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Graphene oxide membranes on ceramic hollow fibers – Microstructural stability and nanofiltration performance

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ABSTRACT

Graphene oxide (GO) membranes have demonstrated great potential in liquid filtration. With the aim of real applications, GO membranes in a hollow fiber shape are of particular interest because of the high-efficiency and easy-assembly features at the module level. We report here that GO membranes on ceramic hollow fiber substrates are unstable at the dry state, mainly due to the drying-related shrinkage. And we demonstrate that these GO hollow fiber membranes can be stabilized by keeping them wet after initial controlled formation of the membranes. The GO hollow fiber membranes show higher permeation fluxes of acetone and methanol than most commercial membranes, and reject molecules larger than 300 Da, showing a great potential in the use of value-added organic solvent nanofiltration processes.

1. Introduction

Graphene oxide, a derivative of graphene, has been considered as a promising material to realize functional thin films such as flexible and transparent electronic or optoelectronic devices because of its two-dimensional structure [1–6]. Each single-layer GO flake has an effective thickness of 0.5 nm [7], and the lateral size is tuneable from hundreds of nanometers up to tens of microns. The very high width-to-thickness ratio enables an easy assembly of ultrathin two-dimensional architectures [8,9]. Besides the uses of the assembled GO sheets in electronics and photonics, a very attractive potential is to use them for membrane separation [10–18]. Thick GO membranes are deemed to be impermeable to most substances [19], but some recent studies showed that when GO membranes are as thin as a few nanometers, the membranes allow gases to permeate with considerable fluxes and very high selectivities [14,16]. GO membranes have also showed good potential in nanofiltration applications where molecules with molecular weights of several hundred can be rejected whereas water can pass through [15,20–22]. Besides, GO membranes have been used to separate water from organic solvents through pervaporation process, and high permeation rates and separation factors were achieved [10,11]. These studies show the perspectives of GO membranes as effective separation barriers in environmental and chemical engineering.

Due to the extremely thin feature, GO membranes have to be supported by a substrate in real separation processes to withstand high pressure difference across the membrane. So far, GO membranes have been made on planar supports but they are difficult for mass production and their membrane area per volume ratio is limited. Hollow fiber membranes, often with a diameter of 1 mm or even less, are, in this context, more favorable for membrane module assembly in industry because they give the highest membrane area to module volume ratios (up to 9000 m^2/m^3), thus greatly reduce the size of separation plants and operating cost. Polymeric hollow fiber nanofiltration membranes coated with a thin GO layer have been recently reported to improve the permeance and selectivity very effectively [23]. Compared to their polymeric counterparts, ceramic hollow fibers would be a better substrate for GO membranes, as they are strong and rigid, giving a good support to the GO membrane. They are also chemically and thermally stable, making them possible to work under harsh operating conditions. The successful use of GO/ceramic hollow fiber composite membrane has been recently reported for dehydration of dimethyl carbonate, and high water flux and separation factors were obtained [11]. We report in this work, however, that GO membranes on ceramic hollow fiber substrates are unstable in the air, mainly due to the drying-related shrinkage. We also demonstrate that GO hollow fiber membranes can be stabilized by keeping them wet after initial linking of GO flakes. The stability requirements imply such GO hollow fiber membranes are not

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suitable for gas separation, but have great potential in wet separation processes such as nanofiltration.

2. Experimental

2.1. Preparation of GO/ceramic hollow fiber membranes and GO flat sheet membranes

The GO dispersion was synthesized by oxidation and exfoliation of graphite powder via a modified Hummer's method [4,24]. Briefly, graphite powder, $NaNO_3$ and 95% pure H_2SO_4 were mixed, and then $KMnO_4$ was gradually added with stirring in an ice water bath. After 5 h till the mixture was cooled down, the ice water bath was removed and the mixture was continuously stirred for 5 days. Then water was added to exfoliate GO and H_2O_2 was added to remove the remaining manganese ions. The resultant GO dispersion obtained was washed with deionized water and centrifuged to grade the size of GO flakes. The final GO dispersion used in this research has a concentration of 0.1 g L^{-1}, and the flake size is determined to be 5–10 μm by a scanning electronic microscope as shown Fig. 1.

The Al_2O_3 and YSZ hollow fibers were fabricated through a combined phase-inversion/sintering process [25], and the green fibers were sintered at 1350 °C and 1150 °C, respectively to gain the mechanical strength.

To deposit GO membrane onto the surface of ceramic hollow fibers, the hollow fiber was immersed into a GO dispersion with one end sealed and the other end connected to a vacuum pump. When a vacuum is applied to the lumen of the fiber, water is sucked into the fiber and the water flow directs GO flakes to the hollow fiber substrate. GO membrane is formed by stacking the flakes layer by layer, with the aid of pressure difference and water permeation. Thickness of the GO membrane was controlled by changing the initial concentration of the GO dispersion and the duration of filtration. After drying in vacuum at 40 °C for four hours, the GO hollow fibers were assembled using epoxy on a stainless steel holder for tests. In another scenario, the wet GO hollow fibers were immersed into methanol or acetone immediately after coating, and were left in the solvent for at least two days to allow a complete solvent displacement. After the solvent displacements, the GO hollow fibers were dried in the air for more than one week before water permeation and dye rejection tests.

