MOF-derived multi-interface carbon-based composites with enhanced polarization loss and efficient microwave absorption

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ABSTRACT
Metal-organic framework materials (MOFs) have been widely studied because of their adjustable composition and controllable structure in the field of microwave absorption (MA). Therein, Prussian blue analogs (PBA) have attracted the attention of researchers with ultra-high metal content. However, the attenuation ability of microwave for PBA-based composites is still unsatisfactory up to now. Therefore, the NiFe/CoFe@C composites were prepared by carbonizing polymetallic PBA (NiCoFe PBA) materials in this work, and the influence of different metal alloy components on MA was explored by adjusting the ratio of metal ions (Ni$^{2+}$/Co$^{2+}$). Moreover, the NiFe/CoFe@C composites have rich interfaces and enhance the polarization loss due to the introduction of Ni and it has an optimal performance at 2.7 mm that is the reflection loss (RL) is $-41.49$ dB and an effective absorption bandwidth (EAB) is 7.12 GHz with 1/1 (Ni$^{2+}$/Co$^{2+}$). The above data provides a research idea for obtaining light and efficient absorbers.

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1. Introduction

When the information age comes, radar detection technology and electromagnetic radiation pollution have a great impact on national military security and person's health [1,2]. Research shows that, research and application of microwave absorbing materials (MAMs) are the important methods to solve this problem [3,4]. Researchers have explored multifarious MAMs so far, including magnetic materials [5], carbon materials [6], ceramic materials [7], conductive polymers [8], and multi-component composites [9,10]. Among them, the magnetic/carbon composites with both dielectric loss and magnetic loss tend to have good impedance matching characteristics and strong loss capacity. This is conducive to the materials to obtain excellent MA performance, that is, strong absorption, wide band, thin thickness and low density [11–13].

MOFs as promising precursors of carbon matrix composites have the advantages of controllable morphology and adjustable composition [14–16]. Importantly, polymetallic MOFs can be constructed by changing the type of metal and generate metal alloys after pyrolysis, thus enhancing the polarization loss and magnetic loss [17–19]. In addition, because of the periodic arrangement of ligands and metal ions, metal particles are evenly dispersed in carbon after carbonization, which can inhibit agglomeration as much as possible [20–22]. Of these are beneficial to improving the MA performance of absorbers. However, high conductive loss and low magnetic content are disadvantageous to optimizing impedance matching, which are the main problems faced by MOFs derived absorbers [23,24]. Therefore, Prussian blue and its analogues as MOF materials have the advantages of MOF materials. In addition, due to the rich metal ions in the ligand, PBA materials have a high metal content, which makes them have low conductivity and enhanced magnetic loss capacity after carbonization. And it is also an important reason why the materials have attracted the attention of researchers. Therefore, metal alloy/carbon composites with both dielectric loss and magnetic loss and good impedance matching characteristics can be prepared by carbonization at high temperature with PBA as precursor [25,26]. For example, Qiu and coworkers synthesized CoFe PBA by ion exchange method with MnFe PBA as a precursor and designed the structure by adjusting the solvent [27]. It is found that the material with the mesoporous structure has a RL of -73.63 dB at 2.6 mm with an EAB of 5 GHz. Furthermore, Luo and his team obtained fibers with different diameters and pores by electrospinning the mixture of NiFe PBA and polyacrylonitrile [28]. Simultaneously, the interlaced fibers constitute a conductive network, which improves conductive loss and promotes the synergy between multiple loss mechanisms. At 2 mm, the RL can reach up to -39.7 dB and the broadest EAB is 4.6 GHz at an ultra-thin thickness of 1.45 mm. As can be seen from the above, PBA can show good MA performance, and the performance can be improved to some extent by optimizing the morphology and structure. In addition, the regulation of composition is also an important means to enhance the performance of PBA [29,30]. Gao et al. prepared NiCo@C nanocubes by low temperature carbonization using NiCo PBA as a precursor [31]. Subsequently, porous MnO2/Mn3O4@Ni-Co/graphitized carbon composites were fabricated by pyrolysis of NiCo@C materials which were oxidated with KMnO4. It can be observed the dielectric loss and magnetic loss of materials can be improved by introducing additional components. This also proves that the influence of composition on material properties is crucial [32]. Nonetheless,
in most of the articles, the preparation process of materials is very complicated. Meanwhile, there is little exploration of the composition of PBA material itself so far. Therefore, this paper mainly explores the influence of different components on the MA performance. Among them, Fe, Co and Ni, as magnetic materials, are widely used as MAMs due to their excellent magnetic loss ability. In addition, for MOFs prepared with Fe$^{3+}$, Co$^{2+}$ and Ni$^{2+}$ as metal ions, metal alloys can be easily obtained by carbonization using self-sacrificing template method. For these reasons, Fe$^{3+}$, Co$^{2+}$ and Ni$^{2+}$ were selected as metal cations to be studied.

