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MoS_2/polyelectrolytes hybrid nanofiltration (NF) membranes with enhanced permselectivity

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ABSTRACT

The layered transition metal dichalcogenides, molybdenum disulfide (MoS_2) have received increasing attention and hold great potential applications in various fields due to its unique properties. In this work, the PDDA modified MoS_2 nanosheets (PDDA@MoS_2 nanosheets) were prepared and then incorporated into polyelectrolyte multilayers through layer-by-layer self-assembly method to get a PDDA@MoS_2-PDDA/PSS hybrid membrane. The morphologies and structures of the resulted PDDA@MoS_2 nanosheets and hybrid membranes were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscopy, X-ray photoelectron spectroscopy, energy dispersive spectroscopy and atom force microscopy. The nanofiltration performance of the hybrid membranes were investigated by retention of dyes and salts from aqueous solution. The result indicated that the hybrid membranes showed 98.4% retention of methyl blue with flux of 194.4 L/m^2 h MPa, which was 2.3 times than that of pure polyelectrolytes membrane with flux of 82.7 L/m^2 h MPa. And the hybrid membrane also showed rejection of salts in the sequence $Na_2SO_4 > MgSO_4 > NaCl > MgCl_2$. Moreover, the flux of the membrane remained around 180.0 L/m^2 h MPa, while the rejection was maintained at about 98.0% during the 165 h running time, displaying good long term stability.

1. Introduction

Nanofiltration (NF) technology is considered as an emerging pressure-driven separation process between reverse osmosis (RO) and ultrafiltration (UF), which have great potentials in water treatment, such as high rejection to organic compounds with molecular weight above 200 Da or multivalent ions and low operating pressure [1–7]. Most currently used NF membrane for water treatment is polymeric NF membrane due to low cost, easy processing, good mechanical stability, and tunable transport properties [8–12]. However, the extensive utilization of polymeric NF membrane is still restricted by some weak points such as trade-off relationship between permeability and selectivity, and poor stability [8,9]. The development of NF membranes with high flux and rejection, and good stability is necessary for water purification under the context of energy efficiency and cost effectiveness [8–12].

Organic/inorganic hybrid NF membranes could combine the characteristics of both organic polymers and inorganic materials, and overcome the trade-off effects showing elevated permselectivity [9]. Numerous inorganic components, such as one-dimensional (1D, like carbon nanotubes) and two-dimensional (2D, like graphene) materials [13–18] have been used in hybrid NF membrane resulting in improved membrane performances. 2D layered materials have been explored increasingly as a fundamental platform to develop separation technologies due to their unique atomic thickness and micrometer lateral dimensions [19]. Wang et al. have assembled 2D structured graphene oxide (GO) into NF membrane, and found that the prepared membrane's separation performance for dye molecules could be effectively enhanced by incorporation GO, exhibiting relatively high flux with a comparable retention [14,20].

MoS_2 is a typical transition metal dichalcogenides. Owing to its anisotropic structure, MoS_2 is prone to form graphene-like 2D morphology that offers large surface area and 2D permeable channels for ion adsorption and transport [21,22]. Therefore, the 2D MoS_2 nanosheets received increasing attention in recent years, due to its unique properties in field-effect transistors [23], photodetectors [24], catalyst [25] and optics [26,27]. More recently, MoS_2 nanosheets are expected to have novel application in the NF technology [28]. Heiranian et al. demonstrated that monolayer MoS_2

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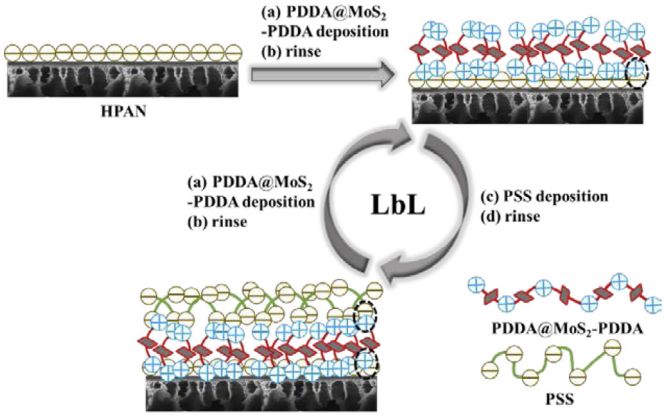

Scheme 1. Schematic illustration of the preparation of MoS_2/polyelectrolytes hybrid NF membranes.

can effectively reject ions and allow transport of water at a high rate through molecular dynamics simulations [29]. Peng et al. reported a laminar MoS_2 membrane composed of monolayer MoS_2 nanosheets with similar ~1.8 μm of thickness and ~3 nm channel size as that of the GO membrane, which exhibited 3- to 5-times higher water flux for retention of Evans blue (EB) molecules [30]. These works revealed that the monolayer MoS_2 nanosheets showed great potential in water-related membrane application. However, exfoliating bulk MoS_2 into thin nanosheets are much costly and unsafe due to use of *n*-butyllithium [31].

