Fe-based material@N-doped carbon composites as environment-friendly microwave absorbers

Qingwei Liu, Min Zeng*, Jue liu*, Baiyu Guo, Xiaozhu Hao, Qian Cao, Yuchen Shang, Xin Sun, Jinzhang Liu, Xuexu Gao, jiheng Li, Jie zhu, Xixiang Zhang, Ronghai Yu*

aSchool of Materials Science and Engineering, Beihang University, Beijing 100191, China.

bState Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China.

cPhysical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 239556900, Saudi Arabia

*Corresponding authors:
E-mail: min_zeng@buaa.edu.cn (Min Zeng); jueliu1992@163.com (Jue Liu); rhyu@buaa.edu.cn (Ronghai Yu)
ABSTRACT:

Environment-friendly Fe-based material@N-doped carbon nanoparticles imbedded in polylactic acid (PLA) matrix are prepared and applied in microwave absorption field. In the synthesis process, polydopamine (PDA) in the precursor could rationally regulate the phases of the iron-based particles and carbon contents. It turns out that optimizing the chemical composition plays a vital role in modulating microwave absorption performance. For instance, the maximum reflection loss ($R_{L\text{max}}$) for Fe@N-doped carbon particles (S-120) reaches $-61.6$ dB (12.56 GHz, 2.1 mm), and the effective bandwidth is 4.48 GHz (from 13.52 GHz to 18 GHz) with a thickness of only 1.7 mm. The excellent microwave absorption performance could be attributed to perfect impedance matching brought by the synergies of multiple components. Moreover, the microwave absorbers display not only high microwave absorption performance but also environment-friendly characteristics that can avoid leaving stubborn waste after failure. The preparation process of the composite is pollution-free and the PLA in the composite can almost be naturally degraded within one month under simulated marine environment. This work may provide a new perspective on preparing high-efficient functional materials which are also harmless to the environment.

**Keywords**: Fe-based material@N-doped carbon, polylactic acid, microwave absorption, reflection loss, environment-friendly.
1. Introduction

With the rapid development and wide application of high-frequency electronic equipment, the emission and interaction of electromagnetic wave become more and more serious in the environment[1]. These electromagnetic radiation can be attenuated by absorbing agents with strong reflection loss (RL) and broad absorption bandwidth[2], such as carbon[3, 4], magnetic metals[5], ferrites[6], and multi-absorbers[7] etc. Among them, Fe/Fe-based oxides as one kind of the magnetic materials have gained much attention due to strong magnetic response, simple preparation, good compatibility and nontoxicity, which make them hold promise in microwave shielding application[8].

Generally, dielectric loss and magnetic loss are believed to contribute to the microwave absorption. However, like most single-phase materials, the impedance matching between Fe/Fe-based oxides and free space is often inferior, easily leading to uncompetitive absorption capacity. The balanced dielectric and magnetic properties may improve impedance matching characteristics and give rise to the microwave absorption[9]. Therefore, combining dielectric materials with magnetic ones is a strategy to obtain strong microwave absorption. Some researchers have incorporated carbon into Fe-based materials to induce considerable dielectric loss, and thus achieve good impedance matching through the synergistic effect between multiple components[10]. Besides, introduction of carbon can modify the agglomeration of nano-sized particles and enhance the stability of the composites in service.

Recently, polydopamine (PDA) used in multilayer particle preparation as a carbon
source has attracted tremendous interest[11, 12]. It can be easily coated on almost all kinds of surfaces and form nano-sized films through self-polymerization of dopamine (DA) [13, 14]. Even after the polymerization process, there may still retain some active groups that helps modify the surface structures of the micro/nano-sized materials[15]. And the carbon, derived from PDA, demonstrates comparable dielectric property with polycrystalline graphite, which is very helpful in enhancing dielectric loss and modulating impedance matching, and thus leading to a stronger microwave absorption[16]. For instance, Ma et al. prepared 1D flower-like ZnFe₂O₄@SiO₂@C@NiCo₂O₄ nanochains with carbon derived from PDA, achieving a strong reflection loss of $-54.29$ dB (2.39 mm)[17].

Meanwhile, there is another issue about green production that needs to be addressed. For functional materials, they should not only meet the requirements of application performance, but also meet the needs of environmental protection to support the sustainable development of human society. As far as we know, microwave absorbers generally involve fillers, which should have good absorption properties and matrixes, which usually play dominated role on attaching fillers. It is found that many of the reported preparation processes of fillers tend to produce pollution and have harmful effects on the environment[12, 18, 19]. Moreover, many traditional matrixes including epoxy[20], polycaprolactone[21], polyvinylidene fluoride[22], and silicone rubber[23], may also cause pollution to the environment due to the toxic raw materials and nondegradable final products, leaving a lot of waste behind[24]. It is urgent to prepare an environment-friendly filler and find an appropriate matrix which could be obtained
greenly and decomposed naturally after failure.

