Ion-Exchange Strategy for Metal-Organic Frameworks-Derived Composites with Tunable Hollow Porous and Microwave Absorption

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Hollow metal-organic frameworks (MOFs) with careful phase engineering have been considered to be suitable candidates for high-performance microwave absorbents. However, there has been a lack of direct methods tailored to MOFs in this area. Here, a facile and safe Ni$^{2+}$-exchange strategy is proposed to synthesize graphite/CoNi alloy hollow porous composites from Ni$^{2+}$ concentration-dependent etching of Zeolite imidazole frame-67 (ZIF-67) MOF and subsequent thermal field regulation. Such a special combination of hollow structure and carefully selected hybrid phase are with optimized impedance matching and electromagnetic attenuation. Especially, the suitable carrier transport model and the rich polarization site enhance the dielectric loss, while more significant hysteresis loss and more natural resonance increase the magnetic loss. As a result, excellent microwave absorbing (MA) performances of both broadband absorption (7.63 GHz) and high-efficiency loss (~63.79 dB) are obtained. Moreover, the applicability and practicability of the strategy are demonstrated. This work illustrates the unique advantages of ion-exchange strategy in structure design, component optimization, and electromagnetic regulation, providing a new reference for the 5G cause and MA field.

1. Introduction

Electromagnetic pollution has been considered to be one of the major cancers of the 5G revolution. The building of
through the Co-N coordination bond that is easily clipped by protons.\cite{24} If protons originate from the hydrolysis of metal salts, free Co\textsuperscript{2+} ions bind to the trivalent metal ions, forming a 2D host layer by sharing the edge of the octahedron coordinated by hydroxyl. The host layer and interlayer anions, such as NO\textsubscript{3}\textsuperscript{-}, Cl\textsuperscript{-}, and SO\textsubscript{4}\textsuperscript{2-}, are assembled into layered double hydroxides (LDHs) on the surface of MOFs.\cite{25} According to the clipping reaction kinetics of Co-N by protons, the etching of MOFs dominates over the growth of LDHs at excessive proton concentrations, which leads to the collapse of the skeleton.\cite{25,26} Instead, ideal hollowing should be achieved only when both the phases of etching (i.e., Co\textsuperscript{2+} and organic matter dissolution) and growth (i.e., other metal ions entry) reach a synchronous dynamic balance,\cite{27,28} as proved directly by the visualization study of cavity evolution of Wang et al.\cite{29} From the perspective of MA, capturing a certain coexisting state of MOFs/LDHs is a prerequisite to harnessing both the composition and structural advantages at the same time. However, such an etching-growth process is fleeting, flexibly adjusting the clipping reaction power and accurately capturing the transient phase between MOFs-LDHs are the two major technical challenges, which have yet to be properly addressed at present.

Furthermore, given that both MOFs and LDHs need to be annealed at elevated temperatures to induce electromagnetic properties suitable for MA,\cite{30,31} a new metal hybrid phase can be then possibly formed by dissimilar metal ions from metal salts for hydrolysis and metal centers of MOFs, disrupting the charge density distribution and manipulating the carrier migration rate. The charge orientation and local current conduction inherit the internal structure of the precursor (Figure 1c–f). With the introduction of Ni\textsuperscript{2+}, the ratio of ZIF-67-O/CoNi-LDHs can be easily adjusted and controlled, which is proved by the crystal surface trace in XRD (Figure S2, supporting information). With the progress of the etching growth process, the (003), (006), (012), and (110) crystal planes of CoNi-LDHs (PDF#40-0216) become clearer,\cite{26} while the diffraction peak of ZIF-67 decreases continuously until it disappears. After vacuum pyrolysis, the particles inherit the internal structure of the precursor (Figure 1c–f). MOF-O and MOF-O1 are with a solid and yolk-shell structure, respectively, while MOF-O2 and MOF-O3 are both with hollow structures. The rough nanoparticles on the surface cover the skeleton, but the octadecahedral shape can still be observed from the depression of the surface (Figure S3, Supporting Information).

