

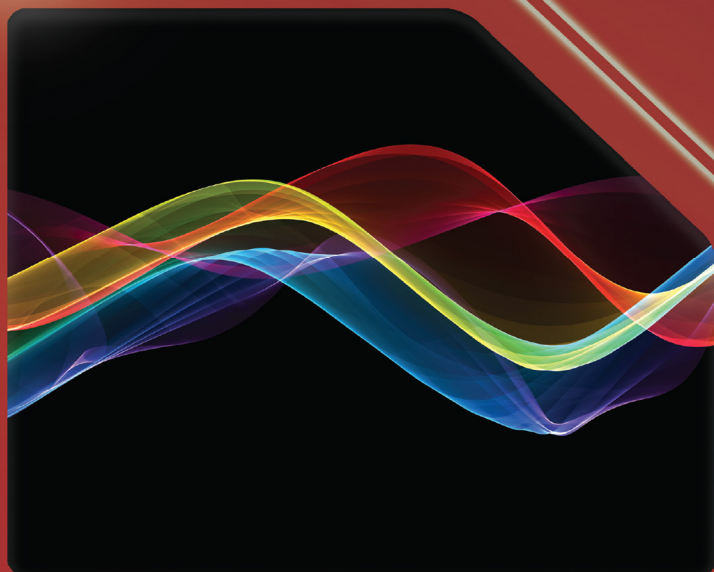
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Electromagnetic Wave Absorbing Materials

**Fundamentals and
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Electromagnetic Wave Absorbing Materials

Fundamentals and Applications

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Overview of the Work

Description

Electromagnetic Wave-Absorbing Materials: Fundamentals and Applications introduces the fundamentals and basic concepts of the mainstream electromagnetic wave absorption materials, including MOF-derived materials, MXene-derived materials, and high-entropy materials. It covers the design and preparation of these wave-absorbing materials, including their characterization, properties, manipulation, and related research. The book provides a comprehensive description of the various microscopic electromagnetic wave loss mechanisms (dielectric loss, magnetic loss) that are currently available, their causes of formation, and effects on the electromagnetic response properties of the materials. It also describes and summarizes the design, preparation, and application of the mainstream electromagnetic wave absorption devices, such as foam, gel, and film-based materials.

The book details the latest methods, technologies, and applications currently available in the field of electromagnetic wave absorption. It will support the studies of academic researchers and graduate students, as well as the many industrial research and development efforts of engineers and materials scientists. In addition, it will be of great value to those directly involved in industrial sectors related to electromagnetic wave absorption materials, as well as researchers in materials science, materials chemistry, nanomaterials, and other electromagnetic materials fields.

Key Features

Electromagnetic Wave-Absorbing Materials: Fundamentals and Applications mainly describes how to design and prepare high-performance electromagnetic wave absorption materials.

The book includes the synthesis of new wave absorption materials and the new technology of regulating the electromagnetic wave-absorbing properties of materials. The latest progress in the field of electromagnetic wave-absorbing materials is reviewed, which provides valuable insights for the future development direction of electromagnetic wave-absorbing materials.

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1

Metal–Organic Framework-Based Electromagnetic Wave Absorption Materials

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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 acetylacetonate (M(acac)) is employed as the metal salt, the resulting acetylacetonate 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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 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 ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$), 1,4-benzene dicarboxylic acid (BDC), DMF, methanol, sodium chloride ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$), 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-M-MOFs 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).

