Omniphobic Polyvinylidene Fluoride (PVDF) Membrane for Desalination of Shale Gas Produced Water by Membrane Distillation

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ABSTRACT: Microporous membranes fabricated from hydrophobic polymers such as polyvinylidene fluoride (PVDF) have been widely used for membrane distillation (MD). However, hydrophobic MD membranes are prone to wetting by low surface tension substances, thereby limiting their use in treating challenging industrial wastewaters, such as shale gas produced water. In this study, we present a facile and scalable approach for the fabrication of omniphobic polyvinylidene fluoride (PVDF) membranes that repel both water and oil. Positive surface charge was imparted to an alkaline-treated PVDF membrane by aminosilane functionalization, which enabled irreversible binding of negatively charged silica nanoparticles (SiNPs) to the membrane through electrostatic attraction. The membrane with grafted SiNPs was then coated with fluoroalkylsilane (perfluorodecyltrichlorosilane) to lower the membrane surface energy. Results from contact angle measurements with mineral oil and surfactant solution demonstrated that overlaying SiNPs with ultralow surface energy significantly enhanced the wetting resistance of the membrane against low surface tension liquids. We also evaluated desalination performance of the modified membrane in direct contact membrane distillation with a synthetic wastewater containing surfactant (sodium dodecyl sulfate) and mineral oil, as well as with shale gas produced water. The omniphobic membrane exhibited a stable MD performance, demonstrating its potential application for desalination of challenging industrial wastewaters containing diverse low surface tension contaminants.
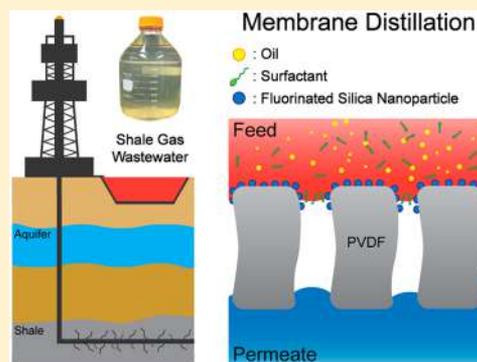
INTRODUCTION

Natural gas from unconventional shale plays has the potential to secure energy supply and reduce carbon dioxide emissions by minimizing the dependence on fossil fuel energy production.[1] Breakthroughs in horizontal drilling and hydraulic fracturing technologies have allowed access to vast natural gas resources from shale formation.[2] However, environmental impacts of shale gas production, including wastewater management and potential groundwater contamination, remain major challenges for efficient exploitation of this emerging energy resource.[3,4]

The Environmental Protection Agency (EPA) estimates 25 000−30 000 new shale gas wells were developed annually in the United States between 2011 and 2014, with two to four million gallons of water used for drilling and hydraulic fracturing of each well.[5,6] Shale gas produced water comprises water trapped in underground formation and flowback from hydraulic fracturing.[7] This waste stream is characterized by high total dissolved solids (TDS) concentrations and hydrocarbon content (i.e., oil and grease) due to the nature of formation water and high levels of chemical additives used in hydraulic fracturing.[8] Shale gas produced water is challenging to treat by conventional water treatment practices due to its high salinity and complex physicochemical composition.[6]

Membrane distillation (MD) is an emerging technology that shows promise for efficient desalination of high salinity industrial wastewaters.[9,10] MD desalination is driven by a vapor pressure gradient between a hot feed stream and a cold permeate (distillate) stream. Performance of this thermal-based separation process is only slightly sensitive to the feed salinity, rendering MD suitable for desalination of highly saline shale gas produced water.[6,11] The temperature of shale gas produced waters, which originates from geothermal heat sources at well sites, can be as high as 100 °C.[6] Hence, the elevated temperature of produced water could be exploited to drive MD desalination.

Despite the advantages of applying MD to produced water desalination, potential wetting of the MD membrane remains a practical shortcoming that hinders its implementation. Shale gas produced water contains high levels of low surface tension contaminants, such as oil and grease, organic solvents, and surfactants.[12] These low surface tension substances can potentially wet conventional hydrophobic MD membranes, resulting in failure of the MD desalination process.

Omniphobic membranes resisting wetting to both water and low surface tension liquids hold promise for MD application in treatment of shale gas produced water.[13,14] Omniphobicity can be realized by constructing surfaces with ultralow interfacial energy and re-entrant structures that together allow a metastable

Cassie−Baxter state for the liquid−solid−vapor interface.[15] Numerous approaches have been attempted to create surfaces that feature a re-entrant structure using electrochemical[16] and plasma etching,[17] anodization,[18] and photolithography,[19] and to achieve ultralow surface energy by silanization[19] and coating[20,21] of fluoroalkyl molecules. However, these techniques have mostly focused on fabricating omniphobic surfaces for impermeable prototype substrates (e.g., silicon wafer)[22] or fabric materials.[23]

Microporous polyvinylidene fluoride (PVDF) membranes have been widely used for MD applications because of their hydrophobic nature, excellent chemical compatibility, and physical robustness.[24] The PVDF membrane structure properties that are ideal for MD, such as high porosity and submicrometer pore size, can be easily controlled by the well-established phase separation fabrication technique.[25] However, conventional hydrophobic PVDF membranes are prone to wetting by low surface tension substances. Furthermore, surface engineering of PVDF membranes to achieve desired chemical and physical properties is challenging because PVDF is chemically inert and possesses no surface groups.