Therefore, in this paper, we fabricated NiCo PBA with different compositions by adjusting the ratio of Ni$^{2+}$/Co$^{2+}$. After carbonization, NiFe/CoFe@C composites were generated and the text detailedly describes their effects on MA performance. It is found the introduction of the Ni element enhances the polarization loss. Meanwhile, it is beneficial to obtain good impedance matching and improve the microwave loss capacity. When Ni$^{2+}$/Co$^{2+}$ is 1/3, the RL value is $-43.6$ dB at 2.8 mm with an EAB of 6.44 GHz. And the maximum EAB is 6.84 GHz with 2.7 mm. When Ni$^{2+}$/Co$^{2+}$ is 1/1, the material has the best performance at 2.7 mm, that is, the RL is $-41.49$ dB and the best EAB is 7.16 GHz. This provides a simple design idea for obtaining efficient absorbers.

2. Experimental section

2.1 Synthesis of NiCoFe PBA precursors

The NiCoFe PBA precursor was synthesized by a simple method. Mainly, 1.2 mmol CoCl$_2$ · 6H$_2$O, 1.2 mmol NiCl$_2$ · 6H$_2$O and 1 g trisodium citrate were added to 80 mL deionized water (DW), and 80 mL aqueous solution with 1.6 mmol potassium ferricyanide was poured into it to form a mixed solution. The solution was left for 24 hours to generate precipitation after continuous stirring for 10 min. The precipitates were then collected and cleaned with DW and ethanol by centrifugation, and dried at 60°C. Finally, NiCoFe PBA was obtained and named PBA-2. In addition, under the same condition, different PBA materials were prepared by changing the Ni$^{2+}$/Co$^{2+}$ ratio to 0/4, 1/3 and 3/1, and labeled as PBA-0, PBA-1 and PBA-3 respectively.

2.2 Synthesis of NiFe/CoFe@C composites

Typically, PBA-0, PBA-1, PBA-2, and PBA-3 were calcined at N$_2$ atmosphere for 2 h at 600°C to form NiFe/CoFe@C composites, called NiFe/CoFe@C-0, NiFe/CoFe@C-1, NiFe/CoFe@C-2, and NiFe/CoFe@C-3, respectively.

3. Results and discussion

Figure 1 shows a brief synthesis process of NiFe/CoFe@C composites. Firstly, NiCo PBA precursors were obtained by coordinating Ni$^{2+}$ and Co$^{2+}$ with Fe (CN)$_6$$^{3-}$. Among them, the citrate anions coordinate with Ni$^{2+}$ and Co$^{2+}$, and then chelate with Fe (CN)$_6$$^{3-}$, which reduces the nucleation rate and is beneficial to the structural integrity of NiCoFe PBA. And the composition was regulated by changing the ratio of Ni$^{2+}$ and Co$^{2+}$. Meanwhile, Ni$^{2+}$ and Co$^{2+}$ are respectively close to Fe$^{3+}$, which forms NiFe and CoFe alloys easily after
carbonization. This also allowed the four PBA precursors to form NiFe/CoFe@C composites with different alloy compositions. Figure 2 shows the SEM images of precursors and NiFe/CoFe@C composites. In general, the PBA precursors have regular morphology and uniform particle size, while the carbonized samples have broken structure and uneven particle size. It can be found that the PBA-0 cubes (Figure 2(a)) have the largest size, with a diameter of about 400 nm. When the Ni$^{2+}$/Co$^{2+}$ ratio is 1/3, the cube size is greatly reduced to about 200 nm in Figure 2(b). With the further increase of Ni content, the size increases to about 300 nm (Figure 2(c,d)). In the SEM figures after heat treatment (Figure 2(e–h)), the cube structures completely disappear and become stacked particles. This is because the NiCoFe PBA precursors have the small size and high metal content, which makes the metal particles polymerize easily after carbonization. So, it is not conducive to maintaining the morphology [33]. Furthermore, many small carbon nanotubes were generated because of the good catalytic effect of NiFe and CoFe alloys on carbon. This is also demonstrated by the TEM diagrams (Figure S1). It can be observed from Figure 2(i) that metal particles are wrapped by carbon, and the oxidation on the surface of metal particles is weakened due to the formation of core-shell structures [34]. The crystal plane spacing of 0.206, 0.212 and 0.34 nm were calculated from the HR-TEM image (Figure 2(j)), which correspond to the (110) crystal planes of CoFe alloy, the (111) crystal planes of NiFe alloy and the (002) crystal planes of carbon. By further analyzing the distribution of different elements in the element mapping diagrams (Figure 2(k–2p)), it can be found that the elements of Fe, Co and Ni are evenly dispersed in carbon with high content.

