

## Full Length Article

# Enhancing CO<sub>2</sub> sequestration efficiency: A comprehensive study of nanostructured MOF-composite membrane for sustainable climate solution



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## ABSTRACT

This study provides a detailed exploration of nanostructured Metal-Organic Frameworks (MOFs)-composite membranes as a novel and efficient solution for CO<sub>2</sub> sequestration process. The integration of MOFs into membrane systems is shown to significantly enhance gas separation performance by improving both selectivity and permeability, thus addressing the inherent limitations of conventional CO<sub>2</sub> capture technologies. A range of synthesis techniques, including solvothermal synthesis, layer-by-layer assembly, and in-situ growth, are discussed, highlighting their role in optimizing the interaction between MOFs and membrane materials. In addition, the CO<sub>2</sub> capture and separation mechanism through the membrane are thoroughly discussed. The analysis further explores the impact of nanostructuring on the mechanical, chemical, and operational stability of the membranes, with particular attention to their potential for industrial scalability. Key challenges, such as MOF regeneration, economic feasibility, and environmental sustainability, are critically assessed. Additionally, the incorporation of advanced computational modelling and green synthesis methods is emphasized as essential in furthering the development of MOF-composite membranes. This study highlights the significant potential of these advanced materials to revolutionize CO<sub>2</sub> capture technologies, contributing to more sustainable and scalable approaches to climate change mitigation.

## 1. Introduction

The continuous increase in atmospheric carbon dioxide (CO<sub>2</sub>) concentrations, primarily driven by the combustion of fossil fuels and the clearance of forests, represents a significant challenge in the current period. This increase in CO<sub>2</sub>, a potent greenhouse gas, is a major contributor to the escalating phenomenon of global climate change, characterized by rising global temperatures, shifting weather patterns, and increasing sea levels. The need for effective strategies to mitigate these CO<sub>2</sub> emissions is not just urgent but essential for the sustainability of our planet (Fu et al., 2022; Koytsoumpa et al., 2018; Roohollahi et al., 2022).

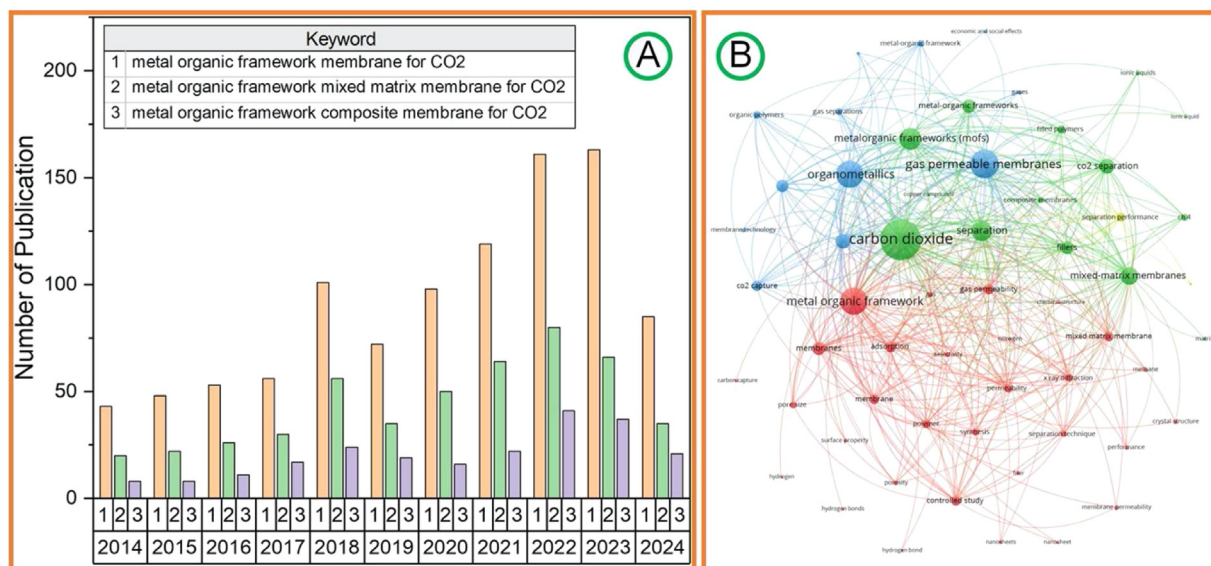
Among a variety of strategies, one that stands out as crucial is CO<sub>2</sub> sequestration. This strategy entails the capturing and storing of atmospheric CO<sub>2</sub> for the long term, whether in geological formations, oceans, or through mineral carbonation (Fu et al., 2022). However, conven-

tional approaches to CO<sub>2</sub> sequestration, like scrubbing with amines, encounter numerous obstacles, such as high operational expenses, energy-intensive procedures, and apprehensions about the stability of long-term storage. These challenges highlight the need for novel, effective, and economically feasible alternatives (Aghel et al., 2022; Fu et al., 2022; Kamran and Park, 2021; Madejski et al., 2022).

Membrane technology is a promising option for CO<sub>2</sub> capture. Advantages include lower energy needs, scalability, and possible integration into current industrial processes. Efficiency relies heavily on the materials utilized. Nanostructured Metal-Organic Frameworks (MOFs) are crucial in enhancing membrane technology ability to capture CO<sub>2</sub> (Song et al., 2024; Wu et al., 2021, 2023). MOFs, with their highly ordered, porous structures and customizable chemical functionalities, offer remarkable CO<sub>2</sub> adsorption capacities. The integration of MOFs into membrane technology, particularly when nanostructured, potentially leads to a significant enhancement in the selectivity and perme-

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**Fig. 1.** (A) Publications related to MOF-based membranes for CO<sub>2</sub> capture (number of publication are obtained from SCOPUS. Keywords network is generated by using VOSViewer; Retrieved on 18 May 2024). Figures presented here illustrate the dynamic of research on MOF-based membranes.

ability of CO<sub>2</sub>. These nanostructured MOF-composite membranes represent a novel class of materials that could potentially redefine the benchmarks of CO<sub>2</sub> capture technology (Essalhi et al., 2023; Fan et al., 2022; Fatemina et al., 2023; Gulbalkan et al., 2024; Ho and Paesani, 2023; Hu et al., 2023; Ren et al., 2019; M. Sun et al., 2023; Usman et al., 2021).

This study aims to perform a thorough investigation on these novel composites. The research will explore into the synthesis and characterization of nanostructured MOF-composite membranes, focusing on the details of their production and the complexities of their structural characteristics. An in-depth analysis of the mechanisms involved in the capture and separation of CO<sub>2</sub> by these composites will be provided, emphasizing the significance of MOFs in improving CO<sub>2</sub> attraction and selectivity. In addition, the study will assess the influence of nanostructuring on membrane performance, examining how these modifications impact overall functionality (Ma et al., 2019; Mohamed et al., 2023; Ni et al., 2023).

The paper will examine the kinetic and thermodynamic elements that are essential for the effectiveness of CO<sub>2</sub> capture, shedding light on the operational parameters and environmental considerations involved. Recent advancements and breakthroughs in the production of such composites will be evaluated, offering an overview of the current state-of-the-art accomplishments in this field. Finally, an examination will be conducted on the technical and economic obstacles encountered by these novel materials as they transition from the laboratory to practical applications, along with the potential they offer within the broader scope of sustainable climate solutions (M. Sun et al., 2023; Wu et al., 2023).

Fig. 1 presents the number of published literatures and networks of keywords associated with MOF-based membranes. These figures collectively demonstrate the expanding research efforts and the evolving focus on improving MOF-based membranes for effective CO<sub>2</sub> capture and separation. In general, these data show that there are active research conducted on the topic related with MOF-based membranes.

In addition, there are review papers on the advancements in MOF-based membranes as presented in Table 1, however, they have distinct focuses and contributions. Previously available review papers primarily concentrate on the design, performance, and application of MOF membranes for CO<sub>2</sub> capture and gas separation. These reviews encompass a variety of critical aspects, including intricate material design, sophisticated fabrication methods, and the enhancement of separation

efficiency through specialized MOF structures. The focus is broad, addressing multiple types of separations (both gas and liquid), different MOF materials, and their composite forms. Other reviews examine the development of high-efficiency MOF membranes, tackling complex issues like framework flexibility, interface compatibility, and achieving optimal separation performance across diverse applications. They emphasize the necessity of engineering CO<sub>2</sub>-philic MOFs and fabricating crack-free membranes, as well as integrating MOFs into mixed matrix membranes (MMMs) to augment gas separation efficiency and stability.

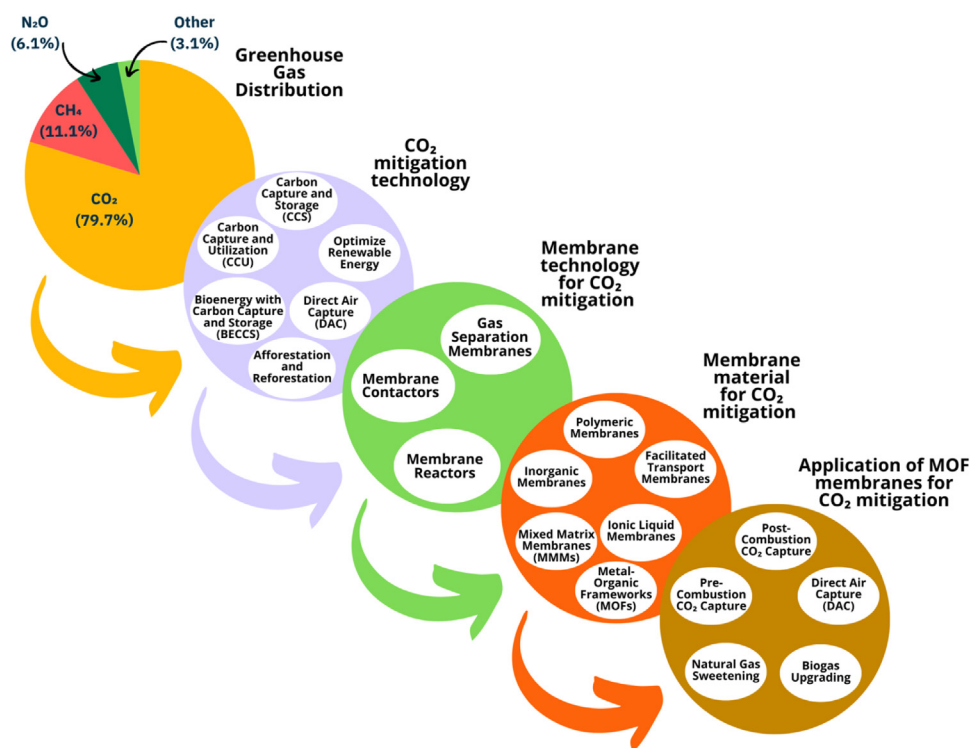
The objectives of this study are to develop and optimize nanostructured MOF-composite membranes for efficient CO<sub>2</sub> sequestration while addressing limitations of conventional capture technologies. The key research questions focus on identifying effective synthesis techniques, understanding the mechanisms of CO<sub>2</sub> capture and separation, evaluating the impact of nanostructuring on membrane performance, and assessing the scalability and challenges for industrial applications. The study also explores the integration of computational modeling and machine learning to enhance performance and sustainability, positioning MOF-composite membranes as a promising solution for climate change mitigation.

## 2. Fundamentals and theoretical background of CO<sub>2</sub> capture and CO<sub>2</sub> capture with MOF-composite membrane

The text provides an in-depth exploration of CO<sub>2</sub> capture technologies, focusing on the integration of Metal-Organic Frameworks (MOFs) with membranes to enhance efficiency and selectivity. Traditional methods like absorption, adsorption, and cryogenic separation face challenges such as high energy demands and environmental concerns, whereas membrane-based techniques offer energy-efficient and scalable alternatives. MOFs, with their high porosity, tunable structures, and selective adsorption capabilities, are increasingly being incorporated into membranes, either as fillers in mixed matrix membranes (MMMs) or as thin films. These MOF-composite membranes employ various mechanisms, including solution-diffusion, molecular sieving, and facilitated transport, to improve CO<sub>2</sub> separation performance. Advances in functionalization, surface modifications, and innovative fabrication methods have further optimized their efficiency. Despite challenges like regeneration complexity and scalability, MOF-composite membranes represent a promising solution for sustainable and efficient CO<sub>2</sub> capture, contributing significantly to climate change mitigation efforts.

**Table 1**  
Analysis of selected review papers on MOF-based membranes.

No.	Focus of review	Contributions	Reference
1	This paper focuses on CO <sub>2</sub> -philic MOFs and crack-free membranes for enhanced permeability and selectivity	<ul style="list-style-type: none"> <li>Material design for CO<sub>2</sub> capture using MOFs.</li> <li>Construction of crack-free membranes for high-efficiency CO<sub>2</sub> capture.</li> </ul>	(Ban et al., 2020)
2	The review paper focuses on the challenges in MOF-based membranes, including flexibility and interface compatibility	<ul style="list-style-type: none"> <li>High-quality MOF-based membranes achieved desired separation performance in gas/liquid separation.</li> <li>MOF membranes showed remarkable molecular sieving performance for gas separation.</li> </ul>	(Duan et al., 2023)
3	This paper focuses on ZIF-8-based membranes for CO <sub>2</sub> capture and separation under various conditions	<ul style="list-style-type: none"> <li>Review of ZIF-8 membranes for CO<sub>2</sub> adsorption and separation.</li> <li>Detailed analysis of ZIF-8 composite membranes for gas separation.</li> </ul>	(Gong et al., 2017)
4	This paper focuses on the historical development and industrial challenges of MOF-based membranes	<ul style="list-style-type: none"> <li>Classification of membranes and historical development of MOF-based membranes.</li> <li>Design strategies, advances, and challenges in MOF-based membranes.</li> </ul>	(Cheng et al., 2022)
5	This paper focuses on MOF fillers in mixed-matrix membranes (MMMs) for gas separation	<ul style="list-style-type: none"> <li>MMMs overcome limitations of polymeric membranes, enhancing separation performance.</li> <li>MOFs enhance stability, broaden applications in gas separation and carbon capture.</li> <li>Artificial intelligence or AI, machine learning optimizes membrane design, guide MOF-polymer selection.</li> </ul>	(Chen et al., 2023)
6	This paper focuses on biogas upgrading with MOFs, specifically targeting methane separation	<ul style="list-style-type: none"> <li>Discusses MOFs for biogas upgrading, CO<sub>2</sub> removal, and commercialization.</li> <li>Highlights progress, challenges, and future prospects of MOFs in biogas upgrading.</li> </ul>	(Khan et al., 2021)
7	This paper focuses on synthesis and modification of MOFs for carbon capture	<ul style="list-style-type: none"> <li>Detailed overview of MOFs for CO<sub>2</sub> capture and conversion.</li> <li>Synthesis methods, modifications, and performance evaluation of MOFs.</li> <li>Assessment of adsorption kinetics models and challenges faced by MOFs.</li> </ul>	(Aniruddha et al., 2020)
8	This paper focuses on MOF adsorbents and membranes for practical separation challenges	<ul style="list-style-type: none"> <li>Summary study of 70,000 MOFs structures, including IRMOFs and ZIFs.</li> <li>Fabrication of chemically stable fluorinated MOF material for gas separation.</li> <li>Review of MOF structural design advantages and related applications.</li> </ul>	(Duan et al., 2018)
9	This paper focuses on emerging microporous materials (MOFs, porous organic frameworks or POFs) for CO <sub>2</sub> separation	<ul style="list-style-type: none"> <li>Focus on MOFs, POFs, and microporous polymers for CO<sub>2</sub> separation membranes.</li> <li>Analysis of membrane performance in CO<sub>2</sub> separation under different conditions.</li> <li>Point out challenges and perspectives for future development in the field.</li> </ul>	(Prasetya et al., 2020)
10	This paper focuses on emerging 2D microporous membranes, such as g-C <sub>3</sub> N <sub>4</sub> , porous graphene oxide or PGO, MOFs, and covalent organic frameworks or COFs, for high-performance CO <sub>2</sub> capture.	<ul style="list-style-type: none"> <li>Review of membrane separation mechanism with focus on membrane materials.</li> <li>Highlight of latest research on emerging 2D microporous membranes for gas separation.</li> <li>Discussion on current challenges and future directions of 2D microporous membranes.</li> </ul>	(Dai et al., 2023)
11	This paper focuses on stability and scalability of MOF and COF-based MMMs for CO <sub>2</sub> separation.	<ul style="list-style-type: none"> <li>Overview of MOF-based MMM stability and manufacturability in non-ideal conditions.</li> <li>Analysis of COFs as fillers in MMMs for CO<sub>2</sub> separation.</li> </ul>	(Shan et al., 2024)
12	This paper focuses on polycrystalline MOF membranes for molecular separations, discussing ZIF-8 membranes, gas separations, and engineering challenges for industrial scale-up	<ul style="list-style-type: none"> <li>Summarizes MOF membrane development for gas separations.</li> <li>Reviews ZIF-8 membranes for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation.</li> <li>Discusses engineering challenges for industrial scale-up of MOF membranes.</li> </ul>	(Abdul Hamid et al., 2021)
13	This paper emphasizing nanostructured MOF-composite membranes, advanced synthesis techniques, computational modeling, and a strong focus on scalability and sustainability. The other papers provide foundational and specific insights into MOF-based materials but do not delve as deeply into the integration of nanostructuring, industrial scalability, or green synthesis as this manuscript does.	<ul style="list-style-type: none"> <li>Synthesis techniques, CO<sub>2</sub> capture mechanisms, and MOF role are elucidated.</li> <li>Economic transformation, job creation, and circular carbon economy are highlighted.</li> <li>Analysis of kinetic, thermodynamic factors, recent advancements, and challenges are discussed.</li> <li>Computational modeling, machine learning integration, and green synthesis methods are emphasized.</li> <li>MOF-composite membranes' significance in advancing CO<sub>2</sub> sequestration technologies is highlighted in this paper.</li> </ul>	This work



**Fig. 2.** Membrane-based CO<sub>2</sub> sequestration techniques. The figure illustrates the distribution of greenhouse gases, CO<sub>2</sub> mitigation technologies, membrane technologies for CO<sub>2</sub> capture, materials used in membranes, and the application of MOF-based membranes for CO<sub>2</sub> mitigation.

## 2.1. Overview of CO<sub>2</sub> capture technologies

In the effort to address the adverse effects of climate change by reducing greenhouse gas emissions, the utilization of CO<sub>2</sub> capture technologies is essential, especially in industries characterized by significant emissions like power production and manufacturing. Conventional techniques such as absorption, which involves the chemical or physical absorption of CO<sub>2</sub> using different solvents, primarily amines, are widely used but encounter issues such as substantial energy requirements for solvent reclamation and environmental hazards linked to solvent disposal (Kammerer et al., 2023; Yu et al., 2023). Adsorption, another common technique, captures CO<sub>2</sub> on solid sorbent surfaces but often struggles with capacity and selectivity, alongside regeneration issues. Cryogenic separation, effective for high-concentration CO<sub>2</sub> streams, requires substantial energy, limiting its applicability to lower concentration scenarios (Kammerer et al., 2023).

Membrane-based separation, noted for its energy efficiency and scalability, utilizes selective membranes that leverage two main mechanisms—solution-diffusion and size-sieve—to separate CO<sub>2</sub> from gas mixtures. These membranes, made from materials such as advanced polymers, ceramics, and composites, operate by allowing different gases to dissolve and diffuse at varying rates, or by physically sieving molecules based on size, effectively capturing smaller molecules like CO<sub>2</sub> (Adot Veetil et al., 2023; Ahmad et al., 2021; Tanvidkar et al., 2022; Yu et al., 2024). As pointed out in Fig. 2, available membrane-based CO<sub>2</sub> capture techniques include gas separation membrane, membrane contactor, and membrane reactor.

Recognizing the limitations of traditional methods, the scientific community is shifting towards innovative technologies that improve efficiency and reduce environmental footprints. These include advanced solvents with lower energy needs, novel sorbents with enhanced selectivity, and cutting-edge separation techniques like the integration of Metal-Organic Frameworks (MOFs) with membranes. MOFs, with their highly porous and customizable structures, offer a significant enhancement in CO<sub>2</sub> capture efficiency when combined with membrane technologies (Åhlén et al., 2023; Damas et al., 2021; Elhenawy et al., 2020;

Kammerer et al., 2023; Li et al., 2022; Qazvini et al., 2021; Trickett et al., 2017). MOF-composite membranes are potential to be applied in not only post combustion capture process, but also in pre combustion capture and direct air capture processes as depicted in Fig. 2.

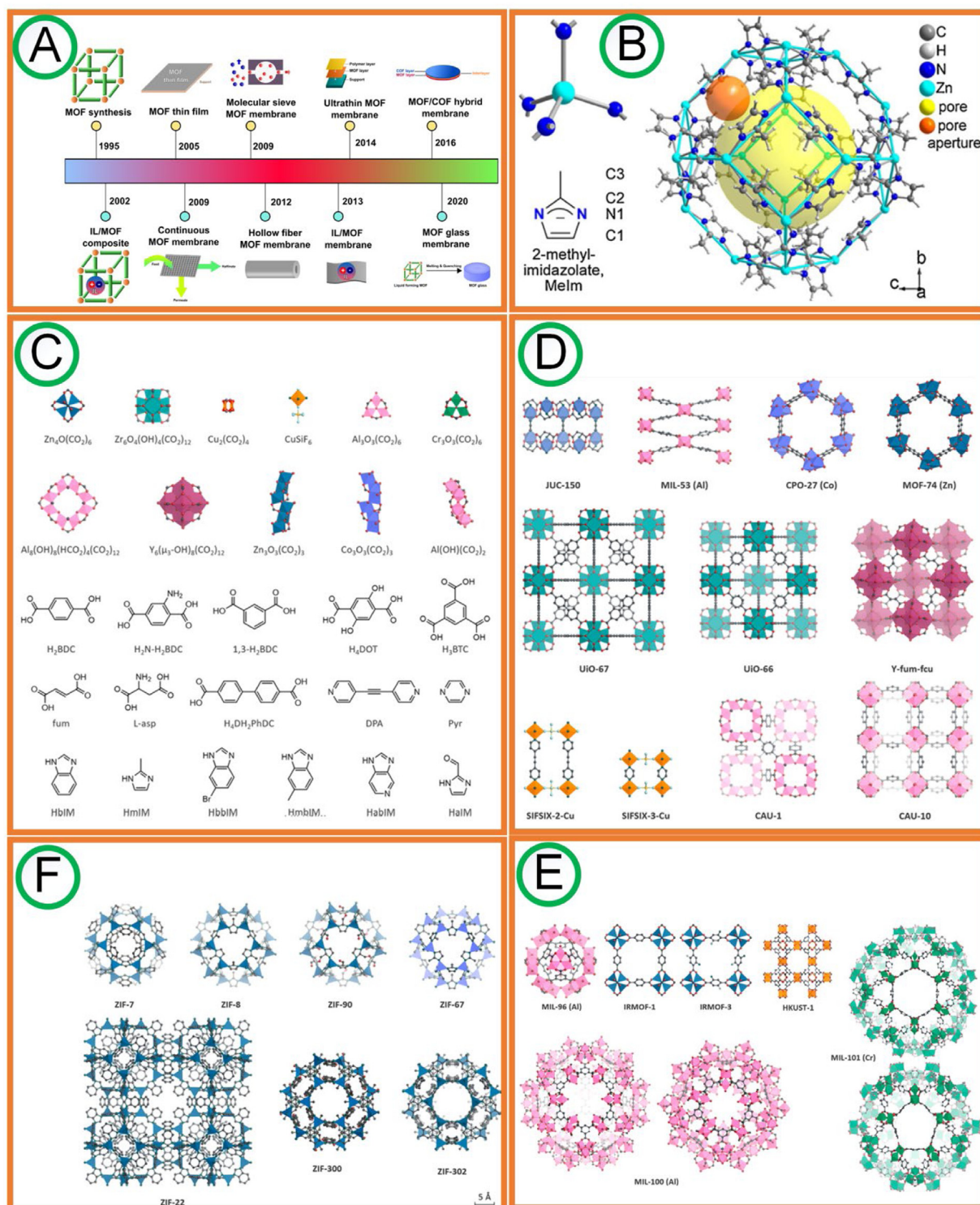
MOF-composite membranes, a novel approach in CO<sub>2</sub> capture technology, promise to revolutionize the field by synergistically enhancing the energy efficiency, selectivity, and capacity of existing methods (Adot Veetil et al., 2023; Damas et al., 2021; Elhenawy et al., 2020; Qazvini et al., 2021). This integration not only increases the efficiency of CO<sub>2</sub> capture but also marks a significant advance towards sustainable and environmentally friendly solutions, potentially offering a viable path for large-scale, effective CO<sub>2</sub> sequestration and a more sustainable future (Åhlén et al., 2023; Bernardo et al., 2009; Damas et al., 2021; Elhenawy et al., 2020; Qazvini et al., 2021; Sutrisna et al., 2017, 2020). Fig. 2 presents the CO<sub>2</sub> sequestration techniques available including MOF-composite membrane as emerging technology.

