ISSN: 2664-9640

Electromagnetic wave absorption performance of three-dimensional porous biomass carbon@Co_3O_4 composite

Haipeng Cui[1], Haitao Zhao[2], Yuxin Fu[3], Benxiang Hu[1], Zhaohan Ding[4]

[1]School of Materials Science and Engineering, Hainan University, Haikou 570228, China.

[2]Southwest Jiaotong University School of Civil Engineering, Chengdu,611756, China.

[3]College of Chemistry and Chemical Engineering, Hunan University, Changsha,410082, China

[4]School of Environmental Engineering, Nanjing Institute of Technology, Nanjing 211167, China

Abstract

A single Co_3O_4 material has a narrow absorbing frequency band and a single microscopic appearance. Therefore, the composite material with micro-nano structure characteristics prepared by combining Co_3O_4 with other nanomaterials has become a current research hotspot of absorbing materials. The bio-carbon material with porous network structure was prepared by physical activation method, and the biomass carbon@Co_3O_4 composite material was prepared by compounding with the porous carbon structure during the synthesis of Co_3O_4. The microstructure and electromagnetic wave absorption properties of the composite material were studied. The results show that: Biocarbon@Co_3O_4 is a porous mesh material with a core-shell structure. It has good impedance matching and attenuation characteristics, and the Z value is close to the ideal value 1, which promotes electromagnetic waves to enter the material to the greatest extent; at 4GHz The minimum reflection loss is -21 dB; when the matching thickness is 1.85 mm, the effective absorption range is 2-18 GHz, and the absorption bandwidth is 5.3 GHz, which has potential broadband absorption capabilities.

Keywords

Electromagnetic, performance , carbon@Co_3O_4 composite.

1. Introduction

In recent years, electronic devices have changed people's lifestyles. However, these high-tech electronic devices not only bring convenience to people's lives, but also cause huge electromagnetic interference (EMI) to the environment and equipment, and cause irreversible harm to the human body. Therefore, in order to solve this problem, the development of a material that can effectively absorb electromagnetic waves and convert them into heat is an urgent and critical solution. Generally, including low filling rate, wide absorption bandwidth, light weight and thin thickness are the key factors to measure the absorption performance. In recent years, Fe, Co, Ni and their alloys have received widespread attention due to their amazing magnetic properties.For example, Gao[1] et al. used dendritic α-FeO to Fe2O, partial and complete reduction of Fe, and reduction and oxidation of γ-FeO to achieve a dendritic microstructure while still retaining the dendritic morphology. Magnetic properties and microwave absorption capacity.Dong[2] et al. successfully prepared Ni/polyaniline (PANi) nanocomposites through chemical polymerization, which exhibits strong natural resonance, which is dominant in microwave magnetic loss.Generally, the complex permittivity（$\varepsilon_r=\varepsilon'-i\varepsilon''$） and complex permeability（$\mu_r=\mu'-i\mu''$）,these are two important electromagnetic parameters that can be used to measure the impedance matching value, dielectric and magnetic loss capabilities of materials[3].On the one hand, good impedance matching requires the values of

μ_r and ε_r to be close; on the other hand, excellent loss capability depends on the higher values of ε" and μ". Due to its good ferromagnetic properties, excellent magnetic loss capability and low cost advantages, magnetic alloy materials have been extensively studied and used in the traditional microwave absorption field[4].

However, in recent years, there has been little research on spherical magnetic alloy materials in the field of microwave absorption. In previous studies, most of them tend to adjust the real and imaginary parts of the dielectric constant at the same time, which makes it impossible to obtain the strength dielectric loss capability and impedance matching at the same time. The capacity of dielectric and magnetic loss mainly depends on ε" and μ". For Co_3O_4 alloy, lower ε'means better impedance matching. Therefore, the best way to improve the microwave absorption capacity of Co_3O_4 materials is to reduce ε'to enhance impedance matching, and increase ε" to increase its dielectric loss ability, so as to obtain better electromagnetic wave absorption. Therefore, how to reasonably combine Co_3O_4 with other materials The combination of materials to achieve the above expectations has become the key to this work[5].