To better analyze the influence of the different ratios of Ni$^{2+}$/Co$^{2+}$ on the composition of materials, the XRD tests were carried out. In Figure 3(a), the peaks of NiCoFe PBA precursors are sharp and correspond to the standard characteristic peaks of Co$_3$(Fe(CN)$_6$)$_2$·10H$_2$O (JCPDS NO. 00–046-0907) and KNiFe (CN)$_6$ (JCPDS NO. 00–051-1897), which proves the successful synthesis of NiCoFe PBA [35]. In addition, due to the effect of trisodium citrate, a small amount of Fe$^{3+}$ ions were reduced to Fe$^{2+}$. So, PBA-0 also has characteristic peaks corresponding to that of Co$_2$Fe (CN)$_6$·2H$_2$O (JCPDS NO. 00–023-0189) [36]. And the characteristic peaks disappeared after the Ni element was introduced. The XRD pattern of the carbonized materials is shown in Figure 3(b). And the materials have characteristic peaks
of CoFe alloy at 44.8° and 65.3°, which is corresponded to (110) and (200) crystal planes respectively (JCPDS NO. 01-071-5029). And the characteristic peaks of NiFe alloy gradually appear at 43.8°, 51.1° and 75.1° and correspond to (111), (200) and (220) crystal planes (JCPDS NO. 01-071-8322) [29]. When the Ni²⁺/Co²⁺ ratio increases, it can be intuitively found that the peak strength of CoFe alloy gradually decreases, on the contrary, the strength of characteristic peaks for NiFe alloy gradually increases. More importantly, when a small amount of Ni element is introduced, NiFe/CoFe@C-1 has no obvious peaks of NiFe alloy, which is also conducive to dispersing Ni uniformly in the materials. The average sizes of CoFe and NiFe alloys in NiFe/CoFe@C composites were calculated by the Scherer formula ($D = \frac{K\lambda}{\beta\cos\theta}$). The grain sizes of CoFe alloys are 25, 27.6, 29.6 and 24.6 nm, respectively, while those of NiFe alloys are 0, 0, 21.3 and 19.7 nm, respectively. Therefore, it can be found that the metal particle size increases first and decreases on the whole. Furthermore, because no characteristic peak of carbon can be observed, it is proved that the carbon in the materials is mainly amorphous. Raman was characterized to specify the degree of graphitization. Among them, there are wide peaks representing D band (around 1350 cm⁻¹) and G band (around 1580 cm⁻¹), which are derived from the defective graphitized lattice and ideal graphitized lattice of the materials. $I_D/I_G$ was calculated to compare the degree of
graphitization of absorbers, that is, the lower the specific value, the higher the graphitization [37]. Therefore, in Figure 3(c), \(I_D/I_G\) values are 1.05, 1.02, 0.94 and 1.00 with the increase of Ni content, respectively. It proves that the co-action of CoFe and NiFe alloy is beneficial to carbon graphitization, and the graphitization degree is best when the Ni\(^{2+}/Co^{2+}\) ratio is 1/1. However, as the catalytic effect of Ni is weaker than that of Co, the graphitization degree of the materials will be weakened when the content of NiFe alloy increases. VSM is used to explain the static magnetism of materials, which mainly includes saturation magnetization \(M_s\) and coercivity \(H_c\). In Figure 3(d), the \(M_s\) values decrease gradually, which is 120.03, 112.96, 106.18 and 93.27 emu g\(^{-1}\), respectively. It is mainly because the magnetic response of NiFe alloys is weaker than that of CoFe alloys. Similarly, the \(H_c\) has a similar pattern and the values are 748.67, 746.01, 706.54 and 535.38 Oe, respectively. \(H_c\) is mainly related to the size and anisotropy of magnetic components [38]. Generally, the smaller the metal particles and the higher the magnetic crystal anisotropy, the greater the \(H_c\) of the materials. According to the grain size calculated by XRD, there is no great difference on NiFe and CoFe alloys. Therefore, magnetocrystalline anisotropy plays a major role. Compared with Co, the magnetic...
crystal anisotropy of Ni is greatly reduced, being $7 \times 10^6$ erg cm$^{-3}$ and $5 \times 10^4$ erg cm$^{-3}$ respectively [39]. Therefore, when the content of NiFe alloy increases, the magnetocrystalline anisotropy decreases and the $H_c$ decreases.