## 2.2. Metal-Organic Frameworks (MOFs) as emerging materials for CO<sub>2</sub> capture process

While conventional CO<sub>2</sub> capture technologies face limitations in energy efficiency and selectivity, the integration of advanced materials, such as MOFs, offers promising solutions. MOFs, with their tunable structures and exceptional adsorption properties, have emerged as a transformative approach to overcoming these challenges. The following section explores the potential of MOFs as next-generation materials for CO<sub>2</sub> capture, highlighting their structural advantages, functional versatility, and practical challenges.

MOFs, with their unique structural and functional characteristics, have emerged as a promising material in the area of CO<sub>2</sub> capture technologies. These compounds are crystalline in nature, comprising metal ions or clusters that are coordinated to organic ligands. This configuration results in a highly porous framework that can be tailored to specific needs (Liu et al., 2023; M. Sun et al., 2023). In addition, the selection of metals and linkers is not just a matter of structural variation but also a strategic approach to fine-tuning the properties of MOFs for optimal gas





**Fig. 3.** (A) A timeline describing the development of MOFs-membrane composite used for CO<sub>2</sub> separation (Figure A is reproduced with permission from (Demir et al., 2022)); (B)-(F) structures of MOFs commonly applied for CO<sub>2</sub> capture. Figure B is reproduced with permission from (Railey et al., 2017)); and Figure C-F are reproduced with permission from (Qian et al., 2020)). All figures showcase the development timeline, structures, and types of MOFs, highlighting their design, coordination, and applications in CO<sub>2</sub> capture and separation processes.

adsorption, especially for CO<sub>2</sub>. Fig. 3 presents several MOFs that have been used in CO<sub>2</sub> separation processes.

One of the most remarkable attributes of MOFs is their exceptionally high surface area and porosity, which facilitate an extensive interface for CO<sub>2</sub> adsorption. This characteristic is critical in enhancing the efficiency of CO<sub>2</sub> capture, as it allows for a greater volume of gas to

be adsorbed per unit of material (Duan et al., 2018; Gulbalkan et al., 2024; Sabetghadam et al., 2018). The tunability of MOFs is another significant aspect; it allows for the precise adjustment of pore sizes and the incorporation of functional groups. These modifications lead to a selective affinity for CO<sub>2</sub> molecules, enabling MOFs to target and capture CO<sub>2</sub> more effectively than other gases present in the mixture

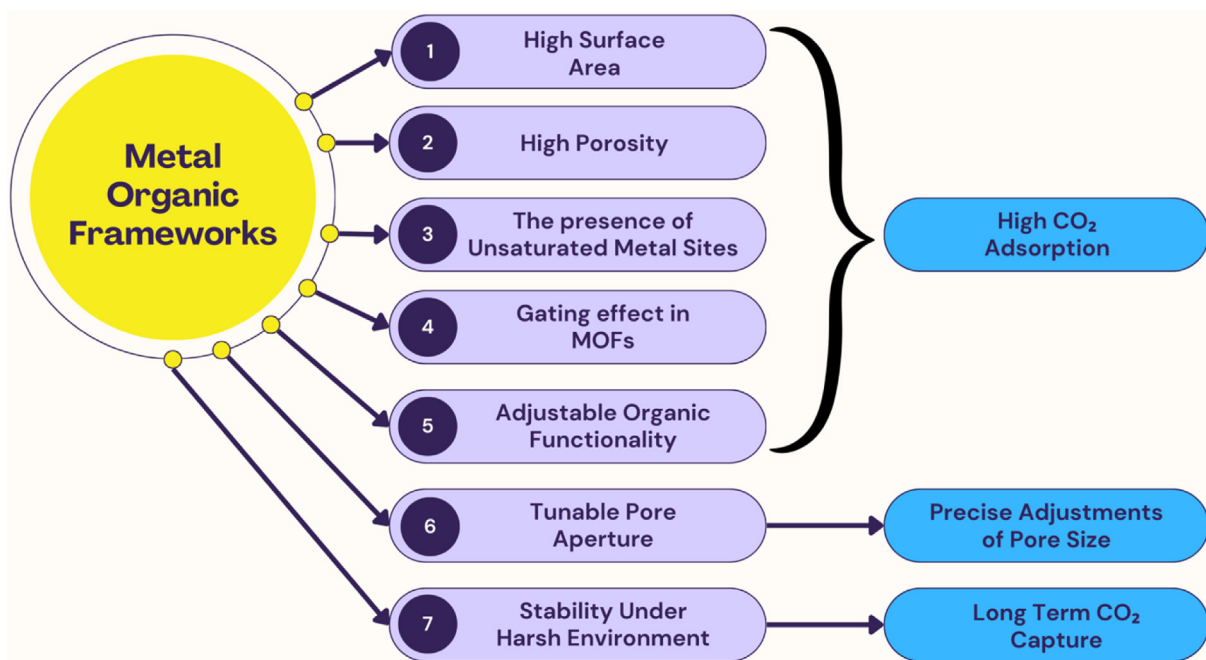


Fig. 4. Several advantages and challenges of MOFs for CO<sub>2</sub> capture. The figure highlights key properties of MOFs that enable high CO<sub>2</sub> adsorption, precise pore size adjustments, and long-term CO<sub>2</sub> capture.

(Gładysiak et al., 2018; He et al., 2020; Lan et al., 2011; Thompson et al., 2013; Wu et al., 2013). During the synthesis of certain MOFs, metal ions may coordinate with non-ligand species, such as water molecules, residual chemicals, or solvents. Upon activation through thermal treatment under dynamic vacuum or chemical processes like solvent exchange, these weakly coordinated species can be removed without destabilizing the framework. This process exposes unsaturated metal sites, which act as electron-deficient Lewis acids capable of reversible interactions with electron-rich molecules, such as CO<sub>2</sub> and hydrocarbons, enhancing the material's adsorption capacity.

Additionally, flexible MOFs represent a subset of stimuli-responsive porous crystals (SPCs) that can transition between multiple stable crystalline phases in response to external physical or chemical stimuli, including guest molecules, mechanical stress, pressure, temperature, light, and unique electrical or magnetic forces (Qian et al., 2020). Fig. 4 summarizes the pros and challenges faced by MOFs for CO<sub>2</sub> capture and separation processes. In addition to Fig. 4, one issue that needs to be considered to apply MOFs inside composite membrane is the complexity of their regeneration process. Once after the MOFs have been saturated with guest molecules, the MOFs require regeneration process to recover their adsorption capacity.

Functionalizing MOFs is essential for enhancing their stability, adsorption capacity, and CO<sub>2</sub> selectivity. By introducing specific functional groups or modifying their structure, scientists can optimize interactions with CO<sub>2</sub> molecules (Güçlü et al., 2021; Jun et al., 2022; Ma et al., 2022). For example, a Zr-based MOF, MOF-808, was functionalized with ethyleneamines like tetraethylenepentamine (TEPA), diethylenetriamine (DETA), and ethylenediamine (ED) for selective CO<sub>2</sub> capture from offgas under low pressure. TEPA was the most effective due to its low basicity. A MOF-808 functionalized with TEPA showed an ideal adsorption solution theory (IAST) selectivity of 256, about seven times higher than the pristine MOF-808, and adsorbed 2.5 times more CO<sub>2</sub> at 15 kPa. The loaded amino groups enabled Lewis acid-base interactions with CO<sub>2</sub> to form carbamates. This modification approach allows for effective CO<sub>2</sub> capture, even in MOFs without open metal sites (Jun et al., 2022).

The stability of MOFs under various environmental conditions, such as humidity and temperature, is crucial for their longevity and effectiveness in practical applications (Lan et al., 2020; Qazvini and Telfer, 2021, 2020; Shi et al., 2020; Ullah et al., 2020). A novel Zn-based three-dimensional framework, Zn(Py)(Atz), demonstrated outstanding stability and performance, with a BET surface area of 764.5 m<sup>2</sup>.g<sup>-1</sup> and a pore volume of 0.32 cm<sup>3</sup>.g<sup>-1</sup>. It exhibited a CO<sub>2</sub> sorption capacity of 52.3 cm<sup>3</sup>.g<sup>-1</sup> at 273 K and achieved a 92.1% propylene carbonate yield with 98% selectivity under mild conditions (60°C, 1.5 MPa). Zn(Py)(Atz) maintained excellent stability in water and in acidic and basic solutions (pH 2–14 for 72 hours) and could be recycled seven times with minimal loss in efficiency (Lan et al., 2020).

Construction of thermally and chemically robust MOFs is essential for post-combustion CO<sub>2</sub> capture from flue gas containing water vapor and acidic gases. By appending amino groups to triazolate linkers, these MOFs exhibit exceptional stability against aqueous, acidic, and basic conditions, with a CO<sub>2</sub>/N<sub>2</sub> thermodynamic adsorption selectivity of 120 and a CO<sub>2</sub>/H<sub>2</sub>O kinetic adsorption selectivity of 70. The best-performing MOF in this series features low regeneration energy, high CO<sub>2</sub> capture utility under humid conditions, and robust cycling performance (Shi et al., 2020).

The incorporation of MOFs into membrane technologies represents a significant leap forward. MOF-embedded membranes can potentially transform CO<sub>2</sub> separation technologies by providing higher selectivity and permeability, addressing limitations such as low throughput and reduced separation efficiency (Anastasiou et al., 2018; Fan et al., 2022; Ferreira et al., 2021; Liu et al., 2023). For instance, new composite materials made of bromide-based ionic liquids (ILs) and MOF MIL-101(Cr) were produced, resulting in powdered composites [PMIM][Br]@MIL-101(Cr) and [BMIM][Br]@MIL-101(Cr). These composites were incorporated into mixed matrix membranes (MMMs) using Matrimid®5218 as the polymeric matrix, with different filler loadings (10, 20, and 30 wt%). Single-gas permeation experiments at 303 K showed that Matrimid®5218/MIL-101(Cr) membranes exhibited superior CO<sub>2</sub> permeability compared to Matrimid®5218/[BMIM][Br]@MIL-101(Cr) membranes. The best CO<sub>2</sub>/N<sub>2</sub> selectivity was achieved with a

20 wt% filler loading, highlighting an optimum loading for membrane performance. Despite the incorporation of ILs reducing gas adsorption capacity and selectivity in powdered composites, the mechanical properties of the MMMs were enhanced by the presence of ILs in the composite fillers (Ferreira et al., 2021).

However, the journey from laboratory to industry is not without challenges. The environmental impact and economic feasibility of utilizing MOFs on a large scale are critical considerations. The synthesis process, scalability, life cycle analysis, and reusability of MOFs must be critically evaluated to ensure that their application in CO<sub>2</sub> capture is both environmentally sustainable and economically viable (Chen et al., 2024; Rasmussen et al., 2020; Rogacka et al., 2021). MOFs present a highly versatile and efficient solution for CO<sub>2</sub> capture, but their practical application necessitates a comprehensive understanding of their properties and challenges.

### 2.3. The integration of MOFs with membrane technology

Building on the exceptional properties of MOFs for CO<sub>2</sub> capture, their integration with membrane technologies has emerged as a groundbreaking approach to enhancing separation performance. By combining the high selectivity and tunability of MOFs with the permeability and robustness of membranes, MOF-based composites address limitations in conventional CO<sub>2</sub> capture systems. The next section explores recent advancements in MOF-membrane integration, focusing on fabrication techniques, performance improvements, and challenges associated with practical applications.

Recent advancements in integrating MOFs with membrane technology, a synergistic combination promising to revolutionize CO<sub>2</sub> sequestration efficiency, highlight innovative design and advanced fabrication techniques of MOF-composite membranes (Fakoori et al., 2021; Goh et al., 2022). Additionally, the exceptional surface areas, customizable pore structures, and chemically functionalizable frameworks of MOFs are intricately combined with the selective permeability and mechanical robustness of membranes (Goh et al., 2022; Jaffar et al., 2022).

The mechanisms of this integration are thoroughly examined, discussing various strategies for embedding MOFs within membranes or coating them on membrane surfaces. This includes an analysis of how these methods affect gas separation performance, CO<sub>2</sub> capture efficiency, and the overall stability of the composite system (Fakoori et al., 2021; Goh et al., 2022). A significant focus is placed on the interface engineering between MOFs and membrane materials. Critical challenges such as achieving uniform MOF dispersion within the membrane matrix, optimizing interfacial adhesion, and ensuring the structural and chemical integrity of the MOFs during processing are addressed (Goh et al., 2022). Recent advancements in nanoengineering and surface chemistry modifications have led to improved compatibility and enhanced performance of the composites as presented in Table 2. In terms of membrane systems, MOFs have been incorporated either as pure thin film on the surface of porous polymeric or inorganic substrate or as filler inside polymer matrix to form mixed matrix membranes. The illustrated gas separation mechanisms through different types of membranes are presented in Fig. 5.

One study investigated modulated UiO-66-based MMMs, finding that a 30 wt% loading showed excellent CO<sub>2</sub>/CH<sub>4</sub> separation performance. The use of amine-functionalized linkers and a modulator significantly enhanced CO<sub>2</sub> transport, increasing mixed gas selectivity and permeability. The stability of the membranes was ensured through covalent linking between fillers and Matrimid (M. Waqas Anjum et al., 2015). Similarly, chemical functionalization of NUS-8 in a NUS-8-CO<sub>2</sub>H/PIM-1 MMM led to a threefold increase in CO<sub>2</sub>/N<sub>2</sub> selectivity and a high CO<sub>2</sub> permeability of 6700 Barrer, as predicted by simulations. This enhancement is attributed to the improved interface between the MOF and the polymer matrix (Dong Li Fan et al., 2022). Surface modification strategies also showed promising results. For instance, a surface-modified UiO-66-NH<sub>2</sub> MOF in a Pebax matrix exhibited a CO<sub>2</sub> perme-

ability of 247 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 56.1 with just 1 wt% loading of PIM-grafted-MOF (Asmaul Husna et al., 2022).

Another study on UiO-66(Hf)-(OH)<sub>2</sub> MOF nanoparticles demonstrated enhanced H<sub>2</sub>/CO<sub>2</sub> separation, achieving excellent H<sub>2</sub> permeability with a 10 wt% loading. These nanoparticles were synthesized via a modulated hydrothermal process and evaluated through mixed-gas permeation tests (Zhigang Hu et al., 2016). Rapid fabrication techniques have led to MMMs with a fourfold enhancement in CO<sub>2</sub> permeability, reaching 2490 Barrer, while maintaining long-term stability and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 37. These membranes were constructed using confined swelling coupled with solvent-controlled crystallization (Shuo Li et al., 2023). Additionally, the encapsulation of ionic liquids (IL) in MOFs was shown to enhance stability under humid conditions, achieving a CO<sub>2</sub> permeability of 13,778 Barrer and a CO<sub>2</sub>/N<sub>2</sub> separation factor of approximately 35.2 (Chenxu Geng et al., 2023).

Thermal cross-linking of NH<sub>2</sub>-UiO-66 with a COOH-PI (polyimide) matrix has improved membrane stability and performance, enhancing mechanical strength and reducing CO<sub>2</sub> plasticization (Zhengong Wang et al., 2021). In another study, NH<sub>2</sub>-MIL-53(Al) MOF incorporated into MMMs enhanced CO<sub>2</sub> permeability while maintaining high separation factors. Techniques such as fast solvent removal and structural analysis using XRD and FIB-SEM were used to optimize the MOF structure and separation performance (Rodenas et al., 2014).

Incorporation of ZIF-8 nanoparticles into a PVAm matrix improved CO<sub>2</sub>/N<sub>2</sub> separation performance, achieving higher gas permselectivity with thinner selective layers. Techniques like X-ray diffraction and SEM were utilized to characterize the chemical structure and nanoparticle dispersion (Song Zhao et al., 2015). Similarly, incorporating podlike PSS-ZIF fillers into Pebax enhanced CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity by 96% and 44% respectively, facilitating efficient CO<sub>2</sub> transport through 1D and 3D pathways (Chao Liang et al., 2023).

Highly oriented Zr-MOF membranes prepared using anisotropic etching and confined contra-diffusion strategies exhibited unprecedented CO<sub>2</sub> separation performance, surpassing polycrystalline MOF membranes in CO<sub>2</sub> permeance and selectivity (Yanwei Sun et al., 2023). A zeolite-like MOF membrane with an ana topology provided optimal pore energetics for CO<sub>2</sub> capture, showing high selectivity for butane/isobutane and effective reverse CO<sub>2</sub>/H<sub>2</sub> separation (Valeriya Chernikova et al., 2023).

Combining MOFs with ILs in composite membranes has enhanced CO<sub>2</sub> separation technology by managing the trade-off between permeability and selectivity, resulting in improved compatibility and interface between the MOF and polymeric membrane (Megawati Zunita et al., 2022). Rapid heat treatment (RHT) at 360°C has improved CO<sub>2</sub> separation performance in ZIF-8 membranes, achieving unprecedented selectivities for CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, and H<sub>2</sub>/CH<sub>4</sub> (Deepu J. Babu et al., 2019).

The solvent-free space-confined conversion (SFSC) approach has enabled the fabrication of free-standing MOF membranes with high H<sub>2</sub>/CO<sub>2</sub> selectivities and permeances, achieving an H<sub>2</sub> permeance of 2653.7 GPU and an H<sub>2</sub>/CO<sub>2</sub> selectivity of 17.1 (Zhuangzhuang Gao et al., 2023). Similarly, the 2D Ni<sub>3</sub>(HITP)<sub>2</sub> MOF membrane fabricated via a contra-diffusion method showed excellent CO<sub>2</sub> permeance and selective permeability over N<sub>2</sub>/CH<sub>4</sub>, with CO<sub>2</sub> permeance of  $1.59 \times 10^{-6}$  mol m<sup>2</sup> s<sup>-1</sup> Pa<sup>-1</sup> and CO<sub>2</sub>/N<sub>2</sub> selectivity of 10.2 (Shuangshuang Jiang et al., 2021). Lastly, ultrathin nanosheet membranes with low-dose amino side groups in Zn<sub>2</sub>(benzimidazolate)<sub>4</sub> have achieved high-speed H<sub>2</sub> transport and precise CO<sub>2</sub> separation, with a mixture separation factor of 1158 and H<sub>2</sub> permeance of 1417 GPU, optimizing H<sub>2</sub>/CO<sub>2</sub> separation (Hongling Song et al., 2023).

The integration of MOFs with membrane technologies has demonstrated significant advancements in enhancing CO<sub>2</sub> separation performance through innovative fabrication and interface engineering. To fully understand the efficiency of these systems, it is essential to explore the underlying mechanisms governing CO<sub>2</sub> capture and separation in MOF-composite membranes. The following section delves into these mechanisms, including solution-diffusion, molecular sieving, and facili-



