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Metal–Organic Framework-Based Electromagnetic Wave Absorption Materials

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CHAPTER MENU

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1.1 Brief Introduction to Metal–Organic Frameworks

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), first proposed by Yaghi and Li et al. in the 1990s, are a class of crystalline porous materials consisting of metal ions/clusters and organic ligands assembled in an orderly manner [1, 2]. MOFs are exquisite porous materials composed of metal ions or clusters and organic ligands. These components are meticulously arranged in a crystalline structure, held together by coordination bonds formed between the metal centers and the organic ligands. Additionally, depending on the specific composition and structure, other forces such as hydrogen bonding, van der Waals forces, and π-π stacking also play a significant role. The composition of MOFs is diverse, covering almost all kinds of metal ions, such as main group, transition group, lanthanides, rare earth metals, and so on, while their organic ligands are mostly polyamines, carboxyl groups, pyridines, porphyrins, cyano groups, crown ethers, and phosphoric acid [3–7]. In recent years, MOFs have gained significant attention due to their remarkable characteristics, including the ability to design and control their components, achieve a regular and highly adjustable pore structure, exhibit high crystallinity, possess a

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large specific surface area, exhibit unique liquid and glassy properties, and showcase diverse topologies. Moreover, their environmentally friendly preparation aligns perfectly with sustainable development strategies [8–11]. Therefore, MOFs and their derived materials have received extensive attention in the fields of catalysis [12, 13], clean energy [14, 15], gas storage and separation [16, 17], sensors [18, 19], and medicine [20, 21]. Up to now, more than 20,000 MOF materials have been synthesized through the selection of various metal centers and organic ligands. Common MOF materials [5, 8, 22] include isotropic metal–organic frameworks (IRMOFs), coordination columnar layers (CCL), zeolitic imidazolate frameworks (ZIFs), porous coordination networks (PhCNs) [23–25], and so on. With the development of science and technology and the rising demand of the times, the types and quantities of MOFs and their derived materials will further increase, and their application scenarios and fields will further expand.

Due to their exceptional flexibility and diverse structural components, MOFs exhibit significant research value and hold great potential for development in the field of electromagnetic wave (EMW) absorption materials. The unique combination of metal and organic components, along with the highly adjustable microstructure, makes MOFs an ideal candidate for EMW absorption materials. Through careful control of the pyrolysis process, organic linkers can be transformed into a porous carbon network while preserving the original porous skeleton. Simultaneously, metal ions/clusters can be reduced to metal composites such as metals, metal oxides, and metal carbides via the carbothermal reduction process. These metal composites are homogeneously embedded within the network structure of the porous carbon, resulting in carbon-based composites with abundant interfaces and defects, a continuous conductive network, and exceptional magnetic response properties [26–29]. By precisely controlling the components, structural form, and composition, MOFs can be combined with other materials to optimize conductive loss, enhance dipole polarization, construct interface polarization, and improve magnetic response. This strategic approach ultimately leads to the development of MOF-based composite wave-absorbing materials that leverage a diverse range of microphysical loss mechanisms. Notably, when compared to other absorbing materials, MOFs and their derivatives offer exceptional versatility in modulating magnetic loss, dielectric loss, and impedance match properties [30–34]. By incorporating diverse component structures and facilitating the in situ generation of metal/metal oxide nanoparticles (NPs) or clusters, MOF-based materials demonstrate an extraordinary ability to attenuate incident EMWs on a substantial scale. This achievement underscores the immense potential of MOFs in the field of EMW absorption [35–37]. In addition, the highly porous structure inherited from the pristine MOFs facilitates the multiple scattering of incident microwaves and the lengthening of the transmission path, thus promoting their absorption of EMWs. Therefore, MOF-based EMW absorption materials are prepared and studied in large quantities at present and are also moving toward more novel and microscopic directions, such as multidimensional design, quantum dot modification, supramolecular cross-linking, and so on.

1.2 Preparation Method of MOF Materials

MOFs and MOF-derived materials have been synthesized by a variety of methods. Theoretically, the conditions for the synthesis of MOFs should be chosen so that metal–ligand bonds can not only be formed but also be broken and reorganized to prompt the structure propagation.

Dynamic bonds can induce changes in the morphology of the materials by breakage and reorganization of the structure under specific conditions. Therefore, dynamic bonds play an important role in the formation of crystals and ordered structures, where any faulty bonding that may lead to disorder or premature structural termination can be corrected [38–43].

1.2.1 Solvothermal Method

Solvothermal synthesis is a widely employed and straightforward method for the preparation of MOFs. Typically, this method involves the combination of metal salts with multipoint organic ligands in high-boiling solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dimethylformamide (DEF). The resulting mixture is heated in a PTFE-lined stainless steel reactor or immersed in a nonflammable silicone-based oil bath on a hot plate within an oven or fume hood. Generally, the reaction is allowed to proceed for 12–48 hours. When selecting a stainless steel reactor, it is important to consider factors such as the reaction size, solvent volume, and target temperature to ensure sufficient space for potential pressure buildup. The hydrothermal reaction method offers the ability to modulate the properties of synthesized MOF materials by systematically varying parameters including reaction temperature, time, solvent, reagent concentration, and pH. These parameters not only impact the material's topology but also influence crystal size and phase purity. It is worth noting that the synthesis of MOFs is a dynamic process and is highly sensitive to even small changes in the reaction mixture. This sensitivity allows for an exceptionally high degree of tunability in MOFs prepared via the hydrothermal method. For instance, the use of a mixture of metal chloride (MCl) and a multipoint carboxylic acid linker can result in the formation of a lesser stoichiometric amount of HCl. This, in turn, can dissolve the forming MOFs and slow down crystal growth to a certain extent. Conversely, if metal acetylacetone (M(acac)) is employed as the metal salt, the resulting acetylacetone by-product does not exert a constraining effect on crystal formation. The hydrothermal method has been extensively utilized to synthesize numerous MOFs and MOF-derived materials, which have found applications in diverse fields. Wang and coworkers [38] synthesized carbon quantum dots (CQD)/Ni-MOF composites by a one-pot hydrothermal method using $NiCl_3$-$6H_2O$ as the metal salt, p-phthalic acid (PTA) as the ligand, and DMF, ethanol, CQD solution, and deionized water as the solvents. By controlling the amount of CQDs, the conductivity and micro-morphology of Ni-MOF can be effectively regulated, and the number of active sites can be controlled, which in turn improves its electrochemical properties. Yuan and coworkers [44] used 2-amino terephthalic acid, tetrabutyl titanate ($C_{16}H_{36}O_4Ti$), 1,4-benzene dicarboxylic acid (BDC), DMF, methanol, sodium chloride ($C_{16}H_{36}O_4Ti$), and methanol (CH_3OH) as raw materials. Two different MOF materials, MIL-125(Ti) and amino-functionalized NH_2-MIL-125(Ti), were successfully synthesized by a solvent-thermal method, and they relied on their valence-electron-transferring properties and exhibited effective photocatalytic activity in visible light for the reduction of Cr(VI) in aqueous solution. Lang and coworkers [45] employed a large-scale bottom-up solvent-based solvatochromic approach to prepare Ni, Fe, Al, Co, Mn, Zn, Cd sulfates, *N*,*N*-dimethylacetamide (DMAC), *N*,*N*-dimethylformamide (DMF), formamide, N-2-methylpyrrolidinone (NMP), *N*,*N*-dimethylformamide (DEF), and Ni-NiMOFs using a large-scale bottom-up solvent-based solvatochromic approach. Ni-M-M-MOF (M = Fe, Al, Co, Mn, Zn, and Cd) nanosheets (NSs) prepared by a large-scale bottom-up solvent-thermal method, with a thickness of only a few atomic layers, are capable of directly acting as highly efficient electrocatalysts for oxygen precipitation reactions (as shown in Figure 1.1).

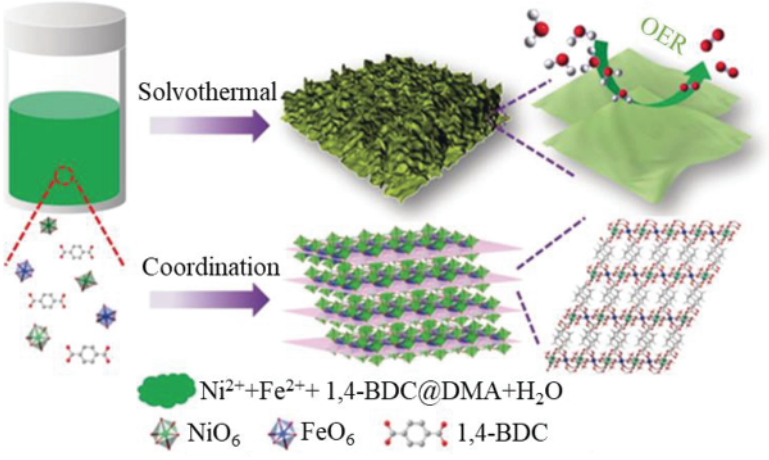

Figure 1.1 Synthetic procedure for the production of ultrathin metal–organic framework nanosheets and their utilization for the oxygen evolution reaction. Source: Li et al. [45]/with permission of John Wiley & Sons.

1.2.2 Microwave-Assisted Synthesis Method

The microwave-assisted method can effectively transfer the energy generated by EMWs to the reactants for more efficient and faster heating. Microwave irradiation, as a more efficient method of energy input than conventional heating methods, is expected to significantly reduce the reaction time without affecting the product yield or the quality of the finished product, and this means is suitable for industrial production. This effect has already been demonstrated by several researchers in laboratory-scale MOF synthesis. Unlike conventional heating methods, during microwave-assisted synthesis, crystallization of the synthesis takes place on hot spots formed by direct heating of the solvent, enabling the formation of small-sized particles in a short period. The theory of efficient thermal conversion by microwaves is favorable for the high-yield synthesis of MOF, but the limited penetration depth of microwaves into the absorbing medium limits the size of the reactor, which then hinders the large-scale industrial production of MOF.

