

Review

Progress and Challenges of Ferrite Matrix Microwave Absorption Materials

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Abstract: Intelligent devices, when subjected to multiple interactions, tend to generate electromagnetic pollution, which can disrupt the normal functioning of electronic components. Ferrite, which acts as a microwave-absorbing material (MAM), offers a promising strategy to overcome this issue. To further enhance the microwave absorption properties of ferrite MAM, numerous works have been conducted, including ion doping and combining with other materials. Notably, the microstructure is also key factor that affects the microwave absorption properties of ferrite-based MAM. Thus, this article provides a comprehensive overview of research progress on the influence of the microstructure on ferrite-based MAM. MAMs with sheet and layered structures are also current important research directions. For core-shell structure composites, the solid core-shell structure, hollow core-shell structure, yolk-eggshell structure, and non-spherical core-shell structure are introduced. For porous composites, the biomass porous structure and other porous structures are presented. Finally, the development trends are summarized, and prospects for the structure design and preparation of high-performance MAMs are predicted.

Keywords: ferrite; microstructure; interface polarization; electromagnetic microwave absorption



Citation: Meng, X.; Xu, W.; Ren, X.; Zhu, M. Progress and Challenges of Ferrite Matrix Microwave Absorption Materials. *Materials* **2024**, *17*, 2315. <https://doi.org/10.3390/ma17102315>

Academic Editor: Gediminas Niaura

Received: 8 April 2024

Revised: 7 May 2024

Accepted: 9 May 2024

Published: 14 May 2024



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1. Introduction

With the advancement of radar and semiconductor technology, unmanned intelligent electronic devices are gradually being applied to various fields, such as intelligent assisted-driving cars, 5G smart base stations, multi-field remote-controlled drones, and unmanned transportation systems in coal mines. However, electromagnetic waves emitted by these devices interfere with each other to form electromagnetic pollution, affecting equipment stability and human health, while posing potential dangers to the human body. Developing high-performance materials resistant to electromagnetic interference is crucial for the stable operation of intelligent electronic devices [1,2]. MAMs possess advantages such as high absorption capacity, broadband performance, low thickness, and strong stability. They dissipate electromagnetic wave energy through specific mechanisms, thereby absorbing the electromagnetic wave, effectively addressing the issue of electromagnetic pollution [3–5]. These materials play a pivotal role in the field of national defense and security [6–8].

The two key factors affecting the performance of MAMs are impedance matching and attenuation characteristics. When an electromagnetic wave impinges upon the material's surface, impedance matching determines the amount of penetration into the material's interior. The closer the impedance matching value to 1, the greater the electromagnetic wave penetration. Attenuation characteristics, or the material's loss capacity, categorize MAMs based on their loss mechanisms: resistive loss materials, dielectric loss materials, and magnetic loss materials [9,10]. In the context of electrical current passage, resistive loss materials undergo a significant number of collisions between free electrons within the material, resulting in the conversion of electrical energy into thermal energy. This phenomenon predominantly occurs in materials with high electrical conductivity, such

as graphene, carbon nanotubes, and conductive polymers. On the other hand, dielectric loss materials, which contain few free electrons, undergo molecular friction, ionization, relaxation, and other processes when exposed to electromagnetic microwaves, without generating a macroscopic current, leading to a certain loss of energy. Examples include materials like Al_2O_3 and SiO_2 . Magnetic loss primarily encompasses mechanisms such as hysteresis loss, eddy current loss, natural resonance, and domain wall resonance. Materials subjected to magnetic loss undergo processes of magnetization or demagnetization in alternating electromagnetic fields, with a portion of the energy being converted into thermal energy [11,12]. Examples include ferrites and nickel-cobalt alloys. As the frequency of the alternating electromagnetic field increases, magnetic loss generally also increases, primarily due to natural resonance and domain wall resonance. Based on this mechanism, the selection of lossy materials is pivotal to the realization of high-performance MAMs. Typically, composites are prepared using two or three lossy materials, amplifying the loss synergism, and enhancing the radar-absorbing effect. Ferrites possess numerous advantages, including excellent magnetic permeability and magnetic loss, outstanding temperature and chemical stability, low cost, and strong microwave-absorbing performance.

Ferrites can be broadly classified into three types, based on their crystal structure: spinel (cubic system), garnet (cubic system), and magnetorheological (hexagonal system). The spinel type of ferrite has the chemical formula MeFe_2O_4 , where Me represents divalent metal ions such as Co^{2+} , Cu^{2+} , and Ni^{2+} , with oxygen ions arranged in a face-centered cubic (fcc) dense packing. Spinel exhibits high magnetic saturation induction, making them one of the most studied and widely applied types. The garnet structure has the formula $\text{R}_3\text{Fe}_5\text{O}_{12}$, where R represents trivalent rare earth ions such as Y^{3+} and Sc^{3+} . The performance of garnets is influenced by their crystal structure, and the properties of this material can be adjusted by varying the type of R. The magnetorheological type has the formula $\text{MeFe}_{12}\text{O}_{19}$, where Me is typically Ba^{2+} , with substitutions for Mn, Zn, Al, etc. This type of ferrite exhibits high magnetic anisotropy and a natural resonant frequency, making it an effective MAM in the centimeter wave band.

The research on ferrite MAMs can be traced back to the 1940s. Due to issues such as poor impedance matching, a single mechanism for magnetic loss, narrow absorption bandwidth, and high density, the materials are greatly limited in their applications. Modifications to ferrites are often achieved by doping metal ions, which cause distortions and defects in the internal structure. These defects can act as polarization centers, leading to electron shifts and enhanced loss to electromagnetic waves. The superior performance is attributed to the intricate design of the microstructure. By regulating and optimizing the material's microstructure, we can enhance and improve various properties of the material, including microwave absorption, physical, chemical, and mechanical properties. This results in the preparation of MAMs with high strength, wide bandwidth, low thickness, and good stability. In recent years, numerous studies have been conducted by scholars on ferrite-based MAMs. This article, from the perspectives of the microstructure, preparation methods, and composition, summarizes the research progress and challenges regarding the microstructure of ferrite-based MAMs, and points out the future development trends.

2. Sheet Structure

The sheet structure possesses a substantial surface area, with each node interconnected to form a unified network entity, providing additional anchor points. Even if some node atoms undergo substitution, it barely affects the overall structure, yet still achieves the goal of modification. Graphene is a prototypical material of the sheet structure, exhibiting a planar hexagonal honeycomb structure, with a pronounced dielectric loss and excellent conductivity. Boundary groups and planar defects can enhance the conductivity loss. The sheet structure is suitable as a carrier for nanoparticles, enabling the preparation of various functional composite materials. For instance, on graphene oxide sheets supported by polymers, the synthesized nanorods are enhanced with carbon nanotubes and chitosan, representing a promising bone filling material. Moreover, it has been extensively studied and

applied in fields such as electromagnetic microwave absorption [13,14], biomedicine [15,16], biosensors, and supercapacitors [17,18]. Assembling graphene with ferrite nanoparticles can effectively achieve a complementation of dielectric loss and magnetic loss, enhancing the electromagnetic wave loss capability.

Graphene oxide (GO) possesses a surface rich in oxygen-containing functional groups, exhibiting high chemical reactivity. Sun et al. utilized a hydrothermal method to synthesize a ternary composite material, copper-cobalt-nickel ferrite@GO@polyaniline (PANI) [19], successfully prepared a coating fabric, using aqueous polyurethane as the matrix. When the ternary composite material is applied in an amount of approximately 40%, the fabric thickness is 2.0 mm and the RL_{max} at 10.8 GHz is -33 dB, with an effective absorption bandwidth (EAB: $RL < -10$ dB) of approximately 6.95 GHz. The shielding performance can reach -47 dB within the frequency range of 300 kHz to 3.0 GHz. After chemical oxidation and stripping of graphite powder, reduced graphene oxide (RGO) sheets are obtained, which exhibit properties similar to those of graphene. However, RGO typically contains more defects and other impurities, leading to a higher conductive loss capacity, making it more suitable as a doping substrate compared to graphene. Wang and colleagues synthesized RGO@Fe₃O₄@PANI nanocomposite material [13] by reducing GO with aniline. From Figure 1a the synthesis schematic diagram and (b) TEM image of RGO/Fe₃O₄/PANI, the anchoring of ferrite particles and PANI onto the surface of GO sheets leads to magnetic losses and enhanced dielectric losses. Molecular dynamics simulations indicate a strong interaction between carboxyl groups at the edges of graphene and iron atoms in the ferrite. When the graphene sheet is introduced from a parallel direction onto the Fe₃O₄(111) surface, the interfacial interaction energy is low, making it easier to form a smooth single-layer structure. In an alternating electromagnetic field, electrons are displaced, resulting in interfacial polarization. Figure 1c shows the RL_{max} of RGO@Fe₃O₄@PANI at 7.4 GHz is -51.5 dB, with an EAB of 4.2 GHz. Compared to graphene-based composite materials, its microwave absorption performance is significantly improved.

Doping can alter the lattice structure of ferrites, modulating their electromagnetic parameters and properties such as magnetic anisotropy [8,9]. Transition metal ions like Ni, Co, and Zn, as well as rare earth elements like Ce, La, and Nd, when doped, cause changes in the lattice structure of ferrites, leading to lattice distortion, disruption of exchange interactions, and local chemical disorder. This increases internal defects, adjusting the electromagnetic parameters and properties such as magnetic anisotropy, and enhances the microwave absorption capability of the ferrites [3,7]. The unpaired 4f electrons and strong spin-orbit coupling of the rare earth element Ce ions enhance the dielectric properties of ferrites, while increasing magnetic anisotropy improves the coercivity of the materials. Under electromagnetic fields, induced dipole polarization enhances the absorption intensity of electromagnetic waves [20]. The incorporation of non-magnetic transition metal ions, such as Zn²⁺, can reduce the coupling between magnetic ions [21], decrease the coercivity, and increase the saturation magnetization, leading to a favorable attenuation effect for high-frequency and ultra-high-frequency signals. Chireh et al. substituted Fe³⁺ in LiFe₅O₈ with Sr²⁺ and Co²⁺. Due to the electronic transition between Fe³⁺ and Fe²⁺, magneto-crystalline anisotropy, exchange anisotropy, and shape anisotropy were caused by substitution of Sr²⁺ and Co²⁺, resulting in higher and lower saturation magnetization and coercivity fields for RGO/LiSr_{0.25}Fe_{4.75}O₈ and RGO/LiCo_{0.25}Fe_{4.75}O₈ nanoparticles than those of pure LiFe₅O₈ ferrite. The magnetic parameter test results show that partial substitution resulted in a larger complex dielectric constant, and the RGO/LiSr_{0.25}Fe_{4.75}O₈ and RGO/LiCo_{0.25}Fe_{4.75}O₈ nanocomposite materials [22] exhibit a broader EAB, with varying degrees of improved RL_{max} compared to LiSr_{0.25}Fe_{4.75}O₈ and LiCo_{0.25}Fe_{4.75}O₈. The RGO/LiCo_{0.25}Fe_{4.75}O₈ composite material, with a sample thickness of 3 mm, exhibits a RL_{max} of -46.80 dB at 13.20 GHz, and an EAB of 6.80 GHz (10.52–17.32 GHz). In contrast to the heat treatment and polymerization methods of Chireh et al., Shu et al. utilized a simpler solvothermal method to synthesize the RGO/ZnFe₂O₄ hybrid nanocomposite material [23], with a RL_{max} of -41.1 dB when the sample thickness is 2.5 mm. The superior microwave

absorption performance of RGO//LiCo_{0.25}Fe_{4.75}O₈ and RGO/ZnFe₂O₄ indicates that it is feasible to anchor sheet-like RGO to ferrite nanoparticles.

