Robust bio-inspired superhydrophilic and underwater superoleophobic membranes for simultaneously fast water and oil recovery

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ABSTRACT: Designing a stable and uniform hydrophilic material for separation of oil and water is strongly desired for sustainable management of oily wastewater. Herein, a stable and uniform bio-inspired coating onto the non-woven fabric substrate with superhydrophilicity and underwater superoleophobicity via rapid co-deposition of dopamine and polyethylenimine was demonstrated. Ammonium persulfate outperformed other oxidants (e.g., Cu^{2+}-H_2O_2 and $NaIO_4$) to rapidly trigger the co-deposition of dopamine and polyethylenimine for homogeneous superhydrophilic and underwater superoleophobic surface engineering. Furthermore, the co-deposition conditions, i.e., concentration of ammonium persulfate and exposure duration, have a positive dependence on the hydrophilicity and underwater oleophobicity of the coated fabric membranes. Specifically, the superhydrophilicity and underwater superoleophobicity (underwater oil contact angle of 165.4±1.1°, sliding angle of 2.5±0.5°) can be obtained for the coated fabric membranes at the optimal co-deposition condition (i.e., 28.5 $mmol \cdot L^{-1}$ persulfate and coating duration of 7 h), showing a great potential in gravitational oil-water separation (permeation flux >115,000 $L \cdot m^{-2} \cdot h^{-1}$; oil rejection >99.2%). Integrating with a superhydrophobic copper mesh, the oil-water mixed solution can be continuously and sufficiently separated, realizing simultaneous recovery of pure oil and water from oily wastewater. In addition, the bio-inspired coating displays a strong long-term chemical robustness and stability in extreme environments (i.e., acidic/alkaline solutions and oils). The study provides a facile, cost-

effective and practical strategy in constructing superhydrophilic and underwater superoleophobic interfaces for sustainable treatment of oily wastewater.

KEYWORDS: Dopamine; Co-deposition; Superhydrophilicity and underwater superoelophobocity; Gravitational oil-water separation; Resource recovery

1. Introduction

Frequent occurrence of marine oil-spill accidents and large-scale discharge of industrial oily wastewaters not only pose serious damage to the eco-system and human health, but also lead to a tremendous loss of valuable resources, *e.g.*, oil and fresh water [1-5]. Various methods, such as *in-situ* burning, physical adsorption and the use of settling tank, have been employed to eliminate the oil species from these polluted oily wastewaters [6]. However, these traditional treatment methods are not environmentally friendly and suffer from a low efficiency with high cost. Therefore, developing a fast, cost-effective and environmentally friendly oil-water separation method is urgently needed for realizing the sufficient recovery of oil and water from the oily wastewaters, in view of advanced sustainability [7-10].

Currently, superwetting interfaces have been proposed to design feasible, sustainable, and cost-effective materials by utilizing a physico-chemical strategy based on mimicking structures of natural products (*e.g.*, lotus leaf, butterfly wing, and water strider leg) for effective oil-water separation [11-13]. These superwetting

materials are typically categorized into two types, i.e., with hydrophobicity & oleophilicity or hydrophilicity & oleophobicity in nature, based on their affinity to oil or water. Initially, superhydrophobic and superoleophilic materials were extensively studied for oil-water separation [14-17]. For instance, Jiang *et al.* constructed superhydrophobic-superoleophilic porous membranes with a >99.95% separation efficiency for oil-water solution by a facile phase inversion method [18]. These superhydrophobic membranes allow the oil to pass through while retaining the water from oil-water mixed solutions. Shang *et al*. fabricated a superhydrophobic nanofiber membrane by *in situ* polymerization of fluorinated polybenzoxazine mixed SiO_2 nanoparticles functional layer on cellulose acetate nanofiber [19], yielding a water contact angle of 161°. Zhou *et al.* designed a superhydrophobic cotton fabric with excellent durability and high separation efficiency (>97.8%) in oil-water solutions via vapor phase deposition [20]. Unfortunately, those superhydrophobic interfaces with nano/microstructures are fragile and can be easily destroyed, resulting in a poor mechanical stability and durability, although they exhibit an acceptable efficacy for oil-water separation [21].

Alternatively, superhydrophilic interfaces are of increasing interest in separation of oil-water mixtures, which are capable of selectively retaining oil from the oil-water mixtures [22-26]. A key advantage regarding superhydrophilic interfaces is that fouling is greatly alleviated by avoiding direct contact between oil and the interfaces. To date, various materials, such as chitosan [27, 28], cellulose [29], hydrogel [30, 31], tannic

84 acid and dopamine [32-34], have been introduced to construct superhydrophilic and
85 underwater superoleophobilc surfaces by physical or chemical techniques. Specifically,
86 dopamine is a typical catecholamine with 3, 4-dihydroxy-L-phenylalanine and lysine,
87 which can self-polymerize in a slightly alkaline environment to form a thin
88 polydopamine (PDA) coating [35]. Due to the strong covalent/non-covalent interaction
89 between catechins and substrates, the dopamine can firm deposit onto various surfaces.
90 Additionally, the abundant hydrophilic groups (i.e., hydroxyl and amino functional
91 groups) derived from the PDA coating can endow the substrate material with a strong
92 hydrophilicity and chemical versatility, which has a great potential for applications [36-
93 38]. However, this dopamine-based surface modification is not impeccable with various
94 issues of concern, *e.g*., slow deposition [39-41], inadequate surface wettability [42] and
95 chemical stability [43]. Huang and his co-workers observed that a porous sponge
96 required at least 8 $g \cdot L^{-1}$ dopamine and 4 hours for surface decoration to form a
97 hierarchically structured PDA coating in a slightly alkaline environment [44]. Various
98 oxidation strategies, e.g., pure oxygen-induced oxidation [45], $CuSO_4/H_2O_2$ oxidation
99 [46], microwave-assisted oxidation [47], UV-assisted oxidation [48], and electric field-
100 triggered oxidation [49], were proposed as triggers to accelerate the bio-inspired
101 coating for tailoring its properties. However, these oxidation-accelerated strategies still
102 have insufficient polymerization kinetics or require complicated steps to rapidly form
103 a stable and homogeneous PDA-based coating on the substrates.

In this study, a highly-efficient, one-step, facile strategy was demonstrated to design robust superhydrophilic non-woven fabric membranes by coating of the PDA and polyethyleneimine (PEI) complex for effective oil-water separation. We confirmed the efficacy of ammonium persulfate as appropriate strong oxidant to rapidly trigger the co-deposition of PDA and PEI complex by scanning electronic microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and water contact angle measurement. The separation performance of the bio-inspired superhydrophilibic fabric membranes in oil-water mixture was studied to evaluate their potential in oil-water separation for sustainable resource recovery through integration with a superhydrophobic copper mesh. Additionally, the bio-inspired superhydrophilic fabric membranes were exposed to extreme conditions to test their long-term stability for practical application.

