Dean&Francis

ISSN 2959-6157

Design Strategies and Application Prospects of Metal–Organic Framework/ Carbon-Based Composite Adsorbents

Ziqing Gu

Department of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin, China
*Corresponding author: SelinaGu060105@outlook.com

Abstract:

Metal-Organic Frameworks (MOFs) are coordination polymers formed by the self-assembly of organic ligands and transition metal ions through coordination bonds, hydrogen bonds, or other weak intermolecular interactions, resulting in one-, two-, or three-dimensional structures. MOFs exhibit high specific surface areas, porous architectures, and tunable functionalities. However, they still face several limitations, including brittleness, poor film-forming ability, low mechanical strength, limited processability, and structural instability under humid or high-temperature conditions. The integration of carbon materials with MOFs can effectively compensate for the poor mechanical strength, aggregation tendency, and limited selective adsorption of MOFs by introducing structural stability, enhanced conductivity, and hierarchical porosity, owing to the robust frameworks of CNTs, the dispersion capability of graphene, and the high surface accessibility of activated carbon. This review summarizes several synthesis strategies for carbon-based material/ MOF composites, including in situ growth, electrostatic self-assembly, impregnation, post-treatment, and surface modification. Additionally, it discusses their adsorption performance for ions such as Cd^{2+}, Ni^{2+}, and As^{5+}, as well as their potential applications in fields like wastewater treatment.

Keywords: MOF; Graphene; Activated Carbon; Carbon Nanotube; Composites.

1. Introduction

The synthesis of metal-organic framework (MOF) coordination polymers has become a major focus in modern molecular design, offering a strategic approach to constructing functional coordination materials with tailored properties. Through molecular design, researchers can purposefully select metal ions as coordination centers (templates), multidentate organic ligands (building blocks), and auxiliary ligands

ISSN 2959-6157

to drive self-assembly, thereby achieving the controlled synthesis of MOFs. Their highly ordered structures and functionalized ligands endow them with excellent gas adsorption selectivity, ion recognition capability, and catalytic activity. Consequently, MOFs have found broad applications in gas separation, energy storage, environmental remediation, and catalysis. However, intrinsic limitations such as poor electrical conductivity, insufficient structural stability, and low mechanical strength restrict their applicability in certain electrochemical and engineering scenarios.

Carbon-based materials, as a class of functional materials with diverse structures and outstanding properties, exhibit excellent electrical conductivity, chemical stability, and mechanical strength. Commonly used in battery electrodes, adsorbents, and catalyst supports, carbon materials are composed of carbon atoms with various hybridization states (e.g., sp^2 or sp^3), resulting in rich structural diversity and excellent physicochemical properties. Depending on their morphology and structure, typical carbon materials include graphene, activated carbon, and carbon nanotubes, all of which feature high specific surface area, good electrical conductivity, chemical inertness, and tunable architecture. These materials have been widely studied and applied in fields such as energy, environment, and catalysis. Moreover, the surfaces of carbon materials are typically rich in functional groups such as carboxyl and hydroxyl, which can participate in adsorption and complexation with metal ions or organic molecules. This makes them highly effective in water treatment, heavy metal ion removal, and electrochemical ion sensing. When integrated with MOFs via in situ growth, electrostatic self-assembly, or physical mixing, carbon materials can further enhance the electrochemical activity, adsorption capacity, and conductivity of the resulting composites. Thanks to their high electrical conductivity, structural tunability, and environmental compatibility, carbon materials are regarded as ideal platforms for constructing high-performance composite adsorbents and energy storage devices. This review focuses on the outstanding properties, synthesis strategies, and ion adsorption applications of graphene/MOF, activated carbon/MOF, and carbon nanotube/MOF composites.

2. C-MOF composite

Metal-Organic Frameworks (MOFs) are a class of highly ordered crystalline materials constructed via the self-assembly of metal ions or clusters and organic ligands through coordination interactions. Their unique structures arise from the formation of one-, two-, or three-dimensional network frameworks, which are built through coordination bonds, hydrogen bonding, π-π stacking, and other intermolecular forces between the metal nodes and organic linkers. This design strategy endows MOFs with remarkable structural diversity and tunability, allowing researchers to precisely tailor pore size, morphology, and functional groups by selecting different metal centers and ligand molecules.

