



## Efficient separation of oil-water emulsions: Competent design of superwetting materials for practical applications

Rajaram S. Sutar<sup>a</sup>, Xinna Wu<sup>a</sup>, Sanjay S. Latthe<sup>a,b</sup>, Bairu Shi<sup>a,c</sup>, Ruimin Xing<sup>a,\*</sup>, Shanhu Liu<sup>a,\*</sup>

<sup>a</sup> Henan Key Laboratory of Polyoxometalate Chemistry, School of Energy Science and Technology, Henan University, Zhengzhou, 450046, P. R. China

<sup>b</sup> Self-cleaning Research Laboratory, Department of Physics, Vivekanand College (Autonomous), (Affiliated to Shivaji University, Kolhapur), Kolhapur 416003, Maharashtra, India

<sup>c</sup> Research Institute of Petroleum Exploration & Development, Beijing 100083, P. R. China

### ARTICLE INFO

Editor: Luigi Rizzo

#### Keywords:

Superwetting  
Oil-in-water emulsion  
Water-in-oil emulsion  
Superhydrophobic  
Superoleophilic

### ABSTRACT

Globally, the issue of oil-water emulsion is continuously ticking in the minds of researchers. The oil-water emulsion is hazardous to marine ecological safety and human health around the globe, indicating that we urgently need to develop efficient strategies to tackle emulsion issues. Materials with porous morphology and selective superwettability towards certain liquids are essential in separating oil-water emulsions. Recently, there has been increased demand for smart oil-absorbent and water-absorbent superwetting porous materials. Over the past decade, several innovative advancements and promising industrial developments to separate oil-water emulsions have been spotted. This review article overviews the latest advancements in the design of superwetting materials for oil-water emulsion separation and thoroughly discusses oil-absorbent and water-absorbent superwetting porous materials, demulsification, and superamphiphilic materials. In each section, the design strategies, base materials and oil-water emulsion separation performance of superwetting porous materials have been systematically discussed. Then, common challenges of superwetting materials in practical application are discussed. Finally, conclusions and future perspectives concerning oil-water emulsion separation based on superwetting porous materials are summarized. This review article can allow helping hand to early career scientists to elegantly understand the oil-water emulsion separation issues.

### 1. Introduction

Oil-water emulsions have become a major global issue due to their detrimental and long-lasting effects on the environment, animals, and plants. Offshore oil spills can produce oil-water emulsion, which can have a negative impact on the fresh water [1–7]. The five largest and disastrous oil spills in history include Gulf War - Persian Gulf (1991), Deepwater Horizon - Mexican Gulf (2010), Ixtoc -1 - Mexican Gulf (1980), Atlantic Empress - Caribbean Sea (1979), and ABT Summer - Offshore Angola (1991) [8]. Additionally, several industrial processes release large volumes of oil containing wastewater into the fresh water annually. In a day, petro-refinery industries generate over 250 million barrels of oily wastewater, out of which around 40% is discarded into the environment [9]. Due to inadequate distribution of oil stores and consumption areas, over 71% of oceans are infected with oil, causing immense damage to marine and human life [10]. Oil creates a layer on the water surface that prevents oxygen from reaching aquatic plants and

animals. Due to the oil layer on the sea surface, the hypothermia effect caused to the sea birds, fishes, seals, and sea otters, which can be fatal. Fish and other sea life can suffer from poisoning, internal injury, ulcers, damage to red blood cells, kidneys, liver, and the immune system after ingesting oil. Whales can die due to clogged blowholes from oil, and humans can suffer various diseases such as lipid pneumonia, lung diseases, folliculitis, and skin diseases due to exposure to oily water [11–14]. The primary source of generation of oil-water emulsion and its impact on the ecosystem is compiled in Fig. 1.

In fact, emulsion separation is a worldwide challenge [15,16]. Conventional methods have been developed to tackle this issue, however find numerous limitations. The heat separation method, for instance, involves heating oil to reduce its viscosity, which releases abundant hydrocarbon components in the environment, causing secondary pollution such as air pollution [17]. On the other hand, gravity separation takes much longer time and relies on the density difference between oil and water [18]. Coalescence separation involves the

\* Corresponding authors.

E-mail addresses: [rmxing@henu.edu.cn](mailto:rmxing@henu.edu.cn) (R. Xing), [liushanhu@vip.henu.edu.cn](mailto:liushanhu@vip.henu.edu.cn) (S. Liu).

<https://doi.org/10.1016/j.jece.2023.111299>

Received 27 June 2023; Received in revised form 20 September 2023; Accepted 20 October 2023

Available online 24 October 2023

2213-3437/© 2023 Elsevier Ltd. All rights reserved.

collision of tiny droplets to form larger ones, which can then be separated [19]. Centrifugation is an industrial-scale process that separates oil-water emulsion using centrifugal force, but its efficiency depends on the specific gravity of components. The coagulation method involves destabilization of emulsion through aggregation and flocculation, but non-biodegradable coagulants used in this process create secondary pollutants. Generally, these conventional methods are inefficient, expensive, and prone to secondary pollution [20–23]. Therefore, cutting-edge techniques are urgently required for easy and sustainable oil-water emulsion separation, using environmentally friendly materials.

The wetting phenomena occurring on many natural surfaces brought the idea of superwetting. A water drop rests on the lotus leaf like a tiny ball due to rough surface morphology and the presence of low surface energy wax crystalloids on the lotus leaf [24,25]. Furthermore, the surface and interfacial studies of fish scales exhibit superhydrophilic (SHL) and underwater superoleophobic (SOP) characteristics [26]. This outstanding wetting characteristic is due to its rough surface structure and outer fish skin secretes a slippery mucus layer consisting of hydroxyl, amine, and carbonyl groups. This principle can be utilized to develop materials that can either absorb oil or water or form a layer that prevents other liquids from passing through the pores [27–30].

As promising alternatives, superwetting materials have many benefits, such as being affordable, easy to make, efficient, and environmentally friendly [31–35]. These materials have demonstrated exceptional performance in various applications, including self-cleaning [36], anti-icing [37], anti-fouling [38], self-healing [39], anti-corrosion [40], and oil-water separation [41–43]. Porous superwetting surfaces were found beneficial for efficient oil-water emulsions.

However, large pore-size materials are unable to separate emulsions effectively. The pore size can be controlled using the size-sieving effect by adjusting the pore size smaller than emulsion droplets for efficient separation [44]. In academic and industrial research, different types of materials, including meshes, polymer membranes, and foams have been used to create superhydrophobic/superoleophilic (SHP/SOL) and superhydrophilic/underwater superoleophobic (SHL/SOP) porous materials. A SHP/SOL porous material can be used to separate water-in-oil (W/O) emulsion, whereas SHL/underwater SOP materials can be adopted to separate oil-in-water (O/W) emulsion. Many attempts have been made to fabricate porous superwetting materials for oil-water emulsion separation [45–48].

Several review articles on oil-water emulsion separation are found in the literature discussing a variety of membranes, polyimide materials, fibrous materials, and natural superwetting materials [49–55].

However, their applications from small laboratory scale to large industrial level have not been summarized well. This review aims to fill this gap by explaining the mechanism of emulsion separation by superwetting materials. We provide an overview of recent advancements in the fabrication of superwetting materials for emulsion separation, consequently adding subsections on oil-absorbent and water-absorbent superwetting porous materials, demulsification, and superamphiphilic materials. In each section, the design strategies, base materials, and oil-water emulsion separation performance of superwetting porous materials have been thoroughly discussed. Moreover, this review highlights the exceptional properties of porous superwetting materials, including their extended wettability, efficiency, reusability, mechanical strength, and scalability in manufacturing, making them ideal for emulsion separation. Consequently, common challenges of superwetting materials in practical applications are briefly discussed. The conclusions and future perspectives concerning oil-water emulsion separation based on superwetting porous materials are briefed at the end.

## 2. Mechanisms of oil-water emulsions and their separation

### 2.1. Basics of oil-water emulsions

An emulsion is a fine mixture of water and oil that contains small droplets of the opposite liquid dispersed throughout. There are two main types of emulsions: oil-in-water (O/W) and water-in-oil (W/O) [56]. In an O/W emulsion, oil droplets are dispersed in a continuous water phase (schematically shown in Fig. 2A, top). In contrast, the continuous and dispersed phases are switched in a W/O emulsion (schematically shown in Fig. 2A, bottom). Stabilized microemulsion droplets are formed when surfactants, biopolymers, or fine particles are present in the emulsion [55,57]. Surfactants have hydrophilic and hydrophobic groups that tend towards the water and oil phases, respectively, which reduce the interfacial tension. Water-soluble surfactants are present in O/W emulsions, while oil-soluble surfactants are present in W/O emulsions.

### 2.2. Oil-water emulsion separation mechanism

For oil-water emulsion separation, the superwetting porous materials can be designed by controlling pore size along with surface morphology and surface energy. The superwetting porous materials can completely wet with one phase of oil-water emulsion and pass through the pores to achieve oil-water emulsion separation. Pore size-sieve plays a significant role in the design of superwetting porous materials for emulsion separation. According to the size-sieving effect, oil-water

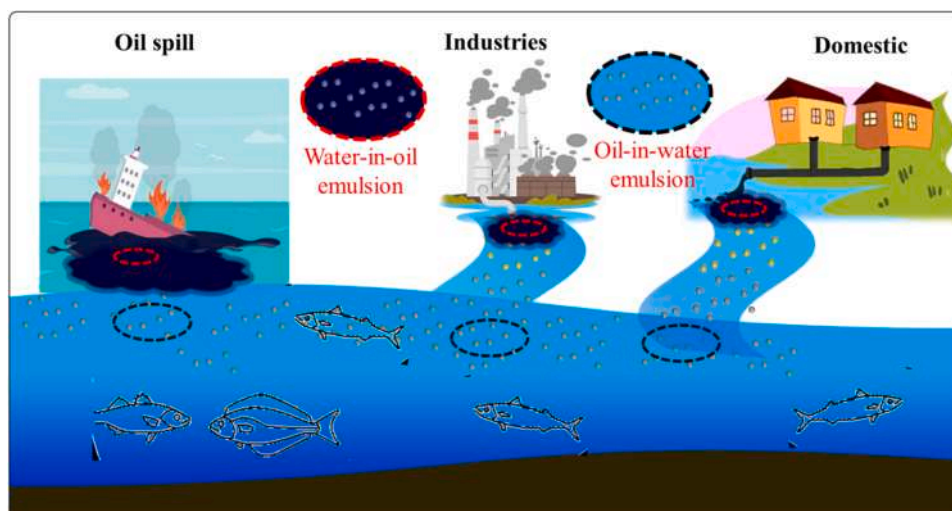
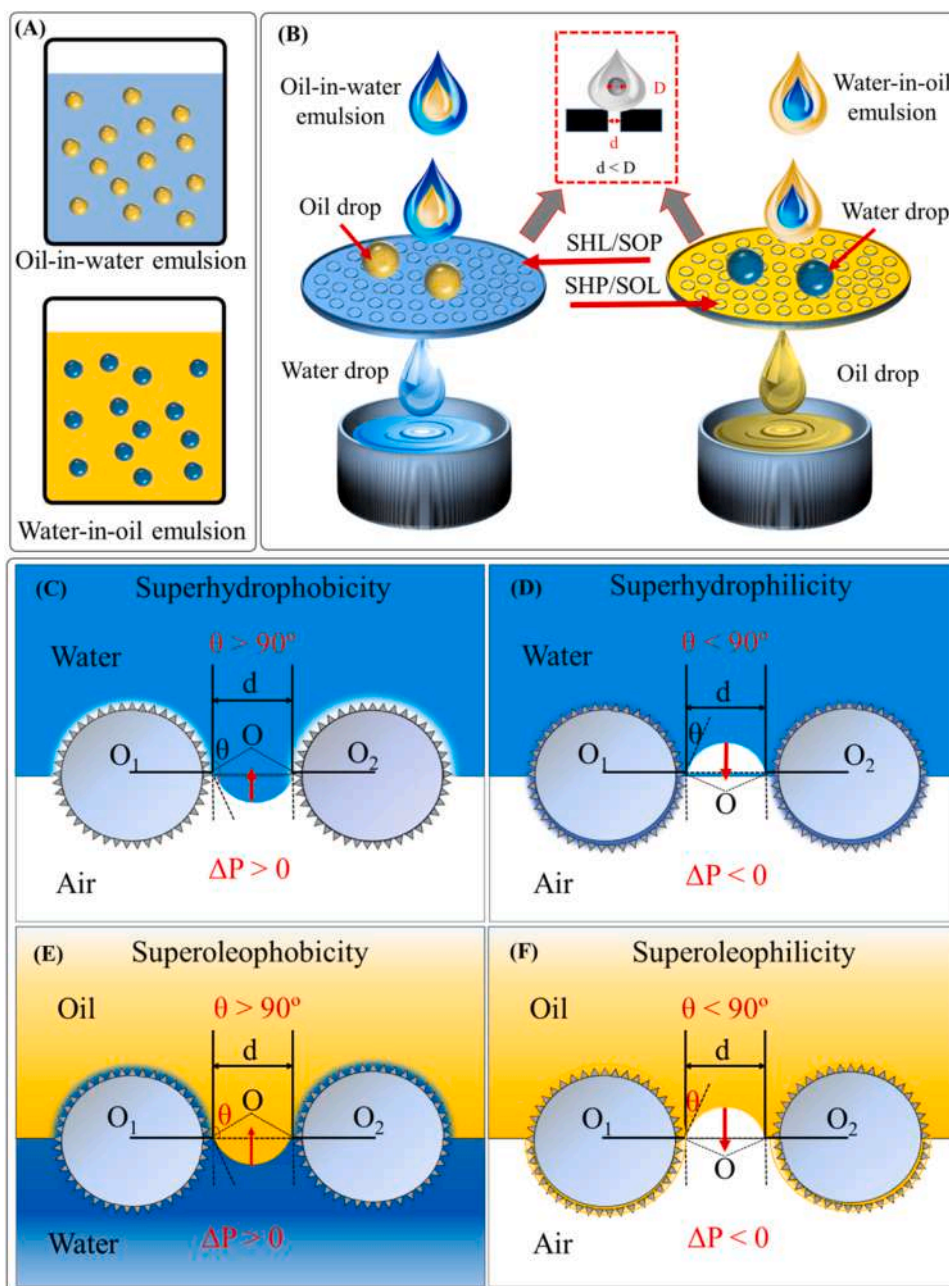


Fig. 1. Suffering of aquatic life due to oil spill and industrial and domestic oily wastewater dumping in water bodies.



**Fig. 2.** (A) Schematics of O/W and W/O emulsion. (B) Schematic representation of the mechanism of separation of oil-water emulsion by superwetting materials with a small pore size based on size-sieving. (C) Water cannot wet a porous surface when CA  $> 90^\circ$  in air. (D) Water can wet a porous surface when WCA  $< 90^\circ$  in air. (E) Oil cannot permeate superoleophobic porous surfaces when prewetted by water. (F) Oil can wet a porous surface when OCA  $< 90^\circ$  in air.

emulsions can be separated by the small pore sized porous materials where the pores are much smaller than the emulsion droplets (schematically shown in Fig. 2B) [58,59]. Another physical characteristic, the intrusion pressure ( $\Delta P$ ), needs to be considered in the emulsion separation process. Intrusion pressure is the maximum pressure that porous materials can withstand without liquid passing through their pores. It is determined by the wettability of the material. Liquid intrusion pressure can be determined using the following equation:

$$\Delta P = - (1 \gamma \cos\theta) / A \quad (1)$$

where  $\gamma$  is surface tension,  $l$  and  $A$  is a pore's circumference and cross-sectional area.  $\theta$  is the liquid contact angle on the flat surface. The superhydrophobic porous material possesses a water contact angle ( $\theta_w$ )  $> 90^\circ$ , enabling it to repel water effectively (Fig. 2C). This is due to the

presence of a thin air film trapped within the porous structure of the material, which acts as a barrier against water intrusion. In contrast, water can enter the superhydrophilic porous material that has  $\theta_w < 90^\circ$  (Fig. 2D). When water prewets a porous surface; it replaces trapped air. The water-prewetted porous surface readily forms a capillary bridge of water between two cylinders of pores and is opposed to the intrusion of oil into the porous structure. As a result, water-prewetted porous materials become superoleophobic with oil contact angle  $\theta_o > 90^\circ$ , indicating external pressure is needed to penetrate oil into pores ( $\Delta P > 0$ ) (Fig. 2E). In the case of superhydrophilic or superoleophilic porous materials, which have a contact angle of less than  $90^\circ$ , only gravity can cause water or oil to penetrate easily. Therefore, these materials have an intrusion pressure of  $\Delta P < 0$  (Fig. 2D and F).