In this paper, a simple one-step hydrothermal method was used to prepare a biomass-based composite material loaded with Co_3O_4 nanosheets. Co_3O_4 nanospheres grow uniformly on the surface of biochar and form a spherical structure. According to the analysis of the measured electromagnetic parameters, it is found that the introduction of Co_3O_4 can effectively improve the dielectric loss ability of the composite material, thereby improving its electromagnetic wave absorption ability[6]. The introduction of biochar not only broadens the absorption bandwidth, but also enhances the reflection loss ability of the biochar flakes. The preparation method of biomass carbon/Co_3O_4 composite materials mentioned in this article provides new ideas for future research on traditional electromagnetic wave absorbers。

2. Test part

2.1. Reagents

Cobalt nitrate (purity 98%) and citric acid monohydrate were purchased from Sinopharm Chemical Reagent Co., Ltd.; Macadamia shell carbon was purchased from Chinese Academy of Agricultural Sciences.

2.2. Preparation of C/Co nanofibers

Weigh 0.7 g of biochar and pour into three small Erlenmeyer flasks containing 9.1 g of cobalt nitrate. Put the Erlenmeyer flask into a water bath and heat and stir at 50 ℃ for about 2 h until the solution is completely mixed. Add 0.2, 0.5 or 0.8 g of biological carbon (BC) to the cobalt nitrate solution, and continue to magnetically stir for about 12 h at room temperature. The collected precursor fibers are fully dried and then placed in a program-controlled box-type electric furnace. They are heated from room temperature to 240℃ at a rate of 2℃/min in an air atmosphere and kept for 3 hours, and then the stabilized fibers are placed again. Into the program-controlled electric furnace, pass high-purity argon gas, heat up from room temperature to 900 ℃ at a rate of 5 ℃/min for carbonization treatment, keep it for 1 h and then cool down to room temperature under the protection of argon gas to obtain Co/C Nanofibers. According to the content of Co salt in the spinning solution, the target products were marked as BC/Co-2, BC/Co-5 and BC/Co-8.

2.3. Characterization method

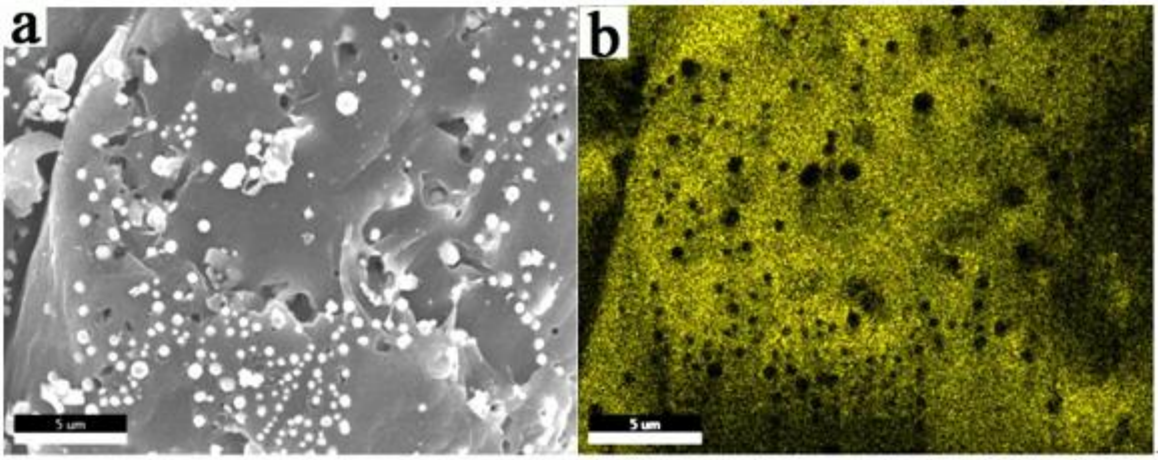
JEOLJSM7001F field emission scanning electron microscope (SEM) and JEM2100 transmission electron microscope (TEM) were used to observe the surface morphology and microstructure of composite nanofibers. The Shimadzu-type thermogravimetric differential thermal simultaneous thermal analyzer (TG-DTA) was used to study the composition of nanofibers.

