ACS APPLIED MATERIALS & INTERFACES

Research Article

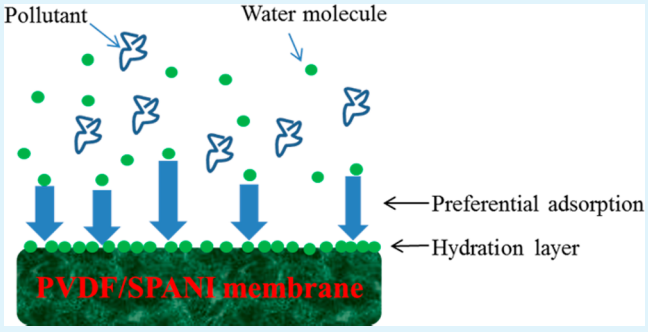
www.acsami.org

Efficient Preparation of Super Antifouling PVDF Ultrafiltration Membrane with One Step Fabricated Zwitterionic Surface

Xinzhen Zhao and Chunju He*

State Key Lab for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

ABSTRACT: On the basis of the excellent fouling resistance of zwitterionic materials, the super antifouling polyvinylidene fluoride (PVDF) membrane was efficiently prepared though one-step sulfonation of PVDF and polyaniline blend membrane in situ. The self-doped sulfonated polyaniline (SPANI) was generated as a novel zwitterionic polymer to improve the antifouling property of PVDF ultrafiltration membrane used in sewage treatment. Surface attenuated total reflection Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, surface zeta potential, and water contact angle demonstrated the successful fabrication of zwitterionic interface by convenient sulfonation modification. The static adsorption fouling test showed the quantified adsorption mass of bovine serum albumin (BSA) pollutant on the PVDF/SPANI membrane surface decreases to 3(±2) $\mu g/cm^2$, and the water flux recovery ratio (FRR) values were no less than 95% for the three model pollutants of BSA, sodium alginate (SA), and humic acid (HA), which were corresponding hydrophobic, hydrophilic, and natural pollutants in sewage, respectively. This Research Article demonstrated the antifouling advantages of zwitterionic SPANI and aimed to provide a simple method for the large scale preparation of zwitterionic antifouling ultrafiltration membranes.



KEYWORDS: *polyvinylidene fluoride, sulfonated polyaniline, zwitterionic surface, antifouling, membrane fouling*

1. INTRODUCTION

Membrane fouling, diminishing the separation performance and shortening the service life of membrane modules, has been the key factor for limiting the advancements of membrane technologies.[1−5] For the commercial used ultrafiltration (UF) membrane such as polyvinylidene fluoride (PVDF) and polyether sulfone (PES), numbers studies have demonstrated that the improved hydrophilicity of UF membrane is the primary approach to effectively reduce the membrane fouling problem.[6−8] PEG based polymer, amphiphilic polymer, hydrophilic nanoparticles, and zwitterionic materials are the most used hydrophilic modifiers for improving the wetting ability of hydrophobic membrane.[9−13]

According to the relevant literature of past five years, zwitterionic materials have been considered to be the most effective antifouling medium due to the excellent antifouling ability, the adsorption mass of zwitterionic polymer brush is as low as 5 ng/cm^2 even in the plasma and serum environment. The conventional zwitterionic polymers such as polymethacryloyloxylethyl phosphorylcholine (PMPC), polysulfobetaine methacrylate (PSBMA) and poly(amino acid) all exhibit the remarkable antifouling properties due to the superior ion hydration effect,[14,15] and Morisaku[16] reveales about 23 H_2O molecules corresponding to per PC repeat unit in the PMPC polymer by thermal analysis, so there are a lot of attempts about using zwitterionic materials to prepare low fouling UF membrane. However, there is a fatal limit for the application of zwitterionic polymer to modify the UF membrane due to the significant difference of solvent, zwitterionic polymer can be dissolved in water, but the super ion hydration capacity make it insoluble in the organic solvent used for the fabrication of PVDF and PES UF membranes. All the reported applications of zwitterionic materials in the UF membranes field are still at experimental stage only by synthesis of harsh precursor and surface graft polymer brushes,[17−19] multistep process and harsh reaction conditions make it is yet a great challenge for the large scale fabrication of zwitterionic antifouling UF membrane.

Polyaniline (PANI), known as a conductive polymer for its facile synthesis, electrical conductivity and environmental stability, can be dissolved in polar aprotic solvents such as *N*-methylpyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF),[20−22] which are used as conventional solvent to prepare UF membranes including PVDF and PES membranes. It is worth noticed that sulfonated polyaniline (SPANI), as self-doped polyaniline derivatives with both positive and negative charges equipped along the polymer chains,[23,24] exhibits the potential as zwitterionic material. This current study aims to introduce a distinct simple method to fabricate novel

