

Article

Pseudo-zwitterions self-assembled from polycation and anion clusters showing exceptional water-cleanable anti-crude-oil-adhesion property

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SUMMARY

It is of great importance and practical value to develop a facile and operable surface treatment method of materials with excellent antipollution and antiadhesion property, but still a huge challenge. In this work, a series of pseudo-zwitterions are prepared from electrostatic assembly of cationic polyethyleneimine and anionic phosphonic clusters. These pseudo-zwitterionic assemblies provide a strong hydration through electrostatic interaction with water and in turn create a barrier against oil foulants, leading to a nearly zero crude oil adhesion force. The pseudo-zwitterions-decorated surfaces exhibit exceptional water-cleanable oil-repellent property, even when they are completely dried and without prehydration before fouled by crude oil. While using these pseudo-zwitterions-modified polymeric membranes for separating surfactant stabilized oil-in-water emulsion, less than 10% decline of permeating flux is observed throughout a 2-h continuous separation experiment, showing excellent emulsion separation ability and antipollution performance for high viscous oil.

INTRODUCTION

Crude oils produced during oil drilling and oil spills pose a serious threat to the environment, ecosystem, and water resources (Cheryan and Rajagopalan, 1998; Fakhru'l-Razi et al., 2009; Peterson et al., 2003). Due to the high adhesion and viscosity of crude oils, the solid surfaces of adsorbents, filters, membranes, and other metal or nonmetal equipments and parts are easily pasted by a thick layer of oil, resulting in rapid failure and invalidation (Ma et al., 2016; Yang et al., 2018; Zhu et al., 2014). It is very difficult to remove these oil deposits and completely restore the function of solid surfaces by general cleaning process or even special chemical or mechanical cleaning methods (Adebajo et al., 2003; Ge et al., 2017; Padaki et al., 2015). Water is green, safe, and the most readily available liquid on earth. Using water to clean and recover crude oils from contaminated surfaces is undoubtedly an ideal strategy. It is predicted that the material surface with water-cleanable anti-crude-oil-adhesion property can solve the knotty problem of crude oil adhesion and innovate the technology of oily wastewater treatment. In order to achieve this expectation, the material surface should interact with water as much as possible so that the oil attached on it can be replaced by water (Lai et al., 2009, 2013).

Among numerous hydrophilic molecules, zwitterions containing equal positive and negative charges are well-known as important molecules (Estephan et al., 2011; Jiang and Cao, 2010; Kobayashi et al., 2012; Singh and Tarannum, 2018). Due to the ionized structure of zwitterions, a strong hydration layer can be formed around zwitterions through the electrostatic attraction with water (Hadjesfandiari and Parambath, 2018; Huang et al., 2015; Leng et al., 2014; Zhao et al., 2014), which could act as physical and energy barriers to the adhesion of proteins (An et al., 2013; Sun et al., 2006), bacteria (Chen et al., 2016; Lu et al., 2017), oil pollutants (Yang et al., 2015; Zhu et al., 2018), and other dirt. More importantly, the interaction between zwitterions and water is a long-range effect (Shi et al., 2016). Therefore, water molecules can be attracted by zwitterionic surfaces to replace oil droplets and other pollutants on the solid surface without prehydration (He et al., 2015; Kobayashi et al., 2012; Zhang et al., 2018). A number of studies have demonstrated that the surfaces grafted with zwitterionic polyelectrolytes can effectively repel oil droplets such as silicone oil, vegetable oil, and heavy oil under water, even if the oil-contaminated surfaces are dry (Chen et al., 2005; Liu et al., 2010). Although zwitterions themselves have excellent hydration ability, a high-density distribution of zwitterions on the surface of material is required to achieve water-cleanable antiadhesion property.

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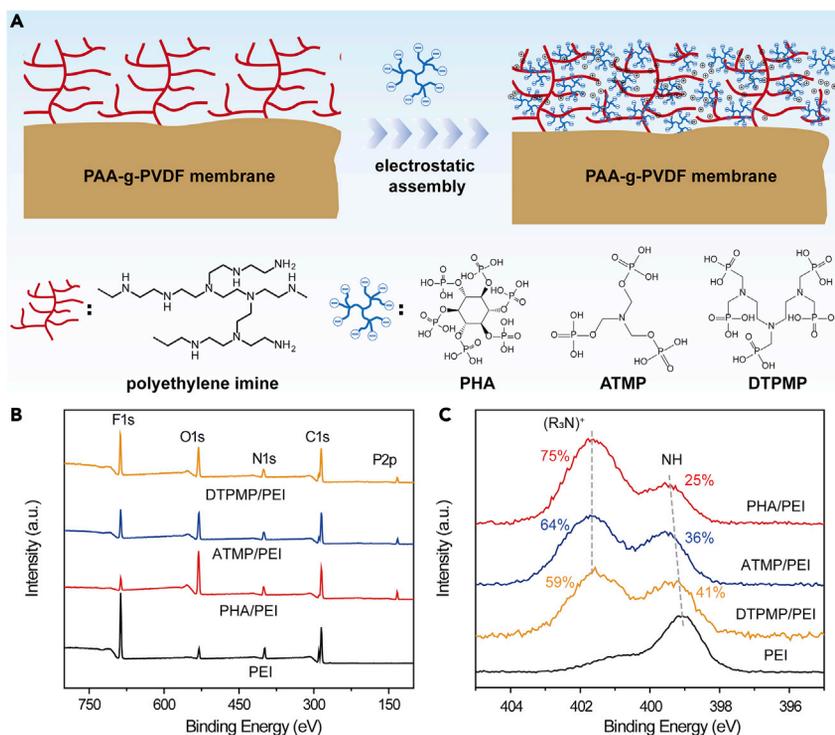