**2. Results and Analysis**

### 2.1. Effect of Ion Exchange Strategy on Structure and Element Composition

The octadecahedral-like ZIF-67 (ZIF-67-O) template was etched by Ni\textsuperscript{2+}, as shown in Figure 1a. In detail, the protons hydrolyzed cut Co-N coordination bonds from outside to inside. In addition, the escaped Co\textsuperscript{2+} is assembled with external Ni\textsuperscript{3+} (Ni\textsuperscript{3+} is oxidized by O\textsubscript{2} and NO\textsubscript{3}-) to form lamellar CoNi-LDHs (Eq S1-S4, Supporting Information). Due to the inhibition of proton clipping power in the ethanol environment, the etching time needs to be prolonged to make CoNi-LDHs fully grow and deposit on the surface of ZIF-67-O. Gradually increase the concentration of Ni\textsuperscript{2+} to promote the dissolution of the core (Figure 1b), making the structure evolve along the solid-yolk shell-hollow path. At the same time, the deposition amount of CoNi-LDHs nanosheets on the surface of the particles is proportional to the concentration of Ni\textsuperscript{2+} (Figure S1a–d, Supporting Information). The ratio of ZIF-67-O/CoNi-LDHs can be easily adjusted and controlled, which is proved by the crystal surface trace in XRD (Figure S2, supporting information). With the progress of the etching growth process, the (003), (006), (012), and (110) crystal planes of CoNi-LDHs (PDF#40-0216) become clearer,\cite{26} while the diffraction peak of ZIF-67 decreases continuously until it disappears.

**Figure** 2a–d presents the high-resolution TEM and element mapping results. The crystal planes of C (002) and Co (111) with a lattice spacing of 0.34 nm and 0.205 nm were observed in MOF-O, respectively. With the introduction of Ni\textsuperscript{2+}, the CoNi crystal planes of (111) appear in MOF-O1 and MOF-O2. After numerous Co\textsuperscript{2+} are replaced, the lattice stripes representing the crystal planes of CoNiO\textsubscript{2} cross each other to obtain an angle of 55.2°, which conforms to the law of angle.\cite{35} The changes in polycrystalline rings and crystal points in all SAED correspond to the changes in lattice stripes. In addition, except for MOF-O, the other three groups of samples all have Ni. Interestingly, the core of MOF-O1 does not have Ni, which proves that the concentration of Ni\textsuperscript{2+} is directly related to the transient stage of the etching-growth process. The element content of the product is shown in Table S2 (Supporting Information). During the etching of ZIF-67, a large amount of organic matter is lost, resulting in the decrease of C (Figure 2e) and N after carbonization. The introduction of OH\textsuperscript{-}, Ni\textsuperscript{3+}, and Co\textsuperscript{2+}, into the growth of CoNi-LDHs, makes the content of carbonized O (Figure 2f), Ni (Figure 2g), and Co increase. From the trend of the variation of element content, the change of MOF-O1 is relatively smaller than that of MOF-O2, while the change of MOF-O3 is significantly large. Once the overgrowth of CoNi-LDHs occurs, the limited carbon content cannot completely reduce it to CoNi, which is not conducive to electrical conductivity and magnetism.
2.2. Effect of Ion Exchange Strategy on Phase Composition and Chemical Properties

The TG curves of the sample are shown in Figure 3a. At 200 °C, the weight of the sample is increased due to metal oxidation, and the more metal content, the more obvious this trend is. When the temperature increases to 800 °C, carbon and nitrogen react with external oxygen to form carbon oxide and nitrogen oxide evaporation, while the weight trend of the remaining metal oxides is consistent with that of Ni²⁺ etching.

