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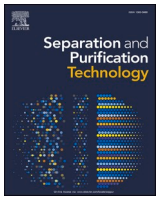

Constructing superwetting membranes by sodium lignosulfonate-modified carbon nanotube for highly efficient crude oil-in-water emulsions separations

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ABSTRACT

For the past few years, superwetting materials had been developed to enhance the treatment process of oily wastewater. Membranes are improved through the combination of surface topography and chemical modifications to achieve superwetting properties for treating oily wastewater effectively. In this work, we prepared an eco-friendly membrane by depositing sodium lignosulfonate (SLS)-modified carbon nanotube (CNT) on a cellulose acetate membrane via vacuum filtration without employing any organic solvents. The SLS@CNT membrane shows superhydrophilicity and underwater superoleophobicity with high stability. Furthermore, the SLS@CNT membrane exhibits outstanding antifouling and self-cleaning properties against crude oil of high viscosity. Most importantly, our SLS@CNT membrane exhibits outstanding oil-in-water emulsions separation performances including crude oil-in-water emulsions. For the surfactant-free and surfactant-stabilized emulsions, fluxes were revealed to reach up to 27,800 L m^{-2} h^{-1} bar^{-1} and 13,800 L m^{-2} h^{-1} bar^{-1}, respectively, with very high separation efficiency (>99.97 % and 99.79 %, respectively). The distinguished performance of our SLS@CNT membrane, and its eco-friendly, low-energy consumption, and cost-effective preparation, demonstrate practical applicability.

1. Introduction

Crude oil and organic solvents are important ingredients in the present industries. However, oil spills that resulted from the increase in crude oil transportation and the emissions of wastewater containing oil/water mixtures and emulsions had led to serious environmental problems [1–4]. The traditional methods for separating oil and water which includes air flotation, gravity separation, chemical demulsification, and absorption possess many disadvantages such as ineffective separation efficiency, use of various chemicals, high energy consumption, and high cost [1,5].

As a preferable alternative to the above-mentioned processes, membrane technology for oil/water separation has received huge attraction owing to its high separation efficiency of tiny emulsion droplets, simple operation process, no chemical addition requirements, and its energy saving aspect. The membrane separation is generally based on a size-sieving mechanism which could exhibit the tradeoff between flux and separation efficiency. Nevertheless, the fouling problem is a tough issue for membranes, that caused the decline in the flux, the separation efficiency, and the lifetime of most existing membranes [6,7]. This is why in recent years, membranes possessing superhydrophilicity and underwater superoleophobicity draw more recognition for treating oily wastewater because of their superior antifouling properties. The superhydrophilic/underwater superoleophobic membranes can be directly wetted by a water droplet, and the trapped water in the membrane serves as an anti-oil barrier which could provide good

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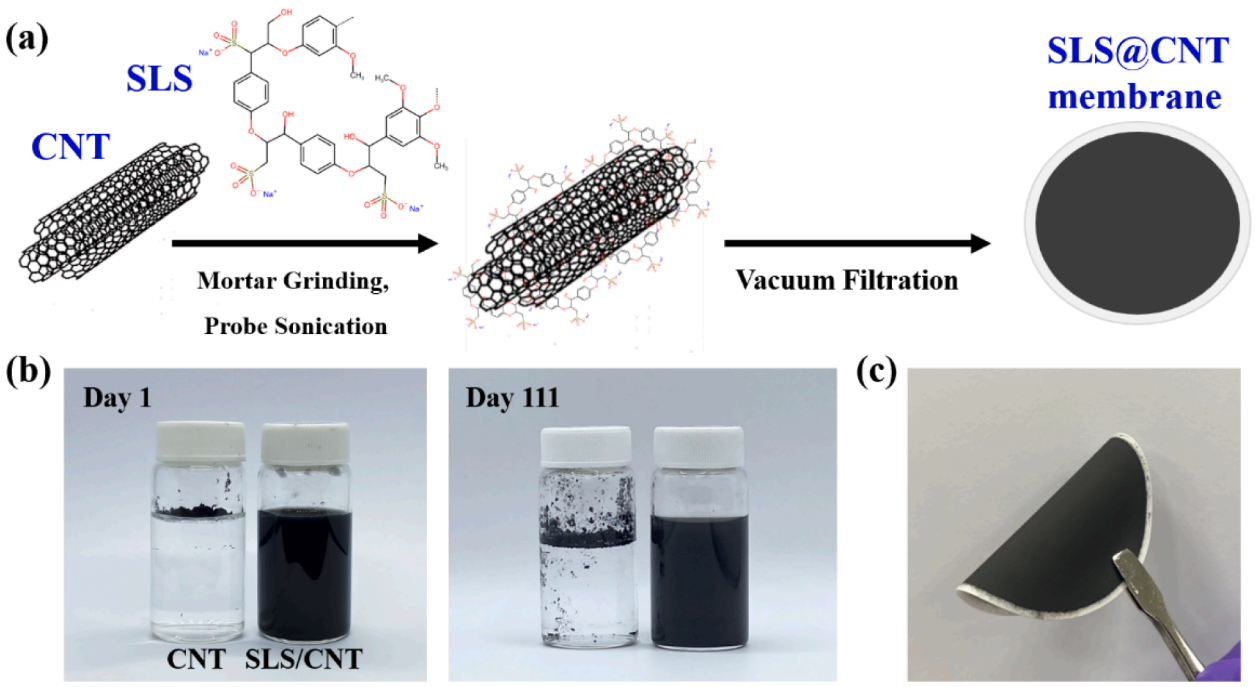

Fig. 1. (a) Schematic illustration of SLS@CNT membrane preparation. (b) Photographic images of CNT (left) and SLS@CNT (right) aqueous suspensions. The SLS/CNT aqueous suspension is stable for 3 months. (c) The SLS@CNT membrane exhibited good flexibility.

oil rejection property. Besides, the water flux can be induced by precipitation through the superhydrophilic membrane's capillary force [8,9]. Recently, many scientists prepared various membranes with superwetting properties for treating emulsions. Zhang et al. prepared a superwettable zwitterionic membrane via modifying polyvinylidene difluoride (PVDF) membrane with co-assembly of 3-aminopropyldimethylamine oxide and dopamine for emulsion separations [10]. Chen et al. reported a method to fabricate a multi-functional fibrous composite membrane from TiO_2 that are anchored onto crumpled graphene oxide and then sprayed onto poly (arylene ether nitrile) fibrous membrane for treating oil–water emulsions [11]. Xi et al. provided superwetting membranes based on cellulose and glass fibers that can be employed in the separation of oil–water emulsions with good separation performance [7]. Feng et al. applied a layer-by-layer strategy to modify polyacrylic acid grafted PVDF membranes for preparing superhydrophilic membranes with ultralow oil adhesion. Their membranes exhibited good separation capabilities for oil-in-water emulsions and showed self-healing properties [12].