In view of the above considerations, we intend to develop a high-efficient microwave absorber with non-toxic filler and naturally degradable matrix from harmless preparation, with a desire to arouse people's environmental awareness. Herein, the filler, Fe-based material@N-doped carbon derived from Fe$_2$O$_3$@PDA, is obtained via an environment-friendly synthesis. For the matrix, we have noted that polylactic acid (PLA) holds promise due to the plant feedstock origination and naturally degradable property[25]. In addition, PLA can be well machined to meet the structural demands when used in variable circumstances[26]. Thus, incorporation Fe-based material@N-doped carbon with PLA matrix provides a strategy to realize highly efficient microwave absorption and avoid additional environmental pollution.

2. Experimental section

2.1. Materials

Analytical iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) and dopamine hydrochloride (C$_8$H$_{11}$NO$_2$·HCl) were obtained from Macklin biochemical (Shanghai, China). Analytical urea (H$_2$NCONH$_2$), ethanol (C$_2$H$_5$OH) and tris-base (C$_4$H$_{11}$NO$_3$) were obtained from Xilong scientific (Guangdong, China), Beijing Chemical (Beijing, China) and Aladdin biochemical (Shanghai, China). Polylactic acid (molecular weight, ~20000) was obtained from Jinan Daigang biomaterial (Shandong, China).

2.2. Synthesis

2.2.1. Precursors

1 mmol of Fe(NO$_3$)$_3$·9H$_2$O and 5 mmol of urea were dissolved in 36 mL deionized
water. Then, the solution was transferred into a 50 mL Teflon-lined autoclave. The autoclave was sealed, maintained at 120 °C for 12 h, and then naturally cooled. The red precipitate, denoted as Pre-0, was collected, washed, and dried. To obtain other precursors, 50 mg of Pre-0 was dispersed in 80 mL Tris-base buffer solution (pH=8.5) ultrasonically, then DA with different amounts (80 mg, 120 mg, and 160 mg, respectively) were added into the solution and stirred for extra 5 hours, forming particles named as Pre-80, Pre-120, and Pre-160, respectively. Afterwards, the precursors were washed and dried.

2.2.2. Fe-based material@N-doped carbon particles

To obtain Fe-based material@N-doped carbon structures, the as-prepared precursors were heated at 600 °C for 2 hours with a heating rate of 2 °C/min in N₂ atmosphere. The series of products are named as S-0, S-80, S-120, and S-160, annealed from Pre-0, Pre-80, Pre-120, and Pre-160, respectively. Detailed preparation process is depicted in Fig. 1.
2.3. Characterization

The samples were characterized with a series of equipment and instruments. The crystal structures were obtained with an X-ray diffraction (XRD, D/MAX-2500, Rigaku). Mossbauer spectrometer (wissel, Germany) was used to identify the phase structure of samples S-0 with 57Co(Pd) radiative source at room temperature. Thermogravimetric (TG) experiments were carried out using thermal gravimetric analyzer (209F3, Netzsch, Germany) in air atmosphere from room temperature to 800°C. Raman spectrometer (LabRam ARAMIS; HORIBA) was used to record the Raman spectra. Surface morphologies were observed with scanning electron microscopy (SEM, JSM 7500, JEOL). Detailed microstructures were investigated with a transmission electron microscopy (TEM, TF30, FEI). The surface valance status was measured with an X-ray photoelectron spectroscopy (XPS, Axis Supra, Kratos). The saturation magnetization was obtained via a vibrating sample magnetometer (VSM, 7404, Lake Shore). The dynamic electromagnetic performance was calculated with complex permittivity and complex permeability, which were obtained with a vector network analyzer (VNA, N5234A, Agilent). For this test, the as-prepared sample was mixed with PLA following a typical process as follows: 50 mg of Fe-based material@N-doped carbon powder was ultrasonically dispersed in 50 mL acetone, and then 50 mg of PLA was added, which was placed for 12 hours to evaporate acetone. Then the obtained composites were pressed into circle rings suitable for VNA testing. For the accelerating degradation test, the used absorber was immersed into sea water and maintained at 50 °C.
for days and months.

