



Impact of trace graphene oxide in coagulation bath on morphology and performance of polysulfone ultrafiltration membrane



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ABSTRACT

This paper aimed to systematically investigate the effect of trace graphene oxide (GO) nanosheets in coagulation bath on the morphology, surface property, mechanical strength and separation property of the polysulfone (PS) membranes fabricated via non-solvent induced phase inversion process. For comparison, PS membranes were fabricated in pure water and GO containing coagulation bath, respectively. The synthesized membranes were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), contact angle goniometry, tensile strength measurement, etc. The hydrophilicity of the PS membranes increased with the increasing of GO concentration. Compared to the PS membranes synthesized in pure water coagulation bath, the skin layer of the PS/GO membranes synthesized in GO containing water coagulation bath was also thicker, which in turn influenced the separation performance. For example, the flux of the PS/GO membrane synthesized in GO solution (20 mg/L, PS/GO-20) decreased by 75.1%. However, the PS/GO membranes had better tensile strength (from 2.31 to 2.87 MPa) and tensile modulus (from 237.86 to 258.47 MPa) compared with PS membrane, although the membrane integrity was destroyed to some extent due to the incorporation of GO nanosheets. The results showed that the trace nanomaterials in the water coagulation bath had significant impact on the surface property, morphology, mechanical strength and resultant separation performance of the synthesized membranes.

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1. Introduction

Nanomaterial–polymer hybrid membranes have been intensively studied in recent years due to their superior properties, such as strong mechanical strength, high thermal stability, excellent permeability and selectivity [1–4]. Phase inversion is the most popular synthesis method of nanomaterial–polymer hybrid membranes. Generally, nanomaterials are blended into a polymer casting solution and then the doping solution is cast onto a glass substrate forming a thin film [5]. Subsequently the glass substrate is immersed into a coagulation bath and a hybrid membrane is formed. Among various nanomaterial, graphene and its derivative graphene oxide (GO), single-atom thick and two-dimensional materials, have attracted great attention for their remarkable electronic [6–12], mechanical [4,13,14], and thermal properties [15,16]. Most recently, great efforts have been made to develop polymer/GO membranes using the phase inversion process. For example, GO nanosheets were incorporated into a polysulfone

(PS) matrix [17], and the results indicated that salt rejection of the PS membrane was improved after GO doping. Similarly, Ionita and co-workers [18] found that PS membranes presented a higher thermal stability when a low amount of GO (0.25 and 0.5 wt.%) was incorporated within the matrix. In another study, Zhao and co-workers [19] embedded reduced graphene oxide (rGO) into PS ultrafiltration (UF) membranes and found that the antifouling property was greatly enhanced. Besides PS membranes, other polymeric membranes, such as polyethersulfone (PES) [20,21] and polyvinylidene fluoride membranes (PVDF) [22–24], also exhibited improved antifouling, hydrophilicity, permeability and mechanical strength after incorporating GO nanosheets.

However, during phase inversion in the coagulation bath, a small fraction of the nanomaterials present in the casting solutions are inevitably dispersed into the coagulation bath due to the exchange between solvent and non-solvent [25–30]. These trace nanomaterials will definitely change the properties of the non-solvent in coagulation bath to some extent. Previous studies have shown that the morphology, structure and performance of membranes are significantly affected if ions or other solvents are present in coagulation bath [5,31,32]. However, no attention has

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been paid to the trace nanomaterials, such as solid impurities, although they may have similar impact as the ions and solvents on the subsequent membrane synthesis. Thus, it is important to study the effect of trace nanomaterials in coagulation bath on the polymer membrane.

In this work, GO nanosheets were chosen as the model nanomaterial to investigate the impact of trace nanomaterials present in coagulation bath on the synthesis of PS membranes. Low concentration GO nanosheets of 5–20 mg/L were dispersed in a coagulation bath. Then PS membranes were fabricated via phase inversion in the GO containing coagulation bath. The synthesized PS membranes were characterized by SEM, contact angle and FTIR, etc. to study the impact of GO on the morphology, hydrophilicity and surface properties of the resultant membranes. The flux, rejection and mechanical strength of the PS membranes were evaluated to assess the impact of GO on the filtration performance. Finally, the effect of trace GO nanosheets on phase inversion was discussed thoroughly based on the characterization and filtration data. To the best of our knowledge, this study is the first investigation of the impact of nanomaterials impurities in coagulation bath on the synthesis of polymeric membranes. The results may provide new insights into the fabrication of polymer/nanomaterial hybrid membranes.

2. Experimental section

2.1. Materials

Natural graphite power, sodium nitrate (NaNO_3), sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), 1-methyl-2-pyrrolidinone (NMP; 99.0%), polyethylene glycol (PEG; with MW of 100 kDa) and hydrochloric acid (HCl; 32%) were purchased from Sigma Aldrich. Polysulfone (PS) was purchased from BASF Co., Ltd., Germany.