Further, the thickness along with the pore size of superwetting porous materials can influence the permeation flux of oil-water

emulsions. The Hagen–Poiseuille relation can be used to calculate the permeation flux ( $F$ ) of the membrane, which depends on the porosity ( $\epsilon$ ), pore radius ( $r_p$ ), thickness of the material ( $L$ ), intrusion pressure ( $\Delta P$ ), and viscosity of the liquid ( $\mu$ ) [60]; is given by following equation,

$$F = \Delta P (\epsilon r_p^2 / 8\mu L) \quad (2)$$

The reduction in the pore size of porous materials decreases separation flux. Moreover, emulsion droplets clogged in small pores, resulting decline in flux. To overcome this issue, the oil-water emulsion can be separated based on demulsification. Superwetting materials can absorb emulsion droplets during demulsification. Emulsion droplets on a superwetting surface coalesce into bigger droplets due to the coalescence effect. The coalesced droplets form a layered oil/water mixture that can be separated. This separation process is not affected by the pore size of superwetable materials and does not require increased flux to be effective [61,62]. Therefore, superwetable materials can lead to the highest possible oil-water emulsion separation.

### 3. Recent progress in the design of superwetting materials for oil-water emulsion separation

Extensive research is being conducted on porous superwetting materials, which are proving highly effective for separating oil-water emulsions. There are two common types of superwetting materials: superhydrophilic and superoleophilic. These materials are designed to exhibit extreme affinity for either water or oil, respectively. Adjusting pore size concerning emulsion droplets and making them robust for industrial applications is challenging. The different types of porous materials, including metal mesh/foam, polymer membranes, polymer sponges, cellulose materials, cotton fabric and filter paper, have been used to prepare superwetting surfaces for emulsion separation (Fig. 3A) [63–66]. The superwetting membranes are popular due to their high porosity, adjustable pore size, thin architecture, and affordability. Different techniques, including spray [67,68], spin [69], dip [70,71], brush coating [72,73], electrospinning, electrospray, electrochemical [74–76] and phase separation [77], have been used to fabricate superwetting porous materials. The common fabrication methods of superwetting porous materials are schematically represented in Fig. 3 (B–G).

Along with wettability and porous morphology, physical and chemical stability are essential factors for superwetting porous materials to be used in oil-water emulsion separation applications. The various durability testing methods, including abrasion test, sand impact test, tape-peeling test, UV exposure, deep corrosive liquid stability, heating, antifouling, and reusability have been mostly used. Fig. 4 (A–H) represents a schematic illustration of durability testing methods for superwetting porous materials. The recent progresses in the design of superwetting materials for oil-water emulsion separation are discussed in the following subsections.

#### 3.1. Oil absorbent superwetting porous materials

Huge amounts of oil-water emulsions are continuously formed as a result of oil spills; the viscosity, temperature, and density differences between the oil and water play significant roles in the formation of emulsions [78]. In addition, W/O emulsions are developed due to water injection during oil extraction, water cooling during petroleum cracking, or long-distance transportation by underground pipelines or oil tankers. The micro emulsion droplets are captured by superoleophilic porous materials, wet the surface completely and pass through the pores. However, water may strike on the surface, resulting in effective W/O emulsion separation [79].

For the first time, a lotus leaf-like surface that strongly repels water and quickly absorbs oil was fabricated by coating low surface energy polytetrafluoroethylene (PTFE) on stainless steel mesh [80]. The mesh separated oil and water mixture successfully, however, it was incapable in separating the oil-water emulsion because of the large pore size. Considering this drawback, researchers have designed superwetting materials with microporous morphology, especially for oil-water emulsion separation [81,82]. Recently, Lin assembled a cobweb-like multi-sized pore-based network on stainless steel mesh (SSM) by a vacuum suction method for W/O emulsion separation [83]. Dispersion of carbon nanofibers (CNFs) and single-walled carbon nanotubes (SWCNTs) was filtered through chemically etched SSM (ESSM) under pressure. The CNFs-SWCNTs network embedded mesh was dipped into polydimethylsiloxane (PDMS) for superhydrophobicity. Fig. 5A depicts the schematic of an embedded network structure of CNFs-SWCNTs-PDMS on ESSM. The dual scaled pore diameters of 500 nm and 200 nm were formed through cross-linking between CNFs and SWCNTs, respectively, which could separate 100 nm sized W/O emulsion with separation flux of  $430 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ . Besides, Stenocara beetle's back structure gives a new idea to design superwetting materials, in which the water droplets get captured from water-in-oil emulsion and improve separation efficiency. The beetle's back structure consists of a unique structure of hydrophilic bumps and superhydrophobic background. Hydrophilic bumps capture atmospheric water molecules and then coalesce and roll down the superhydrophobic area under gravity. Thus, Zeng et al. have simulated the superwetting Stenocara beetle's back structure for collecting micro water droplets dispersed in oil [84]. The schematic of preparation of superhydrophilic bumps–superhydrophobic/superoleophilic stainless steel mesh (SBS-SSM) by electrostatic self-assembly and spin-coating methods is shown in Fig. 5B. The superoleophilicity and superhydrophobicity were achieved by depositing hydrophilic silica particles on SSM having pore size of  $10 \mu\text{m}$  followed by spin-coating of a nano-composite solution of fluoropolymer/SiO<sub>2</sub> nanoparticles. Hydrophilic bumps (due to hydrophilic silica particles) could capture tiny water droplets from emulsion that are smaller than the pore size of the stainless steel mesh. Due to superoleophilicity, oil permeates through the pores of SHP/SOL surface and gets separated (99.95%).

Immoderately small and large sized pores of materials are

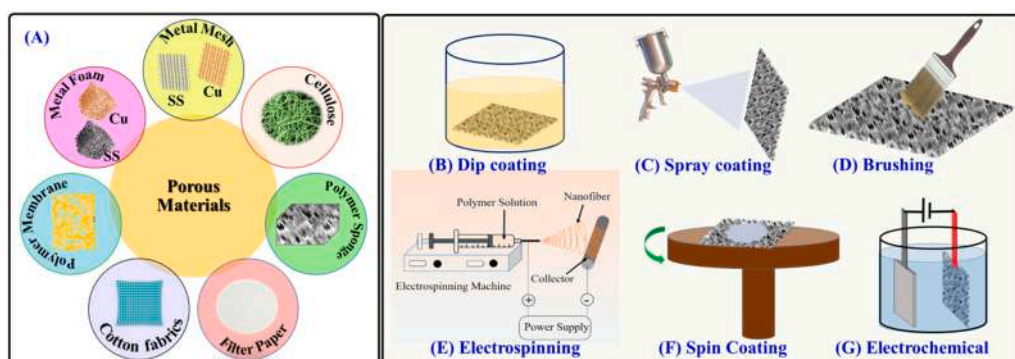


Fig. 3. (A) Schematic of various porous materials. (B–G) Common fabrication methods of superwetting porous materials.

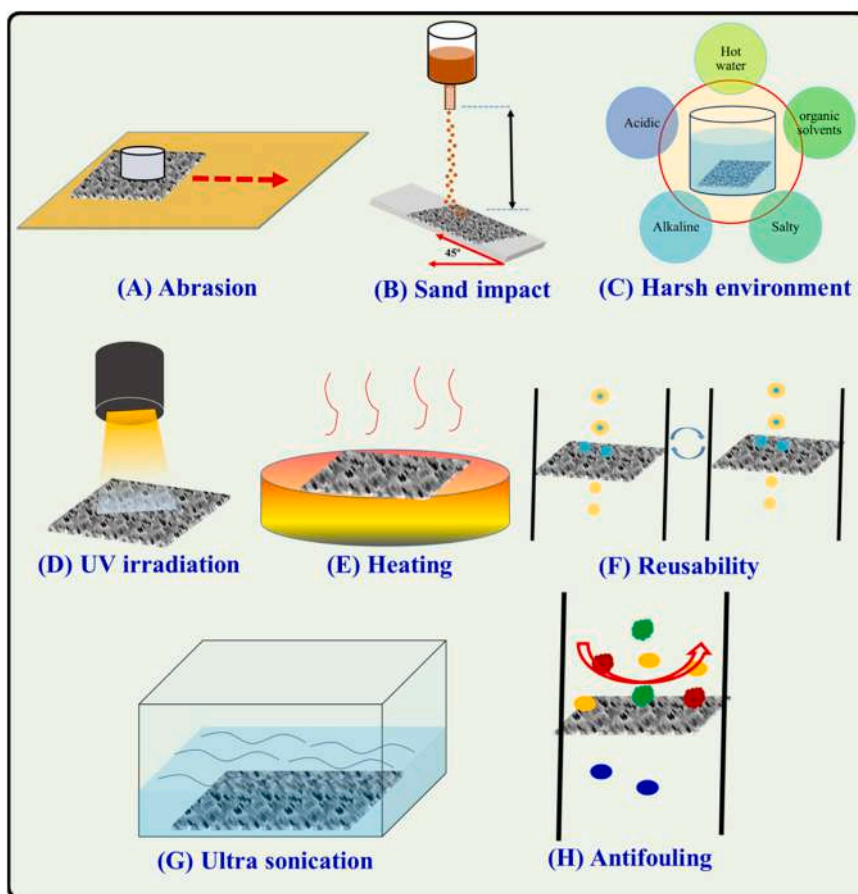


Fig. 4. (A-H) Common durability testing methods of superwetting porous materials.

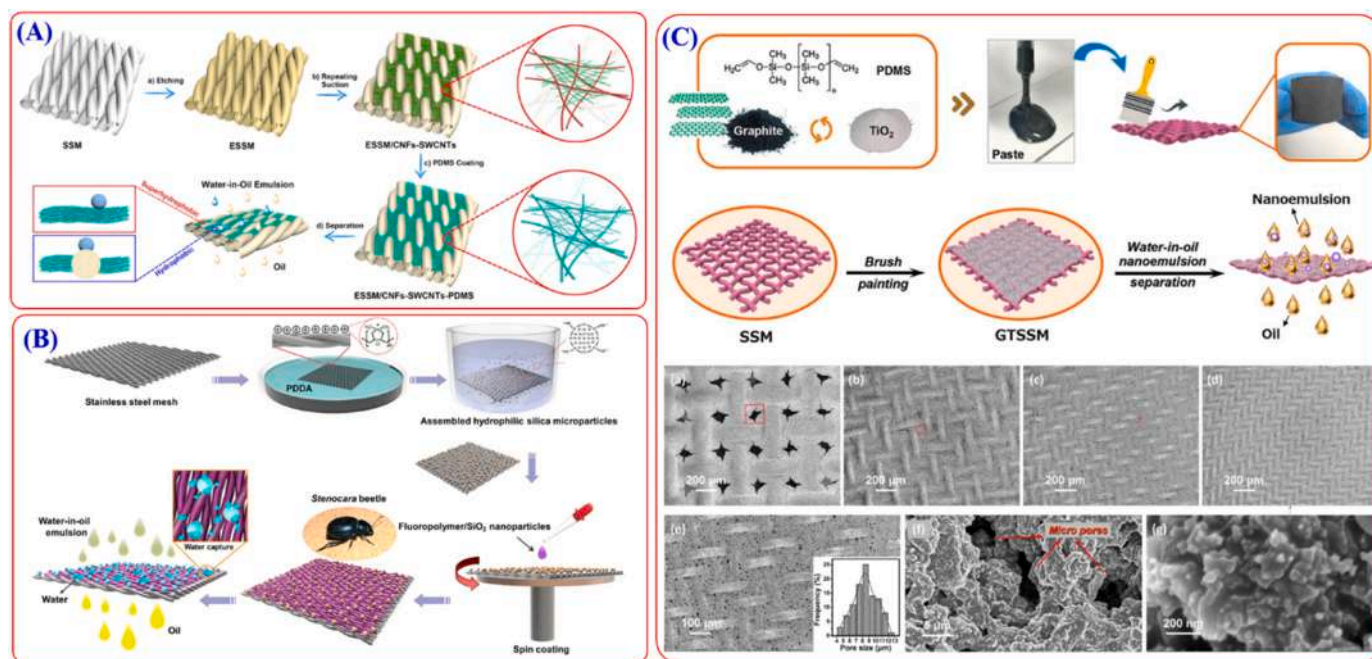


Fig. 5. (A) Schematic of embedded network structure of CNFs-SWCNTs-PDMS on mesh [83]. (Copyright 2017, American Chemical Society. Reproduced with permission from Ref. [83]). (B) Schematic of preparation of SBS-SSM by electrostatic self-assembly and spin-coating methods [84]. (Copyright 2017, American Chemical Society. Reproduced with permission from Ref. [84]). (C) Schematic of preparation of superhydrophobic coating on mesh and SEM images of coated mesh [85]. (Copyright 2019, American Chemical Society. Reproduced with permission from Ref. [85]).

inappropriate for emulsion separation. Du et al. have analyzed the emulsion separation performance against different pore sized SSM [85]. The superhydrophobic paste (graphite, TiO<sub>2</sub> nanoparticles, and polydimethylsiloxane (PDMS) was applied on SSM of different mesh numbers (80, 200, 300 and 400) having different pore diameters as shown in Fig. 5C. The micro- scale graphite and nano-scale TiO<sub>2</sub> were responsible to attain hierarchical micro-/nano- structures on mesh surface and PDMS reduces the overall surface energy, which can eventually enhance the superhydrophobic property of the coating. The 8-9 μm pore size obtained for the paste applied on 300-mesh, could separate W/O emulsion droplets (smaller than 8 nm) of gasoline, isooctane, xylene, dichloromethane, and n-hexane with separation efficiency of 99.9%. In Scanning electron microscopy analysis of coatings (Fig. 5C), it was observed that many rough and irregular protuberances conglomerated on the coating, which enhances oil absorption and water drops strike on oil wetted mesh surface. Along with superwettability and pore size control, mechanical robustness is considered for long time separation of oil-water emulsion. For the fabrication of mechanically robust superhydrophobic surface, Li et al. have used aluminum phosphate (AP) as an inorganic adhesive in the suspension of octadecyltrimethoxysilane-modified attapulgite and spray coated on SSM (Fig. 6 A) [86]. The roughness attained due to attapulgite nanorods and low surface energy by virtue of octadecyltrimethoxysilane executes SHP/SOL SSM. The Si-O bond on octadecyltrimethoxysilane breaks and Si atom makes new bonding with O atom of attapulgite, which eventually produces long-chain of hydrophobic alkyls on the attapulgite surface. Furthermore, there are several hydrogen bonds between the functional groups of the aluminum phosphate binder and the oxygen atoms on the attapulgite, which will aid to improve adhesion. Therefore, the prepared coating has exhibited more robust wetting properties (WCA > 150°) against 200 sandpaper abrasion cycles and sand impact tests (Fig. 6 B and D). Even after 200 sandpaper abrasion cycles, the mesh had showed outstanding emulsion separation (99.4%) (Fig. 6 C). The hydroxyl groups and reactive double bonds (P=O) in AP create cross-linked structures, improving the attractive force and cohesion between nanoparticles and the substrate [87].

Further, polymer-based materials have been extensively utilized for emulsion separation due to their flexibility, controlling pore structure, and low corrosion possibility. The polymeric porous materials are

mostly synthesized by electrospinning and phase inversion [88,89]. In the electrospinning technique, nanofibers attain porous structured membrane. In phase inversion, the porous morphology was developed by non-solvent induced phase separation (NIPS), solvent evaporation-induced phase separation (SEIPS) and thermally induced phase separation (TIPS). Poly (vinylidene fluoride) (PVDF) [90], poly (vinyl alcohol) (PVA) [91], polyurethane (PU) [92], poly(vinyl chloride) (PVC) [93] and poly(arylene ether nitrile) (PEN) [94] are mostly used for fabrication of porous polymeric materials. The pristine polymeric porous materials are hydrophobic in nature, but unsuitable for high wettability and oil-water emulsion separation. The addition of inorganic nanoparticles in polymer matrix substantially improves the wettability, emulsion separation ability and mechanical strength. For example, the addition of SiO<sub>2</sub> nanoparticles and micro-scale fluorinated ethylene propylene particles into the polysulfone/fluorinated ethylene propylene membrane resulted in a hierarchical roughness of 0.712 μm, which revealed a WCA of 153.3° and rolling angle of 6.1° [95]. This membrane effectively separated water-in-kerosene and water-in-diesel emulsions with high efficiency. Xiong et al. have attained PET membrane by electrospinning technique and immersed into ZnO seed solution followed by grafting of hydrophobic functional groups by dipping into sodium laurate solution (Fig. 7A) [96]. The SEM micrograph of PET membrane reveals that the PET membrane consists of smooth PET nanofibers which form porous network structure. After in situ growth of ZnO, nanofiber surface become rougher due to the coverage of ZnO nanopillars (Fig. 7B). The ZnO nanopillars, self-entanglement and network-like pores provide flow channel during emulsion separation. The as fabricated membrane exhibited excellent chemical stability in corrosive liquid and showed separation efficiency of 99.6% even after 10 separation cycles (Fig. 7C).