2. Experimental section

2.1 Materials and chemicals

Dopamine hydrochloride, polyethyleneimine (PEI, M_w=600 Da), tris(hydroxymethyl) aminomethane (Tris), ammonium persulfate, sodium periodate ($NaIO_4$), hydrogen peroxide (H_2O_2) and copper sulfate were supplied from Sigma-Aldrich. Petroleum ether, hexane, kerosene, toluene, paraffin, hydrochloric acid and ethanol were ordered from Sinopharm Chemical Reagent Co., Ltd. (China). The non-woven polyester fabrics were purchased from Freudenberg (Germany). All chemicals were of analytical grade and used as received.

2.2 Bio-inspired coating on non-woven fabrics

The non-woven fabrics were surface-coated via rapid co-deposition of dopamine and PEI triggered by persulfate as trigger (**Fig. 1**). Initially, persulfate with different concentrations (i.e., 0, 9.5, 19.0, 28.5 and 38.0 $mmol \cdot L^{-1}$) was homogeneously dissolved in the Tris buffer solutions (50 mL, pH~8.5), respectively. Then, 100 mg (2.0 $g \cdot L^{-1}$) of PEI and 100 mg (2.0 $g \cdot L^{-1}$) of dopamine were completely mixed into the persulfate-containing buffer solutions. Finally, the non-woven fabric substrates were immediately exposed into the as-prepared dopamine-based solutions for 7 hours. All the coated non-woven fabric membranes were rinsed 4 times with ultrapure water in order to remove the residual unreacted agents. The coated bio-inspired non-woven fabric membranes triggered by different oxidant concentrations (i.e., 0, 9.5, 19.0, 28.5 and 38.0 $mmol \cdot L^{-1}$) were denoted as F/PS-0, F/PS-1, F/PS-2, F/PS-3, and F/PS-4, respectively. The other triggers, i.e., Cu^{2+}-H_2O_2 and $NaIO_4$, with equivalent amounts, were employed to compare with persulfate during the polymerization of dopamine and PEI.

The non-woven fabric substrates were immersed into the dopamine-based solutions at different co-deposition durations, i.e., 1, 2, 3, 4, 5, 6, 7 and 8 hours to investigate the effect of co-deposition duration on the wettability. After that, the coated non-woven fabric membranes were completely cleaned by ultrapure water and dried for further use. Details about the experimental procedure are presented in **Supplementary Table S1**.

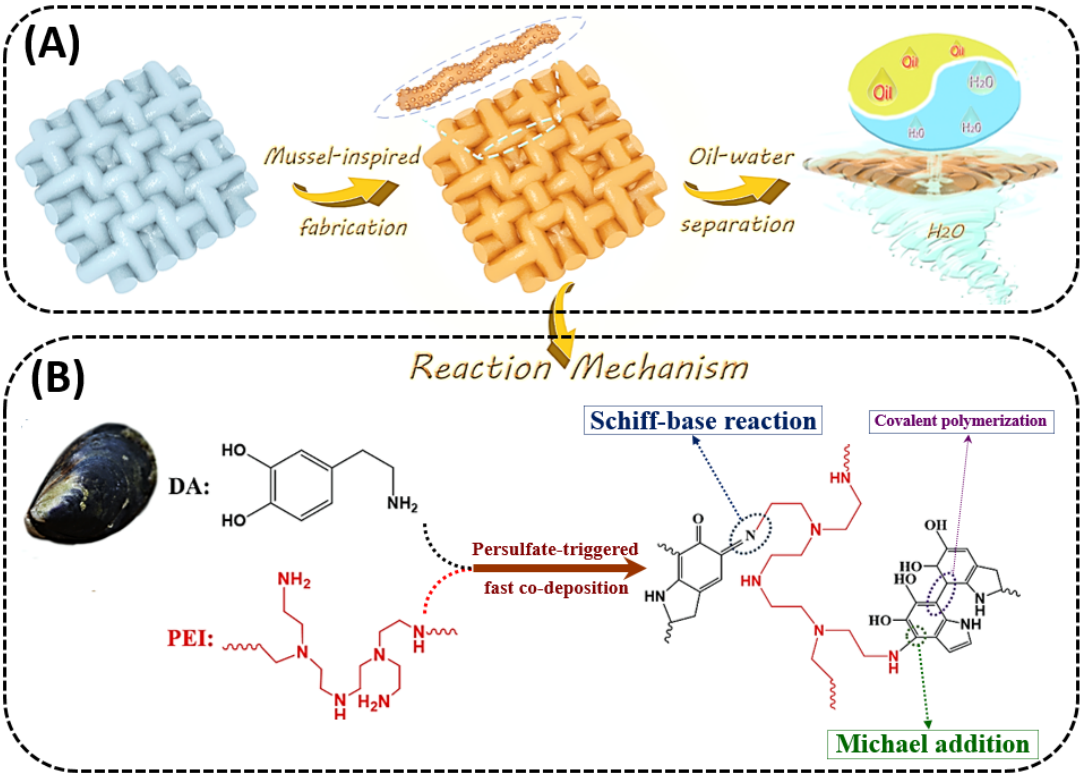


Fig. 1. (A) Schematic diagram of mussel-inspired coating for design of superhydrophilic non-woven fabric membranes; (B) proposed reaction mechanism of fast co-deposition of dopamine (DA) and PEI triggered by persulfate via Michael addition and Schiff-base reaction.

2.3 Characterization

2.3.1 Color variation of dopamine-based solutions

In this study, various oxidants, i.e., air, Cu^{2+}-H_2O_2, $NaIO_4$ and persulfate, were employed as triggers to investigate the polymerization kinetics of dopamine or/and PEI through color variation. UV-vis spectrophotoscopy (UV2600, Tianmei Scientific Instruments Co., Ltd., China) was applied to analyze the absorbance of the dopamine-based solutions at the wavelengths of 357 and 403 nm, respectively [50].

2.3.2 Composition of bio-inspired coating

FTIR measurement was performed through a Vector 22 spectrometer (Bruker Daltonics Inc., Germany) to characterize the chemical functional groups on the surface of the coated fabric membranes at the wavenumbers of 500-4000 cm^{-1}. In addition, XPS measurement was further conducted in a PHI-5000C ESCA System (USA) with Mg Kα excitation radiation (h_v=1253.6 eV).

2.3.3 Surface morphology

SEM measurement was taken through a SEM XL30 FEG (Philips, The Netherlands) to visualize the morphology of the coated non-woven fabric membranes. Before the SEM measurement, the coated non-woven fabric membranes were dried and sputter-coated with gold nanoparticles.