One of the most prominent features of MOFs is their extremely high specific surface area (up to several thousand m^2/g), regular porous structures, and customizable functional sites. These advantages make MOFs highly attractive in fields such as gas adsorption and separation, catalysis, sensing, and drug delivery [1]. Moreover, the flexible design of organic linkers and the variable valence states of metal clusters allow MOFs to serve as intelligent responsive materials or multifunctional catalytic platforms.

Nevertheless, despite their structural versatility, the intrinsic crystalline nature of MOFs also brings about several challenges and limitations in practical applications. Most MOF materials exhibit relatively poor mechanical strength and are prone to fracture under external stress or shear, making it difficult to meet the strength requirements for membrane materials or device integration. In addition, MOFs often suffer from poor film-forming ability, making it challenging to obtain dense and uniform coatings. Furthermore, some MOFs are structurally unstable under humid, strongly acidic/alkaline, or high-temperature conditions, leading to framework collapse or coordination dissociation and consequent loss of functionality. These issues limit their industrial-scale applications and long-term stability under harsh conditions.

To improve the engineering applicability of MOFs, current research efforts frequently involve strategies such as support material integration, post-synthetic modification, or polymer coating. These approaches aim to overcome the inherent brittleness and poor processability of MOFs while retaining their intrinsic advantages, thereby enhancing their structural stability and practical usability.

The combination of carbon materials with MOF can offer several significant advantages. Carbon materials can enhance the electrical conductivity, chemical stability, and mechanical strength of MOF-based composites, while MOFs provide high surface area and tunable porosity for efficient ion storage or adsorption. The simplified structures of various carbon-based materials are shown in Figure 1.

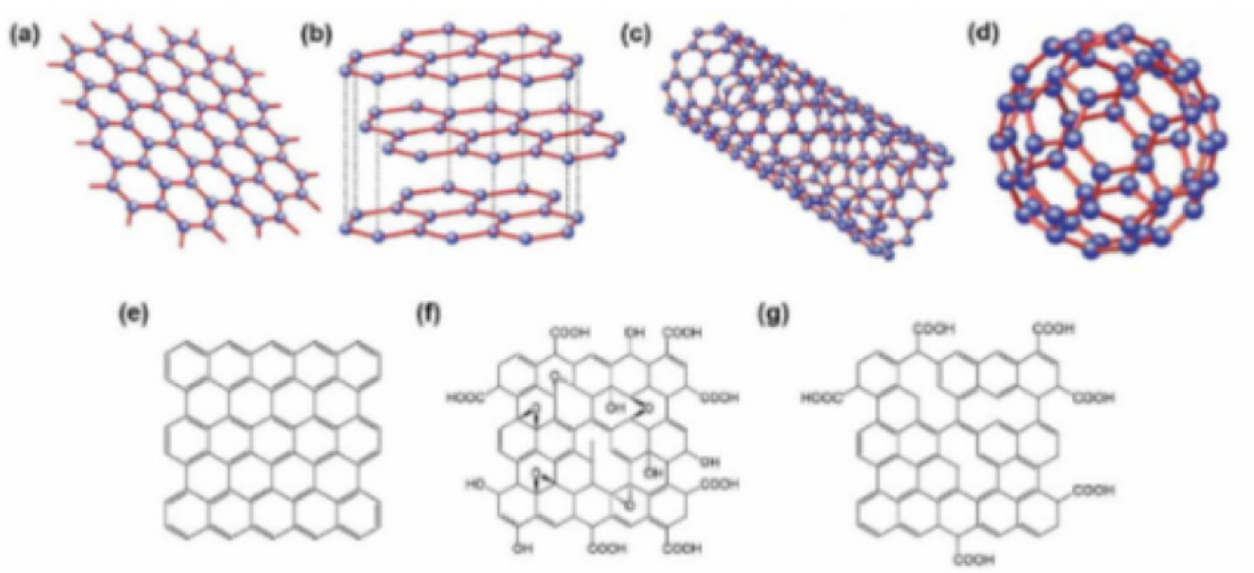

Figure 1 (a) Graphene, (b) Graphite, (c) Carbon nanotubes (d) C60, (e) pristine graphene, (f) Graphene Oxide, (g) Reduced Graphene Oxide [1]