Compared with the two-dimensional superwetting materials, the three-dimensional structure yield space for the storage of oil droplets and its selective superwetting facilitates rapid and effective separation. For continuous and longtime emulsion separation, Xu et al. have designed a novel tubular-like three-dimensional nanofiber membrane using polyvinyl chloride (PVC) and hydrophobic SiO<sub>2</sub> nanoparticles (Fig. 7D) [97]. The tubular-like three-dimensional PVC nanofiber membrane was prepared using three-dimensional microspheres and two-dimensional nanofibers via electrospinning process. The

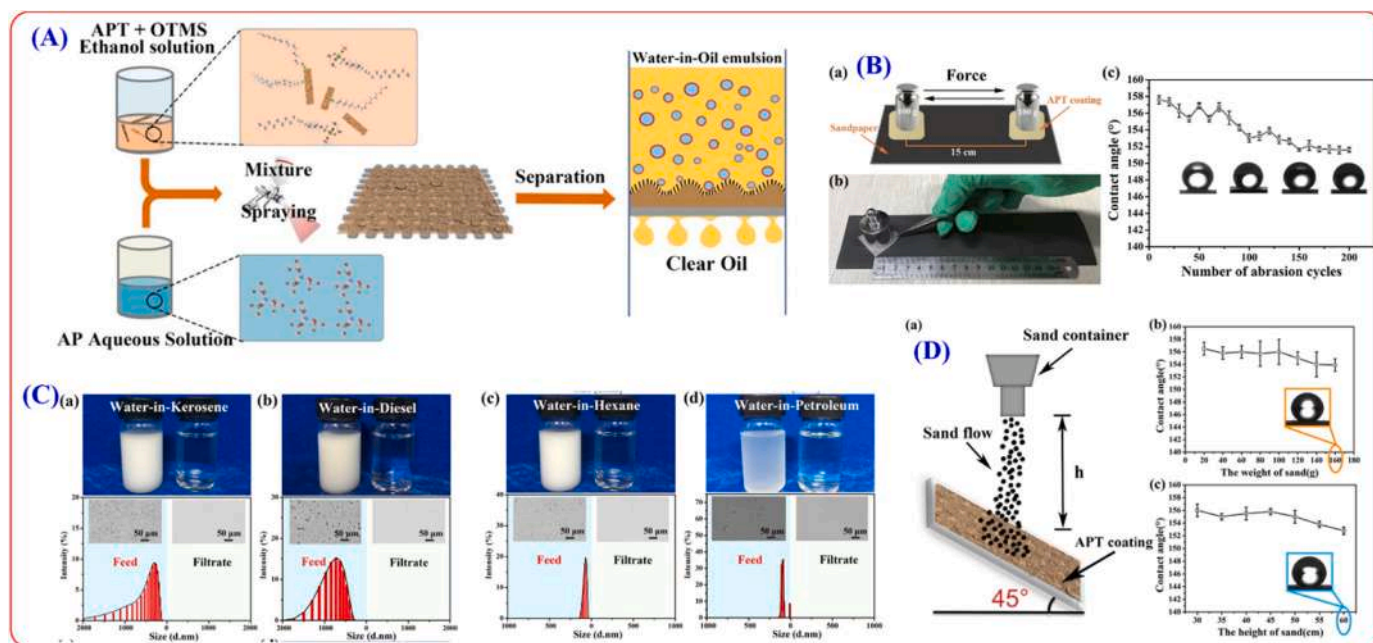


Fig. 6. The experiment process of coating (A), the evolution of mechanical durability (B and D) and the emulsion separation performance (C) of coated mesh [86]. (Copyright 2019, Elsevier. Reproduced with permission from Ref. [86]).

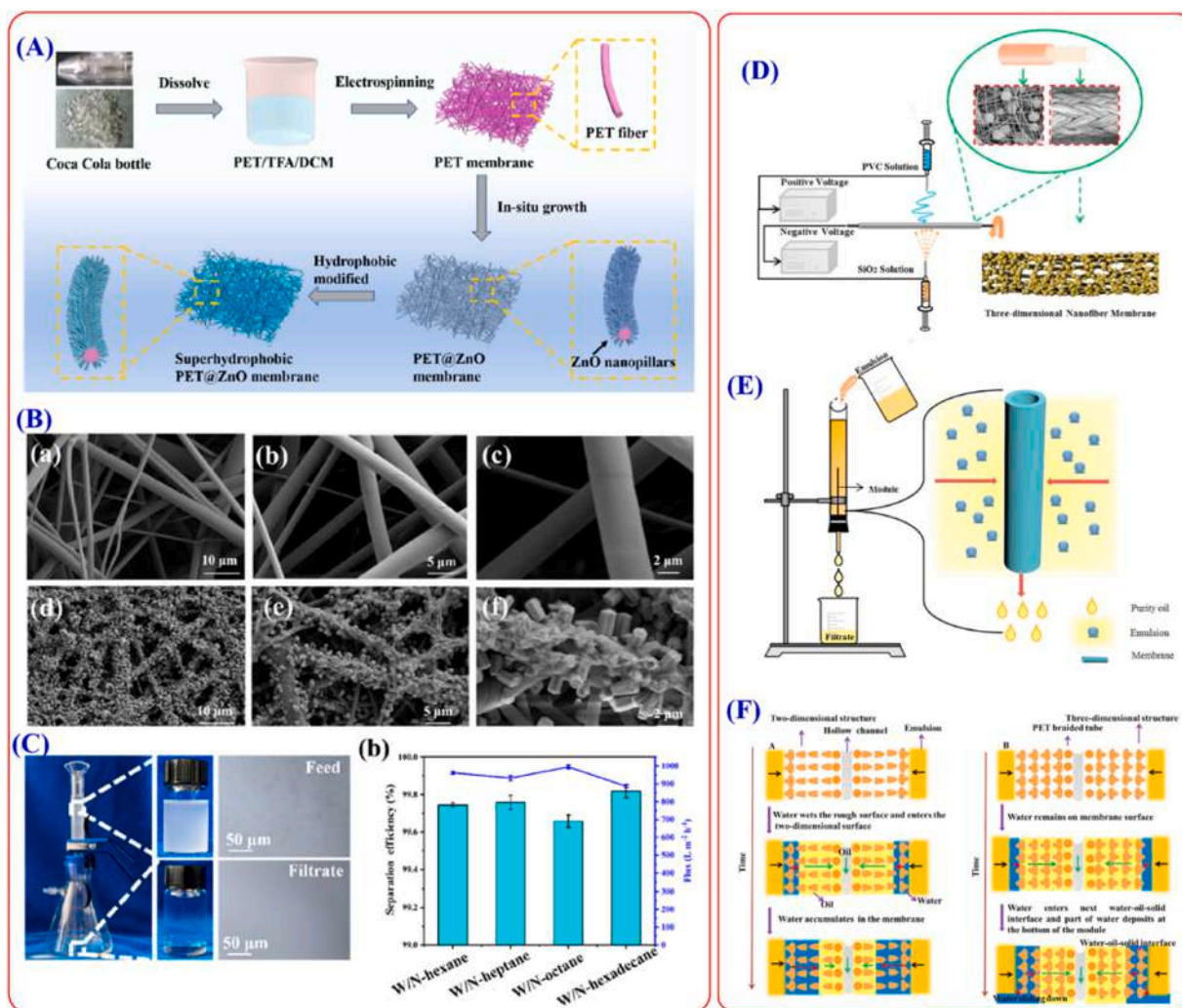


Fig. 7. Schematic of fabrication process of PET membrane (A), SEM images (B) and W/O emulsion separation performance (C) of PET membrane [96]. (Copyright 2022, American Chemical Society. Reproduced with permission from Ref. [96]). Schematic of experimental process of fabrication of PVC/SiO<sub>2</sub> membrane (D), emulsion separation device (E) and wetting behavior of two dimensional and three dimensional membrane (F) [97]. (Copyright 2021, Elsevier. Reproduced with permission from Ref. [97]).

hydrophobic SiO<sub>2</sub> nanoparticles were electrospayed. The as-prepared membrane revealed lipophilicity and under oil superhydrophobicity. Fig. 7E shows the schematic of W/O emulsion separation device. Compared with two dimensional nanofiber membrane, three dimensional nanofiber membranes has fast oil wetting process due to continuous water-oil-solid interface and reduce possibilities of water wetting. After longtime emulsion separation process, the direction of water droplets flow changed from horizontal to vertical, as shown schematically in Fig. 7F.

A nepenthes pitcher plant-inspired slippery liquid-infused porous surfaces (SLIPS) have been designed for emulsion separation [98,99]. Excellent water repellency can be achieved by infusing lubricating oil into the rough micro/nanostructured surface, which enables water drop to slide off. Zhao et al. have developed a slippery liquid-infused membrane for W/O emulsion separation [100]. The hydrophobic trimethoxy (1H,1H,2H,2H-heptadecafluorodecyl) silane (FOTS) functionalized polyethylene terephthalate (PET) membrane with pore size of 4 μm and thickness of 270 μm was infused by oil to obtain a slippery liquid-infused membrane. Such membrane repels water and showed more than 98.6% separation efficiency for low viscous oil-water mixture and more than 99.4% for high viscosity oil-water mixture.

Nevertheless, the emulsion separation research has paid attention to aerogels [101–103], bio-waste materials [104], covalent organic

framework (COF) [105] and metal-organic framework (MOF) membrane [106] in oil-water emulsion separation. Aerogels' unique wettability and 3-D porous structure enables emulsion droplet coalescence and the formation of larger droplets. Apart from this, the framework materials have highly tunable structures and functionalities towards wettability. Table 1 depicts W/O emulsion separation performance of recently developed oil absorbent superwetting porous materials.

### 3.2. Water absorbent superwetting porous materials

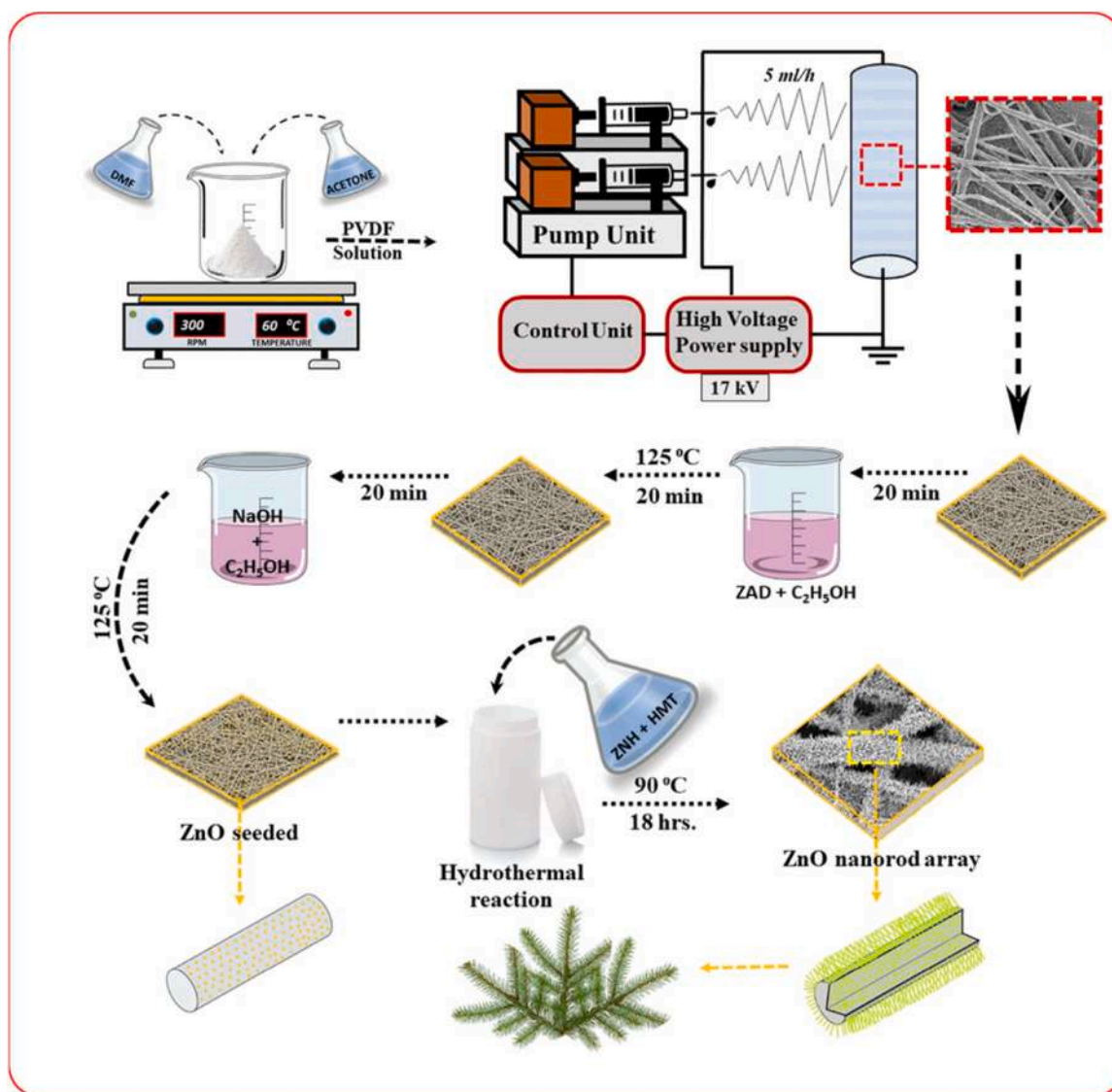
As discussed in the previous section, the reverse wetting property of porous materials towards water and oil makes them superhydrophilic (SHL) and superoleophobic (SOP), which can separate O/W emulsions. The unique hierarchical surface structure and a thin mucus layer on fish skin exhibit SHL/ underwater SOP [116]. To date, many efforts have been made on the design of SHL/underwater SOP porous materials for O/W emulsion separation. Using an in-situ chemical etching method, He et al. have developed a fish scale-like wettability on stainless steel mesh [117]. The vertically grown CuC<sub>2</sub>O<sub>4</sub> nanosheet layer on mesh exhibited high water absorbing ability to firm the water layer into a rough surface and consequently showed superoleophobicity with OCA greater than 150°. A phenomenon of water capturing ability of desert beetle from atmosphere can be adopted to separate O/W emulsion separation by

**Table 1**  
W/O emulsion separation performance of oil absorbent superwetting porous materials.

Materials	Method	flux $L \cdot m^{-2} \cdot h^{-1}$	Separation efficiency (%)	Number of cycles	References
Metal felt, glue and $SiO_2$	Dip	4000	99.7	30	[107]
SSM, Cu NPs, aluminum phosphate and Octadecanethiol	Spray	75	99.975	10	[108]
SSM, copper stearate/ $Fe_3O_4$ Nps	Dip	503	98	10	[109]
SSM, copper (II) chloride, sodium hydroxide, and polyurethane, and n-dodecanethiol	Dip	11.5	99.0	10	[110]
PVDF Membrane	Electro-spinning	88167	99	-	[111]
Carbon Membrane nanotube/poly(vinylidene fluoride-cohexafluoro trimethoxy (1H, 1H, 2H, 2H-heptadecafluorodecyl) silane propylene)	Electro-spinning	632.5	99.9	20	[112]
PET Membrane	Electro-spinning	1100	99.99	40	[113]
PVDF, PMMA, PAN	Electro-spinning	2408	92	5	[114]
SSM, CNFs-PDMS	Vacuum-based filtration	984	-	-	[115]
Copper foam, N-dodecyl mercaptan,	Electro-deposition	6560	99.89	30	[61]

collecting oil droplets from an emulsion. Inspired by the desert beetle back structure, Li et al. have constructed an inverse desert beetle back-like structured membrane for the collection of oil from the emulsion [69]. This membrane consists of oleophilic ZIF-8 bumps and superoleophobic polyacrylonitrile (PAN), that exhibit a similar structure

and opposite wettability that found on desert beetles. The bumps on the material can capture small oil droplets. The process of capturing and demulsifying oil droplets on the surface of ZIF-8 is attributed to both electrostatic attraction and hydrophobic interaction. The positive charge on the surface of ZIF-8 can attract negatively charged oil



**Fig. 8.** Experiment fabrication process of nanofibrous PVDF@ZnO nanorod membrane fabrication [118]. (Copyright 2022, Elsevier. Reproduced with permission from Ref. [118]).



droplets, while the hydrophobic nature of ZIF-8 interacts with the hydrocarbon chains of the oil droplets, which leads to their adsorption. The captured oil droplets form a thin layer on the particle surface; at the same time, further oil droplets get adsorbed and aggregated. With time, size of the oil droplets grows and eventually detach from ZIF-8 particle and these large oil droplets bounce off the superhydrophilic PAN surface. ZIF-8/PAN membrane had showed 99.59% of O/W emulsion separation efficiency.

