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Enhanced pervaporative performance of hybrid membrane by incorporating amphiphilic carbonaceous material

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ABSTRACT

Amphiphilic carbonaceous material (ACM) was blended with sodium alginate (SA) and then deposited onto the polyacrylonitrile (PAN) porous support layer to fabricate SA-ACM/PAN hybrid membranes. As a two-dimensional material, ACM provided anisotropy, horizontal stacking orientation and high aspect ratio. The abundant oxygen-containing functional groups (–NO_2, –SO_3H, –OH, –COOH and epoxy group) on the edge of ACM (proved by X-ray photoelectron spectroscopy and scanning electron microscope with energy dispersive X-ray (EDX) spectrometer) offered the hydrophilic region, while the unoxidized part on the surface of ACM offered hydrophobic region. The hydrophilic region on ACM could preferentially adsorb water molecules and then facilitate water molecules entering the transport channel due to the hydrogen bond, while the hydrophobic region could realize the fast diffusion of water molecules. The small nanosheet size (200–400 nm, observed by atomic force microscopy) could interfere the arrangement of polymer chains more efficiently. The hybrid membranes exhibited the optimal permeation flux of 1778 g/m^2 h and separation factor of 1816 for ethanol dehydration under 76 °C and 10 wt% feed water concentration, which is much higher than that of SA membrane (increased by 139% and 306%, respectively).

1. Introduction

Dimensionality plays an essential role in influencing their fundamental properties, in addition to the composition and arrangement of atoms in materials [1]. Two-dimensional (2D) materials provide a vast and diverse untapped source of layered substance with anisotropy, horizontal stacking orientation and high aspect ratio, which are essential for separation, sensing, catalysis and energy storage applications [2]. Novoselov et al. established a convenient method to prepare a variety of free-standing atomic 2D crystals (especially graphene) by using micromechanical cleavage in 2004, which has made the application of 2D materials in diverse fields a research hotpot [3]. Among those fields, polymer-inorganic hybrid membrane by incorporating 2D materials into the polymer to enhance the separation performance has received tremendous attention [4–7]. In the hybrid membranes, 2D materials prefer to accept the configuration parallel to the membrane surface, which can improve interfacial interactions between polymer-inorganic interfaces more effectively to optimize the structure and property of hybrid membrane [8–11]. The space between stacking layers of 2D materials could form the molecule transport channels, which is beneficial for the separation performance [12]. Meanwhile, the processability and flexibility of polymer could offset the defects generated from the accumulation of 2D materials [13]. Polymer-2D inorganic material hybrid membranes have achieved extensive application in separation performance, due to it can combine the advantages of polymer and 2D inorganic material.

2D materials used for the preparation of polymer-inorganic hybrid membrane mainly include molecular sieve, zeolite, metal organic framework (MOF) and graphene oxide (GO). Among various 2D materials, GO, usually coming from flake graphite, has been widely used due to its special properties, such as high specific surface area (2600 m^2/g), single atomic layer and handy surface modification [14]. It has been proved that both the functional

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groups and size of GO nanosheets have a significant influence on the performance of the polymer-GO hybrid membranes. Compared with graphene, GO with plenty of oxygen-containing groups including hydroxyl, carboxyl and epoxy groups are beneficial for dehydration separation in membranes [15]. Zhao et al. introduced additional oxygen-containing groups, such as $–SO_3H$, onto GO by grafting zwitterionic PSBMA. The PSBMA@GO nanosheets enhanced the hydrophilicity of the sodium alginate (SA) membrane by hydrogen bonds to endow the high-efficiency water permeation [16]. Meanwhile, the small nanosheet size can provide more edge-to-edge slits as penetration paths for water, which construct molecular-sieving channels and structural pores to enhance the separation performance more efficiently [17]. Chen et al. prepared GO membranes consisting of small GO sheets (lateral size of 200–400 nm) for the dehydration of butanol. Benefited from removing the larger GO sheets (lateral size of 4–6 μm), the membrane exhibited better separation performance [18]. Therefore, it can be envisaged that if a novel 2D material is synthesized with more oxygen-containing groups (especially more hydrophilic groups) and smaller size, the performance of the fabricated polymer-inorganic hybrid membranes will be further enhanced.