Piao and coworkers [46] synthesized FeMo-MIL-88B materials by an ultrafast microwave-assisted method using $FeCl_3$-$6H_2O$, urea, DMF, terephthalic acid, and $Na_2MoO_4 \cdot 2H_2O$ as raw materials, which facilitated the hydrogen-extraction reaction (HER), oxygen-extraction reaction (OER), and overall hydrolysis reaction. Huo and coworkers [47] synthesized nickel-iron-based trimetallic MOF NSs through a simple microwave-assisted method using $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, terephthalic acid, and DMF as raw materials, which enabled simultaneous and rapid synthesis and activation of MOFs used for oxygen precipitation reactions. Cai and coworkers [48] prepared a Zn-doped nickel-based metal–organic framework (Ni-MOF) material with a honeycomb-layered spherical structure through the microwave-assisted method using $NiCl_2 \cdot 6H_2O$, PTA, $Zn(Ac)_2 \cdot 2H_2O$, and DMF as the raw materials (as shown in Figure 1.2), and excellent electrochemical properties were obtained by regulating the doping amount of Zn.

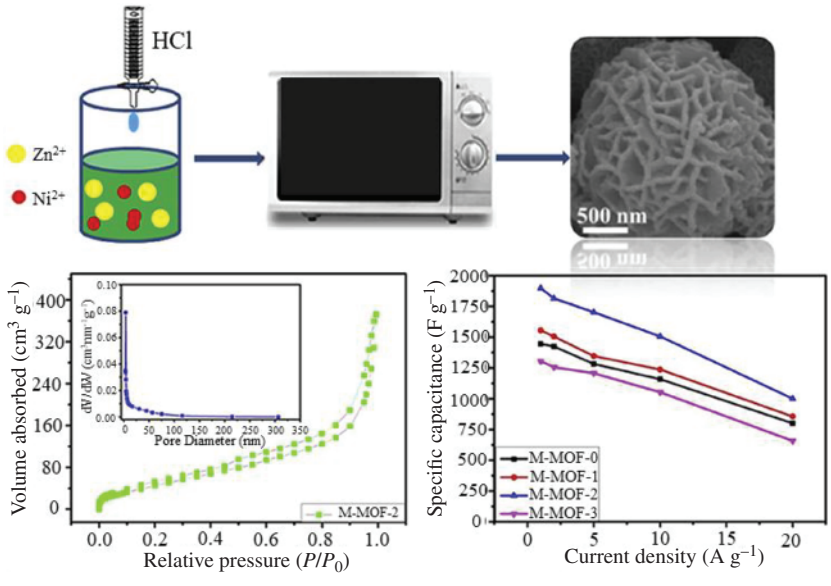

Figure 1.2 Schematic illustration of the overall formation process of the Zn-doped nickel-based metal–organic framework (Ni-MOF). Source: Chen et al. [48]/with permission of Elsevier.

1.2.3 Electrochemical Synthesis Method

Cathodic deposition and anodic dissolution are the two main methods for the electrochemical synthesis of MOFs. In the cathodic deposition method, a solution consisting of metal ions, organic linkers, and metal salts is in contact with the cathode surface. In the anodic dissolution method, a metal electrode rather than a metal salt is used as the metal cation source to avoid corrosion by anions such as nitrates and acetates. This method provides the metal ions continuously required for MOF formation, while organic linkers and electrolytes can be added as needed. Due to the increase in pH near the cathode surface, an electrochemical reduction reaction is triggered, which in turn leads to the deposition of the MOF film. In electrochemical synthesis, the yield and structure of the material are influenced by the electrolyte, solvent, voltage, density, and temperature. Compared to conventional methods, this method has the advantages of a fast reaction rate and low temperature, and the metal source is not salt. In addition, it is a discontinuous process that enables higher synthesis efficiency.

Easun and coworkers [49] prepared Mn-MOF by electrochemical synthesis using 2,5-diamino terephthalic acid and DMF as raw materials and obtained MOF materials with high CO_2 uptake by regulating the crystal synthesis and yield through the parameters of electrochemical synthesis, such as current density, electrolyte dosage, and reaction time (as shown in Figure 1.3a). Limin and coworkers [50] prepared ZIF-8 thin films by electrochemical deposition, which possessed a three-dimensional ordered macroporous metal–organic skeleton with a thickness of 4 cm and excellent optical, catalytic, and biosensing properties (as shown in Figure 1.3b). Liu et al. [51] proposed an electrochemical synthesis method for the preparation of large-area $Cu_3(HHTP)_2$ MOF films on single-crystal Cu anodes by charge-induced molecular assembly to achieve a surface reaction, and the synthesized MOF films possessed high electrical conductivity (as shown in Figure 1.3c).

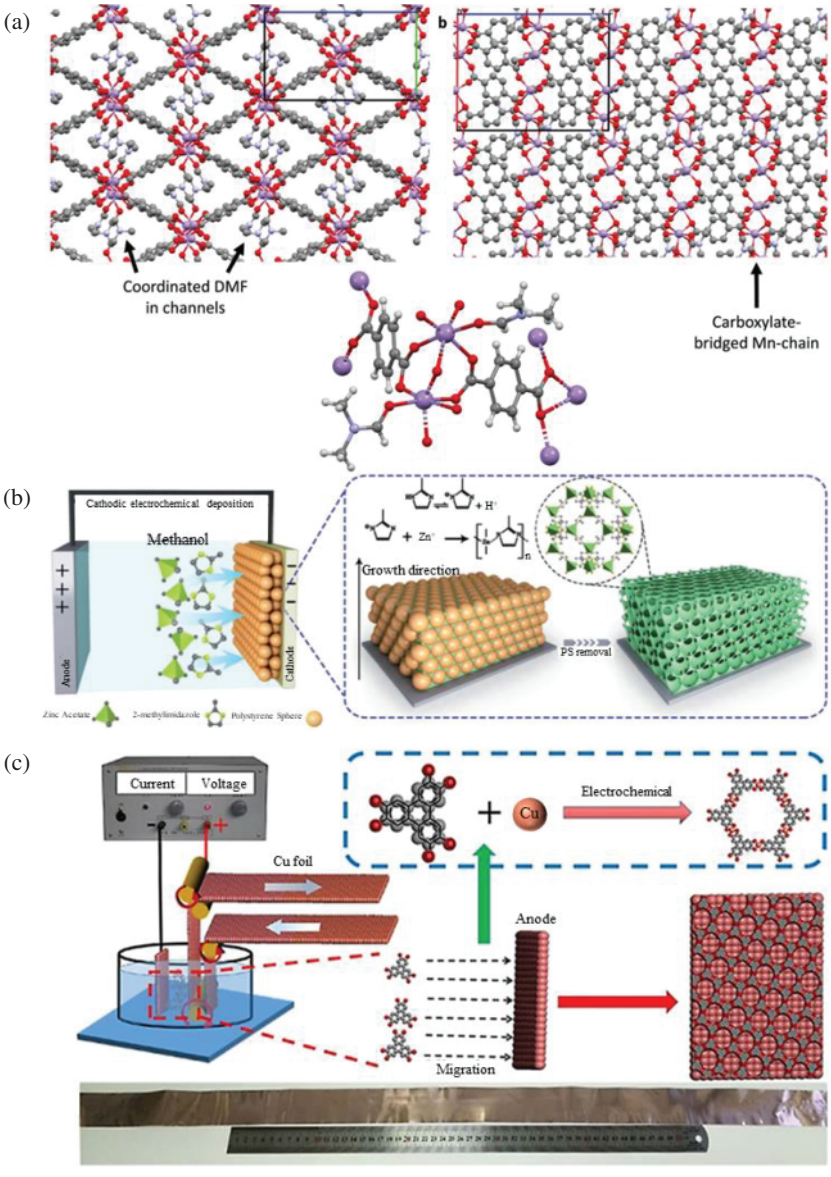

Figure 1.3 (a) Crystal structure of the Mn-MOF. Source: Asghar et al. [49]/Royal Society of Chemistry/CC BY 3.0. (b) Illustration of the fabrication process of a macro-microporous MOF inverse opal film deposited on a fluorine-doped tin oxide (FTO) substrate. Source: Qin et al. [50]/with permission of Royal Society of Chemistry. (c) Electrochemical reaction cell for the preparation of a $Cu_3(HHTP)_2$ film on Cu foil and the schematic diagram of coordination reaction between Cu^{2+} and the HHTP ion. Source: Liu et al. [51]/with permission of John Wiley & Sons.

1.2.4 Ultrasonic Method

The ultrasound (US)-assisted method is a simple, economical, and effective method for the preparation of MOFs. It has been found that US with a frequency of 20 KHz–1 MHz can cause chemical reactions of molecules in the solvent. The process of bubble formation, growth, and rupture during ultrasonication leads to an increase in the local temperature of the solution, which can result in homogeneous nucleation of the material, reduction of the crystallization time, and formation of smaller crystal sizes. Dissolving metal ions and organic ligands in organic solvents and then synergistically preparing MOFs in the presence of US is also an extremely effective approach.

Heydari and coworkers [52] prepared a cerium-organic skeleton (Ce-UIO-66MOF) rapidly and efficiently with 1,4-benzene dicarboxylic acid, DMF, and $(NH_4)_2Ce(NO_3)_6$ as raw materials under high-density US-assisted radiation at 305 W. It showed good catalytic activity for aerobic oxidation reactions. Haque and Jhung [53] compared US-assisted, microwave (MW) irradiation and conventional electrical heating methods for the synthesis of isomeric CPO-27S. The ultrasonic method resulted in faster nucleation and crystallization than the other heating methods due to the strong hot spot of US irradiation. The US-assisted synthesis of CPO-27-Co crystals with the smallest size and the highest porosity demonstrated that the US-assisted method can obtain small-sized MOF crystals with low energy consumption (i.e. shorter reaction time and/or lower temperature). Ding and coworkers [54] investigated the US-assisted rapid synthesis of caffeic acid (CA)-loaded and antimicrobial-use cyclodextrin metal–organic skeletons (U-CD-MOF), which reduced the preparation time to a few minutes (as shown in Figure 1.4c). It was found that ultrasonic power, reaction time, and temperature affected the morphology and size of the resulting crystals and the antimicrobial properties of the materials.