The focus on graphene, activated carbon, and carbon nanotubes (CNTs) in MOF composites arises from their distinct and complementary properties that align well with the specific shortcomings of MOFs. Graphene offers exceptional electrical conductivity and high mechanical strength, along with a large two-dimensional surface that can prevent MOF aggregation and enhance electronic transport pathways. Its planar structure also facilitates good contact with MOF crystals, improving composite stability and charge mobility; Activated carbon features a highly porous, disordered structure with a large surface area and tunable pore size distribution, which complements the crystallinity and uniform porosity of MOFs. When integrated, it helps create hierarchical pore networks that enhance ion diffusion and increase overall adsorption capacity—particularly useful for liquid-phase applications like pollutant removal or supercapacitors; Carbon nanotubes (CNTs) contribute one-dimensional structural support with excellent electrical conductivity and chemical stability. Their tubular framework can interconnect MOF particles, reduce aggregation, and form continuous conductive networks, which is beneficial for electrochemical performance and mechanical reinforcement.

2.1 Graphene/MOF Composites

2.1.1 Graphene/MOF Composites' Preparation

In this study, graphene/metal–organic framework (MOF) composites were prepared via an insitu growth strategy [2]. In-situ growth refers to a material preparation technique where, within a specific substrate or reaction system, the target material is directly generated on the substrate surface or inside the system by regulating reaction conditions (such as temperature, pressure, reactant concentration, reaction time, pH value, etc.), eliminating the need for subsequent transfer or secondary assembly. Taking the preparation of activated carbon and MOF doped materials as an example, the in-situ growth process typically involves the following key steps and technical aspects.

During the preparation process, an appropriate activated carbon is first selected as the substrate. Due to its rich pore structure and large specific surface area, it can provide numerous attachment sites for the growth of MOFs. The pretreated activated carbon is immersed in a precursor solution containing metal ions (such as zinc, copper, iron, etc.) and organic ligands (such as terephthalic acid, imidazole, etc.), allowing the metal ions and organic ligands to adhere to the surface and pores of the activated carbon through physical adsorption or chemical bonding. Subsequently, the system is placed under specific reaction conditions (such as hydrothermal, solvothermal, or normal temperature and pressure reaction environments), and the metal ions and organic ligands undergo coordination reactions on the surface and within the pores of the activated carbon, gradually growing to form MOF crystals.

The in-situ growth technology has significant advantages. On the one hand, this method can achieve uniform distribution and close combination of MOFs on the surface and within the pores of activated carbon, forming a unique interpenetrating network structure. This avoids problems such as weak interfacial bonding force and uneven dispersion caused by traditional mechanical mixing methods,

ISSN 2959-6157

thereby effectively enhancing the comprehensive performance of doped materials. On the other hand, by precisely regulating the reaction conditions, the growth morphology (such as crystal size and shape), pore structure (pore size, pore volume, specific surface area), and loading amount of MOFs can be accurately controlled to meet the performance requirements of different application scenarios. In gas adsorption applications, the growth conditions of MOFs can be controlled to make their pore sizes match the sizes of target gas molecules, improving adsorption selectivity and capacity [3].

However, the in-situ growth technology also faces many challenges. Firstly, the precise control of reaction conditions is difficult. Minor fluctuations in conditions may lead to uneven growth of MOFs and an increase in crystal defects, affecting material performance. Secondly, some MOFs may block the original pores of activated carbon during the growth process, reducing the adsorption performance of the activated carbon itself. Thirdly, during large-scale production, it is difficult to ensure the uniformity and stability of materials in different batches, which places extremely high demands on the repeatability of process parameters and equipment.

This method refers to the direct formation of MOF crystals on the surface and within the structure of carbon materials. Functional groups on the graphene surface first coordinate with metal ions, enabling MOF nucleation and growth directly on the graphene substrate. This leads to composites with enhanced adsorption capacity, electrical conductivity, and cycling stability.

2.1.2 Graphene/MOF Composites' performance

During the insitu process, MOF precursors (metal ions and ligands) nucleate and grow on the carbon material surface, resulting in stable, tightly bound composites. Graphene or graphene oxide, acting as a 2D support, offers surface oxygen-containing functional groups—such as carboxyl, hydroxyl, and epoxy—that coordinate with metal ions and serve as nucleation sites. This promotes uniform MOF crystal growth and prevents uncontrolled particle aggregation. Furthermore, these functional groups enhance interfacial interactions between the two components by acting as chemical anchoring sites.

