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Surface Chemistry

Salt-Induced Fabrication of Superhydrophilic and Underwater Superoleophobic PAA-g-PVDF Membranes for Effective Separation of Oil-in-Water Emulsions**

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Abstract: *Conventional polymer membranes suffer from low flux and serious fouling when used for treating emulsified oil/water mixtures. Reported herein is the fabrication of a novel superhydrophilic and underwater superoleophobic poly(acrylic acid)-grafted PVDF filtration membrane using a salt-induced phase-inversion approach. A hierarchical micro/nanoscale structure is constructed on the membrane surface and endows it with a superhydrophilic/underwater superoleophobic property. The membrane separates both surfactant-free and surfactant-stabilized oil-in-water emulsions under either a small applied pressure (<0.3 bar) or gravity, with high separation efficiency and high flux, which is one to two orders of magnitude higher than those of commercial filtration membranes having a similar permeation property. The membrane exhibits an excellent antifouling property and is easily recycled for long-term use. The outstanding performance of the membrane and the efficient, energy and cost-effective preparation process highlight its potential for practical applications.*

Efficient, energy and cost-effective processes for oil/water separation, especially for treating emulsified oil/water mixtures, are highly desired yet still challenging. The polymer-dominated filtration membranes have been acknowledged as an advanced technology for the separation of various emulsions, especially for surfactant-stabilized emulsions, with acceptable discharge quality and a relatively simple process from an operational point of view.[1] In spite of these advantages, polymeric membranes suffer from low flux, and serious fouling and degradation because of surfactant adsorption and/or pore plugging by oil droplets, which lead to a quick decline of permeation.[2] In addition, the size-sieving mechanism of filtration membranes is relatively energy-consuming since a transmembrane pressure of up to several bars is usually required to allow emulsions to selectively pass through the membranes. The popularly used and thus most important class of membrane-preparation processes is the so-called liquid–liquid phase inversion. A phase inversion can be described as a demixing process whereby there is an exchange of the solvent in the homogeneous polymer solution with the nonsolvent from the coagulation bath, thus resulting in porous polymer film.[3] As a result of the intrinsic property of most of polymers, the traditional polymeric membranes prepared by phase inversion are prone to being oleophilic, which causes the aforementioned fouling issue and decline of flux. To improve the hydrophilicity and antifouling performance of polymeric membranes, many approaches through either surface modification,[4] or polymer grafting,[5] or blending with inorganic nanoparticles and other additives[6,7] have been taken. However, the improvement in performance is still strictly limited and has far less than applicable requirements.

A number of superwetting materials have been fabricated through a combination of surface chemistry and rough structure, and applied to oil/water separation.[8] Although superhydrophobic materials have been extensively investigated, they are limited to the separation of oil-rich oil/water mixtures but not suitable for water-rich oil/water mixtures or oil-in-water emulsions. Recently, a new concept, which takes advantage of high-surface-energy materials having water-favoring property, to construct underwater superoleophobic surfaces has been proposed and used to separate oils from water by the group of Jiang.[9] By using this strategy, superoleophobic surfaces were achieved under water. As water usually has higher density than oils, a water-barrier layer will form on the surface of a superhydrophilic and underwater superoleophobic membrane, thus effectively preventing oil pollution and improving antifouling properties of the membrane during oil/water separation.

Herein, we report the fabrication of a novel superhydrophilic and underwater superoleophobic poly(acrylic acid)-grafted PVDF (PAA-g-PVDF) membrane by a salt-induced phase inversion. Completely different from the general approach of adding salts (such as $LiClO_4$, LiCl), as a pore-forming additive, to a PVDF solution to change the pore structure of the PVDF membrane and thus improve the membrane permeability as reported previously,[10] herein, the salt (NaCl) at a nearly saturated concentration is added into the coagulation bath to function as nucleates at the interface

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of two liquids during the solvent exchange to induce the assembly of PAA-g-PVDF micelles around them. This salt-induced micelle assembly at the interface gives rise to a micro/nanoscale hierarchical structure on the membrane surface to endow the membrane with a superhydrophilic and underwater superoleophobic property. As a consequence, the membrane can separate both surfactant-free and surfactant-stabilized oil-in-water emulsions, under either a small applied pressure (0.1 bar) or solely driven by gravity, with high separation efficiency (water purity in filtrate after one-time separation > 99.99 wt %) and high flux. Most importantly, the membrane exhibits an excellent antifouling property and is easily recycled for long-term use. The outstanding performance of the membrane for the separation of an oil-in-water emulsion and its industrially processable preparation process indicate its great potential for practical applications.

