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ARTICLE

Mussel-inspired Modification of Polymer Membrane for Ultrahigh Water Permeability and Oil-in-Water Emulsion Separation

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Surface structures and properties of a membrane largely determine its in-service performance during a filtration process. Here we report a facile hydrophilization method via co-deposition of mussel-inspired polydopamine (PDA) and polyethyleneimine (PEI) on polypropylene microfiltration membrane. The deposition time is greatly shortened and the surface hydrophilicity is significantly improved compared to those membranes decorated only by PDA. The dopamine/PEI deposition solution can be reused for several times with negligible effect on the surface hydrophilicity of membranes. Moreover, the PDA/PEI coating endows the membranes ultrahigh water permeability, allowing microfiltration separation of oil-in-water emulsions under ordinary pressure.

Introduction

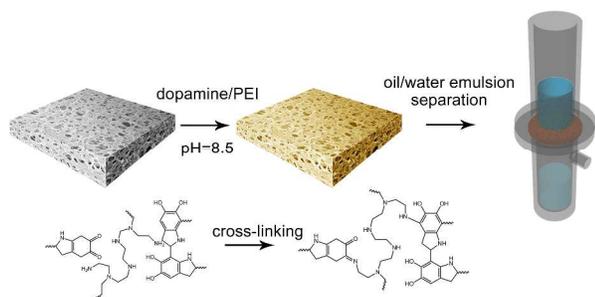
Oil/water separation attracts considerable attention for increasing environmental incidents such as oil spills. Materials with superwetting properties are believed to be one of the most promising solutions to this demand.¹ Superhydrophobic and superhydrophilic (underwater superoleophobic at the same time) materials can be both applied for oil/water separation. In the former case, oil passes through the hydrophobic materials and water is retained.² One problem is oil pollution on this kind of materials caused by oleophilicity in the presence of water. It has been suggested to overcome this problem by inspiration from fish scales and clamshell.^{3,4} Novel concepts, such as underwater low-oil-adhesion superoleophobicity, are then introduced to fabricate oil/water separation materials. Hydrophilic polymers, including polyacrylamide (PAM) and polyethylene glycol (PEG), can form hydration layer as a barrier to repel oil drops,⁵ which can be also achieved by superhydrophilic inorganic coatings.⁶ However, most of the reported materials cannot be used in separation of oil-in-water emulsions due to the large pores they possessed. One promising approach to oil-in-water emulsion separation is membrane filtration, especially microfiltration that has higher flux and less oil pollution than ultrafiltration.^{7,8} It is worth noting that low transmembrane pressure for water is necessary because deformation of the oil droplets and membrane emulsification are possible under high pressure in an emulsifier-contained solution during a microfiltration process.⁹

A series of hydrophilization methods have been developed to reduce operation pressure and membrane fouling for water permeation, enabling an energy-saving and effective filtration process.¹⁰⁻¹⁵ The superhydrophilic modification, compared to the traditional hydrophilic one, endows the polymer membranes with ultrahigh water permeability, and allows the microfiltration process to work under ultralow transmembrane pressure. Nevertheless, most of membranes cannot meet the demand of superhydrophilicity, especially high water permeability. More recently, we have reported a novel hybrid superhydrophilic membrane inspired by biomimetic mineralization in nature.^{16,17} The deposition of CaCO₃-based nano-sized minerals is responsible for the exceeding water permeability.

Mussel-inspired surface chemistry has attracted much interest for its simplicity, versatility and wide applicability.¹⁸ Although the structure of polydopamine (PDA) remains elusive,¹⁹⁻²¹ it has been extensively used in membrane modification for diverse demands such as permeation improvement, antifouling property and structural stability.^{20,22-24} Differing from traditional coating protocols, the deposition of dopamine involves a polymerization process, and the inherent strong adhesion of catechol structure makes it more stable than the case of physical coating. Moreover, this process introduces less damage to membranes and no swelling-induced blocking¹⁶ compared to the graft polymerization induced by UV, plasma or electron beam radiation. However, the deposition of PDA is a time-consuming process, and the resulted hydrophilicity is barely satisfactory for ultralow transmembrane pressure and

high water permeability.²⁵ Besides, PDA oligomers usually form aggregates by non-covalent interactions^{26,27} in solution after long time deposition, which may block the membrane pores and decrease the water permeability. Furthermore, the resulted coating always becomes unstable in strong alkaline environment due to the non-covalent connection in PDA, as revealed by several researchers.^{28,29}