Based on the TG results, the BC/Co-2, BC/Co-5 and BC/Co-8 samples can be calculated The content of metallic Co is approximately 13.1%, 37.8% and 49.7%, respectively. The obtained nanofibers are uniformly mixed with silica gel and curing agent. The fiber content is 5%. Then they are filled into a special stainless steel mold and placed in a vacuum oven at 100°C for about 2 hours to form an outer diameter of 7.0 mm. A ring specimen with an inner diameter of 3.0 mm and a thickness of 2.0 mm. The relative complex permittivity and complex permeability of the composite sample in the frequency range of 2-18 GHz were measured on the Agilent E5071C vector network analyzer (VNA) using the coaxial transmission/reflection method. According to the measured electromagnetic parameters, the theoretical reflection loss of each nanofiber absorbing coating is calculated using transmission line theory, and its microwave absorption performance is evaluated and analyzed.

3. Results and discussion

3.1. The structure and morphology of nanofibers

Figures 1(a)-(d) are the SEM-EDAX-TEM photos of biocarbon/Co3O4 nanofibers. It can be seen from the figure that the products obtained by high-temperature carbonization still maintain a good spherical morphology, and the metal oxide particle size It is relatively uniform, and the Co content has no obvious effect on the diameter of the metal oxide, and the average diameter is about 190-220 nm. However, some particle-like protrusions appeared on the surface of the Co-containing composite nanospheres, and the number gradually increased with the increase of the Co content. At the same time, with the increase of these protrusions, the fiber seems to become a little loose and porous, its continuity is damaged to a certain extent, and it is more prone to breakage. In order to further investigate the microstructure of nanofibers and the characteristics and distribution of Co particles, Figure 3(d) shows the TEM and high-resolution TEM pictures of the C/Co-5 sample. It can be observed from the figure that the formed Co particles are roughly spherical, and are more evenly embedded in the carbon-based nanofibers along the axial direction. The particle size distribution is relatively wide, about 600-800 nm. At the same time, the high-resolution TEM photos show that the carbon around the Co particles is indeed graphitized, and the entire particles are covered by several layers of ordered graphitized carbon layers, which are similar to the formation of a Co particle/graphite core-shell nanostructure, SEM The granular protrusions on the surface of the biochar in the photo are actually Co particles coated with the graphitized carbon layer. The better dispersion of Co particles and the special core-shell microstructure formed are not only conducive to improving their own oxidation and corrosion resistance, but also can establish a good electromagnetic match at the micro-nano scale, thereby helping to improve the material Microwave absorption performance.



