Advances of covalent organic frameworks based on magnetism: classification, synthesis, properties, applications

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Abstract: Magnetic nanoparticles (MNPs) possess outstanding rapid magnetic separation ability due to their excellent superparamagnetism and stability. Covalent organic frameworks (COFs) have the advantages of porous structure, large specific surface area, remarkable acid-base and thermal stability that can form novel magnetic nanocomposites with MNPs. The formed magnetic covalent organic frameworks (MCOFs) composite material owns high saturation magnetization and prominent chemical stability, which is the great potential material in the fields of environmental remediation and biological applications. Based on the current research results, firstly, this review further simplifies the classification according to the composition and functionalization of the composite: primitive MCOFs, functionalized MCOFs, composite of Fe/Co/Ni and its alloys with COFs. Secondly, several major characteristics and diverse synthesis methods of MCOFs composites are described. Thirdly, the applications of MCOFs in adsorption and enrichment detection, catalysis, sensing and biomedical aspect are reviewed in detail, and the mechanisms of these processes have been fully and reasonably explained. Finally, the future development and challenges of MCOFs composite materials have been prospected. This work aims to provide a theoretical basis for the synthesis and design of MCOFs composite materials in the future.

Keywords: Magnetic covalent organic frameworks, Covalent organic frameworks, Magnetic nanoparticles, Functionalization, Environmental remediation

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[1] Abbreviations: Apt= aptamers, AT= ambient temperature, BD-$(NO_2)_2$=3,3,-Dinitrobenzidine, BTA=benzene-1,3,5-tricarbaldehyde, B-R=Britton-Robinson buffer solution, COFs= covalent organic frameworks, CTFs= covalent triazine frameworks, Co-FPy-CON= Co-loaded covalent organic framework nanosheets, DtTb=2,5-dihydroxyterephthalaldehyde (Dt) and 1,3,5-tris(4-aminophenyl) benzene (Tb), DAPS=4,4′-diaminodiphenyldisulfide, DQ-COF=2,6-diaminoanthraquinone (DAAQ) with 1,3,5-triformylphloroglucinol (TFP), DQTP=2,6-diaminoanthraquinone (DQ) and 2,4,6-triformylphloroglucinol (TP), DABA=2,5-diaminobenzenesulfonic acid, DHBD=3,3′-dihydroxybenzidine, EB= ethidium bromide, EA= ethyl aceta, Fe Dha Tph-COF=5,10,15,20-tetra-(4-aminophenyl)-porphyrin Fe (III) chloride (FeTAPPCl) and 2,5-dihydroxyterephthalaldehyde (Dha), GSH= glutathione, HBY-COF-900= metal-encapsulated nitrogen-doping porous carbonaceous materials composed of FeN_4 active sites by introduction of metalloporphyrin into porous COFs, MCOFs=magnetic covalent organic frameworks, MNPs= magnetic nanoparticles, mCTpBD=a magnetic covalent organic framework with inherent hydrophilicity, M-DA= polydopamine modified particles, MAA= mercaptoacetic acid, MPS= mercaptopropanesulphonate, MeOH= methanol, MSPE= magnetic solid phase extraction, NPs= Nanoparticles, N_3−PBA= azide-phenylboronic acid, NiPor= porphyrin nickel, por(5,10,15,20-tetrakis(4-cyanophenyl) porphyrin), NUS-55= a highly porous COF, PI= polyimide, PA= pamidronic acid, Pc= phthalocyanine, PBBA=1,4-phenyleneboronic acid, PMA= phosphomolybdic acid, SPIOs= superparamagnetic iron oxide nanoparticles, TbBd=1,3,5-triformylbenzene (Tb) and benzidine (Bd), TpBD=1,3,5-triformylphloroglucinol (Tp) and Benzidine (BD), TpPa-1=1,3,5-triformylphloroglucinol (Tp) and 1, 4-diaminobenzene (Pa-1), TAPB=1,3, 5- tri (4-aminophenyl) benzene, TFTA=2,3,5, 6-tetrafluoro-p-benzaldehyde, TFP=1,3,5-triformylphloroglucinol, TpND=1,3,5-triformylphoroglucinol (Tp) and 1,5-naphalenediamine (ND), TEOA= triethanolamine, TBPM= tetrahedral tetra-(4-dihydroxyborylphenyl) methane, TT-Por (Co)-COF= a porphyrin-based COF containing donor–acceptor (D–A) heterojunctions, TT= thieno[3,2-b] thiophene-2,5-dicarbaldehyde, β-CD=β-Cyclodextrin, 2-FPBA=2-formylphenylboronic acid.

Contents

1. Introduction

The development of society is accompanied by the two major problems of environmental pollution and resource depletion [1, 2]. It is of great significance to seek a reasonable way to balance the relationship between social development, environmental protection and sustainable energy [3-6]. Currently, it is becoming increasingly popular to study various materials for environmental remediation and energy production [7-9]. Covalent organic frameworks (COFs) are a new type of covalent porous crystalline polymer that is different from traditional polymers [10], which can be designed in advance for topology design and synthesis process control [11]. It is the integration of organic units into highly ordered topologies through strong covalent bonds [12]. In recent years, the excellent development prospect of COFs has been attributed to the entire organic structure and can be modified by a wide range of molecular synthesis tools [13]. Because COFs is formed by the reversible strong covalent bond between the light elements C, O, N, and B, it has a low weight density and high stability. Moreover, COFs enjoy unique morphological characteristics such as pores, cavities and channels, which make it possesses high surface area and can be functionalized [14, 15]. Since the research group of Yaghi et al. first designed and successfully synthesized a COF with high thermal stability, permanent porosity, and high surface area $(C_3H_2BO)_6\cdot(C_9H_{12})_1$ (COF-1) and $C_9H_4BO_2$ (COF-5) [16], a host of articles on the application of COFs have been reported, such as gas storage and separation, adsorption, sensing, catalysis, detection, disinfection, environmental management and other aspects [17-27]. Also, quite a few scholars have made COFs into COFs membranes and applied them in the field of seawater desalination and water treatment [28]. The magnitude of papers about COFs have been published, but all of them face a family of ardous problem that successful separation and easy recovery from solution. Therefore, there is an urgent need to develop more stable COFs based, easily separable composite materials.

In recent decades, nanocomposites have become a hot spot because of their advantages of lightweight, high strength, and excellent electrical conductivity [29]. Magnetic nanoparticles (MNPs), as a relatively new nano adsorbent, have received extensive attention from researchers [30]. MNPs mainly include four types: magnetic metals, metal alloys, metal oxides, and multifunctional nanoparticles (NPs) [31]. Over the course of the past 20 years, individuals have shown a strong interest in metal-doped iron oxide with enhanced magnetic properties. A variety of metals could be doped into iron oxide for the synthesis of spinel metal ferromagnet MFe_2O_4 (such as $MnFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$, M can also be Fe) [32]. The most popular currently used are iron-based nanoparticles, which mainly include nano-zero-valent iron (nZVI), magnetite nanoparticles (Fe_3O_4) and maghemite nanoparticles (γ-Fe_2O_3) [33]. Among the four methods for preparing MNPs (co-precipitation, thermal decomposition, microemulsion, and hydrothermal synthesis), the methods of large-scale preparation are co-precipitation and thermal decomposition [34]. In addition to the small particle size, large specific surface area, and simple nanoparticle preparation process, MNPs are equipped with more exciting properties, namely superparamagnetism [35]. Due to these characteristics , MNPs possess fast kinetics, strong adsorption capacity, and easy separation, which are broadly applied in adsorption and detection [36, 37], catalysis [38-40], capacitors [41], biomedicine [42-44], just to name a few. However, MNPs are subject to certain limitations in practical applications due to their shortcomings, such as easy oxidation, decomposition, aggregation, and environmental factors that may interfere with their magnetic properties and undesirable biocompatibility. Fortunately, the defects can be solved by surface modification, that is, according to the specific reaction needs, different functional groups are selected for the improvement of MNPs [45, 46] to achieve more practical applications [47, 48].