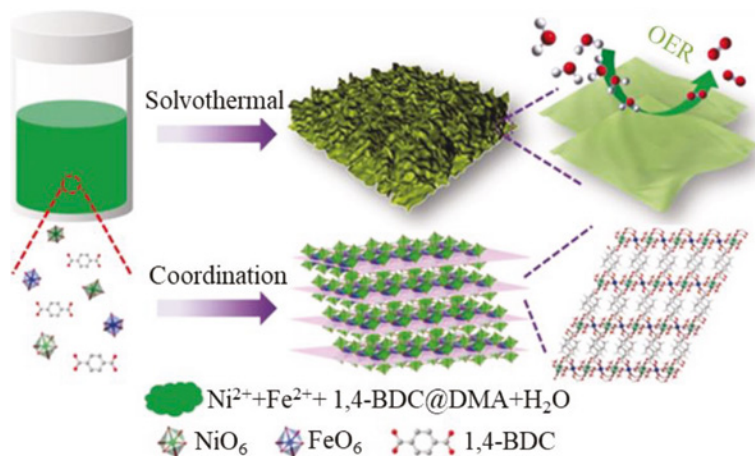


Figure 1.1 Synthetic procedure for the production of ultrathin metal–organic framework nanosheets and their utilization for the oxygen evolution reaction. Source: Li et al. [45]/with permission of John Wiley & Sons.

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 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, urea, DMF, terephthalic acid, and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, PTA, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 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.

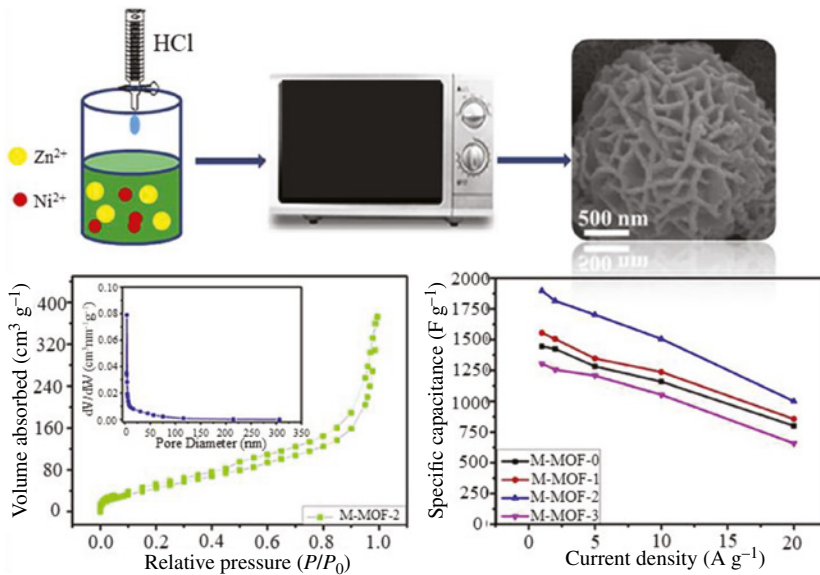


Figure 1.2 Schematic illustration of the overall formation process of the Zn-doped nickel-based metal-organic framework (Ni-MOF). Source: Chen et al. [48]/with permission of Elsevier.

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 $\text{Cu}_3(\text{HHTP})_2$ 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).

