Phosphonium Modified Nanocellulose Membranes with High Permeate Flux and Antibacterial Property for Oily Wastewater Separation

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Abstract

Nanocellulose membranes could efficiently separate oily wastewater because of their superhydrophilic and underwater superoleophobic property and nanoporous structure. However, the practical application and storage of nanocellulose membranes were limited by their low water permeation flux and easy corrosion by bacteria, respectively. Herein, nanocellulose membranes with high permeate flux and antibacterial property were fabricated by grafting tetrakis(hydroxymethyl) phosphonium chloride (THPC) onto the surface of tunicate cellulose nanofibers (TCNFs) via esterification reaction. The introduction of THPC groups with tetrahedral structure on the surface of TCNFs significantly improved the pore size and interlayer space of nanocellulose membranes, resulting in the increasing of water permeation flux. These THPC@TCNF membranes were superhydrophilic and underwater superoleophobic, which could effectively separate various oil/water nanoemulsion. Moreover, THPC@TCNF membranes possessed excellent durability, mechanical stability, and cycling performance. Due to the presence of positively charged phosphonium groups, THPC@TCNF membranes exhibited excellent antibacterial property against \textit{B. subtilis} that is a typical Gram-positive bacterium presenting in oily wastewater. This works provided a facile method to endow nanocellulose membrane with high permeate flux and antibacterial property.

1. Introduction

Oily wastewater produced from petrochemical industry and human daily life have attracted worldwide environmental concerns, therefore, high-performance materials for oil/water separation are imminently required (Gupta et al. 2017; Liu et al. 2019; Peng et al. 2016). In comparison to traditional separation technologies such as coagulation, centrifugation, settling and flotation (Kamcev et al. 2019; Yu et al. 2019; Zheng et al. 2021), membrane separation technology is the preferred technique in the field of oily wastewater purification due to its advantages of high efficiency, simple operation, small footprint, and ability to avoid secondary pollution and so on (Cai et al. 2020; Deng et al. 2020; Peng et al. 2022; Zhan et al. 2018). Various membranes, including polymeric membranes (Damodar et al. 2009; Zhu et al. 2017), ceramic membranes (Benito et al. 2007), and nanomaterial membranes (Shi et al. 2013), are widely applied in oily wastewater purification. However, the majority of reported membranes still face the problems of non-biodegradable, expensive raw materials, and complex fabrication.

Nanocellulose, as the most plentiful natural polymeric nanomaterial on earth, is widely utilized to construct porous nanomaterials due to its high aspect ratio, high elastic modulus, renewability, and biodegradability (Huang et al. 2021; Chen et al. 2018; De France et al. 2021; Heise et al. 2021; Isogai 2021; Wang et al. 2019). For example, nanocellulose membranes obtained by vacuum-assisted filtration could effectively separate oil/water nanoemulsions, which was attributed to the nano-scale pore size and super wettability of the membrane (Cheng et al. 2017). However, the nanoporous structure of membranes produced by dense assembly of nanocellulose always reduced their permeate flux, which severely limited their separation efficiency (Kwon et al. 2021). According to the Hagen–Poiseuille Eq. (1):
\[ J = \epsilon r^2 \Delta p / 8 \mu L \]

where \( J \) is the liquid flux through the membrane, \( \epsilon \) is the surface porosity, \( r \) is the pore size, \( \Delta p \) is the pressure, \( \mu \) is the liquid viscosity, and \( L \) is the thickness of the membrane (Hu et al. 2015). To improve the permeate flux of membranes, enhancing the pore size (or porosity) and lessening the thickness of membrane are two general strategies (Ke et al. 2020; Lamm et al. 2021; Li et al. 2021b). By mixing silica particles with bacterial cellulose, the porosity of membrane was significantly increased (Wahid et al. 2021). The pore size of the membranes could also be enhanced by combining solvent exchange of nanocellulose suspensions with ethanol and the use of a removable template (a mixture of calcium compounds) (Orsolini et al. 2016). On the other hand, ultrathin cellulose Voronoi-nanonet membrane could be fabricated by welding to the electrospinning nanofiber substrate via nonsolvent-induced phase separation (Tang et al. 2020). Although the permeate flux of these cellulose-based membranes could be effectively improved, they could not efficaciously prevent the corrosion of cellulose by microorganisms and the blockage of the membrane, affecting the service life of the membrane.

