Desalination 441 (2018) 77–86

Contents lists available at ScienceDirect

Desalination

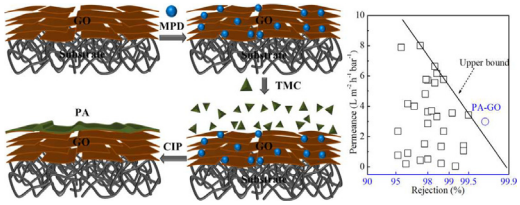
journal homepage: www.elsevier.com/locate/desal

Confined interfacial polymerization of polyamide-graphene oxide composite membranes for water desalination

Jiali Shi, Wufeng Wu, Yan Xia, Zhanjun Li, Wanbin Li*

School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Graphene oxide
Polyamide
Confined interfacial polymerization
Water purification
Reverse osmosis

ABSTRACT

The developments of efficient reverse osmosis (RO) membranes and their fabrication mechanisms are significant for water purification. Graphene oxide (GO) membranes show excellent stability and large permeance, but the large transport nanochannels make it difficult to be applied for RO desalination. Herein, a strategy, confined interfacial polymerization, is reported for preparing ultrathin polyamide (PA)-GO membranes with excellent performance in RO desalination. By making use of the adsorption of negatively charged GO with oxygen-containing groups to meta-phenylene diamine (MPD), the polymerization between MPD and trimesoyl chloride (TMC) at void regions of GO layer is carried out, which can refine the size of transport nanochannels. The resulting PA-GO membrane displays high salt rejection of 99.7%. Because of the 30-nm thickness of and the small amount of formed PA, the large permeance of 3.0 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ is achieved. Moreover, the PA-GO membrane shows good long-term stability, high chemical stability and low fouling propensity.

1. Introduction

The scarcity of clean and safe water becomes a critical issue as growth of population and progress of industrialization [1]. Desalination by membrane-based reverse osmosis (RO) is an energy-efficient technology for obtaining fresh water from seawater, brackish water and wastewater [2]. Most commercial RO membranes are fabricated by depositing polyamide (PA) selective layers on porous substrates [3]. PA selective layers of RO membranes for salt rejection are traditionally synthesized by interfacial polymerization, through immersing porous substrates (usually polysulfone-PSF) with impregnated meta-phenylene diamine (MPD) aqueous solution into trimesoyl chloride (TMC) organic solution [4,5]. The dense PA layers can be formed at the immiscible water/organic interfaces. As the results of the protruding MPD solution, the formed membranes usually have leaf-like structure, which enhances the surface roughness and then increases fouling propensity. Although PA membranes exhibit superior permeability and salt rejection than first-generation cellulose acetate membranes, their chlorine sensitivity and fouling propensity are bottlenecks for better practical application [6–13]. Moreover, development of efficient membranes to break through the limitation of trade-off between permeability and rejection is still the main research interest.

Graphene and its derivatives including graphene oxide (GO) and reduced graphene oxide (rGO), have great advantages for various

* Corresponding author.
E-mail address: gandeylin@126.com (W. Li).

https://doi.org/10.1016/j.desal.2018.04.030
Received 26 January 2018; Received in revised form 26 April 2018; Accepted 30 April 2018

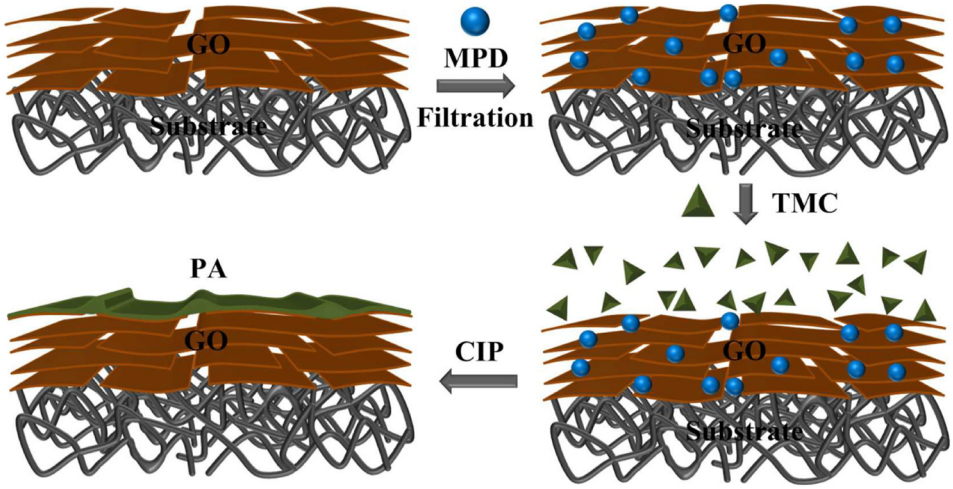


Fig. 1. Schematic illustration of PA-GO membrane formation via confined interfacial polymerization.

