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Tailoring conductive network nanostructures of ZIF-derived cobalt-decorated N-doped graphene/carbon nanotubes for microwave absorption applications

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Abstract

Confronted with microwave pollution issues, there is an urgent need for microwave absorption materials that possess optimal combinations of dielectric loss and magnetic loss properties. While a variety of studies focus on the components, the construction of nanostructure is rarely studied, which is of equivalent significance to microwave absorber design. In this work, Co-ZIF-67 was adopted as self-template to grow N-

doped graphene/carbon nanotube interlinked conductive networks in-situ under a one-step carbonization process with tailored microwave absorption properties. Diverse microwave absorption performance could be achieved by directly adjusting the proportions among ingredients and the calcination temperature, obtaining a maximum value of reflection loss of -65.45 dB at 17.5 GHz with a sample thickness of just 1.5 mm. The effective absorption bandwidth could be tailored from 3.75-18 GHz among different thickness as required. The nanostructures had an apparent impact on the corresponding microwave absorption performance, in which the N-doped carbon-based conductive networks, ferromagnetic cobalt atoms, and interfaces among heterostructure strengthened the dipolar polarization and conductivity loss, magnetic loss, and interfacial polarization, respectively. This synthesis strategy offers a promising pathway for integrating nanostructures and functions, catering to requirements for designing and optimizing prospective microwave absorbers.

1. Introduction

Irradiated electromagnetic pollution problems have aroused widespread attention accompanied by the advancement and evolution of electronic apparatuses.

Radioactive electromagnetic energy plagues humanity by obstructing precise operation in various fields ranging from industrial manufacturing to aerospace equipment, and may threaten the health of the human body [1-3]. It is generally insufficient to focus on the absorption intensity and effective absorption frequency

bandwidth but neglect the application environment. Thin, lightweight, corrosion-resistant, easily-assembled, and upscaled production are also important considerations in developing next-generation microwave absorption devices.

Microwave absorption materials can be classified as dielectric loss materials and magnetic loss materials according to their working mechanism [4, 5]. Amounts of researchers have chosen carbon-based materials[6-9], such as graphene and carbon nanotubes (CNTs), rather than ceramics [10, 11] or conductive polymers [12-15], for their superior advantages including high electrical conductivity, low density, corrosion resistance, high carrier concentration, and adjustable nanostructures [16-18]. Magnetic loss behaviours can be mainly obtained by ferromagnetic particles (Fe, Co, Ni) and their alloy compounds [19-21]. However, the aggregation of magnetic particles at the nanoscale often exerts limited microwave absorption performance at low frequencies with a narrow absorption bandwidth, attributed to the Snoke's limit [22] around bulk magnetic materials. Furthermore, unilateral of composition cannot simultaneously provide sufficient attenuation ability and effective matched impedance in an electromagnetic field. The combination of carbon-based materials and magnetic materials, which have synergetic effects, has gained much attention. Furthermore, the introduction of N atoms in the carbonaceous framework can direct specific dipole movement, which helps adjust the electrical conductivity of N-doped graphene (NG). Apart from the chemical compositions involved, the design of the nanostructure also has an indispensable impact on influencing the material microwave absorption performance, but is rarely emphasized. Notably, carbon-based conductive networks

have been suggested as competitive candidates because the numerous efficient electric transfer pathways within nanocomposites can accumulate space charges, progressively increasing the conductivity loss of the materials. In addition, the increasing interfacial areas in the heterostructure have been proven to strengthen interfacial polarization behaviours. The multi-reflection effect can be facilitated in hollow frameworks at the same time, which are auxiliary methods to transfer and dissipate electromagnetic energy.

Metal-Organic Frameworks (MOFs) are materials composed of organic ligands and metal ions [23]. Their attractive properties of high specific surface area, porosity and active sites have great potential in the fields of energy storage and transformation[24-27]. The popular posttreatment of MOFs [28], namely high-temperature calcination under an inert atmosphere, can transform them into metal/carbon core/shell structures while maintained their porous morphology, enabling upgrading performance in potential applications. Our group [29] synthesized a Co/C core/shell structure by pyrolyzing relative Co-MOF-74 under a N₂ atmosphere to evaluate its microwave absorption performance. The reflection loss reached -62.12 dB with an effective absorption bandwidth (EAB) of 4.6 GHz at a thickness of 2.4 mm. To enhance the microwave absorption performance towards MOF-based materials, researchers [30-34] often modify MOFs on graphene surfaces through two-step processes, including graphene prefabrication and growing MOFs on the surfaces. However, it is difficult to govern uniform MOF nucleation on graphene nanosheets (GNs) due to the irregular distribution of the functional groups. In addition, it requires complicated GN

prefabrication. It is a challenging but highly pursued mission to synthesize nanocomposites with controllable structures and superior functions.

