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ABSTRACT

Mixed matrix membranes (MMMs) composed of sulfonated poly(ether ether ketone) (SPEEK) and amine-functionalized titania submicrospheres were prepared. TiO₂ submicrospheres (~300 nm) were amine-functionalized through a facile two-step method by using dopamine (DA) and polyethyleneimine (PEI) in succession. The resultant TiO₂-DA-PEI microspheres were incorporated into SPEEK with a sulfonation degree of 67%. Grafting PEI with abundant amine groups onto the titania fillers remarkably increased the content of facilitated transport sites in the membranes, leading to an increment in both gas permeability and selectivity. High humidity also contributed to the facilitated transport of CO₂ via the generation of HCO₃⁻. The highest ideal selectivities of the SPEEK/TiO₂-DA-PEI membranes for CO₂/CH₄ and CO₂/N₂ were 58 and 64, respectively, with a CO₂ permeability of 1629 Barrer. Besides, the mechanical and thermal stabilities of the membranes were also enhanced compared to pure SPEEK membrane.

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1. Introduction

Polymer-based gas separation membranes have already emerged as a relatively realistic platform for use in large scale industries [1–4]. The high efficiency offered by polymeric membranes for gas separation and their beneficial advantages in terms of capital investment, operational cost and energy saving in comparison to the conventional processes have attracted much attention toward the membrane gas separation process. However, the instinct trade-off between permeability and selectivity for polymeric materials becomes one of the major obstacles for further improvement in separation performance and industrial scale-up [1]. Mixed matrix membranes (MMMs) based on a bulk polymer matrix and a dispersed inorganic phase [5–10] have been proved to be an effective approach to overcoming this obstacle. Numerous materials have been used as the inorganic phase in MMMs, such as carbon molecular sieves [11,12], zeolites [13–15], mesoporous materials [16], activated carbons [17], carbon nanotubes [18] and metal-organic frameworks [19,20]. The concept of MMMs combines

the advantages of each constituents: high selectivity and desirable mechanical property of the dispersed inorganic fillers and easy processability of the bulk polymers, thus making it possible to surpass the Robeson's upper-bound constraint [21,22].

Facilitated transport is an efficient method commonly used to enhance the CO₂ separation performance by the reversible reaction between facilitated transport carriers and CO₂ molecules [23–28]. The commonly used facilitated transport membranes can be divided into three categories: (1) immobilized liquid membranes, (2) solvent swollen, fixed-site carrier membranes, and (3) solid electrolyte polymer membranes. Although these membranes have shown very high performance with respect to natural gas and hydrocarbon separation, their mechanical and long-term high-performance stabilities are still unsatisfied [29]. Therefore, the practical application of facilitated transport membranes in natural gas separation (CO₂/CH₄) is still pending.

Incorporation of CO₂-facilitated transport fillers (CO₂-FTF) into polymeric membranes has been studied recently. Chung et al. [30] investigated the effect of Ag⁺ ion exchange treatment of zeolite on the CO₂/CH₄ gas separation performance of PES-zeolite AgA MMMs and found that the CO₂ and CH₄ permeability decreased with increasing zeolite content due to partial pore blockage and polymer chain rigidification, whereas the CO₂/CH₄ selectivity

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increased because of the combined effect of the facilitated transport of Ag^+ and the molecular sieving of zeolite. Ismail et al. [31] explored the facilitated transport effect of Ag^+ ion exchanged halloysite nanotubes (HNTs) in membranes on the CO_2/CH_4 gas separation performance. Wang et al. [32,33] prepared high performance membranes with CO_2 -facilitated transport highway constructed by incorporating polyaniline nanoparticles into polyvinylamine matrix for CO_2/N_2 separation. Kim et al. [34] reported an increased CO_2/CH_4 selectivity of polysulfone membranes doped with APTES functionalized MCM-41 particles.

Filler shape (sheet, tube, spheres, etc.) is also an important factor influencing the dispersion in the mixed matrix membranes and the final separation performance. Coronas et al. [35–39] investigated both micro and submicro spheres, and they found that the use of spherical-shaped fillers led to reduced agglomeration due to minimized contact area between particles. Spherical fillers with high mechanical, thermal stability and ease of chemical functionalization have been incorporated into polymer to increase permeability [16,22]. Sulfonated poly(ether ether ketone) (SPEEK) is a glassy polyelectrolyte and has recently been used as a potential gas separation membrane materials [40–44]. In this study, SPEEK was used as the polymer matrix and amine-functionalized titania submicrospheres were used as the filler to fabricate mixed matrix membranes for gas separation. The membrane morphology, polymer chain rigidity, membrane free volume property, mechanical property and thermal stability were characterized and the separation performance was explored for CO_2/CH_4 and CO_2/N_2 mixtures.

2. Experimental

2.1. Chemicals and materials

Poly(ether ether ketone) (PEEK) was purchased from Victrex High-performance Materials (Shanghai, China) Co., Ltd. 3-2-(3,4-dihydroxyphenyl)ethylamine (Dopamine Fig. 1(a)) was purchased from Yuancheng Technology Development Co., Ltd. (Wuhan, China). Polyethyleneimine (PEI, M.W.=1800, 99%, Fig. 1(b)) was purchased from Gracian chemical technology Co., Ltd. (Chengdu, China). Tetrabutyl titanate, hydrochloric acid, ethylene glycol, sulfuric acid, N,N-Dimethyl acetamide (DMAc) and acetone were of analytical grade and purchased from Tianjin Guangfu Fine Chemical Research Institute(Tianjin, China). Tris(hydroxymethyl) aminomethane (Tris) was purchased from Sigma-Aldrich.