**Table 2**  
Selected experimental study on MOF-based nanostructured membranes.

No	Insights	Gas separation performance	Methods Used	Key findings	Reference
1	The study focused on the application of modulated UiO-66-based MMMs for CO <sub>2</sub> /CH <sub>4</sub> separation.	CO <sub>2</sub> permeability (PCO <sub>2</sub> ) = 37.9 Barrer CO <sub>2</sub> /CH <sub>4</sub> selectivity = 47.7 Polymer matrix: Matrimid 9725 Feed pressure: 9 bar	<ul style="list-style-type: none"> <li>Modulation approach with amine-functionalized linkers used for MOF synthesis</li> <li>Covalent linking between fillers and Matrimid for stable membranes</li> </ul>	<ul style="list-style-type: none"> <li>Fillers often lack interfacial compatibility with polymer matrix in MMMs.</li> <li>Modulation of MOFs enhances CO<sub>2</sub> transport in MMMs.</li> </ul>	(M. Waqas Anjum et al., 2015)
2	Another study utilizing modified UiO-66-NH <sub>2</sub> MOF in Pebax polymer matrix to enhance CO <sub>2</sub> transport.	PCO <sub>2</sub> = 247 Barrer CO <sub>2</sub> /CH <sub>4</sub> selectivity = 17 CO <sub>2</sub> /N <sub>2</sub> selectivity = 56.1 Polymer matrix: Pebax Feed pressure: 1 bar	<ul style="list-style-type: none"> <li>Surface-modification strategy for MOF through polymer grafting</li> <li>Engineering MOF-polymer interface in MMMs using Pebax support</li> </ul>	<ul style="list-style-type: none"> <li>Developed a new MMM with PIM-PI-functionalized UiO-66 MOF for CO<sub>2</sub> separation.</li> <li>Used Pebax as a support layer for improved separation performance.</li> </ul>	(Asmaul Husna et al., 2022)
3	Research focused on the application of UiO-66(Hf)-(OH) <sub>2</sub> MOF membranes for CO <sub>2</sub> capture.	PCO <sub>2</sub> = 0.42 Barrer H <sub>2</sub> /CO <sub>2</sub> selectivity = 19.37 Polymer matrix: Polybenzimidazole Feed pressure: 2 - 5 bar	<ul style="list-style-type: none"> <li>Modulated hydrothermal synthesis of UiO-66(Hf)-(OH)<sub>2</sub> MOF nanoparticles</li> <li>Mixed-gas permeation tests for H<sub>2</sub>/CO<sub>2</sub> separation performance evaluation</li> </ul>	<ul style="list-style-type: none"> <li>High-quality MMMs achieved by reducing inorganic filler particle size.</li> <li>Effective modulated hydrothermal synthesis of UiO-66(Hf)-(OH)<sub>2</sub> MOFs.</li> </ul>	(Zhigang Hu et al., 2016)
4	Study focused on rapid fabrication of high-permeability ZIF-8/PEO-based mixed matrix membranes.	PCO <sub>2</sub> = 2490 Barrer CO <sub>2</sub> /N <sub>2</sub> selectivity = 37 Polymer matrix: Polyethylene oxide Feed pressure: 1 - 15 bar	<ul style="list-style-type: none"> <li>Confined swelling coupled solvent-controlled crystallization</li> <li>Rapid construction of defect-free freeway channels for CO<sub>2</sub> transportation</li> </ul>	<ul style="list-style-type: none"> <li>Rapid construction of defect-free freeway channels for CO<sub>2</sub> transportation</li> <li>Fourfold enhancement in CO<sub>2</sub> permeability with long-term stability</li> </ul>	(Shuo Li et al., 2023)
5	The application of mixed matrix MOF membranes with ionic liquid combined with UiO(IL-UiO) for CO <sub>2</sub> separation.	PCO <sub>2</sub> = 13,778 Barrer CO <sub>2</sub> /N <sub>2</sub> selectivity = 35.2 Polymer matrix: Polymer with intrinsic microporosity-1 (PIM-1)	<ul style="list-style-type: none"> <li>Encapsulation of hydrophobic ionic liquid into MOFs</li> <li>Use of polymer of intrinsic microporosity-1 (PIM-1) as matrix</li> </ul>	<ul style="list-style-type: none"> <li>Encapsulation of hydrophobic ionic liquid into MOFs for stable gas separation.</li> <li>Improved CO<sub>2</sub>/N<sub>2</sub> separation performance and stability under humid conditions.</li> </ul>	(Chenxu Geng et al., 2023)
6	Focused of this research was the application of modified UiO-66 based membranes to increase anti-plasticization of membrane during CO <sub>2</sub> capture process.	PCO <sub>2</sub> = 995 Barrer CO <sub>2</sub> /CH <sub>4</sub> selectivity = 25.4 Polymer matrix: Polyimide or PI Feed pressure: 4 bar	<ul style="list-style-type: none"> <li>Thermal cross-linking of NH<sub>2</sub>-UiO-66 with COOH-PI matrix</li> <li>Formation of amide bond at interface under mild conditions</li> </ul>	<ul style="list-style-type: none"> <li>Cross-linking MOFs/PI improves membrane stability and performance.</li> <li>Enhanced mechanical strength, reduced CO<sub>2</sub> plasticization, improved gas separation.</li> </ul>	(Zhengcong Wang et al., 2021)
7	Study focused on NH <sub>2</sub> -MIL-53(Al) MOF mixed matrix membranes for CO <sub>2</sub> capture.	PCO <sub>2</sub> = > 14 Barrer CO <sub>2</sub> /CH <sub>4</sub> selectivity = > 37 Polymer matrix: Polyimide or PI Feed pressure: 3 - 12 bar	<ul style="list-style-type: none"> <li>FIB-SEM for spatial distribution of MOF filler in matrix</li> <li>XRD for MOF powder and membrane structural analysis</li> </ul>	<ul style="list-style-type: none"> <li>Low pressure adsorption isotherm shows complete reversibility.</li> <li>Structural features of MMMs determine mechanical properties and performance.</li> </ul>	(Rodenas et al., 2014)
8	The application of PVAm/ZIF-8-based MMMs for CO <sub>2</sub> /N <sub>2</sub> separation. - ZIF-8 nanoparticles enhanced gas permselectivity in PVAm matrix.	CO <sub>2</sub> permeance = 297 Gas permeation unit (GPU) CO <sub>2</sub> /N <sub>2</sub> selectivity = 83 Polymer matrix: poly-(vinylamine) or (PVAm) Feed pressure: 1.1 bar	<ul style="list-style-type: none"> <li>X-ray diffraction and FTIR for chemical structure characterization</li> <li>SEM for observing dispersion of nanoparticles in polymer matrix</li> </ul>	<ul style="list-style-type: none"> <li>Trade-off between selectivity and permeability in polymer membranes</li> <li>Challenges in fabricating defect-free mixed-matrix membranes</li> </ul>	(Song Zhao et al., 2015)
9	Study focused on synthesis and application of Pebax/PSS-ZIF mixed matrix membranes for CO <sub>2</sub> /CH <sub>4</sub> separation.	PCO <sub>2</sub> = 528 Barrer CO <sub>2</sub> /CH <sub>4</sub> selectivity = 36 Polymer matrix: Copolymer Pebax-1657 Feed pressure: 2 - 8 bar	<ul style="list-style-type: none"> <li>Design of nanosized podlike fillers (PSS-ZIF) for MMMs</li> <li>Incorporation of PSS-ZIF into Pebax for CO<sub>2</sub>/CH<sub>4</sub> separation</li> </ul>	<ul style="list-style-type: none"> <li>Podlike PSS-ZIF fillers enhance CO<sub>2</sub> permeability and selectivity in MMMs.</li> <li>1D and 3D transport pathways expedite CO<sub>2</sub> transport in MMMs.</li> </ul>	(Chao Liang et al., 2023)
10	Experimental study on the synthesis of highly oriented Zr-MOF membrane for CO <sub>2</sub> separation.	CO <sub>2</sub> permeance = 1230 GPU H <sub>2</sub> /CO <sub>2</sub> selectivity = 41.3	<ul style="list-style-type: none"> <li>Anisotropic etching strategy for preparing 40 nm-thick UiO-66 nanosheets seeds</li> <li>Confined contra-diffusion during epitaxial growth for membrane preparation</li> </ul>	<ul style="list-style-type: none"> <li>Prepared highly oriented sub-200-nm-thick Zr-MOF membranes with unprecedented separation performances.</li> <li>Achieved superior CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity surpassing polycrystalline membranes.</li> </ul>	(Yanwei Sun et al., 2023)

(continued on next page)



Table 2 (continued)

No	Insights	Gas separation performance	Methods Used	Key findings	Reference
11	Study focused on the synthesis and application of Zeolite-like MOF membrane for reverse CO <sub>2</sub> /H <sub>2</sub> separation.	PCO <sub>2</sub> = 2919 Barrer CO <sub>2</sub> /H <sub>2</sub> selectivity = 88 Feed pressure: 1.5 bar	<ul style="list-style-type: none"> <li>Fabrication of defect-free membrane based on zeolite-like MOF</li> <li>Utilization of ana-ZMOF structure for gas transport efficiency</li> </ul>	<ul style="list-style-type: none"> <li>Defect-free membrane based on zeolite-like MOF with ana topology</li> <li>Optimum pore size for butane/isobutane selectivity and CO<sub>2</sub>/H<sub>2</sub> separation</li> </ul>	(Valeriya Chernikova et al., 2023)
12	Synthesis of polycrystalline ZIF-8 membrane for CO <sub>2</sub> capture.	CO <sub>2</sub> permeance = $4 \times 10^{-8}$ mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> CO <sub>2</sub> /CH <sub>4</sub> selectivity = 34 CO <sub>2</sub> /N <sub>2</sub> selectivity = 37.3 Feed pressure: 1 bar	<ul style="list-style-type: none"> <li>Rapid heat treatment (RHT) at 360°C</li> <li>Spectroscopic and X-ray diffraction studies</li> </ul>	<ul style="list-style-type: none"> <li>Rapid heat treatment improves CO<sub>2</sub> separation performance in ZIF-8 membranes.</li> <li>Lattice stiffening enhances gas separation selectivities in MOF membranes.</li> </ul>	(Deepu J. Babu et al., 2019)
13	An experimental study on the synthesis of free-standing MOF membranes with high H <sub>2</sub> /CO <sub>2</sub> selectivity.	ZIF-8 membrane: H <sub>2</sub> permeance 2653.7 GPU H <sub>2</sub> /CO <sub>2</sub> selectivity = 17.1 Zn(EtIm) <sub>2</sub> membrane: H <sub>2</sub> /CO <sub>2</sub> selectivity 22.1 H <sub>2</sub> permeance 6268.7 GPU	<ul style="list-style-type: none"> <li>Solvent-free space-confined conversion (SFSC) approach</li> <li>Fabrication of free-standing MOF membranes without solvents or supports</li> </ul>	<ul style="list-style-type: none"> <li>Solvent-free space-confined conversion (SFSC) approach for MOF membrane fabrication</li> <li>Free-standing MOF membranes with high selectivities and permeances</li> </ul>	(Zhuangzhuang Gao et al., 2023)
14	Focused on 2D Ni <sub>3</sub> (HITP) <sub>2</sub> MOF membrane for CO <sub>2</sub> separation.	CO <sub>2</sub> permeance: $1.59 \times 10^{-6}$ mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> CO <sub>2</sub> /N <sub>2</sub> selectivity= 10.2 CO <sub>2</sub> /CH <sub>4</sub> selectivity = 6.9	<ul style="list-style-type: none"> <li>Fabrication of 2D MOF membranes via contra-diffusion method</li> </ul>	<ul style="list-style-type: none"> <li>Fabrication of high-quality 2D MOF membranes via contra-diffusion method</li> <li>Membrane shows excellent CO<sub>2</sub> permeance and selective permeability over N<sub>2</sub> and CH<sub>4</sub></li> </ul>	(Shuangshuang Jiang et al., 2021)
15	A study on the synthesis of ultrathin nanosheet membrane with low dose amino side groups in Zn <sub>2</sub> (benzimidazolate) <sub>4</sub> for CO <sub>2</sub> capture.	H <sub>2</sub> permeance: 1417 GPU H <sub>2</sub> /CO <sub>2</sub> selectivity = 1158 Feed pressure: 1 bar	<ul style="list-style-type: none"> <li>Low dose amino side groups introduced</li> <li>Physisorbed CO<sub>2</sub> used as interlayer linkers</li> </ul>	<ul style="list-style-type: none"> <li>Introduction of low dose amino side groups into the Zn<sub>2</sub>(benzimidazolate)<sub>4</sub> conformation</li> <li>Optimization of amino membranes for ultrathin nanosheet membranes in H<sub>2</sub>/CO<sub>2</sub> separation</li> </ul>	(Hongling Song et al., 2023)

1 Barrer =  $10^{-10}$  cm<sup>3</sup>[STP] cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup> or  $3.35 \times 10^{-16}$  mol m m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>

1 GPU =  $10^{-6}$  cm<sup>3</sup>[STP] cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup> or  $3.348 \times 10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>

tated transport, which collectively contribute to the superior selectivity and permeability of MOF-based membranes.

#### 2.4. The mechanisms of CO<sub>2</sub> capture in membrane-MOF systems

The mechanism of CO<sub>2</sub> capture and separation in MOF-composite membranes is a complex interplay of various processes that synergistically enhance both the selectivity and permeability of CO<sub>2</sub> compared to other gases. In general, MOF-composite membranes can be categorized into MOF-based mixed matrix membrane (MMM) and MOF-based thin film membrane grown on a porous substrate. The gas separation mechanisms in MOF-based MMMs are dominated by solution – diffusion mechanism and facilitated transport mechanism (Dechnik et al., 2017; Katare et al., 2023; Niu et al., 2024). On the other hand, the gas separation mechanisms through MOF-based thin film membranes can be explained by molecular sieving and adsorption mechanisms (Ahmad et al., 2021; Bétard and Fischer, 2012; Shekhah et al., 2011; Zulkifli et al., 2022).

##### 2.4.1. Solution – diffusion mechanism

The solution-diffusion mechanism depends on differences in kinetic diameters and condensation properties of gas molecules. It involves three main steps: (a) adsorption of gas molecules on the membrane surface, (b) diffusion through the membrane, and (c) desorption on the low-pressure side. The driving force behind this process is the pressure gradient across the membrane, alongside other interactive forces. To assess membrane performance, gas permeability and selectivity are key factors to measure (Niu et al., 2024; Reddy et al., 2024; Tanh Jeazet et al., 2012).

This mechanism can be examined in terms of both dissolution selectivity and diffusion selectivity. Dissolution selectivity is improved through the incorporation of polar functional groups, while diffusion selectivity benefits from the pore structure of porous fillers that offer channels for gas movement. Proper pore size reduces diffusion resistance, speeding up molecular diffusion and enhancing selectivity (Niu et al., 2024). Additionally, the interaction between the polymer matrix and the filler at their interface strengthens both diffusion and overall membrane selectivity, particularly when the polymer matrix adheres strongly to the filler, leading to a stiffened structure on the surface of the filler.

Size-based separation also plays a crucial role in gas separation processes, particularly through the use of MOFs. The unique pore structures of MOFs selectively allow the passage of smaller gas molecules like CO<sub>2</sub> while restricting larger ones. This is especially effective in MOFs with pore sizes close to the kinetic diameter of CO<sub>2</sub> (3.3 Å). For instance, ZIF-8, with a pore aperture of 3.4 Å, has been widely incorporated into composite membranes for CO<sub>2</sub> separation, as demonstrated in studies showing significant improvements in both permeability and selectivity compared to pure Matrimid® membranes (Bano et al., 2020).

Furthermore, diffusion-based separation is enhanced in MMMs, where the incorporation of MOFs into polymer matrices creates additional pathways for gas transport. The interfacial voids and increased free volume within the membrane facilitate faster diffusion of CO<sub>2</sub> molecules. This was observed in MOF-801 incorporated PEBA mixed-matrix membranes, where the addition of MOF-801 improved both gas selectivity and permeability compared to pure Pebax membranes (Sun et al., 2019).

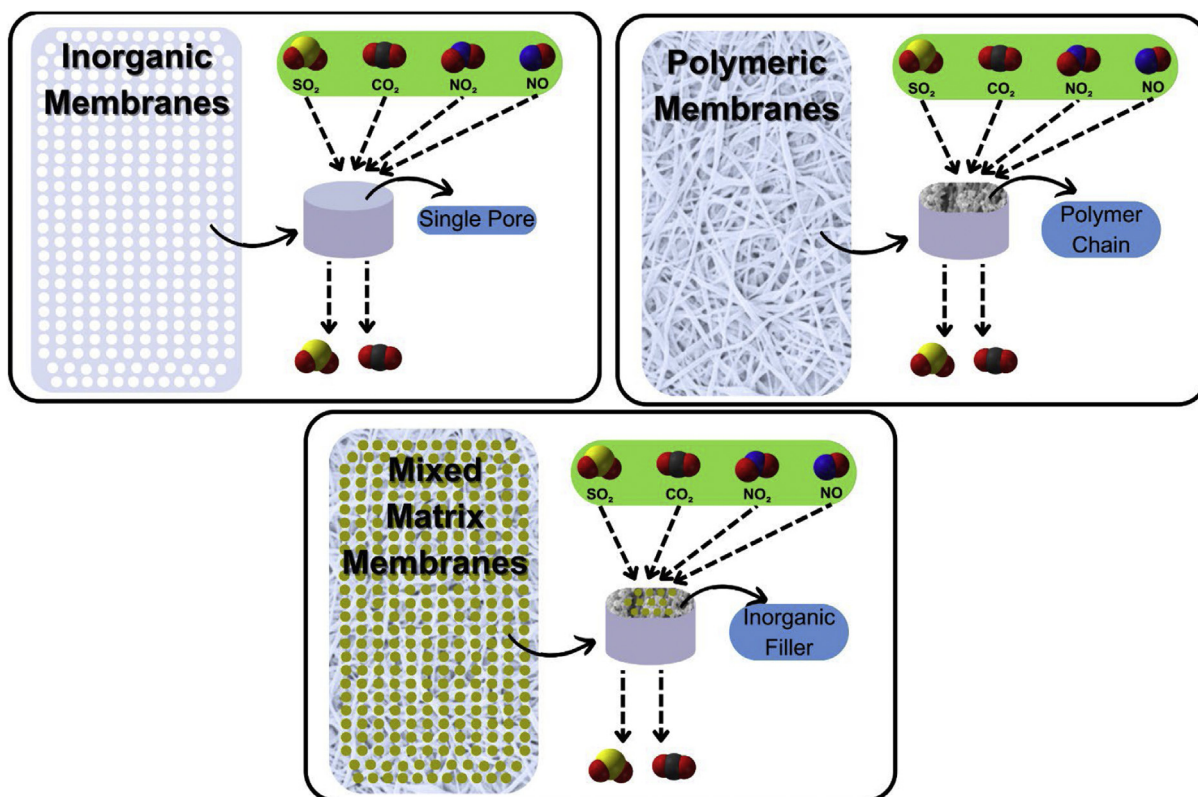


Fig. 5. Gas separation mechanism through different types of membranes. Gas molecules diffuse through (a) single pore of inorganic membrane, (b) polymer chain of polymeric membrane, and (c) inorganic filler of mixed-matrix membrane (MMM). The figure compares inorganic, polymeric, and MMM based on their structures and gas separation mechanisms for  $\text{CO}_2$  and other gases.

#### 2.4.2. Molecular sieving mechanism

The incorporation of inorganic fillers with a well-defined porous structure significantly enhances gas separation performance through the molecular sieving mechanism. This mechanism relies on the precise control of pore sizes within the filler material, allowing for selective gas transport based on their kinetic diameters (Katare et al., 2023). Specifically, when the pore diameter of the filler lies between the kinetic diameters of the gases in the mixture, only gases with a smaller kinetic diameter can pass through the membrane, while those with a larger diameter are effectively blocked. This selective transport is essential for achieving high separation efficiency in mixed matrix membranes (MMMs). One of the critical factors in the success of this mechanism is the small variance in the kinetic diameters of gases, particularly  $\text{CO}_2$  compared to other gases like  $\text{N}_2$  or  $\text{CH}_4$ . Given that these differences are minimal, the pore diameter must be controlled to match the specific requirements of the gas mixture being processed. If the pore size is not carefully tailored, the membrane's selectivity could be compromised, leading to inefficient separation (Katare et al., 2023; Wu et al., 2023).

To achieve the desired separation efficiency, microporous materials with finely controlled pore size distributions are commonly employed as fillers in MMMs. MOFs materials are particularly effective due to their molecular-scale pore sizes and uniform distribution of these pores. These materials exhibit the capability to selectively transport smaller gas molecules while restricting the passage of larger ones, thereby enhancing the overall selectivity of the membrane (Crivello et al., 2021, 2021; Shekhah et al., 2011). The use of such materials allows for the fine-tuning of the membrane's separation characteristics, making them highly suitable for challenging gas separation tasks like  $\text{CO}_2$  capture and separation from natural gas or flue gases. As a result, MMMs incorporating microporous fillers offer a promising solution for applications where both high selectivity and permeability are required, such as in energy-efficient gas separation technologies.

#### 2.4.3. Facilitated transport and other mechanisms

Adsorption-based capture is a fundamental mechanism in MOF-composite membranes, leveraging the high surface area and porous structure of MOFs to provide numerous adsorption sites for  $\text{CO}_2$  molecules. This process involves both physisorption and chemisorption, with the latter occurring at specific functional groups or open metal sites within the MOF structure. The effectiveness of this mechanism is demonstrated in various MOF-composite membranes. For instance, a study on copolymer Pebax/MOF composite membranes showed that incorporating UiO-66 into Pebax at 5% loading resulted in a  $\text{CO}_2/\text{N}_2$  selectivity of 85.94 and a  $\text{CO}_2$  permeability of 189.77 Barrer, surpassing Robeson's Upper bound from 2008 (Tang et al., 2021).

In contrast to the solution-diffusion mechanism, the facilitated transfer mechanism is widely applied in membranes designed for  $\text{CO}_2$  separation by leveraging differences in gas reactivity. This mechanism operates by introducing specific sites within the membrane that interact with  $\text{CO}_2$ , enhancing its transport through the membrane. This facilitated transfer occurs via a reversible reaction between  $\text{CO}_2$  and the carrier within the membrane, allowing for selective separation. While other gases pass through the membrane via the dissolution-diffusion process, only  $\text{CO}_2$  reacts with the carrier, leading to enhanced selectivity and permeability (Katare et al., 2023; Niu et al., 2024). Studies on molecular transfer within biological membranes have shown that incorporating a carrier can significantly improve the transport of a specific gas component. In facilitated transport membranes,  $\text{CO}_2$  separation surpasses the typical trade-offs between permeability and selectivity, often exceeding the Robeson upper bound (Niu et al., 2024).

Chemical affinity-based separation further enhances  $\text{CO}_2$  capture in MOF-composite membranes. Certain MOFs possess strong chemical affinity towards  $\text{CO}_2$  due to specific functional groups or metal sites within their structure. This affinity can be enhanced through functionalization. For example, an amine-functionalized UiO-66 (UiO-66-NH<sub>2</sub>)

embedded in a Pebax matrix demonstrated superior CO<sub>2</sub> capture performance compared to its non-functionalized counterpart, highlighting the role of functional groups in boosting CO<sub>2</sub> affinity (Tang et al., 2021).

Facilitated transport has been utilized in some advanced MOF-composite membranes to significantly improve CO<sub>2</sub> separation. Specific functional groups or metal sites in the MOFs act as carriers, forming reversible complexes with CO<sub>2</sub>, thus facilitating its transport across the membrane. A noteworthy example is the use of core/shell Nylon 6,6/La-TMA MOF nanofiber composite membranes, which achieved a CO<sub>2</sub> adsorption capacity of 0.219 mmol g<sup>-1</sup>. Interestingly, the pure La-TMA MOF demonstrated an even higher CO<sub>2</sub> adsorption capacity of 0.277 mmol g<sup>-1</sup>, further emphasizing the efficiency of MOFs in facilitated transport mechanisms (Fateminia et al., 2023).

To summarize, the superior CO<sub>2</sub> capture and separation performance of MOF-composite membranes results from the synergistic combination of these mechanisms. As research in this field continues to advance, it is likely that even more efficient MOF-composite membranes will be developed, potentially revolutionizing CO<sub>2</sub> capture and separation technologies and contributing significantly to global efforts to mitigate climate change.

The progression from conventional CO<sub>2</sub> capture technologies to advanced MOF materials and their integration with membranes highlights a paradigm shift in separation processes. MOF-composite membranes combine the tunable adsorption properties of MOFs with the selective permeability of membranes, significantly enhancing CO<sub>2</sub> capture performance. Building on the mechanisms and design strategies explored earlier, the next section focuses on the practical advancements, synthesis techniques, and challenges in developing membrane-MOF composites as a scalable solution for industrial CO<sub>2</sub> separation.

### 3. CO<sub>2</sub> Separation Enhancement of MOF-composite membranes

The integration of membrane and Metal-Organic Framework (MOF) composites represents a notable advancement in CO<sub>2</sub> separation technologies, offering significant improvements in capture efficiency. By merging the selective permeability of membranes with the high adsorption capacity and structural versatility of MOFs, these composites enhance both the permeability and selectivity for CO<sub>2</sub>. Various synthesis techniques, such as layer-by-layer assembly, in-situ growth, and physical blending, are utilized to optimize the interaction between MOFs and membrane structures. A central challenge in this field is the balance between selectivity and permeability; however, recent innovations in composite design have demonstrated substantial progress in overcoming this trade-off. These advancements highlight the potential of membrane-MOF composites to meet industrial-scale CO<sub>2</sub> capture demands, offering a scalable and sustainable approach to addressing global climate challenges.

#### 3.1. The roles of materials selection and synthesis techniques of MOF-composite membranes in CO<sub>2</sub> separation enhancement

In the complex process of synthesizing membrane-MOF (Metal-Organic Framework) composites, careful selection of materials and synthesis techniques plays a crucial role in improving the separation performances of MOF-composite membrane. The choice of MOF materials is critical, with a focus on those possessing high surface area and porosity, characteristics vital for effective CO<sub>2</sub> adsorption. MOF-74, ZIF-8, and UiO-66 are among the most popular due to their distinct properties in gas separation, such as high adsorption capacity and selectivity for CO<sub>2</sub> (Kim et al., 2018; Knebel and Caro, 2022).

Concurrently, the selection of membrane materials is equally crucial. These are often polymeric or ceramic bases, like polysulfone or alumina, chosen not only for their compatibility with MOF particles but also for their inherent structural stability and permeability characteristics. The synergy between the MOF materials and the membrane base

is fundamental to the composite's overall performance in CO<sub>2</sub> capture (Knebel and Caro, 2022).

The integration of MOFs into membranes is achieved through several innovative techniques as can be seen diagrammatically in Fig. 6. Solvothermal synthesis, a widely used method, involves dissolving both MOF precursors and membrane polymers in a solvent. This mixture is then subjected to controlled heating, leading to the formation of a composite where MOFs are uniformly distributed within the membrane matrix. This method is particularly noted for its ability to create composites with a high degree of MOF dispersion and integration. In one study, mixed matrix membranes (MMMs) containing zeolitic imidazolate framework-8 (ZIF-8) and UiO-66 as microporous fillers were prepared and evaluated for their potential in gas separation from a methane reforming process. Hydrothermal synthesis produced ZIF-8 crystals ranging from 50 to 70 nm and UiO-66 crystals from 200 to 300 nm. MMMs were prepared with 15 wt.% filler loading for both ZIF-8 and UiO-66. The MMM containing UiO-66 exhibited H<sub>2</sub> permeability of 64.4 Bar·cm and H<sub>2</sub>/CH<sub>4</sub> selectivity of 153.3 for single gas permeation, more than twice the values exhibited by a neat polymer membrane. Similarly, the MMM containing ZIF-8 showed H<sub>2</sub> permeability of 27.1 Bar·cm and H<sub>2</sub>/CH<sub>4</sub> selectivity of 123.2. When a gas mixture consisting of 78% Ar/18% H<sub>2</sub>/4% CH<sub>4</sub> was tested at 5 bar, the H<sub>2</sub> purity increased to as high as 93%. However, no improvement in mixture gas separation performance was observed compared to the neat polymer membrane (Kim et al., 2018).