Carbon nanotube (CNT) is another promising material that has been applied to membrane filtration technology due to its unique structure, superior mechanical strength, chemical resistance, favorable electrical properties, and other unique physical attributes [13,14]. However, one challenge in using CNT is its poor dispersion ability in water. To improve the dispersity of CNTs in water or solvents, scientists develop two approaches: (1) covalently functionalizing the CNT; and (2) allowing noncovalent adsorption of organic molecules on CNT surfaces [15–17]. The noncovalent treatment is more attractive to researchers because it has been reported to generally retain nearly all of the essential characteristics of the CNTs [18]. Lignosulfonates are by-products from the paper industry in the preparation of wood pulp, and one of its forms – sodium lignosulfonates (SLS) that possess aromatic structure along with the hydrophilic sulfonate group have been employed in many fields such as in making hydrogels [19], or as additives in battery [20] and flame retardants [21]. Liu et al. reported that CNTs could be modified by SLS through a simple physical grinding method, and the SLS-modified CNTs showed good dispersibility in water. [18].

In this paper, we revealed an eco-friendly method to prepare superwetting membranes from CNT and SLS without employing organic solvents. Our SLS@CNT membranes exhibited superhydrophilic and underwater superoleophobic features and anti-fouling characteristics even for crude oil with high viscosity. Moreover, the SLS@CNT membranes can be used to separate both surfactant-free and surfactant-stabilized oil-in-water emulsions (SFOWEs and SSOWEs) including crude oil-in-water emulsions. The SLS@CNT membranes showed high flux values of up to 27,800 and 13,800 L m^{-2} h^{-1} bar^{-1} for SFOWEs and SSOWEs, respectively, and with excellent separation efficiencies (>99.79 %). The remarkable performance of the fabricated membranes in emulsion separations, and their environment-friendly production suggest that they possess a substantial capacity to be employed in academic and industrial applications.

2. Experimental section

2.1. Materials

Multiwalled carbon nanotube (CNT) (purity > 99.5 %, diameter: 40–90 nm, length: 10–50 μm,) was acquired from Golden Innovation Business Co., Ltd. (Taiwan). Sodium lignosulfonate (SLS) (Mw 52,000 g/mol) and toluene were supplied by Sigma Aldrich (USA). Cellulose acetate membrane (pore sizes: 0.45 μm) was obtained from Whatman, GE Healthcare Co. Ltd. (USA). Tween 80 was supplied by Acros Organics (USA). Petroleum ether and hexadecane were purchased from Alfa Aesar (USA). n-Hexane, and isooctane were procured from TEDIA Co., Inc. (USA).

2.2. Preparation of CNT and SLS@CNT membranes

CNT suspension was prepared by adding CNT (4 mg) to ethanol (20 mL). The mixture was then subjected to probe ultrasonication for 10 min to obtain a uniform dispersion. The CNT membrane was fabricated via a vacuum-assisted filtration of the obtained CNT suspension onto a cellulose acetate membrane support. SLS/CNT suspension was prepared according to a previous report [22]. First, 4 mg CNT and 4 mg SLS were mixed by mortar grinding for 10 min with a small amount of DI water.

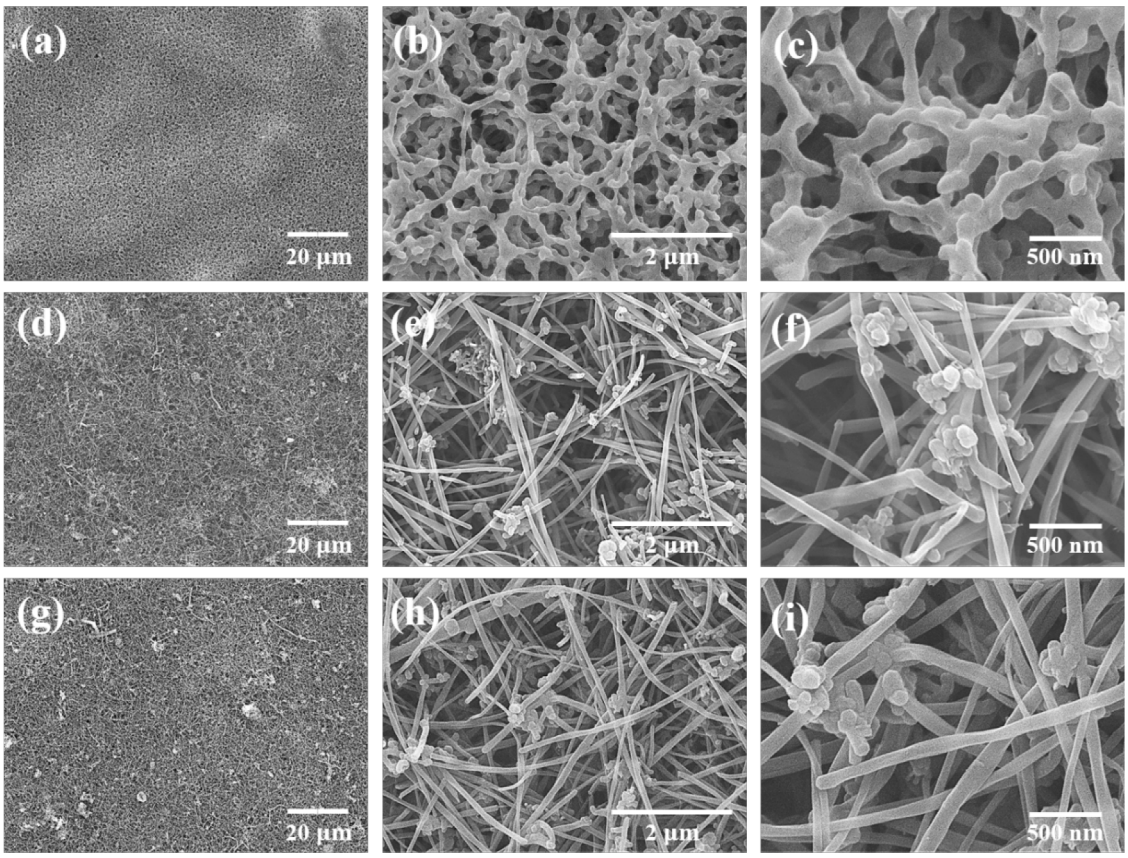

Fig. 2. The SEM images of (a-c) cellulose acetate substrate, (d-f) CNT membrane, and (g-i) SLS@CNT membrane with different magnifications.

Then, more DI water was added to dilute the SLS/CNT suspension to achieve a concentration of 1 mg mL^{-1}. Finally, a uniform dispersion of SLS/CNT was attained by subjecting the suspension to probe ultrasonication for 10 min. The SLS@CNT membrane was also fabricated by filtering the SLS/CNT suspension (4 mL) onto a cellulose acetate membrane with vacuum assistance.

