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Layer-by-layer assembly of graphene oxide membranes via electrostatic interaction

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ABSTRACT

We fabricated a novel type of water purification membrane by layer-by-layer assembling negatively charged graphene oxide (GO) nanosheets on a porous poly(acrylonitrile) support and interconnecting them with positively charged poly(allylamine hydrochloride) (PAH) via electrostatic interaction. A series of characterization techniques were used to confirm the successful assembly of multiple GO–PAH bilayers, quantify their composition and thickness, and understand the structure of the GO membrane. Quartz crystal microbalance-dissipation (QCM-D) results showed that each GO–PAH bilayer in the membrane is around 16.5 nm thick and dominated by GO (mass of GO is 2–5 times higher than that of PAH), indicating multiple layers of GO nanosheets exist in each bilayer. This is most likely because the mass-to-charge ratio of GO is much higher than that of PAH. Transport of water and selected solutes in the GO membrane was investigated in a pressurized system and also in a forward osmosis (FO) and pressure retarded osmosis (PRO) system. Water permeability of the GO membrane was found to be about one order of magnitude higher than that of a commercial FO membrane. The solute flux of the GO membrane for sucrose (as a representative uncharged species) was much lower than that for an ionic species, although the hydrated radius of the ions is comparable to that of sucrose. This is most likely because the GO–PAH bilayers tend to swell in ionic solutions. In solutions of low ionic strength, the GO membrane retained a tight structure and exhibited high rejection to sucrose (~99%), indicating an MWCO of around 342 or an equivalent pore size of around 1 nm. Therefore, at the present stage, the GO membrane can be well suited for applications such as FO-based emergency water purification using sugary draw solutions and water treatment not requiring high ionic strength.

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1. Introduction

As a sheet of carbon atoms arranged in a honeycomb lattice and decorated with oxygenated functional groups (i.e., carboxyl, hydroxyl, epoxy groups), graphene oxide (GO) can be mass-produced by oxidizing and exfoliating graphite [1] and has great potential as building blocks for the fabrication of inexpensive yet high-performance water purification membranes [2–6]. Compared with traditional membrane materials such as polyamide, this two-dimensional (2D) material promisingly offers a number of significant benefits in facilitating the fabrication process and improving the physicochemical properties of membranes. In particular, the unique 2D structure of GO makes it ideal for creating a new class of membrane by stacking GO nanosheets via a layer-by-layer (LbL) assembly technique, which is relatively cost-effective and environmentally friendly because all fabrication steps can be performed in

aqueous solutions while traditional membrane synthesis procedures (e.g., interfacial polymerization) often involve complex chemical reactions and use organic solvents.

Unlike traditional membranes that separate unwanted substances from feed water as water passes through the pores within the membrane active layer, a GO membrane relies on the nano-sized interlayer spaces to filtrate water as it zigzags within the layered GO film deposited on a support substrate. The long slip length caused by the capillary effect makes it possible for water to flow nearly without any friction [4,7], a very desired material property for making high-flux membranes. Recently it has been experimentally shown that a GO membrane can outperform commercial nanofiltration (NF) membranes in terms of water flux (an order of magnitude higher) while demonstrating at least the same level of solute rejection [3]. Besides, it is worth emphasizing that stacking of 2D nanosheets offers a unique opportunity to very flexibly optimize various membrane properties during, as opposed to after, membrane fabrication. For example, membrane selectivity can be tuned by manipulating the spacing between GO nanosheets, membrane antifouling properties can be enhanced by adjusting the

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functional groups and charges on GO nanosheets, and membrane regenerability can be realized via reversible binding interactions between GO nanosheets.

Membrane integrity must be ensured in order for a GO membrane to be practically useful for water-solute separation. So far, most layered GO membranes have been fabricated via a simple solution-filtration process [4,8,9] and hence are highly susceptible to dispersion in an aqueous environment due to the extreme hydrophilicity of GO nanosheets. To resolve this issue, neighboring GO layers need be bonded firmly to each other and so does the outermost layer to the support substrate. There exist different bonding strategies for making a stable GO membrane [10]. One strategy is to establish covalent bonding between GO layers by using appropriate cross-linkers such as trimesoyl chloride (TMC) [3]. Another promising strategy is to bond stacked GO nanosheets through electrostatic interaction. Because GO nanosheets are negatively charged due to the ionization of carboxylate groups in water [11,12], they can act as polyanions and electrostatically bind to positively charged polyelectrolytes such as poly(allylamine hydrochloride) (PAH) [13,14]. Note that although the binding forces between assembled polyelectrolyte layers are mainly contributed by electrostatic interaction, hydrophobic interaction and hydrogen bonding may also be involved but to a lesser extent [15]. Compared with covalent bonding, electrostatic bonding may lead to GO membrane fabrication that advantageously features simpler reaction, more flexible control of chemistry, less usage of organic solvent, and reduction of by-products. In fact, the LbL technique has proven very useful for assembling oppositely charged polyelectrolytes to form thin films or coatings for membranes used in pervaporation [16,17], NF [18–22], solvent resistant NF [23], reverse osmosis [18,24], and forward osmosis (FO) [19,25–28]. An added benefit is that an electrostatically bonded GO membrane is potentially regenerable, that is, existing GO layers on the membrane can be released by varying solution chemistry to, for example, extremely high pH and/or surfactant concentrations, thereby enabling the deposition of fresh GO layers to regain membrane functionality.