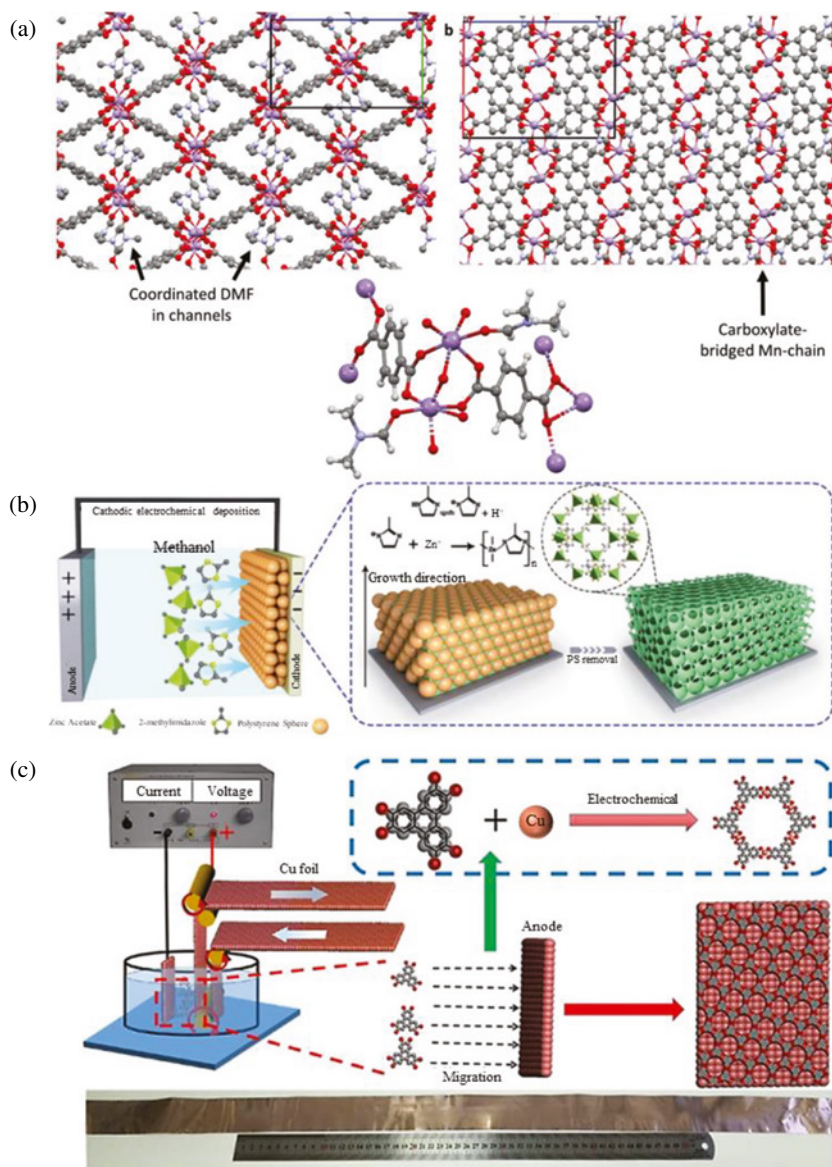


Figure 1.3 (a) Crystal structure of the Mn-MOF. Source: Asghar et al. [49]/Royal Society of Chemistry/CC BY 3.0. (b) Illustration of the fabrication process of a macro-microporous MOF inverse opal film deposited on a fluorine-doped tin oxide (FTO) substrate. Source: Qin et al. [50]/with permission of Royal Society of Chemistry. (c) Electrochemical reaction cell for the preparation of a $\text{Cu}_3(\text{HHTP})_2$ 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 $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ 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.

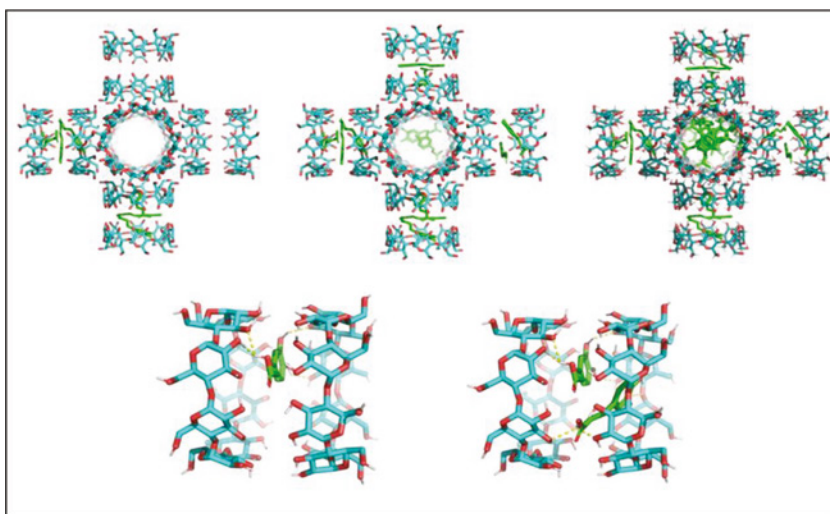


Figure 1.4 Molecular docking simulations of caffeic acid molecules distributed in CD-MOF. Source: Shen et al. [54]/with permission of Elsevier.

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 SF₆. 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.