3. Results and discussion

3.1. Characterization of Fe-based material@N-doped carbon

Fig. S1 shows the crystal structures of precursors and the diffraction peaks are well indexed to Fe₂O₃ phase (JCPDS No. 87–1166). The resulting products are obtained through annealing treatments with XRD patterns shown in Fig. 2a. For S-0, the peaks at 18.5°, 30.2°, 35.6°, 37.3°, 43.3°, 53.6°, 57.1°, and 62.7° are observed and could belong to cubic Fe₃O₄ phase (JCPDS No. 89–0691). However, the similarity of the XRD patterns for γ-Fe₂O₃ and Fe₃O₄ makes it hard to identify the crystal structure only by XRD. Therefore, to further investigate the phase configuration, Mössbauer spectrum was adopted and fitted with least square method. It is observed that two sextets, ascribed to tetrahedral A and octahedral B sites, exist in the spectrum (Fig. 2b).[27] And the corresponding hyperfine parameters, ie, hyperfine magnetic field (B_{hf}), isomer shift (IS), quadrupole shift (QS), width, and area fraction (AF), are shown in Table 1. For one sextet (the red line), the IS and B_{hf} values are 0.31 mm/s and 49.5 T, demonstrating the presence of tetrahedral Fe³⁺. And the Fe³⁺ percentage is 48%. [27] Another sextet (the blue line) with IS and B_{hf} values of 0.66 mm/s and 46.1 T is ascribed to octahedral Fe².5⁺ and the relative percentage is 56%. [27] The ratio of the two sextets is close to 1:1, suggesting the component of S-0 is Fe₃O₄ combined with the XRD pattern. This means that the precursor, Fe₂O₃, is totally transformed to Fe₃O₄. For S-80, two more peaks at 36.3° and 42.2° appear besides peaks indexed to cubic Fe₃O₄ phase, indicating the existence of cubic ferrous oxide (Fe₀.942O phase, JCPDS No. 73–2144). And with
the assistance of Rietveld method, the mass ratio between Fe$_{0.942}$O and Fe$_3$O$_4$ in S-80 is identified as 60:40 (Fig. S2). The coexisting of Fe$_3$O$_4$ and Fe$_{0.942}$O results from the reduction effect of carbon under nitrogen atmosphere[28]. For S-120 and S-160, all peaks of Fe$_3$O$_4$ and Fe$_{0.942}$O disappear and peaks corresponding to cubic Fe phase (JCPDS No. 89–7194) dominate, suggesting the thorough contribution of carbon reduction. To further specify the carbon contents in the samples, TG curves are obtained and shown in Fig. 2c. The weight increases by 2.9% in S-0 mainly due to the phase change from Fe$_3$O$_4$ to Fe$_2$O$_3$. For S-80, the weight loss reaches 14.5%. Further calculation demonstrates that 21% carbon (mass percentage) exists, thus Fe$_{0.942}$O: Fe$_3$O$_4$: C (mass ratio) equals 47:32:21. Since carbon loss and Fe oxidation happen in S-120 and S-160, the weight decreases and then increases in TG curves. The variation magnitudes are 24.1% and 5.8%, respectively, for S-120 and S-160. Through calculation, the corresponding mass ratios of Fe and C are 51:49 and 44:56. These results illustrate that the constituents of Fe-based material@N-doped carbon particles can be rationally controlled by PDA in the precursors, thus modulates the intrinsic dielectric and magnetic properties of the samples.

Since carbon affects the dielectric property remarkably, Raman spectrometer is used to investigate the defects and carbon species derived from PDA in different samples with the corresponding spectra shown in Fig. 2d. For S-0, the broaden peak at ~1400 cm$^{-1}$ could be related to carboxyl group originated from urea in the synthesis process[29]. S-80, S-120 and S-160 exhibit two characteristic peaks located at ~1340 cm$^{-1}$ and ~1580 cm$^{-1}$, corresponding to D-band and G-band, respectively[30]. The D-band is generated
by defective carbon, while G-band represents the existence of graphitic layers[31, 32]. Generally, for carbon-based materials, the graphitization degree is negatively correlated with $I_D/I_G$ (intensity ratio)[33]. The values of $I_D/I_G$ are 1.45, 0.82, and 1.02 for S-80, S-120 and S-160, respectively. It is obvious that S-120 and S-160 possess higher graphitization degree due to Fe acting as a catalyst to generate graphitic carbon from PDA[34]. And S-160 has a declined $I_D/I_G$ value compared with S-120, which might be ascribed to increasing defective carbon brought by more PDA. Overall, S-120 possesses the highest graphitization degree, which may contribute to the conduction loss[32].