Sulfonated poly(ether ether ketone) (SPEEK) (Fig. 1(c)) with different sulfonation degree was prepared by direct sulfonation of PEEK [45]. PEEK was firstly dried in oven at 80°C for 24 h before sulfonation. Then, the dried PEEK (14 g) in triplicate was gradually dissolved into 100 mL sulfuric acid (H_2SO_4 , 95–98%) in a three-neck flask for about 4.5 h at room temperature, followed by vigorous stirring at 50°C for 8 h, 10 h and 12 h, respectively. Afterward, the polymer solutions were gradually precipitated into water under mechanical agitation, respectively. Finally, the polymer precipitate was washed several times with deionized water until pH reached neutral and then dried first at room temperature for 24 h and then at 60°C for another 24 h. The degrees of sulfonation (DS) were determined through acid–base titration method.

2.2. Preparation of amine-functionalized TiO_2 submicrospheres and membranes

TiO_2 submicrospheres (0#) with a particle size of about 300 nm were synthesized by a sol–gel method as described in previous study [46]. Firstly, TBT (0.02 mol) was poured into 100 ml of ethylene glycol under nitrogen atmosphere to prepare the precursor solution. The precursor solution was magnetically stirred

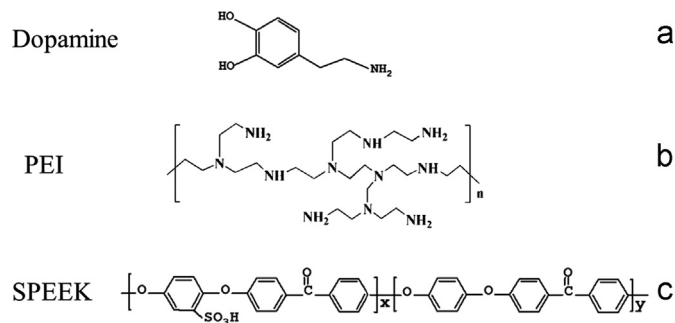


Fig. 1. Chemical structure of (a) dopamine, (b) PEI and (c) SPEEK.

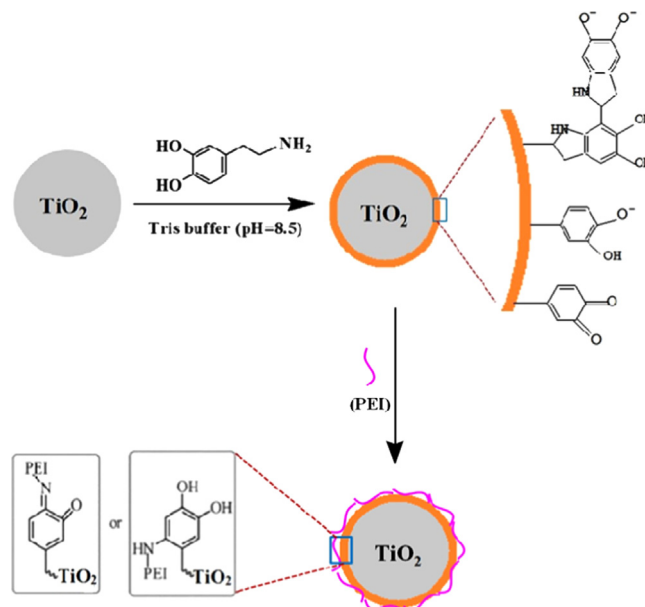


Fig. 2. The grafting mechanism of dopamine and PEI on titania.

for 10 h at room temperature and then added into acetone solution containing 0.3 wt% water. The concentration of TBT in acetone was 0.01 M. For amine-functionalized TiO_2 , dopamine and PEI were subsequently used as modification reagents (Fig. 2). Firstly, a facile chelation procedure was conducted. 0.5 g TiO_2 powders were suspended in 250 ml deionized water under ultrasonic treatment for 2 h to break aggregates, and 1.0 g dopamine was dissolved in 250 ml Tris-HCl (pH=8.5) used as modification reagent solution. The TiO_2 suspension was mixed with the same volume of modification reagent, followed by vigorous stirring for 24 h [47]. The polydopamine-coated TiO_2 submicrospheres were collected by centrifugation, washed with distilled water until neutral and dried in a vacuum oven at 80°C for 24 h. Secondly, 0.5 g polydopamine-coated TiO_2 subsequently reacted with PEI in 5 wt% aqueous solution via Michael addition or Schiff base reactions at 60°C for 6 h [48]. The obtained polydopamine-coated titania and the further PEI-grafted titania were designated as $\text{TiO}_2\text{-DA}$ (1#) and $\text{TiO}_2\text{-DA-PEI}$ (2#), respectively. A color change from white (TiO_2) to dark gray ($\text{TiO}_2\text{-DA}$) and then to brown ($\text{TiO}_2\text{-DA-PEI}$) was observed during the functionalization procedure.

SPEEK (0.6 g) was dissolved in DMAc (8 g) at room temperature. A measured amount of fillers was dispersed in DMAc (4 g) and the resulting suspension was added into SPEEK–DMAc solution under vigorously stirring for 24 h to get a fine dispersion of fillers in the polymer solution. After degasification, the mixture was poured on a clean glass plate and heated overnight at 60°C for

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