In addition, the synthesis of thin-film or pure MOF membranes via solvothermal or hydrothermal methods involves dissolving metal ions and linkers in a solvent, followed by immersing the substrate into the growth solution. This ensures that the diffusion of metal ions and linker molecules occurs in the same direction during MOF film formation. The approach encompasses two main strategies: in situ growth and seeded (secondary) growth (Li et al., 2015). In situ growth entails the direct fabrication of the MOF layer on the substrate using solvothermal or hydrothermal treatments. To enhance adhesion and nucleation on the substrate surface, functional groups are typically introduced through surface modifications. These groups can interact with metal ions or linkers, and the modified substrate is subsequently subjected to solvothermal or hydrothermal conditions to facilitate MOF layer formation.

While this method has been widely applied for synthesizing MOF membranes, it also presents certain drawbacks. Surface modifications or seeding are often necessary to increase the density of heterogeneous nucleation sites on the substrate, thereby complicating the synthesis process. Additionally, as the precursor solution comprises a mixture of metal ions and linkers, MOF crystals may form in the bulk solution, resulting in raw material wastage. Furthermore, this approach is energy-intensive and challenging to scale up, limiting its practical application for large-scale membrane production (Li et al., 2015).

Layer-by-layer assembly, a sophisticated and versatile technique, is employed for crafting thin-film composites and MOF membranes. It involves the sequential deposition of MOF layers and polymer layers onto a substrate, allowing for precise control over membrane thickness and MOF loading. In this method, the metal ion and linker are dissolved in separate solutions. The substrate is alternately coated with one precursor solution, rinsed with solvent to remove excess material, and then immersed in the other precursor solution to facilitate MOF growth at a controlled temperature. Due to the stepwise crystallization process, the thickness of the MOF layer can be accurately regulated by adjusting the number of fabrication cycles (Dehghankar et al., 2023; Li et al., 2015). This technique is widely appreciated for its mild conditions, simplicity, and controllability, making it ideal for tailoring membrane separation properties. However, while it is effective for fabricating thin MOF films, achieving a continuous and defect-free MOF layer in membrane applications remains challenging. In addition, this technique requires long time to achieve defect free membrane. This limitation can hinder the formation of high-quality MOF membranes for practical separations (Lausund et al., 2020; Li et al., 2015; Xiang et al., 2018).



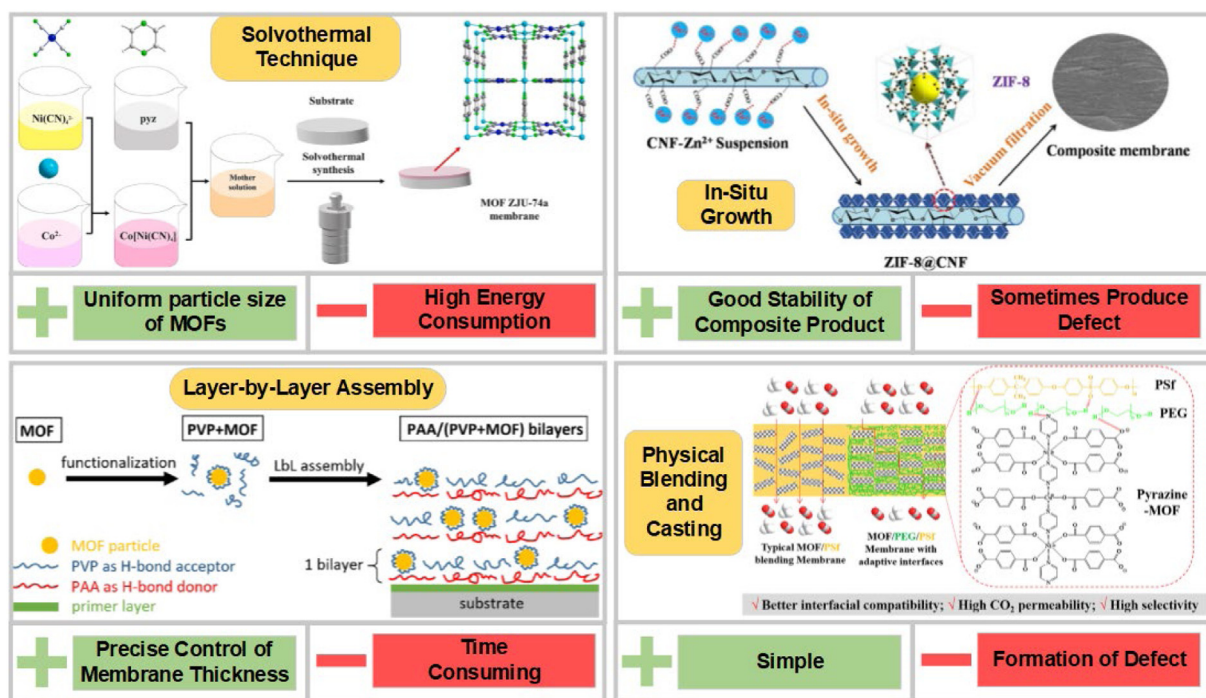


Fig. 6. Synthesis techniques for nanostructured MOFs membrane composite. The figure summarizes four MOF-membrane fabrication techniques, highlighting their advantages and challenges.

Numerous investigators have produced polymer composites containing metal-organic framework (MOF) filler particles to combine the processability of polymers and the gas selectivity of MOF particles. However, filler particle aggregation and weak filler-matrix interaction have sometimes led to poor gas separation performance. In a recent study, polyvinylpyrrolidone (PVP) modified UiO-66-PA particles were combined with poly(acrylic acid) (PAA) through H-bonding assisted layer-by-layer assembly. The resultant PAA/(PVP + MOF) bilayers featured individually dispersed fillers and strong filler-matrix interaction, stronger than the internal strength of fillers. This enabled the polymer/MOF composite membrane, based on PAA/(PVP + MOF) bilayers, to achieve a higher selectivity ( $\text{H}_2/\text{CO}_2 = 20.3$ ) compared to PAA/PVP bilayers ( $\text{H}_2/\text{CO}_2 = 12.5$ ) and several previously reported pure-MOF membranes ( $\text{H}_2/\text{CO}_2 < 10$ ) (Xiang et al., 2018).

In-situ growth is a technique where MOF crystals are directly grown on the membrane surface, ensuring a robust MOF-membrane interaction. This method involves immersing the membrane (substrate) in a solution containing MOF precursors, where crystal growth is induced under specific reaction conditions. Depending on the type of substrate used, the in-situ growth approach can be categorized into two main strategies: the direct growth method and the modified substrate method (Ma et al., 2019). The direct growth method involves the direct contact of the substrate with the reaction solution, leading to the formation of the MOF membrane on its surface. In contrast, the modified substrate method incorporates surface modifications to enhance nucleation and adhesion of MOF crystals. The in-situ growth approach is widely recognized for producing MOF-membrane composites with exceptional mechanical strength and stability, making them particularly suitable for demanding applications such as  $\text{CO}_2$  separation.

A recent study demonstrated the in-situ synergistic growth of crystalline zeolite imidazole framework-8 (ZIF-8) within polybenzimidazole (PBI), creating highly porous structures with high gas permeability. PBI, containing benzimidazole groups similar to the ZIF-8 precursor, induced the formation of amorphous ZIFs, enhancing interfacial compatibility and creating highly size-discriminating bottlenecks. The formation of 15 wt.% ZIF-8 in PBI improved  $\text{H}_2$  permeability and  $\text{H}_2/\text{CO}_2$  selectiv-

ity by approximately 100% at  $35^\circ\text{C}$ , effectively breaking the permeability/selectivity trade-off. This innovative approach unveils a new platform of mixed matrix materials (MMMs) comprising functional polymer-incorporated amorphous ZIFs with hierarchical nanostructures for various applications (Hu et al., 2022).

Physical blending, a simpler and more straightforward method, involves directly mixing MOF particles with polymer solutions before the membrane fabrication process. While this method lacks the sophistication of other techniques, it is effective for bulk applications where high throughput is a priority (Asmaul Husna et al., 2022; Prasetya et al., 2020). Each synthesis method presents its unique set of advantages and limitations. The choice is often dictated by a multitude of factors, including the desired MOF loading, specific properties of the membrane, and the intended application of the composite. For instance, high-performance applications may necessitate the precise control offered by layer-by-layer assembly, whereas large-scale industrial applications might benefit from the simplicity and scalability of physical blending (Nie et al., 2023).

Incorporating MOFs into membrane systems enhances their  $\text{CO}_2$  separation efficiency, thermal and chemical stability, mechanical strength, and gas separation properties, which are invaluable for industrial applications demanding high durability, efficiency, and performance. Recent studies corroborate the potential of MOF-composite membranes, showing significant improvements in  $\text{CO}_2/\text{N}_2$  selectivity, a critical metric for evaluating  $\text{CO}_2$  capture technologies (Shan et al., 2024; Sutrisna et al., 2018, 2017). The empirical evidence from recent studies corroborates the potential of MOF-composite membranes, showcasing remarkable improvements in  $\text{CO}_2/\text{N}_2$  selectivity, a critical metric for evaluating the effectiveness of  $\text{CO}_2$  capture technologies. For instance, polymer-based hollow fiber composite membranes, composed of a porous support, a highly permeable gutter layer, and a thin selective top layer, face challenges in maintaining performance under high pressure or long-term operation. Incorporating ZIF-8 into Pebax-1657 for gas separation membranes increased gas permeability due to higher fractional free volume, despite slightly reduced gas selectivity. The stable ZIF-8 structure and hydrogen bonds with polyamide chains improved polymer chain stiff-



ness, ensuring good operational stability under elevated pressure and overcoming aging issues observed in previous materials, demonstrating long-term operational stability (Sutrisna et al., 2017).

The success of the synthesis process is evaluated based on several criteria: the uniformity of MOF distribution within the membrane, the composite's structural and functional stability, and its effectiveness in CO<sub>2</sub> capture tests. Advanced characterization techniques, such as electron microscopy and gas sorption analyses, are employed to assess these criteria, providing insights into the microstructural and adsorptive properties of the composites. Optimizing these factors is central to the development of efficient MOF-composite membranes. As these composites advance, they hold the promise of revolutionizing CO<sub>2</sub> sequestration technologies, offering a sustainable solution to mitigate the impacts of climate change (Research Institute of Medicine and Pharmacy, Qiqihar Medical University, China et al., 2023). Non-selective interface defects and discontinuous dispersion of MOF particles in polymeric matrices can significantly compromise gas separation performance. Nevertheless, rapid advancements in nanofabrication techniques and materials science are progressively overcoming these obstacles (Dong et al., 2013; Y. Sun et al., 2023). In a recent study, embedding [C5min][BF<sub>4</sub>] encapsulated ZIF-67 (IL@ZIF) composites into a defect-free IL/Pebax ion gel matrix has been shown to form a mixed matrix ion gel membrane without interface defects. With good interfacial compatibility, these membranes achieve relatively continuous and highly selective CO<sub>2</sub> transmission channels. A typical IL@ZIF/IL/Pebax membrane with 80 wt% IL content and 70 wt% IL@ZIF doping exhibits a CO<sub>2</sub> permeability of 408.2 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 97.2, surpassing the latest upper line (Y. Sun et al., 2023). These advancements highlight the potential for constructing high-performance MOF-based MMMs for gas separation.

In the near future, the continuous development of MOF-composite membrane design and functionality shows great promise for the advancement of CO<sub>2</sub> capture technology. There is a growing emphasis in research on upscaling these composites for industrial applications, improving their effectiveness, and assessing their environmental impact. The combination of MOFs with membranes not only signifies a notable advancement in our ability to tackle climate change but also opens up avenues for the development of state-of-the-art materials for environmental preservation. This innovative method highlights the potential for establishing more effective, durable, and expandable CO<sub>2</sub> separation systems, positioning it as a fundamental element in the worldwide endeavour to alleviate the consequences of climate change.

### 3.2. Optimizing selectivity-permeability interaction and operational parameter of MOF-composite membranes for excellent CO<sub>2</sub> capture and separation

The selection of appropriate materials and synthesis techniques for MOF-composite membranes plays a critical role in enhancing their CO<sub>2</sub> separation performance by improving both structural integrity and functional efficiency. However, achieving an optimal balance between selectivity and permeability remains a significant challenge in practical applications. The following section explores strategies for optimizing this selectivity-permeability interaction, alongside the influence of operational parameters such as temperature, pressure, and surface modifications, to further advance the performance and scalability of MOF-composite membranes for CO<sub>2</sub> capture.

The selective permeability of the membrane is the central aspect of this separation technique, cleverly increased by the incorporation of MOFs, known for their customizable pore structure and surface chemistry. This customization facilitates the precise adjustment of the membrane's selectivity, enabling the preferential transport of CO<sub>2</sub> molecules while effectively discriminating against other components of flue gas, such as nitrogen, oxygen, and methane, based on their size, shape, and potential interactions (Adot Veetil et al., 2023; Goh et al., 2022).

The discussion investigates the dynamic interaction between selectivity and permeability, crucial aspects influencing the effectiveness of

CO<sub>2</sub> separation. Typically, balancing high selectivity for CO<sub>2</sub> with the desired permeability impacts the volume of gas processed over time. Advancements in MOF-composite membrane design, such as creating hierarchical pore structures and incorporating functional groups that selectively engage with CO<sub>2</sub> molecules, demonstrate approaches that surpass this compromise, improving both selectivity and flux across the membrane (Shahid et al., 2021; Ullah et al., 2020; Yu et al., 2024). For example, MOF-200, prepared using a direct solution-based and catalyst-free method, exhibited a surface area of 3624 m<sup>2</sup>.g<sup>-1</sup>. Post-synthetic modification with graphene oxide (GO) to form MOF-200/GO resulted in a slight surface area reduction to 3359 m<sup>2</sup>.g<sup>-1</sup>, but enhanced CO<sub>2</sub> uptake by 15% due to the successful attachment of surface functionalities (Ullah et al., 2020). In another study, polyimide-based mixed matrix membranes (MMMs) incorporating hierarchical ZIF-8 (H-ZIF-8) particles showed a four-fold increase in CO<sub>2</sub> and CH<sub>4</sub> permeability and a marked increase in selectivity and plasticization resistance with 30 wt% H-ZIF-8 loading. These advancements highlight the potential of hierarchical structures and functional modifications to enhance the performance of MOF composites in gas separation processes (Shahid et al., 2021).

In addition, analysis is required to study the kinetic and thermodynamic factors influencing the separation process, including the impact of temperature, hydrothermal treatment, and pressure on CO<sub>2</sub> adsorption and desorption cycles, and the role of these parameters in optimizing the separation efficiency and energy consumption of the system (Ho and Paesani, 2023; Xin et al., 2021). Theoretical models and computational simulations that predict the behaviour of these complex systems are discussed, offering insights into the design of next-generation materials and processes (Gulbalkan et al., 2024; Wu et al., 2015). Hierarchical porous composite Mg-MOF-74/MCFs (mesocellular siliceous foams), synthesized via a simple in situ solvothermal method, show improved CO<sub>2</sub> adsorption by integrating nanosized Mg-MOF-74 particles into MCFs. Initially, the composites' CO<sub>2</sub> adsorption capacity is 1.68 mmol.g<sup>-1</sup>, less than pristine Mg-MOF-74. However, post-hydrothermal treatment, this capacity rises to 2.66 mmol.g<sup>-1</sup>, surpassing Mg-MOF-74's 2.39 mmol.g<sup>-1</sup>. This enhancement highlights the importance of optimizing thermodynamic conditions for efficient CO<sub>2</sub> separation (Xin et al., 2021).

Recent advancements highlight cutting-edge research leading to the development of novel MOF materials and membrane configurations (Fateminia et al., 2023; Lan et al., 2020). These innovations promise higher CO<sub>2</sub> capture capacities and selectivities, along with enhanced stability and durability under operational conditions, addressing key challenges in the scalability and practical implementation of CO<sub>2</sub> separation technologies.

## 4. Role of MOFs in MOF-composite membrane in enhancing CO<sub>2</sub> affinity and selectivity

The enhancement of CO<sub>2</sub> affinity and selectivity in MOF-composite membranes is largely attributed to the structural versatility of MOFs, which enables precise tuning of pore sizes and surface functionalities. In general, the incorporation of MOFs are expected to improve the size selectivity and to enhance the chemical affinity of the membrane. The high surface area and tuneable porosity of MOFs are key factors in facilitating both physisorption and chemisorption, significantly increasing their CO<sub>2</sub> adsorption capacity. The functionalization of MOFs with specific chemical groups further optimizes their performance by improving both selectivity and adsorption efficiency (Güçlü et al., 2021; Jun et al., 2022). In addition, the molecular interactions between MOFs and CO<sub>2</sub>, including the underlying kinetics and thermodynamics, are examined to elucidate the mechanisms responsible for their enhanced capture capabilities. Furthermore, nanostructuring techniques that incorporate MOFs into membranes are explored for their potential to enhance permeability, selectivity, and operational stability in CO<sub>2</sub> separation processes.

4.1. Improving size selectivity

Improving the size selectivity of membranes for CO<sub>2</sub> capture is a critical challenge in environmental engineering, directly impacting the efficacy and feasibility of carbon sequestration technologies. The advent of nanostructuring techniques has heralded a new era in membrane development, allowing for unprecedented precision in tuning membrane

properties for enhanced gas separation (Hu et al., 2024; Rodrigues et al., 2018).

The separation performance of polymeric membranes is fundamentally constrained by an intrinsic trade-off between permeability and selectivity, wherein membranes with higher permeability generally exhibit lower selectivity and vice versa (Fig. 7 A). This inherent trade-off is encapsulated by the "Robeson upper bound." To mitigate this limi-

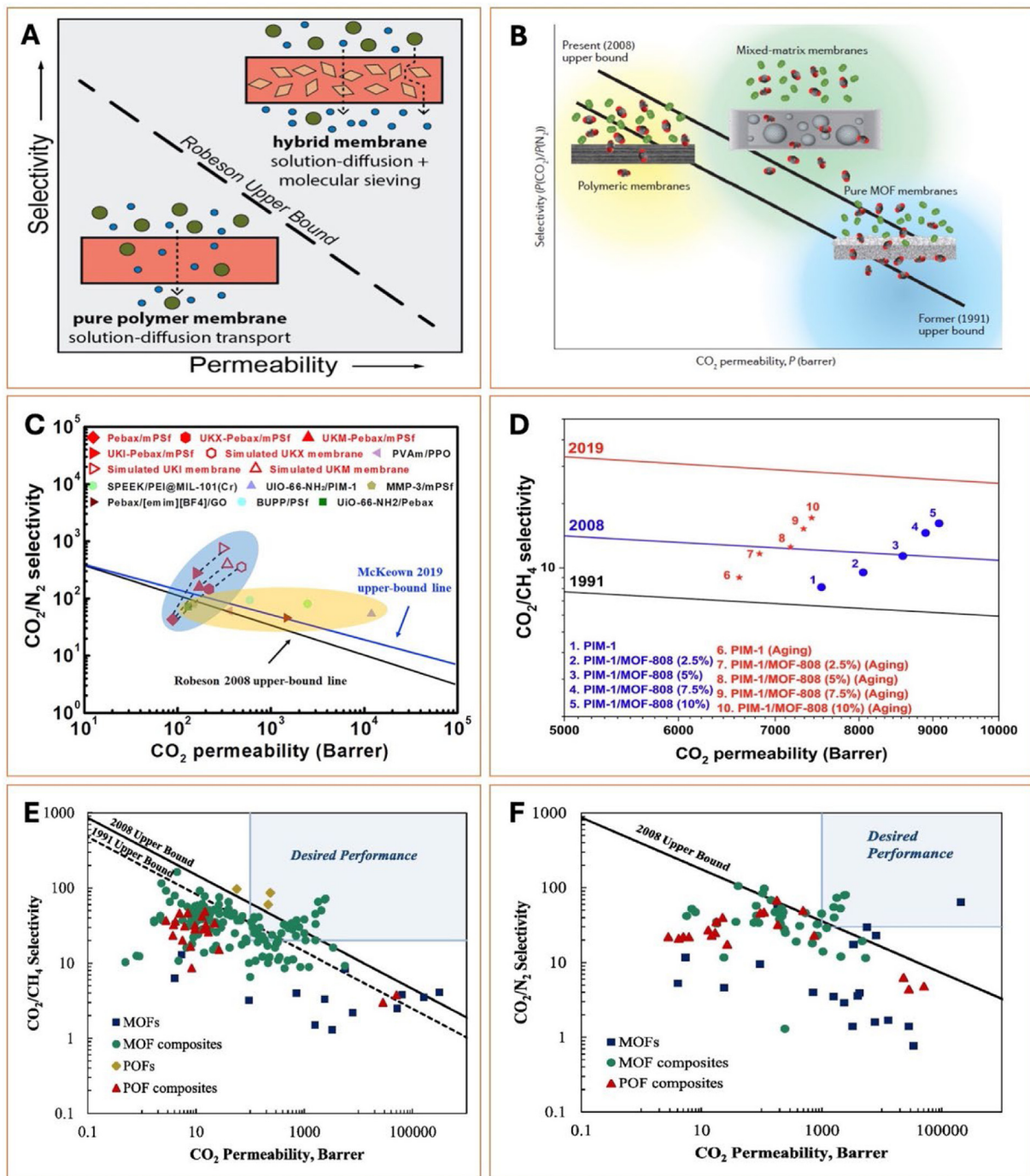


Fig. 7. (A) Gas separation performances of pure polymeric membrane and hybrid membrane (Reproduced with permission from (Pastore and Cook, 2020)); (B) Comparison of selectivity and CO<sub>2</sub> permeability against the Robeson upper bound curves for pure polymeric, mixed-matrix, and pure MOF membranes (Reproduced with permission from (Trickett et al., 2017)); (C) Comparison of the separation performance of CO<sub>2</sub>/N<sub>2</sub> mixed gas in MMMs (Reproduced with permission from (Wang et al., 2021)); and (D) PIM-1 pristine membrane and PIM-1/MOF-808 MMMs (Reproduced with permission from (Yahia et al., 2024)). Performances of MOF, POF, MOF-composite, and POF composite membranes in (E) CO<sub>2</sub>/CH<sub>4</sub> and (F) CO<sub>2</sub>/N<sub>2</sub> gas mixture (E and F are reproduced from (Prasetya et al., 2020)). All figures illustrate the relationship between CO<sub>2</sub> permeability and selectivity for polymeric, mixed-matrix, and MOF-based membranes, showing advancements beyond Robeson's upper bounds over time.

tation, the strategic incorporation of porous fillers within a polymeric matrix has catalysed the evolution of polymer/filler composite membranes, termed mixed-matrix membranes (MMMs). MMMs synergistically integrate the mechanical flexibility and processability of polymers with the molecular sieving precision of porous fillers, thereby achieving enhanced permeability and selectivity (Yang et al., 2023). Significant advancements have been realized with MOF-based membranes, enhancing both selectivity and permeability in CO<sub>2</sub>-containing gas separation processes, as demonstrated in Fig. 7 B-F.

Nanostructured membranes control the design of pore architecture to facilitate selective gas permeation. By engineering pores at dimensions closely matching the kinetic diameter of CO<sub>2</sub> molecules, these membranes can effectively discriminate against larger molecules such as nitrogen and methane, common constituents in flue gases. The precision in pore size not only maximizes CO<sub>2</sub> throughput but also minimizes the energy required for gas separation, addressing one of the major bottlenecks in conventional CO<sub>2</sub> capture processes (Essalhi et al., 2023; Rodrigues et al., 2018).