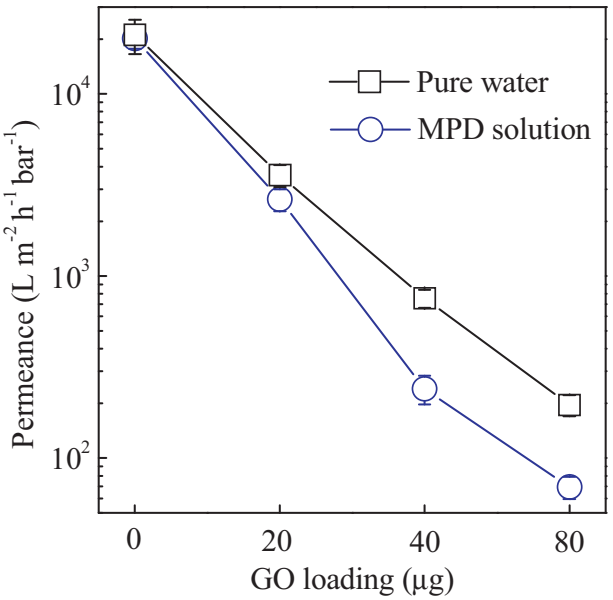


Fig. 2. Permeance of pure water and MPD solution through the GO membranes with different loadings.

applications and for fabricating the separation membranes with excellent chemical stability and large permeance [14–20]. There are two main separation mechanisms of graphene-based membranes, separation by interlayered nanochannels and by transport through defects and pores. For mono-layered and few-layered graphene-based membranes, the artificial pores in graphene or intrinsic defects of GO and rGO are main molecular transport nanochannels. The pore size of defects determines the permselectivity for various molecules [21–27]. The single-layered graphene with subnanometer-sized pores created by oxygen plasma etching can reject salts totally [21]. However, controlling of the pores and scaling up of those membranes are extremely untoward. Meanwhile, the mechanical strength of those membranes is relatively poor. In stacked graphene-based membranes, usually including GO and rGO membranes, with thickness from tens of nanometers to several micrometers, the interlayered spacing between nanosheets are main nanochannels for molecular transport and separation [28–31]. Definitely, the intrinsic defects of GO and rGO sheets also provide transport nanochannels when the membrane thickness is nanometer-sized [32]. Water crowding can prop open the transport nanochannels to approximately 10 Å, hence the stacked graphene-based membranes are usually employed for loose nanofiltration rather than RO desalination [32–36]. Various methods have been proposed to adjust the nanochannels of stacked graphene-based membranes [37–43], but the application of graphene-based membranes in RO for salt rejection remains a great challenge.

Herein, we report a strategy, confined interfacial polymerization, for obtaining PA-GO membranes with excellent performance in RO desalination (Fig. 1). By filtration of MPD solution through ultrathin GO membranes, the negatively charged GO with oxygen-containing groups adsorbs MPD molecules. Then confined interfacial polymerization between MPD and TMC at void regions is carried out to refine the size of transport nanochannels. The PA-GO membranes thus prepared have thickness smaller than 30 nm and exhibit impressive NaCl rejection and permeance. Moreover, the prepared PA-GO membranes also show superior chemical stability in chlorine exposure, good antifouling property to bio-pollutants and long-term stability.

2. Experimental

2.1. Materials

The natural graphite flakes with size of 500 meshes were purchased from XFnano chemical Co., Ltd., China. $KMnO_4$, $NaNO_3$, meta-phenylene diamine (MPD), trimesoyl chloride (TMC), n-hexane, bovine serum albumin (BSA), sodium hypochlorite and other reagents used in this work were purchased from Kutai Chemical Reagent Co., China. Polysulfone ultrafiltration membrane with molecular weight cutoff of 50 kDa and mixed cellulose ester membrane with pore size of 0.22 μm were obtained from Liangwen Chemical Reagent Co., China. The reagents were used without further purification.

2.2. Synthesis of graphite oxide

Natural graphite flake (2.0 g) and $NaNO_3$ (1.0 g) were added gradually into concentrated H_2SO_4 (46 mL) with ice bath. $KMnO_4$ (6.0 g) was added slowly to the above suspension. In this process, the temperature was controlled below 20 °C. After reaction for 2 h in ice bath, the temperature of suspension was increased to 35 °C, and maintained for 1 h. Water (96 mL) was added into suspension slowly, and the temperature of suspension was increased to 98 °C and kept for 40 min. The prepared suspension was treated by 30% H_2O_2 solution. Ultimately, the product was washed by diluted HCl solution, collected and dried.