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Tailoring permeation channels of graphene oxide membranes for precise ion separation

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ABSTRACT

The design and tailoring of membrane permeation channels is crucial for precise separation of ions or molecules. Herein, a method for tuning the permeation channels of graphene oxide (GO) membranes is developed, in which the basal planes and edges of GO flakes are simultaneously crosslinked by dicarboxylic acid and diamine. By altering the chain length of the crosslinkers, the size, structure and properties of the permeation channels are successfully tuned. In the permeation of single metal salt solution, the fluxes of metal ions are related to the swelling degree of GO membranes. In the separation of mixed salt solutions, the fluxes are determined by the radii of hydrated cations, and the crosslinked GO membranes display outstanding size-selectivity. This is the first report about the distinct orders of permeation fluxes of single salt solution and mixed salt solution. With the increasing hydrophobicity of diamines, the permeation fluxes of aqueous solution decrease. The optimized crosslinked GO membranes display excellent fluxes and separation factor, which are more than 2 times and 3 times that of the pristine membranes, respectively. The elastic modulus of the crosslinked GO membranes is double that of the pristine one, and the swelling degree in water is 75 times lower.

1. Introduction

Materials with nanopores and nanochannels such as carbon nanotubes [1,2], nanoporous graphene [3], graphene oxide (GO) [4,5], have attracted significant research interest in recent years due to their potential applications in separation [6]. GO, one of the most important derivatives of graphene, contains hydroxyl and epoxy functional groups on the basal planes, along with carbonyl and carboxyl groups at the flake edges [7]. GO can be exfoliated into aqueous colloidal suspensions of flakes and then assembled into free-standing membranes, thin films or paper-like materials by means of drop-casting, spin-coating [8], vacuum or pressure driven filtration [9], gas–liquid interfacial self-assembly [10], L–B [11], *etc.* Water permeation is expected to proceed through the whole interlayer space including oxidized areas which occupy a major part of the graphene oxide surface [12] and the nonoxidized regions [13,14]. This endows the GO membranes excellent performance in water purification [15,16], liquid pervaporation [17,18] and fuel cells [19].

Although single layered GO flake exhibits outstanding mechanical strength, the weak interaction between GO flakes results in unsatisfactory mechanical performance of GO membranes [20]. The hydrophilic functional groups also lead to unstability and easily damage of GO membranes especially in aqueous solutions [21]. The integral mechanical strength of GO membranes is considered as the critical challenge for the practical separation. To solve these problems, chemical crosslinking of GO membranes with metal ions [22], borate [23], dopamine [24], amino acids, acyl chloride, isocyanates, dicarboxylic acids, diols, polyols [25], silsesquioxane [26], polyallylamine [27], polyetheramine [28], etc., has been reported to produce membranes with improved mechanical properties and stability [29]. Apparently, the molecular structure of the crosslinkers determines the reaction locations (basal planes and/or edges of GO flakes), structure and properties (hydrophilicity, charges, coordination capability, etc.) of GO membranes. Nevertheless, to our best knowledge, there are few reports related to the design and tailoring of micro-structure of GO membranes. Crosslinking both of the basal planes and edges of GO flakes is also seldom addressed. Moreover, the GO membranes are usually applied in the dialysis of single salt solution [30] while the application in the separation of mixed salts solutions is very limited.

Herein, we employed dicarboxylic acids and diamines

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successively to bond both of the basal planes and edges of GO flakes. By adjusting the molecular structure of diamines and dicarboxylic acids, the size, structure and properties of permeation channels are tuned, giving rise to the adjustable permeation, hydrophilicity, mechanical strength and stability of GO membranes. This is critical for precise separation of ions or molecules in practice [31,32]. The permeation performance of GO membranes were conducted in the single salt solution and mixed salts solution (KCl, NaCl, $MgCl_2$ and $NiCl_2$), and distinct orders of permeation fluxes in the two cases were observed for the first time.

2. Experimental

2.1. Materials

H_2SO_4 (>98.0%), H_2O_2 (30%), hydrochloric acid, $KMnO_4$, $NaNO_3$, propandioic acid (PA), hexanedioic acid (HA), ethylene diamine (EDA), propylene diamine (PDA), butanediamine (BDA), hexamethylene diamine (HMDA), *p*-phenylenediamine (PPD), or *o*-phenylenediamine (OPD), KCl, NaCl, $MgCl_2$ and $NiCl_2$. The above chemicals were analytical grade and provided by Beijing Chemical Factory.

2.2. Preparation of GO

GO was prepared by the modified Hummers' method [34,35]. 5 g of graphite was added gradually into 115 mL of H_2SO_4 (containing 2.5 g of $NaNO_3$) and kept below 278 K. Then, 15 g of $KMnO_4$ was added into the mixture under stirring and cooling. After further stirred at 308 K for a certain time, DI water was added, and the temperature was elevated to 371 K. Then DI water and 30% H_2O_2 were added and the color of the mixture changed to bright yellow. The product was washed with hydrochloric acid and DI water until neutral. Exfoliation of graphite oxide in water was achieved by ultrasonic dispersion.