Herein, we tried to fabricate antibacterial nanocellulose membranes with high permeate flux by grafting tetrakis(hydroxymethyl) phosphonium chloride (THPC) onto tunicate cellulose nanofibers (TCNFs). THPC with flame retardancy and antibacterial property is an inexpensive by-product of phosphine tail gas (Olkiewicz et al. 2015). Owing to its tetrahedral structure and broad-spectrum antibacterial characteristics (Palermo et al. 2019; Peng et al. 2020), THPC was employed as pore-forming and antibacterial agent to endow membranes with enlarged pore size and antibacterial property. After esterification reaction, the average pore size and thickness of THPC@TCNF membranes increased to 62.2 ± 2.9 nm and 21.1 µm, respectively. The THPC@TCNF membrane could separate oil/water nanoemulsion with water permeate flux of 1858 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) and oil rejection of 99%. Furthermore, the resultant membrane exhibited good mechanical stability, cycle performance, and antibacterial property.

2. Experimental Section

2.1. Materials

Tunicate (Halocynthia roretzi Drasche) was obtained from Weihai Evergreen Marine science and technology Co. Ltd (Shandong, China). Microporous filter membrane (Nylon 66, cut-off: 0.22 µm, diameter: 50 mm) as a support was bought from Tianjin Jinteng Co., Ltd (Tianjin, China). 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was purchased from Sigma-Aldrich (America). Tetrakis(hydroxymethyl) phosphonium chloride (THPC, 80% aqueous solution), 4-dimethylaminopyridine (DMAP, 99%), were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Sodium hypochlorite (NaClO) was obtained from Alfa Aesar Co., Ltd (Shanghai, China). Sodium bromide (NaBr), sodium hydroxide (NaOH), hydrogen peroxide (H\(_2\)O\(_2\)) and dimethyl sulfoxide (DMSO) were obtained from
2.2. Fabrication of tunicate cellulose nanofibers (TCNFs)

Tunicate cellulose was isolated from the mantle of tunicate by NaOH boiling and H₂O₂ bleaching according to our previous method (Huang et al. 2019). Afterwards, tunicate cellulose (1 g) was dispersed in deionized water (99 g), followed by the addition of NaBr (0.1 g) and TEMPO (0.016 g). After TEMPO was completely dissolved, NaClO (6.2 g, 12%) was used to start the TEMPO oxidation, and NaOH (1 M) was applied to maintain the reaction medium pH of 10 ~ 10.5 under 400 rpm stirring for 12 h. Finally, the TEMPO-oxidized tunicate cellulose suspension was centrifuged and dialyzed to neutrality, and the TCNFs suspension was obtained by mechanical stirring in an ordinary soymilk machine.

2.3. Fabrication of THPC@TCNF membranes

TCNF suspension (12 mL, 0.06 wt%) was freely deposited on the Nylon 66 supported membrane by vacuum-assisted filtration to obtain a TCNF layer (5.73 g m⁻²). Subsequently, the Nylon 66 membrane coated with TCNF layer was dried, and finally stripped from the Nylon 66 support to obtain self-supporting TCNF membrane. Subsequently, a certain amount of THPC (2 ~ 32 wt%) with DMAP (5 wt%) were dissolved in DMSO. The TCNF membranes were then soaked with above solution at room temperature for 24 h. Finally, THPC@TCNF membranes were fabricated by washing with deionized water and drying.

2.4. Characterization

The morphologies of TCNFs and THPC@TCNFs were visualized with transmission electron microscopy (TEM, JEM-2100, Japan). The morphology of membranes was observed with scanning electron microscope (SEM, Zeiss SIGMA, Germany). The chemical structures of THPC@TCNF membranes were analyzed with Fourier transform infrared spectrometer (FTIR, NICOLET 5700, Thermo Fisher Scientific, USA). The constituent elements of the membranes before and after modification were analyzed by X-ray photoelectron spectrometer (XPS, ESCALAB250Xi, Thermo Fisher Scientific, USA). The distribution of P and Cl element was observed with energy disperse spectroscopy (EDS, Oxford UltimMax 40, Oxford, UK). The wettability of membranes was characterized by contact angle measurements (DSA100, Krüss, Germany). The oil concentration of the filtrates was measured with infrared spectrometer oil content analyzer (FYHW-2000B, Fangyuan, China).