The nuances of the crystal structure are identified by XRD, as shown in Figure 3b. For MOF-O, the (002) crystal plane of C and the (111), (200), and (220) crystal plane of Co (PDF#15-0806) appear at the positions of 26.3°, 44.2°, 51.5°, and 75.9°, respectively.[36] For MOF-O1, MOF-O2, and MOF-O3, with the enhancement of Ni²⁺ etching, the diffraction peaks of CoNi alloy become sharper while the peak of C is gradually masked.[37] More importantly, it is found that the three diffraction peaks of CoNi alloy gradually shift to a large angle, which is related to the increase of Ni in the CoNi alloy phase.[38] In addition, obvious CoNiO₂ (PDF#46-1217) diffraction peaks appeared at 36.9°, 42.9°, 62.4°, 74.7°, and 78.7°.[39,40] which were the same as those of TEM.

The valence and bonding of the surface elements were determined by XPS spectra, and obviously, only MOF-O lacks Ni 2p (Figure S4, Supporting Information). The deconvolution results of Co 2p1/2 and Ni 2p3/2 (Figure S5b,c, Supporting Information) show that Ni⁰/Co⁰ increases gradually (Figure 3c), indicating that the content of Ni in the alloy increases. Under the condition of vacuum and high temperature, organic matter and LDHs are pyrolyzed into carbon and metal oxides respectively, while carbon is used as a reducing agent to further reduce metal oxides to metal. This process involves the changes of vacancies formed by atomic evaporation, residual heteroatoms (O, N, H), and dispersed metal particles. As shown in the result of deconvolution of C 1s (Figure S5a, Supporting Information), C-C/C\(^{=}\)C decreases gradually (Figure 3d), while C-O and C\(^{=}\)O increase slowly, which will destroy the long-range order of the carbon atoms network.[41]

In the Raman spectrum (Figure 3e), the D peak at 1340 cm\(^{-1}\) originates from disordered carbon and atomic defects, and the G peak at 1590 cm\(^{-1}\) results from the in-plane stretching vibration of sp² hybrid carbon. The I\(_D\)/I\(_G\) (the degree of graphitization)[42] of MOF-O, MOF-O1, MOF-O2, and MOF-O3 are 0.75, 0.96, 1.06, and 1.16 respectively, which shows a decreasing trend thus indicating that Ni²⁺ etching can bring more defects.

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**Figure 1.** a) Evolution path of the cavity. b) The mechanism of ion etching. TEM images of c) MOF-O, d) MOF-O1, e) MOF-O2, and f) MOF-O3.
Suitable defects help to enhance the defect-induced relaxation polarization,[43] while severely oxidized, such as the NiO characteristic peak in MOF-O3, will be counterproductive.

2.3. Electromagnetic Parameter and Performance

Figure 4a gives the 3D MA performance results of all MOF-Ox at 28 wt.%. Surprisingly, MOF-O2 presents an EAB of 6.45 GHz (from 11 GHz to 17.45 GHz) and a thickness of only 2 mm (Figure 4b). Unfortunately, the lowest reflection loss (RLmin) is only -15.25 dB (a thickness of 2.9 mm). Unexpectedly, MOF-O1 and MOF-O3 do not have qualified MA capabilities in 2–18 GHz. Generally, the interaction process between electromagnetic wave and the material is divided into two stages: electromagnetic wave incidence and electromagnetic wave attenuation, that is, absorbent eats electromagnetic wave and digests it. As shown in Figures 4c,d, MOF-O1 has strong electromagnetic attenuation characteristics, but the reflectivity is too high, while MOF-O3 has good electromagnetic incident characteristics, but cannot digest in time, so neither of them has good MA performance feedback. The drastic change of the complex permittivity is the key factor affecting the incidence and attenuation of electromagnetic waves. With the increase in etching degree, the real permittivity (ε’) of the MOF-Ox increases at first and then decreases (Figure S7a, Supporting Information). Based on the equivalent medium theory and Maxwell-Garnett theory, the dielectric constant of powder/paraffin is closely related to the volume ratio of powder:

**Figure 2.** Lattice stripes, SAED and element mapping of a) MOF-O, b) MOF-O1, c) MOF-O2, and d) MOF-O3. The changes of e) C content, f) O content, and g) Ni content.
Figure 3. a) TG curves and b) XRD patterns. c) The fitting area result Co 2p3/2 and Ni 2p3/2. d) The fitting area result C 1s. e) Raman spectra of MOF-Ox.