This study presents a scalable approach to fabricate omniphobic membranes for desalination of shale gas produced water by membrane distillation. Specifically, we demonstrate surface modification of a conventional hydrophobic PVDF microporous substrate to produce an omniphobic membrane that exhibits surface wetting resistance to low surface tension substances. Desalination performance of the omniphobic membrane was evaluated in direct contact membrane distillation with synthetic wastewaters containing low surface tension contaminants, including surfactants and mineral oil. Produced water from shale gas industry was further employed to evaluate MD performance of the omniphobic membrane. Implications of the results for the use omniphobic membranes in MD to treat challenging industrial wastewaters are evaluated and discussed.

■ MATERIALS AND METHODS

Materials and Chemicals. ACS grade sodium hydroxide (NaOH, J.T. Baker, Phillipsburg, NJ), (3-Aminopropyl)-triethoxysilane (99%, APTES) (Sigma-Aldrich, St. Louis, MO), anhydrous ethanol (100%, Decon Laboratories, Inc., PA), silica nanoparticles (SiNPs) with an average diameter of 0.1 μm (AngstromSphere Monodispersed Silica Powder, Fiber Optic Center Inc., MA), and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (FDTS, Gelest Inc., PA) were used for the surface modification of the PVDF substrate.

Surface Modification of PVDF Membrane. A flat sheet polyvinylidene fluoride (PVDF) membrane with a nominal pore size of 0.45 μm and an average thickness of 125 μm was used as a substrate (HVHP, Millipore, Billerica, MA). The PVDF substrate was immersed in a 7.5 M NaOH solution at ∼70 °C for 3 h to generate hydroxyl surface functionality. To ensure complete soaking of PVDF substrate in the NaOH solution, the membrane was prewetted by ethanol. An alkaline treated PVDF substrate was then soaked in 1% v/v APTES in anhydrous ethanol for 1 h under gentle stirring to functionalize the surface with amine terminal groups, rendering the PVDF substrate positively charged. The APTES-functionalized PVDF substrate was immersed in an aqueous SiNP solution for 1 h under gentle mixing. APTES functionalization and SiNP coating were executed with only the top surface of the membrane in contact with the suspension. The aqueous SiNP solution was prepared by dispersing 0.05 wt % SiNPs in acetate buffer with an ionic strength of ∼1 mM. The pH of the suspension was adjusted to 4

to promote electrostatic attraction between the negatively charged SiNPs and the positively charged PVDF substrate.

After attaching SiNPs to the PVDF substrate, the membrane was coated with perfluorodecyltrichlorosilane (FDTS) via vapor-phase silanization to lower the membrane surface energy. An SiNP-coated PVDF membrane was fixed on the wall of a glass bottle (Septa jars, Thermo Fisher Scientific, Inc., MA) using heat resistant tape (Kapton Polyimide, Uline, WI). The bottle was nitrogen purged for 20 min through the septa cap. After nitrogen purging, 100 μL FDTS was placed in a small Petri dish inside the bottle. Then, the SiNP-coated PVDF membrane was silanized in a vacuum oven (vacuum pressure at ∼80 kPa and temperature at ∼100 °C) for 17 h.

The stability of surface coating with SiNPs and FDTS was assessed by reevaluation of SEM images and contact angles after the modified membranes were subjected to harsh chemical and physical stresses. Chemical stress was applied by exposing the modified PVDF membrane for 20 min to a pH 2 solution (HCl), a pH 12 solution (NaOH), or a 1.0 M NaCl solution, followed by thorough rinse with DI water. Physical stress was exerted by immersing the membranes in a sonicating water bath (Fisher Scientific F60) for 20 min.

Membrane Characterization. Surface morphology of the modified PVDF membranes was investigated by scanning electron microscopy (SEM, Hitachi SU-70). Before imaging, membrane samples were sputter-coated with a chromium layer (BTT-IV, Denton Vacuum, LLC, Moorestown, NJ). To obtain cross-section images, membranes were dried at room temperature and freeze-fractured using liquid nitrogen before the chromium coating. Acceleration voltage of 5.0 kV was applied to image all membrane samples.

Zeta potential of membrane surface was evaluated by a streaming potential analyzer utilizing an asymmetric clamping cell (EKA, Brookhaven Instruments, Holtsville, NY) as described elsewhere.[26] Measurements were performed with a solution containing 1 mM KCl and 0.1 mM KHCO$_3$. Electrophoretic mobility of the silica nanoparticles (SiNPs) was measured in a background electrolyte of 1 mM NaCl using a Zeta Potential Analyzer (ZetaPals, Brookhaven Instruments, Holtsville, NY) at different pH values. The zeta potentials of SiNPs were calculated from electrophoretic mobility measurement by using the tabulated data of Ottewill and Shaw.[27] The elemental composition of the membranes was investigated by Fourier transform infrared (FTIR) spectroscopy with attenuated total reflectance (ATR). Absorbance spectra were measured with 32 scans of each sample at a spectral resolution of 1 cm^{-1}. Background measurements in air were collected before each membrane sample measurement.

