



Review

Metal–Organic Framework-Based Composites for Dual Functionalities: Advances in Microwave Absorption and Flame Retardancy

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Abstract: With the rapid expansion of electronic information technology and rising material safety needs, the creation of composite materials that perform both electromagnetic microwave absorption (EMA) and flame retardancy has arisen as a materials science research hotspot. Metal–organic frameworks (MOFs) have great potential for developing novel multifunctional composite materials due to their unique structural characteristics and customizable functions. This work presents a comprehensive assessment of the most recent research findings on MOF-based EMA-flame retardant dual-functional composites. The fundamental mechanisms of EMA and flame retardancy are covered, including dielectric loss, magnetic loss, and both condensed-phase and gas-phase flame retardancy mechanisms. The development of composites based on Fe-MOF, Co-MOF, Ni-MOF, and polymetallic MOF in terms of EMA and flame retardancy is highlighted. These materials offer exceptional EMA performance and strong flame retardancy effects thanks to their unique structural designs and component regulations. In addition, some materials have great infrared stealth, thermal insulation, hydrophobic, and mechanical qualities. Ultimately, the problems of MOF-based dual-functional composites and their development possibilities are reviewed, giving valuable references for the development of new multifunctional composite materials.



Academic Editor: Soon Hyung Hong

Received: 25 January 2025

Revised: 23 February 2025

Accepted: 3 March 2025

Published: 6 March 2025

Citation: Hu, J.; Jiang, J.; Li, Q.; Cao, J.; Sun, X.; Huo, S.; Pan, Y.-T.; Ma, M. Metal–Organic Framework-Based Composites for Dual Functionalities: Advances in Microwave Absorption and Flame Retardancy. *J. Compos. Sci.* **2025**, *9*, 121. <https://doi.org/10.3390/jcs9030121>

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Keywords: metal–organic framework; microwave absorption; flame retardant; composite

1. Introduction

Electromagnetic microwave pollution and fire safety concerns have gotten worse due to the quick development of electronic information technology, which poses serious risks to public safety and human health [1–3]. On the one hand, electromagnetic radiation can interfere with the normal operation of precision electronic devices and may also pose potential health risks to the human body [4,5]; on the other hand, with the widespread use of new materials and chemicals, the frequency and severity of fire accidents are continuously rising [6,7]. Therefore, developing multifunctional composite materials with excellent electromagnetic microwave absorption (EMA) and flame retardancy properties

holds important practical significance and application value. Particularly in the military field, electromagnetic stealth and fireproof–explosion-proof performance are critical to the safety of equipment; in the civilian sector, electromagnetic protection and flame-retardant materials also have extensive application demands in areas such as electronic devices, building materials, and transportation [8–10].

A type of innovative porous crystalline material, metal–organic frameworks (MOFs) have a high specific surface area, variable pore size, rich functional groups, and outstanding physical–chemical stability, which makes them very applicable in a variety of disciplines [11–13]. MOFs use organic ligands to coordinate metal ions or clusters to create three-dimensional (3D) network architectures. By choosing various metal centers and organic ligands, they can flexibly modify their structure and functioning [14]. Research on MOF materials has steadily shifted in recent years from more conventional domains like gas adsorption, separation, and catalysis to newer application areas including EMA [15–17], flame retardancy [18–20], sensing [21], hybrid supercapacitors [22], and more. Specifically, metal/carbon composites made from MOFs that have been pyrolyzed not only have better conductivity and stability but also preserve the original porous structural characteristics, offering a valuable foundation for the creation of new functional materials [23].

In the EMA field, MOF-based materials can achieve synergistic effects of multiple loss mechanisms due to their unique porous structure and tunable chemical composition [24–26]. Studies have shown that the metal centers in MOF materials can provide magnetic loss, organic ligands and carbonized products can offer dielectric loss, and the porous structure can increase multiple reflections and scattering of electromagnetic microwaves, thereby enabling efficient EMA [27]. Xu et al. [15] constructed a 3D Co/N co-doped hybrid carbon network by pyrolyzing acid-treated bilayer bimetallic zeolitic imidazolate frameworks (ZIFs). The hybrid carbon network exhibited a minimum reflection loss ($RL_{\min}$) of -56.2 dB and an effective absorption bandwidth (EAB) of 5.2 GHz, with a thickness of only 1.8 mm. Zhang et al. [25] prepared a 3D sea cucumber-shaped nanomaterial by pyrolyzing bimetallic FeCo-MOF to self-grow carbon nanotubes (CNTs). When the thickness was 1.38 mm, $RL_{\min}$ was -59.21 dB and EAB was 3.22 GHz.

MOF materials provide special benefits in the area of flame retardancy. The MOFs' metal ions have the ability to encourage charring by creating a barrier that prevents heat and oxygen from passing through [28,29]. Furthermore, MOFs' porous structure can reduce the emission of harmful gasses by adsorbing and catalytically breaking down combustion products [30,31]. By grafting ferrocene aldehyde onto amino-modified ZIF-67, Cao et al. [32] created a novel design that produces a hierarchical nanoporous flame retardant with a yolk-shell structure. The synergistic effect of ferrocene and ZIF expedited the creation of a dense and strong carbon layer in epoxy resin (EP) during combustion, while its porous core structure facilitated the adsorption of hazardous and combustible components. The LOI and UL-94 of the EP composites reached 28.3% and V-0 rating, respectively. The peak heat release rate (pHRR) decreased by 56.5%, the peak smoke production rate (pSPR) by 55.1%, the total smoke production (TSP) by 44.6%, and the peak CO production rate (pCOP) by 71.6%.

However, most current research is still limited to the development of single functionalities, while multifunctionality is the key focus for the future development of materials. Figure 1 presents the recent research progress of MOF-based composite materials with EMA and flame-retardant functions, highlighting the rapid advancement in this field. It is foreseeable that the research on dual-functional MOF-based composites will receive increasing attention and reporting. Developing MOF-based multifunctional composites with excellent EMA and flame-retardant properties is not only of significant scientific importance to meet practical application needs but also provides a feasible technological path

to address pressing environmental and safety issues. The breakthrough research on these multifunctional materials holds strategic significance for advancing the field of materials science. This review systematically summarizes the latest developments in the relevant fields, offering valuable references and guidance for the design and application of future multifunctional MOF composites.

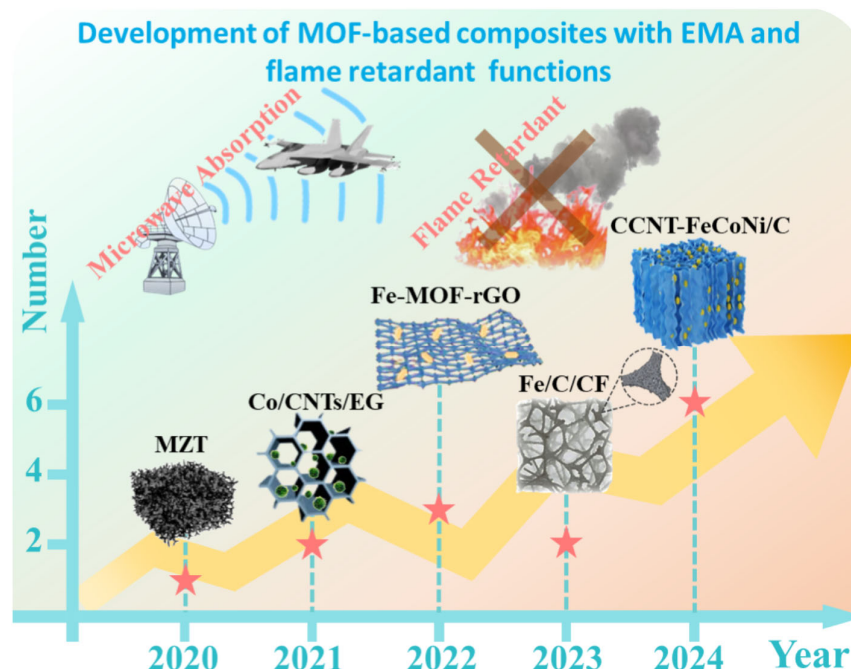


Figure 1. Development of MOF-based dual-functional composites with EMA and flame retardant in recent years (until January 2025).