Figure 4. a) The MA performance of MOF-Ox at 28 wt.%. b) the RL curves of MOF-O2 at 28 wt.%. c) Reflectivity and d) attenuation constant of MOF-Ox at 28 wt.%. e) Specific surface area of MOF-Ox, e1) mass balance of MOF-O and MOF-O1, e2) the filling model of MOF-O1, MOF-O2, and MOF-O3.
where $\varepsilon_0$ is the dielectric constant of paraffin wax, $\varepsilon_2$ is the dielectric constant of powder, and $P$ is the volume ratio of powder. Under slight Ni$^{2+}$ etching, the content of elements does not change much. However, the appearance of the cavity results in a significant decrease in MOF-O1 density (Figure 4e1) and a higher volume ratio, which can be proved by the suddenly increased specific surface area in Figure 4e (stage I). The lightest properties make MOF-O1 occupy the largest volume ratio, so $\varepsilon''$ increases significantly. At the same time, the toughest filling state undoubtedly provides more paths and choices for carrier migration.[10] The strongest electrical conductivity is reflected in the highest imaginary permittivity ($\varepsilon''$) (Figure S7b, Supporting Information), according to the free electron model:

$$\sigma_0 = \omega\varepsilon_0\varepsilon'' = 2\pi f\varepsilon_0\varepsilon''$$

where $\sigma_0$ is the conductivity, $f$ is the frequency and $\varepsilon_0$ is the vacuum permittivity. The enhancement of current accelerates the conversion of electromagnetic energy into thermal energy, but it also produces a reverse electromagnetic field, which hinders the incidence of external electromagnetic waves. At medium Ni$^{2+}$ concentration, the C content of MOF-O2 is decreased by 15.2 wt.%, while elements of O, Co, and Ni are increased by 16.9 wt.% resulting in a decrease in the intrinsic conductivity of the particles and an increase in density (relative decrease in volume ratio). Consequently, $\varepsilon'$ and $\varepsilon''$ are both decreased. In comparison, at high Ni$^{3+}$ concentration, the C content is decreased by 29.9 wt.%, while elements of O, Co, and Ni are increased by 32.4 wt.%. Even though MOF-O3 is hollow, the massive loss of the C component makes the density of particles increase significantly as the severely reduced specific surface area of Figure 4e (stage II) implies, resulting in a loose filling model. In addition, the strong oxidation further weakens the intrinsic conductivity of MOF-O3 and greatly degrades its electromagnetic attenuation ability. Therefore, under the combined influence of structure and chemical composition, the most coordinated reflectivity and electromagnetic attenuation characteristics promote the excellent MA performance of MOFs-O2 (Figure 4e2).

The pure relaxation model is fitted and updated by the least square method to distinguish the conductance loss contribution ($\varepsilon'''$, which is equivalent to the parallel circuit of resistance and capacitor) and the polarization loss contribution ($\varepsilon''''$, equivalent to the series circuit of resistance and capacitor) [45,46].

$$\varepsilon'' = \varepsilon'_p + \varepsilon''_p = (\varepsilon_1 - \varepsilon_{\infty}) \left(\frac{2\pi f\tau}{1 + (2\pi f\tau)^2}\right) + \frac{\sigma}{2\pi f\varepsilon_0}$$

In Figure 5a, the strength of $\varepsilon'''$ is MOF-O1>MOF-O2>MOF-O3, which is directly determined by their conductivity (Figure 5b). In Figure 5c, the change of $\varepsilon''''$ intensity of samples is similar to that of $\varepsilon'''$. The difference is that the dominant range of $\varepsilon''''$ is in the high-frequency region that contains EAB (11–17.45 GHz), which is an important reason for broadband absorption.

