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Antifouling and Antimicrobial Polymer Membranes Based on Bioinspired Polydopamine and Strong Hydrogen-Bonded Poly(*N*-vinyl pyrrolidone)

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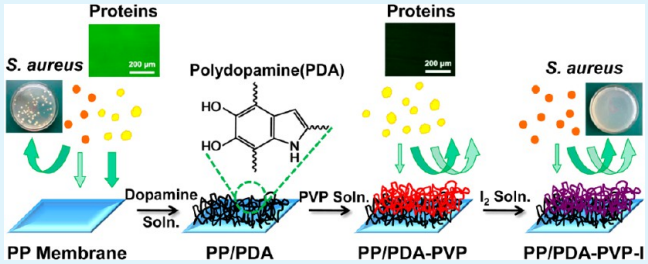
Supporting Information

ABSTRACT: A facile and versatile approach for the preparation of antifouling and antimicrobial polymer membranes has been developed on the basis of bioinspired polydopamine (PDA) in this work. It is well-known that a tightly adherent PDA layer can be generated over a wide range of material surfaces through a simple dip-coating process in dopamine aqueous solution. The resulting PDA coating is prone to be further surface-tailored and functionalized via secondary treatments because of its robust reactivity. Herein, a typical hydrophobic polypropylene (PP) porous membrane was first coated with a PDA layer and then further modified by poly(*N*-vinyl pyrrolidone) (PVP) via multiple hydrogen-bonding interactions between PVP and PDA. Data of water contact angle measurements showed that hydrophilicity and wettability of the membranes were significantly improved after introducing PDA and PVP layers. Both permeation fluxes and antifouling properties of the modified membranes were enhanced as evaluated in oil/water emulsion filtration, protein filtration, and adsorption tests. Furthermore, the modified membranes showed remarkable antimicrobial activity after iodine complexation with the PVP layer. The PVP layer immobilized on the membrane had satisfying long-term stability and durability because of the strong noncovalent forces between PVP and PDA coating. The strategy of material surface modification reported here is substrate-independent, and applicable to a broad range of materials and geometries, which allows effective development of materials with novel functional coatings based on the mussel-inspired surface chemistry.



KEYWORDS: *polydopamine, poly(N-vinyl pyrrolidone), membrane, antifouling, antimicrobial, oil/water separation*

1. INTRODUCTION

Polymer is the most favorable membrane material because of its excellent film forming ability, mechanical strength, chemical and thermal stability, corrosion and oxidation resistance, as well as low cost. Polymer porous membranes have been widely used in chemical industry separation, food, environment, energy resources, biomedical fields, and so on. However, most of synthesized polymer membranes are inherently hydrophobic, which augments resistance to water permeation and increases energy consumption during separation. Moreover, organics, colloids, and organisms in the feed solution are prone to adsorb onto membrane surfaces and into pore walls, leading to membrane fouling and degenerating the comprehensive performances of the membranes. These drawbacks make the hydrophobic membranes unsatisfactory for use in organics/water separation (such as oil/water separation) in water treatment and bioseparation system. Therefore, hydrophilic and antimicrobial modification for synthesized polymer membranes is a pressing demand in overcoming these problems and tailoring the membrane surface with desirable properties.

Poly(*N*-vinyl pyrrolidone) (PVP) is one of the synthesized fine chemicals and is widely used in daily chemical industry, food, biomedical field, etc. It exhibits good chemical stability, complexing ability, colloids characteristics, physiological inertness, biocompatibility, and preeminent solubility in water as well as most conventional organic solvents.[1,2] According to the literatures,[2−5] introducing PVP onto polymer surfaces is able to enhance the hydrophilicity, antifouling properties and hemocompatibility of the hydrophobic polymer materials. Currently, commercial PVP is generally regarded as a promising hydrophilic and antifouling surface modifier comparable to poly(ethylene glycol) (PEG). Various methods such as physical coating,[6] blending modification,[7,8] photochemical grafting,[9] γ-radiation-induced grafting,[10,11] and plasma polymerization[12] have been developed to incorporate hydrophilic PVP into/onto polymer membranes. Nevertheless, there are some major challenges in these modification methods, including loss of PVP coatings because of weak bonding and damage to the bulk properties and membrane structures under polymerization conditions. In addition, these methods are more or less

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complicated and lack a general applicability to diverse polymer materials with complex shapes.[2,13,14]

Recently, Messersmith et al. developed a facile and versatile aqueous surface modification technique using dopamine as a powerful modifier based on mussel-inspired surface chemistry.[15] Dopamine is a kind of catecholamine that contains both catechol and primary amine functional groups. This simple structural mimic of mussel adhesive proteins (MAPs) is a powerful building block for firm attachment of polydopamine (PDA) upon various substrates in wet environments. Under oxidizing conditions, dopamine is able to undergo self-polymerization in aqueous solution, creating a tightly adherent PDA layer onto a substrate that is immersed in the freshly prepared dopamine solution for a period of time. This surface modification strategy can be applied to virtually any solid materials including polymers, noble metals, oxides, semiconductors, and ceramics. And the modified surfaces can serve as useful platforms for secondary reactions and surface functionalization under mild conditions.[15,16] In recent research, hydrophobic polymer membranes or films including polyethylene (PE), poly(vinylidene fluoride) (PVDF), polytetrafluoroethylene (PTFE), etc., were successfully modified with adhesive PDA coatings by dip coating in dopamine solution.[17−22] Diverse functional molecules were further bound onto PDA-coated membranes via covalent immobilization to endow the membranes with superior performance for various applications.[23−25] However, incorporation of hydrophilic PVP molecules onto a PDA-coated surface solely via noncovalent interactions have not been reported yet as far as we know. The motivation of the present work is to explore the strong noncovalent interactions between PDA and PVP and to extend their applications in hydrophilic, antifouling, biocompatible, lubricative as well as anticorrosive modifications for various solid materials.

Many researches have suggested that PVP is capable of adsorbing polyphenols compounds selectively through strong noncovalent interactions. The strength of multiple hydrogen bonding interactions between lactam groups in PVP and phenolic hydroxyl groups in polyphenols is probably comparable to that of covalent interactions.[26−30] Actually, dopamine and its polymerization products have similar catechol moieties to the polyphenols compounds. Recently, Zhang et al.[31] have demonstrated that oxidant-induced dopamine polymerization in aqueous solution can be hindered by PVP because of its strong hydrogen acceptor nature. The hydrogen bond between PVP and catechol species is able to interfere with PDA formation by suppressing both noncovalent self-assembly and covalent polymerization. It is indicated that there are strong noncovalent interactions between PVP and catechol compounds such as dopamine.[27,31] In this work, a hydrophobic polypropylene (PP) membrane was first surface-modified by a layer of PDA (Figure 1). And then hydrophilic PVP was immobilized onto the PDA-coated PP membrane via hydrogen bonding interactions. Antimicrobial iodine was further introduced onto the membrane by complexation with the PVP layer. The effects of surface modification on surface morphologies, chemical compositions, hydrophilicity, permeability, oil/water separation performance, antifouling, and antimicrobial properties of the membranes were investigated in detail.