2. The Mechanism of EMA and Flame Retardant

2.1. EMA

The EMA performance of materials is typically assessed by measuring their electromagnetic parameters, including the complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) and complex permeability ($\mu_r = \mu' - j\mu''$) [33–35]. These parameters reflect the material's dielectric loss and magnetic loss capabilities, which are key to understanding its EMA mechanisms. One of the most commonly used methods for measuring these electromagnetic parameters is the coaxial transmission line method, widely employed for its accuracy and reproducibility. The coaxial transmission line method involves using a vector network analyzer (VNA) to measure the scattering parameters (S-parameters) of samples. The materials under study are typically fabricated into toroidal samples and placed within a coaxial transmission line fixture. S-parameters (S11 and S21) are measured over a specific frequency range, and these values are used to calculate the material's ϵ_r and μ_r . Based on the measured S-parameters, analytical models such as the Nicholson–Ross–Weir (NRW) algorithm [36,37] can be used to extract the material's ϵ_r and μ_r . By analyzing these electromagnetic parameters, further calculations can be performed to determine the material's microwave reflection loss (RL), a key performance indicator of EMA. RL is typically calculated using the following equation [38–40]:

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r} \tanh[j(\frac{2\pi fd}{c}) \sqrt{\mu_r \epsilon_r}]} \quad (1)$$

$$RL = 20 \lg \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (2)$$

where Z_{in} and Z_0 are the material and air impedances, respectively; f is the microwave frequency; d is the absorber thickness; and c is the speed of light. The RL value is an important metric for evaluating the EMA performance of materials since it represents the degree of attenuation of the incident microwave on the material's surface and within. $RL < -10$ dB means 90% absorption efficiency. EAB refers to the frequency range when RL is less than -10 dB. Materials with a broad frequency absorption range are often more useful for practical applications [41]. Most research on EMA materials has focused on the 2–18 GHz range, which is particularly interesting because it aligns with the operational frequencies of many modern radar systems, satellite communications, and wireless networks [42]. Achieving high EMA performance within this range is critical for both civilian and military applications, including electromagnetic compatibility and stealth technology [43].

MOF-based composite materials have significant potential in EMA, owing to their distinctive porous structure and variable chemical composition. Controlling the synthesis conditions of MOFs allows for exact adjustment of their pore size distribution, specific surface area, and framework structure to fulfill the various demands of EMA [44]. MOFs' flexible binding sites on the surface enable hybridization with a variety of materials, resulting in synergistic effects of dielectric and magnetic loss that lead to wideband and efficient EMA performance. The main mechanisms of EMA are dielectric loss and magnetic loss [45,46]. The primary way energy is dissipated is through dielectric loss. The coordination bonds formed between metal elements and organic ligands in MOF materials will be polarized under the action of an alternating electric field. This polarization process consists of electronic polarization, ionic polarization, orientational polarization, and interfacial polarization. Interfacial polarization is especially critical in composite materials because the interfaces between MOFs and other components generate a significant amount of interfacial charge [47,48]. The reciprocating movement of these charges in the electric field causes enormous energy dissipation. It is worth mentioning that the migration of free carriers (such as electrons and holes) under an alternating electric field generates displacement currents and conduction currents, causing conductivity loss, and its loss efficiency is positively correlated with the electrical conductivity of the material [49]. Furthermore, the porosity of MOFs provides various reflection and scattering channels for microwave propagation, increasing absorption path length and energy dissipation. Magnetic loss is also an important mechanism for EMA, especially when magnetic metals (such as Fe, Co, Ni) or their oxides are integrated with MOFs [50,51]. An applied magnetic field causes the magnetic moments of the magnetic components to precess, dissipating microwave energy through natural resonance and exchange resonance during this process. Moreover, the movement of magnetic domain walls and hysteresis loss are also significant energy dissipation pathways. At the same time, the incorporation of magnetic components can match the impedance characteristics of the material with the wave impedance of free space, minimizing the surface reflection of microwaves and allowing more energy to enter the material and be absorbed [52,53].

MOF-based composites exhibit varying electromagnetic responses to electromagnetic waves of different frequencies (1–20 GHz). In the low-frequency range (1–2 GHz), due to the longer wavelength of microwaves, achieving high EMA performance is challenging and requires thicker or more complex material designs. Magnetic MOFs dominate energy dissipation through magnetic resonance effects, while moderate conductivity (such as MOF-derived carbon) aids in dielectric loss and suppresses surface reflection [54]. In this range, material thickness and the content of magnetic components are key design parameters. In the mid-frequency range (2–8 GHz), the synergy between dielectric loss and magnetic loss becomes the core. The hierarchical porosity and heterogeneous interfaces of MOFs enhance interfacial polarization, while the resonance frequencies of magnetic

components cover this frequency band. Optimization of the conductive network (e.g., CNT/MOF composites) can further improve broadband EMA performance [55]. In the high-frequency range (8–20 GHz), dielectric loss (especially interfacial polarization and relaxation effects) dominates. The high specific surface area and nanoscale channels of MOFs provide abundant polarization sites, while the incorporation of conductive fillers (e.g., graphene, MXene) enhances high-frequency EMA through conductive loss and multiple scattering [56].

2.2. Flame Retardant

A variety of testing techniques must be used in order to assess the performance of flame-retardant materials. The UL-94 vertical burning test, the limiting oxygen index (LOI), the cone calorimeter test (CCT), and infrared thermal imaging analysis are examples of common characterization techniques [57]. One important test technique for describing a material's flame-retardant qualities is CCT. It measures a number of crucial factors, such as heat release rate (HRR), total heat release (THR), TSP, and CO production rate (COP), and it models how materials would burn in a fire. These metrics fully reflect the flame-retardant capabilities of the material. A key measure of a material's flame-retardant properties, LOI testing determines the minimum oxygen concentration required to sustain burning. The ability of a material to sustain combustion generally declines as the LOI value rises. Examining a material's ability to extinguish itself and the behavior of molten droplets requires the use of the UL-94 test. With V-0 being the highest, the material is assessed based on its self-extinguishing qualities and droplet features during combustion (e.g., V-0, V-1, V-2). The temperature distribution on the material's surface during combustion can also be tracked in real time using infrared thermal imaging technology, which is crucial for assessing the material's thermal insulation qualities and flame spread behavior. Superior thermal insulation allows for infrared stealth capabilities, which are especially crucial in military and aerospace applications, in addition to efficiently preventing heat transfer.

Because of their exceptional thermal stability, distinctive decomposition behavior, and capacity to adsorb and catalytically degrade combustion products, MOF-based composite materials have clear advantages in the field of flame retardancy [58]. Condensed-phase and gas-phase flame retardancy are the two primary fundamental mechanisms for flame retardancy [59,60]. At high temperatures in the condensed phase, the metal ions in the MOF molecule break down, carbonizing the matrix material and forming a thick protective layer that effectively prevents oxygen and heat transmission [61]. Furthermore, composite materials including MOFs can collect pyrolysis products such as hazardous CO and carbon soot particles, resulting in much lower smoke and harmful gas emissions during burning [62]. MOF-based materials emit non-toxic or low-toxic volatile compounds (such as water vapor and CO₂) during high-temperature decomposition, which contributes to gas-phase flame retardancy [63]. These gasses help reduce the amount of flammable gas in the combustion zone. Furthermore, active metal components (such as Fe, Co, Al, etc.) in some MOF composites can accelerate the production of hydroxyl or peroxy radicals, interrupting the free radical chain reactions of combustion [64,65]. Moreover, the thermal stability and flame-retardant qualities of MOFs can be improved by functional modification (for example, adding N, S, or P groups). Through cooperation with one-dimensional or two-dimensional (2D) materials (e.g., CNTs [66–68], layered double hydroxides [69–71], MXenes [72–74], etc.), MOF-based composites have been able to achieve notable increases in smoke suppression and flame retardancy.

3. EMA and Flame-Retardant Dual-Functional MOF Composites

3.1. Fe-MOF

In recent years, Fe-based MOFs have shown great potential in the fields of EMA and flame retardancy due to their tunable microstructures and excellent functional properties [75,76]. Li et al. [77] used a simple one-pot solvothermal synthesis approach to develop Fe-MOFs on the surface of in situ reduced graphene oxide (rGO), resulting in a unique Fe-MOF-rGO microwave absorber. When the Fe-MOF-rGO content reached 25 wt.% and the thickness was 2.0 mm, the $RL_{\min}$ reached -43.6 dB, and the EAB exceeded 5.0 GHz, meeting the high-efficiency, lightweight, and wide-bandwidth requirements. Furthermore, the addition of 10 wt.% Fe-MOF-rGO into EP resulted in 42.1%, 42.3%, and 17.7% reductions in heat release capacity (HRC), pHRR, and THR, demonstrating excellent flame retardancy.

The flexible coordination between phosphate groups and metals gives metal-based phosphates a variety of electronic structures and electronic conduction pathways, giving them distinct dielectric responses and impedance matching characteristics. Furthermore, metal-based phosphates demonstrate excellent high-temperature and fire-resistant performance [78,79]. Therefore, developing metal-based phosphate/doped heteroatom carbon composites has promise for producing highly efficient and controllable EMA and flame retardancy. Liu et al. [80] prepared fire-resistant Fe-based phosphate-/phosphorus-doped carbon composites by annealing phytic acid-treated MIL-101(Fe) as the precursor. By varying the amount of phytic acid during the preparation process, they were able to obtain the $Fe_2P_4O_{12}$ /phosphorus-doped carbon ($Fe_2P_4O_{12}$ /P-C) composite with the best EMA performance, achieving an EAB of 5.76 GHz ($d = 2.1$ mm) and an $RL_{\min}$ of -67.6 dB ($d = 2.0$ mm). Meanwhile, the $Fe_2P_4O_{12}$ /P-C composite showed good fire resistance. After 3 min of exposure to flame, composite sheets formed from the material retained their macroscopic shape.