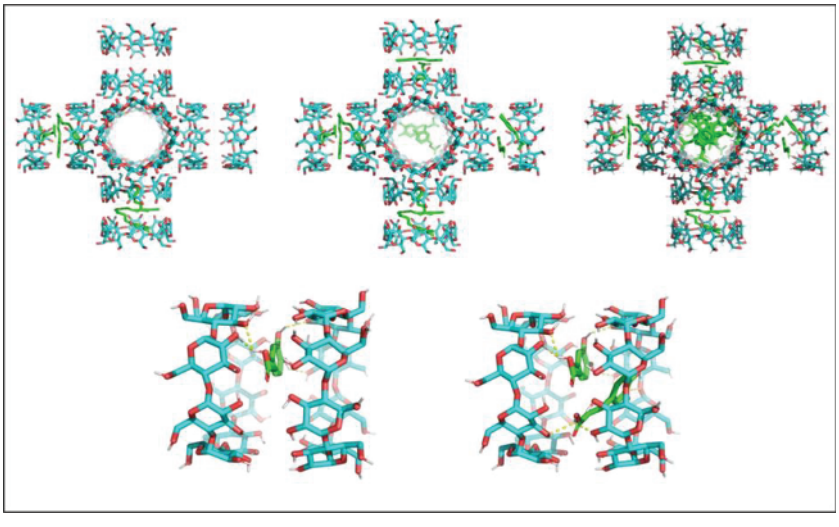

Figure 1.4 Molecular docking simulations of caffeic acid molecules distributed in CD-MOF. Source: Shen et al. [54]/with permission of Elsevier.

1.2.5 Mechanochemistry Method

Mechanochemical synthesis refers to the process of grinding a solid to facilitate a quantitative chemical reaction using grinding; this process usually does not use any solvent or uses only one solvent. This method enables faster and more efficient synthesis of MOFs than traditional hydrothermal methods. Impressively, MOF precursors with low solubility can also be adapted to this method. Typical mechanochemical methods include ball milling, pressure application, and extrusion. The ball milling method is the most common mechanochemical synthesis method of MOFs, which usually adopts a high-energy ball milling process to make solid or solid–liquid mixtures chemically react in a short time. The synthesis process of this method is simple, environmentally friendly, and low cost, which has good application prospects. However, this method still has some drawbacks, such as small yield, long equipment downtime, and difficult product cleaning. The pressurized synthesis method usually uses static/dynamic high pressure to pressurize the reactants to promote interface contact and improve reaction efficiency. This technique simplifies the synthesis process and reduces waste generation. However, this method suffers from low capacity in the large-scale preparation of MOFs because the feedstock is difficult to react completely. Extrusion is also an efficient and continuous mechanochemical method for the preparation of MOFs. The method requires little to no solvent; then the MOF synthesis can be achieved continuously. This mechanochemical technique offers the possibility of large-scale production of MOFs. It should be noted that to make the synthesized MOF have higher structural properties, the chemical ratio of the precursors should be strictly controlled so that the precursors can be as fully reacted as possible, as well as to avoid clogging of the pores by unreacted precursors. In addition, for the mechanochemical synthesis method, to fully carry out the reaction or reduce the generation of by-products, it is necessary to select appropriate precursors to avoid the formation of complex by-products, thus reducing the impact on the pore structure.

Tao and coworkers [55] proposed a simple and rapid mechanochemical synthesis of a series of HKUST-1, which can be used for the efficient adsorption of SF_6. Experiments were carried out using trimeric hexanoic acid (H3BTC) and copper nitrate doped with three different hybrid ligands, namely imidazole (Im), 1,2,4-1*H*-triazole (Trtz), and tetrazole (Tetz), respectively, and three different hetero ligands were successfully prepared. X@HKUST-1 (X = Im, Trtz, or Tetz) was successfully prepared. Notably, the water stability of the doped imidazole Im@HKUST-1 was significantly improved, compared to HUST-1. Xie and coworkers [56] prepared Pt-doped Zn-MOF-74 (PtZn-MOF-74) from Pt-doped ZnO (Pt-ZnO) by mechanochemical transformation. The lack of a large number of solvents limited the solvation and diffusion of the growing substance during the mechanochemical transformation process, thus preventing the agglomeration of the Pt dopant in PtZn-MOF-74. Liu and coworkers [57] formed MOFs by rapid encapsulation of a series of substrates, such as imidazole, phosphonic acid, urea, and amino sulfonic acid, into the pores of MOF NENU-3 via a one-pot mechanochemical synthesis (as shown in Figure 1.5). The synthesis of MOFs loaded with functional guests, which used to take days and require multiple steps, can now be done in one step within minutes. The proton conductivity of the resulting composite is improved by two to three times of magnitude over NENU-3. Compared with other methods of synthesizing MOFs, the mechanochemical technique has an extremely high synthesis efficiency, can significantly reduce the reaction time, and possesses great potential for large-scale and industrial production.

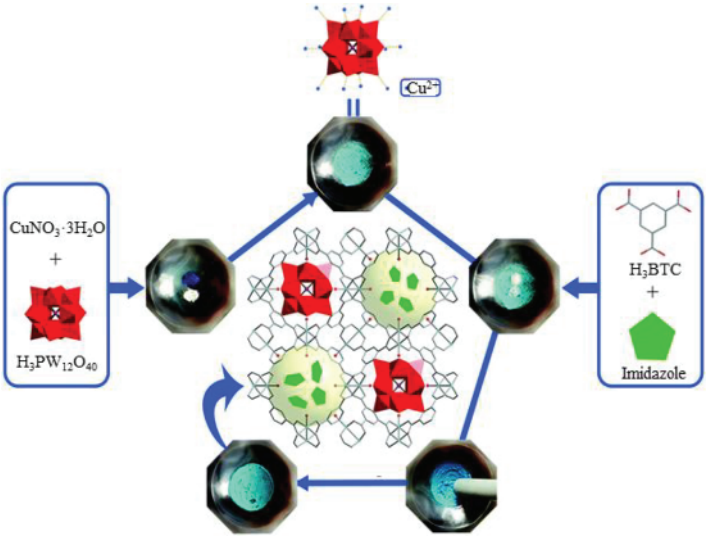

Figure 1.5 The synthesis process of Im@NENU-3 by a one-pot mechanochemical method. Source: Wang et al. [57]/with permission of Royal Society of Chemistry.

1.2.6 Steam-Assisted Conversion Method

Steam-assisted reforming is a method of MOF synthesis that uses small, submicron droplets generated by heating to facilitate a chemical reaction. Steam-assisted reforming typically uses smaller reactors and produces less waste than conventional hydrothermal synthesis. In this method, only a thin layer of mixed reaction precursors is spread in the reaction apparatus to facilitate the completion of the reaction. In addition, the use of a combination of spray drying and constant steam-assisted conversion is effective enough to achieve large-scale preparation of MOF. This combination of spray drying and steam-assisted conversion is expected to be an efficient, simple, low-cost, and low-waste method for MOF production, potentially leading to industrial-scale MOF production.

Dong and coworkers [58] successfully prepared ZIF-8 and ZIF-67 in place of organic DMF in water at 120 °C and 1.9848 bar with high solids concentration and significant solid–liquid separation. Notably, this is the first time that water has been used as the sole solvent for the preparation of ZIF materials. Jhung and coworkers [59] achieved rapid production of nano-porous MIL via steam-assisted conversion of −100(Fe) for rapid production. Here, the use of zero-valent iron, instead of Fe metal salts, avoided the associated negative effects. Furthermore, Kim and coworkers [60] prepared MIL-101(Cr) by steam-assisted conversion in an autoclave containing porous polytetrafluoroethylene plates at 220 °C, achieving a 90% product yield with an SSA of up to 4100 $m^2\ g^{-1}$ and good reproducibility (as shown in Figure 1.6).

1.2.7 Fluid Chemistry Method

Flow chemistry, in which chemical reactions are made to take place in a continuous flowing fluid rather than in a reaction vessel, shows advantages such as high surface area and volume

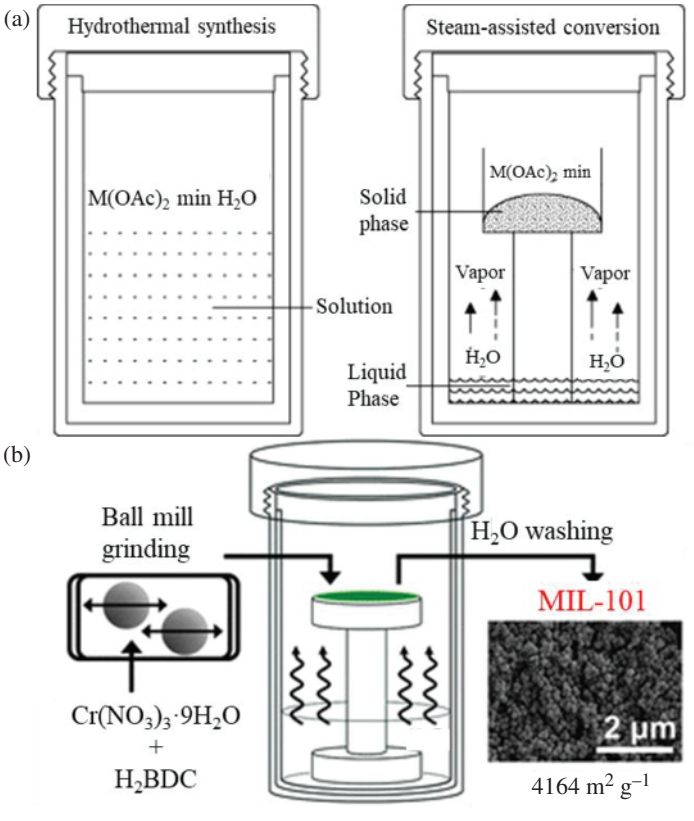

Figure 1.6 (a) Schematic diagram of the reaction vessels for ZIF synthesis. Left: hydrothermal synthesis (HTS), and right: the steam-assisted conversion (SAC) method; M-Zn, Co. Source: Shi et al. [58]/with permission of John Wiley & Sons. (b) Dry-gel conversion synthesis of Cr-MIL-101 aided by grinding. Source: Kim et al. [60]/with permission of Royal Society of Chemistry.

