Review

Recent Advancements in MOF/Biomass and Bio-MOF Multifunctional Materials: A Review

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Abstract: Metal–organic frameworks (MOFs) and their derivatives have delivered perfect answers in detection, separation, solving water and electromagnetic pollution and improving catalysis and energy storage efficiency due to their advantages including their highly tunable porosity, structure and versatility. Recently, MOF/biomass, bio-MOFs and their derivatives have gradually become a shining star in the MOF family due to the improvement in the application performance of MOFs using biomass and biomolecules. However, current studies lack a systematic summary of the synthesis and advancements of MOF/biomass, bio-MOFs and their derivatives. In this review, we describe their research progress in detail from the following two aspects: (1) synthesis of MOF/biomass using biomass as a template to achieve good dispersion and connectivity at the same time; (2) preparing bio-MOFs by replacing traditional organic linkers with biomolecules to enhance the connection stability between metal ions/clusters and ligands and avoid the formation of toxic by-products. This enables MOFs to possess additional unique advantages, such as improved biocompatibility and mechanical strength, ideal reusability and stability and lower production costs. Most importantly, this is a further step towards green and sustainable development. Additionally, we showcase some typical application examples to show their great potential, including in the fields of environmental remediation, energy storage and electromagnetic wave absorption.

Keywords: MOFs; biomass; bio-MOFs; biocompatibility

1. Introduction

Metal–organic frameworks (MOFs), which are advanced porous coordination polymers, comprising metal ions/clusters and organic linkers by orderly self-assembly, have set off a research boom around the world in the 21st century [1,2]. Thanks to the high selectivity of metal ions/clusters and organic linkers, since first being reported, upwards of 90,000 MOFs have been created [3], and they have shown ultra-strong applicability in adsorption [2,4], separation [5,6], sensing [7,8], storage [9,10] and catalysis [11,12], which benefits from their high specific surface area, adjustable pore size and diverse morphology and structure [13–15]. Recently, MOFs have been applied as self-sacrificed templates/precursors to prepare porous carbon by in-situ pyrolysis; the carbon skeleton derived from organic linkers not only retains the morphology and porous structure of MOFs but also protects the metal/metal oxide formed by the carbothermic reduction, which greatly enhances the conductivity and stability [16–18]. Compared to traditional metal/carbon composites, MOF derivatives possess a more ordered pore structure and a more uniform distribution of metals/metal oxides.

However, there are two big obstacles for the further development of MOFs and their derivatives [19,20]: (1) MOFs and their derivatives tend to agglomerate, especially in the process of pyrolysis, which decreases the specific surface area and porosity, and even destroys the morphology of the derivatives, thus having a negative impact on the
application performance. (2) MOFs with poor stability are prone to hydrolyzing in water or acid/alkaline environments due to the weak binding energy between the metal ions and organic ligands. At this time, toxic organic ligands will be released into the environment, which poses a threat to biological safety.

For the former, incorporating MOF precursors with a carbon template, such as graphene [21], carbon nanofibers [22] or carbon nanotubes [23], is a common and effective method to improve the dispersity and structure of MOF derivatives. Nevertheless, carbon nanomaterials consume a lot of fossil resources and funds. As a matter of fact, no other material is better as an ideal template than biomass. Biomass, an abundant, cheap, renewable natural material, is the best potential candidate to replace carbon nanomaterials. Inspiringly, the surface of biomass is rich in hydroxyl and carboxyl, which is helpful to form stable links between MOFs and biomass [24]. The combination of biomass and MOFs illuminates a low-cost and sustainable strategy to prepare advanced function materials with excellent performance [25–27].

For the latter, biomolecules collected from biomass, e.g., amino acids, peptides, bases and polysaccharides, can be used as linkers—replacing traditional organic linkers—to construct metal–biomolecule frameworks (bio-MOFs), in order to avoid the pollution caused by traditional organic linkers with toxicity [28–30]. For example, p-phthalic acid, the organic linker of MOF-5, is harmful to organisms; when exposed to humid air, MOF-5 with poor stability tends to decompose and dissolve into water [31]. Bio-MOFs have several significant advantages in comparison with MOFs [32]: (1) good biocompatibility, strong self-assembly ability, nontoxicity and easy recycling; (2) structural diversity, including rigid and flexible structures, and many different binding sites, forming a variety of coordination modes with metal ions; (3) bio-MOFs constructed with chiral biomolecules show unique recognition and separation capabilities. Due to the rich heteroatom content, bio-MOF derivatives possess more active sites, which is an advantage that can significantly strengthen the electrochemical performance.

To the best of our knowledge, many works on MOFs and their derivatives have been reported [33–35], but there is a lack of comprehensive reviews related to MOF/biomass, bio-MOFs and their derivatives. Thus, in order to highlight the advantages of MOF/biomass, bio-MOFs and their derivatives (Figure 1), the current review aims at recommending research on them, and introducing, in detail, the advancements in the application of them in the field of environmental remediation, energy storage and electromagnetic wave absorption.