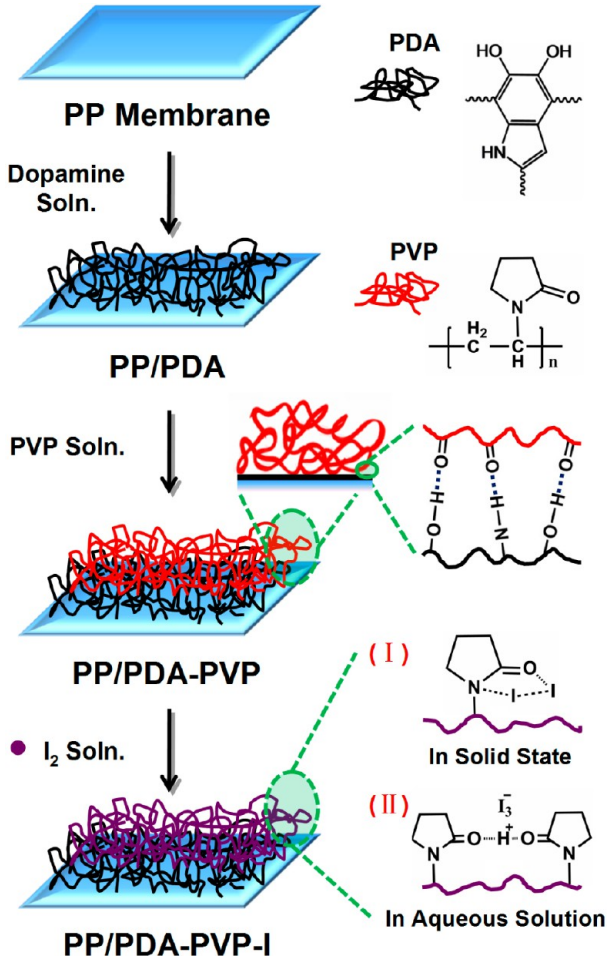

Figure 1. Scheme of coating polydopamine (PDA) on a PP membrane as well as subsequent PVP and iodine complexation.

2. RESULTS AND DISCUSSION

Dopamine is a versatile and powerful biomimetic surface modifier that has been widely used to modify various solid materials with distinctly different chemical compositions and physical morphologies, even for classically adhesion-resistant materials such as poly(tetrafluoroethylene) (PTFE).[15,16] In this study, the hydrophobic PP membrane was first surface modified by dip coating in an aqueous solution of dopamine. During oxidation and self-assembly process of dopamine, a mass of reaction products (PDA) containing stable complexes of (dopamine)$_2$/5,6-dihydroxyindole and high-molecular-weight polymers are generated and deposit on PP membranes simultaneously.[15,32] The as-prepared PDA-coated PP membrane is referred to as PP/PDA for short. The water contact angle of the original hydrophobic PP membrane decreased from 117.2° to 54.3° after PDA treatment for 24 h, which indicated a dramatical hydrophilic conversion for the PP membranes (Figure 2A). The wetting behavior of water droplets on original PP membrane and PP/PDA membrane was totally different as shown in Figure 2B, which agrees well with the reported results.[33,34] The influences of the PDA coating on the surface morphology and chemical composition of the PP membrane were investigated by field emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS). As shown in Figure 2C, both the pores sizes and porosities decreased for the PP/PDA

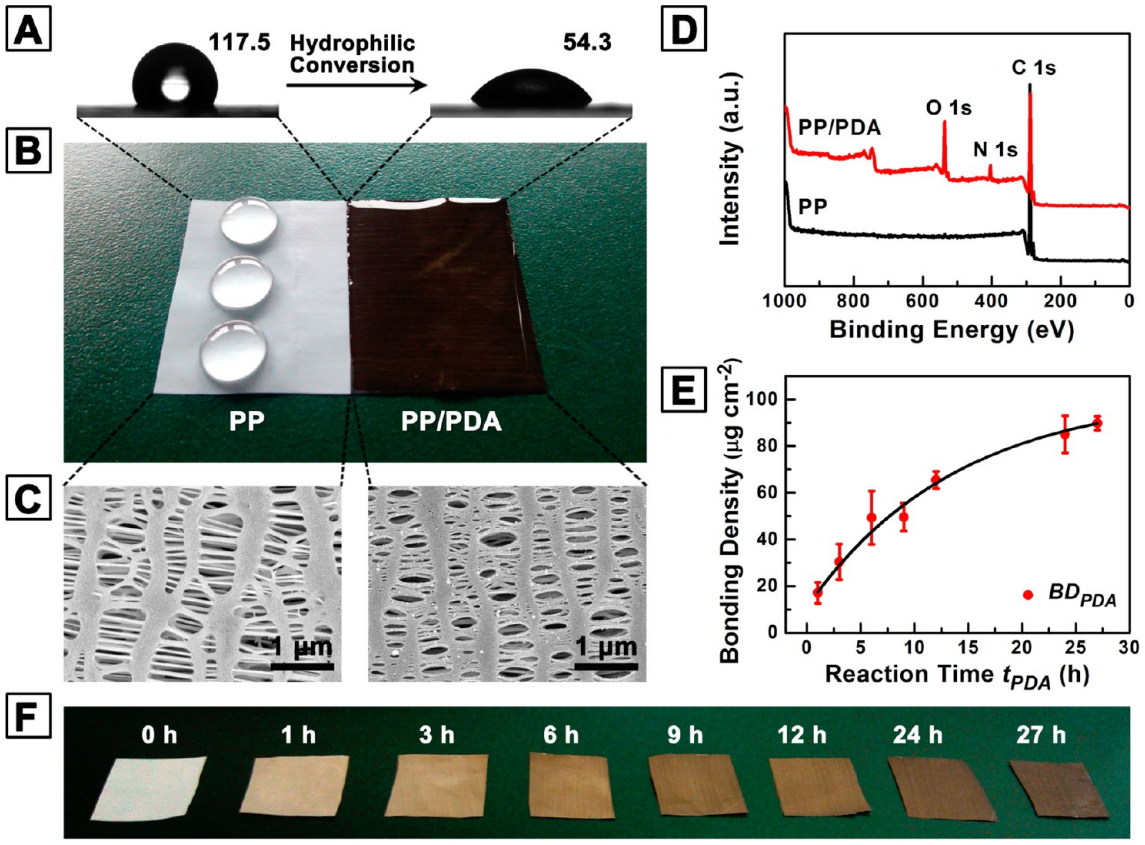

Figure 2. Characterization of the PDA-coated PP membrane (PP/PDA) (t_{PDA} = 24 h for A–D). (A) Water contact angle images of a PP membrane before and after PDA modification. (B) Photograph of wetting behaviors of water droplets on the original PP membrane and PP/PDA membrane. (C) Surface SEM images of the unmodified and modified PP membrane. (D) XPS wide scans for the near surface of PP membrane before and after modification. (E) Variations of surface density for PDA on the modified PP membrane surface with reaction time t_{PDA}. (F) A photograph of changes in colors of PP membranes with reaction time t_{PDA}.

membrane in comparison to the original PP membrane. The generated PDA layer during modification process tightly adhered and covered on the PP membrane, making the membrane surface smoother and denser. As a result of PDA treatment, new peaks, O 1s and N 1s, were observed in the XPS spectra of PP/PDA membrane (Figure 2D) and confirmed the successful introduction of PDA onto the PP membrane. Figure 2E showed an increase in the surface bonding density (BD) of PDA with increasing reaction time t_{PDA}. The growth of BD was fast during the initial 12 h, and then the growth rate decreased and the *BD* gradually approached to a constant value. A BD_{PDA} of 89.8 μg cm^{-2} was obtained for PP/PDA after reacting in an aqueous solution of dopamine for 27 h, and the color of PP/PDA changed from white to dark brown as a result of PDA deposition (Figure 2F).

