Bioinspired Modification of Layer-Stacked Molybdenum Disulfide (MoS$_2$) Membranes for Enhanced Nanofiltration Performance

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ABSTRACT: Inorganic nanofiltration membranes with high flux are urgently needed in water purification processes. Herein, polydopamine (PDA)-modified layer-stacked molybdenum disulfide (MoS$_2$) nanofiltration membranes (NFMs) were fabricated via a pressure-assisted self-assembly process. The separation performance of the as-prepared membranes with various MoS$_2$ loadings at different dopamine polymerization times was evaluated. The pure water permeance of PDA-modified MoS$_2$ NFMs, with MoS$_2$ loading of 0.1103 mg/cm$^2$ at 4 h modification, could reach 135.3 LMH/bar. The rejection toward methylene blue could reach 100% with molecular weight cutoff approximately 671 Da and a high permeability of salts. Furthermore, the resultant membrane also exhibited a satisfactory long-term stability toward dye solution and anti fouling property toward bovine serum albumin. This work may give inspiration to the development of inorganic membranes with high performance, especially high pure water permeance, for water-related processes.

1. INTRODUCTION

According to The United Nation World Water Development Report 2018, the global demand of clean water has been increasing at a rate of about 1% per year, owing to the economic development, population growth, and changing consumption patterns. Hence, clean water is limited, and there is a large requirement of treatment technology for industrial water and domestic water.

Nanofiltration, thanks to its low cost, high efficiency, low energy consumption, and facile operational process, has been widely used in water softening, desalination, wastewater reclamation, and industrial substance separation. In general, nanofiltration is defined as a pressure-driven membrane filtration mode intermediate between reverse osmosis and ultrafiltration, and has a high rejection of species ranging from 0.001 to 0.01 μm with a relatively high water flux. Polymeric nanofiltration membranes (NFMs), although widely used, could suffer from some intrinsic drawbacks such as unsatisfying mechanical strength, thermal properties, and physicochemical stability. Especially, when polymeric NFMs are used in water purification process, swelling is an unavoidable problem. On the other hand, although inorganic NFMs have a better performance on durability and pure water flux compared to polymeric NFMs, some drawbacks may also exist, such as brittleness and incompatibility to flexible substrates used in water purification processes.

Recently, two-dimensional (2D) layered inorganic materials have been widely studied because of their excellent flexible mechanical properties. Particularly, 2D graphene oxide (GO) has been made for a variety of NFMs with exceptional performance. For instance, Zhang et al. prepared a novel GO framework composite NFM via a layer-by-layer approach, endowing it with high rejections toward heavy metal and a water permeability of 4.7 LMH/bar. Mi et al. fabricated GO NFMs via layer-by-layer deposition of GO nanosheets, followed by cross-linking with 1,3,5-benzenetricarbonyl trichloride. The GO NFMs exhibited a high rejection toward Rhodamine WT and a water flux ranging between 8.00 and 27.6 LMH/bar. As a typical transition-metal dichalcogenide, molybdenum disulfide (MoS$_2$) is a new kind of 2D layered inorganic material and a laminar crystal with many unique properties, such as low cost, high surface area, and low cytotoxicity. It can also exhibit structural stability and frictionless smooth surface without oxygen-containing groups. And the layer-stacked MoS$_2$ membranes also have the characteristics of antiswelling and rigid nano-channels. Thus, these properties could endow the MoS$_2$ layer-stacked membrane with higher and steadier water permeance during water filtration process. The group of Mi has discovered that the interlayer spacing with 1.2 nm of fully hydrated MoS$_2$ nanosheets could meet the requirements of moderate molecular rejection and high water permeability.
And with a high pressure, the MoS₂ membrane could exhibit a satisfactory neatly layer-stacked nanostructure to create a condition for stable water flux and rejection performance.²⁶ Wang et al.³⁰ successfully prepared ultrathin single-layered MoS₂-based membranes with controlling thickness well for gas separation. Zhang et al.³¹ prepared a low-pressure nanofiltration membrane comprising MoS₂ nanosheets as spacers in the GO layers through the forward treatment of pressure-assisted assembly and heat. This GO/MoS₂ NFM exhibited a rejection of more than 95% toward different charged dyes with a pure water permeability of 10.2 LMH/bar, which was 13.6 times that of pristine GO NFM. Furthermore, the GO/MoS₂ NFMs also have exhibited satisfactory antifouling properties and stability. Zhou et al.³² prepared a hybrid membrane through layer-by-layer self-assembling polyelectrolyte multilayers with incorporating MoS₂ nanosheets modified by poly(diallyldimethylammonium chloride) (PDDA) (PDDA@MoS₂ nanosheets). The water flux of the hybrid membrane was 2.3 times that of the pure polyelectrolyte membrane with good long-term stability. In the work of Liang et al.³³ the MoS₂ was modified by zwitterion (poly(sulfobetaine methacrylate), PSBMA) to prepare MoS₂−PSBMA/polyethersulfone (PES) composite membranes by the conventional phase inversion method. And the composite membrane exhibited a high rejection toward dye and a high flux of 108.3 LMH at 0.6 MPa.