Received: May 28, 2015
Accepted: July 28, 2015
Published: July 28, 2015

DOI: 10.1021/acsami.5b04648
ACS Appl. Mater. Interfaces 2015, 7, 17947−17953

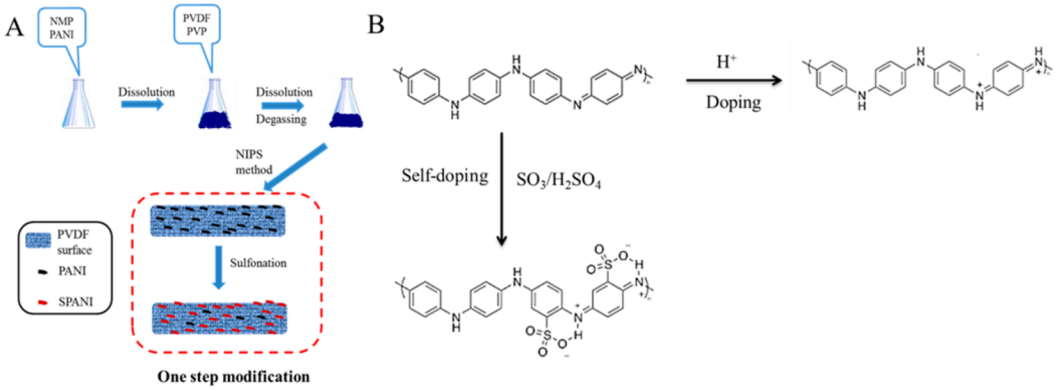


Figure 1. Schematic diagram: (A) Preparation process of PVDF/SPANI membrane. (B) Doping and self-doping effect of PANI.

antifouling PVDF UF membrane, in situ sulfonation method (one step modification) is employed to modify PVDF/PANI blend membrane to introduce the antifouling property of zwitterion. The impacts of different polyaniline derivatives on membrane surface property and the antifouling ability of modified PVDF membrane were investigated with the static adsorption fouling test of bovine serum albumin (BSA) and the dynamic filtration fouling test using different model pollutants. It is expected that this work could provide a convenient and large-scale method to fabricate antifouling membrane with zwitterionic feature.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. PVDF (FR 904) was purchased from 3F New Materials Co. (China), polyaniline emeraldine base (PANI, $M_w \approx 15\,000$) and polyaniline emeraldine salt from *p*-toluenesulfonic acid (PANI-ES, $M_w \approx 20\,000$) were purchased from Alfa Aesar. Bovine serum albumin(BSA, 67 000 Da) and polyvinylpyrrolidone (PVP, K30, $M_w \approx 40\,000$) were purchased from Sinopharm Chemical Reagent Co.(China). Humic acid (HA, fulvic acid >90%) and sodium alginate (SA) were purchased from Aladdin (China). *N*-methylpyrollidone (NMP) and fuming sulfuric acid (20% SO_3) were purchased from the local chemical company and were of analytical grade, all the reagents were used as received without further purification.

2.2. Membranes Preparation. The membrane preparation process was shown in Figure 1A, and all the PVDF membranes were fabricated by the nonsolvent induced phase separation method (NIPS). PANI (0.5 g) was dissolved in 100 mL of NMP solvent; 15 g of PVDF and 1 g of PVP K30 were added into the solution and dissolved by mechanical stirring; the casting solution was casted on a glass plate with the cast knife of 200 μm; and the plate was immediately immersed into water coagulating bath at room temperature. All the prepared membranes were kept in water at least 24 h to remove the residual pore former.

In situ sulfonation modification of PVDF/PANI membrane was executed at room temperature, and the freeze-dried PVDF/PANI membrane was placed into the fuming sulfuric acid for 1 h. After that, the modified membrane was taken out and washed using deionized water sufficiently for the further use. PVDF/PANI-ES blend membrane without sulfonation process was prepared using doped PANI with the same molar proportion of PANI. Neat PVDF membrane were prepared and treated by fuming sulfuric acid as the reference sample.

2.3. Membrane Characterization. Surface and cross-section morphology of membranes were viewed with the field emitting scanning electron microscope (SEM, Hitachi SU8010, Japan), all the samples were coated with gold before observation and fractured by being immersed in liquid nitrogen to obtain the cross section. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 8700) was used to examined the surface composition of PVDF membranes with an aperture angle of 45°. Membrane surface chemical composition was also tested using X-ray photoelectron spectroscopy (XPS, Kratos, AXIS UltraDLD), Al K-α X-ray was used as radioactive source with the takeoff angle at 90°, all survey and high-resolution spectra were recorded with the resolution of 0.68 eV/(C 1s) using a charge neutralization system. The surface zeta potential of neat and modified PVDF membranes were tested using the nanoparticle size analyzer (DelsaNano, Beckman Coulter, USA) by switching to the test mode of zeta potential. Water contact angles (CA) on the membranes were measured by OCA40Micro (Dataphysics Co., Germany) at room temperature to evaluate the surface wetting ability using the drop shape image analysis system.

2.4. Permeation Experiments. The separation properties of all the prepared membranes were measured by a dead end unit with the effective filtration area of 12.5 cm^2, the pressure of filtration cell was supplied by a water pump and all the filtration experiments were carried out at the pressure of 0.1 MPa. The flux volume of filtered water was collected for a certain time and flux was calculated by the following eq 1. The rejection ratio (R) of BSA (1 g/L, pH 7.4) was calculated according to the following eq 2, the feed and the permeate concentrations were tested via UV spectrophotometer (UV-1800, Shimadzu).

$$J = \frac{V}{A \times t} \tag{1}$$

$$R = \left(1 - \frac{C_p}{C}\right) \times 100\% \tag{2}$$

where J (L/m^2h) is the volume of permeated water, t (h) is the permeation time, and A (m^2) is effective area for filtration, and C and C_p are the concentrations of BSA in the feed and permeate, respectively.

