ZIF-67 Derived Co-Ni/C Composites for High-Efficiency Broadband Microwave Absorption

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Abstract: The development of broadband and high-efficiency broadband microwave-absorbing materials is one of the keys to resisting electromagnetic radiation and electromagnetic interference. In this paper, we used zeolitic imidazolate framework-67 (ZIF-67) as the template to obtain Ni-doped ZIF-67 via Ni(NO$_3$)$_2$ etching followed by pyrolysis to prepare Co-Ni/C composites successfully. The morphology and microstructure of Co-Ni/C composites can be well-tuned by altering the Ni doping content. ZIF-67-derived Co-Ni/C porous materials exhibit extremely strong microwave absorption performance thanks to dielectric loss, magnetic loss, and the synergistic effect between different components. When the dosage of Ni(NO$_3$)$_2$ used reaches 0.32 g, the obtained composite possesses the optimal absorbing properties with a maximum reflection loss ($RL$) of $-72.88$ dB and an effective bandwidth ($f_e$, representing $RL \leq -10$ dB) of 7.04 GHz (9.76–16.8 GHz) corresponding to a thickness of 2.53 mm. The results of this work indicate that Co-Ni/C composites have potential application value in the field of microwave absorption.

Keywords: microwave absorption; ZIF-67; Ni doping; composite; electromagnetic parameters

1. Introduction

In recent decades, microwave-absorbing materials have attracted increasing interest, for they can convert electromagnetic energy into heat energy, effectively protecting human health, the safety of military facilities, communication signals, etc. [1]. There are many kinds of microwave-absorbing materials, including ferrite materials, metal-based materials, carbon-based materials, ceramic materials, etc. [2]. However, single-component microwave absorbers usually have only a single microwave loss mechanism of magnetic loss (such as magnetic metal) or dielectric loss (such as carbon-based material), which means it is hard for them to satisfy the requirements of microwave absorption. In recent years, metal/carbon composites have aroused extensive research interest as lightweight microwave absorbers because they benefit from the properties of both carbon materials and metal materials, generating magnetic loss and dielectric loss simultaneously.

As a type of functional material, metal–organic frameworks (MOFs) have been utilized in many fields such as adsorption, catalysis, and sensing due to their diverse structures, high specific surface area, high porosity, and ease of fabrication [3]. Meanwhile, the microstructure of MOFs is considered to be an ideal model for microwave-absorbing materials with the advantages of light weight, excellent absorption performance, and ease of fabrication [4,5]. Therefore, the design and preparation of MOF derivatives in the field of microwave absorption is a hot topic.

Zeolitic imidazolate frameworks (ZIFs), as a class of MOFs, are composed of transition-metal cations (M) and imidazole-based ligands (lm). Among them, ZIF-67 has received a lot of attention in the microwave absorption field [6]. Zheng’s group first used ZIF-67 as a precursor to obtain Co/C composite absorbers by high-temperature pyrolysis [7]. They studied the effect of pyrolysis temperature on microwave absorption performance,
indicating the microwave absorber prepared at 500 °C has optimal performance, with a maximum RL of −35.3 dB and a $f_e$ of 5.80 GHz (8.40 GHz–14.20 GHz). Shortly afterward, microwave-absorbing materials obtained by high-temperature pyrolysis using MOFs as precursors aroused great research interest [8–10]. Che et al. constructed shelled ZIF-67 rhombic dodecahedral cages from tannic acid followed by pyrolysis to obtain hollow Co@N-doped carbon nanocages with uniform heterojunction and hierarchical micro-pores. The maximum reflection loss at 2.4 mm is −60.6 dB, and the corresponding $f_e$ at 1.9 mm reaches 5.1 GHz with 10 wt% filler [11]. Yan et al. successfully prepared CoS$_2$/N-doped carbon nanotube composites (CoS$_2$/NCNT) derived from MOF, indicating CoS$_2$/NCNT with 50% loadings exhibits optimal microwave absorption performance, the $f_e$ almost covering the entire X-band with a thickness of only 1.6 mm [12]. However, further improving the microwave absorption performance of ZIF-67-derived microwave-absorbing materials, especially the design and preparation of broadband (>6 GHz) materials, still needs to be further explored.

In recent years, hollow nanostructures have attracted extensive attention owing to their strong microwave absorption properties [13]. On one hand, hollow nanostructures have a large specific surface area, which is conducive to enhancing the impedance matching performance as well as facilitating multiple scattering of electromagnetic waves. On the other hand, hollow nanostructures introduce more defects and polarization centers, thereby increasing the dielectric loss.