In the context of the two hotspots of MNPs and COFs, combining COFs and MNPs to construct a new type of magnetic nanocomposite is a new development direction. Recently, magnetic covalent organic frameworks (MCOFs) have captured the attention of many scholars because of their simple preparation, unique magnetic properties and stability, and their application in the environment (Fig. 1). For example, simple synthetic method was used to prepare high magnetic responsiveness and specific surface area, uniform pore size, good stability of core-shell Fe_3O_4@TbBd nanospheres, the composite material as an adsorbent applied in the selective separation and enrichment of human urine estrogen [49]. In the past few years, an army of scholars have made gratifying progress in the preparation and application of

MCOFs composites [50-56]. The MCOFs provide more active sites and avoid the aggregation of MNPs. To a certain extent, the enrichment efficiency is improved, the test time and energy consumption are saved, moreover, the test procedure is further simplified while ensuring good stability and reusability.

Compared with similar metal organic frameworks (MOFs), the advantages of COFs are shown in their excellent chemical stability when they exist in acidic and organic solvents [57]. MOFs are coordinated between bridging joints and secondary structures, the weak bond strength leads to insufficient stability [58]. During the past five years, a number of the reported review articles on the magnetic metal organic frameworks (MMOFs) were regarding the preparation method of MMOFs and its application in monitoring and removing harmful environmental pollutants and environmental remediation [59-63]. However, there are currently no review articles describing MCOFs systematically, and many studies are based on the preparation and functionalization of MCOFs to enhance practical applications. Moreover, most applications focus on the use of MCOFs composites as adsorbents in the environment. Therefore, a comprehensive study of the application range of MCOFs is of great significance for exploring the new properties of composite materials. In this article, we first classify the composition or structure of MCOFs complexes, then discuss their synthesis methods, and analyze their physical and chemical properties and mechanism of action. Secondly, the application of MCOFs composite materials in adsorption and enrichment of various pollutants (heavy metals, organic pollutant, etc.), photocatalytic reduction of CO_2, immunosensing and fluorescence sensing, magnetic resonance imaging and targeted drug delivery are elaborated, respectively. Ultimately, the future development and challenges of MCOFs have been prospected. In addition, this review also provides a scientific basis for the development of MCOFs compounds in the future, and it is expected that large-scale applications will be realized in the near future.

2. Types of MCOFs

To better comprehend MCOFs， according to the composition and functionalization of MCOFs composite materials, it can be broadly divided into three categories. The first type is that the primitive MCOFs only contain MNPs and COFs, without other components. The second is functional MCOFs, consists of three or more components: MNPs, COFs and other ingredients (surfactants, precious metals, organic matter, etc.). The third is the composite of Fe/Co/Ni and its alloys with COFs. The MCOFs structure formed by the first two types is mainly a core-shell structure. The MNPs are the core, and the COFs are the shell, as shown in Fig. 2(a-b). The formation of this structure is that MNPs are prone to accumulation, and the COFs shell is wrapped on the surface of MNPs, which can effectively avoid the aggregation of MNPs, thereby increasing the active sites of the reaction. Of course, quite a few scholars have synthesized other shapes of MCOFs through experiments, such as core-shell nanoparticle clusters [64], multi-coated structures [65], microporous and mesoporous structures [66, 67], spherical [68], sea urchin shape [69], cube-shaped

[70], layered sea cucumber shape [71], tubular [72]. The structure of the third type of complex is mainly magnetic metal and its alloy nanoparticles dispersed in COFs (Fig. 2c).

2.1. Primitive MCOFs

The primitive magnetic covalent organic frameworks (MCOFs) only contain MNPs and COFs, and no other components. At present, there are two mainly types of MNPs combined with COFs: iron oxide magnetic nanoparticles and other ferromagnetic nanoparticles. The most representative MNPs are mainly magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) [32], and relatively few nickel and cobalt. Compared with functionalized MCOFs, the formation process of primitive MCOFs is relatively simple, as shown in Fig. 3a. Unlike functional MCOFs composites, the primitive MCOFs do not have a third component.

For example, Tan et al. synthesized a new type of MCOFs composite material ($NiFe_2O_4$@COFs) using $NiFe_2O_4$ as the magnetic core and COFs as the shell at room temperature [73]. Zhang et al. synthesized amine-functionalized magnetic hollow nanospheres (Fe_3O_4-NH_2) and 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAP), respectively. A novel COFs was synthesized by the dehydration reaction of tetraamino porphyrin and 4,4,-biphenyldicarboxaldehyde, then it was decorated on the magnetic Fe_3O_4 to obtain Fe_3O_4@COFs nanospheres with core-shell structure [74]. Xie et al. used 1,3,5-tris(4-aminophenyl) benzene (TAPB) and 2,5-dimethoxyterephaldehyde (DMTP) monomers to prepare TAPB-DMTP-COFs shells, subsequently, Fe_3O_4 was encapsulated in the shell layer to form a core-shell structure MCOFs. The obtained composite material coated on the surface of the glassy carbon electrode could be used as an electrochemical sensor to measure the content of luteolin. The highly ordered porous structure of the composite material (Fe_3O_4@TAPB-DMTP-COFs) could provide more active sites and avoid the aggregation of Fe_3O_4 NPs. Meanwhile, the presence of Fe_3O_4 could significantly increase the electron transfer speed [75]. Table 1 below shows the primitive MCOFs synthesized in recent years.

2.2. Functionalized MCOFs

Functionalized magnetic covalent organic frameworks (MCOFs) are usually a multifunctional composite material, which are synthesized by MNPs, COFs, and functional parts (the third component) according to the expected application and required performance, as shown in Fig. 3b. As for MNPs, magnetite ferroferric oxide (Fe_3O_4) with superparamagnetism and biocompatibility is the most used MNPs, which is an essential part of MCOFs [76].

Both MNPs and COFs can be surface modified and functionalized to prepare corresponding functionalized materials [44, 77]. Thus, the constitution of functionalized MCOFs composite materials can be divided into three categories according to whether they are surface modified and functionalized. The first is that COFs are grafted onto surface-modified Fe_3O_4 NPs. For example, COF-LZU1 was immobilized on polyethyleneimine-functionalized Fe_3O_4 NPs [70]. The second is that surface-modified COFs are grafted onto Fe_3O_4 NPs, such as used the polydopamine modified particles to decorate COF-1 (the first COF developed) and fixed it on cubic Fe_3O_4 [78]. The third is that composite materials are synthesized after both surface modification, such as combining amino-modified Fe_3O_4 with COFs introduced with nitro groups [79]. If the introduction of external functional components can enhance or improve the performance of MCOFs materials, the successful synthesis of functionalized MCOFs materials can be proved.

2.2.1. Functionalization of MNPs

It is well known that bare MNPs possess low stability and will be oxidized when exposed to the air. And due to the high specific surface energy of nanoparticles, the MNPs will agglomerate easily, which is not conducive to their existence in various practical applications. Inspiringly, there are several effective strategies can be used for protecting MNPs from agglomeration [32]. The first strategy is grafted or coated of organic substances (including surfactants and polymers) [80], inorganic layers, such as inorganic metals (gold) [81], inorganic non-metals (graphite) [82], or oxide (silica) [83]. The second strategy is used polymer shells to encapsulate MNPs [84]. The third strategy is encapsulated MNPs in liposomes [32], for instance, high-concentration magnetic colloids can be encapsulated in phospholipid bilayer vesicles, and the stabilization strategy is shown in Fig. 4.

The stability of MNPs particles and their dispersibility in water can be improved by this protective surface strategy, moreover, they can also be further combined with biologically active molecules or targeting ligands to provide functionalization for the obtained multifunctional nanoparticles [85]. Organic matter is coated on the MNPs to reduce aggregation, and humic acid coating Fe_3O_4 is a favorable choice [86]. The polymer shell formed on the external surface of MNPs can provide a higher adsorption load. Studies have shown that with magnetic iron oxide nanoparticles as the core, the nucleotide coordination polymer grows into a complete shell structure on its outer surface [76]. Unlike general physical adsorption, this kind of shell can encapsulate other guest molecules, such as small organic dyes, proteins, DNA, and gold nanoparticles. Consequently, it provides more excellent guest stability and activity than bare magnetic iron, and the core has a higher load capacity. Xu et al. used Fe_3O_4 as the magnetic core and gold or gold/silver as the coating to propose a hybrid nanoparticle system with controllable magnetic and plasma properties. It showed the feasibility of noble metal coating for the long-term stability of the magnetic core and the functionalization of nanoparticles [87]. In addition, when the environment is at low pH, it is an excellent choice to cover the surface of MNPs with a silica coating. And it is not oxidized or dissolved because of the SiO_2 shell has reliable chemical stability, biocompatibility, and surface modification versatility [88]. MNPs functionalization is mainly functionalized at the protection level and ligand exchange. The former is functionalized by introducing specific components (such as functional groups), substituting hydrophobic ligands by small molecules results in the latter, which converts MNPs to water-soluble [34, 89]. Fe_3O_4 NPs can be further modified after being embellished by functional groups, such as grafting polymers to amino-functionalized Fe_3O_4 NPs to form a magnetic composite [90]. The protective layer formed on the surface of MNPs can cooperate with other nanoparticles or various ligands to functionalize MNPs to meet diverse applications. In this respect, Ag NPs were used to modify Fe_3O_4 nanorods coated with SiO_2, and the resulting composite material has a higher catalytic efficiency in degrading organic dyes than exposed Ag NPs [91]. The coating on the surface of MNPs indicates an outstanding protective effect on MNPs and has outstanding modifiability [88].