MOF-derived materials for EMA composites have garnered extensive attention due to their unique structural design flexibility and excellent functional properties. Jiang et al. [81] created a MOF-derived Fe/C/carbon foam (Fe/C/CF) 3D magnetic composite EMA material by using carbon foam as a template and uniformly distributing Prussian blue nanocubes throughout the carbon foam skeleton (Figure 2a). The Fe/C/CF achieved a $RL_{\min}$ of -66.7 dB and the maximum EAB of 6.34 GHz, as shown in Figure 2b,c. Furthermore, the hybrid foam's surface temperature remained nearly unchanged when heated for more than 1 h at a constant 120 °C, demonstrating its excellent thermal insulation performance (Figure 2f). Additionally, since heat-emitting devices are easily detectable by infrared cameras, military equipment requires infrared stealth capability. As illustrated in Figure 2d, the hybrid foam is the same hue as the surroundings, suggesting that the heated hand's infrared stealth has been achieved. Similarly, the target of military equipment concealed with hybrid foam is undetectable to the thermal infrared camera (Figure 2e).

3.2. Co-MOF

ZIFs are a special family of crystalline materials that are a subclass of MOFs. A typical example of one of these is ZIF-67, which has imidazole as the bridging ligand and Co ions as the core metal. Because of its strong electrical conductivity and large number of surface active sites, ZIF-67 has attracted a lot of interest as a precursor for EMA, catalysis, and sensing applications [82–84].

Gu et al. [85] discovered that when melamine serves as the structural matrix, ZIF-67 particles can uniformly grow on the foam surface via hydroxyl radicals. After calcination, they obtained a 3D hybrid foam, MZT, with EMA functionality (Figure 3a). As shown in Figure 3b,c, the hybrid foam achieved a $RL_{\min}$ of -59.82 dB at a thickness of 2.3 mm and an EAB of 5.64 GHz at a relatively thin thickness of 2.1 mm. When the hybrid foam was placed

on a heating platform at 70 °C, the surface temperatures recorded over 5 to 30 min were 18.3, 18.5, 18.9, 19.4, 19.5, and 19.9 °C, respectively, demonstrating its excellent infrared stealth and thermal insulation properties (Figure 3d).

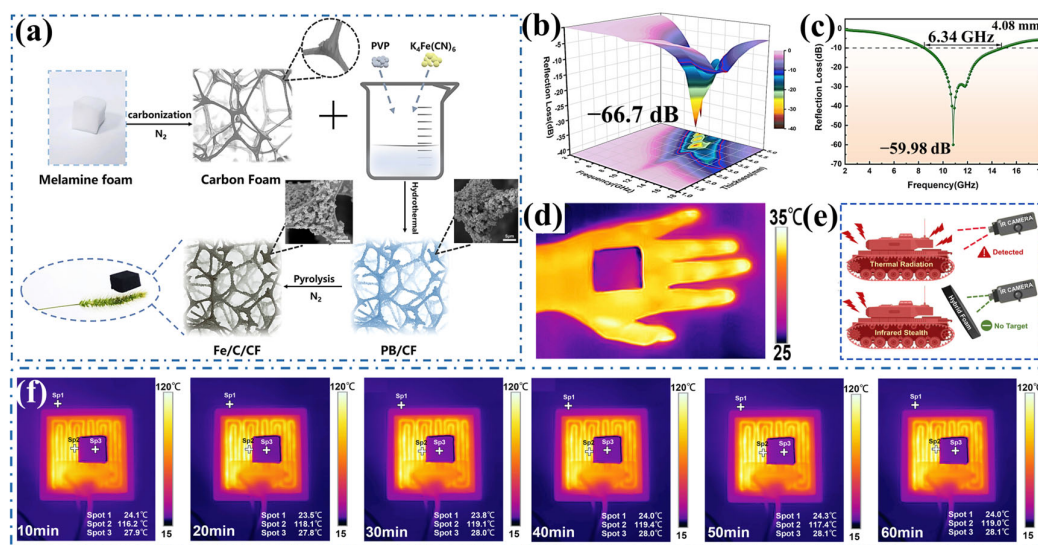


Figure 2. Fe/C/CF: (a) schematic diagram of synthesis process, (b) 3D RL diagram, (c) RL-f curve, (d) thermal infrared image of hand, (e) infrared stealth diagram, and (f) thermal infrared image at 120 °C (reprinted with permission from [81] © 2023 Elsevier).

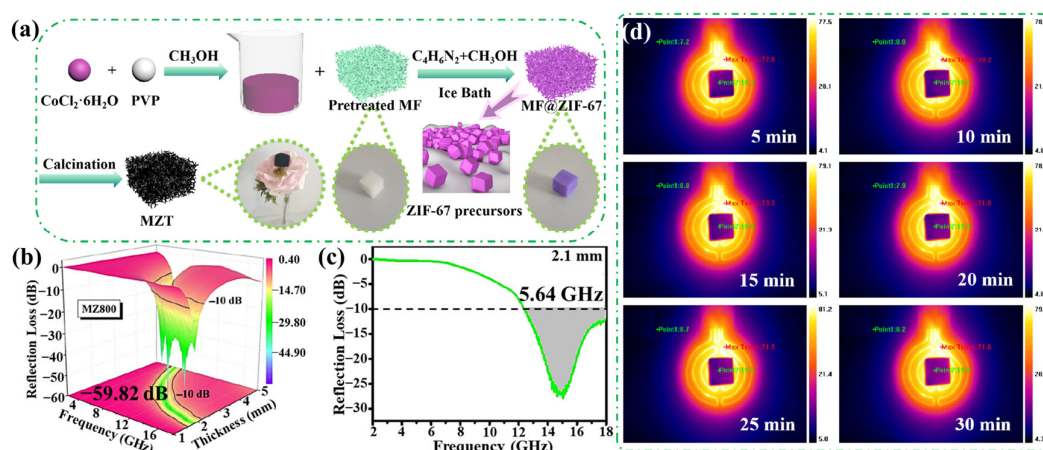


Figure 3. MZT hybrid foam: (a) schematic diagram of the synthesis process, (b) 3D RL diagram, (c) RL-f curve, (d) thermal infrared image at 70 °C (reprinted with permission from [85] © 2020 American Chemical Society).

Xiang et al. [86] designed a porous composite material consisting of Co-MOF-loaded CNTs and expanded graphite (Co/CNTs/EG) (Figure 4a). At an ultra-low filler loading of 3 wt.% and an ultra-thin thickness of 1.4 mm, the Co/CNTs/EG composite achieved a RL_{min} of -67.2 dB and an EAB of 5.1 GHz (Figure 4b,c). Figure 4(d₁,d₂) shows that when the composite was blended into the EP matrix and subjected to a 20 s alcohol lamp test (~ 500 °C), the pure EP was ignited, whereas the Co/CNTs/EG/EP sample held its shape and showed no apparent flames, smoke, or dripping. Figure 4(e₁–e₃) shows infrared thermal pictures of Co/CNTs/EG taken over a period of 3–9 min. These pictures demonstrate that the Co/CNTs/EG composite effectively isolates heat and blocks infrared radiation, showing its suitability for infrared stealth applications. Figure 4(e₄) compares the Co/CNTs/EG composite's infrared shielding efficacy to two other materials (commercial polyurethane foam (PU) and nickel foam (NF)), exhibiting that the Co/CNTs/EG composite

has considerably greater thermal insulation. This highlights its immense application potential in thermal insulation and infrared stealth technologies.