To fulfil the purpose of simultaneously tailoring the microwave absorption performance and controlling the nanostructure, along with integrating the above-mentioned multiple advantages, we chose Co-ZIF-67, melamine and g-C₃N₄ in this work. Hollow voids were created inside the Co-ZIF-67 nanoparticles when introducing tannic acid to create hollow core by surface functionalization-assisted etching strategy. The NG/CNT conductive networks were constructed in-situ with the decoration of nanoscale cobalt under specific conditions. NG nanoshells grew and covered the surfaces of residual cobalt nanoparticles from ZIF-based structures, while the CNTs were interconnected and limited within the ZIF frameworks. Distinct morphologies have direct relationships with microwave absorption performance, which can be precisely adjusted by tailoring the carbonization temperature and composition proportions. Excellent microwave absorption features of thin, lightweight, wide frequency bandwidth, and strong absorption intensity, could be obtained by a facile synthesis process and met strict requirements for next-generation microwave absorption devices.

2. Experimental

2.1 Materials

Sodium Nitrate Hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole (2-mIM), methanol, absolute ethanol (99.7%), melamine, graphitic carbon nitride (g- C_3N_4), and tannic acid (TA) were supplied by Sigma-Aldrich Co., Ltd. All chemicals were used without any further purification.

2.2 Fabrication and pretreatment of Co-ZIF-67

Co-ZIF-67 was prepared according to procedures reported previously[35]. Specifically, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.87 mmol) and 2- -mIM (24.36 mmol) were separately dissolved in methanol (50 mL) under magnetic stirring for 20 minutes at room temperature. The colour of the solution turned purple after mixing them together instantaneously with continuous stirring. The nucleus grew gradually when sealed for 24 hours at constant temperature. It was collected and washed with ethanol under centrifugation, producing Co-ZIF-67 powder. Then, 10 ml of 0.5 g L^{-1} tannic acid was added dropwise into Co-ZIF-67, which was aged for 10 minutes to fabricate a hollow Co-ZIF-67 core, referred to H-Co-ZIF-67 (hollow-Co-ZIF-67).

2.3 Fabrication of Co-N-doped Graphene/Carbon nanotube nanocomposites

The H-Co-ZIF-67 powder was mixed with melamine and graphitic g- C_3N_4 according to different mass ratios (x:1:1, x ranged from 1 to 4) and ground into a uniform mixture. The mixture was then sintered under N_2 atmosphere. The temperature was increased from room temperature to 550°C at a slow rate (2°C min^{-1}), followed by 5°C min^{-1} to a specific temperature (from 600°C to 900°C). NG/CNT conductive

networks were constructed with the nanosized cobalt (Co-NG/CNT) decoration after maintaining the temperature for 3 hours. The nanocomposites were denoted as sample-x-y, where x and y represented the mass ratio of hollow-Co-ZIF-67 and the temperature of calcination, respectively. For example, sample-111-800 had a pyrolysis temperature of 800°C with a mass ratio of hollow-Co-ZIF-67: melamine: g-C₃N₄ of 1:1:1.

2.4 Characterizations

Thermal gravimetric analysis (TGA) measurements were conducted on a TGA system (Pyris 1) at a heating rate of 10°C min⁻¹ from 20°C to 900°C under a N₂ atmosphere to evaluate thermal properties during the carbonization process. The chemical compositions and element valences were analysed using X-ray photoelectron spectroscopy (XPS) on an Axis Ultra DLD spectrometer (Kratos) after the samples had been pressed into tablets. The crystal structures of the samples were obtained by powder X-ray diffraction (pXRD) patterns on a polyfunctional X-ray diffractometer (D8 advance Da Vinci, Bruker) at a scan speed of 5° min⁻¹ using Cu K α radiation ($\lambda=0.15418$ nm). A physical property measurement system (EC-II, Quantum Design) was adopted with a magnetization field ranging from -30 kOe to 30 kOe to evaluate the ferromagnetic behaviours. Dispersive Raman microscopy (Senterra R200-L, Bruker Optics) was used to obtain the Raman spectra ranging from 1000 to 4000 cm⁻¹ on a 532 nm argon ion laser (10 mW), with a spot size of 2 mm and an acceleration voltage of 10 kV. The specific surface area (S_{BET}) and the pore size distribution were

measured by a gas sorption analyser (Autosorb-IQ3). The morphologies were observed by a field-emission scanning electron microscopy system (FE-SEM, Sirion 200) at 10 kV after the samples were fixed on carbon conductive tape and spray-coated with gold. Embedded with epoxy resin in a lacy support film and sliced into ultrathin films with a microtome, a TEM system (Talos F200X G2) was utilized to obtain transmission electron microscopy (TEM) images, high-angle annular dark field (HAADF) images, Element-dispersive X-ray spectroscopy mapping (EDX mapping) and selected area electric diffraction (SAED) patterns.

