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Construction of $Fe_{0.64}Ni_{0.36}$ @graphite nanoparticles *via* corrosion-like transformation from NiFe₂O₄ and surface graphitization in flexible carbon nanofibers to achieve strong wideband microwave absorption



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ABSTRACT

Recently, microwave absorption (MA) materials have attracted intensive research attention for their ability to counteract the effects of ever-growing electromagnetic pollution. However, conventional microwave absorbers suffer from complex fabrication processes, poor stability and different optimal thicknesses for minimum reflection loss (RL_{min}) and widest effective absorption bandwidth (EAB). To address these issues, we have used electrospinning followed by high-temperature annealing in argon to develop a flexible microwave absorber with strong wideband absorption. The MA properties of the carbon nanofibers (CNFs) can be tuned by adjusting annealing temperature, and are dependent on the composition and microstructure of the CNFs. The absorber membrane obtained at 800 °C consists of $Fe_{0.64}Ni_{0.36}@graphite core-shell nanoparticles (NPs) embedded in CNFs, formed$ *via* $a corrosion-like transformation from NiFe₂O₄ to <math>Fe_{0.64}Ni_{0.36}$ followed by surface graphitization. This nanostructure greatly enhances magnetic-dielectric synergistic loss to achieve superior MA properties, with an RL_{min} of -57.7 dB and an EAB of 6.48 GHz (11.20–17.68 GHz) both acquired at a thickness of 2.1 mm. This work provides useful insights into structure–property relationship of the CNFs, sheds light on the formation mechanism of $Fe_{0.64}Ni_{0.36}@graphite NPs$, and offers a simple synthesis route to fabricate light-weight and flexible microwave absorbers.

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1. Introduction

5G telecommunications have the potential to significantly improve productivity and digital connectivity, but come at the cost of increased electromagnetic (EM) radiation and interference. This is considered a new source of pollution which threatens human health and hampers the operation of precision electronic devices. [1–5] Over the past decade, the search for microwave absorption (MA) materials in the GHz range [6–8] has been expedited by the growing need to suppress harm caused by EM pollution. An ideal microwave absorber is light-weight, physically and chemically stable, and achieves a low minimum reflection loss (RL_{min}) and wide effective absorption bandwidth (EAB) at a thin thickness. To date, researchers have mainly focused on improving RL and EAB by constructing various composite materials with rich loss mechanisms and good impedance matching [9–12]. However, improvements to the MA properties alone are unlikely to satisfy the requirements of an ideal absorber.

In the pursuit of ideal microwave absorbers, composites of carbon and magnetic materials (CM composites) stand out as some of the best candidates due to their light weight, high physicochemical stability, and magnetic-dielectric synergistic loss [4]. In recent years, researchers have devoted great efforts to constructing different CM composites. Examples include FeCo/graphene hybrids [10], 3D Fe₃O₄/C and FeNi/C flower nanostructures [11,12], graphene aerogels decorated with magnetic materials [13,14], Fe₃O₄@C core-shell microspheres [15], and 1D NiCo@C/ZnO nanorods [16]. These composites have demonstrated low RL_{min} and wide EAB, while most are achieved at different thicknesses. In addition, fabrication processes tend to be complicated, and the powdered composites usually require high filling factors which can result in high density and agglomeration [3]. These shortcomings seriously hinder their practical application. Therefore, novel CM composites with light weight, simple fabrication processes and excellent MA properties are urgently needed.

To construct novel CM composites, it is essential to design a nanostructure that can greatly enhance MA. Previous investigations have shown that core-shell nanoparticles (NPs) [15] and 1D nanostructures [16,17] can possess excellent MA properties. It is reasonable to infer that core-shell NPs embedded in 1D nanostructures have even better MA properties. Recently, Kuang *et al.* [18] implemented such an idea by constructing FeCo@C core-shell nanoparticles embedded in carbon nanotubes using metal-organic chemical vapor deposition (MOCVD). It was shown that synergistic effects between core-shell FeCo@C NPs and carbon nanotubes could significantly improve the MA capabilities of the composite, with RL_{min} and widest EAB both achieved at the same thickness. Kuang's work corroborates that designing 1D carbon nanostructures embedded with core-shell magnetic NPs is an effective strategy to enhance MA.

For the core-shell NPs embedded in carbon nanostructures, the magnetic loss material in the core of the NPs is essential for MA, as it directly determines the magnetic loss capability of the composite. To adopt a congruent magnetic loss material in our nanostructure design, we look to those used in other nanostructures, which include several ferrites and alloys such as FeCo [10], Fe₃O₄ [11,14], FeNi [12], NiFe₂O₄ [13], CoNi [19]. In particular, FeNi is an environment-friendly alloy with large saturation magnetization, high Curie temperature and high conductivity, which are beneficial for achieving excellent MA properties [10]. In previous work, FeNi was composited with different carbon nanostructures such as 3D structures [12,20], nanotubes [21,22] and NPs [22], all exhibiting good MA properties. Based on these previous efforts, FeNi is chosen herein as the magnetic loss material to obtain FeNi@C core-shell NPs embedded in 1D carbon nanostructure. This nanostructure is expected to have excellent MA properties and rich MA mechanisms due to synergistic effects between the core-shell NPs and 1D carbon nanostructure and existence of many interfaces in this composite. In this work, we focus on constructing this CM composite and investigating its MA mechanism.

To prepare this CM composite, an appropriate fabrication technique is required. In Kuang's work, MOCVD was used to fabricate 1D carbon nanostructures embedded with core-shell NPs [18], but this method has high expense, slow growth speed, and non-flexible end-product. Other approaches to obtain NPs/1D nanostructures include molten-saltassisted CVD [23], and the hydrothermal method followed by pyrolysis and partial etching [24], which are also complicated. In contrast to these techniques, electrospinning is an easy and reliable method to fabricate flexible 1D nanofibers that are tunable in microstructure [25]. Therefore, to implement our strategy, electrospinning followed by annealing in argon (Ar) was chosen for fabrication of core-shell NPs/ carbon nanofibers (CNFs), which can produce flexible and light-weight membranes with reduced fabrication cost. Up to now, no reports have been found on the fabrication of FeNi@C core-shell NPs embedded in 1D carbon nanofibers. In addition, the formation mechanism of FeNi@C NPs in the carbon nanofibers remains poorly understood.

In this work, we used electrospinning followed by annealing in Ar atmosphere at 800 °C to fabricate flexible membranes consisting of faceted Fe0.64Ni0.36@graphite NPs embedded in carbon nanofibers (Fe_{0.64}Ni_{0.36}@graphite/CNFs). MA measurements of these membranes revealed that an $RL_{min}\ \text{of}\ -57.7\ \text{dB}$ and widest EAB of 6.48 GHz were both achieved at a thickness of 2.1 mm. To explore the structure-property relationships, we investigated structural evolution and MA property differences in the CNFs obtained at different annealing temperatures. It was found that NiFe₂O₄ NPs formed in the CNFs when annealing in Ar at 400 °C and a corrosion-like transformation from NiFe₂O₄ to Fe_{0.64}Ni_{0.36} took place at 600 °C. The MA properties of CNFs annealed at 400, 500, 600, and 700 °C were investigated and compared with those annealed at 800 °C. By correlating structural characteristics with MA properties, we found that loss mechanisms including conduction loss, polarization loss, and exchange resonance were closely related to the composition and microstructure of these CNFs.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN, average Mw. 150,000), Iron acetylacetonate [Fe(acac)₃, 98 %], Nickel acetylacetonate [Ni(acac)₂, 98 %], and N, N-Dimethylformamide (DMF, 99.5 %) were purchased from Sinopharm Chemical Reagent Co., Ltd.. All chemicals were of analytical grade and used as received without further purification.