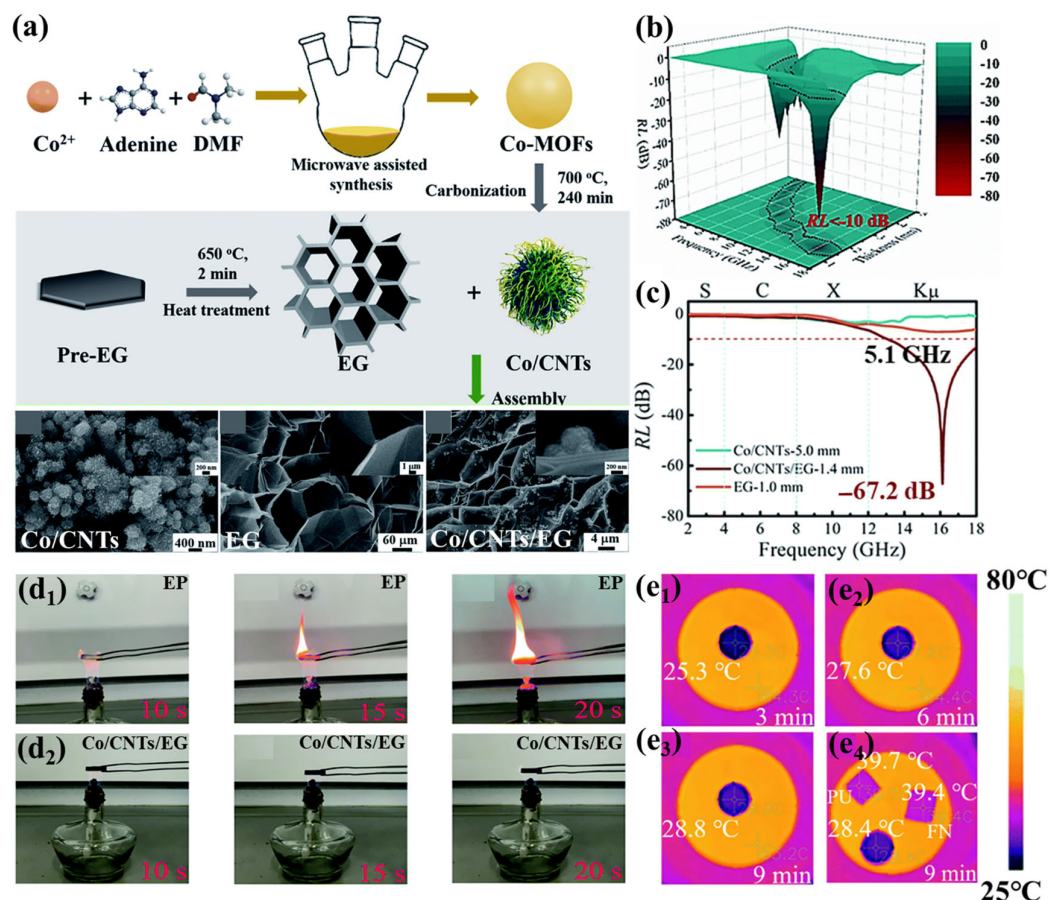


Figure 4. Co/CNTs/EG: (a) schematic diagram of the synthesis process, (b) 3D RL diagram, and (c) RL- f curve; EP (d₁) and Co/CNTs/EG/EP (d₂) alcohol lamp combustion test; (e₁–e₄) thermal infrared images at 63.5 °C (reprinted with permission from [86] © 2021 Royal Society of Chemistry).

3D printing technology has introduced new opportunities for the design and fabrication of multifunctional materials, enabling the creation of complex shapes with unprecedented possibilities. Li et al. [87] selected a polarity-induced rigid–flexible EP/multifluorination/siloxane network as a supporting material and prepared multidimensional nanofillers CoMXene (CoM) and CoNiCNT (CoNiC) through an in situ growth and pyrolysis process of ZIF-67. Stable CoM@CoNiC-F inks were created using C-F $\cdots\pi$ interactions. These inks were utilized to 3D print high-resolution and complex-shaped CoM@CoNiC-F nanocomposites via direct-ink-writing technology (Figure 5a). Additionally, the 3D-printed objects exhibited reliable photothermal-induced shape memory properties, facilitating the fabrication of 4D-printed structures with dynamic shape evolution behavior. The composites demonstrated excellent EMA performance, with a $RL_{\min}$ of -64.78 dB and an EAB of 4.6 GHz (Figure 5b). Simulated results using CST electromagnetic simulation software revealed that the radar cross-section (RCS) values of CoM@CoNiC-F were significantly lower than those of a perfect electric conductor (PEC) (see Figure 5c–e), consistent with the experimental results. The LOI value of CoM@CoNiC-F EP composites reached 30.8%, with a UL-94 rating of V-0. As shown in Figure 5g–j, compared with pure EP, CoM@CoNiC-F significantly reduced the pHRR, THR, pSPR, and pCOP by 70.71%, 43.11%, 71.69%, and 76.03%, respectively. Notably, the CoM@CoNiC-F nanocomposites

exhibited advanced protective multifunctionality, including superamphiphobicity (contact angles of 157° and 153°), long-term corrosion resistance (45 d), and mechanical durability.

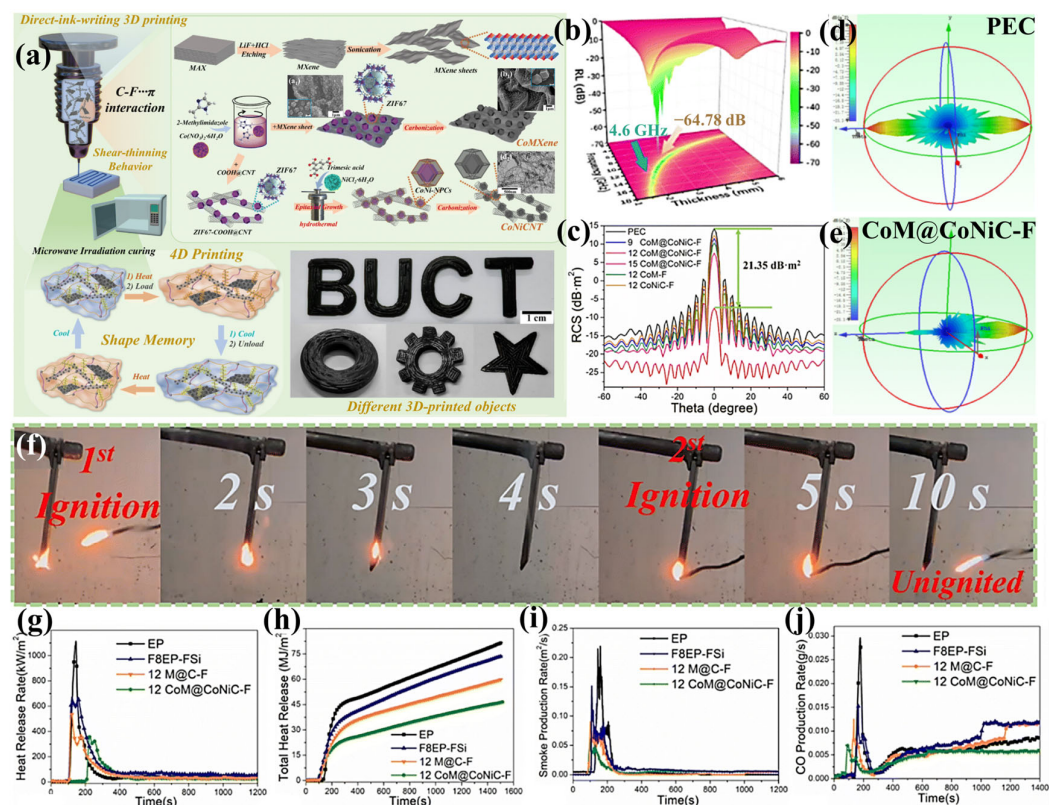


Figure 5. CoM@CoNiC-F: (a) schematic diagram of the synthesis process, (b) 3D RL diagram, (c) 2D RCS diagram, (d,e) 3D RCS diagram, (f) vertical combustion test, (g) HRR, (h) THR, (i) SPR, and (j) COP (reprinted with permission from [87] © 2024 Royal Society of Chemistry).

For wearable, intelligent, and portable composite phase-change materials, improving multifunctionality is essential to meeting the challenges presented by harsh and complicated settings. Li et al. [88] developed a multifunctional composite phase-change material (PW-CMF@Co/NC) based on Co/N co-doped carbon foam by coating melamine foam (MF) with ZIF-67, followed by high-temperature calcination and paraffin wax (PW) melting encapsulation (Figure 6a). This material offers great promise for radiation-resistant smart wearables and customized thermal management by combining dual-temperature thermal management, photothermal heating, waterproofing, flame retardancy, and EMA. As shown in Figure 6b, the PW-CMF@Co/NC composite demonstrated outstanding EMA performance, achieving a $RL_{\min}$ of -57.93 dB at 9.3 GHz with a thickness of 3 mm and an EAB of 3.85 GHz. In CCT, the PW-CMF@Co/NC composite demonstrated outstanding flame retardancy, with a $pHRR$ of only 82.3 kW/m², a THR of 10.0 MJ/m², a $pSPR$ of 3.8 kW/m², and a total smoke release (TSR) of 81.8 MJ/m² (Figure 6e,f). In a vertical burning test using an alcohol lamp (Figure 6g), the PW-CMF@Co/NC composite showed no significant combustion when exposed to flames. After 60 s, the material only exhibited slight shrinkage and carbonization, further confirming its excellent flame retardancy. Infrared thermal imaging was used to record the temperature variation processes of PW and PW-CMF@Co/NC composites (Figure 6c,d). The composite material exhibited a faster temperature rise compared to PW, indicating enhanced heat transfer properties. Moreover, the foam-based composite phase-change material maintained outstanding thermal management, structural stability, and thermal storage stability after 300 heating–cooling cycles.