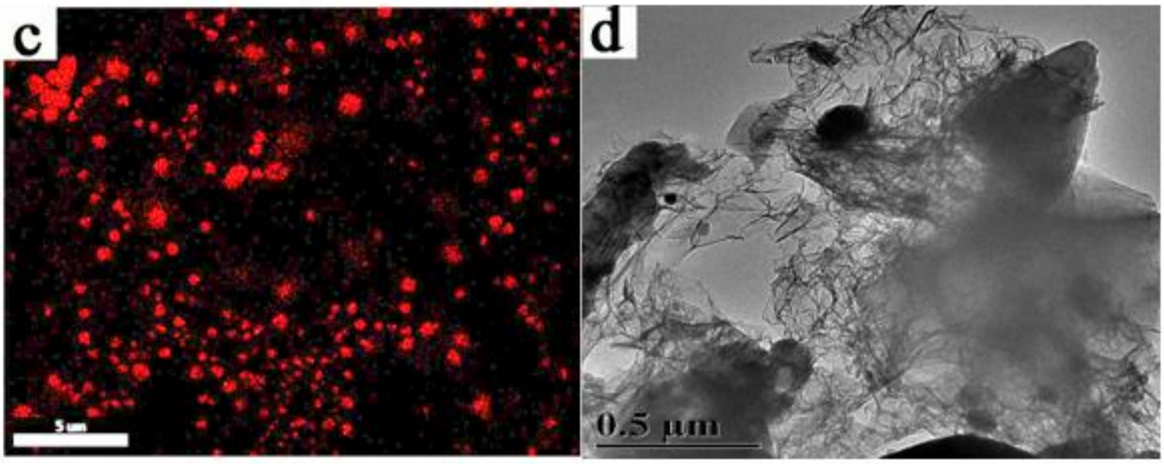


Figure 1: (a)-(d) are SEM-EDAX-TEM photos of biocarbon/Co_3O_4 nanofibers

3.2. Analysis of electromagnetic parameters

Figure 2(a) and Figure 2(b) show the ε′ and ε″ of the BC@Co_3O_4 composite sample. Obviously, the ε′ value of the sample is maintained at about 10-20, while the load of enough Co_3O_4 coating The value of ε′ of the sample is 0.1-10.6, and the peak value at 2 GHz is 10. It can be determined that the sample loaded at 2 GHz and 14.3 GHz has two peaks with values of 10 and 8. Compared with the bio-carbon material, the conductivity is poor. In addition, the reason why the loaded sample has a higher dielectric constant is that the Co_3O_4 nanospheres have a larger surface to enhance the interface polarization. It can also be found that the amount of relaxation peaks Significant increase. The results show that the dielectric loss of the composite material can be significantly increased by incorporating a sufficient content of Co_3O_4. Generally, various polarization effects lead to an increase in ε". In the microwave frequency range, the dielectric loss is mainly caused by the interface polarization effect. The Co_3O_4 layer on the biochar material increases the polarization of the interface between biochar/Co_3O_4/air, resulting in increased dielectric loss. It can be clearly illustrated from the figure that by loading a sufficient content of Co_3O_4 dielectric material, the dielectric loss capacity of the bio-carbon/Co_3O_4 composite material can be broadened to 18 GHz.

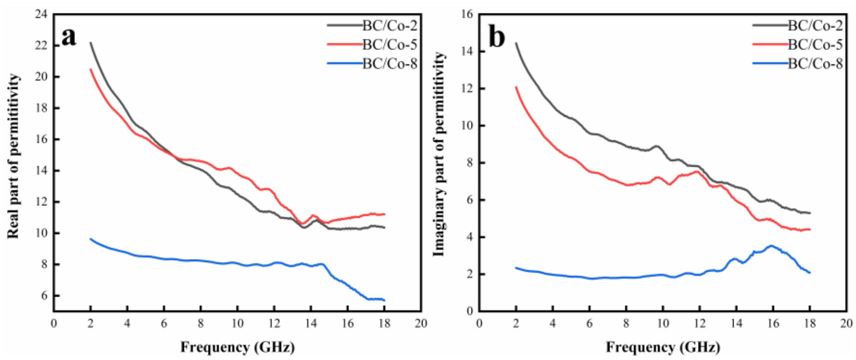


Figure 2: Dielectric constant of composite material

Figure 3(a) and Figure 3(b) show the real part of permeability (μ') and imaginary part (μ") of the composite material. It can be clearly seen from the figure that the permeability of the sample is imaginary The change trend of the part is obviously different. When the Co_3O_4 loading of the sample increases to a certain extent, the permeability of the composite material increases and decreases significantly. The results show that, due to the existence of the Co_3O_4 coating layer, the values of μ'and μ" There is a slight difference. It is worth noting that the change in dielectric constant is not as obvious as the permeability of the composite sample. The reason is that the coated Co_3O_4 layer is very thin, and Co_3O_4 is a dielectric loss material, and the contribution of biocarbon to the magnetic loss ability is negligible. Only when the Co_3O_4 load is large enough can it have a sufficient impact on the magnetic properties of the sample, but the impact is not obvious.

