ACS APPLIED MATERIALS & INTERFACES

www.acsami.org

Review

Recent Progress in Superhydrophilic Carbon-Based Composite Membranes for Oil/Water Emulsion Separation

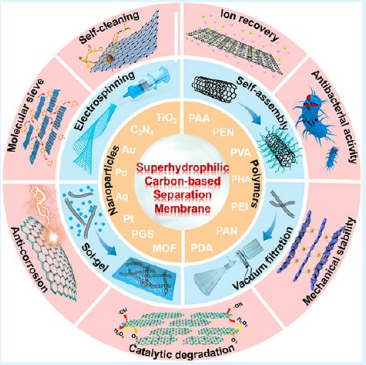
Jincui Gu, Lingtong Ji, Peng Xiao, Chang Zhang, Jian Li, Luke Yan,* and Tao Chen*

Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 36679–36696

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: The purification of stabilized oil/water emulsions is essential to meet the ever increasing demand for monitoring water in the environment, which has been addressed with superwetting carbon-based separation membranes. These include superhydrophilic carbon-based membranes whose progress in recent years and perspectives are reviewed in this paper. The membrane construction strategy is organized into four parts, vacuum-assisted self-assembly, sol−gel process, electrospinning, and vacuum-assisted filtration. In each section, the design strategies and their responding disadvantages have been comprehensively discussed. The challenges and prospects concerning the superhydrophilic carbon-based separation membranes for oily wastewater purification are also summarized to arouse researchers to carry out more studies.



KEYWORDS: *superwettability, carbon-based composite membrane, membrane construction strategy, O/W emulsion separation, function integration*

1. INTRODUCTION

The frequent oil pollution accidents resulting from offshore oil production and marine transportation have become a disastrous global water environment issue.[1−3] Therefore, removing these oil pollutants, especially surfactant-stabilized oily wastewater, draws attention. Traditional separation countermeasures, such as landfill, adsorption, and biological treatment, have been taken to solve these challenging problems, but the bottleneck of their complex process, low efficiency, etc. remains.[4−6] Therefore, it is urgent to develop advanced technology to purify oily wastewater through energy-saving, high-efficiency, and environmentally friendly methods.

Membrane separation technology has been regarded as an effective means for water environment optimization benefiting from its advantages, such as low energy consumption, high separation efficiency, and easy-to-operate.[7−10] To date, enormous efforts have been devoted to constructing separation membranes. Especially, carbon-based membranes, involving carbon nanotubes (CNTs) and graphene oxide (GO), have gained considerable attention in the field of science to explore their transport behavior and purification mechanism.[11−16] For one thing, the CNTs or GO has a large surface area and hydrophilic characteristics, making them ideal options to contact water-soluble contaminations efficiently.[17−19] For another, a continuous structure can be designed through covalent/noncovalent cross-linking or interfacial self-assembly, which is beneficial to capture the target substances.[20−23] Until now, plenty of exciting achievements about carbon-based separation membranes have emerged endlessly. Generally speaking, these membranes are divided into four parts, superhydrophobic carbon-based membranes, superhydrophilic carbon-based membranes, Janus carbon-based membranes, and smart carbon-based membranes.[24−43] These membranes play irreplaceable roles in the field of oil/water purification.

As promising alternatives, superhydrophilic carbon-based membranes are of particular research interest.[44−48] On the one hand, they present excellent antifouling ability benefiting from their special wettability.[28−35] During the demulsification process, these membranes are captured by the continuous water and form hydrophilic layers, hindering oil droplets from passing through the membrane interface.[49−51] On the other hand, some superhydrophilic carbon-based membranes can achieve the on-demand oil/water emulsion separation just only by being prewetted with their responding liquids.[52−58] Their separation process does not require specialized device equipment.

Furthermore, it does not need specific energy consumption (such as light, heat, electrical field), which is more facile than

Received: May 1, 2021
Accepted: July 19, 2021
Published: August 2, 2021

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

the Janus carbon-based membranes and smart carbon-based membranes. Besides, the functional components endow the superhydrophilic carbon-based membranes to remove the harmful substances (ions, bacteria, dyes, etc.) in water efficiently.[55,56] Up until now, more attention has been focused on superhydrophilic carbon-based membranes in the scientific and industrial fields, but inspiring achievements have sprung up. Despite some reviews summarizing the carbon-based membranes for oily wastewater purification, they have not given a systematic summary of superhydrophilic carbon-based membranes from the perspective of membrane construction means.[27,29,43] Herein, we try to provide a detailed overview of the construction methods and properties of the superhydrophilic carbon-based membranes. According to membrane construction strategy, this review is focused on four parts (Figure 1). Coupling microscopic structures with surface free

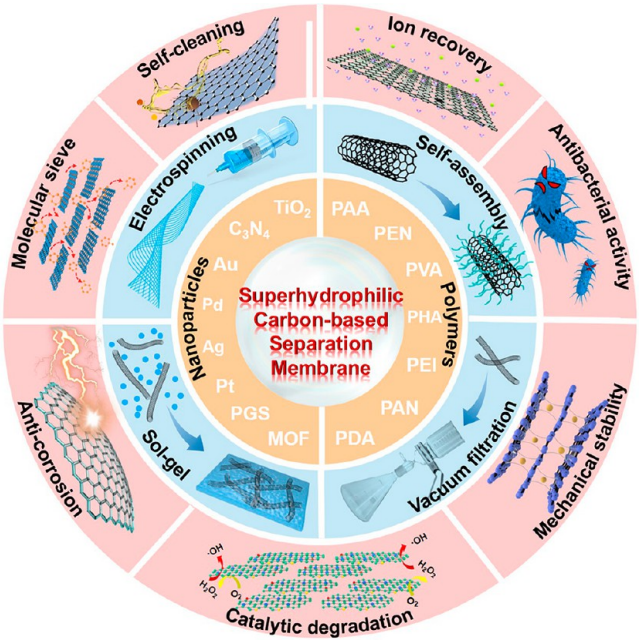


Figure 1. Superhydrophilic carbon-based membrane for oily wastewater purification. The carbon-based materials are modified with nanoparticles or polymers through the sol−gel process, vacuum-assisted self-assembly, electrospinning, and vacuum-assisted filtration. These membranes present oil-in-water emulsion separation performance. Moreover, they show other properties, such as self-cleaning, iron recovery, antibacterial activity, mechanical stability, catalytic degradation, anticorrosion, molecular sieve, etc.

energy, these membranes show excellent separation performance and other properties, such as self-cleaning, catalytic degradation, and screening. The preparation process and performance are comprehensively summarized (Table 1). The challenges and future perspectives of the superhydrophilic carbon-based separation membranes are given at the end.

2. THEORY FOR WETTABILITY AND OIL/WATER SEPARATION

2.1. Theory for Superwetting Surfaces. Wettability is a function of the interfacial property, which can be quantitatively calculated by measuring the contact angle (θ_{CA}) by a liquid between the liquid, gas, and solid three-phase.[59,60] According to Thomas Young's mode, when a droplet is dripped on an ideally smooth surface, it tends to form a spherical shape on

Table 1. Superhydrophilic Carbon-Based Membranes for Oily Water Purification

membranes	performance (flux and other ability)	ref
PEI/GO	135 500 L $m^{-2}h^{-1}$ bar^{-1}	5
GO/PGS	1867 L m^{-2} h^{-1}, antifouling property	28
GO/g-C_3N_4@TiO_2	4536 L $m^{-2}h^{-1}$ bar^{-1}, self-cleaning property	84
CNT@ FeOOH	8000 L m^{-2} h^{-1} bar^{-1}, self-cleaning property	30
PVA@CNTs	600 L m^{-2} h^{-1} bar^{-1}, antifouling property	31
SWCNT/TiO_2	30000 L m^{-2} h^{-1} bar^{-1}, self-cleaning property	32
h-PAN/GO	3500 L m^{-2} h^{-1} bar^{-1}, efficiency ∼ 99%	33
PVA-GO	30 L m^{-2} h^{-1}, efficiency > 99%	91
GO/PEN	1130 L m^{-2} h^{-1}, anticorrosive property	92
DTPA/CNT/TiO_2	943 L m^{-2} h^{-1}, efficiency > 97.4%	93
SiO_2/GO	470 L m^{-2} h^{-1}, efficiency > 99.4%, dye rejection	34
GO/TiO_2	67.4 L m^{-2} h^{-1}, efficiency > 99.5%, dye rejection	96
GO/MCU-C_3N_4	800 L m^{-2} h^{-1}, efficiency > 98%, antifouling property	120
GO/PG/CN@BOC	4600 L m^{-2} h^{-1} bar^{-1}, self-cleaning property	98
CNTs/TiO_2	30 L m^{-2} h^{-1} bar^{-1}, anticorrosive property	99
CNTs/PDA/PEI	6000 L m^{-2} h^{-1} bar^{-1}, anticorrosive property	102
PDA-RGO	3000 L m^{-2} h^{-1} bar^{-1}, efficiency > 99.6%	103
CNTs/PEI	1427 L m^{-2} h^{-1} (0.5 bar), antifouling property	104
Polymer@CNTs	4592 L m^{-2} h^{-1} bar^{-1}, antifouling property	105
CNTs/PAH	250 L m^{-2} h^{-1}, efficiency > 98.6%, ion recovery	106
PDA@CNTs	7240 L m^{-2} h^{-1} bar^{-1}, efficiency about 99.8%	3
RGO/PDA/MXene	200 L m^{-2} h^{-1}, efficiency > 97%, dye rejection	81
RGO/PDA/g-C_3N_4	3400 L m^{-2} h^{-1}, efficiency > 99.4%, self-cleaning property	109
CNTs-PAA/CNMS	5570 L m^{-2} h^{-1}, efficiency > 98.5%, self-cleaning property	110
CNTs/PDA/PSBMA	3400 L $m^{-2}h^{-1}$, efficiency > 99.5%, self-cleaning property	111
g-C_3N_4/RGO/TiO_2	1261 L $m^{-2}h^{-1}$, efficiency > 95.4%, self-cleaning property	121
CNTs@PS@AuNPs	3500 L m^{-2} h^{-1} bar^{-1}, efficiency > 92.6%, catalytic degradation	114
CNTs/Pd@Pt/CNTs	800 L m^{-2} h^{-1} bar^{-1}, efficiency > 99.8%, catalytic degradation	115
CNTs-PAA/MOF@Pt	11000 L m^{-2} h^{-1} bar^{-1}, efficiency > 98.8%, catalytic degradation	116
GO/PDA/HNTs	60.3 L m^{-2} h^{-1}, efficiency > 99%, molecular sieve	117
D-ChNCs/GO	135.6 L m^{-2} h^{-1}, efficiency > 97.8%, molecular sieve	118
Ag/PAA-CNTs	3000 L m^{-2} h^{-1}, efficiency > 97.8%, antibacterial ability	122

this surface (Figure 2A).[59] The θ_{CA} is dependent on the surface tensions of the solid/vapor (γ_{SV}), solid/liquid (γ_{SL}), and liquid/vapor (γ_{LV}) interfaces (eq 1). When $\theta_{CA} < 90°$, the surface is hydrophilic, whereas the surface is hydrophobic when $\theta_{CA} > 90°$.[61]

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

Young's model is only used for a smooth surface, homogeneous chemical composition, and no external force.[62] However, the entire surface does not have perfect smoothness and strict chemical homogeneity. As an intrinsic property, surface wettability is governed by chemical composition and surface microstructure.[63] Among them, the chemical composition is the essence that determines the surface-free energy. The Wenzel model and Cassie model can explain the effect of

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

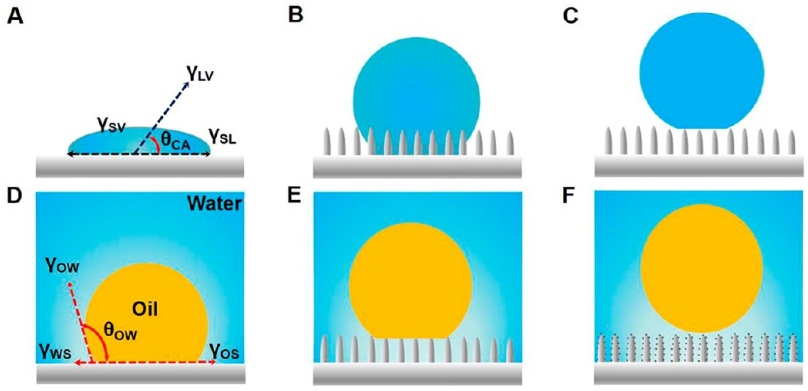


Figure 2. Schematic description of a water droplet on the (A) smooth and (B,C) rough substrates in air. Modified (D) Young's model and (E) Cassie's model of an oil droplet underwater. (F) Enlarged superhyophilicity and underwater oleophobicity produced by a rough surface.[59] Reprinted with permission from ref 59. Copyright 2019 Wiley-VCH.

