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Silica-Decorated Polypropylene Microfiltration Membranes with a Mussel-Inspired Intermediate Layer for Oil-in-Water Emulsion Separation

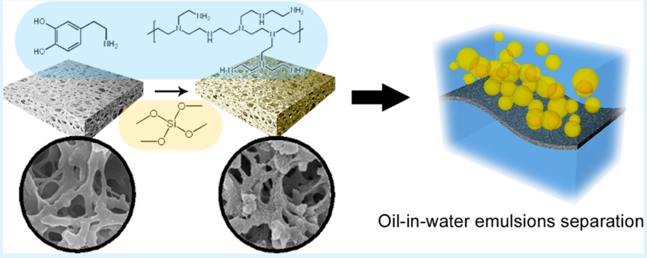
Hao-Cheng Yang,[†] Jun-Ke Pi,[†] Kun-Jian Liao,[†] He Huang,[†] Qing-Yun Wu,[‡] Xiao-Jun Huang,[†] and Zhi-Kang Xu*,[†]

[†]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

[‡]Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China

Supporting Information

ABSTRACT: Silica-decorated polypropylene microfiltration membranes were fabricated via a facile biomimetic silicification process on the polydopamine/polyethylenimine-modified surfaces. The membranes exhibit superhydrophilicity and underwater superoleophobicity derived from the inherent hydrophilicity and the well-defined micronanocomposite structures of the silica-decorated surfaces. They can be applied in varieties of oil-in-water emulsions separation with high permeate flux (above 1200 L/m^{2}h under 0.04 MPa) and oil rejection (above 99%). The membranes also have relatively high oil breakthrough pressure reaching 0.16 MPa due to the microporous structure, showing great potential for practical applications. Furthermore, such mussel-inspired intermediate layer provides us a convenient and powerful tool to fabricate organic−inorganic hybrid membranes for advanced applications.



KEYWORDS: *microfiltration, silicification, superhydrophilicity, underwater superoleophobicity, oil-in-water emulsion separation*

1. INTRODUCTION

In recent years, materials with special wettability have attracted widespread interest for their great application prospect in oil/water separation.[1−5] Surfaces with superwetability play a crucial role in disgushing the adhesion of water or oil. Both superhydrophobic[6] and superhydrophilic[7,8] (also underwater superoleophobic many cases) surfaces are adequate for this purpose. The superhydrophilic materials are preferred in most cases because of their better oil resistance and removal efficiency contrast to the superhydrophobic ones during the separation of oil-in-water suspensions.[9−12] Therefore, superhydrophilic and underwater superoleophobic materials, including hydrogel- and mineral-coated steel meshes, are mostly prepared to separate oil/water mixture.[7,13] However, it still remains challenging to separate emulsified oil drops from water containing surfactants. These emulsified drops are easier to pass through the porous materials by pressure-induced deformation, because they have small size ranging from hundreds to thousands of nanometers and their surface tension is lower than the surfactant-free ones. Membrane filtration, especially microfiltration and ultrafiltration, is the most attractive solution to solve this problem. Moreover, it can continuously remove dispersed oil drops from oily wastewater, which has been widely employed in industrial applications. For instance, cellulose ultrafiltration membranes were widely applied in oil-in-water emulsion separation, as well as the polysulfone ones with hydrophilic additives (such as polyvinylpyrrolidone and polyethylene glycol).[14−16] Jin et al. fabricated microfiltration membranes grafted with poly(acrylic acid) and zwitterionic polymer for efficient separation of emulsified oil/water mixtures under ultralow trans-membrane pressure or gravity.[17,18] Unfortunately, oil fouling is always inevitable for most polymer membranes because of the oleophilic nature of C−H structures in polymer chains even after hydrophilic modifications, which may cause an obvious decline in permeation flux and separation efficiency.