After modifying the PP membrane with PDA, we tried to further introduce a coating of PVP onto the PP/PDA membrane. PVP is a strong hydrogen acceptor and PDA is a hydrogen donor, which makes them prone to form strong hydrogen bonds with each other.[31] First, we confirmed the interactions between PVP and PDA by detecting changes in UV–vis absorption bands of PVP solution before and after adding PDA deposition. The PDA deposition was collected by centrifugation (10 000 rpm) of a 2.0 g L^{-1} aqueous solution of dopamine after reacting at 60 °C for 24 h. Then a certain amount of PDA deposition was added into a 5.0 g L^{-1} aqueous solution of PVP and the mixture was shaken for 24 h. The UV–vis spectra of the PVP solutions were shown in Figure 3A. Seen from the UV–vis spectra, there was no obvious characteristic absorption peak for the PVP solution at wavelength from 250 to 600 nm. After blending PDA with the solution, a distinct band at 280 nm and a shoulder at about 310 nm gradually rose with the increasing dosage of PDA deposition. These new absorption bands are attributed to the unpolymerized dopamine (280 nm) and its oxidation products such as 5,6-dihydroxyindole as well as its oligomers (310 nm), respectively, in the PDA deposition.[35−37] As is known to us, the UV–vis absorption of PDA is monotonic with a broad band from 200 to 800 nm,[38,39] which was also found in Figure S1 in the Supporting Information. The appearance of characteristic absorption bands at 280 and 310 nm suggested that monomers and oligomers were captured from the PDA deposition when exposed to an aqueous solution of PVP. The results indicate that there is strong force between PVP and PDA, thus PVP is capable of grabbing a fraction of nonfirmly adherent PDA (especially monomers such as dopamine and its oxidation products as well as oligomers) from the PDA deposition. Besides, this finding supports the hypothesis that PDA consists of unreacted dopamine and its oxidation products, oligomers, and high-molecular-weight polymers.[32]

Based on the strong interactions between PVP and PDA, PVP was bonded onto the PDA layer via simply immersing PP/PDA membrane into a PVP solution. The resultant PVP-modified membrane is referred to as PP/PDA-PVP for short in the following discussion. As presented in Figure 3B, the hydrophilicity of the PP/PDA-PVP membrane was further

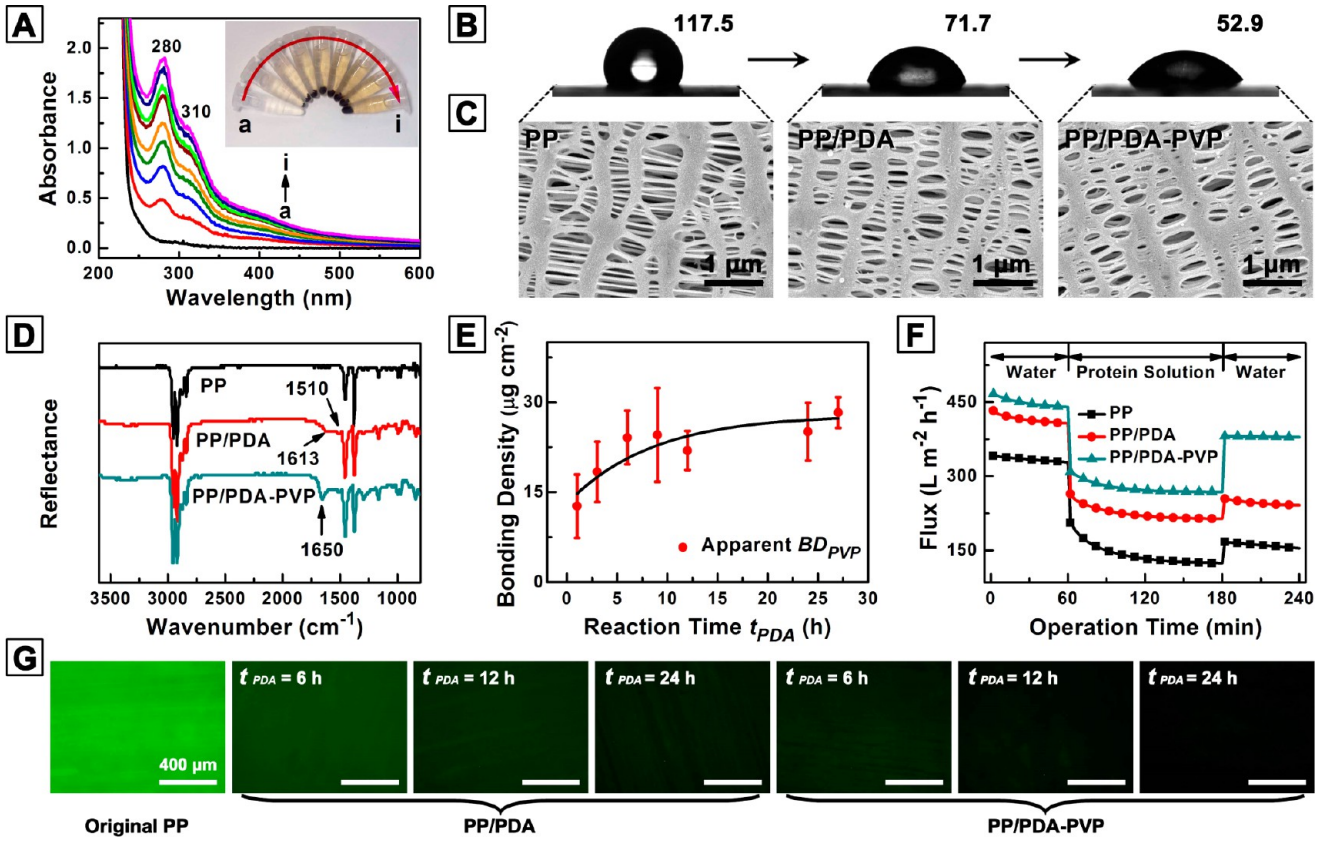

Figure 3. Interactions between PDA and PVP as well as the subsequent characterization of the PVP-modified PP membrane (PP/PDA-PVP). (t_{PDA} = 6 h for 3B–D, 3F) (A) UV–vis spectra of the PVP solutions with PDA concentrations of (a–i) 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 g L^{-1}, respectively. The inset shows the changes in colors of the PVP solutions with the increasing dosage of PDA. (B) Water contact angle images and (C) surface SEM images of the membranes. (D) ATR-FTIR spectra for the near surface of membranes. (E) Variations of apparent surface density for PVP on the modified PP membrane surface with reaction time t_{PDA}. (F) Permeate flux of water and protein solution through the original and modified PP membranes. (G) Representative fluorescence microscopy images of the membranes surfaces after being exposed to a BSA-FITC solution for 8 h.

improved after incorporation of PVP. The surface morphologies and chemical composition of the membranes were investigated with FESEM and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). It was found that the pores sizes and porosities of the PP membrane decreased as a result of the coverage of the PDA and PVP coating (Figure 3C and Figure S2 in the Supporting Information). Seen from the ATR-FTIR spectra shown in Figure 3D, an obvious difference in the spectra of original PP and PP/PDA membrane was detected. New absorption signals at 1613 and 1510 cm^{-1} after PDA modification are ascribed to the superposition of phenylic C═C stretching and N–H bending vibrations (former) as well as N–H shearing vibrations (latter), respectively. It is indicated that PDA is formed and incorporated onto the modified PP membrane surface. For the spectra of the PP/PDA-PVP membrane, a new peak appearing at 1650 cm^{-1} is attributed to C═O stretching (amide I band) in pyrrolidone ring of PVP. The result proved that PVP was incorporated onto the PP membrane surface with success via hydrogen bonding interactions (see Figure S3 in the Supporting Information). Figure 3E showed the apparent BD of PVP on the PP membrane with different reaction time t_{PDA}. It is worth noting that BD for PP/PDA-PVP membrane is labeled as apparent BD_{PVP} because it is not the real BD of PVP. There was weight loss for PP/PDA membrane during PVP modification process. A fraction of nonfirmly adherent PDA was removed from the PDA coatings when the PP/PDA membrane was put into an aqueous solution of PVP (see Figure S4 in the Supporting Information) as confirmed in the Figure 3A and Figure S1 in the Supporting Information. However, the variation of apparent BD_{PVP} basically followed the common rule, and the apparent BD_{PVP} reached 28.3 μg cm^{-2} when reaction time t_{PDA} was 27 h.