2.2. Preparation of CNF membranes

The precursor solution containing DMF, PAN (11 wt.%), Ni(acac)₂ and Fe(acac)₃ (a molar ratio of 1:2) was prepared, and stirred at 30 °C for 6 h to form a viscous mixture. The fiber membranes were obtained by electrospinning under a working voltage of 20 kV with a flow rate of 0.4 mL/h. The distance between needle tip and collecting roll was set as 14 cm. The speed of the receiver and the diameter of the needle were 500 rpm and 0.55 mm, respectively. The temperature and the humidity were 26 °C and 33–36 %. Subsequently, the as-prepared fiber membranes were stabilized in drying oven at 230 °C for 2 h. Finally, the stabilized fiber membranes were annealed at temperatures ranging from 400 to 900 °C for 2 h with a heating rate of 2 °C/min in Ar atmosphere. The CNF membranes obtained at different annealing temperatures were labeled as CNF-T (T stands for annealing temperature).

2.3. Materials characterization

The structure evolution of the CNFs at different annealing temperatures was investigated by *in-situ* X-ray diffraction analysis using a high temperature chamber Anton Paar HTK 1200 N mounted on powder diffractometer (Bruker D8 Advance) with Cu-K α radiation ($\lambda = 1.5406$ Å). The chamber was evacuated by a turbo-molecular pump creating a

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Fig. 1. Typical SEM images of CNF-400 (a), CNF-600 (b) and CNF-800 (c); Aberration-corrected HAADF images of a single nanofiber and an individual NP in CNF-400 (d), CNF-600 (e), and CNF-800 (f); (g) STEM images of NPs in CNF-800 with different aspect ratios; Aberration-corrected HAADF image of a rectangular NP (h) and a near-spherical NP (i) in CNF-800; (j) EDS mapping of Fe, Ni, C and O in a single NP in CNF-800.

pressure about 10^{-2} Pa before measurements. The CNFs were uniformly heated without thermal gradients from room temperature up to 800 °C and exposed for 30 min at 230, 400, 500, 600, 700, and 800 °C. Graphitization of CNFs was investigated by Raman spectroscopy using a confocal Raman spectrometer (Renishaw inVia) with a laser wavelength of 532 nm.

The morphologies of the CNFs were studied using a field-emission scanning electron microscope (FE-SEM, Sigma 500) at an accelerating voltage of 20 kV. Bright-field (BF) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a transmission electron microscope (TEM, JEOL JEM2100F) operating at 200 kV. The high-angle annular dark field (HAADF) scanning-transmission electron microscopy (STEM) imaging was performed using a probecorrected FEI Titan G2 80–200 S/TEM equipped with the ChemiSTEM energy dispersive X-ray spectrometer (EDS) system and a Gatan Quantum ER imaging filter (GIF) for electron energy-loss spectroscopy (EELS). The Titan was operated at an accelerating voltage of 200 kV. The STEM images were acquired using a semi-convergence angle of 21 mrad and a collection angle of 54 mrad. The EELS spectra were obtained in STEM mode with a semi-convergence angle of 21 mrad and a collection angle of 62 mrad.

2.4. Computational methodology

To explore the structure evolution, first-principles simulations were performed using the Perdew-Burke-Ernzerhof (PBE) functional [26] and the ultrasoft pseudopotential method [27] in the CASTEP code. In structural optimization, the energy cutoff for the truncation of plane wave basis was set to be 340 eV and a Brillouin zone k-point sampling with a resolution of $2\pi \times 0.05$ Å⁻¹ was used. The convergence criterion is 0.01 meV/atom for the total energy, 0.03 eV/Å for the forces acting on the atoms, and 0.005 Å for the maximum displacement.

2.5. Microwave absorption measurements and calculations

The permittivity and permeability of each CNF were measured at test frequencies 2 to 18 GHz by a vector network analyzer (Agilent N5234A) using a coaxial method. The CNFs were mixed with melted paraffin wax at a mass ratio of 1:6, and the mixture was pressed into a ring with an inner diameter, outer diameter and thickness of 3.04 mm, 7.00 mm, and 2.00 mm, respectively. The magnetization versus magnetic field hysteresis loops were measured by a vibrating sample magnetometer (VSM) equipped on a physical properties measurement system (PPMS, Quantum Design) at room temperature. The input impedance and RL values are calculated with relative complex permittivity ($\varepsilon_r = \varepsilon'$ -j ε'') and relative complex permeability ($\mu_r = \mu'$ -j μ'') using transmission line theory [28,29].

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left(j\frac{2\pi f d}{c}\sqrt{\varepsilon_r \mu_r}\right)$$
(1)

$$RL(dB) = 20log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|$$
⁽²⁾

where Z_{in} is the input impedance of the absorber, Z_0 is the impedance of free space, f is the frequency of incident EM wave, d is the thickness of absorber layer, and c is the speed of light. The EAB is the frequency range in which RL is less than -10 dB. To determine whether eddy current loss is dominant, the eddy current coefficient C_0 is calculated as follows [30].

$$C_0 = \frac{\mu}{(\mu')^2 f}$$
(3)

To quantify the ability of the CNFs to attenuate EM waves, the attenuation constant (α) is calculated using the following equation [31].

$$\alpha = \frac{\sqrt{2}\pi f}{c} \sqrt{\left(\mu^{'}\varepsilon^{''} - \mu^{'}\varepsilon^{'}\right)} + \sqrt{\left(\mu^{'}\varepsilon^{''} - \mu^{'}\varepsilon^{'}\right)^{2} + \left(\mu^{'}\varepsilon^{''} + \mu^{'}\varepsilon^{'}\right)^{2}}$$
(4)

3. Results and discussion

3.1. Morphology and crystal structure of CNFs

Fig. 1 (a-c) shows typical SEM images of CNF-400, CNF-600 and CNF-800, respectively. From the SEM images, we can see that the nanofibers are intertwined, forming a network, and the nanofiber diameter decreases as annealing temperature increases. In addition, it can be seen from three insets that the surface morphology of the nanofibers becomes rougher as annealing temperature increases. In CNF-400, the surface morphology of nanofibers is smooth, as shown in inset of Fig. 1(a). As annealing temperature increases, small NPs are seen to appear on the surfaces of nanofibers in CNF-600, as shown in inset of Fig. 1(b). For CNF-800, the NPs are larger than those in CNF-600, which can be clearly observed in inset of Fig. 1(c).

To further investigate the composition and microstructure of NPs embedded in the CNFs, extensive STEM examinations were carried out. Fig. 1(d) shows a low-magnification STEM image (left) of an individual nanofiber in CNF-400 and HAADF image (right) of a single NP in this fiber. From the $[0\bar{1}1]$ zone-axis HAADF image of a NP with dimensions around 5 nm, the interplanar spacing is measured to be 4.82 Å, consistent with that of (111) planes of NiFe₂O₄, indicating the formation of NiFe₂O₄ in the CNF-400. EDS elemental mapping of a single nanofiber in CNF-400 further confirms the formation of NiFe₂O₄, as shown in Fig. S1 in the supplementary information (SM). Fig. 1(e) shows a typical STEM

