



Microwave absorption performance of iron oxide/multiwalled carbon nanotubes nanohybrids prepared by electrostatic attraction

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ABSTRACT

Designing the structure with dielectric loss and magnetic loss integrated contributes to expansion of microwave absorption bandwidth. Nanohybrid materials composed of iron oxide (Fe_3O_4) and multiwalled carbon nanotubes (MWCNTs) were prepared through a newly electrostatic attraction method as high-performance microwave absorbers in the 2–18 GHz band. The nanohybrids are characterized by transmission electron microscopy, X-ray diffraction, and vector network analysis. Microstructural analysis showed that Fe_3O_4 and MWCNTs were well-connected through electrostatic interaction in the nanohybrids. The experimental results indicated that MWCNTs/PEDOT: PSS/ Fe_3O_4 possessed higher reflection loss and broader absorption bandwidth than MWCNTs. MWCNTs/SDBS/ Fe_3O_4 had better matching of dielectric loss and magnetic loss, the absorption bandwidth below -10 dB was up to 8 GHz. This work further reveals that the novel electrostatic attraction method could be efficiently enlarged electromagnetic wave attenuation performance in absorb materials.

Introduction

Electromagnetic shielding and attenuation materials based on excellent dielectric and magnetic properties are drawing increasing attention to the significant applications in aircrafts, communication devices, cutting-edge electronics, and health protection [1–7]. Serious electromagnetic interference pollution is so ubiquitous that finding efficient microwave absorbers with superior absorption performances at specific

frequency band is becoming highly desirable and necessary [8].

Based on the absorption mechanism, microwave absorbers can be classified into two categories: dielectric loss absorbers and magnetic loss absorber [9]. Dielectric loss absorbers comprise graphite, carbon nanotube, carbon particles, and SiC. Magnetic loss absorbers include metal compounds such as Fe_3O_4 , magnetic metal (Fe, Ni), and hydroxy-Fe [10]. However, dielectric and magnetic absorbers both

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have shortcoming of low attenuation ability when they are utilized alone in the microwave band of 2–18 GHz. Dielectric loss absorbers have a low absorption efficiency, while magnetic loss absorbers are heavy and poor heat resistance. Nanohybrids composed of those two absorbers with controlled structure and interface interaction may exhibit synergistic properties and show great potential as high-performance microwave absorbers.

Multiwalled carbon nanotubes (MWCNTs) have great potential as microwave absorbers because of their unique chemical structure and electrical and magnetic properties [11–13]. It is necessary to modify MWCNTs by coating, filling, or doping with other nanomaterials in order to improve microwave absorption properties. In the previous studies, three routes were applied to improve the dielectric loss or magnetic loss of MWCNTs. Firstly, coating MWCNTs with conductive polymer. A. Choudhury synthesized the nanohybrids of protonic acid doped poly(*o*-toluidine) with carboxyl-functionalized MWCNTs by in situ chemical oxidation polymerization to improve dielectric constantly and loss significantly [14]. Secondly, MWCNTs hybrids with dielectric materials, some researchers used BaTiO₃ and TiO₂ to develop novel absorption materials. The absorption strength could reach –40 dB, but the bandwidth below –10 dB did not show any enhancement [15, 16]. Thirdly, MWCNTs hybrids with magnetic metal compounds. Bhattacharya et al. [17] used rare metal nitrate-doped MWCNTs as the absorber to achieve the maximum absorption bandwidth up to 5.12 GHz. Zhang doped MWCNTs with Co_{0.5}Ni_{0.5}Fe₂O₄ nanoparticles and achieved the maximum reflection loss value of –24.37 dB, the frequency bandwidth of 5.1 GHz from 7.8 to 12.9 GHz [18]. Wang applies Fe incorporation into the structure of MWCNTs and obtained the highest EMI shielding effectiveness of –41 dB [19]. Mao-Sheng Cao's work [20], the ferrosferric oxide was selected as the phase-in multiwalled carbon nanotube (MWCNT)-based composites for enhancing magnetic properties and improving electromagnetic attenuation. It was confirmed to have the highly efficient microwave absorption and effective absorption bandwidth. Therefore, designing absorbers contained with dielectric loss and magnetic loss components is an efficient way to enlarge the absorption bandwidth.

