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# Recent progress of MOF-derived porous carbon materials for microwave absorption

Mingliang Ma,<sup>a</sup> Yuxin Bi,<sup>a</sup> Zhouyu Tong,<sup>a</sup> Yanyan Liu, <sup>1</sup> \* Ping Lyu,<sup>a</sup> Rongzhen Wang,<sup>a</sup> Yong Ma,<sup>b</sup> Guanglei Wu,<sup>c</sup> Zijian Liao<sup>a</sup> and Yan Chen<sup>a</sup>

Microwave absorbing materials (MAM) have attracted considerable attention over the years in stealth and information technologies. Metal-organic framework (MOF) with a unique microstructure and electronic state has become an attractive focus as self-sacrificing precursors of microwave absorbers. The MOF-derived porous carbon (PC) materials exhibit a high absorbing performance due to the stable three-dimensional structure and homogeneous distribution of metal particles. MOF-derived PC materials are promising for ideal MAM *via* tuning of the structure and composition, resulting in appropriate impedance matching and the synergistic effect between magnetic and dielectric loss. In this review, the MOF-derived PC materials and their basic absorption mechanisms (dielectric loss, magnetic loss and impedance matching) are introduced, as well as the characters of various MOF-derived PC materials. In addition, this review provides a comprehensive introduction and tabulates the recent progress based on the classification of the MOF-derived metallic state, such as pure PC (without reduced metals), monometal/PC, multi-metal/PC, metal oxides/PC and other derived PC composites. Finally, the challenges faced by MOF-derived PC materials are overviewed, and their further development is mentioned.

### 1. Introduction

In recent decades, the world has witnessed an eruptible development in stealth, information technology and electronics industry that bring public convenience and high-efficiency.¹ However, it is worth noting that the living environment has deteriorated dramatically with the explosive growth of modern electronic technology, which not only induces electrical interference with precision equipment and apparatus but also makes an impact on public health.² Thus, developing ideal microwave absorbing materials (MAM) with higher attenuating capacity, wider absorption bandwidth and lighter weight is an urgent proposition.³

Metal-organic framework (MOF) materials attract a lot of attention owing to their intriguing structure with a large pore volume, high surface area and uniformity of metals. MOFs have exhibited significant applications in gas storage and separation, sensing, catalysis, proton conduction, drug delivery and other fields.<sup>4-10</sup> In addition, the synthesis process of MOF materials is simple and environment friendly, which meets the development requirements of green functional materials in modern society.<sup>11</sup>

Up to now, more than twenty thousand monomers of MOF are prepared with different metal ions and organic ligands, exhibiting rich and varied micro-morphology such as sphere-like, flake-like, cube-like, octahedron-like, dodecahedron-like and so on, 12-20 which have received attention from various fields. And the number of MOF materials reported is refreshed constantly with endless emergence of new monomers.

The metal ions cover almost all kinds of metals like main group metals, transition metals, lanthanide metals and rare-earth metals. As for the organic ligands, the common ligands are polyamines (especially amines produced from imidazole, oxalic acid and benzene), carboxylates, pyridyl, porphyrins, cyano groups, crown ethers and phosphonates.<sup>21</sup> Therefore, there are various and complicated classification methods of MOF materials depending on what public focuses on. Different types of MOF can be converted into each other simply by changing the microstructure or one of the elements due to the highly adjustable character.

MOF possesses the advantages of high porosity, low density, large specific surface area, regular channel, adjustable pore structure and topological structure diversity. MOF-derived materials, especially the carbon materials, have become a new member of the microwave absorption field. The publications of MOF (almost all of publications searched are about MOF-derived porous carbon (PC) materials) as microwave absorbers are increasing progressively in recent ten years, as shown in Fig. 1. Compared with the MOF materials, MOF-derived PC materials are more promising as microwave absorbers.

<sup>&</sup>quot;School of Civil Engineering, Qingdao University of Technology, Qingdao 266033, People's Republic of China. E-mail: yanqdlg@163.com

<sup>&</sup>lt;sup>b</sup>School of Material Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, People's Republic of China

<sup>&#</sup>x27;Institute of Materials for Energy and EnvironmentState Key Laboratory of Bio-fibers and Eco-textiles, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, People's Republic of China

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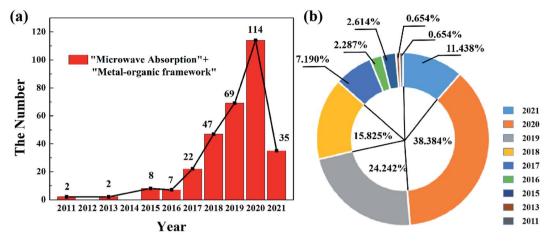


Fig. 1 The number (a) and the proportion (b) of publications on "microwave absorption" and "metal-organic framework" searched by Web of Science

MOF and their composites are used as ideal precursors by controlling pyrolysis and the following postprocessing processes to synthesize MOF-derived PC materials, which have great impedance matching, high porosity and light weight. 22,23 The porous structure and the ordered metal arrangement of MOF precursors are greatly inherited into derived PC materials via carbonizing under inert atmosphere (N2 or Ar). Compared with traditional PC materials, MOF-derived PC materials possess unique metal/carbon microstructure with homogeneous metal embedded. Plenty of researches have revealed that the serious aggregation of metals can be effectively avoided because of the metallic ordered arrangement in the MOFderived metal/carbon construction, so that derived composites often exhibit highly efficient microwave absorbing properties.24 Some of them have confirmed that pure carbon with porous framework can be prepared by calcining or etching the metallic tiny particles. At the same time, with the unique microstructure and composition advantages of MOF, the active ingredients in the derivative materials can be precisely tuned to well overcome the common problems of poor stability and low conductivity for MOF precursors. The tuning progress can provide new reaction sites and expand the applicable reaction range, and also provide great convenience for performance optimization.<sup>25,26</sup>

MOF-derived PC materials have been widely concerned as microwave absorbers, but there are few literatures focus on the derived PC materials from the view of metallic state.27,28 This review summarizes the MOF-derived PC materials with considerable microwave absorption performance, which are just the tip of the iceberg of big MOF material family. In here, MOF-derived PC materials are divided into pure PC (without metals), metal oxides/PC, mono-metal/PC, multi-metal/PC and other PC composites, which is classified on the different MOFderived metallic state. The strengths of MOF-derived PC materials are emphasized via comparing with traditional pure PC, and the basic absorption mechanisms are briefly explained. Additionally, this article herein includes the discussion and summarization of major MOF-derived PC materials reported in the recent years. Finally, the MOF-derived PC materials with different classification are tabulated as tables for comparison.