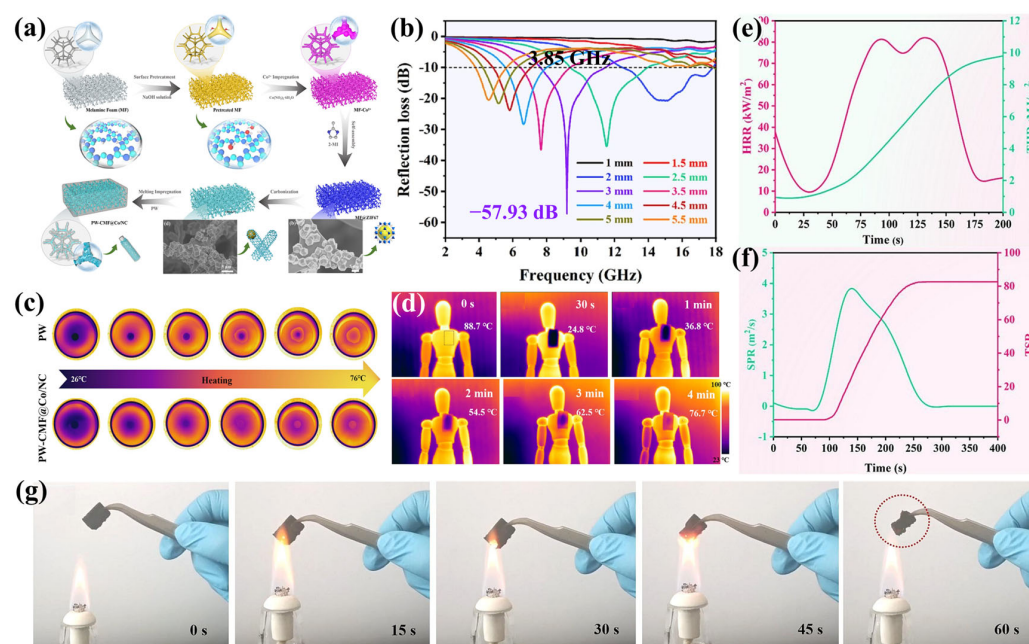


Figure 6. PW-CMF@Co/NC: (a) schematic diagram of the synthesis process, (b) RL–f curve, (c,d) thermal infrared images, (e) HRR and THR, (f) SPR and TSR, and (g) alcohol lamp vertical combustion test (reprinted with permission from [88] © 2024 Elsevier).

3.3. Ni-MOF

In recent years, layered nanocomposites have demonstrated remarkable EMA and infrared shielding capabilities, providing new avenues for the development of multifunctional materials. Xiang et al. [89] reported the synthesis of versatile layered Ni nanoparticle@porous carbon (Ni@C) nanocomposites through the simple carbonization of the Ni-MOF precursor. The results revealed that the layered porous Ni@C nanocomposites exhibited enhanced EMA performance, achieving a $RL_{\min}$ of -59.8 dB and an EAB of 4.5 GHz at a loading of 25 wt.% ($d = 1.5$ mm). Furthermore, thermal infrared imaging and contact angle experiments demonstrated that the layered porous Ni@C nanocomposites possessed certain infrared shielding, thermal insulation, and waterproofing properties. Building upon this, Xiang et al. [90] proposed a controlled assembly strategy to construct nano-/microstructured 2D MXene-encapsulated Ni@C-layered microcubes ($Ti_3CNT_x/Ni@C$) via the thermal decomposition of self-assembled 2D Ni-MOF templates and subsequent electrostatic assembly with Ti_3CNT_x MXene nanosheets (Figure 7a). As shown in Figure 7d–f, the composite material exhibited efficient EMA with a $RL_{\min}$ of -65.7 dB and an EAB of 5.4 GHz at a low loading of 8 wt.% ($d = 1.5$ mm). Figure 7b shows that a $60 \mu\text{m}$ thick $Ti_3CNT_x/Ni@C$ (5 wt%) film burned over an alcohol lamp emitted a red glow for 60 s without igniting and retained its original shape. Additionally, when placed on a heating platform, the film exhibited the slowest temperature rise compared to PU and FN, as illustrated in Figure 7c. These tests confirmed the excellent thermal stability, flame retardancy, thermal insulation, and infrared shielding properties of the layered porous $Ti_3CNT_x/Ni@C$ composites. Moreover, the $Ti_3CNT_x/Ni@C$ layered film demonstrated high electrical conductivity, enabling effective conversion of electrical energy into thermal energy, thereby exhibiting outstanding Joule heating performance.

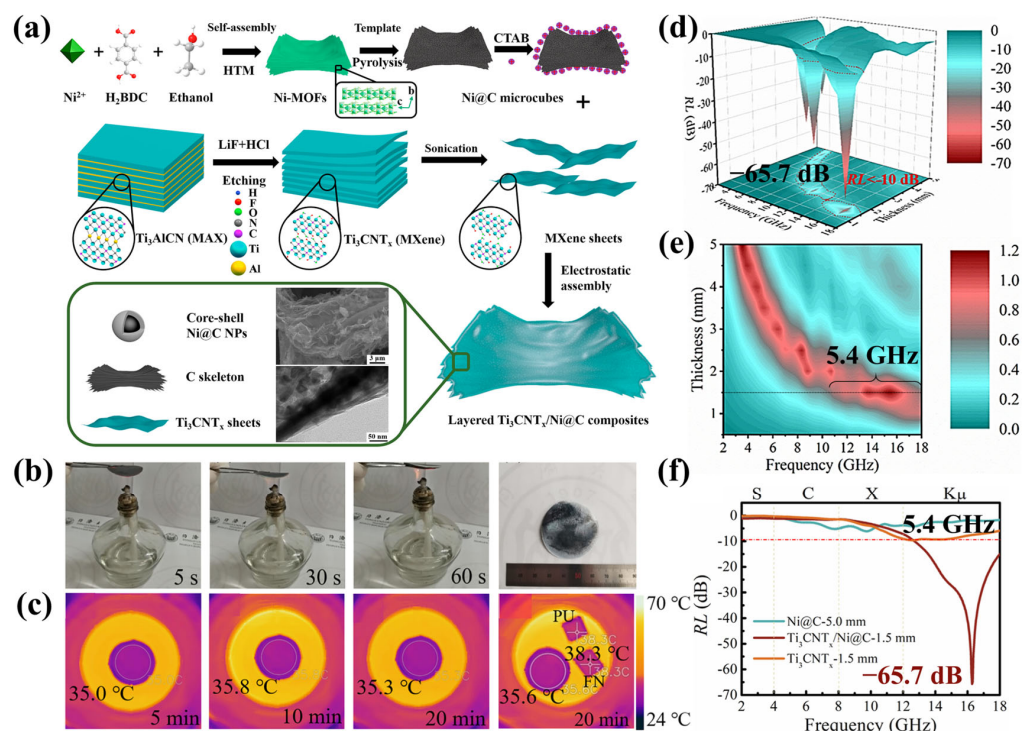


Figure 7. $\text{Ti}_3\text{CNT}_x/\text{Ni@C}$: (a) schematic diagram of the synthesis process, (b) alcohol lamp combustion test, (c) thermal infrared image at 62.0°C , (d) 3D RL diagram, (e) 2D impedance matching plane map, and (f) RL–f curve (reprinted with permission from [90] © 2022 Elsevier).

3.4. Polymetallic MOF

Polymetallic MOFs have received a lot of attention as new functional materials because of their adjustable structures and diverse functions. Composite materials designed based on polymetallic MOFs exhibit excellent EMA, flame retardancy, thermal insulation, and mechanical properties, making them a hot research topic in the development of novel high-performance materials [50,91–93].

As shown in Figure 8a, Li et al. [94] developed a multifunctional CoC@FeNiG-F nanocomposite using an in situ growth and multiphase synergy strategy by combining ZIF-67 and FeNi-MOF. The CoC@FeNiG-F nanocomposite demonstrated exceptional EMA performance, achieving a $\text{RL}_{\min}$ of -75.19 dB with an EAB of 3.95 GHz at a thickness of 2.4 mm (Figure 8b). The combustion behavior of CoC@FeNiG-F -incorporated EP was investigated through LOI and UL-94 vertical burning tests. As shown in Figure 8c, the CoC@FeNiG-F composite achieved a LOI of 31.2% and a UL-94 V-0 rating. CCT further revealed significant reductions in pHRR, THR, pSPR, and pCOP by 68.77% , 36.53% , 48.39% , and 56.14% , respectively, compared to pure EP (Figure 8d–g). Additionally, the composite material exhibited outstanding mechanical properties (80.3 MPa), superamphiphobicity (contact angles of 153° and 151° for water and oil, respectively), long-term corrosion resistance (45 d), and mechanical durability, highlighting its potential for advanced multifunctional applications.

The innovative synthesis methods for trimetallic MOFs have opened new pathways for the study of composite materials. Guo et al. [95] employed a liquid nitrogen directional freezing strategy to load spindle-shaped trimetallic MOFs onto the pore walls of aerogels. After carbonization, they obtained a 3D carbon aerogel composite derived from trimetallic MOFs, named CCNT-FeCoNi/C (Figure 9a). As illustrated in Figure 9b–d, the CCNT-FeCoNi/C composite exhibited remarkable EMA performance. At a loading of $5\text{ wt.}\%$, the composite achieved a $\text{RL}_{\min}$ of -61.55 dB ($d = 2.42\text{ mm}$) and a maximum EAB of 7.2 GHz ($d = 2.82\text{ mm}$). To assess its flame retardancy, a burning test was conducted using

an alcohol lamp. As shown in Figure 9f, the shape of the composite aerogel remained nearly unchanged during the 30 s burning test, demonstrating the excellent flame-retardant properties of CCNT-FeCoNi/C. Furthermore, as shown in Figure 9e, the composite aerogel exhibited thermal insulation properties when placed on a hot platform at 100 °C, further highlighting its multifunctional potential for advanced applications.