![Figure 1](image-url). The advantages of MOF/biomass and bio-MOFs.
2. MOF/Biomass Composites

2.1. MOF/Biomass Extracts

To date, many biomass extracts have shown great promise for use as carbon sources to enhance the performance of MOFs. Recent research indicated that introducing biomass extracts into MOF precursors can not only improve the structure of MOF derivatives but also offset the lack of carbon content of organic linkers [36–38].

For instance, small glucose biomolecules can easily load on the surface or penetrate into the internal pores of MOFs (Figure 2a). Cao et al. used ZIF (zeolitic imidazolate framework)-7/glucose to propose nitrogen-doped porous carbon by in situ pyrolysis, which presented high electrocatalytic activity and excellent stability [39]. Glucose has a significant impact on the microstructure, composition and conductivity of ZIF-7 derivatives. After carbonization, rather than a cubic structure, the porous carbon showed a sheet-like or graphene-like structure of ZIF-7 (Figure 2b). The addition of glucose prevented the formation of macropores, because the glucose-derived graphite carbon could catalytically convert ZnO to the metal Zn; the metal Zn with a low boiling point evaporated from the carbon matrix, thus promoting the formation of micropores, and an improvement in the specific surface area (SSA) and porosity (Figure 2c). Cai et al. used glucose as a sealed reactor to wrap ZIF-8 and found that glucose effectively prevented the loss of pyrrole nitrogen species (Figure 2d), which had a positive effect on the RhB removal performance [40]. In another study, Gu et al. adjusted the structure of CoZn-MOF/glucose-derivatives (ZnO/Co$_3$O$_4$@NC) by regulating the loading ratio of glucose [41]. Zn$^{2+}$ tends to combine with the hydroxy group of sugars [42]; hence, dense snake-like ZnO/C nanorods were induced to grow on the surface of ZnO/Co$_3$O$_4$@NC during pyrolysis. Instead, with the increase in the glucose content, the ZnO/C nanorods became greater in number and larger, which led to the agglomeration of the metallic oxide.

Maji et al. fabricated porous materials by carbonizing amine-functionalized IRMOF-3/sucrose, which achieved good carbon oxide storage by regulating the content of sucrose [43]. The authors concluded that sucrose formed good hydrogen bonding interactions with the MOFs within the pores and did not disrupt the crystal structure of the MOFs. Nitrogen absorption experiments showed that the SSA of the IRMOF-3/sucrose derivatives (nanoporous carbons, NPCs) was several times higher than that of IRMOF-3 and the sucrose derivative. When 300 mg of sucrose was added, the loading of sucrose in IRMOF-3 reached the limit. By this time, an encouraging gas storage capacity was obtained, with the highest SSA of 3119 m$^2$/g and a 1.93 cm$^3$/g pore volume. The experimental results supported that the NPCs could capture 5.1 wt% H$_2$ and 64 wt% CO$_2$, at most, under different conditions.

Recently, chitosan has been widely used for environmental remediation because of its biodegradability, water solubility and nontoxicity [44,45]. However, this substance exhibits poor chemical and mechanical stability, because it will completely dissolve in acid solutions or form a gel in alkaline solutions [46]. Studies have shown that there are strong interactions between pollutants and MOFs/chitosan, including complexation, hydrogen bonds, van der Waals forces and π–π interactions [47,48]. Therefore, the combination of chitosan and MOFs is a powerful alliance, which not only improves the stability of both but also brings about better performance. As Zhu et al. reported, the addition of chitosan improved the ability to adsorb tetracycline [49]. On the one hand, ZIF-8 was evenly distributed in the chitosan matrix, which ensured a higher adsorption capacity of ZIF-8/chitosan. On the other hand, chitosan has many amino and hydroxyl groups which are the active sites of tetracycline absorption. The results showed that each gram of ZIF-8/chitosan could absorb 495.04 mg of tetracycline at most; even after 10 adsorption/desorption cycles, the adsorption efficiency of ZIF-8/chitosan for tetracycline could still reach 90%, illustrating it is a green and reusable bio-adsorbent. Naeem et al. synthesized the dye adsorbent chitosan/Fe-MOF-235 with an absorption capacity of 2833 mg/g (methylene blue) and 2467 mg/g (methyl orange) [50]. After absorbing the dye, the XRD curve of chitosan/Fe-MOF-235 barely changed, which proved that chitosan/Fe-MOF-235 possessed superior stability. Moreover, chitosan/Fe-MOF-235 could achieve efficient absorption under acid/alkaline
conditions or high temperature (10–200 °C) due to its good adaptability. Besides the above, other MOF/chitosan absorbents, such as PAN/chitosan/UiO-66-NH$_2$ [48], HKUST-1/chitosan [49] and MIL-100(Fe)/chitosan [51], have shown great application prospects in the field of environmental remediation.