To measure the electromagnetic parameters (real and imaginary parts of permittivity and permeability), the samples were prepared by homogeneous dispersing the samples in paraffin wax (wave-transparent material) with a presupposed mass ratio (from 15% to 30%) and then reshaped into toroidal rings with ϕ_{out} of 7.0 mm and ϕ_{in} of 3.04 mm. After reshaping, the real and imaginary parts of complex permittivity (ϵ' , ϵ'') and permeability (μ' , μ'') were detected by the transmission/reflection coaxial line method through a vector network analyser (VNA, Agilent N5224A) ranging from 2 to 18 GHz. The value of the reflection loss was calculated with the following equations:

$$Z_{\text{in}} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \left(\frac{2\pi}{c} f d \right) \sqrt{\mu_r \epsilon_r} \right] \quad (1)$$

$$RL = 20 \lg \left| \frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0} \right| \quad (2)$$

$$\epsilon_r = \epsilon' - j\epsilon'' \quad (3)$$

$$\mu_r = \mu' - j\mu'' \quad (4)$$

where Z_{in} and Z_0 (377Ω) are the impedance input of the absorber and free space, respectively; ϵ_r and μ_r refer to the complex permittivity and permeability of the samples, respectively; c is the velocity of light in free space; f is the microwave frequency; and d is the adjustable thickness of the samples as required.

3. Results and discussion

The Co-ZIF-67 synthesis was facile and scalable since mixing methanolic solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-mIM supported the Co-ZIF-67 nucleation at room temperature. Tannic acid (TA) acts as both protecting agent and etching agent during the corrosion process of Co-ZIF-67 [36], which was beneficial to exposing more active sites on interfaces. It also avoided aggregation of nanosized cobalt when compared with the traditional Co-ZIF-67 carbonization process. The carbonization process under a specific temperature in an inert atmosphere was employed to decompose H-Co-ZIF-67 ligands, leaving a porous nanostructure with retained parental morphology. At this moment, the reduced gases decomposed from both the ligands and melamine, played the alternative role of reducing atmosphere rather than the traditional H_2 , thereby providing a much safer atmosphere for the reduction from Co^{2+} ions to Co nanoparticles. Meanwhile, NGs were triggered in-situ to grow on cobalt, while CNT skeletons were immobilized among cobalt nanoparticles, constructing conductive carbon-based networks. By adjusting the raw material proportions, different nanostructures were acquired with various properties. Notably, without enough physical contact among them, CNTs were replaced by porous Co/graphitic-carbon

core/shell structures. A schematic illustration of the fabrication process is shown in **Figure 1**.

TGA measurements were used to analyse the influence of the carbonization temperature on the structure and microwave absorption performance of samples. Three plateaus appeared, which implied two evident mass loss behaviours in **Figure 2a**. The first slip with a mass ratio of 32.32% from 260°C to 320°C was attributed to melamine degradation. Following a steady transition state until 500°C, the organic ligands began to decompose, along with triggering the in-situ synthesis of metastable products. Catalysed by residual cobalt ions at 800°C, NG and/or CNTs emerged, interlinking and constructing conductive carbon-based networks with reduced cobalt nanoparticles. In addition, ex-situ XRD measurements were shown in **Figure S1**. The H-Co-ZIF-67 diffraction pattern exhibited no evident discrepancy compared with Co-ZIF-67 in the previous study, suggesting an intact crystalline structure after tannic acid corrosion. Several characteristic peaks were located at 44.22°, 51.52° and 75.85°, which corresponded to face-centred cubic (FCC) structure of Co (111), (200), and (220) facets (JCPDS No. 15-0806), respectively. In addition, broad bumps at 26.2° appeared when the temperature increased to 800°C, which belonged to the NG/CNT (002) plane. The N 1s peak of the XPS result (**Figure S2**) presented significant changes in the compositions under distinct calcination temperatures, indicating different N configurations during pyrolysis. Larger amounts of graphitic N atoms were substituted into carbon-based networks with increasing calcination temperature, resulting in the enhanced graphitization degree of N-doped graphene. Meanwhile, the

ex-situ morphologies during carbonization were determined from SEM images (**Figure S3**) and indicated that graphene and/or CNTs appeared when the temperature was raised to 800°C. The reflection loss among different temperatures and thicknesses with a filler ratio of 25% were detected and are presented in **Figure S4**. A suitable temperature for the carbonization process is in high demand since low temperature is insufficient to catalyse NG and CNT growth, whereas over-high temperature leads to CNT aggregation, high graphitized carbon crystallinity, and collapse of the diamond dodecahedron structure, which hinders impedance matching. As a result, carbonization temperature of 800°C was selected according to previous studies [29] and comparative experiments in this study. For convenience, the pyrolysis temperature is omitted in the sample name hereafter. For example, the name “sample-111” replaces the former “sample-111-800”.

As shown in the XRD pattern in **Figure 2b**, obvious diffraction peaks were located at the same degree for each sample, which could be indexed to the identical phase of cobalt (JCPDS No. 15-0806) as mentioned above. Characteristic CoO or Co₃O₄ diffraction peaks were not observed, indicating the purity of cobalt. The sharp and intense peaks illustrate the strong crystallization nature of cobalt, with crystal sizes ranging from 12 to 27 nm based on Debye-Scherrer's equation ($D=0.89\lambda/\beta\cos\theta$).