In present study, a newly electrostatic attraction method is applied to prepare nanohybrids with

MWCNTs and Fe₃O₄. The experimental results indicate that the nanohybrid of MWCNTs/Fe₃O₄ possesses high reflection loss and absorption bandwidth, the absorption bandwidth below –10 dB is up to 8 GHz.

Experimental

Materials

Multiwalled carbon nanotubes (MWCNTs) were provided by Chengdu Organic Chemicals Co. Ltd. (Chinese Academy of Sciences) with a diameter of 8 nm and purity of 95 wt%. Iron oxide (20 nm, 99.5 wt%) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) (1.4% in water) were obtained from Aladdin Industrial Corporation and Adamas Reagent Ltd., respectively. Sodium dodecyl benzene sulfonate (SDBS) and cetyl trimethyl ammonium bromide (CTAB) were all purchased from Sinopharm Chemical Reagent Co. Ltd.

Synthesis of MWCNTs/PEDOT: PSS/Fe₃O₄ nanohybrids

An electrostatic adsorption method was applied to fabricate the nanohybrids of MWCNTs/PEDOT: PSS/Fe₃O₄. Initially, MWCNTs (100 mg) were dispersed in a 50 mL PEDOT: PSS solution with the concentration of 0.2 wt% in an ultrasonic bath. This mixture was further sonicated for at least 1 h to get a stable black suspension. The suspension was suction filtrated by a microporous membrane and then dried in a vacuum oven to obtain the sample of MWCNTs/PEDOT: PSS. Then, a stable Fe₃O₄/CTAB suspension was achieved by the same method. Finally, the two solutions were mixed together and mechanically stirred at a slow rate to synthesize MWCNTs/PEDOT: PSS/Fe₃O₄ through electrostatic adsorption effect from PEDOT: PSS and CTAB. The powder of MWCNTs/PEDOT: PSS/Fe₃O₄ was gotten after suction filtrated and dried in a vacuum oven.

Synthesis of MWCNTs/SDBS/Fe₃O₄ nanohybrids

The strategy for fabrication of MWCNTs/SDBS/Fe₃O₄ is the same with that of MWCNTs/PEDOT: PSS/Fe₃O₄ nanohybrids. In this section, SDBS was

applied as coating of the MWCNTs replacing of PEDOT: PSS. Finally, the samples of MWCNTs/SDBS and MWCNTs/SDBS/Fe₃O₄ were gotten, respectively.

Characterization

X-ray diffraction (XRD) patterns of the products were obtained on a Rigaku D/max-2550VB3+/PC diffractometer equipped with a rotating anode and Cu K α source. Transmission electron microscope (TEM) images were taken on a JEM-2100F electron microscope under an accelerating voltage of 300 kV. TEM samples were prepared by dropping a diluted dispersion of the as-prepared products onto amorphous carbon-coated copper grids and drying in air. Electromagnetic parameters were measured on a vector network analyzer (Agilent, N5244A PNA-X) with the transmission-reflection mode in the 2–18 GHz band. Samples containing 25 wt% prepared composites were pressed into a shape with an outer diameter of 7.0 mm, the inner diameter of 3.0 mm, and thickness of about 2.5 mm for microwave measurement, in which paraffin wax was used as the binder. All reported values were obtained by averaging over the data measured from three samples for each kind of nanohybrids.

Results and discussion

Structure of MWCNTs/Fe₃O₄ nanohybrids

The phase composition and morphology of the nanohybrids (MWCNTs/Fe₃O₄) were characterized

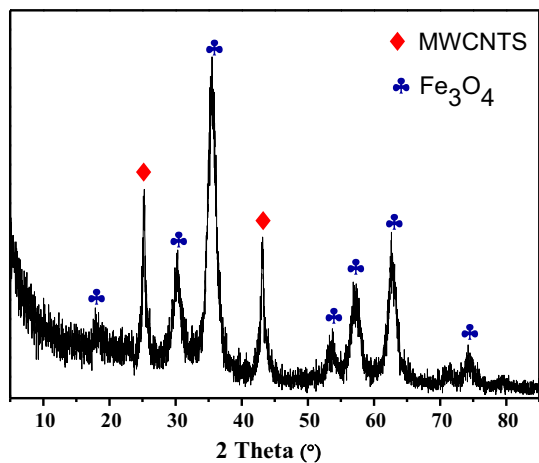


Figure 1 XRD pattern of the MWCNTs/Fe₃O₄ nanohybrids.

