



## Review

## A review from material functionalization to process feasibility on advanced mixed matrix membranes for gas separations

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## ABSTRACT

Carbon capture and hydrocarbon purification via economically viable and energy-efficient membrane systems have recently attracted increased interest. Mixed matrix membranes (MMMs) made from metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and 2-dimensional (2D) materials such as MXenes and layered double hydroxides (LDHs) are particularly attractive for gas separations. This work conducted a critical review of the latest development of MMMs based on advanced filler functionalization strategies, and their performances and stabilities under different operating conditions related to pressure, temperature, and feed gas impurities. Moreover, the upscaling and techno-economic feasibility of MMMs for industrial applications in postcombustion carbon capture, natural gas sweetening, biogas upgrading, hydrogen purification and olefin/paraffin separation were systematically discussed. Advanced MMMs developed at higher technology readiness levels are still challenging to meet their industrial gas separations. Herein, we present the latest ideas for improving fillers for MMMs and optimizing process design with regard to enhancing material properties and

**Abbreviations:** [Bmim][Tf<sub>2</sub>N], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [Emin][Tf<sub>2</sub>N], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; OD, zero-Dimensional; 2D, two-Dimensional; 3D, three-Dimensional; 6FDA, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride; 6FDA-DABA, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride-3,5-diaminobenzoic acid; 6FDA-DAM, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride-diaminomesitylene; 6FDA-ODA, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride-4,4'-oxydianiline; ACOF-1, Azine-linked COF; BDC, 2-hydroxyterephthalic acid; BTB, 1,3,5-Tris (4-carboxyphenyl) benzene; BTC, 1,4-Benzenedicarboxylate; CA, cellulose acetate; CBMNs, co-benzenedicarboxylate MOF nanosheets; CMC, carboxymethyl cellulose; COF, covalent-organic framework; COF-LZU-1, COF-Lanzhou University-1; CTPP, covalent triazine piperazine polymer; DABA, 3,5-diaminobenzoic acid; Dobdc, 2, 5-dihydroxyterephthalic acid; Durene, 2,3,5,6-tetramethyl-1,4-phenylenediamine; EDTA, ethylene diamine tetraacetic acid; FCTF-1, fluorinated covalent triazine framework-1; FIB-SEM, Focused Ion Beam Scanning Electron Microscopy; FTIR, Fourier Transform Infrared Spectrometer; GPU, Gas Permeation Unit; HFDS, 1H,1H,2H,2H-perfluorodecyltriethoxysilane; HKUST-1, Hong Kong University of Science and Technology-1; IPD, isophthalic dihydrazide; LDHs, layered double hydroxides; MIL, Material of Institute Lavoisier; MMMs, Mixed matrix membranes; MOF, Metal-organic framework; MoS<sub>2</sub>, molybdenum disulfide; NIPS, Nonsolvent-induced phase separation; NUS, National University of Singapore; P84, polyimide (PI); PAO-PIM-1, functionalized polymers of intrinsic microporosity; PBI, polybenzimidazole; Pebax, poly (ether-block-amide); PEG, polyethylene glycol; PEGDA, poly (ethylene glycol) diacrylate; PEI, polyethyleneimine; PEO, polyethylene oxide; PI, polyimide; PIEM, poly 2-isocyanatoethyl methacrylate; PIM-1, polymers of intrinsic micro-porosity; PIM-PI-1, polymers of intrinsic microporosity-polyimide; PMMA, polymethyl methacrylate; Psf, polysulfone; PU, polyurethane; PVAc, polyvinyl acetate; PVAm, poly (vinylamine); PVDF, polyvinylidene difluoride; SAPO-34, silicoaluminophosphate-34; SBR, styrene-butadiene rubber; SEM, scanning electron microscope; SNW-1, covalent organic framework Schiff base network-1; SPEEK, sulfonated poly (ether ether ketone); TFC, thin film composite; TpBD, 1, 3, 5-Triformylphloroglucinol-benzidine COF; TpPa-1, 1,3,5-Benzenetricarboxaldehyde, 2,4,6-trihydroxy-, polymer with 1,4-benzenediamine; TRL, Technology Readiness Level; UiO, University of Oslo; WS<sub>2</sub>, Tungsten disulfide; XLPEO, highly tunable crosslinked poly (ethylene oxide); ZIF, Zeolite imidazolate framework; ZSM-5, Zeolite Socony Mobil-5; γ-CD-MOF, γ-cyclodextrin-based metal-organic framework.

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