As the most abundant renewable natural resource on the earth, cellulose can be obtained from lignocellulosic biomass, such as cotton, wood and bamboo [52–54]. Cellulose is easier to use for MOF modification/anchoring thanks to the greater number of hydroxyl groups on the surface in comparison to other biomolecules. Kadib proposed a strategy of preparing cellulose@MOF composites, which can be divided into the following [55]:

1. Physical mixing. There are two fatal disadvantages, i.e., MOFs are unevenly dispersed and can easily leach from the bio-composites, which can only be alleviated by introducing more functional groups on the cellulose surface. Emam et al. oxidized the hydroxyl group of cellulose into a carboxyl group with stronger binding ability using hydrogen peroxide, in order to realize the good binding of Cu-BTC with cotton [56]. In the study of Zou et al. [57], they synthesized graphene nanoplate/C-ZIF-67/cellulose nanofiber films using a similar method with slight adjustments. Cellulose imparted outstanding mechanical properties and excellent electromagnetic interference (EMI) shielding performance to the composite films: the tensile strength was 46.33 MPa and the EMI shielding effectiveness reached 50.5 dB at a low thickness of 0.1 mm.

Figure 2. (a) Mechanism diagram of biomass extract filling in MOFs. Reprinted with permission from Ref. [43]. Copyright 2016, Elsevier; (b) HRTEM images of ZIF-7/glucose derivatives; (c) nitrogen adsorption–desorption isotherms of ZIF-7/glucose, ZIF-7 and glucose derivatives. Reprinted with permission from Ref. [39]. Copyright 2013, Royal Society of Chemistry; (d) proportion of various N-species in the total nitrogen functional groups of carbons. Reprinted with permission from Ref. [40]. Copyright 2021, Elsevier; (e) the formation mechanism of UiO-66-(COOH)$_2$ within cotton fabric to produce a composite. Reprinted with permission from Ref. [58]. Copyright 2018, Elsevier; (f) LBL method for the growth of MOFs by subsequently immersing the cotton fiber in an alternating bath of metal and ligand organic precursor solutions. Reprinted with permission from Ref. [55]. Copyright 2019, Elsevier.
(2) In-situ growth. The preparation process is generally as follows: firstly, cellulose needs to be dispersed in the metal salt/organic linker solution and then immersed in the organic linker/metal salt solution, which enables better dispersion of the MOFs and tighter attachment between the MOFs and biomass. For example, in a typical experimental process, cotton was added to 1,2,4,5-benzenetetracarboxylic dianhydride solution, after aging for 3 h at 70 °C; then, zirconium tetrachloride was added into the solution which continued to be heated at 150 °C; finally, UiO-66-(COOH)$_2$ was grown in the cotton (Figure 2e) [58]. After modifying with UiO-66-(COOH)$_2$, the cotton turned from white to yellow. The simulation results showed that UiO-66-(COOH)$_2$@cotton has the potential to remove creatinine from the blood, where a maximum absorption capacity of 212.8 mg/g was achieved, which was better than that of UiO-66-(COOH)$_2$@cotton synthesized ex-situ (192.3 mg/g). The data of the MOF content sufficiently explained the difference. The loading of MOFs for in-situ composites was 153.26 mg/g, but it was 43.63 mg/g for ex-situ composites.

(3) Layer-by-layer growth. This is illustrated with examples: As seen in Figure 2f, Cu-BTC/cotton was prepared via alternating immersion in aqueous solutions containing copper (II) acetate and the benzene-1,3,5-tricarboxylic acid ligand precursor [59]. This method reduced the formation of free MOFs and realized a high loading rate of Cu-BTC on the surface of the cotton. The efficiency of catalyzing NO release from S-nitroso cysteamine increased by 7–9 times as compared to the catalyzer-free reaction.

2.2. MOF/Biomass

Based on its large number of electronegative groups (-OH, -COOH) from cellulose, hemicellulose and lignin, highly developed directional pore structure, excellent mechanical properties and good biocompatibility [60–62], biomass has been widely used as an ideal template for advanced functional materials to prepare electrodes, supercapacitors, catalysts, adsorbents, absorbers, etc. [63–67]. In addition, biomass with great mechanical properties can serve as a mechanical support to ensure the mechanical stability of composite materials. These characteristics can also be perfectly reflected in MOF/biomass. Here, the application is discussed from the perspective of whether MOF/biomass composites are pyrolyzed or not.