All of these previous studies have made it reasonable to fabricate MoS₂ membranes to improve water flux in nanofiltration process.

Inspired by mussel, dopamine has been widely used to modify different kinds of membrane surfaces because it can nonspecifically adhere to various substrates under weak alkaline and oxygen-containing environment.⁶,³⁴ After modification, various properties of membranes, such as tenacity, antifouling, and surface hydrophilicity, could be improved.³⁵⁻⁵⁹ Hence, we developed a novel layer-stacked MoS₂ nanofiltration membrane via the pressure-assisted self-assembly technique. Subsequently, the surface of MoS₂ membrane was modified by dopamine dip-coating method. In this process, dopamine could polymerize to highly cross-linked adhesive polydopamine (PDA) through the process of consecutive oxidation, intramolecular cyclization, and oligomerization in alkaline oxygen condition, where a coniform coating on the surface of the MoS₂ membrane could be formed. MoS₂ nanosheets and the as-prepared membranes were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), ζ-potential, X-ray diffraction (XRD), Fourier transform infrared spectrometry (FT-IR), and water contact angles. The nanofiltration performance of PDA-modified MoS₂ membranes (PDA/MoS₂ NFMs) with various
MoS₂ loadings at different dopamine polymerization times was investigated in detail. In addition, the molecular weight cutoff (MWCO), antifouling property, and long-term stability of PDA/MoS₂ NFMs were also tested.

2. RESULTS AND DISCUSSION

2.1. Characterization of Exfoliated MoS₂. The morphology of exfoliated MoS₂ nanosheets is shown in Figure 1. The AFM images (Figure 1a,b) indicated that the thickness of the exfoliated MoS₂ nanosheets was about 2–3 nm. And the thickness of a single MoS₂ layer is around 0.9–1.2 nm, therefore, the obtained MoS₂ nanosheets were few-layer nanosheets that were suitable for the membrane formation. The 2D ultrathin nanosheet morphology of exfoliated MoS₂ was further investigated by TEM. As can be seen in Figure 1c, the lamellar size of the individual MoS₂ nanosheets was generally less than 400 nm.

2.2. Characterization of PDA/MoS₂ NFMs. The surface morphology of the membrane was observed by SEM. As shown in Figure 2a, there was irregular bumpiness with some nanostructured papillae on the surface of the membrane at a dopamine polymerization time of 4 h. The catechol group of dopamine could be oxidized to benzoquinone with high reaction activity in a weak alkaline solution in the presence of oxygen. Then, it was self-polymerized to PDA nanoaggregates through the covalent cross-linking and noncovalent self-assembly to form a modification layer onto the MoS₂ membrane surface. Therefore, the surface roughness of
the membrane was ascribed to the accumulation of PDA nanoaggregates. The cross-sectional morphology of the membrane is shown in Figure 2b. The active layer of PDA(4)/MoS2(0.1103) NFM was tightly coated on the porous substrate without interfacial defects. The active layer was a laminar MoS2 layer coated by the PDA nanoaggregates with a uniform thickness of about 2.2 μm.

The surface morphologies of the membranes were further observed by the three-dimensional AFM images (Figure 3). With the increase of polymerization time, more and more PDA nanoaggregates were deposited onto the surfaces of the membranes, which increased the surface roughness and tuned the membrane surface properties.