2.3.4 Hydrophilicity and underwater oelophobocity

The water contact angle and underwater oil contact angle were measured to assess the hydrophilicity and underwater oleophobocity of the fabric membrane samples at 6 different positions by a drop shape analyzer (DSA100, Krüss GmbH, Germany) at ambient conditions.

2.4 Oil-water separation performance

The oil-water separation performance of the non-woven fabric membranes was tested by a filtration system with an effective area of 12.57 cm^2 at room temperature. The volume ratio between oil and water in the oil-water mixture was set at 1:1. Various oil species, *i.e.*, *n*-hexane, kerosene, toluene, petroleum ether and paraffin, were applied to

investigate the oil-water separation performance. Furthermore, the separation efficiency of the coated non-woven fabric membranes was measured solely by gravity force (10-cm hight), which was calculated by Eq. 1:

$$R(\%) = \left(\frac{C_0 - C_p}{C_0} \right) \times 100 \quad (1)$$

where R is the oil rejection. C_p and C_0 are the concentration of oil present in the permeate and feed, as measured by a total organic carbon analyzer.

The permeation flux of the coated non-woven fabric membranes in the oil-water mixtures was determined by recording the volume of the permeate during a fixed time, as shown in Eq. 2:

$$J = \frac{V}{S \cdot \Delta t} \quad (2)$$

where J presents the permeation flux, V denotes the volume of the permeate, S is the effective area of the coated non-woven fabric membranes, and Δt is the time for collecting the permeate.

2.5 Stability/durability of the bio-inspired coating

To assess the chemical stability of the bio-inspired non-woven fabric membranes in the extreme environments, the resultant non-woven fabric membranes were exposed in acidic (pH=2), neutral (pH = 7), & alkaline (pH=12) solutions and different oils for 5 days. Then, the exposed non-woven fabric membranes were dried for underwater oil contact angle measurement. The durability of the coated non-woven fabric membranes was also investigated by a 100-cycles oil-water separation test. After each cycle, the

coated non-woven fabric membranes were rinsed with deionized water for the next measurement.

3. Results and discussion

3.1 Color variation of dopamine-based solutions

The polymerization kinetics behavior of dopamine is vital for the evolution of the hydrophilic coating; these are significantly affected by different conditions, especially oxidants. **Fig. 2** shows the color variation and UV-vis absorbance of the dopamine-based solutions in the presence of different oxidants as triggers.

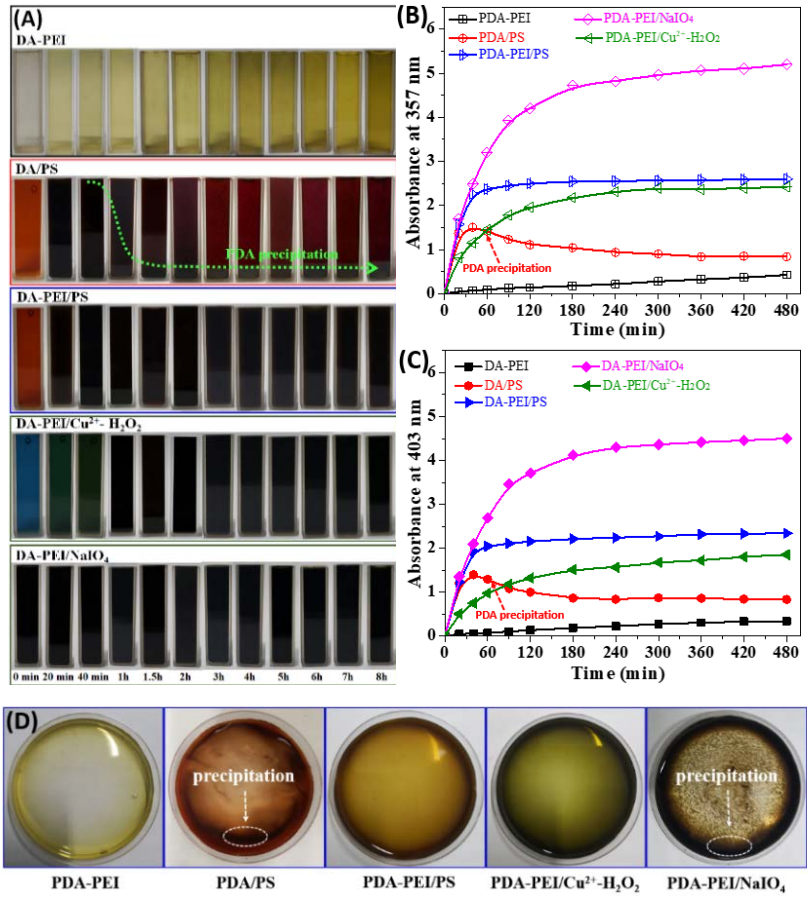


Fig. 2. (A) Color variation of dopamine-based solutions with different triggers, i.e., air, persulfate (PS), Cu^{2+}-H_2O_2, and $NaIO_4$; (B, C) evolution in UV-vis absorbance of

dopamine-based solutions (10-fold dilution before UV-vis measurement) at the wavelengths of 357 and 403 nm, respectively; (D) photographs of various dopamine-based solutions.

As indicated in **Fig. 2A**, the dopamine-PEI solution showed no obvious change in color pattern with the absence of strong oxidants during 8-h exposure duration, which can be reflected by the slight enhancement in the absorbance at the wavelengths of 403 and 357 nm (**Fig. 2B** and **2C**). Under this mildly alkaline condition (pH~8.5), self-polymerization of dopamine or its interconnection with PEI was strongly impeded, since only a trace amount of oxygen was present in the dopamine-PEI solution. On the other hand, the other dopamine-based solutions yielded an impressive color pattern, once they came into contact with the triggers with strong oxidation power, i.e., Cu^{2+}-H_2O_2, persulfate and $NaIO_4$, which can accelerate the oxidation of dopamine for self-polymerization or interconnection with PEI. As the reaction duration extended, these dopamine-based solutions generally exhibited an increasing gradient in depth of color pattern. As illustrated in the UV-vis absorbance at wavelengths of 357 and 403 nm (**Fig. 2B** and **2C**), the slowest oxidation kinetics for dopamine were observed when Cu^{2+}-H_2O_2 was used among these three triggers, since Cu^{2+} ions can chelate with amino groups derived from dopamine or PEI to form the Cu^{2+}-based complexes. This could diminish the generation of reactive oxygen species to some extent for oxidation of dopamine, which limits the evolution of bio-inspired coating onto the fabric substrates

(**Fig. S1**). The strongly oxidizing persulfate allowed for enhanced oxidation kinetics of dopamine, and resulted in aggregation of PDA particles via covalent stacking in the pure dopamine solution, which was demonstrated by the solution color depth and reduced UV-vis absorbance with extending exposure duration. Nevertheless, the presence of PEI would strongly interconnect with dopamine or its oxidized intermediates based on Schiff base or Michael addition reaction induced by persulfate in the dopamine-PEI solution [48].

