance, durability, antiaging, and regeneration of superhydrophobicity. For example, the thermal stability is an important parameter for the real application of SPs. Generally, water contact angle (WCA) before and after heating (or boiling water) has been used to evaluate the thermal stability of SPs in terms of heating and boiling water (Figure 3). Yang et al. found that the superhydrophobic HAP@Fe<sub>3</sub>O<sub>4</sub>@PDMS (HAP = hydroxyapatite) paper can well-maintain its superhydrophobicity after treatment in a wide temperature range from -198 to 250 °C.<sup>4</sup> Du et al. showed that the WCA of a superhydrophobic filter paper can remain unchanged when the paper is placed in an oven and heated at 180 °C for 72 h.<sup>12</sup> Piltan et al. reported that

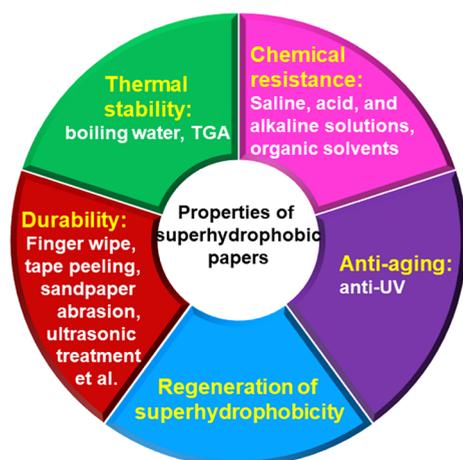


Figure 3. Properties of superhydrophobic papers.

the superhydrophobicity of the as-prepared filter paper can be retained (WCA =  $158^\circ \pm 3^\circ$ , SA =  $8^\circ$ ) when placed in an oven at  $200^\circ\text{C}$  for 2 h.<sup>11</sup> Therefore, the thermal stability of SPs enables the maintenance of surface superhydrophobicity and then extends their potential applications under different heating conditions (i.e.,  $\sim 200^\circ\text{C}$ ).

Immersing SPs in boiling water for a certain time is another approach to evaluate the thermal stability of SPs. For example, He et al. found that the WCA of  $\text{TiO}_2/\text{PDA}$ -based superhydrophobic paper is still  $>158^\circ$  after being immersed in boiling water for 120 s.<sup>1c</sup> Wen and Guo showed that the superhydrophobic paper can tolerate boiling water for 120 s with WCAs  $>150^\circ$ , while the shape of the paper was damaged.<sup>10a</sup> Besides, to verify the thermal stability, the thermogravimetric analysis (TGA) curves of pristine paper and SPs are characterized based on the weight loss.<sup>1c,10,21</sup> The weight loss of SPs is due to the absorbed water, dehydration of the silane group, and degradation of the silane coupling agent, which is usually  $>90\%$ . Thus, the good thermal stability of SPs can extend their applications in relatively high-temperature fields (i.e., fire-resistant materials).

In real application, the degradation of SPs is inevitable. The maintenance of superhydrophobicity for SPs becomes a great challenge. There are many methods to evaluate the durability of SPs, including finger wipe,<sup>4</sup> tape peeling,<sup>4,5,19</sup> knife scratching,<sup>4,19</sup> sandpaper abrasion,<sup>4,5,7b,13c,20,21</sup> bending,<sup>5,13c,20,21</sup> ultrasonic treatment,<sup>5,13c,17b,20,23</sup> flexural rigidity,<sup>23</sup> breaking (or bursting),<sup>23</sup> and scrubbing<sup>24</sup> (see Figure 3). For example, Yang et al. found that the superhydrophobicity of  $\text{HAP}@Fe_3O_4@PDMS$  paper is well-preserved after several mechanical damage tests, including finger wipe, adhesive tape peeling, knife scratching, and sandpaper abrasion.<sup>4</sup> Li et al. investigated the mechanical durabilities of several types of SPs and found that the superhydrophobicity of SPs can be maintained after sandpaper abrasion, bending, and ultrasonic treatment.<sup>5,13c,20</sup> Yang et al. reported that, compared with untreated papers, the flexural rigidity and breaking strength of  $\text{SiO}_2$ -decorated SPs can be enhanced by 22.0% and 20.9%, respectively.<sup>23</sup> For versatile applications, the mechanical durability is a critical parameter that determines the stability of surface superhydrophobicity of SPs and thus influences practical applications.