The coating on the surface of MNPs has a protective effect, however, it may have a particular impact on the magnetic properties of MNPs. Cao et al. studied the influence of silica coating thickness on the superparamagnetism of nanocomposites. The results of experiments suggested that the superparamagnetism decreased with the increase of SiO_2 coating thickness [92]. Interestingly, the content of MNPs is related to magnetism of MCOFs. Ge et al. argued that the modified Fe_3O_4 content had no effect on the structure of the synthesized microporous magnetic Fe_3O_4/M-COFs material. Nevertheless, the magnetic properties of the material could be controlled by changing the content of MNPs in the composite material [67]. Thus, on the one hand, the function of MNPs is to prevent the aggregation of the nanoparticles themselves. On the other hand, it can increase the binding affinity to the COFs. The above studies have shown that the thickness of the coating and the content of MNPs both have a specific effect on the magnetic properties of the composite material. Hence, elaborate design of coating thickness and control of MNPs dosage is of great significance to the development of functionalized MCOFs composite materials.

2.2.2. Functionalization of COFs

To further synthesize and design functional COFs with flexible structure, post-synthesis modification strategy (PSM) and pre-synthesis strategy (bottom-up approach) are invariably used [93, 94] (Fig. 5). The former first synthesizes COFs and then introduces functional parts to obtain COFs with specific functions. The latter includes the functional parts in the building unit before the synthesis of COFs, which has the advantage of homogenizing the available region [14]. Nonetheless, both synthesis strategies possess certain shortcomings. In the pre-synthesis strategy, the harsh preparation conditions of COFs may damage the functional groups. In addition, the type and number of functional groups are limited, as well as the strict structural symmetry and stability requirements of building units, which limits its wide application. Although the post-synthesis modification can add different functional groups according to specific functions, the functional groups may affect the crystal structure of COFs [95].

The functional parts are usually metal ions [96, 97], functional groups [98, 99] including ethyl, acetate, hydroxyl, carboxylic acid, and amino groups, methoxy groups, etc., various organic bonds [10] (such as boronate, boroxine, borosilicate, imine, hydrazone, squaraine, phenazine, azine, imide bonds etc.), organic matter [100], and so on. For instance, Huang et al. published a review on the functionalization of metal-modified COFs, COFs could be used as carriers to disperse and fix metal species and maintain their adsorption and catalytic performance. It showed that metal-modified COFs exhibited well catalytic activity, selectivity, and recyclability in various catalytic reactions [101]. The team of Lin adopted a post-synthesis modification strategy, first of all, they synthesized a triazine-based covalent organic framework (COF-SDU1), and then metal palladium (Pd (II)) was uniformly doped into the triazine-based COFs, finally, a green catalyst that can be recycled multiple times was obtained [102]. Lu et al. designed functionalized COFs of thioether groups. The sulfide groups were uniformly distributed in COFs, and narrow-sized Pt or Pd NPs had been successfully prepared. The even chemical groups distribution was conducive to anchoring and constraining nanoparticles in the pores, which is in favor of stabilizing nanoparticles. The structure of COFs with thioether groups was the key to the successful preparation of nanoparticles with narrow size distribution [103].

A great deal of studies suggested that the composite materials formed by introducing functional parts into COFs can possess better performance. For instance, Ding et al. reported for the first time the COF-LZU1 with a two-dimensional (2D) layered stack structure imine-linked [104]. The metal ion palladium (Pd) was introduced by adding Pd $(OAc)_2$ at room temperature. Pd/COF-LZU1 with a unique structure was prepared by simple post-processing and used to catalyze Suzuki-Miyaura Coupling Reaction. At the same time, the successful synthesis of the material was verified by spectral analysis. This material exhibited engaging catalytic activity, which broadened the range of reactants, improved the yield of reaction products and catalytic stability, and facilitated recovery. The most significant disadvantage of COFs is high hydrophobicity [105], which makes it limited in the practical application of hydrophilic substances. In the functionalized MCOFs composite material, in order to improve the hydrophilicity of COFs, molecules with acidic groups can be added. Modification of COFs enhances the interaction between the composite material and the analyte. Liu et al. synthesized carboxyl functionalized MCOFs nanocomposites, the carboxyl group was successfully added to COFs. According to the principle of similar compatibility, the affinity of carboxylated COFs with higher polarity to the analyte sulfonamide was enhanced [106]. Similarly, Lu et al. applied the nitro-functionalized core-shell structure Fe_3O_4@COF$(NO_2)_2$ to MSPE to determine trace pesticides in vegetable samples, which demonstrated the nitro group improved the hydrophilicity of COFs, thereby increasing the strong hydrophilic interaction between the composite material and the pesticide [79]. The above studies manifested that the introduction of functional components have varied the relevant properties of COFs, such as the hydrophobicity of COFs materials, and multifunctional composite materials based on COFs have been obtained. Thence, the functionalization of COFs has positive significance for the synthesis of MCOFs composite materials.

2.2.3. Functionalized MCOFs

Compared with the primitive MCOFs, the preparation of functionalized MCOFs is usually not obtained by a single method, it is a process of combining synthesis and modification. The synthesis of the core-shell structure of functionalized MCOFs composites generally adopts a multi-step modification strategy, and the preparation process is relatively cumbersome. MCNC@COF@Zr^{4+} is an example of functionalized MCOFs complex, which can be prepared by continuous post-synthesis modification [107]. At first, a solvothermal reaction was used to synthesize high magnetic response magnetic colloidal nanoclusters (MCNCs). The MCNCs were used as the core, and the COFs shell was coated on the surface of MCNCs to make MCNC@COF. Subsequently, a three-step sequential functionalization was used, and the surface functional group of the composite was changed to a hydroxyl-carboxy-phosphate group to obtain PA-MCNC@COF. Finally, Zr^{4+} phosphate was used for coordination, which was fixed on the surface of PA-MCNC@COF to form MCNC@COF@Zr^{4+}. Similarly, Luo et al. used the same method to synthesize glutathione-functionalized magnetic covalent organic framework microspheres (MCNC@COF@GSH)) [108]. The introduction of functional parts in composite materials can not only retain the excellent properties of COFs, but also increase the unique functions of the functional parts. Yang et al. used Au-S bond to fix β-Cyclodextrin on the surface of COFs to prepare β-Cyclodextrin-functionalized MCOF (Fe_3O_4@COF@Au-β-CD) [109]. The fascinating advantages of COFs were preserved, such as large specific surface area, adjustable pore structure, and excellent stability. Meanwhile, it also provided a unique hydrophobic cavity of β-cyclodextrin, and the ability to identify and enrich the target analyte was further improved. In particular, halogen elements (such as fluorine elements) can also be added to MCOFs materials to obtain functionalized MCOFs composite materials. The addition of fluorine-containing ligands made the composite materials as a fluorinated MCOF (Fe_3O_4@TpPa-F4). This material had higher adsorption performance and selectivity for high persistent organic pollutants perfluorocarbons in complex samples. The reason lied in the strong fluorine-fluorine interaction between MCOFs and perfluorocarbons and the fluorinated COF shell. The proposed fluorinated magnetic solid phase extraction (FM-SPE) integrated with HPLC-MS/MS analysis could be opportunely applied to determine six perfluorinated chemical substances in milk samples [110]. Experiments indicated that the introduction of fluorine atoms improved the hydrophobicity of the composite material. A hydrophobic interaction was used between the material and the hydrophobic contaminants polybrominated diphenyl ethers, effectively enriched contaminants [72]. Hence, a number of studies have shown that the preparation of functionalized MCOFs was based on the functionalization of MNPs and COFs. Surprisingly, the grafting of functional parts had no effect on the original core-shell structure of the material. This implied that the grafted functional parts were feasible for synthesizing of core-shell structured MCOFs composite materials.