Structurally, MOF crystals align along the surface or interlayer spaces of graphene, forming a three-dimensional conductive or interpenetrated network. Graphene provides fast electron transport pathways, while simultaneously improving the mechanical flexibility and structural robustness of the composite. The inherent porosity and functional sites of MOFs significantly enhance molecular recognition and selective adsorption of target species.

As a result of these structural synergies, the inherently low-conductive and fragile MOF materials gain improved electronic transport, mechanical support, and interfacial stability, while graphene's limited porosity and lack of selective adsorption sites are compensated. Thus, in situ grown graphene/MOF composites exhibit outstanding synergistic performance in fields such as heavy metal adsorption, energy storage electrodes, and heterogeneous catalysis. Figure 2 presents the structure of the graphene/MOF composite membrane:

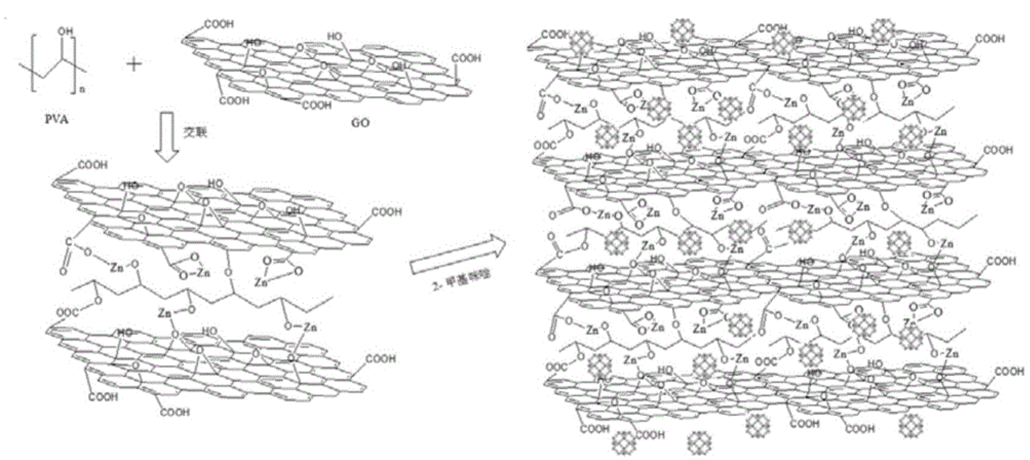

Figure 2 The structure of the graphene/MOF composite [3]

2.1.3 Graphene/MOF Composites' applications

Due to their π–π conjugated structures, these materials exhibit strong affinity toward heavy metal ions such as Pb^{2+}, Cd^{2+}, Hg^{2+}, and various organic pollutants. They can effectively remove heavy metals, radioactive nuclides from industrial wastewater, and contribute to seawater desalination applications.

Recent progress has also been made in the study of separation performance and VOCs removal during photothermal membrane distillation using graphene–MOF-based materials. Numerous studies have reported photothermal membrane distillation systems based on carbon-based materials, primarily graphene. However, the overall photothermal efficiency of these systems remains suboptimal. One of the main reasons is the inherently high thermal conductivity of graphene, which leads to rapid heat dissipation from the surface to the surrounding environment, resulting in significant thermal losses [4].

To address this issue, recent developments have introduced photothermal composite membranes (PTFE-G-ZIF), in which graphene is coated with metal–organic frameworks (MOFs) such as ZIF-67 and ZIF-8 on a PTFE base membrane. This design enhances the utilization efficiency of photothermal energy during the membrane distillation process. Moreover, by leveraging the catalytic activity of MOFs, the composite membrane effectively degrades and removes permeated volatile organic compounds (VOCs) through the activation of peroxymonosulfate (PMS), thereby mitigating the limitations mentioned above.

2.2 Activated Carbon/MOF Composites

2.2.1 Activated Carbon/MOF Composites' preparation

Activated carbon (AC) is an amorphous material with a highly disordered internal structure composed of randomly oriented graphite microcrystallites. Most of its pores are microporous, which contribute significantly to its exceptional adsorption capacity. The elemental composition of AC mainly includes C, H, O, and N, with common surface functional groups such as phenolic, carboxyl, and pyridinic moieties.