VSM measurements were performed to differentiate the magnetic behaviours among different composition ratios. As shown in **Figure 2c**, each sample showed a similar “S”-shaped magnetic hysteresis loop, denoting ferromagnetic behaviours similar to those of the relevant materials [37]. Nonetheless, there were discrepancies among

different samples. The saturation magnetization value (M_s) increased with the H-Co-ZIF-67 proportion in the compositions, from 48.39 emu g⁻¹ to 54.22 emu g⁻¹.

However, it was apparently lower than that of bulk cobalt (168 emu g⁻¹), attributed to the nano-size of Co and the dominant nonmagnetic carbon-based framework. In addition, the remanent magnetization (M_r) and coercivity (H_c) values were measured and shown in **Table 1**. H_c represents the ability of a magnetic material to resist an external reverse magnetic field or other demagnetizing effects, which is strongly affected by the size of the grain. As the grain size decreased, the H_c value increased at first and gradually decreased after the grain size shrunk to a critical size. The critical point of the grain size corresponded to the size of a single domain, ranging from ten to several hundred nanometres for different magnetic nanoparticles. Besides, magnetic anisotropy, doping, pores, and defects affect the value of H_c . In this case, a large H_c value originated from the nanosized cobalt within the critical diameter (70 nm) [38], along with the doping of N atoms and defects. The enhanced H_c value led to blueshift of natural resonance frequency, contributing to enhanced microwave absorption performance in the gigahertz frequency range. The adsorption/desorption isotherms and the pore-size distribution of the samples were obtained by Brunauer–Emmett–Teller (BET) gas sorptometry measurements, as shown in **Figure 2d** and **Figure S5**.

According to the IUPAC classification, all the isotherms corresponded to typical type IV isotherms characteristic of mesoporous materials. The BJH pore-size distribution results, derived from the desorption branch of N₂ isotherms, illustrated an average pore size of less than 5 nm in all the samples except for sample-411, which was

approximately 19 nm. The reason was that it inherited the properties from hollow-Co-ZIF-67 without CNTs growing from the pores, but was replaced by a porous graphitic carbon shell. The mesopore distribution in the samples suggested high mono-porous property of these nanocomposites. The S_{BET} values of the samples were calculated and are listed in **Table 1**, ranging from 270.67 m² g⁻¹ to 333.05 m² g⁻¹. Large S_{BET} areas of the samples offer more interfaces for dipolar polarization and interfacial polarization towards dielectric loss of microwaves.

Raman spectroscopy is a powerful and non-destructive method for studying molecular and defective structures. It was adopted here to obtain the graphitization degree of the samples, as shown in **Figure 2e-h**. The major peaks at 1360 cm⁻¹ and 1580 cm⁻¹ were unambiguously related to the D band and the G band of carbon-based materials, respectively. The D band represents disordered or defective atoms in sp^3 hybridized carbon, while the G band is responsible for sp^2 hybridized carbon atoms from graphitic structures. There was a small blueshift of the D band resulting from N atom doping. The graphitization degree along with the number of defects in carbon-based materials was evaluated through the intensity ratio I ($I=I_D/I_G$). The intensity ratio gradually increased with increasing H-Co-ZIF-67 content from 1.03 to 1.15. This increasing tendency originated from the enhanced defective degree of the carbon-based frameworks, which was consistent with the decreasing trend of carbon sources. As demonstrated in free electronic theory [37], a higher graphitization degree of carbon represents better material electrical conductivity, contributing to conductivity loss. More amorphous carbon leads to a lower graphitization degree, benefiting

microwave penetration. Suitable graphitization degree is consequently suggested to obtain better microwave absorption performance. It was noticed that an obvious peak emerged at approximately 2640 cm^{-1} (2D band, **Figure S6**), which belonged to the multi-layered graphene second-order feature, implying that multi-layered graphene nanosheets emerged during the carbonization process.

XPS spectra revealed the existence and state of the elements. The survey scan spectra in **Figure 3a** presented the existence of Co, C, and N elements in the composite. Due to spin-orbit splitting, the Co 2p spectrum showed two representative peaks located at 778.5 eV and 793.3 eV, which were assigned to 2p $3/2$ and 2p $1/2$ of the Co atom, respectively (**Figure S7**). The predominant peak located at 284.6 eV (**Figure S8**) corresponded to C=C sp^2 bonding in the skeleton, while the C=N sp^2 and C-N sp^3 bonding values were comparable to the literature values of 285.7 eV and 286.9 eV, respectively. The N 1s peak could be distributed into various distinguished domains (**Figure 3b-e**) with binding energies at 398.8 eV, 399.8 eV, and 400.8 eV belonging to pyridinic N, pyrrolic N, and graphitic N configurations, respectively. Pyridinic N can be regarded as active sites that serve as polarization centres [39, 40] which contributed to polarization loss. The graphitic N content dominated the configurations, which reflected the tendency of carbon atoms to be substituted by nitrogen atoms within graphene nanosheets, having a beneficial impact on improving electrical conductivity [41]. Pyridinic N and graphitic N tended to decrease when increasing the ratio of H-Co-ZIF-67, implying marginal dielectric loss behaviour.

