

Highly Hydrophilic Polyvinylidene Fluoride (PVDF) Ultrafiltration Membranes via Postfabrication Grafting of Surface-Tailored Silica Nanoparticles

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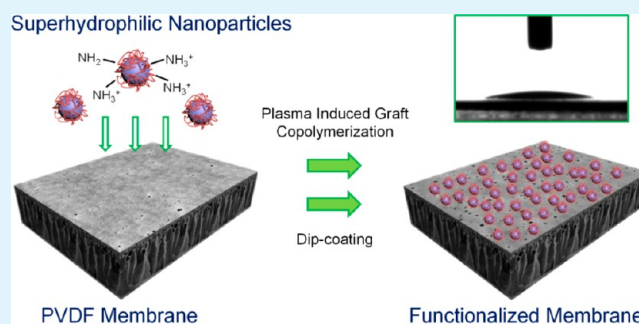
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Supporting Information

ABSTRACT: Polyvinylidene fluoride (PVDF) has drawn much attention as a predominant ultrafiltration (UF) membrane material due to its outstanding mechanical and physicochemical properties. However, current applications suffer from the low fouling resistance of the PVDF membrane due to the intrinsic hydrophobic property of the membrane. The present study demonstrates a novel approach for the fabrication of a highly hydrophilic PVDF UF membrane via postfabrication tethering of superhydrophilic silica nanoparticles (NPs) to the membrane surface. The pristine PVDF membrane was grafted with poly(methacrylic acid) (PMAA) by plasma induced graft copolymerization, providing sufficient carboxyl groups as anchor sites for the binding of silica NPs, which were surface-tailored with amine-terminated cationic ligands. The NP binding was achieved through a remarkably simple and effective dip-coating technique in the presence or absence of the *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC)/*N*-hydroxysuccinimide (NHS) cross-linking process. The properties of the membrane prepared from the modification without EDC/NHS cross-linking were comparable to those for the functionalized membranes, which significantly improved the wettability of the membrane and converted the membrane surface from hydrophobic to highly hydrophilic. The irreversibly bound layer of superhydrophilic silica NPs endowed the membranes with strong antifouling performance as demonstrated by three sequential fouling filtration runs using bovine serum albumin (BSA) as a model organic foulant. The results suggest promising applications of the postfabrication surface modification technique in various membrane separation areas.

KEYWORDS: ultrafiltration, PVDF, fouling, antifouling, superhydrophilic, nanoparticles, membrane functionalization



INTRODUCTION

Ultrafiltration (UF) is a membrane separation process extensively used in various fields, such as the food and dairy industry,^{1,2} biological purification,^{3,4} and water purification,^{5–8} where high separation efficiency is required. While membrane filtration processes, such as UF, are widely used, their long-term operation is hampered by the low resistance of the membranes to fouling. Membrane fouling, caused by the adsorption and accumulation of various foulants on a membrane surface or in a membrane matrix during filtration, results in reduced productivity, additional operating costs, and the need for frequent chemical cleaning that shortens membrane life-span.^{9–13} Membrane surface hydrophilicity is widely accepted as a dominant factor that governs fouling development on the membrane.^{11,12,14} A hydrophilic membrane surface generally

has higher fouling resistance compared with hydrophobic membranes.^{9–11,13}

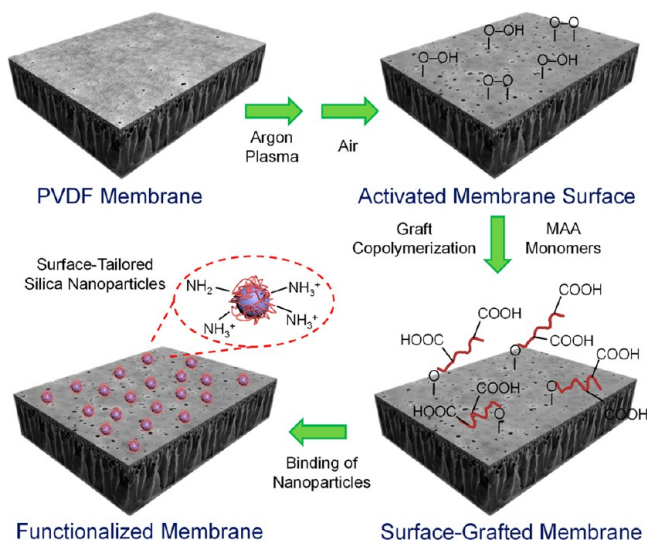
Polyvinylidene fluoride (PVDF) is extensively used as a UF membrane material in a wide range of applications due to its outstanding mechanical strength, chemical resistance, and thermal stability.^{15–17} Nevertheless, the intrinsic hydrophobic property of PVDF is a major challenge for the widespread application of PVDF membranes in separation processes that involve feed solution containing organic and biological substances. The low surface energy of the resultant PVDF

Received: April 21, 2013

Accepted: June 24, 2013

Published: June 24, 2013

Scheme 1. Schematic Protocol of PVDF Membrane Functionalization, Illustrating Argon Plasma Treatment, Graft Copolymerization, and Nanoparticle (NP) Binding^a



^aGraft copolymerization of plasma-activated PVDF membrane with methacrylic acid (MAA) monomers was carried out to introduce carboxyl groups, which acted as binding sites for the surface-tailored silica nanoparticles (NPs). Positively charged ligands, terminated with amine functional groups, were used to tailor the surface of the NPs, rendering them superhydrophilic. Electrostatic and covalent bonds impart stability and durability to the coatings of functionalized NPs on the membrane surface.

membrane results in poor membrane wettability and aggravates the adsorption of organic foulants on the membrane surface.^{9,15}

To mitigate membrane organic fouling, significant efforts have been made to increase the hydrophilicity of the PVDF membrane via blending modification or surface modification.^{10,12,14–16} Ongoing development of inorganic nanomaterials has enabled the incorporation of a variety of hydrophilic nanoparticles (NPs) into polymeric membranes through a simple blending strategy, thereby improving the antifouling performance of the resultant hybrid membranes.^{10,18,19} However, in this strategy, large amounts of NPs are encased in the membrane bulk material, which limits the amount of NPs on the membrane surface and decreases the modification efficiency. Another blending approach using amphiphilic copolymers results in the enrichment of the hydrophilic moieties of the copolymers on the membrane surface by virtue of surface segregation.^{13,20–22} However, the amelioration of the surface hydrophilicity of the resultant membrane using this modification is still limited, since it is hard to decrease the contact angle below 40°, even for the relatively hydrophilic polyacrylonitrile membrane.¹³ Surface modification by growing or coating hydrophilic or superhydrophilic materials on UF membranes provides an efficient and effective strategy for significant improvement of the hydrophilicity and antifouling properties of UF membranes. A surface embedment-growth technique¹² was developed to anchor aluminum oxide particles on the PVDF membrane surface, which cut down the efficiency loss caused by particle encasement compared with the NP-blending strategy. Nevertheless, the large-sized particles grown on the surface might conspicuously decrease the permeability of the resultant membrane. Similar techniques were developed through growing/coating inorganic materials on the membrane

surface.^{23,24} However, none of these methods succeeded in avoiding the adverse effects on the most fundamental and essential membrane functions—solvent permeation and solute separation—which must be seriously considered when designing a membrane modification protocol.