2.3. Fabrication of GO membrane

1.0 mL of 0.1 mol L^{-1} dicarboxylic acid solution was mixed with 4.0 mL of GO aqueous colloidal suspension (7.56 mg mL^{-1}) under ultrasonication, followed by filtration with a PP microfiltration membrane (0.45 μm) to obtain interlocked GO membrane. The esterification reaction was catalyzed by hydrochloric acid (6.0 mol L^{-1}) at 353 k. Then, 1.0 mL of diamine solution was filtrated. As high reaction temperature may result in complete amidation and low permeability [33], we heated the membranes at a relatively lower temperature (353 K) for 30 min in the presence of catalytic hydrochloric acid to form amide partially. After washing with DI water, the crosslinked GO membrane was dried at room temperature.

2.4. Characterization

The FT-IR spectra of GO membranes were determined with a FT-IR spectrometer (Nicolet 380, USA). X-ray photoelectron spectroscopy was analyzed with Thermofisher ESCaLab 250Xi spectrometer. The membrane morphology was observed by scanned electron microscopy (SEM S-4800, Japan) after sputtered with platinum. The XRD patterns of GO membranes (kept in a desiccator overnight to achieve the similar humidity) were measured using Shimadzu XRD-6000 (Cu Kα). The mechanical properties were tested with a universal mechanical testing machine (INSTRON-3366, USA) at stretching speed of 100%/min. In the measurement of swelling degree, the dried membrane is soaked in DI water at room temperature for 3 h. Then the membrane was taken out and the surface water was wiped off with filter paper, and the membrane was weighted immediately. The swelling degree (SD) was calculated as follows,

$$SD = \frac{W_s - W_d}{W_d} \times 100\% \qquad (1)$$

where W_d is the weight of dried membrane and W_s represents the weight of swollen membrane.

Ion penetration experiments were carried out with a homemade U-shaped tube. The feed side contained a single salt solution (0.10 mol L^{-1} of NaCl, KCl, $MgCl_2$ or $NiCl_2$) or mixed salts aqueous solutions (NaCl, KCl, $MgCl_2$ and $NiCl_2$, 0.10 mol L^{-1} for each salt). The permeate side contained DI water. The diameter of GO membrane (22.3 μm in thickness) was 13.0 mm. Both sides were vigorously stirred to promote mass-transfer. The cations concentration in the permeate side was measured by ICP-AES (iCAP 6000 Series, Thermo Scientific).

3. Results and discussion

3.1. Characterization of GO membranes

Fig. 1a and b shows the scanning electron microscope (SEM) images of the as-obtained GO membranes, which displays a wrinkled surface and stacked lamellar structure. In the FTIR spectra (Fig. S1), the broad band at 3214 cm^{-1} is attributed to O–H stretching vibrations. The peak at 1630 cm^{-1} is related to C=C vibration and 1720 cm^{-1} is assigned to carboxyl absorption [36]. The peak at 1380 cm^{-1} is the C–O vibration, and 1049 cm^{-1} is from the epoxy vibration [37]. After crosslinking by diamines, a peak at 1100 cm^{-1} ascribing to C–N stretching appears, and its intensities slowly decrease from EDA to PDA, BDA, HMDA, PPD and OPD.

A typical X-ray photoelectron spectra (XPS) of GO membranes were shown in Fig. S2. It can be seen that the N element appears after crosslinking with diamines (Fig. S2 a). In the curve fitting of C1s spectra, the binding energy of 284.8 eV is assigned to C=C/C–C, and 286.9 eV is ascribed to epoxy/C–OH (Fig. S2 b). The respective binding energy of 288.2 eV and 289.0 eV correspond to C=O and C(O)O [38,39]. After the crosslinking reaction with propandioic acid (PA), the intensity of C=O and C(O)O increases while that of C–OH reduces (Fig. S2 c). After further crosslinking reaction with PDA, a peak (287.5 eV) assigned to C–N appears while the intensity of 286.9 eV (epoxy) as well as 289.0 eV (C(O)O) declines (Fig. S2 d) because of the amidation and epoxy ring–opening reactions. Fig. 1c gives the micro-structure model of GO membranes, in which the dicarboxylic acids covalently bond the hydroxyl groups on the GO flake planes while the diamines react with the epoxy on the planes as well as the carboxyl groups at the edges.

Fig. S3 a gives the XRD patterns of GO membranes. For the pristine GO membrane, the diffraction peak ($2\theta = 11.9°$) indicates an interflake spacing of 7.40 Å. After crosslinked with the diamines, the diffraction peaks generally move to a lower angle, indicating the slight increment in the interflake spacing due to intercalation effects. For PA/EDA, PA/PDA, PA/BDA, PA/HMDA, PA/PPD and PA/OPD crosslinked membranes, the interflake spacing is 7.46 Å, 7.49 Å, 7.40 Å, 7.46 Å, 7.22 Å, 7.70 Å respectively. As the single-layer graphene is around 3.40 Å in thickness, the size of permeation channels are estimated to be in the range of 3.82–4.30 Å (Fig. S3 b).

3.2. Ion penetration through GO membranes

The ion penetration performance of GO membranes was evaluated with a U-shaped tube. The feed side contained 0.10 mol L^{-1} of single salt solution (KCl, NaCl, $MgCl_2$ or $NiCl_2$) or mixed salts