The membrane surface hydrophilicity was demonstrated by the water contact angle analysis. As shown in Figure 4, water contact angles of the membranes were remarkably decreased with the extension of dopamine polymerization time. These phenomena could be explained by that the hydrophilic PDA nanoaggregates, with abundant hydrophilic amine and hydroxyl groups, were deposited gradually along with the polymerization time.43,44 On the one hand, the surface hydrophilicity was enhanced by the deposition of PDA. On the other hand, the surface structure would become more compact with increasing polymerization time. And the relatively compact surface is more beneficial for spreading of water droplets, thereby the water contact angles could be decreased.45

The ζ-potential of membrane surface is an important characteristic that is relevant to the separation property of membranes. According to one of the nanofiltration mechanisms, the Donnan effect, the membrane is tended to reject the molecule with the same electricity as the membrane surface and to infiltrate the molecule with opposite electricity to the membrane surface.45 The results of ζ-potential of hydrolyzed polyacrylonitrile (HPAN) substrate, MoS2 NFM, and PDA/MoS2 NFM are shown in Figure 5. These three kinds of membranes were all proved to be negatively charged at pH 4–10, especially at the neutral application conditions. The polyacrylonitrile (PAN) substrate could generate carboxyl groups (−COOH) after the hydrolyzation of nitrile groups in NaOH solution, which was the main factor of the negative electricity of the HPAN surface at pH 4–10.46,47 In Figure 5, it could also be observed that, compared with HPAN, the electronegativity of NFM loaded with MoS2 was enhanced, which could be ascribed to the electronegativity of MoS2.24,25 Due to the weak electronegativity of PDA, the electronegativity of the membrane surface was slightly lower after PDA modification.48

As shown in Figure 6, there was an intensive peak (002) at 2θ = 14.4° on the XRD spectra of MoS2 NFM and PDA/MoS2 NFM, which was in accordance with the typical hexagonal structure peaks of MoS2 (JCPDS card No. 77-1716).49 FT-IR spectra of HPAN, MoS2 NFM, and PDA/MoS2 NFM samples are shown in Figure 7. The characteristic peak at around 1727 cm⁻¹ corresponded to C=O stretching vibration, which confirmed the hydrolyzation of PAN substrate membrane. This peak became weaker and weaker after MoS2 loading and PDA modification.50,51 For the spectrum of PDA(4)/MoS2(0.1103) NFM, a new peak appeared at 1566 cm⁻¹, which was attributed to the N–H vibration in PDA. And the broad band at around 3400 cm⁻¹ was related to the

![Figure 5. Surface ζ-potentials of membranes at different pH values.](image)

![Figure 6. XRD spectra of MoS2 NFM and PDA/MoS2 NFM.](image)

![Figure 7. FT-IR spectra of HPAN, MoS2 NFM, and PDA(4)/MoS2(0.1103) NFM.](image)
catechol −OH group and N−H group from PDA, which also indicated the effectiveness of PDA modification.  

2.3. Membrane Performance. 2.3.1. Effect of MoS₂ Loading. The influence of MoS₂ loading on the pure water permeance and dye rejection was investigated. As shown in Figure 8, with the increase of MoS₂ loading from 0.03597 to 0.1415 mg/cm², the membrane showed an increase of dye rejection from 45.52 to 100%. Meanwhile, the pure water permeance showed a slight decrease from 141.5 to 129.5 LMH/bar. The separation performance of the membrane, i.e., permeance showed a slight decrease from 141.5 to 129.5 LMH/bar. The separation performance was correlated to the specific MoS₂ loading. The three atomic layers of MoS₂ nanosheets, which could serve as the fluidic nanochannels with stable interlaminar dimensions formed by overlapped MoS₂ nanosheets, which could form a hydration layer, and the membrane by decreasing BSA adhesion due to the high hydrophilicity, which could form a hydration layer, and the negative charge, which could reduce the adhesion of BSA with negative charge at neutral to alkaline pH through electrostatic repulsion. However, with the dopamine polymerization time prolonged further, the PDA nano-aggregates could be generated to block some passages of water transportation and the PDA modification layer also turned too dense and thick, thereby correspondingly decreasing the water permeance. But even at 6 h, the permeance of PDA(6)/MoS₂ NFM was still higher than that of the MoS₂ NFM without PDA modification because of the increased hydrophilicity. The synergy of MoS₂ nanosheets and PDA modification has contributed to the high permeability of PDA/MoS₂ NFMs.