image of an individual nanofiber in the CNF-600. Small NPs can be seen in the nanofibers, consistent with SEM observations of CNF-600. From the $[1 \overline{1} 1]$ zone-axis HAADF image of an individual NP in the nanofiber, it can be seen that the lower part has brighter contrast than the upper part, suggesting that two different phases exist, separated by an interface in this NP. The upper part has an interplanar spacing of 2.95 Å, agreeing well with (220) planes of NiFe₂O₄ (labelled as NFO), and the lower part has an interplanar spacing of 1.27 Å, consistent with (220) planes of Fe_{0.64}Ni_{0.36} (labelled as FeNi). This suggests that a transformation from NiFe₂O₄ to Fe_{0.64}Ni_{0.36} takes place at 600 °C. More observations of $NiFe_2O_4$ and $Fe_{0.64}Ni_{0.36}$ forming an interface in a single NP are presented in Fig. S5, and the EDS elemental mapping of a single nanofiber in CNF-600 can be found in Fig. S2. Fig. 1(f) shows a typical lowmagnification STEM image of an individual nanofiber in CNF-800, from which it can be seen that most particles have a rectangular or square shape. From the HAADF image of a typical NP shown in Fig. 1(f), the interplanar spacing is measured to be 2.07 Å, corresponding to {111} planes of Fe_{0.64}Ni_{0.36} (labelled as FeNi). Careful examination shows that five planes with faint contrast are covered on the particle surface. In HAADF images, the intensity of atomic columns is approximately proportional to $Z^{1.67}$, where Z is the atomic number. [32] Therefore, the faint-contrast planes on the surface of the NP should be composed of low-Z elements. Combining this fact with the interplanar spacings, which are measured to be 3.40 Å, the faint-contrast planes are identified as (002) planes of graphite. From above analysis, it can be concluded that NiFe₂O₄ NPs form in the CNFs at 400 °C, which partially transform into Fe_{0.64}Ni_{0.36} NPs at 600 °C, and completely transform into Fe_{0.64}Ni_{0.36}@graphite NPs at 800 °C. This is further corroborated by the EDS spectra in Fig. S3 and the quantification results in Table S1.

Extensive STEM examinations were carried out to study the NPs in CNF-800 in detail. It was found that most NPs have a rectangular or near-square shape, while quite few have a near-spherical shape. During the high-temperature annealing, formation of low index facets in the NPs such as {111}, {200} and {220} planes is energetically favorable, therefore most NPs are expected to have a rectangular or near-square shape. Fig. 1(g1-g3) shows the Fe0.64Ni0.36 NPs have a rectangular shape with aspect ratios of 1.07, 1.11, and 1.19, respectively. Fig. 1(g₄) shows a NP with a near-spherical shape. It can be seen that there are weak-contrast layers on the surface of these NPs. To explore the composition of the weak-contrast layers, EDS mapping is carried out on a near-square shaped NP, as shown in Fig. 1(j). The EDS elemental mappings match well with the characteristics of a $\mathrm{Fe}_{0.64}\mathrm{Ni}_{0.36}$ NP with strong Fe and Ni intensities. In addition, large traces of C are found on the surface and edges of the NP. The EDS mapping of a near-spherical NP in Fig. S4 also shows a similar elemental distribution. Therefore, the weak-contrast layers in the HAADF images in Fig. 1(g) are determined to be composed of carbon, though it is not clear whether graphitization takes place. Fig. 1(h1) displays a truncated rectangular NP with an aspect ratio of 1.23. Viewed from [011] direction, this NP has (200), (1 $\overline{1}$ 1) and $(0\overline{2} 2)$ facets, as labeled in Fig. 1(h₁). The enlarged image of the $(0\overline{2}2)$ facet is shown in Fig. 1(h₂), from which it can be seen that there is no apparent graphite coating on the surface of the NP. A possible explanation is that there are few (<5) layers of graphite on the NP surface which do not produce enough contrast to be seen in this HAADF image due to the proportionality of image contrast and Z^{1.67}. The FFT pattern of the NP is shown in Fig. $1(h_3)$, in which the diffraction spots corresponding to (200) and (0 $\overline{2}$ 2) facets are labeled. Fig. 1(i) shows a near-spherical-shaped Fe_{0.64}Ni_{0.36} NP with a diameter of 11.0 nm. This NP is clearly observed to be covered with graphite layers, and the (002) planes of graphite and (111) planes of $Fe_{0.64}Ni_{0.36}$ are indicated in Fig. 1 (i). Graphitization of carbon adsorbed on Fe_{0.64}Ni_{0.36} NP surfaces [33,34] through catalysis of Ni [33] can be used to explain the various NP shapes. For rectangular NPs with little C adsorbed, there is little effect on NP growth. Without graphitization, {200} planes grow faster than {220} planes for fcc Fe_{0.64}Ni_{0.36}, hence forming a rectangular NP.



Fig. 2. (a) *In-situ* XRD patterns of the nanofibers (Ni:Fe = 1:2) heated in vacuum up to 800 °C; (b) EELS spectra and (c) Fe $L_{2,3}$ peaks acquired from a single nanofiber in CNF-400, CNF-600 and CNF-800, respectively; HRTEM images of an individual NP in CNF-400 (d), CNF-600 (e), CNF-800 (f, g).

During the formation of near-square shaped NPs, surface graphitization is more effective, and growth of {200} and {220} planes are both hampered, leading to more similar growth speeds for these planes, thus forming a near-square shape. For near-spherical NPs with multiple facets, the graphite layers hinder the growth of all facets, resulting in similar growth speeds for all facets, thus maintaining a near-spherical shape. Though the HAADF images in Fig. 1(f, i) provides strong evidence of graphitization on the surface of $Fe_{0.64}Ni_{0.36}$ NPs, further characterization is required to confirm the universality of this process in the NPs.

3.2. Transformation from NiFe₂O₄ NPs to Fe_{0.64}Ni_{0.36}@graphite NPs

Although many reports have claimed that $Fe_{0.64}Ni_{0.36}$ forms *via* the reduction of NiFe₂O₄ [35–38], no explicit explanation of the transformation process can be found. To clarify the transformation from NiFe₂O₄ to $Fe_{0.64}Ni_{0.36}$ in the CNFs, *in-situ* XRD analysis, EELS and extensive HRTEM examinations were carried out. Fig. 2(a) shows the *in-situ* XRD patterns of as-prepared nanofibers heated up to 800 °C in vacuum. From 230 to 400 °C, the XRD patterns have broad peaks at 20 values around 43.4°, 53.8°, 62.9°, and 75.8°, corresponding to (400),



Fig. 3. Schematic unit cell of (a) the inverse spinel NiFe₂O₄ (space group $Fd \ \overline{3} \ m$) and (b) Fe_{0.64}Ni_{0.36} (space group $Fm \ \overline{3} \ m$). Schematic of (c) stacking order of NiFe₂O₄ atomic layers along the [111] direction, and (d) lowest energy interface of NiFe₂O₄-Fe_{0.64}Ni_{0.36}, terminated with the [Fe]_{tet-1} atomic layer of NiFe₂O₄.

(422), (440), and (622) planes of NiFe₂O₄ (JCPDS card no. 10-0325), respectively. In addition, the intensity of the (400) peak obtained at 400 °C is higher than those obtained at 230 °C and 300 °C, which results from the preferred orientation of the NPs along [400] direction at 400 °C. When the temperature reaches 500 °C, the transformation from NiFe₂O₄ to Fe_{0.64}Ni_{0.36} starts, symbolized by a plateau peak between 42° and 45° , which is caused by the overlapped diffraction from both (400) plane of NiFe₂O₄ and (111) plane of Fe_{0.64}Ni_{0.36}. At 600 °C, the transformation continues, displaying a similar XRD pattern to that obtained at 500 °C. At 700 °C, the XRD pattern exhibits peaks at 20 values 43.6°, 50.8° and 74.7° , corresponding to (111), (200) and (220) planes of Fe0.64Ni0.36 (JCPDS card no. 47-1405), respectively. Therefore, most of NiFe2O4 has converted into Fe0.64Ni0.36 at 700 °C. At 800 °C, the crystallinity of Fe_{0.64}Ni_{0.36} further increases, signified by the sharper diffraction peaks. It should be noted that the peak intensity ratios in Fig. 2(a) differ from those in the JCPDS cards, which is likely due to the preferred orientation of NPs along certain directions [25]. For example, {111} planes are often present in the HRTEM images of Fe_{0.64}Ni_{0.36}, meaning that many NPs are oriented along < 111 > direction. Therefore, the peak at around 43.6° has high intensity in the XRD pattern acquired at 800 °C.