When used in harsh environments, the chemical corrosion resistance is beneficial to the long-term use of SPs, including

soaking in different organic solvents, saline solutions, acid solutions, and alkaline solutions (Figure 3). For example, He et al. found that the WCAs of the  $\text{TiO}_2/\text{PDA}$ -based SPs are still  $>150^\circ$  when being immersed in a HCl solution (pH = 1) for 180 min and in an alkaline solution (pH = 13) for 120 min.<sup>1c</sup> Yang et al. showed that the superhydrophobicity of  $\text{HAP}@Fe_3O_4@PDMS$  paper remains after soaking in organic solvents (i.e., acetone, cyclohexane, isopropanol, methanol, ethanol, *n*-hexane, and ethylene glycol) and being immersed in solutions with different pH values (2.35–12.98) and extremely acid condition (pH = 1.46).<sup>4</sup> Li et al. found that the WCAs of SPs are still kept  $>150^\circ$  after being immersed in different organic solvents (i.e., ethanol, acetone, and *n*-hexane) for 72 h.<sup>5</sup> However, the gradual degradation of surface chemistry and morphologies of SPs becomes unavoidable in corrosive solutions (i.e., organic solvents, saline solutions, acid solutions, and alkaline solutions) as time elapses.

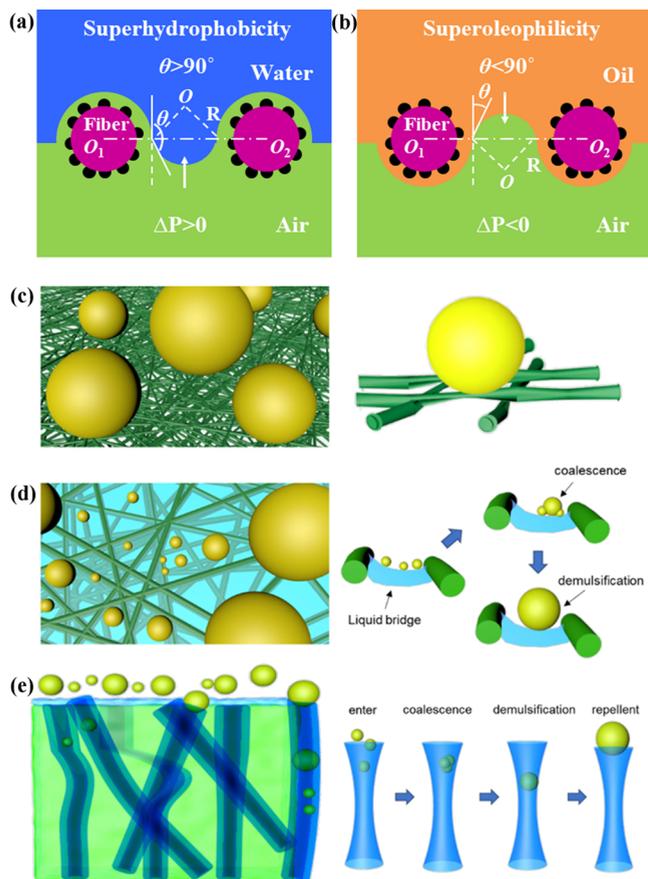
Antianging and antiultraviolet properties of SPs are also very important when utilized in harsh outdoor conditions (Figure 3), which can be realized by the rational design of SPs. For example, Ge et al. evaluated long-term durability by a hydrothermal aging test (i.e., the aging temperature is  $60^\circ\text{C}$  and the humidity is 80%), indicating the stability of SPs.<sup>17b</sup> Du et al. placed SPs under the light of a 48 W ultraviolet (UV) lamp for 72 h, and the SPs showed excellent resistance to ultraviolet irradiation.<sup>12</sup> Gao et al. found that the WCA of SPs still remains  $>151^\circ$  after UV exposure for  $>5$  h, showing good UV resistance.<sup>17c</sup> Li et al. showed that the superhydrophobic  $\text{PDA}@Ag@n\text{-DM}$  paper still kept superhydrophobicity after 6 h of UV exposure, indicating good UV durability.<sup>20</sup> On the basis of the earlier discussions, antiaging and antiultraviolet properties enable SPs' resistance toward different environmental conditions and facilitate the maintenance of long-term stability of SPs in practical applications.