2.5. Oil/water nanoemulsion separation

Four types of emulsions containing oil droplets of 50 ~ 500 nm were prepared by dispersing petroleum ether, chloroform, pump oil, and dimethicone into water with the help of surfactants, respectively. Details on the preparation of various nanoemulsions were provided in the Supporting Information. In a typical oil/water nanoemulsion separation process, the effective filter membrane area was 1.54 cm² and various nanoemulsions were fed into the separation unit at a constant pressure of 0.5 bar. According to the
volume of filtrate collected in 5 min, the water flux \( J \) (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) was calculated by substituting into Eq. (2):

\[
J = \frac{V}{A t \Delta P}
\]

Where \( V \) (L), \( A \) (m\(^2\)), \( t \) (h) and \( \Delta P \) (bar) was water permeate volume, effective filtration membrane area, permeation time, and transmembrane pressure, respectively. Besides, the oil rejection \( R \) (%) was obtained according to Eq. (3):

\[
R = (1 - \frac{C_f}{C_0}) \times 100 \%
\]

where \( C_f \) (mg mL\(^{-1}\)) and \( C_0 \) (mg mL\(^{-1}\)) were the oil concentrations in the filtrate collected after filtration and in the unfiltered oil/water emulsion, respectively. The infrared spectrometer oil content analyzer was used to measure the value of \( C_f \).

For the cycle performance of THPC@TCNF membranes in the oil/water separation process, the membranes were soaked in pure water for a few seconds after each cycle and dried for the next cycle.

### 2.6. Antibacterial property

The antibacterial properties of various membranes were appraised using Bacillus subtilis (\( B. subtilis \)), which is a typical Gram-positive bacterium presenting in oily wastewater. In the blend culture test, a complete membrane was soaked in the diluted \( B. subtilis \) solution (\( 10^7 \) CFU mL\(^{-1}\), 2 mL). After cultured at 37°C for 1 h, bacterial solution (100 µL) was spread on the Luria-Bertani (LB) culture medium. After culturing at 37°C for 24 h, the number of colonies was counted. For the bacterial filtration test, the diluted bacterial liquid (\( 10^2 \) CFU mL\(^{-1}\), 10 mL) was deposited on the membranes by vacuum-assisted filtration. The membranes were kept under wet condition for 1 h, and then the morphology of bacterial was observed by SEM.

### 3. Results And Discussion

#### 3.1. Fabrication and morphology of THPC@TCNF membranes

The fabrication process of THPC@TCNF membrane was displayed in Fig. 1. Firstly, The TEMPO oxidized TCNFs suspension was deposited on nylon 66 supported membrane by vacuum assisted filtration. After drying, the supported membrane was removed to obtain self-supporting TCNF membrane (Figure S1a). After TEMPO oxidation, a lot of carboxyl groups appeared on the surface of TCNFs. By immersing TCNF membrane into THPC solution, THPC was grafted onto the surface of TCNFs in the membrane via
esterification reaction. Finally, THPC@TCNF membrane was obtained after washing with water and drying (Figure S1b). Benefiting from the swelling effect of DMSO, the tetrahedral structure of THPC, and the electrostatic repulsion of positively charged phosphonium groups, the pore size and thickness of THPC@TCNF membrane would be significantly improved in comparison with TCNF membrane. Therefore, THPC@TCNF membrane was expected to have enhanced permeate flux and antibacterial property.

TCNFs prepared by TEMPO-oxidized tunicate cellulose had fiber-like morphology, whose average length, average width, and aspect ratio were 10.0 ± 0.3 µm, 6.5 ± 0.2 nm, and ~ 1540, respectively (Figure S2). The ultralong morphology of TCNFs could be attributed to the high molecular weight and crystallinity of tunicate cellulose (Zhang et al. 2018). Due to the presence of -COO−/-COO− electrostatic repulsion (Isogai et al. 2011), TCNFs dispersed well in water and formed stable and homogeneous suspensions (Figure S3).

After vacuum-assisted filtration, TCNF membrane exhibited nanoporous structure with an average pore size of 50.4 ± 2.5 nm (Fig. 2a), which could generate capillary force and easily form a hydration layer during oil/water separation process (Peng et al. 2022). After modification, THPC@TCNF membrane displayed a relatively loose surface with a larger pore size (62.2 ± 2.9 nm), as shown in Fig. 2b. According to Hagen–Poiseuille equation, the enlarged pore size of membranes would improve their permeate flux during oily wastewater purification. Besides, the thickness of TCNF membrane also augmented from 11.8 µm to 21.1 µm after reacting with THPC, while larger pore could be clearly discovered in the cross-section of THPC@TCNF membrane (Fig. 2c). THPC modified TCNFs that isolated from membrane had fiber-like morphology, and some black dots could be observed on the surface of TCNFs (Figure S4). These results indicated that THPC was successfully grafted onto TCNFs via esterification reaction and the morphology of TCNFs was not changed.