Contact angles of the modified PVDF membranes for liquids with a wide range of surface tensions, including water (γ = 72.8 mN/m), 0.1 mM SDS in 1.0 M NaCl ($\gamma \approx$ 38 mN/m), and mineral oil ($\gamma \approx$ 30 mN/m) were measured by a goniometer (OneAttension, Biolin scientific instrument) using the sessile drop method. A 5-μL liquid droplet was placed on the membrane sample and photographed using a digital camera for 3 min. The left and right contact angles were analyzed from the digital images by a postprocessing software (OneAttension software). The measurements were conducted on a minimum of two random locations with three different membrane samples, and the data were averaged.

Model and Shale Gas Produced Water Feed Solutions. NaCl (1.0 M) solution at 60 °C and DI water at 20 °C were employed as feed and permeate streams, respectively, for the
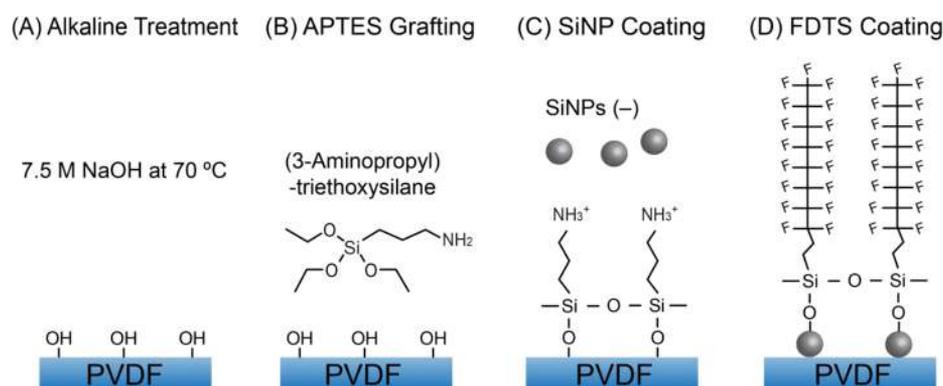
Figure 1. Schematic illustrating the procedure for omniphobic surface modification of PVDF membrane. (A) Hydroxyl groups are generated on the surface of the PVDF substrate by alkaline treatment with a 7.5 M NaOH solution at 70 °C for 3 h. (B) Hydroxyl groups are used for grafting of (3-Aminopropyl)triethoxysilane (APTES). (C) Silica nanoparticles (SiNPs) bind to APTES functionalized PVDF substrate via electrostatic attraction. (D) SiNPs are coated with perfluorodecyltrichlorosilane (FDTS) via vapor-phase silanization.

initial 2 h DCMD runs. After stabilization, sodium dodecyl sulfate (SDS) or mineral oil was added to the feed solution every 2 h during the DCMD experiment to evaluate wetting resistance of the control and the modified PVDF membranes. The SDS concentrations in the feed solution after sequential SDS addition were 0.05, 0.1, and 0.2 mM. Surface tensions with varying SDS concentrations in DI water and 1.0 M NaCl solution were determined by a tensiometer (Sigma 300, KSV Instrument, Helsinki) using the Wilhelmy plate method. Mineral oil-in-water emulsion at concentration of 1% v/v was prepared by adding 0.1% v/v Tween80 (nonionic surfactant) (Sigma-Aldrich, St. Louis, MO) as an emulsifier. The mineral oil concentrations in the feed solution after addition of emulsion every 2 h DCMD were 0.001, 0.005, and 0.01% v/v, which correspond to 8, 40, and 80 mg/L. Size of mineral oil droplets in the feed was analyzed by dynamic light scattering (DLS) measurements (ZetaPals, Brookhaven Instruments, Holtsville, NY). The feed solution (initial volume of 1 L) was replenished every 50 mL loss to maintain variation of SDS or mineral oil concentration within 5%.

Shale gas produced water from the Permian Basin in Texas (provided by Gradiant Corporation) was prefiltered through 16-μm filter (Ashless grade 44, GE Whatman, PA) to remove large particulate and suspended matters before they were supplied to DCMD experiments. The major composition and key properties of the prefiltered shale gas produced water were analyzed by a third-party analyzing laboratory (Environmental Service Laboratories, Inc., PA) (Table S1). The biological activity of the shale gas wastewater was minimized by storing the sample at 4 °C. The DCMD experiments with shale gas wastewater were conducted until the feed solution (initial volume of 1 L) was concentrated by 50% (or until the permeate volume reached 500 mL).

Membrane Distillation Performance Tests. The MD performance of the control and modified PVDF membranes was evaluated by a laboratory-scale direct contact membrane distillation (DCMD) unit. The membrane was inserted into a custom-built transparent acrylic cell with channel dimensions of 77 mm in length, 26 mm in width, and 3 mm in depth. The effective membrane area exposed to feed and permeate (distillate) streams was 20.0 cm². Spacers were inserted in both feed and permeate channels to support and maintain the membrane geometry in the cell. The temperatures of feed and permeate solutions were maintained at 60 and 20 °C, respectively. A slightly higher cross-flow rate for the feed stream,

0.4 L/min (cross-flow velocity of 8.5 cm/s), than for the permeate stream, 0.35 L/min (cross-flow velocity of 7.5 cm/s), was used to facilitate the detection of MD membrane wetting.