The composition and chemical bonds of NiFe/CoFe@C composites were analyzed by XPS tests. It can be proved that the materials have C, N, O, Fe, Co and Ni elements from the survey spectrum (Figure 4(a)). The characteristic peak of Ni increases when the Ni content rises, while that of Co decreases. This also corresponds to the metal proportion and the XRD pattern. The high-resolution spectrums of different elements of NiFe/CoFe@C-2 composites are shown in Figure 4(b–f). In the C 1s spectrum (Figure 4(b)), it can be observed that the peaks at 284.60, 285.65, 286.51 and 288.32 eV correspond to C-C, C-N, C-O and C = O, respectively. Four kinds of chemical bonds for N 1s spectrum can be seen in Figure 4(c), namely pyridinic-N (398.33 eV), pyrrolic-N (399.97 eV), graphitic-N (401.04 eV) and oxidized-N (403.94 eV). Meanwhile, these provide polarization sites for the materials and enhance the polarization loss. In Figure 4(d), Fe$^0$ (707.43 eV), Fe$^{2+}$ (710.47 eV) and Fe$^{3+}$ (713.72 eV) mainly exist in the Fe 2p$_{3/2}$ region, and the peaks at 720.15, 721.90 and 724.08 eV can also put down to Fe$^0$ 2p$_{1/2}$, Fe$^{2+}$ 2p$_{1/2}$ and Fe$^{3+}$ 2p$_{1/2}$. Moreover, due to the coexistence of Fe$^{2+}$ and Fe$^{3+}$, the materials have a satellite peak at 718.00 eV [28]. In Figure 4(e), the five main characteristic peaks are attributed to Co$^0$ of 2p$_{3/2}$ (778.40 eV) and 2p$_{1/2}$ (793.30 eV), Co$^{2+}$ of 2p$_{3/2}$ (781.20 eV) and 2p$_{1/2}$ (796.50 eV) and the satellite peaks (786.85 and 805.63 eV) generated by Co$^{2+}$ high spin. Similar to Co 2p spectrum, in the Ni 2p spectrum (Figure 4(f)), 853.50, 870.00, 855.50 and 872.00 eV also have typical characteristic peaks corresponding to Ni$^0$ of 2p$_{3/2}$ and 2p$_{1/2}$ and Ni$^{2+}$ of 2p$_{3/2}$ and 2p$_{1/2}$, respectively. And there are two satellite peaks at 861.50 and 879.10 eV [40]. In addition, metal chemical bond states of composites are compared and analyzed in Figure S2. It is noteworthy that they all show similar characteristic peaks, indicating that the change in metal content does not have much influence on the overall chemical bond.

![Figure 4](image-url)

**Figure 4.** XPS for (a) wide-scan survey of NiFe/CoFe@C composites and (b) C 1s, (c) N 1s, (d) Fe 2p, (e) Co 2p and (f) Ni 2p of NiFe/CoFe@C-2.
states. However, the relative intensity of Co\(^0\) 2p\(_{3/2}\) characteristic peak increases first and then decreases, proving that a small amount of Ni can promote the generation of CoFe alloy. Meanwhile, the relative strength of Ni\(^0\) characteristic peak increases gradually.