![Fig. 2](image_url)

**Fig. 2.** (a) XRD patterns (●, ◆, and ♦ represent cubic Fe$_3$O$_4$, cubic Fe$_{0.942}$O, and cubic Fe, respectively) for S-0, S-80, S-120, and S-160, (b) Mössbauer spectrum of S-0, (c) TG curves, and (d) Raman spectra for S-0, S-80, S-120 and S-160, respectively.
Table 1. The hyperfine parameters of Mössbauer spectrum for S-0.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>A-site</th>
<th>B-site</th>
</tr>
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<tbody>
<tr>
<td>IS (mm/s)</td>
<td>0.31</td>
<td>0.66</td>
</tr>
<tr>
<td>B_H (T)</td>
<td>49.5</td>
<td>46.1</td>
</tr>
<tr>
<td>QS (mm/s)</td>
<td>−0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Width (mm/s)</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td>AF (%)</td>
<td>48</td>
<td>56</td>
</tr>
</tbody>
</table>

The surface morphologies of the precursors and annealing products are obtained with SEM. Fig. S3 shows that the precursors are spherical with average sizes of about 100 nm. After calcination, the morphologies of the as-prepared products (S-0, S-80, S-120, S-160, sequentially) are shown in Fig. 3a-d, which are inherited from the precursors. It can be observed that the particle size increases slightly and the surface becomes rougher with the increasing content of PDA in precursor. Typically, for S-160, the particles agglomerate obviously due to excess carbon coating.

Insight study of the microstructures is conducted with S-120. Fig. 3e reveals the uniform distribution of Fe particles in the carbon matrix. The magnified image (Fig. 3f) demonstrates that a carbon layer (~5 nm) coats Fe particles evenly. High resolution image (Fig. 3g) indicates the existence of Fe, graphitic carbon and amorphous carbon. The two obvious lattice fringes with the spacing of 0.325 nm and 0.205 nm correspond to the (002) and (110) lattice planes for graphitic carbon and Fe particles, respectively. This crystal lattice structures are consistent with the XRD results.
Fig. 3. SEM images of (a) S-0, (b) S-80, (c) S-120, (d) S-160, (e, f) TEM and (g) HRTEM images of S-120.

(A 2-column fitting image)

S-120 is also selected for the surface elemental status analysis by XPS and the corresponding spectra are shown in Fig. 4. The existence of Fe, O, C, N elements are identified in the survey spectrum (Fig. 4a). In Fe 2p spectrum (Fig. 4b), the existence of Fe\textsubscript{0} is proved by peak at 707.1 eV, while peaks at 711.2 eV and 724.4 eV correspond
to Fe$_{2+}$, and those peaks at 715.3 eV, 719.9 eV, and 728.9 eV belong to Fe$_{3+}$[35]. The existence of Fe$_{2+}$ and Fe$_{3+}$ can be attributed to surface oxidation, which is also reported by Yu et al[36]. For O 1s, the spectrum can be deconvoluted into four peaks at 530.1 eV, 531.7 eV, 532.8 eV, and 533.6 eV, attributed to Fe–O, C=O, C–O, and the adsorbed water, respectively (Fig. 4c)[37]. In Fig. 4d, the spectrum of C 1s reveals the information of carbon functional groups. The deconvoluted three peaks at 284.8 eV, 285.3 eV, and 288.5 eV are assigned to C–C, C–N, and C=O, respectively[38], indicating nitrogen doping into S-120. And the high peak intensity of C–C implies that graphitic carbon is the main species, which is in accordance with Raman spectra.

Fig. S4 shows the hysteresis loops of Fe-based material@N-doped carbon. The saturation magnetization ($M_s$) values of S-0, S-80, S-120 and S-160 are 88.7, 36.0, 210.7, and 43.5 emu/g, respectively, demonstrating that all of the samples are ferromagnetic and S-120 has the strongest magnetization property. The decrease of $M_s$ from S-0 to S-80 can be explained by the existence of non-magnetic Fe$_{0.942}$O and carbon, while the enhanced $M_s$ for S-120 is due to the appearance of pure iron phase with stronger magnetization. However, S-160 possesses a declined $M_s$ value attributed to the presence of more carbon derived from PDA, although it also contains pure iron phase.
Fig. 4. XPS spectra of (a) survey, (b) Fe 2p, (c) O 1s, and (d) C 1s, respectively.