ratios of the reaction mixture, rapid mass, and heat transfer. Flow chemistry is considered to be a cost-effective method to meet the requirements of industrial production. Studies have been carried out to synthesize MOFs using flow chemistry techniques. Microfluidic synthesis is a typical fluid chemistry method. Microfluidic synthesis provides another effective way to synthesize MOFs on a large scale due to its advantages of automatic control and online quality monitoring. Fluid chemistry is globally recognized as a green and safe preparation technology that overturns the traditional synthesis methods. It provides greater flexibility and selectivity in the design of MOF synthesis routes, which can improve the synthesis efficiency and reduce pollution from the source. The fluid chemistry method is an important development trend for future MOF synthesis and is expected to achieve commercial mass production of MOFs for industrial applications in the future.

Herman and coworkers [61] designed a segmented reactor combining continuous flow and microwave radiation for the synthesis of MOF-74(Ni) at a pressure of 2.5 bar with a reagent conversion of 95.5%. Segmented flow improves the mixing state of the feedstock, reduces particle contamination, and allows the reaction to be carried out for a long period, with the

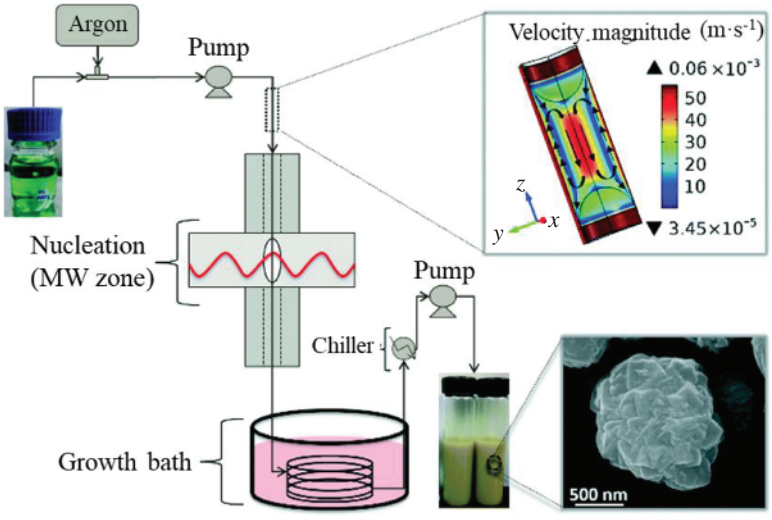

Figure 1.7 Schematic of the segmented, continuous-flow, microwave-assisted synthetic reactor for MOF-74(Ni). The inset on the top right, obtained using Comsol, shows turbulence in-between slugs in segmented flow. Source: Albuquerque et al. [61]/with permission of American Chemical Society.

results possessing a high degree of reproducibility. Thus, this strategy is time-efficient and allows for the continuous preparation of high-quality MOFs and composites, which is a favorable factor for large-scale production (as shown in Figure 1.7).

1.3 MOF-Derived EMW Absorption Materials

With the vigorous development of electronic information technology, the intelligent era is promoting the fourth industrial revolution, and the electronic information physical system based on the internet and intelligent entity system has comprehensively improved the types and application fields of electromagnetic equipment. However, the resulting electromagnetic pollution is also becoming more serious. Therefore, it is of great significance to use EMW absorption materials to absorb useless EMW pollution and eliminate harmful radiation. So far, a variety of nanomaterials with different topological, chemical, and physical properties have been applied to EMW absorption. In particular, MOF-derived materials with a unique composition and structure, owing to their unique micro-topological structure and diversified metal coordination, not only exhibit high EMW absorption performance and a flexible absorption frequency band but also possess abundant absorption mechanisms, thus attracting increasing attention. The design concept and research direction of MOF-derived EMW absorption materials can be summarized in the following stages: (1) selecting organic ligands and metal ions, (2) controlling the topology through self-assembly behavior, (3) obtaining different kinds of derivatives through post-processing, and (4) testing the absorbability of materials to EMWs and analyzing their microscopic electromagnetic response mechanisms.

1.3.1 Monometallic MOF-Derived Absorption Materials

Metals, alloys, ferrites, carbon nanofibers, carbon nanotubes (CNTs), graphene, and conductive polymers all possess certain EMW absorption capabilities. However, metals and alloys have limited applications due to their narrow absorption bands, while pure carbon materials exhibit a single loss mechanism that hinders further improvement in their EMW absorption capabilities. As a result, research has focused on modifying materials by combining carbon materials with single metal materials, leading to the development of materials with advantages such as high absorption strength, lightweight, and broad absorption frequency. Among these materials, MOFs synthesized using transition metal elements such as Fe, Co, Ni, Cu, and Zn serve as excellent precursors. These MOFs can be transformed into magnetic or nonmagnetic metal derivatives/carbon matrix composites at different temperatures. MOF-derived materials with nonmagnetic metals as coordination centers primarily concentrate on constructing microscopic conductive networks and modulating dielectric loss. On the other hand, MOF-derived materials with magnetic metals as coordination centers not only modulate polarization and conductivity loss but also enhance the magnetic loss capability by manipulating magnetic eddy currents and magnetic resonance effects.

Gao and coworkers [62] synthesized rod-like Cu-MOF-74 precursors using 2,5-dihydroxyterephthalic acid as a ligand. The precursor was treated with a KOH alkaline solution for 180 min to transform its morphology into a circular dodecahedron. Subsequently, calcined at 300 °C, the calcined samples were placed in an aqueous Na_2S solution for treatment, resulting in hollow dodecahedrons with Cu_2S shells. After mixing the sample with paraffin wax at 20 wt%, the optimum effective absorption bandwidth of the sample was achieved at 2.3 mm, which reached a value of 6.2 GHz, covering 11.8–18.0 GHz. The material has a large number of defects and nonhomogeneous interfaces, which can effectively generate polarization relaxation. The structure of the hollow core can enhance the multi-scattering ability of the material to a certain degree, further optimizing the impedance-matching properties and improving the EMW absorption performance of the material.

Che and coworkers [63] synthesized octahedral ZIF-67 precursors using 2-methylimidazole as a ligand by controlling the solvent and cobalt/linker molar ratio. After calcination at 500 °C, Co@N-doped carbon composites (Co@NC) were obtained, with the initial MOF precursor determining the distribution of the carbon backbone and magnetic cobalt NPs. The carbonization yielded Co@NC composites with controllable size and shape. Additionally, the magnetic carbon composites have the advantages of rich interfacial polarization and a strong magnetic coupling network, and the MOF-derived dielectric carbon skeleton provides electron transport paths and enhances the conductive dissipation. The optimized octa-decahedral Co@NC sample exhibits the best microwave absorption of −53.0 dB at a thickness of 1.8 mm and an effective absorption bandwidth of 6.2 GHz (as shown in Figure 1.8).

1.3.2 Multi-metal MOF-Derived Absorption Materials

Compared with monometallic MOFs, multi-metal MOFs possess a richer variety of active sites, which are conducive to the improvement of the stability of the material backbone structure, chemical activity, alteration of the state of charge distribution, and magnetic properties of the materials. Numerous parameters of the polymetallic MOFs can be designed and regulated according to the ratio of the adjusting metals so that MOF materials with desired properties can be obtained. Therefore, it is easier to regulate the EMW absorption