Herein, Ni-doped ZIF-67 was prepared by etching nano-cubic ZIF-67 with Ni(NO$_3$)$_2$ followed by high-temperature in-situ pyrolysis in Ar/H$_2$ atmosphere to obtain light-weight and strongly absorbing Co-Ni/C composites as microwave absorbers. Interestingly, the Co-Ni/C composite exhibits extremely strong microwave-absorption properties, with a maximum RL of −72.88 dB and the corresponding $f_e$ reaching 7.04 GHz, indicating it can be used as an excellent microwave absorber in stealth structure design.

2. Experiment and Characterization

2.1. Synthesis of ZIF-67

Co(NO$_3$)$_2$·6H$_2$O (58 mg) and 1 mg cetyltrimethylammonium bromide (CTAB) were added into 2 mL of aqueous solution to form a uniform solution. Then, the mixture was injected into 14 mL of aqueous solution with 908 mg of 2-methylimidazole and vigorously stirred for 20 min. Then, the precipitate yielded was collected by thoroughly washing with absolute alcohol several times before vacuum drying at room temperature overnight.

2.2. Synthesis of Ni-Doped ZIF-67

The as-prepared ZIF-67 nanocubes (0.16 g) were first dispersed in 100 mL of absolute alcohol and then Ni(NO$_3$)$_2$·6H$_2$O with different amounts (0 g, 0.16 g, 0.32 g, 0.64 g) were added into the suspension. After stirring for 20 min, Ni-doped ZIF-67 layered double hydroxides (LDHs) were formed, denoted as Pre-0, Pre-16, Pre-32, and Pre-64, respectively. Then, the products were centrifuged with absolute alcohol several times.

2.3. Synthesis of Co-Ni/C

To obtain Co-Ni/C materials, the as-prepared Ni-doped ZIF-67 was heated at 800 °C for 2 h in an Ar/H$_2$ (95%/5% in volume) atmosphere. The series of products were named S-0, S-16, S-32, and S-64, annealed from Pre-0, Pre-16, Pre-32, and Pre-64, respectively. The whole synthesis process is illustrated in Figure 1.
when the amount of Ni(NO$_3$)$_2$ is 0.16 g, the nanocubes basically maintain the original morphology with slight surface roughness and shrinkage. As the amount of Ni(NO$_3$)$_2$ increases, broken shell cubes are found in Figure 2c, indicating the interior of ZIF-67 has been etched and then turned into hollow cubes, which increase the surface roughness. Surface roughness plays a crucial role in microwave absorption properties since a high surface area provides more active sites for electromagnetic wave reflection and scattering and promotes the repeated absorption process of electromagnetic waves. In addition, a rough surface is more suitable for impedance matching. When the amount of Ni(NO$_3$)$_2$ increased to 0.64 g, the nanocubes were broken, and it was difficult to maintain the original morphology in Figure 2d. The phenomenon mentioned above can be explained as follows: ZIF-67 nanocubes are reacted with Ni(NO$_3$)$_2$ to form Ni-Co LDH on the surface of ZIF-67 nanocubes, while the inner part of ZIF-67 diffuses out of the nanocubes to form ZIF-67@LDH nanoboxes [14].

3.2. Microstructure and Microwave Absorption Properties of Co-Ni/C

Figure 3 exhibits the SEM of Ni-doped ZIF-67 after 800 °C pyrolysis. The surface of the S-0 sample is covered with coiled carbon nanotubes, which is in accord with the research results of Yin et al. [15], indicating the catalytic effect of Co promotes the transformation of carbon in ZIF-67 to carbon nanotubes. When etched by Ni(NO$_3$)$_2$, the carbon source is correspondingly reduced, and only a few short carbon nanotubes are observed as circled in red in Figure 3b,c. When the content of Ni(NO$_3$)$_2$ is further increased, almost no carbon nanotubes are observed, followed by a significant agglomeration in Figure 3d. In general, particle aggregation leads to a decrease in the surface area of the materials and a poor impedance match with the air, which is not conducive to the absorption of electromagnetic waves.
Transmission line theory and metal backplane model were used to calculate $RL$ and corresponding impedance of the test samples, which can be expressed as [16]:

$$RL = 20\log_{10}\left|\frac{Z_1 - Z_0}{Z_1 + Z_0}\right|$$  \hspace{1cm} (1)

$$Z_1 = \sqrt{\mu_1/\varepsilon_1}\tanh[j2\pi f d_1\sqrt{\mu_1\varepsilon_1}/c]$$  \hspace{1cm} (2)

where $Z_0$ is the impedance of free space, $Z_{in}$ is the input impedance of the absorber, and $\varepsilon_1$ and $\mu_1$ are the relative complex permittivity and permeability of the sample, respectively. Additionally, $d_1$ is the thickness of the sample, $f$ is the frequency of the microwave, and $c$ represents the speed of light in free space.

