



Fabrication of assembled membrane from malonate-functionalized graphene and evaluation of its permeation performance



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ABSTRACT

The increasing number of studies on graphene membranes has indicated a great potential of graphene in separation applications. For the first time, this study demonstrates liquid permeation performance of a new graphene membrane that assembled functionalized graphene sheets. Functionalized graphene was synthesized from graphene dispersion based on a Bingel reaction with diethyl bromomalonate, and employed to prepare an assembled membrane using a vacuum filtration method. Thus prepared membrane was subjected to permeation tests using four solvents (hexane, acetone, methanol and water). The chemical functionalization led to two interesting consequences: i) Even a relatively minor extent of functionalization dramatically altered the chemical selectivity of the membrane, and ii) the permeability of the membrane was greatly enhanced, which plausibly arose from the less ordered stacking of the functionalized graphene sheets as compared to the pristine ones.

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1. Introduction

In recent years, graphene membranes for separation applications have attracted great attention from scientists and industrial producers due to the extreme thinness as well as the chemical and physical stability of graphene [1–3]. There are two types of graphene membranes that have been reported to show high efficiency in separation purposes [1]. The first type is porous graphene, which is mono or few-layer graphene with nano-sized (or even sub-nano) pores created on its basal plane [1,3]. Pores are introduced by electron beam irradiation [4], ultraviolet-induced oxidative etching [5], oxygen plasma etching [6] and bottom-up chemical synthesis [7] methods. The second one belongs to assembled graphene membranes that consist of stacking graphene sheets in a layer-by-layer fashion [2,8–10]. The transportation pathway is attributed to the channels created by the interlayer space among graphene layers [2,8,9]. The difference in the permeation speed of different kinds of molecules results in selective permeation and lastly, the separation behavior of the membranes [5,11,12]. In the porous structure, the pore size is the dominant factor determining the

permeability of the membranes, while the shape and chemical nature of the pores can also exert some significant effects [3,5,12]. In the case of the laminate framework, a recent work reported an extremely selective permeation behavior of graphene oxide membranes against water [8]. The origin of the selective permeability has been explained based on the hydrophilic nature of graphene oxide channels whose inter-layer spacing, ~ 7.0 Å, matches with one monolayer of water filled in these nanosized capillaries [8].

In spite of the above promising aspects of these membranes, some challenges still remain for practical applications. As for the porous graphene membrane, its highly selective permeability was mainly demonstrated based on computational simulations [1,6,13]. Nevertheless, the introduction of uniform pores in size without damaging the intrinsic structure of graphene is practically difficult, especially over a large area [3,13]. In fact, few reports have experimentally demonstrated the separation ability of porous graphene membranes [3,13]. In addition, the discontinuation of an aromatic system caused by pore introduction can weaken the mechanical durability of pristine graphene and thus, the membrane cannot withstand the pressure during separation [14]. In the case of the assembled structure, the majority of efforts has been devoted to membranes prepared from graphene oxide and its derivatives [10,15–19]. Contrary to the porous structure, high-quality

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membranes are facilitated by simple and cost-effective approaches such as spin-coating, dip-coating, vacuum filtration, Langmuir-Blodgett methods [2,3,9]. However, the selective permeability of graphene oxide membranes has been still limited to water filtration, even though some research groups have adjusted the chemistry of graphene oxide walls and the interlayer spacing of the channels to a certain extent [16,17,20]. Hence, in order to meet demands in chemical refinery, waste treatment, etc., the selectivity against different liquid/gas molecules in separation needs to be developed and broadened based on advanced graphene membranes.

The present research aimed to fabricate a new generation of assembled membranes from functionalized graphene instead of graphene oxide and to explore their selective aspects for the permeation of different solvents. Pristine graphene was covalently modified based on the Bingel reaction, which is a common approach to modify carbon nanomaterials [21–26] and suitable for post modification through the transesterification of the ester groups. An assembled functionalized graphene membrane was prepared by a vacuum filtration method, and its permeability against different solvents was compared with that of a reference membrane composed of pristine graphene.

2. Experimental

2.1. Materials

Graphite powder (particle size > 45 μm , purity > 98%) and orthodichlorobenzene (ODCB, 98%) were delivered by Wako Pure Chemical Industries, Ltd. Diethyl bromomalonate (98%) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%) were purchased from Sigma Aldrich. All chemicals and solvents were at analytical grade and used without further purification.

Aluminum oxide membranes or Anodisc membranes (AAO) (0.2 μm pore and 47 mm diameter) were supplied by SPI Corp., and PTFE membranes (0.1 μm pore and 47 mm diameter) were delivered by Sterlitech Corp.