The absorption properties are explored by calculating RL values according to the transmission line theory. The specific formulas are shown as follows [41]:

\[
RL = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|
\]

(1)

\[
Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tan h \left[ j \left( \frac{2\pi fd}{c} \right) \sqrt{\frac{\mu_r \varepsilon_r}{\mu_r + \varepsilon_r}} \right]
\]

(2)

here, \(Z_{in}\) is the input impedance, \(Z_0\) denotes the vacuum’s impedance, while \(\mu_r\) and \(\varepsilon_r\) are the complex permeability and complex permittivity. Generally, the frequency range is EAB when RL is less than −10 dB at the same thickness. Meanwhile, when the RL value is smaller and the EAB value is larger, it proves that the material has better properties [42,43]. In addition, the absorption performance of modern practical applications in different environments such as high temperature, intense light, water flow, etc. can also be analyzed [44]. Figure 5(a–h) shows the RL values and 2D RL projection plots of NiFe/CoFe@C composites in 2–18 GHz with the thickness from 1 mm to 5 mm. On the whole, compared with NiFe/CoFe@C-0, the introduction of Ni is helpful to improve the absorption properties. Among them, NiFe/CoFe@C-1 (Figure 5(b,f)) has the best performance at 2.8 mm, that is, the RL value is −43.60 dB and the EAB is 6.44 GHz (10.6 ~ 17.04 GHz). And it has a maximum EAB of 6.84 GHz (11.08 ~ 17.82 GHz) at 2.7 mm. Simultaneously, NiFe/CoFe@C-2 (Figure 5(c,g)) shows an excellent performance at 2.7 mm. It has a RL value of −41.49 dB with 13.76 GHz, while the EAB can be as broad as 7.12 GHz (10.44 ~ 17.60 GHz). In contrast, NiFe/CoFe@C-3 has poor RL (Figure 5(d,h)). Even so, it also has an EAB of 6.7 GHz. The comparison can also be made more intuitively from the 3D RL diagram (Figure S3). Table 1 shows the MA performance of absorbers with PBA as precursors that have been reported so far. The NiFe/CoFe@C composites exhibit the better MA performance at a lower filling amount. This confirms that the optimization of the composition of the material itself contributes to the improvement of performance. As a result, compared with other PBA-derived composites, the materials based on the regulation of composition obtained more excellent MA performance by simple synthesis method, which enhanced the practicability of the absorbers. In addition, the NiFe/CoFe@C composites have a higher metal content than other MOF-derived magnetic-carbon matrix composites, which is conducive to improving the attenuation ability.

The attenuation mechanism of materials is studied by analyzing electromagnetic parameters. Firstly, the introduction of Ni can improve the complex permittivity of materials in Figure 6(a,b). And when the Ni content increases, \(\varepsilon'\) firstly increases and then decreases. Meanwhile, \(\varepsilon''\) shows a similar process. It indicates the occurrence of multiple polarization relaxation processes because the materials have multiple relaxation peaks. The dielectric loss tangent \((\tan \delta_e = \varepsilon''/\varepsilon')\) is used to indicate the dielectric loss capacity [45]. In Figure 6(c), compared with NiFe/CoFe@C-0, the \(\tan \delta_e\) of other composites exhibits better dielectric loss, but decreases with the increase of Ni content. And NiFe/
CoFe@C-2 has a higher loss at 10–14 GHz. The polarization relaxation process of materials was studied by Cole-Cole curves. The specific formula derived from Debye’s theory is shown in Eq. (3) [22]:

\[
\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2
\]

where, \(\varepsilon_s\) represents the static permittivity and \(\varepsilon_\infty\) represents the relative permittivity at infinite frequency. Each Debye semicircle represents a Debye relaxation process. Figure 7(a–d) is the Cole-Cole curves of NiFe/CoFe@C composites. It can be observed that the materials all have multiple Debye semicircles. And the introduction of Ni increases the number of Debye semicircles, which illustrates that the multi-alloy composition can enhance the dielectric loss. Since Debye semicircles are irregular, it is proved that multiple polarization losses coexist. Among them, dipole polarization is caused by C = O and N-containing chemical bonds as the polarization centers and interface polarization arises from the interfaces between NiFe, CoFe, carbon and void. Therefore, NiFe/CoFe@C-1 has better dielectric loss, mainly because of the low content and uniform distribution of Ni in PBA-1, which can generate more interfaces.