2.5. Assessment of Membrane Fouling. To evaluate the antifouling properties of the modified membranes, static adsorption fouling tests were executed though quantitative analysis with BSA as model protein pollutant. All The tested membranes were cut into regular shape of 3 × 3 cm^2 and immersed into 50 mL of BSA (0.5 g/L, pH7.4) phosphate buffer solution, and triplicate samples for each polymer membrane were tested to obtain the mean values. After oscillating incubation for 12 h at room temperature to reach adsorption equilibrium, the adsorption mass (M) were calculated according to the eq 3 based on the changed concentrations of BSA solution before and after adsorption.

$$M = \frac{10^3(C_0 - C_d)V}{2S} \tag{3}$$

where M is the adsorption mass (μg/cm^2), C_0 and C_d are the feed concentrations (g/L) of BSA solution before and after adsorption test, V (L) is the BSA solution volume, and S (cm^2) is membrane area.

On the basis of the dynamic filtration fouling test, the water flux recovery ratio (FRR), the irreversible flux decline ratio (IFR) and

DOI: 10.1021/acsami.5b04648
ACS Appl. Mater. Interfaces 2015, 7, 17947−17953

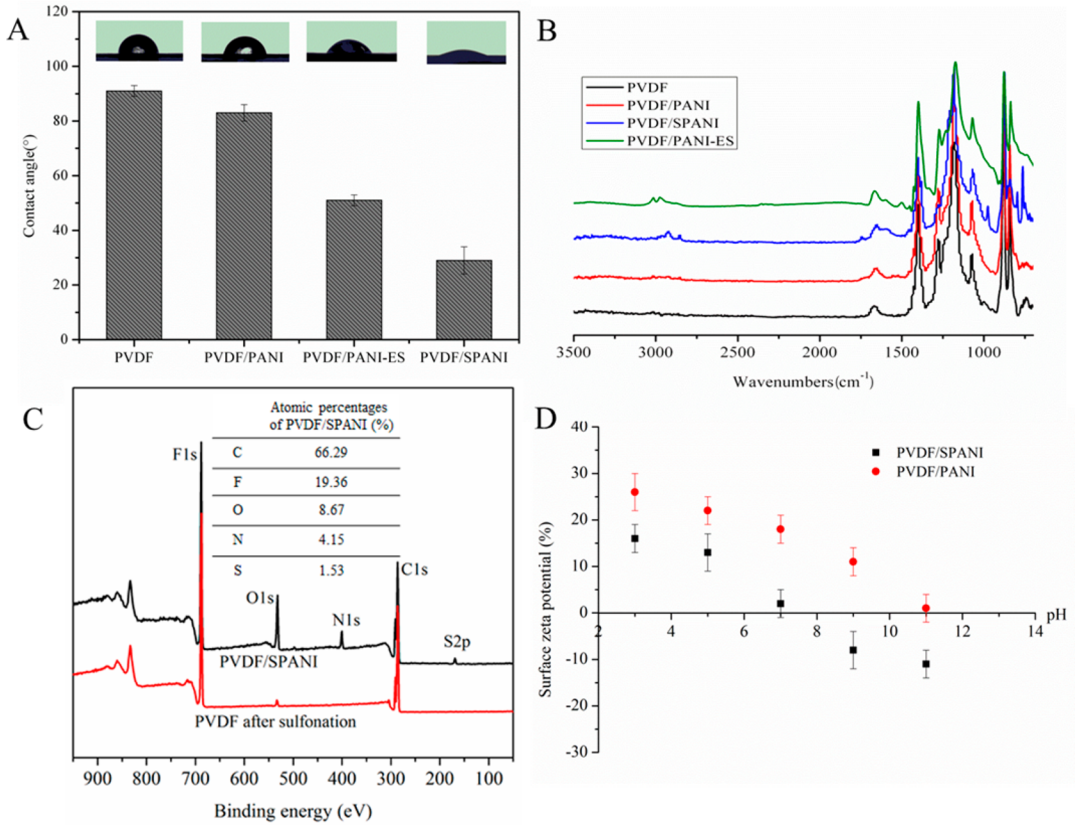


Figure 2. Characterization of prepared membranes: (A) Water contact angle, (B) ATR-FTIR spectra, (C) XPS spectra of PVDF/SPANI and fuming sulfuric acid treated PVDF membranes, and (D) surface zeta potential of PVDF/SPANI and PVDF/PANI membranes.

relative fouled flux ratio (RFR) were employed to the evaluate antifouling ability,[25] it should be notice that the membrane with the higher value of FRR and lower value of IFR indicated the better antifouling properties. The used pollutant solution including BSA (1g/L, pH 7.4), HA (1 g/L), SA(1 g/L), and mixed pollutants as mimetic sewage (0.3 g of BSA, 0.3 g of HA, and 0.4 g of SA in 1 L of water). The loop filtration process was executed consists of three steps, first of all, stable flux (J) was obtained via pure water filtration, second, the feed solution was changed to pollutants solution (BSA, HA, SA, and mimetic sewage) and another stable flux (J_P) was obtained, then a cleaning process was introduced and the membrane was taken out from the filter system to immerse in the phosphate butter for 10 min and rinsed with pure water for 20 min, and reinstalled back into filtration system, the second flux (J_2) of pure water was recorded at the end. All the FRR, IFR, and RFR values were calculated by the eqs 4, 5 and 6, respectively.