To focus the discussion, the focus is placed on MOF-O and MOF-O2, and the source and change of polarization loss are further explained from the point of view of the structure, composition, defect, and functional group, respectively. From Figure 5d, the surface of MOF-O2 is covered with pores visible to the naked eye, with an average size of 19.9 nm. The mesoporous structure is as lightweight as the hollow structure and the rich surface can provide more hanging bonds to enhance the capture of free charge.[47] At this point, the heterogeneous interfaces (Figure 5e) are similar, such as the CoNi-graphite and graphite-amorphous interfaces. Because of the obvious difference in electronegativity between CoNi and graphite, it is easy to attract a charge and induce charge penetration and migration, resulting in interface polarization loss of electromagnetic energy.[48] It is worth mentioning that the layout of metal ions will affect the continuity of the graphite region. Looking back to the high-temperature reduction process of organic matter, Co$^{2+}$ and Ni$^{3+}$ as reducing agents promote the graphitization of surrounding carbon atoms. Therefore, the areas not covered by metal ions are prone to insufficient graphitization.[49] Discontinuous graphite regions, or amorphous regions, usually have poor electrical conductivity and can even be regarded as defects in the graphite matrix. At the junction of the graphite region and the amorphous region, the boundary effect induces a large number of charge accumulation, rotation, and collision, thus converting electromagnetic energy into thermal energy loss.[50,51] The above interfacial polarization caused by surface and heterogeneous interface is greatly affected by structure and composition, so we consider assigning the Cole-Cole semicircle in the low-frequency region (<10 GHz, and seriously affected by electrical conductivity) to them (Figure S9, Supporting Information). Combined with the frequency of $RL_{min}$ and the coverage frequency of EAB, the strong conductivity loss caused by hollow structure and mesoporous structure masks the effect of polarization. So, we preliminarily determine that the relaxation near 4.3 GHz is incidental to the structure, while the polarization induced by the heterogeneous interface is near 77 GHz. All kinds of defects of MOF-O2 can also be observed in TEM, including oxygen vacancy (point defect), non-coherent crystal plane (plane defect), and dislocation (line defect), among which point defect is the most. As mentioned earlier, the Ni$^{2+}$ etching and growth process cuts out a large amount of organic matter and brings in additional O atoms. A large number of O atoms evaporate during pyrolysis, leaving oxygen vacancies and disturbing the order of graphite. In the results of O1s spectral deconvolution (Figure S10, Supporting Information), the oxygen vacancy content of MOF-O2 is higher than that of MOF-O, which means that the defect-induced polarization is enhanced.[52] It is noted that the peak of MOF-O2 has a blue shift of 0.5 eV, indicating that the defect energy level has changed, which leads to the decrease in the frequency of relaxation from 13.1 GHz to 11.9 GHz. Finally, the fourth Cole-Cole semicircle (Figure S9, Supporting Information) at 15.9 GHz is naturally thought to be caused by residual polar functional groups. As shown in Figure S6 (Supporting Information), the number of C-O and C = O increases significantly, which increases the polarization of the dipole[53] and the larger semicircle radius confirms this reasoning. In a word, in terms of dielectric loss, the hollow structure caused by ion etching, the amplified mesoporous structure, and the change of dielectric/magnetic composition enhances the conductivity loss and polarization loss. In particular, the dipole polarization induced by defects and polar groups makes an
irreplaceable contribution to the wide absorption properties of materials at high frequencies.