Li et al. substituted Fe³⁺ with Nd³⁺, utilizing solid solution and hydrothermal synthesis to produce the RGO/Ni_{0.4}Co_{0.2}Zn_{0.4}Nd_xFe_{2-x}O₄ composite materials [24]. As *x* gradually increases, the *RL*_{max} deepens, and at *x* = 0.06, the RGO/Ni_{0.4}Co_{0.2}Zn_{0.4}Nd_{0.06}Fe_{1.94}O₄ composite material exhibits a *RL*_{max} of −58.33 dB at 12.2 GHz, with a matching thickness of 2.33 mm, an *EAB* of 7.5 GHz (5.0–12.5 GHz), and a further enhanced microwave absorption performance.

Zhang et al. synthesized a composite material of RGO/CoFe₂O₄/SnS₂ using the hydrothermal method [25]. Figure 1d,e shows the dielectric polarizations in hollow CoFe₂O₄ NPs and solid CoFe₂O₄ NPs. The material exhibited a saturation magnetization (*M*_S) of 22.9 emu/g and a remanence (*M*_r) of 1.9 emu/g, preserving the excellent magnetic properties of CoFe₂O₄. The *RL*_{max} of the sample at 16.5 GHz reached −54.4 dB, with an *EAB* spanning the entire X-band, up to 12.0 GHz (6.0–18.0 GHz). In Wang et al.'s work, the synthesized NiFe₂O₄@MnO₂@graphene composite material [26] exhibited good impedance matching, primarily due to the increased contact area with air, caused by the gap between MnO₂ and graphene, enhancing impedance matching. The *M*_S of NiFe₂O₄ was 54.8 emu/g, and the *RL*_{max} of the composite sample at 7.4 GHz reached −47.4 dB. It is evident that ferrites such as CoFe₂O₄ and NiFe₂O₄ doped with Ni and Co, improve the electromagnetic microwave absorption capability of the composite material. Yan et al. prepared RGO-PANI-NiFe₂O₄, RGO-polypyrrole (PPy)-NiFe₂O₄, and RGO-3,4-PEDOT-NiFe₂O₄ composite materials [27]. From Figure 1g–i, the NiFe₂O₄ particles impart superparamagnetic to the composite materials, achieving peak *RL*_{max} of −49.7 dB, −44.8 dB, and −45.4 dB, respectively. Gao et al. synthesized a BiFeO₃/RGO composite material through a hydrothermal reaction [28], achieving a *RL*_{max} of −46.7 dB, an *EAB* of 4.7 GHz (12.0–16.7 GHz), and a matching thickness of 1.8 mm.

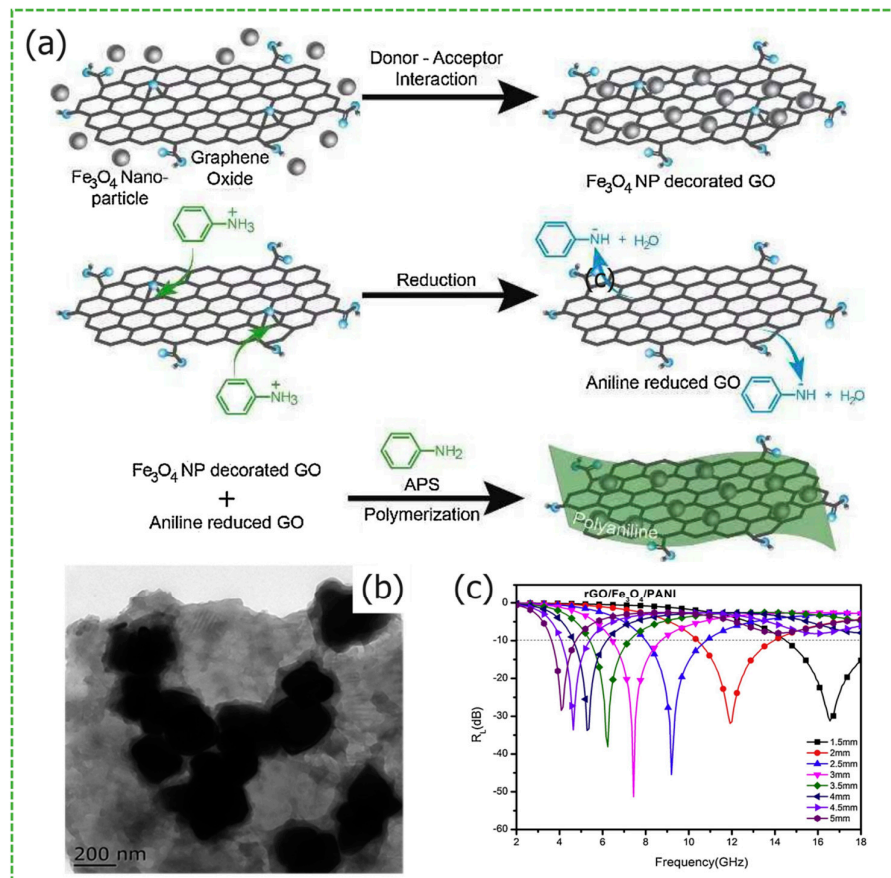


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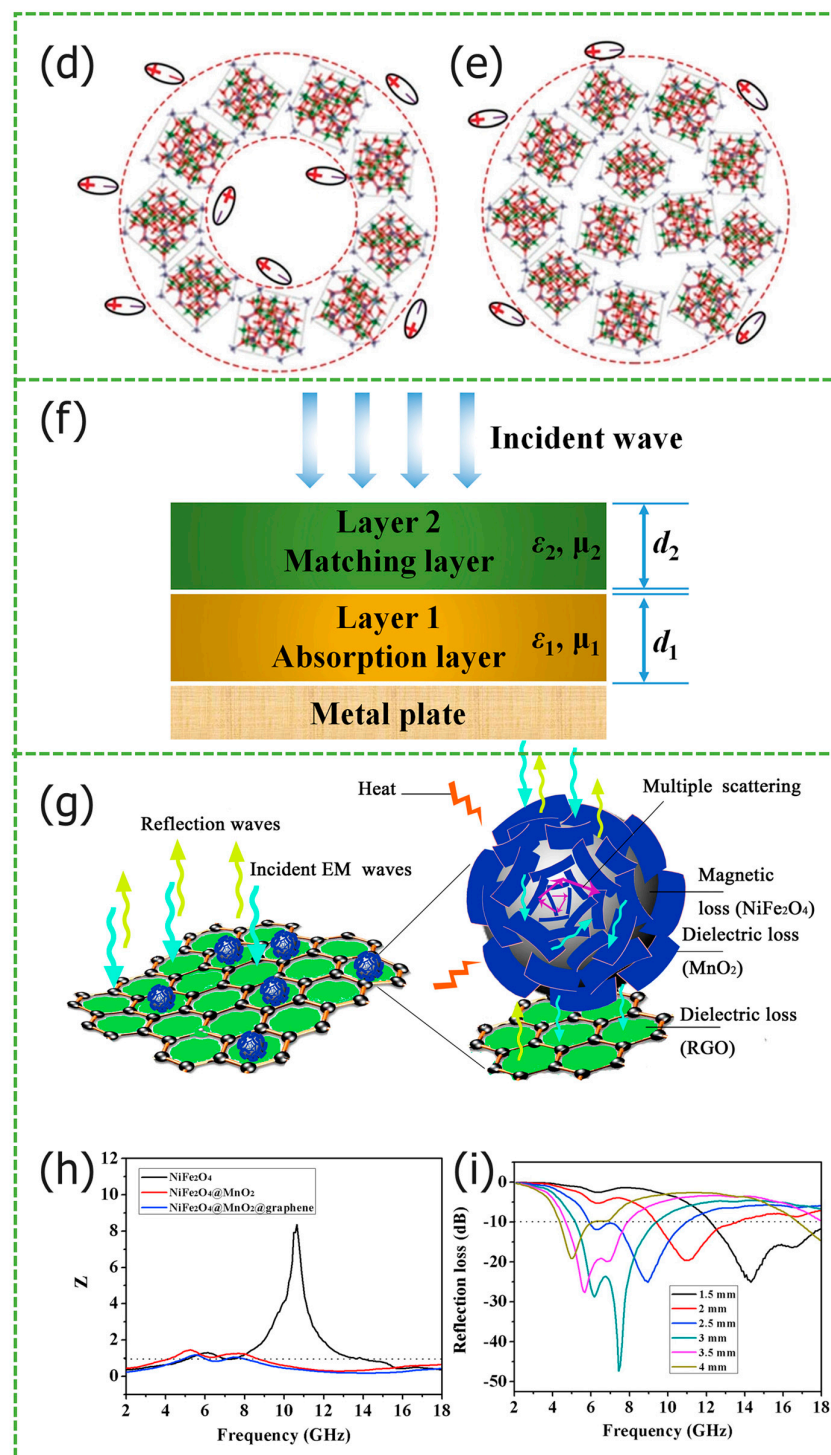


Figure 1. Graphical summary of sheet structure MAMs. (a) The synthesis schematic diagram, (b) TEM image, and (c) the RL for RGO/ Fe_3O_4 /PANI. Reproduced with permission [13] Copyright 2020, Elsevier B.V. (d,e) The dielectric polarizations in hollow CoFe_2O_4 NPs and solid CoFe_2O_4 NPs, respectively. Reproduced with permission [25]. Copyright 2018, Royal Society of Chemistry. (f) Schematic diagram of double-layer MAM. Reproduced with permission [29] Copyright 2017, Elsevier B.V. (g) Schematic illustration for absorption mechanism, (h) impedance matching, and (i) the RL curves of $\text{NiFe}_2\text{O}_4@\text{MnO}_2@\text{graphene}$. Reproduced with permission [27] Copyright 2016, Elsevier B.V.

Unlike others, Min et al. synthesized BaFe₁₂O₁₉/graphite composites using BaFe₁₂O₁₉ and graphite nanosheets as matching and absorbing layers, respectively [14]. However, the improvement in microwave absorption performance by the materials was very limited, with RL_{max} of only −26 dB and narrow *EAB* at a sample thickness of 2.5 mm. The main reason for this result is that the incidence and absorption of electromagnetic microwaves are almost synchronized, and the poor impedance matching of the BaFe₁₂O₁₉ layer results in most of the electromagnetic microwaves being reflected, with only a small amount of them incident on the graphite layer being absorbed. A similar design was used in the work of Liu et al. Co_{0.2}Ni_{0.4}Zn_{0.4}Fe₂O₄ (CNZF) ferrite and RGO were used as matching and absorbing layers for MAM in Figure 1f, respectively [29]. The CNZF exhibits good impedance matching, the double-layer MAM has a RL_{max} of −49.5 dB at 16.9 GHz, and an *EAB* of 6.0 GHz at a mass fraction of 30%, with thickness of 2.5 mm, which is a significant enhancement in the absorbing performance.

The moderate increase in defects and functional groups in the lamellar structure generates more electromagnetic microwave loss mechanisms, enhances multiple synergistic losses, and improves the microwave-absorbing performance.

3. Layered Structure

The layered structure can increase the contact area between materials. When the dielectric constants and conductivities of two materials differ, charge accumulation occurs at the contact interface. The accumulation of positive and negative charges intensifies electron shifts, enhancing the interfacial polarization effect. MXene is a prototypical material with a layered structure, composed of alternating carbon layers and transition metal layers, primarily connected by van der Waals forces between layers. The flexible selection of M and X elements not only endows MXene with superior conductivity and dielectric loss characteristics, but also provides a broader range of tunability. In addition to MXene, stacked graphite and graphene can also form layered structures, and anchoring ferrite nanoparticles between layers is a common approach. This results in a complementation of dielectric loss and magnetic loss.