The water vapor flux, J_w, across the membrane was determined by measuring the increase in permeate weight. Electric conductivity of the permeate solution was monitored to assess the NaCl concentration in the permeate stream, C_P. The cumulative salt mass in the permeate stream, $V_P C_P$, was divided by the volume of water vapor flux to calculate the permeate salt concentration, from which the salt (NaCl) rejection, R_{NaCl}, was determined using

$$R_{NaCl} = \left(1 - \frac{V_P C_P / J_w A_m t}{C_F}\right)100 \tag{1}$$

where V_p is the volume of permeate stream, C_F is the initial NaCl concentration in the feed (1.0 M), A_m is the membrane area, and t is time.

■ RESULTS AND DISCUSSION

Surface Properties of Modified Omniphobic Membrane. Silica nanoparticles (SiNPs) were used for the omniphobic surface modification of a PVDF substrate because SiNP is abundant in hydroxyl functional groups that allow surface fluorination via well-established silane chemistry to lower the membrane surface energy.[28] Further, spherical SiNP is a geometry that provides a re-entrant structure for substrate surface, which is critical for achieving surface omniphobicity.[29]

SiNPs possessing negative surface charge were attached to aminosilane functionalized PVDF substrate via electrostatic attraction (Figure 1). First, a PVDF substrate was treated with high concentration NaOH solution (7.5 M) under high temperatures (~70 °C) to generate hydroxyl functional groups on PVDF polymer chains. Mechanisms for the formation of hydroxyl groups on a PVDF chain by alkaline treatment are well described in previous studies.[30,31] After alkaline treatment, the PVDF substrate was soaked in an aminosilane solution (APTES 1% v/v in anhydrous ethanol) to functionalize the surface with amine terminal groups. The APTES covalently binds to the hydroxyl groups on the PVDF substrate via hydrolysis and condensation, rendering the substrate surface positively charged. Positive surface charge of the APTES-functionalized PVDF membrane enables binding of the negatively charged SiNPs via electrostatic attraction. Grafted SiNPs were then coated with
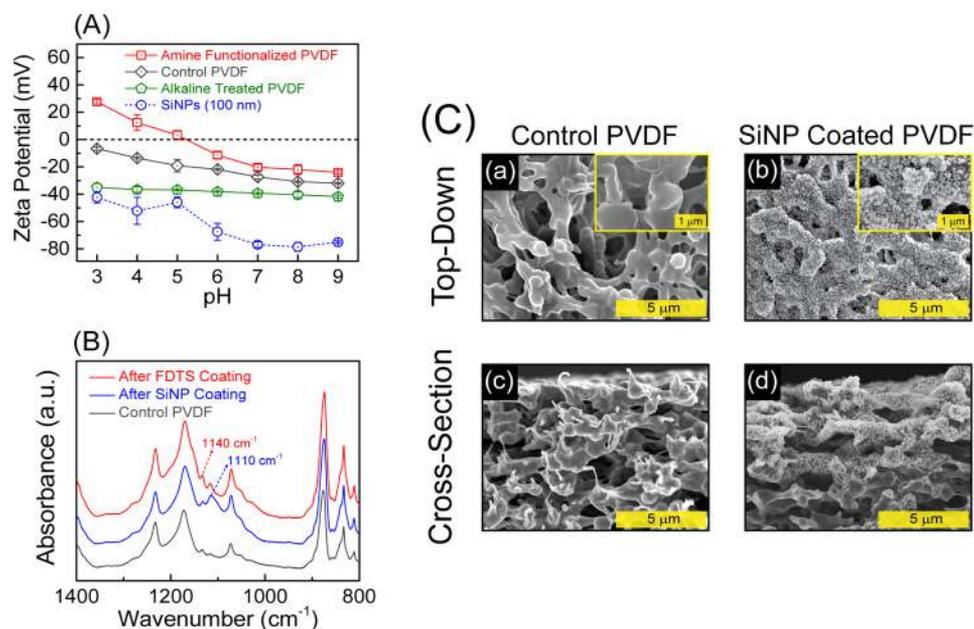
Figure 2. (A) Zeta potential as a function of pH of silica nanoparticles (SiNPs) and PVDF membranes at various stages of surface modification. (B) ATR-FTIR spectra of control, SiNP-coated, and FDTS-coated PVDF membranes. (C) SEM images depicting top-down and cross-section of control and SiNP-coated PVDF membranes.

perfluorodecyltrichlorosilane (FDTS) to lower the surface energy of the membrane.