Inspired by fish scales and clamshell,[10,11] minerals (such as $CaCO_3$, SiO_2, and TiO_2) with inherent superhydrophilicity and underwater oil-repellent ability are acknowledged as the ideal candidates for oily wastewater treatment. Yu et al. prepared a zeolite-decorated steel mesh with high stability for oil/water mixture separation, which could be used under various harsh conditions.[13] Another example is the TiO_2-based mesh coupled with the photodegradation of pollutes, demonstrated by Feng and his co-workers.[19] However, the pore size of the reported meshes is always too large in a few tens of microns to retain the emulsified oil drops. Although an inorganic mesh enveloped by $Cu(OH)_2$ nanowires was used to separate oil/water emulsion,

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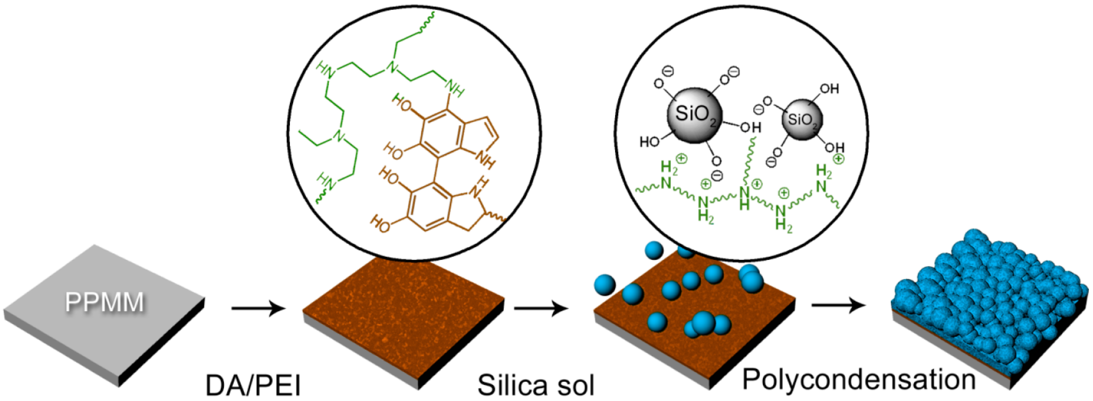

Figure 1. Schematic illustration of the silica-decorated microfiltration membranes fabricated via a biomimetic silicification process induced by a polydopamine/polyethylenimine (PDA/PEI) intermediate layer.

the oil drops were still too lager compared to the stable emulsion.[20] In pursuit of outstanding emulsion separation, a critical demand is to construct mineralized porous membranes with well-defined surface microstructure. By far, several methods have been developed to construct organic−inorganic hybrid membranes.[21−23] For example, various inorganic nanoparticles, including SiO_2, Al_2O_3 and TiO_2, were incorporated into polymer membrane matrixes for separation of oily wastewater.[24,25] However, it is unable to produce high mineral decoration essential to form superhydrophilic surfaces for most of the traditional approaches such as physical blending and *in situ* generation. It is because inorganic nanoparticles or precursors are mostly dispersed in polymer matrix, which can be described as "embedded model". The hence formed inefficient inorganic decoration results in an inferior surface modification effect restricting the applications in catalysis, adsorption, and other fields.

To address these issues, we make an attempt to develop a new kind of organic−inorganic hybrid membrane with high mineral decorated surfaces, accordingly described as "enveloped model". It is suggested that the entire membrane pore surfaces are uniformly decorated by a layer of nanominerals, which endows the membrane with particular features of inorganics (e.g., superhydrophilicity, rigidity, absorbability, and catalytic properties). For this purpose, an intermediate layer is required to robustly connect the membrane surfaces with the inorganic coating. In our previous work, poly(acrylic acid) with negative charges was grafted onto the surfaces of polypropylene microfiltration membranes (PPMM) via UV-induced polymerization, and then on which a nano-$CaCO_3$-based coating with positive charges was fabricated via an alternate soaking process.[26,27] The hybrid membranes show superhigh water permeation and excellent oil-in-water emulsions separation performance. Nevertheless, $CaCO_3$ is unable to withstand long-term operation, and the protein resistance of $CaCO_3$-decorated surfaces is always worrying because this mineral is believed to carry positive charges. Hence, a positively charged intermediate layer is necessary for deposition of the more stable nonionic minerals such as SiO_2, whose sols are always negatively charged. In these research, we fabricate a nanosilica-decorated membrane to separate the emulsified oil-in-water mixtures. Dopamine, a well-known "bio-glue", is introduced as the adhesive component in the intermediate layer for its universal and simple deposition process.[28] Polyethylenimine (PEI), an amino-containing polymer, is codeposited onto the membrane surfaces via covalent connection between the catechol and amino group,[29,30] which is benificial to the polycondensation of silicic acid via a biomineralization process (Figure 1).[31−33] The silica-decorated membranes show expected superhydrophilicity in air and underwater superoleophobicity arising from the surface chemistry and the morphology of the mineral coating, leading to effective filtration of oil-in-water emulsions under low pressure. Furthermore, the microporous membrane structure makes the threshold breakthrough pressure for sodium dodecyl sulfate (SDS) stabilized emulsion reach 0.16 MPa. It is proposed the interactions between the membrane surfaces and the surfactants play an important role in emulsion filtration. Although the dopamine-assisted silicification has been reported in previous work,[34−36] it is still used in oil-in-water emulsions separation for the first time.