The superhydrophilic and underwater superoleophobic PAA-g-PVDF membranes were fabricated by phase inversion, wherein water containing a high concentration of sodium chloride (NaCl) was used as a coagulation bath thus creating a salt-induced phase-inversion process as we describe herein. Figure 1 a shows the schematic of the process for membrane formation. A PAA-g-PVDF-concentrated NMP solution on the substrate is immersed into salty water, and the solvent exchange between water and NMP occurs immediately at the interface of the two liquids. As a result of the instant increase in salt concentration at the interface, NaCl is squeezed out from the water and tends to crystallize into small crystal seeds at the interface. The NaCl seeds could function as accumulation points to gather surrounding PAA-g-PVDF micelles to form micelle aggregates around the seeds. The micelle aggregates grow additionally in the subsequent phase-inversion process into spherical microparticles. The spherical microparticles finally form a skin layer at the membrane surface, and endows the membrane surface with a superhydrophilic and underwater superoleophobic property. The as-prepared PAA-g-PVDF membrane (taken the sample with 2.5 wt % graft ratio of PAA as an example) exhibits good mechanical properties (see Figure S1b in the Supporting Information) and flexibility (Figure 1 b), and no cracks were observed after bending it several (200) times (see Figure S1). Scanning-electron microscopy (SEM) images were used to characterize the morphology and microstructure of the cross-section and top surface of the membrane as shown in Figures 1 c and d. The membrane displays an asymmetric cross-section with fingerlike holes. This structure is similar to those of most of traditional polymeric membranes formed by a phase-inversion process.[11] On the top of the membrane, there is a thin skin layer or a so-called separation layer. The enlarged top-view SEM image of the membrane surface shows that it is composed of numerous spherical microparticles of a sub-micrometer scale. Such a structure is different from the traditional membranes. The microparticles are disorderly arranged but closely connected, thus giving rise to a rather rough surface. On the surfaces of these microparticles there are much finer protrusion structures of the nanometer scale. The micro- and nanoscale composite structure is crucial for obtaining superwetting behavior according to the Cassie model derived from Young's equation.[12] The bottom surface of the membrane is completely different from the top surface. It gives a typical porous structure and no microspheres are observed (see Figure S2). These results indicate that the existence of NaCl in water affect only the microstructure of the top surface of the membrane. In other words, NaCl seeds are only produced at the interface of two liquids during the phase-inversion process just as we proposed above. Energy dispersive X-ray (EDX) analysis on both top and bottom surfaces of the membrane helps to prove this proposal further (see Figure S3). A weak peak at 1.05 keV, ascribed to NaK, is observed for the top surface but not detected for the bottom. The appearance of this peak is a result of the small amount of the NaCl residue on the top surface of the membrane. Figures 1 e and f show the wetting behavior of oil and water on the top surface of the as-prepared PAA-g-PVDF membrane. A water contact angle (CA) of about 0° in air and an underwater oil (1,2-dichloroethane) CA of approximately 160° are observed, thus suggesting a superhydrophilic and underwater superoleophobic property.

