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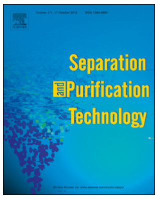

# Mixed-matrix membranes containing nanocage-like hollow ZIF-8 polyhedral nanocrystals in graft copolymers for carbon dioxide/methane separation

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## ABSTRACT

Nanocage-like, hollow ZIF-8 (H-ZIF) polyhedral nanocrystals were synthesized via the use of seed crystals, epitaxial ZIF-8 growth, and excavation of ZIF-67 sacrificial templates. The highly porous and hollow structure of the H-ZIF polyhedral nanocrystals was confirmed by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction (XRD), and Brunauer-Emmett-Teller analysis. The H-ZIF nanocrystals were distributed in an amphiphilic poly(vinyl chloride)-*g*-poly(oxyethylene methacrylate) (PVC-*g*-POEM) graft copolymer matrix to form mixed-matrix membranes (MMMs) for $CO_2/CH_4$ separation. The microphase-separated nature of the structure of the PVC-*g*-POEM was induced by the solubility difference between the hydrophobic PVC backbone and the hydrophilic POEM side chains. Specific interactions between the micro-structured PVC-*g*-POEM polymer matrix and the imidazole moiety of the H-ZIF enhanced the interfacial contact and improved the dispersion of the H-ZIF within the MMM; this was confirmed by XRD, FE-SEM, and differential scanning calorimetry. The hollow structure of the H-ZIF reduced the gas diffusion resistance of the MMM, resulting in increased gas permeability. Moreover, the molecular sieving properties and $CO_2$-philic amine groups in the imidazole linkers of the H-ZIF led to high $CO_2$ separation performance. The PVC-*g*-POEM/H-ZIF MMM exhibited an approximately fivefold increase in $CO_2$ permeability, with a value of 210.6 barrer, compared to 43.5 barrer for a pristine PVC-*g*-POEM membrane with a $CO_2/CH_4$ selectivity of 14.3, which is close to upper bound reported by Robeson in 2008.

## 1. Introduction

Carbon dioxide is a primary cause of the greenhouse effect; it mainly originates from the combustion of fossil fuels and the development of natural gas and biogas. $CO_2$ separation technology has attracted significant attention as a route to clean energy sources and to prevent environmental problems [1–5]. The separation of $CO_2$ from $CO_2/CH_4$ mixtures is an important process in natural gas transportation and storage systems because, in the presence of water, acidic $CO_2$ can cause corrosion [6–10]. Recently, membrane technology has been identified as a promising alternative to conventional industrial processes—such as adsorption, absorption, and cryogenic distillation—due to its many advantages, including easy scale-up, high energy efficiency, and low operating costs [11–15]. However, polymer membranes still suffer from a trade-off between permeability and selectivity [16,17]. Therefore, many approaches to overcoming this limitation on the gas separation performance have been investigated.

Mixed matrix membranes (MMMs), comprising inorganic fillers and an organic polymer matrix, have emerged as a new type of membrane with high gas-separation performances [18]. The incorporation of highly permselective materials in a suitable polymer matrix can enhance the performance of MMMs, overcoming the trade-off inherent in other membranes. Various types of materials have been used as MMM fillers, including carbon nanotubes [19–22], graphene [23,24], zeolites [25–27], porous metal oxides [28–30], and metal-organic frameworks (MOFs) [31–34]. MOFs are a subclass of coordination polymers consisting of organic ligands coordinated to metal ions. MOFs generally have tunable, porous structures with high surface areas and selective

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*Abbreviations:* BET, Brunauer-Emmett-Teller; DSC, differential scanning calorimetry; FE-SEM, field-emission scanning electron microscopy; FT-IR, Fourier-transform infrared; HMTETA, 1,1,4,7,10,10-hexamethyltriethylenetetramine; H-ZIF, hollow ZIF-8; MMM, mixed-matrix membrane; NMP, N-methylpyrrolidone; POEM, poly(oxyethylene methacrylate); PVC, poly (vinyl chloride); TEM, transmission electron microscopy; TGA, thermogravimetric analysis; THF, tetrahydrofuran; XRD, X-ray diffraction; ZIF, zeolitic imidazolate framework

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affinities for gases.