Zeta potentials of the control, alkaline treated, and amine functionalized PVDF membranes were evaluated to confirm a binding mechanism between the SiNPs and the PVDF substrate (Figure 2A). The control PVDF substrate was found to be negatively charged over the entire pH range investigated, consistent with other reported data.[32,33] Because the control PVDF membrane does not possess a fixed surface charge, the observed negative zeta potential may be attributed to the adsorption of anions, such as OH⁻ and Cl⁻ from the background electrolyte, onto the membrane surface, as proposed elsewhere.[34,35] Zeta potential of the PVDF substrate became more negative and stable over the whole pH range after treatment with alkaline solution (7.5 M NaOH). The PVDF membrane became hydrophilic after alkaline treatment due to the formation of hydroxyl groups.[30,31] Increased negative surface charges of the alkaline treated PVDF substrate is likely because the hydrophilic surface offers closer proximity for anions (i.e., OH⁻ and Cl⁻) from the background electrolyte. Functionalization of the substrate surface with APTES reduced the negative zeta potential (i.e., more positive charge) of the PVDF membrane with an extrapolated isoelectric point of ~5.2 (Figure 2A). The SiNP coating was performed under suspension pH at 4, where the zeta potential of the amine functionalized PVDF substrate is positive while that of the SiNPs is negative.

Surface morphology of the PVDF substrates before and after SiNP coating was investigated by scanning electron microscope (SEM). For comparison, top-down and cross-section SEM images of the control PVDF and the SiNP-coated PVDF membranes are shown in Figure 2C. The top-down SEM image shows that dense SiNP coating formed on the surface of the PVDF substrate (Figure 2C-b). In addition, the cross-section SEM image of the SiNP-coated membrane (Figure 2C-d) indicates that SiNPs penetrated into the porous substrate and created a 3−5 μm thick SiNP coating layer. A re-entrant structure developed by a spherical or cylindrical surface geometry creates a

local kinetic barrier for the transition from the metastable Cassie−Baxter state to the fully wetting Wenzel state for low surface tension liquids. Results from the SEM images clearly show a re-entrant surface structure achieved by coating with spherical SiNPs. In addition, SiNP coating inside the pores (Figure 2C-d) is expected to offer multiple kinetic barriers, and thus further increase membrane wetting resistance against low surface tension liquids.

Surface coatings of the PVDF substrate with SiNPs and FDTS were confirmed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy measurement. Figure 2B shows the 1400−800 wavenumber region of the FTIR spectra, covering the characteristic absorbances of the distinct functional groups in the control PVDF substrate and SiNP-, and FDTS-coated PVDF membranes. After surface coating with SiNPs, a new peak at ~1110 cm⁻¹ which corresponds to silanol groups on the SiNPs was detected. An increase in absorbance intensity at ~1140 cm⁻¹, which is ascribed to CF_2 symmetric stretching mode, was observed after coating with FDTS, substantiating successful surface fluorination via vapor-phase silanization.

Wetting Resistance of Modified Omniphobic Membrane. Contact angles for the control and the modified PVDF membranes were measured to evaluate the surface wetting resistance to liquids with a wide range of surface tensions, including water (γ = 72.8 mN/m), 0.1 mM sodium dodecyl sulfate (SDS) in 1.0 M NaCl ($\gamma \approx 38$ mN/m), and mineral oil ($\gamma \approx 30$ mN/m). We have selected SDS and mineral oil as representative surface wetting agents found in shale gas wastewater streams. The SDS solution was prepared with high salinity (1.0 M NaCl) to mimic the high TDS shale gas wastewater. Also, we note that the surface tension of ionic surfactant (i.e., SDS) solution is significantly reduced under high salt concentrations because electrolytes screen the charge of the polar head groups, leading to a higher surfactant density at the liquid−air interface as described in previous studies.[36]

Contact angles of liquids with different surface tensions on the control and the modified PVDF membranes are shown in Figure

3. Due to the dynamic behavior of droplets of certain testing liquids, the contact angles were monitored for 3 min. The control
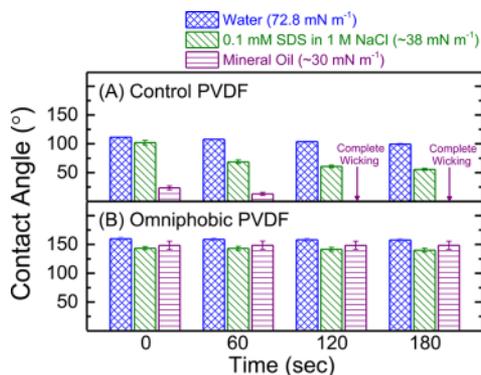
Figure 3. Variation in static contact angle of (A) control PVDF and (B) modified omniphobic PVDF membranes measured with DI water, 0.1 mM SDS in 1 M NaCl, and mineral oil. A 5-μL liquid droplet was placed on the membrane surface and the contact angle was monitored for 3 min (180 s). Error bars represent standard deviations of two contact angles from three different membrane samples. Surface tensions of the liquids are indicated in legends.