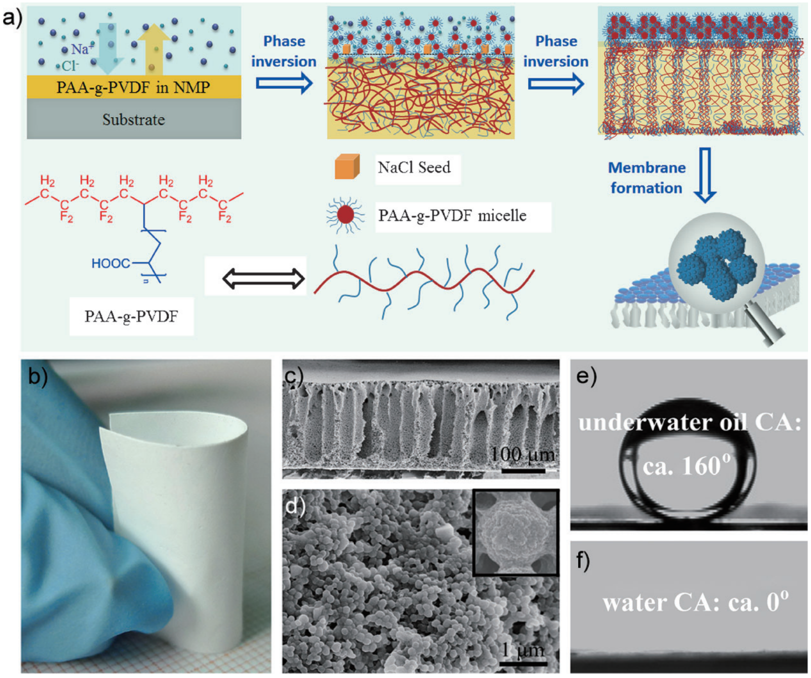

Figure 1. a) Formation of a superhydrophilic underwater superoleophobic PAA-g-PVDF membrane by a salt-induced phase-inversion process. b) Photograph of an as-prepared PAA-g-PVDF membrane. c) Cross-section and d) top-view SEM images of the membrane. Photographs of an underwater oil droplet (e) and a water droplet on the membrane (f). The PAA-g-PVDF membrane was prepared by using PAA-g-PVDF with a graft ratio of 2.5 wt % in the case of a salt concentration of 35 %.

The influence of the NaCl concentration on the microstructure and wettability of

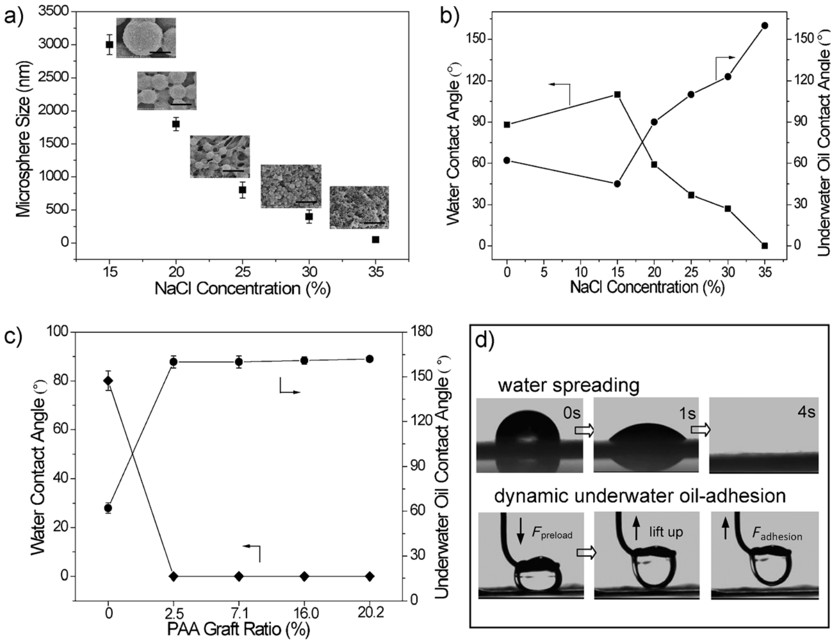

Figure 2. Characterization of microstructure and wettability of PAA-g-PVDF membranes. a) Variation of the particle size of the membranes on the top surfaces with a concentrated NaCl solution in the coagulation bath. b) Variation of the water CA and underwater oil CA of the membrane with the concentration of the NaCl solution in the coagulation bath. c) Variation of the water CA and underwater oil CA of the membrane with the PAA graft ratio. d) Photographs of dynamic measurements of water spreading (top) and underwater oil-adhesion (bottom) on the membrane.