2.3. Preparation of oil-in-water emulsions

We used n-hexane, petroleum ether, isooctane, hexadecane, toluene, and crude oil to formulate SFOWEs and SSOWEs. The SFOWEs was formulated by adding 20 mL of oil into 180 mL DI water followed by a 20-min sonication. The SSOWEs were prepared by adding 2 mL of oil into 200 mL DI water (containing 0.02 g Tween 80) under vigorous stirring for 3 h.

2.4. Oil-in-water emulsion separation

The SFOWEs and SSOWEs separation experiments were carried out using a dead-end filtration set up under an external pressure of 0.5 bar. The flux (J) was calculated using the following equation:

$$\mathbf{J} = \frac{\mathbf{V}}{\mathbf{A} \bullet \Delta \mathbf{t} \bullet \Delta \mathbf{P}} \quad (1)$$

where the J (L m^{-2} h^{-1} bar^{-1}), V (L), A (m^2), Δt (h), and ΔP (bar) are flux, volume of filtrate, effective filtration area, time, and applied external pressure, respectively. A volume of 25 mL of filtrate was collected to calculate the flux. The separation efficiency (R) was calculated using the following equation:

$$\mathbf{R} = \frac{\mathbf{C_f} - \mathbf{C_p}}{\mathbf{C_f}} \times 100\% \quad (2)$$

Where R (%) is the separation efficiency, and C_f and C_p are oil concentration in feed and permeated solution, respectively.

2.5. Instruments and characterizations

Detailed information on the instruments and characterization is presented in Supporting Information.

3. Results and discussion

3.1. Preparation and morphological analysis of membranes

Previous studies had revealed that SLS could be used to modify CNT through a noncovalent method [18,22,23]. In this study, we used a simple filtration method to prepare the SLS@CNT membrane (Fig. 1**a**). As displayed in Fig. 1b, the CNT cannot be dispersed in water, therefore, we used SLS as a dispersant to prepare CNT suspensions. SLS can be absorbed on the CNT surface via the π-π interaction and hydrophobic interactions [18]. At the same time, the high polarity of the sulfonate group and the hydroxyl group in the SLS chemical structure greatly enhanced the hydrophilicity of SLS-modified CNT which resulted in the high stability of the SLS/CNT suspension. This highly-stable SLS/CNT suspension was kept and observed for three months under ambient conditions (Fig. 1**b**). The SLS-modified CNT was deposited on a cellulose acetate membrane via vacuum filtration to prepare SLS@CNT membranes (Fig. 1**a**). The as-prepared SLS@CNT membrane was uniform without any cracks on the surface and showed good flexibility (Fig. 1**c**). Through the use of a scanning electron microscope (SEM), morphological analysis of the fabricated membranes was extensively performed, and the results exhibited that the cellulose acetate membrane possessed a porous microstructure (Fig. 2**a-c**). After the deposition process, CNT layer fully covered the cellulose acetate membranes, constructing a

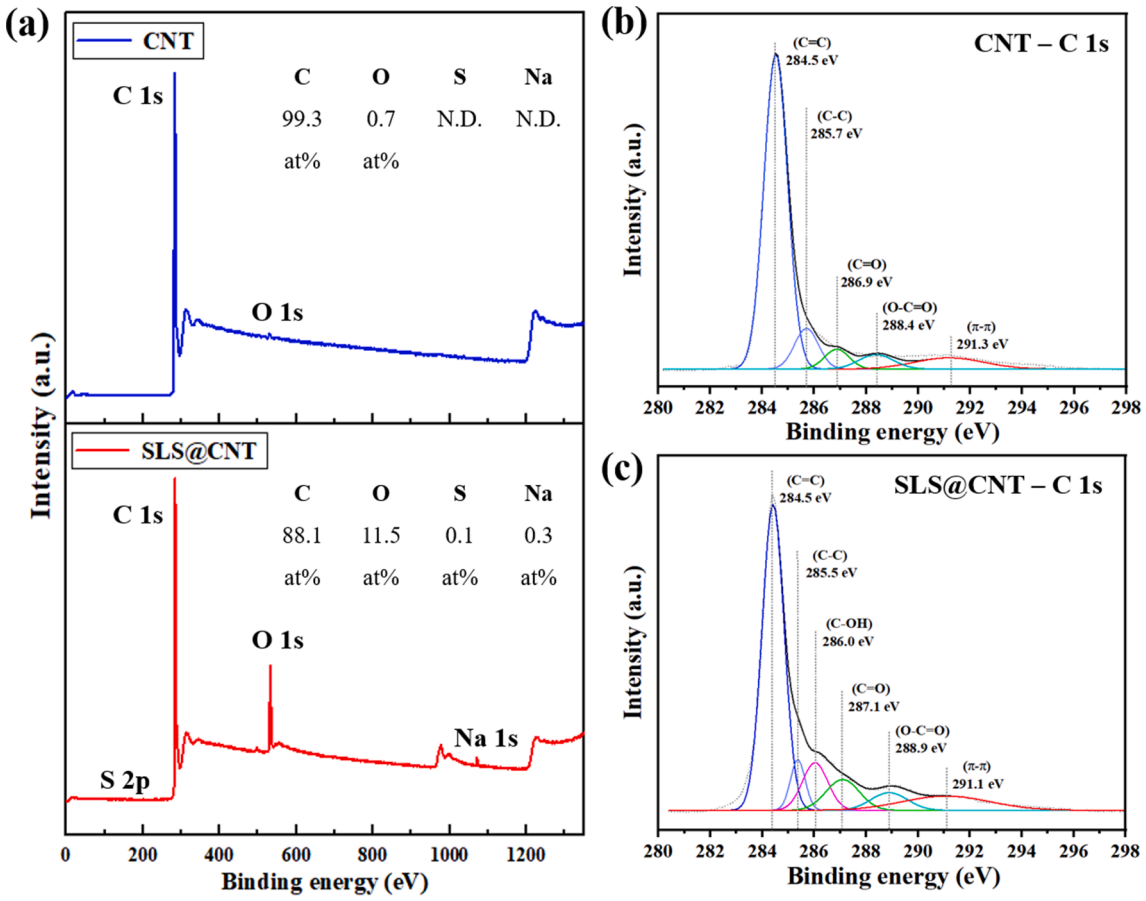

Fig. 3. (a) (a) XPS spectra of the CNT and SLS@CNT membranes. High-resolution C 1s spectra of (b) CNT and (c) SLS@CNT membranes.

defect-free, microporous layer with a rough microstructure (Fig. 2**d-f**). The SLS@CNT membrane exhibited a rough surface morphology (Fig. 2**g-I** and **Fig. S1**) comparable to the characteristics of the CNT membrane. The thickness of the SLS@CNT layer is about 22.8 μm (**Fig. S2**). **Fig. S3** shows the atomic force microscope (AFM) images of the SLS@CNT membrane. It indicated that SLS@CNT membrane possessed rough surface structures with the roughness (Ra) of 163 nm.