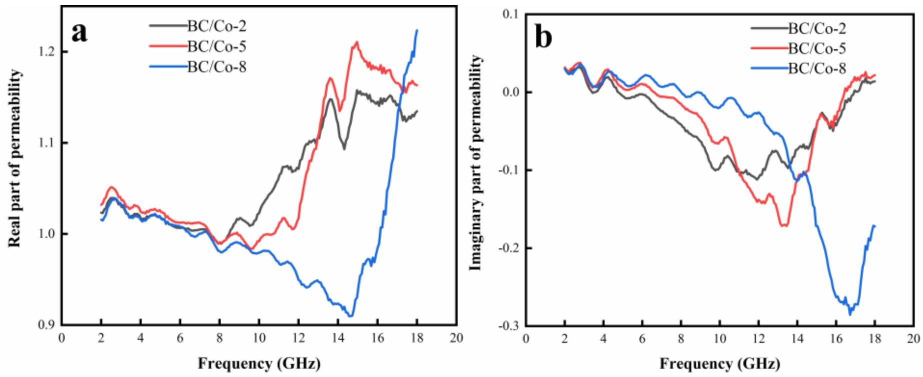


Figure 3: Magnetic permeability of composite materials

4. Analysis of microwave absorption performance

Generally, the reflection loss value and the effective absorption bandwidth are two key factors to measure the electromagnetic wave absorption performance of microwave absorbing materials. The calculation formula of reflection loss is as follows[7-8]:

$$RL = 20log_{10}\left(\frac{Z_{in}-Z_0}{Z_{in}+Z_0}\right)$$

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

Where: RL is the value of reflection loss, Zin is the input impedance of the material, and Z0 is the characteristic impedance of free space. Generally, the absorption region with an RL value lower than -10 dB is called effective absorption, which means that 90% of EM waves can be absorbed.As shown in Figure 4 (a)-Figure 4 (c), Figure 4 (a)-Figure 4 (c) are the two-dimensional reflection loss diagrams of the sample, and Figure 4 is the effective absorption bandwidth of the sample and the corresponding matching thickness picture. Compared with the unloaded sample, the RL value of Co3O4 microspheres coated with biochar has a significant increase. The area where the RL value of the sample is less than -10dB after loading is significantly enhanced. When the matching thickness range is 1-5mm, the effective absorption range is expanded from 4.74 GHz (6.51-11.25 GHz) to 11.15 GHz (6.27-11.58 GHz, 12.16-18 GHz). It can also be seen from the figure that at 7.77 GHz, when the matching thickness is 3.0mm, the minimum RL value of the sample is -20.1dB, but the effective absorption bandwidth (6.5-8.5 GHz) is too narrow to meet the required wide absorption. Bandwidth electromagnetic absorption characteristics. While the sample is at 15.11 GHz, when the matching thickness is 1.5 mm, the minimum RL value can reach -41 dB. In addition, when the matching thickness is 1.6mm, the effective absorption bandwidth can almost cover 13.39-17.94 GHz. We found that due to the addition of Co_3O_4, the relaxation peak in the high frequency range extended the absorption band to high frequencies. Generally, the value of reflection loss is greatly affected by the reflection and attenuation capabilities of the material. In detail, the incident microwave should be propagated into the material to the greatest extent and attenuated to the greatest extent. Based on the above, due to the coating of the dielectric layer Co_3O_4 layer, the ε′ of the series of samples increased slightly, and ε″ increased significantly, showing a peak in the high frequency range. Therefore, good electromagnetic wave attenuation characteristics can be achieved.