The incorporation of MOFs into nanostructured membranes introduces a multifaceted approach to selectivity enhancement. MOFs, with their highly ordered, porous structures, offer customizable adsorption sites that can be chemically tailored to prefer CO<sub>2</sub> molecules. This customization extends to the functionalization of MOF surfaces with specific ligands or active sites that exhibit a high affinity for CO<sub>2</sub>, such as amine groups (Bahamon et al., 2021; Ghalei et al., 2017). These functional groups engage in chemical interactions with CO<sub>2</sub>, such as chemisorption, which significantly enhances the selectivity and capacity of membranes for CO<sub>2</sub> capture. Highly ordered, porous MOFs like NH<sub>2</sub>-MIL-101(Cr) and MIL-101(Cr) grafted with amine groups, such as tetraethylenepentamine (TEPA), are chemically customized to preferentially adsorb CO<sub>2</sub> via chemisorption. For instance, a Matrimid-based membrane incorporating ammoniated PVDF and NH<sub>2</sub>-MIL-101(Cr) exhibited a remarkable increase in CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity by 33% and CO<sub>2</sub> permeability by 39% with 3 wt% NH<sub>2</sub>-PVDF, which further enhanced to 125% and 136%, respectively, with the addition of 5 wt% NH<sub>2</sub>-MIL-101(Cr) (Rajati et al., 2020). In another approach, TEPA-MIL-101(Cr) incorporated into Pebax® 1657 thin-film nanocomposite (TFN) membranes resulted in a 63% increase in CO<sub>2</sub> permeability and doubled the CO<sub>2</sub>/CH<sub>4</sub> selectivity to 46.3 when compared to the neat Pebax membrane (Khoshhal Salestan et al., 2021). These results emphasize the potential of functionalized MOFs within membrane technologies to effectively separate CO<sub>2</sub> at both enhanced selectivity and capacity, pointing towards promising applications in industrial gas separation processes.

Furthermore, the surface modification of nanostructured membranes with selective coatings or functional groups can dramatically improve their CO<sub>2</sub> selectivity. Techniques such as plasma treatment, layer-by-layer assembly, and chemical vapor deposition enable the addition of selective layers or functional moieties that further enhance membrane affinity for CO<sub>2</sub> (Lin et al., 2022; Xiang et al., 2018). These modifications not only increase the physical and chemical interactions with CO<sub>2</sub> but also contribute to the overall stability and durability of the membrane under operational conditions. This aligns with recent advancements in MOF architectures, where designing and regulating porous microenvironments have shown significant scientific interest. Specifically, guest-host dual MOF@MOF heterosystems, constructed by vapor linker processing, demonstrate tailored dual pore geometries and enhanced gas molecule affinities. These heterosystems, formed by solvent-free chemical vapor deposition, bridge pre-impregnated metal precursors in confined MOF pores to create MOF cages with optimal porosity. Notably, MOF@MOF composites exhibit substantial improvements in polymer compatibility and molecular sieving capabilities, achieving remarkable carbon capture performance with 162% CO<sub>2</sub> permeability (14,366 Barrer) and 152% CO<sub>2</sub>/N<sub>2</sub> selectivity compared to pure polymeric membranes (Lin et al., 2022). This study highlights an innovative approach to developing heterogeneous and porous materials for enhanced carbon capture.

Emerging research highlights the potential of combining nanostructuring with MOF integration and surface functionalization. Studies have shown that membranes designed with hierarchical nanostructures and MOF composites exhibit superior selectivity and permeability for CO<sub>2</sub>, significantly outperforming traditional polymeric and inorganic membranes. For instance, mixed matrix membranes (MMMs) using Pebax 2533 and MOFs such as SUM-1 and SUM-9 have demonstrated notable CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity under varying humidity conditions. At 35°C and 2 bar, the CO<sub>2</sub> permeability of Pebax-SUM-1 was 380.9 to 433.1 Barrer, while Pebax-SUM-9 ranged from 387.4 to 452.4 Barrer, with selectivities maintaining around 17.0 to 20.0 (Qin et al., 2023). These findings highlight the challenge of optimizing these complex systems for industrial-scale applications, balancing selectivity, permeability, and operational stability, while considering the impact of environmental factors such as humidity on performance (Knebel et al., 2018; Shahid et al., 2021).

The strategic application of nanostructuring in membrane design presents a promising avenue for advancing CO<sub>2</sub> capture technology. By precisely engineering the pore structure, integrating selective MOF materials, and optimizing surface chemistry, nanostructured membranes achieve unparalleled selectivity for CO<sub>2</sub>. This enhancement not only improves the efficiency of carbon sequestration but also paves the way for more sustainable and economically viable climate mitigation strategies. The ongoing research and development in this field are poised to overcome existing limitations, heralding a new generation of membrane technologies for environmental preservation.

Enhancing size selectivity through precise nanostructuring and MOF integration has significantly improved CO<sub>2</sub> capture efficiency by optimizing the membrane's ability to discriminate gas molecules based on size and shape. However, achieving superior performance requires further advancements in CO<sub>2</sub> affinity, which can be tailored by functionalizing MOFs with targeted chemical groups and metal centers. The following section explores strategies to improve the CO<sub>2</sub> affinity of MOF-composite membranes, highlighting the role of functionalization and molecular interactions in boosting adsorption capacity and selectivity.

#### 4.2. Improving CO<sub>2</sub> affinity of MOF-composite membrane

The affinity of MOFs for CO<sub>2</sub> is foundational to their efficiency in carbon sequestration, distinguishing them as superior candidates for carbon capture technologies. This affinity is primarily attributed to their unparalleled porosity and extensive surface areas, characteristics that enable MOFs to adsorb substantial quantities of CO<sub>2</sub>. The structural configuration of MOFs, characterized by a network of metal ions coordinated to organic linkers, provides a versatile platform for the fine-tuning of pore architectures and surface functionalities, optimizing CO<sub>2</sub> adsorption capacities (Li et al., 2022; Trickett et al., 2017).

A critical aspect of MOFs' CO<sub>2</sub> affinity lies in the strategic engineering of their pore size and functionality. By adjusting these parameters, MOFs can achieve high size and shape selectivity, ensuring efficient CO<sub>2</sub> uptake. The incorporation of specific functional groups, such as amine groups, enhances CO<sub>2</sub> capture through chemisorption, where CO<sub>2</sub> molecules form stable compounds with the functional groups, leading to higher adsorption rates and capacities. For instance, Zr-based MOF-808 functionalized with tetraethylenepentamine (TEPA) showed a remarkable increase in CO<sub>2</sub> adsorption performance. The TEPA-functionalized MOF-808 demonstrated a very high ideal adsorption solution theory selectivity of 256, about seven times that of the pristine MOF-808, and adsorbed approximately 2.5 times more CO<sub>2</sub> at 15 kPa. Similarly, IRMOF-74-III, modified with primary alkylamine functionalities, uptakes CO<sub>2</sub> at low pressures through a chemisorption mechanism, predominantly forming carbamic acid. This reaction shifts to ammonium carbamate in the presence of water vapor, highlighting the importance of geometric constraints and the mediating role of water within the pores of MOFs in controlling CO<sub>2</sub> capture chemistry (Flaig et al., 2017; Jun et al., 2022).



Moreover, the role of the metal centres in MOFs is very important. Different metal ions significantly affect the electronic environment of the MOFs, altering its interaction with CO<sub>2</sub> molecules. Metals with high CO<sub>2</sub> affinity can induce dipole moments that attract CO<sub>2</sub> molecules more effectively, thereby increasing the MOF's overall CO<sub>2</sub> adsorption capacity. For example, MOFs such as MOF-74-Mg, HKUST-1, SIFSIX-3-M (M = Fe, Co, Ni, Cu, Zn), and ZIF-8 demonstrate efficient CO<sub>2</sub> adsorption due to features like open metal sites, ultra-microporosity, and flexible frameworks. These materials exhibit CO<sub>2</sub> capacities comparable to or exceeding standard adsorbents like zeolite 13X and activated carbon, making them promising candidates for carbon capture and sequestration (CCS) technologies. Understanding the CO<sub>2</sub> adsorption mechanisms in these MOFs is crucial for further enhancing their performance, addressing factors such as preferential adsorption sites, water stability, CO<sub>2</sub>-MOF complex configuration, adsorption dynamics, and bonding angles (Renata A. Maia et al., 2021).

The kinetics of CO<sub>2</sub> adsorption within MOFs is another vital consideration. The rate at which CO<sub>2</sub> is adsorbed and subsequently released from the MOFs matrix is crucial for the practical application of these materials in dynamic environments. Factors such as the diffusion of CO<sub>2</sub> molecules into the MOF pores, the accessibility of adsorption sites, and the strength of the CO<sub>2</sub>-MOFs interactions directly influence the adsorption-desorption kinetics (Dong et al., 2013; Renata A. Maia et al., 2021). Advanced characterization techniques, including in situ spectroscopy and computational modelling, have provided insights into these processes, revealing the complex interplay between MOFs structure and CO<sub>2</sub> adsorption dynamics.

To improve CO<sub>2</sub> capture efficiency, researchers have analysed several MOFs, each highlighting specific benefits. MOFs with open metal sites or functionalized with electron-rich groups exhibit particularly high CO<sub>2</sub> affinities due to enhanced CO<sub>2</sub>-MOF interactions (Nandi et al., 2018; Renata A. Maia et al., 2021). For instance, a new ultra-microporous Cu<sub>2</sub> paddlewheel-based MOF exhibits notable features such as a BET surface area of 945 m<sup>2</sup>.g<sup>-1</sup>, a CO<sub>2</sub> capacity of 3.5 mmol.g<sup>-1</sup> at ambient temperature and pressure, a CO<sub>2</sub>/N<sub>2</sub> selectivity of 250, and fast CO<sub>2</sub> diffusion kinetics (D<sub>c</sub> = 2.25 × 10<sup>-9</sup> m<sup>2</sup>.s<sup>-1</sup>). Despite having channels lined by amine and open-metal sites, this MOF displays a moderate heat of adsorption (HOA) of 26 kJ.mol<sup>-1</sup>, as opposed to the typically strong CO<sub>2</sub>-framework interactions seen in other high-performing MOFs with HOA ≥ 38 kJ.mol<sup>-1</sup>. Comparative studies highlight the diversity in CO<sub>2</sub> adsorption performance across different MOF structures, underscoring the importance of molecular design in developing efficient carbon capture materials (Nandi et al., 2018).

The functionalization of Metal-Organic Frameworks (MOFs) represents a transformative strategy in the enhancement of CO<sub>2</sub> capture technologies. By integrating specific functional groups into the MOF structure, scientists can significantly influence the material's CO<sub>2</sub> adsorption dynamics, optimizing both its capacity and selectivity for CO<sub>2</sub> over other atmospheric gases (Ghalei et al., 2017).

Metal-organic frameworks (MOFs) with functional groups like -NH<sub>2</sub> (amines), -COOH (carboxylates), and -OH (hydroxyls) significantly enhance CO<sub>2</sub> capture through strong interactions such as the formation of carbamic acid and carbamate ions at low temperatures. This reversible reaction facilitates easy CO<sub>2</sub> release during regeneration, improving CO<sub>2</sub> uptake and selectivity for CO<sub>2</sub> molecules. The placement of these functional groups influences the distribution and accessibility of adsorption sites within the MOFs, affecting the adsorption kinetics and thermodynamics (Flaig et al., 2017; Gu et al., 2021; Jun et al., 2022; Ma et al., 2022).

A novel approach involves the Cu(adci)-2 MOF, which combines aromatic amine functionalization with ultramicroporosity to achieve an impressive CO<sub>2</sub> adsorption capacity of 2.01 mmol.g<sup>-1</sup> at 298 K and 15 kPa (Fig. 8A-B). The Cu(adci)-2 features oriented NH<sub>2</sub> groups within one-dimensional square-shaped channels, enhancing physisorption through Lewis base-acid and London dispersion interactions. Despite the presence of moisture, its performance remains stable, show-

ing significant potential for flue gas applications (Jo et al., 2022). Furthermore, Mg<sub>2</sub>(dobpdc) MOFs, functionalized using a solvent exchange method with N-ethylethylenediamine, demonstrate a high CO<sub>2</sub> adsorption capacity of 16.5 wt% (Fig. 8C-D). This process stresses the importance of solvent effects on amine functionalization, with density functional theory calculations revealing insights into the chemical interactions that govern diamine grafting and CO<sub>2</sub> capture efficiency (Choi et al., 2021). Additionally, addressing indoor CO<sub>2</sub> levels, the epn-functionalized Mg<sub>2</sub>(dobpdc) MOFs mixed with a hydrophobic polymer and shaped into membranes show a CO<sub>2</sub> adsorption of 2.8 mmol.g<sup>-1</sup> at 1000 ppm (Fig. 8E-F). These composites are robust, maintaining CO<sub>2</sub> removal efficiency over multiple cycles and days, proving their utility in practical indoor air quality management (Seok Chae et al., 2022). These developments highlight the critical role of MOF design in enhancing CO<sub>2</sub> capture through strategic functionalization and innovative material combinations, promising effective solutions for both environmental and indoor air quality improvements.

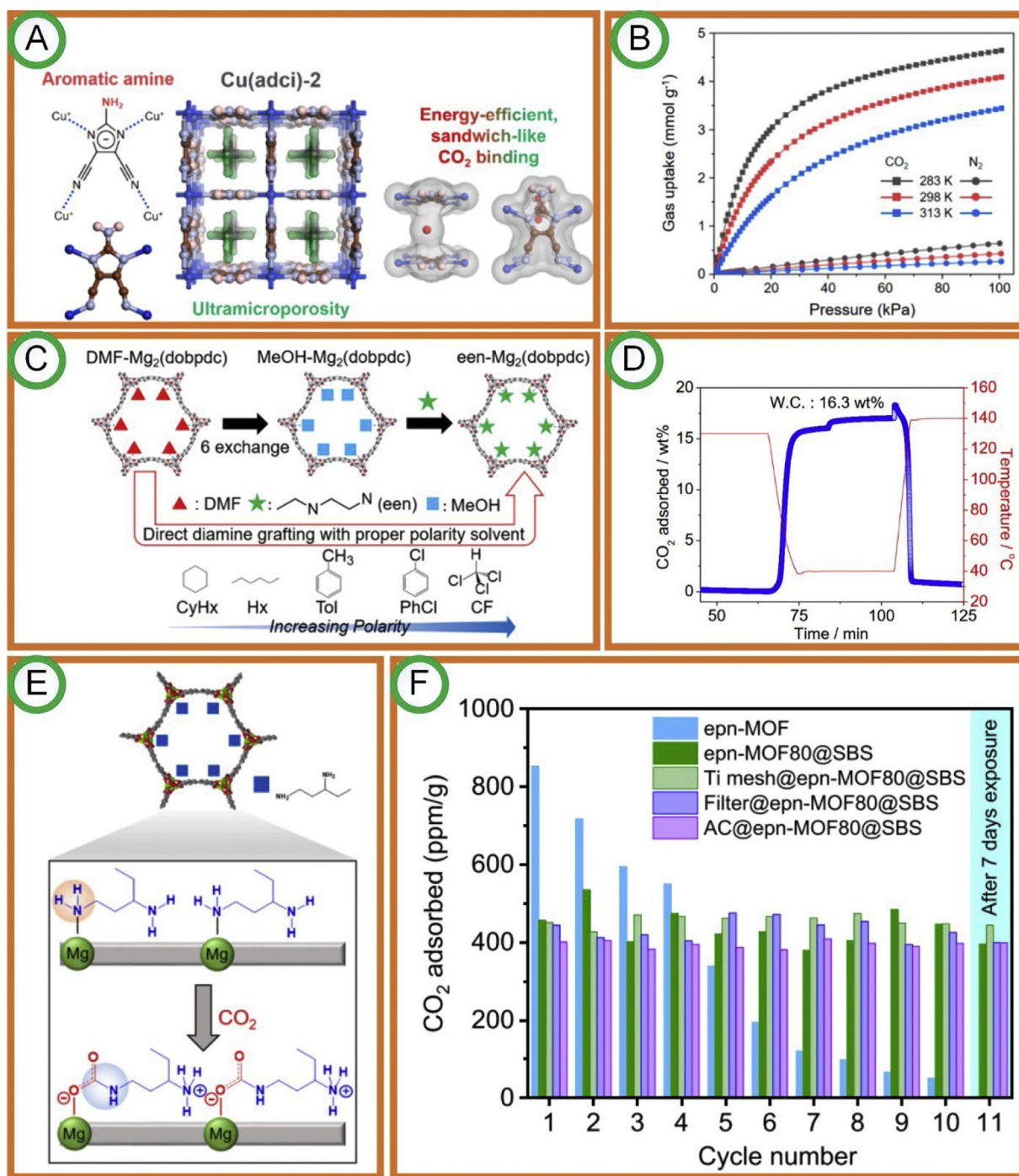
Beyond enhancing CO<sub>2</sub> affinity and selectivity, the functionalization of MOFs also addresses challenges related to the stability and regenerability of these materials in industrial applications. For example, incorporating functional groups that improve chemical resistance and thermal stability makes MOFs more suitable for long-term use in harsh environments, such as flue gas streams containing pollutants (Flaig et al., 2017). Recent advancements have showcased the development of novel functionalized MOFs with remarkable CO<sub>2</sub> capture capabilities. Studies have highlighted how specific functional groups can lower the energy required for regeneration, a critical factor in reducing the overall cost of CO<sub>2</sub> capture processes. Furthermore, the design of multifunctional MOFs, which combine several types of functional groups or incorporate metal sites with catalytic activity, opens new pathways for the simultaneous capture and conversion of CO<sub>2</sub> into valuable chemicals, aligning CO<sub>2</sub> sequestration efforts with sustainable chemistry initiatives (Anastasiou et al., 2018; Renata A. Maia et al., 2021). Mixed-matrix membranes (MMMs) comprising inorganic fillers dispersed in an organic matrix are gaining attention for their potential to enhance separation selectivity, throughput, and material robustness. In a recent study, ZIF-8 MOF and ZIF-8/graphene oxide (GO) hybrid nanofillers were developed and incorporated into a polysulfone (PSF) matrix. Compared to the pristine PSF membrane, the PSF+(ZIF-8/GO) MMMs showed an increase in CO<sub>2</sub> permeability by up to 87% and selectivity by up to 61% for the CO<sub>2</sub>/CH<sub>4</sub> pair. Additionally, the selectivity of the PSF+(ZIF-8/GO) MMM increased up to 7-fold compared to the PSF + ZIF-8 MMM. These results demonstrate that composite fillers combining the functionality of MOFs and GO have the potential to significantly improve the performance of polymeric membranes for CO<sub>2</sub> separation from hydrocarbon gases, flue gas, and related gas mixtures (Anastasiou et al., 2018).

The functionalization of MOFs is a highly promising area of research, offering a versatile platform for the design of next-generation materials for CO<sub>2</sub> capture. By elucidating the mechanisms through which functional groups enhance CO<sub>2</sub> interactions and by leveraging advanced synthetic techniques, the development of functionalized MOFs can lead to more efficient, economical, and environmentally friendly solutions for addressing the challenges of climate change (Philip and Henni, 2023). This exploration underscores the necessity for continued innovation and interdisciplinary collaboration in the quest to refine and apply MOF-based technologies in the global effort to mitigate atmospheric CO<sub>2</sub> levels.

The intricate molecular interactions between Metal-Organic Frameworks (MOFs) and CO<sub>2</sub> molecules are at the heart of the revolutionary advancements in CO<sub>2</sub> capture technology. These interactions, predominantly characterized as physisorption and chemisorption, leverage the unique structural properties of MOFs to address the critical need for efficient CO<sub>2</sub> sequestration methods (Bahamon et al., 2021; Choi et al., 2021; Jo et al., 2022).

Physisorption, characterized by the physical adherence of CO<sub>2</sub> molecules to the MOF surface, is facilitated by the framework's ex-





**Fig. 8.** (A) Amine functionalization of Cu(adci)-2 MOF schematic diagram; (B) Sorption capacity of amine-functionalized Cu(adci)-2 MOF (Reproduced with permission from (Jo et al., 2022)); (C) Functionalization of Mg<sub>2</sub>(dobpdc) MOFs using N- ethylethylenediamine process; (D) Gas sorption of functionalized Mg<sub>2</sub>(dobpdc) MOFs (Reproduced with permission from (Choi et al., 2021)); (E) Schematic diagram of CO<sub>2</sub> insertion mechanism in epn-functionalized Mg<sub>2</sub>(dobpdc); (F) CO<sub>2</sub> adsorption tests at long cycles for different epn-based MOFs (Reproduced with permission from (Seok Chae et al., 2022)). All figures highlight the synthesis, adsorption performance, and cycling stability of MOF-based materials for efficient CO<sub>2</sub> capture and binding.

tensive surface area and the presence of porous channels, which collectively enable substantial CO<sub>2</sub> adsorption (Tovar et al., 2018). This process is governed by van der Waals forces, resulting in relatively low-energy bond formations between CO<sub>2</sub> and the MOF. The reversible nature of physisorption is particularly advantageous for cyclic CO<sub>2</sub> capture and release processes, essential in industrial applications where flexibility and efficiency are paramount (Liu et al., 2021; Tovar et al., 2018).

In contrast, chemisorption offers a more robust solution to CO<sub>2</sub> capture through the formation of chemical bonds between CO<sub>2</sub> molecules and specific active sites within the MOF structure (Bahamon et al., 2021; Choi et al., 2021; Jo et al., 2022). This interaction, significantly stronger than physisorption, can be greatly enhanced by strategically introducing functional groups—such as amines—into the MOF, which are known for their high affinity towards CO<sub>2</sub>. Although chemisorption provides higher selectivity and capacity for CO<sub>2</sub> capture, it often requires more

energy for the release of CO<sub>2</sub>, due to the stronger bonds formed during the capture process (Bahamon et al., 2021; Liu et al., 2021).

The dual mechanism of CO<sub>2</sub> capture presented by MOFs—through both physisorption and chemisorption—highlights the versatility and adaptability of these materials in addressing the challenges of CO<sub>2</sub> sequestration (Bahamon et al., 2021; Liu et al., 2021; Tovar et al., 2018). By fine-tuning the balance between these interactions, researchers aim to develop MOFs that not only capture CO<sub>2</sub> more efficiently but also align with the economic and energetic constraints of large-scale deployment. UiO-66, a highly stable MOF, exemplifies this potential. For small, nonpolar adsorbates like O<sub>2</sub>, physisorption is dominated by weak van der Waals interactions. However, functionalizing UiO-66 with electron donating groups such as -NH<sub>2</sub>, -OH, and -OCF<sub>3</sub> significantly enhances its adsorption properties. For instance, UiO-66-(OH)<sub>2</sub>-p, which has two -OH groups para to one another, shows a significant increase in both binding energy and adsorption capacity for O<sub>2</sub>. Density functional theory (DFT) simulations revealed that the highest energy binding site is on top of the electron  $\pi$ -cloud of the aromatic ring of the ligand, with a direct correlation between binding energy and low-pressure adsorption capacity. These effects were similarly observed for the low-pressure adsorption of N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, highlighting the potential of functionalized MOFs in enhancing adsorption capacity and efficiency across various gases.

The ongoing research in the field of metal-organic frameworks (MOFs) is not only paving the way for innovative materials with optimized pore structures but also enhancing functionalization for improved CO<sub>2</sub> capture (Ullah et al., 2020). These developments are driven by the urgency to mitigate climate change through effective and sustainable carbon sequestration techniques. Notably, a novel nanoporous HKUST-1 aerogel demonstrates significant advances, featuring a hierarchical pore structure that combines high specific surface area (636.62 m<sup>2</sup>.g<sup>-1</sup>) and extreme porosity (99.33%) (Fig. 9A-B). The aerogel's low density (5.86 mg.cm<sup>-3</sup>) and its ability to facilitate gas transfer and CO<sub>2</sub> adsorption through its meso- and micropores respectively, result in a high CO<sub>2</sub> adsorption capacity (7.29 mmol.g<sup>-1</sup>) and excellent selectivity (39 for CO<sub>2</sub>/N<sub>2</sub> and 42 for CO<sub>2</sub>/O<sub>2</sub>) as presented in Fig. 9C (G. Zhao et al., 2023). These attributes mark a substantial progress in MOF research, aligning with global efforts towards a sustainable low-carbon economy by improving handling characteristics and performance in environmental purification.