2.3.2. Effect of Dopamine Polymerization Time. The effect of dopamine polymerization time on dye rejection and pure water permeance was also investigated. As shown in Figure 9, with more and more PDA deposited, a complete PDA modification layer was formed and the membrane hydrophilicity was enhanced, which led to the increase of water permeance. However, with the filter cake being rinsed off, the flux could be recovered during the washing process. Thus, the antifouling property is an important property of membranes. In this work, the antifouling behavior of the membranes was evaluated by four fouling parameters (flux recovery ratio (FRR), total flux decline ratio (DRₜ), reversible flux decline ratio (DRᵣ), and irreversible flux decline ratio (DRᵢ)) using bovine serum albumin (BSA) as model foulant. As we all know, the lower DRₜ and higher FRR values mean more excellent antifouling characteristic of the membrane. For the PDA/MoS₂ NFMs, the layer-stacked MoS₂ nanosheets acted as a barrier and repelled the BSA molecules from the surface layers. And the absence of conjugated structure in MoS₂ could avoid the cation−π and π−π interactions with organic fouling. As shown in Figure 10, with the extension of polymerization time, the FRR increased and the DRₜ decreased, which revealed that PDA modification could enhance the antifouling property of the membrane by decreasing BSA adhesion due to the high hydrophilicity, which could form a hydration layer, and the negative charge, which could reduce the adhesion of BSA with negative charge at neutral to alkaline pH through electrostatic repulsion. As shown in Figure 10, the membrane showed better antifouling performance at 6 h; therefore, if there is a...
higher requirement for antifouling performance, the polymerization time of 6 h is a good choice at the cost of longer preparation time and lower water permeance.

2.3.4. Rejection Performance. The retention performance of the PDA/MoS\(_2\) NFM was characterized through MWCO measurements using the widely used neutral molecule poly(ethylene glycol) (PEG). The MWCO was defined as the molecular weight of PEG at 90% rejection.\(^5\) As shown in Figure 11, the MWCO was estimated to be 671 Da, which was in accordance with the typical nanofiltration characteristic. As calculated by eq 3, the average transport path size of the PDA/MoS\(_2\) NFM was estimated to be ~0.96 nm.

Five kinds of dyes with varying molecular weights and charges were employed to explore the separation mechanism of PDA(4)/MoS\(_2\)(0.1103) NFM. The positively charged dyes are MB and crystal violet (CV), while the negatively charged dyes are methyl orange (MO) and acid fuchsin (AF), and the rhodamine B (RhB) is electroneutral. According to the extended Derjaguin–Landau–Verwey–Overbeek theory, the van der Waals attraction between MoS\(_2\) nanosheets is greater than hydration force and electrostatic repulsion, so the swelling degree of MoS\(_2\) layer is limited in water. And the maximum interlayer spacing of the fully hydrated MoS\(_2\) nanosheets could reach \(~1.2\) nm.\(^2\) However, the kinetic diameter of dye molecules was generally greater than 1.1 nm.\(^5\) This makes it possible for the MoS\(_2\) nanofiltration membrane to obtain a high rejection for dye molecules.

As shown in Figure 12, the rejection toward dyes with the same electronegativity and higher molecular weights was higher, and the rejection toward RhB was as high as 97%, indicating that the steric hindrance effect played an important role in dye rejection. Because the dye molecules could be inclined to aggregate into some larger molecules via hydrophobic interaction or intermolecular hydrogen bonding in the solution, the actual size of dye molecules in the solution could be larger than theoretical values.\(^5\) So, the dye rejection was usually higher than the result from MWCO. The surface of PDA/MoS\(_2\) NFM was negatively charged (Figure 5).\(^2\,4\) Thereby, except size exclusion, the capability of removing MO and AF was also contributed by the Donnan effect. The rejection toward MB and CV was higher than that of AF, due to the possible physical adsorption of dyes with positive charge onto the negatively charged membrane surface. So, the steric hindrance effect and electrostatic effect worked together for the rejection toward dyes.