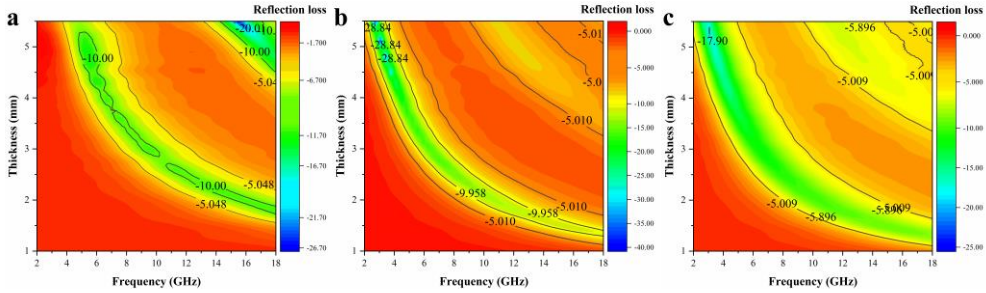


Figure 4： Microwave absorption properties of composite materials

In order to further study the microwave absorption capacity of Co_3O_4 materials without and with different contents, the less electromagnetic waves reflected on the surface of the material, that is, the better the microwave absorption capacity of the material. As shown in Figure 6, it can be confirmed that the impedance matching value of the sample loaded with Co_3O_4 is significantly lower than that of the pure biochar sample, and is closer to 1, which means that most of the electromagnetic waves can be incident into the material. Relatively speaking, the $|Z_{in}/Z_0|$ value of the sample between 0-6 GHz is basically lower than the range of 6-18 GHz, that is, the impedance matching of the sample is better when the frequency is lower. Moreover, it can be found that the impedance matching value of the composite sample is obviously closer to 1 than that of the uncomposited material. In other words, the presence of Co_3O_4 optimizes the impedance matching characteristics of the biomass/Co_3O_4 composite material at different frequencies and thicknesses, and then Improve the wave absorbing ability of composite materials.

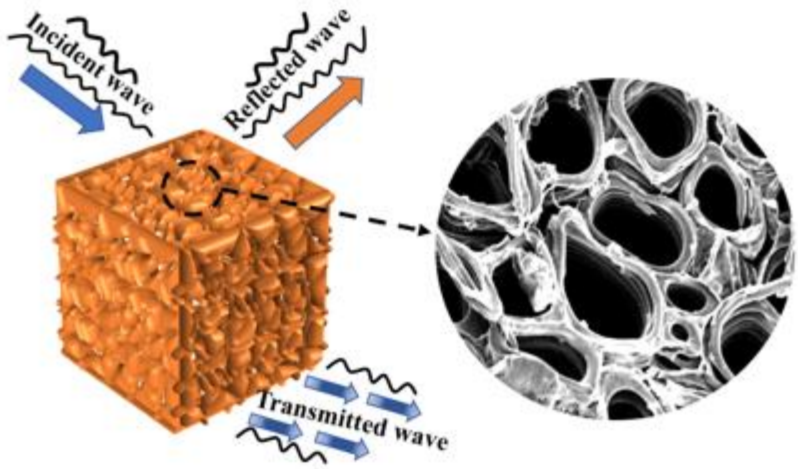


Figure 5: Microwave absorption mechanism diagram of composite materials

5. Conclusion

The bio-carbon-based composite material loaded with Co_3O_4 nanospheres was synthesized by the direct carbonization method. The SEM-EDX test confirmed that the Co_3O_4 nanospheres are evenly loaded on the surface of the biochar. After coating Co_3O_4, a variety of loss mechanisms are introduced, and the dielectric loss ability of the composite material is well enhanced, while the magnetic permeability is slightly reduced. Conductivity loss, interface polarization and magnetic loss significantly increase the electromagnetic wave absorption bandwidth and absorption strength of the composite material. The RL value of the biomass carbon/Co_3O_4 composite at 4.1GHz is -27 dB, and the matching thickness is only 5 mm. When the matching thickness is less than 3 mm, the absorption area can reach 11.15 GHz (6.27-11.58 GHz, 12.16-18 GHz). The high-efficiency microwave attenuation of the bio-carbon-loaded Co_3O_4 spherical composite material is mainly due to its own higher magnetic loss and the dielectric loss capability of the introduced semiconductor material. This research provides new ideas for the optimization of the performance of conventional electromagnetic materials in the future.

