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Cross-linked graphene membrane for high-performance organics separation of emulsions

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ABSTRACT

Recently, graphene oxide (GO) membranes are highly attractive for their exceptional separation performance. However, their sieving characteristics limit GO membranes for some important applications where organics are preferred or organic solvents are employed. In this work, a novel cross-linked graphene (CG) membrane is fabricated through compressing and then reducing a cross-linked GO aerogel. It achieved high-performance of organics separation with high flux ($225 \, \mathrm{L \, m^{-2} \, h^{-1}}$) and purity ($> 99.98\%$) even in a cross-flow separation model, where water was intercepted. Deep insight revealed that both the converted surface wettability and the remaining channels in the CG membrane were crucial for the high-performance of organics separation. Beyond that, this CG membrane offers many advantages, such as facile preparation, self-supporting, structural stability and adaptation in harsh acidic/basic/high-temperature conditions, demonstrating its great potential for practical applications.

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1. Introduction

Graphene oxide (GO), a star nanomaterial in recent years [1–4], contains oxygenated functional groups on the unique two-dimensional and mono-atom thick graphene sheet, rendering it a good candidate for use in various fields, such as nanocomposites, energy-related materials, sensors, paper-like materials, field-effect transistors and biomedical applications [5–9]. Recently, GO membranes are highly attractive for their exceptional separation performance on treating gases, liquids and ions [10–21]. As a breakthrough, Geim's group found that water vapor can pass through a GO membrane as fast as no barrier, while some organic molecules are blocked [10]. Meanwhile, several studies have also demonstrated that GO membrane is an ideal pressure-driven filtration membrane [11,12], especially for water separation due to its high hydrophilicity and low friction for water molecules [13]. However, their sieving characteristics limit GO membranes for some important applications where organics are preferred or organic solvents are employed. For example, the separation of organic emulsions remains a global challenge for industry [22,23].

Energy-saving and high-performance membranes are highly desirable for this purpose.

For organics selective filtration, reduced GO (RGO), which is deoxygenated GO by thermal annealing [24] or chemical reduction [25], is suitable for the demand of interfacial hydrophobicity and lipophilicity. However, the interlayer spacing of RGO is known less than that of GO [26], resulting in blocking or unacceptable permeation flux [12]. For example, Nair's group recently reported that hydroiodic acid reduced GO membrane is a perfect barrier for blocking all gases, liquids and aggressive chemicals [27]. Considering that three-dimensional (3D) cross-linked graphene (CG) aerogel has porous structure and, especially, ultrafast oil absorbability [28], we suggest that using a cross-linked graphene oxide (CGO) membrane with post-reduction treatment can address the issues of organic emulsions separation.

With this strategy, the obtained CG membrane survived the chemical reduction while oxygen-related groups were removed. Both the needed channels within the cross-linked structure and the surface wettability were realized simultaneously. Herein, we present this novel CG membrane. It could achieve fast and selective permeation of organic solvents from various emulsions. Only tens to hundreds of ppm of water were detected in the organic filtrates. We demonstrated that besides the high-performance of organics separation, the designed CG membrane had basic advantages in aspects such as facile preparation, self-supporting, and

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structural stability, even countering the cross-flow separation used in industry [11,29,30].

2. Experimental section

2.1. Preparation of GO

Typically, 2 g graphite (80 mesh, purchased from Qingdao Jinrilai Co., Ltd., Shandong, China) and 1 g sodium nitrate were dispersed in 40 mL sulfuric acid (98%) at 0 °C. 6 g potassium permanganate was added and kept at 35 °C for 2 h. After adding 75 mL deionised water, the mixture was maintained at 98 °C for 15 min. Then, the mixture was diluted with 100 mL deionised water. 15 mL hydrogen peroxide (30%) was added gradually until the mixture turned yellow. After washing with water sufficiently, a GO solution (5 mg mL^{-1}) was obtained by ultrasonic exfoliation and centrifugation.

2.2. Preparation of CG membrane

Briefly, 1 mL ethylenediamine (EDA) and 100 mL GO solution (5 mg mL^{-1}) were sealed in a reactor (18 × 11 cm^2). After heating for 6 h at 95 °C, the CGO hydrogel was obtained with a size of 15 × 9 cm^2 [31]. Subsequently, the CGO aerogel was produced by freeze-drying treatment. After washing with ethanol sufficiently, the 3D-CGO aerogel was compressed to be a membrane at 6 MPa. This CGO membrane was reduced by a hydriodic acid solution (57%) at 95 °C for 10 min. After washing with ethanol sufficiently, the CG membrane was obtained. It can be tailored to a suitable shape and size for use in the separation apparatus (Supporting information, Scheme S1 and Fig. S1).