#### MOF-derived PC materials

Carbon-based materials are widely accepted as high MAM due to the strong electromagnetic attenuation ability, low density and chemical stability. Distinct existence forms of carbon-based materials are reported including carbon nanotubes,29 carbon fibers,30 graphene31,32 and carbon spheres.2,33 However, carbonbased materials have relatively high complex permittivity and poor magnetic permeability. These features lead to the unmatched impedance and single attenuation the development as microwave absorbers.34 In the recent years, PC combined with carbon and porous features gain interests, due to the facial synthesis method and high performance.35 The PC materials have been reported and applied in the field of catalysis, supercapacitor and the microwave absorption, due to the high specific areas, tunable pore sizes and unique structures.36 However, pure PC materials commonly exhibit the single loss mechanism, which cannot show the better absorption capacity. One of the common methods is to blend PC materials with the magnetic loss materials, increasing the complex permeability to satisfy the impedance matching.37,38 For instance, Wu et al. synthesized carbon sphere/Fe-Fe<sub>3</sub>O<sub>4</sub> via loading magnetic quantum dots of Fe-Fe<sub>3</sub>O<sub>4</sub> on the mono-dispersed carbon sphere carbonatized from the phenolic resin sphere.39 The asobtained composites showed excellent electromagnetic absorption properties with the effective absorption bandwidth (EAB) of 5.8 GHz with coating thickness of 1.5 mm. Fan et al. successfully synthesized urchin-like transition metal oxides NiCo2O4 grown on the carbon microsphere, and prepared binary metal oxides ZnO nanoparticles on the surface of C/ NiCo<sub>2</sub>O<sub>4</sub> to improve the impedance matching.<sup>40</sup> The minimum reflection loss (RL) of composites reached -43.61 dB at 11.61 GHz and the EAB covered 4.32 GHz from 9.74 to 14.06 GHz.

The traditional synthetic methods of carbon/magnetic structure are almost more complicated than methods of MOF-derived PC materials synthesis. Recently, studies have found that high-temperature pyrolysis of MOF precursors in inert atmosphere can generate magnetic metal/carbon composite materials, which maintain the original special structure of MOF

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materials. Magnetic particles can also be uniformly dispersed on the surface of PC.41 The preparation process of MOF-derived PC materials is facile, and it is easy to disperse reduced metals or metal oxides inside carbon skeleton. 42 As a result, PC materials derived from MOF become a new focus for light-weight microwave absorbers and increasingly attract a wide variety of attention.

The unique pore microstructure is retained to MOF-derived PC materials with a large extent and can be flexibly adjusted according to the application performance requirements of the crystal size and pore size.43 The periodic and regular arrangement of metal ion nodes in the carbon framework reduces homogenously dispersion of metal particles.44 These characteristics make it possible for MOF to be used as templates and precursors to prepare the PC composites under suitable calcination conditions.45

The existence of derived carbon/magnetic structure not only prevents the generation of magnetic particles in harsh environments, but also provides stronger interface polarization.46 These results are conducive to the dissipation of microwaves. Various MOF-derived PC materials have been successfully manufactured, such as Fe/C, 47,48 Co/C, 49,50 Fe<sub>3</sub>O<sub>4</sub>/C, 51 Co<sub>3</sub>O<sub>4</sub>/C, 52 CoFe/C, 53,54 CoZn/C.55 The MOF-derived PC materials are summarized and tabulated according to different metallic state, so that the composites are easily observed and compared.

# Principle of MOF-derived PC absorbers

Electromagnetic waves are oscillating particle waves derived from mutually perpendicular electric and magnetic fields in space, so the loss of microwave is mainly induced by the interaction of either one of these fields, or both.<sup>56</sup> In the previous literature reported, the mechanisms of absorption could be described as dielectric loss, magnetic loss and their synergistic effect. With unique three-dimensional carbon/ magnetic structure, MOF-derived PC materials possess optimized impedance matching and excellent performance as microwave absorbers. The evaluation of the absorbing performance is mainly based on two key characteristics: impedance matching and attenuation capacity.

#### 3.1 Dielectric loss

Dielectric loss is described that the microwave energy is translated into thermal energy loss via the electronic interaction between MOF-derived PC materials and electric field of incident microwave. The polarity changing of the electric field is sinusoidally and orthogonal to the forward propagation direction of incident microwave. The polarization phenomenon is induced by generating of conductive current in an alternating electric field. The dielectric loss occurs when the polarization changes slower than the rate of the oscillation field, and then the energy of incident microwave is converted into thermal loss through repeated polarization relaxation of the absorbing materials.<sup>57</sup> In addition, the collision and scattering of electrons can be thought as "friction" during transportation of microwave, and

this "friction" induces energy conversion, which manifests as the subsequent generation of heat and reduction of microwave. 58 Generally, relative permittivity ( $\varepsilon_r$ ) is the main parameter for estimating dielectric loss, which is shown in eqn (1):

$$\varepsilon_{\rm r} = \frac{\varepsilon}{\varepsilon_0} = \varepsilon' - i\varepsilon'' \tag{1}$$

It is widely accepted that carbon absorbers not only possess strong dielectric loss property, but also have the advantage of light weight and great thermal stability for practical application.59 These features are especially enhanced and optimized in the MOF-derived PC materials with high porosity and relative permittivity. The porous structure retained from MOF precursors exhibits large of holes. And carbon skeleton around these pores could attain micro-size even nano-size which are much less than the length of incident microwave, greatly reducing the reflection from the PC surface.57 The MOF-derived PC materials with high conductivity can provide a longer transmission channel for dissipating current to enhance dielectric loss.

#### 3.2 Magnetic loss

Magnetic loss is magnetic interaction between absorption materials and magnetic field of incident microwave. In general, magnetic loss includes magnetic hysteresis loss, eddy current loss and resonance effect. In an alternating magnetic field, the change of the magnetization vector lags behind the changing of the magnetic field and the generation of ring eddy current is perpendicular to the direction of the changing magnetic flux, inducing the loss of microwaves. 60 Magnetic metals (Ni, Co, Fe) and metallic compounds (Fe<sub>3</sub>O<sub>4</sub>, γ-Fe<sub>2</sub>O<sub>3</sub>, ferrite) are the most typical MAM.61 Magnetic materials can effectively induce the entrance of incident waves, avoiding the skin effects at high frequencies and convert the electromagnetic energy into thermal energy and losses.38,41

Reduced magnetic metals and metallic compounds of MOF precursors are evenly distributed in carbon framework as nanoscale quantum dots without agglomeration. This character mainly results in eddy current losses and resonance effects.<sup>56</sup> Meanwhile, the nano-size metallic quantum dots have large specific surface area, which cause more interface polarization, multiple scattering and reflections. In addition, the unique quantum size effect of nano-particles can degrade the electron energy level, which causes a new attenuation channel of microwave energy.<sup>57</sup> The relative permeability  $\mu_r$  of absorbers is used to estimate magnetic loss, as shown in eqn (2).

$$\mu_{\rm r} = \frac{\mu}{\mu_0} = \mu' - i\mu'' \tag{2}$$

In eqn (1) and (2), the real part  $(\varepsilon', \mu')$  of the complex permittivity and complex permeability represent the storage capacity of electromagnetic energy, and the imaginary part ( $\varepsilon''$ ,  $\mu''$ ) are often used as key parameters to represent the consumption capacity of electromagnetic energy.