3.2. Surface chemical compositions of the membranes

We used X-ray photoelectron spectroscopy (XPS) analysis to attain relevant information on the surface chemical composition of the membranes (Fig. 3). The XPS spectra of the CNT membrane present quantitative 99.3 at% C and 0.7 at% O. Meanwhile, the SLS@CNT membrane showed significantly increasing prevalence of O content to 11.5 at%, and new peaks corresponding to S and Na elements which demonstrate the presence of SLS (Fig. 3**a**). The C 1s spectra of the CNT membrane were fitted into five peaks (Fig. 3**b**). The major characteristic peaks can be attributed to the aromatic structure C═C/C—C (284.5 eV and 285.5 eV), while the minor peaks can be assigned to the carbon–oxygen species including C═O carbonyl (286.9 eV), O—C═O carboxyl (288.4 eV), and π-π interaction (291.3 eV) [24,25]. On the other hand, the C 1s spectra of the SLS@CNT membrane was deconvoluted into six components with an additional peak at 286.0 eV (Fig. 3**c**), which can be attributed to the presence of the hydroxyl group. The XPS observations confirmed the successful modification of SLS on the SLS@CNT membrane.

3.3. Wettability of the membranes

The hierarchical nanostructure and surface chemical composition are significant factors that substantially contributes to membrane wettability. This was evaluated by measuring the water contact angle (WCA) and underwater oil contact angle (UWOCA) of the membranes, as shown in Fig. 4. On the one hand, the CNT membrane shows superhydrophobicity (Fig. 4**a**). A water droplet was approached and preloaded on the CNT membrane surface. After that, the water droplet was lifted up without any residual left on the CNT membrane surface conforming the superhydrophobicity of the CNT membrane. On the other hand, the SLS@CNT membrane shows superhydrophilic properties as shown in Fig. 4**b**. After contacting with the SLS@CNT membrane surface, the WCA decreased to 0° within one minute. From these results, it can be established that the presence of SLS can turn the wettability from superhydrophobic to superhydrophilic properties. The dynamic crude oil adhesion underwater was performed and shown in Fig. 4**c-d**. When a crude oil approached the CNT membrane surface, the oil droplet was immediately adsorbed by the CNT membrane as seen in Fig. 4**c**. This CNT membrane instance demonstrates the superhydrophobic in air and underwater superoleophilic properties. On the contrary, an abundance of hydrophilic functional groups in the SLS@CNT membrane was observed to be capable of forming a hydration layer to prevent the membrane surface from fouling underwater as shown in Fig. 4**d**. When the crude oil droplet was contacted and pressed onto the SLS@CNT surface, the crude oil could be removed without any residual droplet on surface, indicating the underwater superoleophobic property. The UWOCA of the membranes were further investigated using various types of organic solvents including petroleum ether, n-hexane, isooctane, hexadecane, toluene, and crude oil, with the respective values of 157.3°, 156.3°, 155.0°, 158.9°, 158.0°, and 161.6° **(**Fig. 4**e)**. Once the UWOCA is above 150° and the oil droplet could be removed without any residual droplet on the surface, indicating the Cassie-Baxter model [26]. It could be explained by the synergistic effect of the hydrophilic functional groups and the topological hierarchical nanostructure of the SLS@CNT

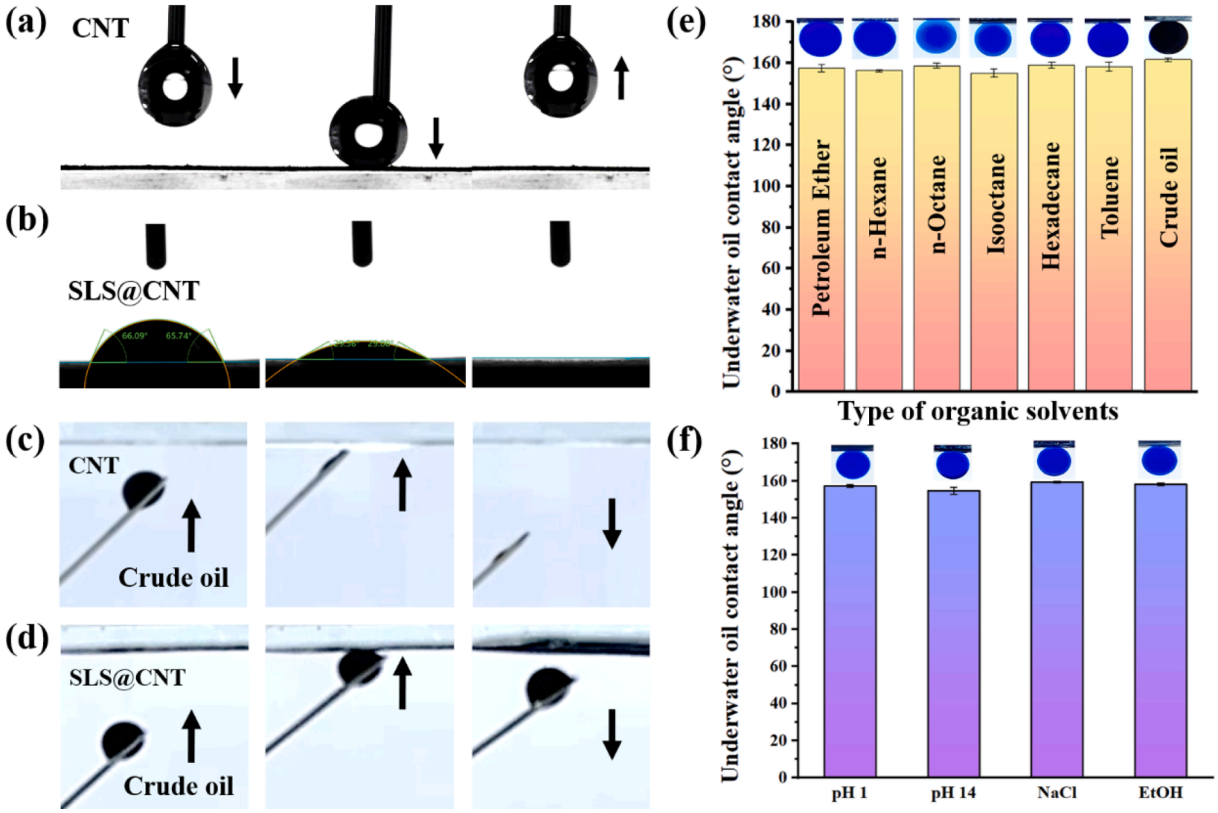

Fig. 4. Approach and contact of a water droplet in air on a syringe needle with respect to the (a) CNT and (b) SLS@CNT membranes. Approach, contact, deformation, and departure of a crude oil droplet underwater on a syringe needle with respect to the (c) CNT and (d) SLS@CNT membranes. (e) UWOCAs on the SLS@CNT membrane of a series of oils. (f) UWOCAs of SLS@CNT membranes after immersion in HCl (pH = 1), NaOH (pH = 14), NaCl (3.5 wt%) aqueous solutions, and ethanol for 7 days.