In this study, AC/MOF composites were synthesized using an impregnation method. The main idea is to immerse activated carbon into a MOF precursor solution, allowing in situ growth of MOF crystals on the AC surface or within its pores through chemical reactions. Initially, the precursors are prepared by dissolving metal salts and organic ligands in solvents such as DMF, water, or methanol. The AC is then activated—commonly via acid treatment or thermal annealing—to increase surface oxygen-containing functional groups (e.g., –COOH, –OH), which promote MOF nucleation. The activated AC is dispersed into the precursor solution with the assistance of ultrasonication, followed by static incubation at room temperature to induce MOF growth. Afterward, the product is recovered by centrifugation or filtration, washed with methanol or DMF to remove unreacted species, and vacuum-dried to obtain the final composite material.

This approach achieves property complementarity: AC's macropores provide rapid ion transport channels, while the microporous MOFs contribute dense adsorption sites, improving selectivity. The resulting composite forms a hierarchical porous network (3D void structure), which facilitates efficient diffusion and selective capture of ionic species.

2.2.2 Activated Carbon/MOF Composites' performance

In the development of high-performance functional adsorbent materials, the combination of traditional activated carbon (AC) with metal–organic frameworks (MOFs) offer an effective strategy to achieve hierarchical pore structure design and harness the complementary structural and functional advantages of both components. Activated carbon possesses a rich distribution of macropores and mesopores, which serve as low-resistance ion transport channels in liquid or gas phases. These larger pores facilitate rapid mass transfer and enhance the overall adsorption kinetics. However, the relatively low proportion of micropores and limited number of surface functional sites in AC often restrict its adsorption selectivity and overall adsorption capacity.

MOF materials, on the other hand, exhibit tremendous potential in adsorption applications due to their highly ordered microporous structures and exceptionally high specific surface areas. The densely distributed open metal sites, functional organic groups, and localized charge regions within MOFs can act as high-density selective adsorption sites, enabling strong affinity and specific recognition toward certain target species, such as heavy metal ions, radioactive ions, and organic pollutants. By embedding or coating MOF units in situ onto the surface and pore walls of activated carbon, the resulting composite provides not only a molecular-scale sieving effect but also significantly improves the selective adsorption performance of the material.

Furthermore, these AC/MOF composites typically form robust three-dimensional porous networks, in which the activated carbon framework offers macroscopic mechanical support, while the MOF component compensates for the lack of microscopic functionality. This multiscale hierarchical pore system enhances both structural stability and regeneration capability, while also mitigating the inherent issues of pure MOFs, such as poor film-forming ability and mechanical fragility. As a result, AC/MOF composites exhibit great promise in engineering applications such as water purification, gas capture, and energy storage devices.

The assembly method and process flow of an asymmetric supercapacitor device incorporating MOF/nitrogen-doped activated carbon are described as Figure 3:

ISSN 2959-6157

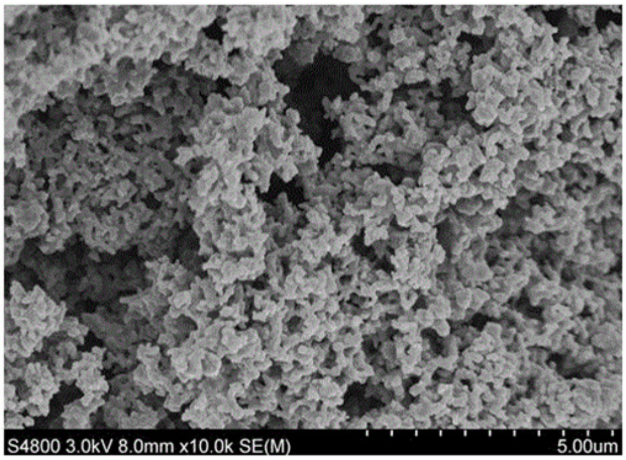

Figure 3 Activated Carbon/MOF Composites SEM pattern [4]

2.2.3 Activated Carbon/MOF Composites' applications

In air purification, activated carbon and MOF doped materials showcase their remarkable adsorption capabilities. Indoor air contains volatile organic compounds (VOCs) such as formaldehyde and benzene, as well as harmful gases like sulfur dioxide and nitrogen oxides. In the doped materials, the abundant pores of activated carbon can initially adsorb these gases, while the special pore structures and rich active sites of MOF materials can selectively capture specific gas molecules. For example, when a copper-based MOF is doped with activated carbon, it exhibits a high affinity for formaldehyde molecules [5]. Through chemical adsorption, it can convert formaldehyde into harmless substances, effectively purifying indoor air and safeguarding people's respiratory health. Additionally, in industrial waste gas treatment, this doped material can also efficiently remove pollutants from waste gases [6], reducing pollution to the atmospheric environment.