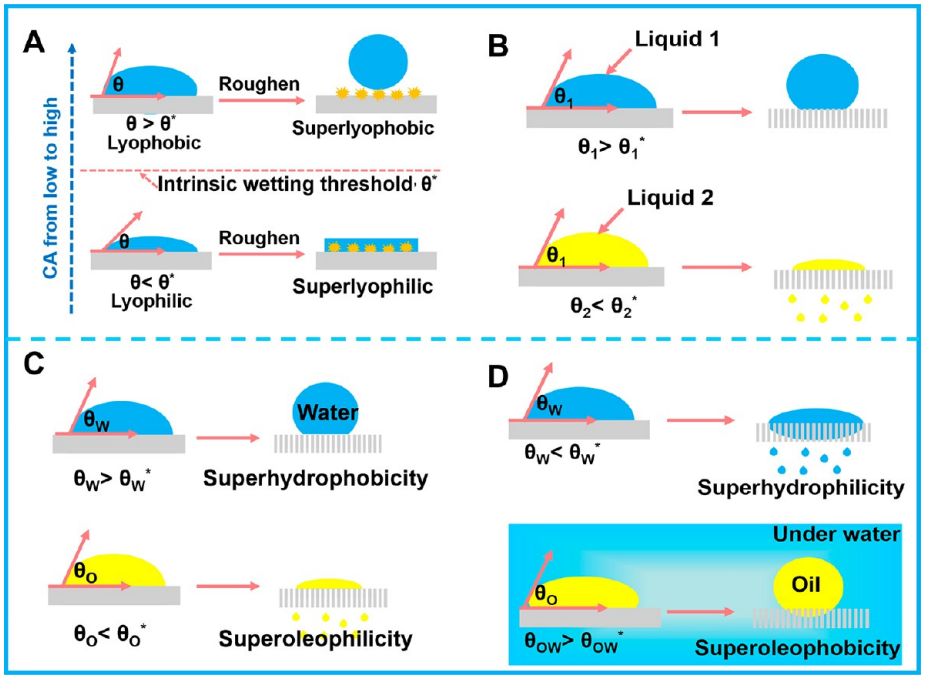


Figure 3. (A) Principle description of the wetting threshold theory. (B) Approach of constructing superwetting materials for separating liquid 1 and liquid 2. (C) Principle of superhydrophobic materials for separating oil from the oil/water mixture. (D) Principle of superhydrophilic/underwater superoleophobic materials for separating water from oil/water mixtures.[66] Reprinted with permission from ref 66. Copyright 2018 Elsevier.

surface morphology on wettability.[64] In Wenzel's model (Figure 2B), the droplet can completely contact the homogeneous wetting state.[59] The Wenzel CA (θ_W) is determined by eq 2, where r is the ratio between actual surface area and apparent area of the rough surface.[65]

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

Wenzel's model is based on two assumptions. One is that the surface roughness is negligible compared with the size of the droplet. The other one is that the surface geometry does not affect the surface area. In Wenzel's model, surface roughness can promote surface wettability, no matter if it is a hydrophilic surface or hydrophobic surface. However, it does not apply when the liquid does not penetrate the rough surface. Cassie–Baxter proposes a more complicated model to deal with the heterogeneous, rough surface. Cassie–Baxter illustrates that the surface with small asperities is surrounded by air and cannot be filled with liquid. In other words, the air is trapped underneath a liquid droplet (Figure 2C).[59] This phenomenon can be expressed by Cassie–Baxter's model (eq 3), where Φ_s represents the friction between the solid and liquid surface.[66]

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

In Cassie–Baxter's model, the droplet can only touch the highest protrusions of the substrate surface. The adhesion between the droplets and solid surface is relatively low. Consequently, the water droplets immediately roll on the surface with the θ_{CA} larger than 150°, which is regarded as a superhydrophobic surface.[67] Based on Young's model, the oil contact angle (θ_{OW}) on a substrate surface underwater (Figure 2D–F) can be modified to eq 4, in which γ_{OS}, γ_{WS}, and γ_{OW} are

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679–36696

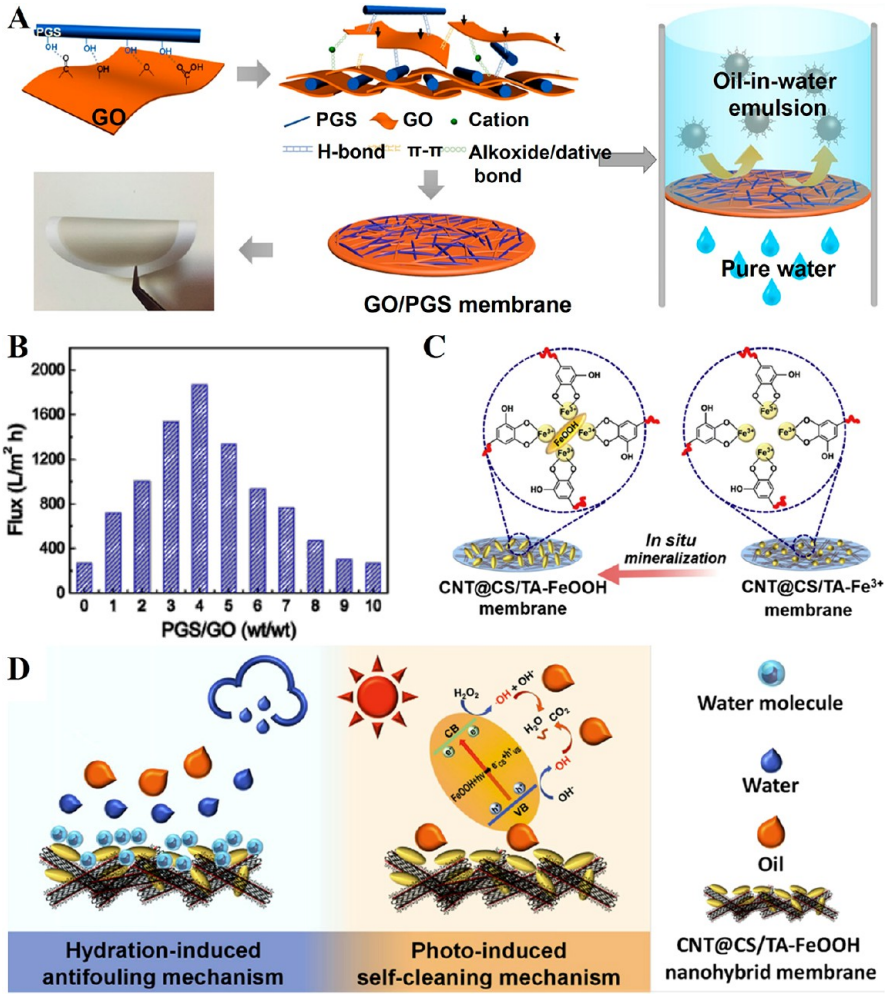


Figure 4. (A) Schematic description of the GO/PGS membrane' fabrication through vacuum-assisted self-assembly and its application for O/W emulsion separation. (B) Flux of the GO/PGS membranes with different mass ratios.[28] (C) Schematic illustration of fabricating the CNTs@CS/TA-FeOOH membrane through self-assembly. (D) Synergistic antifouling mechanism of the CNTs@CS/TA-FeOOH membrane, including hydration-induced and photocatalytic antifouling.[30] Reprinted with permission from ref 28 and ref 30, respectively. Copyright 2016 American Chemical Society and 2020 Elsevier, respectively.

the interface tensions of oil/air, water/air, and oil/water, respectively.

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

2.2. Principle for Oil/Water Separation. To understand the separation process of superwetting membranes, the water and oil penetration process is simulated on the assumption that the porous are arranged approximately in a regular square array and the surface is smooth with a specific chemical composition.[68] In the light of the wetting threshold theory, a border CA (θ^*) exists between the lyophilic and lyophobic interface for a given liquid (Figure 3A).[66] The surface is lyophilic in the case the surface CA (θ) is small than θ^*. Therefore, introducing roughness structures can reduce their wettability to superlyophilicity. In comparison, the rough surface will be superlyophobic when θ is larger than θ^*.

Based on this theory, porous materials with rough structures show inverse wettability for different liquids. Therefore, such material can selectively make liquid 1 pass through but liquid 2 be repelled (Figure 3B).[66] The superlyophobic materials can be manufactured by integrating the appropriate surface morphology and surface free energy. Under the circumstances, the separation of liquid 1 (oil) and liquid 2 (water) can come true (Figure 3C).[66] However, it is intractable to achieve superhydrophilicity because the surface free energy of oils (20−60 mN m^{-1}) is lower than that of water (72 mN m^{-1}).[63] Inspired by natural antifouling phenomena, superhydrophilic materials have been developed by combining an appropriate microstructure and chemical composition.[69] Theoretically, there are two key criteria to dominating the fabrication of superhydrophilic surfaces (Figure 3D).[66,70−72] One is that the intrinsic wetting threshold (θ_{W^*}) is larger than the water contact angle (θ_W) on the smooth surface, and the other is that underwater−oil contact angle (θ_O) is more extensive than its intrinsic underwater−oil wetting threshold (θ_{O^*}). Therefore, the superhydrophilic materials with a specific microscopic topography and chemical composition can be used for oil/water separation.

2.3. Separation Kinetics. Generally, the water droplets with higher density will fall, while the oil droplets with lower density will rise during oil/water mixture separations. These comply with the Stokes theorem (eq 5):[73]

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

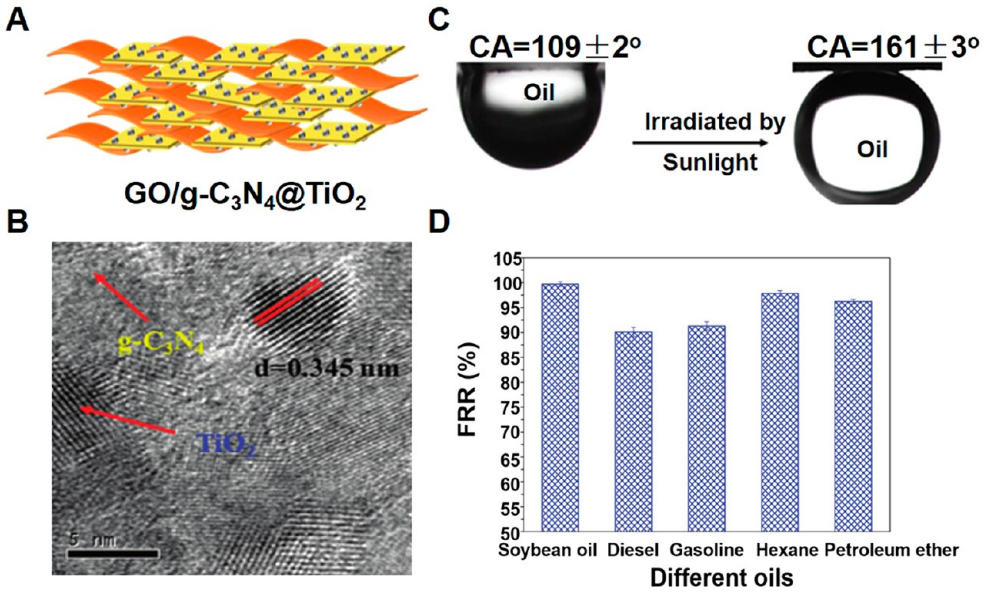


Figure 5. (A) Schematic illustration of the construction of GO/g-C_3N_4@TiO_2 membrane via a self-assembly process. (B) TEM image of the GO/g-C_3N_4@TiO_2 membrane. (C) Oil contact angle underwater of the GO/g-C_3N_4@TiO_2 membrane after being fouled with oil and subsequent irradiation under sunlight. (D) Flux recovery ratio of the GO/g-C_3N_4@TiO_2 membrane for different O/W emulsions.[84] Reprinted with permission from ref 84. Copyright 2018 Wiley-VCH.

$$v = \frac{d_2 g(\rho_w - \rho_o)}{18\mu_w} \quad (5)$$

In this formula, v represents the rising rate of oil droplets, d represents the average diameter of oil droplets, g is the acceleration of gravity, and ρ_o and ρ_w represent the relative densities of oil and water, respectively. μ is the relative viscosity of the water droplets. It can be seen that the rising rate of oil droplets is restricted to the size distribution of the oil droplets.[73] Moreover, it is a positive correlation with the density difference between these two liquids. Hence, the separation flux can be enhanced by increasing their density difference and the average diameter of the oil droplets.

2.4. Carbon-Based Materials for Water Transport. CNTs are regarded as a prominent contender for the water purification process attributed to their exceptional durability, selectivity, and facile processing pathways. It is necessary to fully understand the water transport mechanism through CNTs channels for exploiting its potential application in various fields. On the one hand, present studies found that the high permeability flux and selectivity of CNTs are resulting from its atomic-sized smooth inner wall and molecular ordering phenomena within the nanopores.[74] On the other hand, the CNTs' hollowed structure with a small and precise diameter can form high-energy barriers, which have played an essential role in the fulfillment of the separation performance through the principle of size screening.[75] Furthermore, the hydrophobicity characteristic of CNTs, the capillary effect and low activation energy can facilitate the rapid transport of a water molecule in the CNTs' channels.[76] In addition, targeted specific modification can be implemented on the CNTs without changing or destroying its internal microstructure to facilitate selective water transport.[77] By virtue of these characteristics, CNTs can be seen as a suitable candidate that possesses a bright prospective on the aspect of water purification. Apart from CNTs, GO is also a promising candidate to achieve highly selective permeation owing to its tunable physical and chemical properties. Previous research indicated that the water molecule transport process in the GO' channels is similar to that of CNTs, in which the water molecules are prone to diffuse and move freely in the nonoxidized hydrophobic regions.[76] Furthermore, the interlayer spacing of the GO can be easily tailored through inserting spacers among the GO sheets to create a stable and well-defined water transmission channel.[17,23]

3. CONSTRUCTION STRATEGY

3.1. Vacuum-Assisted Self-Assembly. Vacuum-assisted self-assembly was consistently recognized as an attractive strategy for "bottom-up" nanotechnology.[77] The vacuum-assisted self-assembly method is identified as an attractive strategy to exploit desirable separation membranes. On one hand, their surface/interface microstructures can be tuned, so it is favorable to acquire the targeted membranes with controlled functionalization. On the other hand, it provides numerous opportunities for integrating various inorganic and organic components to construct homogeneous separation membranes for task-oriented applications. By virtue of these advantages, various GO-based nanostructures with different morphologies (particles, membrane, hollow spheres, hydrogel, etc.) can be achieved by the covalent or noncovalent self-assembly.[78] Moreover, particular functions with desirable hybrids and macroscopic architectures can be obtained through the self-assembly behavior of GO architectures.[79] Therefore, GO sheets' self-assembly is an effective strategy for producing visible GO-based materials for further applications, such as photoelectric conversion, energy storage, photocatalysis, and environment optimization.[80] For example, GO is a good choice for constructing high-performance separation membranes. However, GO nanosheets' narrow interlayer distance (<2 nm) has dramatically restrained the water permeability for O/W emulsion separation.[81] To enlarge the GO-based membrane's interlayer distance, Zhao et al. fabricated a hydrophilic and underwater superoleophobic

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

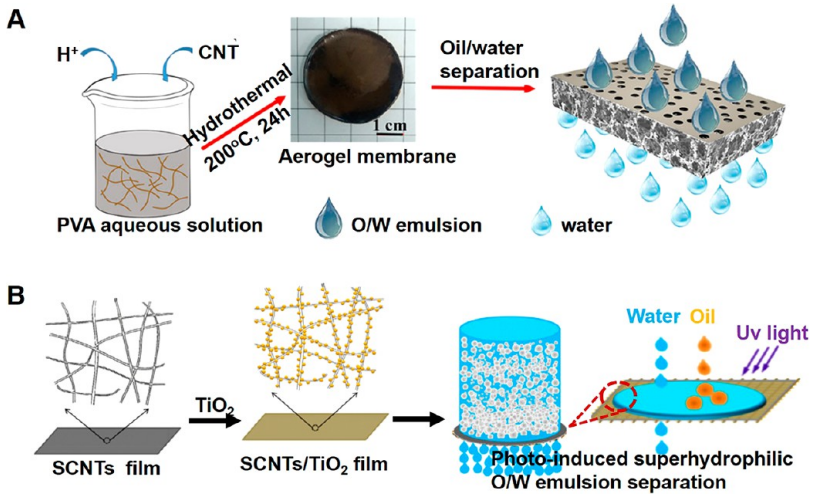


Figure 6. (A) Schematic illustration for constructing PVA@CNTs membrane through a sol–gel process for emulsified oil/water separation.[31] (B) Schematic illustration of the SWCNT/TiO_2 membrane preparation via the sol–gel method for photoresponsive O/W emulsion separation.[32] Reprinted with permission from ref 31 and ref 32, respectively. Copyright 2018 American Chemical Society and 2014 American Chemical Society, respectively.

graphene oxide-palygorskite (GO/PGS) membrane by controlling the PGS nanorods' assembly into the GO nanosheets (Figure 4A).[28] The channel structure and water flux of the GO/PGS membranes can be simultaneously tuned by changing the intercalation between PGS nanorods and GO nanosheets (Figure 4B). The synergistic effect between PGS nanorods and GO nanosheets endowed this membrane with excellent separation performance for hexadecane-in-water emulsion.

