Graphene oxide modified graphitic carbon nitride as a modifier for thin film composite forward osmosis membrane

Yaqin Wang [a,b], Ranwen Ou [a], Huanting Wang [c,*], Tongwen Xu [a,*]

[a] Functional Membrane Laboratory, School of Chemistry and Material Science, University of Science and Technology of China, Anhui, Hefei 230026, PR China
[b] School of Materials and Chemical Engineering, Anhui Jianzhu University, Anhui, Hefei 230026, PR China
[c] Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

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ABSTRACT

Reduced graphene oxide (rGO) modified graphitic carbon nitride (g-C_3N_4), CN/rGO, was synthesized as a modifier for porous polyethersulfone (PES) substrate for the preparation of thin film composite (TFC) polyamide forward osmosis (FO) membrane. The effect of CN/rGO addition on the PES substrate formation was investigated using viscosity and light transmittance measurements, and the PES–CN/rGO substrates and the FO membranes were characterized by SEM, TEM, AFM, XPS and contact angle measurements. The results indicated that the addition of CN/rGO had a significant effect on the membrane properties. The FO membrane with an appropriate amount of CN/rGO in the PES substrate exhibited excellent FO performance. The osmotic water flux with 0.5 wt% CN/rGO in the substrate of TFC membrane reached 41.4 LMH using 2 M NaCl as draw solution and deionized water as feed, which was around 20% greater than with the control membrane without CN/rGO. The FO performance improvement should be attributed to the modified structure of the PES substrate, and thus lower structure parameter and the reduction of ICP. This study suggests that CN/rGO is an effective additive for modifying the porous substrate for the development of FO membranes.

1. Introduction

The forward osmosis (FO) process has attracted growing interest in the development of energy-efficient water treatment technologies since this process requires a very low hydraulic pressure, less energy input, and lower fouling tendency [1,2]. This is because water can spontaneously diffuse across a semipermeable membrane by the chemical potential gradient between the feed and draw solution [3]. However, existing FO membranes often show low water permeability due to internal concentration polarization (ICP) occurring inside the porous substrate layer of membranes; and high salt leakage is another problem of these membranes [4]. It has been widely recognized that an ideal FO membrane should have a thinner, highly porous substrate with low tortuous pore structure to provide a short path from the bulk draw solution to the active layer during osmotic process, thereby alleviating the ICP and achieving a high water flux [5], and a selective layer with high dissolved solute rejection. Recently, many studies have reported the thin film composite (TFC) offers the possibility to optimize support and selective layers separately [6–11].

Several methods have been applied to develop better performance TFC FO membranes, such as optimizing the structure of substrate [6,7,9,10,12–18] by a controlling phase inversion process during the membrane support fabrication, and constructing scaffold-like nanofiber structure using an electrospinning technique [19]. Although high water permeability of TFC membrane with electro-spun nanofibers substrate was reported, the thin film layer-substrate interfacial binding in such membranes is likely much weaker rather than that in the conversion membranes [20]. In addition, greater wettability of the substrate is desired to enhance water transport and less fouling tendency [15]. However, few hydrophilic polymers were used as the substrate of TFC membranes because water might plasticize the hydrophilic support more severely than the rigid selective layer, resulting in delamination of the selective layer [13]. The disadvantages of these polymeric membrane materials have in turn shifted the focus of research away from hydrophilic nanocomposite materials.

Recently, the modification of hydrophobic polymer has attracted considerable attention. Sotto et al. [17] optimized the substrate by incorporation of titanium (TiO_2) nanoparticles into polyethersulfone (PES) matrix with significantly increased water flux through the TFC membranes. The results from Ismail group also confirmed this conclusion by investigating the effect of the loading of TiO_2 on the polysulfone substrate of TFC membrane. Ma et al. [20] reported porous zeolite nanoparticles loaded in the

substrate was effective for ICP control. Our previous research also demonstrated the incorporation of multi-walled carbon nanotubes could modify the PES substrate for FO membranes [21] thanks to the porosity enhanced by the nanotubes. These above studies imply that the incorporation of appropriate additive into polymer substrate of TFC membranes offers a possibility not only to improve the wettability of membranes but also to modify the substrate structure. These features may potentially lead to a greatly reduced ICP.

In this paper, with a goal of combining the benefits of high water/salt selective polyamide as the active layer and the nanocomposite materials as the substrate, we report on a polyethersulfone (PES) composite substrate containing a small amount of nanosheets of reduced oxide graphene (rGO) modified graphitic carbon nitride (g-C_3N_4) (CN/rGO) for the preparation of FO membranes. In recent years, CN/rGO has been of particular interest owing to its catalytic activity and application in photocatalysis [22,23]. In our study, we take advantage of its special architecture and physicochemical properties of CN/rGO; in particular, CN/rGO is porous and consists of many curved nanosheets with lamellar morphology [24], and carbon nitride materials have the potential to enhance the composite substrate wettability due to the formation of hydrogen bonds between the water molecules and the nitrogen atoms of carbon nitride. To date, there has been no report about the use of CN/rGO as a modifier of polymer membranes. In this work, the effects of the loading of CN/rGO nanosheets on the PES composite substrate and the FO performance of TFC membrane are investigated.