In the field of wastewater treatment, activated carbon and MOF doped materials also play a crucial role. Wastewater contains heavy metal ions such as lead, mercury, cadmium, etc, dye molecules, and organic pollutants. The physical adsorption of activated carbon can remove some macromolecular organic substances and pigments, while the coordinatively unsaturated metal sites and organic ligands of MOF materials can specifically bind with heavy metal ions, achieving efficient adsorption and removal of heavy metals. For instance, doping iron-based MOF with activated carbon can effectively adsorb arsenic ions in water, fixing arsenic on the material surface by forming stable iron-arsenic compounds [7]. Meanwhile, for dye molecules like methyl orange and methylene blue in dye wastewater, the doped material can also adsorb and enrich the dye molecules by virtue of its unique pore structure and surface properties, purifying the wastewater and enabling the recycling of water resources [8].

In the preparation of supercapacitor electrode materials, activated carbon and MOF doped materials exhibit excellent electrochemical properties. Activated carbon has excellent electrical conductivity and a high specific surface area, which is conducive to the rapid transmission and storage of charges. MOF materials have rich redox active sites, which can provide additional pseudocapacitance. After doping the two, the former composite materials have unique porous structures and good electron conductivity, which can effectively improve the specific capacitance, power density, and cycle stability of supercapacitors. For example, the electrode material prepared by compositing cobalt-based MOF with activated carbon shows a high specific capacitance and excellent cycle performance in supercapacitors, providing a new material option for the development of high-performance supercapacitors and having broad application prospects in fields such as electric vehicles and portable electronic devices [9, 10].

2.3 Carbon Nanotube/MOF Composites

2.3.1 Carbon Nanotube/MOF Composites' preparation

Pristine carbon nanotubes (CNTs) possess high surface area and excellent electrical conductivity but are generally chemically inert and hydrophobic, showing limited reactivity with metal ions or ligands. As a result, it is difficult to achieve MOF nucleation and growth directly on untreated CNTs. To overcome this, CNTs are typically functionalized by treating them with mixed acids under reflux conditions. This introduces oxygen-containing groups such as carboxyl (–COOH), hydroxyl (–OH), and carbonyl (C=O), which break parts of the graphitic structure, create surface defects, and convert the surface from hydrophobic to hydrophilic. The functionalized CNTs are then ultrasonically dispersed in solvents to form a stable dispersion.

Subsequently, solutions containing metal ions and organic ligands are prepared, and the functionalized CNTs are added to the precursor mixture. Under controlled temperature and reaction time, MOFs nucleate and grow in situ on the CNT surface, forming tightly integrated CNT/MOF composites. The final product is obtained by centrifugation or filtration, washed to remove impurities, and dried.

2.3.2 Carbon Nanotube/MOF Composites' performance

In CNT/MOF composites, CNTs serve as mechanically strong and flexible reinforcing scaffolds, supporting the fragile MOF crystal structures and preventing issues such as pulverization, collapse, or swelling during handling. CNTs form continuous electron-conducting channels across the MOF matrix, enabling efficient charge transport—addressing the insulating nature of pristine MOFs. Their flexibility imparts mechanical resilience to the composite, allowing fabrication into self-standing films, foams, or fibrous morphologies. MOFs, in turn, contribute functional enhancement by offering a tunable micro-/mesoporous structure.

Together, the synergy between CNTs and MOFs enhances the structural, electronic, and adsorption characteristics of the composite [11], making it well-suited for applications in adsorption, catalysis, and electrochemical energy devices.

2.3.3 Carbon Nanotube/MOF Composites' applications

CNT-doped MOF composites have attracted attention in fields such as electrocatalysis and gas sensing due to their enhanced electrical conductivity and improved structural stability. Doping CNTs into MOFs introduces continuous electron pathways, which effectively overcome the poor intrinsic conductivity of most MOFs. For instance, CNT-doped Ni-MOFs have been successfully applied as electrocatalysts for oxygen evolution reactions (OER), where the CNTs facilitate electron transfer and increase active surface exposure [12]. Meanwhile, the CNT/MOF composite exhibits efficient and high-performance degradation of Acid Orange G in catalytic applications [13].