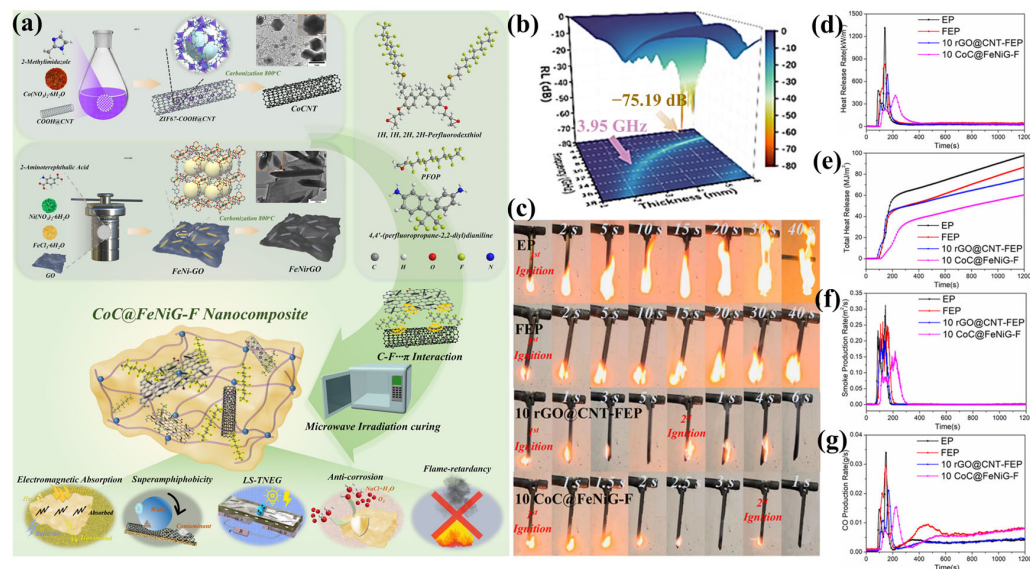


Figure 8. CoC@FeNiG-F: (a) schematic diagram of synthesis process, (b) 3D RL diagram, (c) vertical combustion test, (d) HRR, (e) THR, (f) SPR, and (g) COP ([94] free © 2023 Wiley).

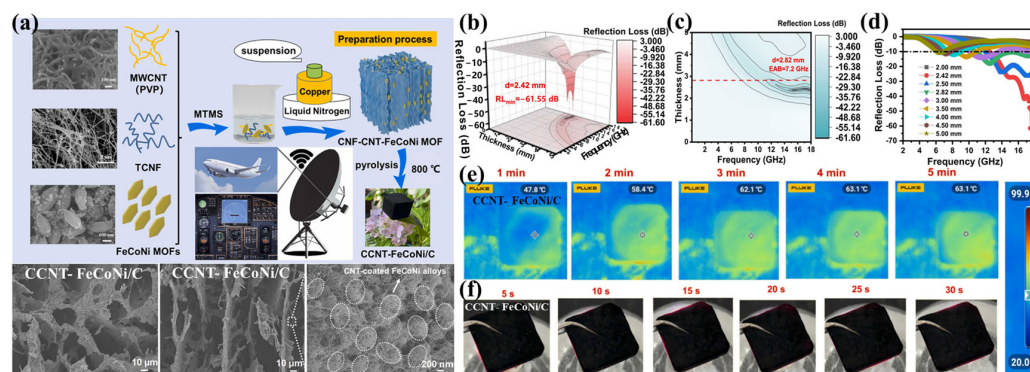


Figure 9. CCNT-FeCoNi/C: (a) schematic diagram of synthesis process and SEM diagram, (b) 3D RL diagram, (c) 2D RL plane map, (d) RL-f curve, (e) thermal infrared image at 100 °C, and (f) alcohol lamp combustion test (reprinted with permission from [95] © 2024 Elsevier).

Using a multidimensional design strategy, Li et al. [96] successfully developed a novel EMA material by combining carboxylated CNTs with graphene oxide (GO) and loading Co/Ni-MOF onto the surface of GO using its rich functional groups. This resulted in the EMA composite CNT-rGO-Co/Ni-MOF (Figure 10a). As shown in Figure 10b–d, CNT-rGO-Co/Ni-MOF exhibited remarkable EMA properties, achieving a significant $RL_{\min}$ of -43.0 dB and an EAB greater than 4.0 GHz at 25 wt.% loading ($d = 1.5$ mm). When 10 wt.% of CNT-rGO-Co/Ni-MOF was added to EP, the composite material did not ignite within 60 s, in stark contrast to pure EP, which rapidly ignited (Figure 10e). Additionally, as shown in Figure 10f, compared to pure EP, the HRC, pHRR, and THR of EP/CNT-rGO-Co/Ni-MOF were reduced by 59.2%, 52.6%, and 20.8%, respectively, demonstrating excellent flame retardancy.

In the research of high-performance composites, using renewable resources as scaffold templates to fabricate novel composites has become a green and efficient strategy.

Peng et al. [97] used a renewable wood-based porous carbon (WPC) scaffold as a template and its highly ordered internal cells as micro-reactors to fabricate an ultralight, flame-retardant, heat-insulating, and cyclically stable CoFe-MOF@Ti₃C₂T_x MXene@sodium alginate@WPC (MMSW) composite material (Figure 11a). As shown in Figure 11b,c, MMSW achieved a RL_{min} of −58.2 dB and an EAB of 5.8 GHz (d = 2.0 mm). By varying the thickness of MMSW from 1.5 to 6.0 mm, the peak RL exceeded −20 dB in the 6–18 GHz range. Compared to tissue paper, MMSW maintained its shape after being heated by an alcohol lamp for 90 s, demonstrating excellent flame retardancy (Figure 11f,g). Moreover, as shown in Figure 11d,e, a tissue paper placed on MMSW remained intact after 90 s, indicating that MMSW possesses excellent thermal stability and heat insulation properties. Additionally, MMSW displayed excellent Joule heating performance, showing high electric–thermal conversion efficiency after continuous voltage application.

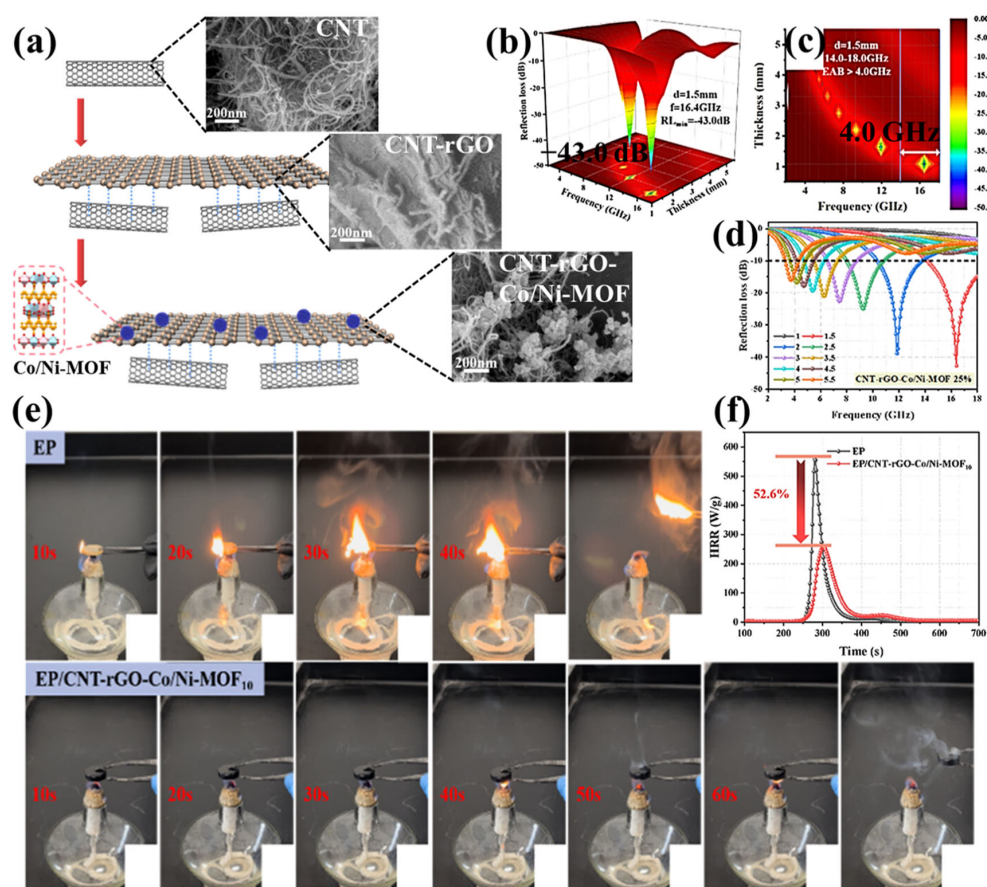


Figure 10. CNT-rGO-Co/Ni-MOF: (a) schematic diagram of synthesis process and SEM diagram, (b) 3D RL diagram, (c) 2D RL plane map, (d) RL–f curve, (e) alcohol lamp combustion test, and (f) HRR (reprinted with permission from [96] © 2024 American Chemical Society).