Although persulfate has the highest standard redox potential, it exhibited a lower oxidation capacity for dopamine, compared to $NaIO_4$, mainly attributed to the fact that persulfate fails to be efficiently decomposed into sulfate radicals with higher oxidation power for dopamine oxidation. $NaIO_4$ showed an advantageous priority to promote the oxidation of dopamine in the dopamine-PEI solutions, as demonstrated by increasing UV-vis absorbance in **Fig. 2B** and **2C**. Unfortunately, $NaIO_4$ allowed for a sufficient conversion of dopamine into polydopamine (PDA) aggregates due to its two-electron oxidant property (**Fig. 2D**) [51]. Such a PDA aggregation is unfavorable for the formation of a PDA-PEI layer on fabric substrates, which can be reflected by the poor and inhomogeneous deposition of the bio-inspired coating (see **Supplementary Fig. S1**). Therefore, persulfate shows a potentially impressive efficacy in triggering the bio-inspired co-deposition on the fabric substrate.

3.2 Air-triggered bio-inspired co-deposition

To investigate the co-deposition behavior of the PDA-PEI coating on the fabric substrate triggered by air, the evolution in hydrophilicity and underwater oleophobicity of the coated fabric membranes was demonstrated (**Fig. 3**).

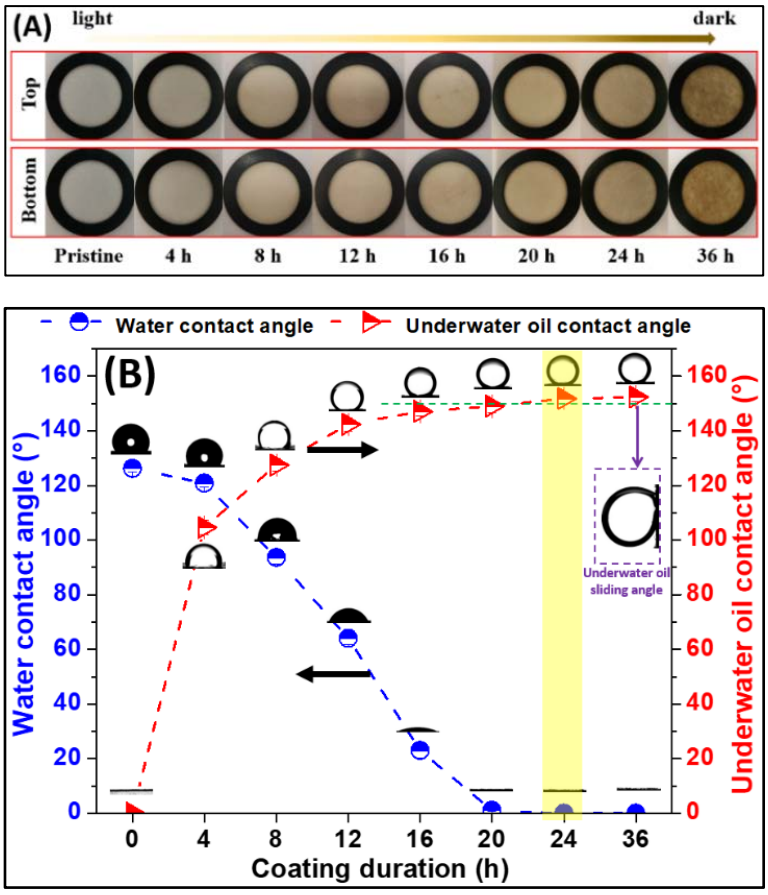


Fig. 3. (A) Photograph of the PDA-PEI coatings triggered by air onto the non-woven fabric substrate; (B) hydrophilicity and underwater oleophobicity of the PDA-PEI coatings triggered by air.

As demonstrated in **Fig. 3A**, the initial color pattern of the coated fabric membranes turned slightly yellow when exposed in the dopamine-based solution for 4 h, suggesting the successful co-deposition of the PDA-PEI complex. As the coating duration

extended, the color depth of the coated fabric membranes became increasingly darkened, since more PDA-PEI complexes were deposited onto the non-woven fabric substrate surfaces. However, such a coating of the PDA-PEI complex was not sufficient, due to the low polymerization kinetics of dopamine triggered by air. Consequently, this led to a less sufficient evolution of hydrophilicity and underwater oleophobicity on the non-woven fabric membranes (**Fig. 3B**). Especially, the coated fabric membranes showed a slight improvement in hydrophilicity with 4-h coating, which can be reflected from the drop of water contact angle by ca. 5.4°. With the extension of coating duration, the hydrophilicity and underwater oleophobicity of the non-woven fabric membranes increased. With 24-h coating, the fabric membranes exhibited a complete wettability for water with acceptably high underwater oleophobicity (i.e., underwater oil contact angle: 151.8±2.1°). When increasing the coating duration to 36 h, the hydrophilicity and underwater oleophobicity of the fabric membranes had no significant improvement. Unfortunately, the oil drops can firmly adhere to the fabric membranes even when placed vertically. The air-triggered bio-inspired co-deposition on the fabric substrate was time-consuming and ineffective to form a PDA-PEI complex layer with acceptable wettability and underwater oleophobicity. Such a moderate underwater oleophobicity is unfavorable for oil-water separation, since the oil could potentially penetrate through the non-woven fabric membranes for reduced oil retention.

3.3 Persulfate-triggered bio-inspired co-deposition

3.3.1 Effect of persulfate content on bio-inspired co-deposition

In order to accelerate the co-deposition of the PDA-PEI complex on the fabric substrate, persulfate was used as trigger. **Fig. 4** shows the effect of the persulfate content on the wettability of the PDA-PEI complex coating.