However, the weakened interlayer $\pi-\pi$ interaction usually resulted in lower structural stability. Moreover, membrane fouling becomes a challenging issue resulting from the enrichment of contaminants, which causes a sharp decrease of the separation flux. Beyond surface hydration, synergistic antifouling technology has recently been suggested to be the design criteria for advanced separation membranes. As an active antifouling strategy, photocatalytic degradation has been recognized as an efficient environmental remediation technology.[82] Graphitic carbon nitride (g-C_3N_4), being metal-free, having a lower bandgap (~2.4–2.8 eV), is visible-light-driven, and has thermal and chemical stabilities, has received growing attention.[83] Jiang et al. fabricated a graphene oxide/graphitic carbon nitride@titanium dioxide (GO/g-C_3N_4@TiO_2) membrane via a vacuum-assisted self-assembly process.[84] The well-aligned layer structure was built due to the multiple noncovalent/covalent interactions between GO nanosheets and g-C_3N_4 nanosheets (Figure 5A,B). Moreover, the GO/g-C_3N_4@TiO_2 membrane' surface topography can be tuned according to the contents of g-C_3N_4 nanosheets in the g-C_3N_4@TiO_2 heterojunction.

Also, the g-C_3N_4@TiO_2 photocatalytic property endowed the GO/g-C_3N_4@TiO_2 membranes with an obvious self-cleaning ability. This membrane's wettability and separation performance can be recovered after being irradiated by sunlight (Figure 5C,D). Apart from g-C_3N_4, FeOOH was also utilized to endow the membranes with photocatalytic and hydrophilic properties for O/W emulsion separation. For example, Zhao et al. prepared an antioil-fouling CNTs composite membrane embedded with FeOOH nanorods.[30] Tannic acid/chitosan (TA/CS) formed a polyphenol-metal coordination network with Fe^{3+} ions through a strong chelation force because it has sufficient catechol or galloyl groups (Figure 4C). The FeOOH nanorods were in situ mineralized and uniformly assembled on the membrane surface, which endowed this membrane with superhydrophilic and antioil-adhesion properties. Therefore, it cannot only achieve a high permeability flux (>8200 L m^{-2} h^{-1} bar^{-1}) and a good separation efficiency (>99%) for various tween 80-stabilized pump oil-in-water emulsion but also has a desirable flux recovery capability (>97%) under the expected effect of a hydrophilic layer and photocatalytic self-cleaning property (Figure 4D).

The vacuum-assisted self-assembly carbon-based membranes with delicate structures show great potential in wastewater purification. Despite these extraordinary processes, the following issues should be given attention. First, the self-assembly mechanism lacks depth studies and understanding, which are critical for effectively controlling the self-assembly process to improve separation performance further.[59] Second, owing to the structural variability and compositional complexity, it remains a significant challenge to construct a membrane with ultrathin, controllable surface chemistry compositions and well-defined micromorphology through the self-assembly method.[71] Finally, it is urgent to integrate more functional units into membranes via self-assembly to obtain advanced separation membranes with unique structures and properties. Meanwhile, it should be noted that homogeneous self-assembly is of particular importance for constructing carbon-based membranes for wastewater purification.

3.2. Sol–gel process. The sol–gel process is another effective measure to prepare functional membranes. It has many advantages, including controllable size and chemical composition, multihole structure, low temperature, and low cost. Therefore, it is widely used in many fields, such as optics, electronics, energy, sensors, medicine, and separation.[85] For example, Jiang et al. prepared a poly(vinyl alcohol)/carbon nanotubes (PVA@CNTs) hydrogel membrane via a sol–gel process (Figure 6A).[31] It showed high separation rejection (>99.0%) for various O/W emulsions with the highest flux of 135 500 L m^{-2} h^{-1} bar^{-1}. Zhang et al. prepared a polyethyleneimine/graphene oxide (PEI/GO) hydrogel membrane via a sol–gel process.[5] This membrane has a micro/

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679–36696

nanoscale rough structure because of the disordered GO sheets.

In addition, PVA was used as a cross-linker to make the assembled GO random rather than a laminated stacked in the membrane. Moreover, its roughness, pore structure, and wettability can be tuned by changing the chemical composition. This membrane is superhydrophilic through the joint action of hydrophilic surface chemistry of PVA and the micro/nanoscale structure of GO. Therefore, this membrane has good separation efficiency for tween 80-stabilized O/W emulsions with a flux up to 600 L m^{-2} h^{-1} bar^{-1}, which was higher than the traditional laminated membrane prepared via the filtration-assisted method. Moreover, this membrane was antifouling and can be easily recycled for long-term use. This work is the first to study the CNTs-based hydrogel membrane in a separation field. Jin et al. prepared a single-walled carbon nanotubes/titanium dioxide (SWCNT/TiO_2) ultrathin membrane via a sol−gel process (Figure 6B).[32] Because of the TiO_2 nanoparticles' photoresponsive property, this membrane achieved the superhydrophilic property with ultraviolet light irradiation. Furthermore, it can separate various sodium dodecyl sulfate (SDS) stabilized-O/W emulsions with a flux up to 30000 L m^{-2} h^{-1} bar^{-1} and a separation efficiency of ∼99%. Although some progress has been made on constructing separation membranes through the sol−gel method, the longtime preparation and uncontrollable pore structures have limited further development.

3.3. Electrospinning Technique. Electrospinning has been recognized as a promising and straightforward approach that can process various inorganic/organic composite materials into ordered and continuous fibers with required surface energy.[86] Moreover, it possesses powerful structural tunability and can meet the requirements to prepare materials with regulated hierarchical micro/nanostructures.[33] Besides, electrospun membranes have excellent properties, in particular, large surface area and good interconnectivity.[87] The former provides abundant reaction sites with contaminant molecules, and the latter ensures smooth channels for the permeability of fluid streams.[88] Thus, electrospun nanofibrous membranes have emerged as promising materials for filtration and adsorption of contaminants in water.

Electrospun nanofibrous membranes can be reinforced with nanocarbons, such as CNTs and GO, due to their superior mechanical and thermal properties.[89] However, the pristine GO or CNTs could easily detach from the fiber due to the weak adhesion between the nanofibers and GO or CNTs, which results in the gradual loss of separation performance.[90] Chen et al. prepared a porous structured polyvinyl alcohol-graphene oxide (PVA-GO) nanofibrous membrane through electrospinning to overcome this problem.[91] By adjusting the relative ratio of the GO in the PVA dispersion, GO sheets can maintain compatibility and avoid aggregation, so this membrane has a continuous hierarchy and uniform structure. This membrane can separate various O/W emulsions with a flux above 30 L m^{-2} h^{-1} and efficiency above 99%. Although this membrane has a high rejection ratio for O/W emulsions, the lower antifouling ability has limited its further development. Given this, two main strategies are adopted to improve the carbon-based membranes' environmental adaptability fabricated by electrospinning.

3.3.1. Physical Antifouling. Designing a specific structure can improve the antifouling ability of membrane separation material. Xue et al. fabricated a hydrolyzed polyacrylonitrile/graphene oxide (h-PAN/GO) three-dimensional porous membrane through electrospinning.[33] The h-PAN/GO nanofibers' average diameter was approximately 450 nm, and the h-PAN/GO membrane possessed high porosity (Figure 7A).

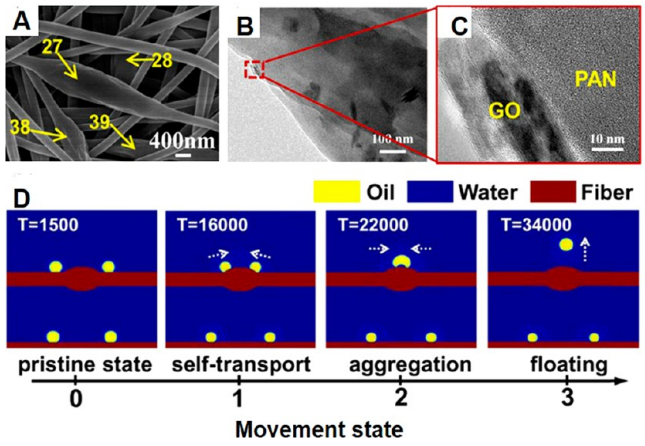


Figure 7. (A) SEM image of the h-PAN/GO membrane. (B,C) TEM image and its high magnification image of the h-PAN/GO membrane. (D) Movement state of the oil droplets on the h-PAN/GO membrane, including pristine state, self-transport, aggregation, and floating away from the membrane surface.[33] Reprinted with permission from ref 33. Copyright 2017 Elsevier.

Moreover, owing to the difference between the size of the GO sheets and the fiber diameter between the polymer matrix and GO, obvious ellipsoids around GO nanosheets can be formed and lead to a unique nanoscale spindle-knot structure (Figure 7B,C). This structure cannot only enhance the hydrophilicity of the h-PAN/GO membrane because of its micro/nanostructures, but also it can endow the h-PAN/GO membrane with high antifouling performance because this structure can cause the motion of oil droplets and finally float away from the membrane surface (Figure 7D).

3.3.2. Chemical Antifouling. Using the material's essential characteristics can also enhance its antifouling ability. Zhan et al. developed a graphene oxide/poly(arylene ether nitrile) (GO/PEN) composite membrane with stable thermal and chemical properties through electrospinning.[92] It showed superhydrophilicity because of the heterogeneous structure and hydrophilic polydopamine. Furthermore, this membrane presented excellent reusability for various O/W emulsions under harsh surroundings, such as high-temperature, strong corrosive acidity (1 mol/L HCl), and basicity (1 mol/L NaOH). This membrane's remarkable antifouling performance resulted from the good inherent properties of PEN, including good solubility, high corrosion resistance, and exceptional thermal stability.

Apart from this, incorporating photocatalytic nanoparticles, such as TiO_2 or MOF, is another promising strategy to improve antifouling properties.[93,94] For example, TiO_2 shows an excellent self-cleaning ability due to the produced electron (e^-_{CB}) in the conduction band and (h^+_{VB}) in the valence band under the excitation of suitable energy. By combining the advantages of GO and TiO_2, Gangasalama et al. prepared a CNTs-based membrane via electrospinning. This membrane can realize the separation of various O/W emulsions with an efficiency of ∼97.4%. Moreover, it can degrade dye molecules into carbon dioxide and water because of the generated

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

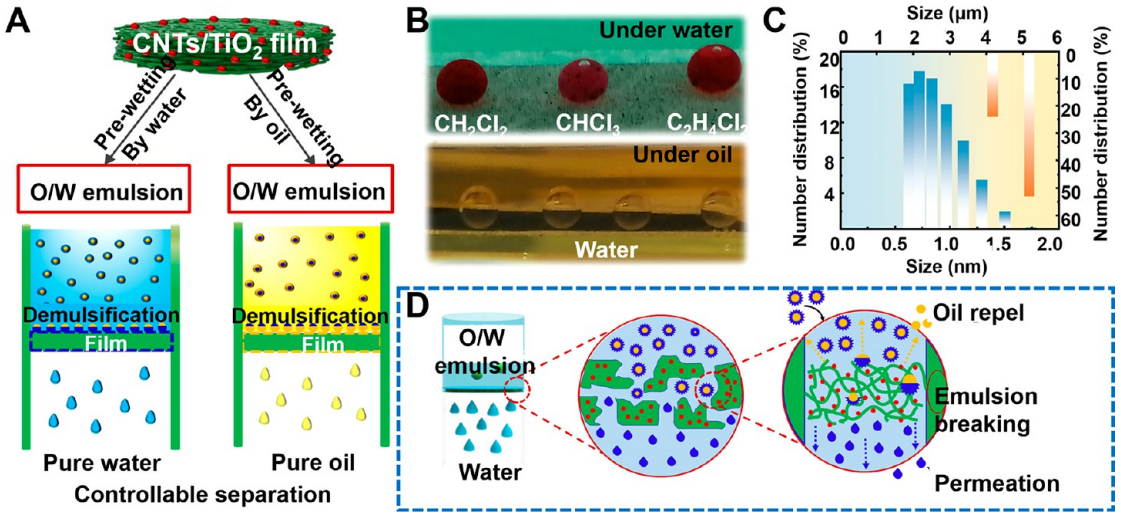


Figure 8. (A) Schematic diagram of the CNTs/TiO_2 membrane's construction process for on-demand emulsion separation. (B) Photographs of the CNTs/TiO_2 membrane's wettability toward different liquids under water and oil, respectively. (C) Particle size distribution of the feed emulsion and filtration. (D) Demulsification mechanism of the CNTs/TiO_2 membrane.[99] Reprinted with permission from ref 99. Copyright 2020 Elsevier.

superoxide radicals ($^{\bullet}O^{2-}$) and hydroperoxyl radicals ($HO_2^{\bullet}$).[93]

Electrospun membranes show a promising application in environmental remediation. However, it remains the primary challenge to disperse the CNTs or GO into the electrospinning solution and eventual nanofiber due to van der Waal's forces.[95] Some properties are inevitably sacrificed despite some techniques, such as covalent or noncovalent modification, being adopted to improve their dispersion. Another limitation is the durability of the electrospun polymer-carbon composite membranes.[96] The rough structures are easy to be damaged under some conditions, which resulted in the loss of the oil/water separation ability. Besides, the nanoparticles may gradually leach from the electrospun carbon-based composite membranes, which will result in secondary contamination during the filtration process.[89] Therefore, it is highly needed to improve the dispersion of nanocarbons and their interface force with nanofiber to develop electrospun carbon-based membranes with excellent stability and antifouling ability.

3.4. Vacuum-Assisted Filtration. Compared with the mentioned membrane construction strategy, vacuum-assisted filtration is demonstrated as the most popular method to achieve membranes on different surfaces because it is simple and highly reproducible and allows precise control in the thickness of the membranes. Many separation membranes were constructed under these merits, such as carbon-based separation membranes, for wastewater purification. According to their different compositions, they are divided into the following three parts.