membrane. The hydrophilic function groups could form a hydration layer to protect the membrane from foulants. Moreover, the carbon nanotube's rough microstructure can improve the antifouling property. In addition, long-term chemical resistance experiments were performed by immersing the SLS@CNT membrane in the following harsh conditions for 7 days: acid (HCl, pH = 1), alkaline (NaOH, pH = 14), saline solution (NaCl, 3.5 wt%), and an organic solvent (ethanol). After immersion, the hexadecane was used to measure the UWOCA as shown in Fig. 4**f**. The UWOCA was>155° for all conditions, indicating that the SLS@CNT membrane possessed well chemical resistance. To further investigate the stability of the SLS@CNT membrane, we also carried out the bending test to determine the mechanical durability of the SLS@CNT membrane. Even after 50 cycle of bending tests, the SLS@CNT layer was still fixed well on the cellulose acetate substrate and the SLS@CNT membrane maintained its superhydrophilicity and underwater superoleophobicity, revealing that SLS@CNT membrane had outstanding mechanical durability (Figure S4). The as-prepared SLS@CNT membrane shows superhydrophilicity in air and underwater superoleophobicity, which are distinguishing features that indicate antifouling properties and the potential for oil-in-water emulsion separations.

3.4. Antifouling and self-cleaning properties of the membranes

Regarding the SLS@CNT membrane's superhydrophilicity in air and its underwater superoleophobicity, the antifouling and self-cleaning attributes were tested by injecting the light oil onto the surface and immersing the prewetted membrane into high-viscosity crude oil as illustrated in Fig. 5. Here, the antifouling test was performed by immersing the membrane in water, followed by injecting 3 mL of isooctane (dyed with blue color) onto the membrane surface. Fig. 5**a** presents the antifouling property of the CNT membrane. It can be seen that the CNT surface appears as silver in color underwater which might be due to its superhydrophobic property. It could prevent water molecules as it traps air on the surface, resulting in a silver color appearance. When oil was injected onto the surface, the CNT membrane easily fouled and absorbed the oil. On the contrary, the SLS@CNT membrane with superhydrophilic property was fully wetted by water. As a result, when oil is introduced onto the surface of the SLS@CNT membrane, the hydration layer can shield the surface from fouling as demonstrated by the clean surface shown in Fig. 5**b**. In order to verify the self-cleaning property, the membranes were first prewetted by water, then immersed into crude oil and allowed to perform self-cleaning by immersing it again in a clean water bath. After that, the membranes were tapped onto a tissue paper to observe the fouling on the surface. Because of its water repellency and underwater superoleophilicity, the CNT membrane was easily fouled by crude oil as seen on the tissue paper (Fig. 5**c**). On the other hand, Fig. 5**d** presents the cleaned SLS@CNT membrane. After being seriously fouled by crude oil, the self-cleaned SLS@CNT membrane reveals the significant observation on the clean tissue paper. The results indicated that the SLS@CNT membrane possessed outstanding antifouling and self-cleaning properties.

3.5. Emulsion separation performance of the SLS@CNT membrane

To address industrial wastewater issues using one of the most promising technologies, the SLS@CNT membrane was used to separate SFOWEs and SSOWEs. First, the SLS@CNT membrane was placed in a dead-end filtration setup and was prewetted by water. Afterward, SFOWEs were poured onto the filtration setup and the emulsion separation was performed under an external pressure of 0.5 bar. The separation of isooctane and crude oil SFOWEs was observed under an optical