Figure 1. The preparation protocols and chemical structure of pseudo-zwitterions

(A) Schematic illustration of the preparation of phosphonic clusters assembled PEI/PAA-g-PVDF membranes via electrostatic self-assembly

(B and C) (B) XPS survey spectra and (C) N1s XPS spectra of PEI/PAA-g-PVDF membrane (PEI) and phosphonic clusters assembled PEI/PAA-g-PVDF membranes (PHA/PEI, ATMP/PEI, and DTPMP/PEI, respectively).

Other than the most reported surface modification strategy based on surface-initiated atomic transfer radical polymerization (SI-ATRP), few methods can graft zwitterions on material surfaces with high density. The catalyst system in SI-ATRP process is very sensitive to oxygen, which makes the SI-ATRP process suffering from harsh and complex operation process (Magenau et al., 2011; Matyjaszewski, 2012; Matyjaszewski and Xia, 2001). Therefore, it is of great significance to explore a new surface modification approach to replace the zwitterion grafting method or to replace the zwitterions with similar functional molecules.

As mentioned above, the feature of zwitterions is the coexistence of an equal amount of positive and negative charge groups on the same molecule. The charge groups are flexible and independent but not dissociated. Inspired by this feature, we report in this work the design of a new type of pseudo-zwitterions via self-assembly of polycation and anion clusters to mimic not only the structure but also the property of common zwitterions. The pseudo-zwitterions are made up of cationic polyethyleneimine (PEI) and a series of anionic phosphonic clusters via a one-step electrostatic self-assembly. The solid surfaces modified by the pseudo-zwitterions exhibit superhydrophilic and exceptional water-cleanable anti-crude-oil-adhesion property even when they are completely dried. It breaks through the limitation of traditional superhydrophilic materials where anti-oil-adhesion performance can only be realized when they are continuously soaked in water. The pseudo-zwitterions-modified microporous membranes show excellent separation performance for oil-in-water emulsions with stable permeating flux and small flux loss in long-term operation. Our work provides a new and effective way to solve the knotty problem of oil adhesion.

RESULTS

As schematically illustrated in Figure 1A, branched PEI molecules with molecule weight of 10,000 Da were firstly tethered on the surface of a polyacrylic-acid-grafted polyvinylidene fluoride (PAA-g-PVDF) microporous membrane via amide reaction between amine group and carboxyl group to form the PEI-grafted PAA-g-PVDF (PEI/PAA-g-PVDF) membrane (see Figures S1 and S2 for detail description of the preparation and characterization of PAA-g-PVDF membrane). Phosphonic clusters of phytic acid

Table 1. Summary of the physicochemical properties of PEI/PAA-g-PVDF membrane and phosphonic clusters assembled PEI/PAA-g-PVDF membranes.

Surface	Atomic ratio of P/N	Zeta potential (mV)	Adhesion force (μN)
PEI	/	46	>37
PHA/PEI	0.79	-71	<1
ATMP/PEI	0.53	10	<1
DTPMP/PEI	0.57	-8	<1

(PHA), amino trimethylene phosphonic acid (ATMP), and diethylenetriaminepentakis (methylphosphonic acid) (DTPMP) were then assembled onto it via electrostatic interaction with PEI molecule, respectively, to form phosphonic clusters assembled PEI/PAA-g-PVDF membranes, named as PHA/PEI, ATMP/PEI, and DTPMP/PEI, correspondingly.

X-ray photoelectron spectroscopy (XPS) analysis was used to probe the surface chemical composition of the membranes. Four peaks of C 1s at 285.0 eV, N 1s at 400.9 eV, O 1s at 530.9 eV, and F 1s at 686.9 eV are detected in the XPS survey spectrum of PEI/PAA-g-PVDF membrane (Figure 1B). A new peak ascribed to P 2p at 131.9 eV appears in the spectra of the three phosphonic clusters assembled PEI/PAA-g-PVDF membranes, proving the existence of phosphonic clusters on the membrane. The atomic ratio of P/N for PHA/PEI, DTPMP/PEI, and ATMP/PEI is 0.79, 0.57 and 0.53, respectively. The difference of atomic ratio of P/N is mainly due to the different amount of phosphonate groups in the phosphonic clusters, which cause in turn the difference of surface charges on the membranes. The curves of zeta potential versus pH show that the zeta potential of PEI/PAA-g-PVDF membrane dramatically decreases from 46 mV to 10 mV, -8 mV, and -71 mV after being assembled with the phosphonic clusters of ATMP, DTPMP, and PHA, respectively (Table 1 and Figure S3).