2. EXPERIMENTAL SECTION

2.1. Deposition of PDA/PEI on the Membrane Surfaces. Polypropylene microfiltration membranes (PPMM, mean pore size 0.2 μm, porosity 75%) from Membrana GmbH (Germany) were cut into rounds with a diameter of 25 mm. The samples were washed by acetone overnight to remove impurities adsorbed on the membrane surfaces and then dried in a vacuum oven at 40 °C to a constant weight. The dried membranes were totally prewetted by ethanol and then immersed into tris-buffer solution (50 mM, pH = 8.5) dissolved by dopamine hydrochloride (Sigma-Aldrich) and polyethylenimine (PEI, M_w = 600 Da, Aladdin, China) with a concentration of 2 mg/mL, respectively. The mass ratio of dopamine/PEI was 1:1 in this solution. After 4 h deposition, the resulting membranes were washed by deionized water overnight. We also investigated the effect of dopamine/PEI mass ratio in deposition solution on the following silicification process.

2.2. Silicification on the PDA/PEI-Deposited membranes. Silification solution was prepared as follows. A 0.15 mL portion of tetramethyl orthosilicate (TMOS, Aladdin, China) was added into 10 mL of HCl solution (1 mM) under stirring for 15 min, and mixed with equal volume phosphate buffer solution (0.2 M, pH = 6.0). Then, the PDA/PEI-deposited membranes were transferred into this solution at 25 °C for a designed of time. After silicification, the membranes were washed by deionized water and dried in a vacuum oven overnight for further use.

2.3. Membrane Characterization. The surface morphology and element distribution of nascent, PDA/PEI-deposited and silica-decorated membranes were observed by field emission scanning electron microscopy (Hitachi, S4800, Japan) with an energy dispersive X-ray detector. The water contact angles and underwater oil contact angles were detected with a contact angle system (MAIST Vision Inspection & Measurement Co. Ltd., DropMeter A-200, China). The surface chemistry was analyzed by both X-ray photoelectron spectrometer (Thermo, ESCALAB250Xi) and attenuated total

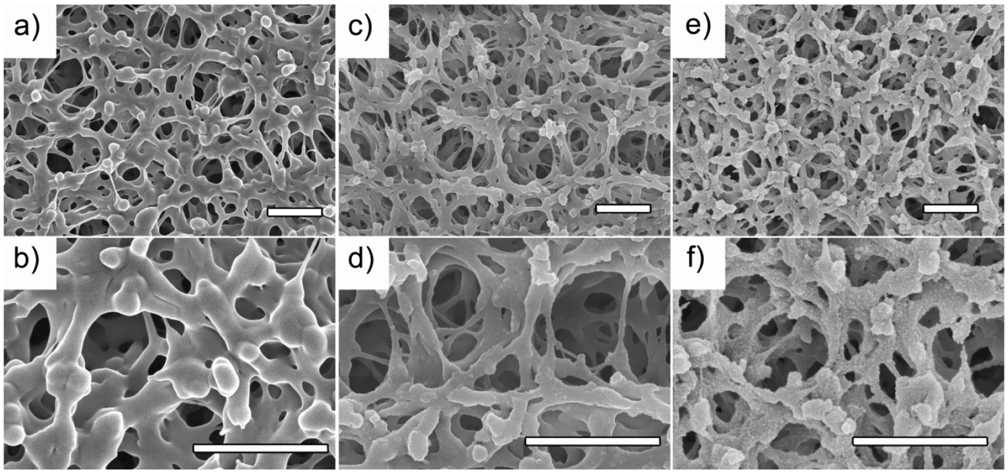

Figure 2. SEM images of the membrane surface for the nascent (a and b), PDA/PEI-deposited (c and d), and silica-decorated (6 h, e and f) membranes at different magnifications. The scale bars are 1 μm in the images.