The salt rejection of the PDA/MoS\(_2\) NFM is shown in Figure 13. The salt rejection was generally below 20%, which was obviously lower than the dye rejection. The contrast was partially due to the aggregation of dye molecules mentioned above. Furthermore, the inorganic MoS\(_2\) layers created rigid nanochannels, which could effectively reject the dye molecules with a large kinetic diameter and infiltrate the salt ions with a relatively lower kinetic diameter.\(^5\) The rejection toward MgSO\(_4\) and Na\(_2\)SO\(_4\) was apparently higher than the rejection toward MgCl\(_2\) and NaCl, which was mainly ascribed to the Donnan effect on the negatively charged surface, which was consistent with the result of the \(\zeta\)-potential measurement. And because of the steric hindrance effect, the MgSO\(_4\) and MgCl\(_2\) retentions were higher than those of Na\(_2\)SO\(_4\) and NaCl.

2.3.5. Long-Term Stability. The PDA(4)/MoS\(_2\)(0.1103) NFM was chosen as a representative to operate dye (MB) solution for 168 h for the long-term stability test. The flux and rejection toward MB were tested every 12 h by the methods mentioned above. Finally, \(P/P_0\) (permeance) and \(R/R_0\)
were used to express the results of long-term stability. From Figure 14, both permeance and rejection showed a slight fluctuation during the long-term stability testing process. This result indicated the high structural stability of PDA(4)/MoS2(0.1103) NFM. This could be on account of the excellent stability of MoS2 and PDA. MoS2 nanosheets possessed antiswelling and rigid nanochannel structure, which contributed to the stability of MoS2 layer-stacked structure during the long-term water filtration process. The PDA with the property of inherently strong adhesion also provided a stable modification layer for the NFM.

2.3.6. Comparison. The separation performance of the as-prepared membrane was compared to that of other state-of-the-art nanofiltration membranes. As shown in Table 1, the PDA(4)/MoS2(0.1103) membrane in this study showed a superior separation performance with high pure water permeance and high dye rejection.

3. CONCLUSIONS

A novel PDA/MoS2 NFM was fabricated via self-assembly of MoS2 nanosheets followed by PDA modification. The membrane was composed of a uniform MoS2 layer and a PDA layer coated on the HPAN substrate. The separation performance of PDA/MoS2 NFMs with various MoS2 loadings and dopamine polymerization times was investigated. With the increase of MoS2 loading, the dye rejection increased and the water permeance decreased. The smooth surface and rigid nanochannels of the exfoliated MoS2 nanosheets endowed the membrane with high water permeance and dye rejection. And the PDA modification effectively enhanced the membrane hydrophilicity, thus increasing the water permeance, and the dye rejection also slightly increased. Furthermore, the antifouling property of the membrane for BSA was also satisfactory with a high flux recovery ratio and a low total fouling ratio due to the increase of hydrophilicity and the electrostatic repulsion. And profited from the stability of MoS2 nanosheets and inherently strong adhesion of PDA, the PDA/MoS2 NFM also exhibited a satisfactory long-term stability. The pure water permeance of PDA(4)/MoS2(0.1103) NFM was 135.3 LMH/bar, and the rejection toward MB was 100%. The developed membrane also maintained high rejection toward various kinds of dyes (MB, CV, MO, RhB, and AF) and high permeability of salts (MgSO4, MgCl2, Na2SO4, and NaCl) with the molecular weight cutoff (MWCO) of 671 Da. This work provided a method to fabricate and modify MoS2 membranes for high-performance nanofiltration process.

4. EXPERIMENTAL SECTION

4.1. Material. Polyacrylonitrile (PAN) ultrafiltration membranes (MWCO = 50 kDa) supplied by Beijing Separate Equipment Co. Ltd. (China) were used as substrates of NFMs. MoS2 (99.5%), methylene blue (MB, 99.0%), methyl orange (MO, 97.0%), crystal violet (CV, 90.0%), lissamine rhodamine BSA: Evans blue; EBT: eriochrome black T; CR: congo red; RO16: reactive orange 16; cyt C: cytochrome C.