To further prove the transformation process at different annealing temperatures, EELS spectra were acquired from single nanofibers in CNF-400, CNF-600 and CNF-800, as shown in Fig. 2(b). It was found that O-K edge, Fe- $L_{2, 3}$, and Ni- $L_{2, 3}$ peaks are all present for CNF-400 and CNF-600 [39–42], but the O-K edge vanishes for CNF-800. The splitting of the O-K edge is due to crystal field splitting, originating from the mixing of O 2*p* states and Fe/Ni 3*d* orbitals [39]. In addition, the highest peak of O-K edge shifts from 539.75 eV for CNF-400 to 540.25 eV for CNF-600, indicating that the partial density of states overlap between the oxygen 2*p* states and metal 3*d* states is weaker for CNF-600 [40]. Quantification of the EELS spectra for CNF-400 shows that the atomic ratio of Ni:Fe:O is close to 1:2:4, which is consistent with the stoichiometry of NiFe₂O₄, while for CNF-800, the atomic ratio of Ni:Fe is close to 1:2, which agrees well with the stoichiometry of Fe_{0.64}Ni_{0.36}. This

demonstrates that a transformation from $NiFe_2O_4$ to $Fe_{0.64}Ni_{0.36}$ takes place during the annealing process, consistent with the XRD analysis above. Detailed analysis of Fe- $L_{2, 3}$ peaks is presented in Fig. 2(c), labeled with the Hartree-Slater background and fitted peaks. The background has two steps set at the positions of L_3 and L_2 peak maxima, and the peak height ratio is 2:1, according to the multiplicity of the initial 2p states (L_3 : four 2p3/2 states; L_2 : two 2p1/2 states) [41]. The area ratios of Fe L_3 and L_2 peaks (L_3/L_2) decrease as annealing temperature increases. For CNF-400, $L_3/L_2 = 4.5$; for CNF-600, $L_3/L_2 = 3.9$; for CNF-800, this ratio decreases to 2.1. In previous work, it was found that L_3/L_2 decreases with decreasing Fe valence state (~5 for Fe³⁺ and ~ 4 for Fe^{2+} [40]), and reaches a value around 2 for Fe^{0} [42]. Therefore, it can be deduced that the Fe valence state changes from Fe³⁺ in CNF-400 to Fe⁰ in CNF-800. This is consistent with our XRD analysis results that $NiFe_2O_4$ (Fe^{3+}) forms at 400 $^\circ C$ and transforms into $Fe_{0.64}Ni_{0.36}$ (Fe^) at 800 °C.

Extensive HRTEM examinations were carried out to clarify how NiFe₂O₄ NPs transform into Fe_{0.64}Ni_{0.36}@graphite NPs. Fig. 2(d) shows a typical HRTEM image of an individual NP in CNF-400, from which it can be seen that the trapezoid NiFe₂O₄ NP (labelled as NFO) has {220} facets. HRTEM images of NPs with defects in CNF-400 can be found in Fig. S6. Fig. 2(e) shows a typical [0 $\overline{1}$ 1] zone-axis HRTEM image of a single NP in CNF-600, where a hemispherical Fe_{0.64}Ni_{0.36} NP (labelled as NFO) on the right forms an interface with the NiFe₂O₄ NP (labelled as NFO) on the left. The orientation relationships are described as follows.

$$(\overline{3}33)_{\text{NiFe}_2O_4} // (111)_{\text{Fe}_{0.64}Ni_{0.36}}$$

 $(311)_{\text{NiFe}_2O_4} // (\overline{1}11)_{\text{Fe}_{0.64}Ni_{0.36}}$ (5)

Due to lattice mismatch, there are several edge dislocations near the interfacial region, which are displayed in Fig. S7. To explore the graphitization of $Fe_{0.64}Ni_{0.36}$ NPs at 800 °C in detail, HRTEM

 $[0\overline{1}1]_{NiFe_2O_4} / [0\overline{1}1]_{Fe_064Ni036}$

examinations were carried out on CNF-800. It was found that around 90 % of NPs are covered with graphite layers (see Fig. S8). This confirms CNF-800 is composed of Fe_{0.64}Ni_{0.36}@graphite/CNFs. Fig. 2(f, g) shows typical HRTEM images of Fe0.64Ni0.36 NPs (labelled as FeNi) in CNF-800, which exhibit obvious surface graphitization. In Fig. 2(f), graphite layers are clearly observed surrounding the rectangular NP and the NP on the bottom left. The rectangular NP has less than 5 graphite layers, with two twin boundaries labeled as (111) planes. Fig. 2(g) shows a near-spherical shaped NP with multiple facets, surrounded by more than 20 graphite layers. It seems that rectangular NPs tend to have less graphite layers than near-spherical NPs. Near-spherical NPs have larger surface area than rectangular NPs, and the catalysis of graphitization by Ni [33] is more effective, hence the near-spherical NPs tend to have more graphite layers. To provide more evidence of graphitization, Raman spectra were performed for all CNFs, as shown in Fig. S9. Two distinct peaks at around 1 367 cm $^{-1}$ and 1587 cm $^{-1}$ are assigned to the D and G bands of carbon, respectively. It is well known that the lower the intensity ratio of D and G bands, the higher the graphitization degree [43]. From Fig. S9, we can see that as the annealing temperature rises, I_D/I_G decreases, dropping to 0.88 for CNF-800. Therefore, the graphitization degree increases with annealing temperature, and CNF-800 has the highest graphitization degree. This is consistent with our TEM observations.

Based on above results, we propose a mechanism for the transformation from NiFe2O4 to Fe0.64Ni0.36@graphite NPs. At 600 °C, transformation from NiFe2O4 to Fe0.64Ni0.36 takes place. In contrast to epitaxial growth, it seems that the Fe_{0.64}Ni_{0.36} lattice grows into the NiFe₂O₄ lattice, *i.e.*, the NiFe₂O₄ lattice being dissolved and transformed into the Fe_{0.64}Ni_{0.36} lattice in a layer-by-layer fashion. This layer-bylayer reduction process is described as a corrosion-like transformation, which has not been reported in previous reviews [44-46]. In Fig. 2(e), the corrosion-like transformation only occurs on the right-sided $(\overline{3} \ 3 \ 3)$ plane. This might result from heavy exposure of the right-sided plane to the reductive atmosphere, or its surface energy being higher than the others. As annealing temperature increases up to 800 °C, the corrosionlike transformation is complete, forming Fe_{0.64}Ni_{0.36} NPs with different facets. During the growth of Fe_{0.64}Ni_{0.36} NPs, carbon is adsorbed onto the NP surfaces, and graphitization occurs through catalysis of Ni. Despite the above characterization, the interface structure between NiFe₂O₄ and Fe_{0.64}Ni_{0.36} as well as the beginning of the corrosion-like transformation remains unclear.