It is known that adsorption of organic contaminants especially proteins on membrane surface and in membrane pores is ordinarily the predominant reason for membrane fouling in separation and purification processes. In practical use, membrane fouling should be minimized as low as possible. BSA is usually used as a model protein to investigate fouling dynamics of membranes[40–42] and was employed to evaluate antifouling performances of the original and modified PP membranes. As shown in Figure 3F, the permeate fluxes of pure water and protein solution for PP/PDA membrane and PP/PDA-PVP membrane (t_{PDA} = 6 h) were both enhanced in comparison to that of the original PP membrane. This is ascribed to the decrease in membrane resistance to water permeation by incorporating hydrophilic PDA and PVP coatings. Besides, membrane fouling caused by adsorbed proteins was effectively minimized by the hydrophilic PVP coating (see Table S1 in the Supporting Information). After modification, water molecules from the protein solution are capable of adsorbing on the membrane surface preferentially,

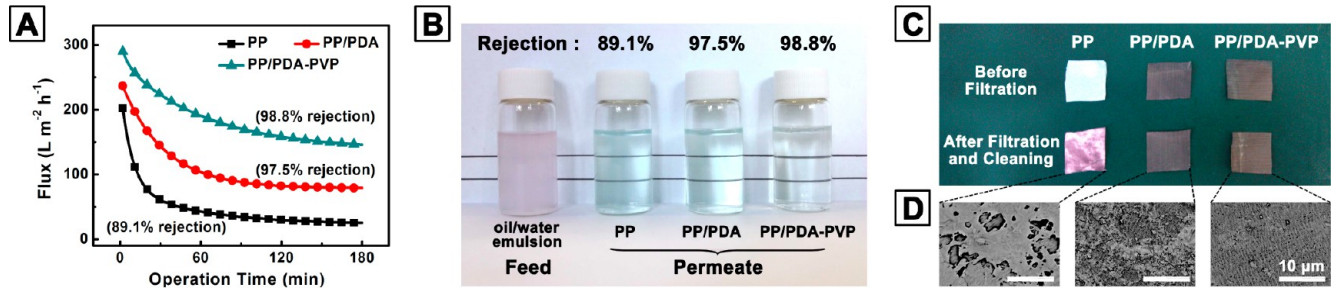

Figure 4. Oil/water separation performances of the PP membrane before and after modification. (t_{PDA} = 6 h) (A) Attenuation curves for permeate fluxes of oil/water emulsion through the membranes. (B) Photograph of feed and permeate taken after filtration test. (C) Photograph of each membrane before and after oil/water emulsion filtration. (D) Surface SEM images of each membrane after oil/water emulsion filtration and membrane-cleaning process.

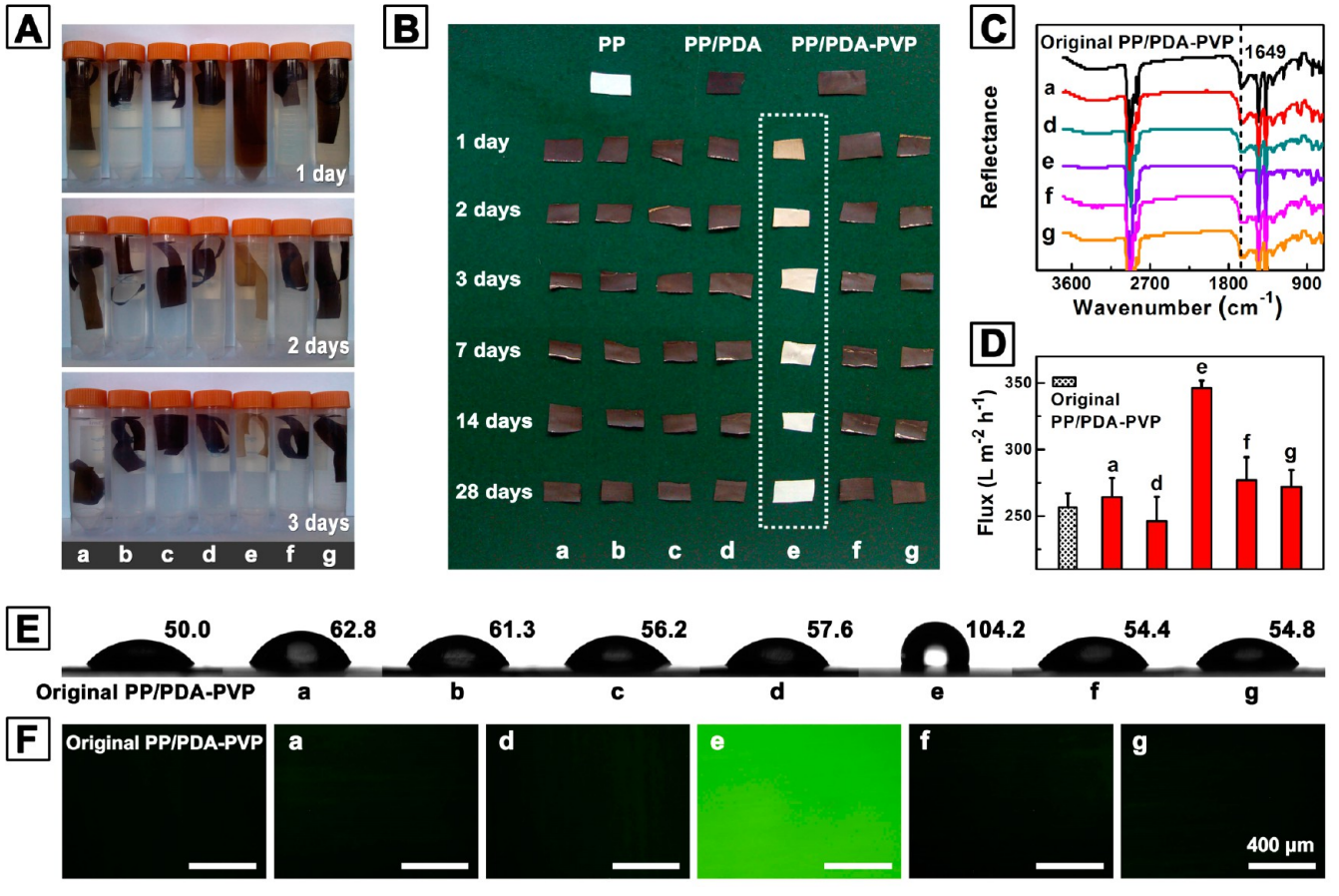

Figure 5. The stability and durability of the PVP coating. (t_{PDA} = 24 h) In this test, the PP/PDA-PVP was washed with aqueous solutions at (a) pH 1, (b) pH 3, (c) pH 7, (d) pH 10, (e) pH 13, as well as aqueous solutions of (f) 2 M DMSO and (g) 8 M urea at room temperature for 28 days. The solutions were replaced daily. (A) Photographs of the different aqueous solutions with PP/PDA-PVP. (B) Photograph of PP/PDA-PVP after shaken in the aqueous solutions for different time. (C) ATR-FTIR spectra, (D) water fluxes, (E) water contact angle images, and (F) fluorescence microscopy images of PP/PDA-PVP membranes before and after shaken in the aqueous solutions for 28 days.

which weakens the interactions of protein molecules with the membrane and reduces membrane fouling as a result.[43,44]

Figure 3G presented fluorescence microscopy images of the membranes surfaces after exposed to a BSA-FITC solution for 8 h. Uniform and intense fluorescence was observed for the original PP membrane, indicating a significant extent of BSA-FITC adsorption on the membrane surface. Compared with the original PP membrane, the fluorescence intensities of the modified membrane decreased obviously, and only faint fluorescence on the surface of the PP/PDA-PVP membrane was visible when t_{PDA} was longer than 6 h. It is associated with the reduced extent of the BSA-FITC adsorption on the modified surfaces. The results are in accordance with those in the filtration test. The hydrophilic coatings preferentially adsorb water molecules and repel organics simultaneously in the separation process, which endows the hydrophobic PP membrane with dramatically improved hydrophilicity, permeability, and fouling resistant capacity.