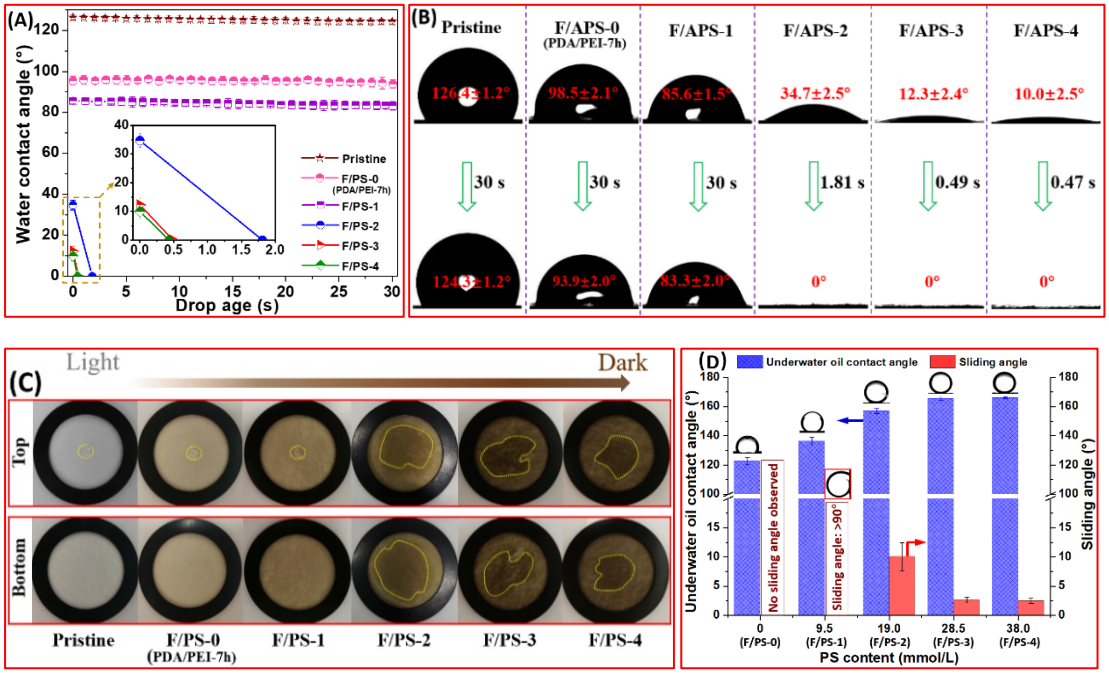


Fig. 4. (A, B) Dynamic water contact angle; (C) digital images (yellow marks denote the wetting of water drop); (D) underwater oil contact angle & sliding angle of persulfate-triggered PDA-PEI coatings at different persulfate contents.

The non-woven fabric substrate showed a moderate hydrophobicity for repelling the water drop after air-triggered PDA-PEI coating with a duration of 7 h (**Fig. 4A** and **4B**). Due to the inferior oxidation capacity of air, the PDA-PEI complex layer was slowly evolved and poorly deposited on the fabric substrate surface, as reflected by the

insignificant change in color development of the fabric substrate surface (**Fig. 4C**) and SEM observation (**Fig. 5A** and **5B**). Additionally, the unpronounced peaks at 1558 cm^{-1} (assigned to the vibration of N-H) [52], 1626 cm^{-1} (assigned to the vibration of C=N) [53] and 3300-3600 cm^{-1} (assigned to the vibration of O-H) [54] in FTIR measurement and low intensity for N 1s peak in XPS spectra of the coated fabric membrane (i.e., F/PS-0) also can confirm the poor adhesion of the air-triggered PDA-PEI complex coating on the fabric substrate surface (**Fig. 6**). This only yielded a slight improvement in surface hydrophilicity with the reduction of water contact angle from 126.4±1.2° to 98.5±2.1°.

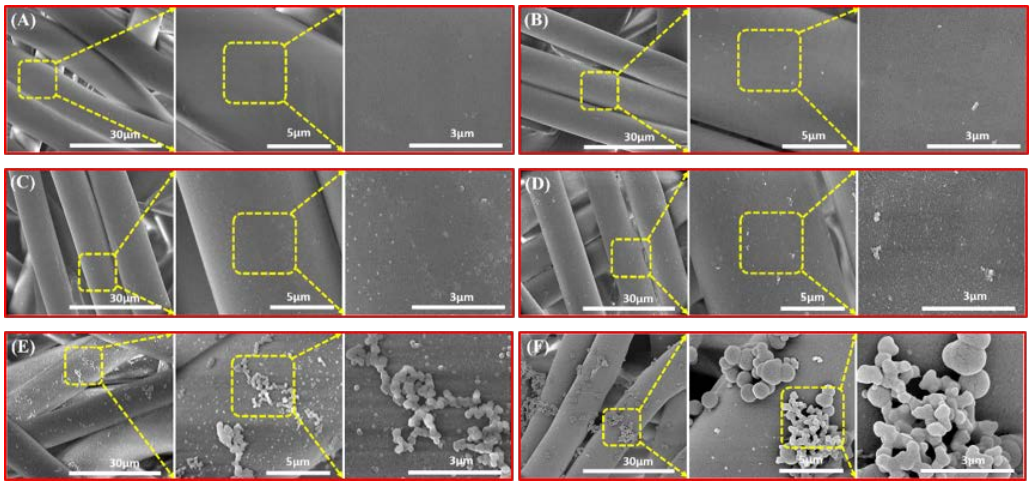
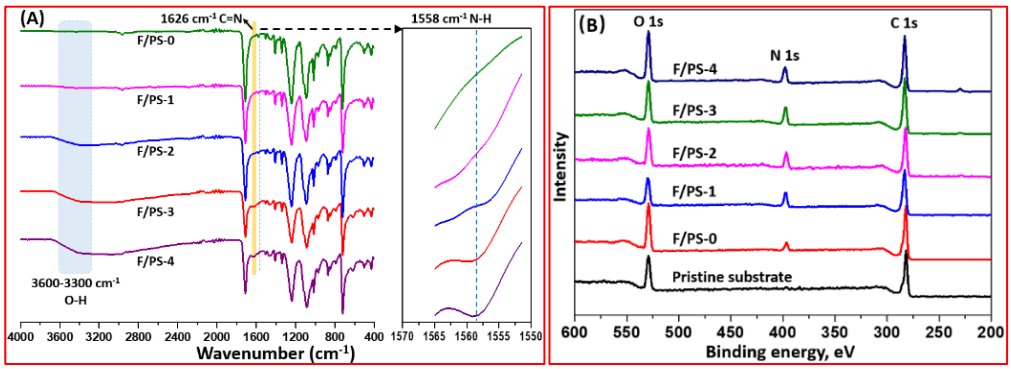


Fig. 5. Surface SEM images of the persulfate-triggered PDA-PEI coatings onto the fabric substrate at various persulfate amounts. (A) Pristine; (B) F/PS-0; (C) F/PS-1; (D) F/PS-2; (E) F/PS-3; (F) F/PS-4.



310

311 **Fig. 6.** (A) FTIR and (B) XPS spectra for the pristine fabric substrate and coated

312 fabric membranes with different persulfate amounts.