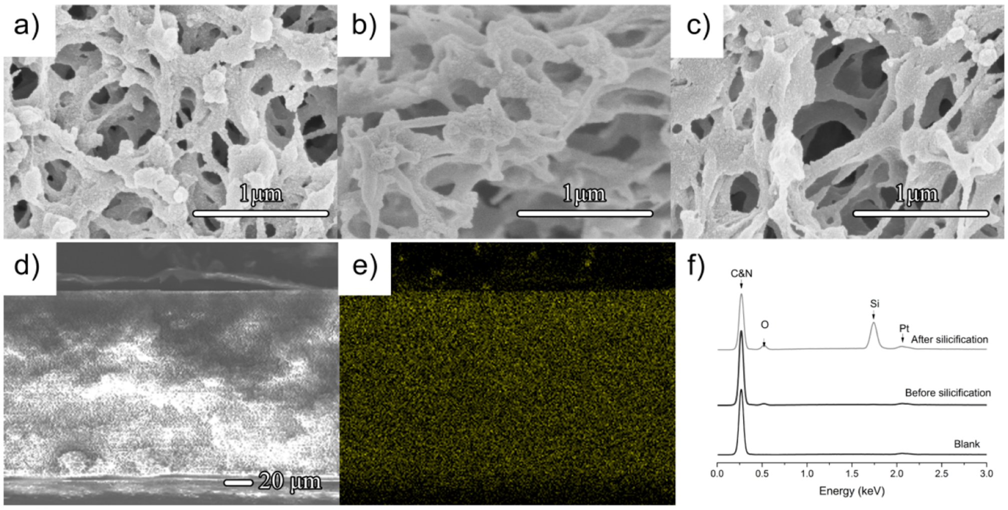

Figure 3. SEM images of (a) the top surface, (b) the cross-section, and (c) the bottom surface of the silica-decorated membrane after silicification for 6 h. (d, e) SEM and EDX scan images of the membrane cross-section. (f) EDX spectra of the nascent, PDA/PEI-deposited, and silica-decorated membranes.

reflectance-Fourier transform infrared spectroscopy (Thermol, Nicolet 6700). The membrane performances were tested with a dead-end filtration equipment from Milipore Co. The surface potential was measured from electrokinetic analyzer for solid surface analysis (Anton Paar, SurPASS, Austria).

2.4. Preparation and Separation of Oil-in-Water Emulsions. The oil-in-water emulsions were prepared as described in previous literature.[18] In brief, diesel-in-water emulsion was obtained by mixing diesel and water in 1/99 (v/v) with dissolving 0.02 mg of sodium dodecyl sulfate (SDS) per mL of emulsion under 3000 rpm stirring for 5 h. The as-prepared emulsion is quite stable during the following tests. Other oil-in-water emulsions were prepared following the similar steps. The properties of these oils are listed in Supporting Information Table S2, and the droplet size distribution of emulsions has been characterized by particle size analyzer (Malvern, ZcEc, UK) in Supporting Information Figure S2.

A dead-end filtration apparatus (Millipore) was applied for measuring the permeate flux (the diameter of membrane is 25 mm), and the trans-membrane pressure was adjusted by a nitrogen tank (Supporting Information Figure S1). The silica-decorated membranes were precompacted at 0.3 MPa by pure water for 20 min, and the permeate fluxes were tested under 0.04 MPa. Considering the flux decrease caused by the accumulation of oil cake, we calculated the permeate flux by averaging the collected solution volume within 5 min. The flux recovery property was evaluated by detecting the real-time flux every 2 min. The membranes were simply rinsed by deionized water three times before the next measurement. To obtain the breakthrough pressure, we measured the oil rejection and permeate flux every 2 min by increasing the operation pressure from 0.02 to 0.2 MPa with an interval of 0.02 MPa. The oil rejection was measured by UV−vis spectrophotometer (Shimadzu, UV 2450, Japan) as reported previously.[27]

