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Sulfur-Containing Metal-Organic Framework

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Abstract:

Metal-organic frameworks (MOFs) have garnered significant attention from scientists due to their unique chemical structures, high amenability to post-synthetic modification, and their ability to combine the rigidity of inorganic materials with the flexibility of organic components. These characteristics endow MOFs with promising application prospects across numerous fields. Sulfur atoms, characterized by their relatively high electronegativity, large atomic radius, and versatile coordination capabilities, can impart a series of distinctive alterations to material properties, thereby attracting widespread interest. Incorporating sulfur into the organic ligands of MOFs modifies a range of their physicochemical properties, leading to unique changes such as enhanced metal ion adsorption, altered catalytic performance, and modified gas adsorption and separation capabilities. This review discusses the influence of sulfur incorporation on the structure and properties of MOF materials, the strategies employed to introduce sulfur into MOFs, and the applications of sulfur-containing MOFs

Keywords: MOF, sulfur-containing materials, improved performance.

1. Introduction

Metal-organic frameworks are a kind of organic-inorganic hybrid materials with crystalline porous network architecture by coordination of metal ions and organic ligands. Metal-organic frameworks (MOFs) have advanced rapidly due to their unique advantages like well chemical-stability, high porosity, large surface area, tunable pore sizes, and the combined characteristics of inorganic rigidity and organic flexibility [1]. These materials have been extensively explored and applied in diverse fields such as adsorption and separation, chemical catalysis, biomedicine, and sensing and response, demonstrating considerable research potential.

In contemporary materials science, the deliberate introduction of heteroatoms, such as N, P, and S, into diverse organic materials, alongside the conventional C, H, and O elements, confers distinctive properties or induces significant modifications in material performance. For instance, chalcogen elements like S, Se possess inherently high molar extinction coefficients. This intrinsic characteristic has consequently attracted considerable scientific interest and found

extensive application in the structural design of high-refractive-index materials [2]. Moreover, Sulfur-containing materials have also been reported to exhibit various remarkable mechanical properties, excellent thermal stability, tunable optical characteristics, intrinsic self-healing capabilities, among other advantageous properties, garnering extensive scientific and industrial attention [2, 3].

Within the organic ligands of MOFs, the incorporation of heteroatoms such as N, P, and S can modify their electronic structures of the framework and ranges of physicochemical properties. This modification thereby induces significant changes in the properties of MOFs, including enhancements in adsorption and separation capabilities, catalytic activity, luminescence intensity, and sensing and response performance [4]. For example, in 2022, Liu group have reported a kind of MOF material which confine FeP/ CoP in N, P co-doped carbon derived. This material exhibits effective electronic catalytic performance over a wide pH range and significant long-term stability, for heteroatoms N, P facilitated the modulation of the electronic structure of carbon and synergize with the metal and porous carbon, the introduction of N, P into the MOFs brought a better electroactivity [5]. Sulfur atoms, characterized by their valence electron configuration of $3s^2 3p^4$, belong to the same group as oxygen in the periodic table. Their relatively large atomic radius and abundant valence states enable diverse chemical reactivity, thereby affording multiple strategies for incorporating sulfur into metal-organic framework architectures. Furthermore, sulfur exhibits exceptional coordination and adsorption capabilities with various metal ions, as evidenced by recent studies. For instance, in 2024, *Qin et al.* synthesized a group of sulfur-incorporated MOFs for electrocatalytic hydrogen evolution. Through deliberate sulfur coordination with cobalt centers, these materials harness synergistic interactions between metal sites and sulfur moieties, generating abundant active sites that significantly enhance catalytic efficiency [4]. Complementarily, in 2020, *Yang et al.* leveraged the high-affinity mercury capture capacity of thiol functionalities to engineer sulfur-functionalized MOFs for selective Hg (II) adsorption and recovery. These materials demonstrate remarkable anti-interference capability against competing ions and exceptional structural stability under operational conditions [6]. Moreover, according to reports, iron sulfides (denoted as Fe_xS_y) represent a class of electrode materials characterized by their low cost and high theoretical capacity. Consequently, they have been extensively studied and are currently the subject of widespread research as promising anode materials for lithium-ion batteries. However, these materials inherently suffer from a series of drawbacks. Significantly, it has been demonstrated that integrating them with MOF-based materials offers a viable strategy to effectively mitigate these limitations, thereby improving the overall electrochemical performance of such composite electrodes. As clearly evidenced by the growing body of research, the strategic incorporation of sulfur atoms into MOFs can induce a spectrum of property modifications and functional enhancements [7].