2.3. Composite of Fe/Co/Ni and its alloys with COFs

This article also introduces other ferromagnetic magnetic metals such as cobalt (Co), nickel (Ni), FeCo alloys and their composites formed by the combination of

COFs. It is noteworthy that except for the combination of iron oxide and COFs, some metals (iron, cobalt, nickel, along with iron-cobalt alloys) and COFs combine to form a MCOFs composite material besides the core-shell structure.

To attain the purpose of dispersing magnetic metals in COFs and avoiding the leaching of metal ions, ligands with distinct contents and functions are frequently introduced into the framework to form forced coordination with metal ions. Besides, the abundant nitrogen content in COFs is also an important factor for the combination of magnetic metal nanoparticles to form coordination interactions. For example, nitrogen-rich COFs were used to combine with Co, and the nitrogen-rich sites contributed to form strong interactions with cobalt nanoparticles and prevented the leaching of Co NPs [111]. Rozhko et al. adapted two different types of COFs that were used as carriers to combine with the molecular catalyst Ni^{2+}. Either in the form of pyridine was quasi bipyridine moieties or as diiminopyridine moieties, Ni^{2+} could coordinate with the framework, due to the large number of N heteroatoms in the framework [112]. Generally speaking, the organic ligands used for metal binding are imine, bipyridine, and porphyrin [101]. For instance, under solvothermal conditions, terephthalaldehyde (TA) and cobalt (II) 5,10,15,20-tetrakis(ρ-tetraphenylamino) porphyrin (Co-TAPP) were co-condensed to prepare Co-COF [113]. Zhong et al. utilized the chelating effect of the pyridine binding unit to design a single nickel site anchored in TpBpy successfully, which was used as a co-catalyst for photocatalytic selective conversion of carbon dioxide [114]. The experimental results indicated that it benefited from the synergy between a single nickel catalytic site and the 2,2′-bipyridine-based COF (TpBpy) framework carrier. In addition to doping a single metal into the framework, there were also reports in the literature that doping iron and cobalt bimetals into COFs. The structure of this hybrid material was different from the general MCOFs. The iron and cobalt particles were anchored on the wall of the frame hole instead of the hybrid material surface [115]. Besides organic ligands, complexes could be used to combine a single metal with the COFs framework. Yu and his colleagues fixed iron ions and PMA to imine COFs through physical adsorption and chemical bond coordination. Iron ions were uniformly dispersed on the framework surface or cavities [116].

Interestingly, the doping of magnetic metal nanoparticles into COFs also has a certain effect on the original chemical properties of COFs. Studies have indicated that inserting Fe atoms between two layers of COFs can better change the electronic properties of COFs [117]. This structure can not only maintain the symmetry of the original structure of COFs, but also adjust the band gap of porous materials [118]. Li et al. synthesized Ni-doped COFs with a square plane Ni(II) coordinate geometry that could improve the low conductivity of COFs and were used in supercapacitors [119]. Ni-doped COFs can also enhance the catalytic performance of material. Chen et al. reported for the first time a photosensitive triazine-based COF that used nickel site modification to form a dual catalyst for organic conversion, showing excellent catalytic performance [120]. Compared with the first two types of MCOFs, this kind of composites obtained by combining metals and their alloys with COFs has been less studied, and more applications in the field of catalysis.

In short, among the three classifications of composite materials, functionalized MCOFs have been studied extensively. Primitive MCOFs and functionalized MCOFs are widely used in adsorption and detection enrichment, which are often combined with magnetic solid phase extraction (MSPE) and separated by an external magnetic field, and the structure (core-shell) is obviously different from the third type (dispersed type). The third type of composite materials compounded with magnetic metals and their alloys and COFs are widely used in the field of catalysis (electrocatalysis, photocatalysis, etc.), but there is little research on adsorption. It is worth noting that the synthesis methods of different types of complexes are not the same.

3. Synthesis method of MCOFs

Composite materials are usually a type of material that combines the advantages of two or more materials and has synergistic properties. According to its expected performance and synergistic effect, there are several ways for synthesizing MCOFs complexes. The synthesis methods mainly include coating method, monomer polymerization method (also known as a one-pot reaction), in-situ growth method, and impregnation method.

3.1. Coating method

The coating method is a standard method for preparing MCOFs so far. By separately synthesizing MNPs and COFs, then the COFs shell is wrapped on MNPs surface. Under relatively mild situation, MCOFs with Fe_3O_4 NPs as core and COFs as shell are synthesized. The coating method for synthesizing MCOFs includes the direct coating method and indirect coating method. The distinction is that the latter contains an intermediate layer, that is, a coating agent. In the preparation process, the two approaches can be distinguished by whether or not using a coating agent. Usually used coating agents are tetraethyl orthosilicate (TEOS), and polydopamine (PDA).

The direct coating method directly wraps the COFs shell on the functionalized MNPs surface. The purpose is to introduce functional groups to avoid the problems of oxidation, decomposition, and aggregation of exposed MNPs, and to improve its dispersibility. You et al. used the direct coating method to synthesize a simple core-shell structure Fe_3O_4@COF material [121]. Initially, the ferroferric oxide nanoparticles were modified and stabilized with amino groups. Then the prepared Fe_3O_4 particles were dispersed in a dimethyl sulfoxide (DMSO) solution containing melamine (MA) and terephthalaldehyde (TPA), at the same time, ultrasound treatment was used to homogenize the solution. The MCOFs composite material directly wrapped by COFs was obtained. The magnet was used as the separated product, while washing with organic solvents (anhydrous methanol, dichloromethane, tetrahydrofuran, etc.) to remove impurities. Similarly, Wei et al. synthesized a MCOF (Fe_3O_4@TpND) in two steps [122]. The first step was to synthesize amino-modified Fe_3O_4, and the second step was to polymerize COF on the surface of Fe_3O_4 by direct coating method.

The indirect coating method is often accompanied by the use of coating agents. For example, Wu et al. synthesized an inherently hydrophilic magnetic covalent organic framework (mCTpBD) by encapsulating with TEOS to stabilize Fe_3O_4 NPs [123]. Firstly, Fe_3O_4 NPs were prepared, and then amino groups modified the surface, which could improve the interplay between the organic coating and the inorganic magnetic core to obtain Fe_3O_4-NH_2 particles. Secondly, CTp (carboxyl-modified 1,3,5-triformylphloroglucinol) was prepared through a nucleophilic addition reaction between diglycolic anhydride (DA) and 1,3,5-triformylphloroglucinol (Tp). Fe_3O_4-NH_2 was dispersed in 1,4-dioxane, acetic acid and CTp sequentially added to the mixed solution. To further make the solution more uniform, ultrasonic treatment was performed. It was then diverted to a teflon-lined stainless-steel autoclave and heated in an atmosphere of 120 ℃ for 1 h to obtain the product Fe_3O_4-NH_2-CTp (Fig. 6b_1). The two monomers were mixed with benzidine (BD), mesitylene, 1,4-dioxane, and acetic acid for ultrasonic treatment. Under the protection of Ar_2, the mixture was stirred at 90 ℃ for 4 h. A magnetic field was applied to separate the product, and finally, it was washed and dried. Moreover, Yan et al. used the indirect coating method to prepare hydrophilic magnetic nanospheres (Fe_3O_4@PDA@TbBd) [124]. Firstly, Fe_3O_4 nanospheres were prepared by hydrothermal reaction, coating dopamine with self-polymerization on the nanospheres to obtain Fe_3O_4@PDA. The COF shell TbBd was synthesized by using 1,3,5-triformylbenzene (Tb) and benzidine (Bd).

Subsequently, under the existence of DMSO solvent, a one-pot reaction was used to obtain hydrophilic magnetic nanospheres (Fe_3O_4@PDA@TbBd) with Fe_3O_4@PDA as the internal core and TbBd as the shell. The prepared composite material used PDA as the intermediate layer, connecting the Fe_3O_4 magnetic core and COF(TbBd) shell (Fig. 6b$_2$). The synthesized composite material was applied to detect phthalates in the environment efficiently, which could achieve the separation effect only with the help of an external magnet.