2. Experimental

2.1. Materials

Graphite powder was purchased from Qingdao Henglide Graphite Co. Ltd. Polyethersulfone was purchased from BASF (Ultrason E3010, Germany). N,N-Dimethylacetamide (DMAc,), N-methyl-2-pyrrolidone (NMP) were obtained from Sinopharm chemical reagent Co., Ltd (CHN). 1,3-phenylenediamine (MPD) and 1,3,5-benzenetricarbonyle trichloride (TMC) with a purity of all over 98% were used. All other reagents were purchased from Alfa Aesar and used as received.

2.2. Synthesis of CN/rGO nanosheets and preparation of membranes

2.2.1. Synthesis of CN/rGO nanosheets

The synthesis process of CN/rGO nanosheets is illustrated in Fig.1. CN/rGO nanosheets were obtained by preparation of GO sheets using Hummers' method [25] and subsequent cyanamide polycondensation on the surface of GO. More details on the synthesis are presented in Supplementary Material.

2.2.2. Fabrication of PES and CN/rGO–PES substrates

All flat-sheet substrates were fabricated using PES casting solutions with different amounts of the additive by the phase inversion method. The modified substrates were prepared by adding CN/rGO, while the control substrate was prepared without the additive. Specifically, 1 g of pre-dried PES polymer powder was dissolved into 5 g of a mixed solvent (the weight ratio of NMP to DMAc is 1:1) to obtain a PES solution. A varied amount of CN/rGO powder (0.2, 0.5, 0.8 and 1.0 wt% on the basis of dry PES powder) was added into 4 g of the mixed solvent, followed by tip sonication in a water bath using a ultrasonicator (SK3310SP) at an output power of 180 W for 3 h to get a CN/rGO dispersion. The modified polymer casting solution with CN/rGO was then prepared by mixing PES solution with CN/rGO dispersion under continuous stirring for 24 h to ensure good dispersion. Prior to casting, the prepared solution was left for degassing at room temperature for 1 day. The casting solution of the control substrate was prepared using the same procedure including the ultrasonification except that no CN/rGO was added. The casting solution was then cast onto a clean glass plate using a casting knife with a gap of 100 μm. After partial evaporation of the solvent for 20 s, the film was immersed into a coagulation bath containing deionized water for 24 h before being stored in water. The thickness of the prepared substrates was measured using a digital micrometer, and the average thickness was about 50 μm. The pristine PES substrate was referred to as control-S, and the PES–CN/rGO nanocomposite substrates were denoted CN/rGO–S-0.2, CN/rGO–S-0.5, CN/rGO–S-0.8, and CN/rGO–S-1.0 according to the mass percentage of CN/rGO in the PES matrix.

2.2.3. Synthesis of polyamide active layer

The polyamide active layer of TFC FO membranes was formed by interfacial polymerization (IP) of polyamide on the surface of a PES or PES–CN/rGO substrate. The substrate was soaked in an aqueous solution of 2 wt% m-phenylenediamine (MPD) containing an equivalent amount of triethylamine (TEA) as an acid acceptor and 0.1 wt% sodium dodecyl sulfate (SDS) as the surfactant for 1 min, and the excessive MPD solution on the substrate surface was removed by blowing air. Subsequently, the substrate was in contact with a solution of 0.15 wt% trimesoyl chloride (TMC) in n-hexane for 1 min. Then, the resulting composite membranes were cured at 60 °C for around 10 min in an oven, then rinsed with a 200 ppm NaOCl aqueous solution for 120 s, followed by rinsing for 30 s with a 1000 ppm NaHSO₃ aqueous solution [8] before they were washed with water and finally stored in fresh distilled water at ambient temperature. The prepared TFC membranes were denoted Control-M, CN/rGO-M-0.5 and CN/rGO-M-1.0, corresponding to the substrates Control-S, CN/rGO–S-0.5 and CN/rGO–S-1.0, respectively.
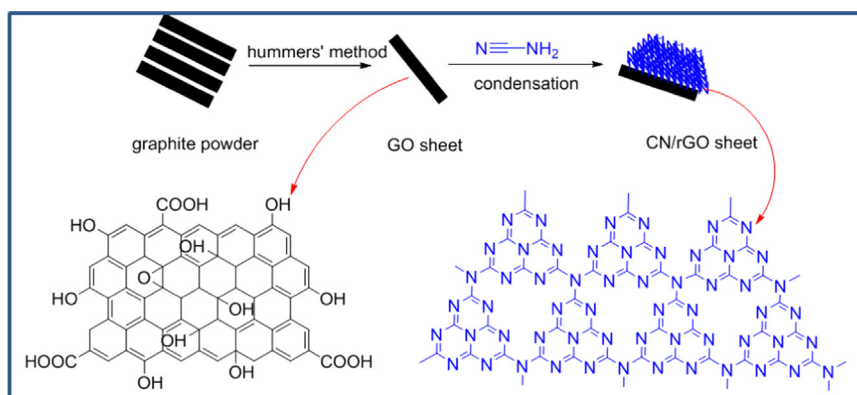

Fig. 1. Schematic illustration of CN/rGO preparation procedure.