3.4.1. Inorganic Nanoparticle Modified Carbon-Based Separation Membranes. GO has gained tremendous attention because of its distinctive characteristics, such as tunable mass transfer channels, large surface area, and ultrafast transporting properties.[19] It can block various molecules/ions through size screening, electrostatic interactions, and interfacial adsorption effects, making it a suitable material to construct advanced membranes for water separation.[24] However, it usually suffers from low separation flux resulting from GO's narrow transport channels and strong interaction between the GO sheets.[95] Lu et al. designed a hierarchically nanostructured GO-TiO_2 membrane through coupling photocatalytic degradation with membrane filtration.[35] The TiO_2 nanoparticles were used as the building blocks to alleviate the overlap tendency of the GO sheets. In addition, its self-cleaning property made this membrane separate various O/W emulsions for long-term operation. Nonetheless, the TiO_2 bandgap energy mismatch and the sunlight spectra made it suffer from low efficiency (less than 6% of the solar energy) and a narrow light response range.[97] Consequently, it is essential to optimize TiO_2 nanoparticles to achieve efficient photoactivation in the visible spectrum.

Combining TiO_2 with g-C_3N_4 demonstrates a promising direction in membrane separation fields. Lu et al. prepared a sunlight-driven self-cleaning GO-based membrane through vacuum-assisted filtration.[98] This membrane showed high permeation flux and good self-cleaning ability (recovery rate > 95%) for separating O/W emulsions. The presence of palygorskite (PG) and graphene carbon nitride@bismuth carbonate (g-C_3N_4@BOC) can avoid the decrease of the interlayer distance of this membrane. The BOC possessed a hydrophilic character, which gave this membrane underwater superoleophobicity. Therefore, this membrane showed a higher gasoline-in-water emulsion separation flux (4600 L m^{-2} h^{-1} bar^{-1}) than that of the pure GO membrane (100 L m^{-2} h^{-1} bar^{-1}). More importantly, the g-C_3N_4@BOC catalyst has an excellent photocatalytic performance in the visible light range, so it can effectively avoid membrane fouling and a sharp decrease of the permeation flux. TiO_2 was also used to modify CNTs to construct an advanced membrane for the separation of the O/W emulsion. For example, Chen et al. prepared a CNTs/TiO_2 membrane with superhydrophilic property through in situ growth TiO_2 nanoparticles on the surface of CNTs (Figure 8A,B).[99] This membrane can achieve multitasking performance for treating tween 80-stabilized O/W emulsions (Figure 8C,D). Furthermore, this membrane has presented antifouling capability owing to its superior wettability. Despite the progress, these nanoparticles inevitably fall off the carbon-based membrane due to their weak interface force, which resulted in the degradation of separation performance and may cause secondary pollution. Therefore,

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

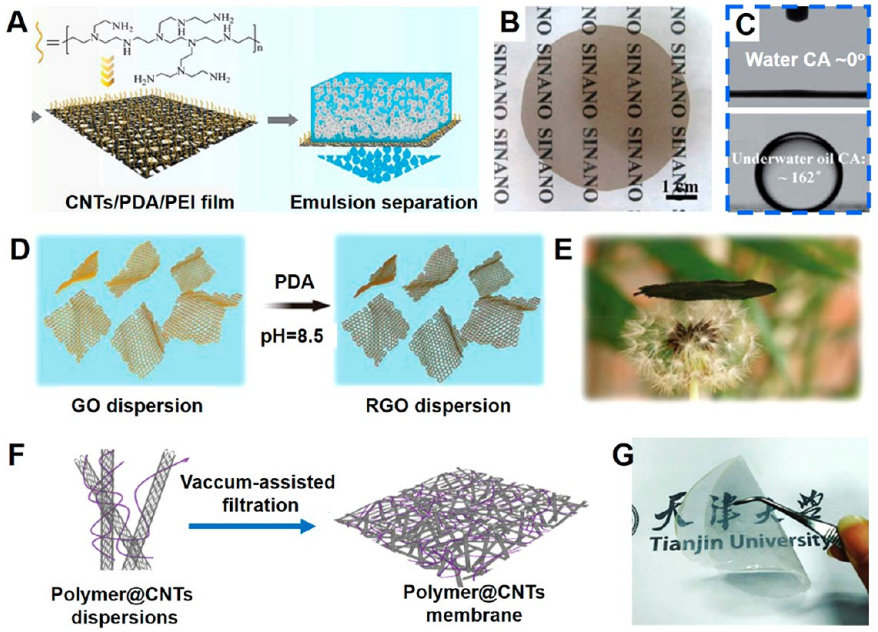


Figure 9. (A) Schematic illustrations of CNTs/PDA/PEI membrane preparation for superhigh O/W emulsion separation. (B) Photograph of CNTs/PDA/PEI membrane on the solution surface.[102] (C) WCA and the CNTs/PDA/PEI membrane's oil contact angle, respectively. (D) Schematic diagram of the reduction process of the GO sheets. (E) Photograph of a free-standing PDA-RGO membrane.[103] (F) Schematic illustration of the synthesis of polymer functionalized CNTs membrane.[105] (G) Photograph of the polymer functionalized CNTs membranes.[104] Reprinted with permission from ref 102, ref 103, ref 104, and ref 105, respectively. Copyright 2015 Royal Society of Chemistry, 2015 Royal Society of Chemistry, 2017 Royal Society of Chemistry, and 2017 Elsevier, respectively.

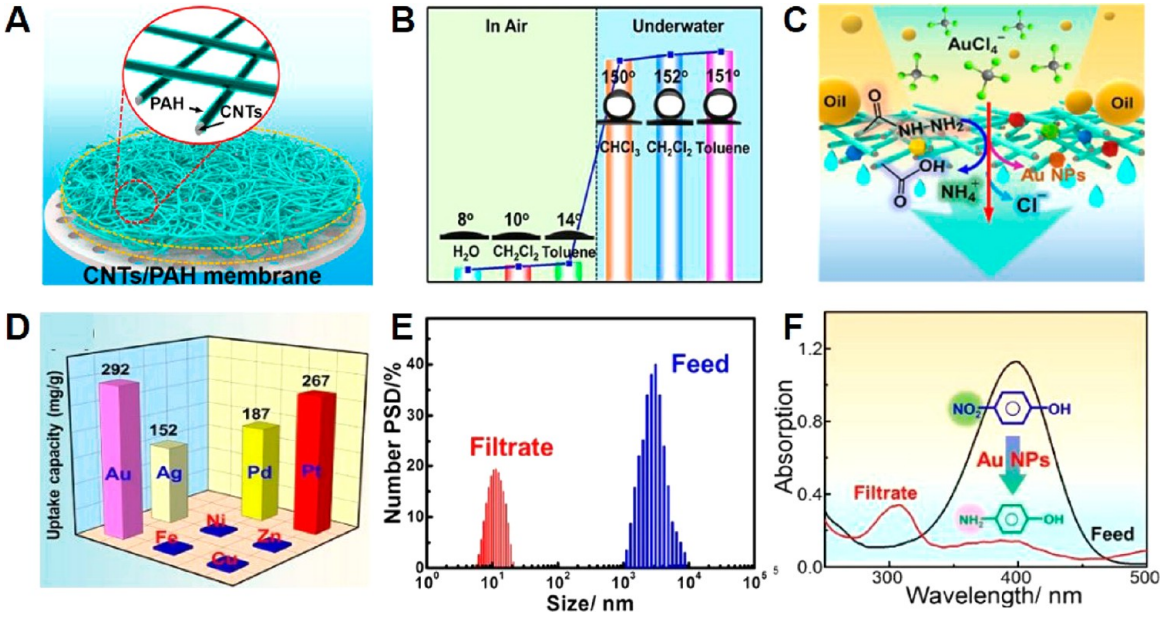


Figure 10. (A) Schematic diagram of the CNTs/PAH membrane and its enlarged responding structure. (B) Wettability of CNTs/PAH membrane in the air (left) and underwater (right). (C) Schematic illustration of the reduction process of the CNTs/PAH membrane. (D) Uptake capacity of CNTs/PAH reductive membrane for different metal ions. (E) Particle distribution of the feed and filtrate solution, respectively. (F) Catalytic degradation ability of the CNTs/PAH@Au membrane.[106] Reprinted with permission from ref 106. Copyright 2018 Royal Society of Chemistry.

appropriate measures need to be taken to improve the membrane microstructure's stability.

3.4.2. Polymer Functionalized Carbon-Based Separation Membranes. In recent years, functional polymers with adjustable surface functional groups, superior physical, chemical, and mechanical properties have played an essential role in the various application fields, such as gas storage, separations, and catalysis.[100] Also, polymers have large structural units, which can adapt to surrounding environments and regulate wettability as well as adhesion of different species.[66] In particular, according to Wenzel's model, hydrophilic polymers can endow the rough interface with the superhydrophilic property.[67] Therefore, colossal research on superhydrophilic polymer functionalized carbon-based membranes has been carried out through a combination of suitable surface chemistry and roughness. For example, polydopamine

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

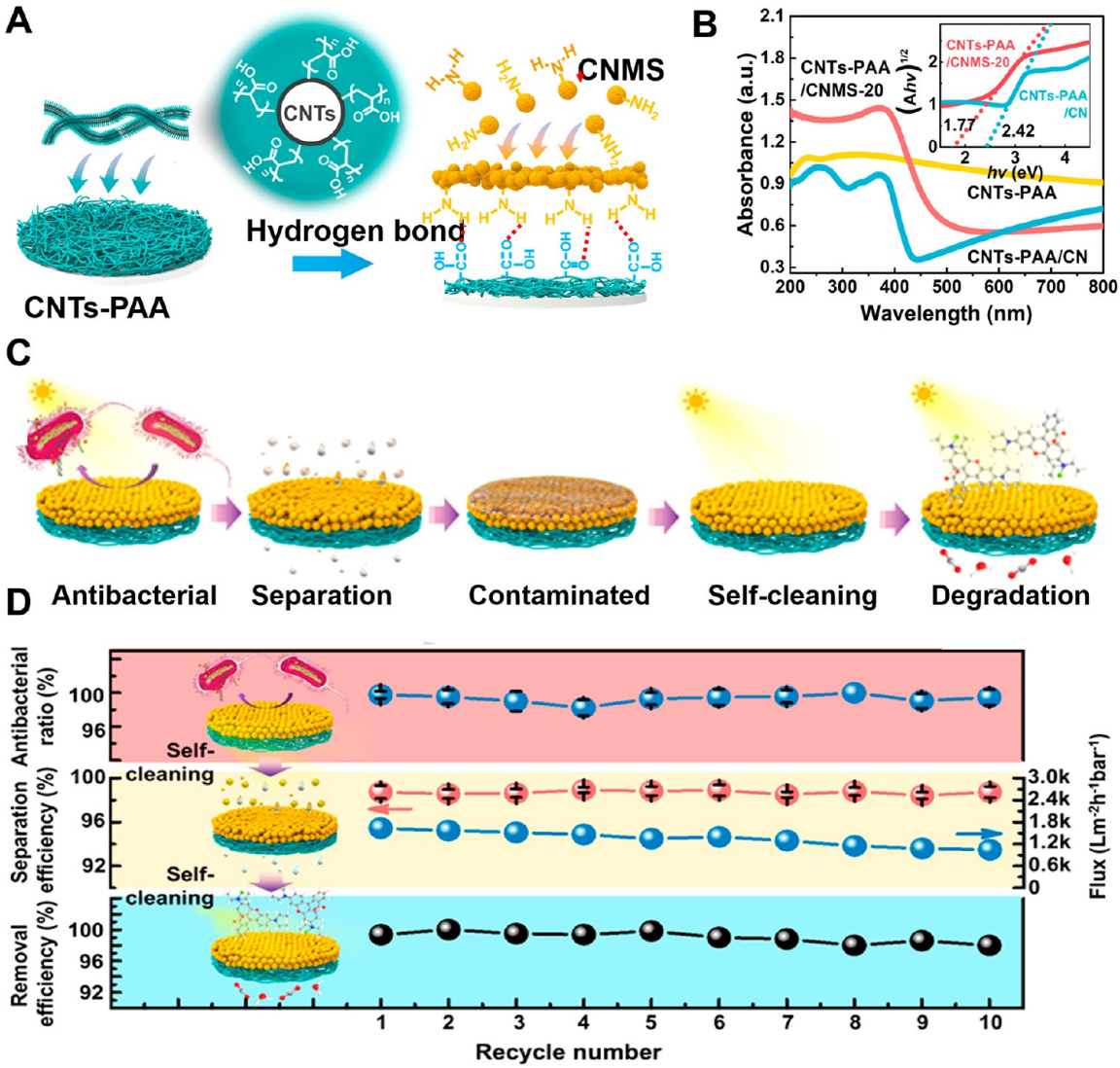


Figure 11. (A) Schematic description of the modification of CNTs-PAA membrane with CNMS particles. (B) UV−vis absorption spectra of different membranes. (C,D) Cyclic and continuous self-cleaning properties of the CNTs-PAA/CNMS-20 membrane, including the antibacterial process, O/W emulsion separation process, and photocatalytic degradation.[110] Reprinted with permission from ref 110. Copyright 2020 Wiley-VCH.

(PDA), with abundant phenolic hydroxyl groups and amino groups, presents extensive adhesion property with various polymers and inorganics, which provides a platform for material engineering functionalization.[101] Jin et al. prepared a CNTs/PDA/PEI membrane via vacuum-assisted filtration (Figure 9A).[102] This membrane presented ultrathin thickness (~158 nm) and a tunable pore size (~10−100 nm) (Figure 9B). Furthermore, due to the hydrophilic groups' existence, this membrane showed good affinity to water with the WCA of about 0° and underwater−oil contact angle above 150°(Figure 9C). Therefore, this membrane exhibited an extremely high separation flux for various tween 80-stabilized O/W emulsions (~3000−6000 L m^{-2} h^{-1} bar^{-1}), which was 10 times higher than the traditional separation materials with a high rejection ability.

Feng et al. prepared a polydopamine@reduced graphene oxide (PDA-RGO) membrane through vacuum-assisted filtration (Figure 9D).[103] This membrane presented splendid superhydrophilic and free-standing properties (Figure 9E). Moreover, it displayed exceptionally superior chemical stability that can withstand several corrosive environments. Apart from PDA, other hydrophilic polymers, such as poly(acrylic acid), polyvinyl alcohol, sodium alginate, and chitosan, can also endow the CNTs membrane superhydrophilic property.[104] For example, to restrain the nonspecific interactions between foulants and the membrane surface, Jiang et al. fabricated a series of polymer functionalized CNTs membranes via synchronously regulating the surface charges, physical morphologies, and hydrophilicity of membranes[105] (Figure 9F,G). The synergistic effect between CNTs with a hierarchical nanostructure and hydrophilic polymers with different surface charges endowed these membranes with excellent antifouling ability for tween 20-stabilized O/W emulsion separation.