Among various MOFs, zeolitic imidazolate frameworks (ZIFs) are promising candidates for use in gas-separation membranes due to their remarkable thermal/chemical stability and structural properties [33,35–37]. ZIFs are composed of transition-metal ions (e.g. Zn, Co) coordinated by imidazolate linkers to form tetrahedral clusters with tunable pore structures and affinities for specific gases. The crystal structures of ZIFs are topologically isomorphic with zeolites, due to the similar metal-imidazole-metal (145°) and Si-O-Si bond angles [37]. In particular, ZIF-8, a representative ZIF, has a sodalite zeolite structure that consists of Zn metal ions and 2-methylimidazole linkers. ZIF-8 has been widely investigated for use in gas-separation membranes due to its large cage size (11.6 Å) and pore size (3.4 Å) that is suitable for molecular sieving. Ordoñez et al. used Matrimid/ZIF-8 MMMs for the separation of various gas mixtures (including $CO_2/CH_4$, $CO_2/C_3H_8$, and $H_2/O_2$) [38]. Compared to a pristine Matrimid membrane, the $CO_2/CH_4$ selectivity of a 50 wt% Matrimid/ZIF-8 MMM increased from 40 to 124 due to the molecular-sieving effect of ZIF-8. Nordin et al. reported polysulfone/ZIF-8 MMMs with varying ZIF-8 sizes [39]. ZIF-8 particles with various sizes were synthesized in aqueous media by varying the concentration of a triethylamine additive and with further heat treating to enhance the pore structure. The use of small-pore ZIF-8 resulted in a decrease in $CO_2$ permeability from 25.7 barrer to 15.6 barrer (1 barrer = $1 \times 10^{-10}\ \text{cm}^3_{\text{STP}}\ \text{cm}\ \text{cm}^{-2}\ \text{s}^{-1}\ \text{cmHg}^{-1}$) but an increase in $CO_2/CH_4$ selectivity, compared to a pure polysulfone membrane, from 19.4 to 28.5.

Recently, Rösler et al. [40] and Yang et al. [41] reported the preparation of nanoscale, hollow ZIF crystals with tunable porosities and multi-functionality. These hollow ZIF crystals are beneficial hosts for catalytically active species and, thus, expected to be effective as MMM fillers. Recently, our group reported the use of MMMs with hollow, spherical ZIF nanoparticles, prepared using polystyrene bead templates, for gas separation [40]; however, the use of nanocage-like H-ZIF polyhedral crystals has not been reported.

In this study, we synthesized nanocage-like hollow ZIF (H-ZIF) polyhedral crystals via a two-step method: the solvothermal synthesis of ZIF-67 crystals followed by epitaxial growth of ZIF-8 on the ZIF-67 nanocrystals via self-sacrifice/excavation of the ZIF-67 crystals. The H-ZIF polyhedral nanocrystals were used as an inorganic filler for the preparation of MMMs containing a poly(vinyl chloride)-*g*-poly(oxyethylene methacrylate) (PVC-*g*-POEM) graft copolymer matrix. The structure and morphology of the membranes were characterized in detail using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). The influence of H-ZIF loading on membrane performance was investigated using pure gas ($CO_2$ and $CH_4$) permeation via the time-lag method.

## 2. Experimental

### 2.1. Materials

For the synthesis of nanocage-like H-ZIF-8 polyhedral nanocrystals, cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 98%) and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 98%), for use as metal sources, and 2-methylimidazole ($C_4H_6N_2$, 98%), for use as an organic ligand, were purchased from Sigma-Aldrich. For the synthesis of the PVC-*g*-POEM copolymer, poly(vinyl chloride) (PVC, average $M_w \sim 233{,}000\ \text{g mol}^{-1}$, average $M_n \sim 99{,}000\ \text{g mol}^{-1}$), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol)methyl ether methacrylate, $M_n \sim 475\ \text{g mol}^{-1}$), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), and copper (I) chloride (CuCl, 99%) were purchased from Sigma-Aldrich. N-Methylpyrrolidone (NMP), tetrahydrofuran (THF), and methanol were obtained from J. T. Baker. All solvents and chemicals were reagent grade and were used as received.