3 Conclusion

This paper highlights the significant advantages of integrating metal–organic frameworks (MOFs) with carbon-based materials such as graphene, activated carbon, and carbon nanotubes (CNTs). The combination effectively addresses the key limitations of pristine MOFs—namely poor mechanical strength, low electrical conductivity, and limited structural stability—by leveraging the complementary properties of carbon materials. Graphene contributes high conductivity and mechanical robustness while preventing MOF aggregation. Activated carbon introduces hierarchical porosity and enhances mass transport, making the composites especially suitable for adsorption in aqueous environments. CNTs serve as conductive frameworks and mechanical supports, improving both structural integrity and electrochemical performance.

The synthesis strategies discussed—including in situ growth and impregnation—enable precise control over morphology and interfacial bonding, ensuring tight integration between the MOF and carbon phases. These composites have demonstrated strong potential in diverse applications such as wastewater treatment, air purification, catalysis, and energy storage. Due to their outstanding properties and versatile functionalities, carbon-doped MOF composites represent a highly promising direction for future research.

References

[1] Li Jiali. Controlled Preparation of ZIF-8-Based Porous Microspheres and Their Adsorption of Gaseous Benzene [D]. Zhengzhou Tobacco Research Institute, China National Tobacco Corporation, 2025.

[2] Qiao, Y. Y., Zhang, X. H., Zhao, X. Z., et al. Preparation and Application of Graphene/Metal-Organic Frameworks Composites [J]. Progress in Chemistry, 2022, 34(5): 1181–1190.

[3] Liu, Y. Z., Liu, X., Li, J. H., et al. In-situ Growth of Fe_3O_4 Derived from Metal-Organic Frameworks on V_2O_5 Surface as Cathode Material for Lithium-Sulfur Batteries [J]. Journal of Materials and Metallurgy, 2025, 24(03): 259–265 + 278.

[4] Li, J. Z. Research on the Separation Performance and VOCs Removal of Photothermal Membrane Distillation Process Based on Graphene-MOF Materials [D]. Donghua University, 2023.

[5] Lu, T. J., Wang, J. H. Preparation of Semi-coke Activated Carbon Supported CuCo-MOF-74 and Its Application in Degrading Bisphenol A in Water by Activating Persulfate [J]. China Environmental Science, 1–14.

[6] Huang Wenjin. Development and Application of Adsorbent Materials in Exhaust Gas Treatment [J]. China Tire Recycling, 2025, 02: 112–114.

[7] Fang Zhendin. Adsorption and Combined Toxic Effects of Functionalized Iron-Based MOFs on Arsenic in Water [D]. Southwest University, 2023.

[8] CHEN Cuifeng, HUANG Jiahong, HU Jianting, et al. Preparation and study of solid waste oxide/carbon composite catalysts for methyl orange oxidative degradation[J]. Environmental Chemistry, 2025, 44: 1-12.

[9] Zhou Gangqiang, Jin Zhao, Xiao Wei, et al. Simple Preparation and Supercapacitor Properties of Fe_3O_4 Nanoparticles/Graphene Composites [J]. New Chemical Materials, 2025, 1–8.

[10] Yu Jiahui, He Ke, Li Mengyu, et al. Research Progress on MOF-Derived Materials in the Field of Energy Storage [J]. Bulletin of the Chinese Ceramic Society, 2025, 1–13.

[11] Wang Yaqing, Su Yun, Li Na, et al. Preparation of Mn-Based Metal–Organic Framework Composite CNT Electrodes and Their Lithium Storage Performance [J]. Microelectronics & Nanoelectronics Technology, 2024, 61(09): 17–23.

[12] ZHANG M, MA L H, PENG K, et al. First principles study on highly efficient two-dimensional bifunctional electrocatalyst Cu_2@ C_2N for ORR/ OER[J]. Journal of Beijing University of Technology, 2025, 51(10): 1153-1161.

[13] Zhang Jun, Chen Ling'en, Zhang Wanting, et al. Catalytic Performance and Mechanism of MOF-Derived Fe/Co-CNT@ NC Metal–Carbon Composite in Degradation of Acid Orange G [J]. Journal of Donghua University (Natural Science Edition), 2025, 1–11.