Graphene oxide modified polyamide reverse osmosis membranes with enhanced chlorine resistance

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ABSTRACT

Improving chlorine resistance of polyamide (PA) reverse osmosis membranes is one of the major challenges in reverse osmosis membrane technology. In this study, few-layered graphene oxide (GO) was assembled onto polyamide thin film composite membrane surfaces through a spin-coating method to address this challenge. The coating solutions were used at different pH values and with different dispersion solvents. It was found that the pH values have great effects on membrane performance including maximizing water flux at a pH value of 6–7. XPS results indicate that the GO layer can protect the PA functional layer by absorbing chlorine radicals to form O−Cl bond. All modified membranes demonstrate a good suppression of membrane degradation in salt rejection upon chlorine exposure, and the degree of resistance to chlorine was enhanced with the increase of the number of GO layers. The GO_1-coated membrane with GO nanosheets dispersed in ethanol showed increased water flux and good chlorine resistance. For instance, salt rejection varied from 95.3% to 91.6% for the first two hours, while unmodified membrane dropped to 80%. After 16 h of chlorine exposure, measured salt rejection of GO_1-coated membrane was 75% but unmodified membrane was a less effective 63%.

1. Introduction

Since graphene was first prepared by Geim and Novoselov et al. in 2004, its unique physical and chemical properties made it immediately become a hot research topic for various fields of study [1,2]. In comparison to graphene, graphene oxide (GO) contains functional groups, and thereby can be well-dispersed in aqueous solution. Moreover, GO nanosheets have good film-forming properties for many methods, such as vacuum filtration, dip-coating, spin-coating and layer by layer self-assembly [3–5]. Remarkably, tunable nanochannels within lamellar GO membranes offer a much more straightforward approach to control the passages for molecules and ions [6], which leads to lots of promising applications in preparation of large flux film, membrane modification, water treatment, gas separation and desalination [7–9].

Polyamide (PA) reverse osmosis membranes are widely used in such fields as sea water desalination, brackish water desalination, and water purification [10]. As we know, these processes normally use chlorine or bleaching powder for sterilization which cause the degradation of amide bond. This results in membrane failing in salt rejection upon chlorine exposure and shortens the membrane service life. Poor chlorine resistance is the biggest hurdle for PA reverse osmosis membranes, and its research seems meaningful.

To date, there has been much progress made in improving the chlorine resistance of PA reverse osmosis membranes. Main methods include synthesizing surface coating protective layers, chemical grafting, and development of new materials [11], such as chemical grafting between membrane surfaces and GO [12–14]. However, a simple and low-cost physical coating method has not been reported for GO-modified reverse osmosis membranes. Spin-coating method was reported as one of physical coating methods in preparing GO membranes for applications in water treatments and solar cells. To our knowledge, GO layers coated on PA reverse osmosis membrane surface by spin-coating method have not been well investigated. Synthesizing surface coating protective layers is considered the most valuable one because of its simple process. However, this technique increases permeation resistance to an undesired reduction in water flux, following typical trade-off relation between performance and durability. Hence, improving chlorine resistance together with increased water flux and salt rejection will be highly desirable for the coating strategy.

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Most chlorine resistance modified materials of PA membrane usually utilize macromolecules or polymers [15–17]. Also, nanomaterials such as zeolite, TiO$_2$, carbon nanotubes, and graphene/TiO$_2$ have been reported as membrane modified materials [18–20]. Carbon nanotubes and graphene can improve the chlorine resistance of membranes: Park et al. [21] added carbon nanotubes into water phase of interfacial polymerization modification and prepared modified membranes. After 4 h of exposure to 6 mg/mL NaClO solution, salt rejection of unmodified membrane fell from 98.3% to 76.5%, while modified membrane dropped from 92.5% to 82.4%. Kim et al. [22] discovered that GO can more effectively improve the resistance to chlorine in comparison to carbon nanotubes. Moreover, PA membranes whose polyamide functional layer mingled with carbon nanotubes and GO show optimal chlorine resistance with 0.02 wt% doping content, and the flux can extend from 5000 mg/(L h) to 15,000 mg/(L h); meanwhile, they indicated that this kind of carbon nanostructure played a role as a potential efficient antioxidant due to the capacity of phenolic hydroxyl which can capture hydroxyl radicals [23–25]. Choi et al. [26] deposited positively charged aminated-GO (AGO) and negatively charged GO onto PA membrane surface by opposite electrostatic adherence, and the l0-layered modified membrane possessed good chlorine resistance without flux decline.