$$\mathrm{FRR} = \frac{J_2}{J} \times 100\% \tag{4}$$

$$\mathrm{IFR} = \left(1 - \frac{J_2}{J}\right) \times 100\% \tag{5}$$

$$\mathrm{RFR} = \frac{J_P}{J} \tag{6}$$

3. RESULTS AND DISCUSSION

As shown in Figure 1A, for the prepared PVDF/PANI membrane with NIPS method, only one step sulfonation was needed to fabricate modified PVDF membrane with SPANI. According to the doping effect of PANI illustrated in Figure1B, PANI can be doped with additional acids to be more hydrophilic because of the positive charge group of N^+ belonging to the quinoid unit. In addition, in the case of self-doping, both positive charge and negative charge are along the chain bones of SPANI after sulfonation reaction with fuming sulfuric acid, exhibiting the characteristic of zwitterionic polymer, which is considered to be one kind of the best antifouling materials.[26] Based on the resistance to strong acid solution of PVDF materials and sulfonated properties of PANI, in situ sulfonation reaction can be employed to generate zwitterionic SPANI on the PVDF/PANI membrane surface by one step modification, which provides the theoretical possibility for the efficient preparation of antifouling membrane with zwitterionic feature.

The physical and chemical characteristics of the membrane surface were studied in details and shown in Figure 2. Figure 2A exhibited the wetting ability of neat and modified PVDF membranes, the water contact angle of neat PVDF was as high as 92°, and there was no obviously improvement for the blended PVDF/PANI membrane. However, the contact angle of PVDF/PANI-ES was declined clearly with doped PANI being added into PVDF membrane due to the improved hydrophilicity of modified membrane surface by the charged PANI. The lowest contact angle of 29° was observed from the PVDF/SPANI membrane, indicating sulfonation in situ was able to improve the wetting ability of PVDF/PANI membrane based on the SPANI formed on the membrane surface, and the improved hydrophilicity also provides the basis for the antifouling properties of PVDF membrane. Surface compositions of PVDF and modified membranes were studied by ATR-FTIR as show in Figure 2B. Two new peaks at 1570 $cm^{-1}$and 1512 cm^{-1} were viewed on the spectra of PVDF/PANI and

DOI: 10.1021/acsami.5b04648
ACS Appl. Mater. Interfaces 2015, 7, 17947−17953

PVDF/PANI-ES membranes, which were attributed to the stretching vibration of C═C ring in PANI backbone. In addition, compared with PVDF/PANI membrane, two additional peaks at 1035 $cm^{-1}$and 715 cm^{-1}were observed from the spectrum of PVDF/SPANI, which were attributed to the symmetric stretching vibration of S═O band and stretching vibration of S−O band belonging to the $-SO_3H$ group in self-doped SPANI,[27] and the $-SO_3H$ group was able to introduce the self-doped effect to PANI to obtain the special characteristics of zwitterionic polymer. As for the XPS results shown in Figure 2C, according to the spectra of PVDF/SPANI membrane and fuming sulfuric acid treated neat PVDF membrane, sulfur (S, 1.53%) element was only detected in the PVDF/SPANI membrane surface, which was assigned to the introduced sulfonated groups on the PVDF/PANI membrane surface. Referring to the characteristic IR absorption peak of $-SO_3H$ in Figure 2B, it was confirmed that the sulfonic acid groups are generated on the membrane surface. Because each S atom corresponded to one pair of charged group, and according to the number of atoms in every unit of PVDF and SPANI (emeraldine base), it could be inferred that the number ratio of CH_2-CF_2 units and zwitterionic units was bout 12:1 on the membrane surface. The surface zeta potential of PVDF/SPANI membrane were shown in Figure 2D, PVDF/PANI membrane exhibited positive charge below the pH value of 11, but PVDF/SPANI membrane exhibited positive charge at low pH value and negative charge at high pH value, which was consistent with the zeta potential feature of zwitterionic materials. It was definite that zwitterionic surface was successfully fabricated. In addition, it was need to know that fuming sulfuric acid as small molecules could enter the membrane pores to sulfonate the pores surface, so all the membrane surface and pores surface should be endowed with zwitterionic property after sulfonation.

To analyze the effect of blend and sulfonation on membrane morphology, SEM was used to investigate the surface and cross section structure of all the prepared PVDF membranes. As shown in Figure 3, according to the images A−D, there were no obviously difference for the cross section morphology of all the PVDF membranes with a large number of finger holes and dense skin layer resulting from NIPS method. In addition, due to the comparison of images a−d, there were no large pores or defects, indicating the product resulting from sulfonation reaction was not directly dissolved in water, so blend and sulfonation method were advantageous for preparing homogeneous PVDF membrane without spoiled skin layer by introducing PANI and its derivatives to PVDF materials.

The pure water fluxes and BSA rejections of neat and modified PVDF membranes were shown in the Figure 4. Obviously, the highest flux value was obtained from PVDF/SPANI membrane based on the improved hydrophilicity as the CA results showed, as a contrast, added hydrophobic PANI was not conducive to enhancing the flux value. The rejections of all the membrane were between 90% and 95% without significant changes. And considering with the SEM results, it can be concluded the modified PVDF membranes with considerable separation performance can be prepared though blend and sulfonation of PANI.