Zhao et al. synthesized carbon nanotubes/expanded graphite/BaFe₁₂O₁₉ (CNT/EG/BF) composite material, using an in-situ sol-gel self-combustion method. From Figure 2a synthesis schematic diagram can be seen that carbon nanotubes serve as a conductive network, connecting the expanded graphite layers and the interlayer bonds of the expanded graphite with BaFe₁₂O₁₉ [30]. According to the absorption mechanism of sandwich CNT/EG/BF in Figure 2b, Figure 2c shows the RL_{max} of −45.8 dB of the sample, with an *EAB* of 4.2 GHz, and a matching thickness of only 1 mm. Compared with the functionally layered BaFe₁₂O₁₉/graphite composites, the microwave-absorbing properties are dramatically improved, taking advantage of the combination of expanded graphite and BaFe₁₂O₁₉. In the work of Li et al., the synthesized Fe₃O₄/RGO composites with a similar sandwich structure have obvious advantages [31]. From Figure 2d schematic diagram of absorption mechanism and (e) SEM image of Fe₃O₄/RGO-3 sandwich composites, the layered structure not only effectively inhibits the aggregation of ferrite particles, but also induces the particles to be uniformly distributed on the surface of RGO, producing interfacial polarization. Figure 2f shows the RL_{max} of −49.9 dB of samples, and *EAB* covers 5.7 GHz. Liu et al. introduced TiO₂ and PANI materials to graphene, and synthesized graphene@Fe₃O₄@PANI composites [32], it decorated with random vertically distributed TiO₂ nanosheets. From Figure 2g schematic illustration of the fabrication and (h) TEM image of composites, TiO₂ further promotes interfacial polarization and impedance matching. Figure 2i shows that when the paraffin doping was 50 wt%, the composites exhibited a RL_{max} of −41.8 dB at 14.4 GHz, with an *EAB* of 3.5 GHz and a matching thickness of only 1.6 mm. Lei et al. prepared two-dimensional Ti₃C₂T_x using HF etching, which was combined with ferrite particles, synthesizing Ti₃C₂T_x/Co-doped NiZn ferrite (CNZFO)/PANI composites [33]. The ferrite particles and PANI chains were attached to the Ti₃C₂T_x structure, contributing to the synergistic enhancement of the loss mechanism. Compared with CNZFO and Ti₃C₂T_x,

the $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNZFO}/\text{PANI}$ composite exhibits a deeper $RL_{\max}$ of -37.1 dB, a wider EAB of 4.1 GHz (8.2 – 12.3 GHz) at 10.2 GHz, and a matched thickness of 2.2 mm.

Li et al. and Guo et al. used similar methods to synthesize $\text{Ti}_3\text{C}_2\text{T}_x/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ [34] and $\text{Ti}_3\text{C}_2\text{T}_x/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ (NZFO) composites [35], respectively. The former $\text{Ti}_3\text{C}_2\text{T}_x$ with 5 wt % doping showed a $RL_{\max}$ of -42.5 dB at 13.5 GHz, while the latter $\text{Ti}_3\text{C}_2\text{T}_x/\text{NZFO}$ -2 showed a $RL_{\max}$ of -66.2 dB at 15.2 GHz, with an EAB of 4.74 GHz, and a thickness of only 1.609 mm. The obvious difference in the $RL_{\max}$ of the two composites may be due to the following factors: the significant ferrite lattice changes due to the different doping amounts of Ni and Zn, as well as the different composite methods used. Although MXene suffers from the problem of self-stacking, the interlayer is prone to agglomeration and re-stacking. By introducing ferrite particles, the above problems can be effectively solved by weakening the excessive conductivity and increasing the magnetic loss capability.

In the study of Swapnalini et al., it was found that MXene anchored moderate CoFe_2O_4 ferrite particles, increasing the dielectric constant and permeability of $\text{Ti}_3\text{C}_2\text{T}_x@\text{CoFe}_2\text{O}_4$ composites [36], probably due to the formation of many defective dipoles by the incorporation of CoFe_2O_4 , which triggers an inhomogeneous local charge distribution. Polyvinyl Butyral/ $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}/\text{Ti}_3\text{C}_2$ MXene composites were synthesized by Yang et al. [37]. MXene nanosheets significantly reduce the saturation magnetization, and varying filler content can optimize electromagnetic parameters, thereby improving the microwave absorption properties. The $RL_{\max}$ of composites is -46.3 dB at 5.8 GHz.

The layered structure has a high surface-area-to-volume ratio, and the gaps between the layers promote the adsorption of ferrite nanoparticles, enhancing the absorption performance of composite materials.

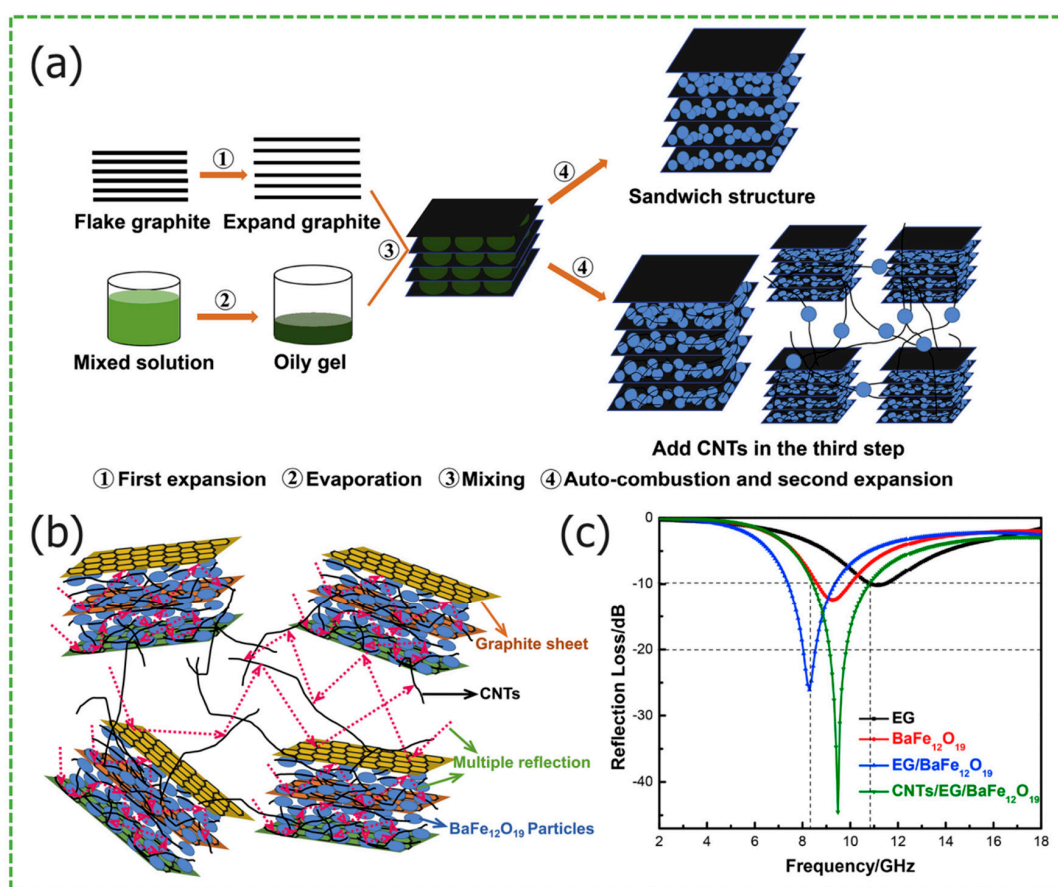


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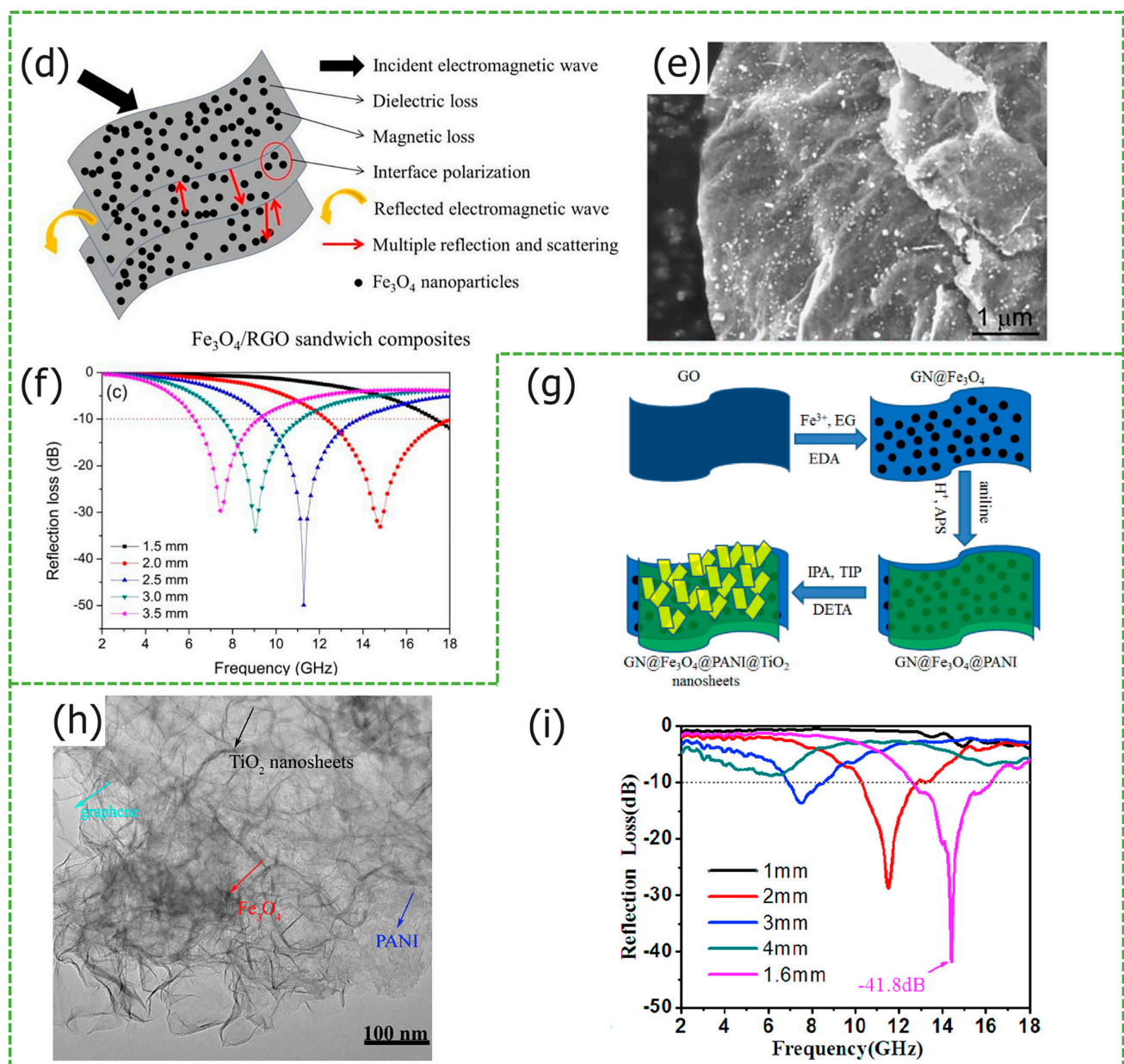


Figure 2. Graphical summary of layered structure MAMs. (a) Synthesis schematic diagram, (b) absorption mechanism, and (c) the RL curves of sandwich CNT/EG/BF nanocomposite. Reproduced with permission [30] Copyright 2017, Elsevier B.V. (d) Schematic diagram of absorption mechanism, (e) SEM image, and (f) the RL curves of $\text{Fe}_3\text{O}_4/\text{RGO}$ -3 sandwich composites. Reproduced with permission [31] Copyright 2023, Elsevier Inc. (g) Schematic illustration of the fabrication, (h) TEM image, and (i) the RL curves of the $\text{GN@Fe}_3\text{O}_4\text{@PANI@TiO}_2$ nanosheets. Reproduced with permission [32] Copyright 2016, Elsevier B.V.