We report an improved one-pot approach to superhydrophilize polypropylene microfiltration membrane (PPMM) by co-deposition of dopamine and low molecular weight polyethyleneimine (PEI), an amino-rich polymer (**Scheme 1**). The deposition time is greatly shortened and the water permeability of the membrane is dramatically improved. The dopamine/PEI solution can be reused at least five times with negligible decrease in water permeability of the PDA/PEI-decorated membranes. The co-decorated membranes show better stability in strong alkaline environment due to the covalent cross-linking between PDA and PEI. Furthermore, the membranes were applied to separate oil-in-water emulsions under ultralow pressure, which holds promising for treatment of oily wastewater through microfiltration process.



Scheme 1 Schematic representation for the surface modification of PPMM by immersing in dopamine/PEI solution and its application in oil-in-water emulsion separation.

Experimental

1. Materials

Polypropylene microfiltration membrane (PPMM, mean pore size 0.2 μm , porosity 75%) is a commercial product of Membrana GmbH (Germany). All membrane samples used were cut into rounds with a diameter of 25 mm, washed by acetone overnight to remove impurities adsorbed on the membrane surfaces and then dried in a vacuum oven at 40 $^{\circ}\text{C}$ to a constant weight. Dopamine hydrochloride and polyethyleneimine (PEI, $M_w = 600$ Da) was purchased from Sigma-Aldrich (USA) and Aladdin (China), respectively. Other reagents such as tris(hydroxymethyl) aminomethane, Tween-80, 1,2-dichloroethane, n-hexane and ethanol were procured from Sinopharm Chemical Reagent Co., Ltd and used as received.

2. Modification of polypropylene microfiltration membrane

Dopamine hydrochloride and PEI were dissolved in Tris buffer solution (pH=8.5, 50 mM) with a mass ratio of 1:1. The concentration was 2 mg/mL for each component in the solution.

PPMM samples were immersed in fresh prepared solution after pretreated by ethanol and shaken for designed time at 28 $^{\circ}\text{C}$. Then, the samples were washed three times by deionized water, and dried in a vacuum at 40 $^{\circ}\text{C}$ overnight. Another group of membranes were only immersed in a dopamine solution without PEI at the same condition for comparison. We will call the membrane from dopamine solution as PDA-decorated membrane, while from dopamine/PEI solution as PDA/PEI-decorated membrane.

3. Characterization and measurement

Surface morphology of the membranes was observed by field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan). X-ray photoelectron spectra were collected by a spectrometer (XPS, PerkinElmer, USA) with Al K α excitation radiation (1486.6 eV). FT-IR/ATR spectra were collected on a Nicolet 6700 infrared spectrophotometer equipped with an ATR accessory (ZnSe crystal, 45 $^{\circ}$). UV-vis absorption of the solutions was measured with an ultraviolet spectrophotometer (Shimadzu, UV 2450) from 700 nm to 240 nm. Both static and dynamic contact angles were detected using a DropMeter A-200 contact angle system (MAIST VisionInspection & Measurement Co. Ltd., China). Pure water flux was measured for the membranes by a dead-end stirred-cell filtration system (Millipore 6700P05, USA). The membranes were compacted at 0.3 MPa for 15 min, and then the water flux was measured at 0.1 MPa after operated under this pressure for 10 min to reach a stable value. The oil-in-water emulsion was prepared as following: 10 mL 1,2-dichloroethane or n-hexane was added into 990 mL deionized water with 20 mg Tween-80 as emulsifier; then the solution was stirring under 3000 rpm for 5 h. The droplet sizes are in the range of several hundred nanometers to 8 μm under optical microscopy observation. The oil rejection was measured according to the former reference.¹⁶

