Carbon 136 (2018) 28–37

Contents lists available at ScienceDirect

Carbon

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

Cross-linking modification with diamine monomers to enhance desalination performance of graphene oxide membranes

Yunlong Qian [a, b], Chen Zhou [b], Aisheng Huang [a, *]

[a] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Dongchuan Road 500, Shanghai 200241, China
[b] Institute of New Energy Technology, Ningbo Institute of Materials Technology and Engineering, CAS, 1219 Zhongguan Road, 315201 Ningbo, China

ARTICLE INFO

Article history:
Received 14 November 2017
Received in revised form
11 April 2018
Accepted 21 April 2018
Available online 24 April 2018

Keywords:
Graphene oxide composite membranes (GOCMs)
Diamine molecule
Covalent modification
Cross-linking
Seawater desalination

ABSTRACT

Two kinds of diamine molecules, including 1, 4-cyclohyxanediamine (CDA) and *p*-phenylenediamine (pPDA), were used as cross-linking for modification of graphene oxide (GO) nanosheets to prepare three-dimensional graphene oxide framework (GOF). Thereafter, graphene oxide composite membranes (GOCMs) were prepared on the polydopamine (PDA) modified α-Al_2O_3 tubes via vacuum filtration of GOF suspension. The separation performance of the GOCMs was tested for seawater desalination by pervaporation. The cross-linking modification, membrane thickness, operation temperature, feed concentration and PDA modification of α-Al_2O_3 tube have great effect on the separation performance of the GOCMs. Attributing to the enhancement of d-spacing and surface hydrophilicity after CDA modification, the CDA-based GOCM (CDA-GOCM) shows a higher water flux (20.1 kg m^{-2} h^{-1} with ion rejection of 99.9%) for desalination of 3.5 wt% seawater at 90 °C, which is higher than that of GO membrane (11.4 kg m^{-2} h^{-1} with ion rejection of 99.9%). However, since the hydrophilicity of the GO markedly decreases after pPDA modification, the pPDA-based GOCM (pPDA-GOCM) show a lower water flux (10.7 kg m^{-2} h^{-1} with ion rejection of 99.8%) at 90 °C. Further, the CDA-GOCM prepared on the PDA-modified α-Al_2O_3 tubes displays high stability for desalination of 3.5 wt% seawater.

1. Introduction

With rapid development of modern industry, population explosion and water pollution, the shortage of freshwater resource has increasingly become a globe issue [1,2]. Seawater desalination has attracted great interest to solve the water crisis since it is expected to provide an unlimited and steady supply of freshwater. Membrane separation is one of the most promising alternative for seawater desalination due to its low energy consumption [3]. In the past years, many membrane separation methods such as reverse osmosis (RO) [4] and electrodialysis (ED) [5] were developed mainly for desalination to obtain drinking water [6]. Meanwhile, membrane distillation (MD) [7], pressure retarded osmosis (PRO) [8,9] and reverse electrodialysis (RED) [10] have emerged, due to recent developments and progresses in membrane technology. Among these separation process, RO have been widely studied in commercial applications [11]. However, a rather high operation pressure (P-based) is needed to provide during the separation process (approximately above 50 bars) [12]. In MD, high temperature (T-based) is essential for the formation of the vapors at the side by heat, and the transportation through the hydrophobic membrane and condensation on the other side [13]. Pervaporation (PV) is a processing method for the separation of liquids mixtures by partial vaporization through a porous membrane through vacuum driving, which has been widely applied for dehydration of bio-alcohols due to its low energy consumption and ease of operation [14–16]. Recently, pervaporation also shows promising and effective for seawater desalination [17–21]. So far, the present membranes used for seawater desalination are mainly polymeric composite membranes, but they are usually low stability due to biofouling, oxidation, abrasion and mineral scaling, thus usually resulting in low rejection and low stability. Therefore, it is highly desired to develop novel membranes with high stability and high separation performance for seawater desalination [17,18,20,22,23].

In the last years, as a monoatomic layer material reported by Geim and Novoselov in 2004, graphene has attracted great interest in water desalination and purification due to their high chemical stability, high tensile strength and multi-functional surface

* Corresponding author.
E-mail address: huangash@chem.ecnu.edu.cn (A. Huang).

https://doi.org/10.1016/j.carbon.2018.04.062
0008-6223/

chemistry [24,25]. As a derivative of graphene, graphene oxide (GO) exhibits similar properties to graphene containing oxygen-rich functional groups like hydroxyl, epoxy groups. Therefore, GO has attracted intense interest to fabricate two-dimensional GO membrane for gas or liquid separation [26–28]. Especially, because of the preferential water adsorption ability and fast water diffusivity as well as narrow spacing between GO nanosheets, it can be expected that the GO membranes can show excellent separation performance in seawater desalination. Indeed, because the effective pore size of GO (0.3 nm) [24] is just between the size of water molecules (0.26 nm) and hydrated ions (e.g. Na^+ 0.72 nm, K^+ 0.66 nm, Ca^{2+} 0.82 nm, Mg^{2+} 0.86 nm, Cl^- 0.66 nm), GO membranes have displayed high salt rejections in seawater desalination [19,29,30].

However, as reported previously [31], even for a submicrometer thick GO membrane, it was almost impermeable to liquids, vapors and gases. In order to increase the permeance of GO membranes, besides the development of ultrathin (nm-sized) GO membranes [32], an alternative road is to enlarge its spacing size between GO nanosheets through inserting nanoparticles or cross-linking modification of GO nanosheets [33–36]. Since there are plenty of oxygen-containing functional groups in the GO framework: hydroxyl and carboxyl groups are located around the edges, whereas carbonyl and epoxide groups are in the center [37–39], GO can be easily intercalated or cross-linked with aliphatic amines, amino acids, diaminoalkanes, aromatic amines [35,40,41], isocyanates [42,43], and acyl chloride [44], forming three dimensional graphene oxide-framework (GOF). Therefore, on one hand, the flexibility and hydrophilicity of GO membrane can be improved; on the other hand, the interlayer spacing of GO can be expanded and thus increasing the performance of GO membranes.