However, excessive electrical conductivity indicates unbalanced between dielectric

loss and magnetic loss, which could ultimately result in microwave reflection instead of absorption. Hence, suitable pyridinic N to graphitic N content is recommended for optimal microwave absorption performance.

The morphology, nanoparticle crystallinity, and distribution of divergent elements could be articulated through SEM and TEM images, as revealed in **Figure 4** and **Figure S9**. After treating Co-ZIF-67 with tannic acid, a hollow core (**Figure S9a-b**) was created inside while the as-prepared precursors essentially retained their uniform diamond dodecahedron structure with a diameter of approximately 500 nm. This result indicates that pre-treatment with tannic acid could effectively increase the interfacial areas, providing more space for NG and CNT growth and reducing the weight, thereby enhancing interfacial polarization and multi-reflection effect within the hollow structures. A number of CNT clusters were randomly distributed on the surfaces of the ZIF cores and entangled together in both sample-111 (**Figure 4a**) and sample-211 (**Figure 4b**) after the carbonization process. This observation was attributed to excess melamine and g-C₃N₄. The stacking of frameworks had a detrimental impact on absorbing and depleting microwave energy since the high-electrical-conductivity CNT clusters served as shielding shells that prevented the microwave from entering the materials. Tailoring the mass ratio of the materials in a suitable range (3:1:1), both CNTs (with diameters of 32 nm, **Figure S9c**) and NGs appeared and interlinked together, constructing the proposed conductive networks (**Figure 4c and e**). The characteristic spacing of 0.13 nm for the FCC metallic cobalt (220) lattice plane was displayed in HR-TEM images (**Figure 4f**). In addition,

nanosized cobalt particles offered more interfaces for few-layer (0.76 nm, equivalent to 4-layer or so) NG nanosheets to cover, which improved interfacial polarization. A HAADF image (**Figure 4g**) provided a more detailed view of the carbonaceous nanostructures. The relatively brighter spots represented the cobalt nanoparticles with 10 nm in diameter, while the darker clusters originated from carbon nanotubes and graphene nanosheets. (EDX mapping characterization (**Figure 4h**) showed the uniform distribution of cobalt nanoparticles in the N-doped carbon-based skeleton. However, the conductive network collapsed so that no evident CNTs could be found (**Figure 4d**) when reducing the proportions of carbon sources (decomposed by melamine and g-C₃N₄). Amorphous carbon shells were replaced since these atoms failed to cover and diffuse on the surfaces of large amounts of cobalt nanoparticles. Furthermore, the porous structure could be evidently confirmed by the TEM images. In general, the real and imaginary parts of the complex permittivity and permeability correspond to the storage and the dissipation capability of electric and magnetic energy, respectively. The optimal combination of them makes a compromising impedance match possible along with enhanced microwave absorption performance. **Figure 5a** exhibited the ϵ' -frequency curves of different samples. Following the frequency dispersion effect [42], the value of ϵ' displayed a downward trend towards the frequency of each sample. In addition, the value of ϵ' decreased with the ratio of H-Co-ZIF-67, which was attributed to the weaker electrical conductivity. Specifically, the value of ϵ' declined from 31.52 to 21.47 for sample-111; a similar tendency was found for sample-211 from 27.89 to 14.29. In comparison, the decreased behaviour

was gentler for sample-311 from 13.92 to 8.40, and the characteristic peak located at 10 GHz originated from relaxation behaviour. Furthermore, more frequent curve fluctuation appeared when increasing the proportion of H-Co-ZIF-67, indicating the emergence of more relaxation behaviours. The value of ϵ'' versus frequency curves declined towards both the frequency and the ratio of H-Co-ZIF-67 corresponding to the ϵ' curves. It has been widely accepted that dielectric loss can be reflected by complex permittivity, which is determined by two dominant factors, namely conduction loss and polarization loss, according to the Debye theory [43]. Electrical conductivity has an instrumental impact on the conductivity loss by affecting the value of ϵ'' , which could be improved by constructing a GN/CNT conductive network along with doping N atoms. Intrinsic and hopping conduction, frequently observed among carbon-based materials, brought about conductivity loss of the samples as well. Evidently, characterized peaks in the plots emerged from the polarization relaxation behaviours. In this case, polarization loss exists as dipolar orientation polarization and interfacial polarization. The polarized centres were generated from multiple defects introduced by dopants in the carbon-based skeleton, which accelerated the consumption of electromagnetic energy by orientation polarization loss under an altering electromagnetic field. Moreover, heterointerfaces among 0D Co nanoparticles, 1D CNTs, and 2D GNs induced plentiful movement of the space charges, boosting the interfacial polarization effect. The Debye relaxation equation is used to theoretically demonstrate the polarization and relaxation process, which can be expressed as:

$$\varepsilon' = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} + \varepsilon_\infty \quad (5)$$