(A single fitting image)

3.2. Microwave absorption performance

Generally, the dielectric and magnetic properties of absorbers work together to affect the microwave absorption properties. The complex permittivities are shown in Fig. 5a, b. In the range of 2–18 GHz, the real part, $\varepsilon'$, of S-0 demonstrates little fluctuation between 7.35–8.82, close to the results reported by Li et al[39]. And S-80 possesses similar $\varepsilon'$ values with S-0 in most frequency ranges. S-120 presents $\varepsilon'$ values ranging from 9.35–10.86 and S-160 shows a higher value of 12.00 at 2 GHz and decreases to 7.16 at 18 GHz. As mentioned above, the crystal configurations could be rationally controlled with the introduction of DA in the synthesis process. S-0 is constituted with
pure Fe$_3$O$_4$. Smaller amount of DA makes the crystal structure of S-80 turn from pure Fe$_3$O$_4$ to mixed-phases of Fe$_3$O$_4$, Fe$_{0.942}$O, and carbon. The comparable $\varepsilon'$ of S-80 with that of S-0 might be explained as follows: on one hand, carbon derived from PDA helps enhance the conductivity; on the other hand, excess interfaces among Fe$_3$O$_4$, Fe$_{0.942}$O and carbon hinder the electron transfer in the sample. With further increasing amount of DA, S-120 and S-160 are composed of cubic Fe and carbon, and their corresponding larger $\varepsilon'$ values could be attributed to the good conductivities of the materials.[40]

The imaginary part, $\varepsilon''$, reveals the attenuation of electric energy, which is affected by the heterostructure and intrinsic electric property through generating interfacial and dipole polarization, respectively[41]. S-0 possesses relatively small $\varepsilon''$ values probably because of its single phase. For S-80, multiple interfaces among Fe$_3$O$_4$, Fe$_{0.942}$O and carbon help enhance the interfacial polarization due to disparate electric properties of each component. Moreover, many defects, proved by Raman spectra, generate dipole polarization. Both of them lead to larger $\varepsilon''$ values (1.23–2.34). S-120 presents comparable $\varepsilon''$ values with S-0, possibly explained by relatively simple phase interfacial interaction between Fe and carbon and the existence of less defects. In S-160, excess carbon provides more phase interfaces and abundant defects, arousing stronger interfacial polarization and dipole polarization, which lead to larger $\varepsilon''$ values.[42]
Fig. 5. (a, b) complex permittivity, (c, d) complex permeability, (e) dielectric loss and (f) magnetic loss of the samples.

(A single column fitting image)

Normally, large permittivity values may favor strong dielectric loss capability. The dielectric loss tangents ($\tan \delta_e = \varepsilon''/\varepsilon'$) of the samples are plotted in Fig. 5c, being closely dependent on the frequency as the complex permittivity. Roughly, the values of S-0, S-80 and S-160 follow an increasing order before 12 GHz because of the increasing
permittivity values induced by growing carbon content, while S-120 presents the smallest values lining at the bottom as shown in Fig. 5b, which is consistent with the imaginary permittivity. When subjected to the frequencies higher than 12 GHz, all the curves possess several large fluctuations, which are likely to trigger strong microwave dissipation through polarization relaxation[43].

Generally, macroscopic electric moment induced by the charge accumulation and depletion accounts for the polarization relaxation process, and the interfacial polarization makes additional contribution[44]. To further investigate the contribution of polarization relaxation to dielectric loss, the Cole–Cole curves were plotted and shown in Fig. S5. A semicircle represents a polarization relaxation process. All the samples show several semicircles, suggesting the key role of polarization in generating dielectric loss. The complex semicircles of S-0 and S-80 might be generated mostly by multiple interfaces and defects, while the curves of S-120 and S-160 present small tails, which come from good conductivity induced by Fe and carbon[45]. Through polarization process, the microwave energy converts into thermal energy, and dissipates.