To further investigate the antifouling properties of modified PVDF membranes, the adsorbed mass of BSA on the neat and modified PVDF membranes were quantitated as static fouling test. As shown in Figure 5, the BSA adsorption mass of hydrophobic PVDF membranes was as high as about 30 $\mu g/cm^2$, as a contrast, the BSA adsorption value of PVDF/SPANI was as low as $3(\pm 2)$ $\mu g/cm^2$, indicating the antiadsorption capacity of PVDF membrane can be improved by introducing zwitterionic SPANI onto membrane surface. Zwitterionic surface could significantly reduce the anchor sites of pollutants and effectively inhibit the nonspecial adsorption of hydrophobic pollutants to decrease the total amount of adsorbed pollutants on the PVDF membrane surface, this result was better than the reported values of absorbed BSA mass in the literature.[28,29]

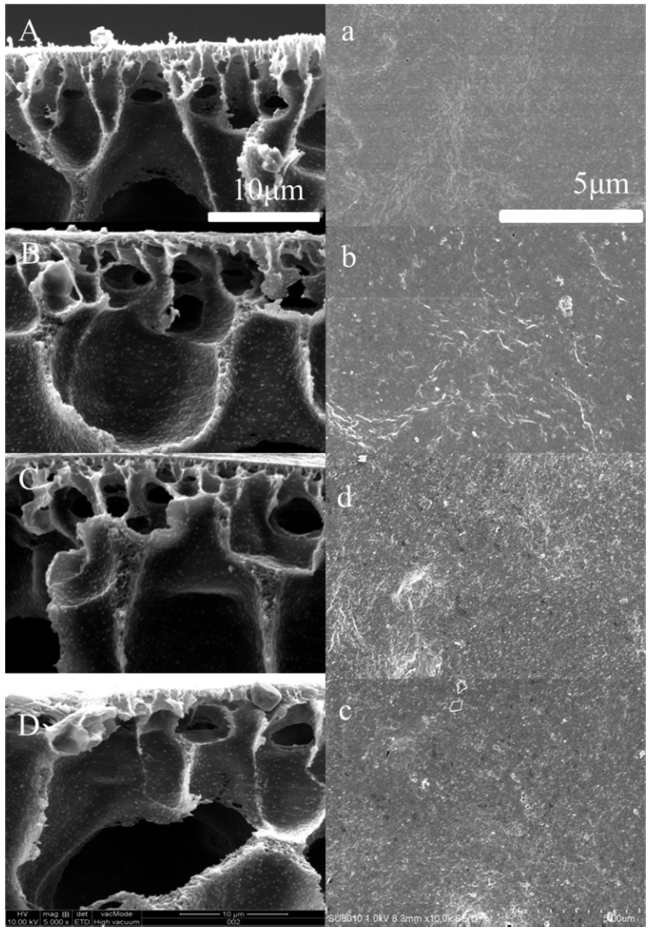


Figure 3. Cross section and surface SEM images of prepared membranes: (A, a) PVDF, (B, b) PVDF/PANI, (C, c) PVDF/SPANI, and (D, d) PVDF/PANI-ES. A−D: Cross section. a−d: Surface.

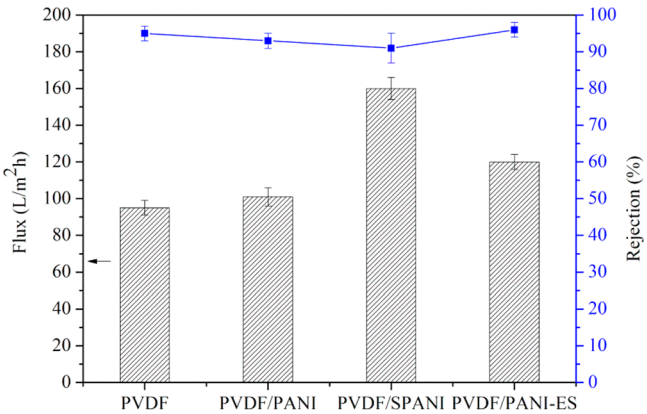


Figure 4. Separation performance of prepared PVDF membranes.

DOI: 10.1021/acsami.5b04648
ACS Appl. Mater. Interfaces 2015, 7, 17947−17953

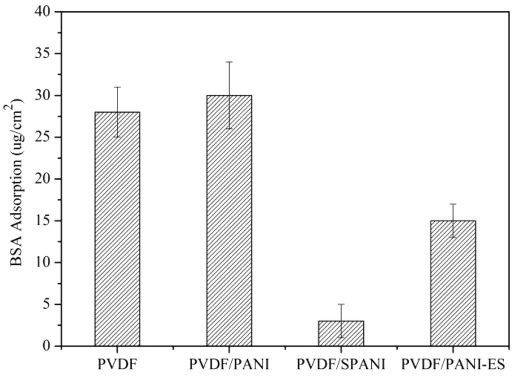


Figure 5. Adsorption mass of BSA on all the prepared PVDF membranes.