3. RESULTS AND DISCUSSION

3.1. Structures of the Silica-Decorated Membranes. For advanced performance in oil/water separation, the membranes are supposed to be fantastic at both oil resistance and water permeation. Therefore, this work focuses on regulating and controlling the surface chemistry and morphology, which directly contribute to the wettability and oil-repelling property of the membrane surface. Figure 2 shows the SEM images of the membrane surfaces before and after silicification. No apparent change is observed between the PDA/PEI-deposited membrane and the nascent one, which has also been demonstrated in our previous work.[37] We found uniform deposition of PDA/PEI layer on the membrane surface

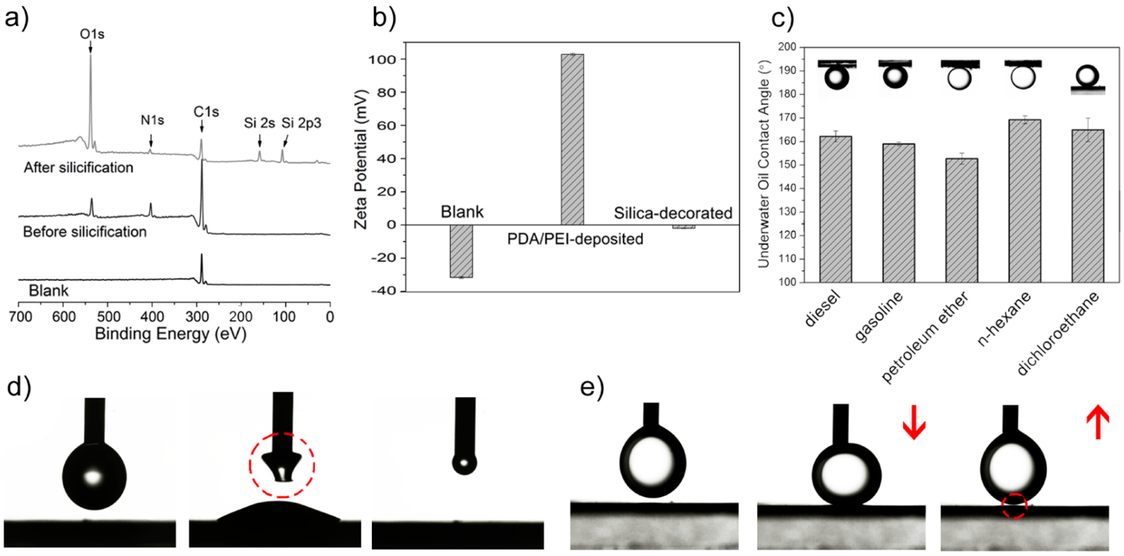

Figure 4. (a) XPS spectra of the nascent, PDA/PEI-deposited, and silica-decorated membranes. (b) Zeta potentials of the membrane surfaces before and after silicification at pH = 6.0. (c) Underwater oil contact angles (OCAs) of different oils (diesel, gasoline, petroleum ether, *n*-hexane, and dichloroethane). Images of (d) water contact angle (WCA) and (e) underwater OCA test of the silica-decorated membranes. The water drop permeates through the membrane in air rapidly, while the oil drop shows little adhesion on the membrane surface under water. The oil selected in this experiment is 1,2-dichloroethane.

and in the membrane pores, which ensures the good silicification process through the whole membrane. Moreover, the coating shows improved stability in acidic or basic environment due to the covalent connection between PEI and PDA. However, the membrane surfaces are indeed decorated by silica coating in nanosize after silicification yet with negligible decrease in the pore size. These silica nanoparticles are combined with the inherent microporous structure of the membrane surface, which is responsible for the excellent wettability and the oil repelling property of the prepared membranes as shown below. SEM images are also presented in Figure 3a−d for the membrane morphologies at different positions. The whole membrane is well silicified, and the silica layers are uniformly distributed in the membrane cross-section as revealed by EDX scan image in Figure 3e. The mineral particles attached on the inner pores enhance the water permeation, enabling high permeation flux under relatively low trans-membrane pressure to prevent oil drop deformation.