PVDF substrate maintained a relatively high ($\sim$110°) and stable water contact angle during 3 min of observation. However, the control PVDF substrate failed to resist wetting by surfactant (SDS) solution and mineral oil (Figure 3A). The contact angle of 0.1 mM SDS solution reduced from $\sim$100° to $\sim$55° during the 3 min measurement interval and complete wetting was found 2 min after placing mineral oil on the control PVDF substrate. The modified PVDF membrane exhibited superhydrophobicity with a water contact angle >150° (Figure 3B). The observed significantly high water contact angle on the modified PVDF membrane is attributed to vapor/air pockets developed between SiNPs attached on the substrate and ultralow surface energy achieved by FDTS coating. Notably, the modified PVDF membrane exhibited high (>130°) and stable (for 3 min observation) contact angles with both SDS solution and mineral oil. An omniphobic surface that repels both water and low surface tension liquids (e.g., oil and alcohol) is available only when the surface has features with a re-entrant structure and ultralow surface energy. The observed wetting resistances of the modified PVDF membrane to SDS solution and mineral oil demonstrate that substrate coatings with SiNP and FDTS successfully imparted surface omniphobicity to the control PVDF membrane.

The irreversibility of SiNP and FDTS coatings on the substrate surface and subsequent membrane wetting resistance were assessed by subjecting the modified PVDF membranes to harsh chemical (i.e., pH 2, pH 12, or 1.0 M NaCl) and physical (i.e., bath sonication for 20 min) stresses. SEM micrographs taken after stress protocols showed no significant difference compared to the results obtained from the SiNP-coated membrane not subjected to stresses (see Figure S1 in the Supporting Information). The results indicated that electrostatic attraction between the negatively charged SiNPs and the positively charged PVDF substrate was strong enough to render the SiNP coating irreversible. Liquid contact angles can be used as a proxy to appraise the stability of SiNP and FDTS coatings because the apparent contact angle is determined by both surface morphology and chemistry. Figure 4 presents the contact angles of water, 0.1 mM SDS in 1.0 M NaCl, and mineral oil on the modified PVDF membranes before and after chemical and
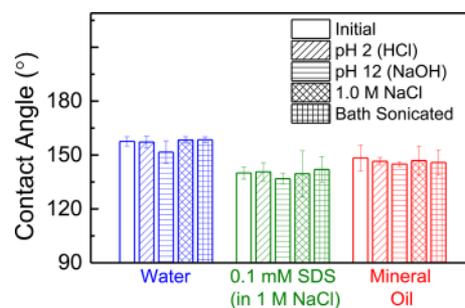
Figure 4. Contact angles of DI water, 0.1 mM SDS in 1 M NaCl, and mineral oil on the membrane surface measured immediately after surface modification (indicated as initial) and after the modified membranes were subjected to the indicated physical and chemical stresses. Contact angles 3 min after placing 5 μL of the testing liquid were determined to be a steady-state value. The variation in liquid volume during the 3 min measurement was within 0.5 μL. Error bars represent standard deviations of two contact angles from three different membrane samples.

physical stresses. Contact angles did not change significantly for all tested liquids, compared to those analyzed immediately after surface modification (indicated as initial in Figure 4). We attribute the observed stable wetting resistance of the modified PVDF membrane to the robust SiNP binding by electrostatic attraction and the strong covalent Si—O—Si linking between FDTS and SiNP achieved via silanization (Figure 1). The confirmed stable wetting resistance of the modified PVDF membrane ensures a long-term omniphobic functionalization under typical MD operational conditions.

Desalination Performance with High Salinity, Low Surface Tension Feed Water. To investigate the desalination performance of the control PVDF and modified omniphobic membranes with feedwater containing low surface tension contaminants, we performed direct contact membrane distillation (DCMD) experiments using feed solutions with varying concentrations of sodium dodecyl sulfate (SDS, anionic surfactant) and mineral oil. SDS and mineral oil were sequentially introduced to the feed every 2 h during the DCMD experiment after an initial 2 h stabilization period with a 1.0 M NaCl feed solution. Water (vapor) flux and salt (NaCl) rejection were monitored for 8 h.

Surfactants are amphiphilic organic compounds comprising a hydrophilic polar head and a hydrophobic nonpolar tail.[37] Below the critical micelle concentration (CMC), diffusion of surfactant toward the air—liquid interface is triggered by the hydrophobic tail, which results in a decrease of the solution surface tension. When surfactants are present in a solution of high salinity, they significantly reduce the surface tension of the medium because the charge of the surfactant polar headgroup is screened by counterions, leading to a higher surfactant density at the liquid—air interface.[38] Surface tensions of the SDS solution measured using a tensiometer were much lower in 1.0 M NaCl than in DI water (Figure S2-A, Supporting Information). We added 0.05, 0.1, and 0.2 mM SDS into the feed solution (1.0 M NaCl at 60 °C) every 2 h during the DCMD experiments to progressively lower the feed surface tensions to $\sim$53, $\sim$ 42, and $\sim$33 mN/m, respectively.[36]