2.2. Synthesis of graphene

Graphene was produced by exfoliating graphite powder in ODCB using an ultra-sonication bath (ASONE-ASU 10, 40 kHz, 500 W). Graphite powder (7.0 mg) and ODCB (2.0 mL) were added in a vial, then sonicated for 6 h at around 40 $^{\circ}\text{C}$ to afford a black mixture. The mixture was centrifuged at 4000 rpm for 2 h and carefully decanted to obtain graphene dispersion in ODCB. The graphene concentration in the dispersion was determined as 0.18 ± 0.02 mg/mL by UV–vis spectroscopy (JASCO V-670 UV-VIS-NIR Spectrophotometer).

2.3. Synthesis of functionalized graphene via Bingel reaction

The graphene dispersion was covalently modified with malonate moieties based on the Bingel reaction. DBU (50 mmol) and diethyl bromomalonate (50 mmol) were added to 60 mL of the graphene dispersion under N_2 , followed by stirring for 24 h at room temperature. The product was filtered and washed on a PTFE membrane with methanol to obtain a black solid. This solid was redispersed in methanol and centrifuged (4000 rpm, 2 h) to remove supernatant. The procedure was repeated for 2 times to obtain purified samples.

2.4. Membrane preparation

In this study, we used a vacuum filtration method to fabricate

membranes from graphene dispersion. Functionalized graphene was dispersed in 30 mL of methanol by sonication for 1 h. An AAO membrane was employed as a support for the deposition of graphene sheets. The initial pressure of a pump was set at 0.98 bar. 10 mL of the dispersion was poured onto the AAO support, followed by gradually decreasing pressure from 0.98 bar to 0.50 bar (differential pressure: 0.48 bar) for 3 min. After the deposition, the pressure was released to the atmospheric pressure. The same procedure was repeated for 3 times, pouring 30 mL of the dispersion in total. It was expected that the stepwise deposition would enhance the uniformity of the membranes. Finally, drying the resultant membranes for 12 h afforded functionalized graphene membranes (termed as FG membranes) for permeation tests as well as for characterization.

Membranes were also prepared from pristine graphene (termed as PG membranes) based on a similar procedure: 10 mL of graphene dispersion in ODCB was repeatedly deposited onto the AAO support for 6 times (60 mL in total). The differential pressure was set to 0.98 bar.

2.5. Characterization

The progress of graphene functionalization was investigated by infrared spectroscopy (IR) and thermogravimetric analysis (TGA). Powder samples were recovered from the corresponding dispersion by vacuum drying for 6 h. Transmittance IR spectra were acquired on JASCO FT/IR-6100 using KBr pellets in the range of 400–4000 cm^{-1} with the resolution of 4 cm^{-1} . TGA was performed on Mettler Toledo DSC 820 under N_2 atmosphere in the range of 30–600 $^{\circ}\text{C}$ at a heating rate of 5 $^{\circ}\text{C}/\text{min}$. Samples were loaded in Al pans and covered by Al lids. The morphology of pristine and functionalized graphene was observed by transmission electron microscopy (TEM, Hitachi H-7100, 100 kV) and atomic force microscopy (AFM, HITACHI SII SPI-3800/SPA400, SI-DF40 cantilever). The graphene dispersion was deposited onto a Cu grid and a Si substrate for TEM and AFM measurements, respectively, and dried overnight at room temperature prior to the measurements.

X-ray diffraction (XRD) patterns of membranes were recorded on Rigaku SMARTLAB at a voltage of 40 kV and a current of 30 mA with Cu $K\alpha$ (1.5418 \AA) radiation. A step scan mode was employed in the 2θ range of 5–60 $^{\circ}$ at the speed of 0.3 $^{\circ}$ per min and the step size of 0.05 $^{\circ}$. The microstructure and the thickness of the membranes were observed by scanning electron microscopy (SEM, Hitachi, S-4100) at an accelerating voltage of 20 kV. A membrane was fractured into small pieces and pasted onto a carbon double-side tape. These pieces of the membranes were coated with a thin layer of Pt-Pd in an ion sputter (Hitachi, E-1030) before imaging.

2.6. Permeation experiments

The permeability of the membranes was tested against four solvents: hexane, acetone, methanol and water. A typical permeation experiment was done by pouring 20 mL of a solvent on a membrane. The pressure was reduced from 0.98 bar to a specific point that was adjusted according to the type of solvents and membranes. Table 1 summarizes the applied differential pressure. The applied pressure was lower for hexane, acetone and methanol than that for water, while higher pressure was applied for the less permeable PG membrane than for the FG membrane.

3. Results and discussion

3.1. Preparation of functionalized graphene

The chemical structures of pristine graphene and functionalized

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