The electrospinning technique can be adopted to attain randomly oriented nanofibers of polymers that have a high surface-to-volume ratio and form ultrahigh porosity, which leads to a high permeation flux to liquids. The addition of hydrophilic nanomaterials in the membrane makes it best for separating O/W emulsions. Ahmed et al. have hydrothermally decorated ZnO nanorods on PVDF nanofibrous membrane (Fig. 8) [118]. Due to the high surface energy and rough micro-/nano structure of PVDF@ZnO nanorods, water droplets spread on the membrane and form an infused water layer on the surface; consequently, it repels oil. Due to the photocatalytic activity of ZnO, the membrane could easily decompose methyl orange and ciprofloxacin, which are major pollutants in organic dyes and pharmaceutical wastewater. The photocatalytic degradation of organic pollutants (stearic acid) by the membrane was due to the photocatalytic nature of ZnO existing in PVDF membrane. The WCA was measured to confirm photocatalytic degradation and self-cleaning capability. Such membrane exhibited high water flux and separation efficiency of 99% for O/W emulsion and exhibited good chemical stability in acidic, alkaline, hot, and cold surroundings.

In another work, Qing et al. have grown SiO<sub>2</sub> nanoparticles on the PVA nanofibers [119]. The hydrophilic PVA nanofibrous membrane was attained using PVA by electrospinning technique (Fig. 9A). During this process, the average diameter of nanofibers increased (from 460 nm to 770 nm); meanwhile, the pore size slightly decreased ( $532 \pm 3$  nm to  $433 \pm 5$  nm). Such membrane efficiently separated kerosene-in-water emulsion having a droplet size of 1.36  $\mu$ m. Membrane shows high water permeation flux, while n-heptane, kerosene, toluene, and chloroform are strongly repelled (Fig. 9B). Based on practical applications

like wastewater treatment, authors have studied the effect of oil densities on emulsion separation performance. They concluded that the oils have lower densities than water and showed higher permeation flux and good oil rejection than higher-density oils. The oil density is one of the critical factors during the emulsion separation process; the separation of lighter and higher-density oil from water is hypothetically shown in Fig. 9C.

Compared with membrane materials, three dimensional superwetting porous materials are most promising in O/W emulsion separation [120]. Due to high porosity, these materials could collect more oil droplets from emulsion and exhibited high separation efficiency. Recently, Li et al. have prepared phenolic-resin-based sponge composed of entangled nanofibers using phenol, 2-aminobenzimidazole, and CTAB via a simple hydrothermal method [121]. He et al. have prepared a magnetic SHP sponge using Fe<sub>3</sub>O<sub>4</sub> particles and stearic acid through immersion [122]. The magnetic SHP sponge drove magnetically to collect oil from the O/W emulsion, avoiding direct contact with toxic and hazardous solvents. The as-prepared sponge showed more than 90% of separation efficiency, with good chemical resistance (soaking for 7 days) and good mechanical stability against 80 times cyclic compression by 200 g of weight. Table 2 shows the list of recently developed water absorbent superwetting porous materials for O/W emulsion separation.

### 3.3. Demulsification

As discussed in previous sections, superwetting technologies for separating oil-water emulsions have several issues, such as fouling, pore blocking, and inadequate mechanical strength. Therefore, these techniques slightly fail to produce satisfactory results. However, demulsification is a promising method that overcomes the drawbacks of previous methods. Unlike chemical and heating methods, demulsification based on superwetting is fast, inexpensive, and eco-friendly. This method uses the coalescence effect to merge emulsion droplets into larger ones before separating them. Materials with selective wettability capture and coalesce emulsion droplets, forming larger droplets that eventually detach from the surface. Water droplets coalesce readily on a SHL surface, while

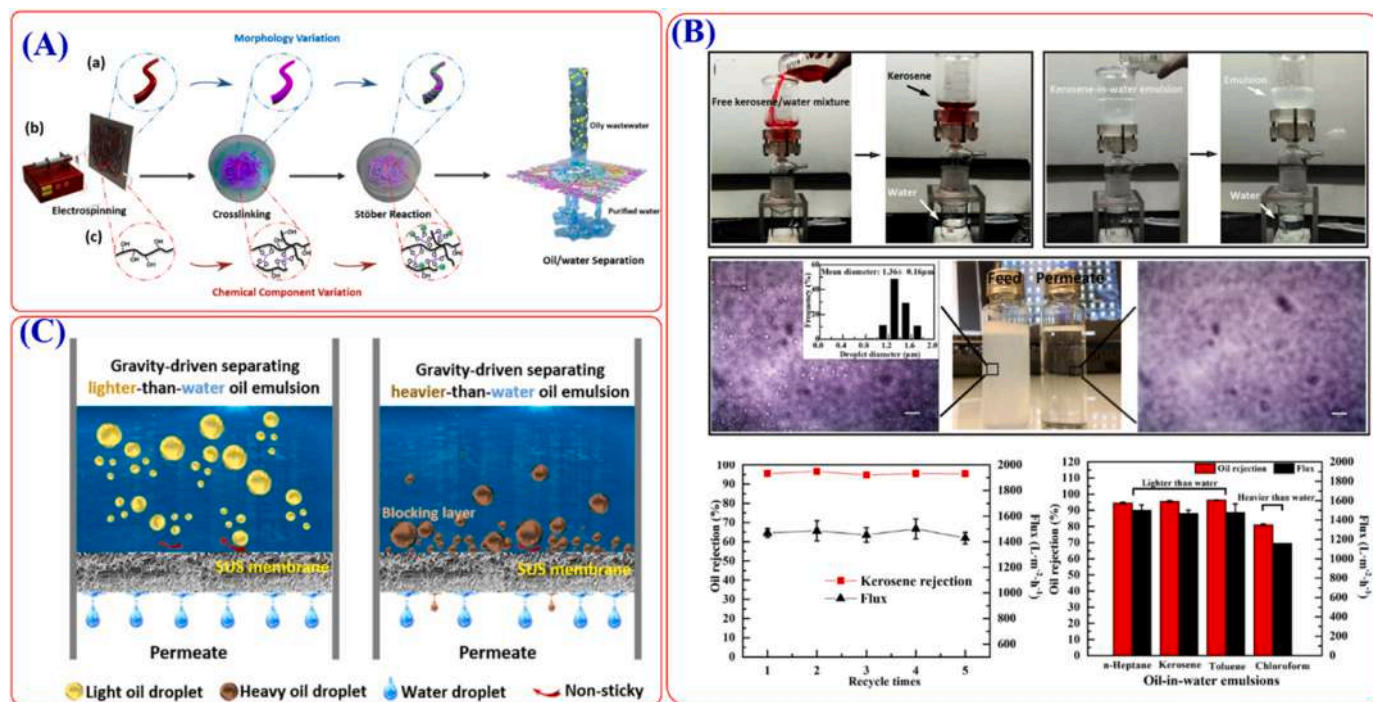


Fig. 9. (A) Schematic representation of experimental procedure and variation of morphology and chemical components during preparation. (B) Oil/water emulsion separation performance of SiO<sub>2</sub>@PVA membrane. (C) Hypothetical illustration of emulsion separation based on different densities of oil in the emulsion [119]. (Copyright 2020, Elsevier. Reproduced with permission from Ref. [119]).

**Table 2**  
O/W emulsion separation performance of water absorbent superwetting porous materials.

Materials	Method	flux $L \cdot m^{-2} \cdot h^{-1}$	Separation efficiency (%)	Number of cycles	References
SSM, polyurethane@graphitic-carbon nitride@perfluorooctanoic acid	Dip coating	50.5	99		[123]
Cellulose acetate membrane, chitosan and $TiO_2$	vacuum-assisted filtration technique	6002.5	97	10	[124]
SSM, $TiO_2$ nanowires	Casting	5859.54	99.1	30	[125]
Glass fibrous membrane, poly (diallyldimethylammonium chloride), $TiO_2$	Dip	2329	94.75		[126]
Wood membrane, sodium hydroxide, sodium sulfite and hydrogen peroxide	Chemical treatment	460.8	99.43	10	[127]
3D cellulose sponge, Row cotton, Zinc chloride, sodium sulfate	Freeze drying	290	99.3	10	[128]

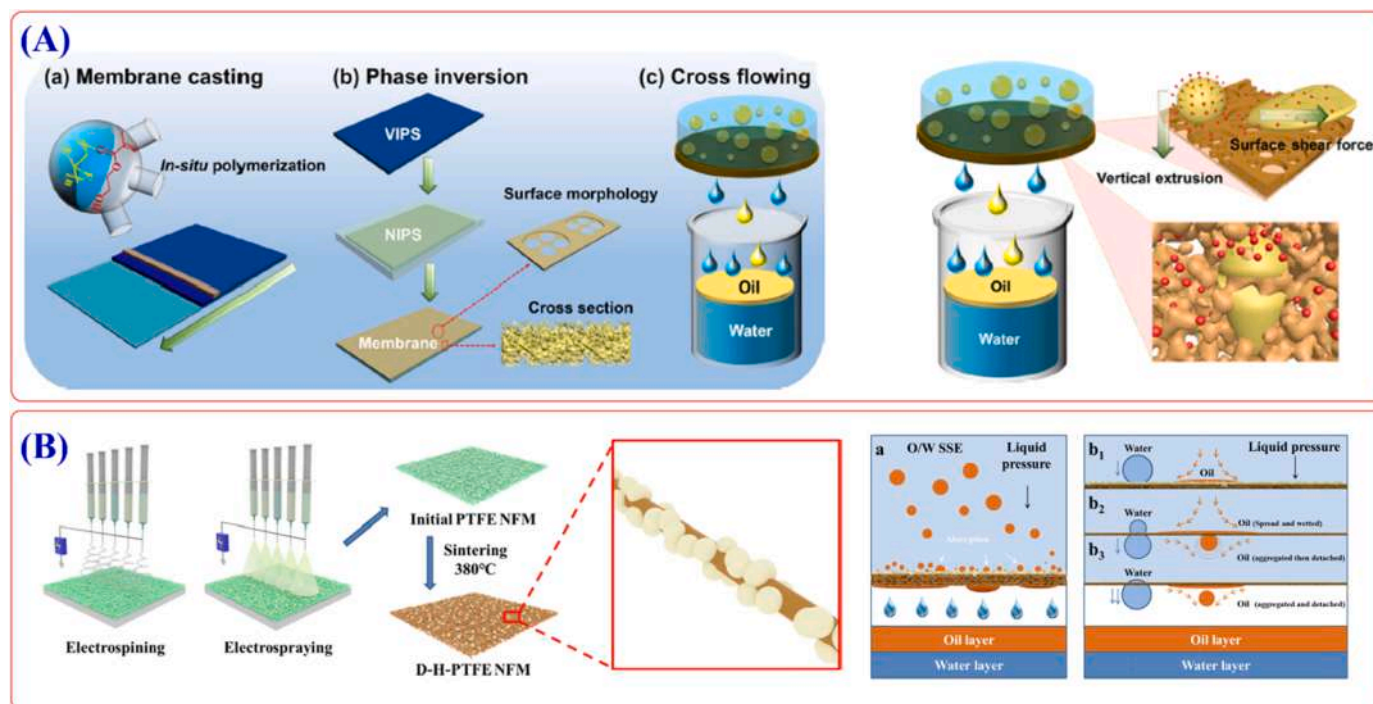
oil droplets coalesce on a SOL surface [129]. Emulsion droplets move toward the surface of the coalescing medium due to hydrodynamic, electric, or other forces and coalesce to form a layered oil/water mixture that can be easily separated. Recently, Wang et al. have developed a PVDF membrane with a dual-scale hyperporous structure that can continuously separate oil-water emulsions by demulsification (Fig. 10A) [130]. The membrane has two layers with different pore sizes: the exterior layer has pores ranging from 0.5 to 2.5  $\mu m$ , while the interior layer has pores ranging from 0.1 to 0.3  $\mu m$ . The membrane revealed a WCA of  $59 \pm 1^\circ$  and an OCA of  $174 \pm 1^\circ$ . It showed a high permeability of  $1078 \pm 50 L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$  and can separate toluene-in-water and D5-in-water emulsions with 99% efficiency under 1.0 bar pressure.

Cao et al. have developed a SHP nanofiber membrane (NFM) made of polytetrafluoroethylene (PTFE) using electrospinning and electro-spraying techniques [131]. The membrane was capable of separating O/W and W/O emulsions through demulsification. The PTFE and polyacrylonitrile (PAN) solution was spun out simultaneously by an electrospinning machine to create the PTFE NFM. Subsequently, the PTFE solution was sprayed onto the NFM using electro-spray, forming microspheres of PTFE, which get attached firmly on the NFM. This NFM was finally sintered at 380  $^\circ C$  for 10 minutes (Fig. 10B). The developed

NFM showed a flux of  $1867.93 L \cdot m^{-2} \cdot h^{-1}$  and a separation rate of 98.46% for W/O emulsions and a flux of  $122 L \cdot m^{-2} \cdot h^{-1}$  and a separation rate of 98.40% for O/W emulsions in multiple cycles. In the demulsification process, oil droplets quickly spread and completely wet the fiber surface, while the water phase flowed through the NFM continuously under pressure. As continuous pressure drove the attached tiny oil droplets to aggregate into larger oil droplets, the aggregated oil droplets would fall off the attaching site, pass through the NFM and seep out from the bottom. However, new oil droplets would attach to the locations where the previous ones were attached, and oil passes through NFM under pressure. The aggregated oil droplets and permeated water form a stable layered oil/water mixture. The demulsification performance is illustrated in Fig. 10B. The comparative survey of the performance of demulsification based on superwetting materials is summarized in Table 3.

### 3.4. Superamphiphilic porous materials

Porous materials which are superamphiphilic in nature can absorb both oil and water, making them useful for separating W/O and O/W emulsions. These materials can change their wettability between



**Fig. 10.** (A) Schematic representation of the membrane fabrication and membrane demulsification process of PVDF membrane [130]. (Copyright 2021, American Chemical Society. Reproduced with permission from Ref. [130]). (B) Schematic illustration of preparing PTFE electrospun NFM and converting O/W emulsion to stratified oil/water mixture through demulsifying tiny oil droplets under pressure [131]. (Copyright 2022, Elsevier. Reproduced with permission from Ref. [131]).

**Table 3**  
Water-in-oil emulsion separation performance based on demulsification.

Materials	Method	flux $L \cdot m^{-2} \cdot h^{-1}$	Separation efficiency (%)	Number of cycles	References
SSM, poly-(N,N-dimethylaminoethyl methacrylate) and poly (divinylbenzene)	Immersion	1200	99.32	10	[132]
Copper mesh, TiO <sub>2</sub>	Immersion	750	99.97	20	[46]
PVA/SiO <sub>2</sub>	Electro-spinning	2398	-	10	[133]
Glass wool, glass fiber and cellulose fiber, thermoplastic polyurethane resin		11,000	99.3		[134]
Cotton fabric, TiO <sub>2</sub> , Silver nitrate, octadecyl trichlorosilane, Melamine sponges, asphaltenes and polyethyleneimine	spray Dip	924.16 15945	98.99 98.7	60 10	[135] [136]

superhydrophobic and superhydrophilic states due to external factors like pH value, temperature, electric field, and light illumination. The selective oil-water emulsion separation was achieved based on these materials.

Using a simple, eco-friendly, and cost-effective electrochemical method, Lei et al. have created a superamphiphilic SSM [137]. The process involved electroplating of the mesh with CuSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solution and then anodic oxidation with NaOH solution. These reactions could change the surface wettability of the mesh to superamphiphilic in nature. The superamphiphilic mesh had over 99% separation efficiency for O/W and W/O emulsions. Additionally, it showed good mechanical resistance against sand impact tests and anti-fouling against reusable experiments. In another work, amphiphilic bamboo powder and PVDF composite foam was successfully used to create underwater superoleophobicity and underoil SHP [138]. The foam was prewetted with water and can repel oil droplets in an O/W emulsion. The unstable oil droplets coalesce with each other and form larger oil droplets on the foam surface. The coalesced larger oil droplets then float towards the water surface from the low adhesion foam surface and form an oil layer. Table 1 gives a comparative survey on the performance of oil-water emulsion separation by recently developed superamphiphilic porous materials. Table 4

#### 4. Challenges in practical applications

The previous sections have covered various methods for separating oil-water emulsions using superwetting porous materials. Though these methods are effective, the short lifespan of these materials limits their use in industrial applications. There are still challenges in real-time applications of superwetting materials for oil-water emulsion separation, such as recyclability, durability, and resistance to fouling. These issues and potential solutions are discussed in detail.