Permeability, as another decisive parameter of microwave absorption, also needs to be analyzed in detail. The magnetism of the alloy is mainly due to the spin effect of extranuclear electrons, which is easily affected by structure, dielectric composition, and the proportion of metal atoms. Under a small amount of Ni²⁺ etching, the cavity and decreased carbon matrix weaken the inhibition of the electron spin effect, so that the magnetic saturation (Ms) intensity of MOF-O1 is higher than that of MOF-O. In the later continuous Ni²⁺ etching process, even though the carbon is still decreasing, the increase of Ni (atomic magnetic moment less than Co) content and the oxidation of the alloy make the Ms of the material decrease. As shown in Figure 5g, the Ms values of samples are 38.2, 87, 67.8, and 34.2 emu g⁻¹, respectively. In addition, the coercivity (Hc) of samples are 38.2, 87, 67.8, and 14.9 Oe, respectively, reflecting the changes in magnetocrystalline anisotropy and the amounts of impurities, holes, or defects under the different Ni²⁺ etching degrees. Finally, high Ms and suitable Hc cause the μ’ and μ’’ of MOF-O1 and MOF-O2 larger than those of MOF-O and MOF-O3 (Figure S7d,e, Supporting Information).

Usually, magnetic loss results from dynamic magnetization mechanisms such as natural resonance, exchange resonance, hysteresis loss, eddy current loss, and so on. The eddy current loss factor (C₀ = μ’’(μ’⁻²)⁻¹f⁻¹) is used to analyze the action degree and main frequency range of various magnetic loss mechanisms, such as Figure 5h. The C₀ curve of the sample shows a sharp steep drop in the low-frequency region, and the steep drop slows down along the high-frequency direction, which implies the existence of hysteresis loss. It has been proved that magnetic coupling units (such as Co nanoparticles and CoNi nanoparticles) spontaneously generate magnetic domains to balance random magnetization vectors under strong magnetic fields, resulting in magnetic crystal anisotropy and magnetic pole orientation deflection. When magnetization lags behind the alternating electromagnetic field, hysteresis loss will occur, such as irreversible displacement/rotation of
domain walls, which will consume electromagnetic energy.\(^{[62,63]}\)

From the decreasing trend of the Co curves, MOF-O1 and MOF-O2 have higher hysteresis loss. The representation of formants in the Co curve is attributed to natural resonance (2–5 GHz) and exchange resonance (5–18 GHz) while MOF-O1 and MOF-O2 have stronger and more formants in the natural resonance band. In addition, the magnetic loss mechanism of electromagnetic energy also includes the eddy current loss. However, according to the Co value in the high-frequency region (>10 GHz), it can be inferred that the intensity of eddy current loss does not change obviously.

Based on the above reasoning, we have revealed the source of excellent MA performance of MOF-O2:

I. suitable Ni\(^{2+}\) etching integrates the advantages of structure and composition, adjusts the filling mode, and coordinates impedance matching and electromagnetic attenuation.

II. the cavity and mesopores optimize the carrier transport model and enhance the conductance loss. Abundant heterogeneous interfaces, defects, and polar functional groups enhance interfacial polarization, defect-induced polarization, and dipole polarization, respectively.

III. CoNi alloy shows more obvious hysteretic loss and natural resonance than that of Co alloy, which enhances the magnetic loss.

2.4. Applicability and Practicability of Ion Exchange Strategy

After confirming the unique contribution of the ion-exchange strategy to MA, we try to verify the universality of this strategy. We use water and CTAB to suppress the \(\{100\}\) crystal planes of the precursor and obtain an improved cubic ZIF-67-C (Figure S11, Supporting Information). Then, MOFs etching and LDHs growth were carried out in Ni\(^{2+}\) ethanol solution with the same concentration as the above experiments (Figure S12a,b and Figure S13, Supporting Information). Unlike ZIF-67-O, ZIF-67-C is more sensitive to Ni\(^{2+}\) concentration and requires a more diluted Ni\(^{2+}\) environment to form a yolk-shell structure (Figure S14, Supporting Information). After vacuum pyrolysis at 600 °C, the skeleton of MOF-Cx is well preserved and the hollow structure is obvious (Figure 6a–d; Figure S12e–h, Supporting Information). At the same time, the changing trend of elements, components, physicochemical properties, and electromagnetic parameters of MOF-Cx with Ni\(^{2+}\) etching is consistent with that of ZIF-67-O (Figure S15–S18, Supporting Information). Surprisingly, MOF-C2 got 6.83 GHz (2.01 mm) of EAB at 28 wt.%, covering the entire K-band. As expected, RL\(_{\text{min}}\) still has not made any progress (Figure S19 and S20, Supporting Information). We tried to fine-tune the fill model manually to further improve MA performance. As shown in Figure 6b and Figure S21,S22 (Supporting Information), MOF-O2 and MOF-C2 achieved EAB for 6.95 GHz (2.07 mm) and 763 GHz (2.42 mm) at 24 wt.%. When the filling amount was 20 wt.%, the RL\(_{\text{min}}\) of -36.43 dB and -63.79 dB are obtained for MOF-O2 and MOF-C2 respectively. Even among the micron and nanometer carbon-based absorbents recently derived from MOFs, MOF-O2, and MOF-C2 are very competitive in terms of light-weight, thin thickness, broadband absorption, and strong reflection loss (Figure 6c; Table S4, Supporting Information).