Figure 4 shows the calculated results of the frequency-dependent $RL$ properties of Co-Ni/C composites with variable absorber thicknesses (d) from 1.0 to 5.0 mm. Although all the samples can work as microwave absorbers, their properties are greatly distinguishable. The maximum $RL$ of sample S-0 is $-58.85$ dB (1.84 mm, 13.12 GHz) while the corresponding effective absorption bandwidth is only 3.84 GHz (1.68 mm, 12.72–16.56 GHz), indicating that although strong absorption of microwaves is achieved, the effective absorption bandwidth is relatively narrow. With the increase in the amount of Ni(NO$_3$)$_2$, the $RL$ value of samples can be significantly enhanced, and the maximum $RL$ for S-16, S-32, and S-64 reach up to $-72.88$ dB (2.7 mm, 12.24 GHz), $-68.12$ dB (2.21 mm, 14.24 GHz), and $-59.05$ dB (1.47 mm, 17.28 GHz), with the corresponding $f_e$ reaching 6.08 GHz (2.34 mm, 11.92–18 GHz), 7.04 GHz (2.53 mm, 9.76–16.8 GHz), and 3.68 GHz (1.49 mm, 12.4–16.08 GHz), respectively. The results indicate that tunable microwave absorption performance can be achieved by changing the amount of Ni(NO$_3$)$_2$. 

Figure 2. SEM of ZIF-67 precursor treated with different amounts of Ni(NO$_3$)$_2$: (a) Pre-0, (b) Pre-16, (c) Pre-32, (d) Pre-64.
Figure 3. SEM of Ni-doped ZIF-67 after 800 °C pyrolysis: (a) S-0, (b) S-16, (c) S-32, (d) S-64.

Figure 4. RL of Ni-doped ZIF-67 after 800 °C pyrolysis: (a) S-0, (b) S-16, (c) S-32, (d) S-64.
3.3. Microwave Absorption Mechanism of Co-Ni/C

RL is determined by electromagnetic parameters, which are the key to understanding the electromagnetic properties of materials. Thus, analyzing the relationship between electromagnetic parameters and frequency is helpful for insight into the underlying mechanism of microwave absorption. In the frequency range of 2–18 GHz, the electromagnetic parameters of Co-Ni/C are measured, and the corresponding results are exhibited in Figure 5. The real part ($\epsilon'$ and $\mu'$) represents the ability to store microwave energy, and the corresponding imaginary part ($\epsilon''$ and $\mu''$) represents the ability to consume microwave energy [17]. In Figure 5a, $\epsilon'$ decreases with increasing frequency which can be due to the increased hysteresis effect of the polarized charge. The S-0 and S-64 samples have larger $\epsilon'$ values, indicating the influence of material composition is crucial. According to the free electron theory, the S-0 sample has a high degree of graphitization under the catalysis of Ni, corresponding to a high $\epsilon'$ value [18]. Generally, the dielectric loss of material in the GHz frequency band is attributed to interface polarization, conductivity loss, and dipole polarization [19]. In alternating electromagnetic fields, space charges will accumulate at the heterogeneous interface between different mediums, resulting in interface polarization. The interfaces in Co-Ni/C include the Co-Ni interface, Co-C interface, and Ni-C interface as well as the interface between Co-Ni/C and epoxy resin. The presence of C and N defects in the sample results in an asymmetric distribution of charges, causing dipole polarization [20]. There are two obvious resonance peaks in $\epsilon''$ of the S-32 sample, indicating the existence of two extremely strong polarization processes. According to the analysis above, the two resonance peaks correspond to interface polarization and dipole polarization.