##### 4.1. Recyclability

Superwetting materials can be evaluated for their long-term usability through cyclic separation tests. These materials have a high affinity for

**Table 4**  
Water-oil emulsion separation performance based on superamphiphilic porous materials.

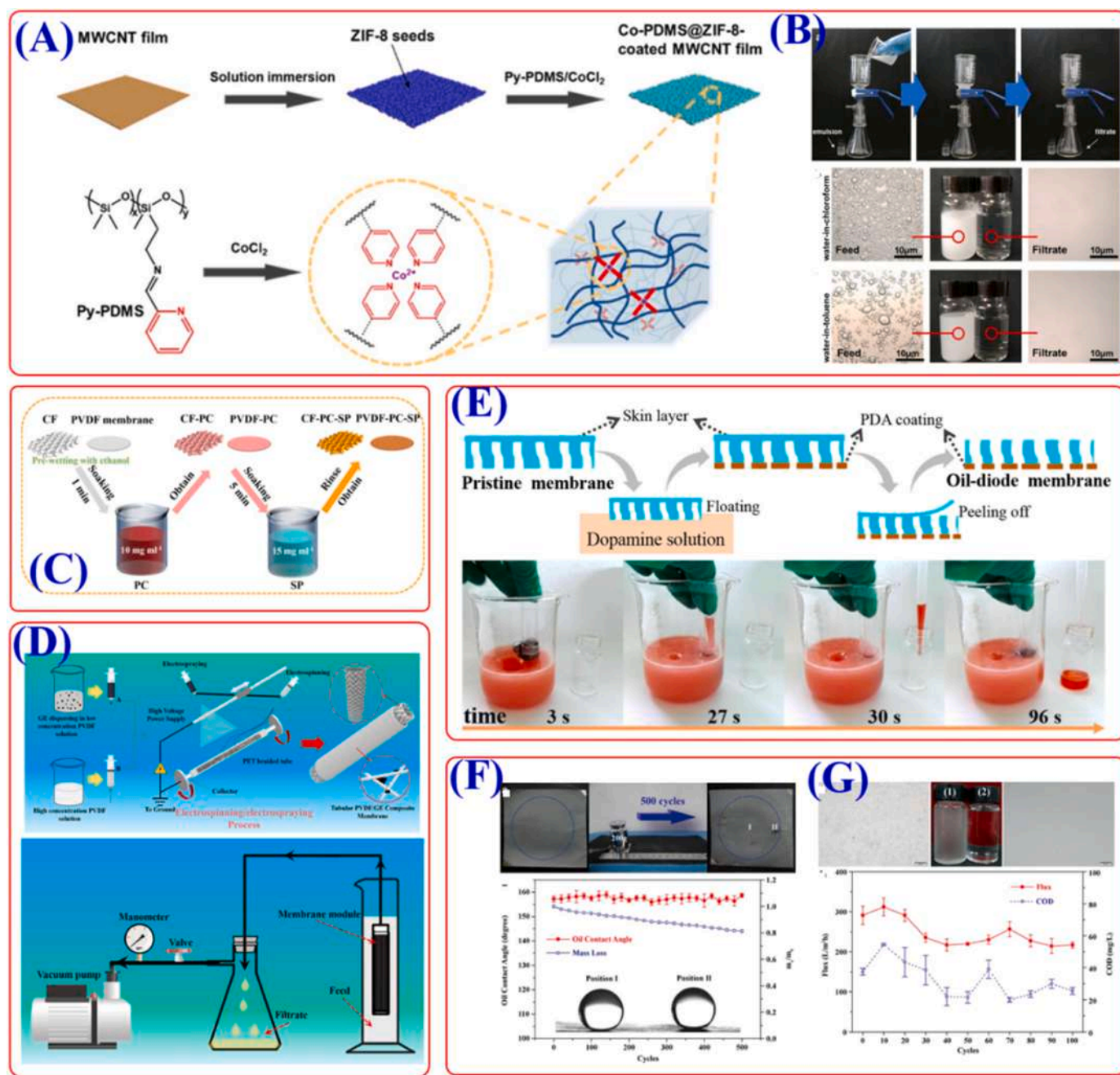
Materials	Method	flux $L \cdot m^{-2} \cdot h^{-1}$	Separation efficiency (%)	Number of cycles	References
SSM, zeolitic imidazolate framework-8/PVA	Immersion	457.6	98.6	10	[139]
Polyurethane/fluorine-modified silica	Electro-spinning	428	99	10	[140]
Candle soot, waterborne polyurethane (PU)	leaching	75	99.9	7	[141]
Poly(N,N-dimethylamino-2-ethyl methacrylate)		-	99.6	-	[142]
Graphene oxide (GO), PVDF	vapor-induced phase separation	-	98	-	[143]
Cellulose diacetate, Sodium hydroxide	Electro-spinning /immersion	38,000	96.9	10	[144]
Polydopamine (PDA)/Cu/Zn, SiO <sub>2</sub> and Zn(OH) <sub>2</sub> nanoparticles	Electro-deposition/dip	115.97	99.91	10	[145]
Nitrocellulose membranes, Dopamine hydrochloride, Tris(hydroxymethyl) aminomethane and polyethylenimine	immersion	1400	99.9	10	[146]

liquids, which quickly get adsorbed. In the continuous wetting process, superwetting surfaces are diminishing. As a result, the separation efficiency and permeation flux decrease. In most of the studies, superwetting porous materials are washed/re-modified after every emulsion separation cycle to maintain permeation flux, which is a hectic process.

For example, Ye et al. have modified multiwalled carbon nanotube film (MWCNT) by zeolitic imidazolate framework (ZIF)-8 and Copolydimethylsiloxane (Co-PDMS) to obtain SHP/SOL membrane (Fig. 11 A-B) [147]. In situ, growth of ZIF-8 formed a micro-/nanolayered structure on the MWCNT and Co-PDMS coating, which provides 0.62  $\mu m$  of average pore size. Four types of W/O emulsions were prepared using chloroform, toluene, xylene and n-hexane with span-80 as an emulsifier. In the recyclability test, an equal amount of emulsion was used for the separation test and the membrane was washed by ethanol during the cyclic interval. Even after ten separation cycles, the separation efficiency (>99.9%) and flux ( $177.6 L \cdot m^{-2} \cdot h^{-1}$ ) remained unaltered. Zhang et al. have fabricated a tubular composite membrane by electrospinning PVDF/graphene (GE) composite into an electrospun PVDF nanofibrous network. The combination of PVDF micro/nanospheres and GE nanosheets with the PVDF nanofibrous network produces a 3D rough composite membrane [148]. A laboratory scale setup was designed to separate W/O emulsions using a vacuum suction process (Fig. 11 D). The separation efficiency of the membrane was up to 99.8%, and it sustained its separation efficiency up to 10 cycles for four types of emulsions, namely, water-in-kerosene (W-K), water-in-toluene (W-T), water-in-chloroform (W-C), and water-in-diesel (W-D). After each cycle, the membrane was washed with ethyl alcohol and dried in the oven for reuse. In conclusion, superwetting porous materials are found promising for oil-water emulsion separation, but need improvement in recyclability for practical applications.

##### 4.2. Mechanical durability

Mechanical durability is one of the important factors of superwetting materials that limit its application in oil-water emulsion separation. The superwetting ability of porous materials is influenced by their surface microstructure. The mechanical contact or continuous oil-water



**Fig. 11.** (A-B) Schematic of the Fabrication of the ZIF-8- and Co-polydimethylsiloxane (PDMS)-Modified MWCNT Films and photographs of the water-in-toluene emulsion separation process [147]. (Copyright 2019, American Chemical Society. Reproduced with permission from Ref. [147]). (C) The fabrication process of the SHL CF-PC-SP and PVDF-PC-SP [149]. (Copyright 2022, Elsevier. Reproduced with permission from Ref. [149]). (D) Schematic illustrating the fabrication process of the tubular PVDF/GE composite membrane and continuous W/O emulsions separation setup [148]. (Copyright 2021, Elsevier. Reproduced with permission from Ref. [148]). (E) Schematic fabrication illustration of oil-diode Janus membrane (JM-O) via the floating coating and peeling off strategy and the snapshots about trapping oil from SDS stabilized toluene-in-water emulsion by a homemade collector capped by the JM-O (the hydrophilic layer faced outward) at one end [150]. (Copyright 2018, Elsevier. Reproduced with permission from Ref. [150]). (F-G) Wetting behavior and separation performance of mesh after abrasion test [151]. (Copyright 2017, American Chemical Society. Reproduced with permission from Ref. [151]).

emulsion separation can damage the micro/nanoscale hierarchical rough architecture, causing the surface to become smoother and lose its superwetting state. Consequently, it fails in oil-water emulsion separation. The mechanical robustness was determined by various mechanical tests such as abrasion, bending, and ultrasonication [152,153]. Therefore, highly robust superwetting porous materials are on demand for practical applications. To address this problem, Liu et al. have produced superwetting coating on a stainless steel mesh by spraying a titanium dioxide (TiO<sub>2</sub>) suspension in combination with aluminum phosphate

(AP) as an adhesive [151]. The mechanical durability of the stainless steel mesh was assessed through a sandpaper abrasion test. The mesh was dragged on sandpaper (grit no. 320) under 200 g weight by an external force for 10 cm and then returned to complete one cycle. Even after 500 sandpaper abrasion cycles, the mesh maintained its superwettability. The as-prepared TiO<sub>2</sub>-AP coated mesh was used to separate three types of O/W emulsions prepared by mixing oil (hexane, petroleum ether, and isooctane) in water. This mesh sustains a separation efficiency of more than 99.98% even after 100 abrasion cycles (Fig. 11

F-G). Additionally, the mesh showed excellent photocatalytic self-cleaning and anti-fouling characteristics against oleic acid and oleic oil, and remained stable up to 100 abrasion cycles. This study demonstrates that combining inorganic adhesives with functional nanomaterials can extend the service life of superwetting materials for practical applications.

#### 4.3. Chemical stability

Surface energy, along with the surface structure of porous materials, plays a significant role in determining the affinity of the surface of a material to oil and water. However, in practical applications, harsh chemical environments such as acidic, alkaline, salty, and organic solvents can destroy specific functional groups that alter the wetting characteristics of superwetting materials. Therefore, developing chemically stable superwetting materials is crucial to maintain their long-term wetting characteristics.

He et al. have fabricated a chemically stable SHP paper for separating W/O emulsions [154]. The polydopamine (PDA) layer was applied on the paper by dipping in PDA solution, followed by dipping in TiO<sub>2</sub> nanoparticles suspension. Finally, the TiO<sub>2</sub>/PDA paper was modified using n-hexane solution of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) to achieve superhydrophobicity. The SHP paper was kept in different solvents, acidic and alkaline solutions for different times to determine its chemical stability. The SHP paper has maintained water contact angles (WCA) of over 158°, even after being immersed in 3.5 wt % NaCl solution, n-hexane, ethanol, and DMF for 60 minutes. When immersed in HCl and NaOH for 120 minutes, the WCAs remained greater than 151°, indicating the high chemical stability of the SHP paper. Besides, SHP TiO<sub>2</sub>/PDA paper showed thermal stability, mechanical durability and high emulsion separation efficiency.

#### 4.4. Fouling resistant

The problem with porous material is that the pore sizes are too small, causing liquid droplets to get stuck and obstruct permeation, leading to fouling. Surfactant-stabilized emulsions can also contain contaminants contributing to fouling [155–160]. Therefore, anti-fouling surfaces must be designed.

Zhang et al. have fabricated anti-oil fouling SHL PVDF membrane for oil-water emulsion separation [149]. The PVDF membrane was first dipped into a proanthocyanidin buffer solution prepared in tris-hydrochloride and then dipped in an aqueous sodium periodate solution. (Fig. 11C). The SHL PVDF membrane showed a maximum flux and efficiency of 108 L·m<sup>-2</sup>·h<sup>-1</sup> and 99.7% under gravity-driven O/W emulsion and under external pressure, it showed 681 L·m<sup>-2</sup>·h<sup>-1</sup> and 99.5%. The flux and efficiency remained the same even after five cycles of separation. The authors also studied the oil-fouling-resistant properties and found that the prepared SHL fabric and membrane had excellent anti-oil-fouling properties.

#### 4.5. Universal strategy

The gravity-driven emulsion separation method is a cost-effective and easy approach that does not require external energy. It is also highly efficient in separation compared with other methods that rely on external pressure. However, it has some limitations when used in large-scale applications or harsh conditions. Hence, the design of superwetting materials needs to be improved significantly to achieve better results.

Yang et al. have developed a Janus oil-unidirectional membrane to separate O/W emulsion [150]. A Janus membrane has a thin hydrophilic layer and a thick hydrophobic layer over hydrophobic PET/PDMS composite porous membrane. The hydrophilic layer was prepared by floating the membrane on dopamine hydrochloride and tris(hydroxymethyl) aminomethane solution, while the other side was glued with adhesive tape. A homemade collector was constructed with a

transparent tube capped by a Janus membrane with a hydrophilic layer towards the emulsion for oil collection. Before collection, the hydrophilic layer was pre-wetted with water, and the hydrophobic layer was wetted with oil. The collector was dipped into the emulsion for oil collection. The fabrication of the Janus membrane and collection of oil is shown in Fig. 11 E.

Sheng et al. have coated the melamine formaldehyde (MF) sponge by iron (III) chloride solution and then modified using PDMS through an immersion technique [161]. The sponge was then loaded into a stainless steel cylinder, where it was compressed to achieve an average pore size of about 45 μm. On a large-scale experiment, the sponge could separate 2 L of 1000 ppm O/W emulsion composed of refined mineral oils with hydrocarbons from C10 to C34 and additives. The separation efficiency reached to 98.8% in 10 minutes and up to 99.8% in 30 minutes. The O/W emulsion separator and separation result is shown in Fig. 12 (A-B). This ultrahigh efficiency makes it ideal for decanting applications, where recovered water on a temporary storage device may be decanted if the total petroleum hydrocarbons are below a specific amount, for example, 15 ppm. The sponge also exhibited long-term robustness, remained stable for up to 10 cycles, and separated 40 L of emulsion.

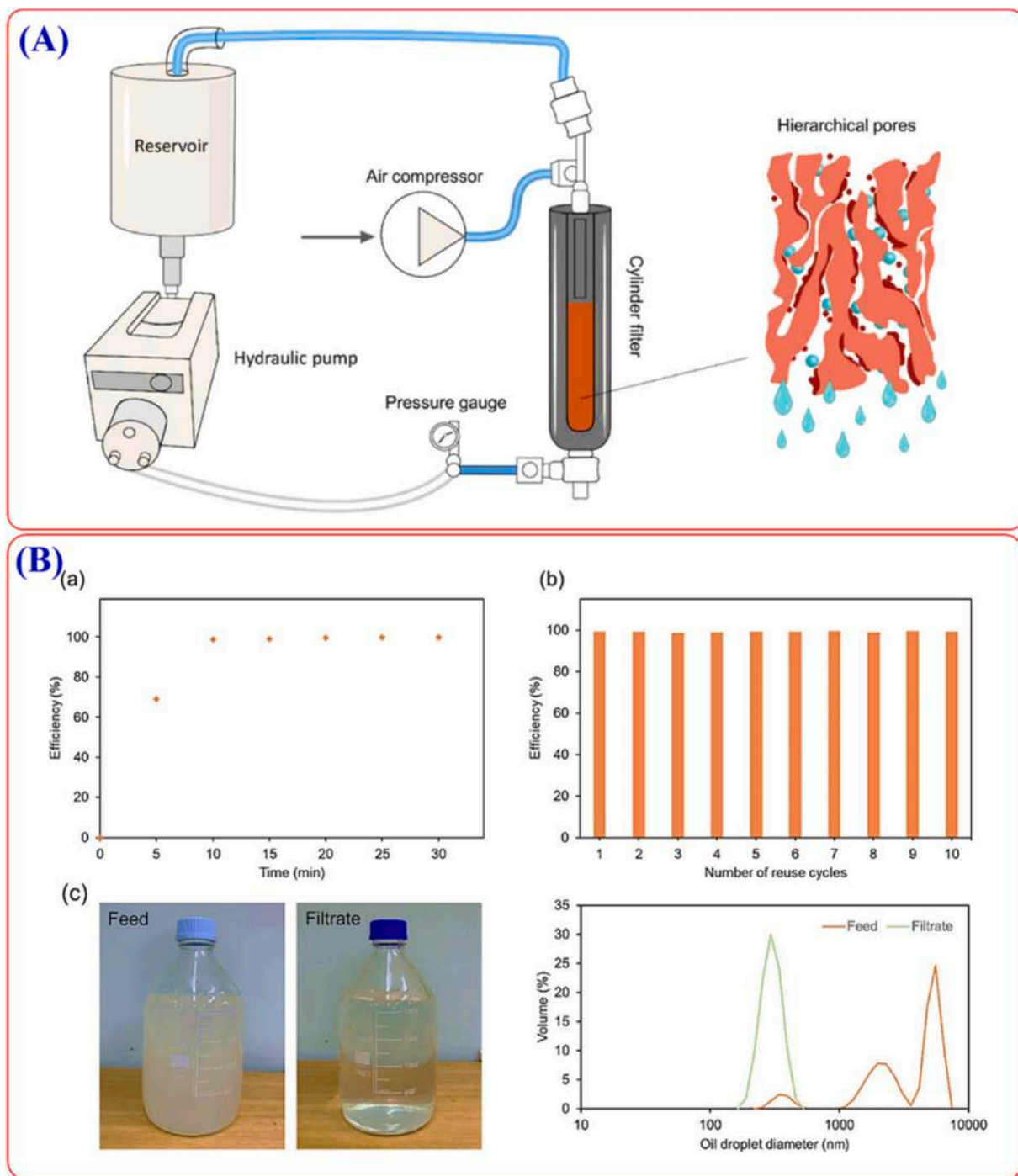
Tuteja et al. have used the dip coating technique to create SHL and underwater SOP porous membranes for continuous oil-water emulsion separation [162]. The porous substrates, including stainless steel, polyester fabric, and filter paper, were first coated with hydrophilic poly(ethylene glycol) diacrylate (PEGDA) and then modified with low surface energy material 1H, 1H, 2H, 2H - Heptadecafluorodecyl polyhedral oligomeric silsequioxane (F-POSS). The PEGDA-coated substrate exhibited HL/OL; while coated with (F - POSS), the surface becomes SHL/SOP. They used a gravity-assisted capillary force-driven separation (CFDS) device consisting of a membrane sandwiched between two vertical glass tubes to separate O/W emulsion and W/O emulsion. The membrane showed continuous separation of both types of emulsion for over 24 hours with self-cleaning and fouling-resistance ability. This work was registered under United States Patent in 2019.