Besides, the regeneration of surface superhydrophobicity is a vital ability for the reusability of SPs (Figure 3). For example, Ren et al. reported that the superhydrophobicity can be restored by heating the coated material at  $80^\circ\text{C}$  for 15 min.<sup>24</sup> Satapathy et al. showed that the superhydrophobicity of damaged/scratched surfaces can be regenerated by the solution-casting method.<sup>19</sup> Now that the degradation and loss of surface superhydrophobicity are unavoidable, the regeneration ability (or self-healing property) makes it possible for SPs to have stable and long-term utilization during practical applications.

## ■ SUPERHYDROPHOBIC PAPERS FOR OIL/WATER SEPARATION

Due to excellent surface superhydrophobicity, SPs have been utilized in various practical applications. Among them, oil/water separation is crucial to the treatment of oceanic oil spill incidents and the discharge of oily wastewaters. Thus, the performances of SPs on separating oily wastewaters are highly important when used in oil/water separation, including separation efficiency, permeation flux, recyclability, and so on (see Table 1). Recently, the mechanisms of SPs for oil/water separation have aroused much interest from researchers. Usually, SPs possess superhydrophobicity (i.e., water droplets in the Cassie–Baxter state) and superoleophilicity (i.e., oil droplets in the Wenzel state). When oil/water mixtures (or emulsions) have contact with SPs, water droplets can be blocked by surface superhydrophobicity and oil can easily permeate into the cellulosic fibers of SPs because of the

superoleophilicity.<sup>1c</sup> Generally, a stable oil/paper interface can be generated during a separation process and, thus, effectively block the permeation of water droplets.<sup>1c,10a</sup> When the intrusion pressure is positive ( $\Delta P > 0$ ) (Figure 4a), water cannot go through cellulosic fibers. Once the intrusion pressure is negative ( $\Delta P < 0$ ), oil can easily enter into fibers (Figure 4b).



**Figure 4.** Separation mechanisms of (a) oil/water mixtures and (b) oil/water emulsions. (b–e) Adapted with permission from ref 7b. Copyright 2021 Springer.

However, the efficient separation of oil/water emulsions is still a challenge for SPs due to the stability and the small droplet size of oil/water emulsions. When separating oil/water emulsions, the pore size of SPs and the droplet size of oil/water emulsions are of great importance to demulsification processes.<sup>5,13c,20,23</sup> If the size of the oil/water emulsion droplet is smaller than the pore size of the SPs, oil droplets can be easily separated.<sup>7a</sup> When the oil droplets are larger than the pore size of the SPs, they can be held (Figure 4c).<sup>7b</sup> Because of superhydrophobicity, the liquid bridges can be formed among the fiber pores, and thus small oil droplets can leave and permeate through the cellulosic fibers (Figure 4d).<sup>7b</sup> Xi et al. thought that the existence of the liquid bridge can result in the coalescence of oil droplets and thus induce the demulsification of emulsions (Figure 4e).<sup>7b</sup> Although the separation efficiency of SPs is high, the tiny nanoemulsions are still difficult to be separated. For example, Ren et al. found that the size of the emulsions ranges from 300 to 1500 nm before separation, while the droplet sizes in the filtrate are between 3 and 12 nm after separation by using SPs.<sup>24</sup> Shi et al. reported that the

particle size of emulsions is distributed between 1000 and 2500 nm, while the particle size of emulsions in the filtrate is between 4 and 18 nm.<sup>1a</sup> Therefore, the separation of tiny nanoemulsions (i.e., size < 20 nm) needs to be fundamentally investigated by the rational design of SPs (i.e., the size of the pores).