313 With the triggering by persulfate, the bio-inspired coating was rapidly evolved and

314 constructed on the fabric substrate, as demonstrated by spot-like structure with

315 increasing surface roughness in **Fig. 5C-5F**. Specifically, the vibration of N-H at 1558

316 cm^{-1}, C=N at 1626 cm^{-1} and O-H at 3300-3600 cm^{-1} in the coated fabric membranes

317 during FTIR measurement was intensified with increasing persulfate concentration

318 (**Fig. 6A**). Furthermore, the increasing intensity for N 1s peak in XPS spectra confirms

319 that a sufficient amount of PEI with higher atomic percentage of N element was

320 interconnected with dopamine via Michael addition and Schiff base reactions (**Fig. 6B**)

321 [50]. Such a rapid bio-inspired coating greatly enhances the hydrophilicity and

322 underwater oleophobicity of the fabric membranes. However, the surface wettability of

323 the fabric membranes was strongly dependent on the amount of persulfate, which

324 dominated the polymerization kinetics of the PDA-PEI complex. Therefore, a sufficient

325 amount of persulfate is required to yield an acceptable hydrophilicity and underwater

326 oleophobicity for the coated fabric membranes. Specifically, the addition of 9.5

mmol·L^{-1} persulfate resulted in no pronounced improvement in surface hydrophilicity, and the water still cannot easily penetrate through the coated fabric membrane surface (**Fig. 4C**). As the amount of persulfate was raised to 28.5 mmol·L^{-1}, the water drop can rapidly spread on the coated fabric surface (i.e., F/PS-3) within 0.5 s. In addition, an underwater oil contact angle of 165.4±1.1° with an extremely low sliding angle (2.5±0.5°) was obtained, demonstrating a superior hydrophilicity and underwater oleophobicity (**Supplementary Fig. S2**). As the amount of persulfate further increased, the fabric surface showed a plateau in the superhydrophilicity and underwater oleophobicity. Therefore, a concentration of 28.5 mmol·L^{-1} for persulfate is sufficient to trigger the bio-inspired coating for superwetting interface engineering.

3.3.2 Effect of exposure duration on bio-inspired co-deposition

It is crucial to establish a defect-free dopamine-based coating to ensure an acceptable and uniformly high hydrophilicity and underwater oleophobicity, in view of water-oil separation. Therefore, it calls for a sufficient evolution in PDA-PEI coating onto the fabric surface. **Fig. 7** shows the effect of exposure duration on the wettability of the PDA-PEI complex layer.

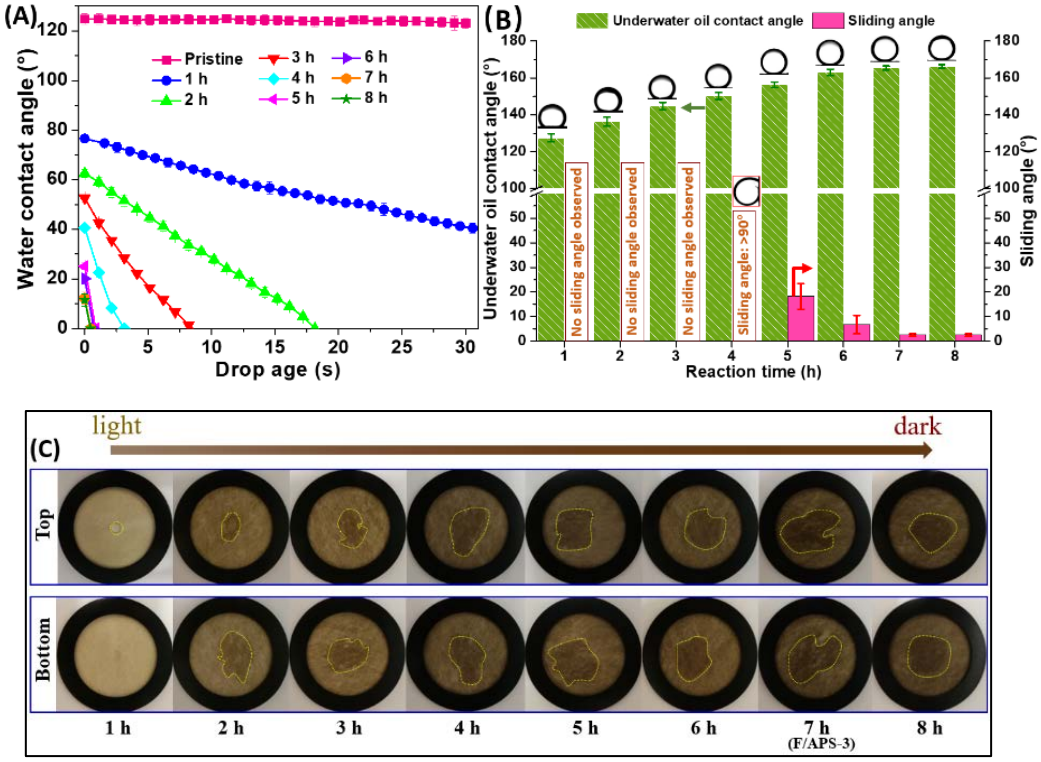


Fig. 7. (A) Dynamic water contact angles; (B) underwater oil contact angle & sliding angle; (C) digital images (yellow marks denote the wetting of water drop) of persulfate-triggered PDA-PEI coatings at various exposure durations.

As shown in **Fig. 7A**, the hydrophilicity of the fabric surfaces was significantly enhanced with exposure duration, due to the coating of the PDA-PEI complex. During an exposure duration of 1 h, the PDA-PEI complex was not sufficiently evolved onto the fabric surface, as demonstrated in digital images (**Fig. 7C**), SEM (**Fig. 8**), FTIR and XPS measurements (**Fig. 9**). The insufficient co-deposition of the PDA-PEI complex led to an insignificant boost in surface hydrophilicity and the water drop failed to penetrate through the fabric surface. As the exposure duration extended, more PDA-PEI complex was involved in co-deposition on the fabric surface via Michael addition

and Schiff-base reactions as triggered by persulfate. This resulted in an elevated hydrophilicity on the surface of the coated fabric membranes. Especially, the coated fabric membranes showed superhydrophilic and underwater superoleophobic properties with an oil sliding angle of 2.5±0.5° when the exposure duration increased to 7 h (**Fig. 7B** and **Supplementary Fig. S2**), since the PDA-PEI complex coating was homogeneously co-deposited on the fabric surface (EDS mapping in **Supplementary Fig. S3**), endowing a superior water adhesion and penetration into the fabric surface. Additionally, the extension of exposure duration does not enable a significant boost in the wettability of the fabric surface. Therefore, the exposure duration of 7 h can be considered optimal in the dopamine-PEI solution with 28.5 mmol·L^{-1} persulfate as trigger for surface engineering of the superhydrophilic fabric membranes.