The present paper demonstrates a novel approach for the fabrication of a highly hydrophilic PVDF membrane via postfabrication tethering of superhydrophilic silica NPs to the membrane surface (Scheme 1). Silica NPs were surface-tailored with superhydrophilic cationic ligands that were terminated with amine functional groups. The pristine PVDF membrane was grafted with poly(methacrylic acid) (PMAA) through plasma induced graft copolymerization, providing sufficient carboxyl groups as anchor sites for NP binding. Afterward, the surface-tailored superhydrophilic NPs were covalently or ionically bound to the PMAA-grafted membrane via a remarkably simple and effective dip-coating method in the presence or absence of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC)/*N*-hydroxysuccinimide (NHS) cross-linking. The NP-functionalized membranes were extensively characterized, and the effect of the EDC/NHS cross-linking on NP binding was investigated. Filtration experiments with protein (bovine serum albumin, BSA) solution demonstrate the remarkable antifouling property of the fabricated membranes.

MATERIALS AND METHODS

PVDF Membrane Casting. PVDF membranes were fabricated using nonsolvent induced phase separation as described previously.¹⁰

Table 1. Recipes of Different Casting Solutions for PVDF Membrane Fabrication

recipe	PVDF/PVP ^a (w/w)	solvent (w/w) NMP ^b /DMF ^c	coagulation bath (v/v) NMP ^b /water
I	15:0	4:1	1:9
II	17:1	1:6	0:10
III	17:1	6:1	1:9

^aPolyvinylpyrrolidone. ^b*N*-Methyl-2-pyrrolidinone. ^c*N,N*-Dimethylformamide.

Three different types of casting solutions were prepared to fabricate membranes with different pore sizes and surface hydrophilicity following the recipes in Table 1. To prepare the casting solution, PVDF (average MW ~534 000, Aldrich) and PVP (average MW ~10 000, Sigma–Aldrich) were dissolved in a mixture of NMP (anhydrous, 99.5%, Sigma–Aldrich) and DMF (anhydrous, 99.8%, Sigma–Aldrich) at different ratios (Table 1) under vigorous stirring at room temperature (23 ± 1 °C) for at least 8 h. The obtained casting solution was stored at room temperature for at least 12 h to remove bubbles and heated at 50 °C for 1 h before membrane casting. To cast the membrane, the casting solution was spread onto a flat glass plate at a thickness of 254 μm using a doctor blade (Gardco, Pompano Beach, FL). After a 30 s exposure to air, the plate was immersed in a deionized (DI) water coagulation bath, where the membrane formed slowly through polymer precipitation. After 10 min, the membrane was detached from the plate and soaked in DI water overnight. Finally, the membrane was annealed for 5 min in an 80 °C DI water bath and stored in a fresh DI water bath prior to use.

Preparation of Superhydrophilic Nanoparticles. Superhydrophilic NPs were synthesized through surface modification of silica NPs (Ludox HS-30, 30%, Sigma–Aldrich). A suspension of silica NPs was prepared by dispersing 6 g of NPs in 30 mL of DI water and sonicating for 30 min at a power output of 20 W (Branson 2510, Branson Instruments, US). The obtained suspension was mixed with a freshly prepared silane solution comprising 2.1 g of (3-aminopropyl)-

trimethoxysilane (97%, Sigma–Aldrich) and 24 mL of DI water under vigorous stirring. After the pH was adjusted to ~5 by 0.1 M HCl, the mixture was heated and stirred at 70 °C for 24 h. Finally, the suspension was dialyzed in DI water using SnakeSkin tubing (7 k MWCO, Pierce) for 48 h and stored at 4 °C prior to use. The stock NP suspension was diluted 3-fold when used for membrane functionalization.

Plasma Induced Graft Copolymerization and Membrane Functionalization. A modified graft copolymerization method was developed following the procedures described by Kaur et al.²⁵ A pristine PVDF membrane sheet was air-dried at room temperature (23 ± 1 °C) before being cut into several strips of the same dimension (3 cm × 5 cm). The membrane strip was affixed on a glass plate with the active layer (top) surface facing up, and placed in the chamber of a plasma cleaner (PDC-32G, Harrick Scientific, Ithaca, NY), which was connected to an argon gas cylinder (UHP 300, Airgas Inc., US). An argon gas flow with a pressure of ~0.037 kPa, controlled using a digital vacuum gauge (DVG-64, OMEGA Engineering Inc., Stamford, CT), was introduced to the chamber, where the argon plasma was generated at a power of 18 W and radio frequency of 8–12 MHz. After a certain treatment time, ranging from 0 to 120 s, the membrane strip was exposed to air for 10 min to facilitate the formation of peroxides and hydroperoxides on the membrane surface before graft copolymerization.^{25–27} For 0 s, the membrane strip was placed in the chamber under vacuum without turning on the plasma power. Subsequently, the membrane strip was immersed in a bottle containing 10% (v/v) methacrylic acid (MAA, 99%, Aldrich) solution that was subjected to vacuum for 15 min to reduce the amount of inhibitors. To remove dissolved oxygen, the bottle was repeatedly vacuumed and aerated with argon gas for 10 min and kept sealed for the following graft copolymerization process. Graft copolymerization was initiated by heating the bottle in an 80 °C water bath for 1 h. Then the PMAA-grafted membrane strip was taken out, rinsed with copious amounts of DI water, and soaked in a 0.1 M NaOH solution for 12 h under gentle shaking to remove any adsorbed homopolymers or unreacted monomers.²⁵ Thereafter, the grafted membrane strip was thoroughly washed with DI water, in preparation for surface functionalization with silica NPs.

NP binding to the PMAA-grafted membrane was achieved with a simple dipping method in the presence or absence of EDC (Thermo Scientific, US)/NHS (98%, Aldrich) cross-linking, which hereafter are designated as the EDC/NHS method or the direct method, respectively. For the EDC/NHS method, the PMAA-grafted membrane was dipped into a solution of 2 mM EDC and 5 mM NHS, buffered with 10 mM 2-(*N*-morpholino)ethanesulfonic acid (MES, ≥99%, Sigma) at pH ~5 for 15 min. Subsequently, the membrane was transferred into the NP suspension (pH of 7–7.2) and immersed for 12 h. For the direct method, the membrane was immersed into the NP suspension (pH 7–7.2) for 12 h. The surface functionalized membrane was washed with copious amounts of DI water and stored in DI water at 4 °C prior to characterization. The schematic protocol of the membrane functionalization is shown in Scheme 1.

To minimize variations in membrane properties between separately cast or functionalized membranes, membrane samples used for each comparison were cut from the same membrane sheet and functionalized in the same batch. Graft copolymerization was performed on three types of PVDF membranes, which were cast following different recipes (Table 1). Membrane fabrication following recipe II was chosen as the optimal recipe for the subsequent surface functionalization, characterization, and fouling experiments.