According to the current membrane technology, oil/water separation on the basis of microfiltration, ultrafiltration, nanofiltration and reverse osmosis is able to effectively decrease industry wastewater in polluting environments. However, oil

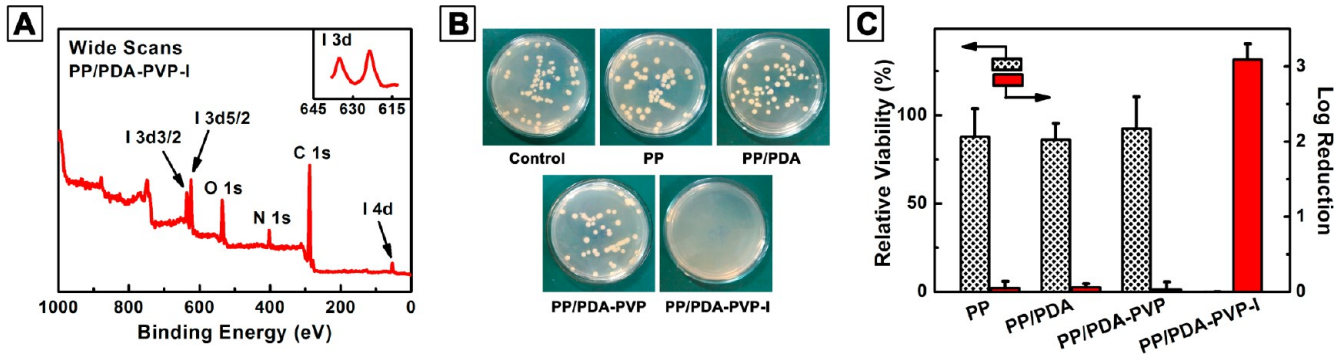

Figure 6. Characterization of the iodine-containing PP membrane (PP/PDA-PVP-I). (t_{PDA} = 6 h) (A) Typical XPS wide scans for the PP/PDA-PVP-I membrane. (B) Antimicrobial activities of each membrane against *S. aureus* and (C) relative viability and log reduction of *S. aureus* after 24 h contact time of each membrane sample.

emulsion fouling is a key challenge during water purification and oil recovery process in membrane-based oily water treatment. Seen from Figure 4**A**, the attenuation of oil/water emulsion flux ($J_{W/O}$) for the original PP membrane was the fastest compared with that of the modified membranes. After 3 h of oil/water emulsion permeation, the $J_{W/O}$ of the PP membrane declined to 12.4% of its initial flux, while this value was 33.5% for PP/PDA membrane and 50.4% for PP/PDA-PVP membrane, respectively. It is suggested that the PP membrane is prone to be fouled by oil because of its hydrophobicity, while hydrophilic PDA or PVP coating is helpful for water to permeate through the membrane and decreasing membrane fouling. Besides, the wetting of the PP membrane by oil during separation increased the likelihood of oil permeation through the membrane. After hydrophilic modification, the oil from the feed was more difficult to permeate through the membranes due to an elevated resistance. As a result, an increased oil rejection for the PP/PDA and PP/PDA-PVP membrane was observed (Figure 4B). After emulsion filtration and membrane-cleaning process, the PP membrane showed a reddish and streaky surface (Figure 4C), which was fully covered by a thick layer of oil contaminants (Figure 4D). For the PP/PDA and PP/PDA-PVP membranes, most of the contaminants were removed through cleaning, and only a few was observed on the PP/PDA-PVP membrane surface. The results are in accord with those in protein filtration test. It is implied that membrane fouling caused by organics such as proteins and oil could be remarkably suppressed by incorporating a hydrophilic coating onto PP membrane surface, and the as-prepared PP/PDA-PVP membrane is quite useful for oily wastewater treatment in practical applications.

The stability and durability of the hydrogen-bonded PVP coatings on the modified PP membranes are important in practice. Generally, temperature and pH value are two dominant factors influencing the strength of hydrogen bonding in aqueous solutions. Two powerful hydrogen-bond-breaking agents, DMSO and urea, were also used to examine the strength of the hydrogen bonds forming between PVP and PDA molecules.[45−47] In this test, the as-prepared PP/PDA-PVP membrane was shaken in aqueous solutions at pH 1, 3, 7, 10, and 13, as well as aqueous solution of 2 M DMSO and 8 M urea at speed of 100 rpm at room temperature for continuous 28 days. The solutions were replaced daily. It was found that the colors of these solutions changed from colorless to brown especially at pH 13 after washing for 1 day (Figure 5**A**). That means some of nonfirmly adherent PDA on the membranes is removed from the membranes into the solutions when rinsed in aqueous solutions at pH 1, 10, 13, and 8 M urea. In the strongly alkaline solution, most of PDA is able to be dissolved,[48,49] which was the case of the PP/PDA-PVP membrane shaken in aqueous solution at pH 13. As a result of dissolution of PDA, the color of the solution became dark brown and the washed PP/PDA-PVP membrane changed from dark drown to nearly white gradually (Figure 5B). However, the remaining PDA coatings on the membranes tended to be stable after washed for 3 days, for nearly no changes in colors was observed for all the aqueous solutions and washed PP/PDA-PVP membranes. The ATR-FTIR spectra, water fluxes and water contact angle images of the PP/PDA-PVP membranes before and after 28 days were shown in Figure 5C−E. Few differences in the surface chemical compositions and a slight decrease in surface hydrophilicity were found for the washed membranes in comparison to that of the original PP/PDA-PVP membrane except for the one shaken in aqueous solution at pH 13. Seen from Figure 5D, the water flux of the original PP/PDA-PVP membrane (t_{PDA} = 24 h) was 256.5 L m^{-2} h^{-1}. It was lower than that of the original PP membrane (334.3 L m^{-2} h^{-1}) as shown in Figure S5 in the Supporting Information because of the excessive coverage of the coating layer over the membrane surface. After immersion in the solution of pH 13, the water flux of the PP/PDA-PVP membrane (346.2 L m^{-2} h^{-1}) changed back to the level of the original PP membrane, suggesting the removal of coatings after washing. While the fluxes of the membranes washed under other conditions did not change much. Figure 5F presented the fluorescence microscopy images of each PP/PDA-PVP membrane after exposed to a BSA-FITC solution for 8 h. The fouling resistant capacity of each membrane almost kept unchanged after washing for 28 days apart from the one immersed in the solution of pH 13. It is indicated that the coatings are stable in aqueous solution with wide pH range (pH 1−10), and the interactions between PDA and PVP are strong enough to resist the disruption by 2 M DMSO and 8 M urea solution. The good stability of the PVP coatings was probably attributed to the strong multiple hydrogen bonding interactions assisted by other potential noncovalent interactions[50−52] between PDA and PVP molecules. Moreover, the PVP layers are capable of bearing a relatively high temperature at least 60 °C (see Figure S6 in the Supporting Information). These results proved that the PVP coatings possess of satisfying thermal and chemical stability, which meets the actual demands for applications in water treatment.

PVP−iodine complex, an iodophor, is a widely used broad spectrum bacteriocidal agent without known bacterial resistance. In this work, iodine was further bonded onto the PVP-modified polymer membranes to endow the membranes with antimicrobial activities. The as-prepared iodine-containing membrane is referred to as PP/PDA-PVP-I for short. The surface chemical composition of the PP/PDA-PVP-I membrane was analyzed by XPS. As shown in Figure 6A, several strong peaks such as *I3d* and *I4d* appeared in the wide-scan spectra of the PP membrane after iodine complexation, which confirmed the introduction of iodine molecules onto the PP membrane. As is known to all, PVP−iodine is able to eradicate commonly seen microorganisms including bacteria, fungi, molds, viruses, and so on.[53] One of the Gram-positive bacteria, *S. aureus*, was chosen to authenticate the antimicrobial activity of the PP/PDA-PVP-I membrane. Panels B and C in Figure 6 showed the antimicrobial activities of each membrane sample against *S. aureus*. It was found that the count for viable colonies of *S. aureus* decreased sharply after contacting with PP/PDA-PVP-I membrane for 24 h. The relative viability of the *S. aureus* was lower than 0.1% and the log reduction reached more than 3 for the PP/PDA-PVP-I membrane. This implied that 99.9% of the *S. aureus* were killed and the PP/PDA-PVP-I membrane had excellent antimicrobial activity against Gram-positive *S. aureus*. Actually, free molecular iodine (I_2) that is released from the PP/PDA-PVP-I surface is almost entirely responsible for the observed antimicrobial activity.[54] Molecular I_2 is able to freely enter cells of microorganisms, and works via a series of pathways to eradicate the microorganisms on the basis of its powerful electrophilic character.[53] Therefore, an antimicrobial PP membrane can be obtained by the introduction of iodine onto the membrane through complexation with the PVP coating layer.