via XRD and TEM. As shown in Figs. 1 and 2. In Fig. 1, nine major diffraction peaks could be observed in the MWCNTs/Fe₃O₄ nanohybrids. The peaks at 26° and 44° are assigned to (002) and (100) planes of the MWCNTs, respectively. Other peaks at 18°, 30°, 35.5°, 53°, 57°, 62.5°, and 74.5° represent the Bragg reflection from (111) (220), (311), (422), (511), (440), and (533) planes of the cubic spinel crystal structure of Fe₃O₄. These results indicate that the nanohybrids of MWCNTs/Fe₃O₄ have been successfully prepared with electrostatic adsorption method.

The structure of MWCNTs/Fe₃O₄ nanohybrids is further measured by TEM, as displayed in Fig. 2. The structure of floccule could be observed in Fig. 2a because electrostatic interaction between PEDOT: PSS and CTAB promotes MWCNTs and Fe₃O₄ to form the structure of floccule. The microstructure of floccule can be analyzed from Fig. 2b, the enlarged view of a red circle in Fig. 2a. Lots of lattice planes (in the red bars) can be seen in the light-colored district, which is the obvious characteristic of Fe₃O₄ and MWCNTs. In addition, lattice planes of different directions can be also observed, which indicates that MWCNTs and Fe₃O₄ have well interaction.

The composition of dark grains was analyzed by EDS, as illustrated in Table 1. As can be seen in Table 1, the grains only contain Fe and O elements. And the atomic ratio and mass ratio match the ideal state of pure Fe₃O₄. Accordingly, the dark grains can be recognized as ferrosferric oxide. It can be confirmed that MWCNTs and Fe₃O₄ have been connected through the analysis of XRD patterns and TEM images.

Electromagnetic performance of MWCNTs/PEDOT: PSS/Fe₃O₄ nanohybrids

Microwave propagation in electromagnetic media is largely determined by the complex permittivity and permeability of the materials. MWCNTs, a typical dielectric loss material, have the relatively higher values of complex permittivity compared to other media. Coating conductive polymers on MWCNTs is an effective method to improve the complex permittivity (as presented in Figs. 3 and 4). That is due to the formation of a π - π non-covalent interaction between the conductive polymer (PEDOT: PSS) and MWCNTs, which can promote electronic transition.

Figures 3 and 4 show the same tendency about real and imaginary part of the three samples. MWCNTs/

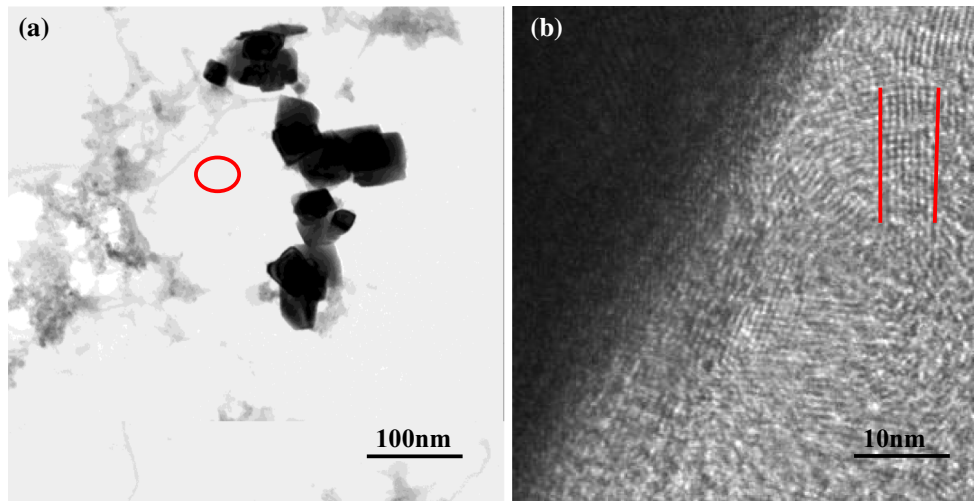


Figure 2 TEM images of the MWCNTs/Fe₃O₄ nanohybrids **a** the morphology of the nanohybrids, **b** the enlarged view of red circle in (a).