As depicted in Figure 3a, Keplinger et al. synthesized ZIF-8/beech composites by in-situ growth of ZIF-8 within beech [68]. They first pretreated the beech with NaOH solution to deprotonate the carboxyl groups and etch the beech surface, which ensured that ZIF-8 would grow effectively. The hierarchical ZIF-8/beech presented an absorption selectivity function, because the pore aperture of ZIF-8 only allowed the transport of CO$_2$ but hindered the diffusion of N$_2$, and the carboxyl group of beech could absorb CO$_2$ but not N$_2$. Moreover, the adsorption and separation of gases are usually carried out under pressurized conditions, so good mechanical properties are the basis for ensuring the stable operation and high reusability of composite systems. ZIF-8/beech exhibited outstanding mechanical strength: the compressive strength and ultimate tensile stress reached up to 100 MPa and 74 MPa, respectively (Figure 3c,d), demonstrating the wood support template can offer a more significant improvement in the mechanical properties of MOFs involved composites in comparison with polymer templates [69,70]. Most importantly, the authors verified that this synthesis strategy was universal and could be applied to different MOFs and various woods (Figure 3b). In Wang and co-workers’ research, the natural pores of wood not only facilitated the load of MOFs but also limited organic pollutants’ transmission channels [71]. The water containing organic pollutants could only be transmitted along the open and elongated channels of the wood, which effectively improved the contact probability of organic pollutants with UiO-66. Then, UiO-66 in the channel adsorbed the organic pollutants through electrostatic interaction, in order to achieve a high removal efficiency (98%).

Biomass is vulnerable to fungi due to the high amounts of starch, polysaccharide and other nutrients [67,72], resulting in a decline in product performance. In such a context, Qin et al. explored the antibacterial properties of MOF-modified bamboo and wood [73].
The results showed that bamboo and wood exhibited significantly improved antibacterial properties, without affecting the stability of MOF-199, and fungi interacted with copper ions on the surface of MOF-199, thus resulting in cell dissolution (Figure 3e).

By analyzing the example of MOF/biomass, the principle of the stable loading of MOF crystals on the biomass surface can be summarized as (1) the electrostatic interaction between the MOFs and carboxylate, (2) and the hydrogen bond formed with hydroxyl [74]. Therefore, the surface quality of biomass affects the crystallinity and size of MOFs. Fewer hydroxyl and carboxyl groups are exposed on the smooth surface, which leads to lower crystallinity and a larger crystal size [75]. However, even if the biomass surface is pretreated with an activator, the loading ratio of MOFs in MOF/biomass is only less than 5% [68,71]. Consequently, it is extremely urgent to develop an innovative method to improve the loading ratio of MOFs. To break through the bottleneck, magnetic induction heating (MIH) has timely emerged [76,77]. Drawing on the experience of MIH, Li et al. synthesized UiO-66-NH$_2$@Fe$_3$O$_4$-wood twice by in-situ growth [78]. Firstly, Fe$_3$O$_4$ nanoparticles were synthesized in situ in wood, and then MOFs were induced to grow for 8 h in the magnetic wood under a 27 mT magnetic field (Figure 3f). In the magnetic field, the Joule heat generated by magnetic induction gathers around the matrix, which not only makes MOFs more inclined to nucleate in the wood but also improves the crystallization rate and yield of MOFs. It is worth mentioning that the growth of MOF can be further regulated by the loading rate of magnetic particles and the magnetic field strength. Under the condition of oil heat, due to the uniform heat dispersion, a large number of free MOFs are produced (Figure 3g). Compared with MOF/biomass prepared by the oil-bath method, the yield of MOFs in UiO-66-NH$_2$@Fe$_3$O$_4$-wood was dramatically increased to 49.6 wt%. The external magnetic field served as a dynamic switch that determines the uptake and release of methylene blue (MB). When UiO-66-NH$_2$@Fe$_3$O$_4$-wood was exposed to a 7.8 mT magnetic field, MB absorption of 96.3% was achieved in 20 min, and no organic linkers were detected in the MB aqueous solution, which demonstrated its excellent hydrolytic stability. By virtue of similar protocols to the synthesis of UiO-66-NH$_2$@Fe$_3$O$_4$-wood, the yield of MIL-100(Fe)@Fe$_3$O$_4$-wood and HKUST-1@Fe$_3$O$_4$-wood can also reach up to 58.4 wt% and 39.7 wt%.

2.3. MOF/Biomass Derivatives

MOF-derived carbon materials have excellent properties and wide applications, but organic ligands are mostly heterocyclic molecules, which leads to the fact that MOF-derived carbon is mostly amorphous carbon with poor conductivity, greatly weakening its electrochemical performance [65,79]. Consequently, there is a need to introduce a material that not only improves the electrical conductivity but also acts as a bridge to facilitate the transport of electrons between mutually independent MOF derivative particles. Until now, many materials have been used to build continuous structures with MOF-derived carbon; as a result, biomass carbon stands out from many materials due to its natural 3D hierarchical structure, sustainability and light weight [80,81].