Fig. 5d, e present the complex permeability of the samples. The maximum values are achieved at 2 GHz, then decrease to the first minimum values at around 6 GHz because of the Snoek’s limits[34]. The peak values are 1.40, 1.27, 1.48, and 1.32 for S-0, S-80, S-120 and S-160 at 2 GHz, respectively. It is S-120 that shows the highest $\mu'$ peak value due to the stronger magnetization of Fe than that of Fe$_3$O$_4$ or Fe$_{0.942}$O in S-0 and S-80. While for S-160, despite Fe in it, the increasing carbon will dilute the magnetic response. And in 6–18 GHz, weakened fluctuations occur since the response of the
magnetic moments is more suppressed in higher frequency region. The corresponding \( \mu'' \) curves show resonant peaks at the frequencies lower than 6 GHz, which are attributed to natural ferromagnetic resonance(Fig. 5e)[46][47]. Generally, the natural ferromagnetic resonant frequency \( (f_r) \) of most ferrite or iron bulks is commonly located under megahertz, far away from gigahertz[48]. It could shift to gigahertz ascribed to small size effect (less than submicron). From the SEM and TEM results, most particles are about 100 nm in size. In this case, an enhanced anisotropy constant \( K \) results in an increasing anisotropy field \( H_a \) \( (K=2\pi M_s H_a) \), leading to a considerable large \( f_r \) \( (f_r=\gamma H_a/2\pi) \) at gigahertz[49]. Other several peaks in the region higher than 6 GHz come from the exchange resonance[50]. Specially, S-120 has the largest \( \mu'' \) value of 0.68 at 3.0 GHz, and displays obviously larger values than the others almost in the whole investigated region, implying intense magnetic loss is triggered in it. Besides, \( \mu'' \) values of S-160 in higher frequency are also higher than those of S-0 and S-80, suggesting Fe in S-120 and S-160 instead of Fe-based oxides in S-0 and S-80 helps enhance Snoek’s limitation[51], maintain good magnetic response in high frequency, and achieve broadband absorption performance.

In addition, the complex permeability is used to define the magnetic loss, i.e. magnetic loss tangent \( (\tan \delta_m = \mu''/\mu') \), of the material. And \( \tan \delta_m \) versus frequency will follow a similar dependent trend mostly with \( \mu'' \) on the frequency. As expected, S-120 shows the strongest magnetic loss in Fig. 5f. The corresponding curve begins from 0.4 at 2 GHz and drops to 0.41 at 7.5 GHz after scrambling up to 0.7 at 4.50 GHz, and then continually slopes gently with several weakened fluctuations along with the increasing
frequency. The values exceed 0.3 within 2–18 GHz and are the biggest among all the samples, demonstrating that a remarkable absorbing property induced by magnetic dissipation is very possible. For other samples, the values of S-0 maintain a second place from 2.0 GHz to 13.5 GHz, and are suppressed by S-160 in 13.5-18.0 GHz, which is because that high Snoek’s limitation of Fe in S-160 helps maintain performance advantage at high frequency, as mentioned in earlier section. S-80 has an inferior magnetic loss, resulted from the existence of nonmagnetic component of FeO.942O.

As well known, magnetic loss may originate from natural ferromagnetic resonance, exchange resonance, and eddy current effect[46]. Among them, eddy current effect contributes if $C_0=\mu''(\mu'-2f^{-1})$ does not vary with frequency[52]. By investigating the relationship between $C_0$ and $f$ in Fig. S6, eddy current effect is not the main reason for the frequency dependent variations. Therefore, natural ferromagnetic resonance and exchange resonance primarily account for magnetic loss, which is also identified in $\mu''$ curves[53].

In general, the intrinsic dielectric and magnetic properties affect the microwave absorption performance. To evaluate the microwave dissipation intuitively, attenuation constant $\alpha$ and impedance matching are introduced and analyzed as follows: firstly, attenuation constant $\alpha$, representing the microwave absorption performance directly, is expressed as Equation 1[54].

$$\alpha = \frac{\sqrt{2\pi f}}{c} \sqrt{(\mu'' \varepsilon' - \mu' \varepsilon') + \sqrt{(\mu'' \varepsilon' - \mu' \varepsilon')^2 + (\mu \varepsilon'' + \mu' \varepsilon')^2}} \quad (1)$$

It is obvious that dielectric and magnetic properties work together to affect the attenuation performance. As shown in Fig. 6a, $\alpha$ values increase with frequency for all
the samples. Higher value of $\alpha$ suggests a better microwave attenuation capability. S-0 presents the smallest $\alpha$ values compared to that of the others, especially in 8–18 GHz. This could be possibly related to remarkable cut-off magnetic loss induced by Snoek’s limitation, although the dielectric loss is not the smallest one[16]. S-80, S-120, and S-160 exhibit similar $\alpha$ values within 2–18 GHz, suggesting that dielectric loss and magnetic loss work together to achieve an increase. For instance, the strong magnetic loss of S-120 makes up its shortage of dielectric property.