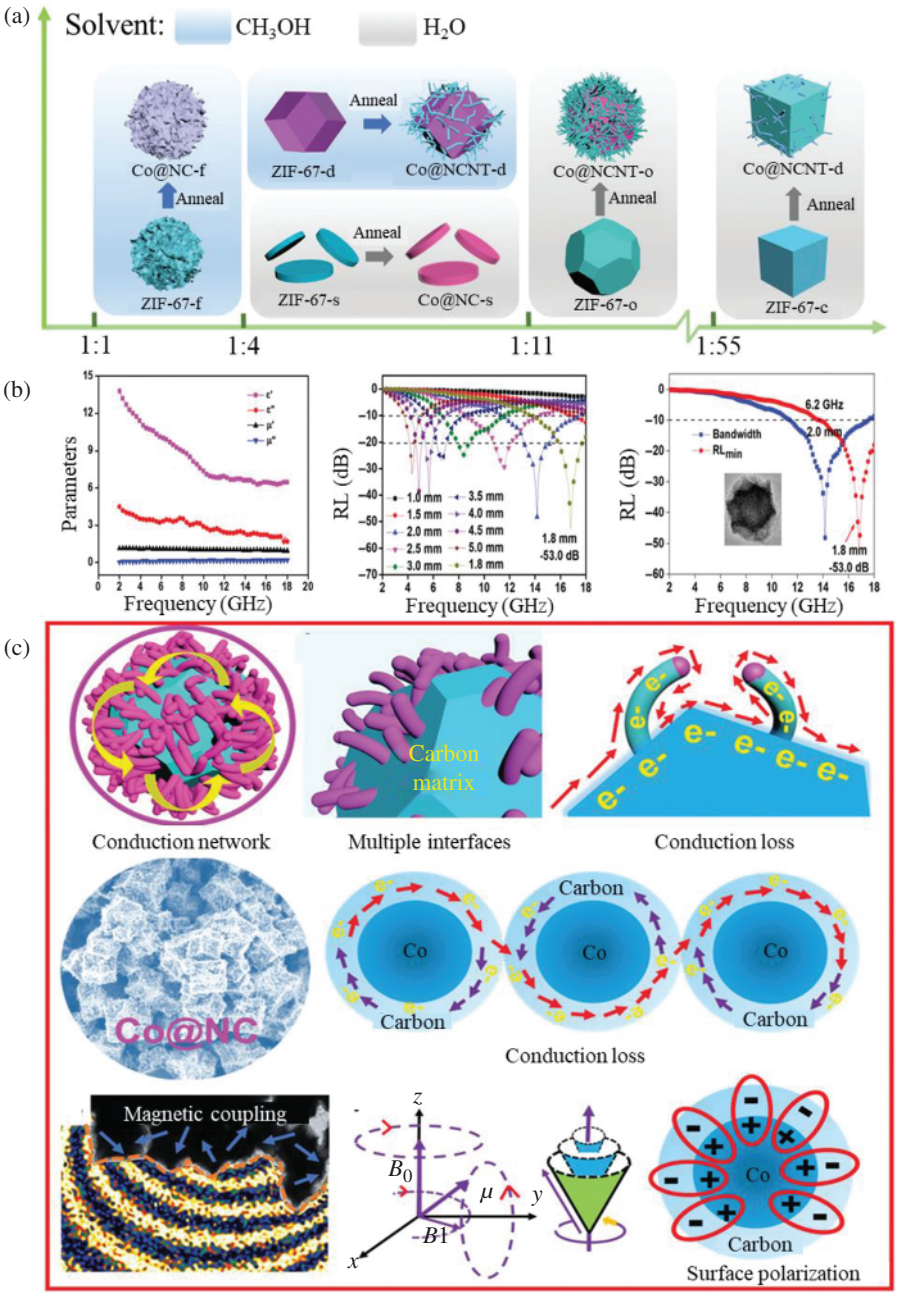

Figure 1.8 (a) Schematic preparation process of Co@NC composites. (b) Frequency dependencies of electromagnetic parameters, calculated reflection loss curves, maximum microwave RL curves, and EAB of Co@NC composites. (c) Schematic illustration of the EMW absorption mechanism. Source: Huang et al. [63]/with permission of John Wiley & Sons.

properties of polymetallic MOFs with different morphologies in the metal centers with different electronic configurations. Their electromagnetic parameters can be easily optimized by reasonable control of temperature. In recent research, the studies of multi-metal MOF-derived absorption materials focused primarily on the bimetallic MOF-derived and tri-metal MOF-derived materials.

Ouyang et al. [64] prepared hollow trimetallic spherical FeCoNi@C EMW-absorbing materials using high-temperature carbonization with FeCoNi-based MOF-74 (FeCoNi-MOF) as the precursor. The FeCoNi-MOF-74, treated by annealing at 700 °C, exhibits excellent EMW-absorbing ability, and the maximum effective absorbing bandwidth of 8.08 GHz (9.92–18 GHz) is obtained at a material thickness of 2.47 mm. The composites of FeCoNi ternary alloy and carbon matrix polymorphs are not only equipped with the magnetic loss brought by magnetic metals but also made the interfacial polarization and dipole polarization of the material increase, which greatly enhances the dielectric loss capability and impedance matching characteristics of the material. In addition, the electronic leaps generated in the alternating electromagnetic field between the conductive FeCoNi NPs and the amorphous carbon will jointly form a highly conductive network, thus enhancing the conductive loss.

Kong and coworkers [65] successfully prepared hollow-cage or solid-box magnetic/dielectric Fe/C/C and dielectric Fe/Mn/C EMW-absorbing nanomaterials by pyrolyzing Prussian blue analogs with controllable topology and phase composition (as shown in Figure 1.9a). The solid box–shaped Fe/Co/C and hollow cage–shaped Fe/Mn/C have a wide effective absorption bandwidth and a minimum reflection loss of −54.6 dB. The solid box–shaped Fe/Co/C nano-compound prepared at 900 °C exhibits an effective absorption bandwidth of 8.8 GHz at a thickness of 2.5 mm (as shown in Figure 1.9b).

Hu and coworkers [66] synthesized tunable Co NPs embedded in porous nitrogen-doped carbon (Co/NC) nanorods by direct, thermal cleavage of a bimetallic organic framework (CoZn-ZIF) precursor. By adjusting the ratio of Co^{2+} in the MOF precursor, the content and distribution of the Co NPs in the composite absorber change accordingly (as shown in Figure 1.10a). When the molar ratio of Co^{2+} to Zn^{2+} was 3:1, the carbonized composite had the largest external surface area and the best EMW absorption performance. When the filler mass loading is only 15 wt%, the minimum reflection loss reaches −52.3 dB at 10.1 GHz for a thin layer thickness of 2.5 mm. The maximum effective absorption bandwidth is 5.0 GHz for a 2.0 mm thick sample (as shown in Figure 1.10b). Enhanced conductive and magnetic losses, abundant interfacial polarization, dipole polarization, defect-induced dipole polarization, layered pore structure, and geometrical effects result in better impedance matching and enhanced EMW attenuation of Co/NC absorbing materials (as shown in Figure 1.10c).

1.3.3 MOF-Carbon Composite Absorption Materials

Most of the monometallic/multi-metal MOF-derived EMW-absorbing materials are made through high-temperature carbonization of the MOF precursor. The processed MOF can form a composite material of metal or metal oxide and carbon, which has excellent dielectric and magnetic losses. However, its inherent disadvantage is the lack of a good conductive network, which also restricts the ion transmission rate and prevents the further enhancement of the wave-absorbing properties. Carbon-based materials themselves have a good attenuation ability for EMWs and lower density, which possesses strong stability. The composite with MOF is expected to address the lack of a conductive network [67]. Common carbon

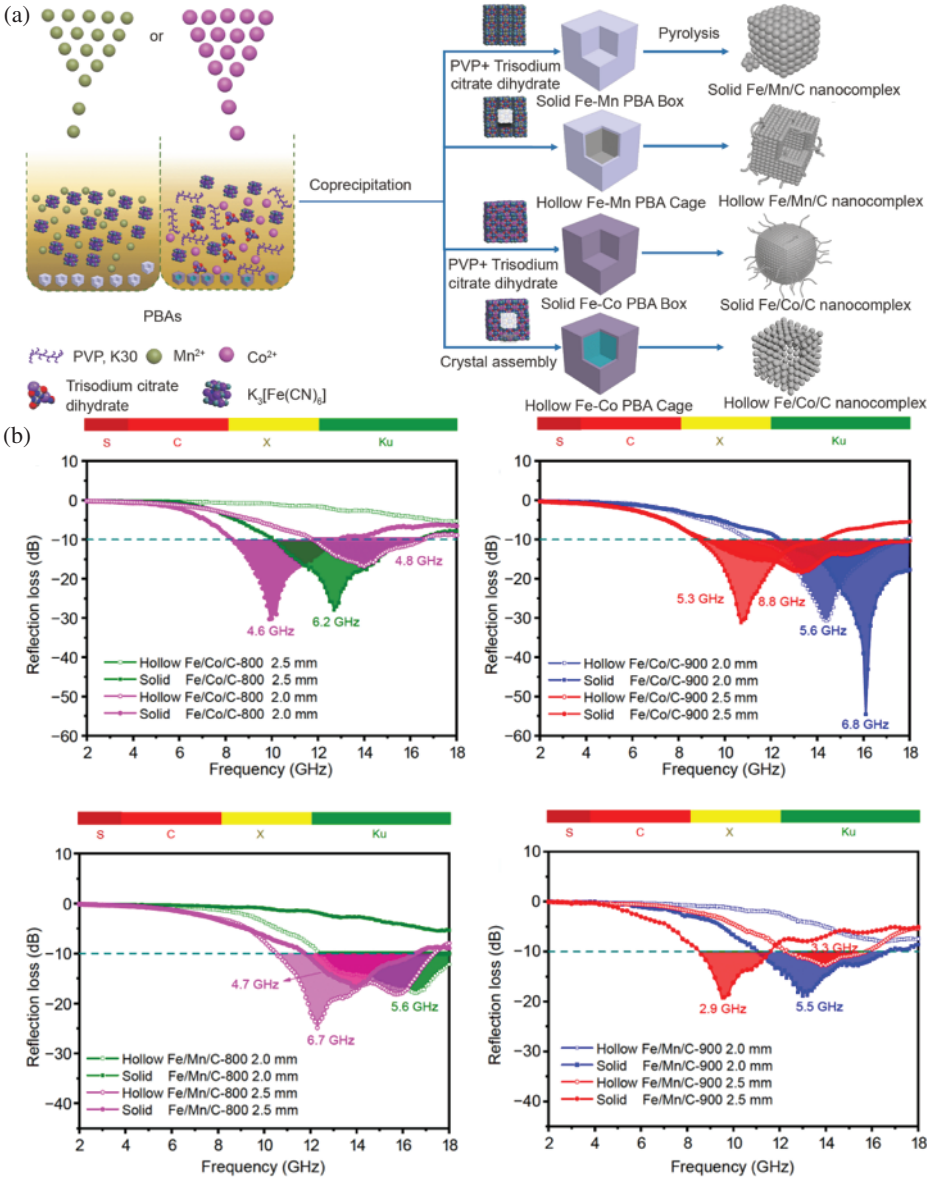

Figure 1.9 (a) Schematic illustration of the fabrication route toward hollow Prussian blue analogs (PBA) cages and solid PBA boxes and their derived nanocomplexes. (b) The comparison of electromagnetic wave absorption performance for pyrolyzed Fe/Co/C and Fe/Mn/C nanocomplexes. Source: Miao et al. [65]/with permission of Springer Nature.