Within the scope of this comprehensive review, we will delineate the diverse synthetic methodologies developed for introducing sulfur functionalities into MOF architectures, ranging from direct ligand functionalization and post-synthetic modification to coordinative anchoring via thiolate groups. Furthermore, this work critically examines an extensive collection of experimentally demonstrated sulfur-integrated MOF systems reported to date, providing detailed analyses of their implementation across cutting-edge applications including but not limited to: energy conversion like electrocatalytic water splitting, heavy metal capture, gas storage and separation, and stimuli-responsive drug delivery platforms.

2. Synthesis of sulfur-containing MOFs

2.1 Synthesis from sulfur-containing organic monomers

The incorporation of sulfur into MOFs via the utilization of sulfur-containing organic monomers during synthesis represents a well-established and prevalent methodology. Sulfur-functional groups, encompassing heterocyclic moieties such as thiazole, tetrahydrofuran, and thiophene, as well as functionalities including thiols (mercaptans), thioethers (sulfides), and thiocarbonyl groups (C=S bonds), are extensively employed across diverse material systems. Their integration confers a suite of distinctive and often enhanced properties upon the resulting materials. For instance, in 2020, *Wang et al.* reported the development of a novel MOF material, designated UiO-66-MTD, constructed from an organic linker featuring a mercapto-1,3,4-thiadiazole moiety. This material was specifically engineered and demonstrated for the adsorptive separation of trivalent gold ions Au (III) from solution. The underlying rationale for its efficacy stems from the inherent nature of Au (III) as a soft acid. This characteristic enables it to form strong, favorable interactions with sulfur-containing functional groups, a phenomenon that manifests effectively in both organic solvents and aqueous phases. Consequently, the strategic introduction of the mercapto-1,3,4-thiadiazole ligand endowed UiO-66-MTD with a robust adsorption capacity specifically tailored for Au (III) ions. Crucially, this adsorption capability proved resilient under acidic conditions, allowing the material to maintain significant

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performance over a minimum of three consecutive adsorption-desorption cycles, highlighting its potential for practical application and recyclability [8]. Additionally, also in 2020, *Helena Montes-Andrés et al.* documented the synthesis and characterization of three distinct flexible MOF materials: Co-URJC-5, Cu-URJC-6, and Zn-URJC-7. *Helena Montes-Andrés* synthesis these frameworks from organic monomers possessing a diphenyl thioether structure [9]. The diphenyl thioether structures were introduced into MOFs through chemical reactions, and this moiety grants the organic struts within the framework a degree of conformational freedom, enabling free rotation around the S atom through a certain angular range, this impacted MOFs more flexible structures and enabled MOFs interact with the analytes easier.

2.2 Synthesis from Metal sulfides (MSs)

Apart from synthesizing sulfur-containing MOFs by utilizing sulfur-containing organic monomers in chemical reactions, researchers also employ a calcination strategy to introduce metal sulfides into MOFs, ultimately transforming them into porous sulfides. This methodology serves as a highly effective pathway to significantly enhance the electrical conductivity of the majority of coordination polymers. Furthermore, the inherent characteristics of MOFs - particularly their tunable metal nodes and unique structural frameworks - establish them as exceptionally versatile and ideal precursor materials for the targeted synthesis of metal sulfides (MS). Illustrative of this approach, in 2021, *Li et al.* demonstrated a sophisticated synthesis route. They initially incorporated Fe_2O_3 nanorods into a MOF matrix, followed by an in-situ vulcanization process. This yielded a complex nanocomposite designated as Fe_7S_8@C-S, characterized by sulfur doping and a protective carbon coating [10]. The strategic integration of Fe_7S_8 within the MOF-derived architecture endowed the resulting composite with exceptional electrochemical attributes pertinent to lithium-ion batteries. These included a high lithium storage capacity, outstanding long-term cycling stability (indicative of robust structural integrity), and remarkable rate capability (denoting excellent performance at high charge/discharge currents). Collectively, these properties manifested in superior overall battery performance. Concurrently in 2021, *Zhou et al*. pursued a related strategy focused on electrocatalysis. They subjected a NiCo-based MOF, pre-deposited onto carbon paper (CP), to a controlled sulfidation treatment. This process successfully generated a class of sulfide nanosheets, specifically identified as $NiCo_2S_4$/CP [11]. The sulfidation step proved pivotal in modifying the material's fundamental properties. It substantially boosted the intrinsic electrical conductivity of the derived material. More critically, it enhanced the material's propensity to adsorb key reaction intermediates involved in both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). This synergistic improvement in conductivity and intermediate adsorption kinetics directly translated into a dramatically enhanced electrocatalytic capability for overall water splitting. Consequently, the $NiCo_2S_4$/CP nanosheets emerged as a highly efficient bifunctional electrocatalyst, showcasing the significant potential of MOF-derived sulfides in advancing sustainable energy conversion technologies like water electrolysis.