In addition to dielectric loss, the introduction of Ni and Co metal particles also produces a strong magnetic loss. As shown in Figure 5d, the S-64 sample has strong resonance peaks in the low and high-frequency bands, indicating the existence of natural resonance and exchange resonance [21]. The S-64 sample has relatively low carbon content as well as high Ni content, and thus exhibits enhanced magnetic loss, which is exhibited in Figure 5f. The microwave absorption performance is determined by two factors. One is the ability of the material to absorb microwaves, which is defined as impedance matching ($|Z_{\text{in}}/Z_0|$), and the other is the ability to attenuate microwave energy [22]. Generally speaking, the intrinsic dielectric and magnetic properties affect microwave absorption efficiency. To further evaluate the microwave absorption efficiency of materials, the attenuation constant $\alpha$ and impedance matching property were analyzed. Attenuation constant $\alpha$ can be expressed by the following equation [23]:

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

Figure 6a exhibits the impedance matching property of Co-Ni/C, indicating the impedance matching of S-16 and S-32 samples are relatively optimal and more microwave incident into the material. Figure 6b exhibits the attenuation constant of Co-Ni/C, indicating the S-64 sample possesses the strongest attenuation capability. Generally speaking, when $|Z_{\text{in}}/Z_0|$ equals 1, electromagnetic waves enter the material and are not reflected at the interface. Considering both impedance matching and attenuation, S-16 and S-32 have the optimal microwave absorption efficiency. On the one hand, the unique microstructure and adjustable electrical properties of Co-Ni/C contribute to impedance matching. On the other hand, metal/carbon composites have both magnetic and dielectric loss mechanisms to effectively consume incidence microwave energy. Table 1 compares the microwave absorption efficiency of prepared Co-Ni/C in this work with other reported MOF derivatives, indicating the absorber prepared in this work has excellent microwave absorption efficiency.
Figure 5. Electromagnetic parameters of Co-Ni/C: (a,b) real and imaginary part of permittivity, (c,d) real and imaginary part of permeability, (e,f) dielectric and magnetic loss tangent.

Figure 6. Impedance matching (a) and attenuation constant (b) of Co-Ni/C composites.
Table 1. Comparison of microwave absorption properties of microwave absorbers in this work with other reported MOF-derived microwave absorbers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorber Thickness (mm)</th>
<th>$RL_{\text{max}}$ (dB)</th>
<th>Effective Bandwidth (GHz)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/C-800</td>
<td>2</td>
<td>−32.4</td>
<td>3.8 (10.7–14.3)</td>
<td>[24]</td>
</tr>
<tr>
<td>Co/NPC@Void@Cl</td>
<td>2.2</td>
<td>−49.2</td>
<td>6.72 (10.56–17.28)</td>
<td>[23]</td>
</tr>
<tr>
<td>CoS$_2$/NCNTs</td>
<td>2.5</td>
<td>−35</td>
<td>4.5 (5.5–10)</td>
<td>[12]</td>
</tr>
<tr>
<td>Co/C-HS-600</td>
<td>2</td>
<td>−31.3</td>
<td>4.4 (11.0–15.4)</td>
<td>[26]</td>
</tr>
<tr>
<td>Fe$_2$P$<em>4$O$</em>{12}$/phosphorus-doped carbon</td>
<td>2.1</td>
<td>−67.6</td>
<td>5.76 (12.24–18)</td>
<td>[16]</td>
</tr>
<tr>
<td>CoNi@NG-NCP</td>
<td>2.5</td>
<td>−24.03</td>
<td>4.32</td>
<td>[13]</td>
</tr>
<tr>
<td>S-16</td>
<td>2.7</td>
<td>−72.88</td>
<td>6.08 (11.92–18)</td>
<td>This work</td>
</tr>
<tr>
<td>S-32</td>
<td>2.21</td>
<td>−68.12</td>
<td>7.04 (9.76–16.8)</td>
<td>This work</td>
</tr>
</tbody>
</table>

4. Conclusions

In this paper, we synthesized a nano-porous Co-Ni/C composite using nano-cubic ZIF-67. After being etched by Ni(NO$_3$)$_2$ and in situ pyrolysis at 800 °C in Ar/H$_2$ atmosphere, lightweight, high-efficiency Co-Ni/C microwave absorbers were prepared. Interestingly, the Co-Ni/C composites exhibited extremely strong microwave absorption efficiency, with a $RL$ value of $-72.88$ dB and, more importantly, a $f_r$ reaching 7.04 GHz, indicating Co-Ni/C prepared in this work can be used as a high-efficiency broadband microwave absorber in stealth structure design.

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References

20. Liu, J.; Meng, C.; Liu, Q.; Li, N.; Yu, R.; Zeng, M. Fire-resistant Iron-Based Phosphates/Phosphorus-Doped Carbon Composites Derived from Phytic Acid-Treated Metal Organic Frameworks as High-Efficiency Microwave Absorbers. *Carbon* 2022, 200, 472–482. [CrossRef]  