2.3. Membrane characterization

A HITACHI S4700 scanning electron microscopy (SEM) was used to image the unique characteristic of the CG membrane, as well as to perform the energy dispersive spectrometry (EDS) analysis. X-ray diffraction (XRD) patterns were recorded on a D/Max 2500 VB2+/PC in the range of $2\theta = 5$–$90°$. Contact angle (CA) measurements were measured on a Dataphysics OCA20 at room temperature. De-ionized water and hexane (oil) were used here. Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo TGA/DSC1/1100SF. Porosity was obtained by the Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System V4.01. The N$_2$ volume was at standard temperature and pressure (STP). The P/P_0 represented the partial pressure of N$_2$ at equilibrium at 77 K. About 0.2 g of the samples was used in the test. The Derjaguin–Müller–Toporov (DMT) modulus was determined with a Bruker MultiMode 8 atomic force microscope (AFM). The values of the DMT modulus were determined at the corresponding vertical frequency values.

2.4. Preparation of emulsions

The emulsions were produced with a C25 emulsifying homogenizer (Shang Hai HENC Mechanical Equipment Co., Ltd.) at 16,000 rpm for 30 min. Surfactant-free emulsions were prepared from organic and water at a ratio of approximately 9:1. The emulsions of toluene, isooctane, petroleum ether, gasoline, diesel and soybean oil were termed from E-1 to E-6, respectively. Two surfactants, S-170 (RYOTO sugar esters) and LAS (linear-alkylbenzenesulfonic acid), were used in the preparation of surfactant-stabilised emulsions and strong acidic/basic emulsions. The compositions of the emulsions were shown in below: S-1 (toluene/water/S-170, 11.4 mL/100 μL/50 mg), S-2 (toluene/water/S-170,

5.8 mL/5.8 mL/50 mg), A-1 (toluene/HCl/LAS, 11.4 mL/100 μL/10 mg), B-1 (toluene/NaOH/LAS, 11.4 mL/100 μL/10 mg). 12 M HCl and NaOH solution were used here. The high-temperature emulsion was named T-1, which was composed of toluene (90%) and water (10%), mixed at 65 °C.

2.5. Separation of emulsions

A CG membrane was sealed between one vertical glass tube with a diameter of 15.5 mm and one sand-core filter plate (Fig. S2). The oil/water emulsions were poured onto the CG membrane and spontaneously permeated. The finally obtained organic filtrate was collected for purity tests. The flux was determined by calculating the permeated volume of the organic filtrate within 5 min.

For the cross-flow separation, the separation instrument was fabricated first. Briefly, a hatch (5 mm × 2 mm) was made on a hard tube. Then, the tube was partially attached by a sellotape with an aligned hatch. Finally, the hatch of the sellotape was covered by a piece of the CG membrane, and the CG membrane was grasped on the tube with the sellotape. When the separation instrument was generated, it was connected to a peristaltic pump with a soft silicone tube. The S-1 emulsion was continuously pumped into the instrument with a flow velocity of 5.5 L h^{-1}. Toluene permeated through the CG membrane and was collected for purity tests. The flux was determined by the above method.

3. Results and discussions

3.1. Characterization of the CG membrane

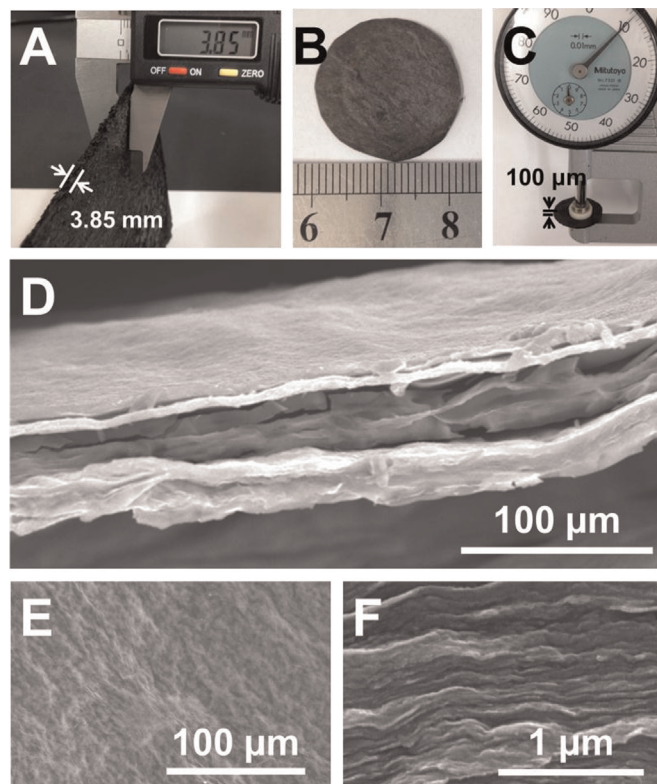Fig. 1A shows that the thickness of the porous CGO aerogel

Fig. 1. The characterization of the CG membrane. (A) The thickness of the 3D CGO aerogel. (B) The tailored CG membrane. (C) The thickness of the CG membrane. (D) Cross-sectional SEM image of the CG membrane. A continuous thin surface layer could be found. (E) SEM image of the uniform membrane surface. (F) High-magnification SEM image of the stacked arrangement of cross-linked graphene sheets.