3.2. Monomer polymerization method

In the monomer polymerization method, all the monomers are mixed, which is a one-pot reaction to prepare composite materials. During the process, a catalyst is often added to speed up the reaction rate. For example, Wang et al.[125] synthesized Fe_3O_4@COF with a core-shell structure (Fig. 6c). Fe_3O_4 NPs were synthesized through the solvothermal reaction, which was then added to the round bottom flask and mixed with 1,3,5-tris(p-formylphenyl)benzene, 4,4”-diamino-p-terphenyl, and DMSO. To accelerate the reaction rate, acetic acid was added as a catalyst, and the compound was rapidly reacted at a temperature of 75℃. The material was segregated by an external magnetic field, washed, and dried.

3.3. In-situ growth method

The in-situ growth method refers to the functionalization of MNPs by introducing functional groups on the surface of MNPs to prevent the magnetic core from gathering. Subsequently, the monomer is grafted to the functionalized magnetic nano-material surface, and the shell-like COF is generated through the reaction to synthesize the core-shell structure MCOFs. For instance, Yang et al. used a monomer-mediated method to prepare core-shell Fe_3O_4@TpBD nanospheres based on an in-situ growth strategy [126]. Similarly, Wang et al. firstly synthesized Fe_3O_4 NPs (Fe_3O_4@SiO_2-NH_2) coated with amino-functional silica. The monomer 1,3,5-Triformylphloroglucinol (Tp) was grafted onto the Fe_3O_4@SiO_2-NH_2 surface by Schiff base reaction. Then the in-situ growth method was used to uniformly modify the COF shell on the magnetic core surface. Finally, the post-synthesis modification strategy was used to obtain boric acid functionalized MCOFs (Fe_3O_4@COF@2-FPBA) [95] (Fig. 7a). It was worth noting that in the study of Wei et al., the Fe_3O_4-NH_2 was combined with Tp molecules through the Schiff base reaction to form an intermediate product Fe_3O_4-NH_2@Tp. Then it was used as a monomer to polymerize with COF [122] (Fig. 7b).

3.4. Impregnation method

The impregnation method is to mix the synthesized COFs and the metal precursor material in an organic solvent and prepare by stirring. Then excess organic solvent is used to wash the synthesized material, the purpose is to remove impurities. Finally, the hybrid material is obtained by vacuum drying. The impregnation method mainly refers to COFs doped with magnetic metal iron, nickel, and cobalt ions. For example, Yu et al. prepared imine-based COFs using a reactor, and then immobilized iron ions and PMA on the framework support by the impregnation method [116].

Interestingly, Fe-Co bimetallic could be doped into a COF [115] (Fig. 8a). Cobalt-modified covalent organic framework containing bipyridine (Co-TpBpy), cobalt ion was coordinated with a bipyridine nitrogen atom in COFs framework [127] (Fig. 8b). A known quantity of TpBpy was mixed with methanolic cobalt acetate solution and stirred for 4 h, then washed with excess dry methanol. Finally, the resulting material was vacuum dried at 60 ℃. For the three-dimensional COF (DBA-3D-COF 1) including π-electron conjugated dehydrobenzoannulene (DBA) units, added 10 wt% $Ni(COD)_2$ dissolved in dry toluene, then mixed and stirred to obtain a dark purple crystalline powder of Ni-DBA-3D-COF (Fig. 8c). Finally, the aim of dry toluene washing was to remove excess $Ni(COD)_2$ [128]. Some scholars have adopted the same method to synthesize Ni-DBA-2D-COF using 2D COFs [129].

Briefly, the direct coating method is simple and convenient to operate, requires mild reaction conditions, and can form a regular spherical core-shell structure. However, the size of the obtained composite magnetic core and the thickness of the COFs shell are also not exactly the same due to the difference in monomers and preparation conditions. The indirect coating method is more complicated than the direct coating method because the use of the coating agent, and the properties of the coating layer and the COFs layer determine the effect and mechanism of the composite adsorbing pollutants. Compared with the coating method, the catalyst in the monomer polymerization method controls the reaction speed, the reaction is interfered by the monomers, the temperature requirements are strict, the crystallinity of the product is lower. So, the monomer polymerization method is used less. In the in-situ growth method, the COFs shell can be uniformly modified, while maintaining the unique structure of COFs, and overcoming the limitations of temperature and catalyst in the monomer polymerization method. The saturation magnetization of the product obtained by impregnation method is relatively high, and the COFs and the MNPs are highly merged by doping in the framework, but the large amount of use of organic solvents increases the preparation cost. Overall, several methods have certain shortcomings. At present, they are still unable to achieve large-scale applications. In the future, we can explore ways to reduce pollution and save costs from the source, and minimize the use of solvents.

4. Physical and chemical properties of MCOFs

In line with the composition of the MCOFs composite material, the properties of material combine the characteristics of MNPs and COFs. In various applications of MCOFs, magnetic properties, structural properties, catalytic properties, electrochemical properties, and reusability are the most essential properties.

4.1. Magnetism

The magnetic property of MCOFs composites is usually measured at room temperature with a vibration sample magnetometer (VSM) [130]. In the hysteresis loop, the saturation magnetization (Ms) is used to characterize the magnetism. If there is no apparent hysteresis, remanence, and coercivity in the curve, it indicates that the synthetic material has superparamagnetism [131]. The superparamagnetism of the material enables the magnetic separation process to further decrease the time of the contaminant concentration process [132]. It is shown that the saturation magnetization value after the formation of the MCOFs composite is lower than the initial MNPs (Table 1), the reason is that the COFs layer covers the MNPs surface [133]. The magnetic properties of the composite material can be adjusted by changing the content of the magnetic metal precursor substance during the synthesis process [134]. Superparamagnetism is a characteristic property of MCOFs materials. It can be quickly separated by using superparamagnetism under the effect of an external magnetic field (Fig. 9). The traditional filtering steps are avoided, and the experiment time is saved. Table 4 lists the time required for material separation by an external magnetic field in recent years.

4.2. Structure

MCOFs composites mainly possess a high specific surface area, ordered topological structure, pore volume, pore size, and other structural characteristics. The pore structure of composite materials is usually indicated by N_2 adsorption-desorption isotherm, and Brunauer-Emmett-Teller (BET) method is used to determine porosity. The large porosity and high surface area enable the composite material to provide more adsorption sites when applied to adsorb pollutants [135]. Under normal circumstances, the surface structure of the synthetic material is characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM) to obtain the corresponding size and shape. Energy dispersive X-ray spectroscopy (EDS) is used to analyze whether the elements are uniformly distributed. The structure of iron oxide in MNPs mainly includes ellipsoidal polycrystalline and spherical particles, as shown in Fig. 10(a-c) [32]. The core-shell structure of MCOFs composite magnetic cores mostly adapts spherical particles of MNPs. The MCOFs composite material doped with gold nanoparticles was taken as an example [136]. Compared with the primitive MCOFs, as shown in Fig. 11(a-c), in the functionalized MCOFs composite, as shown in Fig. 11(d-f), gold nanoparticles were fixed in the framework channel. The transparent layer and rough surface demonstrated that the COFs layer was successfully combined on the MNPs surface. The third type of structure is magnetic metal nanoparticles Co, Ni, etc. dispersed in the COFs frame, as shown in Fig. 11(g-i). For COFs composites doped with magnetic metals or metal alloys, MNPs are uniformly dispersed in the framework. Taking cobalt as an example, the structure of the Co@COF composite did not change significantly before and after used [111]. Fig. 10(d-e) showed that the morphology of the samples before and after catalyzed had little changed. The fineness and uniform appearance of the cyan line in Fig. 10f indicated that the cobalt nanoparticles did not self-aggregate, suggesting that they were uniformly dispersed in the COFs.

In addition, the chemical structure of the material is obtained by analyzing the functional group composition of the material by Fourier transform infrared spectroscopy (FT-IR). X-ray photoelectron (XPS) spectroscopy was used for qualitative and quantitative analysis. Thermogravimetric analysis (TGA) is used to examine the thermal and chemical stability of materials. The functionalized composite material was taken as an example [108]. In order to further confirm the success of the COF shell and GSH modification in the composite material MCNC@COF@GSH, FT-IR, XPS, electronic dispersive x-ray (EDX) and TGA were used to analysis, as shown in Fig. 12.