In the present study, we explored the potential use of layered GO membrane in FO and pressure retarded osmosis (PRO) processes. As an energy-inexpensive alternative to the conventional pressure-driven membrane processes, the FO/PRO membrane technology has experienced an accelerated development over the past decade [29–32]. In contrast to other types of water purification membranes, FO/PRO membranes must have a relatively thin, hydrophilic support in order to reduce internal concentration polarization (ICP), which is caused by the hindered solute transport within the support layer and can significantly reduce membrane flux and aggravate membrane fouling. To date, the existing commercial FO/PRO membranes can be categorized into cellulose-based membranes and thin-film composite (TFC) membranes. Synthesized via phase separation, cellulose-based membranes have excellent antifouling properties but exhibit relatively low water flux and high salt passage and only work within a narrow pH range [33–35]. In comparison, TFC membranes show excellent salt rejection at the cost of low pure water flux due to the ICP effect of the thick, dense membrane support [33,36]. Therefore, development of high-performance FO/PRO membranes has been a major task in the journey of achieving the full benefit of such a sustainable technology [31,33].

Herein we propose to electrostatically bond layered GO nanosheets to form a stable GO membrane and test its suitability for FO/PRO processes. Briefly speaking, the LbL technique was employed to assemble oppositely charged GO and PAH layers on both sides of a charged support substrate in order to minimize internal concentration polarization. The GO membrane was then characterized using a series of techniques to confirm the

successful assembly of multiple GO–PAH bilayers, quantify their composition and thickness, and understand the structure and charge properties of the GO membrane. Next, we tested the GO membrane in cross-flow pressurized and also in FO/PRO membrane systems in order to characterize the transport of water and solutes within the GO membrane, using a commercially available FO membrane as a baseline.

2. Materials and methods

2.1. Membrane support preparation

The membrane support substrate was made of polyacrylonitrile (PAN) through phase inversion and partial hydrolysis. First, a PAN solution was prepared by dissolving 18 g PAN ($M_w \approx 150,000$) and 2 g LiCl in 80 g *N,N*-dimethylformamide (DMF) ($\geq 99.8\%$) at 60 °C. All the chemicals were obtained from Sigma-Aldrich (St. Louis, MO). After cooling to room temperature, the PAN solution was stored overnight in a vacuum desiccator. Next, the PAN solution was cast on a clean glass plate using an aluminum casting rod with a gate height of 125 μm . Then, the glass plate along with the cast PAN film was immediately soaked in a DI water bath for 10 min, during which phase inversion took place to form the PAN support, which finally underwent partial hydrolysis in 1.5 M NaOH for 1.5 h at 45 °C [17,26] and was thoroughly rinsed with DI water.

2.2. GO membrane fabrication

The GO membrane was synthesized via the LbL assembly of GO and PAH on the hydrolyzed PAN (hPAN) support substrate. The GO solution (1 g/L, pH 4) was prepared in our lab using the modified Hummers method [37,38], with the detailed procedure described in a previous study [3]. The PAH solution was prepared by dissolving 1 g/L PAH in DI water and the pH was adjusted from 4.6 to 4 using HCl and NaOH solutions. To fabricate the layered GO membrane, a typical assembly cycle involved soaking the hPAN support in the PAH solution for 30 min and then in the GO solution for another 30 min, thereby adding one GO–PAH bilayer onto each side of the hPAN support. Repeating a prescribed number of such soaking cycles led to a GO membrane with a desired number of GO–PAH bilayers on each side of the hPAN support. The GO membrane was thoroughly rinsed with DI water between successive soaking treatments.

2.3. Characterization of membrane properties

The hPAN membrane support with or without assembled GO–PAH bilayers was characterized by Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700, Thermo Scientific, Marietta, OH) and scanning electron microscopy (SEM) (SU-70, Hitachi High Technologies America, Gaithersburg, MD). Their elemental compositions were analyzed using X-ray photoelectron spectroscopy (XPS) (Kratos AXIS 165, Kratos Analytical, Spring Valley, NY).

2.4. Quantification of LbL assembly

Quartz crystal microbalance with dissipation (QCM-D) (E-4, Biolin Scientific, Linthicum Heights, MD) was used to monitor the process of assembling GO–PAH bilayers on an hPAN film. A QCM-D gold sensor (14 mm in diameter) was coated with a PAN film, hydrolyzed in 1.5 M NaOH solution, and mounted in a QCM-D chamber. The sensor was successively exposed to PAH (1 g/L, pH 4) and GO (1 g/L, pH 4) solutions to mimic the LbL assembly of a GO membrane. The mass of GO or PAH deposited on a sensor was quantified by monitoring and then model-fitting the changes in

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