Zhang et al. fabricated a superhydrophilic carbon nanotubes/polyacryloyl hydrazide (CNTs/PAH) membrane for synchronous extracted noble metal ions and separated O/W emulsion (Figure 10A,B).[106] A large amount of small-sized noble metal nanoparticles, involving Ag, Pd, Pt, Au, were in situ produced on the membrane surface due to the reducibility

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

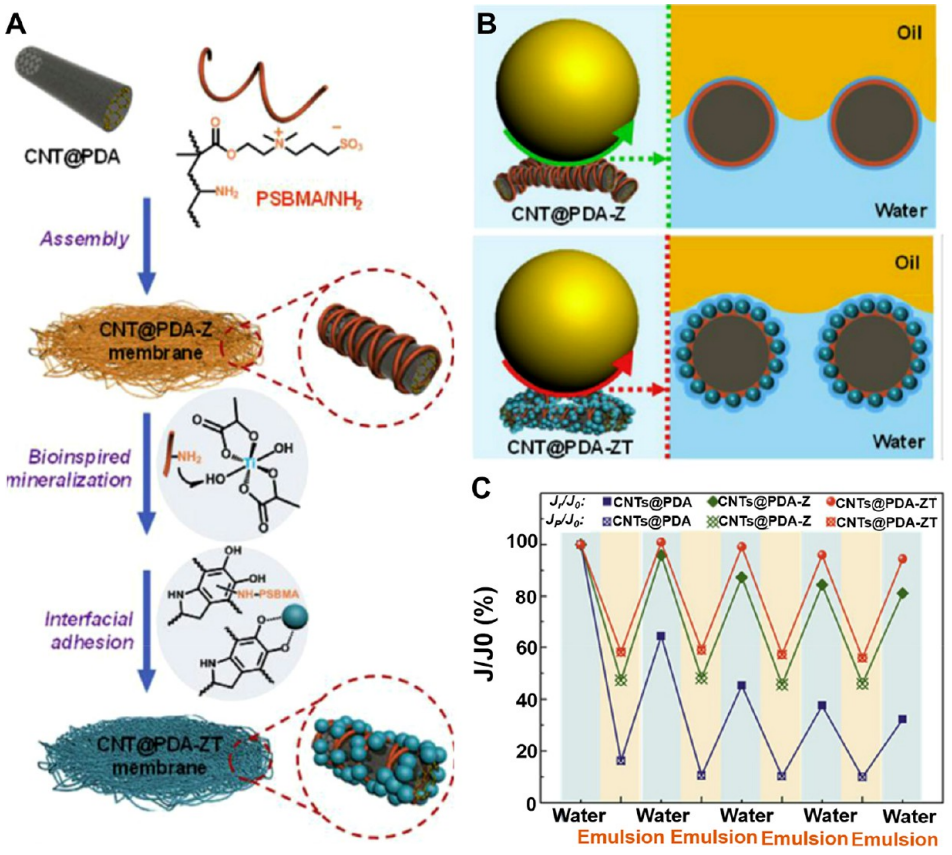


Figure 12. (A) Schematic illustration of fabricating the CNT@PDA-ZT membrane and its (B) antifouling state. (C) Separation flux recovery of the CNT@PDA, CNT@PDA-Z, and CNT@PDA-ZT membranes for O/W emulsion separation.[111] Reprinted with permission from ref 111. Copyright 2019 Elsevier.

of the CNTs/PAH membrane. Furthermore, due to the different reduced rates arising from reduction potentials, the restored noble metal nanoparticles presented various sizes and uptake capacities (Figure 10C,D). This membrane with noble metal nanoparticles anchored can realize the separation of tween 80-stabilized O/W emulsions and comprehensively be applied for catalytic decomposition of dye molecules to achieve the recycling utilization of wasted noble metal ions (Figure 10E,F). Although polymer functionalized carbon-based membranes have provided an effective solution for O/W emulsion separation, these membranes' antifouling ability is attributed to the hydration mechanism that the hydrophilic membranes are infiltrated with water and subsequently block the sufficient contact of oil. However, during the separation process, these hydration layers usually lose their antifouling ability because of the long-term pollutant adsorption, infiltration, accumulation, and migration. Therefore, advanced functional polymers should be exploited to guarantee the carbon-based membranes with the stable antifouling ability through adjusting the interfacial adhesion between the carbon materials and the polymer matrix.

3.4.3. Polymer/Inorganic Hybrid Carbon-Based Separation Membranes. Nowadays, nanoparticles and polymers' collaborative surface functionalization have been considered effective strategies to improve carbon-based membranes' purification performance.[107] On the one hand, the polymer/inorganic carbon-based membranes can retain their inherent essence and possess higher processability and stability through these three counterparts' joint combinations. On the other hand, the nanoparticles are independent within the polymer matrix and avoid aggregation or even falling from the separation membranes, thus can provide more interaction sites with the target pollutants.[108] A series of polymer/inorganic hybrid carbon-based membranes are constructed by combining the advantages of polymers, nanoparticles, and carbon materials. According to their functions, they are mainly divided into the following three parts.

(1) Self-cleaning and O/W emulsion separation. Incorporating photocatalytic nanoparticles with the membrane separation, such as g-C_3N_4, has been regarded as a potentially effective manner to reduce membrane fouling.[79] For example, Yu et al. fabricated an RGO/PDA/g-C_3N_4 membrane by vacuum-assisted filtration.[109] The g-C_3N_4 sheets can widen the interlayer spacing of RGO and thus enhance the separation flux. Moreover, the RGO was served as a semiconductor to improve the photocatalytic performance of g-C_3N_4 sheets. In addition, the introduction of PDA cannot only increase the interface attachment between RGO and g-C_3N_4 sheets but also can provide more active sites for water purification. Therefore, this membrane can separate SDS-stabilized O/W emulsions containing dye molecules with an efficiency above 99%. Furthermore, it can keep its separation flux and rejection ability after five cycles of separation only under the drive of sunlight. Nevertheless, the g-C_3N_4 with a layered structure restrains solar energy use because of its large bandgap (2.9 eV). Chen et al. designed a sunlight-activated separation membrane by coupling graphitic carbon nitride nanomicrospheres (CNMS) and a CNTs-PAA membrane (Figure 11A).[110]

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

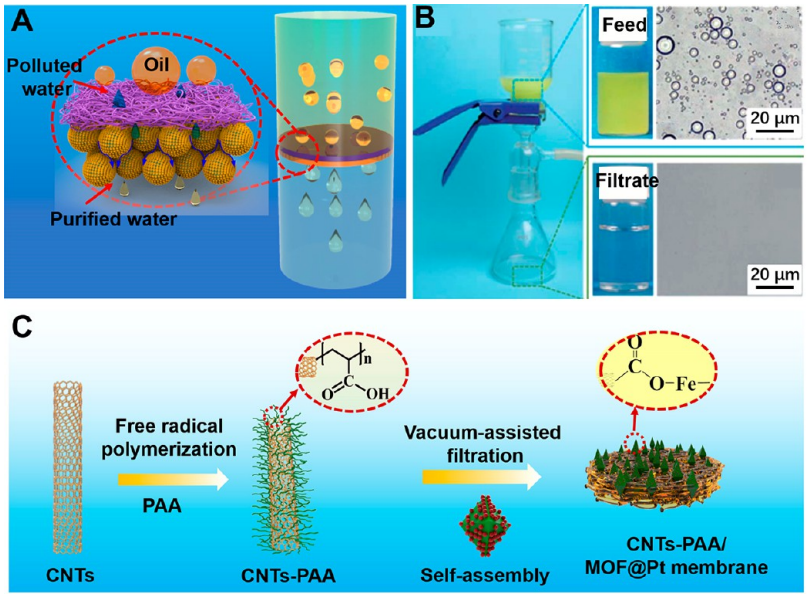


Figure 13. (A) Microstructure model of the CNTs/PS@AuNPs membrane for synchronous water purification. (B) Separation efficiency of the CNTs/PS@AuNPs membrane for O/W emulsions containing dyes.[114] (C) Schematic illustration of the construction process of the CNTs-PAA/MOF@Pt membrane.[116] Reprinted with permission from ref 114 and ref 116, respectively. Copyright 2016 Royal Society of Chemistry and 2021 Elsevier, respectively.

This membrane presented superhydrophilicity and underwater superoleophobicity under the joint effort of the unique structure and chemistry property. Compared with traditional g-C_3N_4 sheets-based membranes, it was endowed with a smaller bandgap (~1.77 eV) to enhance visible-light sensitivity to remove pollutants (Figure 11B). Therefore, this membrane possessed excellent self-cleaning performance, realizing all-in-one purification of wastewater with coexisting contaminations, including tween 80-stabilized oils, dye molecules and bacteria (Figure 11C,D). In addition, the combination of photocatalytic nanoparticles and zwitterion can provide an effective solution for improving the antifouling ability. Zhao et al. synthesized a polyzwitterion/titania PDA@CNTs (CNTs@PDA-ZT) membrane by a dual-bioinspired strategy.[111] First, PDA was modified on the surface of CNTs to form a hydrophilic layer, which acted as an adhesion interface for further modification. Second, polyzwitterion with amino segments (PSBMA/NH_2) can form hydrogen bonding and cation−π interactions with CNTs@PDA via Michael addition/Schiff base reactions. Lastly, TiO_2 nanoparticles were loaded on the CNTs@PDA membrane through the hydrogen bonding and electrostatic interactions between TiO_2 and the CNTs@PDA-PSBMA/NH_2 membrane (Figure 12A). The synergistic effect between TiO_2 and PSBMA/NH_2 formed a concrete highly hydrated barrier, improving the antifouling property of the CNTs@PDA membrane (Figure 12B). Therefore, this membrane kept its separation flux and exhibited antifouling performance for SDS-stabilized O/W emulsion separation (Figure 12C).Despite this progress, some problems still need to be solved. On the one hand, most of the photocatalytic nanoparticles suffered from relatively low efficiency and stability, which are far from the requirements of practical applications. Therefore, it is essential to develop new strategies to explore novel photocatalytic nanoparticles with a highly porous architecture, a larger surface area, higher chemical tunability, and prolonged light-harvesting ability for efficient solar-to-chemical applications.[112] On the other hand, zwitterionic polymers have drawn significant attention for membrane separation due to their impressive hydrophilicity and antifouling properties. However, seldom have reports focused on developing zwitterionic polymers/carbon-based membranes with mechanical strength and thermal and ion selectivity stabilities to the best of our knowledge. Besides, most of these membranes with self-cleaning ability are limited with single adsorption or short-period, which cannot sufficiently reflect these membranes' antipollution performance under the long-term coexistence of multiple pollutants.[113] Therefore, novel carbon-based separation with stable self-cleaning performance for dynamic domestic sewage treatment should be urgently developed.

(2) Catalytic degradation and O/W emulsion separation. Soluble organic dye molecules bring severe damage to the natural environment. Combining appropriate photocatalyst with carbon-based membranes is known as a practicable means to eliminate various substances simultaneously. Zhang et al. fabricated carbon nanotubes/polystyrene@gold nanoparticles (CNTs/PS@AuNPs) through covalent polymerization and subsequent vacuum-assisted filtration (Figure 13A).[114] The upper surface of this membrane presented superhydrophilicity due to the hydrophilicity of PAA, and the underlayer showed catalytic ability because of the presence of Au nanoparticles. This structure made this membrane effectively separate tween 80-stabilized O/W emulsions with flux as high as 3500 L m^{-2} h^{-1} bar^{-1}. Moreover, it showed catalytic degradation ability when the dye molecules contacted the tortuous channels between PS@AuNPs microspheres. However, the sophisticated fabrication process has limited its practical efficiency. Chen et al. furthered fabricated a CNTs-based membrane with a sandwich structure through vacuum-assisted filtration.[115] The palladium@platinum (Pd@Pt) nanoparticles were embedded closely inside the CNTs network and distributed uniformly. This membrane can simultaneously separate tween 80-stabilized O/W emulsions and decompose organic pollutants via the catalytic Pd@Pt nanoparticles (Figure 13B).

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

Even so, these membranes face several critical issues, such as the lower structural stability resulting from the nanoparticles' weak interfacial combination ability. Given the preceding, Gu et al. presented a novel carbon-based membrane by taking MOFs' advantages, such as photocatalyst, high specific surface areas, large pore volumes, stable structures, and environmental friendliness.[116] The MOFs nanoparticles were tightly embedded into the CNTs membrane and formed a catalytic layer via electrostatic interaction (Figure 13C). Therefore, this membrane can synchronously degrade dye molecules and separate tween 80-stabilized O/W emulsions. The separation flux reached up to 11000 L m^{-2} h^{-1} bar^{-1}. Furthermore, this membrane has stable catalytic degradation efficiency (>98.5%) after five cycles of separation. In addition, this membrane presented structural and chemical stability. Despite the progress, many aspects should be improved for future applications. First, it is not easy to produce these metal nanoparticle catalysts in kilogram quantities within a short period because of its complex preparation process, which has hindered their further practical applications. Second, these catalysts are unstable in water and usually reunited into large particles, weakening or even losing their catalytic degradation ability. Third, most of them suffered from weak mechanical properties and bad processability, which hinder their effective combination with carbon-based membranes. Lastly, these catalysts may bring a burden to the environment. Consequently, it is still challenging to achieve cheap, stable, and efficient catalysts for practical water purification.

(3) Molecular sieving and O/W emulsion separation. As mentioned above, the purification of polluted water containing dye molecules and metal ions is an intractable task concerned with water resources. GO membranes have exhibited superior gating performances due to their special wettability and unmatched 2D nanochannels.[20] For one thing, the hydrophilic functional groups and huge specific surface area make the GO an excellent choice to achieve efficient contact with water-soluble dye molecules.[21] For another, the GO sheets' shell-like architecture can serve as an inhibitor layer to block dye molecules from passing.[24] Using these features, Su et al. designed a SiO_2/EDA/GO composite membrane through the vacuum-assisted filtration method.[34] SiO_2 nanoparticles provided a rough structure on the GO nanosheets and endowed this membrane with excellent hydrophilicity. Therefore, this membrane showed perfect separation property for SDS-stabilized O/W emulsions with flux up to 470 L m^{-2} h^{-1} and a separation efficiency of ∼99.4%. Moreover, it showed a good rejection ability for dyes with an efficiency of ∼100%. Liu et al. fabricated an RGO-based separation membrane by halloysite nanotubes assembly and PDA modification.[117] The halloysite nanotube can enlarge the RGO interlayer's space from 0.44 to 0.73 nm, thus promoting the separation flux of surfactant-stabilized O/W emulsions from ∼40 L m^{-2} h^{-1} to ∼273 L m^{-2} h^{-1}. Moreover, the PDA can increase the adhesion ability between the halloysite nanotube and RGO. In addition, the introduced PDA can provide more active sites for adsorbing dye molecules. Therefore, this membrane can separate various O/W emulsions with an efficiency of ∼99.85% and achieve effective rejection of dye molecules and heavy metal ions (such as Cu^{2+}, Cr^{3+}) with an efficiency of ∼99.7%. Apart from this work, Ou et al. developed a free-standing GO-based membrane through vacuum-assisted filtration.[118] Chitin nanocrystals were used to enhance the GO layer's distance and endow the GO membrane with superhydrophilicity. This membrane exhibited a high rejection ratio for dyes molecular and separation efficiency for SDS-stabilized O/W emulsions (>97.5%). However, these membranes showed lower water permeation due to their increasing interface resistance, which is arisen from the concentration polarization across these isotropic interfaces. In addition, dye molecules and metal ions may penetrate the inside of the membrane, which may inhibit the water molecules' transmission.[96] Therefore, it is crucial to develop advanced carbon-based separation membranes with particular structures, such as the Janus structure, to impede the concentration polarization for long-term application.[97,119] Despite the technology that has been widely applied in various domains, there are also some issues that need to be resolved. For one thing, the vacuum-assisted filtration process is highly dependent on the composition and pore size of the substrate and the suction filter's size. Therefore, it is difficult to obtain a composite membrane with a controllable space size through vacuum filtration like a self-assembly method. Moreover, the existence of the substrate cannot only lead to an increase in the production cost, but also it may bring on an adverse effect on the membrane's separation performance. For another, the filter components usually fall off from the substance due to their weak interface force, resulting in the degradation of separation performance. Therefore, we should adopt appropriate measures to enhance the stability of the membranes in the substance.