To confirm the versatility of this modification strategy, we also surface modified two other hydrophobic polymer membranes, polysulfone (PSF) and polyethylene (PE), by the same procedure as to the PP membranes (see Figure S7−S11 and Tabls S1 in the Supporting Information). It is implied that this strategy is an efficient and versatile method for surface modification of various materials.

3. CONCLUSIONS

A facile and versatile approach for preparation of antifouling and antimicrobial polymer membranes is described based on the strong noncovalent interactions between PDA and PVP. Hydrophobic PP membranes were successfully modified with strong adherent PDA layers and then further coated with PVP polymers via the multiple hydrogen bonding interactions between PVP and PDA layers. The hydrophilicity and wettability of the PP membrane were significantly improved after PDA and PVP modification. And the permeate fluxes and antifouling properties of the PVP-modified membranes were also greatly enhanced. The rejection of the PP/PDA-PVP in oil/water emulsion filtration was higher than 98%, indicating the membrane was quite useful for oily wastewater treatment in practical applications. Moreover, the PP membranes were endowed with high antimicrobial activity after iodine complexation, being able to suppress the formation of biofilm on membrane surface during separation process. Although the PVP coating was bonded in a noncovalent manner, it showed good long-term stability and durability in aqueous solution with wide pH range (pH 1−10). Hydrogen bond breaking agents and a relatively high temperature of 60 °C could not cause any noticeable disruption of the interactions between PDA and PVP either. This surface modification method is applicable to nearly any substrates without limit to their surface chemical characteristics, shapes and sizes, which allows the development of novel functional materials on the basis of bioinspired PDA coating. In addition, PVP was proved to be capable of grabbing fractional nonfirmly bonded PDA from the polymerization product of dopamine, especially monomers and oligomers in PDA deposition or PDA coatings on PP/PDA membranes. These fundamental findings will lead to a better understanding of the interactions between PVP and PDA, giving further insight into the PDA characters.

4. EXPERIMENTAL SECTION

Materials and Reagents. Polypropylene (PP) membrane (Celgard 2500, porosity 51%) was got from Celgard Company. 3,4-dihydroxyphenethylamine (dopamine hydrochloride) was obtained from Sigma-Aldrich and used as received. Poly(*N*-vinyl pyrrolidone) (PVP, K-30), bovine serum albumin (BSA, purity of ≥98%), and iodine (I_2, purity of ≥99.8%) were purchased from Sinopharm Chemical Reagent Co. Fluorescein isothiocyanate (FITC) and Sudan IV were obtained from Aladdin Reagent Co. Soybean oil (Golden Dragon Fish) was purchased from a local supermarket. DC193 nonionic surfactant was got from Dow Corning Corp. Staphyloccocus aureus Rosenbach (*S. aureus*) was provided by the College of Life Sciences, Zhejiang University, China. All other chemicals were of commercial analytical grade and were used without further purification.

Surface Modification of Polymer Membranes. A 1.0 g L^{-1} aqueous solution of dopamine was prepared by dissolving 0.25 g of dopamine in 250 mL of deionized water in an open vessel. Then 1 mL of 1 M NaOH solution was added into the solution to adjust the pH of the solution to about 9. Clean PP membranes (5 × 5 cm^2) were soaked in ethanol for 1 h, and then immediately immersed in the freshly prepared dopamine solution with continuous stirring at 15 °C, in contact with atmospheric oxygen. After reacting for a predesigned time (t_{PDA}), the membranes were taken out and washed with deionized water and ethanol alternately to remove nonfirmly adsorbed PDA particles. The resultant PDA-coated PP membranes (PP/PDA) were dried to constant weight in a vacuum oven at 40 °C and used for characterization or further surface modification. For permeation test, the PP/PDA membranes were stored in deionized water without drying step.

The PP/PDA membranes were immersed into a 2.0 g L^{-1} aqueous solution of PVP with continuous stirring at 15 °C for 24 h. Then the membranes were taken out and rinsed with deionized water thoroughly to remove nonfirmly bonded PVP. After being dried to constant weight in a vacuum oven at 40 °C, the resultant PVP-modified membranes (PP/PDA-PVP) were used for characterization or further surface modification. For permeation test, the PP/PDA-PVP membranes were stored in deionized water without drying step.

The bonding density of PDA (BD_{PDA}, $\mu g\ cm^{-2}$) and PVP (BD_{PVP}, $\mu g\ cm^{-2}$) on the polymer membranes were determined by measuring the weight changes of membranes before and after modification with an electronic balance with 0.0001 accuracy. They were calculated according to eqs 1 and 2

$$BD_{PDA} = \frac{W_{PDA} - W_{MEM}}{A_{MEM}} \quad (1)$$

$$BD_{PVP} = \frac{W_{PVP} - W_{PDA}}{A_{MEM}} \quad (2)$$

where W_{MEM}, W_{PDA}, and W_{PVP} (μg) are the weight of the original PP, PP/PDA and PP/PDA-PVP membranes, respectively. A_{MEM} (cm^2) represents the surface area of the membrane. Each result is an average of at least three parallel experiments.

Iodine complexation onto the PP/PDA-PVP membranes was performed following a reported procedure.[55−57] A 5 wt % iodine

solution (100% ethanol as solvent) was prepared in advance and then the PP/PDA-PVP membranes were impregnated in the solution at 10 °C for 24 h. It should be noted that a higher reaction temperature might cause damage to the PDA coatings. To remove the free iodine from the membranes, the resultant membranes were first washed with ethanol three times and then incubated in n-heptane. After incubating overnight, the membranes were further washed with n-heptane twice. The washed solution was colorless and not detected with free iodine by using UV−vis spectroscopy. Then the resultant membranes (PP/PDA-PVP-I) were dried in air at room temperature and used for characterization.

Surface Characterization. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 6700, USA) were employed to analyze the changes in the functional groups on the surfaces of PP membranes after modification. An X-ray photoelectron spectroscopy (XPS, PHI 5000 C ESCA System, USA) with Mg Kα excitation radiation ($h\nu$ = 1253.6 eV) was utilized to detect the chemical compositions in the near surfaces of the membranes, at a takeoff angle of 60°. The whole scan spectra of all the elements with high resolution were both recorded by RBD 147 interface (RBD Enterprises, USA) through the software. A field-emission scanning electron microscope (FESEM, Hitachi S-4800, Japan) was used to observe the surface morphologies of the PP membranes. Water contact angle measurement (CA, Dataphysics OCA20, Germany) was employed to characterize the surface hydrophilicity of the PP membranes. Five measurements were performed for each membrane at 20 °C and 70% relative humidity, and the mean value was taken as the reported result.