Figure 1C is the N 1s XPS spectra of PEI/PAA-g-PVDF membrane and corresponding phosphonic clusters assembled PEI/PAA-g-PVDF membranes. Only amino group (NH) at 399.1 eV is detected in the spectrum of PEI/PAA-g-PVDF membrane. Using this peak as reference, a new peak at 401.6 eV ascribed to amino cation (R_3N^+) group (Graf et al., 2009; Lawrie et al., 2007) appears in the spectra of phosphonic clusters assembled PEI/PAA-g-PVDF membranes, indicating the occurrence of ionization of NH group after assembling with PEI. Quantitative analysis of the peak area reveals that the percentage of these R_3N^+ groups is 75% for PHA/PEI, 64% for ATMP/PEI, and 59% for DTPMP/PEI. The ionization of PEI occurs during the assembly process, which is caused by the proton transfer between phosphonic cluster and amine group, resulting in the coexistence of amino cation and phosphonate anion on the membrane surface. In this way, pseudo-zwitterions are constructed on the surface of PAA-g-PVDF membrane by self-assembly.

The surface wettability of the phosphonic clusters assembled PEI/PAA-g-PVDF membrane is significantly enhanced. The water contact angle (CA) rapidly drops to 0° in a very short time of less than 2.6 s. In comparison, the water CA of PEI/PAA-g-PVDF membrane is $\sim 70^\circ$, and gradually decreases to 0° within 70 s (Figure S4). The change of water CA with time suggests that the phosphonic clusters assembled PEI/PAA-g-PVDF membranes possess the superhydrophilic property that could rival against common zwitterions (He et al., 2016; Liu et al., 2014; Schlenoff, 2014; Yang et al., 2015). When the crude oil droplet is used as a probe to contact the membrane surfaces, very small deformation is observed as presented in Figure S4. The underwater adhesion forces of crude oil on these surfaces are nearly zero with all adhesion forces $< 1 \mu\text{N}$ (Figure S5). When the membranes are immersed in water, the crude oil spontaneously escapes from the wetted surface (Figure S6). Similar underwater adhesion properties are also obtained when other oils such as soybean oil, silicone oil, n-hexadecane, and isooctane are used as probes (Figure S7). The environmental tolerance of the membranes was evaluated by exposing them to aqueous solutions with different pH values (pH 1–10) and different kinds of salt solutions (NaCl, MgCl_2 , CaCl_2 , seawater) (Figure S8). The results of crude oil adhesion test show that the crude oil adhesion force of these membranes is almost unchanged in these environments, indicating that the assembly structure formed by phosphonic cluster and PEI has good stability and environmental tolerance.

To understand and clarify the hydrophilicity and crude-oil-adhesion properties of the phosphonic cluster and PEI assembly structure at the molecular level, molecular dynamics (MD) simulation and sum frequency

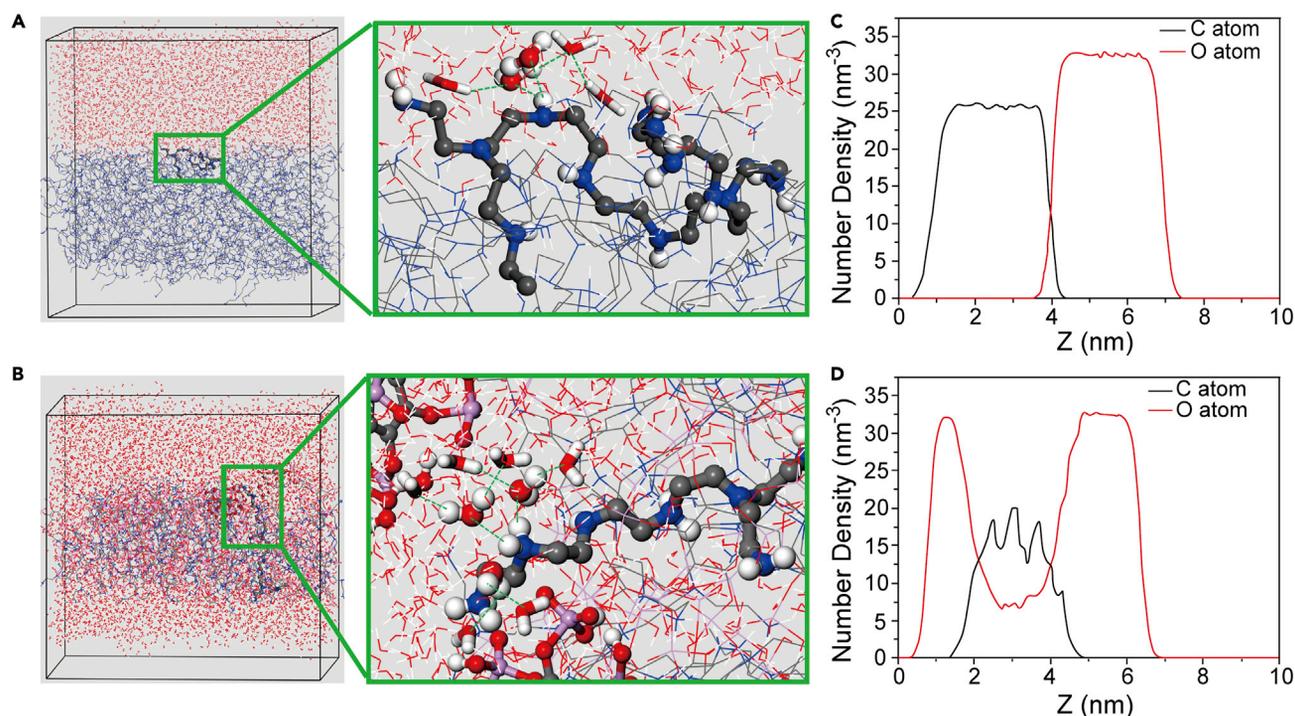


Figure 2. Molecular dynamics simulation

(A–D) Equilibrium molecular structure of (A) PEI and (B) PHA/PEI with water after 20 ns MD simulation. Corresponding atomic density profile of C and O atoms along z axis of (C) PEI/PAA-g-PVDF and (D) PHA assembled PEI/PAA-g-PVDF membrane.