4. Core–Shell Structure

The core-shell structure is typically achieved through various techniques [38,39], such as solvothermal, templated, hydrothermal, or modified Stöber methods, by the orderly assembly of one or more materials. The interplay of atomic forces promotes the tight encapsulation of the core by the outer layer material, resulting in a layered core-shell structure in which all or part of the core's surface is enveloped. The properties of each core and shell, as well as the interface region formed by their interactions, collectively determine the nature and performance of the core-shell structure. For instance, by establishing a unique core-shell heterojunction structure, S@NiFe-LDH enhances the photocatalytic activity and

stability of the catalyst [40]. Core-shell materials have been extensively studied and applied in various fields such as electromagnetic microwave absorption, batteries [41–43], supercapacitors [44–46], sensors [47], biomedicine [48], semiconductors [49,50], and stain and corrosion prevention [51]. Ferrite microspheres are wrapped on the surface of the shell, and electromagnetic waves are incident into the core-shell structure; multiple reflections and scatterings occur within it, resulting in tight encapsulation between materials and enhanced electromagnetic synergies, leading to a loss in electromagnetic wave energy. Based on their microscopic morphology and internal composition, core-shell structures are classified into four types: solid core-shell structures, hollow core-shell structures, yolk-shell structures, and non-spherical core-shell structures.

4.1. Solid Core-Shell Structure

The solid core-shell is the most fundamental type of core-shell structural system, where the outer layer material directly wraps around the core, forming a more polarized interface structure. The shell material usually has higher mechanical strength than the core material, avoiding oxidation or damage to the core material.

Shi et al. utilized dopamine as a carbon source, synthesizing $\text{Fe}_3\text{O}_4@\text{C}$ composite materials through continuous high-temperature carbonization [38]. The microspheres exhibit a layered structure, with the carbon shell encapsulating Fe_3O_4 microspheres, forming a multi-interface heterostructure, and resulting in a synergistic electromagnetic interaction. This approach effectively prevents aggregation among magnetic core microspheres, enhancing magnetic responsiveness. In contrast to the $\text{Fe}_3\text{O}_4@\text{C}$ microspheres prepared by Du et al., using in situ polymerization and high-temperature carbonization [52], which have a $RL_{\max}$ of approximately -36 dB and a narrow EAB , the layered $\text{Fe}_3\text{O}_4@\text{C}$ microspheres, with a thickness of 2.0 mm, achieve a $RL_{\max}$ of -55.4 dB and an EAB spanning 9.5 GHz (8.5–18 GHz), significantly enhancing their microwave absorption performance. Using ferrite microspheres as the matrix, selecting different materials as carbon layers is a common method for preparing solid core-shell materials. Based on $\text{Fe}_3\text{O}_4@\text{C}$, Jia et al. introduced Ni atoms and SiO_2 , which play the roles of enhancing the magnetic loss capability and optimizing the impedance matching, respectively. The preparation diagram is shown in Figure 3a [53], Figure 3b SEM image shows $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C}/\text{Ni}$ composites with a double-core-shell structure, where the electromagnetic wave multiple reflection and scattering loss is further enhanced. The Fe_3O_4 integrity is well preserved due to the protective effect of SiO_2 . Figure 3c electromagnetic parameter test displays the $RL_{\max}$ of -38.9 dB and EAB reaches 10.1 GHz for $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C}/\text{Ni}$, at a thickness of 3.5 mm. Due to the alternating benzene rings and nitrogen atoms on the carbon chain of conductive polymer PANI, it has special electrical and photoelectric properties, and is widely used in the fields of batteries and capacitors. Wang et al. synthesized $\text{Fe}_3\text{O}_4@\text{PANI}$ core-shell nanorods [54]. In Figure 3f, the dielectric loss of conductive PANI and the magnetic loss of Fe_3O_4 nanorods effectively complement each other. However, From Figure 3g SEM image can be seen that particles stick together. The $\text{Fe}_3\text{O}_4@\text{PANI}$ show that the $RL_{\max}$ at 17.3 GHz is -55.5 dB, and the matching thickness is only 1.6 mm from Figure 3h. In order to pursue MAMs with higher strength, wider bandwidth, etc., they are usually constructed using $\text{Fe}_3\text{O}_4@\text{C}$. On this basis, other dielectric materials and magnetic loss materials are introduced to further enhance the polarization between interfaces. Zha et al. used nitrogen doping and $\text{Ti}_3\text{C}_2\text{T}_x$ composite to prepare $\text{Fe}_3\text{O}_4/\text{NC}@\text{MXene}$ (FNCM) composite materials [55]. The interface polarization between $\text{Ti}_3\text{C}_2\text{T}_x$ and ferrite microspheres increases, and nitrogen doping causes the charge distribution in the carbon layer to rearrange, enhancing dipole polarization and conductivity loss. The EAB of the sample FNCM-2 is 7.32 GHz and the $RL_{\max}$ is -54.41 dB at a thickness of 2 mm. TiO_2 has a high dielectric constant. Shi et al. introduced black TiO_{2-x} into $\text{Fe}_3\text{O}_4@\text{TiO}_2$ to prepare $\text{Fe}_3\text{O}_4@\text{b-TiO}_{2-x}$ [56]. Compared to the traditional Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{TiO}_2$ microspheres, this novel core-shell heterostructure significantly enhances the microwave-absorbing properties. With a matching thickness of 2.9 mm, $\text{Fe}_3\text{O}_4@\text{b-TiO}_{2-x}$ achieves a $RL_{\max}$ of -47.6 dB, and the EAB reaches up to 13.0 GHz.

Chen et al. prepared $C@Ni_xCo_{1-x}Fe_2O_4$ composite nanospheres including $NiFe_2O_4$, cobalt-doped nickel ferrite, nickel-cobalt ferrite, nickel-doped cobalt ferrite, and various types of nickel-doped cobalt ferrite using a solvothermal reaction [57]. As the Co content increases, the crystal structure parameters change, and lattice distortion and local chemical disorder lead to a gradual increase in the coercivity of the composite nanospheres. $C@CoFe_2O_4$ exhibits the highest magnetization, reaching 332.1 Oe. The electromagnetic parameter test results showed that, with a Ni doping ratio of 0.75 and Co doping ratio of 0.25, the prepared $C@Ni_{0.75}Co_{0.25}Fe_2O_4$ nanospheres have the strongest microwave-absorbing performance: the RL_{max} was -51 dB, the EAB was 3.3 GHz, and the corresponding matching thickness was only 1.9 mm. Ge et al. prepared $ZnFe_2O_4@polydopamine(PDA)@PPy$ composites using the hydrothermal method and in situ polymerization of PDA [58], Figure 3d shows the synergistic effect of multiple loss mechanisms, when dopamine hydrochloride was used in the amount of 0.1 g, the EAB covered the range of 18–40 GHz, and the RL_{max} at 24.46 GHz was -65.66 dB from Figure 3e.

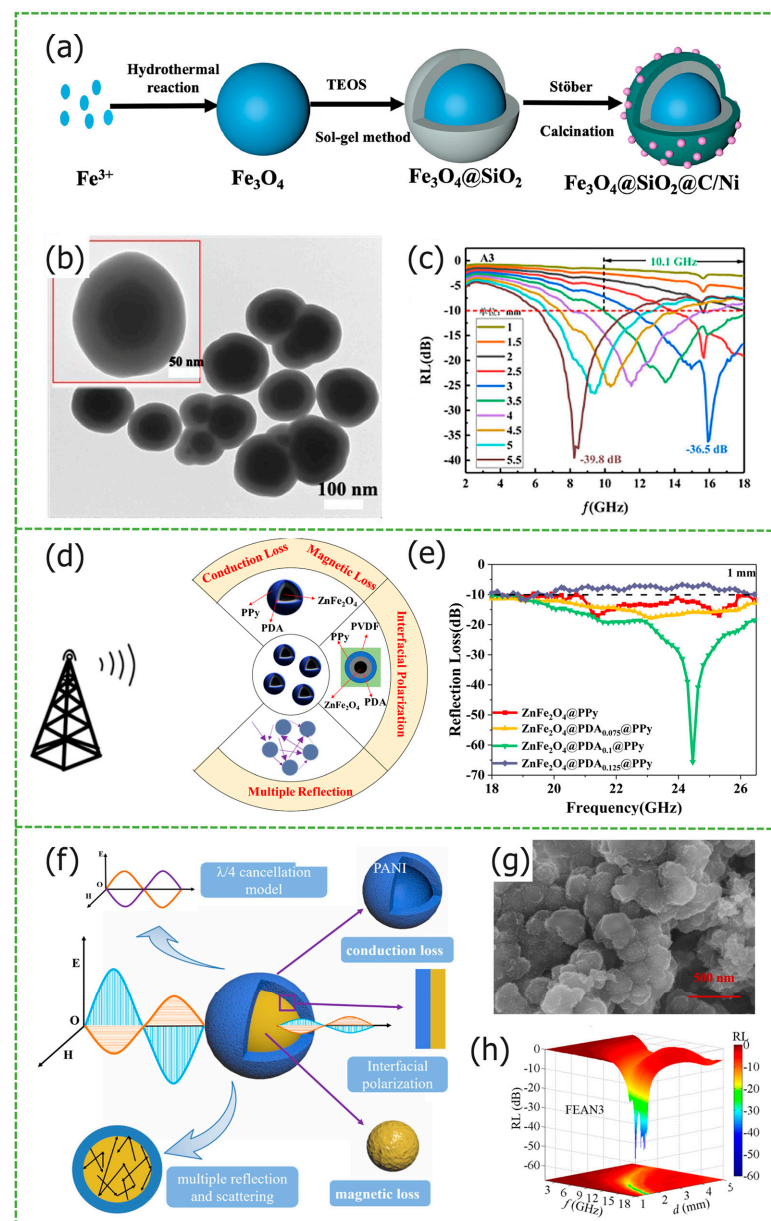


Figure 3. Graphical summary of solid core-shell structure MAMs. (a) Schematic illustration of the preparation, (b) SEM image, and (c) the RL value of $Fe_3O_4@SiO_2@C/Ni$. Reproduced with

permission [53] Copyright 2023, Elsevier B.V. (d) Absorption mechanism and (e) RL maps of $\text{ZnFe}_2\text{O}_4@\text{PDA}_{0.1}@\text{PPy}$. Reproduced with permission [58] Copyright 2021, Springer US. (f) Schematic diagram of absorption mechanism, (g) SEM image, and (h) 3D RL contour maps of FEAN3. Reproduced with permission [54] Copyright 2022, Elsevier B.V.

The tight combination of core and outer core materials results in a large amount of interface polarization in the core-shell structure material, where electrons gather and enhance the loss in electromagnetic waves.

4.2. Hollow Core-Shell Structure

In a hollow core-shell structure, the outer layer material wraps around the core, forming a hollow area in the middle, effectively reducing the mass of the core-shell structure. Increasing the contact area between the hollow area and the air, and optimizing impedance matching, are beneficial for the occurrence of multiple reflections and scattering of incident electromagnetic waves.