Moreover, the impedance matching, expressed as $|Z_{in}/Z_0|$, where $Z_{in}$ and $Z_0$ are the input impedance and free space impedance, respectively, is another factor that directly affects the microwave absorption performance[55]. Generally, when $Z_{in}/Z_0$ equals to 1, no microwave reflection happens at the interface, suggesting good matching performance is obtained. For these samples, the impedance matching (shown in Fig. 6b) is modulated via the chemical state of Fe-based material and carbon content. Obviously, the values of S-0 are far away from 1 except for the cross point, suggesting an impedance mismatch condition. S-80 possesses better impedance matching characteristics in comparison with S-0. Evidently, the best impedance matching property with values close to 1 in a wide range of 12–15 GHz is detected in S-120. This is because perfect combination of conductive carbon layers and magnetic iron particles helps balance the dielectric and magnetic properties. However, further enhancement of carbon will break the dielectric and magnetic match again, resulting in a worse impedance match for S-160. Based on these results, S-120 might hold promise in achieving good microwave absorption performance.
Fig. 6. (a) attenuation constant $\alpha$, (b) impedance matching ($\left| \frac{Z_{in}}{Z_0} \right|$) of the samples.

(A single column fitting image)

$R_L$ deduced from the electromagnetic wave transmission theory is the direct criterion of microwave absorbing performance, employing relative complex permittivity ($\varepsilon=\varepsilon'-j\varepsilon''$) and relative complex permeability ($\mu=\mu'-j\mu''$). It is obtained from the equations as follows[56][57]:

$$Z_0 = \left( \frac{\mu_0}{\varepsilon_0} \right)^{1/2}$$  \hspace{1cm} (2)

$$Z_{in} = Z_0 \frac{\mu}{\varepsilon} \tanh \left[ j \left( \frac{2\pi f t}{c} \right) \sqrt{\mu\varepsilon} \right]$$ \hspace{1cm} (3)

$$R_L = 20 \log \left| \frac{Z_{in}-Z_0}{Z_{in}+Z_0} \right|$$ \hspace{1cm} (4)

where $\varepsilon$ and $\mu$ refer to complex permittivity and complex permeability of the sample, respectively. $\varepsilon_0$ and $\mu_0$ are the corresponding parts of free space, respectively. And $f$, $t$, and $c$ are frequency, thickness, and light velocity, respectively.
$R_L$ versus variables of $f$ and $t$ is plotted and shown in Fig. 7. In Fig. 7a, S-0 demonstrates a $R_{L_{\text{max}}}$ value of $-59.8$ dB ($3.2$ mm). Apart from $R_L$, the bandwidth (in which $R_L \leq -10$ dB, meaning over 90% of the wave energy is absorbed) also needs to be taken into consideration for application purpose[18]. The corresponding effective bandwidth of S-0 is $3.52$ GHz ($7.36\text{–}10.88$ GHz). For S-80, the $R_{L_{\text{max}}}$ value reaches $-54.0$ dB with the thickness of $5.3$ mm (Fig. 7b). When further increasing carbon, S-120 in Fig. 7c shows the highest $R_{L_{\text{max}}}$ value of $-61.6$ dB at $12.56$ GHz ($2.1$ mm). The effective absorption bandwidth reaches up to $-4.48$ GHz ($13.52\text{–}18$ GHz) with a thickness of only $1.7$ mm. As discussed above, excellent impedance matching and relatively high magnetic loss contribute to optimum performance. For S-160 in Fig. 7d, the $R_{L_{\text{max}}}$ value decreases to $-51.2$ dB at $3.2$ mm that might be due to excess carbon breaking excellent impedance matching condition.

From Fig. 7a–d, it can be observed that the $R_{L_{\text{max}}}$ values move towards lower frequencies with an increasing thickness of layer. This is attributed to the quarter-wavelength model, saying that two microwaves would interfere with each other when they are out of phase, resulting in the appearance of $R_{L_{\text{max}}}$. The matching between thickness and frequency for $R_{L_{\text{max}}}$ can be expressed in the following equation[58]:

$$t_m = \frac{nc}{4f\sqrt{\varepsilon\mu}} (n = 1, 3, 5, \ldots)$$

(5)

Fig. 7e demonstrates the calculated $t_m$ versus frequency obtained for $R_{L_{\text{max}}}$ with S-120, which meet the experimental one very well.
Fig. 7. $R_{\text{r, max}}$ of (a) S-0, (b) S-80, (c) S-120, (d) S-160, and (e) thickness ($t_m$) vs. frequency at wavelengths of $\lambda/4$ of S-120.

(A 2-column fitting image)
As shown in Table 2, the performance of as-prepared Fe@N-doped carbon is competitive with other Fe-based particles/carbon composites reported in other literatures. The as-prepared samples, especially S-120, possess excellent microwave absorption performance, which might be attributed to the following aspects depicted in Fig. 8. Firstly, the interfacial polarization induced by heterostructures and dipole polarization originated from different electronegativity of multi-components contribute to dielectric loss. Secondly, the existence of magnetic components helps generate natural resonance and exchange resonance, resulting in an enhanced magnetic loss. Thirdly, the graphitized carbon provides free electrons, and iron particles work as electron donor, which helps form conductive network, leading to effective conduction loss. Finally, perfect impedance matching could be achieved with the adjusted iron and carbon content.