Membrane Characterization. Membrane water permeability and solute selectivity were evaluated using a dead-end filtration system. The sample membrane disk was precompact in a stirred cell (Amicon 8010, Millipore, Billerica, MA) with DI water for 30 min at 70 kPa and the pure water flux was subsequently recorded at 20, 40, and 60 kPa. For quantifying membrane selectivity, filtration experiments were carried out with solutions containing 1 g L⁻¹ of 100 and 200 kDa poly(ethylene oxide) (PEO, Aldrich) at 120 kPa. Total organic carbon (TOC) analyses were performed on the collected

permeate and feed samples using a TOC analyzer (TOC-VCSH, Shimadzu, Kyoto, Japan) to determine solute rejection ($R = 1 - C_{\text{Permeate}}/C_{\text{Feed}}$).

Zeta potential of the membrane surface was determined using a streaming potential analyzer utilizing an asymmetric clamping cell (EKA, Brookhaven Instruments, Holtsville, NY). Measurements were taken with a solution containing 1 mM KCl and 0.1 mM KHCO₃. Aliquots of HCl and KOH were used for pH adjustment to investigate the variation of zeta potential with solution pH (pH range from 4 to 9). For each membrane type, three separately cast and functionalized membranes were tested. Detailed experimental procedure and calculation of zeta potential from the measured streaming potential are described elsewhere.²⁸

Membrane samples were air-dried at room temperature for subsequent surface characterizations. X-ray photoelectron spectroscopy (XPS) was performed to determine the elemental composition of the membrane surface using a Surface Science Instrument SSX-100 UHV system (monochromated for Al K α X-rays with 1486.6 eV). Membrane surface morphology was observed through a field emission scanning electron microscope (FE-SEM, SU-70, Hitachi, Japan). Before observation, membrane samples were vacuum-dried and sputter-coated (DESK V, Denton Vacuum, LLC, Moorestown, NJ) with a 10-nm-thick layer of chrome. The obtained SEM images were analyzed to determine the average membrane pore size using the statistical method described by Xiao et al.¹¹ Membrane surface roughness was characterized using an atomic force microscope (AFM, Dimension 5000, Bruker AXS, Santa Barbara, CA) in tapping mode. Symmetric silicon probes with 30-nm-thick aluminum reflex coating were employed (Tap300AI-G, Innovative Solutions Bulgaria Ltd., Sofia, Bulgaria). The probe has a resonant frequency of 300 kHz, force constant of 40 N/m, cantilever length of 125 ± 10 μ m, and tip radius of <10 nm. For each membrane type, at least nine randomly selected scan positions on three separately cast and functionalized membranes were tested. The surface roughness of each membrane type was characterized as root-mean-square (RMS) roughness, maximum roughness R_{max} , average roughness R_{av} , and surface area difference (SAD).

Water contact angle measurements were performed (VCA-2000, AST Products Inc., Billerica, MA) to indirectly verify (in conjunction with the XPS analyses) the success of graft copolymerization on the membrane surface, characterize the NP-functionalized membranes (via the direct method and the EDC/NHS method), and confirm the irreversibility of the NP–membrane bond. To measure the contact angle, the instantaneous picture of a water droplet on sample surface was taken within 0.3 s, ensuring that observable vibration of the water droplet had already ceased. A software program (VCA Optima XE) was employed to fit the shape profile of the water droplet on the sample surface for contact angle calculation. For each membrane sample, at least seven measurements were conducted at random locations. Water droplet pictures taken at 1 and 10 s were also taken for the pristine and NP-functionalized membrane samples.

To confirm the irreversibility of NP binding, the NP-functionalized membranes were subjected to chemical and physical stresses. Chemical stress was applied by immersing a freshly functionalized membrane for 15 min in a pH 2 solution (HCl), a pH 12 solution (NaOH), or a 5 M NaCl solution, followed by a thorough rinse with DI water. Physical stress was induced by dipping the membrane in a water bath of an ultrasonic cleaner (FS60, Fisher Scientific, Canada) for 1 min and repeating once again after a 1 min interval. After subjecting the membranes to physical and chemical stresses, contact angles were measured to assess changes in the membrane surface properties. For the pristine membrane (recipe II, Table 1) and the NP-functionalized membranes before and after the chemical or physical stress, the final contact angle was determined from the average of at least 21 measurements on three separately cast and functionalized membranes.

The relative wettability of the membranes was evaluated by calculating the membrane–liquid interfacial free energy ($-\Delta G_{\text{ML}}$, here the liquid refers to water) using a modified form of the Young–Dupré equation:^{29–31}

$$-\Delta G_{ML} = \gamma_L \left(1 + \frac{\cos \theta}{1 + SAD} \right) \quad (1)$$

where θ is the measured average water contact angle and γ_L is the pure water surface tension (72.8 mJ m^{-2} at 20°C).²⁹ The effect of surface roughness on contact angle measurement was accounted for via the roughness area parameter, $1 + SAD$ (i.e., the ratio of actual area of the membrane surface to the geometric area).³⁰ A larger value of $-\Delta G_{ML}$ suggests a more wettable surface.³²

The Lifshitz–van der Waals (γ^{LW}) and Lewis acid–base (γ^{AB} , including electron acceptor γ^{AB+} and electron donor γ^{AB-}) components of the membrane surface tension were quantified using the extended Young–Dupr  equation:³³

$$\gamma_L \left(1 + \frac{\cos \theta}{1 + SAD} \right) = 2 \left(\sqrt{\gamma_M^{LW} \gamma_L^{LW}} + \sqrt{\gamma_M^{AB+} \gamma_L^{AB-}} + \sqrt{\gamma_M^{AB-} \gamma_L^{AB+}} \right) \quad (2)$$

where the subscripts M and L refer to the membrane and liquid (water), respectively. Additional contact angle measurements were performed using glycerol ($\geq 99\%$, polar) and diiodomethane ($\geq 99\%$, apolar), the surface tension components of which have been precisely determined (assuming $\gamma_W^{AB+} = \gamma_W^{AB-} = 25.5 \text{ mJ m}^{-2}$, where the subscript W stands for water).²⁹ In conjunction with the surface tension values of water, γ_M^{LW} , γ_M^{AB+} , and γ_M^{AB-} of the membrane can be obtained from the solution of eq 2. The total surface energy can be expressed as $\gamma^{TOT} = \gamma^{LW} + \gamma^{AB}$ where $\gamma^{AB} = 2(\gamma^{AB+} \gamma^{AB-})^{1/2}$. Using the surface tension components of membrane and water, the interfacial free energy of cohesion of membrane interfaces immersed in water (ΔG_{MLM}^{TOT} , commonly termed as “hydrophilicity”) was also calculated.³¹

Filtration Experiments to Evaluate Fouling Resistance. Three sequential cycles of dead-end filtration were performed for the three different types of membrane: the pristine membrane, which served as the control, the NP-functionalized membrane via the direct binding method, and the NP-functionalized membrane via the EDC/NHS binding method. The membrane was first precompactated at 70 kPa with DI water for 0.5 h until the flux reached a plateau. For each membrane, the initial flux was set to $\sim 100 \text{ L m}^{-2} \text{ h}^{-1}$ by adjusting the applied pressure. After a 10-min period of recording the water flux, filtration of a solution of 15 mg L^{-1} BSA and 10 mM ionic strength (9.9 mM NaCl and 0.1 mM NaHCO_3) was carried out for 1 h. A “physical” cleaning step was carried out in the stirred cell at the completion of the BSA fouling run, indicating the end of one filtration cycle. For physical cleaning, the membrane surface was flushed with a BSA-free solution under vigorous stirring (400 rpm) for 5 min. All filtration experiments were conducted at room temperature ($23 \pm 1^\circ\text{C}$) at a stirring rate of 300 rpm.