3. Applications of sulfur-containing MOFs

3.1 Catalysts

Electrocatalytic water splitting for the OER and HER is a widely researched approach for obtaining clean energy. Beyond traditional noble metal catalysts like RuO_2 and IrO_2, significant efforts focus on developing non-noble metal electrocatalysts that are abundant, cost-effective, and exhibit stable performance. Sulfide-based materials are highly promising catalysts for electrocatalytic hydrogen evolution due to their advantages: low cost, ability to modify the electronic structure of carbon materials to enhance electrocatalytic activity, and effectiveness in reducing the adsorption energy barriers for both OER and HER. However, they suffer from limitations such as poor dispersion and insufficient active electrocatalytic sites. Introducing sulfur into MOF materials leverages the tunable porous structure, large surface area, abundant unsaturated metal sites, and numerous functional groups characteristic of MOFs. This effectively addresses the issues of poor dispersion and insufficient catalytic sites encountered by sulfides in electrocatalysis. Thus, sulfur-containing MOF materials represent a highly promising class of catalysts for electrocatalytic water splitting [12]. For instance, in 2024, *Qin et al.* synthesized two structurally analogous Co-MOFs via a solvothermal method—one incorporating a sulfur-containing ligand and the other sulfur-free. Characterization revealed that the sulfur-containing Co-MOF exhibited significantly enhanced electrocatalytic hydrogen evolution (HER) activity compared to its sulfur-free counterpart. The introduction of sulfur strengthened the coordination environment around the Co centers and optimized their electronic structure. This led to a greater abundance of active sites, thereby improving the overall HER performance of the sulfur-containing Co-MOF [13]. Furthermore, also in 2024, *Munisamy et al.* reported a sul-

fur-doped MOF material, denoted S/FeNiP@C, prepared solvothermally. Incorporating sulfur into this MOF effectively reduced its charge transfer resistance, increased its electrochemical surface area, ensured sustained exposure of active species, and accelerated reaction kinetics. Consequently, the S/FeNiP@C material demonstrated outstanding electrocatalytic performance for both the HER and the oxygen evolution reaction (OER) under alkaline conditions [14].

Beyond their established role in electrocatalytic water splitting, sulfur-containing metal-organic frameworks (MOFs) exhibit significant promise as versatile photocatalysts for the degradation of organic pollutants. A compelling example was reported by *Qiu et al.* in 2022, Their work involved the synthesis of a composite material, denoted Ag NPs@Zr-TTFTB, where silver nanoparticles (Ag NPs) were strategically embedded within a sulfur-bearing zirconium-based MOF framework (Zr-TTFTB) [15]. This engineered composite demonstrated remarkable efficacy in the photocatalytic degradation of sulfamethoxazole (SMZ), a commonly encountered organic contaminant and antibiotic residue. The synergistic interaction between the Ag NPs and the sulfur-functionalized MOF matrix significantly enhanced the material's light-harvesting capabilities and charge separation efficiency, thereby driving the efficient breakdown of the SMZ molecule under light irradiation.

Furthermore, sulfur-incorporated MOFs demonstrate considerable potential as efficient catalysts for ORR, this enables them own a wide range of research prospects in fuel cells fields. Illustrating this application, *Song et al.* documented in 2017 the development of nitrogen and sulfur co-doped MOF-derived materials [16]. These materials possessed an exceptionally high specific surface area, providing a vast platform for catalytic activity. Crucially, the synergistic coupling of nitrogen (N) and sulfur (S) heteroatoms within the carbon framework generated a high density of catalytically active sites specifically favorable for the ORR. This N, S co-doping strategy effectively modulated the electronic structure and surface properties of the material, leading to demonstrably enhanced ORR catalytic performance, including improved onset potential and kinetic current density, compared to counterparts lacking this dual heteroatom doping.

Additionally, leveraging the well-documented exceptional catalytic efficacy of sulfur-centered radicals in facilitating hydrogen atom transfer (HAT) reactions, coupled with the inherent advantageous properties of MOFs (such as high porosity, tunable structure, and large surface area), sulfur-containing MOFs have emerged as promising platforms for photocatalytic HAT processes. The unique environment within the MOF pores can stabilize reactive sulfur radical species generated photochemically. These stabilized radicals can then efficiently abstract hydrogen atoms from a diverse range of organic substrates. Consequently, sulfur-MOFs have been successfully applied as heterogeneous photocatalysts to drive a spectrum of synthetically valuable HAT reactions, offering advantages in selectivity and sustainability for transformations traditionally reliant on harsh conditions or stoichiometric reagents. This expanding application domain underscores the remarkable versatility and broad utility of sulfur-functionalized MOF materials across multiple cutting-edge areas of catalysis.

3.2 Absorbent

Leveraging the unique electronic structure and properties of sulfur atoms, sulfur-containing functional groups typically exhibit strong adsorption affinities for diverse substances, including metal ions and gas molecules. Concurrently, MOFs have emerged as a major focal point in adsorption science due to their inherent advantages, such as highly porous architectures, exceptionally large specific surface areas, and exceptional structural tunability. This synergy positions sulfur-containing MOFs as particularly potent adsorbents.