Molybdenum carbide (MoC) integrated into carbon matrices is renowned for its strong interfacial polarization functionality, making it a promising ultra-light microwave absorber. As shown in Figure 12a, Zhang et al. [98] synthesized ZnMo-HZIF foam materials using a solvent-free ball milling method by controlling the milling time. The multifunctional MoC-incorporated carbon matrix (MoC-C) was then synthesized by impregnation deposition thermal reduction from MF and ZnMo-HZIF. The target sample exhibited excellent EMA performance. At a 15 wt.% loading and 2.5 mm thickness, it achieved a RL_{min} of −47.56 dB and an EAB of 4.4 GHz, covering almost the entire X-band (Figure 12b,c). To evaluate the sample's EMA capability in practical scenarios, CST simulation software was used to model the RCS of a PEC plate coated with a uniform absorber. As shown in Figure 12d,e, the RCS

value of the MoC-C remained below $-10 \text{ dB} \cdot \text{m}^2$ across the entire detection angle range, demonstrating the superior EMA capability compared to other samples. In Figure 12f, MoC-C and pure MF were exposed to an alcohol lamp flame for 20 s. Pure MF quickly shrank, and its structural integrity was severely compromised, while MoC-C showed minimal shrinkage and carbonization, maintaining its original shape. This indicates that the incorporation of ZnMo-HZIF significantly enhanced the flame retardancy of the MF-based material. To test the thermal insulation stability of MoC-C, its infrared thermal imaging temperature was compared with several commercial insulating materials, including NF, high-density polyurethane foam (HPU), and polystyrene foam (PS). After exposure to a heating platform set at 150°C and 200°C for 10 min, as shown in Figure 12h, MoC-C maintained a lower temperature than NF, HPU, and PS throughout the heating process, demonstrating its excellent thermal insulation performance. Figure 12g shows that when an infrared camera captured the heated aircraft model, MoC-C displayed outstanding stealth capability under infrared radiation. Additionally, MoC-C exhibited excellent hydrophobicity and resistance to chemical corrosion, further enhancing its multifunctional properties.

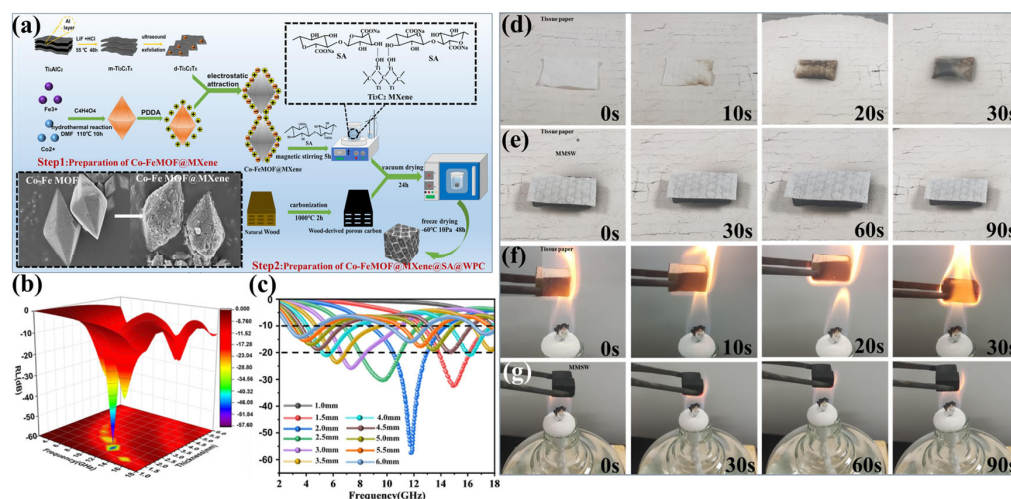


Figure 11. MMSW: (a) schematic diagram of synthesis process and SEM diagram, (b) 3D RL diagram, (c) RL-f curve, and (d–g) alcohol lamp combustion test (reprinted with permission from [97] © 2024 Elsevier).

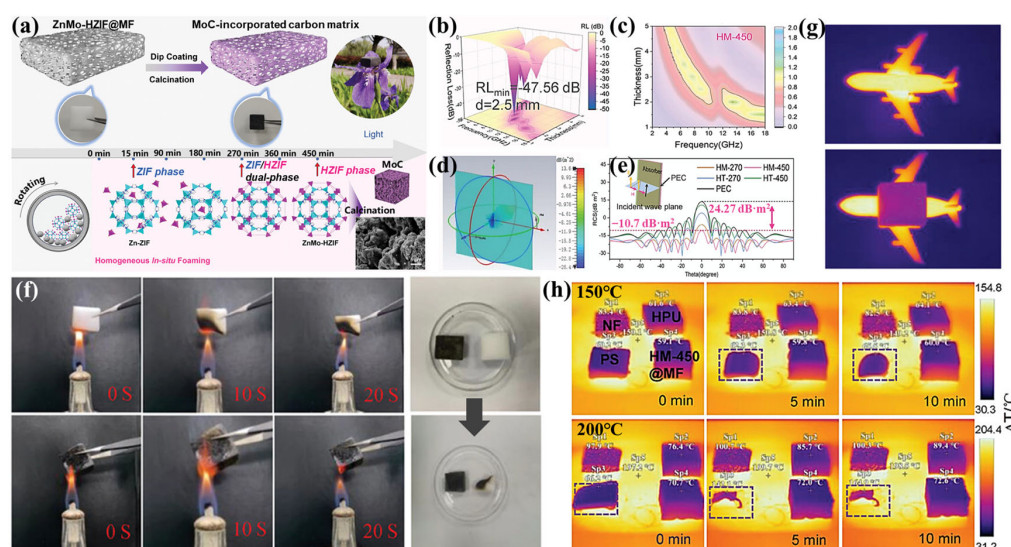


Figure 12. MoC-C: (a) schematic diagram of synthesis process, (b) 3D RL diagram, (c) 2D impedance matching plane map, (d) 3D RCS diagram, (e) 2D RCS diagram, (f) alcohol lamp combustion test, and (g,h) thermal infrared image (reprinted with permission from [98] © 2024 Wiley).

4. Conclusions and Prospects

This review systematically summarizes the research progress of MOF-based EMA flame-retardant dual-functional composites, with the EMA and flame-retardant performance of all discussed materials collected in Table 1. To provide a more intuitive comparison of the performance of different materials across various parameters, Figure 13 presents a comprehensive comparison of these materials in terms of EMA levels, flame retardancy, and other key properties. Additionally, the following main conclusions can be drawn:

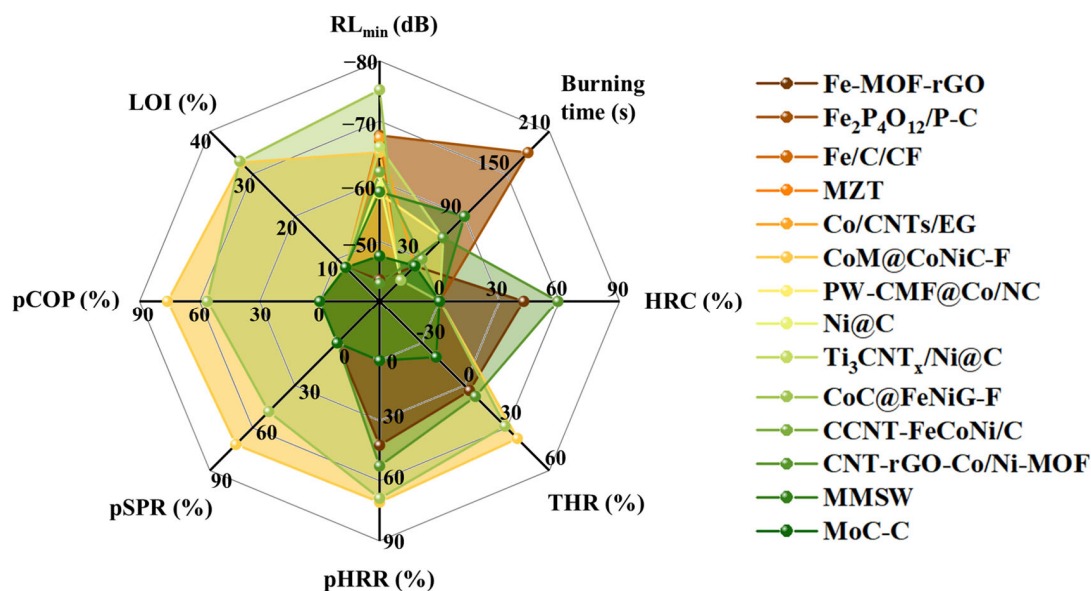


Figure 13. Radar chart of EMA–flame retardancy levels of all MOF-based dual-functional composites.

(1) Through the rational design of the structure and composition of MOFs, synergistic enhancement of both EMA and flame-retardant properties can be achieved. The selection of metal centers plays a key role in the material's performance. Typical magnetic metals (such as Fe, Co, and Ni) can provide a certain degree of magnetic loss capability while also exhibiting excellent dielectric loss characteristics, demonstrating outstanding impedance matching performance. Polymetallic MOFs further enhance performance through the synergistic effect of multiple components.