A slight increase in water flux and a decrease in salt rejection were observed with the control PVDF membrane after the addition of 0.05 mM SDS to the feed solution (Figure 5A). Because we applied a slightly higher cross-flow rate for the feed stream than the permeate stream (cross-flow velocities of 8.5
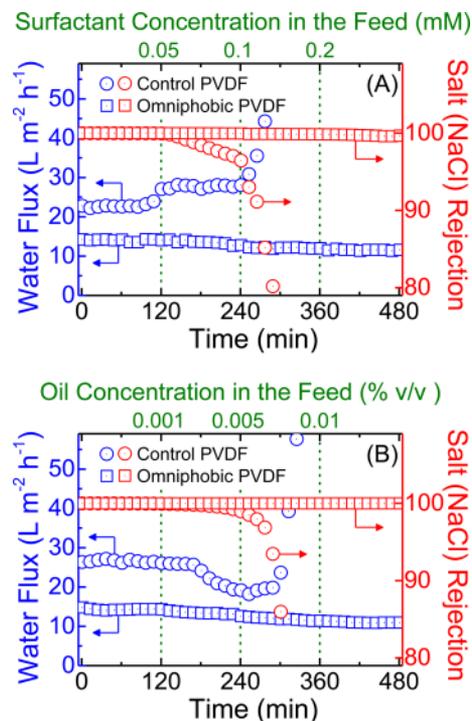
Figure 5. Water flux and salt rejection of control and modified PVDF membranes measured in DCMD using 1 M NaCl at 60 °C with varying (A) SDS and (B) mineral oil concentrations as feed solution and DI water at 20 °C as permeate solution. The SDS concentrations in the feed after sequential additions every 2 h were 0.05, 0.1, and 0.2 mM, and the corresponding estimated surface tensions of the feed solutions were ~53, ~42, and ~33 mN/m, respectively. The mineral oil concentrations in the feed after sequential additions every 2 h were 0.001, 0.005, and 0.01% v/v, which correspond to 8, 40, and 80 mg/L. The feed solution (initial volume of 1 L) was replenished after every 50 mL volume loss to maintain the variation of contaminant (SDS and mineral oil) concentrations within less than 5%.

cm/s versus 7.5 cm/s for feed and permeate streams, respectively), the feed solution penetrates through the MD membrane to the permeate side when pores are wetted. The increase in water flux and the concomitant decrease in salt rejection observed for the control PVDF membrane are evidence of pore wetting due to the reduced solution surface tension resulting from the added surfactant (SDS) in the feed. Further SDS addition to the feed (i.e., 0.1 mM SDS) leads to a more

drastic water flux increase and sudden decrease of salt rejection, suggesting more severe or even complete membrane pore wetting. The modified omniphobic membrane, on the other hand, showed stable water flux and complete salt rejection even after the addition of 0.2 mM SDS to the feed, which corresponds to a solution surface tension of ~33 mN/m, demonstrating wetting resistance of the omniphobic membrane to the low surface tension feedwater.

The effect of oil in the feed solution on MD desalination performance of the control and modified PVDF membranes is presented in Figure 5B. A homogeneous oil stock solution was prepared by mixing mineral oil (1% v/v) and nonionic surfactant (0.1% v/v) in water. The prepared oil emulsion was sequentially added to the feed to achieve mineral oil concentrations of 8, 40, and 80 mg/L. The average diameter of the mineral oil droplets in the feed solution measured by dynamic light scattering (DLS) was ~0.7 μm (Figure S2-B, Supporting Information). The prepared feed solution simulates the wastewaters contaminated by emulsified oils with droplet sizes below several micrometers, which are challenging to treat by conventional pretreatment practices, such as oil skimmers, coalescers, settling tanks, and depth filters.[39]

At a relatively low mineral oil concentration (0.001% v/v or 8 mg/L) in the feed, the control PVDF membrane exhibited water flux decline without a significant change in salt rejection (Figure 5B). Nonpolar oils easily adhere to the PVDF membrane by hydrophobic interactions,[40] thereby causing membrane fouling.[41] The observed water flux decline without significant change in salt rejection at 0.001% v/v mineral oil concentration in the feed is likely because the water and salt passage was blocked by the accumulated oils within the porous structure. At a higher mineral oil concentration (0.005% v/v or 40 mg/L), however, the control PVDF membrane was totally wetted by the feed solution as evidenced by drastically increased water flux and reduced salt rejection, similar to the results obtained with the SDS feed solutions.

In contrast, the omniphobic membrane showed stable water flux and complete salt rejection with feed solution mineral oil concentrations up to 0.01% v/v or 80 mg/L (Figure 5B). Mineral oil droplets are expected to adhere to the omniphobic membrane via nonpolar-nonpolar interaction as they adsorb on hydrophobic surfaces. However, contrary to the hydrophobic control PVDF membrane, the modified omniphobic membrane resists wetting by mineral oils, thereby preventing penetration of the oils
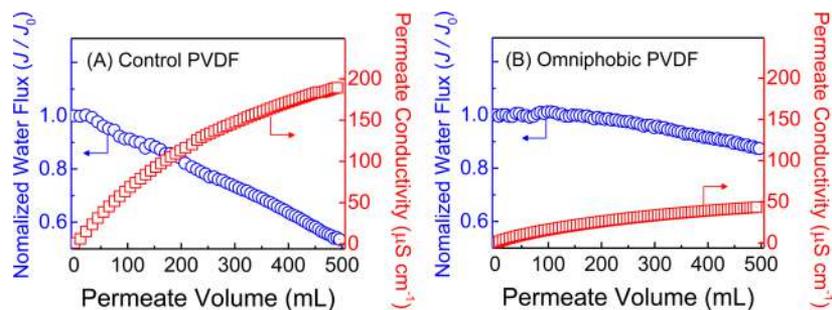
Figure 6. Desalination performances of (A) control PVDF and (B) modified omniphobic PVDF membranes with brines from shale produced water. Water vapor flux and permeate conductivity were measured in DCMD until the cumulative permeate volume reached 500 mL, using shale gas wastewater at 60 °C as a feed stream and DI water at 20 °C as a permeate stream. Properties of the prefiltered (16 μm filter) shale gas wastewater are described in Table S1 (Supporting Information). Initial water flux, J_0, was determined by averaging the permeate flux from the onset of the experiment until the permeate volume reached 25 mL. The obtained initial water fluxes were 23.5 and 13.6 L m^{-2} h^{-1} for the control and omniphobic PVDF membranes, respectively. Water flux performance is expressed as a normalized water flux, J/J_0, based on the initial water flux.