Similar to the preparation method of solid core-shell structures, the synthesis of hollow core-shell structures are usually carried out in the $\text{Fe}_3\text{O}_4@\text{C}$. On this basis, other dielectric materials and magnetic loss materials are introduced. However, there are slight differences in the use of raw materials and synthesis methods, resulting in cavity structures. In the work of Zhu et al., Fe_3O_4 @porous carbon composites with hollow core-shell structures were prepared [59]. The porous structure optimizes impedance matching, enhancing the specific surface area and facilitating the dissipation of incident electromagnetic wave energy. The carbon-derived sample FC-700, synthesized at 700 °C, exhibits outstanding microwave absorption properties, achieving a $RL_{\max}$ of -50.05 dB at 1.8 mm thickness and an EAB of 5.20 GHz. Mainly through carbonization, amorphous carbon is generated and there are many defects. Chai et al. obtained hollow microspheres by etching silica with hydrofluoric acid, and synthesized $\text{ZnFe}_2\text{O}_4@\text{C}$ composite materials through self-assembly and in situ preparation techniques. Additionally, Figure 4d shows that numerous uniform micropores are formed on the surface, improving impedance matching [60]. The carbon microspheres exhibit a porous hollow structure, leading to multiple reflections and scatterings of electromagnetic waves within the microspheres, coupled with the formation of numerous uniform micropores on the surface, which improves impedance matching. Notably, for the sample ZFO@C-1, with a thickness of 4.8 mm, the $RL_{\max}$ at 7.2 GHz is -51.43 dB, and the EAB is 3.52 GHz from Figure 4e. The residual carbon from the fine slag of coal gasification, characterized by a distinct graphitized structure [61,62], was utilized by Gao et al. as a cost-effective carbon source to synthesize Fe_3O_4 @residual carbon composites [63]. The absorption mechanism is shown in Figure 4c. When the filler content is 40 wt%, the thickness of sample ranges from 1.5 mm to 5 mm, and the EAB covers Ku, X, and C bands, with a $RL_{\max}$ of -32.6 dB at a thickness of 2.0 mm. Dong et al. synthesized a composite material consisting of $\text{Fe}_3\text{O}_4@\text{PPy}@\text{RGO}$ [64]. Flake RGO connects hollow microspheres, synergistically optimizing dielectric and electromagnetic losses, and enhancing absorption performance. The $RL_{\max}$ of the sample with 1.89 mm thickness is -61.20 dB.

The biomimetic sea urchin-shaped hollow core-shell structure is lightweight, and the gaps between the fine needles increase the specific surface area, optimizing impedance matching. The sea urchin-shaped $\text{SrFe}_{12}\text{O}_{19}$ prepared by Chen et al. [65] has a $RL_{\max}$ of -22.8 dB and an EAB of 5.6 GHz (12.4–18.0 GHz) at 15.1 GHz, with a thickness of 3 mm. Wu et al. chose to use $\alpha\text{-FeOOH}$ as a precursor to synthesize sea urchin-like structures, using hydrothermal and annealing methods for a $\text{Fe}_3\text{O}_4@\text{C}$ composite material, the preparation process is shown in Figure 4a [66]. When the mass ratio of $\alpha\text{-FeOOH}$ to glucose is 1:1, the $\text{Fe}_3\text{O}_4@\text{C}$ with a thickness of 3.23 mm shows an $RL_{\max}$ of -73.5 dB. The sea urchin-like core-shell structure enhances interfacial polarization, leading to an electron shift in an alternating electromagnetic field. The absorption mechanism is displayed in Figure 4b, which includes multiple loss mechanisms.

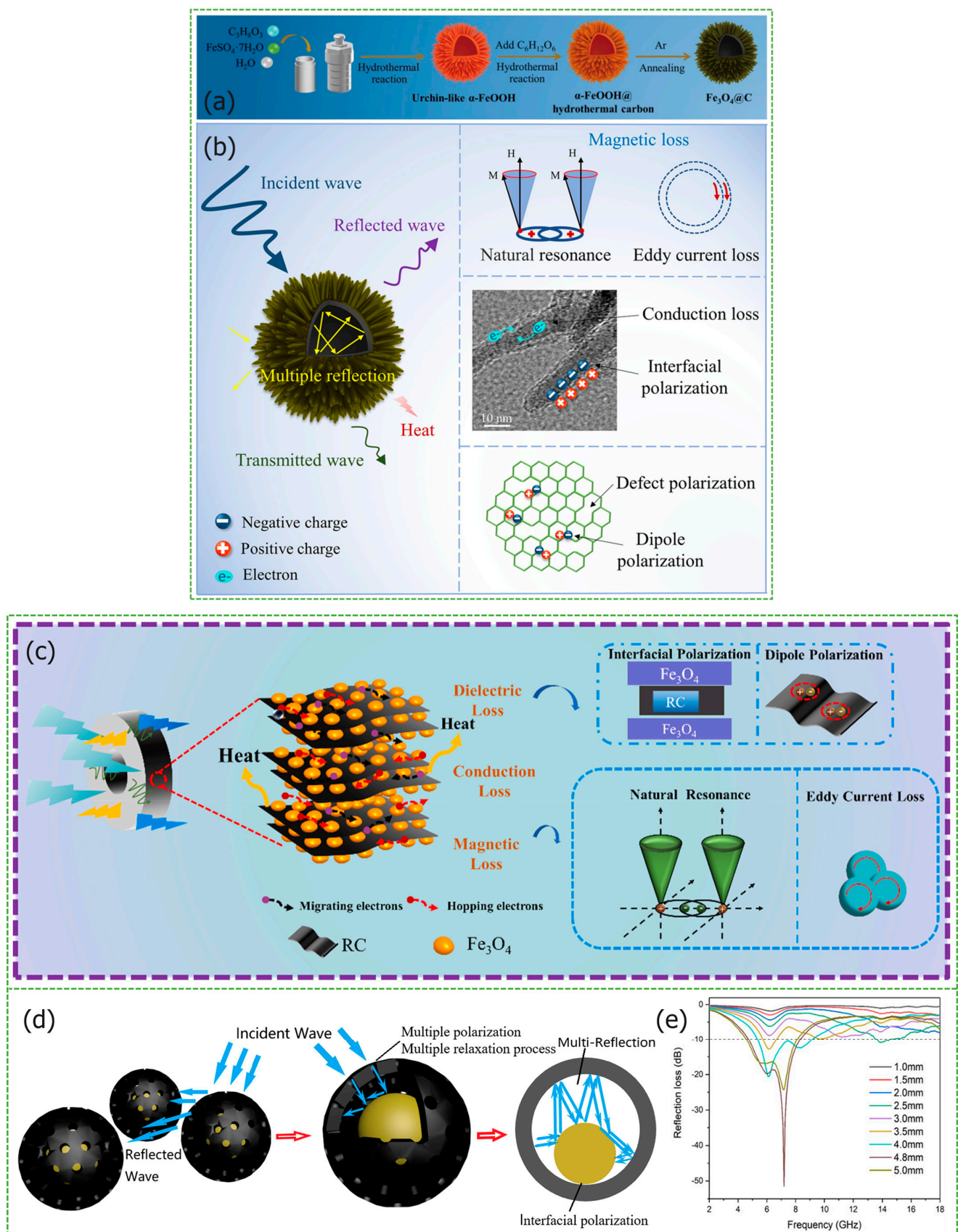


Figure 4. Graphical summary of hollow core-shell structure MAMs. **(a,b)** Schematic diagram of the preparation process and absorption mechanisms of $\text{Fe}_3\text{O}_4@\text{C}$. Reproduced with permission [66].

Copyright 2023, Elsevier Inc. (c) The potential absorbing mechanisms of Fe_3O_4 NPs@RC. Reproduced with permission [63]. Copyright 2023, Elsevier Ltd. and Techna S.r.l. (d,e) Absorption mechanism and RL curves of ZnFe_2O_4 @porous hollow carbon microspheres. Reproduced with permission [60]. Copyright 2021, Elsevier Inc.

Zhang et al. prepared CoFe_2O_4 @carbon nanotube composite materials by replacing Fe^{3+} with Co^{2+} through the chemical vapor precipitation method. The carbon nanotubes are coated on the surface of CoFe_2O_4 hollow microspheres [67]. The $RL_{\max}$ of the sample at 11.7 GHz is -32.8 dB, with a thickness of merely 2 mm.

An appropriate number of voids can reduce the quality of MAMs, optimize impedance matching, and promote the strongest performance of composite materials.

4.3. Yolk-Eggshell Structure

Yolk-eggshell is a structure that lies between a solid core-shell and a hollow core-shell, similar to an egg. There is a certain gap between the inner and outer cores, while maintaining a solid structure inside. Under external forces, the internal solid has a certain degree of mobility, offsetting external work done.

Liu et al. synthesized Fe_3O_4 @ SiO_2 core-shell microspheres, using the enhanced Stöber method. Building upon prior research, they found that a silica coating on Fe_3O_4 particles could effectively modify their surface properties [68]. Subsequently, they hydrothermally deposited SnO_2 , resulting in a Fe_3O_4 @ SnO_2 double-shell structure with a yolk-like structure [39]. These microspheres exhibit a high specific surface area and uniform dimensions, which is attributed to the favorable electromagnetic interaction between the core and shell. When the sample MTO-3 is 2 mm thick, its $RL_{\max}$ at 7 GHz is 36.5 dB, with an EAB spanning from 2 to 18 GHz. The reflection loss is consistently below -20 dB. Compared to Fe_3O_4 particles, it demonstrates superior microwave absorption performance. In another study by Liu et al., by replacing SnO_2 with TiO_2 , Fe_3O_4 @ TiO_2 layered yolk-shell microspheres were prepared using a template method, including in various sizes [69]. Figure 5d,e shows the presence of pores between the outer TiO_2 nanosheets, resulting a large specific surface area, optimizing impedance matching and allowing more electromagnetic waves to be incident on the inside of the yolk shell. At a thickness of 2 mm at 7 GHz, Fe_3O_4 @ TiO_2 exhibited an EAB of nearly 14.5 GHz, significantly surpassing Fe_3O_4 and Fe_3O_4 @ SiO_2 @ TiO_2 microspheres [5]. The $RL_{\max}$ was -33.4 dB.

The non-homogeneous interface of ferrite is prone to polarization, and the charge distribution at the interface is uneven, making it prone to the polarization phenomenon. Zhang et al. utilized this characteristic to synthesize $(\text{Fe}/\text{FeO}_x)\text{@C}$ composites [70], which exhibit better absorption performance than Fe@C . At a thickness of 2 mm, the EAB of $(\text{Fe}/\text{FeO}_x)\text{@C}$ -2 increased by 26.3%, reaching 7.3 GHz (10.7–18.0 GHz). He et al. used N doping to regulate the electronic structure of carbon materials and prepared $\text{Fe}_3\text{O}_4\text{@C@Co/N-Doped C}$ (FCCNC) composite materials, increasing dipole polarization. Figure 5a shows its loss mechanism. The conductive network generated by ZIF-67 carbonization, which connects Fe_3O_4 ferrite and carbon layers, enables dielectric-electromagnetic synergy and impedance matching, which is optimized and enhanced [71]. As shown in Figure 5c, the particles appear spherical in shape. The $RL_{\max}$ of FCCNC reaches -66.39 dB, with a matching thickness of just 1.9 mm from Figure 5b.

The electromagnetic parameters and impedance matching characteristics of yolk-eggshell optimized materials are carbonized to form a carbon layer that combines with ferrite, thereby reducing reflection loss and improving absorption performance.

