



Mixed matrix membranes composed of WS₂ nanosheets and fluorinated poly(2,6-dimethyl-1,4-phenylene oxide) via Suzuki reaction for improved CO₂ separation



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ABSTRACT

A method of introducing trifluoromethyl group (-CF₃) to the polymer backbone by Suzuki reaction was developed to prepare fluorinated polymers for gas separation. The CO₂ permeability increased 119% after the -CF₃ group was substituted. Tungsten disulfide (WS₂), a graphene-like two-dimensional material, was used for first time as an inorganic filler to prepare composite MMMs to separate CO₂, N₂ and CH₄. The introduction of WS₂ nanosheets increases more transport channels for gas molecules, which lead to the permeability and selectivity of MMMs obviously improved in comparison with the pristine FPPO membrane. The CO₂/N₂ selectivity and CO₂/CH₄ selectivity of 10 wt% WS₂-FPPO MMMs reached a maximum about 29.6 and 39.4, respectively, with a CO₂ permeability of 472 Barrer at 10 psig and 291 K. The best performance of MMMs for CO₂/N₂ and CO₂/CH₄ surpasses the Robeson's upper bound line. The MMMs showed strong stability in long-term observation. The results indicated a new direction for CO₂ separation by introducing -CF₃ group to polymer and using 2D WS₂ nanosheets as nanofiller.

1. Introduction

During the past few decades, polymeric membrane-based gas separation has received a great deal of attention due to low capital cost, high energy efficiency, ease of processing, simple process equipment, ease of operation, and environmental friendliness [1–3]. A large number of polymer membranes have been applied in hydrogen separation, nitrogen recovery, oxygen and nitrogen enrichment, and natural gas purification [4,5]. However, most of the current polymeric membranes are restricted by a trade-off between permeability and selectivity, as suggested by Robeson [6,7]. Recently, a breakthrough has been followed to boost the performance of polymeric membranes by embedding filler materials. The resultant mixed matrix membranes (MMM), which generally consist of a polymer matrix and a dispersed phase, exhibit the good processability and mechanical properties of the polymer with high separation capabilities of the filler particles [8,9]. To date, advances in this regard have led to the fabrication of fillers including carbon molecular sieves [10,11], zeolites [12], silica [13], and metal organic frameworks [14,15]. Nevertheless, the challenge of

highly selective membranes with significant flux still remains.

Two-dimensional layered materials such as graphene, and graphene oxide (GO) have attracted increasing interest due to their unique and tunable properties for applications in gas separation. Park et al. fabricated the polymer-supported thin GO membranes with high CO₂/N₂ selectivity [16]. Yu et al. reported the preparation of ultrathin GO membranes with a thickness approaching 1.8 nm for high H₂ separation [17]. On the other hand, the analogue of graphene, a series of two-dimensional (2D) layered materials is developed due to their unique and tunable properties for applications as membrane materials. In particular, the graphene-like material, tungsten disulfide (WS₂) and molybdenum disulfide (MoS₂), is newly developed, in which metal atoms in a layer are sandwiched between two sulfur atoms sheets (the crystalline structure of WS₂ is shown in Fig. 1a). WS₂ and MoS₂ have been widely applied in electronic and optical devices, water purification, energy storage units, and biological systems due to their unique and tunable properties [18–21]. However, few works have been reported about gas separation. Wang et al. first time applied a single-layered MoS₂ based ultrathin membrane to separate H₂/CO₂ gases,

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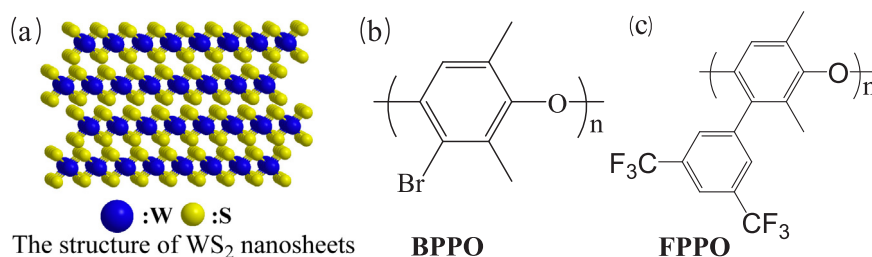


Fig. 1. (a) The structure of WS₂ nanosheets; chemical structure of (b) BPPO and (c) FPPO.

wherein the membranes demonstrated superior H₂/CO₂ separation performance [22]. Compare to many gases, MoS₂ shows high affinity to selected NO₂ and CO₂ owing to the high adsorption energy of these gas molecules onto the basal surface of MoS₂ [23]. Additionally, developed novel high-performance lamellar separation membranes for CO₂ separation are expected.