The possibility of notable advancements in technology for CO<sub>2</sub> sequestration is becoming more evident as the interaction between MOF and CO<sub>2</sub> is further investigated for its molecular dynamics (Roohollahi et al., 2022; M. Sun et al., 2023; Usman et al., 2021). The ability to harness and refine these interactions offers a path towards developing more effective, energy-efficient, and economically feasible CO<sub>2</sub> capture systems (Fateminia et al., 2023; Ma et al., 2019; M. Sun et al., 2023; Usman et al., 2021). This ongoing research, not only contributing to the basic understanding of gas adsorption mechanisms, but also highlights the crucial role of material science in securing a viable future (Fateminia et al., 2023; Ma et al., 2019; Roohollahi et al., 2022; M. Sun et al., 2023; Usman et al., 2021).

Improving the CO<sub>2</sub> affinity of MOF-composite membranes through strategic functionalization has significantly enhanced their adsorption capacity and selectivity. However, for these materials to achieve practical, long-term implementation, their mechanical stability and durability under industrial conditions must be ensured. The following section explores advancements in enhancing the structural resilience and operational longevity of MOF-based membranes, addressing challenges such as plasticization, interfacial compatibility, and environmental stability to further optimize CO<sub>2</sub> separation performance.

#### 4.3. Enhancing mechanical stability and durability

The operational and mechanical stability of nanostructured membranes are critical for effective long-term CO<sub>2</sub> sequestration. Nanostructuring techniques enhance both mechanical and chemical resilience, en-

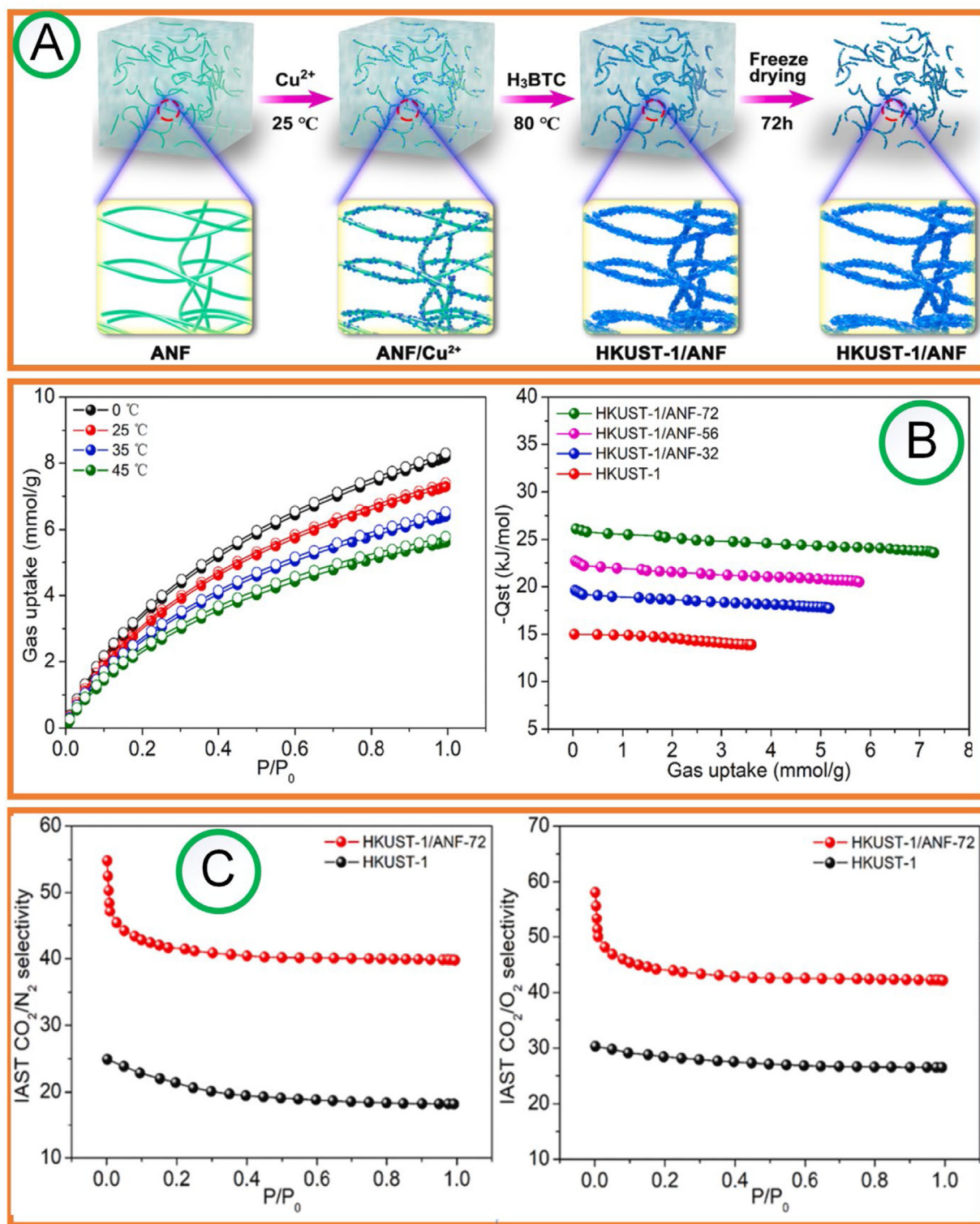
abling membranes to withstand extreme pressures, fluctuating temperatures, and corrosive gases. Incorporating robust MOFs significantly increases structural integrity, providing a scaffold that improves mechanical strength and chemical stability, thus maintaining CO<sub>2</sub> capture capabilities over extended periods without degradation (Shan et al., 2024; Sutrisna et al., 2017). In the development of plasticization-resistant membranes, blending polymers with MOFs, as seen in Matrimid® and PSf blend membranes containing ZIF-8 nanoparticles, demonstrates improved performance under high-pressure gas separations. High ZIF-8 loadings in these mixed matrix membranes (MMMs) enhance CO<sub>2</sub> permeability by 136% compared to pure polymers, while maintaining selectivity. This is attributed to increased gas sorption capacity and faster diffusion rates through ZIF-8 particles. The blend MMMs show increased resistance to plasticization, with a plasticization pressure increased from about 18 bar in native PI/PSf membranes to approximately 25 bar at 30wt% ZIF-8 loading (Shahid and Nijmeijer, 2017).

Similarly, Pebax-based composite hollow fiber membranes, when enhanced with up to 80 wt% UiO-66, particularly (-NH<sub>2</sub>) functionalized versions, show marked improvements in CO<sub>2</sub> permeance and selectivity, alongside enhanced operational stability under high pressures. The effective loading of UiO-66 in Pebax and control over interfacial microvoids are crucial to realizing these performance gains, pointing to a robust strategy for industrial gas separation applications that involve higher CO<sub>2</sub> partial pressures (Sutrisna et al., 2018).

The tailored design of nanostructured membranes is crucial for optimizing surface properties and pore architectures, enhancing fouling resistance, and minimizing performance degradation, which is vital in industrial applications where impurities can drastically impact CO<sub>2</sub> separation efficiency. Post combustion capture, a significant area for CO<sub>2</sub> capture, faces challenges due to high water content affecting mixed matrix membranes (MMMs) performance (Shan et al., 2024). Studies using MOFs like SUM-1 and SUM-9 in Pebax-2533 to test CO<sub>2</sub>/N<sub>2</sub> separation at various humidity levels have shown that while CO<sub>2</sub> permeability and selectivity vary with humidity, the large-pore MOFs mainly provide transport channels rather than selective screening, suggesting that optimal humidity levels could enhance MMM performance (Qin et al., 2023). A novel approach, demonstrated in recent studies (Liu et al., 2020), involves the use of UiO-66 particles modified post-synthetically with branched polyethyleneimine (PEI) and coated with ionic liquid [bmim][Tf2N], improving the interfacial morphology and gas separation properties of mixed matrix membranes (Fig. 10A). The amino groups in UiO-66-PEI enhance CO<sub>2</sub> adsorption, while the ionic liquid facilitates smoother interface interactions, significantly increasing CO<sub>2</sub> transport by engaging in reversible reactions with the amine groups as illustrated in Fig. 10B. The membranes containing 15 wt% of this nanocomposite filler exhibit an optimum CO<sub>2</sub>/CH<sub>4</sub> selectivity of 59.99 (Fig. 10C), demonstrating their potential to revolutionize carbon capture and sequestration technologies.

Additionally, CuBTC, known for its adsorption selectivity, faces challenges in humid conditions. This issue was addressed by synthesizing Gly@CuBTC, where CuBTC was grafted with glycine to improve its moisture stability and CO<sub>2</sub> adsorption capacity where the separation mechanism is presented in Fig. 10D. Embedding Gly@CuBTC in Pebax MH 1657 enhanced interfacial compatibility as can be seen from SEM images of the membranes in Fig. 10E and mechanical strength of the MMMs, significantly improving CO<sub>2</sub>/CH<sub>4</sub> separation performance. Particularly, MMMs with 5 wt% Gly@CuBTC exhibited superior CO<sub>2</sub> permeability of 175 Barrer and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 29 (Fig. 10F), demonstrating excellent stability in humid conditions. These advancements indicate that Gly@CuBTC could be a promising filler for developing industrial-scale MMMs for gas separation and purification, aligning with efforts to mitigate performance losses due to environmental factors like humidity (Wu et al., 2022).

Despite the advancements in nanostructured membranes, challenges persist due to the complexity of their construction. The interfacial stability between materials such as MOFs and polymer matrices is critical, as



**Fig. 9.** (A) Schematic illustration of HKUST-1 aerogel; (B) SEM images of HKUST-1 aerogel with different magnifications; (C)  $\text{CO}_2$  adsorption capacity at different temperatures for HKUST-1/ANF-72 aerogel, Isosteric heat of  $\text{CO}_2$  adsorption for HKUST-1 crystal and HKUST-1 aerogel and TPD spectra of  $\text{CO}_2$  at five different heating rates for HKUST-1 crystal and HKUST-1/ANF-72 aerogel (Reproduced with permission from (G. Zhao et al., 2023)). The figures show the synthesis, gas adsorption capacity, and  $\text{CO}_2$  selectivity performance of HKUST-1/ANF composites under different conditions.

incompatibilities or weak interactions can lead to delamination or structural failure under operational stress. Addressing these requires a deep understanding of material interactions and novel synthesis techniques that enhance interfacial bonding (Y. Sun et al., 2023; Teesdale et al., 2023). In tackling such challenges, the innovative use of  $[\text{C5min}][\text{BF}_4]$

encapsulated ZIF-67 (IL@ZIF) composites in defect-free IL/Pebax ion gel matrices shows promise. These mixed matrix ion gel membranes effectively mitigate non-selective interface defects often seen under high MOF loading conditions. The discontinuous dispersion of MOF particles, a typical challenge in polymer matrices which impedes efficient



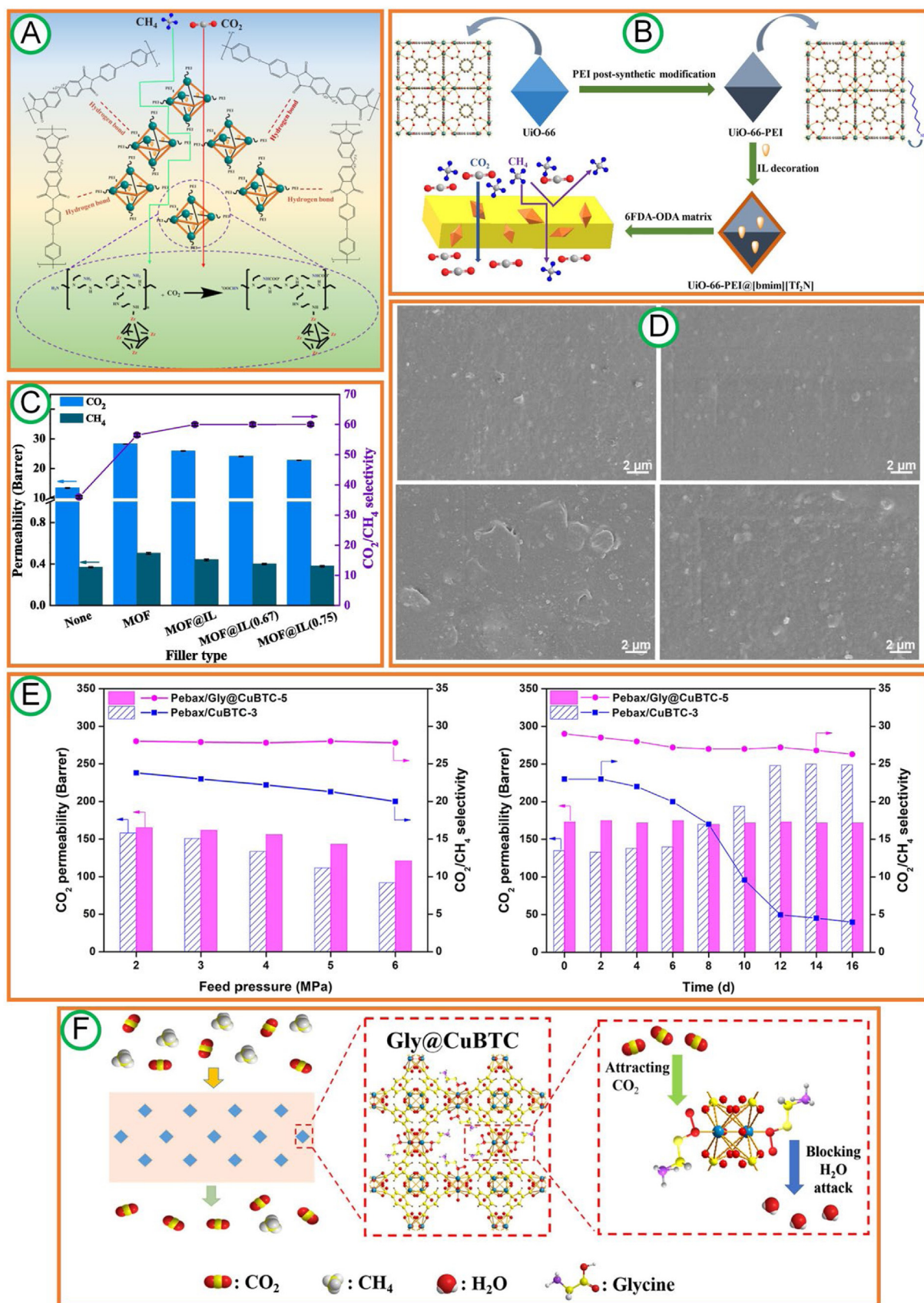


Fig. 10. (A) Scheme of composite membrane synthesis; (B) gas separation mechanism diagram through composite membrane; (C) gas separation membrane through the composite membranes (Figs. 10A-C are reproduced with permission from (Liu et al., 2020)); (D) gas separation mechanism through CuBTC-based mixed matrix membranes or MMMs; (E) SEM images of MMMs; and (F) gas separation performance of CuBTC-based MMMs (Figs. 10D-F are reproduced with permission from (Wu et al., 2022)). The figures illustrate the synthesis, performance, and stability of MOF-based composite membranes for enhanced CO<sub>2</sub> permeability and selectivity under various conditions.



molecular transfer, is addressed by creating continuous and highly selective CO<sub>2</sub> transmission channels through increased filler loading. The IL@ZIF/IL/Pebax membrane, with a high filler content of 80 wt% IL and 70 wt% IL@ZIF, showcases a CO<sub>2</sub> permeability of 408.2 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 97.2, surpassing the latest performance benchmarks (Y. Sun et al., 2023). This approach not only improves the durability of the composite membrane but also enhances its gas separation performance, setting a high reference value for the development of MOF-based MMMs in gas separation.

While nanostructured membranes offer significant advantages in terms of stability and durability for CO<sub>2</sub> capture, ongoing research is essential to fully understand and mitigate the challenges associated with their complex structures. The future of these innovative materials depends on our ability to balance performance enhancements with long-term resilience and environmental sustainability, ensuring their role as a cornerstone technology in the fight against climate change.

Enhancements in size selectivity, CO<sub>2</sub> affinity, and mechanical stability have collectively advanced the performance of MOF-composite membranes, addressing critical challenges in CO<sub>2</sub> capture technologies. These improvements highlight the potential of MOF-based systems for practical applications, yet further innovation is required to overcome barriers related to scalability and cost efficiency. The following section discusses recent advancements in the development of MOF-composite membranes, including novel fabrication techniques, sustainable energy integration, and strategies aimed at enabling their commercial viability for large-scale CO<sub>2</sub> sequestration.

## 5. Recent advancement in MOF-composite membranes development

Recent advancements in the development of MOF-composite membranes have emerged as critical innovations in the field of CO<sub>2</sub> sequestration technologies. These composites are designed to enhance the porosity, durability, and CO<sub>2</sub> selectivity of Metal-Organic Frameworks (MOFs), while simultaneously improving the structural and functional properties of membranes. (Duan et al., 2023). Key developments include the use of advanced materials and fabrication techniques, such as atomic and molecular layer deposition and 3D printing, which allow for precise control over membrane architectures and gas separation performance. Additionally, the integration of MOF-based membranes with renewable energy sources provides a more sustainable approach to powering CO<sub>2</sub> capture processes, reducing both energy consumption and the overall carbon footprint. Despite these significant advancements, challenges related to scalability and commercial viability remain, necessitating further innovations in mass production, cost reduction, and regulatory support. Addressing these challenges is essential for the widespread adoption of MOF-composite membranes as a viable and scalable solution for industrial-scale carbon capture.

### 5.1. Innovative materials and fabrication techniques

The next-generation MOFs are characterized by unprecedented porosity and surface area metrics, with chemical functionalities that have been tailored to optimize CO<sub>2</sub> capture processes. (Aniruddha et al., 2020; Lopez and Perez, 2023). Innovations in MOF chemistry, including the incorporation of amine-functionalized frameworks and the strategic placement of metal centers, exemplify the design strategies employed to maximize CO<sub>2</sub> adsorption properties (Bahamon et al., 2021).

The discussion extends to complex manufacturing techniques crucial for the development of MOF-composite membranes, particularly focusing on detail procedures like molecular and atomic layer deposition (ALD/MLD). These techniques facilitate the precise adjustment of MOF crystal formation on membrane substrates, thereby ensuring a smooth interface for effective gas separation (Crivello et al., 2021; Lausund et al., 2020). Recently, the repertoire of gas-phase MOF thin

film synthesis via ALD/MLD has been expanded to include organic linkers such as 2,6-naphthalenedicarboxylate (2,6-NDC) and biphenyl-4,4'-dicarboxylate (BP-4,4'-DC). The films, deposited using ZrCl<sub>4</sub> with H<sub>2</sub>-2,6-NDC or H<sub>2</sub>-BP-4,4'-DC, initially form in an amorphous state and achieve crystalline MOF structures upon treatment with acetic acid vapor at 160°C. Characterized by techniques such as spectroscopic ellipsometry, photoluminescence, scanning electron microscopy, grazing incidence X-ray diffraction, and X-ray reflectivity, these films have been explored for potential applications in areas benefiting from their porosity, luminescent, and antibacterial properties. This advancement not only broadens the possibilities for MOF applications but also enhances the control over thin film structures with varied pore sizes (Lausund et al., 2020).

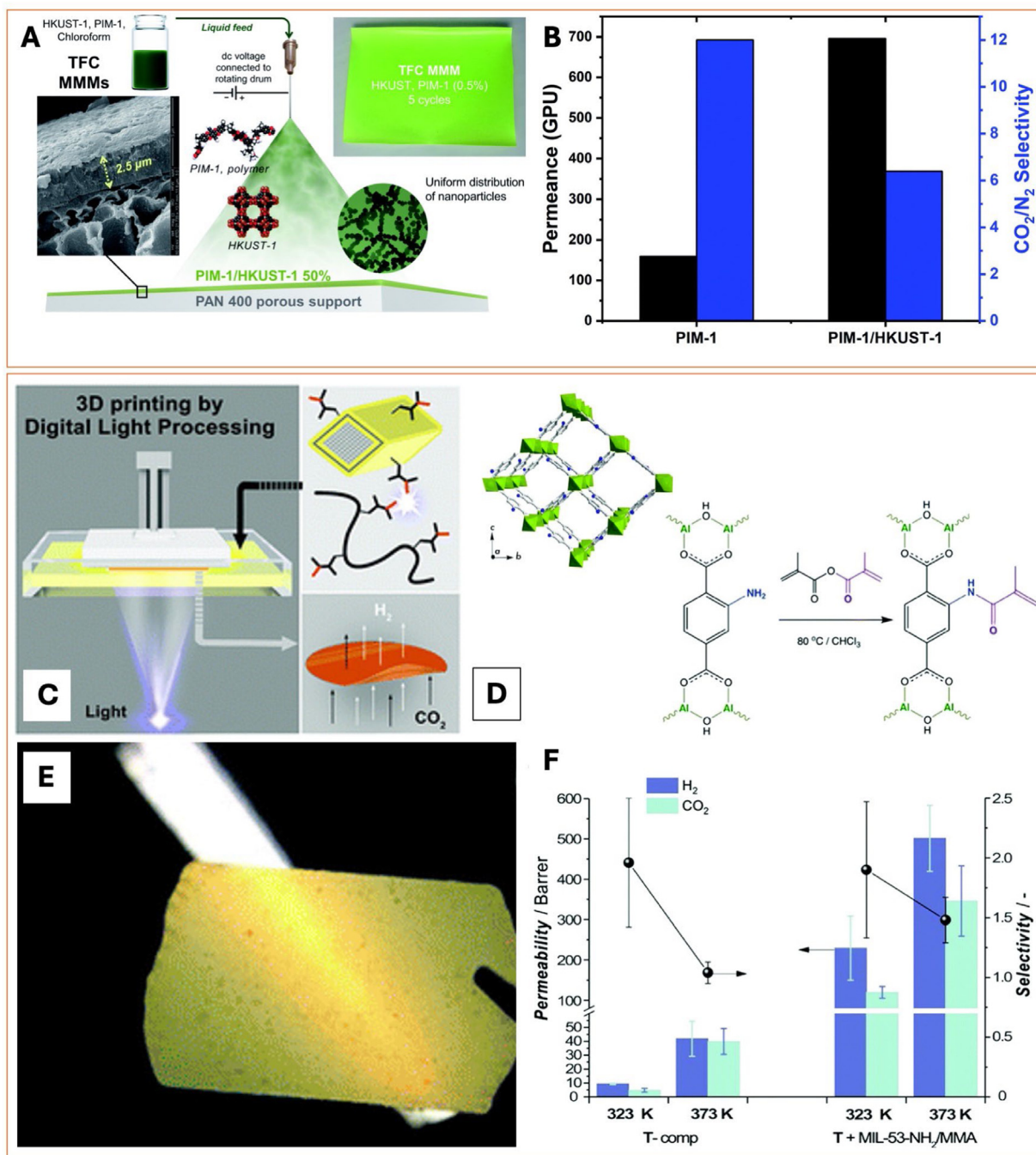
The advent of 3D printing technologies, also known as additive manufacturing, has introduced a paradigm shift in designing and prototyping membrane structures, enabling the creation of complex, hierarchical porosities and geometries previously unattainable. This technological leap not only enhances the mechanical strength and durability of the composites but also allows for the customization of membrane architectures to specific gas separation tasks. (Elsaidi et al., 2021; Pustovarenko et al., 2021). Particularly, MOF-based mixed-matrix membranes (MMMs) have gained attention for their significant separation performance and facile processability in applications like CO<sub>2</sub> separation from flue gas. Using 3D printing techniques such as digital light processing (DLP) and electro spray printing, thin-film composite mixed-matrix membranes (TFC MMMs) with precise control over shape, size, and thickness can be produced. For instance, robust TFC MMMs fabricated using a 3D printing technique demonstrated three times higher CO<sub>2</sub> permeance than neat PIM-1 membranes by adjusting the casting concentration to avoid microscale defects as can be observed in Fig. 11A-B (Elsaidi et al., 2021). Additionally, MOF-based printable inks formulated with commercially available acrylate oligomers and MIL-53(Al)-NH<sub>2</sub> additives post-synthetically modified have been used for fast prototyping of MOF-based MMMs, confirming the applicability of 3D DLP technology for gas separation applications, particularly H<sub>2</sub>/CO<sub>2</sub> separation, while maintaining selectivity and enhancing overall permeability (Fig. 11C-F) (Pustovarenko et al., 2021).