For example, in the field of EMW absorption, MOFs and biomass are both attractive raw materials for the preparation of absorbers [74,82–84]; combining MOFs and biomass is likely a win-win strategy and a desirable means to prepare state-of-the-art absorbers [85,86]. Che et al. added Co(NO$_3$)$_2$·6H$_2$O to a modified cotton fiber pre-immersed in 2-miM solution, and ZIF-67 grew in situ evenly and fully on the surface of the cotton fibers during aging, following which the cotton fiber@ZIF-67 was annealed at 900 °C under a mixed H$_2$/Ar atmosphere [87]. The hollow cotton fibers connected Co/C nano-dodecahedron particles modified with villus-like carbon nanotubes to form a strong conductive network, which enhanced the conductivity loss (Figure 4a). Notably, the hollow cotton fibers not only prolonged the transmission path of the electromagnetic wave (EMW) but also induced multiple Debye dipolar relaxations through the oxygen-containing groups of their surface (Figure 4b). Compared with pure ZIF-67 derivatives [88], the reflection loss and effective absorption bandwidth (EAB) were remarkably optimized. In Huang and co-workers’
research [89], CoNi-MOF/bamboo fiber derivatives possessed a superior EMW absorption performance, and the reflection loss could reach $-75.19$ dB with a 2.66 mm thickness (Figure 4c,d). The authors concluded that the bamboo fibers greatly enhanced the EMW absorption capacity by optimizing the impedance matching and interface polarization. Ni/NC/C composites derived from Ni-MOF/loofah exhibited excellent EMW absorption performance, as reported by Li et al., and the minimum reflection loss was $-63.10$ dB at 2.0 mm with a 16% filling ratio; furthermore, the effective absorption bandwidth could reach up to 35.44 GHz [90]. On the one hand, the 3D hollow structure of the loofahs provided a channel for the conduction of electrons and heat energy and enhanced the conductivity loss; on the other hand, the rich interface defects of the Ni/NC/C composites improved the polarization probability (Figure 4e). In addition, the Ni/C derived from the Ni-MOF induced strong magnetic loss and optimized the impedance matching. In addition to loofahs, pine nutshells containing nitrogen [86] or highly wood aerogels [91] also posed a great influence on the EMW absorption performance of MOF/biomass-derived carbon.

MOF/biomass derivatives can not only be used for EMW absorption but can also be devoted to environmental remediation. For instance, Co@N-PC was prepared by pyrolyzing ZIF-67@poplar sawdust synthesized in situ, which demonstrated a strong organic dye...
removal performance [85]. Taking poplar sawdust as the carrier improved the utilization rate of the biomass and reduced the cost of water treatment, but the uniform -3D conductive structure composed of poplar sawdust and ZIF also promoted the material transfer and electron transfer in the process of dye removal. As shown in Figure 4f, Co@N-PC displayed a much better dye degradation efficiency than other catalysts. In another study, Li et al. studied the absorption capacity of an MB absorbent which combined Cu-BTC and activated carbon derived from agricultural waste; its maximum absorption capacity exceeded 400 mg/g [92], but it cannot be recycled and reused like Co@N-PC using magnetic recovery. MOF/biomass derivatives have also made achievements in the field of sensors. Co$_3$O$_4$/BC was prepared by the pyrolysis of ZIF-67 grown in situ on the surface of biomass (hemp stems) carbon. As illustrated in Figure 4h, Co$_3$O$_4$/BC exhibited good application prospects as a green, environmentally friendly NO$_2$ gas sensor thanks to the excellent synergistic effect between the two components [93]. The pores of biomass carbon provided a natural channel for gas adsorption, analysis and diffusion. The catalytic effect of Co$_3$O$_4$ improved the graphitization degree of biomass carbon, which was conducive to the rapid transfer of electrons, in order to enhance the gas sensitivity (Figure 4g).

![Figure 4](image-url)

**Figure 4.** (a) Dielectric loss tangent of HCF, HCF@CZ and HCF@CZ-CNTs; (b) Cole–Cole semicircle plots of HCF@CZ-CNTs. Reprinted with permission from Ref. [94]. Copyright 2020, Elsevier; (c) reflection loss curve of CN-ABF; (d) EMW absorption mechanism diagram of CN-ABF. Reprinted with permission from Ref. [89]. Copyright 2021, Academic Press Inc.; (e) mechanism of the absorption of electromagnetic waves by the Ni/NC/C composite. Reprinted with permission from Ref. [90]. Copyright 2022, Elsevier; (f) degradation efficiency of MB in different reaction systems within 30 min. Reprinted with permission from Ref. [85]. Copyright 2021, Elsevier; (g) gas sensing detection schematic diagram of CoBC-700; (h) selective testing of the response of the CoBC-700 sensor to various gases. Reprinted with permission from Ref. [93]. Copyright 2021, Elsevier.
3. Bio-MOFs