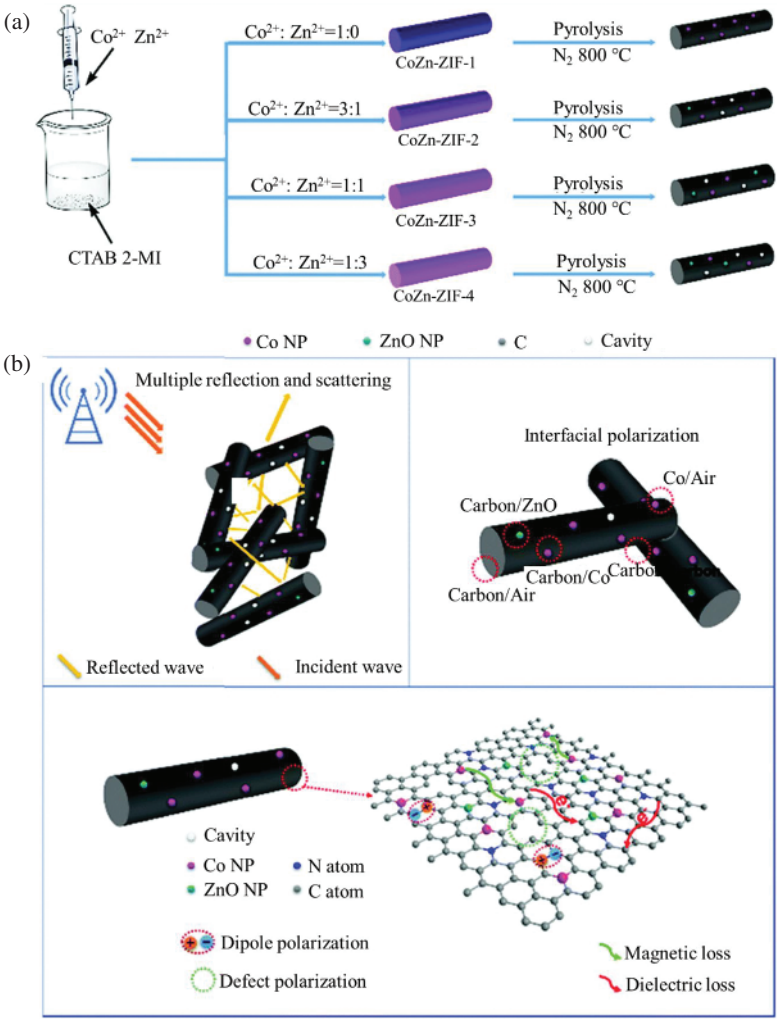

Figure 1.10 (a) Schematic illustration of the synthesis process of Co/NC nanorods. (b) Calculated RL curves and 3D reflection loss map presentations of Co/NC-1, Co/NC-2, Co/NC-3, and Co/NC-4 nanorods, respectively. (c) Schematic diagram of microwave attenuation in the Co/NC composites.
Source: Pan et al. [66]/with permission of Royal Society of Chemistry.

materials include carbon black [68], carbon fiber [69], CNTs [70], and graphene [71], and their derivatives. The introduction of carbon materials is not only conducive to the construction of a wide range of conductive networks to improve charge transport efficiency, but also the structural defects and non-uniform interfaces of carbon materials in MOFs can enhance dielectric loss, which can effectively improve the overall wave absorption performance of the materials. Carbon nanotubes are characterized by a large range of π-bonds formed by the P electrons on the carbon atoms, which give them special electrical properties due to the remarkable properties of conjugation effects. Carbon nanotubes have a

one-dimensional hollow tubular structure, the wall of which is surrounded by a single layer or multiple layers of graphene sheets, and their properties change depending on the way the graphene sheets are curled, reflecting metallic or semiconducting properties. Their electrical conductivity has a close relationship with their diameters and chirality, which reflect highly tunable properties. Therefore, they are widely used in EMW-absorbing materials. In recent years, a large amount of the MOF-CNT absorption materials has been successfully prepared.

Gu and coworkers [72] successfully prepared three-dimensional hybrid nanostructures (CNT/FeCoNi@C) consisting of MOF-derived magnetic nanospheres and Fe-filled CNT sponges. The minimum reflection loss and effective absorption bandwidth of the prepared CNT/FeCoNi@C sponges reached −51.7 dB and 6.0 GHz, respectively, which is better than most reported MOF-based EMW-absorbing materials. One-dimensional CNTs have excellent conductive channels to dissipate current, resulting in large conductive losses. CNTs, FeCoNi, and carbon can construct a large number of heterogeneous interfaces with each other, resulting in interface polarization loss. At the same time, there are a large number of defects in the FeCoNi@C multiphase alloy formed after carbonization, which can form abundant defect-induced dipole polarization, resulting in polarization relaxation loss. In addition, the porous cavities of CNT sponges and FeCoNi@C microspheres can enhance the scattering ability of the materials against EMWs and optimize the impedance-matching characteristics.

Carbon fiber, with its more than 90% carbon content and high-strength fiber characteristics, makes it an excellent material for manufacturing aerospace and other equipment. It has the characteristics such as low specific gravity, high strength, stable physical and chemical properties, excellent electrical conductivity, excellent elastic modulus, and a thermal expansion coefficient close to zero or even negative. Therefore, it is widely used in strategies such as mechanical strength enhancement and electrical conductivity optimization of materials.

Liu and coworkers [73] successfully synthesized a layered composite hollow carbon fiber@nitrogen-doped carbon/Co (HCF@NC/Co) by in situ growing two-dimensional Co metal–organic skeleton (ZIF-67) NSs on the surface of hollow luffa fiber (HLF) and calcination at a high temperature. The aggregation of carbonized MOFs is effectively avoided, and a uniform hierarchical one-dimensional structure is constructed. When the mass ratio of HCF@NC/Co to paraffin wax is 14 wt% and the material thickness is 2.25 mm, the minimum reflection loss of HCF@NC/Co is −50.14 dB, and the maximum effective absorption bandwidth reaches 7.36 GHz. The electrons excited by alternating electromagnetic fields migrate and jump in the one-dimensional conductive network constructed by HCF@NC/Co, converting electromagnetic energy into heat energy and causing conduction loss. Secondly, a large number of heterogeneous interfaces can induce strong interfacial polarization and improve dielectric loss capacity. The doped N and Co particles in graphitic carbon and the defect sites in the lattice also lead to a large number of dipole polarization losses. The magnetic Co particles also provide magnetic loss through eddy current loss, exchange resonance, and natural resonance.

Hu and coworkers [74] prepared a series of NiCo@nanoporous carbon@carbon fiber nanocomposites (NiCo@NPC@CF) consisting of micro- and nanoscale porous carbon structures and flower-like NiCo@C particles using Ni/Co-MOF particles and biomass cotton as precursors (as shown in Figure 1.11a). The hierarchically structured NiCo@NPC@CF at 3.5 mm thickness possesses a minimum reflection loss of −46.5 dB and an effective absorption bandwidth of 10.0 GHz (as shown in Figure 1.11b). The three-dimensional carbon fiber

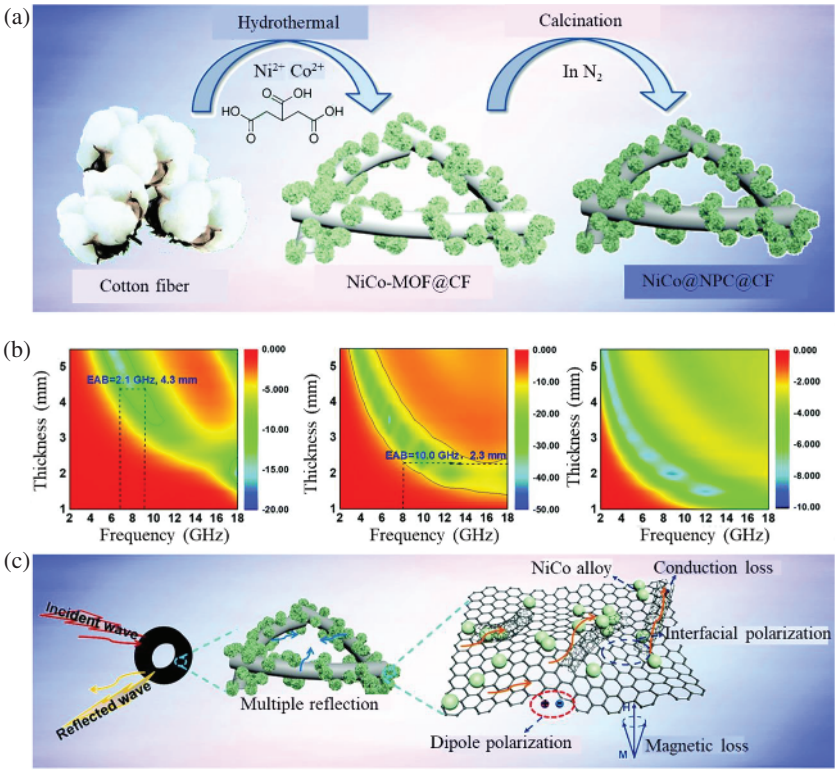

Figure 1.11 (a) Schematic of the synthetic procedure for NiCo@NPC@CF composites. (b) The corresponding 2D curves of NiCo@NPC@CF. (c) Microwave absorption mechanisms of the NiCo@NPC@CF composite. Source: Jin et al. [74]/with permission of Royal Society of Chemistry.

interconnecting network derived from biomass cotton can increase the electrical conductivity and thus enhance the conductive loss. Multiple interfaces between NiCo alloys, CNTs, and carbon fibers are conducive to enhancing the interfacial polarization effect and the loss capability. In addition, the magnetic NiCo alloy can further enhance the electromagnetic loss capability of NiCo@NPC@CF through natural resonance and exchange resonance (as shown in Figure 1.11c).