Results and discussion

1. Surface morphology and chemical component of the decorated membranes

Surface morphology of the membranes was characterized by using FESEM (**Fig. 1a-f**). Several particles are attached to the top surface of PPMM after 6 hr deposition in pure dopamine solution. By contrast, no visible aggregates can be observed on the membrane surfaces decorated with PDA/PEI, which is similar to the nascent ones. The appearance of dopamine solution exhibits black and opaque after deposition, whereas the dopamine/PEI one is in brown and transparent (inset in **Fig. 3a**). These phenomena can be rationalized by the destruction of non-covalent interactions in PDA aggregates, arising from the incorporating of PEI through the cross-linking among catechol and amino groups. Although the PDA aggregates are too small to block the membrane pores in microfiltration, it would be detrimental to the performance of membranes with small pores such as those in ultrafiltration and nanofiltration.²⁴ Therefore, the dopamine/PEI deposition solution holds promise for hydrophilization of ultrafiltration or even nanofiltration membranes with neglected flux decrease caused by blocking.

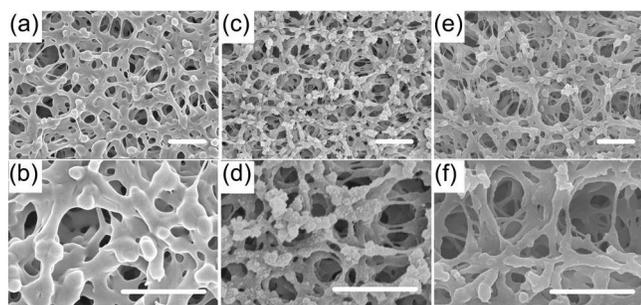


Fig. 1 Surface morphologies of the nascent (a and b), PDA-decorated (c and d), and PDA/PEI-decorated (e and f) PPMMs. The scale bar is 1 μm .

PEI is able to react with dopamine through Michael addition or Schiff base reaction between amine and catechol.^{30,31} The chemical structure was analysed by FT-IR/ATR, XPS and UV-vis spectroscopies. FT-IR/ATR spectra of the membrane surfaces (**Fig. 2a**) present absorption peaks at 1602 cm^{-1} and 1509 cm^{-1} , assigned to C=C resonance vibration in aromatic ring and N-H bending vibration in PDA, respectively. Addition of PEI results in a new absorption band at 1660 cm^{-1} , ascribed to the formation of C=N bond between PEI and PDA. Similarly, UV-vis spectrum of dopamine/PEI solution shows a relative strong absorption around 368 nm associated with the formation of C=C-C=N and C=C-C=O, replacing a weak peak at 403 nm in the case of dopamine solution for the same reaction time (**Fig. 3a**). Interestingly, green fluorescence was observed when the dopamine/PEI solution was excited by a UV lamp at 365 nm (**Fig. 3b**), which is caused by the formation of Schiff base structure.³² Chemical composition of the membrane surfaces was also revealed by XPS spectra. As shown in **Fig. 2b**, the nascent membrane only displays a peak of C1s at 284.6 eV. Peaks of O1s and N1s arise after decoration with PDA or PDA/PEI. N/O ratio for the PDA-decorated surface is 0.4 (the theoretical value is 0.5), while it reaches 1 for the PDA/PEI-decorated membrane. The high-resolution N1s spectra also suggest the formation of C=N bond between PEI and PDA.³¹

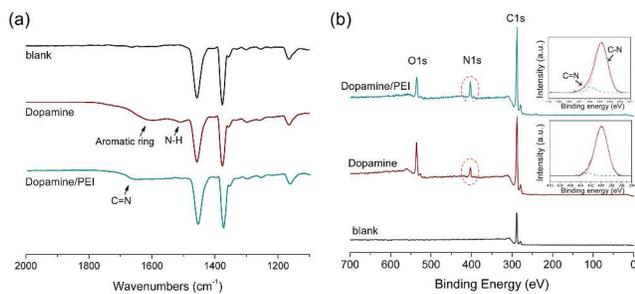


Fig. 2 (a) FT-IR/ATR and (b) XPS spectra of the nascent membrane and those membranes modified by immersing in dopamine and dopamine/PEI solution for 4 hr.