3.1. Biomolecules for Bio-MOFs

Organic linkers are one of the key factors to determine the topology of MOFs, which indirectly determines the application properties of MOFs. However, at present, the high price of commercial organic linkers increases the cost of industrial production. In addition, toxic organic solvents need to be used in the synthesis of MOFs, and the decomposition of MOFs leads to the outflow of toxic organic ligands, which will cause subtle damage to the environment [87]. Biomolecules, including amino acids, nucleobases, peptides, cyclodextrins and saccharides, can serve as organic linkers for MOF synthesis due to their rich resources, nontoxicity, good biocompatibility and structural diversity [20]. Therefore, they have been successfully applied to separation, detection, catalysis, antimicrobials, biomedicine, biosensing, etc. [28].

α-Amino acids, which belong to amphoteric organic compounds, have many carboxyl and amino groups which are ideal binding sites for metal ions. There are three main types of bio-MOFs constructed by α-amino acids [95]: (1) direct chelation; (2) addition of additional polydentate organic ligands and bridging anions; and (3) chemically modified amino acids. Dae-Won Park’s group synthesized the 3D water-soluble zinc-glutamate-MOF (ZnGlu) from natural L-glutamate, which is an eco-friendly catalyst for CO$_2$ conversion [96]. Compared with conventional MOF-based catalysts, it has the advantages of a high catalytic selectivity, high thermochemical stability and easy separation. Peptides are biomolecules in which amino acids are connected by peptide bonds, and they can be used to synthesize functional 2D and 3D bio-MOFs due to their inherent chirality and recognition properties. Chiral and rigid ladder-type building units, Co-L-GG, are constructed by the chiral dipeptide glycine-L(S)-glutamic acid, which can be used to prepare reticulated peptide MOFs [97]. The yield, thermal stability and porosity of peptidyl MOFs are decided by the type and size of the building units, and the enantioselective adsorption performance depends heavily on the pore size of the MOFs. Other studies have proved that the conformation and stability of peptide-based MOFs are affected by the flexible/rigid properties of peptides and will determine the biological application performance of MOFs [87,98].

Nucleobases are rich in oxygen- and nitrogen-containing groups and aromatic rings; all of them can interact with metal ions through coordination, π-π stacking or hydrogen bonding [30,99]. There are two types of bases: purine and pyrimidine. Purine bases have more coordination sites, so they are more widely used. Bio-MOF-1 is the first purine-derived 3D porous MOF consisting of a Zn (II)-ade octahedral cage with an anionic nature that allows it to be used for the storage of cationic drug molecules; the pores can also be modified by a cation exchange strategy for special applications [100]. With this in mind, Nathaniel L. Rosi’s group changed the structure and function of MOFs by controlling the coordination mode, where the specific surface area reached 4300 m$^2$/g and the pore volume was 4.3 cm$^3$/g [101].

Carbohydrates, including monosaccharides, disaccharides, oligosaccharides and polysaccharides [102], need to be oxidized before being used as linkers. The most common are α-CD, β-CD and γ-CD [29,103]. Among them, γ-CD has been extensively studied because of its better structural symmetry. CD-MOF-2 ([γ-CD](MOH)$_2$, where M is K$^+$ or Rb$^+$) synthesized with γ-CD has good thermal stability and architectural stability; inspiringly, there was no obvious weight loss or pore change even at 200 °C [104].

There are other biomolecules that naturally exist in humans, animals or plants, that contain several groups that can coordinate with metal ions and that can also be used as bio-MOF linkers. Table 1 lists the -bio-MOF building units and -bio-MOF structures with unique characteristics that cannot be obtained with traditional ligands. For example, 3D [Fe$_3$O(MeOH)$_3$](fum)$_3$(CO$_2$CH$_3$)$_4$.5MeOH formed by the coordination of Fe$^{3+}$ and fumaric acid and medi-MOF-1 formed by the coordination of Zn$^{2+}$ and curcumin both show great application potential.
### Table 1. Bio-organic ligand building blocks and characterization of bio-MOFs. Adapted with permission from Ref. [105]. Copyright 2021, American Chemical Society.