The chemical components were further characterized by XPS and FI-TR/ATR for the as-prepared membrane surfaces. As shown in Figure 4a, both N 1s and O 1s peaks appear on the PDA/PEI-deposited membrane. It is clear that the membrane surface shows a dramatic decrease of C 1s with a sharp increase in O 1s and the appearance of Si peaks after silicification. The amount of silica increases with the silicification time as illustrated by FT-IR/ATR spectra and SEM images (Figures S3 and S4 in Supporting Information). It seems the mass ratio of dopamine/PEI in solution has no significant effect on the silica content, whereas the PEI content increase may cause undesirable blocking during the following silicification process (Figure S4 in Supporting Information). Zeta potentials were measured for the membrane surfaces. As revealed by Figure 4b, the PDA/PEI-deposited membrane surfaces are positively charged (102.8 ± 0.69 mV when pH = 6.0). They can absorb silicic acid from the sol solution by electrostatic interaction and form silica coating via the hydrolysis following polycondensation process, which consequently reverses the surface charge. We also evaluated the wettability and permeability of the silica-decorated membranes by measuring water contact angle (CA). As shown in Figure 4d, the water drop broke into two parts and permeated through the membrane rapidly, indicating appreciable hydrophilicity derived from high amount of silicon hydroxyl and well-defined micronanostructure. In our previous study, we also demonstrated the excellent hydrophilicity of the PDA/PEI-deposited membranes.[37] By contrast, the silica-decorated membranes show better water permeation performance, although the water drops can permeate through both PDA/PEI-deposited and silica-decorated membranes. When the water drops contact the membrane with excellent hydrophilicity, it diffuses in three dimensions including spreading along the membrane surface and permeating through the membrane cross-section. The silica-decorated membranes show faster permeation along the membrane cross-section, leading to smaller spreading radius on the top surface and wetting area ratio of front to back ($S_{\text{front}}/S_{\text{back}}$) (Figure S6 in Supporting Information), which is consistent with the result of water permeation test. They also exhibit superior pure water permeation flux compared to that of to the nascent ones, especially under low precompacting pressure (Figure S7 in Supporting Information).

As anticipated, such a good hydrophilic property endows the membrane with outstanding oleophobicity in water environment. Moreover, the water trapped in the micro/nanostructures leads to the "Cassie−Baxter" state at the water/oil/solid interface, which contributes to the superoleophobicity rather than ordinary oleophobicity. 1,2-Dichloroethane was selected as a model oil to characterize the underwater superoleophobicity and oil repelling property because of its higher density than water. The membrane has a large underwater oil contact angle (OCA) of 164.9° ± 5.0° and small sliding angle 2.5° ± 1.4°, and no significant deformation was observed during the contact test (Figure 4e), demonstrating pretty low oil adhesion of the membrane surfaces. The OCAs of other oils such as diesel, gasoline, petroleum ether, and *n*-hexane are 162.1° ± 2.3°, 159.0° ± 0.7°, 152.7° ± 2.4°, and 169.2° ± 1.7°, respectively, which all donate the membrane's excellent underwater superoleophobicity (Figure 4c). However, the underwater OCA and adhesion force test cannot totally reflect the antioil fouling property for the membranes during the filtration process of emulsified oil-in-water mixtures because of the existence of surfactant. For example, we used sodium dodecyl sulfate (SDS) as the emulsifier in our filtration experiment, which can extremely lower the interfacial energy between the oil drop and the water environment through the ionic hydration of sulfate groups and make the drop surface negatively charged.