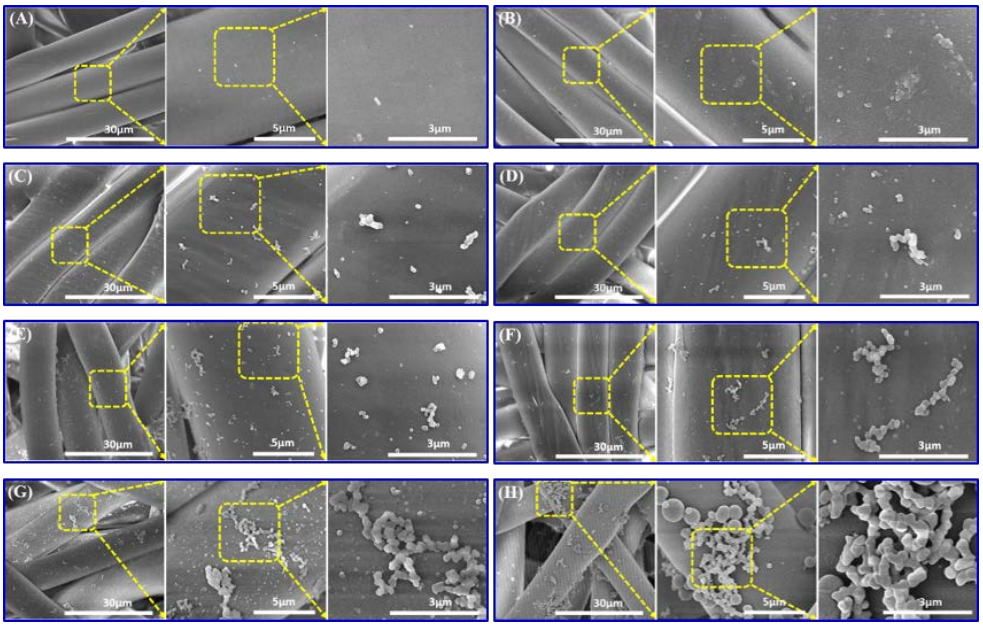


Fig. 8. Surface SEM images of the persulfate-triggered PDA-PEI coating at various exposure durations. (A) 1 h; (B) 2 h; (C) 3 h; (D) 4 h; (E) 5 h; (F) 6 h; (G) 7 h; (H) 8 h.

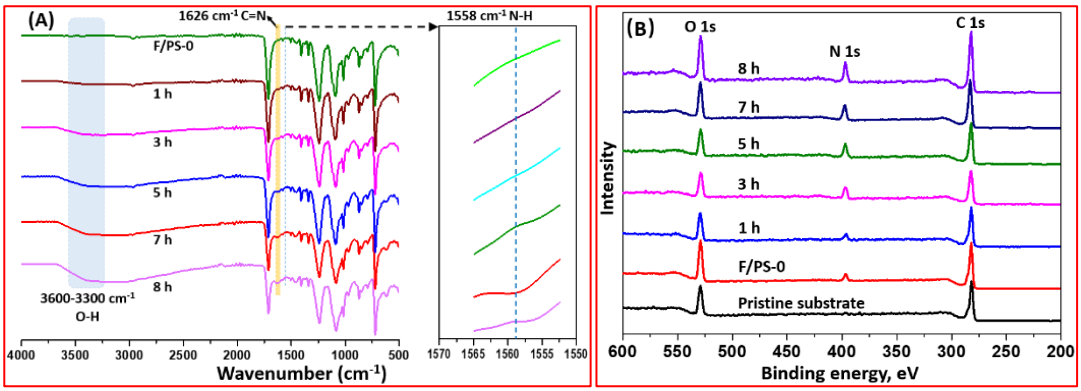


Fig. 9. (A) FTIR and (B) XPS spectra for the pristine and the persulfate-triggered PDA-PEI coatings at various exposure durations.

3.4 Oil-water separation

Due to the impressive underwater oleophobicity, the as-prepared PDA-PEI co-deposited fabric membranes show a promising potential in oil-water separation. A series of tests were conducted to evaluate the oil-water separation efficacy of the PDA-PEI coated fabric membranes triggered by persulfate (i.e., F/PS-3) in various oil-water solutions (**Fig. 10**).