| Bioligands | Characteristics | Representative Molecules | Metal Ion | Case |
|------------|----------------|--------------------------|-----------|------|
| Amino acids | —Metal binding sites containing carboxylic (COO-) and amino (H$_3$N$^+$) groups | —L-Glutamic acid | Zn$^{2+}$ | [96,97] |
|            | —Chains with hydrophobic (nonpolar) and hydrophilic (polar) ends | —1,3-Benzene dicarboxylate | Co$^{2+}$ | |
|            | —Inherent chirality | —L-Aspartate acid | | |
|            | —Low dimensionality (additional organic ligands or bridging anions usually required to increase dimensionality) | —L-Tryptophan | | |
| Peptides   | —Short amino acid chains with reactive groups | —Carnosine | Zn$^{2+}$ | [106,107] |
|            | —Inherent chirality | —Gly-L-Phe | | |
|            | —React appropriately with metal ions, are flexible and exhibit dynamic responses for guest diffusion | —Fmoc-His-Asp-Gly-Arg | | |
|            | —Can covalently bond with linkers through different coordination configurations | | | |
|            | —Flexible | | | |
| Nucleobases | —Key constituents of nucleic acids | —Adenine | Zn$^{2+}$ | [108,109] |
|            | —Self-assembling capability including purines and pyrimidines | —Guanine | Ni$^+$ | |
|            | —Accessible lone electron pairs on nitrogen and oxygen atoms to act as multidentate ligands | | Cu$^{2+}$ | |
|            | —Sometimes coupled with auxiliary ligands, e.g., carboxylic acid | | | |
|            | —Diverse interactions (π–π stacking, coordinate bonding and hydrogen bonding) | | | |
| Saccharides | —Include monosaccharides, disaccharides, oligosaccharides and polysaccharides | —α-Cyclodextrin | K$^+$ | [110,111] |
|            | —Still rare; become the binding modes of bio-MOFs | —β-Cyclodextrin | Na$^+$ | |
|            | —Present in many fruits, vegetables and mammals | —γ-Cyclodextrin | | |
| Porphyrins | —Four modified subunits connected by α-carbons | —Dipyridyl porphyrin | Fe$^{3+}$ | [112,113] |
|            | —Some metal ions, such as Al (III), Fe (II), Zn (II), Co (II) and Cd (II), have been constructed with this ligand | —Tetrakis (4-carboxylphenyl) porphyrin | Zr$^{2+}$ | |
| Proteins   | —Long amino acid sequences | —Fluorescent protein | In$^{3+}$ | [114,115] |
|            | —Complex, flexible, difficult to control | —Catalase | Zn$^{2+}$ | |
|            | —Bind to metal ions at specific positions | | | |
|            | —Chemically and structurally diverse | | | |

#### 3.2. Bio-MOF Derivatives

Bio-MOFs are attractive precursors for the preparation of functional carbon materials. Firstly, they have a high permanent porosity; secondly, the rich nitrogen and active functional groups in the biomolecules can still be inherited by the derived carbon materials after carbonization, which are beneficial to improve the physicochemical properties and play a role in enhancing the catalytic and adsorption properties.

Bio-MOF-1 is an MOF crystal formed by the interaction of Zn$^{2+}$ with adenine (C$_5$H$_5$N$_5$) and biphenyl dicarboxylate. The flow chart of preparing derivative carbon materials with bio-MOF-1 is shown in Figure 4a. In a high-temperature N$_2$ atmosphere, for N-rich bio-MOFs, CNTs and a large number of active centers were induced, which endow the material with excellent electrocatalytic activity [116]. This is because nitrogen in the carbon structure would lead to a pulsed effect, which promotes the formation of CNTs [117,118]. Tian et al. went a further step to study the effect of temperature on the growth of CNTs [119]. When the temperature was higher than 800 °C, the amount of CNTs increased significantly, which resulted in an increase in the SSA. Additionally, the pyrolysis time is also an important
factor affecting the properties of bio-MOF derivatives [120–122]. An appropriate extension of the pyrolysis time could evaporate more Zn, increase the proportion of micropores and improve the graphitization degree and conductivity (the more graphitic N, the higher the conductivity; graphitic N is exhibited in Figure 5b), which is conducive to enhancing the adsorption and catalytic properties of bio-MOF derivatives. Moreover, Qiu et al. systematically investigated the effect of K\(^+\)-doped on the structure of bio-MOF-1-derived carbon [121]. K\(^+\) acted as an activator during the pyrolysis process; compared with the bio-MOF-1-derived carbon dominated by mesopores, many new micropores were produced in the K\(^+\)-@bio-MOF-1-derived carbon (KBM). Consequently, KBM not only showed selective adsorption of carbon dioxide but also had excellent electrochemical cycle stability.

**Figure 5.** (a) Schematic illustration of the synthesis of bio-MOF-1 derivatives; (b) schematic representation of various N types in nitrogen-doped carbon materials. Reprinted with permission from Ref. [121]. Copyright 2019, Academic Press Inc.; (c) schematic illustration of the preparation of ML-Ni/C composites; (d) comparison of the relative input impedance (\(|Z_{in}/Z_0|\)) at a thickness of 2.4 mm for ML-Ni/C composites. Reprinted with permission from Ref. [122]. Copyright 2021, Royal Society of Chemistry; (e) synthetic scheme for the preparation of 3D hierarchical RBC@CNT composites; (f) TEM images of RBC@CNT composites. Reprinted with permission from Ref. [123]. Copyright 2020, Elsevier.