Typical high permeability absorbers mainly include magnetic metals and metallic compounds, which can be (a) Incident Waves

Conduction loss

Multiple scattering reflection waves

Multiple scattering reflection waves

Multiple scattering reflection waves

Interfacial and Dipole polarization

Waves

Microwaves

Electron

Debye dipole polarization

Debye dipole polarization

Electron polarization

Debye dipole polarization

Electron polarization

Electron polarization

Debye dipole polarization

Electron polarization

Electron polarization

Conductivity loss

Transmitted Microwave

Transmitted Microwave

Transmitted Microwave

Transmitted Microwave

Transmitted Microwave

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Fig. 2 Schematic diagram of microwave absorption mechanism of MOF-derived metal/C composites, this figure has been adapted from ref. 41, 70 and 71 with permission from Applied Surface Science, Copyright 2020, Composites Communications, Copyright 2020 and Applied Surface Science, Copyright 2020, respectively.

produced *via* pyrolysis in inert atmosphere. And the absorbers effectively combined with metallic components exhibit improving Debye dipole polarization and multiple interface reflection. <sup>62</sup> Diversiform metals and metallic compounds can be combined *via* simple doping method. As a simple example, FeCo alloy is an ideal absorber for constructing a composite of magnetic material and carbon material with high saturation magnetization, Curie temperature and conductivity, which are better than those of PC doped with Co only. <sup>14</sup> In addition, FeCo or FeNi alloys generally exhibit greater permeability, Snoek's limit and higher saturation magnetization than ferrites, which avail the modification and tuning of absorbing properties. <sup>63</sup>

#### 3.3 Synergistic effect of magnetic/dielectric loss

The strong microwave energy loss is common achieved through a multitude of loss mechanism.64 Microwave absorbers composited of dielectric and magnetic loss materials are promising with optimized impedance matching and synergistic effect between dielectric loss and magnetic loss. And the impedance matching characteristic is typically represented by reflectivity R and term  $Z_{\rm in}$ , as shown in eqn (3)–(5). 65 Nearly all of microwaves can enter into absorbing materials when  $Z_{\rm in}$  is close to 1 (nearly zero reflection at interface). The single-component carbon materials are not conducive to impedance matching because of the large dielectric constant, low magnetic permeability and narrow EAB. And single metal materials with overhigh magnetic loss are difficult to meet an ideal microwave absorber. Some of incident waves are reflected with only high eddy current loss, which is not conducive to the absorbing property.66 MOF-derived PC materials are coupled with carbon

skeleton and metal particles, and carbon skeleton not only improves the corrosion resistance to some degree, but also effectively isolates metal particles, reducing eddy current losses to maintain excellent absorbing performance.<sup>62</sup>

$$Z_{\rm in} = \left(\sqrt{\frac{\mu_{\rm r}}{\varepsilon_{\rm r}}}\right) \tanh \left[j\left(\frac{2\pi f d}{c}\right)\left(\sqrt{\mu_{\rm r}\varepsilon_{\rm r}}\right)\right] \tag{3}$$

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \tag{4}$$

$$R = \frac{Z_{\rm in} - Z_0}{Z_{\rm in} + Z_0} \tag{5}$$

The impedance matching and the absorbing characteristic should be considered comprehensively for an ideal absorber, and the absorbing property is generally indicated by the RL, which is expressed as eqn (6).

$$RL = 20 \lg \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|$$
 (6)

For MOF-derived PC materials, the unique embedded structure of the metals and carbon exhibits abundant interfaces with a large amount of free charge accumulating on them, resulting in the interface polarization. Besides, multiple scattering reflection and interfacial polarization are increased in the porous structure of MOF-derived PC materials, enhancing the absorption performance.<sup>38</sup> For instance, Li *et al.* obtained magnetic Co-C@C composites from ZIF materials. The composites showed the smaller RL of -58.0 dB and wider

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bandwidth of 5.7 GHz compared with previously reported composites, due to the favorable impedance matching and strong attenuation.<sup>67</sup> The size of metal nanoparticles and pores is adjusted with the different pyrolysis temperature, which can tune the impedance matching.<sup>68</sup> The introduction of pores could decrease the density of the absorbers and have an effect on the permittivity of carbon materials. Ding *et al.* studied MIL-53(Fe) derived MCC/rGO composites by gradient temperature calcination and discussed the effect of temperature for absorption performance.<sup>69</sup> The framework enhanced the internal scattering, and the graphene provided a larger absorption surface, efficiently enhancing the absorbing performance.

In a word, compared with common materials, the MOF-derived PC materials with nanoscale quantum dots exhibit better absorbing performance. The synergistic effect of absorbers can achieve excellent impedance matching and high absorbing capacity,<sup>53</sup> as shown in Fig. 2.

# 4. MOF-derived PC materials for microwave absorption

The MOF-derived PC composites exhibit huge potential application as high-performance microwave absorption materials. And the derived PC mentioned herein from recent literatures are divided into a series of subsets for categorization. Based on the metal state, MOF-derived PC composites can be classified as pure PC, mono-metal/PC, multi-metal/PC, metal oxides/PC and

other MOF-derived PC composites. The derived pure PC also be employed not only as absorbers but also as reactive materials.

#### 4.1 Pure PC

As mentioned above, PC exhibits potential application for microwave absorption. MOF-derived pure PC is a high porosity carbon material without metals, which is generally obtained *via* high temperature pyrolyzation process to remove low-boiling point metals. In addition, it can also be prepared through acid etching to remove reduced active metals. MOF-derived pure PC absorbers are often composited with other loss materials because of their restriction as wide frequency bandwidth microwave absorbers.

Various composite forms of derived pure PC are reported. Some are applied as central core of core-shell or yolk-shell structure with other cooperate materials assembling upon their surface. Besides, some are grown on the matrix to construct the porous and stable carbon shell. Derived pure PC can also be combined with two-dimensional materials to play a disperse and dopant role. Zhao and co-workers synthesized nanopolyhedron PC decorating on the surface of reduced graphene oxide (rGO) by in situ pyrolysis.72 ZIF (zeolitic imidazolate framework) is a typical precursor to obtain pure PC materials, such as ZIF-8 (Zn-MOF). It is demonstrated that the grown of ZIF-8 particles is restrained by GO and the derived PC reduces the re-stacking of rGO nanosheets, which yield optimized performance with minimum RL value of -66.2 dB at the thickness of 2.89 mm at 6.2 GHz (as shown in Fig. 3). Because of the low boiling point of metal Zn, ZIF-8 has played a significant

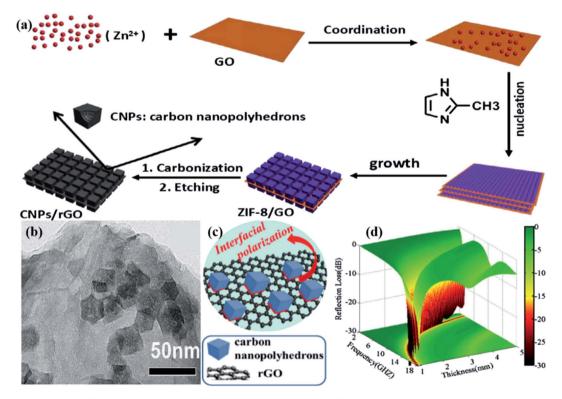


Fig. 3 The fabrication of CNPs/GO derived from ZIF-8/GO (a), TEM images of CNPs/GO (b), interaction (c) and the RL of CNPs/GO (d). This figure has been reproduced from ref. 72 with permission from Journal of Colloid and Interface Science, Copyright 2018.

