Multifunctional Polydopamine Particles as a Thermal Stability Modifier to Prepare Antifouling Melt Blend Composite Membranes

Rong Liu, Yunan Zhu, Fei Jiang, Yijun Fu, Wei Zhang, Yu Zhang, and Guangyu Zhang*

ABSTRACT: This study reports a novel, multifunctional, and easily obtained modifier to support the rapid advancements in the field of filtration. Polydopamine (PDA) particles (PDAPs) have been reported as a filler for constructing polymer composites, but because of their poor thermal stability, the use of PDAPs in high-temperature blend melt systems to construct antifouling membranes was rare. In this paper, high-thermal-stability methoxy polyethylene glycol amine (mPEG-NH2)-functionalized PDA nanoparticles (mPDAPs) were first used as a modifier in high-temperature blend melt polymer composites to construct antifouling composite membranes. First, high-thermal-stability mPDAPs with an average diameter of about 390 nm were prepared by immobilized mPEG-NH2 on the PDAP surface, then melt blend mPDAPs with ultrahigh-molecular-weight polyethylene/liquid paraffin (LP) solution and thermally reduced phase separation (TIPS) to construct antifouling membranes. A combination of properties including mechanical properties, filtration efficiency, and antifouling properties of hybrid composite membranes was investigated and demonstrated that mPDAPs were an efficient modifier for high-temperature melt blending systems. The aim of this study was to provide an effective approach to improve the membrane filtration performance by bulk hybrid modification of multifunctional nanoparticles.

1. INTRODUCTION

Recently, separation technology had an irreplaceable position in today’s life when water resources were becoming increasingly tight. Therefore, the preparation of separation membranes with high separation efficiency, low cost, and antifouling properties has great practical significance and a great economic value.1−3 As a new type of membrane material, ultrahigh-molecular-weight polyethylene (UHMWPE) has excellent comprehensive performance, such as chemical resistance, abrasion resistance, aging resistance, nontoxicity, and standing mechanical strength.4,5 Therefore, exploring UHMWPE separation membranes with high separation efficiency and antifouling properties becomes a hot spot for increasing scientific researchers. During our previous study, a UHMWPE/fabric composite membrane with excellent separation properties was successfully fabricated by the composite UHMWPE with fabrics.6 However, UHMWPE exhibited extremely low surface free energy because there are no polar groups on the linear molecule long chain, so it exhibits strong hydrophobicity. Therefore, this strong hydrophobicity will cause the following problems during the sewage treatment process. Firstly, natural organic substances such as proteins, colloidal particles, solute macromolecules are easily adsorbed and deposited on the surface of the membrane, causing the blockage of the membrane pores, resulting in a decrease in membrane separation efficiency.8−10 Secondly, because of the poor surface wettability of the hydrophobic UHMWPE membrane, an increased external pressure is needed to allow water molecules to pass through the separation membrane.11 Therefore, an effective and simple approach to improve the antifouling properties of the UHMWPE composite membrane has become an emergency issue.

Bulk hybridization modification has attracted increasing attention in the construction of an antifouling separation membrane.12 For example, some hydrophilic polymers, inorganic nanoparticles, and carbon nanotube materials are added as common modifiers to the separation membrane for antifouling modification to improve the overall hydrophilic and antifouling capacity of the separation membrane.9,13−15 Polydopamine (PDA) particles (PDA(Ps) have been reported as a filler for constructing polymer composites16−20 because of their excellent properties (such as simplicity, self-polymer-
ization, biocompatibility, and antioxidant properties). For example, Liang et al. reported immobilized PDA/silver composite nanospheres on an oxidized sodium alginate sponge surface to fabricate antimicrobial sponges; 21 Xiong et al. prepared PDAP/poly(vinylalcohol) biocomposites using different diameters of PDAPs as a filler; 18 and Wang et al. used PDA interfacial cross-linking on a porous supporting layer to fabricate thin-film nanocomposite membranes. 19 However, PDAPs are rarely used in melt blending composite systems 22 because of their unstable thermal resistance.

Hence, in this study, high thermal stability metoxy polyethylene glycol amine (mPEG-NH₂)-functionalized PDA nanoparticles (mPDAPs) with an average diameter of about 390 nm were prepared by immobilized mPEG-NH₂ on the PDAP surface, which not only have excellent thermal properties but also introduce functional groups to the PDAP surface. Then melt mPDAPs with UHMWPE/liquid paraffin (LP) and thermally reduced phase separation (TIPS) to introduce the excellent functionalities of mPDAPs into the overall composite membrane matrix. The effect of nanoparticle addition on the mechanical properties, crystallization properties, separation properties, and antifouling properties of the composite membrane was investigated. This paper aims to provide an effective approach to improve the membrane filtration performance by bulk hybrid modification of multifunctional nanoparticles.