Membrane fouling during membrane separation process was an extremely common problem, in order to investigate the antifouling properties of modified PVDF membranes during dynamic filtration fouling test, three model pollutants of BSA, SA and HA (corresponding hydrophobic, hydrophilic and natural pollutants, respectively) were employed to evaluate the antifouling ability by FRR, IFR, and RFR values. According to the time dependent flux dates in the Figure 6A using BSA as pollutant solution, when the solution was changed to pollutant solution, flux values of all the membranes declined promptly, after 3 circle filtration fouling, there was almost no decline in the water flux of modified PVDF/SPANI membrane. As shown in Figure 6B, the neat PVDF and PVDF/PANI exhibited high IFR values, indicating hydrophobic membrane were more likely to be fouled. On the other side, PVDF/PANI membrane exhibited the highest RFR value based on similar rejection, indicating the improved the penetration ability for pollutant feed. After membrane cleaning process, the tiny IFR value (5%) was observed from PVDF/SPANI membrane due to the better hydrophilicity and stronger hydrated ability of zwitterionic surface to inhibit pollutants blocking membrane pores, and the detected FRR value was higher than the reported results in the similar literature.[30,31] For the other pollutants such as HA and SA (Figure 6B and 6C), the FRR and IFR values showed the same trend with BSA pollutant, the PVDF/SPANI membrane exhibited the highest FRR values no less than 95%. Due to the zwitterionic surface resulting from sulfonation reaction in situ, water molecules were preferential adsorbed onto the membrane surface and pores surface based on the excellent ion hydration ability to inhibit the absorption of pollutants, and the reduction of anchor sites for pollutants in the entire UF membrane increased the removable possibility of pollutants by water flushing. Figure 7 showed the dynamic fouling test with the mimetic sewage (complex pollutants feed), the FRR value was close to 100%, indicating the excellent prospect of zwitterionic UF membrane used in sewage treatment.

4. CONCLUSIONS

A novel PVDF UF membrane was efficient prepared though one step modification, zwitterionic SPANI was fabricated in situ to generate zwitterionic surface used in sewage treatment. The PVDF/SPANI exhibited excellent antifouling property for the three model pollutant such as BSA, HA and SA with the FRR values no less than 95%, and the adsorption mass of BSA on membrane surface was as low as 3(±2) $\mu g/cm^2$, the irreversible fouling in UF membrane was distinctly remitted due to the antifouling features of zwitterion. This paper aimed to provide a

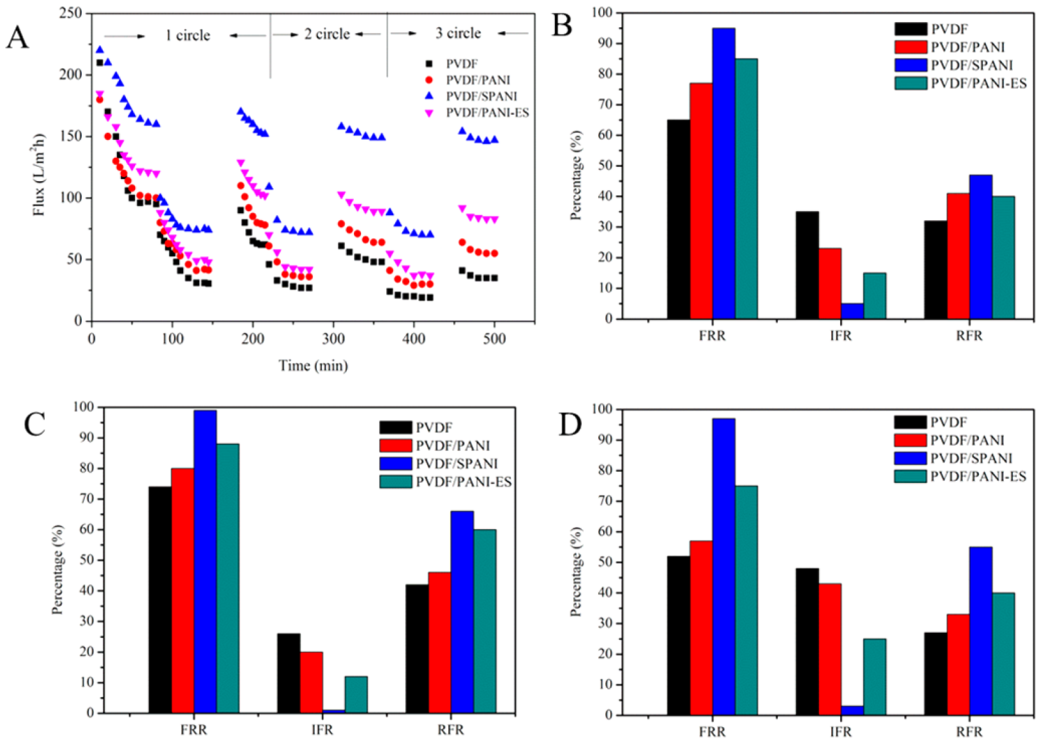


Figure 6. Antifouling property of membranes: (A) Time dependent flux variation with BSA as pollutant. (B) FRR, IFR, and RFR values with BSA as pollutant. (C) FRR, IFR, and RFR values with HA as pollutant. (D) FRR, IFR, and RFR values with SA as pollutant. All the FRR, IFR, and RFR were calculated according to the first circle fouling).