Table 1 The microwave absorbing performance of MOF-derived pure PC materials

Absorbers	Loading (wt%)	$\mathrm{RL}_{\mathrm{min}}$		EAB		
		Thickness (mm)	Value (dB)	Thickness (mm)	Value (GHz)	Ref.
CNPs/GO	40	2.89	-66.2	1.5	3.6	72
Co@NPC	25	1.45	-48	1.65	5.2	73
Hollow GO@PC	10	3.7	-32.43	3.5	4.2	74
N-doped PC	50	4.0	-39.7	4.0	4.3	75
MCCMs	30	2.0	-28.5	1.8	5.7	76
NPC@CPI-2	50	1.9	-46.86	1.65	3.74	77
C@Co/NC	25	2.2	-52.5	2.2	4.4	78
Fe/C	60	3.0	-40.0	1.5	6.0	79
Fe-N/C	33.3	1.7	-30.98	1.7	5.04	80

role in acting as admirable templates to obtain pure PC materials. 34,73,74 Wu's group also used ZIF-8 as the derived loose PC precursor to prepare high-performance absorbers. 55 By the way, the MOF-derived composites are reported that they can be effectively dispersed in one-dimensional and two-dimensional materials such as carbon fiber and graphene, which play a role in avoiding agglomeration.

It is feasible to obtain pure PC *via* using other metal-based MOF-derived composites as precursors and adding acid solution to get rid of metals. For example, Du *et al.* used Ni-MOF as templates to synthesize the multi-chamber carbon microspheres (MCCMs) *via* the pyrolysis progress and etching treatment.<sup>76</sup> The unique multi-chamber structure possessed better impedance matching characteristic than hollow carbon microspheres. Peng *et al.* obtained PC though removing Cu from the prepared HKUST-1 (Cu-MOF) and studied the microwave attenuation of the derived PC composites.<sup>77</sup>

Similar to above absorbers of MOF-derived PC, an increasing number of PC composites have been developed with other magnetic loss and dielectric loss materials to induce microwave absorption, through the increased research of MOF precursors. The minimum RL and EAB with their corresponding loading and thickness of these similar materials are tabulated in Table 1.

#### 4.2 Mono-metal/PC

The derived-PC composites filled with metallic particles possess the increased magnetic interaction with incident microwave and the optimized impedance matching. As a result, the efforts of developing novel microwave absorbers have been devoted to study compounds of carbon materials and magnetic metal nanoparticles in recent years. When MOF-derived PC composites are combined with single component metal and carbon, the composites can be classified as MOF-derived mono-metal/PC materials. Typical magnetic loss absorbing metallic materials

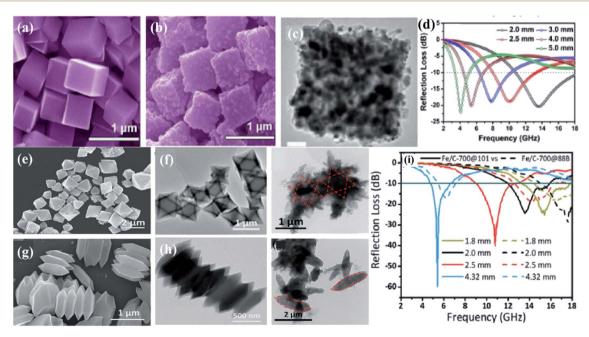


Fig. 4 SEM and TEM images of PB (a), Fe/C-PB (b and c), MIL-101-Fe (e), Fe/Fe<sub>3</sub>C/C-800@101 (f), MIL-88B-Fe (g), and Fe/Fe<sub>3</sub>C/C-800@88B (h), respectively. RL of Fe/C-PB (d), Fe/C-700@101 and Fe/C-700@88B (i), respectively. This figure has been reproduced from ref. 18 and 83 with permission from Advanced Materials Interfaces, Copyright 2020 and Journal of Materials Chemistry A, Copyright 2015.

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includes Fe, Co and Ni, which are also mainly applied in the MOF-derived PC materials. 49,81,82

Prussian blue (PB) is one of common Fe-based MOF which consists of Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub> (a mixed-valence iron(III) hexacyanoferrate(II) compound) with a face-centered-cubic (fcc) crystal structure. And it is an eligible precursor candidate for derived Fe/C composites because of abundant contents of carbon and iron species.83-85 Xu et al. used PB as a MOF precursor to fabricate core-shell Fe@graphitic carbon nanoparticles under different pyrolysis temperature (600-700 °C), and the results displayed strong dielectric loss and magnetic loss properties (Fig. 4).83 The PB derived Fe/C and its composites have been noticed as new microwave absorbers.85 In addition, the more efforts are devoted on MIL (named based on the discovery place: Materials of Institut Lavoisier) series for Febased PC derivatives. Miao et al. reported the morphology effect on microwave absorbing by annealing the two MOF precursors (MIL-101-Fe and MIL-88B-Fe).18 Both of them had almost identical chemical composition and microstructure, including element content, valence state, pore size and volume, but with different topology. The Fe/C-700@101 and Fe/Fe<sub>3</sub>C/C-800@101 (the pyrolysis temperature of MIL-101 precursor was 700 °C and 800 °C) were reduced at high temperature from ferric oxide by CO and reductive carbon generated, showing the excellent performance, as shown in Fig. 4. However, in comparison with pure iron, ferric oxides exhibit chemical stability and have wider application for microwave absorption, which are tabulated in the fourth part of this chapter.

The Ni/C composites with the shape of porous spheres are formed by H<sub>3</sub>BTC (BTC = benzene-1,3,5-tricarboxylate) and Ni<sup>2+</sup>. The amorphous spheres formed with Ni<sup>2+</sup> and H<sub>3</sub>BTC ligands dissolved and diffused to the surface in the process of

crystallization, resulting in rough surface of Ni-based MOF precursors. 15,22,86-88 Liu et al. successfully prepared waxberry-like Ni@C core-shell microspheres with hierarchical architecture.15 The composites obtained after pyrolysis at 700 °C showed optimum absorbing performance, including the RL value of -73.2 dB and the EAB of 4.8 GHz with only 1.8 mm applied thickness (Fig. 5). Similarly, the hollow Ni-MOF spheres were synthesized with different surface morphology by tuning the time of hydrothermal reaction, as shown in Fig. 5.88 And it was found that the samples with 8 h reaction time could reach a broad EAB of about 6.8 GHz with only 1.8 mm thickness. Moreover, rod-like,86 flower-like,89 accordion-like90 and other sphere-like Ni/C composites87 derived from Ni-based MOF also exhibited strong microwave absorption and attenuation performance, and these results are listed in Table 2.