To test the practical value of the ion-exchange strategy, we use CST software to simulate the RSC of a \(300 \times 300 \text{ mm}^2\) coating plate to obtain the real far-field microwave absorption property (Figure 6d). Specifically, 20 wt.% MOF-O2 and MOF-C2 are covered on the surface of the perfectly conductive layer (PEC), and the electromagnetic wave is incident from -60° to 60° at 14 GHz. The 3D radar wave scattering of PEC is very strong (Figure S25, Supporting Information), while MOF-O2 and MOF-C2 are very weak (Figure 6e,f). More precisely, MOF-C2 has almost no scattered signals, indicating that electromagnetic waves are fully absorbed. In the RSC curve (Figure 6f), when the electromagnetic wave is incident vertically, it will cause the maximum reflection, but with the deviation of the incident angle, the RSC value fluctuates and decreases, and the coverage range of MOF-C2 below -10 dB m\(^2\) is wider. Using PEC to subtract the RSC value of the sample, it is found that the radar wave attenuation characteristics of MOF-O2 and MOF-C2 perfectly cover the range of -60° to 60°, and the highest is even more than 30 dB m\(^2\). Due to the strong electromagnetic matching characteristics, MOF-O2 and MOF-C2 can obtain excellent RL\(_{\text{min}}\) at 20 wt.% (Figure 6h; Figure S24, Supporting Information). To sum up, this ion exchange strategy can achieve a strong MA optimization effect and has good applicability. In addition, the absorbent obtained by this strategy has good practicability, which provides a new idea for the design of other MOFs-derived absorbing materials.

3. Conclusion

We successfully designed a simple and safe ion-exchange strategy from the point of view of proton clapping kinetics, which can regulate the MOFs etching-LDHs growth process and capture the transient phase only by changing the Ni\(^{2+}\) concentration. The thermal motion of molecules was stimulated by vacuum high temperature, and the graphite/CoNi composites with optimized structure, components, and electromagnetic properties were obtained. The advantages of this strategy are as follows: 1) Natural porous framework and artificial adjustable cavity improve the carrier transport model and enhance impedance matching and electromagnetic attenuation. 2) A large number of heterogeneous interfaces, defects, and polarity sites are introduced into the ion exchange and reduction process, which enriches and enhances the polarization loss. 3) The hysteretic loss and natural resonance are enhanced, thus increasing the magnetic loss to the electromagnetic wave. 4) Ultra-wideband absorption (7.63 GHz, 24 wt.%) and high efficiency reflection loss (-63.79 dB, 20 wt.%). 5) It is suitable for a variety of MOFs and meets the practical application scenarios. Therefore, this strategy is expected to become a new choice to solve electromagnetic pollution and promote the 5G revolution.