DOI: 10.1021/acsami.5b04648
ACS Appl. Mater. Interfaces 2015, 7, 17947−17953

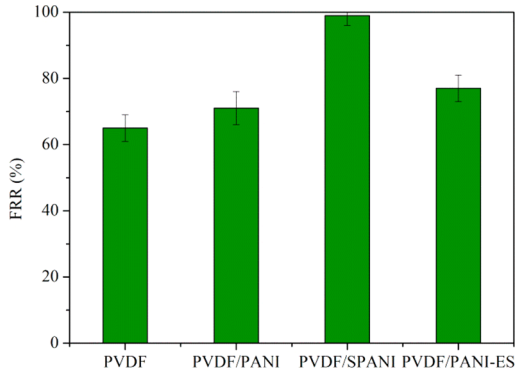


Figure 7. FRR values of all the PVDF membranes with mimetic sewage as feed.

convenient method for the large scale preparation of zwitterionic antifouling UF membrane.

AUTHOR INFORMATION

Corresponding Author

*Email: chunjuhe@dhu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by grants from the National Science Foundation of China (No. 21174027), Program for New Century Excellent Talents in University (No. NCET-12-0827), Program of Introducing Talents of Discipline to Universities (No. 111-2-04), and Innovation Funds for PhD Students of Donghua University (CUSF-DH-D-2015027).

REFERENCES

(1) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M. Science and Technology for Water Purification in the Coming Decades. *Nature* **2008**, *452*, 301−310.

(2) Elimelech, M.; Phillip, W. A. The Future of Seawater Desalination: Energy, Technology, and the Environment. *Science* **2011**, *333*, 712−717.

(3) Rana, D.; Matsuura, T. Surface Modifications for Antifouling Membranes. *Chem. Rev.* **2010**, *110* (4), 2448−2471.

(4) Banerjee, I.; Pangule, R. C.; Kane, R. S. Antifouling Coatings: Recent Developments in the Design of Surfaces That Prevent Fouling by Proteins, Bacteria, and Marine Organisms. *Adv. Mater.* **2011**, *23*, 690−718.

(5) Chen, W.; Su, Y.; Peng, J.; Zhao, X.; Jiang, Z.; Dong, Y.; Zhang, Y.; Liang, Y.; Liu, J. Efficient Wastewater Treatment by Membranes through Constructing Tunable Antifouling Membrane Surfaces. *Environ. Sci. Technol.* **2011**, *45*, 6545−6552.

(6) McCloskey, B. D.; Park, H. B.; Ju, H.; Rowe, B. W.; Miller, D. J.; Chun, B. J.; Kin, K.; Freeman, B. D. Influence of Polydopamine Deposition Conditions on Pure Water Flux and Foulant Adhesion Resistance of Reverse Osmosis, Ultrafiltration, And Microfiltration Membranes. *Polymer* **2010**, *51* (15), 3472−3485.

(7) Chang, Y.; Ko, C. Y.; Shih, Y. J.; Quemener, D.; Deratani, A.; Wei, T. C.; Wang, D. M.; Lai, J. Y. Surface Grafting Control of Pegylated Poly(Vinylidene Fluoride) Antifouling Membrane via Surface-Initiated Radical Graft Copolymerization. *J. Membr. Sci.* **2009**, *345*, 160−169.

(8) Cho, Y.; Sundaram, H. S.; Weinman, C. J.; Paik, M. Y.; Dimitriou, M. D.; Finlay, J. A.; Callow, M. E.; Callow, J. A.; Kramer, E. J.; Ober, C. K. Fluorine-Free Mixed Amphiphilic Polymers Based on PDMS and PEG Side Chains for Fouling Release Applications. *Macromolecules* **2011**, *44*, 4783−4792.

(9) Murphy, E. F.; Lu, J. R.; Brewer, J.; Russell, J.; Penfold, J. The Reduced Adsorption of Proteins at the Phosphoryl Choline Incorporated Polymer-water Interface. *Langmuir* **1999**, *15* (4), 1313−1322.

(10) Kobayashi, M.; Terayama, Y.; Kikuchi, M.; Takahara, A. Chain Dimensions and Surface Characterization of Superhydrophilic Polymer Brushes with Zwitterion Side Groups. *Soft Matter* **2013**, *9* (21), 5138−5148.

(11) Kobayashi, M.; Terayama, Y.; Yamaguchi, H.; Terada, M.; Murakami, D.; Ishihara, K.; Takahara, A. Wettability and Antifouling Behavior on the Surfaces of Superhydrophilic Polymer Brushes. *Langmuir* **2012**, *28* (18), 7212−7222.

(12) Schlenoff, J. B.; Rmaile, A. H.; Bucur, C. B. Hydration Contributions to Association in Polyelectrolyte Multilayers and Complexes: Visualizing Hydrophobicity. *J. Am. Chem. Soc.* **2008**, *130* (41), 13589−13597.

(13) Yang, Q.; Ulbricht, M. Novel Membrane Adsorbers with Grafted Zwitterionic Polymers Synthesized by Surface-Initiated ATRP and Their Salt-Modulated Permeability and Protein Binding Properties. *Chem. Mater.* **2012**, *24* (15), 2943−2951.

(14) Lowe, A. B.; Billingham, N. C.; Armes, S. P. Synthesis and Properties of Low Polydispersity Poly(sulfopropylbetaine)s and TheirBlock Copolymers. *Macromolecules* **1999**, *32* (7), 2141−2148.

(15) Chen, S. F.; Zheng, J.; Li, L. Y.; Jiang, S. Y. Strong Resistance of Phosphorylcholine Self-assembled Monolayers to Protein Adsorption: Insights into Nonfouling Properties of Zwitterionic Materials. *J. Am. Chem. Soc.* **2005**, *127* (41), 14473−14478.