3.2. Structure of THPC@TCNF membranes

To comprehend the chemical structure of THPC@TCNF membrane, FTIR spectra of TCNF membrane and THPC@TCNF membrane were contrasted. As displayed in Fig. 3a, a new absorption band appeared at 1725 cm⁻¹ in the spectrum of THPC@TCNF membrane, which was ascribed to νC=O in the ester bond formed through esterification of -COOH and -OH (Kang et al. 2017). The absorption band located at 3426 cm⁻¹ corresponding to -OH stretching vibration became stronger in the spectrum of THPC@TCNF membrane due to the introduction of THPC. Moreover, a new characteristic peak at 133.5 eV could be discovered in the XPS spectrum of THPC@TCNF membrane (Fig. 3b), which could be assigned to phosphor element of THPC. In the high-resolution P 2p spectra, the characteristic peak could only be found in the spectrum of THPC@TCNF membrane (Figure S5), revealing the presence of phosphonium groups in the membrane. In the C 1s spectrum of THPC (Fig. 3c), different types of carbon atoms mainly included aliphatic carbon (C–H, 284.68 eV), hydroxyls (C–O, 286.30 eV), and carbon-phosphorus covalent bond (C–P, 286.80 eV), where related peaks shifted to 284.91 eV, 286.55eV, and 288.15eV, respectively, in the spectrum of THPC@TCNF membrane (Fig. 3d), indicating that the binding of THPC and TCNFs resulted
in a higher binding energy of various types of carbon atoms. Furthermore, a new XPS peak at 288.15 eV in C_{1s} spectrum of THPC@TCNF membrane, which was assigned to carboxyl groups (O–C = O) due to presence of TCNFs.

In addition, the distribution of phosphonium groups in the membrane was also investigated by EDS mapping of P and Cl elements. As shown in Fig. 3e and Figure S6, green and red dots were uniformly distributed in the images, revealing that phosphonium groups were uniformly distributed in the membrane. To determine degree of substitution of phosphonium groups, the carboxyl content of THPC@TCNF membranes prepared with different dosage of THPC was measured by conductance titration. As displayed in the Fig. 3f, the carboxyl group content of TCNF membrane was 1.25 mmol g^{-1}, because TCNFs were prepared by TEMPO-oxidization strategy and carboxyl groups generated on the surface of TCNFs. When the dosage of THPC increased from 0–16%, carboxyl content gradually decreased from 1.25 mmol g^{-1} to 0.28 mmol g^{-1}. As the dosage of THPC further increased to 32%, the carboxyl content changed slightly because of the steric hindrance effect of phosphonium groups.

### 3.3. Wettability and separation performance of THPC@TCNF membranes

The wettability of the membranes is strong depended on their chemical composition and surface topography, which is crucial to the separation efficiency and fouling resistance during oily wastewater purification (Li et al. 2021a; Zhang et al. 2017). As shown in Fig. 4a, a water droplet could quickly spread out on the surface of THPC@TCNF membrane in air, indicating the superhydrophilicity of membrane. Four kinds of oils, including petroleum ether, pump oil, dimethicone, and chloroform, were employed to study the wettability of THPC@TCNF membrane. The underwater oil contact angles were 158.7°, 164.6°, 160.4°, and 158.1°, for petroleum ether, pump oil, dimethicone, and chloroform, respectively (Fig. 4b). These results indicated that various oil droplets with different density and viscosity could be repelled by the THPC@TCNF membranes, revealing their underwater superoleophobic properties. The wettability of THPC@TCNF membranes was consistent with that of TCNF membranes (Figure S7), which confirmed that the introduction of THPC into TCNF membranes did not change their wettability.

As exhibited in Fig. 4c, the underwater anti-oil adhesion property of the THPC@TCNF membrane was evaluated with dynamic approach-compress-detach test. Under water, after contacting the surface of the THPC@TCNF membrane, the chloroform droplets were slowly compressed downward to form an ellipse. When gradually lifted, the chloroform droplets could quickly overcome the adhesion force and detach from the THPC@TCNF membrane surface without any deformation. The results illustrated that the THPC@TCNF membrane was expected to have low oil adhesion and excellent antifouling performance during oil/water separation.