4. SUMMARY

The rapid development of membrane-separation materials and the advantages of carbon-based materials have effectively tackled the emulsified oil/water mixture, mainly containing other compositions. This review has emphasized the construction of superhydrophilic carbon-based membranes that play key water environmental protection roles. The fundamental theories of wettability, oil/water separation mechanism, and kinetics are explained in detail. Furthermore, the superhydrophilic carbon-based membranes are divided into four parts according to the membrane construction strategy. The detailed research advances during the past 10 years and their responding disadvantages are elaborated on in each region. Despite the remarkable progress of the superhydrophilic carbon-based separation membranes, some critical challenges should be urgently overcome for further development.

For one thing, mechanical stability is an essential factor that should be emphasized. The carbon-based membrane can achieve excellent separation performance through structural adjustment and performance optimization but at the expense of mechanical stability to a certain degree. Typically, structural durability can be acquired by introducing advanced materials, such as polymers with a self-healing ability or functional nanoparticles, into the carbon-based interfacial membranes through polymerization grafting, interfacial assembly, and electrochemical deposition.

For another, most of these carbon-based membranes are subjected to severe membrane interfacial fouling due to the nonspecific deposition or adsorption between the membrane surface and contaminations, such as salts, particles, colloids, macromolecules. The membrane fouling leads to a sharp decline in separation flux and selectivity during purification operation and even reduces service life. Combining hydrophilic polymers or nanoparticles (for example, TiO_2, g-C_3N_4, MOF,

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

etc.) with the carbon-based membrane can improve their antifouling ability based on hydration and the photocatalytic mechanism. However, their antifouling abilities are only applied for static and short-time adsorption, which are unsuitable for the dynamic and long-term antifouling process. Therefore, we should devote sustained efforts to exploring novel nanoparticles/polymers or adopting advanced technology to improve the carbon-based membranes' antifouling ability. On the one hand, we can improve photocatalytic nanoparticles' light utilization efficiency by controlling the morphology (rod, spherical, octahedron, etc.) of the nanoparticles, mesoporous structure, roughness, size, or chemical doping of the nanoparticles. On the other hand, we can exploit novel zwitterions with superior rejection ability to endow the carbon-based membrane with self-cleaning properties. In addition, some advanced strategies, such as electrocatalysis, chemical deposition, supercritical fluid chemistry, plasma technology, 3D printing, surface patterning, etc., should be widely adopted to fulfill an all-round structure and composition adjustment for unparalleled self-cleaning functionality.

In addition, it should be emphasized that there is a large gap between scientific research and amplified application. The current preparation process cannot realize large-scale production. The carbon-based membrane can only achieve the purification of small volumes of oil/water mixtures and cannot meet practical applications. We believe this review will arouse researchers from various domains (surface/interface chemistry, functional materials, etc.) to carry out more scientific research aiming to construct advanced carbon-based separation membranes to meet the ultimate wastewater goal purification.

AUTHOR INFORMATION

Corresponding Authors

Luke Yan − *Polymer Materials & Engineering Department, School of Materials Science & Engineering, Chang'an University, Xi'an 710064, China;* orcid.org/0000-0001-5225-5812; Email: yanlk_79@hotmail.com

Tao Chen − *Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China; University of Chinese Academy of Science, School of Chemical Sciences, Beijing 100049, China; Polymer Materials & Engineering Department, School of Materials Science & Engineering, Chang'an University, Xi'an 710064, China;* orcid.org/0000-0001-9704-9545; Email: tao.chen@nimte.ac.cn

Authors

Jincui Gu − *Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China; University of Chinese Academy of Science, School of Chemical Sciences, Beijing 100049, China*

Lingtong Ji − *Polymer Materials & Engineering Department, School of Materials Science & Engineering, Chang'an University, Xi'an 710064, China*

Peng Xiao − *Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China;* orcid.org/0000-0003-2231-9824

Chang Zhang − *Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China; University of Chinese Academy of Science, School of Chemical Sciences, Beijing 100049, China*

Jian Li − *College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China;* orcid.org/0000-0001-5104-1564

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.1c07737

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the support from the National Key Research and Development Program of China (Grant 2019YFC1606603), the K. C. Wong Education Foundation (Grant GJTD-2019-13), the Open Research Fund of Key Laboratory of Marine Materials and Related Technologies (Grants 2013DP173296 and 2019K03), the Bureau of Frontier Science and Education of Chinese Academy of Sciences (Grant QYZDB-SSW-SLH036), Shaanxi Key Research and Development Project (Grant 2020ZDLGY13-08), and the Shaanxi Key Research and Development Project (Grant 2021GY199).

REFERENCES

(1) Ge, J.; Zhao, H. Y.; Zhu, H. W.; Huang, J.; Shi, L. A.; Yu, S. H. Advanced Sorbents for Oil-Spill Cleanup: Recent Advances and Future Perspectives. *Adv. Mater.* **2016**, *28*, 10459−10490.

(2) Wan, W. C.; Lin, Y. H.; Prakash, A.; Zhou, Y. Three-dimensional Carbon-Based Architectures for Oil Remediation: from Synthesis and Modification to Functionalization. *J. Mater. Chem. A* **2016**, *4* (48), 18687−18705.

(3) Huang, X. W.; Zhang, S.; Xiao, W.; Luo, J. C.; Li, B.; Wang, L.; Xue, H. G.; Gao, J. F. Flexible PDA@ACNTs Decorated Polymer Nanofiber Composite with Superhydrophilicity and Underwater Superoleophobicity for Efficient Separation of Oil-in-Water Emulsion. *J. Membr. Sci.* **2020**, *614*, 118500.

(4) Pan, Y. L.; Liu, L. M.; Zhang, Z. J.; Huang, S. C.; Hao, Z.; Zhao, X. Z. Surfaces with Controllable Super-wettability and Applications for Smart Oil-Water Separation. *Chem. Eng. J.* **2019**, *378*, 122178.

(5) Huang, T. F.; Zhang, L.; Chen, H. L.; Gao, C. J. Sol-Gel Fabrication of a Non-Laminated Graphene Oxide Membrane for Oil/Water Separation. *J. Mater. Chem. A* **2015**, *3* (38), 19517−19524.

(6) Yang, J.; Li, H. N.; Chen, Z. X.; He, A.; Zhong, Q. Z.; Xu, Z. K. Janus Membranes with Controllable Asymmetric Configurations for Highly Efficient Separation of Oil-in-Water Emulsions. *J. Mater. Chem. A* **2019**, *7* (13), 7907−7917.

(7) Kang, Y.; Xia, Y.; Wang, H. T.; Zhang, X. W. 2D Laminar Membranes for Selective Water and Ion Transport. *Adv. Funct. Mater.* **2019**, *29* (29), 1902014.

(8) Chen, X. F.; Mohammed, S.; Yang, G.; Qian, T. Y.; Chen, Y.; Ma, H. Y.; Xie, Z. L.; Zhang, X. W.; Simon, G. P.; Wang, H. T. Selective Permeation of Water through Angstrom-channel Graphene Membranes for Bioethanol Concentration. *Adv. Mater.* **2020**, *32* (33), 2002320.

(9) Yang, Y. B.; Yang, X. D.; Liang, L.; Gao, Y. Y.; Cheng, H. Y.; Li, X. M.; Zou, M. C.; Cao, A. Y.; Ma, R. Z.; Yuan, Q.; Duan, X. F. Large-area Graphene-Nanomesh/Carbon-Nanotube Hybrid Membranes for

Ionic and Molecular Nanofiltration. *Science* **2019**, *364* (6445), 1057−1062.
(10) Cheng, X. Q.; Sun, Z. K.; Yang, X. B.; Li, Z. X.; Zhang, Y. J.; Wang, P.; Liang, H.; Ma, J.; Shao, L. In Situ Asymmetry Engineering Constructing Superhydrophilic Hierarchical Polyacrylonitrile Nanofiber Membrane for Unprecedently Ultrafast Oil-Water Emulsion Separation. *J. Mater. Chem. A* **2020**, *8* (33), 16933−16942.
(11) Zhang, M. C.; Mao, Y. Y.; Liu, G. Z.; Liu, G. P; Fan, Y. Q.; Jin, W. Q. Molecular Mridges Stabilize Graphene Oxide Membranes in Water. *Angew. Chem., Int. Ed.* **2020**, *59* (4), 1689−1695.
(12) Liu, J. C.; Yu, L. J.; Yue, G. C.; Wang, N.; Cui, Z. M.; Hou, L. L.; Li, J. H.; Li, Q. Z.; Karton, A.; Cheng, Q. F.; Jiang, L.; Zhao, Y. Thermoresponsive Graphene Membranes with Reversible Gating Regularity for Smart Fluid Control. *Adv. Funct. Mater.* **2019**, *29* (12), 1808501.
(13) Zhang, M. C.; Guan, K. C.; Ji, Y. F.; Liu, G. P.; Jin, W. Q.; Xu, N. P. Controllable Ion Transport by Surface-Charged Graphene Oxide Membrane. *Nat. Commun.* **2019**, *10*, 1253.
(14) Khalilifard, M.; Javadian, S. Magnetic Superhydrophobic Polyurethane Sponge Loaded with Fe_3O_4@oleic Acid@Graphene Oxide as High Performance Adsorbent Oil from Water. *Chem. Eng. J.* **2021**, *408*, 127369.
(15) Nie, L. N.; Goh, K. L.; Wang, Y.; Lee, J.; Huang, Y. J.; Karahan, H. E.; Zhou, K.; Guiver, M. D.; Bae, T. H. Realizing Small-Flake Graphene Oxide Membranes for Ultrafast Size-Dependent Organic Solvent Nanofiltration. *Sci. Adv.* **2020**, *6*, No. eaaz9184.
(16) Sui, X.; Yuan, Z. W.; Liu, C.; Wei, L.; Xu, M. Y.; Liu, F.; Montoya, A.; Goh, K.; Chen, Y. Graphene Oxide Laminates Intercalated with 2D Covalent-Organic Frameworks as a Robust Nanofiltration Membrane. *J. Mater. Chem. A* **2020**, *8* (19), 9713−9725.
(17) Han, R. Y.; Wu, P. Y. High-Performance Graphene Oxide Nanofiltration Membrane with Continuous Nanochannels Prepared by the in Situ Oxidation of MXene. *J. Mater. Chem. A* **2019**, *7* (11), 6475−6481.
(18) Zhang, P.; Gong, J. L.; Zeng, G. M.; Song, B.; Cao, W. C.; Liu, H. Y.; Huan, S. Y.; Peng, P. Novel "Loose" GO/MoS_2 Composites Membranes with Enhanced Permeability for Effective Salts and Dyes Rejection at Low Pressure. *J. Membr. Sci.* **2019**, *574* (15), 112−123.
(19) Wang, L. D.; Boutilier, M. S. H.; Kidambi, P. R.; Jang, D. J.; Hadjiconstantinou, N. G.; Karnik, R. Fundamental Transport Mechanisms, Fabrication and Potential Applications of Nanoporous Atomically Thin Membranes. *Nat. Nanotechnol.* **2017**, *12*, 509−522.
(20) Zhang, Y. Q.; Ma, J.; Shao, L. Ultra-Thin Trinity Coating Enabled by Competitive Reactions for Unparalleled Molecular Separation. *J. Mater. Chem. A* **2020**, *8* (10), 5078−5085.
(21) Choi, Y.; Kim, S. S.; Kim, J. H.; Kang, J.; Choi, E.; Choi, S. E.; Kim, J. P.; Kwon, O.; Kim, D. W. Graphene Oxide Nanoribbon Hydrogel: Viscoelastic Behavior and Use as a Molecular Separation Membrane. *ACS Nano* **2020**, *14* (9), 12195−12202.
(22) Huang, H. B.; Shi, H. D.; Das, P.; Qin, J. Q.; Li, Y. G.; Wang, X.; Su, F.; Wen, P. C.; Li, S. Y.; Lu, P. F.; Liu, F. Y.; Li, Y. J.; Zhang, Y.; Wang, Y.; Wu, Z. S.; Cheng, H. M. The Chemistry and Promising Applications of Graphene and Porous Graphene Materials. *Adv. Funct. Mater.* **2020**, *30* (41), 1909035.
(23) Liu, Y.; Zhang, F. R.; Zhu, W. X.; Su, D.; Sang, Z. Y.; Yan, X.; Li, S.; Liang, J.; Dou, S. X. A Multifunctional Hierarchical Porous SiO_2/GO Membrane for High Efficiency Oil/Water Separation and Dye Removal. *Carbon* **2020**, *160* (30), 88−97.
(24) Shi, Z.; Zhang, W. B.; Zhang, F.; Liu, X.; Wang, D.; Jin, J.; Jiang, L. Ultrafast Separation of Emulsified Oil/Water Mixtures by Ultrathin Free-Standing Single-Walled Carbon Nanotube Network Films. *Adv. Mater.* **2013**, *25* (17), 2422−2427.
(25) Gu, J. C.; Xiao, P.; Chen, J.; Liu, F.; Huang, Y. J.; Li, G. Y.; Zhang, J. W.; Chen, T. 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* **2014**, *2* (37), 15268−15272.
(26) Gu, J. C.; Xiao, P.; Huang, Y. J.; Zhang, J. W.; Chen, T. Controlled Functionalization of Carbon Nanotubes as Superhydrophobic Materials for Adjustable Oil/Water Separation. *J. Mater. Chem. A* **2015**, *3* (8), 4124−4128.
(27) Junaidi, N. F. D.; Othman, N. H.; Fuzil, N. S.; Mat Shayuti, M. S.; Alias, N. H.; Shahruddin, M. Z.; Marpani, F.; Lau, W. J.; Ismail, A. F.; Aba, N. D. Recent Development of Graphene Oxide-Based Membranes for Oil-Water Separation: A Review. *Sep. Purif. Technol.* **2021**, *258*, 118000.
(28) Zhao, X. T.; Su, Y. L.; Liu, Y. N.; Li, Y. F.; Jiang, Z. Y. Free-Standing Graphene Oxide-Palygorskite Nanohybrid Membrane for Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2016**, *8* (12), 8247−8256.
(29) Ma, L. N.; Dong, X. F.; Chen, M. L.; Zhu, L.; Wang, C. X.; Yang, F. L.; Dong, Y. C. Fabrication and Water Treatment Application of Carbon Nanotubes (CNTs)-Based Composite Membranes: A Review. *Membranes* **2017**, *7*, 16.
(30) Zhao, X. T.; Cheng, L. J.; Jia, N.; Wang, R. X.; Liu, L. F.; Gao, C. J. Polyphenol-Metal Manipulated Nanohybridization of CNT Membranes with FeOOH Nanorods for High-Flux, Anti-Fouling and Self-Cleaning Oil/Water Separation. *J. Membr. Sci.* **2020**, *600*, 117857.
(31) Liu, Y. N.; Su, Y. L.; Guan, J. Y.; Cao, J. L.; Zhang, R. N.; He, M. R.; Jiang, Z. Y. Asymmetric Aerogel Membranes with Ultrafast Water Permeation for the Separation of Oil-in-Water Emulsion. *ACS Appl. Mater. Interfaces* **2018**, *10*, 26546−26554.
(32) Gao, S. J.; Shi, Z.; Zhang, W. B.; Zhang, F.; Jin, J. Photoinduced Superwetting Single-Walled Carbon Nanotube/TiO_2 Ultrathin Network Films for Ultrafast Separation of Oil-in-Water Emulsions. *ACS Nano* **2014**, *8* (6), 6344−6352.
(33) Zhang, J. Q.; Pan, X. L.; Xue, Q. Z.; He, D. L.; Zhu, L.; Guo, Q. K. Anti-Fouling Hydrolyzed Polyacrylonitrile/Graphene Oxide Membrane with Spindle-Knotted Structure for Highly Effective Separation of Oil-Water Emulsion. *J. Membr. Sci.* **2017**, *532*, 38−46.
(34) Liu, Y.; Zhang, F. R.; Zhu, W. X.; Su, D.; Sang, Z. Y.; Yan, X.; Li, S.; Liang, J.; Dou, S. X. A Multifunctional Hierarchical Porous SiO_2/GO Membrane for High Efficiency Oil/Water Separation and Dye Removal. *Carbon* **2020**, *160*, 88−97.
(35) Li, H.; Li, J.; Ai, Z. H.; Jia, F. L.; Zhang, L. Z. Oxygen Vacancy-Mediated Photocatalysis of BiOCl: Reactivity, Selectivity, and Perspectives. *Angew. Chem., Int. Ed.* **2018**, *57* (1), 122−138.
(36) Gu, J. C.; Xiao, P.; Chen, J.; Zhang, J. W.; Huang, Y. J.; Chen, T. Janus Polymer/Carbon Nanotube Hybrid Membranes for Water/Oil Separation. *ACS Appl. Mater. Interfaces* **2014**, *6*, 16204−16209.
(37) Hu, L.; Gao, S. J.; Zhu, Y. Z.; Zhang, F.; Jiang, L.; Jin, J. An Ultrathin Bilayer Membrane with Asymmetric Wettability for Pressure Responsive Oil/Water Emulsion Separation. *J. Mater. Chem. A* **2015**, *3*, 23477−23482.
(38) Jiang, Y. S.; Hou, J. W.; Xu, J.; Shan, B. T. Switchable Oil/Water Separation with Efficient and Robust Janus Nanofiber Membranes. *Carbon* **2017**, *115*, 477−485.
(39) An, Y. P.; Yang, J.; Yang, H. C.; Wu, M. B.; Xu, Z. K. Janus Membranes with Charged Carbon Nanotube Coatings for Deemulsification and Separation of Oil-in-Water Emulsions. *ACS Appl. Mater. Interfaces* **2018**, *10*, 9832−9840.
(40) Zhang, C.; He, S.; Wang, D. F.; Xu, F.; Zhang, F. X.; Zhang, G. X. Facile Fabricate a Bioinspired Janus Membrane with Heterogeneous Wettability for Unidirectional Water Transfer and Controllable Oil-Water Separation. *J. Mater. Sci.* **2018**, *53*, 14398−14411.
(41) Qu, R. X.; Li, X. Y.; Zhang, W. F.; Liu, Y. N.; Zhai, H. J.; Wei, Y.; Feng, L. Photothermally Induced in Situ Double Emulsion Separation by a Carbon Nanotube/poly(nisopropylacrylamide) Modified Membrane with Superwetting Properties. *J. Mater. Chem. A* **2020**, *8*, 7677−7686.
(42) Hu, L.; Gao, S. J.; Ding, X. G.; Wang, D.; Jiang, J.; Jin, J.; Jiang, L. Photothermal-Responsive Single Walled Carbon Nanotube-Based Ultrathin Membranes for On/Off Switchable Separation of Oil-in-Water Nanoemulsions. *ACS Nano* **2015**, *9*, 4835−4842.