Filtration and Antifouling Performance Assessment. A homemade dead-end filtration apparatus with a tested membrane area of 4.9 cm^2 was used to characterize the filtration performance as well as protein solution fouling dynamics of the PP membranes. Original PP membrane was soaked in a 50% ethanol aqueous solution for 1 h to completely infiltrate the hydrophobic membrane before use. And then the membrane was taken out and rinsed with deionized water to thoroughly remove the residual ethanol in the membrane pores. The PP/PDA or PP/PDA-PVP membranes were kept in deionized water and used for characterization directly. The filtration and antifouling performance assessment was performed according to a reported procedure.[40−43] A 1.0 g L^{-1} protein solution was prepared by dissolving BSA in PBS buffer solution (pH 7.2−7.4). A 1500 ppm oil/water emulsion was prepared by blending 3.0 g of DC193 surfactant and 27.0 g of soybean oil (dyed by Sudan IV) in 2 L of deionized water under high speed stirring, and then the mixture was diluted to a total volume of 20 L using deionized water. All the filtration experiments were operated at a pressure of 0.1 MPa. The pure water flux (J_W, L m^{-2} h^{-1}), protein solution flux (J_P, L m^{-2} h^{-1}) and oil/water emulsion flux ($J_{O/W}$, L m^{-2} h^{-1}) were recorded from time to time until steady and calculated according to eqs 3−5

$$J_W = \frac{V_W}{A\Delta t} \tag{3}$$

$$J_P = \frac{V_P}{A\Delta t} \tag{4}$$

$$J_{O/W} = \frac{V_{O/W}}{A\Delta t} \tag{5}$$

where V_W (L), V_P (L), and $V_{O/W}$ (L) are the volume of the permeated pure water, BSA protein solution and oil/water emulsion, A (cm^2) represents the effective filtration area (A = 4.9 cm^2), and Δt (h) is the recorded time.

In the protein filtration test, after 1 h of pure water permeation, the feed solution was displaced by the protein solution, and the J_P was recorded until a steady flux was obtained. After 2 h of protein solution permeation, the membrane sample was washed with PBS buffer solution (pH 7.2−7.4) and shaken in deionized water overnight at room temperature to remove the reversibly adsorbed protein. Then pure water permeation for the washed membrane was performed for 1 h again. The degree of water flux recovery (FR_W) can be calculated by eq 6

$$FR_W(\%) = \left(\frac{J_{W2}}{J_{W1}}\right)100 \tag{6}$$

where J_{W1} and J_{W2} are steady pure water flux (consecutive recorded values differed by less than 2%)[40] of the tested membrane before and after protein solution permeation, respectively. To evaluate the antifouling properties of the polymer membranes, the degree of flux loss caused by total protein fouling (R_t) was defined as eq 7

$$R_t(\%) = \left(\frac{J_{W1} - J_P}{J_{W1}}\right)100 \tag{7}$$

The flux loss was resulted from both reversible and irreversible protein fouling (R_r and R_{ir}), which were defined as eqs 8 and 9:

$$R_r(\%) = \left(\frac{J_{W2} - J_P}{J_{W1}}\right)100 \tag{8}$$

$$R_{ir}(\%) = \left(\frac{J_{W1} - J_{W2}}{J_{W1}}\right)100 = 100\% - FR_W \tag{9}$$

In the oil/water emulsion filtration test, after 3 h of emulsion permeation, the membrane was taken out and cleaned by shaken in deionized water for 1 h. Then the membrane was observed with FESEM. The oil rejection (R) was calculated using eq 10

$$R(\%) = \left(1 - \frac{C_P}{C_f}\right)100 \tag{10}$$

where C_p and C_f are the soybean oil concentration in the permeate and feed, respectively. The soybean oil concentration was measured with a spectrophotometer (Shimadzu, UV-1601) at 520 nm.

Protein Adsorption Test. FITC-labeled BSA (BSA-FITC) was prepared following a reported procedure.[58,59] BSA (10 mg) and FITC (1 mg) were added in 10 mL of 0.1 M $NaHCO_3$ buffer solution (pH 9). After stirred for 3 h at room temperature, the mixture was dialyzed for 5 days at 4 °C to remove the unreacted FITC. Then the resultant BSA-FITC solution was diluted to a concentration of 20 μg mL^{-1} with PBS buffer solution (pH 7.2−7.4). The solution was stored at 4 °C and used for protein adsorption test. The dye/protein ratio was determined by spectrophotometry to be 4.5−5.0:1. It should be noted that the BSA-FITC was always kept away from light during synthesis, purification and storage process.

In the protein adsorption test, a membrane sample (2 × 2 cm^2) was put into a tube containing 5 mL of the BSA-FITC solution and was shaken in a dark place at room temperature for 8 h. Then the membrane was rinsed with PBS buffer solution three times to remove the nonfirmly adsorbed proteins. The adsorption of BSA-FITC on the membrane sample was observed with a Zeiss Axiovert 200 inverted microscope (Axio-vert 200 M, Zeiss, Germany) using 10× apochromat objectives.

Antimicrobial Assay. The antimicrobial activity of original and modified membranes against *S. aureus* was quantitatively evaluated by counting the Colony Forming Unit (CFU). In a typical procedure, a membrane sample (1 × 6 cm^2) was put into a test tube containing 10 mL of the original *S. aureus* suspension and was incubated at 37 °C for 24 h. Then 100 μL of the *S. aureus* suspensions and 100 μL of their 100 times dilutions were dropped onto culture vessels containing agar medium, respectively. The culture vessels were incubated at 37 °C for 24 h, then the count for viable colonies of *S. aureus* were recorded and represented as CFU_M. The CFU of the *S. aureus* suspension in PBS incubated at 37 °C for 24 h without using any membranes was referred to as CFU_C (6.5×10^5 CFU mL^{-1}) and used as control. Three measurements were carried out and the mean value was reported in the results. The relative viability and log reduction of *S. aureus* was expressed as eqs 11 and 12:

$$\text{relative viability (\%)} = \frac{\text{CFU}_M}{\text{CFU}_C} 100\% \quad (11)$$

$$\log \text{reduction} = \log(\text{CFU}_C) - \log(\text{CFU}_M) \quad (12)$$

■ ASSOCIATED CONTENT

Supporting Information

Confirmation of interactions between PDA and PVP, thermal stability of PVP coatings, surface modification and characterization of PP, PSF, and PE membranes. 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.