In this study, few-layered GO was assembled to polyamide thin film composite (PA-TFC) membrane surface serving as a protective layer to improve membrane chlorine resistance. Specifically, GO layers were deposited on the membrane surface through a spin-coating method as it is simple and more likely to form relatively thin GO coating. Effects of different solvents and pH values of the coating solution on water flux and salt rejection were initially investigated. Then, the chlorine resistance of pristine and GO modified membranes was examined by comparing their performance before and after chlorination. X-ray photoelectron spectroscopy (XPS) was used to obtain the information about composition and bonding chemistry for the surface layer and the results indicate that the GO layer can protect PA functional layer by absorbing chlorine radicals to form O–Cl. All GO-modified membranes showed good chlorine resistance in suppressing the degradation of salt rejection upon chlorine exposure compared to pristine PA membrane. Moreover, GO$_1$-coated PA membrane with GO nanosheets dispersed in 70% ethanol water solution presented optimal performance comprehensively considering membrane performances and chlorine resistance. The process shows an improved water flux and excellent chlorine resistance without salt rejection declination. In the first two hours, salt rejection of GO$_1$-coated membrane varied from 95.3% to 91.6%, while pristine membrane dropped to about 80%. After 16 h of exposure, salt rejection of GO$_1$-coated PA membrane was 75% but pristine membrane was only about 63%. This demonstrates the important influence of pH values on membrane performance, and under the condition of the pH value being 6–7, the flux reached its maximum value.

2. Experimental

2.1. Materials

The chemicals were used as follows: GO powder (G139803, Aladdin Corp. The powder was prepared by the improved Hummers method, and the oxidization degree was 56.2% obtained by the XPS test, as shown in Fig. S1 in Supplementary Information), sodium chloride (NaCl, Aladdin), sodium hypochlorite (NaOCl, 10% aq., Aladdin), sodium hydroxide (NaOH, Aladdin), ethanol (> 95%, Aladdin), deionized (DI) water, PA-TFC membrane (LCLE-4040, Dow Corp), and carbon membrane support (Beijing Xinxing Brain Technology Co).

2.2. Surface modification of PA-TFC membrane with GO layer

GO layers were coated onto selective surface of PA-TFC membrane through a spin-coating method. The PA-TFC membrane used was LCLE-4040 reverse osmosis membrane purchased from Dow Corp. Firstly, the preparation of GO water dispersion: GO powder was added in water and sonicated for 1 h to form a homogenous solution. Next, for the preparation of GO ethanol water dispersion, GO water dispersion was used to confect GO ethanol/water dispersion with GO concentration of 0.075 mg/mL. The proportion of water to ethanol was adjustable until the solution appeared obviously turbid. Two different solvents, water and 70% ethanol in water, with 0.075 mg/mL GO were used as coating solutions. Prior to the coating process, we proceeded to clean PA-TFC membranes in water at a pH value of 11, and then spin coated the solution at 60 °C onto the membrane with a speed of 600 rpm [27,28]. The first layered membrane was naturally dried before next coating. At last, after a few coating processes, few-layered GO nanosheets on PA-TFC membrane were prepared.

2.3. Characterization of GO nanosheets and membranes

The morphology and dimension of GO nanosheets were observed using transmission electron microscope (TEM, JEM-1011, JEOL). Chemical structures were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet iN10, Thermo). Surface morphologies of the membrane were examined by scanning electron microscopy (SEM, HItachi-s-4800) and atomic force microscopy (AFM, Multimode 8, Bruker). Water contact angles were measured with a goniometer (3250-DS3210, Kruss Instrument, Germany).

2.4. X-ray photoelectron spectroscopy (XPS)

XPS (Escalab 250Xi) was used to obtain the information about composition and bonding chemistry for the surface layer. The membrane after chlorination was tested by XPS, and the difference of the bonding chemistry between pristine PA and GO-coated PA can help to explain the good chlorine resistance of the GO-coated PA membrane. XPS full-scan spectra were recorded within the range from 0 to 1400 eV with 1 eV resolution with a monochromatic aluminum Kα X-ray source at 1486.7 eV.

2.5. Membrane performance tests

Water flux and salt rejection were tested with 1 mg/mL NaCl aqueous solution in a cross flow system under an operating pressure of 1.5 MPa at room temperature. Water flux (F) can be calculated by F=V/At, where F, V, A, and t respectively represent permeation rate (L/m^{2}h), the volume of water permeation, effective membrane area (m^2), and operation time (h). Salt rejection (R) was calculated by the following equation: R (%)=100×(1−C$_p$/C$_f$), where C$_p$ and C$_f$ were the salt concentrations of permeate and feed side NaCl solution, measured by a conductivity meter (LF39, Sensortechnik Meinsberg).

2.6. Membrane chlorine stability tests

Membrane chlorine stability was characterized by variation of water flux and salt rejection before and after chlorine, especially salt rejection. If there is smaller declination in the salt rejection after chlorine, it indicates that the membrane has better chlorine resistance. Therefore, it is necessary to measure water flux and salt rejection before chlorine exposure as control data. A commercial sodium hypochlorite solution (10% NaOCl aq.) was diluted in DI water to make the chlorine solution with a concentration of 6 mg/mL and