generation (SFG) vibrational spectroscopy characterization were carried out, where PHA/PEI membrane is used as a representative and PEI/PAA-g-PVDF (abbreviated as PEI) membrane as a control. As for MD simulation, the two samples with size of 6.8 nm (length) × 6.8 nm (width) × 2 nm (height) were firstly constructed. A water layer with 3.0-nm thick was then added along the z axis of each sample. The snapshots of the configurations of the two samples after performing equilibrium dynamic simulations to 20 ns are shown in [Figures 2A](#) and [2B](#). The water molecules above the PHA/PEI sample penetrate into the membrane within 20 ns, while no similar phenomenon is observed in the case of PEI sample. Moreover, to quantitatively assess the distribution of water molecules in the two polymer membranes, the number density profile of C atom originated from PEI and O atom originated from water molecule along z axis of the samples were calculated after performing equilibrium dynamic simulation to 20 ns. As shown in [Figures 2C](#) and [2D](#), few water molecules enter into the inner space of PEI sample, while the water molecules completely fill the whole space of PHA/PEI sample based on the overlap of C atom and O atom density profile. Dynamic behaviors of water molecules in the two samples in terms of their diffusion coefficient and residence time were further analyzed to evaluate the interaction strength between water molecule and sample surface (see detailed description in [Figures S9](#), [S10](#), and [Table S1](#)). The water diffusion coefficients near the surfaces of PEI and PHA/PEI are 3.12×10^{-5} and 2.18×10^{-5} cm² s⁻¹ and the corresponding mean residence times are 27.2 ps and 68.7 ps, respectively. The lower the water diffusion coefficient and the longer the mean residence time, the stronger affinity between water and sample is. MD calculation results show that the interaction between water and the surface of membrane is greatly enhanced by the assembly of phosphonic cluster and PEI. It also proves that the assembly structure formed by phosphonic cluster and PEI has strong hydration ability. The strong water affinity of PHA/PEI assembly is mainly attributed to the high density of hydrogen bond network (see detailed description in [Table S1](#)).

SFG vibrational spectroscopy is based on a second-order nonlinear optical process and is a surface-sensitive spectroscopy for detecting molecular structure of polymer surface and interfacial water at various interfaces ([Leng et al., 2015](#); [Shen and Ostroverkhov, 2006](#); [Singla et al., 2018](#); [Uosaki et al., 2010](#)). As shown in [Figure 3A](#), no signals are detected at the range of 1,800–2,500 cm⁻¹ in the spectrum of PHA/PEI membrane in the dry state. When the membrane is fully soaked with water, multipeaks with high adsorption intensity at