2. EXPERIMENTAL SECTION

2.1. Materials. UHMWPE (Mₜ = 4,000,000) was purchased by Beijing Eastern Petrochemical Co., Ltd. Liquid paraffin (LP) was supplied from Hangzhou Refinery (China). mPEG-NH₂ (Mₜ = 51,000) was supplied by Ponsure Biotechnology (Shanghai, China). Xylene and ethanol (chemically pure, ≥99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Irganox 1076 (purity 92%) was supplied by Ciba (Switzerland) and used as the antioxidant. Bovine serum albumin (BSA, purity 96%), sodium alginate (purity 95%), and humic acid (HA, fulvic acid >90%) were all purchased from J&K Chemical Technology (Shanghai, China). Polyester woven fabric was purchased from Shanghai Textile Industry; the linear density of the polyester yarn was 90 dtex.

2.2. Preparation of mPDAP Hybrid Composite Membranes. The mPDAP hybrid composite membranes were fabricated by hot-pressing the homogeneous mixture with the fabric; the specific process was according to our previous studies, 6 and the composite membranes were uniform and with an average thickness of 120 mm.

2.3. Preparation of mPDAP Hybrid Composite Membranes. The mPDAP hybrid composite membranes were prepared via the TIPS process. First, the required amount of mPDAPs was ultrasonically dispersed in LP for 30 min and then mixed with 5% wt UHMWPE; the mass ratios of mPDAPs were 1, 3, and 5% by weight of UHMWPE. Second, the premix was added to a batch mixer (XSS-300, Shanghai Kechang Rubber & Plastic Equipment Co., China) at 200 °C for 20 min to obtain the mPDAPs/UHMWPE/LP homogeneous mixture. After this, the hybrid composite membranes were fabricated by hot-pressing the homogeneous mixture with the fabric.

2.4. Membrane Characterization. Fourier transform infrared (FT-IR) spectra were recorded using attenuated total reflectance FT-IR spectroscopy (ATR–FT-IR, NEXUS-670, Bruker Optics, Germany). Thermogravimetric (TG) analysis (TGA) was performed using a PerkinElmer TGA2050 instrument at a heating rate of 20 °C min⁻¹ under nitrogen. The melting temperature (T_m), crystallization temperature (T_c), and degree of crystallinity (X_c) of the membranes were investigated by differential scanning calorimetry (DSC, Mettler DSC 822, Switzerland), and the heating and cooling rates were all 10 °C min⁻¹. The structure of the composite membrane surfaces was characterized by field emission scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEOL2100F, Japan). The functional nanoparticle size distribution was determined using a laser particle size distribution analyzer (Nano ZS, Malvern, England). An Instron 4465 instrument was used to record the tensile measurements at room temperature with the humidity set at about 45% and at a cross-head speed of 40 mm min⁻¹, and the gauge length and width were 50 and 5 mm, respectively. A contact angle goniometer (OCA40Micro, Malvern, UK) was used to record the hydrophilicity of the composite membrane, and the droplet volume was 5 μL.

Membrane permeation performance evaluation including pure water flux, BSA rejection, and static and dynamic antifouling properties was according to our previous study. 24,25 During the antifouling test, BSA (0.5 g/L, pH 7.4) was used to simulate protein pollution, and HA (0.5 g/L), which is the main component of organic matter in natural water, was also used for the dynamic filtration pollution test. Meanwhile, the dynamic cycle test used to evaluate the antifouling performance of different hybrid composite membranes increased from one round to three rounds. Flux recovery rate (FRR) and irreversible pollution flux attenuation rate were used to characterize the antifouling capability of these hybrid composite membranes.

3. RESULTS AND DISCUSSION

3.1. Characterization of mPDAP Nanoparticles. It is demonstrated that the nanoparticle hybrid method could conspicuously increase the functionality performance of matrix materials. 18,26,27 Hence, functionalized PDA nanoparticles were used as an effective modifier to improve the membrane

![Figure 1. Schematic of mPEG-NH₂ surface-functionalized dopamine spheres.](image-url)
antifouling properties. The process developed by Ai et al. was used to prepare mPDAPs. A schematic outline for mPDAP preparation is shown in Figure 2. First, dopamine was spontaneously polymerized into spherical particles (PDAPs) via intramolecular/intermolecular cross-linking. The obtained PDAP surface contained plenty of reactive quinone groups, which could covalently bond with mPEG-NH₂ molecules via a Schiff base reaction to construct high-thermal-stability mPEG-NH₂-functionalized PDA nanoparticles.