To clarify the interfacial structure and the accurate NiFe2O4 {111} plane on which the transformation begins, we carried out density functional theory calculations [47] using a model slab with NiFe₂O₄ and Fe_{0.64}Ni_{0.36} layers. A virtual crystal approximation (VCA) was used to treat the bulk disordered phase effect [48] for $Fe_{0.64}Ni_{0.36}$, where the configuration averaged potential of a mixture atom occupying a site in the $Fe_{0.64}Ni_{0.36}$ lattice is defined as $V_{VCA}=0.64V_{Fe}+0.36V_{Ni}.$ Fig. 3(a, b) shows schematic unit cells of $\rm NiFe_2O_4$ and $\rm Fe_{0.64}Ni_{0.36},$ respectively. The $Fe_{0.64}Ni_{0.36}$ lattice has mixture atoms occupying fcc lattice points. In NiFe2O4, all Ni atoms occupy octahedral sites (Nioct), while Fe atoms occupy both tetrahedral (Fe_{tet}) and octahedral (Fe_{oct}) sites. For the interfacial structure simulations, (1 1 1) planes of both NiFe₂O₄ and Fe_{0.64}Ni_{0.36} are adopted, in accordance with the orientation relationship in Fig. 2(e). For Fe_{0.64}Ni_{0.36}, only one type of (1 1 1) plane is considered, while for NiFe₂O₄, there are six types of (1 1 1) termination layers as shown in Fig. 3(c). Therefore, there are six possible interface structures depending on the termination layer. Schematics of these six interface structures after optimization can be found in Fig. S10, and the calculation results of interface energies can be found in Table S2. It is found that the lowest energy interface is terminated with the [Fe]_{tet-I} atomic layer, and after optimization, [Fe]_{tet-I}, [FeNi]_{oct} and [Fe]_{tet-II} are assembled in the same atomic layer, as shown in Fig. 3(d). The atoms in the leftmost three layers of NiFe2O4 are fixed to their positions in bulk during the structure optimization process. After relaxation, the Fe and Ni atoms in [Fe]tet-I, [FeNi]oct and [Fe]tet-II layers closest to the interface are

 Table 1

 The formation energies of point defects in NiFe₂O₄.

Point defect	Formation energy (eV)		
Ni _{oct}	-0.40		
Feoct	0.94		
Fe _{tet}	1.14		
0	3.70		

approximately located on the same (111) atomic layer. In addition, the $[Fe]_{tet-I}$ - $[FeNi]_{oct}$ - $[Fe]_{tet-II}$ atomic layer has longer bond length than that of the equilibrium structure, indicating that Fe and Ni atoms have weaker bonding with O in this layer, and can easily exsolve from the NiFe₂O₄ lattice. Calculation results of bond length can be found in Table S3 in the SM.

Besides the interface structure, point defect formation energies were calculated to analyze how the transformation process begins, which are summarized in Table 1. Calculation details of point defect formation energies can be found in section 2.3 of the SM, in which the parameters are listed in Table S4. It shows that Ni and Fe atoms at octahedral sites have the lowest formation energies of point defect. In addition, Ni_{oct} has negative defect formation energy, suggesting that the Ni_{oct}-O bonds will break preferentially during the transformation, consistent with the results in previous reports [49]. Oxygen has the highest defect formation energy, and does not easily exsolve from the lattice. Therefore, the metal atoms, rather than O atoms, preferentially leave the NiFe₂O₄ lattice at the very beginning of transformation process.

Based on the above analysis, we propose a transformation mechanism as follows. First, three different atomic layers, $[Fe]_{tet-I}$, $[FeNi]_{oct}$ and $[Fe]_{tet-II}$, are assembled on the same (111) atomic layer to lower the surface energy of this system. Then, the Fe and Ni atoms in these layers exsolve from the lattice of NiFe₂O₄, and reconstruct a more stable Fe_{0.64}Ni_{0.36} lattice. Subsequently, the O_I, $[FeNi]_{3oct}$ and O_{II} layers exsolve from the NiFe₂O₄ lattice layer-by-layer [see Fig. S10(d-f) for interface schematics], with the Fe and Ni atoms from the [FeNi]_{3oct} layer attached to the Fe_{0.64}Ni_{0.36} lattice. After this process, the next [Fe]_{tet-I}, [FeNi]_{oct} and [Fe]_{tet-II} atomic layers assemble on the same (111) atomic layer, forming an interface with Fe_{0.64}Ni_{0.36} as shown in Fig. 3(d). The periodical repetition of the above transformation process continues until the annealing process is finished, and a final interface forms between NiFe₂O₄ and Fe_{0.64}Ni_{0.36} which was displayed in Fig. 2(e).

3.3. Microwave absorption properties

The μ_r and ε_r were measured at frequencies 2–18 GHz, and the RL values at different thicknesses (d) and frequencies (f) were calculated using Eqs. (1) and (2). Fig. 4 shows the 3D-plots of RL against d and f for the fiber membranes obtained at different annealing temperatures. Fig. 4(a) shows the 3D plot of RL against d and f for CNF-400, consisting of NiFe2O4/CNFs. The RLmin value is -32.8 dB at frequency 17.68 GHz and thickness 9.1 mm, and the widest EAB is 1.12 GHz at 6.5 mm. From Fig. 4(a), it can be seen that CNF-400 has strong absorption at frequencies of both 6.24 GHz and 17.68 GHz, which are attributed to natural and exchange resonance peaks of NiFe₂O₄, respectively. [12,50] At these two frequencies, the RL values are less than -10 dB in thickness ranges 4.3-8.2 mm and 8.3-10 mm, respectively. For CNF-500, the EAB of 1.12 GHz is achieved at a thickness of 6.7 mm, and the RL_{min} value is -27.8 dB at f = 17.44 GHz and d = 6.4 mm, as shown in Fig. 4(b). Compared to CNF-400, CNF-500 has a lower absolute value of RLmin at a lower frequency. In CNF-500, the transformation from NiFe₂O₄ to Fe_{0.64}Ni_{0.36} has just begun. Therefore, CNF-500 is mainly composed of NiFe₂O₄/CNFs, and its MA is still dominated by NiFe₂O₄. It is reported that the exchange resonance peak shifts to lower frequencies as NP size increases [51]. Compared to CNF-400, CNF-500 has larger NPs, thus leading to the shift of exchange resonance to lower frequencies. As the NPs grow, the NP size distribution becomes more disperse, which causes



Fig. 4. 3D plot of the MA properties for (a) CNF-400, (b) CNF-500, (c) CNF-600, (d) CNF-700, and (e) CNF-800, (f) contour plot of MA properties for CNF-800, showing the bandwidth and RL_{min} at d = 2.1 mm, and (g, h) Comparison of MA properties between CNF-800 and the other absorbers in previous work.

Table 2

MA properties for all the CNF membranes.

CNF membrane	RL _{min} (dB)	d _{RL} (mm)	EAB (GHz)	d _{EAB} (mm)
CNF-400	-32.8	9.1	1.12	6.5
CNF-500	-27.8	6.4	1.12	6.7
CNF-600	-44.6	7.7	5.20	8.3
CNF-700	-46.4	4.7	5.76	6.2
CNF-800	-57.7	2.1	6.48	2.1
CNF-900	-64.1	5.4	4.48	2.3

Table 3

Comparison of MA properties for CNF-800 and other absorbers reported in literature.