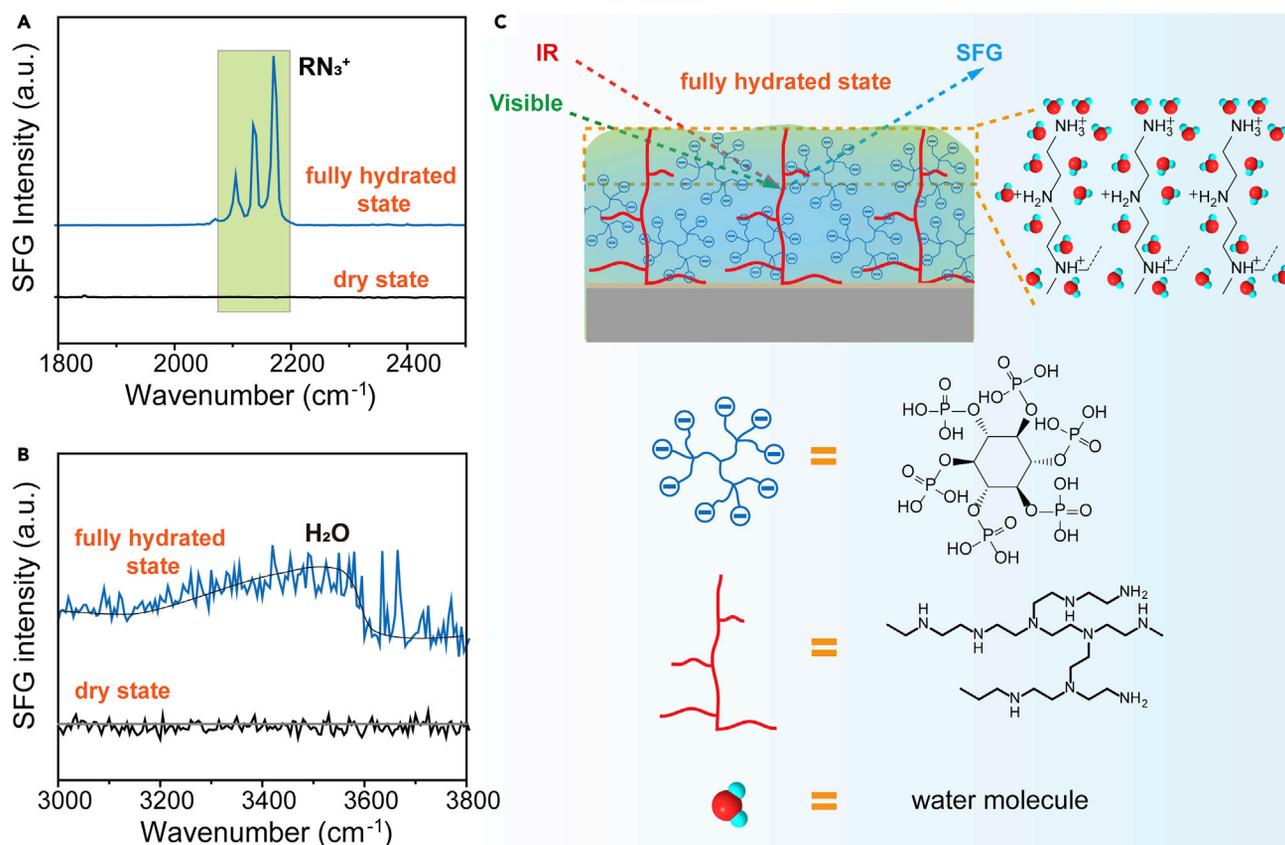


Figure 3. Surface molecular structure of pseudo-zwitterions modified membrane characterized by SFG spectra

(A and B) SFG spectra of PHA assembled PEI/PAA-g-PVDF membrane under dry state and fully hydrated state.

(C) Proposed molecular arrangement of PEI and PHA assembly on membrane surface under fully hydrated state during SFG test.

2,000–2,200 cm^{-1} appear, which are ascribed to the C-H stretching signals of methylene in protonated PEI. Figure 3B is the change of water signals with respect to the wetting state of surface water. A broad peak at 3,200–3,600 cm^{-1} originated from O-H stretching vibration of water molecule is observed in the fully hydrated state. The intensity of C-H stretching signal is so strong that the molecular chains of protonated PEI are considered to be of directional arrangement on the membrane surface as schematically illustrated in Figure 3C. Meanwhile, the occurrence of H₂O signal indicates that the water molecules are regularly adsorbed around protonated PEI chains to form a stable hydrated layer. The directional arrangement of hydrated PEI chains has a greater barrier effect on pollutants, which makes the crude oil foulants strongly repelled by the membrane surface.

The exceptionally water-cleanable antiadhesion property of the self-assembled phosphonic clusters/PEI pseudo-zwitterions was further confirmed by a series of demonstration experiment. A piece of PHA/PEI membrane was first thoroughly dried in an oven (Figure 4A). A drop of crude oil was then dropped on it and immersed in water (Figure 4B). It can be seen that the L-shaped oil droplet on the membrane surface gradually contracts and splits into two small round droplets within 1–3 min. After slightly washing with pure water, the oil droplets are completely removed from the surface, and no crude oil residue is observed. Similarly, such antiadhesion effect can be seen in the experiment as shown in Figure 4C where silicone oil is used. A dried PHA/PEI membrane is immersed in silicone oil died by Oracet Blue B and then immersed in water. The contaminated oil droplets quickly detach from the membrane surface within less than 2 s. Since the viscosity of silicone oil is lower than that of crude oil, its detachment is much faster.

DISCUSSION

We think that the long-range electrostatic interaction between pseudo-zwitterions and water is responsible for the unprecedented antiadhesion property of the phosphonic clusters assembled PEI/PAA-g-PVDF