(2) The EMA performance of MOF-based composites is mainly influenced by the following factors: the pore structure of MOFs provides abundant interfacial polarization sites and multiple reflection channels; the introduction of metal centers and conductive components enhances the material's magnetic loss and dielectric loss capabilities; rational structural design contributes to the optimization of impedance matching. Reported MOF-based composites have achieved RL values ranging from -40 dB to -75 dB and EAB values from 3 GHz to 7 GHz.

(3) The flame-retardant mechanism of MOF-based composites mainly includes the following: the catalytic promotion of charring by the metal centers to form a dense protective layer; the porous structure facilitating the adsorption and catalytic decomposition of toxic gases; and the introduction of functional groups such as P and N further enhancing the flame-retardant effect. Some materials have achieved V-0 flame-retardant performance and a LOI of over 30%.

Table 1. EMA and flame-retardant performance of MOF-based dual-functional composites.

Sample	Structure	Loading (wt.%)	RL _{min} /d (dB/mm)	EAB/d (GHz/mm)	Main Flame-Retardant and Thermal Insulation Results	Advantages/Disadvantages	Ref.
Fe-MOF-rGO	Heterostructure composed of 2D rGO and 3D Fe-MOF	25	−43.6/2.0	5.0/2.0	Alcohol lamp burning 20 s without deformation; HRC, pHRR and THR decreased by 42.1%, 42.3% and 17.7%, respectively.	Lightweight, easy to prepare/high-proportion requirements	[77]
Fe ₂ P ₄ O ₁₂ /P-C	Complex network structure composed of octahedral Fe ₂ P ₄ O ₁₂ and layered carbon	30	−67.6/2.0	5.76/2.1	Alcohol lamp burning 180 s without deformation.	High-temperature fire resistance/complex preparation process and high-proportion requirements	[80]
Fe/C/CF	3D porous structure composed of Fe/C nanotubes and carbon foam	-	−66.7/4.18	6.34/4.08	Thermal insulation and infrared stealth.	Lightweight, easy to prepare/long-term stability and weather resistance to be proven	[81]
MZT	Highly ordered 3D pore network	20	−59.82/2.3	5.64/2.1	Thermal insulation and infrared stealth.	Lightweight/requires precise control of calcining conditions	[85]
Co/CNTs/EG	3D porous structure of urchin-like Co/CNTs distributed in honeycomb EG	3	−67.2/1.4	5.1/1.4	Alcohol lamp burning 20 s without deformation; thermal insulation and infrared stealth.	Lightweight, low proportion/long-term stability and weather resistance to be proven	[86]
CoM@CoNiC-F	Multiphase structure composed of 2D CoMXene and 1D CoNiCNT	-	−64.78/2.3	4.6/1.7	LOI was 30.8%; UL-94 V-0 rating; pHRR, THR, pSPR, and pCOP decreased by 70.71%, 43.11%, 71.69%, and 76.03%, respectively. (Heat flux was 35 kW/m ² .)	Shape memory and 4D printing capability/complex preparation process	[87]
PW-CMF@Co/NC	3D porous carbon foam structure with polyhedron growth, and the surface covered with dense carbon nanotubes	-	−57.93/3.0	3.85/3.0	Alcohol lamp burning 60 s without deformation; heat conduction function; pHRR, THR, pSPR, and TSR were 82.3 kW/m ² , 10.0 MJ/m ² , 3.8 kW/m ² , and 81.8 MJ/m ² . (Heat flux was 50 kW/m ² .)	Efficient photothermal conversion capability, excellent thermal storage stability/practical application limitations	[88]
Ni@C	Laminated porous structure formed by assembling 2D carbon sheets	25	−59.8/1.5	4.5/1.5	Thermal insulation and infrared stealth.	Lightweight, hydrophobic/mechanical strength may be insufficient	[89]
Ti ₃ CNT _x /Ni@C	Layered porous structure composed of 2D MXene sheets and Ni@C microcubes.	8	−65.7/1.5	5.4/1.5	Alcohol lamp burning 60 s without deformation; thermal insulation and infrared stealth.	Lightweight, low proportion/MXene easy to stack and agglomerate	[90]
CoC@FeNiG-F	Multidimensional carbon structure composed of 1D CNTs, 2D rGO, and 3D carbon skeleton	-	−75.19/2.4	3.95/2.4	LOI was 31.2%; UL-94 V-0 rating; pHRR, THR, pSPR, and pCOP decreased by 68.77%, 36.53%, 48.39%, and 56.14%, respectively. (Heat flux was 35 kW/m ² .)	Can be used for liquid–solid triboelectric nanogenerator/complex preparation process	[94]
CCNT-FeCoNi/C	3D porous aerogel structure of FeCoNi alloy grown on the surface	5	−61.55/2.42	7.2/2.82	Alcohol lamp burning 30 s without deformation; thermal insulation and infrared stealth.	Lightweight, low proportion/complex preparation process	[95]
CNT-rGO-Co/Ni-MOF	Multidimensional heterogeneous structures composed of CNT, rGO, and Co/Ni-MOF	25	−43.0/1.5	4.0/1.5	Alcohol lamp burning 60 s without deformation; HRC, pHRR, and THR decreased by 59.2%, 52.6%, and 20.8%.	Lightweight, multi-mechanism synergies/high-proportion requirements	[96]
MMSW	Highly ordered cellular porous carbon foam structure	-	−58.2/2.0	5.8/2.0	Alcohol lamp burning 90 s without deformation; thermal insulation.	Lightweight, excellent Joule thermal properties/mechanical strength may be insufficient	[97]
MoC-C	3D foam structure containing a large number of bubbles and hierarchical pores	15	−47.56/2.5	4.4/2.5	Alcohol lamp burning 20 s without deformation; thermal insulation and infrared stealth.	Lightweight, green preparation/mechanical strength may be insufficient	[98]

Figure 14 visually illustrates the challenges and development directions that research on MOF-based dual-functional composites still faces. In-depth studies on the structure–performance relationships of materials are needed to establish synergistic enhancement mechanisms for EMA and flame-retardant properties, providing theoretical guidance for the rational design of materials. New synthesis strategies and processing techniques should be developed to improve the scalability of material preparation and enhance their

practical application performance. Environmentally friendly and sustainable preparation methods need to be explored to reduce material costs and increase their economic feasibility and practicality. Expanding the application fields of MOF-based composites, such as in smart wearable devices and aerospace materials, will facilitate the further integration and optimization of material functionalities. In conclusion, MOF-based dual-functional composites show a wide range of potential applications. It is anticipated that new high-performance, versatile, and innovative composites will be created via ongoing technical advancement and thorough study, offering practical answers to the problems of fire safety and electromagnetic pollution.

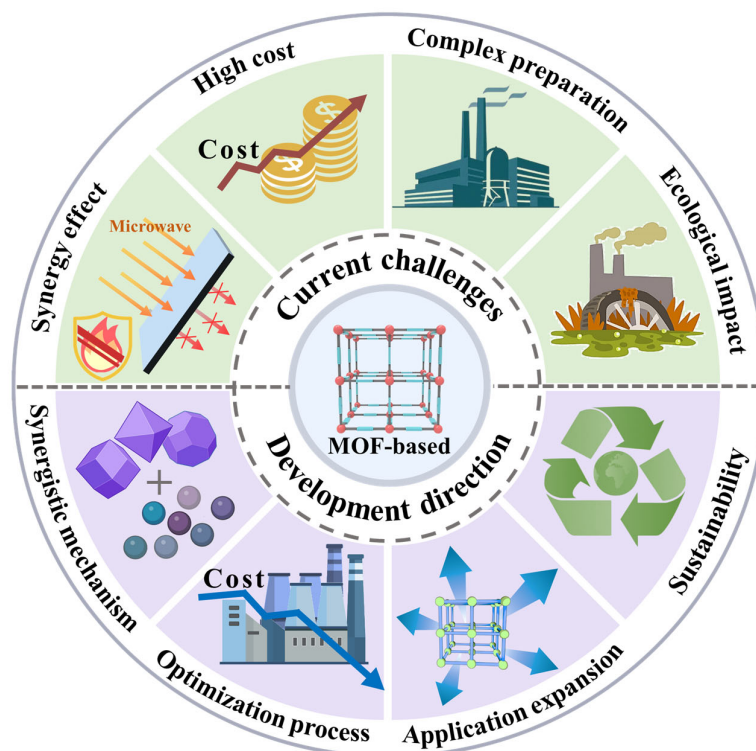


Figure 14. Perspective view of MOF-based dual-functional composites.

Author Contributions: Conceptualization, Y.-T.P.; Witing—original draft, J.H.; Writing—review and editing and Visualization, J.H. and J.J.; Investigation, Q.L., J.C. and X.S.; Supervision, S.H. and M.M. All authors have read and agreed to the published version of the manuscript.

Funding: The National Natural Science Foundation of China (No. 22375023), the Natural Science Foundation of Chongqing (CSTB2024NSCQ-MSX0452), the Natural Science Foundation of Hebei Province (E2024105006) and the Natural Science Foundation of Shandong Province (ZR2024ME040) provided funding for this work.

Data Availability Statement: No new data were created or analyzed in this study.

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

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