The SEM and TEM images shown in Figure 3A(a),B(b) proved the successful synthesis of PDAPs and mPDAPs. Both PDAPs and mPDAPs were uniform spherical particles; after immobilization with mPEG-NH₂, a layer with a thickness of about 50 nm appeared on the PDAP surface, and the particle diameter increased slightly. Meanwhile, as shown in Figure 3C, the average values of diameters displayed a Gaussian distribution with about 270 and 390 nm for PDAPs and mPDAPs, respectively, suggesting that the particle size of mPDAPs increased after immobilization with mPEG-NH₂. The chemical structure changes of the nanoparticle surface before and after mPEG-NH₂ immobilization are shown in FT-IR spectra (Figure 3D). Both PDAPs and mPDAPs had broad peaks at 940–1800 cm⁻¹, which represented the complex chemical structure of PDA and were consistent with recent research studies. After mPEG-NH₂ was functionalized on the PDAP surface, the stretching vibration peaks representing the methyl and methylene groups appeared at 2700 cm⁻¹, and the N−H/O−H absorption peak at 3400 cm⁻¹ became broader, which indicates that mPEG-NH₂ has been successfully immobilized on the PDAP surface. Figure 3F shows the wide scans for PDAPs and mPDAPs. After immobilization with mPEG-NH₂, the O 1s concentration on the surface of PDAPs increased significantly, which also proved the successful immobilization of mPEG-NH₂ onto PDAPs.

The preparation of hybrid membranes in this study needed a melt-blended modifier with UHMWPE/LP at 200 °C for 30 min, which required the modifier with good thermal stability. As shown in Figure 3E, PDAPs exhibited a multistep degradation, suggesting a heterogeneous structure and complicated chemical composition of PDA which had been verified by many research studies. However, after the surface was incorporated with mPEG-NH₂, the thermal stability of...
mPDAPs improved and the initial decomposition temperature increased to about 400 °C. This is due to the fact that mPEG-NH₂ itself has high thermal stability; after mPEG-NH₂ reacted with the active α-quinone on the PDAP surface, the mPEG-NH₂ layer encapsulating PDAPs and the decomposition temperature of mPDAPs increased significantly. Hence, after functionalization with mPEG-NH₂, mPDAPs can be fully used in the high-temperature melt blending systems. Furthermore, the introduction of mPEG-NH₂ improved the hydrophilic properties of PDAPs, which was expected to further enhance the overall hydrophilicity of the hybrid membrane.

3.2. Characterization of Physicochemical Properties of Hybrid Composite Membranes. After composite UHMWPE membranes with a trace amount of mPDAPs, the effect of mPDAP addition on the physicochemical properties of hybrid composite membranes was investigated. As shown in Figure 4, in contrast to the surface of the neat membrane (Figure 4A), there were plentiful circular projections on the composite membrane surface which were unquestionably mPDAPs. For the composites with modifier loadings of 1 and 3 wt %, mPDAPs uniformly distributed over the composites. However, when the loading of PDAPs increased to 5 wt %, some agglomerations appeared, which should be due to the increased probability of agglomeration caused by the excessive addition of mPDAPs. To further study the effects of mPPDAPs loading on membrane properties, ATR-FTIR was carried out to investigate the surface chemical properties changes before and after membrane hybridization. The results were shown in Figure 5, compared with neat membrane, there were no significant changes on the spectrum of mPPDAPs-1% membrane. However, when the amount of mPPDAPs loading reached 3% and 5%, several new absorption peaks appeared, these new peaks at 1369 cm⁻¹ (phenolic O−H bending), 1519 cm⁻¹ (N−H shearing vibrations), 1610 cm⁻¹ (the overlap of C−C resonance vibrations in aromatic ring and N−H bending vibrations) and 1296 cm⁻¹ (C−O stretching) in the spectrum of mPPDAPs-3% and mPPDAPs-5% membrane, and the broad peaks between 3600 and 3100 cm⁻¹ corresponding to N-H/O-H stretching vibrations, representing the mPPDAPs hybridization. Moreover, the peak intensity of mPPDAPs-5% membrane increased significantly, indicating the presence of mPPDAPs in the composite membrane increased, the increased hydrophilic mPPDAPs hybridization is beneficial to improve the filtration properties of UHMWPE composite membrane.