### Table 1. The MA performance of NiFe/CoFe@C composites and the absorbers with PBA as precursors.

| Absorbers                  | Precursors                  | RL (dB) (thickness (mm)) | EAB (GHz) (range (GHz), thickness (mm)) | Ratio (%) | Ref.  |
|---------------------------|-----------------------------|--------------------------|-----------------------------------------|-----------|-------|
| NiCo@C                    | NiCo PBA@phenolic resin     | -68.4 (2.14)             | 5.8 (12.2–18, 2)                        | 40        | [46]  |
| FeCo@Carbon               | FeCo PBA@PDA                | -67.8 (1.75)             | 5.3 (10–16.3, 2)                        | 50        | [20]  |
| CoFe alloy/Carbon         | CoFe PBA                    | -57.4 (1.26)             | 4.6 (12.4–17, 1.5)                      | 40        | [33]  |
| CoFe@N-doped C/rGO        | CoFe PBA/GO                 | -53 (2.4)                | 4.48 (12.96–17.44, 1.7)                 | 35        | [47]  |
| CoNi@CNT                  | CoCo PBA                    | -64.01 (3.4)             | 5.73 (1/2)                              | 20        | [48]  |
| PB/MoS₂                   | PB                          | -42.83 (2.1)             | 7.44 (9.82–17.36, 2.4)                  | 40        | [30]  |
| NiFe@C nanocubes@GO       | NiFe PBA@GO                 | -51 (2.8)                | 5.97 (1/2)                              | 30        | [49]  |
| NiFe/CoFe@C-1 NiCoFe@C-1  | NiCoFe PBA                  | -43.6 (2.8)              | 6.84 (11.08–17.92, 2.7)                 | 18        | This work |
| NiFe/CoFe@C-2 NiCoFe@C-1  | NiCoFe PBA                  | -41.49 (2.7)             | 7.16 (10.44–17.6, 2.7)                  | 18        | This work |

Figure 5. RL values and 2D RL projection plots of (a, e) NiFe/CoFe@C-0, (b, f) NiFe/CoFe@C-1, (c, g) NiFe/CoFe@C-2 and (d, h) NiFe/CoFe@C-3.
after carbonization and enhance the interface polarization loss. In addition, the dielectric loss of NiFe/CoFe@C-2 is enhanced due to its optimal graphitization degree.

Figure 6(d,e) illustrates the $\mu'$ and $\mu''$ of NiFe/CoFe@C composites respectively, both of which show a decreasing trend at 2–18 GHz. Due to the low filling amount and similar magnetic content, the $\mu_r$ of four samples does not change much. The magnetic loss tangent ($\tan\delta_\mu = \mu''/\mu'$) denotes the magnetic loss capacity of materials. Because the $\tan\delta_\mu$ (Figure 6(f)) is lower than the $\tan\delta_\varepsilon$, the main loss mechanism of NiFe/CoFe@C composites...
is dielectric loss. Magnetic losses mainly include ferromagnetic resonance and eddy current loss and can be analyzed by calculating eddy current losses as shown in Eq. (4) below [50]:

\[ \mu'' = 2\pi\mu_0(\mu')^2\sigma d^2f/3 \]  

(4)

here, \( \mu_0 \) is the vacuum permeability. When \( C_0 \) (\( C_0 = \mu''(\mu')^{-2}f^{-1} \)) is constant, the main magnetic loss mechanism is eddy current loss. However, it can be observed from Figure 7(e) that eddy current loss isn’t primary. Therefore, due to the interaction between NiFe and CoFe alloy, the materials have stronger natural resonance at the low frequency. And they also have exchange resonance and eddy current losses at 8–18 GHz. In conclusion, the multi-alloy composition is helpful to promote the microwave loss of materials.