ZIF materials are designed through the expansion of the zeolite topology with larger pores and higher porosity.91 ZIF-67 and ZIF-8, with the same microporous structure and organic ligands, are formed by bridging the 2-methylimidazolate anions and metal cations (Co2+ and Zn2+), respectively. Due to high porosity, easy preparation and large apertures, ZIF-67 is widely applied as precursor of Co-based highly PC matrix absorbers in the recent years. Lu et al. fabricated porous Co/C composites by the directly decomposing ZIF-67 at different temperatures (500 °C, 600 °C and 800 °C). To Co/C composites obtained at 500 °C exhibited best absorbing performance with the minimum RL of -35.3 dB, EAB of 5.80 GHz and the absorbing thickness of 2.5 mm. Chen et al. designed and synthesized rodlike Co/C composites derived from cubic Co-based MOF via hydrothermal and calcination processes.92 The prepared composites exhibited optimized absorbing ability with the minimum RL of -47.6 dB with 2.0 mm. In addition, Co-based

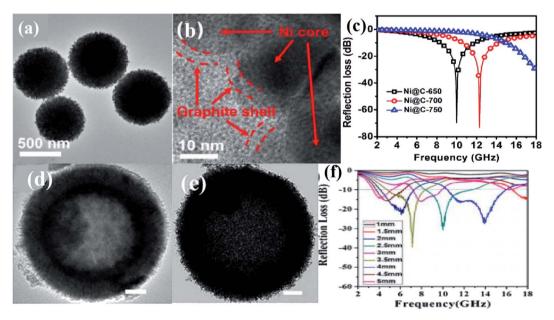


Fig. 5 SEM (a), TEM (b) images and RL (c) of waxberry-like hierarchical Ni/C (annealing at 650 °C), TEM images of Ni-MOF precursors with 8 h (e), Ni/C annealed at 600 °C (d) and RL of Ni/C-8 h (f). This figure has been reproduced from ref. 15 and 88 with permission from Journal of Materials Chemistry C, Copyright 2019 and ACS Applied Nano Materials, Copyright 2019.

Table 2 The microwave absorbing performance of mono-metal/PC materials

Absorbers	Loading (wt%)	$\mathrm{RL}_{\mathrm{min}}$		EAB		
		Thickness (mm)	Value (dB)	Thickness (mm)	Value (GHz)	Ref
Fe/carbon	15	2.5	-29.5	2.5	4.3	48
Fe <sub>3</sub> O <sub>4</sub> @PB	60	1.55	-48.04	2.6	4.5	58
Fe/carbon	40	2.0	-20.3	2.0	7.2	83
Fe/C@Co <sub>3</sub> O <sub>4</sub>	50	1.5	-38.1	2.5	7.65	98
Fe <sub>3</sub> O <sub>4</sub> -C/RGO	15	3.6	-60.5	1.5	5.5	98
Fe/NPC	20	1.8	$\sim$ $-28$	1.8	5.6	99
Ni@C	33	3.5	-45.8	3.5	5.1	22
Ni@C	40	2.7	-86.8	2.7	7.4	22
Ni/C rod	40	2.6	-51.8	2.6	3.48	86
Ni@C@ZnO	25	2.5	-55.8	2.0	4.1	87
Ni/C-8 h	50	_	_	1.8	6.8	88
Ni@C	25	1.8	-86.9	1.8	6.6	90
Ni@C	30	1.85	-57	1.85	6.0	100
Ni/C nanosheets	10	2.2	-71.6	2.2	4.7	101
Co/C	40	4.0	-35.3	2.5	5.8	17
Co/C	40	2.8	-41	2.0	5.6	46
Rod-like Co/C	22	2.0	-47.6	2.0	5.11	92
Co/C	60	2.0	-26.4	2.0	6.6	93
Co@NCNT	25	1.8	-53	2.0	6.2	95
Co@NPC@TiO <sub>2</sub>	50	1.5	-31.7	1.0-5.0	13	96
Co/C	25	3.0	-30.31	3.0	4.93	102
Co/N-doped C	20	2.5	-65.1	3.2	9.4	103
Co/NC@MnO <sub>2</sub>	15	3.7	-58.9	3.7	5.56	11
Co/C@ZnO@GO	30	2.0	-45.4	2.0	5.4	97
Co@C@RGO	20	2.6	-67.5	2.0	5.4	104
Co@C@NRGO	20	2.0	-73.4	2.0	5.3	105
Co-C-MWCNTs	17.5	0.9	-25.27	1.6	2.38	106
Co/C@V <sub>2</sub> O <sub>3</sub>	50	1.5	-40.1	1.5	4.64	107
CNT/Co/C	10	2.9	-53.3	1.6	8.02	108
Mo <sub>2</sub> C/Co@C	35	1.7	-47.98	1.6	6.0	109

MOF can also be synthesized with different organic ligands (glucose, 2,5-dihydroxyterephthalic acid and so on) in a more convenient and environment-friendly way. One Composites with multi-dimensional shapes (sheet-, flower-, cube-, dodecahedron- and octahedron-like) from ZIF-67 precursors were fabricated *via* regulating the anion/linker ratio and the solvent. The observed results provide the way to fabricate high-absorbing MAM with controlled morphology. Other similar Co-based MOF derived PC composite materials are listed at Table 2.

Core–shell structure is a significant research direction for MOF-derived microwave absorbers. For example, Ji *et al.* developed novel multi-interfaced yolk–shell Co@NPC@TiO<sub>2</sub>.96 As a typical semiconductor, TiO<sub>2</sub> is widely applied as a supplemental material to optimize impedance matching owing to its strong dielectric loss. In addition, the porous core–shell Co/C@ZnO-decorated rGO was synthesized *via* a facile method, displaying the exceptional microwave absorbency (Fig. 6).97

The MOF-derived PC materials are not only applied as the central core, but also the lightweight carbon shell of the composites. Recently, Liu *et al.* prepared two different types of ZIF to synthesize nano core–shell carbon cages, made up of N-doped carbon inner shell from ZIF-8 and Co/N-doped carbon outer shell from ZIF-67.<sup>78</sup> Derived core–shell composites

exhibited hierarchical porous, high specific surface area and thin thickness, which induced excellent microwave attenuating performance. The strong RL reached -52.5 dB with 25 wt% filler loading of composites, and the EAB of 4.4 GHz with the thickness of 2.2 mm. The results provided a new strategy of carbon nanocages fabrication with tunable chemical composition and the impedance matching. Besides the examples discussed above, other mono-metal/PC composites with excellent microwave absorbing performance are tabulated in following Table 2.

#### 4.3 Multi-metal/PC

The MOF-derived multi-metal/PC composites (with two or more metals embedded in the derived carbon matrix) often show the better absorption performance than mono-metal/PC, due to the multi-metal/PC composites artfully integrating the advantages of multi metals and carbon. Effective doping of other metallic components to compose functional multi-metal MOF is served as a prospective approach. The compositions and the structures can be optimized to achieve efficient microwave attenuation like improving Debye dipole polarization and multiple interface loss.<sup>110,111</sup> The optimizing absorption properties are due to the synergetic effects of the high porous structure and the multiple

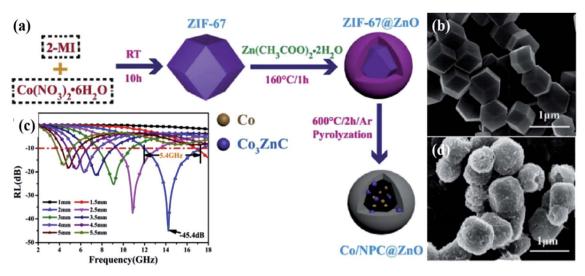


Fig. 6 The scheme for the synthesis of Co/NPC@ZnO/rGO (a), SEM images of ZIF-67 (b) and Co/NPC@ZnO/rGO (d), and the RL of Co/NPC@ZnO/rGO (c). This figure has been adapted from ref. 97 with permission from Journal of alloys and compound, Copyright 2020.

components. This expansion method not only provides interesting references for further studying MOF derived carbon-based lightweight MAM, but also broadens the application of MOF materials.