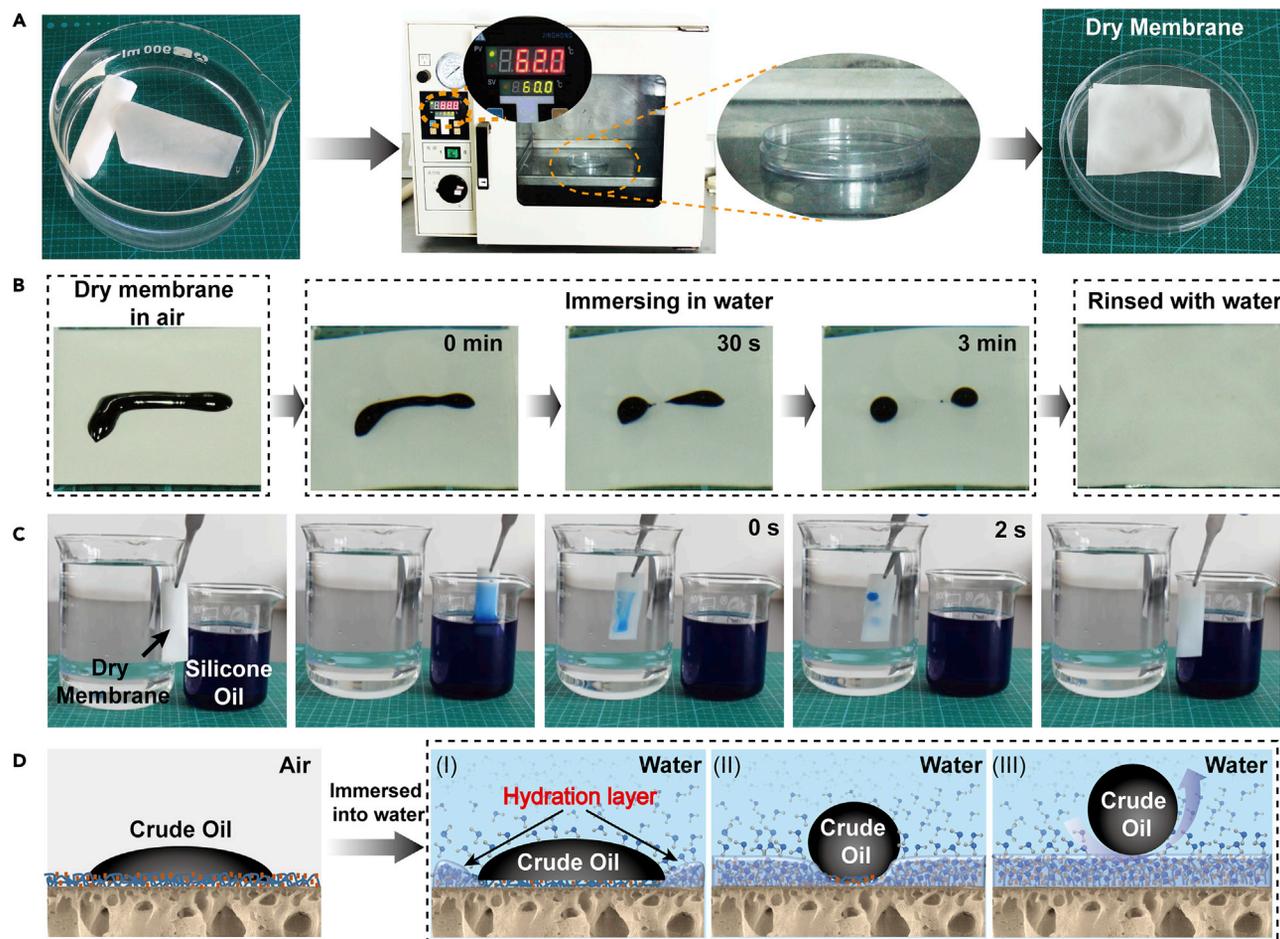


Figure 4. Description of the water-cleanable anti-oil adhesion performance of pseudo-zwitterions modified membranes

(A–C) (A) Dry process of the PHA assembled PEI/PAA-g-PVDF membrane. Demonstration of water-cleanable anti-oil adhesion property of the dried membrane fouled by crude oil (B) and silicone oil (C) without prehydration.

(D) Schematic illustration of the mechanism of water-cleanable anti-crude oil adhesion property of pseudo-zwitterions modified PAA-g-PVDF membrane while the membrane is fouled by crude oil at dry state.

membranes. As schematically described in Figure 4D, when the membrane surface is polluted by crude oil without prehydration, the high-density pseudo-zwitterions on the membrane surface prevent its direct contact with crude oil. When the membrane is immersed in water, pseudo-zwitterions attract water molecules through long-range electrostatic interaction, forming a stable hydration layer, which will gradually occupy the space between the oil pollutant and membrane surface. Therefore, the adhered oil can be easily removed by simply water cleaning.

The phosphonic clusters assembled PEI/PAA-g-PVDF membrane was used to examine the practical application effect for separating surfactant-stabilized oil-in-water emulsions. Figure 5A is the SEM image of PHA/PEI membrane. In comparison with the SEM image of PEI/PAA-g-PVDF membrane (Figure S11A), the introduction of PHA makes the membrane surface smoother. Similar results are observed on other membranes (Figure S11). The mean pore size of the PEI/PAA-g-PVDF membrane is 0.47 μm . After assembled with phosphonic clusters, the mean pore size is 0.28 μm for PHA/PEI, 0.32 μm for ATMP/PHA, and 0.35 μm for DTPMP/PHA (Figure 5B). The obvious changes of surface morphology and pore size verify the formation of high-density pseudo-zwitterion layer. Besides the surface, the inner pores of the membrane are also decorated by pseudo-zwitterions as confirmed by the P elemental mapping image (Figure S12). When Tween-80-stabilized hexadecane-in-water emulsions filtrate through the three membranes (Figures S13 and S14), they all show slight decrease of fluxes. After 2-h continuous filtration, all flux attenuations are less than 10%, indicating excellent anti-oil-fouling property (Figure 5C and Table S2). In contrast,