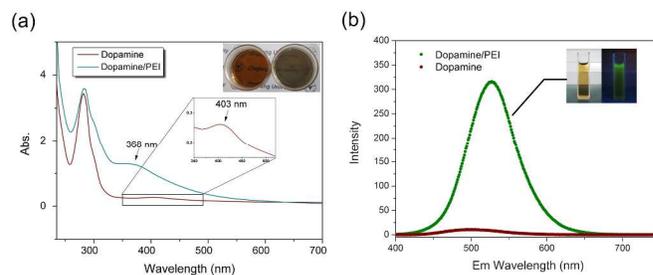


Fig. 3 (a) UV-vis spectra of dopamine and dopamine/PEI solutions after 4 hr deposition. The inset image is the digital photos of dopamine solution (left) and dopamine/PEI solution (right); (b) Fluorescence spectra of dopamine and dopamine/PEI solutions after 4 hr deposition. The inset shows images of diluted dopamine/PEI excited by 365 nm UV light.

2. Surface wettability of the modified membranes

The PDA-decorated surfaces are always hydrophilic with static water contact angle about 40° – 60° .¹⁸ Interestingly, surface hydrophilicity of the modified membranes can be greatly improved after incorporating PEI in the coatings. Wettability of the modified membranes was evaluated by time-dependent water contact angle (WCA) measurement (**Fig. 4a**). For the PDA-decorated membranes, WCA decreases with the increase of deposition time. When the deposition time is 1 hr, the static WCA is around 120° , which is similar to the value of the nascent membrane. Then, it declines to $31.4^{\circ} \pm 2.3^{\circ}$ after deposition more than 2 hr, and reaches $10.2^{\circ} \pm 1.4^{\circ}$ when extending the deposition time to 6 hr. This low WCA is attributed to both the hydrophilic nature of PDA and the porous structure of PPMM. On the other hand, the water drop permeates through the membrane and exhibits an “apparent” WCA of 0° after the membrane surfaces were co-deposited with dopamine/PEI for above 2 hr (**Fig. 5a**). We also detected the weight gain of membranes in dopamine or dopamine/PEI solution after rinsing and drying (**Fig. 4b**). It shows higher deposition rate and weight gain in dopamine/PEI solution than in dopamine one, which may account for the results of WCA measurements. It is clear that PEI plays a crucial role in membrane hydrophilization during the deposition process. Inherent abundant amino group of PEI improves the hydrophilicity of coating remarkably, and crosslinking reaction between PDA and PEI accelerates the deposition process, as well as promotes diffusion of PDA/PEI complexes into the membrane pores. It should be emphasized that the deposition process of PDA is rather time-consuming because it is mainly controlled by the oxygen diffusion gradient in dopamine solution,³³ and also suppressed by air bubbles in the hydrophobic membrane pores. Therefore, vibration and prewetting are essential for improving the deposition efficiency and the membrane properties.

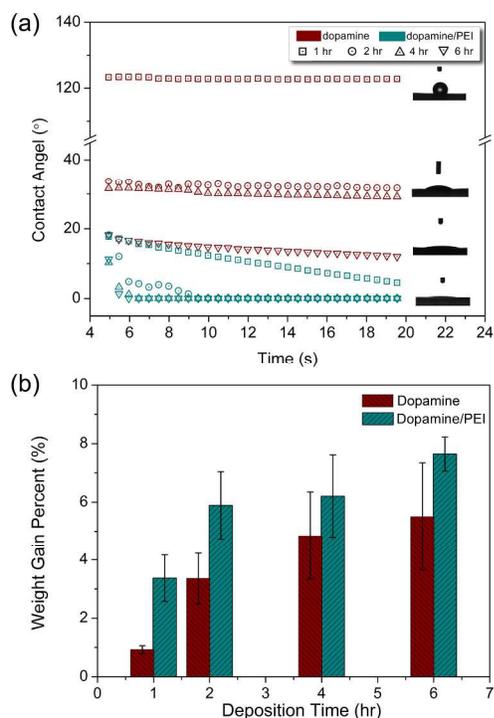


Fig. 4 Water contact angle (a) and weight gain (b) of the membranes modified by immersing in dopamine or dopamine/PEI solution for 1, 2, 4 and 6 hr.