Table 2. List of microwave absorption performances of this work and other literatures

<table>
<thead>
<tr>
<th>Absorber</th>
<th>Thickness (mm)</th>
<th>$R_{L_{max}}$ (dB)</th>
<th>Effective bandwidth (GHz)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$/Fe composites</td>
<td>1.25</td>
<td>–25.9</td>
<td>4.2</td>
<td>[59]</td>
</tr>
<tr>
<td>Double-layer Fe/C</td>
<td>2.00</td>
<td>–23.9</td>
<td>1.3</td>
<td>[60]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/SiO$_2$/PVDF</td>
<td>2.5</td>
<td>–28.6</td>
<td>–</td>
<td>[61]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ NP</td>
<td>6.0</td>
<td>–21.2</td>
<td>3.6</td>
<td>[62]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/C nanospindles</td>
<td>2.1</td>
<td>–38.8</td>
<td>–</td>
<td>[63]</td>
</tr>
<tr>
<td>Fe microflakes</td>
<td>1.1</td>
<td>–15.3</td>
<td>4.4</td>
<td>[64]</td>
</tr>
<tr>
<td>Fe−FeC@C</td>
<td>3.0</td>
<td>−28.10</td>
<td>4.10</td>
<td>[65]</td>
</tr>
<tr>
<td>------------------</td>
<td>-----</td>
<td>--------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>carbonyl</td>
<td>1.7</td>
<td>−25.7</td>
<td>6.9</td>
<td>[7]</td>
</tr>
<tr>
<td>iron@void@nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe@N-doped C</td>
<td>2.1</td>
<td>−60.0</td>
<td>4.48</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Fig. 8.** The proposed microwave absorption mechanism

(A single column fitting image)

### 3.3. Degradation performance

So far, these samples have demonstrated promising microwave absorption properties. The other thing we need to pay attention to is to avoid leaving pollution behind after service. Therefore, environment-friendly filler and matrix are adopted, especially PLA matrix, which is produced with plants and can be degraded after service. The
decomposition performance of the microwave absorber is studied in marine environment and shown in Fig. 9.

![Decomposition rate of the composites](image)

**Fig. 9.** Decomposition rate of the composites

(A single column fitting image)

It is obvious that the residual weight decreases day by day. The weight losses are 0.98 % and 4.95 % after 2 days and 4 days. And the residual weight reaches 46.18 % with the sample immersed in seawater for one month. When the immersion time prolongs to half a year, the residual weight ends as 49.35%, indicating the PLA matrix could almost be completely degraded within one month. Moreover, when the sample is stored in lab environment or placed in normal service condition, the microwave absorption property reveals little attenuation. The decomposition experiment here is to further show the environment-friendly characteristic of the composites that they are naturally degradable after failure, only leaving harmless debris of the filler. Meanwhile, the time for
decomposition of the composites in harsh environment is predictable from the experiment. That is to say, this material, which is composed of Fe-based material@N-doped carbon as filler and PLA as matrix, demonstrates good microwave absorption performance and environment-friendly property.

4. Conclusion

Spherical Fe-based materials@N-doped carbon have been developed as microwave absorbers. PDA is used to regulate the phases of the iron-based particles and generate different carbon species in the synthesis process. The microwave absorbers, Fe-based material@N-doped carbon cooperated with PLA as matrix, demonstrates excellent microwave absorption performance. The $R_{l_{max}}$ value of S-120 reaches −61.6 dB at 12.56 GHz with the corresponding thickness of 2.1 mm, and the effective absorption bandwidth reaches up to −4.48 GHz (from 13.52 GHz to 18 GHz) with a thickness of only 1.7 mm. The high absorption could be ascribed to strong magnetic loss generated by metal Fe, boosted dielectric polarization induced by graphitized carbon, and the achieved perfect impedance matching. Meanwhile, through decomposition experiment, it is observed that the residual weight of absorbers reaches 46.18% and 49.35% with the absorbers immersed in seawater for one month and six months, indicating the PLA matrix could almost be degraded within one month and only debris of the filler remains. Thus, the composites are environment-friendly because Fe-based material@N-doped carbon is synthesized via a green process and PLA is produced with plants and can be degraded naturally after failure. This work provides a new strategy to prepare
environment-friendly microwave absorbers, meeting the requirement of high-efficient microwave absorption and sustainable development of modern society.

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Declaration

The authors declare no competing interests.

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