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \cdot \omega \tau \quad (6)$$

$$\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2} \right)^2 \quad (7)$$

where ω , τ , ε_s , and ε_∞ represent the angular frequency, relaxation time, static permittivity, and relative permittivity at the high-frequency limit, respectively [44]. Each Debye relaxation behaviour is indicated with corresponding semicircles (denoted as the Cole-Cole semicircle) in the plots. **Figure S10** showed several Cole-Cole semicircles in the plots, primarily representing independent relaxation behaviours by interfacial polarization. Generally, microwaves should be absorbed in order to counter reflection. Specifically, a small value of ε_r can hardly satisfy microwave dissipation, whereas an excessive value of ε_r brings about secondary microwave pollution since the domination of reflection mechanism. Therefore, a rational value of ε_r over the whole frequency range is required. The Maxwell–Garnett (MG) theory [45] explains effective permittivity, where ε_1 and ε_2 represent the permittivity of the solid and void medium, respectively, and P is the volume fraction of the void. The situation that CNT clusters were replaced by numerous pores, leading to the decreasing of the nanocomposite density, effectively reducing the value of ε_{eff} into a suitable range and eventually achieving microwave absorption.

$$\varepsilon_{\text{eff}} = \varepsilon_1 \frac{(\varepsilon_2 + 2\varepsilon_1) + 2P(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_2 + 2\varepsilon_1) - P(\varepsilon_2 - \varepsilon_1)} \quad (8)$$

The dielectric loss tangent ($\tan \delta\varepsilon$), namely, the ratio of ε'' to ε' , is commonly adopted as a direct indicator of material dielectric dissipation ability. The curves followed the

variation of ε'' (**Figure 5c**). Specifically, excessive $\tan \delta\varepsilon$ values of sample-111 were ascribed to its large ε'' value from its intrinsic electrical conductivity, which hindered microwave penetration and led to microwave reflection rather than absorption. By reducing the CNT content in the structure, the $\tan \delta\varepsilon$ values decreased to appropriate values, facilitating the microwave energy absorption and dissipation.

The complex permeability reflects the magnetic loss of the microwave absorber. It is usually believed that different magnetic behaviours dominate at different frequency ranges[46]. **Figures 5d-e** showed the variations in μ' and μ'' with frequencies ranging from 2 to 18 GHz. The samples exhibited representative ferromagnetic behaviours with values neighbouring approximately 1.1. There were obvious peaks recognizing in different curves, where the former peak originated from natural resonance and the latter peak resulted from exchange resonance behaviour. The nonmagnetic carbon-based framework was responsible for the decline in magnetism, resulting in the deviation of those peak positions. It is noteworthy that the μ'' value was less than 0 in some positions. This phenomenon could be explained by the magnetic energy produced from the motions under varying electric fields in the carbon-based frameworks according to the Maxwell equations, which was in accordance with previous researches[47]. To evaluate whether the eddy current effect contributed to the magnetic loss, the characteristic equation is proposed as follows[48]:

$$\mu'' \mu'^{-2} f^{-1} = \frac{2}{3} \pi \mu_0 d^2 \sigma \quad (9)$$

where μ_0 , σ , and d represent the vacuum permeability, electrical conductivity, and thickness of the sample, respectively. Each of them is invariant for an individual

sample. Therefore, if the value on the left side remains constant (denoted as C_0) under the changing frequency, the only factor that results in magnetic loss would be the eddy current effect. Under these circumstances (**Figure S11**), all of the curves fluctuated over the whole frequency range for all the samples, implying that the eddy current effect, accompanied with multiple resonance behaviours, contributed to magnetic loss together. The values of the magnetic loss tangent ($\tan \delta\mu$) were calculated to reveal the magnetic energy dissipation, which was presented in **Figure 5f**. The tendency of the $\tan \delta\mu$ curves followed the counterparts of μ'' , illustrating that the combination of multiple resonance behaviours dedicated the dominant magnetic loss behaviours. Furthermore, the value of $\tan \delta\epsilon$ was stronger than that of $\tan \delta\mu$ in all samples, indicating that the dielectric loss occupied a more predominant stage than the magnetic loss at the evaluated frequency bandwidth.

The reflection loss (RL)-characteristic curves exhibited the absorption intensity, effective absorption bandwidth (EAB, the frequency range with the value of RL below -10 dB) and the corresponding thickness of the samples, all of which were critical to evaluate sample microwave absorption performance. Primarily, the mass ratio of the filler in the paraffin wax had to be unified. Nanocomposites were isolated from each other when the filler ratio was inadequate, while excessive filler loading led to aggregation. A filler content from 15 wt% to 30 wt% was adopted to evaluate the intensity and EAB at a thickness of 1.5 mm (**Figure S12**). The RL value reached -22.17 dB when the filler ratio was 15 wt%. More flourishing connective networks could be built up by raising the content to 20 wt%, enhancing the RL value by 195%

to -65.45 dB. Both the interfaces and interconnected conductive networks favourably impacted microwave absorption performance. Further increasing Co-NG/CNT to 25 wt% into the matrix would dramatically decrease the value of RL to -38.84 dB with a similar bandwidth. The high electrical conductivity prompted the reflection behaviour rather than the absorption. When the filler content increased to 30 wt%, the EAB broadened to more than 7 GHz, whereas impairing RL intensity and limiting the microwave energy consumption eventually. As a result, a mass ratio of 20% was chosen as the criterion for judging the microwave absorption performance in this case.