In addition, the synergistic effects achieved through the integration of nanoengineering techniques with traditional membrane fabrication are also very important. Nanoscale manipulation of membrane surfaces, combined with the strategic incorporation of MOF nanoparticles, results in composites with significantly improved gas permeability and selectivity ratios. This nanostructuring approach not only amplifies the intrinsic properties of the MOFs but also optimizes the overall morphology of the composite, leading to enhanced separation efficiencies and operational stability (Rodenas et al., 2014; Rodrigues et al., 2018).

In addressing the scalability and commercial viability of these technologies, recent industrial-scale productions and pilot projects that demonstrate the practical applicability of these advanced MOF-composite membranes need to be explored. The challenges of upscaling, including maintaining material consistency, performance under real-world conditions, and cost-effectiveness, are critically examined (Goh et al., 2022; Liu et al., 2023; Tanvidkar et al., 2022).

### 5.2. Integration with renewable energy sources

The integration of renewable energy significantly enhances the efficiency and effectiveness of CO<sub>2</sub> separation processes, primarily by providing clean energy to power these systems and by acting as a form of energy storage to counter the intermittency of renewable sources. For instance, the integration of renewables with flexible CO<sub>2</sub> capture systems connected to fossil power plants can reduce carbon capture costs and improve operational flexibility, making it a cost-effective and sustainable measure for reducing CO<sub>2</sub> emissions. This integration is heralded as a paradigm shift towards the realization of greener, more sustainable CO<sub>2</sub> capture methodologies that are not only environmentally benign



**Fig. 11.** (A) Scheme of the electrospay 3D printing technique; (B) gas separation performances of produced membranes (Figs. 11A-B are reproduced with permission from (Elsaidi et al., 2021)); (C) Schematic diagram of 3D printing by digital light processing; (D) The chemical structure of MIL-53(Al)-NH<sub>2</sub> structure; (E) images of printed film; and (F) gas separation performances of produced membranes (Fig. 11C-F are reproduced with permission from (Pustovarenko et al., 2021)). All figures show MOF-based membrane fabrication and performance using electrospay 3D printing and digital light processing.

but also economically feasible. The power of solar, wind, and geothermal energies is harnessed to facilitate the adsorption and regeneration phases of the CO<sub>2</sub> capture process, significantly diminishing the carbon footprint and energy consumption traditionally associated with carbon sequestration operations. Additionally, the use of renewable energy-derived hydrogen in CO<sub>2</sub> capture and utilization technologies, such as converting CO<sub>2</sub> to fuel or chemicals, has been promoted to save costs and improve efficiency. The integrated energy system (IES) approach, which combines heat and power generation with carbon capture, electricity to gas, and energy storage, significantly improves renewable energy efficiency and reduces carbon emissions and daily operating costs

compared to traditional models (Fan et al., 2022; Fateminia et al., 2023; Tang et al., 2021).

Integrating MOF-based membranes with renewable energy sources such as solar, wind, and bioenergy can revolutionize energy-intensive processes like gas separation. For instance, solar thermal energy can be used to regenerate MOF materials after gas adsorption without the need for high-energy-consuming thermal processes typically used in traditional gas separation methods. This integration not only reduces the carbon footprint associated with gas separation but also enhances the overall energy efficiency of the system (He et al., 2022). In gas separation fields, the integration of renewable energy with MOF-based mem-

branes can be applied for carbon capture, hydrogen production, and air purification. In carbon capture, MOF-based membranes can be integrated with solar-powered systems to capture CO<sub>2</sub> from industrial emissions and atmospheric air. The use of renewable energy for regeneration of the MOFs after CO<sub>2</sub> adsorption makes the process more sustainable and cost-effective. For example, a study demonstrated that a universal bottom-up method for in situ nanosized MOF assembly within polymer matrices significantly enhanced MOF dispersion, interfacial compatibility, and loading to an unprecedented 67.2 wt % in synthesized mixed matrix membranes (MMMs), which synergistically ameliorated CO<sub>2</sub> solubility (Goh et al., 2022). In hydrogen production, MOF membranes can separate hydrogen from other gases like nitrogen and carbon monoxide in processes such as steam methane reforming or biogas upgrading. Utilizing wind or solar energy to power these separation processes could significantly reduce the environmental impact and improve the economic viability of hydrogen as a clean fuel (Nigiz and Ünügül, 2024). In addition, for air purification, MOF membranes can effectively remove pollutants and toxic gases from the air. Coupling these membranes with bioenergy-generated power sources in ventilation systems could provide a greener and more efficient approach to air purification in both industrial and residential settings (Boone et al., 2022).

Furthermore, the inherent challenges posed by the variability and geographical dependency of renewable energy resources, proposing innovative solutions such as hybrid energy systems and advanced energy storage technologies to ensure a steady and dependable energy supply need to be addressed (Silva et al., 2018; Zantye et al., 2021). In addition, the regulatory, economic, and infrastructural considerations imperative for the widespread adoption of these integrated carbon capture and renewable energy systems, including incentives for renewable energy use, investment in infrastructure development, and advancements in grid integration technologies are required to be considered before implementing the CO<sub>2</sub> capture technologies (Silva et al., 2018).

### 5.3. Scalability and commercial viability

Addressing the scalability and commercial viability of MOF-composite membranes for CO<sub>2</sub> sequestration requires an intricate balance between technological innovation and economic practicality to transition from laboratory success to industrial application. Significant advancements have been made in refining manufacturing processes, with novel methodologies emerging to scale up the production of MOF materials and integrate them into membrane systems without compromising quality or functionality (Liu et al., 2023; Tanvidkar et al., 2022). This encompasses breakthroughs in chemical synthesis, automation, and modular design, which collectively contribute to reducing costs and enhancing the environmental sustainability of production processes.

Evaluating the durability and performance consistency of MOF-composite membranes under varied industrial operational conditions reveals significant advancements in material engineering. These advancements have increased resilience to mechanical stress, chemical degradation, and fluctuating temperatures, thereby extending the lifespan of the composites and reducing maintenance costs (Shan et al., 2024; Sutrisna et al., 2017; Yoo et al., 2016). For instance, a series of metal-organic frameworks (MOFs), M<sub>2</sub>(dobpdc) (M=Mn, Co, Ni, Zn; H4dobpdc=4,4'-dihydroxy-1,1'-biphenyl-3,3'-dicarboxylic acid), have shown high CO<sub>2</sub> binding affinity and structural stability in challenging environments. The structural stability of Ni<sub>2</sub>(dobpdc) is particularly notable; it has proven durable in water vapor, liquid water, and even in refluxing conditions, maintaining integrity across a wide pH range (2–13). This resilience is crucial for their use in separation applications where they must be assembled into thin, continuous, macroscopic films (Yoo et al., 2016). An example includes the ultrathin, continuous zeolitic imidazolate framework (ZIF-8) membranes prepared on titania-functionalized porous polymeric supports. These membranes are not only flexible and well-adhered but also exhibit molecular sieving behaviour close to the theoretical permeability of ZIF-8, demonstrating

significant opportunities for exploiting MOF properties in the fabrication of advanced separation and sensing devices (Hou et al., 2016).

Additionally, the integration of membrane-MOF systems into existing infrastructure is crucial, with attention to the design and logistical considerations that facilitate their adoption without necessitating extensive modifications to current facilities. This includes the compatibility of these systems with existing flue gas treatment processes and their adaptability to different industrial scales and settings (Gkotsis et al., 2023). Lastly, There are challenges that need to be addressed before widespread commercialization of MOF-composite membranes, such as the need for further cost reductions, the optimization of MOF synthesis for mass production, and the establishment of clear regulatory frameworks (Ankit et al., 2024; Gkotsis et al., 2023). In addition, further research is required, particularly focusing on innovative material science, economic analysis, and the exploration of policy incentives that could accelerate the market readiness of these composites for CO<sub>2</sub> capture. One particular attention should be on the efforts to fabricate mixed matrix membranes in hollow fibre configuration that are usually applied in industrial application to capture CO<sub>2</sub> gas (An et al., 2023; Ding et al., 2023; Kamaludin et al., 2023; Zeeshan et al., 2024). For instance, hollow fibre mixed matrix membranes (HFMMMs) utilizing cellulose triacetate (CTA) and amine-functionalized MOF (NH<sub>2</sub>\_MIL-125(Ti)) have shown promising results. The NH<sub>2</sub>\_MIL-125(Ti)/CTA HFMMMs demonstrated a CO<sub>2</sub>/CH<sub>4</sub> ideal gas selectivity of 6.87 and a CO<sub>2</sub> permeability of 26.46 GPU when spun at an air gap of 1 cm (Sunder et al., 2023). These findings highlight the potential of HFMMMs in CO<sub>2</sub> capture and the need for further advancements to contribute significantly to global climate change mitigation efforts.

Enhancing gas separation membranes for industrial applications is critical to improving energy efficiency and reducing environmental impacts. Central to this enhancement is the membrane module, where individual membranes in flat sheet or hollow fiber configurations are integrated for large-scale application. Hollow fiber mixed matrix membranes (HF-MMMs) stand out due to their superior packing density, advantageous surface-area-to-volume ratio, and lower production costs per unit area compared to flat sheet membranes, despite their more intricate fabrication processes (Hua et al., 2024). Numerous studies have demonstrated the promising performance of HF-MMMs, particularly for CO<sub>2</sub> separation, through the incorporation of advanced fillers such as metal-organic frameworks (MOFs). For example, Liu et al. embedded Y-fumfuc-MOF into 6FDA-DAM for CO<sub>2</sub> and H<sub>2</sub>S removal, achieving enhanced gas separation capabilities (Liu et al., 2018). Similarly, ZIF-8 fillers incorporated into polybenzimidazole (PBI) hollow fibers improved H<sub>2</sub> permeance from 65 to 107 GPU while maintaining H<sub>2</sub>/CO<sub>2</sub> selectivity of 18 under 150°C and 7 bar conditions (Exteberria-Benavides et al., 2020). In another study, the addition of ZIF-8 into poly(styrene-ionic liquid) hollow fiber membranes (p(SIL) HFMs) enhanced CO<sub>2</sub> permeance by 33%, reaching 6 GPU with CO<sub>2</sub>/N<sub>2</sub> selectivity of 30 at optimal filler loading (Lai et al., 2022). Furthermore, amine-modified SiO<sub>2</sub>/ZIF-8 nanofillers in polysulfone (PSf) matrices improved CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivities by 61.46% and 89.75%, respectively, while achieving a CO<sub>2</sub> permeability of 4.25 barrer through facilitated transport mechanisms (Sasikumar et al., 2021). Incorporating UiO-66-NH<sub>2</sub> into Pebax-based HF-MMMs further enhanced CO<sub>2</sub> permeance by 80% and CO<sub>2</sub>/CH<sub>4</sub> selectivity by 170% due to improved interfacial compatibility and CO<sub>2</sub> affinity of the amine groups (Sutrisna et al., 2018). While challenges such as plasticization and filler agglomeration remain, the combination of high-performing MOFs with hollow fiber membranes underscores their transformative potential for scalable, industrial gas separation processes.

The advancements in MOF-composite membrane development outlined in Chapter 5 highlight significant progress in material design, fabrication techniques, and renewable energy integration, paving the way for efficient and scalable CO<sub>2</sub> capture technologies. However, as discussed in Chapter 6, translating these innovations into industrial-scale solutions requires addressing key challenges, including material stabil-



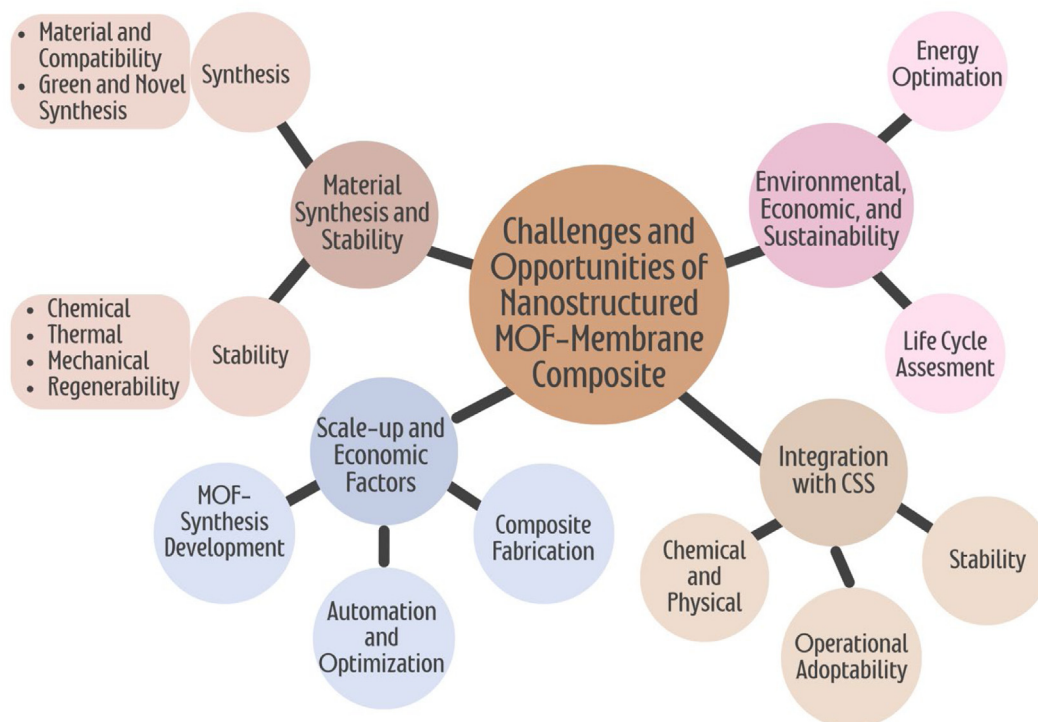


Fig. 12. Challenges and opportunities of nanostructured MOF-membrane composite used in CO<sub>2</sub> sequestration processes. The figure outlines the challenges and opportunities of nanostructured MOF-membrane composites for CO<sub>2</sub> sequestration, including synthesis, stability, scalability, economic factors, and sustainability.

ity, economic viability, and system integration. By bridging the gap between laboratory success and real-world applications, continued research and interdisciplinary collaboration can unlock the full potential of MOF-composite membranes, driving their adoption as a sustainable and economically feasible solution for global CO<sub>2</sub> sequestration efforts.

## 6. Challenges and opportunities

In the pursuit of effective CO<sub>2</sub> sequestration, the development of nanostructured MOF-composite membranes encounters several significant hurdles including material synthesis challenges, scale-up issues, and integration complexities. Yet, this field also presents remarkable opportunities through advancements in material science, which promise enhanced CO<sub>2</sub> capture efficiencies and stability (Goh et al., 2022). Moreover, the potential environmental benefits and market opportunities of these composites align with global sustainability efforts and the urgent need to address climate change. As such, continued innovation could lead to substantial societal impacts by providing viable solutions to mitigate greenhouse gas emissions and promote a circular carbon economy. Fig. 12 illustrates some challenges and opportunities for MOFs based membranes applied in CO<sub>2</sub> capture and separation processes.

### 6.1. Material synthesis and stability

The challenge of material synthesis and stability is crucial in the advancement of nanostructured MOF-composite membranes, particularly for applications in CO<sub>2</sub> sequestration. The intricate process of embedding MOFs within membrane matrices demands not only precision in the composite's fabrication but also a deep understanding of the interaction between MOF particles and the polymer matrix. Achieving a homogeneous distribution of MOFs across the membrane is crucial, as it directly influences the composite's selectivity and permeability towards CO<sub>2</sub>. This uniformity ensures that each part of the membrane contributes equally to CO<sub>2</sub> capture, optimizing the overall efficiency of the process (Karakiliç et al., 2019; Yu et al., 2024).

Moreover, the chemical and physical stability of MOFs within composites under operational conditions remains a significant concern. Environmental factors such as humidity, temperature variations, and the presence of other gases can impact the structural integrity and functionality of MOFs. For instance, moisture can induce structural changes or degradation in some MOFs, leading to a loss in adsorption capacity and selectivity for CO<sub>2</sub>. Similarly, thermal stability is essential for applications involving high temperatures, where some MOFs might decompose or lose their CO<sub>2</sub> capturing abilities (Seok Chae et al., 2022; Xin et al., 2021). Research has shown that despite these challenges, innovations in MOF composites have yielded promising results. For example, the epn-functionalized Mg<sub>2</sub>(dobpdc) composites mixed with a hydrophobic polymer were shaped into membranes (epn-MOF80@SBS), exhibiting a significant CO<sub>2</sub> adsorption capacity of 2.8 mmol.g<sup>-1</sup> at 1000 ppm. These composites maintained their CO<sub>2</sub> removal performance over multiple cycles and even after prolonged exposure to a humid environment (60% relative humidity), demonstrating their potential for practical indoor CO<sub>2</sub> capture applications (Seok Chae et al., 2022).

Similarly, hierarchical porous composite Mg-MOF-74/MCFs, synthesized via a facile solvothermal method, showed enhanced CO<sub>2</sub> adsorption properties after hydrothermal treatment. The composites initially displayed a CO<sub>2</sub> adsorption capacity of 1.68 mmol.g<sup>-1</sup>, which increased to 2.66 mmol.g<sup>-1</sup> post-treatment, surpassing that of pristine Mg-MOF-74 (2.39 mmol.g<sup>-1</sup>). This improvement highlights the impact of composite formation and post-synthesis treatment on enhancing the stability and functionality of MOFs in varying environmental conditions (Xin et al., 2021). These advancements highlight the potential of MOF composites to address the dual challenges of chemical stability and efficient CO<sub>2</sub> capture, offering viable solutions for reducing indoor CO<sub>2</sub> levels to safe concentrations while mitigating the effects of environmental factors on MOF performance.

Addressing these challenges requires a multidisciplinary approach, integrating advancements in materials science, chemistry, and engineering. Innovations in MOF design, such as the development of more robust frameworks and the functionalization of MOFs with specific groups to

enhance interaction with the polymer matrix, are under exploration. Additionally, the exploration of advanced synthesis techniques that allow for better control over MOF particle size, distribution, and incorporation into membranes is crucial. This includes solvothermal synthesis, microwave-assisted synthesis, and layer-by-layer assembly, each offering unique advantages in terms of MOF integration and composite stability (Li et al., 2023; Sutrisna et al., 2020).

Furthermore, the long-term stability and regenerability of MOF-composite membranes under cyclic CO<sub>2</sub> adsorption-desorption processes are critical for their commercial viability. Research into the development of composites that maintain their structural integrity and performance over extended periods and under varying conditions is essential. This not only improves the economic feasibility of these materials for CO<sub>2</sub> capture but also contributes to the sustainability of the technology. (Sutrisna et al., 2018, 2017). The synthesis and stability of MOF-composite membranes for CO<sub>2</sub> sequestration encompass a complex array of challenges that require innovative solutions. Pebax-based composite hollow fiber membranes have emerged as promising candidates for industrial gas separation but are limited by the inherent separation performance of polymeric materials and poor operational stability, especially under elevated pressures. The incorporation of metal-organic frameworks (MOFs) has been extensively investigated as a potential solution. Notably, zirconium-based MOF (UiO-66) with carboxyl (-COOH) and amino (-NH<sub>2</sub>) surface modifications showed significant enhancements in CO<sub>2</sub> permeance and stability under high pressure (Sutrisna et al., 2018). Further advancements include embedding glycine-grafted CuBTC (Gly@CuBTC) into Pebax MH 1657, which demonstrated improved moisture stability and CO<sub>2</sub> adsorption capacity. Pebax/Gly@CuBTC MMMs exhibited a CO<sub>2</sub> permeability of 175 Barrer and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 29 with 5 wt% Gly@CuBTC, showing excellent stability against moisture. These developments highlight the potential to significantly enhance CO<sub>2</sub> sequestration technologies, contributing to global climate change mitigation efforts (Wu et al., 2022).

## 6.2. Scale-up and economic viability

Scaling up the production and ensuring the economic viability of nanostructured MOF-composite membranes for CO<sub>2</sub> sequestration are paramount challenges that stand at the forefront of transitioning this promising technology from the confines of research laboratories to the global industrial area. The intricacies involved in upscaling—such as achieving homogeneity in MOF distribution within the membranes, preserving the delicate structural integrity and functionality of MOFs at increased scales, and overcoming the substantial costs associated with high-grade materials and sophisticated manufacturing processes—pose considerable obstacles (Liu et al., 2023; Y. Sun et al., 2023; Yu et al., 2024). These challenges are compounded by the rigorous demands for chemical and thermal stability of the composites under operational conditions, which are critical for their long-term performance and reliability.

The economic hurdles are not just confined to the raw material and production costs but also encompass the energy-intensive nature of conventional MOF synthesis methods and the specialized equipment required for composite fabrication. Despite these barriers, the sector is ripe with opportunities for innovation and cost reduction. Emerging methodologies in MOF synthesis, such as the development of greener, less energy-consuming approaches and the utilization of cheaper, more abundant precursor materials, are beginning to show potential for minimizing costs (Gao et al., 2021). For instance, the novel bimetallic Zn/Mg-MOF-74 synthesized by a facile one-pot method demonstrated excellent CO<sub>2</sub> adsorption capacity (128.3 cm<sup>3</sup>.g<sup>-1</sup> at 273 K and 1 bar) and efficient catalytic activity for converting CO<sub>2</sub> and epoxides to cyclic carbonates with over 99% yield and selectivity under mild conditions (60°C, 0.8 MPa). This catalyst also exhibited good recyclability for at least five runs and versatility to various substrates, showcasing a competitive avenue for integrating CO<sub>2</sub> adsorption and catalytic conversion,

thereby contributing to the overall reduction of economic barriers in MOF applications (Gao et al., 2021). Similarly, advances in membrane technology that focus on scalable manufacturing techniques and the integration of automation and process optimization can further reduce production expenses and enhance the feasibility of large-scale operations (Kamaludin et al., 2023; Zeeshan et al., 2024).

Moreover, the environmental benefits and the strategic importance of MOF-composite membranes in mitigating CO<sub>2</sub> emissions introduce a compelling economic rationale for investment in this technology. Governmental incentives, such as subsidies, tax breaks, and grants for green technologies, alongside partnerships between academic institutions, government agencies, and industry players, can significantly alleviate financial burdens and stimulate market readiness. Additionally, the development of robust business models that leverage the unique advantages of these composites—such as their superior selectivity and efficiency in CO<sub>2</sub> capture—can open up new markets and applications, from industrial gas separation to direct air capture, further enhancing their economic attractiveness (M. Zhao et al., 2023).