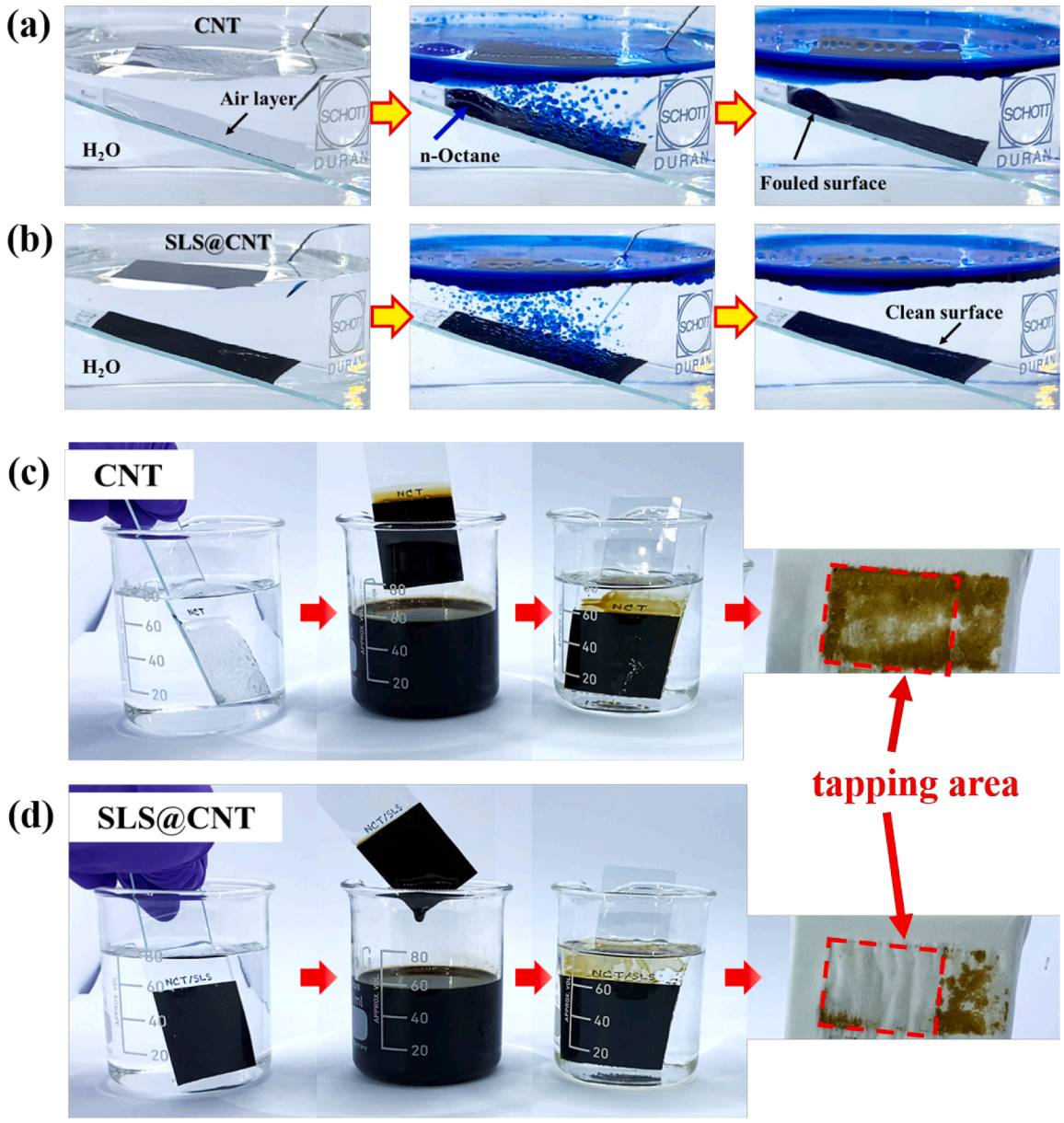

Fig. 5. Comparison of the antifouling and self-cleaning properties of the CNT and the SLS@CNT membranes. The (a) CNT and (b) SLS@CNT membranes were injected with isooctane underwater. The prewetted (c) CNT and (d) SLS@CNT membranes were immersed in crude oil, cleaned by water and tapped on tissue papers.

microscope and the images prior to and after the separation process are presented in Fig. 6**a**. After turning the vacuum pump on and the milky white or brown emulsions were filtered using SLS@CNT membrane, the oil droplets in SFOWEs could be rejected and the clean water permeates were collected into the flask. As displayed in the optical microscopic images, the permeate did not present any residual droplet in the microscale. The SLS@CNT membrane was used to filter a series of SFOWEs including petroleum ether, n-hexane, isooctane, hexadecane, toluene, and crude oil. The fluxes were approximately 24400 ± 1600, 20000 ± 1000, 26400 ± 2900, 27800 ± 1800, 23700 ± 300, and 5050 ± 230 L m^{-2} h^{-1} bar^{-1}, respectively. The separation efficiencies of all SFOW emulsions were higher than 99.97 % (Fig. 6**b**).

Furthermore, we examined the SSOWEs separation performance of the SLS@CNT membrane. The SSOWEs were prepared by using Tween 80 as an emulsifier. It is well known that the presence of a surfactant makes the emulsion separation more difficult to deal with since the surfactant may be absorbed on the membrane surface, causing caking, resulting in a reduction of the flux and separation efficiency. The photographs and optical microscopic images of isooctane and crude oil SSOWEs before and after separation are shown in Fig. 6**c**. It can be seen that the emulsion feed has a milky white or dark brown color for surfactant stabilized isooctane or crude oil emulsion, respectively. After the filtration process, the permeates are shown to be crystal clear without any observable droplets on the optical microscope. The particle size distributions of the SSOWEs (isooctane and crude oil) before and after separation were measured using dynamic light scattering (DLS) (Fig. S5 and S6). DLS data indicated that the particle size of the water droplets in the feed emulsions were 4343 nm (for the isooctane-in-water emulsion) and 3023 nm (for the crude oil-in-water emulsion), and only below 100 nm size particles are observed in all filtrates. The series of the SSOWEs separation performance including petroleum ether, n-hexane, isooctane, hexadecane, toluene, and crude oil emulsions had flux of 13800 ± 1100, 10500 ± 1000, 8500 ± 1100, 7500 ± 350, 10700 ± 1100, 12300 ± 1700, and 4860 ± 450 L m^{-2} h^{-1} bar^{-1}, respectively. The separation efficiencies were higher than 99.79 % for all SSOWEs (Fig. 6**d**).

The SLS@CNT membrane's recyclability for emulsion separation

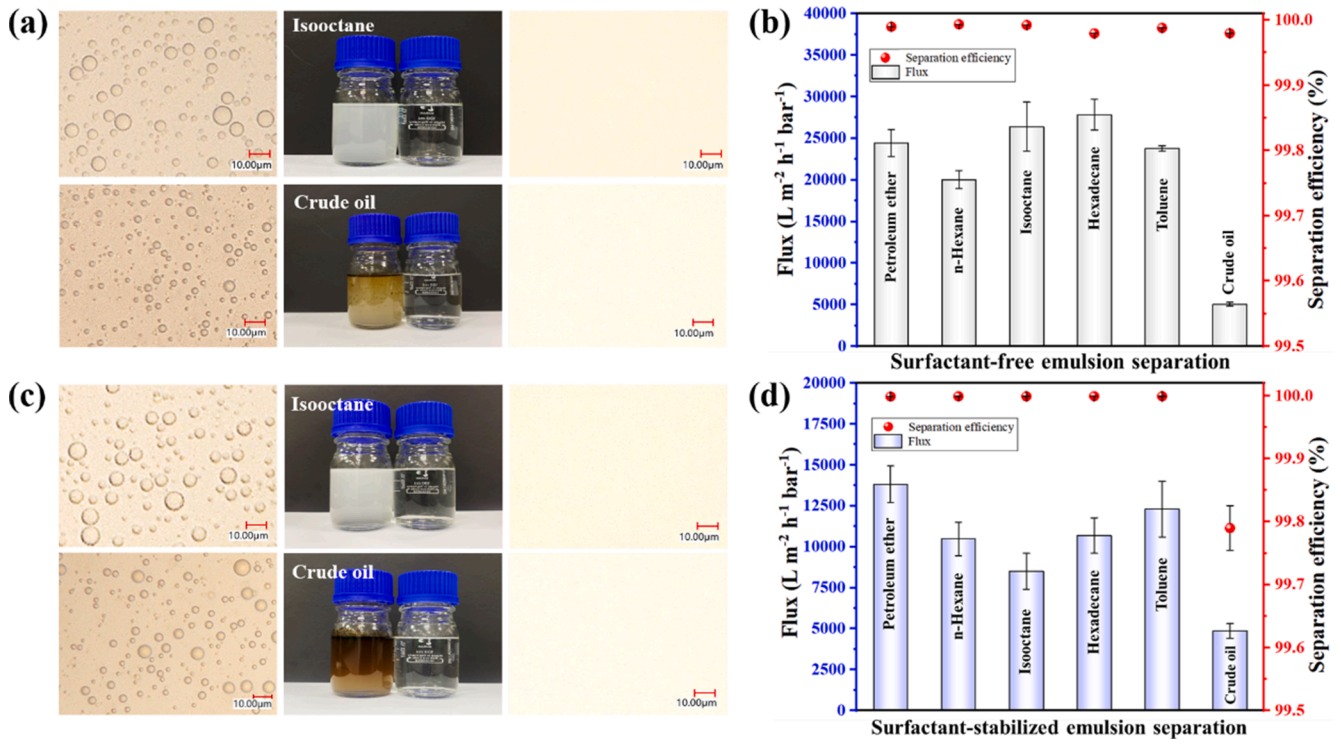

Fig. 6. (a) Actual images of isooctane and crude oil SFOWEs before and after filtration using the fabricated SLS@CNT membrane. (b) Separation performance against SFOWEs of the SLS@CNT membrane. (c) Actual images of isooctane and crude oil SSOWEs before and after filtration using the SLS@CNT membrane. (d) Separation performance against SSOWEs of the SLS@CNT membrane.