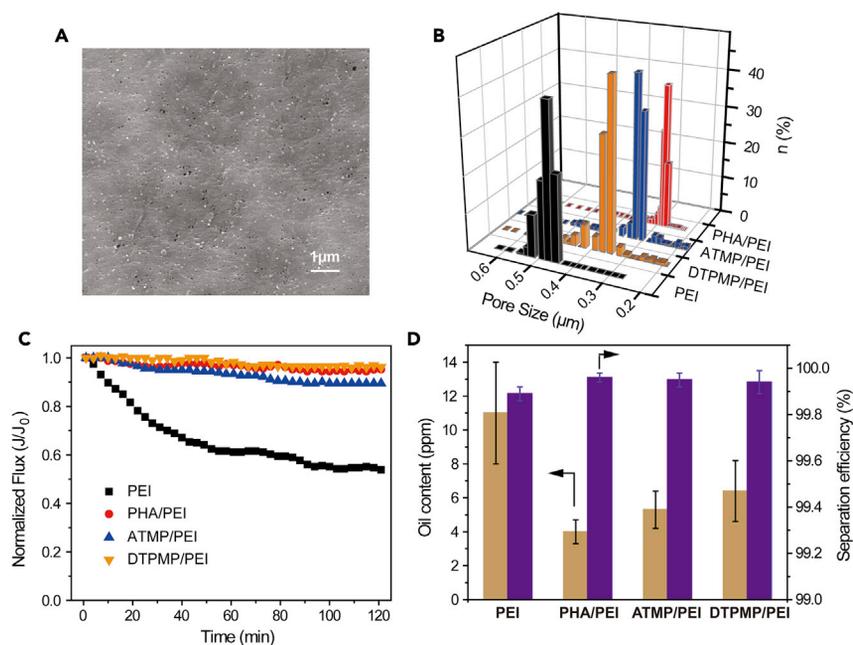


Figure 5. The structure of pseudo-zwitterions modified membranes and corresponding performance for oil-in-water emulsion separation

(A) Top-view SEM image of PHA assembled PAA-g-PVDF membrane.

(B) Pore size distribution of phosphonic clusters assembled PAA-g-PVDF membranes.

(C) Change of normalized permeating flux versus time of surfactant-stabilized hexadecane-in-water emulsion permeating various membranes (feed concentration: 10,000 ppm; applied pressure: 0.1 bar).

(D) Measured oil contents in the collected filtrates and corresponding separation efficiencies. The error bars represent the standard deviation of data from three replicate measurements

the permeating flux of PEI/PAA-g-PVDF membrane decreases significantly, and only less than 60% of the flux remains after 2 h. The oil content in the collected filtrate is 11 ppm for the PEI/PAA-g-PVDF membrane, while the oil contents in the collected filtrates are all less than 8 ppm for the three phosphonic clusters assembled PEI/PAA-g-PVDF membranes with all separation efficiency >99.9% (Figure 5D).

In summary, we report for the first time the successful construction of ion pairs composed of phosphonic clusters and PEI via electrostatic self-assembly on solid surface, called pseudo-zwitterions, to mimic the characteristic of zwitterionic compounds in antipollutant adhesion. The pseudo-zwitterions-modified solid surfaces exhibit exceptional water-cleanable antiadhesion property, even when they are completely dried and without prehydration before fouled by crude oil. This characteristic is superior to the common superhydrophilic materials reported so far which cannot be stored out of the water environment. When the pseudo-zwitterions-modified membranes are used to separate surfactant-stabilized oil-in-water emulsions, the permeating flux decreases a little during the long-term filtration process. Different from the traditional methods of relying on chemical synthesis and surface grafting in strict environment, we propose herein a novel and facile strategy to construct pseudo-zwitterions on solid surface by a simple self-assembly. It opens up a new way to endow the solid surface with excellent antipollution and antiadhesion property. The pseudo-zwitterions-modified materials have promising potentials in the application of crude oil transportation, separation, and purification of oil field productions, treatment of offshore crude oil leakage, and so on.

Limitation of the study

In this study, the pseudo-zwitterion is constructed by the assembly of PEI and phosphonic acid clusters (e.g., phytic acid), while the PEI molecules are tethered on the membrane surface by amide reaction between carboxyl groups in membrane surface and amine groups in PEI. Obviously, the pseudo-zwitterion is emerged as a kind of coating, and carboxyl group functionalized surface is necessary for preparing it, which will limit its large-scale application in the field of surface modification. We would like to address this issue by exploring a strategy to synthesize the solution or dispersion of pseudo-zwitterion.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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 - Oil-in-water emulsion separation
- **QUANTIFICATION AND STATISTICAL ANALYSIS**

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2021.102964>.

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AUTHOR CONTRIBUTIONS

Y.Z and J.J designed the experiments and developed the theory. Y.Z performed the experiment including membrane fabrication, characterization. Y.Z, A.W, and W. F contributed to the performance test. J.S and S.Y performed molecular dynamic (MD) simulation. H.L performed the SFG characterization. All coauthors discussed the results. Y.Z, W.F and J.J all contribute to writing the manuscript.

DECLARATION OF INTERESTS

The authors declare no conflict of interest.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Polyethylene imine (MW 10000 Da, 99%)	Aladdin	CAS: 9002-98-6
Phytic acid (PHA, aqueous solution with concentration of 50 wt%)	Aladdin	CAS:83-86-3
Amino trimethylene phosphonic acid (ATMP, aqueous solution with concentration of 50 wt%)	Aladdin	CAS: 6419-19-8
Diethylenetriaminepentakis (methylphosphonic acid) (aqueous solution with concentration of 50 wt%)	Aladdin	CAS:15827-60-8
2-(N-Morpholino) ethanesulfonic acid monohydrate (MES·H ₂ O, 99%)	Aladdin	CAS:145224-94-8
1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl, 98%)	Aladdin	CAS: 25952-53-8
N-Hydroxy succinimide (NHS, 98%)	J&K Scientific Co. Ltd.	CAS: 6066-82-6

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Prof. Jian Jin (jjin@suda.edu.cn).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All data reported in this paper will be shared by the lead contact upon request. This paper does not report original code. Any additional information required to reanalyze the data reported in this paper are available from the lead contact upon request.