4.3. Catalysis

The catalytic properties of MCOFs composite materials are used to convert environmental pollutants into products that are less harmful or have economic value. Corresponds explicitly to the catalytic application in Section 5. Catalysis can accelerate the chemical reactions process, which is one of the properties of MCOFs composites that have exploratory value in environmental remediation. Fenton-like catalysis, electrocatalysis, and photocatalysis are the primary catalytic forms of MCOFs composite materials in environmental remediation [116, 137-139]. COFs combined with the magnetic metal iron, cobalt, nickel and its alloys possess excellent electrocatalytic activity in electrocatalytic oxygen release and carbon dioxide reduction. Precious metals, such as gold, platinum, palladium, and other catalytically active nanoparticles were introduced into MCOFs materials, which have significant catalytic activity on the degradation of organics and dyes [136]. COFs possess photocatalytic properties, and the composite materials formed by compounding with MNPs also enjoy photocatalytic properties. In energy production and environmental restoration, photocatalysis is a green and efficient technology [140, 141].

Photogenerated electrons (e^-) and holes (h^+) play a major role in the photocatalytic process [142]. Under visible light irradiation, a COF containing a single nickel site selectively reduced CO_2 to CO, and electrons were transferred from the photosensitizer to the nickel site [114].

4.4. Electrochemistry

The electrochemical properties of the MCOFs composites correspond to the sensing applications in Section 5. The highly ordered porous COFs in MCOFs can provide active sites, and MNPs accelerate electron transport. Therefore, MCOFs can be used as materials for sensors [75]. Studies have suggested that when Fe_3O_4 NPs were used to wrap the bare glassy carbon electrode, the peak current was approximately 2.2 times higher than that of the bare glassy carbon electrode. It indicated that the way for Fe_3O_4 NPs to enhance the electron transfer efficiency was to promote the electron flow by introducing magnetization in the electric field [143].

The excellent electrochemical performance of the MCOFs composite material is mainly as the following reasons: (1) The COFs constituting the composite material possess a large specific surface area, can provide more electrochemical active sites, and effectively boost the electrochemical response. (2) COFs are composed of organic ligands, and the π-π interaction makes them have strong adsorption capacity and affinity for pollutants. (3) Fe_3O_4 NPs enjoy strong electrical and magnetic properties, large specific surface area, and high biocompatibility, which are dispersed in COFs without agglomeration, introducing catalytic centers and electrical centers. A conductive composite material with enhanced conductivity and functionality is acquired.

4.5. Reusability

Reusability is an essential feature of MCOFs composite materials in environmental remediation. Since COFs are expensive to prepare as adsorbents, it is of great significance to compound MNPs and COFs to obtain more economical materials. In order to test the reusability of the composite material in the removal of contaminants, repeated adsorption-desorption cycles are performed. The specific number of adsorption-desorption can be acquired from the experimental process. Generally speaking, the more the number of cycles, the gradually lower the recovery rate. However, the adsorption capacity of the material still maintains a high level [131], which implies that the obtained material is environmentally friendly and economical. Besides, it can be enriched or separated quickly and efficiently on the external magnetic field effect.

In short, different types of materials have diverse emphasis on property. Primitive MCOFs and functionalized MCOFs focus on magnetism and reusability, while Fe/Co/Ni and its alloys and COFs mainly emphasize on catalysis and electrochemistry. The magnetic properties of the material make it to be quickly separated and recovered (within 5 min) under an external magnetic field, corresponding to the recyclability. The unique structure can provide more reaction sites and improve efficiency. Catalysis has been widely used in energy production and conversion of environmental pollutants. Electrochemistry is the basis for MCOFs to be used as sensing materials.

5. Applications of MCOFs

Based on the post-synthesis modification, the MCOFs composites modified with diverse functional groups exhibit stronger interactions between pollutants. Molecules with specific functions are often added to MCOFs through post-synthesis modification, due to the lack of excellent selectivity for target analytes. The resulting functionalized composite material has outstanding selective extraction efficiency for analytes [95]. Although the content of various trace pollutants in the environment is low, the impact on human health cannot be ignored. For instance, perfluorocarbons are potentially carcinogenic to humans [144]. Trace levels of diclofenac sodium (DS) can lead to various risks under longtime exposure, such as drug resistance, stomach ulcers and increased risk of heart attack [145]. As a synthetic organic pollutant, perfluoroalkyl acids (PFAAs) have been frequently detected in various environmental substrates, which could still result in environmental and health risks because of toxic and bioaccumulative, even at low concentrations [146]. Thereby, the monitoring and removal of trace substances have positive and vital significance for environmental protection and human health. Since the excellent properties of MCOFs, they are broadly used in the adsorption and enrichment of ecological pollutants, biology (proteome analysis, medical treatment), catalysis (electrocatalytic O_2 release and CO_2 reduction, photocatalysis, etc.), sensing (electrochemical immunosensing, fluorescence sensing, etc.) (Fig. 13).

5.1. Environmental remediation

5.1.1. Adsorption and enrichment detection

Standard treatment methods for pollutants (heavy metals and organic pollutants) in the water environments include chemical reduction and precipitation, adsorption, ion exchange, membrane separation, and electrodialysis, among these technologies, adsorption is favored by most researchers owing to its low cost, uncomplicated operation, and high efficiency [147]. MCOFs composite materials are usually used in the process of pollution remediation in the water environment, and the successfully achieved is attributed to the performance synergy of the materials [72]. Adsorption is the main method in pollutants decontamination, and detection and enrichment is the primary solution of analyzing contaminants [148]. When MCOFs are used as adsorbents to remove contaminants, they are frequently used combined with various eluents. The adsorption performance of the synthesized composite material is evaluated by whether its performance is reduced after multiple continuous cycles [149].

The adsorption performance of MCOFs depend on superparamagnetism, hydrogen bonding, electrostatic interaction, ion exchange, π-π stacking, cation π interaction, and hydrophobic interaction [65, 124, 126]. For instance, experiments have suggested that in the obtained MCOFs, Fe_3O_4 does not actually participate in the adsorption, but through the hydrogen bond interaction between pollutants and functional groups on the surface of COFs to realize adsorption, as shown in Fig. 14(a-b) [122]. Apart from the above factors, the coordination reaction between composite materials and pollutants is also a crucial factor. When the prepared Fe_3O_4@COF@Zr^{4+} composite material was used as adsorbent for MSPE to adsorb organophosphorus pesticides (OPPs) in vegetable samples, excepting the π-π stacking interaction and hydrogen bonding, the Zr^{4+}-phosphate coordination reaction also played an important role [131]. Moreover, the pore structure and large specific surface area of the MCOFs composite can provide more adsorption sites [150]. Various functional groups on the COFs pore walls possess different adsorption capacities for gas molecules. Surface-engineered COF-5 frameworks with different densities and various groups also showed different adsorption capabilities when adsorbing various gas molecules, and might have a high probability of selective adsorption [151]. Therefore, the pore surface is also an essential factor affecting the adsorption performance of COFs. The MCOFs composite materials can be used as magnetic adsorbents in MSPE, which have a positive enrichment ability for trace substances [146]. After using the MCOFs composite material to adsorb the pollutants in MSPE, the external magnet is adopted to separate them from the aqueous solution. If the magnet is taken away, the composite material can be quickly dispersed again. As a result, applying external magnet is conducive to the collection, regeneration, and utilization of MCOFs [152].

