



Vacuum-assisted assembly of ZIF-8@GO composite membranes on ceramic tube with enhanced organic solvent nanofiltration performance



Hengyu Yang, Naixin Wang*, Lin Wang, Hong-Xia Liu, Quan-Fu An, Shulan Ji

Beijing Key Laboratory for Green Catalysis and Separation, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, PR China

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ABSTRACT

Organic solvent nanofiltration (OSN) is an emerging technology for molecular separation and purification in organic media. The separation performances are mainly depended on the material and structure of the membrane. In this study, Zeolitic Imidazolate Framework (ZIF-8) nanoparticles were *in situ* growth onto the surface of graphene oxide (GO) sheets to form ZIF-8@GO composites, which were co-deposited with polyethyleneimine (PEI) matrix on tubular ceramic substrate through a vacuum-assisted assembly method. The dispersion of ZIF-8 nanoparticles in PEI matrix as well as the compactness and uniformity of the composite membranes were readily improved due to the templating effect of lamellar GO sheets and the transmembrane pressure. Membrane performance in OSN was evaluated on the basis of methanol permeance and retention of dye molecules. Methanol permeance increased when ZIF-8@GO laminates were embedded into the PEI layer, whereas the retention remained higher than 99%. The improvement of separation performance may be due to the well dispersion of ZIF-8 nanoparticles in PEI matrix, which offers more well-defined pathways for solvent molecules. Building on these findings, we demonstrate a simple scalable method to obtain robust ZIF-8@GO based membranes with enhanced OSN performance.

1. Introduction

Organic solvent nanofiltration (OSN) can be used in the field of petrochemistry, food, biotechnology, and pharmaceutical industries [1]. Compared with distillation, extraction and other traditional separation process, OSN is an energy-saving and waste-reductive process to separate organic solvent from mixtures [2–4]. The main challenge for OSN membranes is the design and fabrication of new material and construction of novel structure to obtain high solute rejection, desired flux and stable separation performance [5].

Recently, thin film composite (TFC) membrane, which consist of an ultra-thin separating barrier layer on top of a porous support, has been developed to reduce the mass transfer resistance of solvent molecules in the separation process [6,7]. The support usually provides the mechanical strength, whereas the separation layer is responsible for the high separation performance [8]. The advantage of TFC membrane is that the porous support and separation layer can independently be optimized to improve the selectivity and permeability of the composite membrane. To further improve the separation performance, nanoparticles with molecular sieving capacity were incorporated into the separation layer to form thin film nanocomposite (TFN) membranes [9,10]. However, the morphology, structure, size, dispersion, loading,

and compatibility of the nanoparticles should be controlled to maximize their synergistic function and avoid the interfacial defects between the phases [11–13].

As a porous crystalline material comprised by metal ions and organic ligands, metal organic frameworks (MOFs) has attracted increased interest to be used as a molecular sieve in mixed matrix membranes (MMMs). Because of the high surface area, modulated porosity, rich surface chemistry, and flexible structure of MOFs crystal, the MOF-based MMMs can be used in gas separation, pervaporation, and nanofiltration [14–16]. In spite of several advantages for MOF-based membranes, many problems are still needed to be solved, such as the dispersion of MOF particles in polymer, the uniformity of particle size and the interface defect between MOF particles. Many strategies have been used to solve these problems through changing the preparation methods and controlling the fabrication conditions. For example, Fan et al. used simultaneous spray self-assembly method to obtain a maximum loading of ZIF-8 nanoparticles while maintaining uniform dispersion in the polymer [17]. The well-dispersed ZIF-8-PDMS nanohybrid membranes exhibited exceptionally high biobutanol-permselective pervaporation performance. Zhang et al. reported a co-ordination-driven *in situ* self-assembly strategy to prepare a uniformly dispersed robust MOF hybrid membrane [18]. On the basis of the

* Corresponding author.

E-mail address: wangnx@bjut.edu.cn (N. Wang).

coordination interactions between metal ions and ligands and/or the functional groups of the organic polymer, the membrane showed outstanding nanofiltration performance. These results indicated that a homogeneous MOF nanohybrid membrane with a thin selective layer is critical to obtain high separation performance.

Except for modulating the preparation strategies to overcome the agglomeration of nanoparticles, the modification of MOF particles is another approach to improve their arrangement and distribution in the polymer. Graphene oxide (GO) nanosheet, which contains oxygen-rich functional groups with an atomic layer thick, offers a great potential for making uniform, stable and functional MMMs with high separation performance [19–21]. The incorporation of GO nanosheets can effectively inhibit the swelling of the membrane by organic solvent, but decrease the permeate flux due to the strong barrier effect of GO nanosheets on solvent molecules [22]. Recently, MOF particles were anchored on GO sheets to form MOF@GO nanocomposites for combining the advantages of the two materials, such as MOF-5@GO, HKUST-1@GO, MIL-53@GO, ZIF-67@GO and ZIF-8@GO [23–27]. The MOF@GO nanocomposites thus obtained high surface areas, large pore volumes, laminated structure, and alterable pore functionalities. Meanwhile, the *in situ* growth of MOF particles onto GO surface can largely obliterate the agglomeration of MOF in the membrane owing to the coordination between metal ions and carboxyl groups of GO which can disperse MOF particles uniformly in the GO surface [28]. The MOF@GO nanocomposites have been used as fillers to prepare composite membranes in gas separation [29,30], pervaporation [31], and nanofiltration in aqueous solution [32]. To our best knowledge, the using of MOF@GO nanocomposites in OSN has not been reported yet.