To ascertain the optimal dosage of THPC, the water permeate flux of different THPC@TCNF membranes was shown in Figure S8. As THPC dosage increased from 0 to 16 wt%, the water flux of membranes increased from 1208 ± 35 L m^{-2} h^{-1} bar^{-1} to 1931 ± 64 L m^{-2} h^{-1} bar^{-1}, which was attributed to the
enlarged pore size of the membranes. When the dosage of THPC increased to 32 wt%, the water permeate flux of membrane was $1928 \pm 63 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. This result was agreed with the result of carboxyl content, suggesting that the water permeate flux of membrane was dependence of carboxyl content in the membrane. Thus, THPC@TCNF membrane that was prepared by using 16% THPC was selected for the purification of oily wastewater. Four kinds of oil/water nanoemulsions with average particle size of 200 nm were prepared, which showed bright pathway under the irradiation of a laser pen because of Tyndall effect (Fig. 5a-d).

After separation, the size of particles in filtrate was reduced to about 2 nm (surfactants), indicating that the oil droplets in the emulsions could be effectively separated by THPC@TCNF membranes. Moreover, the water permeate fluxes and oil rejections of TCNF membrane and THPC@TCNF membrane for the separation of the four nanoemulsions were compared. The water fluxes of TCNF membrane for petroleum ether, chloroform, pump oil, and dimethicone nanoemulsions were $1115 \pm 35$, $989 \pm 28$, $1056 \pm 34$, and $1094 \pm 35 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, respectively, whereas those of THPC@TCNF membrane were $1858 \pm 58$, $1453 \pm 48$, $1625 \pm 45$, and $1719 \pm 51 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, respectively (Fig. 5e). These datas indicated that the introduction of THPC significantly improved the permeate flux of membrane. Simultaneously, the oil rejections of TCNF membranes for petroleum ether, chloroform, pump oil, and dimethicone nanoemulsions were $99.45 \pm 0.41\%$, $99.19 \pm 0.16\%$, $99.65 \pm 0.31\%$, and $99.69 \pm 0.28\%$, respectively. While the oil rejections of THPC@TCNF membranes for petroleum ether, chloroform, pump oil, and dimethicone nanoemulsions were $99.51 \pm 0.46\%$, $99.23 \pm 0.23\%$, $99.69 \pm 0.27\%$, and $99.74 \pm 0.24\%$, respectively (Fig. 5f). Despite the introduction of THPC enlarged the pore size and enhanced water permeate flux of the membrane, the oil rejections of THPC@TCNF membranes changed slightly and maintained at high values.

To investigate the durability of THPC@TCNF membrane, the separation of petroleum ether/water nanoemulsion for 60 min was displayed in Fig. 5g. During the continuous separation of petroleum ether/water nanoemulsion, the water permeate flux of THPC@TCNF membrane was stable, which remained at $1735 \pm 58 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ after 60 min separation. Until 180 min, the flux was still higher than half of the initial flux and remained at $1121 \pm 35 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (Figure S9a). In addition, as shown in Fig. 5h, the cycle performance of THPC@TCNF membrane was also measured. Both water permeate flux and oil rejection of THPC@TCNF membrane hardly decreased after 10 cycles. Even after 20 cycles, the water flux slightly decreased to $1523 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, while the oil rejection was still as high as $99.02\%$ (Figure S9b), demonstrating excellent durability of THPC@TCNF membrane.

### 3.4. Antibacterial activity and mechanical stability

The presence of bacteria in oily wastewater could decrease the separation efficiency of membranes during long-term use (Bethke et al. 2018), so antibacterial properties of membranes are critical for the practical application of membranes. As shown in Fig. 6a, a slight increase in the colony forming units on the TCNF membrane could be observed in comparison with the control group, because cellulose is a kind of polysaccharide. Impressively, no colony of *B. subtilis* was observed on THPC@TCNF membrane,
because all *B. subtilis* were effectively killed after contacting with THPC@TCNF membrane for 1 h. Compared to control and TCNF membrane, the antibacterial efficiency of THPC@TCNF membrane calculated according to the colony forming units before and after contact almost 100% (Fig. 6b). After contacting with membranes for 1 h, the morphology of *B. subtilis* cultured on TCNF membrane was *B. subtilis*, whereas the surface of *B. subtilis* cultured on THPC@TCNF membrane became loose and fractured, as shown in Fig. 6c and Figure S10, because quaternary phosphonium salts are capable of destroying a wide range of microorganisms by destabilizing bacterial cell walls (Peng et al. 2020). The antibacterial property of HPC@TCNF membrane would be benefitting to prevent the corrosion of bacteria.