Graphene, as a two-dimensional atomic crystal, has excellent mechanical stiffness, strength, and elasticity, as well as very high electrical and thermal conductivity, which suggests that graphene can replace other materials in existing applications. Many properties of graphene exceed those obtained in any other material, and its electron migration rate, Young's modulus, and thermal conductivity all reach the limits predicted by theory. Moreover, due to its easy chemical functionalization, it has been widely modified and applied in various fields. In recent years, many graphene composites have been frequently applied to EMW absorption.

Zhao and coworkers [75] successfully synthesized Fe–Co/N-doped carbon/reduced graphene oxide (Fe–Co/NC/rGO) composites with a layered porous structure by in situ growth of Fe–Co organic framework on porous cocoon-like rGO sheets and then calcination at high temperature (as shown in Figure 1.12a). When the sample thickness was 2.5 mm, the

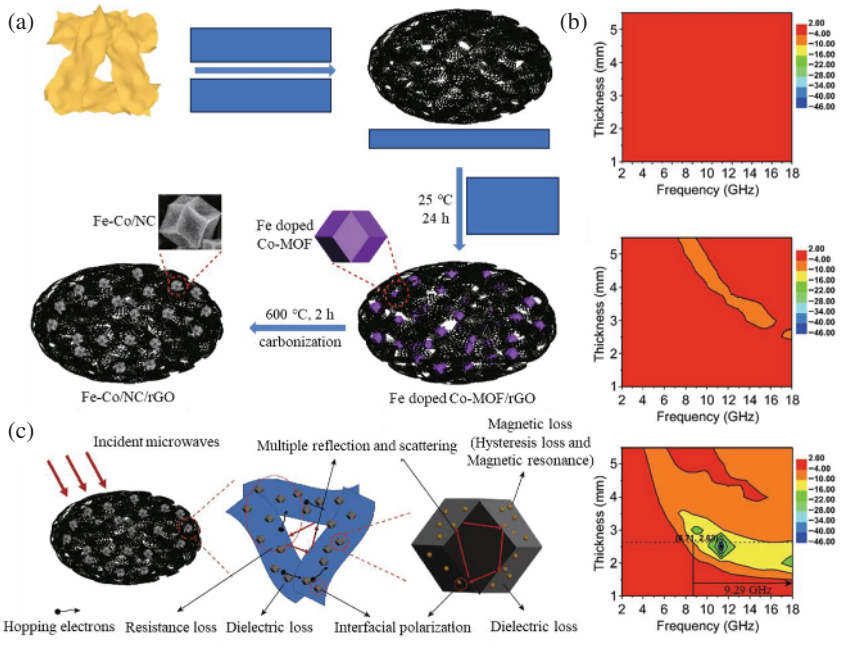

Figure 1.12 (a) Schematic drawings illustrating the fabrication process of hierarchically porous Fe–Co/NC/rGO. (b) Calculated 2D reflection loss of Co/NC, Fe–Co/NC, and Fe–Co/NC/rGO with a mass filling ratio of 25 wt%. (c) Schematic diagram of the microwave absorption mechanism of Fe–Co/NC/rGO. Source: Wang et al. [75]/Springer Nature/CC BY 4.0.

effective absorption bandwidth is as high as 9.12 GHz (8.88–18.0 GHz), and the minimum reflection loss value reaches −48.26 dB at 11.28 GHz (as shown in Figure 1.12b). The magnetic hysteresis loss and magnetic resonance of Fe and Co magnetic metals are the causes of the magnetic loss of composite materials. FeCo alloy embedded in N-doped C can form many interfaces, which greatly enhance the interfacial polarization of the material. After the carbonization of FeCo-MOF, N doping introduces a large number of defect sites into the C lattice and the rGO, thereby enhancing defect-induced dipole polarization. In addition, the conductive network formed by overlapping graphene oxide (GO) sheets can further enhance the conductivity loss (as shown in Figure 1.12c).

Che and coworkers [76] successfully synthesized accordion-like CeO_{2-x}/reduced graphene oxide (CeO_{2-x}/rGO) hybrid materials by converting Ce-MOF into NPs and combining with GO, inducing two-dimensional GO assembly into three-dimensional accordion-like composite materials (as shown in Figure 1.13a). The prepared lightweight, 3D layered CeO_{2-x}/RGO composite has excellent EMW absorption ability; its effective absorption bandwidth reaches 5.84 GHz, and the minimum reflection loss reaches −50.6 dB (as shown in Figure 1.13b). The charge accumulation at the interface caused by the inherent conductivity difference between CeO_{2-x}, NPs, and RGO enhances the interface polarization effect of the material. The residual oxygen functional groups and structural defects in RGO produce abundant polarization sites, which further enhance the dipole polarization. In addition, the highly conductive GO promotes the conductivity loss within the GO sheet (as shown in Figure 1.13c).

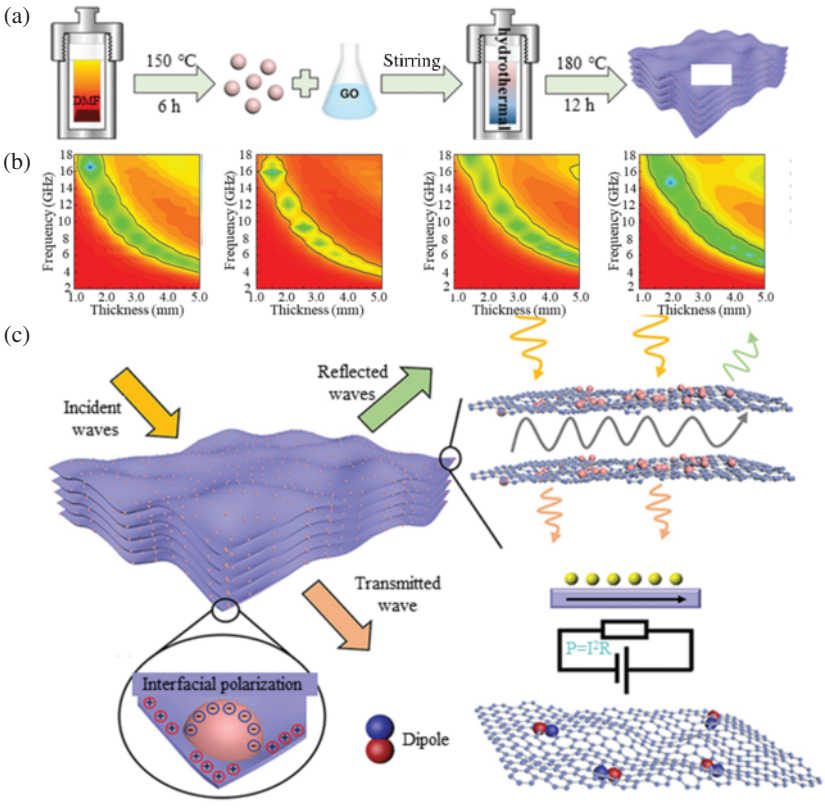

Figure 1.13 (a) Preparation scheme of the accordion-like CeO_{2-x}/RGO composite. (b) Contour map of absolute values of the accordion-like CeO_{2-x}/RGO composite. (c) The schematic of microwave mechanisms of accordion-like CeO_{2-x}/RGO absorbers. Source: Li et al. [76]/with permission of John Wiley & Sons.

1.3.4 MOF-MXene Composite Absorption Materials

Among two-dimensional nanomaterials, transition metal carbides, nitrides, or carbon-nitrides (MXenes) have demonstrated excellent performance in a wide range of applications spanning energy storage, sensing, optoelectronics, catalysis, and biomedicine due to their unique metal conductivity, solution processability, high mechanical properties, and broadly tunable properties. In recent years, MXene and its derivative materials have been widely used for EMW absorption.

Zhang and coworkers [77] constructed an interwoven one-dimensional heterostructure using the assembly of MXene and MOF and controlled the growth of CNTs by adjusting the load of CoNi-MOF on MXene, thus achieving the regulation of electromagnetic parameters. When the matching thickness of the prepared sample is 1.6 mm, the minimum reflection loss of the absorber reaches −51.6 dB, and the effective absorption bandwidth covers 4.5 GHz (13.2–17.7 GHz). The synergistic effect of the double one-dimensional heterostructure and the construction of the three-dimensional conductive network give excellent impedance match characteristics and conductance loss capability. A large number of one-dimensional

heterostructural heterogeneous interfaces between CoNi alloy, CNTs, MXene, and TiO_2 greatly improved the interfacial polarization effect. Defects introduced after carbonization and dipole polarization induced by CoNi NPs further enhance the dielectric loss capacity of the material. In addition, the natural resonance and eddy current loss of CoNi alloy can further increase the magnetic loss capacity of the material.

Lu and coworkers [78] designed and successfully prepared a novel sandwich-like two-dimensional layered Fe&TiO_2 nanoparticles@C nanocomposite based on MXene-MOF hybrid (as shown in Figure 1.14a). The composite obtained a wide effective absorption bandwidth of 6.5 GHz at a thickness of only 1.6 mm and a minimum reflection loss of −51.8 dB at 6.6 GHz (as shown in Figure 1.14b). The conductive network composed of conductive carbon sheets formed by MXene can enhance the conductivity loss ability of the material.