RESULTS AND DISCUSSION

Graft Copolymerization on Membranes with Different Pore Size and Hydrophilicity. Sufficient carboxyl groups, which facilitated the binding of surface-tailored silica NPs, were introduced by the formation of PMAA on the membrane surface through plasma induced graft copolymerization. To verify the success of the polymerization, the surface [O]/[F] ratio, as calculated from the percent atomic concentration of O 1s and F 1s, was determined through XPS analysis. The results for the pristine (control) and surface-grafted membranes as a function of plasma treatment time are presented in Figure 1A. In general, longer plasma treatment times (within 120 s) resulted in a higher [O]/[F] ratio due to the defluorination (decrease in [F]) caused by Ar plasma^{26,27,34,35} and the grafting of PMAA (increase in [O]).^{25,36} The oxidation reaction (i.e., the formation of oxides or peroxides)^{26,27} on the plasma-treated membrane surface during the air exposure stage might also slightly contribute to the increase of [O].

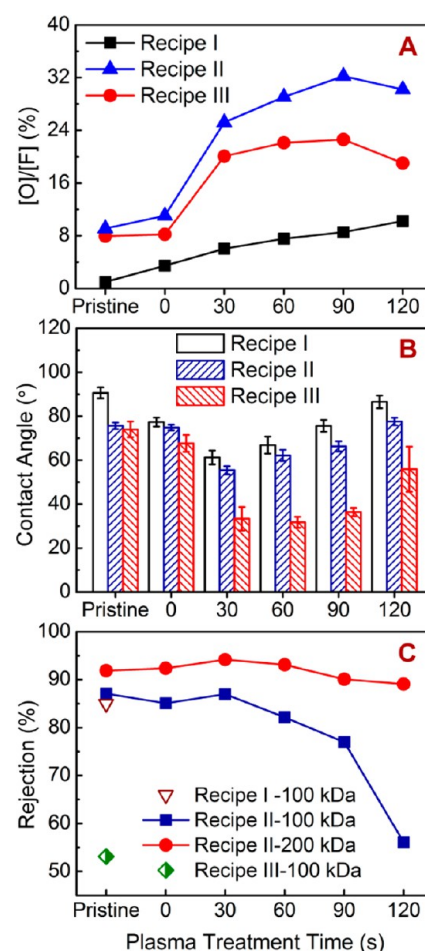


Figure 1. Characteristics of the pristine and surface-grafted membranes. (A) Surface analyses by XPS of the pristine and surface-grafted membranes fabricated by the three different recipes described in Table 1. For each recipe, the calculated ratio of percent atomic concentration of O to F (obtained from XPS data) as a function of plasma treatment time is presented. (B) Contact angles of deionized (DI) water on the pristine and surface-grafted membranes fabricated following the three different recipes as a function of plasma treatment time. Each value was averaged from at least 10 measurements. (C) Rejection of 100 and 200 kDa PEO by the pristine and surface-grafted membranes fabricated following the three different recipes as a function of plasma treatment time. Measurements were conducted by filtering the 1 g L^{-1} of PEO solutions at 70 kPa at room temperature ($23 \pm 1^\circ\text{C}$).

Three recipes (Table 1) were employed for PVDF membrane fabrication. For recipe I, no additives were added to the casting PVDF solution, resulting in an approximate zero [O]/[F] ratio for the pristine membrane. The linear increase of the [O]/[F] ratio with plasma treatment time is attributed to the formation of PMAA on the plasma-activated membrane surface. The oxygen signal in sample 0 (i.e., no plasma treatment) was probably caused by residual absorbed MAA monomers or PMAA polymers, which remained on the surface after the 0.1 M NaOH cleaning process. For recipes II and III, PVP, which contains oxygen, was used as an additive to improve membrane porosity and hydrophilicity,^{10,15} resulting in an increase in the [O]/[F] ratio of the pristine membranes to ~ 0.08 . Membrane pore size or selectivity was controlled by adjusting the proportion of NMP to DMF in the mixed solvent (Table 1). As shown in Figure 1C, pristine membranes

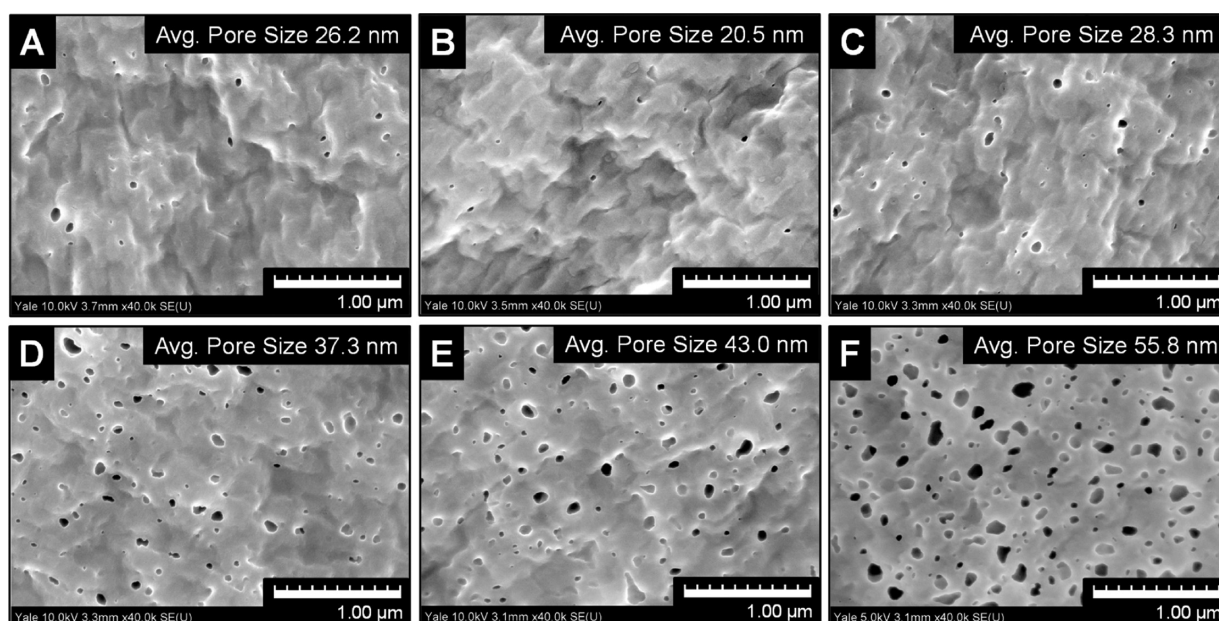


Figure 2. Top views by SEM of (A) the pristine and (B–F) the surface-grafted membranes for different plasma treatment times: (B) 0, (C) 30, (D) 60, (E) 90, and (F) 120 s. The average pore size for each membrane is indicated in the corresponding image.