## 5. Conclusions and future perspectives

The challenge of separating oil-water emulsions is a global concern. The use of superwetting porous material provides a promising solution to address this challenge. The superwettability and pores of materials are crucial in separating oil-water emulsions. This review presented the latest advancement in fabricating superwetting porous materials that can effectively separate oil-water emulsions with ease. The SHP/SOL and SHL/underwater SOP surfaces are used to separate W/O and O/W emulsions, respectively. Several factors, such as separation effectiveness, flux rate, antifouling, reusability, physical stability and chemical stability have proven that superwetting porous material is an excellent candidate for emulsion separation. However, there is limited literature on the practical application of separating oil-water emulsions using superwetting porous materials. The practical products are expected to be cost-effective, optimum separation efficiency, switchable wettability, multifunctional features, multiple reusabilities, and easy fabrication processes for smart superwetting porous materials and operation.

The future perspectives of superwetting materials for oil-water emulsion separation are outlined and graphically represented (Fig. 13),

- 1) The superwetting porous materials at the lab scale showed excellent oil-water emulsion separation ability. For real-life use, it is necessary to produce them in an environmentally friendly and scalable manner. For large-scale application of superwetting porous materials for oil-water emulsion separation, it's essential to simplify the synthesis process and reduce preparation costs.
- 2) Gravity-driven oil-water emulsion separation is fascinating field that expands the application of superwetting porous materials. Additionally, chemically stable, anti-fouling and robust superwetting



**Fig. 12.** (A) Schematic of an O/W emulsion separator with an HCP sorbent filter. (B) O/W separation efficiency of MF-HCP-PDMS as a function of (a) time and (b) number of reuse cycles. (c) Picture of before and after emulsion separation and the size distribution of emulsions in the feed (average 3.6  $\mu\text{m}$ ) and filtrate (average 0.35  $\mu\text{m}$ ) [161]. (Copyright 2022, American Chemical Society. Reproduced with permission from Ref. [161]).

porous materials should be extended their application in oil-water emulsion separation.

- 3) The phenomenon of superwetting occurs at the liquid-solid interface, and surface structure can be easily damaged by repeated separation, fouling, surface contamination (microorganisms, inorganic salts, and dyes), and physical and chemical contact. To address these challenges, a multifunctional surface that is self-cleaning, self-repairing, and photocatalytic must be designed.
- 4) Until now, most superwetting materials have effectively separated low-viscosity oil-water emulsions. They often fail to separate highly viscous oil and oily wastewater. It is crucial to enhance

demulsification technologies by combining selective pore size and wettability of porous materials to separate high-viscosity oil-water emulsions effectively.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

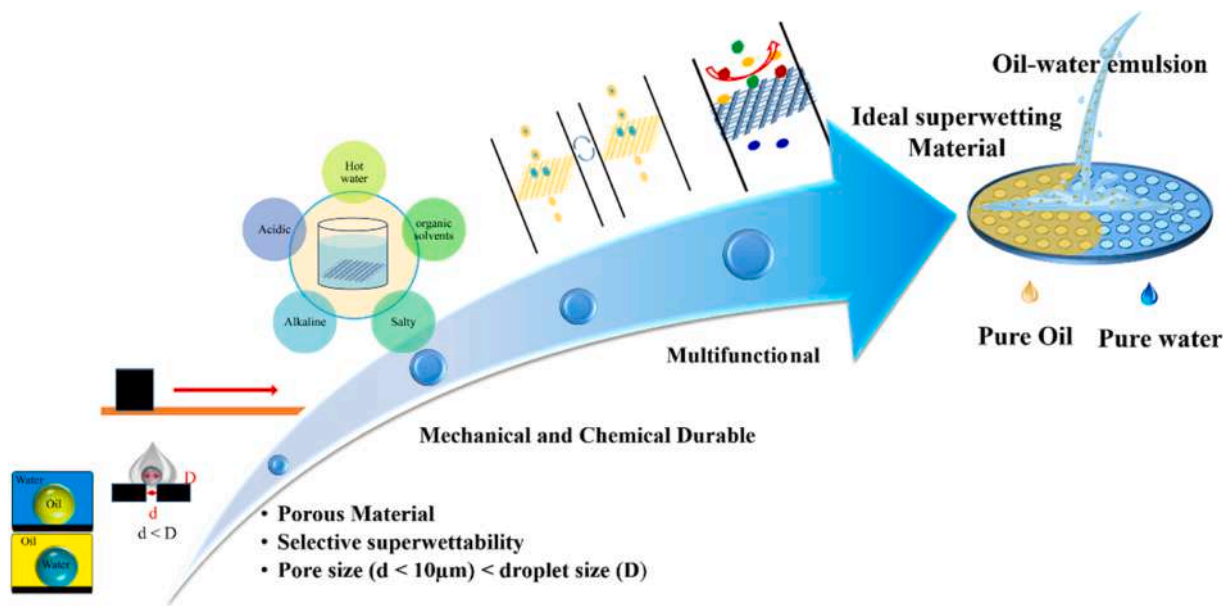


Fig. 13. Future outlook of porous superwetting materials for smart oil-water emulsion separation.

#### Data Availability

No data was used for the research described in the article.

#### Acknowledgments

We greatly appreciate the support of the National Natural Science Foundation of China (21950410531) and the support of the Petro-China Research Institute of Petroleum Exploration & Development (RIPED-2019-CL-186).

#### References

- [1] D. Ashton, M. Hilton, K. Thomas, Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom, *Sci. Total Environ.* 333 (1–3) (2004) 167–184.
- [2] T.J. Crone, M. Tolstoy, Magnitude of the 2010 Gulf of Mexico oil leak, *Science* 330 (2010), 634–634.
- [3] T. Dalton, D. Jin, Extent and frequency of vessel oil spills in US marine protected areas, *Mar. Pollut. Bull.* 60 (11) (2010) 1939–1945.
- [4] B. Dubansky, A. Whitehead, J.T. Miller, C.D. Rice, F. Galvez, Multitissue molecular, genomic, and developmental effects of the Deepwater Horizon oil spill on resident Gulf killifish (*Fundulus grandis*), *Environ. Sci. Technol.* 47 (10) (2013) 5074–5082.
- [5] J. Schaum, M. Cohen, S. Perry, R. Artz, R. Draxler, J.B. Frithsen, D. Heist, M. Lorber, L. Phillips, Screening level assessment of risks due to dioxin emissions from burning oil from the BP Deepwater Horizon Gulf of Mexico spill, *Environ. Sci. Technol.* 44 (24) (2010) 9383–9389.
- [6] M. Schroppe, Deep wounds, *Nature* 472 (2011) 152.
- [7] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A. M. Mayes, Science and technology for water purification in the coming decades, *Nature* 452 (2008) 301–310.
- [8] A. Galieriková, M. Materna, World seaborne trade with oil: One of main cause for oil spills? *Transp. Res. Procedia* 44 (2020) 297–304.
- [9] E.T. Igunnu, G.Z. Chen, Produced water treatment technologies, *Int. J. Low-Carbon Technol.* 9 (3) (2014) 157–177.
- [10] M. Lee, J.Y. Jung, Pollution risk assessment of oil spill accidents in Garorim Bay of Korea, *Mar. Pollut. Bull.* 100 (1) (2015) 297–303.
- [11] M.G. Barron, D.N. Vivian, R.A. Heintz, U.H. Yim, Long-term ecological impacts from oil spills: comparison of Exxon Valdez, Hebei Spirit, and Deepwater Horizon, *Environ. Sci. Technol.* 54 (11) (2020) 6456–6467.
- [12] M. Kammerer, O. Mastain, S. Le Dréan-Queñec'h du, H. Pouliquen, M. Larhantec, Liver and kidney concentrations of vanadium in oiled seabirds after the Erika wreck, *Sci. Total Environ.* 333 (1–3) (2004) 295–301.
- [13] M.D. King, J.E. Elliott, T.D. Williams, Effects of petroleum exposure on birds: a review, *Sci. Total Environ.* 755 (2021), 142834.
- [14] G. Prasad, M. Anuprakash, Pollution due to oil spills in marine environment and control measures, *J. Environ. Sci., Toxicol. Food Technol.* 10 (2016) 01–08.
- [15] I.F. Guha, K.K. Varanasi, Separating nanoscale emulsions: progress and challenges to date, *Curr. Opin. Colloid Interface Sci.* 36 (2018) 110–117.
- [16] W. Zhang, N. Liu, Y. Cao, X. Lin, Y. Liu, L. Feng, Superwetting porous materials for wastewater treatment: from immiscible oil/water mixture to emulsion separation, *Adv. Mater. Interfaces* 4 (10) (2017), 1600029.
- [17] E.R. Binner, J.P. Robinson, S.W. Kingman, E.H. Lester, B.J. Azzopardi, G. Dimitrakis, J. Briggs, Separation of oil/water emulsions in continuous flow using microwave heating, *Energy Fuels* 27 (6) (2013) 3173–3178.
- [18] M. Sato, I. Sumita, Experiments on gravitational phase separation of binary immiscible fluids, *J. Fluid Mech.* 591 (2007) 289–319.
- [19] H. Gong, W. Li, X. Zhang, Y. Peng, B. Yu, Y. Mou, Simulation of the coalescence and breakup of water-in-oil emulsion in a separation device strengthened by coupling electric and swirling centrifugal fields, *Sep. Purif. Technol.* 238 (2020), 116397.
- [20] A. Al-Shamrani, A. James, H. Xiao, Separation of oil from water by dissolved air flotation, *Colloids Surf. A: Physicochem. Eng. Asp.* 209 (1) (2002) 15–26.
- [21] D. Ge, L. Yang, C. Wang, E. Lee, Y. Zhang, S. Yang, A multi-functional oil–water separator from a selectively pre-wetted superamphiphobic paper, *Chem. Commun.* 51 (28) (2015) 6149–6152.
- [22] J. Križan Milić, A. Murić, I. Petriñić, M. Simonič, Recent developments in membrane treatment of spent cutting-oils: a review, *Ind. Eng. Chem. Res.* 52 (23) (2013) 7603–7616.
- [23] G. Wang, Y. He, H. Wang, L. Zhang, Q. Yu, S. Peng, X. Wu, T. Ren, Z. Zeng, Q. Xue, A cellulose sponge with robust superhydrophilicity and under-water superoleophobicity for highly effective oil/water separation, *Green. Chem.* 17 (5) (2015) 3093–3099.
- [24] X. Feng, L. Jiang, Design and creation of superwetting/antiwetting surfaces, *Adv. Mater.* 18 (23) (2006) 3063–3078.
- [25] C. Neinhuis, W. Barthlott, Characterization and distribution of water-repellent, self-cleaning plant surfaces, *Ann. Bot.* 79 (6) (1997) 667–677.
- [26] M. Liu, S. Wang, Z. Wei, Y. Song, L. Jiang, Bioinspired design of a superoleophobic and low adhesive water/solid interface, *Adv. Mater.* 21 (6) (2009) 665–669.
- [27] S.S. Latthe, V.S. Kodag, R.S. Sutar, A.K. Bhosale, S. Nagappan, C.S. Ha, K. K. Sadasivuni, S.R. Kulal, S. Liu, R. Xing, Sawdust-based superhydrophobic pellets for efficient oil-water separation, *Mater. Chem. Phys.* 243 (2020), 122634.
- [28] S.S. Latthe, R.S. Sutar, T.B. Shinde, S.B. Pawar, T.M. Khot, A.K. Bhosale, K. K. Sadasivuni, R. Xing, L. Mao, S. Liu, Superhydrophobic leaf mesh decorated with SiO<sub>2</sub> nanoparticle–polystyrene nanocomposite for oil–water separation, *ACS Appl. Nano Mater.* 2 (2) (2019) 799–805.
- [29] S. Liu, Q. Xu, S.S. Latthe, A.B. Gurav, R. Xing, Superhydrophobic/superoleophilic magnetic polyurethane sponge for oil/water separation, *Rsc Adv.* 5 (84) (2015) 68293–68298.
- [30] I. Prasanthi, B.R. Bora, K. Raidongia, K.K.R. Datta, Fluorinated graphene nanosheet supported halloysite nanoarchitectonics: super-wetting coatings for efficient and recyclable oil sorption, *Sep. Purif. Technol.* 301 (2022), 122049.
- [31] S.P. Dalawai, M.A.S. Aly, S.S. Latthe, R. Xing, R.S. Sutar, S. Nagappan, C.S. Ha, K. K. Sadasivuni, S. Liu, Recent advances in durability of superhydrophobic self-cleaning technology: a critical review, *Prog. Org. Coat.* 138 (2020), 105381.
- [32] M. Shahid, S. Maiti, R.V. Adivarekar, S. Liu, Biomaterial based fabrication of superhydrophobic textiles—a review, *Mater. Today Chem.* 24 (2022), 100940.
- [33] Y. Si, Z. Dong, L. Jiang, Bioinspired designs of superhydrophobic and superhydrophilic materials, *ACS Cent. Sci.* 4 (9) (2018) 1102–1112.
- [34] S. Wang, K. Liu, X. Yao, L. Jiang, Bioinspired surfaces with superwettability: new insight on theory, design, and applications, *Chem. Rev.* 115 (16) (2015) 8230–8293.