Material	RL _{min} (dB)	d _{RL} (mm)	EAB (GHz)	d _{EAB} (mm)	Ref.
FeNi@graphite/ CNF	-57.7	2.1	6.48	2.1	This work
Co _x Ni _y in C nanosheets	-43.7	1.7	5.70	1.8	[8]
Organic C aerogel	-42.4	2.9	5.92	1.8	[9]
Fe ₃ O ₄ /C nanoflower	-54.6	4.3	6.00	2.1	[11]
NiCo@C/ZnO nanorod	-61.0	2.3	6.08	2.0	[16]
FeNi/C nanofibers	-24.8	2.7	4.40	1.8	[53]
FeNi/SWCNT	-42.8	2.7	4.90	2.1	[54]
1D Fe ₃ N@C	-29.5	2.3	5.80	1.7	[57]
MOF-71 & derivatives	-59.8	3.0	5.70	3.0	[58]
FeNi/CNF in C aerogel	-39.4	2.0	4.70	1.8	[59]
Ti ₃ C ₂ T _x aerogel	-40.5	2.5	5.66	3.0	[60]
SiC NW/G aerogel	-54.8	3.6	6.50	2.0	[61]
NiAl-LDH/G	-41.5	1.4	4.40	1.6	[62]

Note: G = graphene, SWCNT = single-walled carbon nanotube, NW = nanowire, LDH = layered double hydroxide.

the broadening and intensity decrease of the exchange resonance peak, resulting in a smaller absolute value of RLmin. Fig. 4(c) shows MA properties of CNF-600, with both NiFe2O4 and Fe0.64Ni0.36 present. CNF-600 has an RL_{min} of -44.6 dB at f = 17.28 GHz, d = 7.7 mm, and an EAB value of 5.20 GHz at d = 8.3 mm. Compared to CNF-400 and 500, there is a major improvement in MA properties of CNF-600, hinting that the newly-formed Fe0.64Ni0.36 has better MA properties than that of NiFe₂O₄. As shown in Fig. 4(d), CNF-700 has an RL_{min} value of -46.4 dB at f = 6.80 GHz, d = 4.7 mm, and an EAB value of 5.76 GHz at d = 6.2 mm. Compared to CNF-600, CNF-700 demonstrates enhanced MA properties due to the increasing composition of Fe_{0.64}Ni_{0.36} in the NPs. To better exhibit their MA properties, the contour plots for CNF-400 to 700 are shown in Fig. S11. In Fig. 4(e), CNF-800, consisting of $\mathrm{Fe}_{0.64}\mathrm{Ni}_{0.36}$ @graphite/CNFs, have the best MA properties among the CNFs, achieving an $RL_{min} \mbox{ of } -57.7 \mbox{ dB}$ at f=14.08 GHz, and an EAB value of 6.48 GHz both at $d=2.1\ \text{mm}.$ These values are clearly labelled in the contour plot Fig. 4(f), showing that the bandwidth ranges from 11.20 GHz to 17.68 GHz, covering almost all the K_u band (12.0-18.0 GHz) [52]. For comparison, 3D and contour plots of the MA properties of CNF-900 are shown in Fig. S12. Compared to CNF-800, CNF-900 has a lower RL_{min} of -64.1 dB, but at a larger thickness of 5.4 mm. In addition, the EAB of 4.48 GHz is less than that of CNF-800. Hence, CNF-800 has overall better absorption properties.

To summarize and compare the MA properties of all CNFs, their RL_{min} , widest EAB, and corresponding d values are presented in Table 2. It can be seen that RL_{min} values increase with annealing temperature with an exception at 500 °C, while EAB values increase with annealing temperature up to 800 °C and then decrease at 900 °C. The thicknesses for RL_{min} and EAB coincide for CNF-800, while other CNFs show large thicknesses that do not coincide. For CNF-400 and 500, the RL_{min} and EAB values are low. At annealing temperatures higher than 600 °C, the CNFs show a remarkable increase in both RL_{min} and EAB, revealing that Fe_{0.64}Ni_{0.36} has superior MA properties compared to NiFe₂O₄. To better understand this, we will explore the MA mechanisms of CNF-400 to CNF-800 in section 3.4.



Fig. 5. (a) Real and (b) imaginary parts of permittivity and (c) tan\delta_e for all CNFs; The Cole-Cole curves of (d) CNF-400, (e) CNF-600 and (f) CNF-800.



Fig. 6. (a) Real and (b) imaginary parts of permeability, (c) $tan \delta_{\mu}$, (d) C_0 , and (e) hysteresis loops for all CNFs.

A comparison of the MA properties between CNF-800 and microwave absorbers in previous work is shown in Fig. 4(g) and (h), and their MA parameters are summarized in Table 3. From Fig. 4(g), it can be seen that CNF-800 in this work has coinciding thickness of 2.1 mm for RL_{min} and widest EAB, which is very practical for strong wideband MA applications. Comparisons were made with other 1D FeNi/C composite absorbers, *i.e.*, FeNi/C nanofibers [53] and FeNi/single-walled carbon nanotubes [54]. From Fig. 4(g), it can be seen that both composites have non-coinciding thickness. Furthermore, from Fig. 4(g), the RL_{min} and EAB values are inferior to those of CNF-800. The biggest discrepancy between CNF-800 and previous 1D-nanostructure absorbers is that in CNF-800, FeNi NPs are faceted and form a core–shell structure with graphite. The advantage of these faceted core–shell NPs is that they greatly enhance interface polarization loss, as the core–shell structure provides more interfaces, and the facets induce charge distribution asymmetry [55,56]. Therefore, the nanostructure of CNF-800 plays an

important part in the superior MA properties of CNF-800. Other composite absorbers for comparison include carbon nanostructures [8,11,16,57–60], aerogels [9,61], and graphene composites [62]. Though some absorbers achieved a lower thickness for both RL_{min} and EAB [8,59,62], their corresponding d values did not coincide, and the RL_{min} and widest EAB values of these work are inferior to CNF-800, which is shown in Fig. 4(h). Although an aerogel composite [61] also achieved a coinciding d value, the thickness is 3 mm, and the absolute value of RL_{min} is lower than CNF-800. From Fig. 4(h), it can be seen that CNF-800 satisfies both strong and wideband absorption. Considering strong wideband absorption and coinciding thickness, CNF-800 is a promising candidate as a flexible MA fabric that absorbs K_u band microwaves, which has wide applications in satellite communications.

By tuning the annealing temperature, different MA properties can be achieved for the CNFs. CNF-400 consists of NiFe₂O₄/CNFs, and has strong absorptions at frequencies 6.24 GHz and 17.68 GHz. Starting from CNF-500, as annealing temperature increases, the EAB becomes wider and the absorption capacity increases. For CNF-800, a hierarchical nanostructure $Fe_{0.64}Ni_{0.36}$ @graphite/CNFs forms, demonstrating strong wideband MA. It is shown that MA properties are closely related to microstructure of CNFs. The design of core–shell NP/CNF structure meets our expectations, and succeeds in achieving outstanding MA properties.

3.4. Microwave absorption mechanisms

To explore the microwave absorption mechanisms in these CNFs, their EM parameters were carefully analyzed. Fig. 5 presents the plots of ϵ and $tan\delta_\epsilon$ with respect to frequency, as well as Cole-Cole curves of three CNFs. These plots were used to investigate dielectric loss mechanisms in the CNFs. For ε , ε' , the lossless parameter, quantifies the dielectric interaction that results in energy storage, while ε ", the lossy parameter, quantifies the dielectric interaction that results in energy dissipation [6]. The energy dissipation can also be quantified by $\tan \delta_{\epsilon}$. Generally, the higher the $tan \delta_{\epsilon}$ value, the greater the energy dissipation [6]. Fig. 5(a) shows the real part (ϵ') of permittivity plotted against frequency. It shows that the ϵ' values of the CNFs have different characteristics. CNF-400 and 500 have low ε' values around 2.50 that do not change significantly with frequency. For CNF-600, there is a small decrease in ϵ' from 3.31 to 2.93 in the 2–18 GHz range. For CNF-700 and 800, their ε' shows an evident decreasing trend. For CNF-700, ε' decreases from 6.36 to 4.84, and for CNF-800 the ε' values decrease from 9.40 to 6.43, which is the largest decrease in ε' among the CNFs. The decrease in ε' values is a typical characteristic of permittivity, according to the Debye equations [63].

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2} \tag{6}$$

$$\varepsilon^{'} = \frac{(\varepsilon_s - \varepsilon_{\infty})\omega\tau}{1 + \omega^2\tau^2}$$
(7)

where τ is the relaxation time constant, $\omega = 2\pi f$, ε_s is the static permittivity, and ε_{∞} is the permittivity at the high-frequency limit. The dielectric loss mechanisms can be revealed by ε'' and tan δ_{ε} plots in Fig. 5 (b, c), in which large ε'' and tan δ_{ε} indicate strong conduction loss [6], and fluctuations of ε'' and tan δ_{ε} suggest there is polarization loss [16].