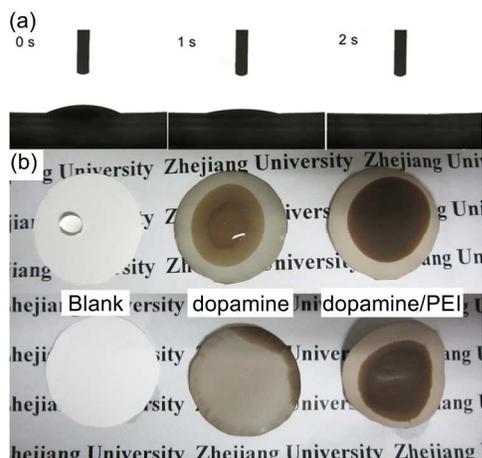


Fig. 5 (a) Dynamic water contact angle on the PDA/PEI-decorated membrane from 4 hr deposition; (b) Photographic images of a water drop on the surfaces of the nascent, the PDA-decorated and PDA/PEI-decorated membranes (above) and the reverse sides of the membranes (below). The deposition time is 4 hr.

The PDA/PEI-decorated membranes exhibit excellent surface hydrophilicity. **Fig. 5b** shows typical photographic images of water drops on the membranes. The nascent PPM is hydrophobic and the drop stays on it with a WCA larger than 150° . The PDA-decorated membrane presents an improved hydrophilicity and the water drop spreads on the membrane surface. However, the water cannot permeate through the membrane pores. As anticipated, the water drop fast permeates through the whole membrane decorated with PDA/PEI.

3. Water permeability of the membranes and reusability of the solutions

Water permeability can be used to reflect the dynamic hydrophilicity of the membrane. There are two common methods for the measurement of pure water permeability, namely ethanol-pretreated method and high-pressure method. The latter one can reflect the intrinsic hydrophilicity of the membrane. As indicated in **Fig. 6a**, pure water permeability is pretty low for the PDA-decorated membrane when the deposition time is less than 2 hr. It is due to that majority of the membrane pores are unmodified in this case, which remain unwetted during the measurement process. The pure water permeability increases to 2730 ± 750 L/m²h and 6796 ± 260 L/m²h with deposition time extending to 4 hr and 6 hr, respectively. However, the PDA-decorated membranes show unstable water permeation performance with a large relative error standard deviation of $\sim 36\%$ for samples deposited for 4 hr. On the other hand, the water permeability is as high as 2750 ± 260 L/m²h for the membranes deposited with PDA/PEI only for 1 hr. Moreover, it keeps about 7000 L/m²h for those membranes as the deposition time is longer than 2 hr. This is because almost all the membrane pores are easily wetted for these PDA/PEI-decorated membranes, and the maximum flux is reached at a measurement pressure of 0.1 MPa. Furthermore, the results suggest that the PDA/PEI-decorated membranes can permeate water even under ordinary pressure, with a flux of 147.7 L/m²h (90 mm water column), while water cannot permeate through the PDA-decorated membranes under the same condition.

