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Preparation and properties of PVDF/SiO_2@GO nanohybrid membranes *via* thermally induced phase separation method

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ABSTRACT

Graphene oxide (GO), one of the most promising filter materials, is intensively employed to prepare the membranes *via* non-solvent induced phase separation(NIPS) method, but it has not been found to modify polymeric membranes *via* thermally induced phase separation (TIPS) method. In this work, the derivative of GO, SiO_2@GO nanohybrid, is fabricated and employed to synthesize PVDF/SiO_2@GO nanohybrid membranes *via* TIPS method for the first time. The results indicate that the PVDF/SiO_2@GO nanohybrid membranes experience liquid-liquid phase separation mechanism, and exhibit bi-continual and asymmetric structure. The included SiO_2@GO nanohybrid is uniformly dispersed in the membrane matrix. With the addition of SiO_2@GO, the top surface becomes denser and the pore size decreases; but overhigh SiO_2@GO addition for membrane M-5 triggers in the adverse trend. This is caused by the combined actions of nucleation and growth of PVDF and viscosity increase of cast solution due to the addition SiO_2@GO nanohybrid. The BSA rejection of membrane gradually increases with the addition of PVDF/SiO_2@GO nanohybrid accompanied with the decline of pure water permeation flux. As the SiO_2@GO content increases to 0.9 wt%, the PVDF/SiO_2@GO nanohybrid membrane M-4 presents the highest BSA rejection of 91.7% and the lowest permeation flux of 182.6 $L\,m^{-2}\,h^{-1}\,bar^{-1}$. However, the overhigh SiO_2@GO addition (1.2 wt%) leads to the outstanding pure water permeation flux of 679.1 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ and a much lower BSA rejection. The addition of PVDF/SiO_2@GO nanohybrid evidently improves the surface hydrophilicity and antifouling ability of resultant membranes. The XRD patterns and FTIR spectra of membranes verify the exclusive α-phase of PVDF, and the melting temperature(T_m) and crystallinity(x_c) evidently increase with the addition of SiO_2@GO nanohybrid up to 0.9 wt% in the dopes. Overhigh SiO_2@GO addition (1.2 wt%) leads to small decline for these parameters.

1. Introduction

Membrane separation technology is widely used to remove various water contaminants, which have significant adverse health and/or environmental effects [1,2]. Due to the outstanding properties such as high thermal stability, good chemical resistance, high mechanical strength, good aging resistance and membrane forming properties, poly(vinylidene fluoride)(PVDF) membranes were applied to a range of scientific researches and industrial processes [3,4]. To date, most commercial and lab membranes are produced *via* a phase inversion process. Thermally induced phase separation (TIPS) method was recognized since the late 1980s; and from then on much more works were devoted to prepare porous membranes *via* TIPS method [5,6]. Apart from the polymers such as polypropylene (PP) [7] and polyethylene (PE), the PVDF membranes [8–11] prepared by TIPS methods were found more significant in mechanical strength, pore size distribution and permeation performances compared with those produced by non-solvent induced phase separation(NIPS) method.

In the past years, most works in membrane preparations *via* TIPS process were intensively concentrated on the selection and effects of diluents on the membrane structure and permeation performance [9,12–18]. For instance, Atkinson et al. [12,13] employed isotactic polypropylene (iPP) and diphenyl ether (DPE) to produce flat membranes with an anisotropic structure *via* TIPS, which underwent a liquid-liquid phase separation mechanism. Ji et al. [14] selected dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) as diluents to prepare PVDF hollow fiber membranes.

In fact, the additives also markedly influence the membrane structure and performance in TIPS process, which is similar to NIPS process. Nevertheless, only a few works were paid on this side. For example, Li et al. [19] reported that $CaCO_3$ influenced the crystallization kinetics of ternary mixture of PVDF/$CaCO_3$/DBP in

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preparing membranes via TIPS. Cui et al. [11] found that a certain amount of micro-sized SiO_2 promoted the water flux of PVDF/SiO_2 blend membranes and induced the formation of spherulitic morphology. Xu et al. [10] fabricated the PVDF/oxidized multi-wall carbon nanotubes(O-MWNTs) flat membranes with bi-continuous structures.

Graphene and its derivatives(such as graphene oxide, GO) are considered as one of the most promising filter materials [20,21]. Although they were intensively employed to prepare the membranes with high anti-fouling and rejection performances *via* non-solvent induced phase separation (NIPS) method [22–28], the graphene and its derivatives (such as GO) have not been found to modify polymeric membranes *via* TIPS method. The low thermal stability of GO may be one factor inhibiting its applications in TIPS process.