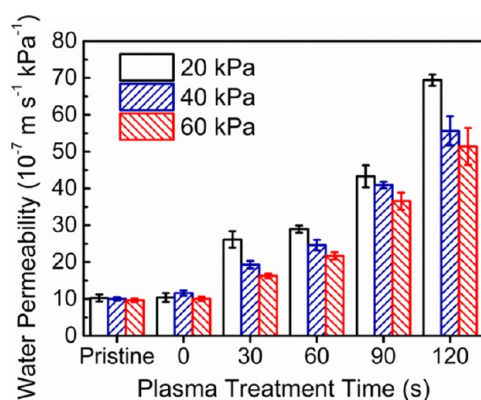


Figure 3. Water permeability of the pristine and surface-grafted membranes as a function of plasma treatment time as determined from filtration experiments with DI water at three different pressures: 20, 40, and 60 kPa. Temperature during the filtration experiments was kept at 23 ± 1 °C.

of recipes I and II have a similar PEO (100 kDa) rejection, while the pristine membrane of recipe III has a much lower rejection, indicating larger pore size. Compared with recipe I (Figure 1A), the increase in the [O]/[F] ratio for recipes II and III after surface polymerization is much more significant, likely due to the role of PVP in the plasma induced copolymerization, which facilitates the formation of PMAA. However, the [O]/[F] ratio approaches an asymptotic value and tends to decrease at Ar plasma treatment times greater than 90 s. This observation is probably due to the etching effect of Ar plasma (as shown in Figure 2) and is consistent with previous studies.^{25,26,34}

As shown in Figure 1B, the hydrophilic moieties of PMAA rendered the surface-grafted membranes more hydrophilic, with minimum contact angles at a plasma treatment time around 30 s. However, for all three recipes, the contact angle linearly increased for plasma treatment times longer than 30 s. This observation could be due to two possible consequences of

plasma etching (as shown in Figure 2): a weakened boundary layer^{27,37,38} and trapped air pockets^{25,38–41} on the membrane surface.

Based on the above results, recipe II was chosen as the optimal recipe for PVDF membrane fabrication. A 60 s plasma treatment was employed in the surface copolymerization step for further functionalization by surface-tailored NPs.

Impact of Ar Plasma Treatment on Membrane Morphology and Permeability. The influence of Ar plasma on membrane morphology was examined through SEM. Surface pore size and porosity of the plasma-treated, surface-grafted membranes increased with increasing plasma treatment time (Figure 2) due to the etching effect of plasma treatment. Consequently, water permeability of the grafted membranes gradually increased (Figure 3). For each membrane type, water permeability was tested under three different pressures: 20, 40, and 60 kPa. For the pristine and 0 s treated membranes, the permeability remained very stable at all pressures, but for the surface-grafted membranes (30–120 s), the permeability decreased under larger pressures. This observation may be attributed to narrowing/blocking of the pores by the PMAA polymers at higher pressure (Scheme 1).

Silica NPs are Irreversibly Bound to Membrane Surface by a Simple Dipping Method and Render the PVDF Membrane Highly Hydrophilic. Figure 4A presents the SEM top views of the pristine and two types of NP-functionalized PVDF membranes: via the direct method and the EDC/NHS method. SEM images indicate that both methods achieved comparable binding, with no significant differences between the membranes. After functionalization, both membrane surfaces were finely covered by a layer of silica NPs, which rendered the PVDF membrane highly hydrophilic. The average contact angles of the two different types of NP-functionalized membranes decreased from $\sim 76^\circ$ (Figure 4B, pristine) to $\sim 17^\circ$ and $\sim 20^\circ$ (Figure 4B, as functionalized), respectively. Moreover, the water droplet was promptly absorbed by the membrane after touching the membrane surface during the contact angle measurement (illustrated in

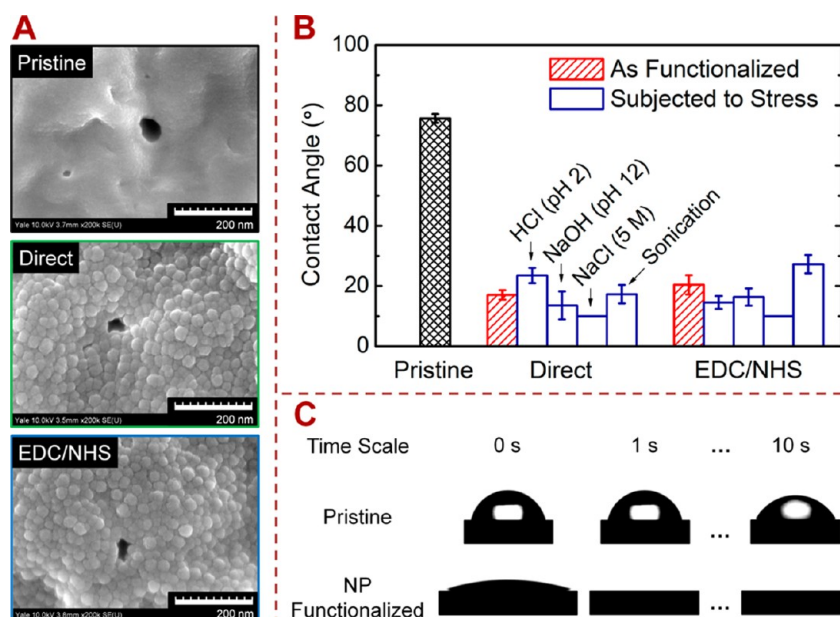


Figure 4. (A) SEM top views of the pristine membrane, silica NP-functionalized membrane via the direct binding method, and silica NP-functionalized membrane via the EDC/NHS binding method. (B) Comparison of contact angles of the pristine membrane (black patterned) and two types of NP-functionalized membranes (i.e., by the direct binding method and the EDC/NHS binding method). For each type, the contact angles of the membrane as functionalized (red patterned) and of the membranes subjected to the indicated chemical and physical stresses (blue hollow) are presented. Each contact angle value is an average of at least 21 measurements (based on the images taken within 1 s) from three separately cast and functionalized membrane samples. When the water droplet was absorbed too fast to perform the measurement, a value of 10° was assumed. (C) Typical images of DI water droplets on the pristine and NP-functionalized membranes, illustrating the contact angle variations along the time scale (shown for illustration only). All measurements were performed at $23 \pm 1^\circ\text{C}$.

Figure 4C), indicating the highly hydrophilic property of the NP-functionalized membranes.