First, we focus on the conduction loss of the CNFs. CNF-400 and 500 have ε'' and $\tan \delta_{\varepsilon}$ values close to 0, meaning the conduction loss is weak. CNF-600 has larger ε'' and $\tan \delta_{\varepsilon}$ values than CNF-400 and 500, but its ε'' values are smaller than 1. CNF-700 has ε'' values around 2, and $\tan \delta_{\varepsilon}$ values a little smaller than that of CNF-800, which has the largest ε'' and $\tan \delta_{\varepsilon}$ values, indicating the conduction loss is strong in CNF-800. It can be seen that the strength of conduction loss increases with annealing temperature, which is ascribed to the fact that Fe_{0.64}Ni_{0.36} NPs formed at high temperatures have better conduction properties than NiFe₂O₄ NPs.

In addition, the good conduction properties are credited to the conducting network formed by intertwining CNFs, which promotes the current flow between nanofibers.

Then, we elaborate on the polarization loss in the CNFs. In Fig. 5(b) and (c), fluctuations of ε'' and $\tan \delta_{\varepsilon}$ at high-frequency bands are present in all CNFs. For CNF-400 and 500, there are fluctuations around 9 and 14 GHz. For CNF-600, the fluctuations are at 12.5 and 16 GHz. For CNF-700, multiple fluctuations exist at frequencies 9, 12.5, 16, and 17 GHz, and the largest fluctuation is at 9 GHz. These fluctuations indicate that there is polarization loss in CNF-400, 500, 600, and 700. For CNF-800, there are multiple large fluctuations at frequencies higher than 8 GHz, suggesting a strong polarization loss. The strong polarization loss of CNF-800 is attributed to the facets, defects, and abundant interfaces in the CNFs, which cause asymmetric distribution of charge, charge accumulation, and dipole formation [55,56].

Fig. 5 (d-f) shows the Cole-Cole plots of CNF-400, 600, and 800, and Fig. S13 presents Cole-Cole plots of CNF-500 and 700. These plots were used to study the polarization loss for the CNFs in detail. The Debye relaxation processes, which results in polarization loss, are revealed by semicircles in the Cole-Cole curves. The semicircles are described using Eq. (8), derived from Eqs. (6) and (7) [64].

$$\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_{\infty}}{2}\right)^2 + \left(\varepsilon'\right)^2 = \left(\frac{\varepsilon_s - \varepsilon_{\infty}}{2}\right)^2 \tag{8}$$

It can be observed that as annealing temperature increases, more semicircles appear, meaning that there are more relaxation processes. This observation can be related to the microstructure in these CNFs. In general, polarization is caused by interfaces and defects in a material. For the CNFs, microstructural defects are present in all CNFs, but the interface structures vary as the microstructure of the NPs evolves with annealing temperature, which causes change in the interface polarization for different CNFs. In CNF-400, only NiFe₂O₄/C interfaces exist, while in CNF-600, there are NiFe₂O₄/C, Fe_{0.64}Ni_{0.36}/C and NiFe₂O₄/Fe_{0.64}Ni_{0.36} interfaces, resulting in an increase of interface polarization. CNF-800 has a large amount of faceted Fe_{0.64}Ni_{0.36}/graphite interfaces and graphite/amorphous C interfaces, leading to strong interfacial polarization, and thus CNF-800 has the most Debye relaxation processes.

Fig. 6 shows plots of μ , tan δ_{μ} , C₀ with respect to frequency, and hysteresis loops for all CNFs, from which magnetic loss mechanisms are explored in the CNFs. Similar to ε , for μ , μ' quantifies the lossless magnetic interaction which results in energy storage, while μ " and tan δ_{μ} quantify the lossy magnetic interaction which results in energy dissipation. From Fig. 6(a), it can be seen that all CNFs have a similar characteristic shape and similar values for μ' up to 16 GHz. Note that there are large fluctuations at 5-8 GHz for all the CNFs, and in particular, large fluctuations appear at 16-18 GHz for CNF-400, 500 and 600. Fig. 6(b, c) show plots of μ'' and $\tan \delta_{\mu}$, in which the peaks appear at the same frequency ranges as the fluctuations of μ' shown in Fig. 6(a). The peaks between 5-8 GHz for all CNFs are attributed to natural resonance [12,50], as labelled in Fig. 6(c). While for CNF-400, 500 and 600, the peaks at frequencies higher than 15 GHz are caused by exchange resonance, labeled in Fig. 6(c), which is often present at high frequencies in small nanostructures with interfaces [12,50]. As can be seen from Fig. 6 (b, c), the exchange resonance peak intensity changes for different CNFs. In CNF-400, the exchange resonance is dominant, while the resonance intensity drops drastically in CNF-500, and decreases further in CNF-600. In CNF-700 and 800, exchange resonance is weak or not present, probably due to the widespread NP size in these CNFs. Thus, it can be concluded that the exchange resonance intensity decreases as annealing temperature increases. Fig. 6(d) shows plots of C_0 , which is commonly used to reveal eddy current loss processes. When eddy current loss is dominant, C₀ does not fluctuate significantly with frequency [30]. Therefore, eddy current loss is dominant for the flat regions of the C₀ curve in Fig. 6(d). It can be seen from Fig. 6(d) that flat regions of C_0 exist in all CNFs, so eddy current loss is an important magnetic loss

Table 4

Magnetic parameters obtained from the hysteresis loops of the CNFs.

			•	-	
Parameter	CNF-400	CNF-500	CNF-600	CNF-700	CNF-800
M_s (emu/g)	1.99	8.65	27.19	36.63	43.96
H _c (Oe)	37	70	87	123	191

mechanism present in all CNFs. The light-blue shades in Fig. 6(d) represent the frequencies where eddy current loss is dominant for all CNFs. For CNF-800, eddy current loss is dominant in frequency ranges 8.5–11 GHz and 13–18 GHz. For CNF-700, eddy current loss is dominant in a wide frequency range of 8.5–18 GHz. For the other three CNFs, the eddy current dominant frequency range is interrupted by the exchange resonance. In CNF-600, the 8.5–16 GHz region is dominated by eddy current loss, while 16–18 GHz is the exchange resonance. For CNF-400 and 500, eddy current loss is dominant from 8.5 GHz up to 17.5 GHz, while 17.5–18 GHz represents the exchange resonance.

The hysteresis loops for the CNFs, as shown in Fig. 6(e), are used to investigate hysteresis loss. The magnetic parameters for all the CNFs are summarized in Table 4. As the annealing temperature increases, the magnetic properties of the CNFs improve. CNF-400 only has an M_s of 1.99 emu/g, an M_r of 0.03 emu/g, and an H_c of 37 Oe, due to its poor crystallinity and low content of magnetic material. CNF-800 has an M_s of 43.96 emu/g, an M_r of 8.92 emu/g, and an H_c of 191 Oe, which are the best magnetic properties among the CNFs. Hysteresis loops for all the CNFs show soft magnetic characteristics, since the magnetic materials, NiFe₂O₄ and Fe_{0.64}Ni_{0.36}, are well-known soft magnets. For such soft

magnetic materials, hysteresis loss at low field is negligible [65]. Therefore, the main magnetic loss mechanisms in the CNFs are the magnetic resonances and eddy current loss.