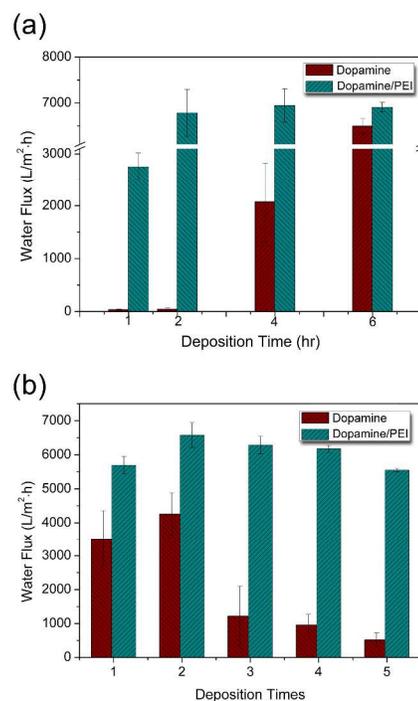


Fig. 6 (a) Pure water permeability of the PDA-decorated and PDA/PEI-decorated membranes prepared with different deposition times; (b) Reusability of the dopamine and dopamine/PEI solutions for membrane modification. The deposition time is 4 hr for each cycle.

During the deposition process of pure dopamine, visible aggregates were formed and precipitated from solution after long time reaction. That is to say, the majority of dopamine is useless and the solution cannot be reused for further surface modification. However, PEI added deposition solution can solve this problem. The reusability was evaluated by repeating deposition experiment, and the result is shown in Fig. 6b. Pristine membranes were immersed in the same solution with 4-hour cycle separately, followed by drying in vacuum and pure water flux measurement. For PDA solution, the flux decreases dramatically after twice depositions, while it keeps near 6000 L/m²h in the case of PDA/PEI. We can also find that the maximum flux is reached at the second 4-hour deposition for both dopamine and dopamine/PEI solution, which suggests that the deposition will be more effective after a period of pre-oxidation in air.

The stability of modifying layer is crucial to the practical applications of the membranes. The PDA coating shows excellent stability in acidic, neutral and weak basic solution, whereas disintegrates in strong alkaline environment.^{28,29} We compared the stability of the PDA- and PDA/PEI-decorated membranes in acidic and alkaline environment. As shown in Fig. 7, both the PDA and PDA/PEI coatings show excellent stability in acidic solution with pH=2. However, the solution containing the PDA-decorated membrane turns a little yellow after 12 hr rinsing at pH=12, and the membrane is bleached at pH=14. By contrast, the PDA/PEI-decorated membrane is more stable in solutions with pH=12 and 14 due to the covalent cross-linking even some non-covalent connected oligomers may be washed away. The hydrophilicity lose is neglected for the PDA/PEI-decorated membranes, while a great hydrophobic recovery can be observed for the PDA-decorated membrane after rinsing in the solution with pH=14.

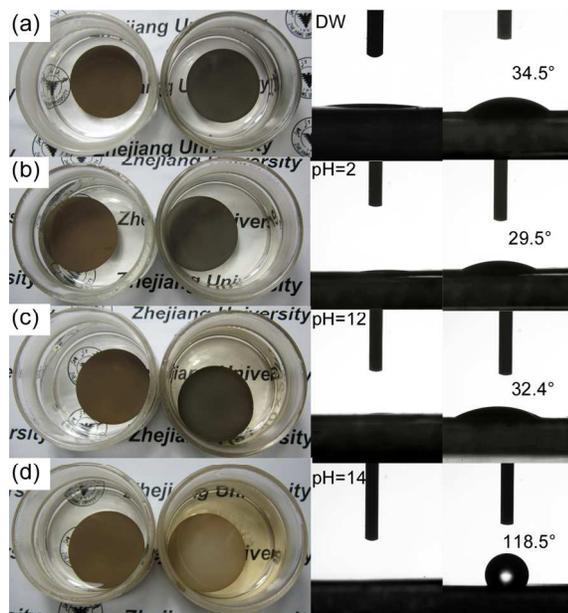


Fig. 7 Digital photos and water contact angles of the PDA/PEI- (left) and PDA-decorated (right) membranes rinsed by the solution with different pH values for 12 hr. DW means deionized water.