Similarly, flat-sheet GO membranes were made through the vacuum-facilitated filtration method using a polyethersulfone (PES) microfiltration flat sheet filter. The flat sheet GO membranes are about 10 μm thick, and they can be peeled off carefully from the PES filter to form free-standing GO membranes for other measurements.

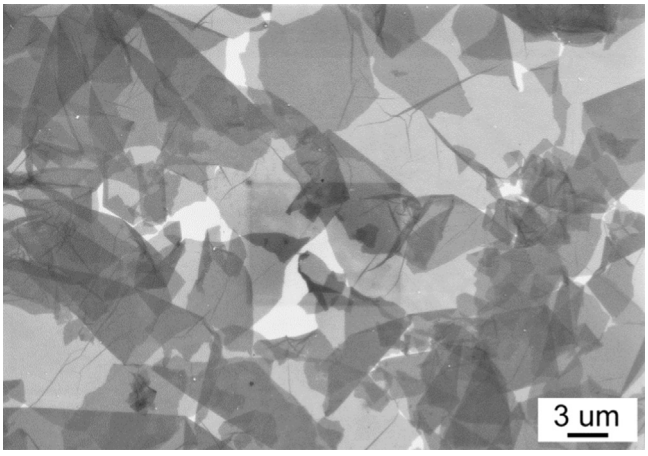

Fig. 1. SEM image of the GO flakes used in this research.

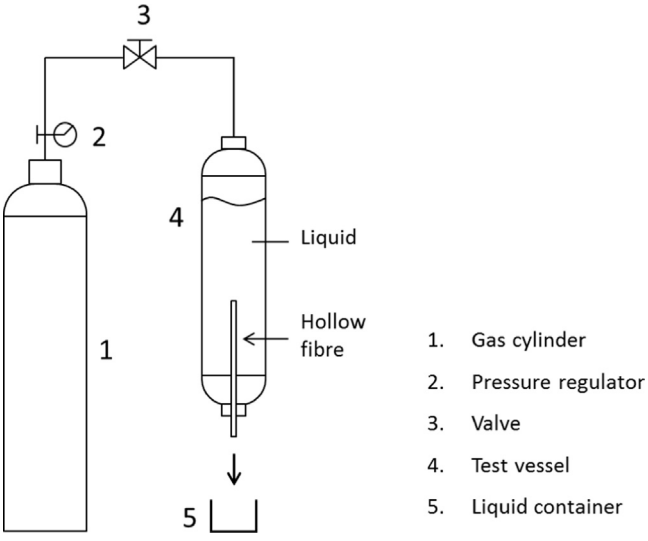

Fig. 2. Scheme of the setup used in this research for pure solvent permeation and nanofiltration tests.

2.2. Pure solvent permeation, nanofiltration and gas permeation tests

The pure solvent permeation and nanofiltration tests were conducted using a dead-end mode. The scheme of the testing setup is shown in Fig. 2. The GO hollow fiber membrane was mounted into the sample cylinder of the setup, in which the pure solvent or a dye solution was filled and pressurized to 10 bars. The permeate through the membrane was collected with a bottle, which was sealed with parafilm to prevent evaporation during the collection. The permeance of the solvent was determined by the weight gain and the duration of the permeation test; the dye concentration of the feed and the permeate were determined by a UV-spectrometer (UV-2101PC, Shimadzu, UK), and the rejection is calculated through the below definition:

$$R_{dye} = \left(\frac{1-c_p}{c_f}\right) \times 100\% \quad (1)$$

where R_{dye} is the rejection of the GO membrane to the dye, c_p and c_f are the concentration of the permeate and the feed, respectively.

Epoxy resin was used to seal the hollow fiber membrane. In the cases of methanol and acetone, a solvent-resist epoxy resin was used to ensure there was no leak through the sealant.

Gas permeation was conducted on a setup similar to Fig. 2, except gas instead of liquid was pressurized in the sample cylinder, and a bubble meter was used to measure the flow rate of the downstream permeated gas.

2.3. Materials characterization

Morphology of the membranes was observed by a scanning electronic microscope (LEO Gemini 1525 FEGSEM). X-ray diffraction (XRD, X'pert Pro PANalytical) was used to determine the average interspace between GO flakes in GO membranes, note here that flat GO membranes were used instead of hollow fibers to ensure accurate diffraction angles. Contact angles of water, methanol and acetone on GO membrane were measured using a drop shape analyzer (DSA 10 MK2, Krüss GmbH, Hamburg, Germany).