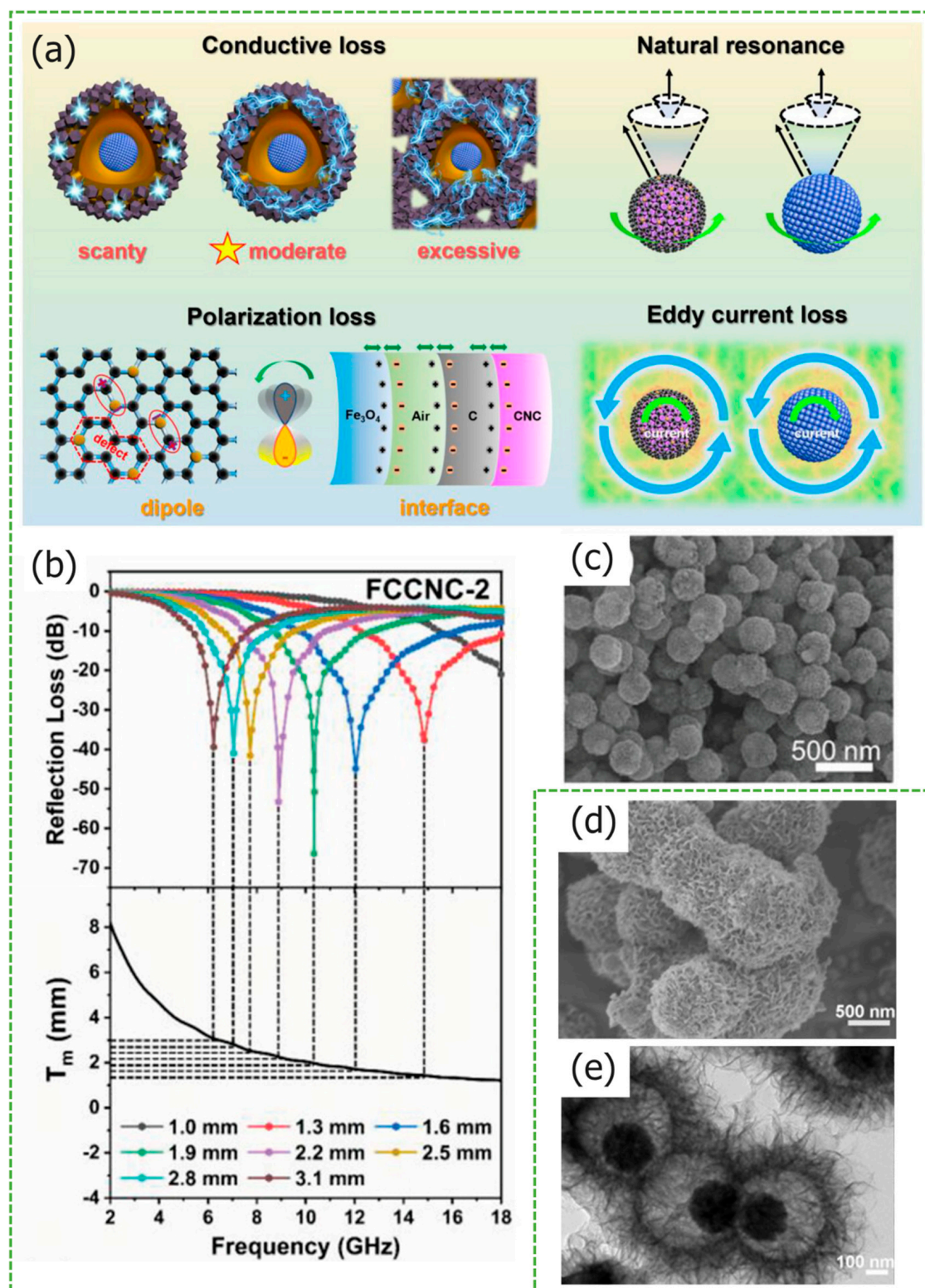


Figure 5. Graphical summary of yolk-eggshell structure MAMs. (a) The specific electromagnetic mechanism of absorption and (b) the RL curves of FCCNC-2. (c) FESEM images of yolk-shell $\text{Fe}_3\text{O}_4@C@Co/N$ -doped C. Reproduced with permission [71] Copyright 2023, Wiley. (d) FESEM and (e) TEM images of the $\text{Fe}_3\text{O}_4@TiO_2$ yolk-shell microspheres. Reproduced with permission [69] Copyright 2013, Easton, Pa. [etc.] American Chemical Society [etc.].

4.4. Non-Spherical Core-Shell Structure

Besides the common spherical core-shell structures, there are also some non-spherical core-shell structures. Examples of these structures are spindle, ellipsoid, rod, nano-axis, and capsule. The size anisotropy influences interfacial polarization, leading to the unique properties of non-spherical core-shell structure MAMs. Xu et al. prepared $\text{Fe}_3\text{O}_4@\text{CuSiO}_3$ nanoparticle composites utilizing a modified Stöber method [72]. The aspect ratio and dimensions of the elliptical structure influence interfacial scattering and polarization. Compared to spherical nanoparticles, the complex dielectric constant exhibits a double resonant peak in its real part, indicating a more intense interfacial polarization, and exhibiting anisotropy in its microwave absorption properties. The sea urchin-shaped external CuSiO_3 shell wraps around the internal Fe_3O_4 magnetic core, creating a synergistic effect to help absorb electromagnetic waves, avoiding oxidation when exposed to air. At a sample thickness of 2 mm, the $RL_{\max}$ is -30.8 dB and the EAB is 8 GHz. In the work of You et al., the synthesized $\gamma\text{-Fe}_2\text{O}_3@\text{C}@\alpha\text{-MnO}_2$ nano-axis composites [73] also exhibit anisotropy in terms of absorption performance. By controlling different ion concentration ratios, crystal growth direction can be guided, and a unique bipolar distribution cavity core-shell structure can be synthesized. Due to the high-temperature condensation properties of dopamine, an $\alpha\text{-Fe}_2\text{O}_3$ ellipsoid is wrapped to form a carbon layer, optimizing impedance matching and the magnetic dielectric synergistic effect. When the sample thickness is 2 mm, the $RL_{\max}$ at 9.36 GHz is -45 dB, with an EAB of 3.89 GHz (7.66–11.55 GHz). Compared to traditional core-shell MAMs, it demonstrates a pronounced microwave absorption property. Lei et al. synthesized X-shaped $\text{Fe}_3\text{O}_4@\text{C}$ composites using the hydrothermal surface coating sintering method, the preparation diagram is shown in Figure 6f [74]; these also have a similar adjustment mechanism, and their absorption performance is adjusted through the proportion of X-shaped dimensions. The sample exhibits a $RL_{\max}$ of -64.92 dB at 15.04 GHz, with an EAB of 4.64 GHz (13.04–17.68 GHz) from Figure 6g. The matching thickness is only 1.75 mm, demonstrating outstanding microwave absorption performance.

By anchoring ferrite particles onto the surface of carbon fibers, Dai et al. developed core-shell structured C/ Fe_3O_4 composites [75]. The many heterogeneous interfaces formed between graphite nanocrystals and amorphous carbon in carbon fibers lead to charge transfers and electron reconstruction at the interface. At the same time, new heterogeneous interfaces are formed between Fe_3O_4 particles and the surface of carbon fibers, ensuring C/ Fe_3O_4 composite fibers have excellent absorption performance. The $RL_{\max}$ at 17 GHz is -55.98 dB, with a matching thickness of only 1.0 mm. Liu et al. synthesized $\text{Fe}/\text{Fe}_3\text{O}_4@\text{C}@\text{MoS}_2$ composites with a capsule-like structure [76]. The preparation diagram is shown in Figure 6d. Upon reduction of a small amount of Fe_3O_4 to Fe, the magnetic loss capability of the composite material is enhanced. For samples with a thickness of 1.8 mm, the EAB is 5.4 GHz in Figure 6e.

Biomass materials are widely available and possess a high carbon content. Wu et al. replaced Fe^{3+} with Ni^{2+} and Zn^{2+} doping, and synthesized $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ @bamboo charcoal (BC) core-shell nanocomposites utilizing the hydrothermal reaction technique [77]. The NiZn ferrite with an unsaturated coordination is encapsulated on the surface of BC from Figure 6a. The internal lattice defects act as ion relaxation polarization centers, accumulating a significant amount of charge, thereby enhancing polarization loss. The peak-to-peak amplitude of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ @BC core-shell nanocomposites increase with increasing temperature, at temperatures ranging from 300 to 470 K. Due to the weakening of magnetic crystal anisotropy, the peak-to-peak linewidth decreases with increasing temperature. When the BC is present in a 30% volume, it exhibits superior microwave absorption properties in the Ka band. Within the broad frequency range of 2–40 GHz in Figure 6b,c, the $RL_{\max}$ reaches -32.7 dB.

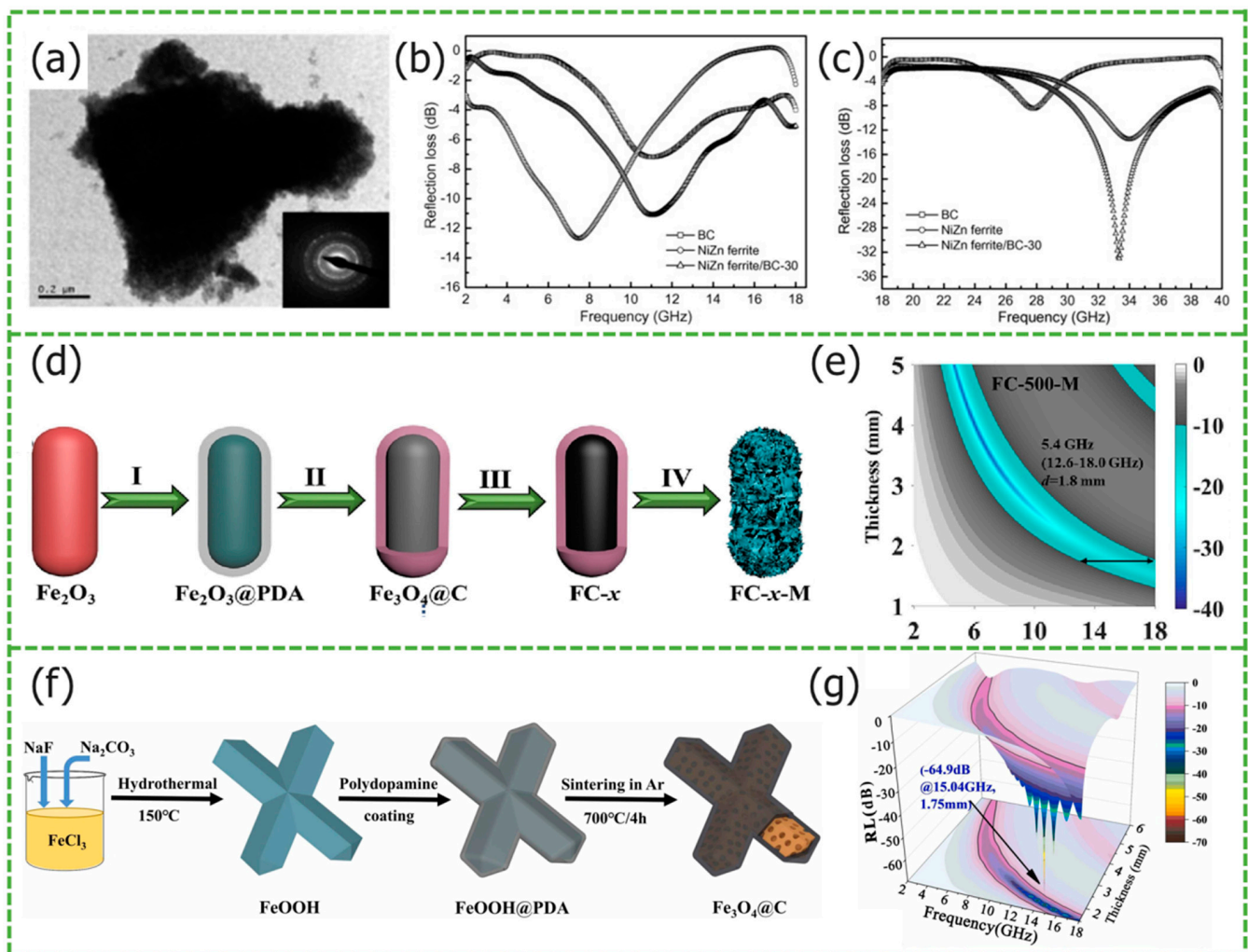


Figure 6. Graphical summary of irregular core-shell structure MAMs. (a) TEM photograph and the RL at (b) 2–18 GHz and (c) 18–40 GHz of NiZn ferrite/BC-30. Reproduced with permission [77] Copyright 2008, Elsevier Ltd. (d) Schematic of the preparation and (e) planar RL maps of FC-500-M. Reproduced with permission [76] Copyright 2023, Elsevier B.V. (f) Illustrated schematic for the preparation process and (g) 3D RL plots of $\text{Fe}_3\text{O}_4@\text{C}-60$. Reproduced with permission [74] Copyright 2024, Elsevier B.V.