In order to overcome the drawback of graphene and its derivatives, SiO_2@GO nanohybrid was produced *via in situ* hydrolysis and condensation of TEOS on the surfaces of graphene oxide (GO) nanosheets, and then used to decorate PVDF membranes *via* TIPS. This study aims to synthesize PVDF/SiO_2@GO nanohybrid membranes for the first time. The influences of SiO_2@GO nanohybrid on the membrane structure and permeation performances were detailed investigated upon a series of characterizations.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF, FR904) was purchased from Shanghai 3F New Material Co. Ltd. (China). Graphite powder (325 mesh) and tetraethoxysilane (TEOS, 98%) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Ammonia solution ($NH_3 \cdot H_2O$, 25 wt%), dibutyl phthalate (DBP), hydrochloric acid(HCl, 36–38 wt%), H_2SO_4 (98 wt%) and absolute ethanol were provided by Shanghai Chemical Agent Co. Ltd.(China). Deionized water (DI) was produced by a reverse osmosis (RO) system. Bovine serum albumin (BSA, M_W=67,000) was purchased from Shanghai Bio Co. Ltd. (China). All chemicals were used without further purification.

2.2. Preparation of inorganic particles

2.2.1. Synthesis of GO nanosheets

Graphene oxide was synthesized from oxidized natural graphite flakes by a modified Hummers method [29,30]. In a typical procedure, 3.0 g graphite flakes and 18.0 g $KMnO_4$ were added to a mixed H_2SO_4/H_3PO_4 (volume ratio=360:40) solution; then the mixture was stirred and reacted at 50 °C for 12 h. After the reaction, the mixtures were cooled to room temperature and poured into the ice bath with adding 3 ml 30% H_2O_2, and then the remaining solid material was washed with DI water, 30% HCl aqueous solution, and absolute ethanol in succession. The solid was dried in vacuum oven at room temperature and stored for further study.

2.2.2. Synthesis of SiO_2@GO nanohybrid

Silica nanoparticles were deposited on GO nanosheets by *in situ* hydrolysis and condensation of TEOS [31]. In a typical procedure, 0.5 g GO was dispersed in 420 ml alcohol–water (5/1, *v*/*v*) solution by sonication for 1 h. After that, the pH of reaction mixture was adjusted to approximate 9.0 with ammonia solution, and then 5.5 ml TEOS was added into the solution drop by drop. After being vigorously dispersed in ultrasonic bath for 1.5 h, the mixture was stood for 24 h at room temperature (25 °C). Then, the SiO_2@GO suspension was centrifuged, washed for 5 times with alcohol, dried in vacuum. The obtained SiO_2@GO nanohybrid was stored for further study.

2.2.3. Characterizations of GO and SiO_2@GO

The synthesized GO nanosheets and GO-SiO_2 nanohybrids were detected by Fourier-transform infrared spectroscopy (FTIR Electron Corp Nicolet 380, US) in the range of 4000–400 cm^{-1} at room temperature.

The thermal stability of GO nanosheets and SiO_2@GO nanohybrid was measured by a thermal gravimetric analyzer (Perkin-Elmer Pyris 6 TGA instrument) at a heating rate of 10 °C/min from 35 °C to 800 °C under nitrogen atmosphere.

The morphologies of GO nanosheets and SiO_2@GO nanohybrid were detected with a field emission transmission electron microscope (FETEM, JEM-2010, Japan) at 200 kV.

2.3. Membranes

2.3.1. Membrane preparation

The PVDF/SiO_2@GO nanohybrid membranes were prepared *via* TIPS process. The predetermined amount of SiO_2@GO nanohybrid was completely dispersed in the measured amount of DBP diluent under ultrasonic bath for 1 h. Then 25 g of PVDF powder was added into the mixing solution. The homogenous casting solution was obtained by vigorous stirring at 200 °C for 6 h. After fully degassing, the casting solution was uniformly spread onto a heated stainless steel plate (200 °C) with a knife gap of 450 μm, and then immediately immersed into quenching bath (ice water bath) until totally solidification. To eliminate diluent, the nascent membranes were immersed into ethanol liquid for 12 h, and then soaked in DI water to extract the residual ethanol. The resulted membranes were then stored in DI water for further study in details. The detailed preparation parameters for the membranes are were listed in Table 1. The PVDF and SiO_2@GO contents in Table 1 represent the ones in the casting solutions.

2.3.2. Characterizations of membranes

The membrane surfaces were analyzed by the attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) (Thermo Electron Corp., Nicolet 380, USA).

The morphologies of the as-prepared membranes were detected using a field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) equipped with an energy-dispersive spectrometry (EDS) under an accelerating voltage of 5.0 kV. Before recording the cross-section SEM images, the membrane samples were fractured in a liquid nitrogen and then sputtered with gold for 120 s. The AFM images of top surfaces were performed on an atomic-force microscopy (AFM, BioScope TM, USA) with tapping mode. The surface was imaged at a scan size of 2 μm × 2 μm at a speed of 2 Hz.

The hydrophilicity of hybrid membrane was evaluated by water contact angle system (KRUSS DSA30 German) equipped with video

Table 1
Compositions of dope solutions and preparation temperature for PVDF/SiO_2@GO membranes.

Membrane no	Mass ratio			Membrane preparation temperature (°C)	Quenching temperature (°C)
	PVDF (g)	DBP (g)	SiO_2@GO (g)		
M-1	25	75	0	200	0
M-2	25	75	0.3	200	0
M-3	25	75	0.6	200	0
M-4	25	75	0.9	200	0
M-5	25	75	1.2	200	0