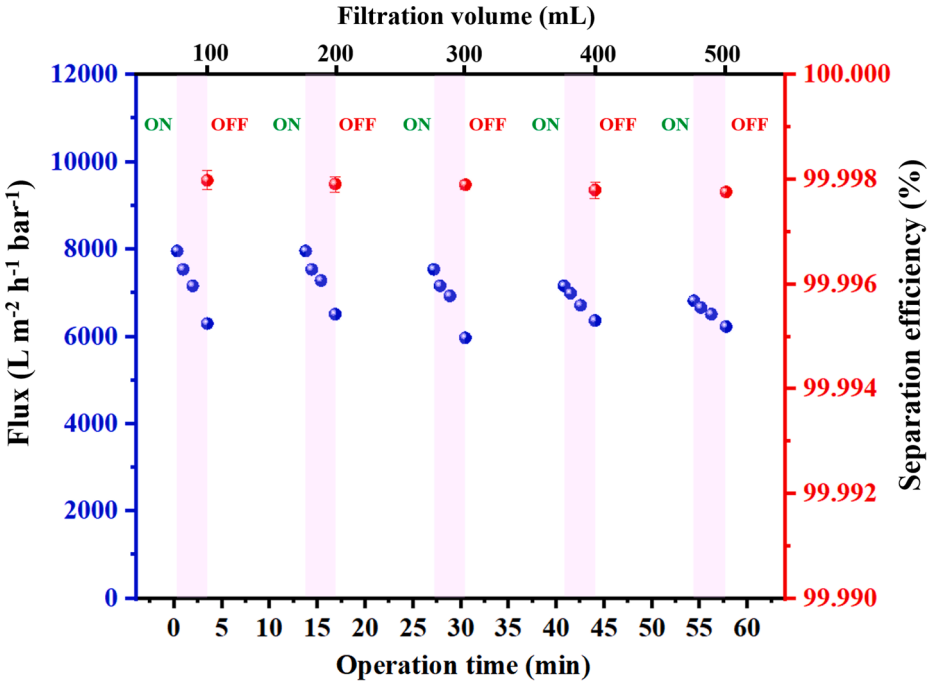

Fig. 7. SLS@CNT membrane's flux and separation efficiency during the separation cycles against SSOWEs.

was also investigated by using an isooctane SSOWE. A 100 mL emulsion was allowed to pass through the prewetted SLS@CNT membrane for each of the five cycles, and the separation was carried out under external pressure (0.5 bar). When the filtrate reached 100 mL, the vacuum pump was turned off and the permeate was collected to measure its oil content. Meanwhile, the used SLS@CNT membrane was washed on the surface with a small amount of water and was allowed to rest for 10 min without any organic solvent treatment or backwashing. As shown in Fig. 7, the flux declined from 8,000 L m^{-2} h^{-1} bar^{-1} to 6,000 L m^{-2} h^{-1} bar^{-1} due to the increase in intrusion pressure from caking and pore blocking. But after the cleaning process, the flux recovery could return up to 100 % in the second cycle and 85.7 % in the fifth cycle. Moreover, after 5 cycles of isooctane SSOWE separation, the SLS@CNT membrane could still maintain a separation efficiency above 99.99 %.

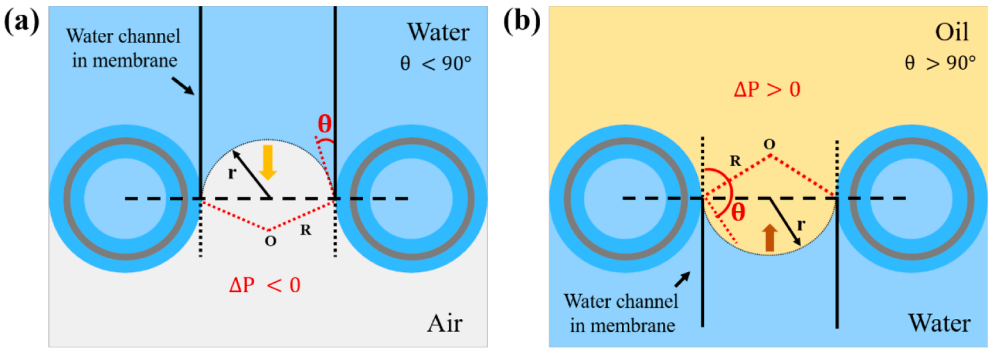

Fig. 8. Schematic diagram showing the wetting models of SLS@CNT membrane. (a) Water could permeate the SLS@CNT membrane. (b) Oil could not permeate the water-prewetted SLS@CNT membrane.