A prime example of their application in metal ion recovery was demonstrated by *Wang et al.* in 2020 [8]. They functionalized a zirconium-based MOF by incorporating mercapto-1,3,4-thiadiazole (MTD) ligands, successfully synthesizing a novel material designated UiO-66-MTD. This engineered S-MOF proved highly effective for the selective adsorption and recovery of Au (III)) directly from acidic wastewater streams. The sulfur moieties within the framework provided specific binding sites for the precious metal ions. Furthermore, in 2023, *Li et al.* reported another significant advancement using sulfur-containing MOFs for Au (III) recovery. They developed a composite material, Fe-BTC/ poly (thioctic acid) (Fe-BTC/ pTA) [17], specifically designed for the highly efficient and reusable adsorption of Au (III) ions, such as those leached from electronic waste (e-waste). The adsorption mechanism involved not only coordination to sulfur sites but also an intriguing redox reaction occurring in situ between the adsorbed Au(III) ions and the sulfur-containing functional groups within the composite. This reaction led to the direct reduction of Au (III) to elemental gold, resulting in the formation of gold nanoparticles (Au NPs) embedded within the adsorbent material, thereby facilitating both recovery and potential valorization.

Apart from metal-ions absorption, sulfur-containing MOFs were reported to be ultilized in clean energy fields like hygrogen absorption materials. For instance, in 2020,

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Helena Montes-Andrés et al. synthesized a series of sulfur-containing MOF materials which could be used in hydrogen adsorption field. Three kinds of distinct flexible MOFs: Co-URJC-5, Cu-URJC-6, and Zn-URJC-7 [9], their diphenyl thioether structures are designed in these MOFs. This moiety grants the organic struts within the framework a degree of conformational freedom, enabling free rotation around the S atom through a certain angular range. This inherent flexibility imparts a dynamic character to the overall framework structure. This dynamic nature directly translates to their hydrogen adsorption profile, where the uptake process at room temperature and under low pressures exhibited a characteristic „gate-opening" type adsorption mechanism. This mechanism typically involves a structural transformation or pore opening triggered by the adsorbate (hydrogen in this case), leading to a step-like increase in adsorption isotherms, a phenomenon directly enabled by the conformational flexibility originating from the thioether groups.

3.3 Batteries materials

Currently, the search for battery materials with higher capacity and greater efficiency is a major research focus. Among them, MS have garnered significant attention due to their unique advantages as anode materials for lithium-ion batteries, sodium-ion batteries, fuel cells, and other energy storage devices [18]. Researchers have found that compared to metal oxides (MO), MS possess distinct benefits including lower volume expansion, stronger adsorption capacity for metal ions, easier initiation of redox reactions, and higher electrical conductivity [19]. However, as battery anodes, MS still suffer from drawbacks such as relatively high volume expansion, degradation/corrosion issues, and consequently, relatively low electrical conductivity. To address these limitations, scientists have incorporated MS into metal-organic framework (MOF) materials. This leverages the excellent electrical conductivity and mechanical properties of carbon materials to mitigate the issues of high volume expansion and nonspecific electron transfer in MS [7].

For instance, in 2019, *Tai et al.* reported a type of porous carbon material, NC-ZIF, derived from the high-temperature calcination of Zeolitic Imidazolate Framework-8 (ZIF-8) for use as an anode material in lithium-ion batteries. This kind of MOF behaved a regular polyhedral morphology, high specific surface area, and porous structure, which significantly enhance lithium-ion transport efficiency. Concurrently, the carbon framework effectively suppresses volume expansion of the material. The capacity remains at 440.5 $mAh \cdot g^{-1}$ after 100 cycles at a current density of 100 $mA \cdot g^{-1}$, demonstrating a high capacity retention rate of 94.7% [20]. In addition to lithium battery electrode materials, *Zhang et al.* reported in 2024 a type of MOF material incorporating mixed nickel-manganese sulfides (NiMnS) for use as an anode material in sodium-ion batteries. This work demonstrates the advantages of mixed metal sulfide-MOF materials as battery electrodes and provides design suggestions for MS-based electrode materials [21].

4. Conclusion

Herein, we have elucidated a series of distinctive properties inherent in sulfur-containing MOFs. The incorporation of sulfur atoms induces structural modifications in molecular architecture, coordination capabilities, active site configurations, and electrical conductivity. These transformations enable the versatile application of such materials across diverse fields. In this review, we present two synthetic strategies for sulfur-containing MOFs: Synthesis from sulfur-containing organic monomers or metal sulfides. Furthermore, we systematically examine their applications in catalysis, adsorption, and battery electrode materials, demonstrating the promising potential for extensive utilization of sulfur-containing MOFs.

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