References:

[1] Sun G , Dong B , Cao M , et al. Hierarchical Dendrite-Like Magnetic Materials of Fe3O4, γ-Fe2O3, and Fe with High Performance of Microwave Absorption[J]. Chemistry of Materials, 2011, 23(6):1587-1593.

[2] Dong X L , Zhang X F , Huang H , et al. Enhanced microwave absorption in Ni/polyaniline nanocomposites by dual dielectric relaxations[J]. Applied Physics Letters, 2008, 92(1):301.

Hansman R J J . Microwave Absorption Measurements of Melting Spherical and Nonspherical Hydrometeors.[J]. Journal of the Atmospheric Sciences, 1986, 43(15):1643-1649.

[3] Zhang X F , Dong X L , Huang H , et al. Microwave absorption properties of the carbon-coated nickel nanocapsules[J]. Applied Physics Letters, 2006, 89(5):1679-1083.

[4] Xu H , Wen S , Xu Q , et al. Structural, magnetic and microwave absorption properties of Ni-doped ZnO nanofibers[J]. Journal of Materials Science: Materials in Electronics, 2017, 28(3):2803-2811.

[5] Zhong X , Cheng J W , Liu Y , et al. Effect of annealing temperature on structure, magnetic and microwave absorption properties of Fe–B submicrometer particles[J]. Journal of Materials Research, 2016, 31(22):3619-3628.

[6] Peng K , Wu Y , Liu C , et al. The tunable microwave absorption performance of the oriented flaky Fe-Co-Nd with a broad bandwidth absorption at a thin thickness[J]. Journal of Magnetism and Magnetic Materials, 2020, 510:166925.

[7] Bao S , Hou T , Tan Q , et al. Immobilization of Zinc Oxide Nanoparticles on Graphene Sheets for Lithium ion Storage and Electromagnetic Microwave Absorption[J]. Materials Chemistry and Physics, 2020, 245:122766.

[8] Sc A , Jhy A , Cyb A , et al. Enhanced microwave absorption properties of Zn-substituted SrW-type hexaferrite composites in the Ku-band[J]. Ceramics International, 2021, 47(6):7571-7581.

[9] Sun Y , Sun Y . Precursor infiltration and pyrolysis cycle-dependent mechanical and microwave absorption performances of continuous carbon fibers-reinforced boron-containing phenolic resins for low-density carbon-carbon composites - ScienceDirect[J]. Ceramics International, 2020, 46(10):15167-15175.

[10] Wang Z , Cheng Z , Fang C , et al. Recent advances in MXenes composites for electromagnetic interference shielding and microwave absorption[J]. Composites Part A Applied Science and Manufacturing, 2020, 136:105956.

[11] Ji C , Liu Y , Li Y , et al. Facile Preparation and Excellent Microwave Absorption Properties of Cobalt-iron/ Porous Carbon Composite Materials[J]. Journal of Magnetism and Magnetic Materials, 2021, 527(20):167776.

[12] Li Y , Zheng W , Zhang A , et al. Effect of Nickel Shell Thickness of Ni-microsphere on Microwave Absorption Properties of Ni-microsphere@MWCNTs Hybrids[J]. Journal of Magnetism and Magnetic Materials, 2020, 513:167218.

[13] Singh S , Kumar A , Agarwal S , et al. Synthesis and tunable microwave absorption characteristics of flower-like Ni/SiC composites[J]. Journal of magnetism and magnetic materials, 2020, 503(Jun.):166616.1-166616.10.

[14] Liu P , Chen S , Yao M , et al. Double-layer absorbers based on hierarchical MXene composites for microwave absorption through optimal combination[J]. Journal of Materials Research, 2020, 35(11):1-11.