- [35] W. Zhang, Y. Liu, F. Tao, Y. An, Y. Zhong, Z. Liu, Z. Hu, X. Zhang, X. Wang, An overview of biomass-based Oil/Water separation materials, *Sep. Purif. Technol.* (2023), 123767.
- [36] S.S. Latthe, R.S. Sutar, V.S. Kodag, A.K. Bhosale, A.M. Kumar, K.K. Sadasivuni, R. Xing, S. Liu, Self-cleaning superhydrophobic coatings: potential industrial applications, *Prog. Org. Coat.* 128 (2019) 52–58.
- [37] S.S. Latthe, R.S. Sutar, A.K. Bhosale, S. Nagappan, C.S. Ha, K.K. Sadasivuni, S. Liu, R. Xing, Recent developments in air-trapped superhydrophobic and liquid-infused slippery surfaces for anti-icing application, *Prog. Org. Coat.* 137 (2019), 105373.
- [38] Z. Li, Z. Guo, Bioinspired surfaces with wettability for antifouling application, *Nanoscale* 11 (47) (2019) 22636–22663.
- [39] C. Zhang, F. Liang, W. Zhang, H. Liu, M. Ge, Y. Zhang, J. Dai, H. Wang, G. Xing, Y. Lai, Y. Tang, Constructing mechanochemical durable and self-healing superhydrophobic surfaces, *ACS Omega* 5 (2) (2020) 986–994.
- [40] S.S. Latthe, P. Sudhagar, A. Devadoss, A.M. Kumar, S. Liu, C. Terashima, K. Nakata, A. Fujishima, A mechanically bendable superhydrophobic steel surface with self-cleaning and corrosion-resistant properties, *J. Mater. Chem. A* 3 (27) (2015) 14263–14271.
- [41] J. Cui, F. Li, Y. Wang, Q. Zhang, W. Ma, C. Huang, Electrospun nanofiber membranes for wastewater treatment applications, *Sep. Purif. Technol.* 250 (2020), 117116.
- [42] R.S. Sutar, S.S. Latthe, N.B. Garge, P.P. Gaikwad, A.R. Jundle, S.S. Ingole, R. A. Ekunde, S. Nagappan, K.H. Park, A.K. Bhosale, S. Liu, Facile approach to fabricate a high-performance superhydrophobic PS/OTS modified SS mesh for oil-water separation, *Colloids Surf. A: Physicochem. Eng. Asp.* 657 (2023), 130561.
- [43] M. Wang, Z. Xu, Y. Hou, P. Li, H. Sun, Q.J. Niu, Fabrication of a superhydrophilic PVDF membrane with excellent chemical and mechanical stability for highly efficient emulsion separation, *Sep. Purif. Technol.* 251 (2020), 117408.
- [44] W. Ma, Q. Zhang, D. Hua, R. Xiong, J. Zhao, W. Rao, S. Huang, X. Zhan, F. Chen, C. Huang, Electrospun fibers for oil-water separation, *Rsc Adv.* 6 (16) (2016) 12868–12884.
- [45] Y. Jin, L. Huang, K. Zheng, S. Zhou, Blending electrostatic spinning fabrication of superhydrophilic/underwater superoleophobic polysulfonamide/polyvinylpyrrolidone nanofibrous membranes for efficient oil-water emulsion separation, *Langmuir* 38 (27) (2022) 8241–8251.
- [46] X. Lin, Y. Chen, N. Liu, Y. Cao, L. Xu, W. Zhang, L. Feng, In situ ultrafast separation and purification of oil/water emulsions by superwetting TiO<sub>2</sub> nanocluster-based mesh, *Nanoscale* 8 (16) (2016) 8525–8529.
- [47] L. Qiu, J. Zhang, Z. Guo, W. Liu, Asymmetric superwetting stainless steel meshes for on-demand and highly effective oil-water emulsion separation, *Sep. Purif. Technol.* 273 (2021), 118994.
- [48] C.F. Wang, S.Y. Yang, S.W. Kuo, Eco-friendly superwetting material for highly effective separations of oil/water mixtures and oil-in-water emulsions, *Sci. Rep.* 7 (1) (2017) 1–9.
- [49] U. Baig, M. Faizan, M. Dastageer, Polyimide based super-wettable membranes/materials for high performance oil/water mixture and emulsion separation: A review, *Adv. Colloid Interface Sci.* 297 (2021), 102525.
- [50] Y. Cai, S.Q. Shi, Z. Fang, J. Li, Design, development, and outlook of superwettability membranes in oil/water emulsions separation, *Adv. Mater. Interfaces* 8 (18) (2021), 2100799.
- [51] F. Esmaelion, H. Tavanai, A.A.M. Beigi, M. Bazarganipour, Application of fibrous structures in separation of water and oil emulsions: a review, *J. Environ. Chem. Eng.* (2022), 107999.
- [52] Y. Si, Z. Guo, Superwetting materials of oil-water emulsion separation, *Chem. Lett.* 44 (7) (2015) 874–883.
- [53] J. Yong, J. Huo, F. Chen, Q. Yang, X. Hou, Oil/water separation based on natural materials with super-wettability: recent advances, *Phys. Chem. Chem. Phys.* 20 (39) (2018) 25140–25163.
- [54] N. Zhang, X. Yang, Y. Wang, Y. Qi, Y. Zhang, J. Luo, P. Cui, W. Jiang, A review on oil/water emulsion separation membrane material, *J. Environ. Chem. Eng.* (2022), 107257.
- [55] Q. Zhu, Y. Pan, X. Jia, J. Li, M. Zhang, L. Yin, Review on the stability mechanism and application of water-in-oil emulsions encapsulating various additives, *Compr. Rev. Food Sci. Food Saf.* 18 (6) (2019) 1660–1675.
- [56] S. Kokal, Crude-oil emulsions: a state-of-the-art review, *SPE Prod. Facil.* 20 (01) (2005) 5–13.
- [57] M. Zembyla, B.S. Murray, A. Sarkar, Water-in-oil emulsions stabilized by surfactants, biopolymers and/or particles: a review, *Trends Food Sci. Technol.* 104 (2020) 49–59.
- [58] J. Gu, P. Xiao, J. Chen, F. Liu, Y. Huang, G. Li, J. Zhang, T. Chen, Robust preparation of superhydrophobic polymer/carbon nanotube hybrid membranes for highly effective removal of oils and separation of water-in-oil emulsions, *J. Mater. Chem. A* 2 (37) (2014) 15268–15272.
- [59] A. Raza, B. Ding, G. Zainab, M. El-Newehy, S.S. Al-Deyab, J. Yu, In situ cross-linked superwetting nanofibrous membranes for ultrafast oil-water separation, *J. Mater. Chem. A* 2 (26) (2014) 10137–10145.
- [60] X. Chen, Y. Li, L. Xu, D. Zhang, Y. Guan, L. Dong, M. Bao, Z. Wang, Thermosensitive microfibril cellulose/MnO<sub>2</sub> membrane: dual network structure, photothermal smart modulation for switchable emulsion separation, *ACS Sustain. Chem. Eng.* (2023).
- [61] Z. Wang, C. Xiao, Z. Wu, Y. Wang, X. Du, W. Kong, D. Pan, G. Guan, X. Hao, A novel 3D porous modified material with cage-like structure: fabrication and its demulsification effect for efficient oil/water separation, *J. Mater. Chem. A* 5 (12) (2017) 5895–5904.
- [62] Y. Zhu, W. Xie, F. Zhang, T. Xing, J. Jin, Superhydrophilic in-situ-cross-linked zwitterionic polyelectrolyte/PVDF-blend membrane for highly efficient oil/water emulsion separation, *ACS Appl. Mater. Interfaces* 9 (11) (2017) 9603–9613.
- [63] Y. Cao, Y. Chen, N. Liu, X. Lin, L. Feng, Y. Wei, Mussel-inspired chemistry and Stöber method for highly stabilized water-in-oil emulsions separation, *J. Mater. Chem. A* 2 (48) (2014) 20439–20443.
- [64] D.D. Ejeta, F.H. Tan, A. Mathivathanan, T.Y. Juang, M.M. Abu-Omar, C.F. Wang, C.H. Lin, J.Y. Lai, Preparation of fluorine-and nanoparticle-free superwetting polybenzoxazine/cellulose composites for efficient oil/water separations, *Sep. Purif. Technol.* 288 (2022), 120675.
- [65] T. Zhang, C. Zhang, G. Zhao, C. Li, L. Liu, J. Yu, F. Jiao, Electrospun composite membrane with superhydrophobic-superoleophilic for efficient water-in-oil emulsion separation and oil adsorption, *Colloids Surf. A: Physicochem. Eng. Asp.* 602 (2020), 125158.
- [66] J. Zhu, L. Li, L. Han, M. Dong, Z. Zeng, L. Sun, Mask waste: a sustainable mask-based epoxy Resin/SiO<sub>2</sub> composite for efficient purification of water-in-oil emulsions, *ACS Appl. Polym. Mater.* 4 (7) (2022) 5180–5188.
- [67] H. Liu, J. Huang, Z. Chen, G. Chen, K.Q. Zhang, S.S. Al-Deyab, Y. Lai, Robust translucent superhydrophobic PDMS/PMMA film by facile one-step spray for self-cleaning and efficient emulsion separation, *Chem. Eng. J.* 330 (2017) 26–35.
- [68] W. Liu, M. Cui, Y. Shen, P. Mu, Y. Yang, J. Li, Efficient separation of crude oil-in-water emulsion based on a robust underwater superoleophilic titanium dioxide-coated mesh, *N. J. Chem.* 44 (7) (2020) 2705–2713.
- [69] H. Li, P. Mu, J. Li, Q. Wang, Inverse desert beetle-like ZIF-8/PAN composite nanofibrous membrane for highly efficient separation of oil-in-water emulsions, *J. Mater. Chem. A* 9 (7) (2021) 4167–4175.
- [70] H. Shi, Y. He, Y. Pan, H. Di, G. Zeng, L. Zhang, C. Zhang, A modified mussel-inspired method to fabricate TiO<sub>2</sub> decorated superhydrophilic PVDF membrane for oil/water separation, *J. Membr. Sci.* 506 (2016) 60–70.
- [71] Y. Zhao, X. Yang, L. Yan, Y. Bai, S. Li, P. Sorokin, L. Shao, Biomimetic nanoparticle-engineered superwettability membranes for efficient oil/water separation, *J. Membr. Sci.* 618 (2021), 118525.
- [72] X. Zeng, Y. Shen, Y. Liu, J. Du, L. Chen, W. Zhou, H. Yang, J. Zuo, C. Zhou, J. Lin, A cross-linked coating decorated mesh prepared by brush-painting method for oil-in-water emulsions separation, *Mater. Chem. Phys.* 242 (2020), 122541.
- [73] J. Zuo, Y. Zhou, Z. Chen, T. Zhao, Q. Tan, C. Zhou, X. Zeng, S. Xu, J. Cheng, X. Wen, A superwetting stainless steel mesh with Janus surface charges for efficient emulsion separation, *J. Hazard. Mater.* 430 (2022), 128378.
- [74] M. Cao, Y. Chen, X. Huang, L. Sun, J. Xu, K. Yang, X. Zhao, L. Lin, Construction of PA6-rGO nanofiber membrane via electrospinning combining electrospinning processes for emulsified oily sewage purification, *J. Taiwan Inst. Chem. Eng.* 118 (2021) 232–244.
- [75] F. Ebrahimi, S.R. Nabavi, A. Omrani, Fabrication of hydrophilic special sandwich structure of PAN/GO/SiO<sub>2</sub> electrospun membrane decorated with SiO<sub>2</sub> nanoparticles for oil/water separation, *J. Water Process Eng.* 48 (2022), 102926.
- [76] Y. Zhao, J. Guo, Y. Li, X. Zhang, A.K. An, Z. Wang, Superhydrophobic and superoleophilic PH-CNT membrane for emulsified oil-water separation, *Desalination* 526 (2022), 115536.
- [77] W. Miao, D. Jiao, C. Wang, S. Han, Q. Shen, J. Wang, X. Han, T. Hou, J. Liu, Y. Zhang, Ethanol-induced one-step fabrication of superhydrophobic-superoleophilic poly(vinylidene fluoride) membrane for efficient oil/water emulsions separation, *J. Water Process Eng.* 34 (2020), 101121.
- [78] A.B. Nordvik, J.L. Simmons, K.R. Biting, A. Lewis, T. Strøm-Kristiansen, Oil and water separation in marine oil spill clean-up operations, *Spill Sci. Technol. Bull.* 3 (3) (1996) 107–122.
- [79] H.H. Tseng, J.C. Wu, Y.C. Lin, G.L. Zhuang, Superoleophilic and quality separation of trace water-in-oil emulsions, *J. Membr. Sci.* 559 (2018) 148–158.
- [80] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water, *Angew. Chem.* 116 (15) (2004) 2046–2048.
- [81] S.J. Gao, Z. Shi, W.B. Zhang, F. Zhang, J. Jin, Photoinduced superwetting single-walled carbon nanotube/TiO<sub>2</sub> ultrathin network films for ultrafast separation of oil-in-water emulsions, *ACS nano* 8 (6) (2014) 6344–6352.
- [82] C.F. Wang, L.T. Chen, Preparation of superwetting porous materials for ultrafast separation of water-in-oil emulsions, *Langmuir* 33 (8) (2017) 1969–1973.
- [83] X. Lin, M. Choi, J. Heo, H. Jeong, S. Park, J. Hong, Cobweb-inspired superhydrophobic multiscaled gating membrane with embedded network structure for robust water-in-oil emulsion separation, *ACS Sustain. Chem. Eng.* 5 (4) (2017) 3448–3455.
- [84] X. Zeng, L. Qian, X. Yuan, C. Zhou, Z. Li, J. Cheng, S. Xu, S. Wang, P. Pi, X. Wen, Inspired by stenocara beetles: from water collection to high-efficiency water-in-oil emulsion separation, *ACS Nano* 11 (1) (2017) 760–769.
- [85] J. Du, C. Zhou, L. Chen, J. Cheng, P. Pi, J. Zuo, W. Shen, S. Jin, L. Tan, L. Dong, Gate-embedding strategy for pore size manipulation on stainless steel mesh: toward highly efficient water-in-oil nanoemulsions separation, *Ind. Eng. Chem. Res.* 58 (33) (2019) 15288–15296.
- [86] H. Li, G. Zhu, Y. Shen, Z. Han, J. Zhang, J. Li, Robust superhydrophobic attapulgite meshes for effective separation of water-in-oil emulsions, *J. Colloid Interface Sci.* 557 (2019) 84–93.
- [87] K. Dong, L. Bian, Y. Liu, Z. Guan, Superhydrophobic coating based on organic/inorganic double component adhesive and functionalized nanoparticles with good durability and anti-corrosion for protection of galvanized steel, *Colloids Surf. A: Physicochem. Eng. Asp.* 640 (2022), 128360.
- [88] D.D. Ejeta, C.F. Wang, C.H. Lin, S.W. Kuo, J.K. Chen, H.C. Tsai, W.S. Hung, C. C. Hu, J.Y. Lai, Preparation of a main-chain-type polybenzoxazine-modified