Amphiphilic carbonaceous material (ACM), as another typical 2D GO-like material, was firstly synthesized by Fujii et al. [19–22]. Besides the typical 2D characters, ACM nanosheets are amphiphilic: the region connected with oxygen-containing functional groups is hydrophilic, while the unoxidized region is hydrophobic. The abundant oxygen-containing groups attached on the nanosheets of ACM mainly contain $–NO_2$, $–SO_3H$, –OH, –COOH and epoxy group [23]. The hydrophilicity of $–NO_2$ and $–SO_3H$ is stronger than that of –COOH and –OH, due to their larger electronegativity providing stronger ability to attract electron and form hydrogen bonds with water molecules. Due to the introduction of oxygen-containing groups ($–NO_2$, $–SO_3H$) with larger volume, the distance between ACM layers is large enough to make the material dispersing steadily in water [24]. Meanwhile, the small nanosheet size (200–400 nm) could enhance the interaction between inorganic filler and polymer to interfere the arrangement of polymer chains more efficiently [25]. Last but not least, the raw material of ACM is green needle coke, refined from petroleum residual oil. By means of the mixed acid process, no organic solvent is used in the preparation of ACM [24]. This can realize the recycling of the industry trash, in order to save resources and protect the environment. It is rare to find the applications of ACM nanosheets in fabricating hybrid membrane in the existing researches.

In this study, the ACM was blended with SA and deposited onto polyacrylonitrile (PAN) ultrafiltration membranes to prepare the hybrid membranes. Due to the hydrophilic property, SA polymer had been widely used as membrane material in pervaporation dehydration [26]. The physical morphology, chemical structure and thermal stability of both the ACM nanosheets as well as the SA-ACM hybrid membranes were characterized. The pervaporation dehydration performance of the hybrid membranes was evaluated using ethanol-water mixtures. The effects of ACM content, operation temperature and feed concentration on the membrane separation performance were investigated, and the long-term operation stability was also evaluated.

2. Experiment

2.1. Materials

Green needle coke (NC) was supplied by Jinzhou Petrochemical Co. Ltd. (Jinzhou, China). Sodium alginate (SA) was supplied by Qingdao Bright Moon seaweed Group Co. Ltd. (Shandong, China). Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), absolute ethanol and silver nitrate ($AgNO_3$) were bought from Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China). Concentrated sulfuric acid (H_2SO_4, 98 wt%), concentrated nitric acid (HNO_3), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were gained from Tianjin Kewei Ltd. (Tianjin, China). Polyacrylonitrile (PAN) ultrafiltration membranes used as membrane substrates with a molecular weight cut-off of 100 kDa were obtained from Shanghai Mega Vision Membrane Engineering & Technology Co. Ltd. (Shanghai, China).

All the reagents were of analytical grade and used without further purification. Deionized water through a Millipore system (MillisQ) was used in all experiments.

2.2. Membrane preparation

2.2.1. Preparation of ACM nanosheets

ACM was prepared from green needle coke with high carbon content, low volatile and ash content, by the mixed acid process. NC of 20–50 μm prepared by crushing and sieving was blended uniformly with a mixture of concentrated nitric acid and sulfuric acid. The reaction was terminated by putting the reactant into cold distilled water. The mixture was washed with distilled water until the filtrate was neutral. The solid collected from the mixture was mixed with NaOH solution ($pH > 12$) and stirred to dissolve at 80 °C. Then hydrochloric acid was added to the filtrate ($pH < 1.8$). ACM was washed by distilled water and gained after stoving [27].

2.2.2. Fabrication of SA-ACM hybrid membranes

The hybrid membranes were fabricated by spin-coating membrane casting solutions blending with SA polymer and ACM nanosheets onto PAN ultrafiltration membranes. The PAN ultrafiltration membranes soaked in deionized water were cut into sizes of 0.1 m × 0.1 m, then hung up and dried at room temperature for 3 h for preparation to serve as support layers. In a typical procedure, an appropriate amount of SA polymer was dissolved in deionized water stirring at 30 °C for 1 h. Certain amounts of ACM nanosheets were dispersed in aqueous solution by ultrasonic vibration (achieved by Noise Isolating Tamber SCIENTZ-IID) for 5 min. The solution was dropwise added into the SA solution and stirred vigorously for another 5 h. After filtration and deaeration by gauze, the membrane casting solution was spin-coated onto PAN substrates, with the spin coating at 500 rpm for 25 s then 800 rpm for 40 s using WS-400BZ-6NPP/LITE spin coater. The hybrid membranes were placed at room temperature for 24 h to evaporate the solvent. After immersed in 0.5 M $CaCl_2$ solution for 10 min and rinsed with abundant water, the cross-linked membranes were obtained.

For simplicity, the hybrid membranes were designated as SA-ACM-X/PAN, where X represented the content of ACM in SA (wt%). The X varied from 1 to 3 for SA-ACM-X/PAN. For characterization and swelling study, the corresponding homogeneous membranes were fabricated on glass plates instead of PAN substrates following a similar preparation procedure and denoted as SA-ACM-X.

2.3. Characterizations

The morphology of the ACM nanosheets was determined by transmission electron microscopy (TEM, JEOL JEM-100CXII) and atomic force microscopy (AFM, CSPM5000). The apparent and cross-section morphologies of the ACM nanosheets and hybrid membranes were measured using field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan), while the category and distribution of atoms on the ACM surface were probed in combination with energy dispersive X-ray (EDX) spectrometer (SEM/EDX).