The unique shape of the non-spherical core-shell structure, with size anisotropy to regulate the absorption performance, makes it easier to synthesize high-performance MAMs. The electromagnetic testing of the above-mentioned ferrite MAMs shows that the core-shell structure has significant advantages in preparing MAMs.

5. Porous Structure

The microstructure of materials is distinctive, and through etching, unexpected porous structures can be produced. These gaps not only increase the contact area between the material and air, effectively reducing material quality and improving impedance matching, but also allow more electromagnetic waves to penetrate the material's interior, enhancing the multiple RL of electromagnetic wave energy. Based on the formation mechanism of porous structure, they can be divided into two categories: one is the use of biomass carbon-based materials, with natural porous microstructures; the other type is prepared through reactive composting.

5.1. Biomass Porous Structure

Biomass-based carbon materials currently represent a research hotspot, possessing advantages such as high sustainability, low cost, novel structural designs, diverse synthesis methods, and high carbon content. The integration of biomass carbon with ferrite materials results in the preparation of porous MAMs. The perfect complementarity between their microwave-absorbing mechanisms ensures their outstanding performance, presenting a broad application potential in the field of microwave absorption. Biomass materials come from a wide range of sources, such as agricultural waste, fruit shells, and animal and plant materials. Typically, after undergoing high-temperature carbonization and activation processes, the microstructure of biomass carbon undergoes significant alterations. Biomass carbons produced by carbonization at 600 °C exhibit a higher density of disordered carbon layer defects, yet the porous structure retains its integrity relatively well. Ferrite after atomic doping replacement is chosen, and the composite material synthesized with it has stronger magnetic properties.

Wang et al. synthesized porous carbon @ NiFe₂O₄ composite materials using pomelo peel as a carbon source by replacing Fe³⁺ with Ni²⁺ [78]. From Figure 7e, layers of carbon are superimposed to form a 3D conductive network, with natural micropores distributed across the surface, enhancing the contact area with air, and optimizing impedance matching. The loss mechanism is shown in Figure 7d. When the composite material has a 2.5 mm thickness, its RL_{max} at 14.3 GHz is −50.8 dB, and the corresponding EAB is 4.9 GHz (12.4–17.3 GHz) in Figure 7f. Corn stover is one of the major agricultural wastes, and recycling it is of great significance. Using corn straw and grapefruit peel as raw materials, Sun et al. replaced Fe³⁺ with Ni²⁺ and Co²⁺, prepared Ni_{0.5}Co_{0.5}Fe₂O₄/corn straw/grapefruit peel composites, which possess a 3D layered porous structure [79]. When the sample thickness is 3 mm, the RL_{max} is −43.95 dB, with an EAB of 4.81 GHz. Huang et al. used Co²⁺ to replace Fe³⁺ and synthesized C@CoFe₂O₄ nanocomposites, using the eggshell membrane impregnation method, the preparation process is shown in Figure 7g [80]. Figure 7h shows that the CoFe₂O₄ particles are anchored onto the porous carbon matrix, resulting in a strong synergistic effect of electromagnetic interaction between the two, and enhancing the material's microwave absorption performance, which was also confirmed by simulation experiments. When the sample is filled with 30% paraffin matrix, the RL_{max} at 9.2 GHz is −49.6 dB in Figure 7i.

Compared to hydrothermal and solvothermal methods, simple solution impregnation and high-temperature carbonization treatment are more convenient. Wang et al. prepared porous carbon/Fe₃O₄@Fe composites by immersing sponge with Fe(NO₃)₃ solution and high-temperature carbonization [81]. From Figure 7a,b, it can be observed that the porous structure and ferrite particle distribution are distinct, respectively. Under the carbonization temperature of 600 °C, the sample exhibits a relatively high attenuation constant. When the thickness is as thin as 2 mm, the EAB range is between 13 and 18 GHz, with the RL_{max} reaching −49.6 dB at 15.9 GHz in Figure 7c, highlighting outstanding microwave-absorbing capabilities. Fang et al. immersed cotton in an Fe(NO₃)₃·9H₂O solution, subjecting it to carbonization treatments at various elevated temperatures, thereby preparing Fe₃O₄/C composites [82]. Fe₃O₄ nanoparticles of different sizes are dispersed on the hollow fiber wall of cotton, and the nanopores on the fiber surface help improve impedance matching, absorbing more electromagnetic waves. When prepared by carbonization at 600 °C, the sample with a thickness of 2.0 mm exhibits an EAB of 4.4 GHz (11.4–15.8 GHz), the RL_{max} is only −22.1 dB, and the absorption performance is poor. In the work of Zhang et al., biochar/ferrite porous composites were prepared using bamboo as the carbon source. The pyrolysis temperature was set at 800 °C, and the sample matching thickness was 2.0 mm, the RL_{max} reached −43.2 dB, and EAB was 14.2 GHz [83].

The preparation method for biomass porous MAMs is relatively simple. They have light weight and high absorption strength, are suitable for large-scale preparation, and have significant advantages compared to other structures.

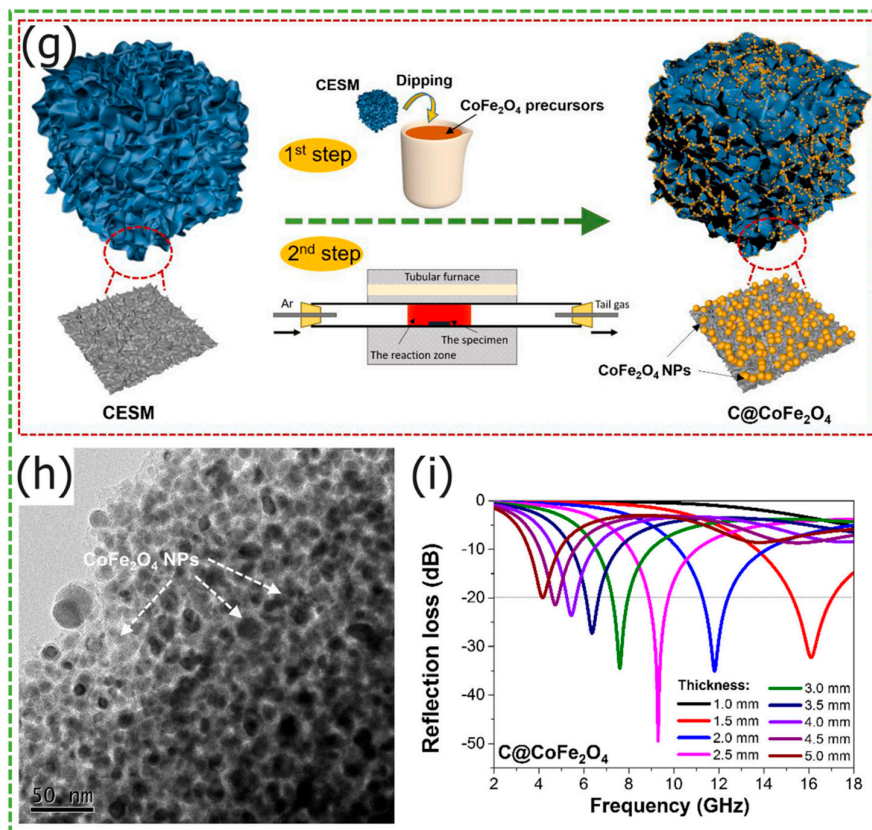
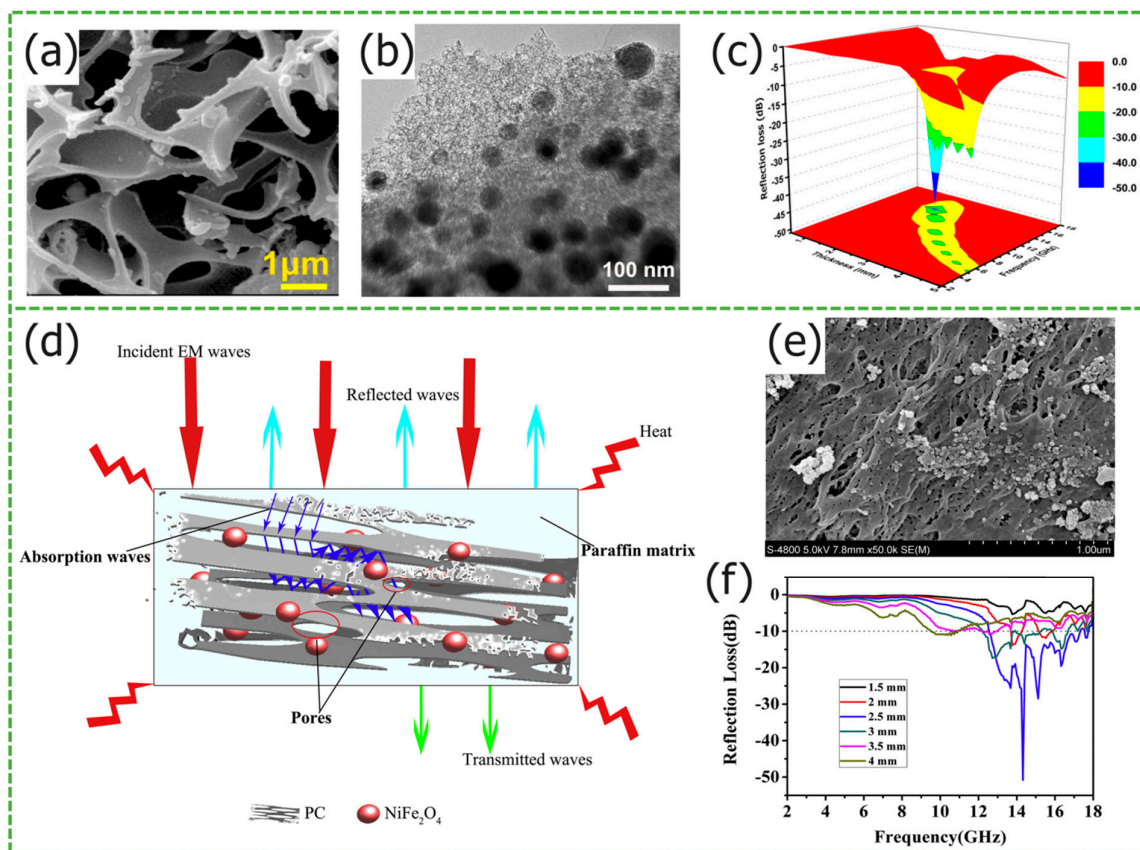


Figure 7. Graphical summary of biomass porous structure MAMs. (a) SEM image, (b) TEM image, and (c) 3D plots of RL of the MPC600. Reproduced with permission [81] Copyright 2018, American

Chemical Society. (d) Schematic illustration of absorption mechanisms, (e) FESEM images, and (f) the RL curves of porous carbon@NiFe₂O₄. Reproduced with permission [78] Copyright 2019, Elsevier B.V. (g) Schematic illustration for preparation, (h) transmission electron microscope images, and (i) RL values of C/CoFe₂O₄. Reproduced with permission [80] Copyright 2019, Elsevier Ltd.

5.2. Other Porous Structure

In addition to porous carbon materials, there are also porous microspheres, aerogels, porous foam, and other structures. The interior is filled with many pores, which not only reduce the mass and increase the specific surface area, but can also adhere to ferrite particles, optimize electromagnetic parameters, and enhance electromagnetic wave loss capacity.

Cui et al. synthesized RGO/MXene/Fe₃O₄ microspheres using the ultrasonic spray drying technique, the preparation process is shown in Figure 8a [84]. Under the influence of surface tension, droplets form into microspheres, which rapidly evaporate at high temperatures and adsorb Fe₃O₄ nanoparticles. These nanoparticles are distributed throughout the nanoplates assembled from RGO and MXene, leading to an irregular arrangement of nanoplates in Figure 8b that creates a porous structure, optimizing impedance matching. The synergistic effect of the three materials, while retaining their respective advantages, gives the microspheres enhanced microwave-absorbing properties. When the sample FMCM-3 is filled with 35% and has a thickness of 2.9 mm, its RL_{max} at 11.1 GHz is −51.2 dB, with an EAB of 4.7 GHz from Figure 8c.