### 2.2. Synthesis of nanocage-like H-ZIF polyhedral nanocrystals

Nanocage-like H-ZIF polyhedral nanocrystals were prepared based on the procedure reported in the literature [40], with some modifications. First, ZIF-67 nanocrystals with sizes of 200 nm–300 nm were synthesized for use as the sacrificial template. Ligand and metal solutions were prepared by dissolving 9.75 g of 2-methylimidazole and 4.32 g of cobalt nitrate hexahydrate in 300 mL of methanol. Then the two solutions were mixed vigorously by stirring for 3 min, followed by aging at room temperature for 24 h without stirring. Afterwards, the synthesized ZIF-67 nanocrystals were washed by three cycles of centrifugation at 7000 rpm and sonication in fresh methanol for 5 min; this was followed by vacuum drying at 80 °C for 12 h and then use as a sacrificial template for the synthesis of the H-ZIF nanocrystals.

Second, to synthesize the H-ZIF nanocrystals, 0.1 g of the synthesized ZIF-67 nanocrystals was dispersed in 60 mL of methanol by sonicating for 5 min. Then, 0.372 g of zinc nitrate hexahydrate and 0.103 g of 2-methylimidazole were sequentially added into the ZIF-67 nanocrystal dispersion, which was then stirred for 10 min. The mixture was then treated solvothermally in a 100 mL Teflon-lined autoclave at 100 °C for 12 h, followed by washing and drying by the same protocol used for the ZIF-67 nanocrystal synthesis.

### 2.3. Synthesis of the PVC-g-POEM graft copolymer

The PVC-*g*-POEM graft copolymer was synthesized according to our previously reported procedure [42]. Six grams of PVC was dissolved in 50 mL of NMP by stirring at 90 °C for 3 h, until complete dissolution. After the solution was cooled to room temperature, 24 mL of POEM, 0.1 g of CuCl, and 0.23 mL of HMTETA were added. After purging with nitrogen gas for 1 h, the mixture was placed in an oil bath. The polymerization reaction was carried out at 90 °C for 20 h. After the polymerization, the resultant mixture was diluted with THF and passed through a column filled with activated $Al_2O_3$ to remove the catalyst. The polymer was precipitated into methanol. To purify the final product, the precipitation process was repeated three times, and then the PVC-*g*-POEM graft copolymer was vacuum dried at 50 °C to remove the residual solvent.

### 2.4. Preparation of the MMMs

The nanocage-like H-ZIF polyhedral nanocrystals were dispersed in THF by sonicating for 1 h. Separately, the PVC-*g*-POEM graft copolymer was dissolved in THF by vigorous stirring at room temperature. The mixed solution was sonicated for 30 min to achieve a well-dispersed state and the removal of gas bubbles. The PVC-*g*-POEM/H-ZIF solutions were poured into round Teflon dishes and covered with perforated aluminium foil to control evaporation rate. The membranes were fabricated at room temperature for 1 d. The membranes were detached from the Teflon dishes and dried in a vacuum oven overnight to eliminate residual solvent. As the proportion of H-ZIF increased, the color of membrane changed from yellow to brown, as shown in Fig. 1.

### 2.5. Characterization

Brunauer-Emmett-Teller (BET) isotherms and specific surface areas of the ZIF-67 particles and H-ZIF nanocrystals were determined from $N_2$ adsorption–desorption data acquired at 77 K using a Belsorp Max instrument. The crystallographic structure and crystallinity of the samples were analyzed by XRD using a Rigaku MAC-18XHF X-ray diffractometer equipped with a CuKα radiation source ($\lambda = 1.54056$ Å) and operated at a scan rate of $10^\circ\ \text{min}^{-1}$ from 3° to 40°. The morphologies of the ZIF-67 particles and H-ZIF particles were observed, and surface images recorded, using a high-resolution FE-SEM (MERLIN, Carl Zeiss STM, Germany). To confirm the hollow-shell structure, field-emission TEM was performed using a JEM-2100F (JEOL). Fourier-transform infrared