4. Experimental Section

Synthesis of MOF-Ox and MOF-Cx (Take MOF-O1 as an example): 154 mg ZIF-67-O and 108 mg nickel nitrate hexahydrate (Ni(NO\(_3\))\(_2\)·6H\(_2\)O) were dissolved in 40 mL and 10 mL absolute ethanol (Et\(_2\)OH), respectively. Then the Ni\(^{2+}\) solution was rapidly injected into the purple solution and ultrasonic for 2 h. The light purple powder was
obtained by vacuum drying after centrifuging with ethanol 3 times for 12 h. The powder was heated to 600 °C at 2 °C min⁻¹ in an Ar atmosphere and kept for 6 h. After natural cooling, the black powder was obtained, which was marked as MOF-O1. According to the variety of ZIF-67 and the dosage of Ni(NO₃)₂·6H₂O, the powder could be marked as MOF-Oₓ and MOF-Cₓ. The samples obtained by direct calcination of ZIF-67-O and ZIF-67-C were recorded as MOF-O and MOF-C. For specific experimental parameters, see Table S1 (Supporting Information).

**Characterization:** The apparent morphology and structure of the powders were characterized by scanning electron microscopy (SEM, Hitachi, Smur4800) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100F), respectively. Combined with the energy-dispersive X-ray spectroscopy (EDX), the distribution and proportion of elements were obtained. The thermal stability was tested by thermogravimetric analysis (TG). The crystal information of precursors and carbides was obtained by X-ray diffractometer (XRD, D8 Advance). The graphite ordering degree of carbides was characterized by Raman spectroscopy (Raman, Horiba LabRAM HR). The electronic properties of the near-surface elements were studied by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB). N₂ adsorption-desorption isotherms (BET, Micrometrics ASAP 2460) were recorded by chemisorption analyzer, and the specific surface area and pore size distribution were obtained by the Brunauer-Emmett-Teller model and Barrett-Joyner-Halenda method. The static magnetic properties of the powder were measured by a vibrating sample magnetometer (VSM, Quantum, MPMS XL-7). The electromagnetic parameters of the coaxial ring (R_out = 7 mm, R_in = 3.04 mm, d = 1.9 mm) were obtained by a vector network analyzer (VNA, Ceyear, 3672B). The MA properties of the samples in the range of 1–10 mm were deduced by utilizing the following formulas.

\[ RL = 20 \log \left| \frac{Z_m - 1}{Z_m + 1} \right| \]  

\[ Z_m = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left[ \frac{j(2\pi f d / c)}{\sqrt{\mu_r \varepsilon_r}} \right] \]

where Z_m is the normalized input impedance, d is the thickness of the coaxial ring, f is the frequency, \( \varepsilon_r \) and \( \mu_r \) are complex permittivity and complex permeability, respectively.

**RCS Simulation:** A square model of 300 × 300 mm² was established with CST Studio Suite 2019, which contained the absorption layer of 2.6 mm and the perfect conductive layer (PEC) of 1.0 mm. The RCS reduction values of MOF-O₂ and MOF-C₂ were obtained by utilizing the following formulas.

\[ RL = 20 \log \left| \frac{Z_m - 1}{Z_m + 1} \right| \]

\[ Z_m = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left[ \frac{j(2\pi f d / c)}{\sqrt{\mu_r \varepsilon_r}} \right] \]

where Z_m is the normalized input impedance, d is the thickness of the coaxial ring, f is the frequency, \( \varepsilon_r \) and \( \mu_r \) are complex permittivity and complex permeability, respectively.
open boundary condition and selected the monitoring frequency of 14 GHz. The incident angle of the electromagnetic wave was adjusted (−60°−60°), and the value was calculated by $S$ (the area of the simulation model), $\lambda$ (electromagnetic wave wavelength), $E$ (the electric field intensity), and $\varepsilon$ (the incident wave).\(^\text{[64]}\)

$$RSC_{(dBm^2)} = 10\log[(4\pi S / \lambda^3) |E_s / E|]^2$$ \hspace{1cm} (6)

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

hollow structures, ion-exchange strategy, microwave absorption, MOFs, ZIF-67/CoNi-LDHs

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