The irreversibility of the interaction between NPs and grafted membrane surface was examined through contact angle measurements, SEM observation, and XPS analyses (discussed in the next section) of the surfaces of the functionalized membranes after being subjected to chemical and physical stresses. After subjection to chemical stress (pH 2 HCl, pH 12 NaOH, or 5 M NaCl), no significant change in the average contact angle was observed for the two types of functionalized membranes. In general, the contact angle values of the functionalized membranes via the EDC/NHS method appear to be more stable than those via the direct method, suggesting the reinforcement effect by the EDC/NHS cross-linking process.^{42,43} However, after the destructive disturbance by physical stress (1 min sonication, twice), the average contact angle of the functionalized membrane via the EDC/NHS method underwent a relatively larger increase than that via the direct method. In general, the difference in contact angles between these two methods was insignificant, indicating comparable effectiveness of the two methods in membrane modification. SEM images revealed no significant difference between the freshly functionalized membranes and those subjected to chemical and physical stresses (Supporting Information Figure S1). The remarkably stable results from contact angle and SEM imaging demonstrate that the binding between NPs and surface-grafted PVDF membranes is irreversible.

Nanoparticle binding was also performed on a pristine PVDF membrane surface using the direct method. The contact angle of the pristine membrane decreased from $\sim 80^\circ$ to $\sim 40^\circ$ after functionalization, and the membrane surface was partially covered by NPs under SEM observation (Supporting

Information Figure S2A). However, the NP binding did not withstand the sonication stress treatment (1 min, twice, Supporting Information Figure S2B), following which the contact angle increased back to $\sim 80^\circ$. This observation underscores the essential role that surface graft copolymerization played throughout the modification protocol.

The interfacial free energy and surface energy of the membranes were analyzed by the contact angle method,²⁹ with two polar liquids, water, and glycerol, and an apolar liquid, diiodomethane. The pristine PVDF membrane was found to be relatively wetting ($-\Delta G_{\text{ML}} = 78.0 \text{ mJ m}^{-2}$), but hydrophobic ($\Delta G_{\text{MLM}}^{\text{TOT}} = -42.2 \text{ mJ m}^{-2}$) when immersed in DI water (Figure 5A). This is due to the relatively low surface energy ($\sim 33.3 \text{ mJ m}^{-2}$, Figure 5B, consistent with the data in previous studies^{44,45}), which is nearly exclusively contributed by the Lifshitz–van der Waals component (Figure 5C). This observation indicates that the PVDF membrane surface primarily interacts with water through van der Waals forces.

Significant changes were observed after functionalization with the superhydrophilic silica NPs. The two types of functionalized membranes both acquired much higher surface energy (almost doubled, Figure 5B), resulting in higher interfacial surface energy (i.e., wettability, Figure 5A). This dramatic increase is attributed to the increase of both the Lifshitz–van der Waals ($\Delta\gamma^{\text{LW}}$) and Lewis acid–base ($\Delta\gamma^{\text{AB}}$) components, with the $\Delta\gamma^{\text{LW}}$ contributing more than the $\Delta\gamma^{\text{AB}}$ (Figure 5C). Moreover, the sharp increase in the electron donor parameter $\gamma^{\text{AB-}}$ dramatically enhanced the monopolar functionality of the membrane surface, consistent with the properties of ligands coating the NP surface.⁴⁶ The electron donor monopolar surface had a strong interaction with the bipolar water molecules, which formed a tightly bound hydration layer on the membrane surface and promoted the

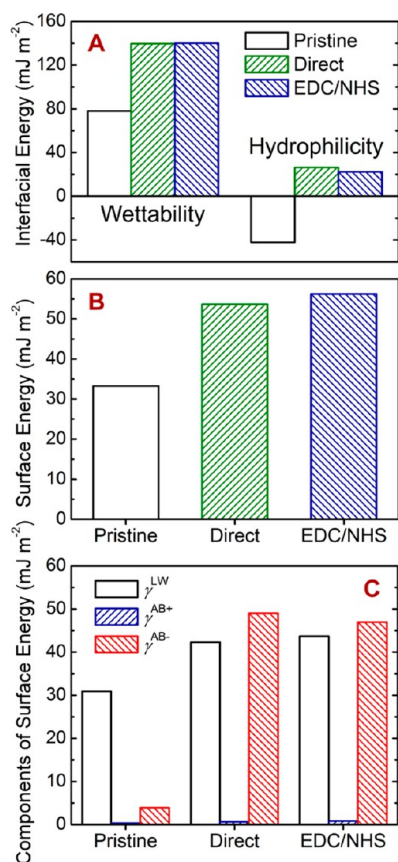


Figure 5. Analyses of interfacial free energy and surface energy of the different membranes. (A) Membrane–liquid (water) interfacial free energy or wettability, $-\Delta G_{ML}$, and interfacial energy of cohesion, ΔG_{MLM}^{TOT} , of the pristine membrane (open bar), NP-functionalized membrane via the direct binding method (green patterned), and NP-functionalized membrane via the EDC/NHS binding method (blue patterned). (B) Calculated values of surface energy, γ^{TOT} , and (C) the Lifshitz–van der Waals (γ^{LW} , black hollow) and the acid–base (γ^{AB+} , blue patterned, and γ^{AB-} , red patterned) components of the total surface energy of the three different membranes. The surface energy parameters were calculated from the average contact angles measured using DI water, glycerol, and diiodomethane at room temperature (23 ± 1 °C), without any adjustment of ionic strength or pH.

conversion of the surface interfacial free energy of cohesion to positive values, i.e., highly hydrophilic properties^{7,47,48} (Figure 5A).

Physicochemical Properties of the Functionalized Membrane Surface. The elemental composition of the pristine and functionalized membrane surfaces was determined through XPS analyses. The spectra are shown in stack lines in Figure 6A for qualitative comparison. The energy peaks detected for the pristine membrane surface (black) are mainly attributed to fluorine, oxygen, nitrogen, and carbon, with fluorine and carbon being the dominating elements. The relatively small peak of oxygen was due to the addition of PVP to the casting solution in membrane fabrication. Silica related peaks were detected for the functionalized membrane surfaces (blue and green), which confirmed the presence of silica NPs on the functionalized surfaces. In addition, a decrease in the intensity of fluorine and an increase in the intensity of oxygen were also observed for the functionalized membranes (Figure 6B). This could be attributed to the plasma induced graft copolymerization reaction, which was discussed in the previous

section. Moreover, the blocking of the XPS signal by the silica NPs on the surface would also lead to a decrease in fluorine intensity, because XPS only analyzes the superficial portion of the membrane surface. The irreversibility of the silica NP binding was also investigated by comparing the area fraction of energy peaks of silica on the functionalized membrane surfaces before and after the various stress treatments. As presented in Figure 6C, the area fraction of the silica peaks remained very stable after the stress treatments, confirming the strong binding between silica NPs and membrane surface.