Table 1 Element content analysis of dark grains

Element	Weight (%)	Atomic (%)
O	25.70	54.70
Fe	74.30	45.30

PEDOT: PSS/Fe₃O₄ has higher complex permittivity than MWCNTs, but lower than MWCNTs/PEDOT: PSS. This phenomenon is attributed to Fe₃O₄ with a large mass fraction in the nanohybrids. Coating conductive polymer improves the dielectric properties of MWCNTs, contributes to further improve the reflection loss of the nanohybrids.

The complex permeability of MWCNTs/PEDOT: PSS/Fe₃O₄ and MWCNTs can be obtained from Fig. 5. The real part of the complex permeability of

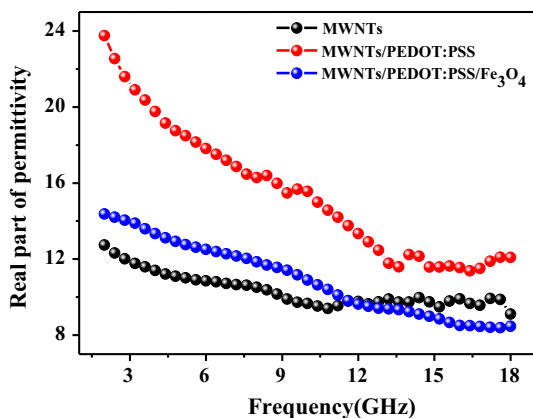


Figure 3 Real part of complex permittivity spectra in the 2–18 GHz range.

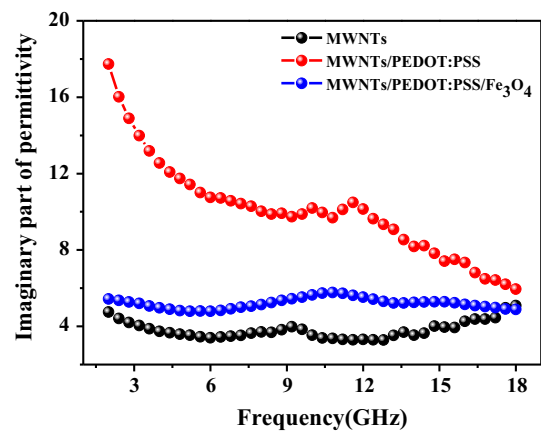


Figure 4 Imaginary part of complex permittivity spectra in the 2–18 GHz range.

MWCNTs is almost 1, and the imaginary part is almost zero. That is to say, MWCNTs do not have magnetic loss capabilities. While the complex permeability of MWCNTs/PEDOT: PSS/Fe₃O₄ gets an enhancing compared to MWCNTs, the sample exhibits a certain degree of magnetic loss. This indicates that the electrostatic adsorption method to connect MWCNTs and Fe₃O₄ used in this study is effective.

Microwave absorption performances of the samples are evaluated by the reflection loss on the basis of the transmission line theory. The equations are as follows:

$$Z = \frac{Z_{in}}{Z_0} = \sqrt{\frac{\mu_r}{\epsilon_r} \tanh\left(j \frac{2\pi f d}{\lambda_0} \cdot \sqrt{\mu_r \epsilon_r}\right)}$$