In this study, a MOF@GO based composite membrane was prepared for OSN. As shown in Fig. 1, ZIF-8 nanoparticles were *in situ* grown on the surface of GO sheets to form ZIF-8@GO laminates with ZIF-8 nanoparticles regularly arranged on GO sheets. The ZIF-8@GO laminates and polyethyleneimine (PEI) were co-deposited onto the outer surface of the tubular ceramic substrate by a vacuum-assisted assembly method. ZIF-8@GO laminates were embedded in PEI matrix under the transmembrane pressure. PEI was used as a bridging agent to improve the bonding force between separation layer and the substrate. Moreover, PEI is easy to be chemically cross-linked because of the abundant amine groups in the molecular chains. The obtained composite membrane was then cross-linked with glutaraldehyde (GA) to make it more stable. The ZIF-8@GO laminates and the as-synthesized membranes with “brick-and-mortar” structure were explored by powder X-Ray diffraction (PXRD), Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy

(XPS) and atomic force microscopy (AFM). The OSN performance of the composite membranes were investigated through removing dyes from methanol. It should be emphasized that the ceramic substrates have advantages of good chemical stability, high temperature tolerance, and well mechanical strength [33,34]. Furthermore, the ceramic substrate has an excellent anti-swelling property to organic solvent, which is very important in OSN. Meanwhile, tubular membrane modules are valuable in industry because of their high packing density [35,36]. Therefore, the ZIF-8@GO/PEI composite membrane formed on tubular ceramic substrate may have a great potential in industrial applications.

2. Experimental

2.1. Chemicals and materials

Graphene oxide (GO) was obtained from Nanjing XFNANO materials Tech Co., Ltd (China). Aqueous solution (50%) of branched Polyethyleneimine (PEI, Mw = 60,000 Da) was purchased from ACROS. 2-Methylimidazole (Hmim) was purchased from Aldrich. Zn (NO₃)₂·6H₂O, glutaraldehyde (GA, 25% aqueous solution), methanol, and methyl blue, were provided by the Beijing Chemical Factory. All chemicals were used as received without further purification. 50 mm-long tubular ceramic substrate with 8.5 mm inner and 13.5 mm outer diameters were supplied by JieXi LiShun Technology Co., Ltd., China. The tubular ceramic substrate is composed of the support layer and the dense layer. The thickness of the dense layer is approximately 5 μm. The pore size is approximately 100 nm.

2.2. Synthesis of lamellar ZIF-8@GO composite

GO was first dispersed in deionized water and sonicated for 4 h. Then, the suspension was centrifuged for 15 min to remove the GO sheets with large size. The ZIF-8@GO composite was synthesized using the following method [37]. Zn(NO₃)₂·6H₂O (0.366 g) and 2-methylimidazole (Hmim, 0.811 g) were dissolved in 12 mL and 20 mL methanol, respectively. Meanwhile, 8 mL GO suspension was added to the Hmim solution. Then, the Zn(NO₃)₂ solution was added to the mixed solution of Hmim and GO under constant stirring at room temperature. The final concentration of GO in the precursor solution was 0.1 g/L, 0.2 g/L, 0.3 g/L and 0.4 g/L, respectively. The precipitation was collected by centrifugation (6000 rpm for 15 min) and washed with methanol for three times, and then dried in a freeze drier. For comparison, pristine ZIF-8 particles were also prepared.

2.3. Membrane preparation

To prepare the composite membrane, ZIF-8@GO suspension with different concentrations (0.0025 wt%, 0.005 wt%, 0.0075 wt%, 0.01 wt %) were prepared by dispersing a certain amount of ZIF-8@GO in methanol. The suspension was sonicated for 1 h and stirred for 12 h to make the ZIF-8@GO disperse well. Then, PEI was added to the suspension under stirring for another 30 min. The ZIF-8@GO/PEI composite membranes were prepared via a vacuum-assisted assembly method. The ceramic tube was immersed in the ZIF-8@GO/PEI suspension with one end was sealed and the other end was connected with a vacuum pump. Subsequently, the ZIF-8@GO/PEI composite was deposited on the outer surface of the ceramic tube under the driving force of transmembrane pressure at -0.09 MPa. After 3 min at room temperature, the composite membrane was taken out and immersed into 0.05 wt% GA solution for crosslinking with 1 min. Finally, the resulting composite membrane was dried at 40 °C for 12 h. For comparison, ZIF-8/PEI and GO/PEI were also deposited on the surface of the ceramic tube to form composite membranes with the same method.

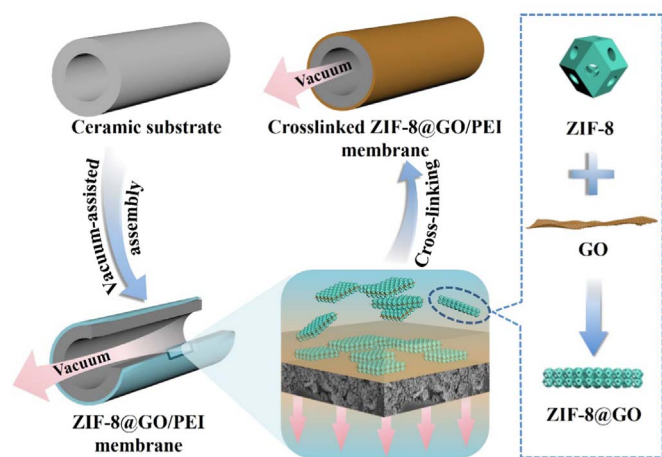


Fig. 1. Schematic illustration of fabrication of crosslinked ZIF-8@GO/PEI composite membrane on tubular ceramic substrate via a vacuum-assisted assembly method.

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