4. Separation of oil-in-water emulsions with the PDA/PEI-decorated membranes

The high water permeability of the PDA/PEI-decorated membranes provides novel approach to separate “soft” pollutant such as dispersed oil from oily wastewater, which needs operate at ultralow pressure by microfiltration. Furthermore, the superhydrophilic surfaces always show underwater superoleophobicity,^{3,34} one of whose potential applications is oil/water separation.^{5,6} However, most of reported materials cannot be used in separation of oil-in-water emulsions due to their large pores. We selected 1,2-dichloroethane as an oil phase for its high density. Our PDA/PEI-decorated membranes show underwater oil contact angle of $164.9^{\circ} \pm 2.8^{\circ}$, and low oil adhesion with slide angle of $2.9^{\circ} \pm 0.8^{\circ}$ (Fig. 8a). It can be used to separate cloudy oil-in-water emulsion under ordinary pressure (Fig. 8b and c). For the oil-in-water emulsion with dichloroethane/water = 1/100, the maximum flux can reach about 100 L/m²h and the oil rejection is higher than 98%. With the increase of filtration time, the flux decreases sharply because of surface fouling by the oil, and it can be recovered after simply rinsing with ethanol and then water (Fig. 8d). On the other hand, it shows no obvious flux and rejection decrease for n-hexane-in-water emulsion, which is ascribed to both the lower density of hexane than water (dichloroethane is denser than water) and the low operation pressure applied. We also found that the oil drops pass through the membranes under high pressure (>0.1 MPa), which further confirms the advantages of superhydrophilic microfiltration membrane for oil-in-water emulsion separation. Moreover, our method can be applied for membranes with smaller pore size, which can improve breakthrough pressure during the filtration process.

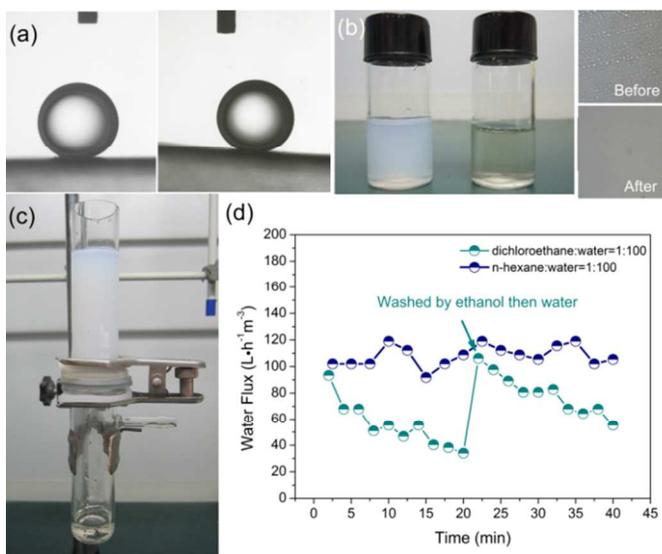


Fig. 8 (a) Underwater oil contact angle and slide angle on the PDA/PEI-decorated membrane surface; (b) Feed and filtrate after filtration by the PDA/PEI-decorated membrane; (c) Oil-in-water emulsion separation by the PDA/PEI-decorated membrane under ordinary pressure. The oil phase is dichloroethane. (d) Water flux of dichloroethane-in-water (1:100, v/v) and n-hexane-in-water emulsion separation (1:100, v/v).

Conclusion

In summary, we fabricated microfiltration membranes with superhydrophilic surfaces by simple co-deposition of PDA and PEI, in which PEI reacted with PDA through crosslinking reaction between amino and catechol. This co-deposition strategy provides a universal, efficient and reusable process. The modified membranes show excellent wettability after a short deposition time. Moreover, the stability of the co-decorated membranes is greatly improved due to the covalent cross-linking between PDA and PEI. The ultrahigh water permeability of the prepared membranes enables a filtration process under ultralow pressure, which is promising for oil-in-water emulsion separation via a microfiltration process.

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Notes and references

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Polydopamine/polyethyleneimine-decorated membranes were fabricated with excellent surface hydrophilicity and high water permeability for oil/water emulsion separation under ordinary pressure.