As is well known, the hybridization of the modifier into a matrix can affect the polymer crystallization properties, which in turn affect membrane pores during phase separation. Therefore, DSC measurements were carried out to evaluate the mPDAPs/UHMWPE composites; both heating and cooling scans were recorded and are shown in Figure 6, and the results are listed in Table 1. The significant increased peak intensity of the hybrid membrane in both the cooling and heating processes can be observed, which implies that the crystallinity of composites increased with the increased amount of mPDAP loading. The crystallinity (χc) was calculated using eq 1, where ΔH represents the change of enthalpy of the sample in the whole test and ΔHf is the enthalpy of wholly crystallized polyethylene, and the value of ΔHf was assigned as 293 J/g.31

$$\chi_c = \left( \frac{\Delta H}{\Delta H_f} \right) \times 100\% \quad (1)$$

The results illustrated that as the amount of mPDAPs increased, the crystallinity of the composite increased, compared with that of the neat membrane (46.57%). The crystallinity of mPDAPs-1/3/5% membranes increased to 54.99, 59.88, and 61.22%, respectively, during the heating process, and the cooling process showed the same trend. This is due to the fact that mPDAPs will act as a heterogeneous nucleating agent, accelerate the crystallization of UHMWPE, and increase the initial crystallization temperature of composites.14,32 Meanwhile, the hybridization of mPDAPs may affect the compatibility of the UHMWPE/LP system; we conducted DSC and used a polarizing microscope to record the initial dynamic crystallization temperature Tc,b and the cloud point Tcloud of composites, as shown in Table 1, and the values of Tc,b and Tcloud were similar, which imply that the hybridization of mPDAPs did not change the phase separation method of composites, and it still showed solid−liquid phase separation. In the solid−liquid phase separation process dominated by crystallization, the increase in crystallinity will make the membrane pores dense, which could be clearly seen from the SEM images (Figure 4).

Meanwhile, the increased membrane crystallization could directly contribute to the increase of membrane strength. As shown in Figure 7A, when the addition amount of mPDAPs increased from 0 to 3%, the tensile strength showed an upward trend, and the tensile strength increased to the highest point of 14.02 MPa when the addition amount reached 3%. However,
when the amount of mPDAPs increased to 5%, the tensile strength dropped, but it was still higher than that of the neat membrane. This is due to the increased probability of agglomeration caused by the excessive addition of mPDAPs which could be observed in Figure 4D, and these larger agglomerated particles will form visible defects in the composite membrane matrix. When subjected to an external force, the defect will break first because of stress concentration, which will cause the reduction of membrane strength. In general, the results of tensile strength indicated that the addition of nanoparticles was beneficial to improve the mechanical properties of composite membranes.

Figure 7B shows the TG and derivative thermogravimetric (DTG) curves of the neat and hybrid composite membranes. It could be clearly seen that the TG and DTG curves of the neat and hybrid composite membranes are similar. In addition, all membranes showed an obvious two-stage degradation; the initial temperature of the first-stage degradation was 337 °C, which corresponded to the initial temperature of the fabric, and the temperature of second-order degradation was 444–478 °C, which corresponds to the degradation of the UHMWPE component in the composite membrane. Meanwhile, the neat and hybrid composite membranes showed different residual masses because of the different additions of mPPDAP amounts, and with the increased mPPDAP addition amount, the residual mass gradually increased. This is due to the fact that the added mPPDAPs will gradually be carbonized into nanospheres, which cannot be completely degraded and have a certain residual mass.

3.3. Filtration Performance. After hybridization of the UHMWPE membrane with a small amount of mPDAPs, the filtration performance including water flux and rejection of hybrid composite membranes was investigated in detail. Figure 8A shows the separation performance of the neat membrane and hybrid composite membranes, compared with that of the neat membrane; when the mPDAP loading increased to 3%, the pure water flux of the composite membrane increased from 452 to 581 L m⁻² h⁻¹, but when the amount of mPPDAPs increased from 3 to 5%, the increasing trend of the pure water flux slowed down. Meanwhile, the rejection of hybrid composite membranes exhibited the same trend; in contrast to the neat membrane, the rejection of the hybrid composite membrane could be up to 93%. The simultaneously increased flux and rejection indicated that the addition of mPDAPs was beneficial to improve the separation property of the UHMWPE membrane. The enhanced separation performance resulted in an increased water flux and a decreased rejection rate. In addition, the rejection performance of the hybrid composite membranes was also higher than that of the neat membrane when the mPDAP loading was 3% or 5%.