Herein, in this work, poly (diallyldimethylammonium chloride) (PDDA) modified MoS_2 (PDDA@MoS_2) nanosheets were first prepared by hydrothermal method in the presence of PDDA inducing a widened interlayer spacing. Then, the positively charged PDDA@MoS_2 nanosheets were incorporated into PDDA and poly(sodium 4-styrenesulfonate) (PSS) polyelectrolytes (PEs) membrane to get a hybrid NF membrane using layer-by-layer (LbL) self-assembly method as Scheme 1. The NF performance of the PDDA@MoS_2-PDDA/PSS hybrid membranes were investigated by retention of dyes and salts from aqueous solution. Also, the long-term stabilities of the hybrid membranes were investigated.

2. Experimentals

2.1. Materials and chemicals

The flat-sheet polyacrylonitrile (PAN) ultrafiltration membrane was supplied by Spero Membranes Inc. (USA). Poly (diallyldimethylammonium chloride) (PDDA, Mw = 750,000), Poly (sodium 4-styrenesulfonate) (PSS, Mw = 1,000,000), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), and thiourea ($CH_4N_2S$) were all purchased from Sigma-Aldrich Co. (USA). NaOH, ethanol, methyl blue (MB), congo red (CR), xylenol orange (XO), Na_2SO_4, $MgSO_4$, NaCl, and $MgCl_2$ were obtained from Beijing Chemical Factory (Beijing, China). De-ionized (DI) water with a resistance of 18.2 MΩ was used in all experiments. The chemicals were used as received without further purification.

2.2. Synthesis of PDDA modified MoS_2 (PDDA@MoS_2)

PDDA modified MoS_2 (PDDA@MoS_2) nanosheets were synthesized by hydrothermal method. Typically, 8 mL 62.5 g/L ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) and 125.0 g/L thiourea (CH_4N_2S) mixed aqueous solution were added to 10 mL of 100.0 g/L PDDA aqueous solution with continuous stirring for 24 h. After that, the mixed solution was transferred into a 25 mL Teflon-lined stainless steel autoclave and maintained at 220 °C for 18 h. The reaction system was allowed to cool to room temperature. The final product was thoroughly washed with water and absolute ethanol to remove the redundant ions, and dried at 60 °C. For the comparison, the controlled MoS_2 nanosheets were prepared by the similar method without PDDA added.

2.3. Preparation of PDDA@MoS_2 hybrid membrane

The hydrolyzed PAN (HPAN) membrane was immersed into 5.0 g/L PDDA solution which contained 0.4 g/L PDDA@MoS_2 nanosheets. After 20 min, the membrane was taken out and rinsed with de-ionized water. Subsequently, the membrane was immersed into 1.0 g/L PSS solution for 20 min, and then rinsed by de-ionized water. The steps were repeated for three times to obtain the $(PDDA@MoS_2\text{-}PDDA/PSS)_{4.0}$ hybrid membrane. As a comparison, the $(PDDA/PSS)_{4.0}$ PEs membrane was prepared by the similar method [32], but none of the PDDA@MoS_2 were added.

2.4. Characterizations

X-ray diffractometer (XRD) was performed on a D8 advance diffractometer (Bruker/AXS, Germany) with Cu Kα radiation ($\lambda = 1.5406$ Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on an Escalab 250Xi (Thermo Fisher, USA) with a monochromatic Al Kα X-ray source. The scanning electron microscopy (SEM) images were taken on a SU8020 (Hitachi, Japan), prior to observations, all samples were coated with gold nanoparticles in a vacuum to increase their conductivity. Elemental compositions of the membranes were analyzed using an energy dispersive spectroscopy (EDS) apparatus along with SEM. The transmission electron microscopy (TEM) was carried out on a JEM-2100 microscope (JEOL, Ltd., Japan). Zeta potential of the obtained MoS_2 nanosheets was measured using Zeta Potential/Particle Sizer (NICOMP™ 380ZLS, USA) and the zeta potential of the membrane surface was determined using an electrokinetic analyzer (Anton Paar, SurPASS, Germany) with 0.83 mmol/L of KCl solution and 0.03 MPa of the operation pressure. Both zeta potentials were measured under neutral condition with pH value at 7. Atom force microscopy was taken with a PicoScan™ 2500 Microscope System (Agilent Technologies, USA) via the tapping mode under air atmosphere and ambient temperature. The roughness was manifested by root mean-square (RMS) with average of height deviations taken from the mean image data plane.

2.5. Nanofiltration performance

Nanofiltration performance was evaluated using a cross flow NF system which contained membrane cell, plunger pump, pressure gauge, and solution vessel as our previous work [32–36]. The nanofiltration membrane was loaded into the membrane cell for filtration with effective membrane area of 33.17 cm^2. The feed solution was pressurized with a plunger pump. The filtration pressure was maintained at 0.4 MPa. During the NF process, the concentrate was recirculated to the feed vessel while permeate was collected in permeate vessel. The flux J was calculated by: $J = V/t \times A \times P$ (L/m^2 h MPa), where V (L) is volume of the permeate sample, t (h) is time for collecting sample, A is the membrane area (m^2), P is operation pressure (MPa). The solute rejection rate R was calculated by: $R = (1 - C_P/C_F) \times 100\%$, where C_p is the solute concentration in the permeate and C_F represents solute concentration in the feed. The dye concentrations were measured by an ultraviolet-visible spectrophotometer (UV-3200, Shanghai Mapada Instruments Co. Ltd., China) at the maximal absorption wavelength of the dye. The salt concentrations were measured using a conductivity meter (Inesa Scientific Instrument Co. Ltd., China). In all

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