Impedance matching and attenuation constant (\( \alpha \)) are two vital factors affecting MA performance. When \( |Z_{in}/Z_0| \) closes to 1, it is proved that the microwaves can enter the absorbers mostly, instead of reflecting off the surface of the materials [51]. Figure 8 reveals the impedance matching projection plots at 2–18 GHz, where the green area indicates that the impedance matching is close to 1. Meanwhile, Figure S4 further illustrates the impedance matching of materials at particular thicknesses. Therefore, it can be concluded

![Figure 8](image-url)
that NiFe/CoFe@C-1 and NiFe/CoFe@C-2 have better impedance matching characteristics. $\alpha$ mainly illustrates the microwave loss capacity of the materials. The corresponding calculation formula is as follows [52]:

$$\alpha = \frac{\sqrt{2\pi f}}{c} \times \sqrt{\left(\mu'_r\varepsilon'_r - \mu'_i\varepsilon'_i\right) + \sqrt{\left(\mu'_r\varepsilon'_r - \mu'_i\varepsilon'_i\right)^2 + \left(\mu'_i\varepsilon'_i + \mu'_i\varepsilon'_i\right)^2}}$$

(5)

In Figure 7(f), the variation of $\alpha$ is consistent with $\tan\delta_\alpha$, that is, NiFe/CoFe@C-1 shows better loss capacity on the whole and NiFe/CoFe@C-2 has higher attenuation at 8–12 GHz. Hence, in combination with the impedance matching diagram, NiFe/CoFe@C - 1 has the good MA in 2–18 GHz. It is mainly because microwaves can enter into the material as far as possible and have a strong attenuation. Meanwhile, the relatively good impedance matching and better attenuation capabilities of NiFe/CoFe@C-2 contribute to the optimal absorption performance at 13.76 GHz. Furthermore, according to a quarter wavelength theory, destructive interference occurs when the difference between the incident electromagnetic wave and the reflected electromagnetic wave is an odd multiple of half a wavelength. The specific formula is as follows [53]:

$$d_m = \frac{nc}{4f_m\sqrt{\varepsilon_r\mu}} \quad (n = 1, 3, 5 \ldots)$$

(6)

It can be observed in Figure S5 that the thickness corresponding to RL and $1/f$ curves of materials is the same at the same frequency. It is also proved that destructive interference of electromagnetic waves can occur in NiFe/CoFe@C composites, which is conducive to the further microwave attenuation.

The MA mechanism of NiFe/CoFe@C composites is described in detail in Figure 9. Firstly, the NiFe alloys are formed due to the introduction of a small amount of Ni, and they are evenly dispersed into the carbon, resulting in more interfaces being generated, which enhances interfacial polarization loss. Then, a large number of defects such as C = O and N-containing functional groups serve as polarization sites in carbon, promoting dipole polarization loss. Moreover, owing to the interaction between NiFe and CoFe

![Figure 9. The possible MA mechanism of NiFe/CoFe@C composites.](image)
alloys, natural resonance, exchange resonance and eddy current loss occur, which improves the magnetic loss capacity. More importantly, the synergy between impedance matching and $\alpha$ enables the materials to have better MA performance. Finally, due to the morphology of small stacked nanoparticles, there are pores between the particles, which is conducive to multiple diffraction of microwaves. At the same time, in the process of continuous attenuation of microwaves, it is inevitable to produce a small amount of scattering due to rough surface. These will prolong the attenuation process and improve the loss ability [54,55].

4. Conclusion

In this work, NiFe/CoFe@C composites derived from NiCoFe PBA precursors were successfully prepared, and the influence of different alloy components on the MA performance was investigated by changing the ratio of Ni$^{2+}$/Co$^{2+}$. The introduction of the Ni element can promote the dielectric loss of materials because the formation of NiFe alloy makes the material have more interfaces, which enhances the interface polarization loss. However, when the content of NiFe alloy exceeds CoFe alloy, the loss ability of materials decreases greatly. In addition, the materials exhibit good impedance matching characteristics and strong attenuation ability because of the synergistic action of dielectric loss and magnetic loss. Hence, the RL and EAB of NiFe/CoFe@C-1 at 13.36 GHz and 2.8 mm are −43.60 dB and 6.44 GHz respectively and the material also has a maximum EAB of 6.84 GHz with 2.7 mm. Furthermore, NiFe/CoFe@C-2 has optimal performance at 13.76 GHz due to its stronger attenuation capability at 10–14 GHz. That is, the RL is −41.49 dB and the ultra-wide EAB is 7.16 GHz with 2.7 mm.

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