Table 1. Separation Performance Comparison of PDA(4)/MoS2(0.1103) NFM with the State-of-the-Art NFMs

| membrane material | PWP (LMH bar⁻¹) | solute | rejection (%) | applied pressure (bar) | ref |
|-------------------|-----------------|--------|---------------|-------------------------|-----|
| PEI−PDA/PES       | 7.2             | MB     | 96.5          | 2                       | 56  |
| PDA + CuNPs       | 25.5            | CR     | 97.5          | 6                       | 59  |
| Ru−PDA/PEI-1      | 26.2            | RO16   | 98.1          | 4                       | 45  |
| ultrathin GO      | 21.8            | MB     | 99.2          | 1                       | 11  |
| T3C2T−GO          | 25              | MB     | 99.5          | 5                       | 60  |
| g-C3N4            | 93              | EB     | 87            | 0.5                     | 62  |
| SG@GO composite   | 33              | EBT    | 98            | 0.5                     | 62  |
| nanosand-channeled WS2 nanosheets | 930            | EB     | 83            | 3                       | 63  |
| MoS2              | 245             | MB     | 89            | 1                       | 49  |
| PDA(4)/MoS2(0.1103) | 135.3          | MB     | 100           | 2                       | this work |

"EB: Evans blue; EBT: eriochrome black T; CR: congo red; RO16: reactive orange 16; cyt C: cytochrome C."
Figure 15. Schematic of the preparation process of PDA/MoS₂ NFMs.

B (Rhb, 99.0%), and acid fuchsin (AF, 99.0%) were provided by Shanghai Aladdin Bio-Chem Technology Co. Ltd. Magnesium sulfate (MgSO₄, 99.0%), magnesium chloride (MgCl₂, 98.0%), sodium sulfate (Na₂SO₄, 99.0%), and sodium chloride (NaCl, 99.5%) were supplied by Tianjin Fengchuan Chemical Reagent Technologies Co. Ltd. Poly(ethylene glycol) (PEG, 99.0%) with molecular weights of 200, 400, 600, 800, and 1000 Da were all from Damao Chemical Reagent Factory. Tris(hydroxymethyl)aminomethane (99.5%) was supplied by Biosharp. Bovine serum albumin (BSA, 98%) and dopamine hydrochloride (99.0%) were obtained from Sigma-Aldrich. Other chemicals, including sodium hydroxide (96.0%), ethanol (99.7%), and hydrochloric acid solution (37 wt %), were obtained from Shanghai Chemical Reagent Co. Ltd., respectively. Other chemicals, including sodium hydroxide (96.0%), ethanol (99.7%), and hydrochloric acid solution (37 wt %), were provided by Tianjin Fengchuan Chemical Reagent Technologies Co. Ltd. and used without any further purification. Water used in this work was ultrapure water prepared by reverse osmosis.

B. 4.2. Exfoliation of Multilayered MoS₂. The 2D MoS₂ nanosheets were prepared by a mixed-solvent mechanical exfoliation strategy. First, 10 mL of ethanol/water with an ethanol volume fraction of 45% was dispersed in a 15 mL pressure flask with 30 mg of MoS₂ powder. The dispersion was treated by ultrasound (QT3120, Ruipu, China) under 120 W for 8 h. Subsequently, the obtained dispersion was centrifuged at 3000 rpm for 20 min for removing multilayer MoS₂. Then, the supernatant was centrifuged at 10 000 rpm for 10 min to obtain exfoliated MoS₂ nanosheets. The as-prepared PDA-modified MoS₂ NFMs were named PDA(X)/MoS₂(Y) NFMs, where X is the polymerization time of dopamine (h) and Y is the loading of MoS₂ (mg/cm²).

4.4. Characterization. 4.4.1. Exfoliated MoS₂ Characterization. The morphologies of exfoliated MoS₂ nanosheets were investigated by transmission electron microscopy (TEM) analysis conducted with a JEM-2100 microscope. The thickness of exfoliated MoS₂ nanosheets was measured by atomic force microscopy (AFM, BioScope Catalyst, Bruker, Germany) on a mica plate. The samples for all analyses were dispersed in ethanol with the help of ultrasound.