3.2. Separation Property of the Silica-Decorated Membranes for Oil-in-Water Emulsions.

The superhydrophilicity and underwater superoleophobicity enable the silica-decorated membranes to get great potential in treatment of oil-containing wastewater. Among all the oily sewage, emulsified oil/water mixtures have always been a challenge due to the small drop size and the low interfacial energy. We assessed the separation performance of various oil-in-water emulsions via a dead-end filtration apparatus. The results indicate that the silica-decorated membranes can effectively intercept the oil drops with relative high water permeation flux and oil rejection. As shown in Figure 5a, the water permeation flux are 1228 ± 80 L/m^2 h, 1296 ± 42 L/m^2 h, 1431 ± 64 L/m^2 h, and 1419 ± 56 L/m^{2}h, respectively, for those oil-in water emulsions containing diesel, gasoline, petroleum ether, and *n*-hexane, while the oil rejection is higher than 99% to each oil (99.93 ± 0.15%, 99.13 ± 0.06%, 99.30 ± 0.10%, and 99.27 ± 0.40%). The permeate fluxes of petroleum ether and *n*-hexane are higher because their droplet size is much larger than those of diesel and gasoline with the same SDS content. For diesel-in-water emulsion, we found the flux decreased with the increase of emulsifier content, which is attributed to the smaller size of oil droplets (Supporting Information Figure S8). It should be noted that the PDA/PEI-deposited membranes can also be used to separate oil-in-water emulsions under low trans-membrane pressure as described in our previous work.[37] However, the permeate fluxes of these membranes are only a quarter of the silica-decorated ones under the same condition. The water permeation flux with evolution of filtration time was further measured in real time to evaluate the flux recovery and reusability of the silica-decorated membranes. Figure 5b indicates that the permeation flux declines dramatically in the first 2 min because of the "oil drops cake" formed on the membrane surfaces during the dead-end filtration, and then decreases slowly after the formation of the soft cake layer. Interestingly, we found a demulsified oil layer in the pipe after a period of dead-end separation under 0.04 MPa. This result originates from the demulsification of large oil drops and can be removed easier than the emulsified oil drops. The process was repeated at least three times, and the silica-decorated membranes show excellent flux recovery after simply rising with water.

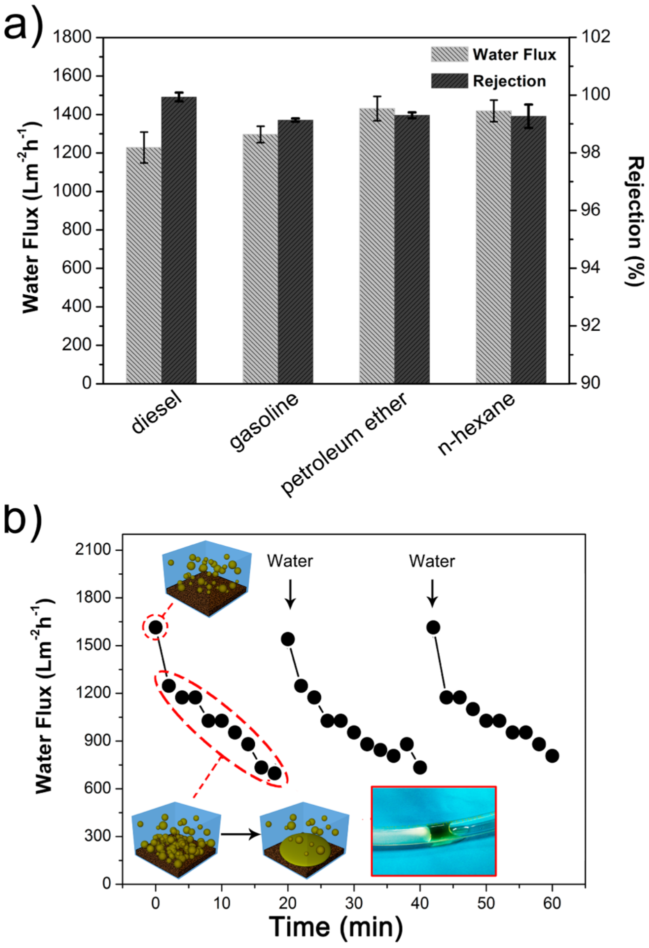

Figure 5. (a) Water permeation flux and oil rejection of the silica-decorated membranes for oil-in-water emulsions containg diesel, gasoline, petroleum ether, and *n*-hexane, respectively. (b) Evolution of the water flux and flux recovery of SDS-stabilized diesel-in-water emulsion over three cycles. The operation pressure is 0.04 MPa.