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■ REFERENCES

(1) Bühler, V., *Polyvinylpyrrolidone Excipients for Pharmaceuticals: Povidone, Crospovidone and Copovidone*; Springer−Verlag: Berlin, 2005; pp 88−108.
(2) Liu, X.; Xu, Y.; Wu, Z.; Chen, H. *Macromol. Biosci.* **2013**, *13*, 147−154.
(3) Higuchi, A.; Shirano, K.; Harashima, M.; Yoon, B. O.; Hara, M.; Hattori, M.; Imamura, K. *Biomaterials* **2002**, *23*, 2659−2666.
(4) Wu, Z.; Tong, W.; Jiang, W.; Liu, X.; Wang, Y.; Chen, H. *Colloids Surf., B* **2012**, *96*, 37−43.
(5) Zhang, Q.; Liu, Y.; Chen, K. C.; Zhang, G.; Shi, X.; Chen, H. *Colloids Surf., B* **2013**, *102*, 354−360.
(6) Robinson, S.; Williams, P. A. *Langmuir* **2002**, *18*, 8743−8748.
(7) Wang, H.; Yu, T.; Zhao, C.; Du, Q. *Fibers Polym.* **2009**, *10*, 1−5.
(8) Wang, P.; Ma, J.; Wang, Z.; Shi, F.; Liu, Q. *Langmuir* **2012**, *28*, 4776−4786.
(9) Pieracci, J.; Crivello, J. V.; Belfort, G. *J. Membr. Sci.* **1999**, *156*, 223−240.
(10) Liu, Z.-M.; Xu, Z.-K.; Wang, J.-Q.; Wu, J.; Fu, J.-J. *Eur. Polym. J.* **2004**, *40*, 2077−2087.
(11) El-Sawy, N. M.; Elassar, A. Z. A. *Eur. Polym. J.* **1998**, *34*, 1073−1080.
(12) Liu, Z.-M.; Xu, Z.-K.; Wan, L.-S.; Wu, J.; Ulbricht, M. *J. Membr. Sci.* **2005**, *249*, 21−31.
(13) Nady, N.; Franssen, M. C. R.; Zuilhof, H.; Eldin, M. S. M.; Boom, R.; Schroën, K. *Desalination* **2011**, *275*, 1−9.
(14) Wan, L.-S.; Xu, Z.-K.; Wang, Z.-G. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 1490−1498.
(15) Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. *Science* **2007**, *318*, 426−430.
(16) Waite, J. H. *Nat. Mater.* **2008**, *7*, 8−9.
(17) Sureshkumar, M.; Lee, P.-N.; Lee, C.-K. *J. Mater. Chem.* **2011**, *21*, 12316−12320.
(18) Sureshkumar, M.; Lee, P.-N.; Lee, C.-K. *RSC Adv.* **2012**, *2*, 5127−5129.
(19) Cheng, C.; Li, S.; Zhao, W.; Wei, Q.; Nie, S.; Sun, S.; Zhao, C. *J. Membr. Sci.* **2012**, *417−418*, 228−236.
(20) Xi, Z.-Y.; Xu, Y.-Y.; Zhu, L.-P.; Wang, Y.; Zhu, B.-K. *J. Membr. Sci.* **2009**, *327*, 244−253.
(21) Jiang, J.; Zhu, L.; Zhu, L.; Zhu, B.; Xu, Y. *Langmuir* **2011**, *27*, 14180−14187.
(22) Li, X.-l.; Zhu, L.-p.; Jiang, J.-h.; Yi, Z.; Zhu, B.-k.; Xu, Y. *Chin. J. Polym. Sci.* **2012**, *30*, 152−163.
(23) Sui, Y.; Gao, X.; Wang, Z.; Gao, C. *J. Membr. Sci.* **2012**, *394−395*, 107−119.
(24) Zhu, L.-P.; Jiang, J.-H.; Zhu, B.-K.; Xu, Y.-Y. *Colloids Surf., B* **2011**, *86*, 111−118.
(25) Jiang, J.-H.; Zhu, L.-P.; Li, X.-L.; Xu, Y.-Y.; Zhu, B.-K. *J. .Membr. Sci.* **2010**, *364*, 194−202.
(26) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48−76.
(27) Liu, Q.; Zhu, X.; Huo, Z.; He, X.; Liang, Y.; Xu, M. *Talanta* **2012**, *97*, 557−562.
(28) Loomis, W. D.; Battaile, J. *Phytochemistry* **1966**, *5*, 423−438.
(29) Laborde, B.; Moine-Ledoux, V.; Richard, T.; Saucier, C.; Dubourdieu, D.; Monti, J.-P. *J. Agric. Food Chem.* **2006**, *54*, 4383−4389.
(30) Ciavatta, C.; Govi, M. *J. Chromatogr., A* **1993**, *643*, 261−270.
(31) Zhang, Y.; Thingholm, B.; Goldie, K. N.; Ogaki, R.; Städler, B. *Langmuir* **2012**, *28*, 17585−17592.
(32) Hong, S.; Na, Y. S.; Choi, S.; Song, I. T.; Kim, W. Y.; Lee, H. *Adv. Funct. Mater.* **2012**, *22*, 4711−4717.
(33) Kang, S. M.; You, I.; Cho, W. K.; Shon, H. K.; Lee, T. G.; Choi, I. S.; Karp, J. M.; Lee, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 9401−9404.
(34) Kim, B. H.; Lee, D. H.; Kim, J. Y.; Shin, D. O.; Jeong, H. Y.; Hong, S.; Yun, J. M.; Koo, C. M.; Lee, H.; Kim, S. O. *Adv. Mater.* **2011**, *23*, 5618−5622.
(35) Pezzella, A.; Panzella, L.; Crescenzi, O.; Napolitano, A.; Navaratman, S.; Edge, R.; Land, E. J.; Barone, V.; d'Ischia, M. *J. Am. Chem. Soc.* **2006**, *128*, 15490−15498.
(36) Bisaglia, M.; Mammi, S.; Bubacco, L. *J. Biol. Chem.* **2007**, *282*, 15597−15605.
(37) Barreto, W. J.; Ponzoni, S.; Sassi, P. *Spectrochim. Acta, Part A* **1998**, *55*, 65−72.
(38) Ju, K.-Y.; Lee, Y.; Lee, S.; Park, S. B.; Lee, J.-K. *Biomacromolecules* **2011**, *12*, 625−632.
(39) Bernsmann, F.; Ball, V.; Addiego, F. d. r.; Ponche, A.; Michel, M.; Gracio, J. J. d. A.; Toniazzo, V. r.; Ruch, D. *Langmuir* **2011**, *27*, 2819−2825.
(40) Zhu, L.-P.; Dong, H.-B.; Wei, X.-Z.; Yi, Z.; Zhu, B.-K.; Xu, Y.-Y. *J. Membr. Sci.* **2008**, *320*, 407−415.
(41) Chiang, Y.-C.; Chang, Y.; Higuchi, A.; Chen, W.-Y.; Ruaan, R.-C. *J. Membr. Sci.* **2009**, *339*, 151−159.
(42) Zhao, Y.-H.; Wee, K.-H.; Bai, R. *J. Membr. Sci.* **2010**, *362*, 326−333.
(43) McCloskey, B. D.; Park, H. B.; Ju, H.; Rowe, B. W.; Miller, D. J.; Freeman, B. D. *J. Membr. Sci.* **2012**, *413−414*, 82−90.
(44) Kasemset, S.; Lee, A.; Miller, D. J.; Freeman, B. D.; Sharma, M. M. *J. Membr. Sci.* **2013**, *425−426*, 208−216.
(45) Andersen, R. A.; Sowers, J. A. *Phytochemistry* **1968**, *7*, 293−301.
(46) Rangavajhyala, N.; Ghorpade, V.; Hanna, M. *J. Agric. Food Chem.* **1997**, *45*, 4204−4208.
(47) Huo, Q.; Russell, K. C.; Leblanc, R. M. *Langmuir* **1998**, *14*, 2174−2186.
(48) Bernsmann, F.; Ponche, A.; Ringwald, C.; Hemmerlé, J.; Raya, J.; Bechinger, B.; Voegel, J.-C.; Schaaf, P.; Ball, V. *J. Phys. Chem. C* **2009**, *113*, 8234−8242.
(49) Dreyer, D. R.; Miller, D. J.; Freeman, B. D.; Paul, D. R.; Bielawski, C. W. *Langmuir* **2012**, *28*, 6428−6435.
(50) Lee, H.; Scherer, N. F.; Messersmith, P. B. *Proc. Natl. Acad. Sci., U.S.A.* **2006**, *103*, 12999−13003.
(51) Ye, Q.; Zhou, F.; Liu, W. *Chem. Soc. Rev.* **2011**, *40*, 4244−4258.
(52) Yu, J.; Kan, Y. J.; Rapp, M.; Danner, E.; Wei, W.; Das, S.; Miller, D. R.; Chen, Y. F.; Waite, J. H.; Israelachvili, J. N. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 15680−15685.
(53) Kara Capriotti, M.; Capriotti, J. A. *Dermatol. Online J.* **2012**, *18*, 1.
(54) Gottardi, W. *J. Hosp. Infect* **1985**, *6* (Suppl A), 1−11.

(55) Xing, C.-M.; Deng, J.-P.; Yang, W.-T. *J. Appl. Polym. Sci.* **2005**, *97*, 2026−2031.
(56) Gao, B.; Wang, Z.; Liu, Q.; Du, R. *Colloids Surf. B* **2010**, *79*, 446−451.
(57) Ahmad, S. I.; Mazumdar, N.; Kumar, S. *Carbohydr. Polym.* **2013**, *92*, 497−502.
(58) Blawas, A. S.; Oliver, T. F.; Pirrung, M. C.; Reichert, W. M. *Langmuir* **1998**, *14*, 4243−4250.
(59) Delehanty, J. B.; Shaffer, K. M.; Lin, B. *Anal. Chem.* **2004**, *76*, 7323−7328.