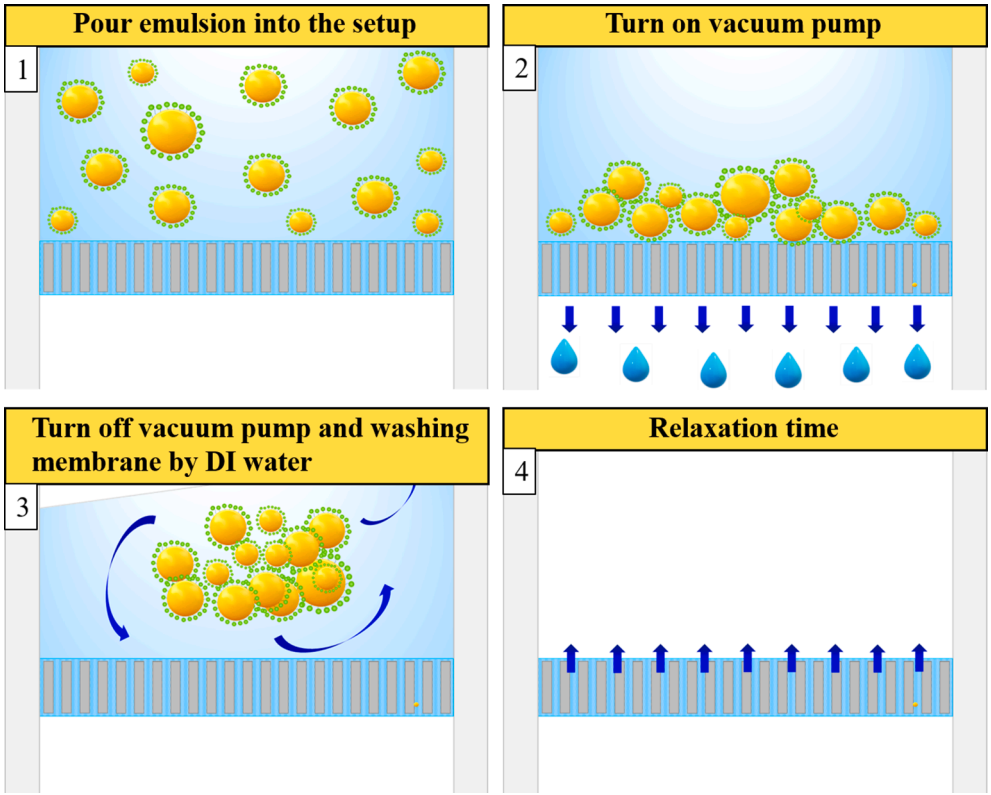

Fig. 9. Schematic diagram showing the emulsion separation and the self-cleaning mechanisms of the SLS@CNT membrane.

3.6. Emulsion separation mechanism

Since the liquid intrusion pressure (ΔP) could be used to describe the wetting and penetration behavior of the SLS@CNT membrane, the simplified Young-Laplace equation was shown in eq. (4) could be used:

$$\Delta P = -\frac{2\gamma_{W,A}\cos\theta_W}{r} \quad (3)$$

where ΔP is the intrusion pressure, $\gamma_{W,A}$ is the surface tension of a liquid (e.g., water) in air, θ_W is the water contact angle on the membrane surface, and r is the radius of the water surface inside the membrane pore. Once the θ_W is close to 0° or it possesses superhydrophilicity in air, then the $\Delta P < 0$, which indicates that the water can permeate through the membrane by gravity forces (Fig. 8**a**). In order to explain the underwater anti oil fouling or water/oil environment, the Young-Laplace equation can be modulated to the following equation:

$$\Delta P_w = -\frac{2\gamma_{L_W L_O}\cos\theta_O}{r} \quad (4)$$

where ΔP_w is the intrusion pressure of the water in the prewetted membrane. When UWOCA is above 150° or it exhibits underwater superoleophobicity, then $\Delta P_w > 0$, indicating that the oil droplet cannot be absorbed into the water-prewetted membrane and requires external pressure for penetration [27,28] (Fig. 8**b**). The separation mechanism could be attributed to the size-sieving effect and the underwater superoleophobicity of the SLS@CNT membrane. Hence, when an external force was applied to draw the emulsion, the oil droplet was rejected and returned to the emulsion stream since they were blocked by the smaller pores of the membrane. The hydrophilic functional groups on the SLS@CNT membrane produced intermolecular hydrogen bonds with water, establishing a protective hydration layer. This encapsulated water on the membrane surface is beneficial for the performance of oil rejection and antifouling, while the hydrophilic pore is accompanied by enhanced water flux through capillary force (Fig. 9). Furthermore, the

Table 1
Comparison of various CNT membranes for separation of oil-in-water emulsions*.

S.N.	Material	Surfactant-free emulsion		Surfactant-stabilized emulsion		Crude oil separation ability	Ref.
		Flux ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	Eff. (%)	Flux ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	Eff. (%)		
1	PVA-MWCNT membrane	–	–	1880	99.6	–	29
2	CNT@PDA-ZT membrane	–	–	2000	99.3	–	25
3	PAA-CNTs/Pd@Pt/PAA-CNTs composite membrane	4284	99.7	400	99	–	30
4	CNT@CS/TA-FeOOH	–	–	1660	99.1	–	31
5	CNT/TA/PVP membrane	7570	99.99	2634	99.41	Yes	32
6	SLS@CNT membrane	27,800	99.97	13,800	99.79	Yes	This work

* -Not Reported. PVA; polyvinyl alcohol, PDA: polydopamine, PAA: polyacrylic acid, CS: chitosan, TA: tannic acid, PVP: polyvinylpyrrolidone.

antifouling and self-cleaning features of the fabricated SLS@CNT membrane could demonstrate the mechanism for the cycle test results using the SLS@CNT membrane. When the used SLS@CNT membrane was rinsed with water to eliminate the oil layer on the surface, the encapsulated water in the membrane pore could induce self-cleaning through capillary force and restore the high flux (Fig. 9).

In comparison to other superwetting CNT membranes [25,29–32], the SLS@CNT membrane exhibited very high fluxes and excellent separation efficiencies for separating SFOWEs and SSOWEs (Table 1). Furthermore, the SLS@CNT membrane possessed remarkable crude oil-in-water emulsion separation abilities. Multistep artificial fabrication, demanding preparation requirements, and the employment of unsafe chemicals have restricted the practical applicability of numerous CNT membranes. The fabrication approach that we reported here offers the advantages of being straightforward, affordable, environmentally friendly, and free of the use of dangerous chemicals.

4. Conclusion

In summary, the SLS@CNT membrane was successfully prepared via a vacuum filtration method. It can be noted that the preparation procedure is a green process without using any organic solvent. The SLS could be absorbed on the CNT surface by π-π stacking and its hydrophilic functional groups could provide a hydrophilic unit to let SLS-modified CNTs be dispersed in water. As-prepared SLS@CNT membrane showed superhydrophilicity in air (WCA about 0°) and underwater superoleophobic properties (UWOCA > 150°). In addition, the presence of the hydrophilic functional group could generate a hydration layer on the surface of the SLS@CNT membrane underwater to acquire exceptional antifouling and self-cleaning qualities. The SLS@CNT shows SFOWEs and SSOWEs separation fluxes up to 27,800 and 13,800 $L\ m^{-2}\ h^{-1}\ bar^{-1}$, with separation efficiency>99.97 % and 99.79 %, respectively. Overall, the distinguished separation performance for different oil-in-water emulsions, green preparation process, inexpensive, and recyclability of the superwetting SLS@CNT membrane make it an excellent candidate for practical applications.

CRediT authorship contribution statement

Jittrakorn Udomsin: Conceptualization, Methodology, Investigation, Writing – original draft. **Chien-Chieh Hu:** Resources, Supervision, Conceptualization. **Chih-Feng Wang:** Resources, Supervision, Conceptualization, Writing – review & editing. **Jem-Kun Chen:** Resources, Formal analysis. **Hsieh-Chih Tsai:** Resources, Formal analysis. **Shiao-Wei Kuo:** Resources, Formal analysis. **Wei-Song Hung:** Resources, Formal analysis. **Juin-Yih Lai:** Resources, Funding acquisition, Supervision.

Declaration of Competing Interest

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

Data availability

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

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.124349.

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