Nowadays, FeCo particles and their composites derived from MOF have been widely reported as microwave absorbers. For example, Ji *et al.* developed carbon composite with FeCo bimetal nanoparticles embedded *via* pyrolysis process of ZIF-

67.<sup>14</sup> The composites showed a strong RL of -21.7 dB with the thin thickness of only 1.2 mm and a broad EAB of 5.8 GHz (covering from 12.2 GHz to 18 GHz). The saturation magnetization gradually increased with the augment of Fe element content. Compared with pure Co/NPC derived from ZIF-67, Fe-Co/NPC exhibited effectively microwave absorption properties, as showed in Fig. 7.

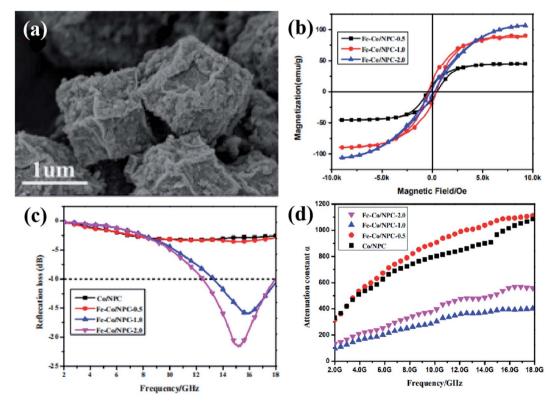


Fig. 7 SEM image of Fe-Co/NPC (a), field-dependent magnetization curve of Fe-Co/NPC (b), the RL (c) and attenuation constant (d) of the Co/NPC, Fe-Co/NPC. This figure has been adapted from ref. 14 with permission from Nanoscale, Copyright 2015.

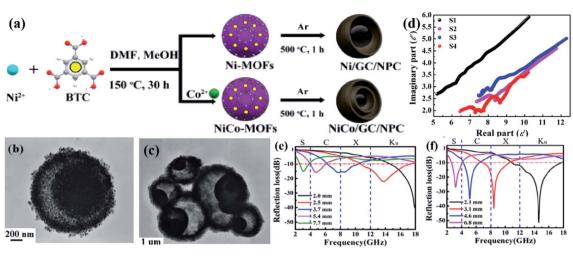


Fig. 8 The schematic formation process of the NiCo/GC/NPC composites (a), TEM images of S1 (b), S4 (c), the Cole–Cole semicircles of S1–S4 (d), the RL with various thicknesses for S1 (e), S4 (f) (S1 represents Ni/GC/NPC, and the content of Co increases from S1 to S4). This figure has been reproduced from ref. 71 with permission from Applied Surface Science, Copyright 2020.

Besides, hollow sphere-like FeCoNi@C absorbers were obtained *via* high-temperature carbonization, which used trimetallic FeCoNi-MOF as the precursor, and more excellent absorption properties are obtained compared with the carbonized mono-metal MOF or bi-metal MOF. Doping with metallic elements can also be achieved through opposite direction, which illustrates the replaceability of similar valence transition metals. Dielectric loss material manganese dioxide (MnO<sub>2</sub>) with flower nanostructures was assembled on the derived CoFe@C nanocube *via* a hydrothermal reaction, giving rise to the improvement of the impedance matching. The Co element was added into the PB nanocube and reduced to Co magnetic metallic nanoparticles at the high annealing temperature. The

CoFe@C@MnO $_2$  achieved a minimum RL of -64 dB and a maximum EAB of 9.2 GHz from 8.8 GHz to 18 GHz with a thickness of 1.3 mm and 1.6 mm, respectively. Yang *et al.* designed NiFe@C nanocubes derived from NiFe PB on the GO nanosheets, having a minimum RL of -51 dB at a thin thickness of 2.8 mm.<sup>114</sup>

Sometimes the doping elements can not only enrich the composition, but also result in a novel structure. Lu and his group designed the MOF derived nanocomposites NiCo/GC/NPC with hierarchical double yolk–shell structure, which were synthesized by regulating Co elements doped into Ni-based MOF.<sup>71</sup> The emergence of yolk–shell could be ascribed to the heterogeneous decomposition induced by Co and Ni

Table 3 The microwave absorbing performance of multi-metal/PC materials

Absorbers	Loading (wt%)	$\mathrm{RL}_{\mathrm{min}}$		EAB		
		Thickness (mm)	Value (dB)	Thickness (mm)	Value (GHz)	Ref.
Fe-Co/NPC	50	1.2	-21.7	1.2	5.8	14
CoFe@C@MnO <sub>2</sub>	50	1.3	-64	1.6	9.2	113
CoFe@C	10	2.8	-61.8	2.8	9.2	117
Solid Fe/Co/C	33	2.0	-54.6	2.5	8.8	118
FeCoNi@C	38	2.1	-64.75	2.47	8.08	112
NiFe/C@GO	40	3.0	-65.5	3.0	4.5	114
CoZn/C/graphene	6	1.5	-47.31	2.2	4.01	2
CoZn/C	40	2.5	-45.2	2.5	5.7	41
CoZn/NPC	30	2.0	-49.0	2.0	5.3	119
CoNi/C-650	30	1.8	-74.7	1.8	15.1	24
Air@NC/Ni-Co	25	2.2	-36.5	2.3	6.55	70
NiCo/GC/NPC	30	2.1	-52.2	2.1	7.2	71
CoNi/C	10	2.0	-61.02	2.0	5.2	115
Ni <sub>0.8</sub> Co <sub>0.2</sub> @C	25	3.5	-39.3	2.0	4.8	116
G/CoNi@NCNTA	10	2.0	-44.23	1.6	4.63	120
CoNi@NG-NCPs	35	3.0	-45.73	2.5	4.32	121
MoW-NC	30	2.8	-55.6	2.8	8.8	122
CoMo@NC	30	2.5	-44.8	2.5	6.56	123

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component, which not only decreases the density of composites, but also facilitates the multiple interfacial polarization (Fig. 8). Similarly, the additional metal Ni was introduced into the derived porous Co/C composites to obtain hollow structure, which yield the RL of -61.02 dB and the EAB of 5.2 GHz.<sup>115</sup> Similarly, Che *et al.* successfully synthesized porous Ni<sub>1-x</sub>-Co<sub>x</sub>@C composites derived from MOF with different Ni, Co millimole content.<sup>116</sup> The generated carbon/alloy particles acted as catalysis to encourage the carbon sp<sup>2</sup> arrangement through the thermal decomposition, forming special micro architecture. Other MOF-derived multi-metal/PC composites mentioned above are tabulated in Table 3.