Fluorine containing polymers play an important role in gas separation applications, because these polymers show lower surface energy, extraordinary chemical and high thermal stability [24]. As a result of high fractional free volume, high hydrophobicity, and the dipole-quadrupole interaction between C–F and CO₂, the fluorinated polymers with highly polar C–F bonds showed very good performance in CO₂ separation [25]. The most widely used strategies to obtain fluorinated polymers are introduction of trifluoromethyl group (-CF₃) in the polymer structure. Okamoto and his coworkers reported that polyimides with -CF₃ linkages showed lower chain packing density, higher permeability, and higher selectivity compared to non-fluorinated polyimides in gas separation [26]. In our previous work, the brominated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (shown in Fig. 1b) exhibits satisfactory gas permselectivity [27]. Herein, in order to improve the gas permeability on the premise of maintaining high selectivity, the -CF₃ and phenyl groups were introduced to the PPO polymer backbone by Suzuki reaction to get poly(3-(3',5'-bis(trifluoromethyl)phenyl)-2,6-dimethyl-1,4-phenylene oxide) (FPPO) (shown in Fig. 1c), which produced more free spaces and provided rigid main chain. To prepare composite MMMs for separating CO₂/N₂ and CO₂/CH₄ gases, the perfectly crystallized WS₂ nanosheets material were used for the first time. The -CF₃ group from polymer and WS₂ nanosheets were expected to construct continuous CO₂ transport channels and improve CO₂ solubility selectivity. The thermal stability, membrane morphology and gas separation performance of these MMMs were evaluated. The relationships between gas separation performance and microstructure of MMMs were discussed in detail.

2. Materials and methods

2.1. Materials

PPO ($M_n \sim 25,000$; polydispersity ~ 2.0 ; density $\sim 1.07 \text{ g cm}^{-3}$) were purchased from Aldrich and used as received. Powder of WS₂ was purchased from Adamas Reagent Co., Ltd. (Shanghai, China). 3,5-Bis(trifluoromethyl)phenylboronic acid and tetrakis(triphenylphosphine) palladium(0) (Pd(PPh₃)₄) were obtained from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). The other solvents and all commercially available reagents were used without further purification.

2.2. Exfoliation of multilayered WS₂

In order to improve the dispersity of the WS₂ powder, it is essential to exfoliate the bulk material for the multilayered WS₂ nanosheets. The commercial WS₂ powder was exfoliated to WS₂ nanosheets by solvent exfoliation method [28]. 0.5 g of WS₂ powder was dispersed in 100 mL of H₂O, in 500 mL serum bottle and kept sonication for 3 h to exfoliate WS₂ powder by an ultrasonic cell pulverizer. After that, the solution

was sonicated by an ordinary ultrasonic washer for 6 h. Finally, the homogeneous WS₂ nanosheet dispersion was obtained.

2.3. Synthesis of FPPO

The poly(3-bromo-2,6-dimethyl-1,4-phenylene oxide) (BPPO) was prepared according to our previous report [26]. To a suspension of PPO (6 g, 0.24 mmol) in CHCl₃ (50 mL) was added dropwise a solution of Br₂ (5 mL, 100 mmol) in CHCl₃ (10 mL) over 30 min at ambient temperature. The suspension was stirred until the solution completely decolorized. The precipitate was obtained from ethanol. FPPO was synthesized by Suzuki reaction. Typically, A mixture of BPPO (0.42 g, 0.008 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (4.30 g, 1.66 mmol), aqueous K₂CO₃ (2 M (mol dm⁻³), 3.76 mL) and Pd(PPh₃)₄ (92.4 mg) in toluene (13 mL) was refluxed with vigorous stirring for 72 h under a nitrogen atmosphere. After the mixture was cooled to room temperature, the resultant polymer was precipitated from methanol/HCl aq, and reprecipitated from methanol/NH₃ aq and from methanol, respectively. Finally, the product was dried under vacuum, affording a gray solid. ¹⁹F NMR (376 MHz, CDCl₃, δ ppm): peak centered at -62.69 (-CF₃).

2.4. Preparation of MMMs

For the preparation of polymeric and MMMs, the conventional solution casting and evaporation technique was used. The FPPO and WS₂ were dried at 80 °C for 24 h to remove the adsorbed water before the membrane preparation. Specifically, for pure FPPO membrane fabrication, the desired amount of polymer (20 wt%) was dissolved in chloroform under stirring for 24 h. For MMMs fabrication, a measured amount of WS₂ defined by Eq. (1) corresponding to the WS₂ loading, was predispersed in chloroform. Then the suspension was placed in ultrasonic bath for 20 min before added into the FPPO solution.

$$\text{WS}_2 \text{ weight percentage (wt\%)} = \left(\frac{\text{wt. WS}_2}{\text{wt. WS}_2 + \text{wt. FPPO}} \right) \times 100\% \quad (1)$$

To obtain a homogeneous dispersion of the WS₂ suspension, the obtained solution was further stirred overnight. The solution was ultrasonically treated for 20 min before MMMs casting, so as to remove the trapped bubbles. After degasification, the mixture was poured on a clean polytetrafluoroethylene plate and covered by an inverted funnel to delay chloroform evaporation from the nascent membranes. The solvent was evaporated under ambient conditions for 24 h. The membranes were peeled off from the plate and dried at 85 °C for 12 h in a vacuum oven to further remove the residual solvent. Before characterization or gas permeation test, the as-prepared membranes were placed in a vacuum oven at 60 °C for 2 h.

2.5. MMMs characterization

Fourier transform infrared (FTIR) spectroscopy was conducted using a MAGNA-IR550, Thermo Nicolet Corporation. The tablet of FPPO and MMMs mixed with KBr were prepared under press force. The spectra were recorded in a spectral range of 400–4000 cm⁻¹ with a resolution

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