membranes was investigated. As shown in Figure 2a, for a wide range (15% to 35%) of NaCl concentrations, the top surfaces of the membranes are all composed of spherical particles but with quite different sizes. With increasing NaCl concentration, the particle size quickly decreases. With a NaCl concentration of 15%, the particle size is as large as 2–4 μm. When the NaCl concentration is as high as 35%, the average particle size is reduced to a few tens of nanometers. We think that the particle size is directly influenced by the size of the NaCl seeds. The higher the NaCl concentration, the smaller the NaCl seeds formed at the interface of two liquids. The microstructure of the top surface of the membranes, that is the size of spherical particles, has great influence on the wettability of water and underwater oils. As shown in Figure 2b, the membrane prepared from pure water coagulation bath exhibits a water CA of 88° and an underwater oil CA of 62°. With addition of 15% NaCl, the water CA increases to 110° and the underwater oil CA decreases slightly to 45°. After that, the water CA and underwater oil CA change inversely with an increase of the NaCl concentration. The former decreases and the latter increases quickly. With up to 35% NaCl, the membrane displays about a 0° water CA and approximately a 160° underwater oil CA, thus exhibiting a superhydrophilic and underwater superoleophobic wetting behavior. This result indicates that the variation of wettability is mainly relevant to the size of the particles on the membrane surface. As for a rough surface, its contact angle can be interpreted by Wenzel's model where the surface roughness is considered as an important factor which influences the wettability.[13] The roughness can enhance both the wetting and anti-wetting behavior of a liquid on a solid. According to the definition of roughness by R. N. Wenzel, the roughness factor is the ratio between the actual surface area and the geometric surface area of a rough surface.[14] Therefore, as for a particle-composed surface, a smaller particle size usually brings about a greater roughness. To further prove this conclusion, the membranes formed by PAA-g-PVDF with a different PAA graft ratio (namely 2.5 wt%, 7.1 wt%, 16.0 wt%, and 20.2 wt%) were prepared for 35% concentration of NaCl and their surface morphology and membrane wettability were investigated (see Figure S4). It can be seen that the different graft ratio of PAA in the PAA-g-PVDF polymer has little effect on the structure of the top surface of the membrane. No matter what the graft ratio, all the top surfaces of the membranes are composed of spherical particles with a similar size (sub-micrometer scale). Correspondingly, the membranes exhibit similar wetting properties with about a 0° water CA and 160° underwater oil CA (Figure 2c).

To examine the dynamic wetting behavior of water on the membrane, a high-speed camera system was used to record the spreading process of a water droplet. When a water droplet (3 μL) contacts the membrane surface, it spreads out quickly and a nearly zero CA is reached within 4 seconds (Figure 2d, top). The oil wettability of the membrane was characterized by measuring the oil CAs and adhesion force under water. The oil exhibits a high underwater CA of about 160°, thus indicating the excellent underwater superoleophobic property. Water usually has a higher density than oils. The superhydrophilic and underwater superoleophobic property ensures water-layer formation on the membrane surface and avoids direct contact between oils and membrane surfaces during oil/water separation. It could greatly enhance the antifouling property of the membrane and keep separation efficiency stable with time. Simultaneously, the membrane behaves as a superior anti-oil adhesion property. Figure 2d (bottom) shows the photographs of a 3 μL oil droplet (1,2-dichloroethane is taken as an example) touching and leaving the membrane surface. The droplet was forced to sufficiently contact the membrane surface with an obvious deformation, and it was then lifted up. There is no deformation observed and no detectable adhesion force could be measured during the leaving process, thus indicating an extremely low-oil adhesion force. This characteristic is also advantageous to an antifouling performance of the membrane.