![Figure 6. DSC curves of the neat membrane and hybrid composite membranes (A: heating, B: cooling).](image)

**Table 1. Thermal Properties of the mPDAPs/UHMWPE Hybrid Composite Membranes from DSC Measurements and the Microplariscope**

| mPDAP content (wt %) | UHMWPE/LP | UHMWPE/LP |
|----------------------|-----------|-----------|
|                      | X_c,m (%) | T_m(°C)  |
| 0                    | 46.57     | 117.4     |
| 1                    | 54.99     | 118.3     |
| 3                    | 59.88     | 119.4     |
| 5                    | 61.12     | 119.4     |

|                      | X_c,c (%) | T_c,b(°C) | T_cloud(°C) |
|----------------------|-----------|-----------|-------------|
| 0                    | 45.34     | 96.3      | 96.8        |
| 1                    | 50.78     | 97.2      | 97.0        |
| 3                    | 56.34     | 97.8      | 98.1        |
| 5                    | 58.02     | 98.2      | 98.5        |
Figure 8. (A) Pure water flux and BSA rejection of the neat and hybrid composite membranes, (B) time-dependent water flux of mPDAPs-3% hybrid composite membranes at 0.1 MPa, (C) water contact angle of the neat and hybrid composite membranes, and (D) schematic of the hybrid composite membrane.

Figure 9. (A) Static adsorption of the BSA solution for the neat and hybrid composite membranes, dynamic fouling performance of the neat membrane and hybrid composite membranes (B: BSA solution, C: HA solution), (D) repeat antifouling performance of mPDAPs-3% hybrid composite membranes (three times, BSA as a pollutant), and (E) time-dependent flux variation under three cycles with BSA as a pollutant (at 0.1 MPa).
of hybrid composite membranes should be due to the enhanced wetting ability on the membrane surface and matrix. As shown in Figure 8C, the hybrid composite membrane displayed an improved wetting ability with the membrane contact angle of the neat membrane and mPDAPs-5% membrane decreased from 130° to 76°, respectively. At the same time, the stability of the modified membrane during the separation process was the key issue to membrane hybrid modification. Therefore, we conducted a long-term separation performance test on mPDAP hybrid-modified composite membranes to characterize the stability of the hybrid material in the composite membrane. The test results are shown in Figure 8B, and it can be clearly seen that the water flux of the mPDAPs-3% hybrid composite membrane was hardly changed in the continuous test of 12 h, indicating that the improvement of membrane flux was long-term with high stability during the filtration process. Through the above characterization, we can find that the melt-blended hydrophilic mPDAPs in the UHMWPE/LP mixture are conducive to increase the overall wetting ability of the hybridization membrane. Meanwhile, the mPDAPs acted as a heterogeneous nucleating agent, accelerating the crystallization of UHMWPE in the solid-liquid phase separation process dominated by crystallization; the increase in crystallinity will make the membrane pores dense, which could be observed in Figure 4, and the hybridization membrane pores became denser. However, the excessive addition of mPDAPs formed visible agglomeration, which would affect the comprehensive performance of the membrane. Hence, the optimal addition ratio of mPDAPs was 3%.

3.4. Antifouling Performance. It can be clearly observed from the above characterization that the addition of hydrophilic mPDAPs can significantly improve the wetting ability of the composite membrane. Many studies had proved that the improved wetting ability was conducive to enhance the membrane antifouling property. Therefore, static adsorption and dynamic filtration were employed to further test the antifouling performance of composite membranes before and after hybridization. Figure 9A shows the BSA static adsorption data of the neat membrane and hybrid composite membranes; after hybridization, the BSA adsorption mass decreased rapidly. In addition, the dynamic antifouling performances of hybrid composite membranes were tested using BSA and HA as two typical pollutants. The flux recovery ratio of the washed membrane (FRR) and total flux attenuation ratio (TFR) were used to depict the membrane antifouling abilities; the higher FRR value or the lower TFR value represented the better antifouling property of hybridization membranes. From the FRR and TFR values obtained from the dynamic antipollution test in Figure 9B, the FRR value of the mPDAP hybrid-modified composite membrane was significantly higher than that of the neat membrane, and the FFR values decreased with the increased mPDAP loading rate, indicating that the addition of hydrophilic mPDAPs could effectively increase the membrane antifouling performance. The results should be due to the antifouling characteristics of mPDAPs. After mPDAPs being uniformly dispersed on the surface and in the matrix of the UHMWPE membrane, the functionalized hydrophilicity of mPDAPs could change the surrounding microenvironment of the composite membrane; the improved membrane microenvironment was conducive to reduce the pollutant adsorption and accumulation in the membrane matrix, transforming the original irreversible pollutants into reversible pollutants, which can be easily washed away by rinsing to obtain a higher FRR value. From the dynamic pollution test results of HA in Figure 9C, the effect of mPDAP addition on the FRR and TFR values of the composite membrane showed the same trend. When the amount of mPDAPs reaches 3%, the FRR value is as high as 86%.