Liu et al. synthesized NiFe₂O₄@Ni@C composites, using a three-step process of a hydrothermal approach, in situ polymerization, and calcination, with porous and empty cavities inside the honeycomb structure [85], which promotes the electromagnetic wave energy loss, the preparation process is shown in Figure 8d. Figure 8e shows that porosity and cavities inside honeycomb structures. NiFe₂O₄ magnetic loss further enhances the absorption of microwaves, the RL_{max} of the NiFe₂O₄@Ni@C sample is −66.70 dB, with an EAB of 5.16 GHz in Figure 8f.

Aerogel and porous foam have many interconnected pores, and a high specific surface area is conducive to increasing reaction sites and improving reaction efficiency. In the work of Xu et al., magnetic graphene foam@Fe₃O₄ composites were synthesized [86]. After the sample was subjected to acid treatment, it maintained a RL_{max} of −49.4 dB at a thickness of 2.3 mm, with an EAB of 6.3 GHz (11.7–18.0 GHz). Fe₃O₄-modified carbon aerogel composites and SiO₂/MXene/Fe₃O₄ aerogels were prepared by Ye et al. and He et al., respectively [87,88]. The porous structure optimizes the impedance matching, and the heterogeneous structure promotes the dielectric-magnetic synergy. The SiO₂/MXene/Fe₃O₄ aerogel, with a thickness of merely 1 mm, exhibits an EAB reaching 8.8 GHz.

Similarly, using CoFe₂O₄ ferrite as the magnetic component, Shen et al. and Li et al. prepared CoFe₂O₄/ordered mesoporous carbon (NOMC) and CoFe₂O₄/carbon nanofiber (CNF) composites [89,90], respectively. In comparison to single components, the electromagnetic microwave absorption performance of composites is significantly enhanced. NOMC structure is shown in the Figure 8g,h, When the thickness of the 40-F/NOMC sample is a mere 1.5 mm, its EAB is 5.0 GHz (11.9–16.9 GHz) in Figure 8i. However, when CoFe₂O₄ doped with 20 wt% of quality, the CoFe₂O₄/CNF composites only exhibit an EAB of 3.6 GHz, with a matching thickness of 2.5 mm. This may be caused by poor impedance matching.

A porous structure with high porosity helps to increase the adsorption capacity of microspheres, facilitate their combination with other materials, and improve the absorption performance of ferrite composite materials.

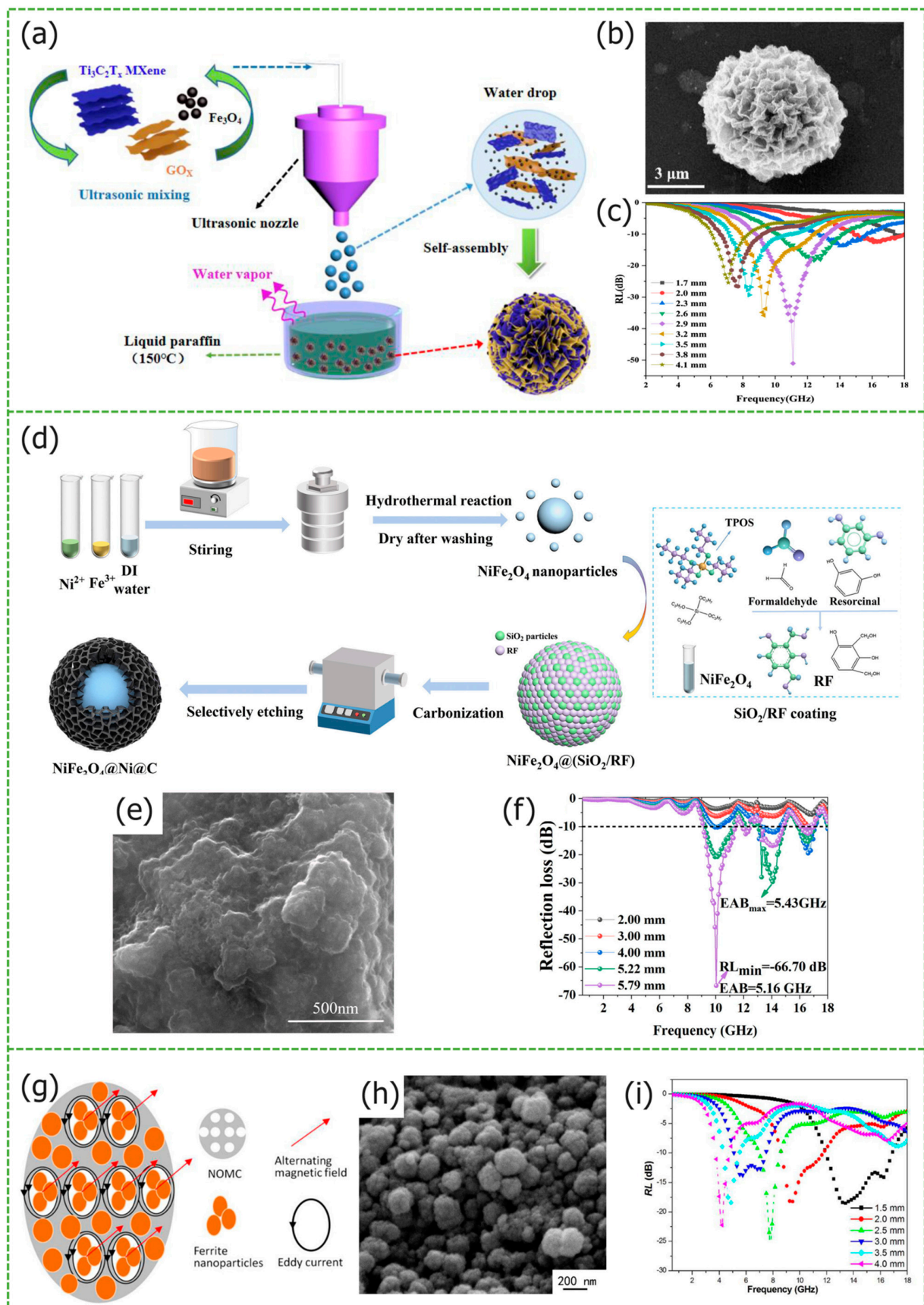


Figure 8. Graphical summary of other porous structure MAMs. (a) Experimental synthesized porous structure, (b) SEM images, and (c) the 2D RL plots of FMCM-3. Reproduced with permission [84]

Copyright 2021, Elsevier Ltd. (d) Schematic diagram of preparation, (e) SEM images, and (f) RL of $\text{NiFe}_2\text{O}_4/\text{Ni}@C-3$. Reproduced with permission [85] Copyright 2022, Elsevier Inc. (g) Forming mechanism of eddy current, (h) SEM images, and (i) the RL curves of 40-F/NOMC. Reproduced with permission [89] Copyright 2020, Elsevier B.V.

6. Conclusions and Outlook

The development of MAMs with wide EAB values and a strong RL is the goal pursued by many researchers. Through continuous efforts, various structures of ferrite-based MAM have been explored, and are starting to be applied in the field of national defense and security. The above structures each have their own advantages. Using Fe_3O_4 ferrite as the matrix, a longitudinal comparative analysis was conducted on the absorption performance of composite materials. Table 1 shows absorption performance data of Fe_3O_4 MAMs with eight structures. Among them, the X-shaped $\text{Fe}_3\text{O}_4@C$ composite material has the highest RL_{max} , reaching -64.92 dB, but the EAB is relatively narrow. For the yolk-eggshell structure $\text{Fe}_3\text{O}_4@SiO_2$, the RL_{max} of the composite materials is only -36.5 dB, and the EAB covers 2–18 GHz, which means that the entire frequency range can absorb more than 90% of the electromagnetic microwave energy, demonstrating excellent performance. Compared with other structures, this indicates that the yolk-eggshell structure has significant advantages. The larger contact area between materials enhances interface polarization, and intensifies electron shift, electromagnetic microwave multiple reflections, and scattering of energy losses. Further research on the yolk-eggshell structure can be conducted, which also points out the direction for future research.

Table 1. Absorption performance data of Fe_3O_4 MAMs with eight structures.

Material	Structure Category	RL_{max}/dB	EAB/GHz	Matching Thickness/mm	Ref.
$\text{RGO}@Fe_3O_4@PANI$	sheet structure	-51.5	4.2	3.0	[13]
Fe_3O_4/RGO	Layered structure	-49.9	5.7	2.5	[31]
$Fe_3O_4@C$	Solid core-shell structure	-55.4	9.5	2.0	[52]
$Fe_3O_4@PPy@RGO$	hollow core-shell structure	-61.2	5.26	1.89	[64]
$Fe_3O_4@SiO_2$	yolk-eggshell structure	-36.5	16	2.0	[68]
$Fe_3O_4@C$	non-spherical core-shell structure	-64.92	4.64	1.75	[74]
porouscarbon/ $Fe_3O_4@Fe$	biomass porous structure	-49.6	5.0	2.0	[81]
Magnetic graphene foam/ Fe_3O_4	other porous structures	-49.4	6.3	2.3	[86]

The integration of diverse materials can yield unique microstructures, while the multi-component synergistic optimization of the loss mechanism produces unexpected performances. This paper reviews the research progress on the structures of ferrite-based MAMs. Typically, ferrite is used to prepare composites with carbon-based compounds or MXene. The optimization of the microstructure of the synthesized composites faces numerous challenges.

In summary, the future structure of ferrite-based MAM can be approached from the following aspects:

(1) Design of new structures of ferrite MAMs. Based on the yolk–eggshell structure, the coating layer of the material is modified with pores to design a porous yolk–eggshell structure. For non-spherical core–shell structures, multi-layer hollow absorbing materials can be designed with different aspect ratios in different directions, which affect the synergistic loss mechanism between components. Determining how to synthesize these structures through experimental methods is currently a challenge that requires further research. The underlying mechanism of the influence of a material’s structure on its performance needs to be further explored to improve material stability.

(2) Optimization of the specific gravity of ferrite composites. An ideal MAM should be lightweight. Hence, reducing the specific gravity of ferrite composites is imperative. The reduction in specific gravity is a crucial method for altering the microstructure of materials. For instance, the test results demonstrated that aerogels and porous foam MAMs possess outstanding microwave absorption properties, effectively reducing their specific gravity. According to the density principle of composite materials, light weight should be achieved by introducing materials with lower density and combining them with ferrites. In composites, the distribution and morphology of dispersion have a significant impact on performance, and many research structures are currently randomly distributed. Determining how to control the dispersion of ferrites on the substrate, thereby achieving a controllable distribution, is one of the future directions.

(3) Development of multifunctional ferrite absorbing materials. Combining MAMs with other functional materials, such as catalysts and sensors, and integrating them with smart devices, can effectively improve the flexibility and intelligence level of the system in fields such as radio spectrum monitoring and antenna design, reduce the impact on the environment, improve electromagnetic compatibility and anti-interference ability, realize multifunctionality, and improve the application value. This integration can be achieved by applying absorbing materials to the external surface or internal structure of smart devices. The current difficulty lies in selecting suitable materials having a low cost, wide absorption bandwidth, and strong absorption ability, which restricts their application.

(4) Investigation of the degradation protection and technological scalability of ferrite MAMs. The degradation mechanism is a complex process that is influenced by environmental factors, such as high-temperature resistance, corrosion resistance, water and moisture resistance, and seismic protection. It is necessary to strengthen the corrosion resistance of materials to maintain good absorption performance in harsh environments and improve the service life of absorption materials. Realizing the large-scale manufacturing of MAMs is an important link for successful application. It is necessary to evaluate whether existing technologies can expand the manufacturing process scale, including the adaptability and feasibility of equipment, process flow, and raw materials, to enhance practical application.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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