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

(43) Ma, J. X.; Ping, D.; Dong, X. F. Recent Developments of Graphene Oxide-Based Membranes: A Review. *Membranes* **2017**, *7*, 52.
(44) Peng, Y. B.; Guo, Z. G. Recent Advances in Biomimetic Thin Membranes Applied in Emulsified Oil/Water Separation. *J. Mater. Chem. A* **2016**, *4* (41), 15749−15770.
(45) Jayaramulu, K.; Geyer, F.; Schneemann, A.; Kment, Š.; Otyepka, M.; Zboril, R.; Vollmer, D.; Fischer, R. A. Hydrophobic Metal-Organic Frameworks. *Adv. Mater.* **2019**, *31* (32), 1900820.
(46) Meng, F. N.; Zhang, M. Q.; Ding, K.; Zhang, T.; Gong, Y. K. Cell Membrane Mimetic PVDF Microfiltration Membrane with Enhanced Anti-Fouling and Separation Performance for Oil/Water Mixture. *J. Mater. Chem. A* **2018**, *6* (7), 3231−3241.
(47) Liu, J. T.; Hua, D.; Zhang, Y.; Japip, S.; Chung, T. S. Precise Molecular Sieving Architectures with Janus Pathways for Both Polar and Nonpolar Molecules. *Adv. Mater.* **2018**, *30* (11), 1705933.
(48) Jing, X. S.; Guo, Z. G. Biomimetic Super Durable and Stable Surfaces with Superhydrophobicity. *J. Mater. Chem. A* **2018**, *6* (35), 16731−16768.
(49) Ries, L.; Petit, E.; Michel, T.; Diogo, C. C.; Gervais, C.; Salameh, C.; Bechelany, M.; Balme, S.; Miele, P.; Onofrio, N.; Voiry, D. Enhanced Sieving from Exfoliated MoS_2 Membranes Via Covalent Functionalization. *Nat. Mater.* **2019**, *18*, 1112−1117.
(50) Jian, M. P.; Qiu, R. S.; Xia, Y.; Lu, J.; Chen, Y.; Gu, Q. F.; Liu, R. P.; Hu, C. Z.; Qu, J. H.; Wang, H. T.; Zhang, X. W. Ultrathin Water-Stable Metal-Organic Framework Membranes for Ion Separation. *Sci. Adv.* **2020**, *6*, eaay3998.
(51) Liu, G. Z.; Shen, J.; Ji, Y. F.; Liu, Q.; Liu, G. P.; Yang, J.; Jin, W. Q. Two-Dimensional Ti_2CTx MXene Membranes with Integrated and Ordered Nanochannels for Efficient Solvent Dehydration. *J. Mater. Chem. A* **2019**, *7* (19), 12095−12104.
(52) Liu, Y. N.; Qu, R. X.; Zhang, W. F.; Li, X. Y.; Wei, Y.; Feng, L. Lotus- and Mussel-Inspired PDA-PET/PTFE Janus Membrane: Toward Integrated Separation of Light and Heavy Oils from Water, ACS Appl. *ACS Appl. Mater. Interfaces* **2019**, *11*, 20545−20556.
(53) Pan, Y. L.; Liu, L. M.; Zhang, Z. J.; Huang, S. C.; Hao, Z.; Zhao, X. Z. Surfaces with Controllable Super-Wettability and Applications for Smart Oil-Water Separation. *Chem. Eng. J.* **2019**, *378*, 122178.
(54) Fan, Y. Y.; Wei, L. Y.; Meng, X. X.; Zhang, W. M.; Yang, N. T.; Jin, Y.; Wang, X. B.; Zhao, M. W.; Liu, S. M. An Unprecedented High-Temperature-Tolerance 2D Laminar Mxene Membrane for Ultrafast Hydrogen Sieving. *J. Membr. Sci.* **2019**, *569*, 117−123.
(55) Ye, C.; Voet, V. S. D.; Folkersma, R.; Loos, K. Robust Superamphiphilic Membrane with a Closed-Loop Life cycle. *Adv. Mater.* **2021**, *33*, 2008460.
(56) Han, X. T.; Guo, Z. G. Graphene and its Derivative Composite Materials with Special Wettability: Potential Application in Oil-Water Separation. *Carbon* **2021**, *172*, 647−681.
(57) Noamani, S.; Niroomand, S.; Rastgar, M.; Sadrzadeh, M. Carbon-Based Polymer Nanocomposite Membranes for Oily Wastewater Treatment. *NPG Clean Water* **2019**, *2*, 20.
(58) Guan, L. Z.; Zhao, L.; Wan, Y. J.; Tang, L. C. Three-Dimensional Graphene-Based Polymer Nanocomposites: Preparation, Properties and Applications. *Nanoscale* **2018**, *10* (31), 14788−14811.
(59) Lin, X. D.; Hong, J. Recent Advances in Robust Superwettable Membranes for Oil-Water Separation. *Adv. Mater. Interfaces* **2019**, *6* (12), 1900126.
(60) Chu, Z. L.; Feng, Y. J.; Seeger, S. Oil/Water Separation with Selective Superantiwetting/Superwetting Surface Materials. *Angew. Chem., Int. Ed.* **2015**, *54* (8), 2328−2338.
(61) Qiu, L.; Sun, Y. H.; Guo, Z. G. Designing Novel Superwetting Surfaces for High-Efficiency Oil-Water Separation: Design Principles, Opportunities, Trends and Challenges. *J. Mater. Chem. A* **2020**, *8* (33), 16831−16853.
(62) Wang, Y. F.; Ma, K. K.; Xin, J. H. Stimuli-Responsive Bioinspired Materials for Controllable Liquid Manipulation: Principles, Fabrication, and Applications. *Adv. Funct. Mater.* **2018**, *28* (6), 1705128.
(63) Su, B.; Tian, Y.; Jiang, L. Bioinspired Interfaces with Superwettability: from Materials to Chemistry. *J. Am. Chem. Soc.* **2016**, *138* (6), 1727−1748.
(64) Ma, Q. L.; Cheng, H. F.; Fane, A. G.; Wang, R.; Zhang, H. Recent Development of Advanced Materials with Special Wettability for Selective Oil/Water Separation. *Small* **2016**, *12* (16), 2186−2202.
(65) Ge, J.; Zhao, H. Y.; Zhu, H. W.; Huang, J.; Shi, L. A.; Yu, S. H. Advanced Sorbents for Oil-Spill Cleanup: Recent Advances and Future Perspectives. *Adv. Mater.* **2016**, *28* (47), 10459−10490.
(66) Li, J. J.; Zhou, Y. N.; Luo, Z. H. Polymeric Materials with Switchable Superwettability for Controllable Oil/Water Separation: A Comprehensive Review. *Prog. Polym. Sci.* **2018**, *87*, 1−33.
(67) Ghasemlou, M.; Daver, F.; Ivanova, E. P.; Adhikari, B. Bio-Inspired Sustainable and Durable Superhydrophobic Materials: from Nature to Market. *J. Mater. Chem. A* **2019**, *7* (28), 16643−16670.
(68) Hu, Y.; Chen, Z.; Zhuo, H.; Zhong, L.; Peng, X.; Sun, R.-C. Advanced Compressible and Elastic 3D Monoliths beyond Hydrogels. *Adv. Funct. Mater.* **2019**, *29* (44), 1904472.
(69) Vogler, E. A. Structure and Reactivity of Water at Biomaterial Surfaces. *Adv. Colloid Interface Sci.* **1998**, *74* (3), 69−117.
(70) Zhang, J.; Liu, H.; Jiang, L. Membrane-Based Strategy for Efficient Ionic Liquids/Water Separation Assisted by Superwettability. *Adv. Funct. Mater.* **2017**, *27* (20), 1606544.
(71) Jung, Y. C; Bhushan, B. Wetting Behavior of Water and Oil Droplets in Three-Phase Interfaces for Hydrophobicity/Philicity and Oleophobicity/Philicity. *Langmuir* **2009**, *25* (24), 14165−14173.
(72) Zheng, W. W.; Huang, J. Y.; Li, S. H.; Ge, M. Z.; Teng, L.; Chen, Z.; Lai, Y. K. Advanced Materials with Special Wettability toward Intelligent Oily Wastewater Remediation. *ACS Appl. Mater. Interfaces* **2021**, *13* (1), 67−87.
(73) Qiu, L.; Sun, Y. H.; Guo, Z. G. Designing Novel Superwetting Surfaces for High-Efficiency Oil-Water Separation: Design Principles, Opportunities, Trends and Challenges. *J. Mater. Chem. A* **2020**, *8* (33), 16831−16853.
(74) De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. Carbon Nanotubes: Present and Future Commercial Applications. *Science* **2013**, *339* (6119), 535−539.
(75) Das, R.; Ali, M. E.; Hamid, S. B. A.; Ramakrishna, S.; Chowdhury, Z. Z. Carbon Nanotube Membranes for Water Purification: A Bright Future in Water Desalination. *Desalination* **2014**, *336*, 97−109.
(76) Goh, K. L.; Karahan, H. E.; Wei, L.; Bae, T. H.; Fane, A. G.; Wang, R.; Chen, Y. *Carbon* **2016**, *109*, 694−710.
(77) Yuan, Z. K.; Xiao, X. F.; Li, J.; Zhao, Z.; Yu, D. S.; Li, Q. Self-Assembled Graphene-Based Architectures and Their Applications. *Adv. Sci.* **2018**, *5*, 1700626.
(78) Shao, J. J.; Lv, W.; Yang, Q. H. Self-Assembly of Graphene Oxide at Interfaces. *Adv. Mater.* **2014**, *26* (32), 5586−5612.
(79) Chen, C. M.; Yang, Q. H.; Yang, Y. G.; Lv, W.; Wen, Y. F.; Hou, P. X.; Wang, M. Z.; Cheng, H. M. Self-Assembled Free-Standing Graphite Oxide Membrane. *Adv. Mater.* **2009**, *21* (29), 3007−3011.
(80) Xu, Y. X.; Sheng, K. X.; Li, C.; Shi, G. Q. Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process. *ACS Nano* **2010**, *4*, 4324.
(81) Feng, X.; Yu, Z.; Long, R.; Sun, Y.; Wang, M.; Li, X.; Zeng, G. Polydopamine Intimate Contacted Two-Dimensional Ultrathin Nylon Basement Membrane Supported RGO/PDA/MXene Composite Material for Oil-Water Separation and Dye Removal. *Sep. Purif. Technol.* **2020**, *247*, 116945.
(82) Shi, Y. H.; Huang, J. H.; Zeng, G. M.; Cheng, W. J.; Hu, J. L. Photocatalytic Membrane in Water Purification: Is It Stepping Closer to Be Driven by Visible Light? *J. Membr. Sci.* **2019**, *584*, 364−392.
(83) Wang, Y.; Wu, N. N.; Wang, Y.; Ma, H.; Zhang, J. X.; Xu, L. L.; Albolkany, M. K.; Liu, B. Graphite Phase Carbon Nitride Based Membrane for Selective Permeation. *Nat. Commun.* **2019**, *10*, 2500.
(84) Liu, Y. N.; Su, Y. L.; Guan, J. Y.; Cao, J. L.; Zhang, R. N.; He, M. R.; Gao, K.; Zhou, L. J.; Jiang, Z. Y. 2D Heterostructure Membranes with Sunlight-Driven Self-Cleaning Ability for Highly