Fig. 7(a, b) shows the attenuation constant (α) and normalized impedance at 2.1 mm for the CNFs. In Fig. 7(c), the point of minimum RL at different thickness of CNF-800 is matched with the quarterwavelength model and normalized impedance, which helps to understand the origin of the strong wideband absorption at thin thickness. In Fig. 7(a), the attenuation constant (α) of the CNFs varies with frequency, calculated using Eq. (4). For an incoming EM wave, its intensity decays exponentially as $I(x) = I_0 e^{-\alpha x}$, where x is the distance travelled, and I_0 is the initial intensity [66]. From the above equation, we can see that α is a measure of the ability to attenuate EM waves. The α values of all CNFs are enhanced around natural and exchange resonant frequencies. The highest α value is achieved in CNF-400, reaching 337.1 at the exchange resonance 17.68 GHz. This impressive value shows CNF-400 has strong absorbing ability around the exchange resonance. From CNF-400 to 800, except for the exchange resonance frequencies, α values gradually increase. Therefore, the overall capability to attenuate EM waves from 2-18 GHz increases. CNF-800 has the overall highest α values in a wide frequency range, with $\alpha > 100$ (skin depth 1 cm) for frequencies 4.8–18 GHz. Fig. 7(b) shows the normalized impedance for the five CNFs at d =2.1 mm. Theoretically, when $|Z_{in}/Z_0|$ is equal to 1, no reflection of the EM wave occurs at the air-absorber interface, and the wave is perfectly transmitted into the absorber, which results in low RL values. CNF-800 has the best impedance matching at 2.1 mm, with $|Z_{in}/Z_0|$ values close to 1 from 10 GHz to 15 GHz. Based on impedance matching theory above, strong absorption capacity is expected for the frequency range



Fig. 7. (a) Attenuation constant *a* and (b) normalized impedance at 2.1 mm for all CNFs; (c) RL at different thicknesses correlated to the quarter-wavelength model and normalized impedance for CNF-800.



Scheme 1. Illustration of MA mechanisms in CNF-400, 600, and 800.

10–15 GHz, which indeed has large overlap with the EAB at 2.1 mm from 11.20 to 17.68 GHz. Therefore, we deduce that the wide EAB of CNF-800 originates from good impedance matching over a large frequency range. In Fig. 7(c), the RL curves of CNF-800 exhibit relatively strong absorption at thicknesses of 1.8 mm, 2.1 mm, 2.5 mm, and 3.1 mm. However, the minimum RL values are achieved at different frequencies for these thicknesses. To explain this phenomenon, the RL curves of CNF-800 at these thicknesses are correlated with the quarter-wavelength model and normalized impedance. The quarter-wavelength matching condition is given as follows. [67]

$$t_m = \frac{n\lambda}{4} = \frac{nc}{4f\sqrt{\mu_r \varepsilon_r}} \tag{9}$$

where t_m is the matching thickness, n is an odd positive integer, and λ is the wavelength of the EM wave. When the matching condition in Eq. (9) is satisfied, the incoming and reflected waves cancel inside the absorber, and an optimal RL should be obtained. It was found from Fig. 7(c) that the t_m at the frequency of minimum RL is close or equal to the absorber thickness (1.8 mm, 2.1 mm, 2.5 mm, and 3.1 mm), and the normalized impedance is close or equal to 1. Focusing on the RL curve when d=2.1 mm, the RL_min point appears at 14.08 GHz, and corresponds to $t_m=2.05$ mm and $|Z_{in}/Z_0|=1$. This means that CNF-800 achieves its RL_min value when the quarter-wavelength condition is satisfied and Z_{in} matches Z_0 .

Fig. S14 presents correlation plots with the quarter-wavelength condition and impedance matching for other CNFs. It can be seen that RL curves of CNF-400 and 500 do not agree with the quarter wavelength condition. Due to the dominant magnetic resonance, they exhibit strong absorption at resonant frequencies, independent of thickness. As the content of Fe0.64Ni0.36 in the CNFs increases, this thickness independency diminishes. CNF-600 demonstrates better compliance with the quarter-wavelength condition than CNF-500, while for CNF-700, the RL curves almost match the quarter-wavelength condition, but still have some offset. From the discussion above, we can see that unlike CNF-800, the other CNFs do not match the quarter-wavelength condition very well. Considering the impedance matching, CNF-400 and 500 have high normalized impedance, while CNF-600 and 700 have lower values closer to 1, accounting for their wider EAB. From this, we can conclude that Fe_{0.64}Ni_{0.36}@graphite/CNFs produce better impedance matching than NiFe₂O₄/CNFs. It should be noted that the above CNFs only showed impedance matching around local minima of RL, whereas CNF-800 exhibited impedance matching in a wide frequency range, especially at low thickness. Through the above analysis, we further confirm the strong wideband MA of CNF-800 originates from wideband impedance matching and good agreement with the quarter-wavelength condition, which are characteristics exclusive to CNF-800.

A summary of the MA mechanisms is shown in Scheme 1. The

excellent MA properties in these CNFs originate from dielectricmagnetic synergistic loss. For CNF-400, magnetic loss mechanisms contain strong natural and exchange resonances, as well as eddy current loss, while dielectric loss mechanisms include interfacial and dipole polarization loss. For CNF-800, the magnetic loss mechanisms include natural resonance and eddy current loss, and dielectric loss mechanisms include conduction loss, interfacial polarization, and dipole polarization loss. From CNF-400 to 800, the exchange resonance gradually weakens, but the conduction loss becomes stronger. Impedance matching and the quarter wavelength model play an important part in determining the thicknesses and frequencies at which good MA is achieved. For CNF-800, strong MA comes from various loss mechanisms, and its wide EAB originates from good impedance matching in a wide frequency range. Furthermore, the strong wideband MA of CNF-800 is achieved at a thin matching thickness according to the quarter-wavelength model.

4. Conclusion

In this work, flexible absorber membranes are produced by electrospinning followed by annealing in Ar atmosphere at different temperatures. The MA properties of the CNFs can be tuned by adjusting temperature. CNF-800 membranes annealing composed of Fe_{0.64}Ni_{0.36}@graphite/CNFs show the best MA properties, achieving an RL_{min} of -57.7 dB and an EAB of 6.48 GHz (11.20-17.68 GHz) both at the thickness 2.1 mm. For CNF-600, the NPs consist of both NiFe₂O₄ and Fe_{0.64}Ni_{0.36}, and the MA properties are inferior to those of CNF-800. CNF-400 consists of NiFe₂O₄/CNFs, which has strong natural and exchange resonance at 6.24 GHz and 17.68 GHz, respectively. The formation process of Fe_{0.64}Ni_{0.36}@graphite NPs involves a transformation from $\rm NiFe_2O_4$ NPs to $\rm Fe_{0.64}Ni_{0.36}$ NPs followed by surface graphitization. For the transition from $NiFe_2O_4$ to $Fe_{0.64}Ni_{0.36}$, a corrosion-like transformation mechanism is proposed. Correlation between structure and MA properties shows that the MA properties of the CNFs are closely related to the composition and microstructure of the CNFs. Careful analysis of the MA mechanisms shows that as the annealing temperature increases, the conduction loss intensifies, while the exchange resonance weakens for the CNFs. The outstanding properties of CNF-800, i.e., strong MA capacity, wide EAB and thin thickness, are attributed to dielectric and magnetic loss mechanisms, good impedance matching, and compliance with the quarter wavelength condition, respectively. This work presents a simple fabrication technique for microwave absorbers together with a good microstructure design that can achieve outstanding absorption properties. The methodology in this work can be expanded for other composite materials, opening a new path in the search for the ideal microwave absorber.

CRediT authorship contribution statement

Jiaju Wang: Investigation, Data curation, Formal analysis, Writing – original draft. Xiaoli Sheng: Investigation. Shujin Hao: Resources. Guanting Liu: Resources, Methodology. Rongsheng Cai: Data curation, Validation. Xuyan Xue: Supervision, Software. Yiqian Wang: Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2023.11.145.

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