2.2. Preparation of GO nanosheets and PS membranes

2.2.1. Preparation of GO nanosheets

NaNO_3 (1.25 g) and natural graphite (2.5 g) were first mixed in a 500 ml glass bottle, which was then kept in an ice water bath for 10 min. Then 60 ml of sulfuric acid was added slowly under vigorous stirring. After 30 min, 7.5 g of KMnO_4 was added into the mixture, and stirred for 2 h. After that, the ice water bath was removed and the mixture was further stirred overnight at room temperature. Subsequently, 135 ml of deionized (DI) water and 25 mL of H_2O_2 was added in sequence. A bright yellow mixture was obtained after the solution cooled down. GO nanosheets were obtained after the mixture was washed several times with DI water and then 32% hydrochloric acid. TEM image of the GO nanosheets is shown in Fig. 1. It can be seen that the sizes of GO nanosheets are from several hundred nanometers to several microns.

2.2.2. Preparation of PS membranes

The PS membranes were prepared via phase inversion in a water coagulation bath containing trace GO nanosheets (0, 5, 10 and 20 mg/L, respectively). In accordance with typical casting methods, a PS casting solution of 15 wt.% was first prepared by dissolving PS into NMP solution. After the PS solution was cast on a clean glass plate by an adjustable micrometer film applicator (stainless steel blade at a gap of 150 μm , Elcometer 3580) at room temperature, it was immersed into the water coagulation bath containing GO nanosheets. After 24 h, the membranes were moved to fresh DI water and stored for later use. The membranes fabricated in the water coagulation bath containing 0, 5, 10 and 20 mg/L GO were named PS, PS/GO-5, PS/GO-10 and PS/GO-20, respectively.

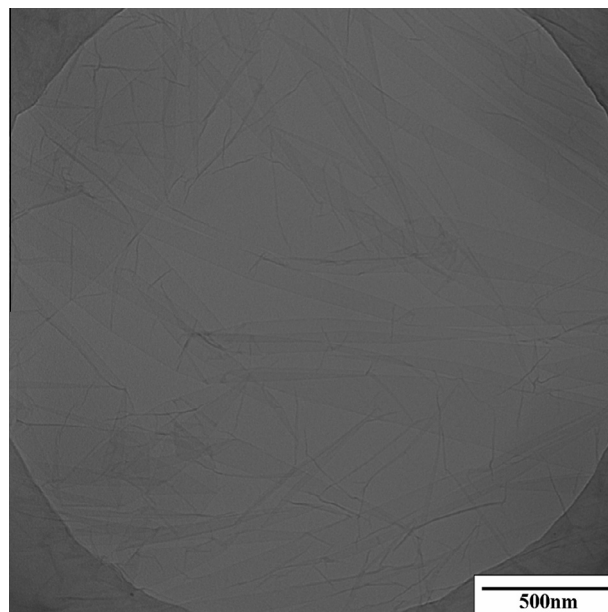


Fig. 1. TEM image of GO nanosheets.

2.3. Characterization of GO and PS/GO membranes

The structure and morphology of GO were characterized by a transmission electron microscopy (TEM; FEI Tecnai G2 T20 TWIN LaB6 TEM). The functional groups and structure of the GO and PS membranes were analyzed by a Fourier transform infrared spectrometer (FTIR spectrometer, PerkinElmer, Australia). The surface and cross-section morphologies of the PS/GO membranes were examined by a field emission scanning electron microscopy (FESEM; Magellan 400 and Nova NanoSEM 450, FEI, USA). All the SEM samples were coated with Platinum (Pt). For the surface samples, the coating time was 15 s. For the cross-section samples, the coating time was 30 s. Imaging settings are listed as follows: HV (5 kV), WD (4.8 mm), det (ETD) and spot (4.0). To prepare SEM samples, the membranes were cut into small pieces and immersed into liquid nitrogen for 60–90 s. The frozen membranes were then broken by a pair of tweezers. After drying at room temperature, the samples were adhered to the SEM sample holder with conductive tape and coated with a thin layer of Pt. Membrane hydrophilicity was analyzed via contact angle measurements (OCA-15EC, Dataphysics, Germany). One μL of deionized water was dropped onto the membrane surface with a microsyringe, and the contact angle was measured after the water drop stabilized.

2.4. Membrane performance evaluation

2.4.1. Membrane permeability and selectivity

Membrane flux was used to characterize the permeability performance of the PS/GO membranes. The pure water flux and polyethylene glycol (PEG) rejection were measured using a dead-end filtration system. The filtration setup comprised of a tank, a balance and a 300 mL filtration cup which housed the membrane. The effective membrane area was 14.2 cm^2 . The detailed procedure is described as follows: (1) The membrane was compacted at 2 bars for 3 h to obtain a steady flux; (2) The flux was then recorded at 1 bar every 30 s and at least 100 readings were collected to obtain an average value; (3) The pure water was replaced by PEG (100 K). The concentration of PEG in the permeation and feed solution were measured by a total organic carbon analyzer (TOC). Permeate flux was calculated on the basis of permeate mass divided by effective

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