(16) Holmlin, R. E.; Chen, X. X.; Chapman, R. G.; Takayama, S.; Whitesides, G. M. Zwitterionic Sams That Resist Nonspecific Adsorption Of Protein From Aqueous Buffer. *Langmuir* **2001**, *17* (9), 2841−2850.

(17) Yang, Q.; Ulbricht, M. Novel Membrane Adsorbers with Grafted Zwitterionic Polymers Synthesized by Surface-Initiated ATRP and Their Salt-Modulated Permeability and Protein Binding Properties. *Chem. Mater.* **2012**, *24*, 2943−2951.

(18) Chen, S. H.; Chang, Y.; Lee, K. R.; Wei, T. C.; Higuchi, A.; Ho, F. M.; Tsou, C. C.; Ho, H. T.; Lai, J. Y. Hemocompatible Control of Sulfobetaine-Grafted Polypropylene Fibrous Membranes in Human Whole Blood via Plasma-Induced Surface Zwitterionization. *Langmuir* **2012**, *28* (51), 17733−17742.

(19) Jhong, J. F.; Venault, A.; Hou, C. C.; Chen, S. H.; Wei, T. C.; Zheng, J.; Huang, J.; Chang, Y. Surface Zwitterionization of Expanded Poly(tetrafluoroethylene) Membranes via Atmospheric Plasma-Induced Polymerization for Enhanced Skin Wound Healing. *ACS Appl. Mater. Interfaces* **2013**, *5* (14), 6732−6742.

(20) Pud, A.; Ogurtsov, N.; Korzhenko, A.; Shapoval, G. Some Aspects of Preparation Methods and Properties of Polyaniline Blends and Composites with Organic Polymers. *Prog. Polym. Sci.* **2003**, *28*, 1701−1753.

(21) Lu, X. F.; Yu, Y. H.; Chen, L. A.; Mao, H. P.; Zhang, W. J.; Wei, Y. Poly(Acrylic Acid)-Guided Synthesis of Helical Polyaniline Microwires. *Polymer* **2005**, *46*, 5329−5333.

(22) Zhao, S.; Wang, Z.; Wei, X.; Zhao, B.; Wang, J.; Yang, S.; Wang, S. Performance Improvement of Polysulfone Ultrafiltration Membrane Using Panieb as Both Pore Forming Agent and Hydrophilic Modifier. *J. Membr. Sci.* **2011**, *385*, 251−262.

(23) Yue, J.; Epstein, A. J. Syntheisis of self-doped conducting polyaniline. *J. Am. Chem. Soc.* **1990**, *112*, 2800−2801.

(24) Huang, J.; Kaner, R. B. A General Chemcial Route to Polyaniline Nanofibers. *J. Am. Chem. Soc.* **2004**, *126*, 851−855.

(25) Zhao, X.; Su, Y.; Li, Y.; Zhang, R.; Zhao, J.; Jiang, Z. Engineering Amphiphilic Membrane Surfaces Based on PEO and PDMS Segments for Improved Antifouling Performances. *J. Membr. Sci.* **2014**, *450*, 111−123.

(26) McVerry, B. T.; Temple, J. A.; Huang, X. W.; Marsh, K. L.; Hoek, E. M.; Kaner, R. B. Fabrication of Low-Fouling Ultrafiltration Membranes Using a Hydrophilic, Self-Doping Polyaniline Additive. *Chem. Mater.* **2013**, *25*, 3597−3602.

DOI: 10.1021/acsami.5b04648
ACS Appl. Mater. Interfaces 2015, 7, 17947−17953

(27) Chen, S. A.; Hwang, G. W. Structure Characterization of Self-Acid-Doped Sulfonic Acid Ring-Substituted Polyaniline in Its Aqueous Solutions and as Solid Film. *Macromolecules* **1996**, *29*, 3950−3955.
(28) Wang, L. J.; Su, Y. L.; Zheng, L. L.; Chen, W. J.; Jiang, Z. Y. Highly Efficient Antifouling Ultrafiltration Membranes Incorporating Zwitterionic Poly([3 (methacryloylamino) propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide). *J. Membr. Sci.* **2009**, *340*, 164−170.
(29) Li, M. Z.; Li, J. H.; Shao, X. S.; Miao, J.; Wang, J. B.; Zhang, Q. Q.; Xu, X. P. Grafting Zwitterionic Brush on The Surface Of PVDF Membrane Using Physisorbed Free Radical Grafting Technique. *J. Membr. Sci.* **2012**, *405*, 141−148.
(30) Zhao, Y. F.; Zhu, L. P.; Yi, Z.; Zhu, B. K.; Xu, Y. Y. Zwitterionic Hydrogel Thin Films as Antifouling Surface Layers of Polyethersulfone Ultrafiltration Membranes Anchored via Reactive Copolymer Additive. *J. Membr. Sci.* **2014**, *470*, 148−158.
(31) Liu, Y. N.; Su, Y. L.; Zhao, X. T.; Li, Y. F.; Zhang, R. N.; Jiang, Z. Y. Improved Antifouling Properties of Polyethersulfone Membrane by Blending The Amphiphilic Surface Modifier with Crosslinked Hydrophobic Segments. *J. Membr. Sci.* **2015**, *486*, 195−206.

DOI: 10.1021/acsami.5b04648
ACS Appl. Mater. Interfaces 2015, 7, 17947−17953