In the present work, based on chemical grafting of amine to the GO via acylation reactions and nucleophilic addition reactions where amines react with carboxyl groups and epoxy groups [18,37], diamine molecules, including 1, 4-cyclohyxanediamine (CDA) and *p*-phenylenediamine (pPDA), are firstly used as cross-linking for covalent modification of GO nanosheets to prepare GOF. And then, micron-thickness graphene oxide composite membranes (GOCMs) are prepared on the polydopamine (PDA) modified α-Al_2O_3 tubes via vacuum filtration of GOF suspension (Fig. 1). The effect of cross-linking modification, membrane thickness, operation temperature, feed concentration and PDA modification of α-Al_2O_3 tubes on the desalination performance of the developed GOCMs were investigated.

2. Experimental

2.1. Materials

All reagents were used as received without further purification: concentrated sulfuric acid (H_2SO_4, AR, 98%), sodium nitrate ($NaNO_3$, AR, 99%), hydrogen peroxide (H_2O_2, AR, 30 wt%), *p*-phenylenediamine (pPDA, AR, 99.9%) and potassium permanganate ($KMnO_4$, AR, 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); Graphite powder (G; 2000 mesh) and 1, 4-cyclohyxanediamine (CDA, AR, 99%) were supported by Macklin Co., Ltd. (Shanghai, China); Dopamine hydrochloride (DPA-HCl, 99%) was gotten from sigma; Tris (hydroxymethyl) aminomethane (Tris, 99.9%) was obtained from Aladdin; Sea salt (Zhejiang blue starfish salt product Co., Ltd., China) was used for preparation of sea water; Deionized (DI) water (18.4 MΩ cm at 25 °C) was provided by a water purification machine (UPT-II-10T, Ulupure, China); Porous α-Al_2O_3 supports (12 mm outside diameter, 9 mm inside diameter, 75 mm length, ca. 1.0 μm pore size, 30% porosity, Jiexi Lishun Technology Co. Guangdong, China) were used as supports.

2.2. Preparation of GO and diamine modified GO nanosheets

GO aqueous suspension was prepared by the modified Hummers method [45] using flake graphite powder as a starting material according to the procedure described elsewhere [18]. The resulting GO aqueous dispersion was sonicated for 30 min followed

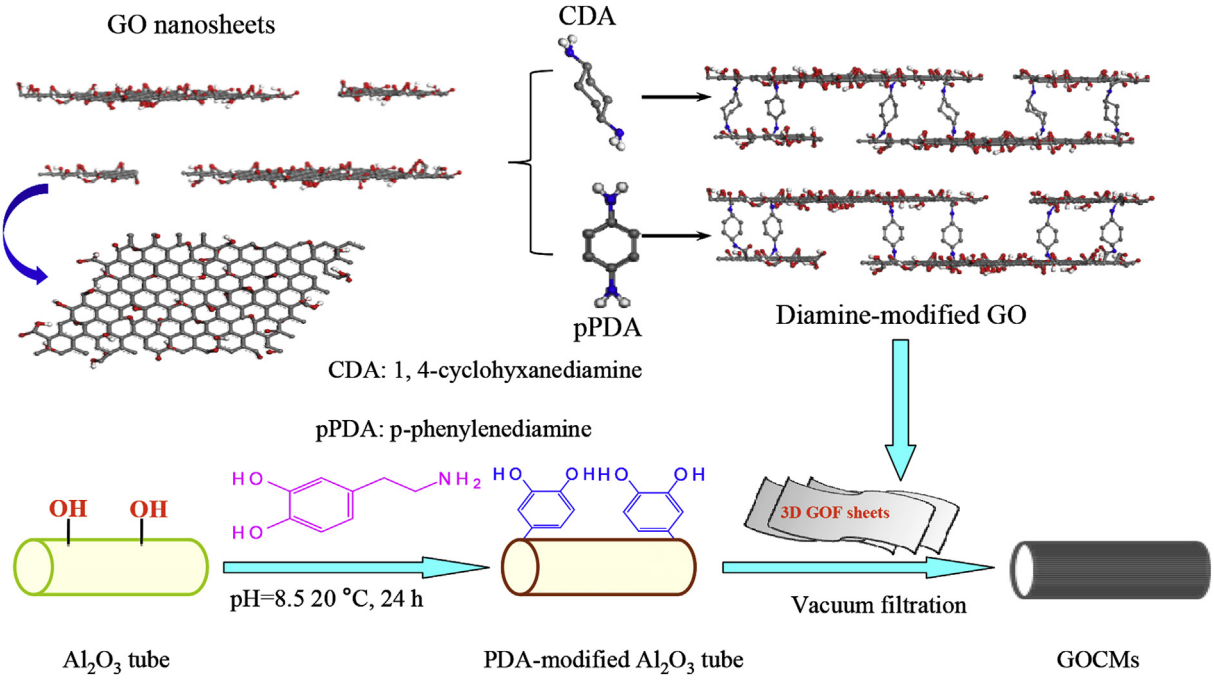

Fig. 1. Scheme of the synthesis of graphene oxide composite membranes (GOCMs) through vacuum filtration of diamine-modified GO suspension on polydopamine (PDA) functionalized α-Al_2O_3 tubes. (A colour version of this figure can be viewed online.)