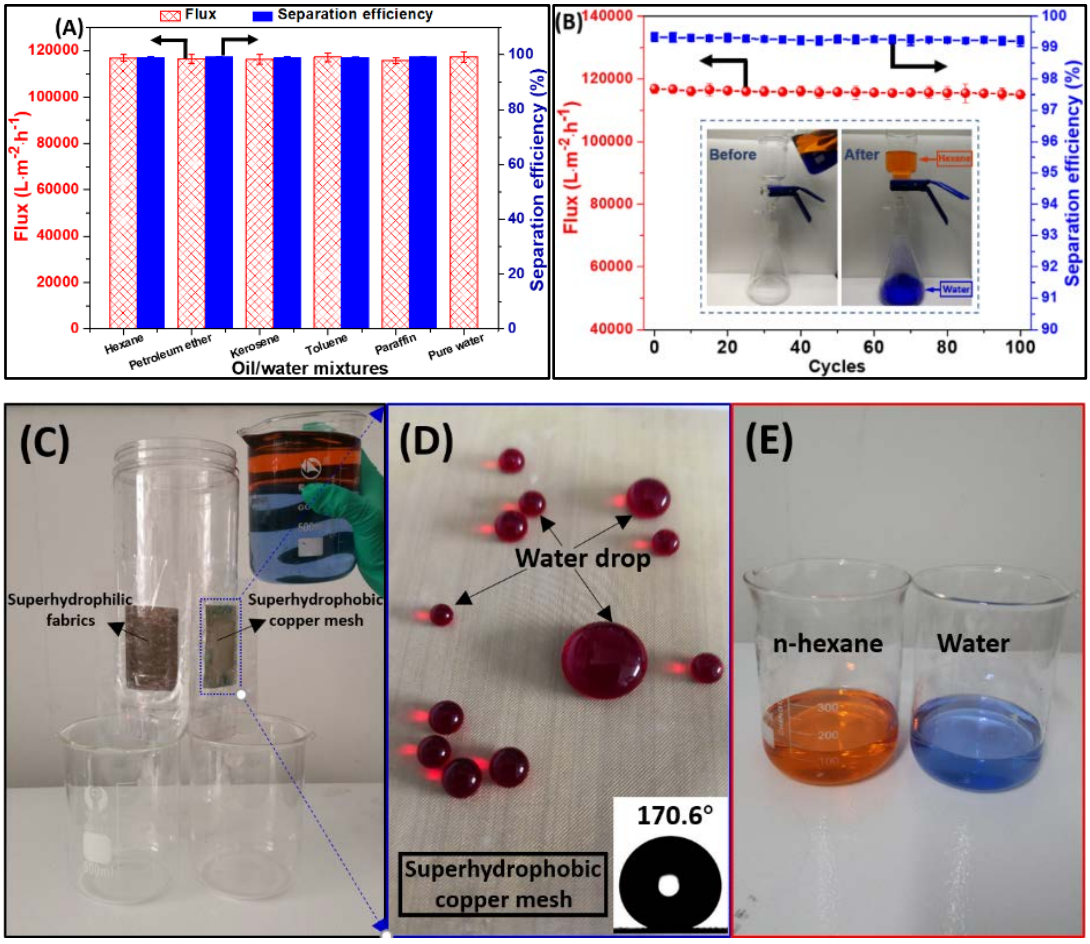


Fig. 10. (A) Separation performance of the PDA-PEI coated fabric membrane (F/PS-3) triggered by persulfate in different oil-water solutions; (B) separation performance of the F/PS-3 fabric membrane in the hexane-water mixture over 100 cycles; (C) oil-water separator by integrating superhydrophilic fabric membrane and superhydrophobic copper mesh for simultaneously fast separation of n-hexane and water mixture; (D) superhydrophobic copper mesh fabricated by spray-coating of fluorinated nanoparticles; (E) digital picture of the separated oil and water.

As indicated in **Fig. 10A**, the PDA-PEI coated fabric membrane (F/PS-3) showed an extremely high permeation flux (ranging from 115,000 to 117,000 $L \cdot m^{-2} \cdot h^{-1}$) in various oil-water solutions using gravity as driving force, with a >99.2% separation efficiency. These permeation fluxes of the coated fabric membrane in various oil-water solutions are comparable to that in pure water, showing a strong applicability for fast separation of oil and water. As reflected in **Fig. 10B**, the separation efficiency of the F/PS-3 fabric membrane in hexane-water solution remained unchanged (i.e., 115,000-116,800 $L \cdot m^{-2} \cdot h^{-1}$ permeation flux; 99.21-99.34% oil rejection) over 100 filtration cycles, implying that the PDA-PEI complex coating triggered by persulfate can endow the coated fabric membrane with a robust and impressive underwater oleopholicity for water-oil separation, which is confirmed by little change in the membrane surface morphology and composition after continuous oil-water separation (see SEM and XPS results in **Supplementary Fig. S4**). Furthermore, integrating with the superhydrophobic copper mesh, which was spray-coated with fluorinated nanoparticles (**Fig. 10C**, **10D** and **10E**) [55], the oil-water mixed solution can be continuously and sufficiently separated (**Supplementary Video S1**), potentially realizing the simultaneous recovery of pure oil and water, in view of sustainable treatment of oily wastewater.

3.5 Stability tests

The long-term stability of the bio-inspired coating is essential for oil and water separation, especially under extreme environmental conditions (i.e., acidic or alkaline solutions, and oils) which may cause severe damage to the bio-inspired coating and

consequently compromise the oil-water separation efficacy. As indicated in **Fig. 11A**, although the coated non-woven fabric membrane (i.e., F/PS-3) was exposed in the aqueous solutions with pH 2, 7 or 12 for 5 days, it still had a high underwater oleophobicity on the surface. Simultaneously, with exposure in various oils (i.e., n-hexane, petroleum ether, toluene, kerosene, and paraffin) for 5 days, only a negligible reduction (reduction of underwater oil angle was less than 1°) in the underwater oleophobicity of the F/PS-3 fabric membrane was observed (**Fig. 11B**). These results demonstrate the impressive chemical robustness and stability of the bio-inspired coating triggered by persulfate for effective oil-water separation.

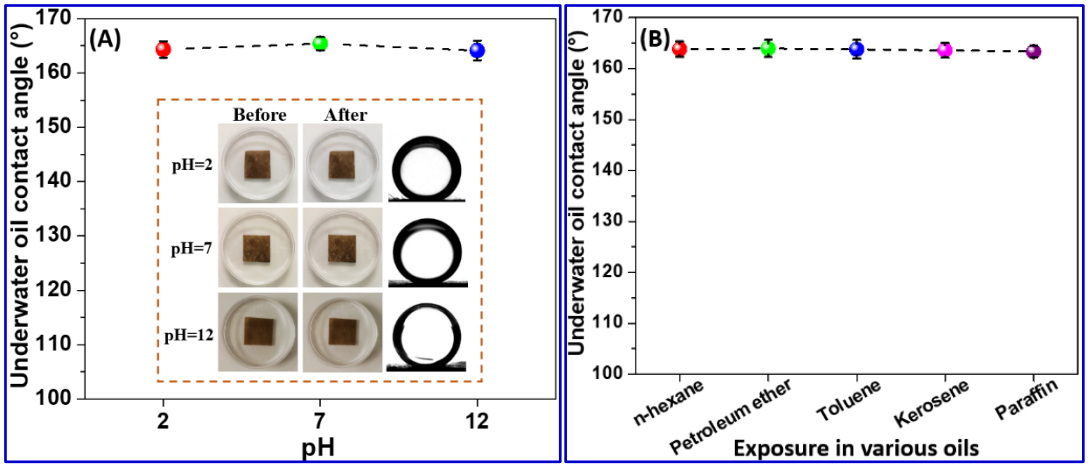


Fig. 11. Underwater oil contact angles of the F/PS-3 fabric exposed in (A) acidic, neutral & alkaline solutions and (B) different oils for 5 days.

4. Conclusion

In this study, a facile, cost-effective strategy based on bio-inspired coating is proposed to tailor-make superhydrophilic and underwater superoleophobic interfaces onto non-woven fabric substrate for highly efficient oil-water separation. Through

introducing persulfate as a strong trigger, the coating time of dopamine-PEI complex onto the non-woven fabric substrate was greatly shortened, simultaneously resulting in a uniform and stable bio-inspired coating. Specifically, at the optimal coating conditions (i.e., 28.5 $mmol \cdot L^{-1}$ persulfate and 7-h coating duration), a superhydrophilic and underwater superoleophobic bio-inspired PDA-PEI complex coating (underwater oil contact angle of 165.4±1.1°, oil sliding angle of 2.5±0.5°) was achieved, conferring the coated fabric membrane with a significant feasibility in oil-water separation. Such a coated superhydrophilic fabric membrane allowed for an extremely high permeation flux of 115,000-118,000 $L \cdot m^{-2} \cdot h^{-1}$ with >99.2% oil rejection in gravitational oil-water separation. Furthermore, the oil-water mixture can be simultaneously, continuously and efficiently separated through integrating the superhydrophilic fabric with the superhydrophobic copper mesh, potentially recovering pure oil and water from the oily wastewater. With exposure in extreme environments (i.e., acidic/alkaline solutions and oils), the bio-inspired coating exhibited strong long-term chemical robustness and stability, demonstrating an impressive efficacy of the persulfate-triggered bio-inspired coating in superhydrophilic and underwater superhydrophobic interface engineering.

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