Figure 6 exhibited the value of reflection loss determined by the frequency and thickness of different samples. Increasing the thickness of the samples led to the peaks redshift to a lower frequency, which followed the quarter-wavelength theory (**Equation S1**). It is more important to understand reasons for performance discrepancies. For sample-111, the RL value was only -4.5 dB with a thickness of 1 mm. This was attributed to the excessive growth of CNT clusters hindering the microwave energy from entering the nanocomposites. The performance of sample-211 was similar, whose RL value reached -11.23 dB with a narrow EAB covering 10.8-13.4 GHz obtained at 1.5 mm. The RL intensity was insufficient to meet the demand in practical applications due to unbalance between magnetic loss and dielectric loss. Tailoring the proportions to 3:1:1 could modify the nanostructure while enhancing microwave absorption performance simultaneously. The maximum RL value of -65.45 dB at 17.5 GHz was obtained from sample-311 at 1.5 mm, giving a RL intensity with normalized thickness of $-436.33 \text{ dB}\cdot\text{cm}^{-1}$. EAB covered from 14.8

GHz to 18 GHz at this thickness. In addition, an ultrawide EAB was achieved at 4.3 GHz with a thickness of 2 mm. More than 90% of the microwave could be absorbed by tuning the thickness from 1 to 5 mm under the specific demand frequency regions from 3.75 GHz to 18 GHz. The decreasing ratio of NG/CNTs to ferromagnetic cobalt nanoparticles in this situation offered more opportunities for microwaves to enter the nanostructure. Besides, larger interfaces improved the interfacial polarization, which made indispensable contributions towards both optimizing the RL intensity and broadening the EAB. The impedance match behaviours[49] were verified by dividing Z_{in} (the value of impedance inside the absorber) by Z_0 (the value of impedance in air, 377 Ω). The samples would obtain the best impedance match capability when the parameter was close to 1. It can be indicated that sample-311 followed the impedance match better than the other samples with appropriate impedance value originated from balanced dielectric loss to magnetic loss. However, continued H-Co-ZIF-67 addition indicated the insufficient coverage of carbon atoms on the metallic cobalt surface. In other words, neither CNTs nor NGs germinated and constructed into conductive network. Coated of amorphous carbon on the surface of cobalt nanoparticles degraded the microwave absorption performance of sample-411, with the maximum RL value unfortunately reaching only -13.08 dB at a thickness of 3 mm.

Apart from the impedance match, the attenuation capability also has a considerable impact on dissipating the microwave energy. Hence, the attenuation constant α is introduced as follows [50]:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' + \mu''\varepsilon')^2}} \quad (10)$$

As presented in **Figure S13**, all samples had increasing values in pace with frequency.

In addition, the dissipation abilities were stronger with the samples that possessed larger values of the imaginary parts of permittivity and permeability. Since sample-311 existed with remarkable impedance matching as well as sufficient attenuation capability, it is reasonable to demonstrate optimal microwave absorption performance.

The superior performance of microwave absorption could be demonstrated as follows.

(1) The customized construction of NG/CNT conductive networks on heterostructures were evaluated. Compared with the amorphous carbonaceous shell, the interlinked networks increased the electrical conductivity of the samples, making inevitable contributions to conductivity loss. (2) Large areas of interfaces were generated among the skeletons. Different charge densities aside from the interfaces could be regarded as micro-capacitor structures, consequently inducing directional movement of the space-charges and facilitating the transfer of electromagnetic energy into heat energy by the interfacial polarization process. (3) The dopants of numerous N atoms served as active sites in the frameworks. These defective centres assisted in strengthening the absorption intensity as well as broadening the EAB through dipolar polarization behaviour. (4) A suitable proportion of modified ferromagnetic cobalt nanoparticles endowed effective magnetic loss by multiple resonance behaviours. The balanced impedance match was satisfied with the synergistic effect between dielectric loss and magnetic loss, guaranteeing the penetration of the microwave into the nanocomposites

rather than reflection from the surface. (5) The multi-reflection effect promoted microwave energy dissipation. When the microwave permeated into the nanostructure, the energy began to attenuate due to the migration pathways created by pores and interfaces. Declined with prolonged propagation, the microwave energy was transformed into heat energy and ultimately exhausted by the multi-reflection effect. Based on these key factors in designing an outstanding microwave absorber, it can be concluded that the multiple loss mechanisms created by Co-NG/CNT conductive networks exhibit attractive impact on microwave absorption performance with enhanced absorption intensity, broader effective frequency bandwidth, thinner thickness, and lighter weight when compared with the relative materials shown in **Table 2**. These prominent microwave absorption performances fulfilled the strict demands of next-generation microwave absorbers. The microwave absorption mechanism is illustrated in **Figure 7**.