During a separation process of oil/water emulsions, a stable liquid/solid interface can be formed that effectively blocks the contact between oil (or water) and the SPs.<sup>1c,10a</sup> As for the oil/water separation, oil/water mixtures (or emulsions) can be realized via a gravity-driven separation by using SPs, while the intrusion pressures for separating different oils are usually different.<sup>1c</sup> Yang et al. found that the intrusion pressures of water and emulsions as well as the working pressure during emulsion separation are 10.39, 3.71, and 0.36 kPa, respectively.<sup>23</sup> The small working pressure guarantees the block of water passing through SPs, achieving the efficient separation of oil/water emulsions. Thus, the intrusion pressure and working pressure should be considered when separating oil/water mixtures (or emulsions).

Viscous oil/water mixtures or emulsions (i.e., crude oils) are another challenge in the field of oil/water separation. Very recently, an external stimulus (i.e., electrothermal or photothermal heating) could be considered to enhance the oil/water separation. For example, the photothermal effect has been demonstrated to increase the surface temperature and thus facilitate the mobility of crude oils.<sup>2a,25</sup> Once the viscosity of viscous oil/water mixtures (or emulsions) is reduced at high surface temperature, the adsorption (or separation) efficiency will increase. This photothermal effect promoted strategy provides new insights into the cleanup of viscous crude oils and other viscous oily wastewaters. Besides, the morphologies of SPs may change after several oil/water separation cycles.<sup>1c</sup> The recycling performances of SPs should also be considered for long-term use in oil/water separation.

## CONCLUSIONS AND OUTLOOK

In summary, this mini-review introduces the design, preparation, and properties of SPs for their application in the field of oil/water separation. The SPs are cellulosic fiber-based materials, consisting of porous structures, microtextures, and rich hydrophilic functional groups. The excellent properties of SPs (i.e., self-cleaning, durability, chemical corrosion resistance, and reusability) enable the efficient oil/water mixtures (or emulsions). Thus, as abundant sustainable resources, SPs are promising candidates in the field of oily wastewater treatment.

In the future, the rational design of SPs needs to be realized to meet the requirements (i.e., thermal stability, chemical resistance, durability, antiaging (or anti-UV), and reusability) of practical applications (i.e., oil/water separation). When utilized in oil/water separation, two main challenges (i.e., the separation of emulsions and the separation of viscous oil/water mixtures) exist. By adjusting the pore size of the SPs and the working pressure, oil/water emulsions can be efficiently separated. However, nanoemulsions (with droplet size < 20 nm) are still difficult to separate. The separation efficiency of nanoemulsions probably can be improved by the combination of the following two methods: (1) the introduction of an external stimulus (i.e., electrothermal or photothermal heating and magnetic field) in the separation of oil/water emulsions is beneficial to the demulsification processes; (2) a multistep process can be employed by utilizing SPs with different pore

sizes to realize the separation of nanoemulsions. As for viscous oil/water mixtures, electrothermal or photothermal heating has been demonstrated to enhance the separation of oil/water mixtures, while the recyclability of SPs should be improved after several cycles of viscous oil/water separation. Of course, SPs also have disadvantages for oil/water separation. For example, the adsorption capacity of SPs for oil/water mixtures (or emulsions) is much lower than that of sponges and porous materials. Thus, in the practical application of oil/water separation, suitable separation materials can be selected to meet different conditions and environments (i.e., viscous oils, nanoemulsions, light oils, and heavy oils). All in all, low-cost and renewable SPs are promising candidates in the field of oily wastewater treatment, providing a great potential use in different harsh environments.

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### Notes

The authors declare no competing financial interest.

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