From the results of the above static adsorption and dynamic filtration tests, it can be clearly seen that the addition of mPDAPs could effectively reduce the irreversible pollution caused by pollutants on the membrane surface and inside the membrane matrix. At the same time, in order to investigate the long-term effectiveness of antipollution performance of the hybrid composite membrane, three cyclic repeated tests of the time-dependent water flux of the hybrid composite membrane at 0.1 MPa were carried out and are shown in Figure 9D,E. After three cycle filtrations, the FRR value was still up to 82%, which indicated that the overall improvement of hydrophilic performance of composite membranes showed a stable excellent antifouling performance.

4. CONCLUSIONS

In conclusion, functional mPDAPs were first used as a modifier in high-temperature blend melt polymer composites. A stable antifouling hydrophilic UHMWPE composite membrane with different modifier contents was constructed via the TIPS method. The crystallinity of the hybrid composite membrane was increased because of the nucleation effect of mPDAPs. Meanwhile, the improved crystallinity increased the mechanical properties of the composite membrane, and the membrane pores became denser. Moreover, mPEG-NH₂-functionalyzed mPDAPs provided excellent hydrophilicity to the UHMWPE membrane with the water contact angle decreased from 130 to 76° simultaneously. With the increased amount of mPDAPs, the filtration properties of the composite membrane increased evidently, the water flux of the mPDAPs-3% hybrid composite membrane was 501 L m⁻² h⁻¹, and the rejection rate to BSA was 90%; the values are steady-state. Besides, the hybridization of the UHMWPE composite membrane exhibited excellent and universal antifouling properties; the FRR values were 89 and 92% for BSA and HA as typical pollutants, respectively. After three cycle dynamic filtration tests, the FRR value of the hybrid composite membrane to BSA can still be maintained at about 83%. In this study, the antifouling performance of the hydrophobic UHMWPE composite membrane has been significantly improved, which is attributed to the bulk hybrid modification of hydrophilic functionalized nanoparticles. This simple and effective technology can be used by the industry for the antifouling treatment of UHMWPE and other similar inert materials and employed on various substrates with customized configurations.

■ AUTHOR INFORMATION

Corresponding Author
Guangyu Zhang — School of Textile & Clothing, National & Local Joint Engineering Research Center of Technical Fiber Composites for Safety and Health, Nantong University, Nantong 226019, P. R. China; orcid.org/0000-0002-1364-3350; Phone: +86 21 85012837; Email: zgyu85@ntu.edu.cn

Authors
Rong Liu — School of Textile & Clothing, National & Local Joint Engineering Research Center of Technical Fiber
Composites for Safety and Health, Nantong University, Nantong 226019, P. R. China
Yunan Zhu — School of Textile & Clothing, National & Local Joint Engineering Research Center of Technical Fiber
Composites for Safety and Health, Nantong University, Nantong 226019, P. R. China
Fei Jiang — Hefei Food and Drug Inspection Center, Hefei 230088, P. R. China
Yijun Fu — School of Textile & Clothing, National & Local Joint Engineering Research Center of Technical Fiber
Composites for Safety and Health, Nantong University, Nantong 226019, P. R. China
Wei Zhang — School of Textile & Clothing, National & Local Joint Engineering Research Center of Technical Fiber
Composites for Safety and Health, Nantong University, Nantong 226019, P. R. China
Yu Zhang — School of Textile & Clothing, National & Local Joint Engineering Research Center of Technical Fiber
Composites for Safety and Health, Nantong University, Nantong 226019, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04915

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors thank the National Natural Science Foundation of China (Nos. 51473031 and 51803094), the Natural Science Foundation of Jiangsu Province (BK20190927), the Talent Introduction Foundation of Nantong University (No. 03081185), and the Large Instruments Open Foundation of Nantong University for the support.