MCOFs composite materials can remove heavy metals and synthetic organic compounds from water pollution as adsorbents. Hexavalent chromium and bisphenol A are respectively carcinogenic heavy metals and persistent organic pollutants in the water circumstance. The prepared MCOFs (Fe_3O_4@TpPa-1) were applied to adsorb these pollutants, and showed excellent adsorption capacity on hexavalent chromium (245.45 mg g^{-1}) and bisphenol A (1220.97 mg g^{-1}) [68]. Specifically, the two pollutants were wrapped in the pore cage of the COFs framework, and the uniform imine and carbonyl functional groups in the framework allowed them to anchor heavy metals and organic pollutants (Fig. 14c). Simultaneously, MCOFs can also remove inorganic contaminants (such as arsenic and mercury) in water. The equilibrium concentration after adsorption by the composite material Fe_2O_3@CTF-1 could reach the standard limit of arsenic and mercury in drinking water. Compared with CTF-1 alone and other iron-based materials, this hybrid material had a higher adsorption capacity for arsenic and mercury in aqueous media, which could be used repeatedly and had an extremely high practical application value [153]. Studies have suggested that by assembling nano-zero-valent iron (nZVI) on the surface of COFs, the prepared Fe^0@COFs could adsorb arsenic up to 135.78 mg g^{-1} [154], and this process was chemical adsorption. Also, MCOFs can adsorb and remove drugs in water. As known to all, the medicine flowing into the water environment will result in specific harm to aquatic organisms and human health. MCOFs composite materials as adsorbents to remove drugs show the practicality of material [155]. Apart from the adsorption and removal of pollutants in water bodies, MCOFs composite materials can also be applied to plants for detection and analysis. In sample pretreatment, MCOFs were used for MSPE of plant growth regulators contained in vegetables and fruits, and plant growth regulators were detected and analyzed by high performance liquid chromatography diode array detectors [156].

It is worth noting that MCOFs composites can simultaneously selectively enrich and ionize analytes, such as selective enrichment and ionization of bisphenol, rapid enrichment, and determination of polycyclic aromatic hydrocarbons in PM2.5 [157]. Besides, combining it with the surface-enhanced laser desorption/ionization time-of-flight mass spectrometry (SELDI-TOF-MS) method can be used for high-throughput screening of bisphenols in drugs and personal care products (PPCPs) (Fig. 15) [158]. Consequently, the rapid identification of harmful compounds by MCOFs composite materials can be further explored. To enhance the ability of MCOFs to enrich pollutants, the structure can be further designed based on the core-shell structure. For example, He et al. combined the shape of flowers and gypsophila to create and successfully synthesized bouquet-like magnetic TpPa-1. The designed structure was further beneficial to magnetic recovery than monodisperse core-shell structure dispersed particles, and had better enrichment performance, using for the extraction of polycyclic aromatic hydrocarbons [159]. In addition to the design of the structure of MCOFs, it is also possible to hybridize the MCOFs composite with other materials to synthesize a novel structure. For instance, using the photochemical synthesis method, magnetic $CoFe_2O_4$ nanoparticles were first filled into carbon nanotubes（CNT) to prepare magnetic carbon nanotubes (MCNT). Then, the synthesized COF shell (CTC-COF) of cyclic tricarboxylic acid was wrapped on the surface of MCNT to obtain a layered sea cucumber-like composite CTC-COF@MCNT [71]. The combination of magnetic Fe_3O_4 NPs, MOFs, and COFs could produce a new type of magnetic composite material, which could effectively extract and pre-concentrate Cu^{2+} in the aqueous solution. The surface of this new type of material contained higher density nitrogen-containing and oxygen-containing functional groups. And after Cu^{2+} was adsorbed, it was separated rapidly within the 30 s under the outer magnet. Then, MSPE and UV-spectrophotometry were used to detect Cu^{2+}. The sensitivity of detecting Cu^{2+} was greatly improved, and the anti-interference ability in multi-component solutions was also further enhanced [160]. In summary, on the basis of current existing studies, the application of MCOFs composite materials in environmental adsorption and enrichment detection is relatively common.

5.1.2. Catalysis

In recent years, with the rapid economic development, excessive carbon dioxide emissions from excessive use of fossil fuels have resulted in environmental problems. A green way to use renewable energy for carbon dioxide conversion is electrocatalytic carbon dioxide reduction [161]. The TM-COFs obtained by combining 2D COFs with transition metal TM (eg, Fe, Co, Mn) exhibited excellent electrocatalytic activity for oxygen reduction reaction (ORR) [162]. In particular, the hybridization of magnetic iron, cobalt, and nickel ions with COFs also has an outstanding catalytic effect. For instance, cobalt-doped COFs electrocatalysis O_2 release [127] and CO_2 reduction [163]. Nickel doping into COFs could electrocatalytically reduce CO_2 [164]. COFs modified with iron-doped titanium dioxide nanoparticles were used for photocatalytic degradation of methylene blue [138]. When composite materials were used for photocatalysis, cobalt-doped COFs tended to reduce CO_2 to CO. However, nickel-doped COFs produced almost equal amounts of CO and HCOOH when reducing CO_2 [165]. The corresponding mechanism was shown in the following Fig. 16a. Lin et al. used a COF containing cobalt porphyrin to reduce CO_2 in a neutral aqueous solution, which indicated the prepared COF-366-Co had a obviously catalytic effect on reducing of carbon dioxide, and the main reduction product was CO [166]. In particular, Gong et al. found that the spin state transition of Co had an important role in regulating the photocatalytic performance of COF-367-Co [167]. By controlling the spin state of Co in COFs to acquire composite materials for CO_2 reduction experiments, COF-367-Co^{III} exhibited outstanding activity, and significantly enhanced the selectivity to HCOOH, thereby greatly decreased the activity and CO and CH_4 selectivity, which was in sharp contrast with COF-367-Co^{II} (Fig. 16b). The coordination of magnetic iron, cobalt, and nickel ions with COFs improves the reduction ability of CO_2, but it may be because the ability of these three metals to capture CO_2 and the electron coordination environment are different, resulting in various reduction products (carbon monoxide or/and glycolic acid) [101].

In particular, the introduction of noble metal nanoparticles (gold, platinum, palladium) into the MCOFs composite has excellent catalytic activity for the degradation of pollutants. Xu et al. reported a preparation strategy of immobilizing ultrafine gold nanoparticles (4.0 nm) in the Fe_3O_4@COF (TAPB-DMTP) shell, which was successfully used to reduce 4-nitrophenol and methylene blue with sodium borohydride. The composite material exhibited significant catalytic activity, and the proposed strategy was also applicable to prepare Fe_3O_4@COF-Pt and Fe_3O_4@COF-Pd [136]. But introducing precious metals is not the only choice. Ni $(OH)_2$ modified COFs materials could prepare composite materials with excellent photocatalytic hydrogen evolution activity [168]. Furthermore, MCOFs are also promising Fenton-like catalysts in terms of catalytic degradation of pollutants [139]. To control the growth of Fe_2O_3 in COFs nanochannels, a nano-flower-shaped morphology MCOFs composite material was prepared for sulfamethazine (SMT) degradation in an aqueous solution, SMT molecules were adsorbed in the porous composite material. The catalytic ability of the material was attributed to Fe_2O_3 NPs confined to the nanochannels. In the presence of Fe_2O_3 as a catalyst, H_2O_2 generated hydroxyl radicals in the limited space of the COFs. The SMT molecules adsorbed in the COFs pores were degraded and removed by the attack of hydroxyl radicals.

5.1.3. Sensing

In electrochemical immunosensing applications, MCOFs can be used as a signal amplification material to generate and amplify electrochemical signals. The essence is a process of stabilization and enhancement. First of all, COFs possess the excellent enrichment ability. Probe molecules can be incorporated into the pores of COFs, because the porous structure of COFs. Then through a variety of non-covalent interactions (π-π stacking, electrostatic interaction, and hydrophobic interaction) to make it stably enriched in COFs, the aim is to ameliorate the electrochemical signal. Afterwards, MNPs can efficiently catalyze the electrochemical oxidation reaction of probe molecules so that the redox signal can be enhanced [169].

When MCOFs composite materials are used as electrochemical sensors, they have high electrochemical activity and excellent stability, which can monitor the aromatic nitro compounds in the water. Besides, by control the surface morphology of this material can enhance its sensitivity and reliability to analytes. Wang et al. did not use any surfactants, templates, or structure-directing agents at room temperature, and only adjusted the reaction solvent content to synthesize a hierarchical Fe_3O_4@AT-COF material with a controllable surface morphology and structure [51]. It was directly modified on the magnetic glassy carbon electrode (MGCE) to obtain a new electrochemical sensor (Fig. 17). This sensor could simultaneously detect p-nitrophenol (PNP) and o-nitrophenol (ONP), which had a broad linear detection range (10-3000 μM) and a low detection limit (0.2361 μM and 0.6568 μM). Adjusting the content of acetic acid (HAc, 36%) to the optimal amount of 2.0 mL was conducive to gradually forming a more uniform three-dimensional core-shell AT-COF on Fe_3O_4 surface. The pore structure of the material is increased, the surface area is more extensive, and the stability is higher. The signal amplification of Fe_3O_4@AT-COF is significantly enhanced, which facilitates electron transfer and fast mass transfer. Moreover, MCOFs as a support material can also be used for fluorescence sensing combined with other materials. Wang et al. combined MCOFs with molecularly imprinted polymers (MIPs) and carbon dots (CDs) [170]. A new type of fluorescence sensor was synthesized, which could sensitively and selectively detect 2,4,6-trinitrophenol (TNP).