#### 4.4 Metal oxides/PC

If the obtained derived PC is formed by metal oxides and reduced carbon, it can be categorized as MOF-derived metal oxides/PC composites. The saturation magnetization and the compatible dielectric loss of metal oxides are lower than those of magnetic metal nanoparticles (*e.g.* Fe, Co, Ni and related alloys).<sup>83</sup> However, they have the great chemical stability, characteristic magnetic property and facile manipulation. Some metal oxides like Fe<sub>3</sub>O<sub>4</sub>, have been often served as magnetic promoters for the enhancement of microwave absorbing, and

other non-magnetic metallic oxide (ZnO,  $Co_3O_4$ ) applied to optimize impedance matching. In addition, it is reported that MOF-derived metal or metal oxide particles carbon composites are mainly based on the reduction potential of metal ions at the pyrolysis process. The metal oxides nanoparticles tend to form when the reduction potential of metal ions is lower than -0.27 V. On the contrary, the metal nanoparticles tend to form at a reduction potential higher than -0.27 V.<sup>124</sup>

 ${\rm Fe_3O_4}$  is one of the widely accepted magnetic metal oxide microwave absorbers because of its low cost, chemical stability and high absorption performances. And it exhibits optimized impedance matching after being composed with other materials. Xiang *et al.* obtained magnetic  ${\rm Fe_3O_4@NPC}$  composites through two thermolysis processes with increasing saturation magnetization. The sample exhibited excellent absorbing properties, including a strong RL of -65.5 dB as well as a broad EAB of 4.5 GHz with a matching thickness of 3.0 mm. Similarly, Shu *et al.* compounded MOF-derived  ${\rm Fe_3O_4@C}$  and rGO by solvothermal and pyrolysis. The obtained  ${\rm Fe_3O_4-C/RGO}$  displayed the minimum RL of -60.5 dB with a thickness of 3.6 mm and the EAB of 5.5 GHz with an ultrathin thickness of merely 1.5 mm. Moreover, derived metal oxides can translate into stronger dielectric loss absorbers as the raw materials. Currently, metal

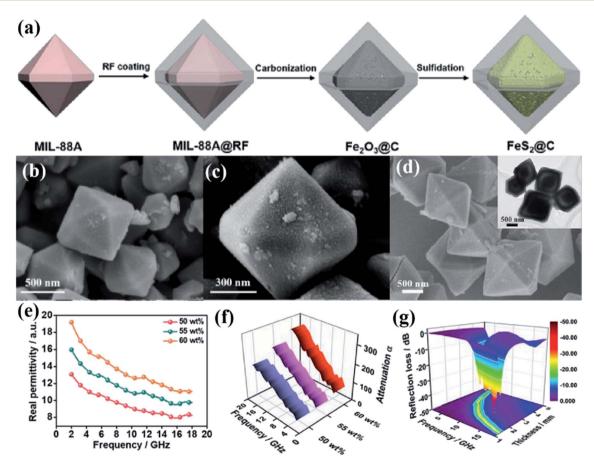


Fig. 9 The schematic formation process of  $FeS_2/C$  composites (a), SEM images of Fe-MOF (b),  $Fe_3O_4/C$  (c), SEM and TEM images of  $FeS_2/C$  (d), the real permittivity (e), attenuation constant (f) and the RL of  $FeS_2/C$  composites (g). This figure has been reproduced from ref. 16 with permission from Nano Letters, Copyright 2020.

Table 4 The microwave absorbing performance of metal oxides/PC materials

Absorbers	Loading (wt%)	$\mathrm{RL}_{\mathrm{min}}$		EAB		
		Thickness (mm)	Value (dB)	Thickness (mm)	Value (GHz)	Ref.
FeS <sub>2</sub> @C	55	1.45	-45	1.2-5.0	15.4	16
Fe <sub>3</sub> O <sub>4</sub> @NPC	40	3.0	-65.5	3.0	9.8	51
Fe <sub>3</sub> O <sub>4</sub> -C/RGO	15	3.6	-60.5	1.5	5.5	98
Fe <sub>3</sub> O <sub>4</sub> /RGO	5	2.2	-67.1	1.8	5.24	131
γ-Fe <sub>2</sub> O <sub>3</sub> /CrGO	50	3.25	-43.13	3.6	11.68	132
Fe <sub>3</sub> O <sub>4</sub> @NC@rGO	25	2.0	-72.6	2.0	5.5	133
ZnO/NPC	40	1.55	-25	_	_	125
ZnO/NPC/RGO	40	2.4	-50.5	2.6	7.4	126
NC-Co <sub>3</sub> O <sub>4</sub> /CP	40	1.6	-41.27	_	_	52
$Co_3O_4/N-C$	40	1.5	-42.63	1.5	4.14	127
ZrO <sub>2</sub> /C	50	1.5	-58.7	_	_	128
TiO <sub>2</sub> /C	60	1.6	-49.6	1.6	4.6	129
CoO/Co/C	25	3.3	-66.7	5.1	1.8	130
Co <sub>3</sub> O <sub>4</sub> @C@α-Fe <sub>2</sub> O <sub>3</sub>	20	3.7	-52.2	2.5	6.6	134
CoO/Co@C	70	1.5	-38.46	2.0	4.8	135
SnO <sub>2</sub> /Co <sub>3</sub> Sn <sub>2</sub> @C	30	2.0	-46.8	2.5	4.8	136

sulfides such as MoS<sub>2</sub>, CdS and CuS develop fast owing to their remarkable RL value. Based on this, Man *et al.* reported a yolk–shell FeS<sub>2</sub>@C nanocomposite for microwave absorption. The MIL nano-spindles were firstly synthesized and then converted to Fe<sub>2</sub>O<sub>3</sub>@C after annealing in N<sub>2</sub> atmosphere. Finally, the FeS<sub>2</sub>@C was obtained *via* a sulfidation process. The asfabricated composites showed excellent absorbing properties having the RL of –45 dB with the matching thickness of 1.45 mm, and the broad bandwidth of 15.4 GHz, as shown in Fig. 9.

It is accepted that nonmagnetic metal oxides can be used to tune impedance matching. For example, Liang et al. designed a hetero-structured ZnO/NPC by using Zn-based MOF ZIF-8 as precursor materials, and the minimum RL achieved -25 dB with merely 1.55 mm of absorber thickness. 125 Similarly, Ji et al. compounded the rGO and ZnO/NPC composites through the simple hydrothermal method.126 Thereinto, the ZnO/NPC were obtained via high-temperature carbonization at 700 °C under N<sub>2</sub> flow. The minimum RL of ZnO/NPC/RGO could reach -50.5 dB with a thin thickness of 2.4 mm. Ji and his group synthesized Co<sub>3</sub>O<sub>4</sub> nanoparticles embedded in the carbon matrix, and the Co<sub>3</sub>O<sub>4</sub> nanoparticles grow on the carbon paper, which exhibited the excellent absorbing properties. The samples showed RL value of -41.38 dB at 7.32 GHz with the absorbing thickness of 2.3 mm.52 Besides, Bai et al. fabricated stratiform Co<sub>3</sub>O<sub>4</sub>/Ndoped carbon using a Co-based MOF as the precursor. 127 The optimal RL of the samples reached -42.63 dB with the thickness of only 1.5 mm. Besides the above metal oxides/PC composites, some similar composites and other certain elements derived materials like ZrO2/C, 128 TiO2/C129 and CoO/ Co/C130 are listed in Table 4.