Membrane surface charge properties also play an important role in membrane performance and fouling resistance.¹¹ Figure 7 presents the zeta potential of the pristine and functionalized membranes measured over a pH range of 4–9. The pristine membrane was found to be negatively charged and stable over the whole pH range (Figure 7A), consistent with other reported data.⁴⁹ In contrast with the pristine membrane, the two types of functionalized membranes possessed significantly different surface charge characteristics. In general, the zeta potential for both functionalized membranes was highly positive at low pH and, linearly, became negative as the pH increased (Figure 7B and C). No obvious difference was distinguished between the two functionalized membranes. This zeta potential behavior was in accordance with the functionalities present at both the NPs and the membrane surface.⁵⁰ The terminal primary amino groups ($-\text{NH}_2$, $pK_a \sim 10$) on the silica NPs (zeta potential $\sim +45$ – 50 mV) are assumed to react with the abundant carboxyl groups on the grafted membrane surface, thus neutralizing many of the charges present on both reacting surfaces. The redundant amino groups and unreacted carboxyl groups determine the overall zeta potential behavior as a function of solution pH. At low pH, the amino groups are protonated while the carboxyl groups are uncharged, resulting in an overall positive zeta potential. As the pH is increased, the overall zeta potential progressively becomes more negative due to the deprotonation of the amino and carboxyl functional groups. The overall zeta potential is close to zero around pH 7, which is close to the pH of many potential feed solutions, such as natural and waste waters. Furthermore, the presence of NPs on the surface of the functionalized membrane is indirectly confirmed by the zeta potential results, which also provide some information about the type of particle–membrane interactions.

The surface roughness of the membranes before and after functionalization was analyzed by AFM. Figure 8 presents the roughness parameters for the pristine membrane and two types of functionalized membranes. Both functionalized membranes exhibited almost identical roughness values, which were only slightly lower than those of the pristine membrane. Moreover, no difference could be visually observed through comparison of the AFM images (Supporting Information Figure S3), further supporting our conclusion that the surface modification method presented in this paper does not influence the surface roughness of the membrane.

Influence of Functionalization on Membrane Selectivity and Water Permeability. The most fundamental and essential properties of a membrane are solute separation and solvent permeation, which must be seriously considered when designing a membrane modification protocol. The solute selectivity and solvent permeability of the pristine and functionalized membranes were evaluated by measuring the rejection of PEO macromolecules (100 and 200 kDa) and pure water permeability, respectively. The properties of the PMAA-

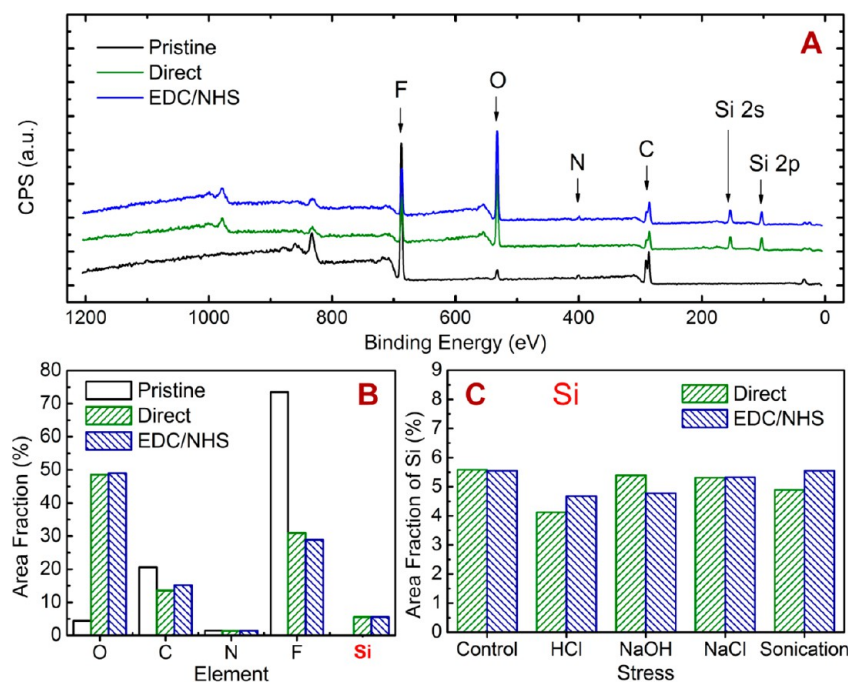


Figure 6. XPS surface analyses of the different membranes. (A) XPS survey scan of the pristine membrane (black), the NP-functionalized membranes via the direct binding method (green), and the NP-functionalized membranes via the EDC/NHS binding method (blue). (B) Area fractions of oxygen (O), carbon (C), nitrogen (N), fluorine (F), and silicon (Si) relative to the sum of these elements present at the surface of the three different membranes. (C) Area fractions of Si on the surface of the two different functionalized membranes after being subjected to the indicated chemical and physical stresses, as well as the membranes before being subjected to the chemical/physical stresses (serves as a control).

grafted membrane were also determined. As shown in Figure 9, the 60 s plasma induced graft copolymerization resulted in a reduced membrane rejection of the 100 kDa PEO and a marked increase in water permeability. This observation is attributed to the etching effect of the plasma treatment and is consistent with other studies.^{37,51} After functionalization, the silica NPs on the membrane surface acted as an additional selective barrier, thus decreasing the water permeability to about the same level as the pristine membrane. Furthermore, no significant change was observed for the membrane rejection of the 200 kDa PEO (Figure 9A). In general, our observations suggest that the surface modification method presented in this paper does not significantly influence membrane selectivity and permeability.

NP Surface Functionalization Imparts Antifouling Property to the PVDF Membrane. The antifouling performance of the functionalized membranes was evaluated through multicycle-filtration runs with a 15 mg L⁻¹ BSA solution (Figure 10). All filtration runs started at the same initial flux (~ 100 L m⁻² h⁻¹ at $t = 0$) under similar applied pressures (~ 70 kPa). In the first filtration cycle, the pristine membrane suffered a rapid flux decline due to fouling and concentration polarization and, then, attained a plateau at $\sim 20\%$ of the initial water flux. After physical cleaning (i.e., rinsing with BSA-free solution at 400 rpm with no applied pressure), the pristine membrane water flux only recovered to $\sim 30\%$ of the initial flux, indicating the poor antifouling property. This poor antifouling performance of the pristine PVDF membrane was also observed in the subsequent two cycles of filtration. In marked contrast, both functionalized membranes attained a water flux $\sim 40\%$ of the initial value as BSA solutes accumulated at the membrane surface due to concentration polarization and some fouling and achieved more than 80% water flux recovery after the simple physical cleaning

operation. This high antifouling performance was also observed in the further two filtration cycles, demonstrating the antifouling property of the functionalized membranes.

As discussed in the previous sections, the electron donor monopolar surface of the NP-functionalized membrane forms a tightly bound hydration layer on the membrane surface. This tightly bound hydration layer exhibits repulsive interactions with the protein molecules, which are also electron donor monopolar.⁴⁷ These repulsive interactions render the functionalized membranes antifouling, which results in low irreversible adsorption of BSA molecules to the functionalized membrane surface and, thereby, very high recovery of water flux after physical cleaning.