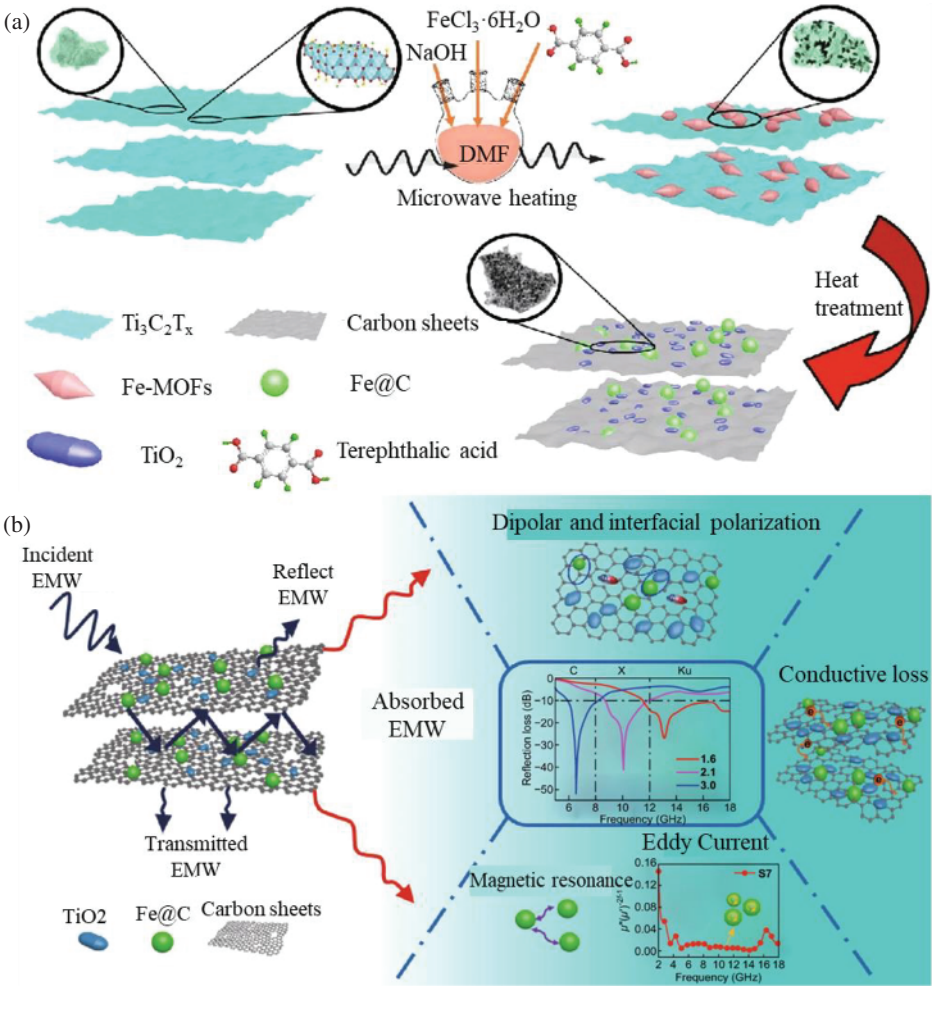

Figure 1.14 (a) Schematic representation of the facile synthesis route of the Fe&TiO_2@C by the heating reaction followed by heat treatment. (b) Illustration of electromagnetic microwave absorption mechanisms for Fe&TiO_2@C nanocomposites. Source: Deng et al. [78]/Springer Nature/CC BY 4.0.

The dipoles in Fe, TiO_2, and carbon can provide a large amount of dipole polarization loss. In addition, the dielectric loss generated by the capacitance-like interface between them will make a significant contribution to the conversion of EM energy into heat. Moreover, Fe, TiO_2 NPs, and carbon sheets with different electrical conductivity can form a capacitance-like effect, which can cause the accumulation and rearrangement of space charges, resulting in a large amount of interface polarization.

1.3.5 MOF-Conductive Polymer Composite Absorption Materials

Conductive polymers are also often combined with MOFs as excellent absorbing materials due to their high dielectric properties, low density, flexibility, corrosion resistance, low cost, and tunable absorption frequency properties [79, 80]. Commonly used conductive polymers are polyaniline (PANI) [81] and polypyrrole (PPy) [82]. When a conductive polymer with adjustable conductivity is combined with the MOF, the electromagnetic parameters of the material can be adjusted so that the absorbent can move toward a lower filling rate and a thinner thickness, while still ensuring a good effective absorption bandwidth.

Ma and coworkers [83] successfully prepared CoZn/C@MoS_2@PPy composite by applying the MOF self-template method and coating polypyridine on the surface of CoZn/C@MoS_2 through chemical polymerization. When the thickness of the prepared CoZn/C@MoS_2@PPy composite is 2.0 mm, the effective absorption bandwidth reaches 4.56 GHz, and the minimum reflection loss is −49.18 dB. The introduction of Zn and Co particles into the carbon matrix, as well as MoS_2 and PPy, provides rich interfacial polarization. The presence of a large number of metal particles in the carbon matrix can cause dipole polarization, which leads to the enhancement of dielectric loss. Graphitized carbon substrates and highly conductive PPy provide greater conductive losses. In addition, the exchange resonance induced by magnetic metal Co and Zn particles and the natural ferromagnetic resonance enhance the magnetic loss ability of the material. Ye and coworkers [84] synthesized $LaCrO_3$/PANI and $LaCrO_3$/PPy composites by in situ chemical oxidation polymerization. The introduction of a conductive polymer (PANI or PPy) significantly improved the EMW absorption properties of the composite compared to pure $LaCrO_3$ (as shown in Figure 1.15a). The optimal $LaCrO_3$/PANI sample achieved an effective absorption bandwidth of 5.8 GHz, covering almost the entire Ku band with a thickness of only 2.5 mm. The optimal $LaCrO_3$/PPy sample showed a minimum RL of −45 dB and a matching thickness of only 3 mm (as shown in Figure 1.15b).

1.4 Summarize and Prospect

MOF is considered as one of the most promising precursors of high-performance EMW absorption materials due to its flexible topological structure, various preparation processes, low cost, high thermal stability, large specific surface area, and high porosity. When MOF is directly used as a template or precursor, due to the inherent characteristics of MOF, most of the composite carbon materials obtained after carbonization show a microporous structure. In addition, the high-temperature calcination process may also cause part of the structure to collapse, which is not conducive to the transport and transfer of electrons/ions. It is a common way to improve the dielectric properties of MOF by constructing or combining a conductive network with high conductivity efficiency. Furthermore, the structure of MOF

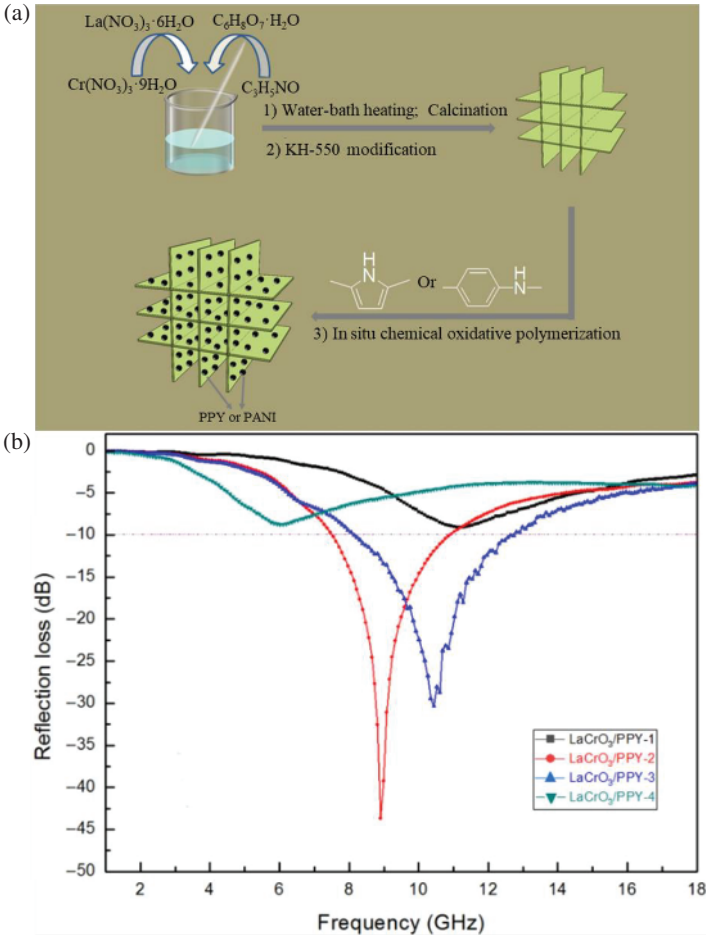

Figure 1.15 (a) Schematic representation of the facile synthesis route of the $LaCrO_3$/PANI and $LaCrO_3$/PPy composites. (b) Frequency dependence of RL values at different thicknesses for $LaCrO_3$/PANI and $LaCrO_3$/PPy composites. Source: Yu et al. [84]/Springer Nature.

derivatives also affects their electromagnetic response characteristics, and the different topological structures of MOF have significant effects on the dielectric and magnetic properties of materials. The regulation of structures and the design and construction of new structures show great potential in the development of new MOF-derived wave-absorbing materials. Defect engineering and interface engineering also improve the polarization loss (interface polarization and dipole polarization) ability of MOF-derived materials, but the quantitative estimation of the influence of various mechanisms still lacks sufficient theoretical support, so both classification and quantification need to be further explored. Hybrid engineering is a very promising research direction because it can create many active sites that promote the absorption of EMWs. However, at present, many researchers pursue the reflection loss value and effective absorption bandwidth of absorbing materials too much, which makes the development of MOF-derived absorbing materials seriously disconnected from practical

applications. Most of the current MOF-derived materials exist in powder form. To cope with the development trend of lightweight, miniaturization, and integration in the current electronic information technology and communication industry and to realize the timely absorption of materials, it is inevitable to prepare MOF-derived absorbing materials with high mechanical properties such as films, fabrics, fibers, gels, and foams. In addition, to adapt to diverse and demanding practical application scenarios such as high altitude or deep sea, these materials should also have high durability, corrosion resistance, low density, sustainability, wear resistance, high- and low-temperature resistance, transparency, and other characteristics. Therefore, in this era of rapid development, the development of multifunctional intelligent devices based on MOF-derived MAMs will be a promising field. Over the past decade, MOF's novel conditioning technology has made encouraging progress in structural optimization and performance regulation of EMW absorption materials. Despite the promising prospects, it is clear that much work remains to be done. It is hoped that this chapter can promote the innovative development of MOF-derived EMW absorption materials and overcome the bottleneck of MOF design in the field of EMW absorption materials.

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