REFERENCES
(1) Wang, P.; Chung, T.-S. Recent advances in membrane distillation processes: Membrane development, con Figureuration design and application exploring. J. Membr. Sci. 2015, 474, 39–56.
(2) Warsinger, D. M.; Chakrabarty, S.; Tow, E. W.; Plumlee, M. H.; Bellona, C.; Loutatidou, S.; Karimi, L.; Mikolowski, A. M.; Achill, A.; Ghassemi, A.; Padhye, L. P.; Snyder, S. A.; Curcio, S.; Vecitis, C. D.; Arafat, H. A.; Lienhard, J. H. Review of polymeric membranes and processes for potable water reuse. Prog. Polym. Sci. 2018, 81, 209–237.
(3) Zhu, T.; Cheng, Y.; Huang, J. Y.; Xiong, J. Qi; Ge, M.; Mao, J. J.; Liu, Z.; Dong, X. L.; Chen, Z.; Lai, Y. K. A transparent superhydrophobic coating with mechanochemical robustness for anti-icing, photocatalysis and self-cleaning. Chem. Eng. J. 2020, 399, 125746.
(4) Liu, S.; Yu, W.; Zhou, C. Tuning the water permeability of ultra-high molecular weight polyethylene microporous membrane by molecular self-assembly and flow field. Polymer 2014, 55, 2113–2124.
(5) Otto, C.; Handge, U. A.; Georgopanos, P.; Aschenbrøner, O.; Kerwitz, J.; Abetz, C.; Metze, A. L.; Abetz, V. Porous UHMWPE Membranes and Composites Filled with Carbon Nanotubes: Permeability, Mechanical, and Electrical Properties. Macromol. Mater. Eng. 2016, 302, 1600405.
(6) Liu, R.; Wang, X.; Yu, J.; Wang, Y.; Zhu, J.; Hu, Z. Development and evaluation of UHMWPE/woven fabric composite microlitration membranes via thermally induced phase separation. RSC Adv. 2016, 6, 90701–90710.
(7) Guo, H.; Geng, C.; Qin, Z.; Chen, C. Hydrophilic modification of HDPE microfiltration membrane by corona-induced graft polymerization. Desalin. Water Treat. 2013, 51, 3810–3813.
(8) Zhang, R.; Liu, Y.; He, M.; Su, Y.; Zhao, X.; Elimelech, M.; Jiang, Z. Antifouling membranes for sustainable water puriﬁcation: strategies and mechanisms. Chem. Soc. Rev. 2016, 45, 5888–5924.
(9) Iyer, K. A.; Torkelson, J. M. Importance of superior dispersion versus ﬁller surface modiﬁcation in producing robust polymer nanocomposites: The example of polypropylene/nanosilica hybrids. Polymer 2015, 68, 147–157.
(10) Ge, M.; Cao, C.; Liang, F.; Liu, R.; Zhang, Y.; Zhang, W.; Zhu, T.; Yu, B.; Tang, Y.; Lai, Y. A "PDMS-in-water" emulsion enables mechanochemically robust superhydrophobic surfaces with self-healing nature. Nanoscale Horiz. 2020, 5, 65–73.
(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, 7212–7222.
(12) Li, D.; Yan, Y.; Wang, H. Recent advances in polymer and polymeric composite membranes for reverse and forward osmosis processes. Prog. Polym. 2016, 61, 104–155.
(13) Li, N.; Xiao, C. Effect of the preparation conditions on the permeation of ultrahigh-molecular-weight polyethylene/silicon dioxide hybrid membranes. J. Appl. Polym. Sci. 2010, 117, 2817–2824.
(14) Hassan, A. E.-S. M.; Eid, A. I.; El-Sheikh, M.; Ali, W. Y. Effect of Graphene Nanoplatelets and Parafﬁn Oil Addition on the Mechanical and Tribological Properties of Low-Density Polyethylene Nanocomposites. Arabian J. Sci. Eng. 2018, 43, 1435–1443.
(15) Zhao, X.; Chen, Y.; Xuan, H.; He, C. Investigation of one-dimensional multi-functional zwitterionic Ag nanowires as a novel modifier for PVDF ultraﬁltration membranes. New J. Chem. 2016, 40, 441–446.
(16) Lv, J.; Wang, H. Z.; Liu, Y.; Chen, J. F.; Chen, H. B.; Xu, J. J.; Sun, J.; Zhao, H. X.; Zhu, C. H. Nanocomposite enhanced radiation resistant effects in polyurethane Elastomer with low fraction of polydopamine nanoparticles. Compos. Sci. Technol. 2020, 186, 107908.
(17) Obiweluozor, F. O.; GhavamiNejad, A.; Park, C. H.; Kim, C. S. Mussel inspired locomotive: the moisture induced actuation in a poly(vinyl alcohol) film containing melanin-like dopamine nano spheres. RSC Adv. 2016, 6, 65089–65094.
(18) Xiong, S.; Wang, Y.; Yu, J.; Chen, L.; Zhu, J.; Hu, Z. Polydopamine particles for next-generation multifunctional biocomposites. J. Mater. Chem. A 2014, 2, 7578–7587.
(19) Wang, F.; Wang, N.; Han, X.; et al. Core-shell FeCoCarbon nanoparticles encapsulated in polydopamine-derived carbon nanocages for efﬁcient microwave absorption. Carbon 2019, 145, 701–711.
(20) Vatanpour, V.; Madaeni, S. S.; Rajabi, L.; Zinadini, S.; Derakhshan, A. A. Boehmite nanoparticles as a new nanofiller for preparation of antifouling mixed matrix membranes. J. Membr. Sci. 2012, 401–402, 132–143.
(21) Liang, L.; Hou, T. T.; Ouyang, Q.; Q.; Xie, L.; Zhong, S. Y.; Li, P. W.; Li, S. D.; Li, C. P. Antimicrobial sodium alginate dressing immobilized with polydopamine-silver composite nanospheres. Composites, Part B 2020, 188, 107877.
(22) Liebscher, J.; Mrówczyński, R.; Scheidt, H. A.; Filip, C.; Häände, N. D.; Turcu, R.; Bende, A.; Beck, S. Structure of Polydopamine: A Never-Ending Story! Langmuir 2013, 29, 10539.
(23) Yan, J.; Yang, L.; Lin, M.-F.; Ma, J.; Lu, X.; Lee, P. S. Polydopamine Spheres as Active Templates for Convenient Synthesis of Various Nanostructures. Small 2013, 9, 596–603.
(24) Liu, R.; Wang, X. W.; Yu, J. R.; Wang, Y.; Zhu, J.; Hu, Z. M. Surface modification of UHMWPE/fabric composite membrane via self-polymerized polydopamine followed by mPEG-NH2 immobilization. J. Appl. Polym. Sci. 2018, 135, 46428.
(25) Liu, R.; Liu, S. S.; Yu, J. R.; Zhang, W.; Dai, J. M.; Zhang, Y.; Zhang, G. Y. The Construction of a Hydrophilic Inorganic Layer Enables Mechanochemically Robust Super Antifouling UHMWPE Composite Membrane Surfaces. Polymers 2020, 12, 569.
(26) Zhu, J.; Zhao, X.; He, C. Zwitterionic SiO2 nanoparticles as novel additives to improve the antifouling properties of PVDF membranes. RSC Adv. 2015, 5, S3653–S3659.
(27) Cao, C.; Yi, B.; Zhang, J. Q.; Hou, C. S.; Wang, Z. Y.; Lu, G.; Huang, X.; Yao, X. Sprayable superhydrophobic coating with high processibility and rapid damage-healing nature. *Chem. Eng. J.* 2020, 392, 124834.