One significant advancement contributing to the scalability and economic viability of MOF materials, including those used in MOF-composite membranes, is the development of novel large-scale manufacturing processes. A recently introduced method utilizes supercritical carbon dioxide (scCO<sub>2</sub>) for the continuous synthesis of the zirconium-based MOF, UiO-66. This process employs a custom counter-current mixer, enhancing heat and mass transfer to MOF precursor materials, facilitating a rapid reaction time of less than 3 seconds and achieving a production rate of 104 g.h<sup>-1</sup> for UiO-66, confirmed via SEM images, PXRD spectra, and physisorption analysis. This method also allows for the recovery of effluent and unreacted material, addressing challenges often encountered in hydrothermal and supercritical water-based systems (Rasmussen et al., 2020). Similarly, the high-throughput synthesis and characterization of nanocrystalline porphyrinic zirconium MOFs, as demonstrated by Kelty et al. (2016), employs a programmable liquid handler to prepare up to 96 reactions simultaneously, with subsequent analysis via high-throughput PXRD (Kelty et al., 2016). This method resulted in the isolation of MOF-525, MOF-545, and PCN-223 at the nanoscale, with MOF-525 cubic crystals having edge sizes of 122(20), 256(39), and 341(62) nm, MOF-545 rod-shaped crystals measuring 117(22) × 34(7), 203(35) × 52(11), and 502(95) × 122(30) nm, and PCN-223 ellipsoidal crystals with dimensions of 535(51) × 331(32), 679(159) × 383(74), and 804(133) × 400(59) nm. These methods highlight the potential for large-scale and economically viable production of MOFs, suitable for various applications including catalysis, light harvesting, photodynamic therapy, and chemical sensing (Kelty et al., 2016).

This scalable synthesis approach not only supports the feasibility of deploying MOFs in various applications, including CO<sub>2</sub> sequestration, but also aligns with strategic financial mechanisms aimed at commercializing MOF-composite membranes. By combining innovations in material science, manufacturing technologies, and strategic financial mechanisms, a multidisciplinary approach can unlock the full potential of this technology. Such advancements are not only important for the commercial success of MOF-composite membranes but also for their critical role in offering a sustainable solution to one of the most pressing environmental issues of our time—climate change.

## 6.3. Integration and System Compatibility

The integration and system compatibility of nanostructured MOF-composite membranes within the broader carbon capture and storage (CCS) ecosystem represents a crucial yet intricate challenge that requires attention. This challenge is multifaceted, involving not only the physical and chemical integration of these advanced materials into existing and future CCS technologies but also their operational adaptability across a spectrum of environmental conditions and industrial processes. A critical aspect of this integration involves ensuring that MOF-composite

membranes can maintain high performance levels—specifically in terms of CO<sub>2</sub> capture efficiency and selectivity—when subjected to the dynamic and often harsh conditions characteristic of industrial-scale operations (Dong et al., 2013; Wu et al., 2021).

A recent development that showcases this capability in practice is the versatile pilot-scale two-stage membrane plant designed for CO<sub>2</sub> capture from different simulated exhaust gases, akin to those emitted by coal-fired power plants, steel mills, and cement plants, with typical CO<sub>2</sub> concentrations of 14%, 25%, and 35% respectively (Wu et al., 2021). The plant's performance was rigorously tested under varying operational pressures, humidifier temperatures, and stage-cuts. Remarkably, the CO<sub>2</sub> capture rates achieved were 61.3%, 60.7%, and 53.9% for the different gas compositions, while the resulting CO<sub>2</sub> purities in the product gas reached 78.5%, 87.2%, and 96.3% respectively. This pilot project not only demonstrated the practical feasibility and adaptability of membrane technology in industrial applications but also laid the groundwork for the future construction of a three-stage and three-step membrane plant in Nanjing, China, expected to achieve 95% CO<sub>2</sub> product purity and 90% CO<sub>2</sub> capture rate by early 2021. The experience and insights gained from this study could significantly accelerate the industrial application of MOF-composite membranes in CO<sub>2</sub> capture, addressing the intricate challenges of integrating these advanced materials into large-scale operations.

The task of integrating these composites extends beyond mere material compatibility; it requires a holistic approach that considers the operational, economic, and environmental sustainability of incorporating such materials into the existing CCS infrastructure. This includes evaluating the durability of MOF-composite membranes under prolonged exposure to mixed gas streams, their resistance to fouling and chemical degradation, and their ability to be regenerated with minimal energy input (Dong et al., 2013). In a recent study, carbonic anhydrase (CA) molecules were embedded into MOFs (CA@ZIF-8) and encapsulated in poly(vinyl alcohol) (PVA)-chitosan (CS) hydrogel networks to create CA@ZIF-8-PVA-CS composite hydrogels. These composite membranes demonstrated high activity, stability, and reusability, with an immobilization efficiency of over 70%. They showed greater stability against high temperatures, denaturants, and acids compared to free CA and CA@ZIF-8. Notably, the amount of calcium carbonate obtained by PVA/CS/CA@ZIF-8 hydrogel membranes was 20- and 1.63-fold higher than that of free CA and CA@ZIF-8 composites, respectively. The hydrogel membranes maintained 50% of their original activity after 11 cycles, whereas CA@ZIF-8 completely lost activity. These results indicate that PVA/CS/CA@ZIF-8 membranes can be efficiently applied to CO<sub>2</sub> sequestration, underscoring the potential for these advanced materials in sustainable CCS solutions (Ren et al., 2019).

Moreover, the economic implications of adopting membrane-MOF technologies on a large scale, such as the cost of material production, the lifespan of the composites, and the overall impact on the cost-per-ton of captured CO<sub>2</sub>, must be rigorously assessed to ensure that these innovative solutions are not only technically viable but also commercially competitive (Cheng et al., 2022; Dong et al., 2013; Wu et al., 2021).

In addition, the seamless integration of MOF-composite membranes into the CCS value chain—spanning CO<sub>2</sub> capture, purification, transportation, and storage phases—demands innovative engineering solutions. These solutions should aim to optimize the interface between the composites and existing infrastructure, developing new module designs and process configurations that leverage the unique properties of MOFs for enhanced CO<sub>2</sub> sequestration (Cheng et al., 2022; Wu et al., 2021). Addressing these integration challenges is essential for advancing the deployment of MOF-composite membranes as a viable and sustainable technology for combating climate change. Success in this endeavour requires a concerted effort from researchers, engineers, policymakers, and industry stakeholders to navigate the complex interplay between material science, engineering design, and economic feasibility. By overcoming these hurdles, we can unlock the transformative potential of MOF-composite membranes, paving the way for their significant contribution

to global CO<sub>2</sub> reduction efforts and the transition towards a more sustainable and low-carbon future.

#### 6.4. Innovations in material science

The field of material science is at the forefront of revolutionizing CO<sub>2</sub> sequestration technologies, with a particular focus on the refinement and application of nanostructured MOF-composite membranes. This innovative domain presents a plethora of opportunities for tailoring material properties to address the specific challenges of CO<sub>2</sub> capture and separation. One of the most promising avenues of research involves the development of novel MOFs characterized by their exceptional surface areas, tunable pore structures, and functionalized sites, which are designed to enhance CO<sub>2</sub> adsorption capacity and selectivity significantly (Cheng et al., 2022; Goh et al., 2022). Furthermore, advancements in nanotechnology have enabled the engineering of membranes with nanostructured interfaces, which are crucial for facilitating higher gas permeability and ensuring robustness against the harsh conditions often encountered during CO<sub>2</sub> capture processes.

Moreover, the integration of computational modeling and machine learning techniques into material science research has catalyzed the discovery and optimization of MOF-composite membranes. These tools allow for the prediction of material performance and the identification of optimal synthesis conditions, thereby streamlining the development process and reducing the time from concept to application. To fully harness this potential, a multiscale analytical approach employing density functional theory (DFT), grand canonical Monte Carlo (GCMC), and machine learning (ML) has been utilized to elucidate the most influential features of MOFs for CO<sub>2</sub> capture. Computational synthesis methods were deployed to create sets of MOFs combining 16 topologies with 13 functionalized molecular building blocks, resulting in a comprehensive exploration of 31 parent MOFs and their derivatives. The CO<sub>2</sub> capture efficacy of these materials was found to be strongly influenced by the type of functionalization—hydroxyl, thiol, cyano, amino, or nitro groups—each contributing differently based on the pore topology. Machine learning models, including decision trees, were trained to predict the impact of these chemical modifications on CO<sub>2</sub> capture metrics, helping to identify without human bias the most critical structural and topological factors (Anderson et al., 2018).

Additionally, the exploration of green synthesis methods and the utilization of sustainable resources for MOF and membrane fabrication emphasizes the commitment to environmental stewardship within the field. One study has successfully prepared a metal-organic framework/MOF-covalent organic framework/COF (IRMOF3-TzDa) composite. Prepared via microwave-assisted solvothermal methods, this composite demonstrated a remarkable capacity for Cu<sup>2+</sup> adsorption, reaching 86 mg·g<sup>-1</sup>, as determined by Langmuir isotherm model fitting. In mixed metal ion solutions, the IRMOF3-TzDa exhibited high selectivity for Cu<sup>2+</sup>, facilitated by the strong affinity and rapid  $\pi$  electron transfer between the material and Cu<sup>2+</sup>. This property was leveraged to develop a fluorescence sensing platform for Cu<sup>2+</sup> detection, achieving a detection limit of 2.2  $\mu$ M with excellent precision and a linear range of 10–500  $\mu$ M. Such capabilities not only emphasize the versatility of MOF-COF composites in environmental applications but also their potential in contributing to more sustainable technologies in CCS and beyond (Ankit et al., 2024).

The implications of these material science innovations extend beyond the technical enhancements of CO<sub>2</sub> sequestration technologies; they also offer a sustainable pathway to mitigate climate change impact. By reducing the energy requirements and increasing the efficiency of CO<sub>2</sub> capture processes, these advancements contribute to the development of economically viable and environmentally friendly solutions. Furthermore, the scalable production and integration of these advanced materials into existing industrial infrastructures could significantly decrease global CO<sub>2</sub> emissions, paving the way for a cleaner, more sustainable future (Ban et al., 2020; Goh et al., 2022; Kalaj et al., 2020). The continuous exploration and application of cutting-edge material science



innovations in developing nanostructured MOF-composite membranes are crucial for advancing CO<sub>2</sub> sequestration technologies. These efforts not only promise to surmount current limitations through enhanced material performance but also align with broader environmental goals, illustrating the critical role of material science in achieving a sustainable balance between industrial development and climate change mitigation.

The practical deployment of MOFs in industrial processes hinges on their ability to undergo efficient regeneration—a process crucial for ensuring economic and environmental sustainability. Recent advancements have significantly expanded our understanding and capability in regenerating MOFs, enabling repeated cycles of adsorption and desorption while maintaining their structural integrity and performance (Hashemi et al., 2022).

#### 6.4.1. Thermal Regeneration Techniques

Thermal regeneration is one of the most established methods for restoring MOFs. Temperature Swing Adsorption (TSA) involves heating the adsorbent with inert gases such as nitrogen, helium, or argon to desorb retained molecules. Studies have demonstrated the effectiveness of TSA in regenerating MOFs like MIL-101(Cr), achieving over 95% CO<sub>2</sub> desorption efficiency after five cycles at 75°C and 20 kPa (Liu et al., 2013). However, TSA's reliance on elevated temperatures and prolonged heating poses energy efficiency challenges. To address this, Vacuum-Temperature Swing Adsorption (VTSA) combines reduced pressure with moderate heating, improving desorption rates while lowering energy consumption. For example, MIL-101(Cr) demonstrated near-complete regeneration under VTSA conditions, with CO<sub>2</sub> desorption efficiencies approaching 99% after multiple cycles (Hashemi et al., 2022; Liu et al., 2013).

Further, research using CuBTC and MIL-53(Al) under vacuum-pressure swing adsorption or VPSA regeneration conditions revealed the complete desorption of CO<sub>2</sub> during thermogravimetric analysis, showcasing their stability and ability to maintain performance over multiple cycles. This highlights the potential of VPSA as an efficient method for industrial-scale regeneration (Majchrzak-Kuceba and Bukalak-Gaik, 2016).

Innovative thermal techniques have also emerged to enhance regeneration efficiency. Microwave Swing Adsorption (MSA) uses electromagnetic waves to induce localized heating, significantly reducing the time and energy required for desorption. Experiments with HKUST-1 and UiO-66 have shown complete desorption within 4–35 minutes, a stark contrast to conventional TSA's extended heating durations (Lee et al., 2019). Similarly, Magnetic Induction Swing Adsorption (MISA) integrates magnetic nanoparticles into MOFs, enabling targeted heating through magnetic fields. This method has achieved CO<sub>2</sub> desorption efficiencies of up to 97.7% for UiO-66, with energy costs 45% lower than those of traditional materials (Tao et al., 2019).

#### 6.4.2. Non-Thermal Regeneration Methods

Non-thermal methods offer alternatives that reduce energy demands and preserve MOF integrity. Solvent-assisted regeneration has proven effective for removing adsorbates through chemical extraction. For instance, TMU-5, when treated with methanol and dried at 110°C, maintained 90% of its adsorption capacity after four cycles (Bagheri et al., 2017). This method is particularly advantageous for MOFs sensitive to high temperatures, as it operates under more moderate conditions. Similarly, purging with inert gases such as helium or nitrogen is another non-thermal technique. UiO-66(NH<sub>2</sub>), for example, retained 95% of its adsorption capacity after three cycles of nitrogen purging at ambient temperature (Vellingiri et al., 2017). These methods are highly effective in scenarios where thermal degradation of the framework is a concern.

Vacuum Swing Adsorption (VSA), Pressure Swing Adsorption (PSA), and Vacuum-Pressure Swing Adsorption (VPSA) are also widely utilized for regenerating MOFs used in gas separations. VPSA, a hybrid method, combines the strengths of VSA and PSA by operating at higher

adsorption pressures and sub-atmospheric desorption pressures. This approach has demonstrated exceptional efficiency in applications such as CO<sub>2</sub> capture, where it minimizes the energy needed for gas evacuation (Hashemi et al., 2022; Majchrzak-Kuceba and Bukalak-Gaik, 2016).

#### 6.4.3. Reconstruction Techniques

In cases of partial or complete structural degradation, reconstruction offers a means to restore MOFs to their original functionality. Moisture-sensitive MOFs, for example, often decompose into metal hydroxides and protonated linkers. By employing solvent-assisted reconstruction, such degraded materials can be reassembled. HKUST-1, after decomposition, was regenerated by exposure to ethanol under mild stirring at room temperature, regaining 94% of its original porosity and 85% of its CO<sub>2</sub> adsorption capacity (Majano et al., 2014). Chemical treatment methods further extend the scope of reconstruction. For instance, UiO-66, after being digested in bicarbonate solutions, was re-synthesized under solvothermal conditions, achieving comparable performance to freshly prepared samples (Chu et al., 2020).

Moreover, studies on MOF-derived Ni-Ce catalysts used in dry reforming of methane (DRM) demonstrated that two-cycle regeneration at 700°C under CO<sub>2</sub> flow retained excellent activity and selectivity, achieving CH<sub>4</sub> and CO<sub>2</sub> conversions of 96% and 99%, respectively. These findings underscore the stability of reconstructed MOFs for catalytic applications under harsh conditions (Alli et al., 2025).

The feasibility of MOF regeneration is closely tied to cost. Certain MOFs, such as MOF-74, are priced as high as \$41,250 per kilogram, emphasizing the need for cost-effective regeneration techniques (Hashemi et al., 2022). Efficient methods like MISA and VTSA significantly reduce operational costs by lowering energy consumption and extending the material's lifespan. These advancements are critical for transitioning MOFs from laboratory-scale research to large-scale industrial applications.

In addition, Cu-MOF hybrids, synthesized within SBA-15 mesopore channels, have shown remarkable regeneration performance for CH<sub>3</sub>SH adsorption, achieving 1.7 mol CH<sub>3</sub>SH per mol Cu—a capacity far exceeding that of standalone Cu-MOFs (0.7 mol CH<sub>3</sub>SH per mol Cu). Regeneration was achieved hydrothermally at 80°C, maintaining over 70% capacity across six cycles, demonstrating their potential as cost-effective, regenerable adsorbents (Jiang et al., 2025).

While significant progress has been made, challenges remain in optimizing regeneration processes to balance energy efficiency, structural stability, and performance retention. Innovative approaches, such as combined magnetic-light induction swing adsorption, show promise as scalable, low-energy solutions (Hashemi et al., 2022). Furthermore, expanding the understanding of adsorption and desorption mechanisms will guide the development of tailored regeneration strategies for diverse industrial applications. Integrating reconstruction methods into regeneration cycles could also mitigate the gradual degradation of MOFs, enhancing their durability and broadening their applicability (Chu et al., 2020; Hashemi et al., 2022; Jiang et al., 2025).

The regeneration of MOFs represents a dynamic field with substantial implications for their industrial viability. By leveraging advancements in thermal, non-thermal, and reconstruction techniques, researchers have laid the groundwork for sustainable and efficient MOF applications. Continued innovation in this area will not only enhance the economic feasibility of MOFs but also pave the way for their adoption in large-scale processes, contributing to cleaner and more efficient technologies across various industries.

#### 6.5. Environmental impact and sustainability

Exploring the environmental impact and sustainability of nanostructured MOF-composite membranes for CO<sub>2</sub> sequestration elucidates their transformative potential in steering global efforts towards a more sustainable and climate-resilient future. The advent of these composites represents a significant leap forward in carbon capture technology, not

only by enhancing the efficiency of CO<sub>2</sub> sequestration but also by embodying the principles of green chemistry and sustainable engineering. The synthesis of MOF-composite membranes, when approached with an emphasis on minimizing energy consumption and utilizing renewable or less environmentally damaging resources, sets a new benchmark for eco-friendly innovation in material science (Annamalai et al., 2022; Research Institute of Medicine and Pharmacy, Qiqihar Medical University, China et al., 2023). Moreover, the lifecycle assessment of these composites is critical, encompassing the energy and resource inputs from synthesis to end-of-life disposal or recycling, thereby ensuring that their environmental footprint is minimized across all stages. Such comprehensive evaluations help in identifying and mitigating any potential ecological impacts, reinforcing the sustainability credentials of these materials.

The role of nanostructured MOF-composite membranes extends beyond mere CO<sub>2</sub> capture; they embody a paradigm shift towards circular carbon economies, where captured CO<sub>2</sub> is not seen merely as waste but as a resource for further utilization in various industrial applications, thus contributing to a reduction in the overall carbon footprint (Liu et al., 2023). This holistic approach to carbon management not only aids in combating climate change but also promotes sustainable development by integrating economic, environmental, and societal benefits.

Furthermore, the scalability and adaptability of these composites to diverse industrial settings prove their potential to replace more energy-intensive CO<sub>2</sub> capture technologies, thereby reducing operational costs and enhancing the sustainability profile of industries (Duan et al., 2018; Liu et al., 2023). By fostering the development and deployment of such advanced materials, we edge closer to achieving the United Nations Sustainable Development Goals, particularly those related to industry, innovation, and infrastructure (Goal 9), responsible consumption and production (Goal 12), and climate action (Goal 13). Nanostructured MOF-composite membranes for CO<sub>2</sub> sequestration stand at the confluence of environmental science, material innovation, and sustainable industrial practice. Their development and application offer a promising pathway to not only mitigate the adverse effects of climate change but also propel society towards a more sustainable and environmentally conscious future.

#### 6.6. Market potential and societal impact

The exploration and eventual commercialization of nanostructured MOF-composite membranes for CO<sub>2</sub> sequestration not only hold substantial market potential but also promise significant societal impacts, marking a significant advancement in global efforts to combat climate change. As the urgency to mitigate atmospheric CO<sub>2</sub> emissions intensifies, the demand for innovative, efficient, and sustainable carbon capture solutions escalates. These composites, with their unparalleled CO<sub>2</sub> capture efficiency and selectivity, stand at the forefront of this technological revolution, offering a scalable solution that could be integrated across a wide range of industries, from energy production to manufacturing sectors (Gkotsis et al., 2023; M. Zhao et al., 2023). This integration signals a substantial shift towards cleaner technologies, aligning with international commitments to reduce carbon emissions and fostering a transition to a low-carbon economy. Beyond the environmental imperative, the deployment of MOF-composite membranes is poised to drive significant economic transformation. The development, manufacturing, and maintenance of these technologies are expected to generate new green jobs, stimulating economic activity in the clean tech sector. This economic ripple effect extends to the creation of markets for captured CO<sub>2</sub>, potentially utilized in various industries, including agriculture, manufacturing, and energy, thereby promoting a circular carbon economy.

Moreover, the societal impact of widespread adoption of such carbon capture technologies cannot be overstated. By directly addressing the root cause of climate change, these innovations contribute to a healthier

planet, with cleaner air leading to improved public health outcomes and the preservation of biodiversity and ecosystems critical to our survival. The proactive adoption of MOF-composite membranes also embodies a collective move towards environmental stewardship, setting a precedent for future generations and highlighting the role of advanced technologies in achieving sustainable development goals (Liu et al., 2023). Nanostructured MOF-composite membranes for CO<sub>2</sub> sequestration embody a transformative potential that transcends environmental benefits, catalyzing economic growth and fostering a societal shift towards sustainability. As these technologies advance towards commercial viability, they offer a beacon of hope, illustrating the tangible benefits of marrying scientific innovation with climate action to pave the way for a sustainable and prosperous future.

## 7. Conclusion

The development and integration of nanostructured Metal-Organic Framework (MOF)-composite membranes represent a transformative advancement in CO<sub>2</sub> sequestration technologies. This study has demonstrated that MOF-composite membranes significantly enhance CO<sub>2</sub> separation performance by improving selectivity and permeability while maintaining mechanical and chemical stability. Various synthesis techniques, including solvothermal synthesis, in-situ growth, and layer-by-layer assembly, have been explored to optimize the interaction between MOFs and membrane matrices, enabling more efficient and scalable CO<sub>2</sub> capture processes. However, to fully realize the potential of MOF-composite membranes, several challenges and opportunities remain to be addressed.

Future research must focus on overcoming key technical bottlenecks, such as improving MOF regeneration processes to ensure long-term adsorption efficiency while minimizing energy input. Hybrid regeneration techniques, such as combining thermal, chemical, and electrochemical methods, should be explored to reduce operational costs. Another critical challenge lies in enhancing the compatibility between MOFs and polymeric matrices. Research into advanced functionalization strategies and molecular grafting can help mitigate interfacial defects and particle agglomeration, leading to improved membrane uniformity and performance.

Additionally, the scalability of MOF-composite membrane production must be prioritized. Developing cost-effective and continuous fabrication methods, such as roll-to-roll manufacturing, will facilitate industrial-scale deployment while maintaining performance consistency. Comprehensive life-cycle assessments (LCA) and techno-economic analyses are also essential to evaluate the environmental impact and economic feasibility of these materials. Green synthesis pathways must be pursued to ensure sustainability across the production chain.

To ensure practical applicability, MOF-composite membranes need to be tested under real-world conditions, such as humid flue gas streams with varying pressures and contaminants. Long-term stability and operational robustness must be validated for industrial applications. Furthermore, leveraging computational tools, including molecular dynamics simulations and machine learning algorithms, can accelerate the discovery of optimized MOF structures and membrane designs, streamlining material development and performance prediction.

Finally, expanding the applicability of these membranes to broader industrial contexts, such as biogas upgrading, pre-combustion CO<sub>2</sub> capture, direct air capture (DAC), and hydrogen production, will unlock new opportunities for mitigating greenhouse gas emissions. Collaborating with industries to conduct pilot-scale demonstrations will bridge the gap between laboratory advancements and large-scale implementation. By addressing these challenges, MOF-composite membranes can emerge as a scalable, efficient, and sustainable solution for CO<sub>2</sub> sequestration, making significant contributions to global climate change mitigation efforts and driving innovation in clean energy technologies.

## Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT 4.0 in writing process in order to improve readability and language. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRedit authorship contribution statement

**Putu Doddy Sutrisna:** Writing – original draft. **Sibudjing Kawi:** Writing – review & editing. **Khoiruddin Khoiruddin:** Writing – original draft. **Pra Cipta W.B. Mustika:** Writing – original draft. **Nicholaus Prasetya:** Writing – review & editing. **I Gede Wenten:** Writing – review & editing, Conceptualization.

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