To test separation capability of the PAA-g-PVDF membranes for oil-in-water emulsions, both surfactant-free and surfactant-stabilized emulsions, namely hexadecane-in-H_2O (hexadecane/H_2O), toluene-in-H_2O (toluene/H_2O), diesel-in-

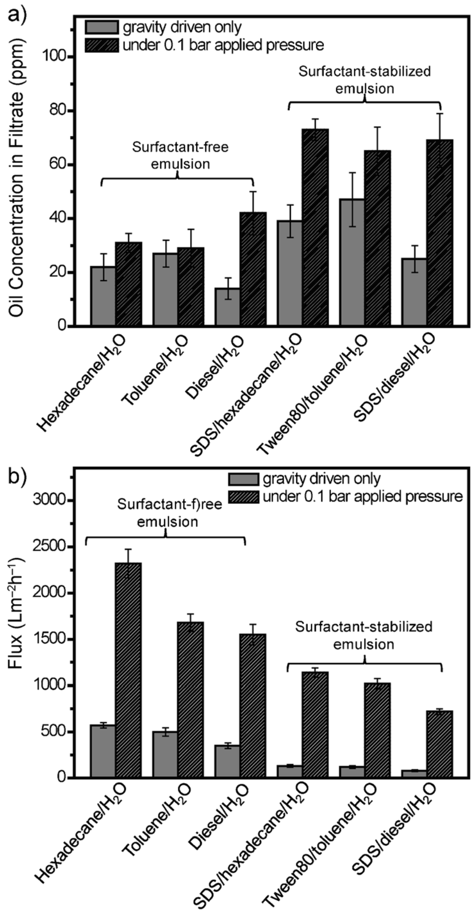

Figure 3. Results for the separation of various oil-in-water emulsions. a) Oil concentration in the corresponding filtrate and b) flux for a series of surfactant-free and surfactant-stabilized oil-in-water emulsions permeating the membrane.

H_2O (diesel/H_2O), SDS-stabilized hexadecane-in-H_2O (SDS/hexadecane/H_2O), Tween 80-stabilized toluene-in-H_2O (Tween 80/toluene/H_2O), and SDS-stabilized diesel-in-H_2O (SDS/diesel/H_2O) with a 1 % oil volume percentage and an oil droplet size of 2–10 μm for surfactant-free emulsions, and several hundreths of a nanometer to 5 μm for surfactant-stabilized emulsions, were prepared. The as-prepared emulsions were then poured onto PAA-g-PVDF membranes to carry out filtration separation driven by either a small applied transmembrane pressure (0.1 bar used in this work) or solely gravity. All emulsions were successfully separated in one step. The oil content in water after a one-time separation was measured by a total organic carbon (TOC) analyzer. As shown in Figure 3 a, for the surfactant-free emulsions, the oil content in the filtrates are all below 40 ppm and for the surfactant-stabilized emulsions, the oil content in the filtrates are all below 80 ppm. It reveals a high separation efficiency of the membrane. The higher oil content obtained for surfactant-stabilized emulsions is probably due to the disturbance of dissolved surfactants in the filtrate. The TOC value is the sum of both oil and surfactant residues in the filtrate. A conductivity experiment has confirmed that there is 12–15 ppm SDS in the filtrate for the SDS/hexadecane/H_2O emulsion. In general, the oil content treated under 0.1 bar of applied pressure is slightly higher than that driven by gravity only. Probably, in the former case, a tiny amount of oil droplets are forced to pass through the membranes accompanied by deformation. The fluxes of the membrane were calculated by measuring the time needed for completely permeating a certain volume of various oil-in-water emulsions. As shown in Figure 3 b, all the emulsions exhibit high fluxes with 0.1 bar of applied pressure across the membrane. The fluxes of 2320, 1680, 1550, 1140, 1020, 720 $L\,m^{-2}h^{-1}$ for hexadecane/H_2O, toluene/H_2O, diesel/H_2O, SDS/hexadecane/H_2O, and Tween 80/toluene/H_2O and SDS/diesel/H_2O, respectively, are obtained. These values are several times higher than those of traditional filtration membranes with similar permeation properties. For the separations driven by gravity, the corresponding fluxes are 570, 500, 350, 130, 120, 80 $L\,m^{-2}\,h^{-1}$. These values are comparable to those of reported membranes used with an applied pressure. Given that the permeation was driven solely by gravity, such separation performance is very attractive from the viewpoint of energy conservation, as compared to the traditional filtration membranes such as ultrafiltration membranes where a transmembrane pressure of one to several bars is usually applied to accomplish emulsion separation. To observe the separation effect, an optical microscope was used to observe the difference between the original emulsion and the corresponding collected filtrates (see Figure S6). For both surfactant-free and surfactant-stabilized emulsions, dense oil droplets of the micrometer and sub-micrometer scale are observed clearly in the starting emulsions. Correspondingly, in the collected filtrates, no droplets are observed in the image. The maximum transmembrane pressure (e.g. intrusion pressure), which indicates the maximum height of liquid that the membrane can support, is one of the important parameters for practical applications. The intrusion pressure of our PAA-g-PVDF membrane was measured, using a water pump, to be 0.3 bar. This pressure is equivalent to a 3.1 m height water.