(28) Ai, K.; Liu, Y.; Ruan, C.; Lu, L.; Lu, G. M. Sp2 C-Dominant N-Doped Carbon Sub-micrometer Spheres with a Tunable Size: A Versatile Platform for Highly Efficient Oxygen-Reduction Catalysts. *Adv. Mater.* 2013, 25, 998–1003.

(29) Ju, K.-Y.; Lee, Y.; Lee, S.; Park, S. B.; Lee, J.-K. Bioinspired polymerization of dopamine to generate melanin-like nanoparticles having an excellent free-radical-scavenging property. *Biomacromolecules* 2011, 12, 625–632.

(30) Shanmuganathan, K.; Cho, J. H.; Iyer, P.; Baranowitz, S.; Ellison, C. J. Thermooxidative Stabilization of Polymers Using Natural and Synthetic Melanins. *Macromolecules* 2016, 44, 9499–9507.

(31) Paul, S.; Chanzy, H. D.; Rotzinger, B. P. Drawing of virgin ultrahigh molecular weight polyethylene: An alternative route to high strength/high modulus materials. *J. Mater. Sci.* 1987, 22, 523.

(32) Gu, M.; Zhang, J.; Wang, X.; Ma, W. Crystallization behavior of PVDF in PVDF-DMP system via thermally induced phase separation. *J. Appl. Polym. Sci.* 2006, 102, 3714–3719.

(33) Lepage, M. L.; Simhadri, C.; Liu, C.; Takaffoli, M.; Bi, L.; Crawford, B.; Milani, A. S.; Wulff, J. E. A broadly applicable cross-linker for aliphatic polymers containing C-H bonds. *Science* 2019, 366, 875–878.

(34) Ghanbari, M.; Emadzadeh, D.; Lau, W. J.; Matsuura, T.; Davoodi, M.; Ismail, A. F. Super hydrophilic TiO2/HNT nanocomposites as a new approach for fabrication of high performance thin film nanocomposite membranes for FO application. *Desalination* 2015, 371, 104–114.