#### 4.5 Other MOF-derived PC

In addition to those mentioned above, there are some PC composites with other composition, such as rare-earth metal, bimetal oxides and so on. Up to now, the rare-earth metal

organic frameworks (RE-MOFs) for microwave absorption are barely reported. However, RE-MOFs are one of the attractive members of MOFs family in the recent years due to the unique 4f electron layer of RE metal ions. And the highly connected structures of RE-MOFs would induce ultra-high surface areas, resulting in excellent absorbing performance. The et al. synthesized four RE-MOFs by hydrothermal reactions for microwave absorption with synergetic and complementary of permittivity and permeability. The microwave absorption with synergetic and complementary of permittivity and permeability.

Metal and metal oxides encapsulated in MOF-derived PC are generally received more attention. And multiple component composites are significant candidates with high property as microwave absorbers. Xu et al. synthesized flower-like heterogeneous Co/MnO@C, deriving from Co/Mn bimetal oxides MOF derivatives.139 When the molar ratio of Co and MnO reached 2: 1, composites exhibited an optimized RL of -55.3 dB with an absorber thickness of 2.4 mm and the EAB of 4.6 GHz from 7.4 GHz to 12.0 GHz. Moreover, necklace-like CNFs@Co/CoO composites derived from ZIF-67 penetrated throughout the carbon nanofibers were synthesized by simple carbonization process (Fig. 10).140 Attributed to the unique conductive network and the synergistic effect of dielectric loss, magnetic loss and impedance matching, the incident microwaves would be sufficiently absorbed after the multiple reflections, scattering and attenuation. The more similar composites are tabulated in Table 5.

Bimetal oxides are explored to act as microwave absorbers. Bi et al. found the unique polaron excitations-enhanced absorbing properties via synthesizing PC with CoNiO<sub>2</sub> through ZIF-67. This properties effectively improved electron polarization, multiple internal reflections and high RL.<sup>141</sup> In addition, metal sulfides and selenides can be homogeneously dispersed in the derived PC under the appropriate reaction conditions. For example, the CoS<sub>2</sub> was obtained after the carbonization and sulphidation process of Co-MOF precursors.<sup>142</sup> Mao et al.

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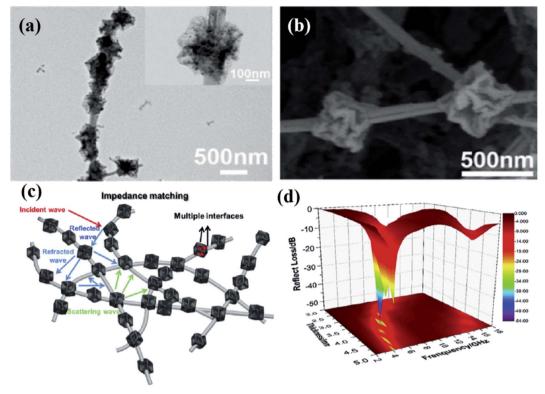


Fig. 10 TEM (a) and SEM (b) images, schematic diagram of microwave absorption mechanisms (c) and the RL (d) of CNFs@Co/CoO composites. This figure has been reproduced from ref. 140 with permission from Journal of Alloys and Compound, Copyright 2018.

Table 5 The microwave absorbing performance of other MOF-derived PC materials

		$\mathrm{RL}_{\mathrm{min}}$		EAB		
Absorbers	Loading (wt%)	Thickness (mm)	Value (dB)	Thickness (mm)	Value (GHz)	Ref.
$[\operatorname{Er}_2(\operatorname{MH})_6]_n$	20	5	-22.78	5	2.24	138
$[Yb_2(MH)_6]_n$	20	4.5	-19.99	4.5	2.12	138
Co/MnO@C	25	2.4	-55.3	2.4	4.6	139
CNFs@Co/CoO	20	3.54	-53.1	2.0-5.0	13.52	140
C/CoNiO <sub>2</sub>	40	2.5	-53	_	_	141
C@NC/CoS <sub>2</sub>	30	2.8	-59.6	2.8	7.2	142
NiSe/C	50	3.7	-59.70	2.1	4.67	143
Co/ZnO/C	30	3.0	-52.6	2.5	5.8	144
Fe/Fe <sub>2</sub> O <sub>3</sub>	30	2.2	-70.2	2.2	5.2	145
Fe <sub>2</sub> N@NC	50	1.55	-59.3	1.9	4.32	146
NiO/Ni/C@Air@NiO/Ni/C	50	1.7	-34.5	1.7	$\sim$ 5.5	147
ZnO/C@Co/C	50	1.9	-28.8	1.9	4.2	148

successfully synthesized rod-like NiSe/C composites *via* the *in situ* selenization of Ni-MOFs with excellent microwave absorption properties.<sup>143</sup> The results and the performance of other MOF-derived PC materials are displayed in the Table 5.

# 5. Summary and conclusions

In the past few decades, MOF-derived PC composites have been increasingly reported for microwave absorption. And the diverse and unique chemical structures (light-weight, specific surface area, chemical stability and high porosity), tunable properties

(electronic conductivity, impedance matching) and facile preparation methods make derived PC composites be sought-after. The varied microstructures and compositions of derived PC are ascribed to the special nature of MOF, and the porosity can be adjusted *via* controlling the carbonization temperatures. These indicate that MOF-derived PC composites are admirable candidates of microwave absorbers.

The synergistic effect between the dielectric loss and the magnetic loss contributes to the efficient and strong attenuation capability, which can be tuned by well designing the constitution of derived PC materials and other microwave

absorbers and adjusting the proportion of effective constituent. Up to now, the MOF-derived PC composited magnetic metals or metal oxides and nano-PC are growing fast, which can overcome the problem of nano-scale particles agglomeration and protect the metal particles from external corrosion. The present of derived carbon skeleton with rich pores establishes the conductive path for electron migrating and hopping, and enhances the interfacial polarization and multiple reflections.

However, there are still some challenges for MOF-derived PC materials to face. For example, the toxic solvents and harsh fabrication condition are generally required in the fabrication process of MOF materials. It is highly desirable to design an environment friendly and facile fabrication strategy to construct MOF materials. The compositions of current absorbers of MOFderived carbon materials are mainly large density metal like Fe, Co and Ni, which have been studied comprehensively in the previous research. However, the chemical composition is much dependent on the corresponding MOF precursors to be tuned, besides, the heavy metal composites often lead to the high filler loading. Thus, it is significant to find novel composite, diverse and lightweight MOF-based PC composites to achieve preferable microwave absorption. In addition, the research progress is almost theoretical stage. The practical applications as microwave absorbers are rarely reported due to the challenge of mass production. Based on this, MOF-derived PC materials are expected to be one of admirable candidates with efficient microwave absorption performance and facile preparation process. With the widespread attentions, MOF-derived PC materials would increasingly promote the advancement of microwave absorption field.

#### **Author contributions**

Ma Mingliang: conceptualization, resources, writing-reviewing and editing Bi Yuxin: conceptualization, investigation, writing-original draft preparation, writing-review and editing Tong Zhouyu: writing-reviewing and investigation Liu Yanyan: editing Lyu Ping: supervision Wang Rongzhen: investigation Ma Yong: writing-review and editing Wu Guanglei: editing Liao Zijian: investigation Chen Yan: investigation.

#### Conflicts of interest

There are no conflicts to declare.

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