Although the oil-in-water emulsions can be separated by the silica-decorated membranes under ultralow pressure, the filtration process is always operated under high pressure (e.g., 0.1 MPa for microfiltration) for practical application. We detected the breakthrough pressure (permeate flux and oil rejection at the same time) of the membranes before and after silicification by increasing the operation pressure progressively (0.02 MPa for each 2 min, Figure 6). For the PDA/PEI-deposited membranes, the flux declines to zero after a short period of filtration until breakthrough under the pressure of 0.14 MPa (different from our previous study using Tween-80, a nonionic emulsifier, instead of SDS).[37] It can be interpreted by the adhesion of oil drops onto the membrane surfaces via electrostatic interaction.[38] As mentioned above (Figure 3b), the PDA/PEI-deposited membrane is positively charged due to the high density of the amino groups, while the oil drops stabilized by SDS carry opposite charges from the sulfate groups. Even though the oil rejection after breakthrough is about 94% for the diminished pores by oil fouling, it still cannot meet the emission standard and permeation flux for actual application. On the other hand, the water flux of the silica-decorated membranes decreases slightly due to the initial formation of "oil cake" at the beginning as shown in Figure 5b. Although the flux should decrease with the filtration time due to the oil droplets accumulation, it also increases with the operation pressure derived from their excellent antioil fouling property. When the operation pressure reaches 0.16 MPa, the oil rejection declines to near 92%, which can be rationalized by both the breakthrough of concentrated oil-drop layer and a possible re-emulsification process. The filtrate returns to clarified solution as we decrease the pressure to 0.04 MPa again. The zeta potential of the membrane surfaces decreases from 102.3 ± 0.69 mV to −2.0 ± 0.19 mV after silicification, which helps to repel the oil drops stabilized by anionic surfactants like SDS. The results also support a latest research of PAA-grafted PVDF membrane for highly efficient oil-in-water emulsion separa-

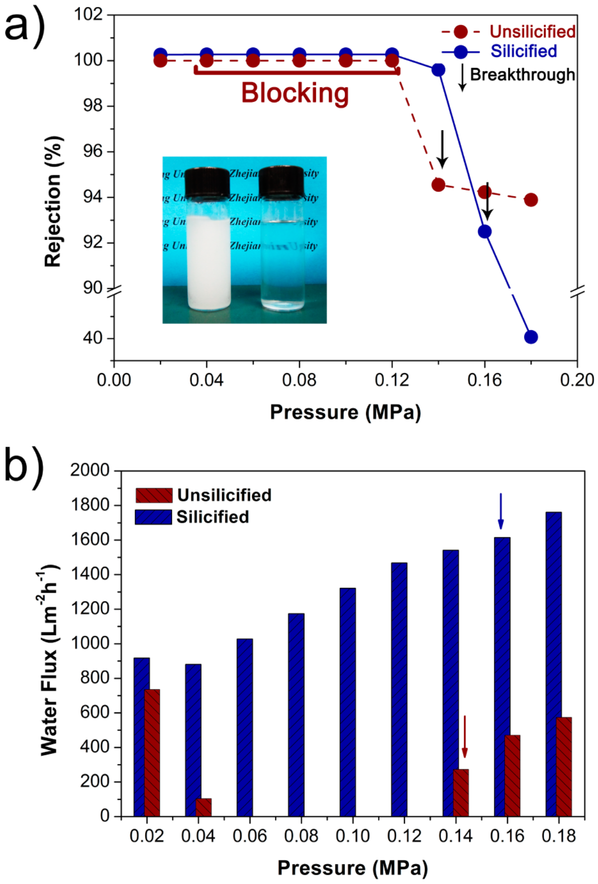

Figure 6. (a) Oil rejection of diesel-in-water emulsion with increased pressure for the membranes before and after silicification. (b) Water permeation flux corresponding to the breakthrough pressure test in part a.

tion.[18] It has also been reported during the ultrafiltration process for this flux decline caused by adsorption between ionic surfant-stabilized oil drops and oppositely charged surfaces.[38,39]

4. CONCLUSION

In conclusion, we demonstrate a novel silica-decorated microfiltration membrane mediated by mussel-inspired polydopamine/polyethylenimine layer via a biomimetic silicification process. The membranes show high water permeation flux and oil rejection for kinds of oil-in-water emulsions, due to the robust superhydrophilicity and underwater superoleophobicity. Moreover, the membranes also have a high breakthrough pressure which can satisfy the industrial application, leading to the demulsification of surfactant-stabilized oil drops. On the other hand, the mussel-inspired intermediate layer provides us with a powerful tool to construct various mineral-coated membranes for further applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

ATR-FTIR spectra and SEM images of silica-decorated membranes with different silicification time. Surface wettability test and water permeation flux of both un-silica-decorated and silica-decorated membranes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xuzk@zju.edu.cn.

Notes

The authors declare no competing financial interest.

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