into the porous substrate. Also, mineral oil droplets adhered to the membrane can be readily removed by hydrodynamic shear force in cross-flow DCMD operation due to the ultralow interfacial energy of the omniphobic surface.[42,43]

Desalination Performance with Shale Gas Produced Water. We further tested the desalination performance of the modified omniphobic membrane by employing a brine from the shale gas industry as a feed stream in DCMD. The shale gas brine has very high total dissolved solids (TDS) concentration (101 000 mg/L) and contains substances which can potentially foul and wet the MD membranes (Table S1, Supporting Information). In particular, oil and grease, surfactants, and organic loading in the shale gas wastewater feed threaten the antiwetting properties of conventional hydrophobic membranes.

Figure 6 presents flux decline curves, expressed as normalized water flux, and permeate conductivity obtained from DCMD experiments for the control PVDF and the omniphobic membranes with the shale gas wastewater as feed solution (60 °C) and DI water as permeate solution (20 °C). To allow meaningful comparison of membrane performance at different initial water fluxes (23.5 and 13.6 L m^{-2} h^{-1} for the control PVDF and the omniphobic membranes, respectively), data are presented as a function of cumulative permeate volume. Experiments were continued until the feed recovery reached 50% (or permeate volume of 500 mL was attained), which took 13.3 h for experiments with the control PVDF membrane and 16.2 h for the omniphobic membrane. Other conditions were identical to those employed in the DCMD experiments described in the previous subsection.

As presented in Figure 6, the omniphobic membrane experienced a much lower flux decline and reduced salt passage compared to the control PVDF membrane. The observed significant performance deterioration of the control PVDF membrane can be attributed to various factors, including wetting, fouling, and scaling of the membrane, given the complex physicochemical composition of the shale gas produced water used. Of these, membrane wetting is expected to be the main factor that caused performance degradation of the control PVDF membrane in the early DCMD stage because wetting is a phenomenon that affects MD performance much faster than fouling and scaling.[44,45] Results obtained from a DCMD experiment using a clean 1.7 M NaCl feed solution (salinity identical to the shale gas produced water) without surface wetting substances further demonstrated a stable desalination performance of the control PVDF membrane in the early MD stage (Figure S3-A of Supporting Information).

The omniphobic membrane exhibited stable MD performance with shale gas wastewater feed (Figure 6B), which was comparable to the results obtained using a clean NaCl feed solution with a salinity (~1.7 M NaCl) identical to the shale gas produced water (Figure S3-B of Supporting Information). Although in both cases (i.e., shale gas produced water and 1.7 M NaCl solution feed) a slight flux decline and a small conductivity increase in the permeate were observed in a long-term DCMD run, likely caused by intrinsic membrane defects, the omniphobic membrane exhibited much more stable desalination performance than the control PVDF membrane. The observed stable desalination performance in MD with a shale gas produced water sample containing a variety of low surface tension contaminants is attributable to the enhanced wetting resistance of the omniphobic membrane achieved by surface modification with silica nanoparticles and low surface energy materials (i.e., fluoroalkylsilane).

In summary, we demonstrated a facile and scalable surface engineering technique to fabricate an omniphobic membrane that exhibits wetting resistance to low surface tension substances. Our omniphobic membrane showed a stable performance in MD for desalination of shale gas produced water, demonstrating the potential benefits of omniphobic membranes in treating high salinity wastewaters that contain diverse low surface tension contaminants. Application of MD with omniphobic membranes can be beneficial for a wide range of industries, considering the increasing demand for efficient treatment of challenging industrial wastewaters and stricter regulations for disposal of such wastewaters.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03882.

> Major composition and key properties of prefiltered shale gas produced water (Table S1); SEM images of modified PVDF membranes taken after chemical and physical stresses (Figure S1); surface tension of SDS solution in DI water and in 1 M NaCl (Figure S2-A) and size distribution of mineral oil droplets (Figure S2−B); water (vapor) flux and permeate conductivity obtained from DCMD experiments for unmodified PVDF and modified PVDF membranes with 1.7 M NaCl feed solution and DI water permeate solution (Figure S3) (PDF)

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Notes

The authors declare no competing financial interest.

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