Judging from the above, it is feasible to apply bio-MOF derivatives to solve EM pollution. For example, a new rod-shaped Ni-MOF was formed by the coordination of Ni\(^{2+}\) and pyrazine. Even when calcined in a non-reducing atmosphere, a large number of CNTs can be grown in situ on the surface of its derivative Ni/C [122]. However, its finite performance cannot meet the requirements of advanced EMW absorbers. For this reason, Lin and co-workers further used a mixed ligand strategy to optimize the performance of Ni/C. In the process of the coordination of pyrazine and Ni\(^{2+}\), trimesic acid was introduced to change the topological structure and color of Ni-MOF. As observed in Figure 5c, the rod-shaped structure of ML-Ni/C-0 became a regular flower but without CNTs. When the molar ratio of trimesic acid/pyrazine was 1:1, ML-Ni/C-2 showed a stronger absorption
capacity as a result of the improved impedance matching (Figure 5d), and the maximum reflection loss was $-65.3\, \text{dB}$ with a 5.1 GHz EAB. As depicted in Figure 5e, a rambutan-like bimetallic/carbon@CNT (RBC@CNT) 3D hierarchical composite was designed by pyrolyzing bimetallic Co/Zn-MOF-11 [123], which achieved a stronger EMW dissipation capacity than Co/Zn-ZIF-derived composites [124]. The special structure led to multiple reflections and scattering, and the improved interfacial polarization, conductivity loss due to the intertwined CNTs (Figure 5f) and magnetic loss of the metallic cobalt jointly promoted the enhancement of the EMW absorption capability.

4. Conclusions and Prospects

The combination of biomass and MOFs provides a new idea for researchers to prepare high-performance functional materials. In MOF/biomass, the biomass provides mechanical support for the MOFs and imparts a higher porosity and larger specific surface area. In addition, the biomass not only solves the problem of MOF aggregation but also connects independent MOF crystals, which significantly improves the performance of MOFs. Bio-MOFs with biomolecules as ligands show stronger attraction in comparison with traditional MOFs. Firstly, biomolecules have multiple coordination sites, which can form a variety of coordination modes with metal ions, meaning they have higher structural adjustability. Secondly, bio-MOFs have special chiral properties, which enables them to have a specific recognition function, good biocompatibility and -nontoxic properties, which broaden their applications in biology. In brief, biomass and biomolecules are a low-cost, abundant renewable resource; in today’s extreme pursuit of sustainable development, rational and efficient utilization of biomass and biomolecules is in line with the requirements of green development.

Along with all the advantages mentioned above, MOF/biomass and bio-MOFs still suffer many challenges, including, but not limited to, the following:

(1) The low loading ratio of MOFs in biomass. As the main phase of functional materials, the loading ratio of MOFs directly determines the properties of MOF/biomass composites. Therefore, in most experiments, the biomass needs to be pretreated to create more binding sites for the MOFs. However, the synthetic strategies, such as physical mixing, in-situ growth or layer-by-layer growth, cannot make MOFs nucleate quickly and efficiently on the surface of the biomass.

(2) The interaction between the composite systems is relative. In the process of in-situ synthesis, the competition between the surface functional groups of the biomass and organic linkers affects the crystallinity and morphology of the MOFs.

(3) The stability of the biomass. The premise of improving the stability of MOFs is to ensure the stability of the biomass. Biomass is easily affected by the environment, such as ultraviolet light and fungi, which will accelerate its degradation. Meanwhile, modifying the biomass with a chemical method makes the preparation process of MOF/biomass composites complicated.

Keeping these pros and cons in mind, MOF/biomass and bio-MOFs still have considerable prospects. First of all, we need to move forward with research on MOF/biomass and bio-MOFs: for example, we need to continue to seek more suitable biomasses and test more biomolecules to prepare new bio-MOFs. Secondly, we should deeply study the composite mechanism between MOFs and biomass to reduce the influence of the biomass surface quality on the morphology and crystallinity of MOFs. Moreover, the purpose of developing new functional materials is for application, so more advanced technology needs to be developed for industrialization. In particular, it is necessary to reduce the energy consumption in the preparation of MOF/biomass and bio-MOF derivatives.

Author Contributions: J.L.: writing and conceptualization; Y.L.: investigation; Z.L.: funding acquisition. All authors have read and agreed to the published version of the manuscript.
Funding: This research was funded by the Jiangsu Agricultural Science and Technology Independent Innovation Fund (CX(20)0301), the National Natural Science Foundation of China (No. 31971740), the Research Project of Jiangxi Forestry Bureau (No. 202134) and the Nanping Science and Technology Planning Project (N2020Z001).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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