To test the antifouling property of the membrane, a home-made apparatus was used for continuous separation of an oil-in-water emulsion (inset in Figure 4 a). In the apparatus, water could continuously pass through the membrane and oil accumulated above the membrane could cross-flow away to avoid blocking water permeation. By using this apparatus, continuous separation of the hexadecane/H_2O emulsion for up to 30 hours was done and the flux was detected in real time. During the process, no obvious flux decline is observed. The flux decreases from 570 to 530 $L\,m^{-2}\,h^{-1}$ with a decline rate of less than 7 % (Figure 4 a). The cycling performance of the membrane for treatment of the SDS/hexadecane/H_2O emulsion was also carried out. For each cycle, a certain volume of emulsion permeated the membrane and then the membrane was simply rinsed with water to recover the flux. The variation of the flux during this process was performed and is shown in Figure 4 b. It can be seen that the flux decreases gradually with time within one cycle, then it recovers completely to the starting flux after cleaning. These results indicate an excellent antifouling property of the PAA-g-PVDF membrane for long-term use.

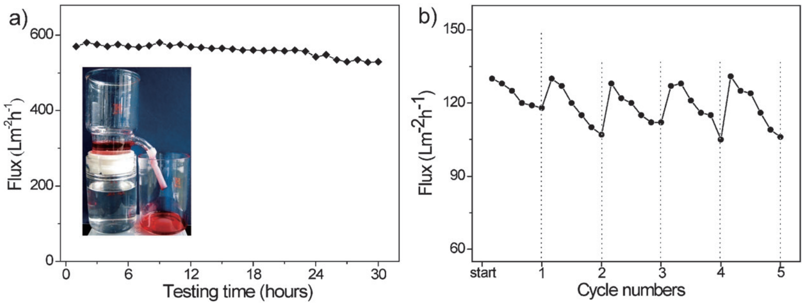

Figure 4. Study of the antifouling property of PAA-g-PVDF membrane. a) Real-time monitoring of the variation of flux as a function of time for up to a 30 h separation of a hexadecane/H_2O emulsion. The inset shows a homemade apparatus for continuous separation where the oil is dyed red. b) Change of the flux and flux recovery in the separation of a SDS/hexadecane/H_2O emulsion over five cycles. In each cycle, the flux was monitored hourly and six points were recorded within a cycle. After one cycle the membrane was rinsed with water only to remove surface adsorbent.

In summary, a superhydrophilic and underwater superoleophobic PAA-g-PVDF membrane have been fabricated by a salt-induced phase-inversion method. The as-prepared membranes, using only gravity or a small applied transmembrane pressure, can effectively separate oil-in-water emulsions with high separation efficiency and much higher fluxes than traditional polymeric filtration membranes with similar permeation properties. Therefore, the PAA-g-PVDF-membrane-based separation methodology is expected to be highly energy efficient. The underwater superoleophobic wettability endows the membrane with a superior antifouling property and easy recycling for long-term use, which matches well with the requirements for oil/water separation in a large volume. Our membrane is promising for practical applications for treating wastewater produced in industry and daily life.

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