4. Conclusions

In conclusion, Co-ZIF-67 was adopted as a self-template to synthesize N-doped graphene/carbon nanotube interlinked conductive networks modified with cobalt nanoparticles through a facile carbonization process. Both the morphology and the microwave absorption performance could be precisely controlled by either tailoring the content of the precursor or the carbonization temperature. Appropriate ratios and calcination temperatures not only guaranteed the construction of conductive networks but also prevented the graphitization or amorphousness of carbonaceous shells,

leading to impedance matching. Through representative characterizations, it can be demonstrated that the nanostructure devoted indispensable impact on microwave absorption. The designed Co-NG/CNT conductive networks revealed enhanced microwave absorption properties, in which the maximum value of reflection loss was -65.45 dB with a frequency of 17.5 GHz and thickness of just 1.5 mm. The effective absorption bandwidth was enlarged at 4.3 GHz when the thickness was 2 mm. It could also be tailored from 3.75 to 18 GHz by changing the thickness from 1 to 5 mm. Furthermore, the maximum value of S_{RL} reached $-436.33 \text{ dB}\cdot\text{cm}^{-1}$, which advanced development of promising microwave absorption materials. The enhanced microwave absorption performance could be ascribed to conductivity loss from the high electrical conductivity of the conductive network, interfacial polarization from heterointerfaces, dipolar polarization from doping atoms, multiple resonances from ferromagnetic nanoparticles, and multi-reflection effect from the nanostructure. Exhibiting superior microwave absorption performance with the facile synthesis process, this impressive result broadens the horizons for designing next-generation microwave absorbers within decades.

Figure 1. Schematic illustration of the Co-NG/CNT nanocomposites.

Figure 2. (a) TGA, (b) XRD, (c) VSM, and (d) N₂ adsorption-desorption measurements of samples; Raman spectra of: (e) sample-111, (f) sample-211, (g) sample-311, and (h) sample-411.

Figure 3. (a) XPS spectrum of samples; N configurations of (b) sample-111, (c) sample-211, (d) sample-311, (e) sample-411 and (f) corresponding proportions.

Figure 4. SEM images of (a) sample-111, (b) sample-211, (c) sample-311, and (d) sample-411; (e) TEM images, (f) HR-TEM image, (g) HAADF image and (h) EDX-mapping images of sample-311.

Figure 5. Complex permittivity (a, b), permeability (d, e), and corresponding tangent values (c, f) of samples.

Figure 6. Reflection loss behaviors, impedance match and corresponding matching thickness of samples: (a) sample-111, (b) sample-211, (c) sample-311, and (d) sample-411.

Figure 7. Microwave absorption mechanism of Co-NG/CNT.

Table 1. The values of magnetic properties, S_{BET} , pore sizes distribution and the intensity ratio of the samples.

sample	111	211	311	411
M_s (emu/g)	48.39	49.53	51.97	54.22
M_r (emu/g)	9.79	10.92	13.09	10.80
H_c (Oe)	284.38	315.26	324.36	338.60
S_{BET} (m^2/g)	333.05	270.67	310.75	273.20
Pore Radius (nm)	3.83	3.84	3.83	19.12
I_D/I_G	1.03	1.05	1.11	1.15

Table 2. Microwave absorption performance of relative materials

sample	mass ratio (%)	optimal R_L value (dB)	f at optimal R_L (GHz)	d (mm)	EAB at this thickness (GHz)	specific R_L ($dB\ cm^{-1}$)	Ref.
Fe_3O_4/NG	70	-53.6	6	4.1	~1.8	-130.73	[51]
Fe_3O_4 -MWCNT	20	-52.8	12.8	6.8	~1.7	-77.65	[52]
NC- Co_3O_4/CP	40	-41.38	7.32	2.3	~2.0	-179.91	[53]
Fe_3O_4/CNT	30	-43	15.2	1.5	~5.7	-245.71	[54]
ZnO-Ni@CNT	50	-58.6	12	2.3	~3.8	-254.78	[55]
Ni/C	40	-51.8	10.4	2.6	3.48	-199.23	[56]
Fe/C	15	-29.5	17.2	2.5	~5	-118.00	[57]
PAN/CNT/ Fe_3O_4	/	-59.85	16.4	1.5	~3.5	-399.00	[58]
FeNi@CNT/CNR	25	-47	10	2.3	~2.8	-204.35	[59]

Fe ₃ O ₄ /CNT	10	-24.8	9	3.2	4.2	-77.50	[60]
Co-NG/CNT	20	-65.45	17.5	1.5	4.3	-436.33	This work

Supplementary information

The XRD, XPS, SEM, Raman spectra, pore size distribution, Debye relaxation, eddy current effect, attenuation constant, microwave absorption performance of the corresponding samples, along with the quarter-wavelength theory are shown in the supplementary section.

Conflicts of interest

There are no conflicts to declare.

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.

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