- melamine sponge via non-solvent-induced phase inversion for oil absorption and very-high-flux separation of water-in-oil emulsions, *Sep. Purif. Technol.* 263 (2021), 118387.
- [89] J.X. Wu, J. Zhang, Y.L. Kang, G. Wu, S.C. Chen, Y.Z. Wang, Reusable and recyclable superhydrophilic electrospun nanofibrous membranes with in situ co-cross-linked polymer–chitin nanowhisker network for robust oil-in-water emulsion separation, *ACS Sustain. Chem. Eng.* 6 (2) (2018) 1753–1762.
- [90] J. Yan, C. Xiao, C. Wang, Robust preparation of braid-reinforced hollow fiber membrane covered by PVDF nanofibers and PVDF/SiO<sub>2</sub> micro/nanospheres for highly efficient emulsion separation, *Sep. Purif. Technol.* 298 (2022), 121593.
- [91] O. Duman, H. Uğurlu, C.Ö. Diker, S. Tunç, Fabrication of highly hydrophobic or superhydrophobic electrospun PVA and agar/PVA membrane materials for efficient and selective oil/water separation, *J. Environ. Chem. Eng.* 10 (3) (2022), 107405.
- [92] W. Fang, L. Liu, T. Li, Z. Dang, C. Qiao, J. Xu, Y. Wang, Electrospun N-substituted polyurethane membranes with self-healing ability for self-cleaning and oil/water separation, *Chem. Eur. J.* 22 (3) (2016) 878–883.
- [93] F. Kazemi, Y. Jafarzadeh, S. Masoumi, M. Rostamizadeh, Oil-in-water emulsion separation by PVC membranes embedded with GO-ZnO nanoparticles, *J. Environ. Chem. Eng.* 9 (1) (2021), 104992.
- [94] A. Sun, Y. Zhan, W. Yang, Q. Feng, H. Dong, X. Chen, Y. Chen, Design of poly (arylene ether nitrile)@ SiO<sub>2</sub> nanoparticles super-wetting membrane for the fast separation of oil-in-water emulsions fabricated through physical confinement effect and dopamine-assisted bio-inspired deposition, *J. Environ. Chem. Eng.* 10 (4) (2022), 108118.
- [95] D. Ji, C. Xiao, S. An, H. Liu, K. Chen, J. Hao, T. Zhang, Preparation of PSF/FEP mixed matrix membrane with super hydrophobic surface for efficient water-in-oil emulsion separation, *RSC Adv.* 8 (18) (2018) 10097–10106.
- [96] Q. Xiong, Q. Tian, X. Yue, J. Xu, X. He, F. Qiu, T. Zhang, Superhydrophobic PET@ ZnO nanofibrous membrane extract from waste plastic for efficient water-in-oil emulsion separation, *Ind. Eng. Chem. Res.* 61 (32) (2022) 11804–11814.
- [97] H. Xu, H. Liu, Y. Huang, C. Xiao, Three-dimensional structure design of tubular polyvinyl chloride hybrid nanofiber membranes for water-in-oil emulsion separation, *J. Membr. Sci.* 620 (2021), 118905.
- [98] H. Bazyar, N. van de Beek, R.G. Lammertink, Liquid-infused membranes with oil-in-water emulsions, *Langmuir* 35 (29) (2019) 9513–9520.
- [99] C. Song, G.C. Rutledge, Electrospun liquid-infused membranes for emulsified oil/water separation, *Langmuir* 38 (7) (2022) 2301–2313.
- [100] L. Zhao, R. Li, R. Xu, D. Si, Y. Shang, H. Ye, Y. Zhang, H. Ye, Q. Xin, Antifouling slippery liquid-infused membrane for separation of water-in-oil emulsions, *J. Membr. Sci.* 611 (2020), 118289.
- [101] J.P. Chaudhary, N. Vadodariya, S.K. Nataraj, R. Meena, Chitosan-based aerogel membrane for robust oil-in-water emulsion separation, *ACS Appl. Mater. Interfaces* 7 (44) (2015) 24957–24962.
- [102] J. Wang, H. Wang, Ultra-hydrophobic and mesoporous silica aerogel membranes for efficient separation of surfactant-stabilized water-in-oil emulsion separation, *Sep. Purif. Technol.* 212 (2019) 597–604.
- [103] X. Yue, W. Li, Z. Li, F. Qiu, J. Pan, T. Zhang, Laminated superwetting aerogel/membrane composite with large pore sizes for efficient separation of surfactant-stabilized water-in-oil emulsions, *Chem. Eng. Sci.* 215 (2020), 115450.
- [104] H. Yuan, F. Ye, G. Ai, G. Zeng, L. Chen, L. Shen, Y. Yang, X. Feng, Z. Zhang, Y. Mi, Preparation of an environmentally friendly demulsifier using waste rice husk as raw materials for oil–water emulsion separation, *J. Mol. Liq.* 367 (2022), 120497.
- [105] L. Chen, C. Zhou, H. Yang, J. Lin, Y. Ge, W. Zhou, C. Lu, L. Tan, L. Dong, Room-temperature fabrication of superhydrophobic covalent organic framework (COF) decorated cotton fabric for high-flux water-in-oil emulsion separation, *Chem. Commun.* 57 (87) (2021) 11533–11536.
- [106] Y. Cai, D. Chen, N. Li, Q. Xu, H. Li, J. He, J. Lu, Superhydrophobic metal–organic framework membrane with self-repairing for high-efficiency oil/water emulsion separation, *ACS Sustain. Chem. Eng.* 7 (2) (2018) 2709–2717.
- [107] C. Chen, S. Chen, L. Chen, Y. Yu, D. Weng, A. Mahmood, J. Wang, I.P. Parkin, C. J. Carmalt, Underoil superhydrophilic metal felt fabricated by modifying ultrathin fumed silica coatings for the separation of water-in-oil emulsions, *ACS Appl. Mater. Interfaces* 12 (24) (2020) 27663–27671.
- [108] J. Zhang, L. Zhu, S. Zhao, D. Wang, Z. Guo, A robust and repairable copper-based superhydrophobic microfiltration membrane for high-efficiency water-in-oil emulsion separation, *Sep. Purif. Technol.* 256 (2021), 117751.
- [109] C. Cao, J. Cheng, Fabrication of superhydrophobic copper stearate@ Fe<sub>3</sub>O<sub>4</sub> coating on stainless steel meshes by dip-coating for oil/water separation, *Surf. Coat. Technol.* 349 (2018) 296–302.
- [110] X. Yin, Z. Wang, Y. Shen, P. Mu, G. Zhu, J. Li, Facile fabrication of superhydrophobic copper hydroxide coated mesh for effective separation of water-in-oil emulsions, *Sep. Purif. Technol.* 230 (2020), 115856.
- [111] J. Wu, Y. Ding, J. Wang, T. Li, H. Lin, J. Wang, F. Liu, Facile fabrication of nanofiber-and micro/nanosphere-coordinated PVDF membrane with ultrahigh permeability of viscous water-in-oil emulsions, *J. Mater. Chem. A* 6 (16) (2018) 7014–7020.
- [112] Y. Wang, G. Yue, D. Li, L. Hou, X. Zhao, Z. Cui, J. Bai, N. Wang, Y. Zhao, A robust carbon nanotube and PVDF-HFP nanofiber composite superwettability membrane for high-efficiency emulsion separation, *Macromol. Rapid Commun.* 41 (10) (2020), 2000089.
- [113] H. Chen, Z. Zuo, Q. Tian, S. Xue, F. Qiu, X. Peng, T. Zhang, Waste to treasure: a superwetting fiber membrane from waste PET plastic for water-in-oil emulsion separation, *J. Clean. Prod.* 396 (2023), 136502.
- [114] D. Wang, J. Zang, Q. Wang, W. Cheng, G. Han, S. Huan, Hierarchical composite membrane with multiscale roughness structures for water-in-oil emulsion separation, *Appl. Surf. Sci.* 566 (2021), 150666.
- [115] X. Lin, J. Heo, H. Jeong, M. Choi, M. Chang, J. Hong, Robust superhydrophobic carbon nanofiber network inlay-gated mesh for water-in-oil emulsion separation with high flux, *J. Mater. Chem. A* 4 (46) (2016) 17970–17980.
- [116] P.R. Waghmare, N.S.K. Gunda, S.K. Mitra, Under-water superoleophobicity of fish scales, *Sci. Rep.* 4 (1) (2014) 1–5.
- [117] H. He, T.C. Zhang, Z. Li, Y. Liang, S. Yuan, Superhydrophilic fish-scale-like Cu<sub>2</sub>O nanosheets wrapped copper mesh with underwater super oil-repellent properties for effective separation of oil-in-water emulsions, *Colloids Surf. A: Physicochem. Eng. Asp.* 627 (2021), 127133.
- [118] F.U. Ahmed, D. Upadhyaya, D.D. Purkayastha, M.G. Krishna, Stable hydrophilic and underwater superoleophobic ZnO nanorod decorated nanofibrous membrane and its application in wastewater treatment, *J. Membr. Sci.* 659 (2022), 120803.
- [119] W. Qing, X. Li, Y. Wu, S. Shao, H. Guo, Z. Yao, Y. Chen, W. Zhang, C.Y. Tang, In situ silica growth for superhydrophilic-underwater superoleophobic Silica/PVA nanofibrous membrane for gravity-driven oil-in-water emulsion separation, *J. Membr. Sci.* 612 (2020), 118476.
- [120] H. Wang, F. Gao, R. Ren, Z. Wang, R. Yue, J. Wei, X. Wang, Z. Kong, H. Zhang, X. Zhang, Caffeic acid polymer rapidly modified sponge with excellent anti-oil-adhesion property and efficient separation of oil-in-water emulsions, *J. Hazard. Mater.* 404 (2021), 124197.
- [121] X. Li, L. You, Y. Song, L. Gao, Y. Liu, W. Chen, L. Mao, Preparation of a phenolic-resin-based polymer sponge composed of intertwined nanofibers with tunable wettability for high-efficiency separation of oil–water emulsions, *Langmuir* 35 (46) (2019) 14902–14912.
- [122] J. He, Y. Zhang, J. Wang, L. Ma, Y. Zhao, Y. Zhou, Z. Yang, M. Qu, Eco-friendly, magnetic-driven, superhydrophobic sponge for oil/water separation and emulsion purification, *J. Mater. Sci.* 55 (2020) 6708–6720.
- [123] S. Mir, A. Rahidi, A. Naderifar, M. Alaei, A novel and facile preparation of Superhydrophilic/Superoleophobic nanofilter using carbon nitride nanosheet for W/O emulsion separation, *Sep. Purif. Technol.* 284 (2022), 120279.
- [124] Y. Du, Y. Li, T. Wu, A superhydrophilic and underwater superoleophobic chitosan–TiO<sub>2</sub> composite membrane for fast oil-in-water emulsion separation, *RSC Adv.* 7 (66) (2017) 41838–41846.
- [125] K. Yutang, Stainless steel mesh supported TiO<sub>2</sub> nanowires membrane with ultra-high flux for separation of oil-in-water mixtures and emulsions, *J. Surf. Coat. Technol.* 375 (2019) 518–526.
- [126] C. Chen, L. Chen, S. Chen, Y. Yu, D. Weng, A. Mahmood, G. Wang, J. Wang, Preparation of underwater superoleophobic membranes via TiO<sub>2</sub> electrostatic self-assembly for separation of stratified oil/water mixtures and emulsions, *J. Membr. Sci.* 602 (2020), 117976.
- [127] S. Kim, K. Kim, G. Jun, W. Hwang, Wood-nanotechnology-based membrane for the efficient purification of oil-in-water emulsions, *ACS Nano* 14 (12) (2020) 17233–17240.
- [128] S. Yang, L. Chen, S. Liu, W. Hou, J. Zhu, P. Zhao, Q. Zhang, Facile and sustainable fabrication of high-performance cellulose sponge from cotton for oil-in-water emulsion separation, *J. Hazard. Mater.* 408 (2021), 124408.
- [129] Y. Li, L. Cao, D. Hu, C. Yang, Uncommon wetting on a special coating and its relevance to coalescence separation of emulsified water from diesel fuel, *Sep. Purif. Technol.* 176 (2017) 313–322.
- [130] J. Wang, B. He, Y. Ding, T. Li, W. Zhang, Y. Zhang, F. Liu, C.Y. Tang, Beyond superwetting surfaces: dual-scale hyperporous membrane with rational wettability for “nonfouling” emulsion separation via coalescence demulsification, *ACS Appl. Mater. Interfaces* 13 (3) (2021) 4731–4739.
- [131] M. Cao, F. Xiao, Z. Yang, Y. Chen, L. Lin, Construction of Polytetrafluoroethylene nanofiber membrane via continuous electrospinning/electrospraying strategy for oil-water separation and demulsification, *Sep. Purif. Technol.* 287 (2022), 120575.
- [132] Y. Cai, D. Chen, N. Li, Q. Xu, H. Li, J. He, J. Lu, A facile method to fabricate a double-layer stainless steel mesh for effective separation of water-in-oil emulsions with high flux, *J. Mater. Chem. A* 4 (48) (2016) 18815–18821.
- [133] P.M. Gurave, S. Dubey, B. Nandan, R.K. Srivastava, Pickering emulsion-templated nanocomposite membranes for excellent demulsification and oil–water separation, *ACS Appl. Mater. Interfaces* 14 (48) (2022) 54233–54244.
- [134] D. Hu, X. Li, L. Li, C. Yang, Designing high-caliber nonwoven filter mats for coalescence filtration of oil/water emulsions, *Sep. Purif. Technol.* 149 (2015) 65–73.
- [135] M. Zhang, D. Liang, W. Jiang, J. Shi, Ag@ TiO<sub>2</sub> NPs/PU composite fabric with special wettability for separating various water–oil emulsions, *RSC Adv.* 10 (58) (2020) 35341–35348.
- [136] D. Gao, F. Cheng, Y. Wang, C. Li, E.M. Yang, C. Li, L. Zhang, G. Cheng, Versatile superhydrophobic sponge for separating both emulsions and immiscible oil/water mixtures, *Colloids Surf. A: Physicochem. Eng. Asp.* 666 (2023), 131267.
- [137] J. Lei, Z. Guo, Superamphiphilic stainless steel mesh for oil/water emulsion separation on-demand, *Colloids Surf. A: Physicochem. Eng. Asp.* 630 (2021), 127574.
- [138] D. Wu, S. Hu, B. Lu, Y. Hu, M. Wang, W. Yu, G.G. Wang, J. Zhang, Waste to treasure: Superwetting foam enhanced by bamboo powder for sustainable on-demand oil-water separation, *J. Hazard. Mater.* 441 (2023), 129829.
- [139] X. Gao, Q. Ma, Z. Jin, P. Nian, Z. Wang, Switchable superlyophobic zeolitic imidazolate framework-8 film-coated stainless-steel meshes for selective oil–water emulsion separation with high flux, *N. J. Chem.* 44 (32) (2020) 13534–13541.

- [140] W. Fang, L. Liu, G. Guo, Tunable wettability of electrospun polyurethane/silica composite membranes for effective separation of water-in-oil and oil-in-water emulsions, *Chem. Eur. J.* 23 (47) (2017) 11253–11260.
- [141] J. Li, Z. Zhao, D. Li, H. Tian, F. Zha, H. Feng, L. Guo, Smart candle soot coated membranes for on-demand immiscible oil/water mixture and emulsion switchable separation, *Nanoscale* 9 (36) (2017) 13610–13617.
- [142] Y. Li, L. Zhu, N. Grishkewich, K.C. Tam, J. Yuan, Z. Mao, X. Sui, CO<sub>2</sub>-responsive cellulose nanofibers aerogels for switchable oil–water separation, *ACS Appl. Mater. Interfaces* 11 (9) (2019) 9367–9373.
- [143] A. Venault, C.H. Chiang, H.Y. Chang, W.S. Hung, Y. Chang, Graphene oxide/PVDF VIPS membranes for switchable, versatile and gravity-driven separation of oil and water, *J. Membr. Sci.* 565 (2018) 131–144.
- [144] W. Wang, J. Lin, J. Cheng, Z. Cui, J. Si, Q. Wang, X. Peng, L.S. Turng, Dual superamphiphilic modified cellulose acetate nanofiber membranes with highly efficient oil/water separation and excellent antifouling properties, *J. Hazard. Mater.* 385 (2020), 121582.
- [145] Q. Zeng, L. Qiu, S. Zhao, J. Zhang, J. Huang, Z. Guo, Two-step facile fabrication of a superamphiphilic biomimic membrane with a micro–nano structure for oil–water emulsion separation on-demand, *N. J. Chem.* 46 (29) (2022) 14140–14145.
- [146] R. Zhang, Z. Guo, Facile preparation of a superamphiphilic nitrocellulose membrane enabling on-demand and energy-efficient separation of oil/water mixtures and emulsions by prewetting, *Biomater. Sci.* 9 (16) (2021) 5559–5568.
- [147] H. Ye, D. Chen, N. Li, Q. Xu, H. Li, J. He, J. Lu, Durable and robust self-healing superhydrophobic Co-PDMS@ ZIF-8-coated MWCNT films for extremely efficient emulsion separation, *ACS Appl. Mater. Interfaces* 11 (41) (2019) 38313–38320.
- [148] T. Zhang, C. Xiao, J. Zhao, X. Liu, D. Ji, H. Xu, One-step preparation of tubular nanofibers and micro/nanospheres covered membrane with 3D micro/nano structure for highly efficient emulsified oil/water separation, *J. Taiwan Inst. Chem. Eng.* 122 (2021) 210–221.
- [149] G. Zhang, Y. Liu, C. Chen, C. Huang, L. Long, S. Zhang, G. Yang, F. Shen, X. Zhang, Y. Zhang, Green, robust self-cleaning superhydrophilic coating and on-demand oil–water separation, *Appl. Surf. Sci.* 595 (2022), 153472.
- [150] X. Yang, Z. Wang, L. Shao, Construction of oil-unidirectional membrane for integrated oil collection with lossless transportation and oil-in-water emulsion purification, *J. Membr. Sci.* 549 (2018) 67–74.
- [151] M. Liu, J. Li, Y. Hou, Z. Guo, Inorganic adhesives for robust superwetting surfaces, *ACS Nano* 11 (1) (2017) 1113–1119.
- [152] Q. Sun, B. Xiang, P. Mu, J. Li, Green preparation of a carboxymethyl cellulose-coated membrane for highly efficient separation of crude oil-in-water emulsions, *Langmuir* 38 (22) (2022) 7067–7076.
- [153] L. Zhang, L. Cheng, H. Wu, T. Yoshioka, H. Matsuyama, One-step fabrication of robust and anti-oil-fouling aliphatic polyketone composite membranes for sustainable and efficient filtration of oil-in-water emulsions, *Journal of Materials Chemistry A*. 6(47) (2018) 24641–24650.
- [154] Z. He, H. Wu, Z. Shi, X. Gao, Y. Sun, X. Liu, Mussel-inspired durable TiO<sub>2</sub>/PDA-based superhydrophobic paper with excellent self-cleaning, high chemical stability, and efficient oil/water separation properties, *Langmuir* 38 (19) (2022) 6086–6098.
- [155] S. Shao, Y. Liu, D. Shi, W. Qing, W. Fu, J. Li, Z. Fang, Y. Chen, Control of organic and surfactant fouling using dynamic membranes in the separation of oil-in-water emulsions, *J. Colloid Interface Sci.* 560 (2020) 787–794.
- [156] Q. Sun, Z. Yang, Z. Wang, L. Wu, Anti-fouling performance investigation of micron-submicron hierarchical structure PVDF membranes in water-in-oil emulsion separation, *J. Environ. Chem. Eng.* 10 (3) (2022), 107497.
- [157] Y. Sun, Y. Lin, L. Fang, L. Zhang, L. Cheng, T. Yoshioka, H. Matsuyama, Facile development of poly (tetrafluoro ethylene-r-vinylpyrrolidone) modified PVDF membrane with comprehensive antifouling property for highly-efficient challenging oil-in-water emulsions separation, *J. Membr. Sci.* 584 (2019) 161–172.
- [158] G. Zhang, L. Li, Y. Huang, A. Hozumi, T. Sonoda, Z. Su, Fouling-resistant membranes for separation of oil-in-water emulsions, *RSC Adv.* 8 (10) (2018) 5306–5311.
- [159] L. Zhang, R. Takagi, S. Wang, Y. Lin, K. Guan, L. Cheng, H. Matsuyama, In situ formation of ultrathin polyampholyte layer on porous polyketone membrane via a one-step dopamine co-deposition strategy for oil/water separation with ultralow fouling, *J. Membr. Sci.* 619 (2021), 118789.
- [160] N. Zhang, K. Cheng, J. Zhang, N. Li, X. Yang, Z. Wang, A dual-biomimetic strategy to construct zwitterionic anti-fouling membrane with superior emulsion separation performance, *J. Membr. Sci.* 660 (2022), 120829.
- [161] Q. Sheng, W. Tian, C.D. Wood, Hyper-cross-linked polymer-decorated surfaces with ultrahigh efficiency for oil/water emulsion separation and recovery, *ACS Appl. Mater. Interfaces* 13 (33) (2021) 39925–39933.
- [162] A. Tuteja, A.K. Kota, G. Kwon, J.M. Mabry, Superhydrophilic and oleophobic porous materials and methods for making and using the same. U.S. Patent 9,186,631, issued November 17, 2015.