Furthermore, both bending test and abrasion test were employed for evaluating the mechanical stability of the THPC@TCNF membranes. As presented in Fig. 6d, the pump oil contact angle still maintained at 163° after 200 bending cycles. The surface morphology of THPC@TCNF membrane hardly changed before and after bending test (Fig. 6e). Additionally, abrasion test of THPC@TCNF membrane was also carried out by rubbing THPC@TCNF membrane on a 2000 mesh sandpaper (Fig. 6f). The THPC@TCNF membrane was adhered to a glass slide with a weight of 100 g, and the membrane was subsequently dragged on the sandpaper for 10 cm in the horizontal and vertical directions, which was a wear cycle. After 30 cycles, some fine moving traces appeared on the surface of the THPC@TCNF membrane, the complete structure of the membrane was not destroyed (Fig. 6g). Simultaneously, the underwater OCA remained at an angle of 159° (Fig. 6f), showing underwater superoleophobicity of the membrane. These results revealed that the THPC@TCNF membranes have good bending and wear resistance properties. Mechanical stability is a necessary condition to ensure long-term high-efficiency oil/water separation, which was beneficial to the practical application of THPC@TCNF membranes in the field of oil/water separation.

**4. Conclusions**

We successfully fabricated THPC@TCNF membranes through grafting tetrahedral-structured THPC onto the surface of TCNFs via esterification reaction. THPC effectively increased the surface average pore size and interlayer spacing of TCNF membranes, resulting in the enhancement of water permeate flux of membrane. On the other hand, the positively charged phosphonium groups endowed the TCNF membrane with good antibacterial properties, which could prevent the membrane from the corrosion of bacteria. These THPC@TCNF membranes exhibited good superhydrophilicity, underwater superoleophobicity, and nanoporous structure, which enabled them to separate various oil/water nanoemulsions. Moreover, THPC@TCNF membranes possessed excellent durability, mechanical stability, and cycle performance. This work provided a simple strategy for fabricating high water permeate flux and antibacterial membranes, which had great potential in oily wastewater treatment.

**Declarations**

**Notes**
The authors declare no competing financial interest.

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CRediT authorship contribution statement

Kun Peng: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing - original draft, Writing - review & editing. Chenglong Wang: Resources, Formal analysis. Chunyu Chang: Conceptualization, Project administration, Supervision, Writing - review & editing. Na Peng: Conceptualization, Project administration, Supervision.

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.

References


Figures

Figure 1

Schematic illustration for the fabrication, morphology, oil/water separation process and antibacterial process of THPC@TCNF membrane.
Figure 2

SEM images of surface and pore size distribution of (a) TCNF membrane and (b) THPC@TCNF membrane. (c) SEM images of cross-section of TCNF membrane (left) and THPC@TCNF membrane (right).
Figure 3

(a) FTIR spectra and (b) XPS spectra of TCNF membrane and THPC@TCNF membrane. High-resolution C$_{1s}$ spectra of (c) THPC and (d) THPC@TCNF membrane. (e) EDS mapping of phosphor element on THPC@TCNF membrane. (f) Relationship between carboxyl content of THPC@TCNF and THPC dosage.

Figure 4
Contact angle measurement of THPC@TCNF membranes with respect to wettability. Photograph of a water drop in air (a), underwater various types of oil drops on THPC@TCNF membranes (b). Dynamic approach-compress-detach oil-adhesion test photograph for THPC@TCNF membrane (c).

**Figure 5**

(a-d) Size distribution and photographs of oil/water nanoemulsions (petroleum ether, chloroform, pump oil, and dimethicone) before (top) and after filtration (bottom). (e) Water permeate flux and (f) oil rejection of TCNF membrane and THPC@TCNF membrane. (g) The relationship between water permeate flux of THPC@TCNF membrane and separation time. (h) Cycle performance of THPC@TCNF membrane for the separation of petroleum ether/water nanoemulsion.
Figure 6

(a) Colony photographs after immersion test of control group, TCNF membrane, and THPC@TCNF membrane against *B. subtilis* bacteria, respectively. (b) Corresponding statistics of the colony forming units and antibacterial efficiency. (c) SEM images of *B. subtilis* after contacting with TCNF membrane and THPC@TCNF membrane for 1 h. (d) Underwater OCA and (e) SEM image of THPC@TCNF membrane before and after bending test. (f) Underwater OCA and (g) SEM image of THPC@TCNF membrane before and after abrasion test.

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