5.2. Biology

At present, the application of MCOFs composite materials in biology has been rapidly developed. The biological applications of MCOFs composite materials are mainly glycoproteome enrichment analysis, biomedical disease treatment (magnetic resonance imaging, targeted drug delivery, etc.).

The MCOFs complex exhibited superior properties in the enrichment analysis of glycoproteome than naked Fe_3O_4. Under the same conditions, the enrichment capacity of a single magnetic nanosphere for multiple glycopeptides was lower than that of composite materials formed by COFs wrapping, because the nitrogen-rich skeleton and amino-rich end were contained in COFs. The mixed digest of human serum immunoglobulin G (IgG) and bovine serum albumin (BSA) was used to verify the feasibility of the obtained MCOFs composite material to enrich glycopeptides specifically. The horseradish peroxidase (HRP) digest was adopted to testify the universality of its enrichment of glycopeptides. The results indicated that the Fe_3O_4@TpPa-1 obtained had excellent selectivity, specificity, and versatility for glycopeptide enrichment [69].

MCOFs can be used as a new and effective drug carrier. Zhao and colleagues first reported the application of MCOFs (Fe_3O_4@COF) in drug targeted delivery and chemo-photothermal therapy of cancer [171]. The composite was modified with bovine serum albumin and folic acid (BSA-FA), and the excellent dispersion of the composite through π-π interaction and hydrogen bonding resulted in a high loading capacity for doxorubicin (DOX) (Fig. 18). The purpose of using BSA modification was that BSA could be adsorbed by COFs through non-covalent interaction, which could greatly improve the biocompatibility and stability of the material in the medium. The effect of FA was to give composite nano-carrier materials special selectivity to cancer cells. Combining COFs and MNPs to construct a nanocomposite that can load drugs for delivery, tumor environmental response, and thermomagnetic properties are of great value for expanding the application of MCOFs composites. At the same time, it has positive significance for human health. Benyetton reported for the first time that COFs were linked to nanoimines combined with magnetic iron oxide nanoparticles (γ-Fe_2O_3 NPs). The anticancer drug Dox was loaded in the nCOF porous network, and then 10 nm γ-Fe_2O_3 NPs were coated on the surface [172]. The γ-Fe_2O_3 NPs interacted with the nCOF surface by N-Fe bonds. Because γ-SD itself was more inclined to aggregation and precipitation, to prevent the magnetic drug loaded nanocomposite particles from forming larger aggregates, the outer surface of the particles was wrapped with the polymer. A shell of Poly (L-lysine) cationic polymer

(PLL) was used to stabilize through a simple impregnation procedure to obtain the magnetic nCOF complex γ-SD/PLL. The interaction between the porous structure of nCOF and the polymer coating could be used for thermochemotherapy and magnetic resonance imaging. The anticancer drug Dox was released by magnetic heating in an acidic pH environment to treat cancer. The results showed that this complex was not toxic to any cells and had good biological safety.

MCOFs can not only be used as adsorbents to adsorb and detect pollutants in the environment (organic, inorganic, heavy metals, etc.), but also can be used as a carrier to deliver anticancer drugs for cancer treatment. In catalytic applications, the photochemical properties of magnetic metals and their alloys are fully demonstrated, and the products obtained by reducing CO_2 with various magnetic metals are different. And MCOFs materials are used in electrochemical immunosensing (as signal amplification materials) to generate and amplify signals and fluorescence sensing (as support materials), due to the electrochemical properties. In short, through a comprehensive investigation of the application of MCOFs materials in various aspects, it is concluded that the materials have vigorous prospects in the fields of environmental remediation and biomedicine.

6. Summary and outlook

In summary, MCOFs produced by the combination MNPs and COFs are used as a new type of organic porous magnetic material that can detect pollutants in the environment by adsorption and enrichment. Magnetism and reusability are the main advantages of MCOFs. Moreover, sensors based on MCOFs materials can be used for biomedical diagnosis, but currently there is no commercial application for making them into portable sensors, so commercialization is a great challenge.

Although the application of MCOFs in various fields has been significantly developed in recent years, there are still some shortcomings. The future development can be considered from the following aspects:

(1) Expand the scope of application. The preparation of MCOFs composite materials enhances the advantages of COFs in separation and enrichment to a certain extent. It can achieve rapid solid-liquid separation by applying an external magnetic field. But applications in other areas still need to be explored. In MCOFs, catalysis study can be further developed towards clean energy. Since the stable π-π stacked crystal structure of COFs can greatly enhance the light absorption capacity, it has the potential for photocatalytic hydrogen production. Combined with the current research on the catalytic performance of composite materials, the main focus is on the reduction of carbon dioxide by magnetic metal-doped COFs, and future research can be in-depth in the direction of catalytic hydrogen production. Besides, the environment pollutants include not only chemical substances but also microorganisms. Considering that there is no works on the application of composite materials in disinfection and sterilization at this stage, biological disinfection and sterilization can be considered in the next step. It is necessary to study the toxicity of nanomaterials to ensure that long-term use of this material will not have an impact on health and

circumstance.

(2) Diversification of composition and structure. According to the current research results, the MNPs for the synthesis of MCOFs composites are relatively singular, iron oxides (such as Fe_3O_4, γ-Fe_2O_3) are generally used. Further research may consider the use of metal alloys and COFs hybridization. For example, $MnFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$, etc., are combined with COFs. Besides, the structure of the obtained MCOFs composite is mainly a core-shell type, and other shapes are rarely studied, diversifying the structure of composite materials remains a challenge. Combining the ellipsoidal polycrystalline shape of magnetic iron oxide, it is feasible to combine it with COFs to design a new composites structure. Further, according to the designability of the pore size of the COFs, MNPs and various functional parts can be doped into pores of different shapes to form composite materials with specific functions.

(3) Preparation cost and efficiency. Most of the current researches tend to develop towards the functionalization of MCOFs. The high cost of monomers used to synthesize COFs leads to high cost of preparation of composite materials, which is not economical. Moreover, the high surface energy of MNPs can lead to the aggregation of nanoparticles, thereby affecting the properties of the nanoparticles themselves. To obtain stable nanoparticles, a substrate is added for protection (such as silica, polydopamine, etc.). On account of the hydrophobic nature of COFs in MCOFs composites, which are not suitable for applications related to hydrophilicity. To

improve the hydrophobicity, certain functional groups are added to prepare composites with specific functions. The introduction of substrates, functional groups, metals, etc. will undoubtedly increase the cost of material preparation. Therefore, looking for cost-effective functional components to reduce input costs and boost manufacturing efficiency is a significant topic for future research.

(4) Simple and large-scale preparation method. The preparation process of MCOFs is relatively cumbersome, and the preparation at this stage is still in the laboratory stage. Simultaneously, many studies focus on the use of MCOFs on the experimental bench and the use of hand-held magnets for separation. This method is unrealistic when the processing object is a large amount of water or flowing water. To date, none of the methods developed is perfect and all are far from ready to be used in commercial systems. The simplification of the preparation method in the future should take into account the large-scale production. Optimize the preparation conditions of each method. For example, it is feasible to find better alternative monomers for COFs synthesis in the monomer polymerization method to overcome the temperature limitation. In the impregnation method, the cost is saved by exploring the optimal use amount of organic solvents.

Acknowledgements

The study was financially supported by the National Natural Science Foundation of China (51979103, 51679085), the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17), the Funds of Hunan Science and

Technology Innovation Project (2018RS3115, 2020RC5012), the Key Research and Development Project of Hunan Province of China (2017SK2241), the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17), the National Natural Science Foundation of China (52100181, 51979103, 51679085, 51521006, 51508177), the Project funded by China Postdoctoral Science Foundation (2021T140192, 2021M690054), the Funds of Hunan Science and Technology Innovation Project (2018RS3115, 2020RC5012). The authors also gratefully acknowledge the National Supercomputing Center in Changsha for providing the computing resources.

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