4.4.2. Membrane Characterization. The surface and cross-sectional morphologies of the PDA/MoS₂ NFMs were observed utilizing scanning electron microscopy (SEM, Nova Nano SEM450 field emission microscope with an accelerating voltage of 10 KV). AFM was employed to examine the morphological changes of the membrane surface at difference dopamine polymerization times. The hydrophilicity of the membrane surface was investigated by water contact angle using a DAS30 video contact angle system (KRUS, Germany). The chemical structure of the membranes was analyzed by Fourier transform infrared spectrometry (FT-IR, VERTEX 70, Bruker, Germany). The transmittance spectra were collected in the wavenumber range of 4000–400 cm⁻¹. The X-ray diffraction (XRD) spectra of MoS₂ NFMs and PDA/MoS₂ NFMs were characterized by an X-ray diffractometer (D8 Discover, BRUKER AXS GMBH, Germany) with a Cu Kα anode (λ = 0.15438 nm) at 40 kV and 40 mA. And the ζ-potential of the surface of PDA/MoS₂ NFMs was determined by an electrokinetic analyzer (SurPASS, Anton Paar, AUS) in the pH range of 3–10 controlled by adding a certain amount of NaOH (0.1 M) or HCl (0.1 M) solution.

4.5. Membrane Flux and Rejection Tests. The nanofiltration performance in terms of pure water permeance and dye rejection was evaluated using a pressurized membrane filtration system with an Amicon cell under a certain pressure. The membrane sample with an effective area of 28.274 cm² was precompacted with ultrapure water for 0.5 h at 2 bar to obtain a steady permeance before performance evaluation. The pure water permeance (J, L m⁻² h⁻¹ bar⁻¹, abbreviated as LMH/bar) was tested at 1 bar using ultrapure water as the feed. Various salt and dye solutions were used to evaluate the rejection (R, %) of the membrane. The concentrations of salt and dye solution were evaluated, respectively, by an electrical conductivity meter (DDSJ-308A, Rex, CHN) and a UV–vis...
spectrophotometer (UV-1100, Mapada, China). The pure water permeance and rejection were calculated according to the following equations, respectively

\[
J = \frac{V}{A \times t \times P}
\]

where \( V \) is the total volume (L) of permeate pure water collected in a certain time \( t \) (h), and \( A \) (m\(^2\)) and \( P \) (bar) represent the effective membrane area and operation pressure, respectively.

\[
R = \left(1 - \frac{C_f}{C_i}\right) \times 100\%
\]

where \( C_f \) and \( C_i \) are the solute concentrations (mg/L) of feed and permeate solutions, respectively.

Furthermore, a series of PEG solutions with molecular weights ranging from 200 to 1000 Da were used as feed solution to test the MWCO of the as-prepared membrane. According to the following equation, the Stokes radius \( (r) \) of PEG molecule could be calculated

\[
\log r = -1.3363 + 0.359 \log (M_w)
\]

where \( M_w \) is the molecular weight of PEG.

**4.6. Antifouling Property.** BSA solution (500 mg/L) was used as the foulant to evaluate the antifouling property of the membrane carried on the same pressurized membrane filtration system with Amicon cell at 1 bar. The membrane sample was initially pressurized with ultrapure water for 0.5 h to ensure the membrane reaching a steady state, and the pure water permeance \( (P_0) \) was measured. Then, by BSA solution replacing the ultrapure water, the foulant solution permeance \( (P_f) \) was measured after 120 min and filtrated through the membrane in Amicon cell. Finally, the ultrapure water was filtrated through the membrane for 0.5 h to wash the membrane. The following pure water permeance \( (P_0) \) was measured. The total flux recovery ratio (FRR), the total flux decline ratio \( (DR_t) \), the reversible flux decline ratio \( (DR_r) \), and the irreversible flux decline ratio \( (DR_i) \), the antifouling characteristics of the membrane, were calculated according to the following equations, respectively

\[
\text{FRR} = \frac{P_f}{P_0} \times 100\%
\]

\[
\text{DR}_t = \left(1 - \frac{P_f}{P_0}\right) \times 100\%
\]

\[
\text{DR}_r = \left(\frac{P_0 - P_f}{P_0}\right) \times 100\%
\]

\[
\text{DR}_i = \left(\frac{P_0 - P_f}{P_0}\right) \times 100\%
\]

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**Notes**

The authors declare no competing financial interest.

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