Efficient Oil-Water Separation. *Adv. Funct. Mater.* **2018**, *28* (13), 1706545.
(85) Lei, Q.; Guo, J.; Noureddine, A.; Wang, A.; Wuttke, S.; Brinker, C. J.; Zhu, W. Sol-Gel-Based Advanced Porous Silica Materials for Biomedical Applications. *Adv. Funct. Mater.* **2020**, *30* (41), 1909539.
(86) Xue, J. J.; Wu, T.; Dai, Y. Q.; Xia, Y. N. Electrospinning and Electrospun Nanofibers: Methods, Materials, and Applications. *Chem. Rev.* **2019**, *119* (8), 5298−5415.
(87) Zhang, J. C.; Zhang, F.; Song, J.; Liu, L. F.; Si, Y.; Yu, J. Y.; Ding, B. Electrospun Flexible Nanofibrous Membranes for Oil/Water Separation. *J. Mater. Chem. A* **2019**, *7* (35), 20075−20102.
(88) Yoon, J.; Yang, H. S.; Lee, B. S.; Yu, W. R. Recent Progress in Coaxial Electrospinning: New Parameters, Various Structures, and Wide Applications. *Adv. Mater.* **2018**, *30* (42), 1704765.
(89) Lee, J. K. Y.; Chen, N.; Peng, S.; Li, L.; Tian, L.; Thakor, N.; Ramakrishna, S. Polymer-Based Composites by Electrospinning: Preparation & Functionalization with Nanocarbons. *Prog. Polym. Sci.* **2018**, *86*, 40−84.
(90) Liu, Q.; Chen, Z. W.; Pei, X. Y.; Guo, C. S.; Teng, K. Y.; Hu, Y. L.; Xu, Z. W.; Qian, X. M. Review: Applications, Effects and the Prospects for Electrospun Nanofibrous Mats in Membrane Separation. *J. Mater. Sci.* **2020**, *55*, 893−924.
(91) Ghaffar, A.; Chen, C.; Zhu, X. Y.; Chen, B. L. Underwater Superoleophobic PVA-GO Nanofibrous Membranes for Emulsified Oily Water Purification. *Environ. Sci.: Nano* **2019**, *6* (12), 3723−3733.
(92) Zhan, Y. Q.; He, S. J.; Wan, X. Y.; Zhao, S. M.; Bai, Y. L. Thermally and Chemically Stable Poly(arylene ether nitrile)/Halloysite Nanotubes Intercalated Graphene Oxide Nanofibrous Composite Membranes for Highly Efficient Oil/Water Emulsion Separation in Harsh Environment. *J. Membr. Sci.* **2018**, *567*, 76−88.
(93) Venkatesh, K.; Arthanareeswaran, G.; Chandra Bose, A.; Suresh Kumar, P.; Kweon, J. Diethylenetriaminepentaacetic Acid-functionalized Multi-walled Carbon Nanotubes/Titanium Oxide-PVDF Nanofiber Membrane for Effective Separation of Oil/Water Emulsion. *Sep. Purif. Technol.* **2021**, *257*, 117926.
(94) Ma, W. J.; Li, Y. S.; Zhang, M. J.; Gao, S. T.; Cui, J. X.; Huang, C. B.; Fu, G. D. Biomimetic Durable Multifunctional Self-Cleaning Nanofibrous Membrane with Outstanding Oil/Water Separation, Photodegradation of Organic Contaminants, and Antibacterial Performances. *ACS Appl. Mater. Interfaces* **2020**, *12* (31), 34999−35010.
(95) Zhu, F.; Zheng, Y. M.; Zhang, B. G.; Dai, Y. R. A Critical Review on the Electrospun Nanofibrous Membranes for the Adsorption of Heavy Metals in Water Treatment. *J. Hazard. Mater.* **2021**, *401*, 123608.
(96) Bao, Z.; Chen, D. Y.; Li, N. J.; Xu, Q. F.; Li, H.; He, J. H.; Lu, J. M. Superamphiphilic and Underwater Superoleophobic Membrane for Oil/Water Emulsion Separation and Organic Dye Degradation. *J. Membr. Sci.* **2020**, *598*, 117804.
(97) Chen, T. Y.; Xia, J. Y.; Gu, J. C.; Lu, G. M.; Xue, Q. J.; Liu, C. H.; Yan, L. K.; Chen, T. Engineering Janus CNTs/OCS Composite Membrane at Air/Water Interface for Excellent Dye Molecules Screening. *Chem. Eng. J.* **2021**, *417*, 127947.
(98) Cai, Y. H.; Chen, D. Y.; Li, N. J.; Xu, Q. F.; Li, H.; He, J. H.; Lu, J. M. A Self-Cleaning Heterostructured Membrane for Efficient Oil-in-Water Emulsion Separation with Stable Flux. *Adv. Mater.* **2020**, *32* (25), 2001265.
(99) Yan, L. K.; Liu, C. H.; Xia, J. Y.; Chao, M.; Wang, W. Q.; Gu, J. C.; Chen, T. CNTs/TiO_2 Composite Membrane with Adaptable Wettability for On-Demand Oil/Water Separation. *J. Cleaner Prod.* **2020**, *275*, 124011.
(100) Dawson, R.; Cooper, A. I.; Adams, D. J. Nanoporous Organic Polymer Networks. *Prog. Polym. Sci.* **2012**, *37* (4), 530−563.
(101) Cheng, W.; Zeng, X. W.; Chen, H. Z.; Li, Z. M.; Zeng, W. F.; Mei, L.; Zhao, Y. L. Versatile Polydopamine Platforms: Synthesis and Promising Applications for Surface Modification and Advanced Nanomedicine. *ACS Nano* **2019**, *13* (8), 8537−8565.
(102) Gao, S. J.; Zhu, Y. Z.; Zhang, F.; Jin, J. Superwetting Polymer-Decorated SWCNT Composite Ultrathin Films for Ultrafast Separation of Oil-in-Water Nano emulsions. *J. Mater. Chem. A* **2015**, *3* (6), 2895−2902.
(103) Liu, N.; Zhang, M.; Zhang, W. F.; Cao, Y. Z.; Chen, Y. N.; Lin, X.; Xu, L. X.; Li, C.; Feng, L.; Wei, Y. Ultralight Free-Standing Reduced Graphene Oxide Membranes for Oil-in-Water Emulsion Separation. *J. Mater. Chem. A* **2015**, *3* (40), 20113−20117.
(104) Liu, Y. N.; Su, Y. L.; Cao, J. L.; Guan, J. Y.; Xu, L. Y.; Zhang, R. N.; He, M. R.; Zhang, Q.; Fan, L.; Jiang, Z. Y. Synergy of the Mechanical, Anti-Fouling and Permeation Properties of a Carbon Nanotube Nanohybrid Membrane for Efficient Oil/Water Separation. *Nanoscale* **2017**, *9* (22), 7508−7518.
(105) Liu, Y. N.; Su, Y. L.; Cao, J. L.; Guan, J. Y.; Zhang, R. N.; He, M. R.; Fan, L.; Zhang, Q.; Jiang, Z. Y. Anti-Fouling, High-Flux Oil/Water Separation Carbon Nanotube Membranes by Polymer-Mediated Surface Charging and Hydrophilization. *J. Membr. Sci.* **2017**, *542*, 254−263.
(106) Zhang, L.; Zha, X.; Zhang, G.; Gu, J.; Zhang, W.; Huang, Y.; Zhang, J.; Chen, T. Designing a Reductive Hybrid Membrane to Selectively Capture Noble Metallic Ions during Oil/Water Emulsion Separation with Further Function Enhancement. *J. Mater. Chem. A* **2018**, *6* (22), 10217−10225.
(107) Xu, T. T.; Qiao, Q. Q. Conjugated Polymer-Inorganic Semiconductor Hybrid Solar Cells. *Energy Environ. Sci.* **2011**, *4* (8), 2700−2720.
(108) Beija, M.; Marty, J. D.; Destarac, M. RAFT/Madix Polymers for the Preparation of Polymer/Inorganic Nanohybrids. *Prog. Polym. Sci.* **2011**, *36* (7), 845−886.
(109) Li, F.; Yu, Z. X.; Shi, H.; Yang, Q. B.; Chen, Q.; Pan, Y.; Zeng, G. Y.; Yan, L. A Mussel-Inspired Method to Fabricate Reduced Graphene Oxide/g-C_3N_4 Composites Membranes for Catalytic Decomposition and Oil-in-Water. *Chem. Eng. J.* **2017**, *322*, 33−45.
(110) Ji, L. T.; Yan, L. K.; Chao, M.; Li, M. R.; Gu, J. C.; Lei, M.; Zhang, Y. M.; Wang, X.; Xia, J. Y.; Chen, T. Y.; Nie, Y. J.; Chen, T. Sphagnum Inspired g-C_3N_4 Nano/Microspheres with Smaller Bandgap in Heterojunction Membranes for Sunlight-Driven Water Purification. *Small* **2021**, *17* (12), 2007122.
(111) Zhao, X. T.; Cheng, L. J.; Wang, R. X.; Jia, N.; Liu, L. F.; Gao, C. J. Bioinspired Synthesis of Polyzwitterion/Titania Functionalized Carbon Nanotube Membrane with Superwetting Property for Efficient Oil-in-Water Emulsion Separation. *J. Membr. Sci.* **2019**, *589*, 117257.
(112) Wang, T.; Wu, H. Y.; Zhao, S.; Zhang, W.; Tahir, M.; Wang, Z.; Wang, J. X. Interfacial Polymerized and Pore-Variable Covalent Organic Framework Composite Membrane for Dye Separation. *Chem. Eng. J.* **2020**, *384*, 123347.
(113) Li, R. J.; Li, J. Y.; Rao, L. H.; Lin, H. J.; Shen, L. G.; Xu, Y. C.; Chen, J. R.; Liao, B. Q. Inkjet Printing of Dopamine Followed by UV Light Irradiation to Modify Mussel-Inspired PVDF Membrane for Efficient Oil-Water Separation. *J. Membr. Sci.* **2021**, *619*, 118790.
(114) Zhang, L.; Gu, J. C.; Song, L. P.; Chen, L.; Huang, Y. J.; Zhang, J. W.; Chen, T. Underwater Superoleophobic Carbon Nanotubes/Core-Shell Polystyrene@Au Nanoparticles Composite Membrane for Flow-Through Catalytic Decomposition and Oil/Water Separation. *J. Mater. Chem. A* **2016**, *4* (28), 10810−10815.
(115) Yan, L. K.; Zhang, G.; Zhang, L.; Zhang, W.; Gu, J. C.; Huang, Y. J.; Zhang, J. W.; Chen, T. Robust Construction of Underwater Superoleophobic CNTs/nanoparticles Multifunctional Hybrid Membranes via Interception Effect for Oily Wastewater Purification. *J. Membr. Sci.* **2019**, *569*, 32−40.
(116) Liu, C. H.; Xia, J. Y.; Gu, J. C.; Wang, W. Q.; Liu, Q. Q.; Yan, L. K.; Chen, T. Multifunctional CNTs-PAA/MIL101(Fe)@Pt Composite Membrane for High-throughput Oily Wastewater Remediation. *J. Hazard. Mater.* **2021**, *403*, 123547.
(117) Liu, Y. C.; Tu, W. W.; Chen, M. Y.; Ma, L. L.; Yang, B.; Liang, Q. L.; Chen, Y. Y. A Mussel-Induced Method to Fabricate Reduced Graphene Oxide/Halloysite Nanotubes Membranes for Multifunctional Applications in Water Purification and Oil/Water Separation. *Chem. Eng. J.* **2018**, *336*, 263−277.

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696

(118) Ou, X. F.; Yang, X. H.; Zheng, J. Q.; Liu, M. X. Free-Standing Graphene Oxide-Chitin Nanocrystal Composite Membrane for Dye Adsorption and Oil/Qater Separation. *ACS Sustainable Chem. Eng.* **2019**, *7* (15), 13379−13390.
(119) Zhu, Z. G.; Zhong, L. L.; Chen, X. M.; Zheng, W.; Zuo, J. L.; Zeng, G. F.; Wang, W. Monolithic and Self-Roughened Janus Fibrous Membrane with Superhydrophilic/Omniphobic Surface for Robust Anti-fouling and Antiwetting Membrane Distillation. *J. Membr. Sci.* **2020**, *615*, 118499.
(120) Bao, Z.; Chen, D. Y.; Li, N. J.; Xu, Q. F.; Li, H.; He, J. H.; Lu, J. M. Superamphiphilic and Underwater Superoleophobic Membrane for Oil/Water Emulsion Separation and Organic Dye Degradation. *J. Membr. Sci.* **2020**, *598*, 117804.
(121) Venkatesh, K.; Arthanareeswaran, G.; Bose, C. A.; Kumar, P. S. Hydrophilic Hierarchical Carbon with TiO_2 Nanofiber Membrane for High Separation Efficiency of Dye and Oil-Water Emulsion. *Sep. Purif. Technol.* **2020**, *241*, 116709.
(122) Gu, J. C.; Xiao, P.; Zhang, L.; Lu, W.; Zhang, G. G.; Huang, Y. J.; Zhang, J. W.; Chen, T. Construction of Superhydrophilic and Under-water Superoleophobic Carbon-Based Membranes for Water Purification. *RSC Adv.* **2016**, *6*, 73399−73403.

https://doi.org/10.1021/acsami.1c07737
ACS Appl. Mater. Interfaces 2021, 13, 36679−36696