METHOD DETAILS

Characterization

Water contact angle (CA) measurement was performed on an OCA20 instrument (Data-Physics, Germany) at ambient temperature, in which 2 μ L water was used as prober. Dynamic underwater oil adhesion force was measured by using a high-sensitivity micro-electro-mechanical balance system (Data-Physics DCAT11, Germany), and a crude oil droplet with volume of 5 μ L was used as prober. FTIR spectra were collected by using a Fourier transform infrared (FT-IR) spectrometer (Nicolet 6700). X-ray photoemission spectroscopy (XPS) was used to detect the surface elements and detailed chemical composition by using a Thermo Fisher Scientific ESCALAB 250Xi X-Ray photoelectron spectrometer. The SEM images and EDX mapping images were all obtained by using an FEI Quanta 250 FEG field emission scanning electron microscopy under a standard vacuum environment. Before performing SEM, all samples were dried in vacuum drying oven under 60°C for 24 h and sprayed with a thin gold layer under 10 mA for 60 s by Emitech K550X sputter. The pore size of as-prepared membranes was characterized via bubble point method on a Beishide pore analyzer (3H-2000PB), in which the pore tunnels of membrane were filled with ethanol. The sum frequency generation (SFG) spectrometer was set up by EKSPILA with a copropagating configuration. The visible laser pulses at 532 nm. The incident angle is 60° for the visible beam, and 55° for the IR beam. The energy of the visible and IR beams is generally less than 200 mJ and no photo-damage is observed during the measurements. The polarization combination for the IR, visible and SFG signal beams is typically ppp during the experiment. The membrane was placed in a Teflon cell, which is lidded with a half-cylinder CaF₂ prism

as an optical window. Then, water steam was continuously pumped into the cell. At the last, the water was directly dipped on the surface of membrane to ensure the membrane was completely soaked with water. The assembled cell is put on a x-y-z sample stage, and the leveling and z-position of the sample plane are carefully adjusted to make sure the SFG signal is collected from the membrane surface. The oil content was measured by an Aurora 1030w O-I-Analytical TOC.

Preparation of PEI/PAA-g-PVDF membrane

PEI/PAA-g-PVDF membrane was prepared according to our previous works (Zhu et al., 2015, 2018). In detail, 2 g Polyacrylic acid grafted PVDF (the grafting ratio of PAA is 8 wt%) powder was dissolved by 20 mL N-Methyl pyrrolidone (NMP) under vigorous stirring at 80°C for 24 h. The solution was then continuously heated under 80°C without any turbulence for other 8 h to remove bubbles. After cooled to room temperature, the PAA-g-PVDF solution was casted onto a glass plate using a doctor blade at a gate height of 300 μm. The glass plate was immediately immersed in water for 30 min. The obtained PAA-g-PVDF membrane was taken out from coagulation bath and washed with pure water for 3–5 times to remove the residual solvent. The PAA-g-PVDF membrane was then immersed into 10 mM 2-morpholinoethanesulfonic acid (MES) solution containing 2 mM N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and 5 mM N-hydroxysuccinimide (NHS) for 1 h at room temperature, and transferred into PBS buffer solution containing 10 g/L PEI for other 24 h under 40°C. After washed by PBS buffer solution and pure water, PEI/PAA-g-PVDF membrane was obtained and stored in water for further use.

Preparation of phosphonic clusters assembled PEI/PAA-g-PVDF membranes

Phosphonic clusters assembled PEI/PAA-g-PVDF membranes were constructed via electrostatic self-assembly of PEI and phosphonic anion clusters. Taken PHA/PEI membrane as an example, the preparation procedure is as follow: PEI/PAA-g-PVDF membrane was soaked with 1 wt% acetic acid solution for 5 min, and then the membrane was immersed in 1 wt% PHA aqueous solution for other 1 h. After taken out from the solution, the membrane was thoroughly washed with pure water to remove the excess PHA, and PHA/PEI membrane was obtained. The other phosphonic clusters, ATMP and DTPMP, were assembled onto PEI/PAA-g-PVDF membranes in the same procedures.

Oil-in-water emulsion separation

Oil-in-water emulsion separation test was performed on a lab-scale cross-flow instrument with circular cells (the effective filtration area of this cell is 4.5 cm²) at room temperature. Tween 80 stabilized hexadecane-in-water emulsion with concentration of 10,000 ppm was used as feed solution. The emulsion was prepared by mixing 20 g hexadecane and 2 g Tween 80 into 2000 mL water under vigorous stirring for 5 min and sonicating under a power of 270 W for 30 min. The transmembrane pressure for separation process is 0.1 bar. The permeating flux of prepared membranes was calculated by the following equation:

$$J = \frac{\Delta V}{A \Delta t \Delta P}$$

where ΔV is the volume of collected permeate within the period time of Δt . ΔP the transmembrane pressure, and A is the effective filtration area of membrane.

QUANTIFICATION AND STATISTICAL ANALYSIS

The type of statistical test that was performed for each experiment is indicated in the figure or table legends.