CONCLUSION

A novel, highly hydrophilic PVDF UF membrane is fabricated via a postfabrication method. Superhydrophilic silica NPs are irreversibly bound to the PMAA graft-copolymerized PVDF membrane surface via a simple dip-coating technique. The resultant functionalized membrane in the absence of EDC/NHS cross-linking strongly compares with the one fabricated in the presence of EDC/NHS cross-linking, implying the remarkable adsorption ability of the surface-tailored silica NPs. Both modifications significantly improve the wettability of the membranes and convert the membrane surface from hydrophobic to hydrophilic. Moreover, the functionalized membrane forms a tightly bound hydration layer on the membrane surface, which serves as a repulsive boundary barrier and endows the membrane with remarkable antifouling properties, suggesting great potential for the functionalized membrane to be used in a variety of applications.

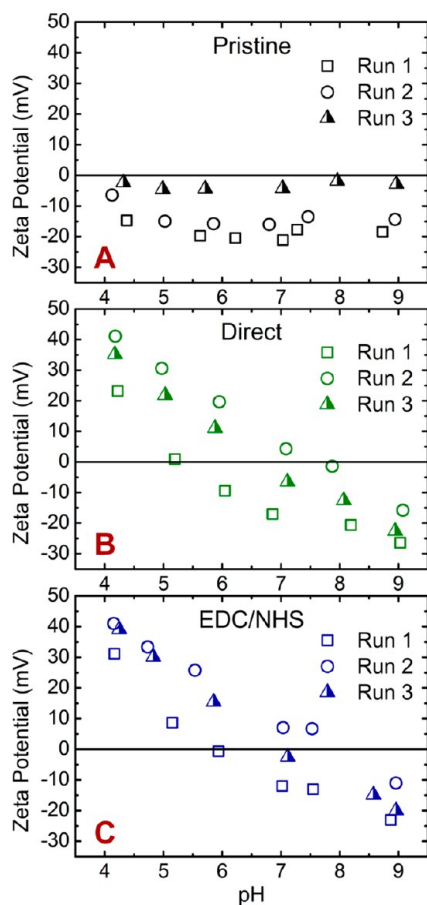


Figure 7. Surface zeta potential as a function of solution pH for (A) pristine membrane, (B) NP-functionalized membrane via the direct binding method, and (C) NP-functionalized membrane via the EDC/NHS binding method. For each type of membrane, zeta potentials of at least three separately cast and functionalized samples were measured (indicated with different symbols). Measurements were carried out in a solution of 0.1 mM KHCO_3 and 1 mM KCl at room temperature ($23 \pm 1^\circ\text{C}$).

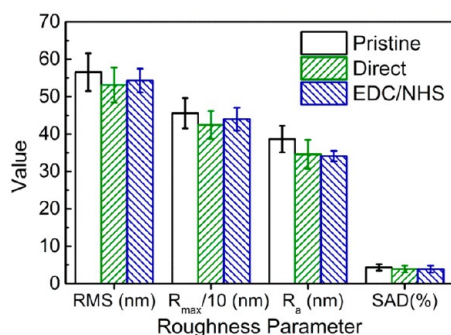


Figure 8. Analyses of surface roughness by AFM of the pristine membrane, NP-functionalized membrane via the direct binding method (green patterned), and NP-functionalized membrane via the EDC/NHS binding method (blue patterned). Roughness parameters, including root-mean-square of roughness (RMS), maximum roughness divided by a factor of 10 ($R_{\text{max}}/10$), average roughness (R_a), and surface area difference (SAD), were measured by tapping mode AFM. The roughness results represent the average of measurements taken from at least nine random spots on three separately cast and functionalized membranes.

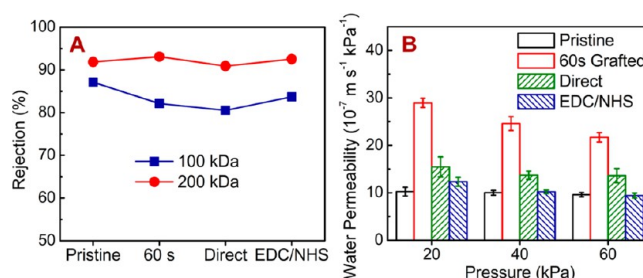


Figure 9. (A) Variation of rejection of PEO macromolecules (100 and 200 kDa) for different membranes: pristine, 60 s grafted, NP-functionalized (direct binding), and NP-functionalized (EDC/NHS binding). (B) Pure water permeability of the membranes described in A as measured at three different applied pressures.

ASSOCIATED CONTENT

Supporting Information

SEM top views of the two types of functionalized membranes after being subjected to chemical and physical stresses (Figure S1). SEM top views of the pristine membrane after NP binding with the direct method and after ultrasonication stress treatment (Figure S2). Typical AFM images of the pristine membrane, NP-functionalized membrane via the direct binding method, and NP-functionalized membrane via the EDC/NHS binding method (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This publication is based on work supported by Award No. KUS-C1-018-02, granted by King Abdullah University of Science and Technology (KAUST). We also acknowledge the postgraduate scholarship program of the China Scholarship Council (CSC) and the use of facilities supported by YINQE and NSF MRSEC DMR 1119826.

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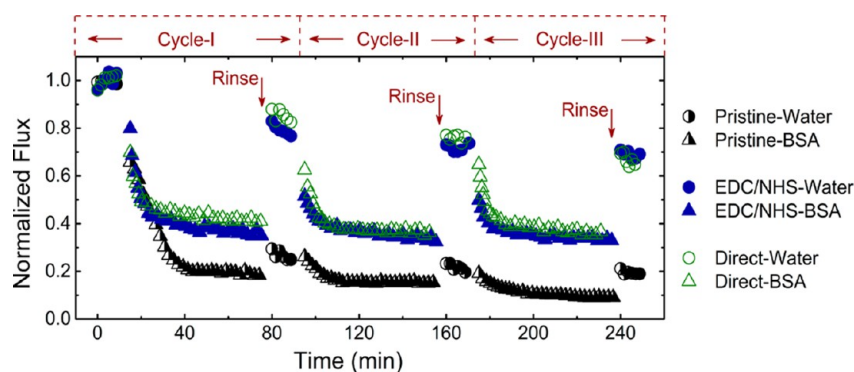


Figure 10. Fouling behavior with BSA solution obtained in three sequential dead-end filtration cycles for three membranes: pristine or control (black patterned), NP-functionalized via direct binding (green hollow), and NP-functionalized via EDC/NHS binding (blue solid). For the first cycle, the water flux with no BSA foulant was measured first (circles), then fouling was initiated by adding BSA resulting in flux decline (triangles), and then the membrane was rinsed with BSA-free solution and the water flux was measured again (circles) to determine the flux recovery. Experimental conditions for all filtration cycles were the following: 15 mg L⁻¹ BSA, 10 mM ionic strength (9.9 mM NaCl and 0.1 mM NaHCO₃), 400 rpm stirring rate, room temperature (23 ± 1 °C), and an initial flux of 100 L m⁻² h⁻¹ (adjusted for each experiment by controlling the applied pressure).

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