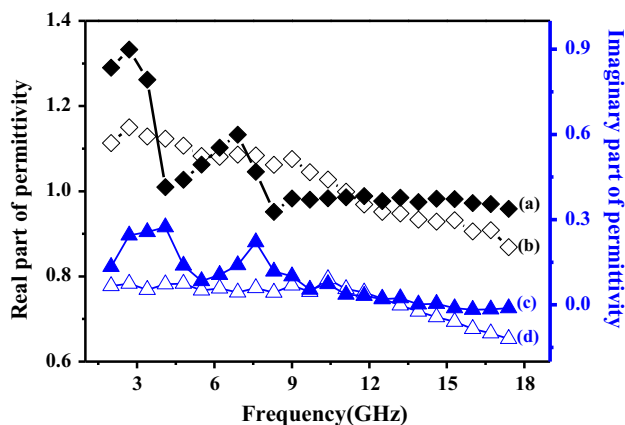


Figure 5 Complex permeability spectra in the 2–18 GHz range. **a** Real part of complex permeability of MWCNTs/PEDOT:PSS/Fe₃O₄, **b** real part of complex permeability of MWCNTs, **c** imaginary part of complex permeability of MWCNTs/PEDOT:PSS/Fe₃O₄, **d** imaginary part of complex permeability of MWCNTs.

$$R(\text{dB}) = 20 \lg \left| \frac{Z - 1}{Z + 1} \right|$$

where f is the frequency of the electromagnetic waves, d is the thickness of the absorber, c is the velocity of electromagnetic waves in free space, μ_r and ϵ_r are the relative complex permeability and permittivity, respectively, Z_0 is the impedance of air, and Z_{in} is the input impedance of the absorber. Reflection loss of the MWCNTs/PEDOT:PSS/Fe₃O₄ nanohybrids was measured in the 2–18 GHz band and is shown in Fig. 6. The lowest reflection loss for all the three samples is -43 dB in 7.8 GHz appearing in the MWCNTs. Pure MWCNTs exhibit strong microwave absorption but lacks of the absorption

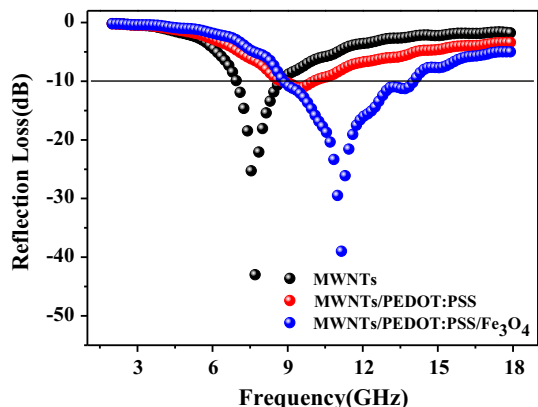


Figure 6 Reflection loss of MWCNTs/PEDOT:PSS/Fe₃O₄ in the 2–18 GHz range.

bandwidth. The absorption bandwidth with a reflection loss below -10 dB is about 2 GHz (from 7 to 9 GHz) for the MWCNTs. MWCNTs/PEDOT:PSS can significantly improve the complex permittivity, but the reflection loss has largely declined to -10 dB nearly. Because of the imaginary part of the complex permittivity of MWCNTs/PEDOT:PSS is too high to enhance the Z_{in} that microwaves are reflected. MWCNTs/PEDOT:PSS/Fe₃O₄ shows excellent absorption performance with reflection loss of -39 dB at 11 GHz and absorption width up to 4.5 GHz. The combination of dielectric loss (MWCNTs/PEDOT:PSS) and magnetic loss (Fe₃O₄) effectively broadens the absorption bandwidth.

Electromagnetic performance of MWCNTs/SDBS/Fe₃O₄ nanohybrids

The use of PEDOT:PSS makes the imaginary part of the complex permittivity raises too much, which limits the enhancement of absorption bandwidth. In this section, anionic surfactant SDBS is used to coat on the MWCNTs to generate the electrostatic adsorption effect with Fe₃O₄/CTAB. Complex permittivity of MWCNTs/SDBS/Fe₃O₄ is shown in Fig. 7. The real part of the complex permittivity of MWCNTs/SDBS/Fe₃O₄ attains to 7–11, which is lower than that of MWCNTs. The imaginary part also has the trend. While the real part and imaginary part of complex permeability attain 1.1–1.4 and 0–0.25 (as shown in Fig. 8), respectively, which is higher than that of MWCNTs/PEDOT:PSS/Fe₃O₄.

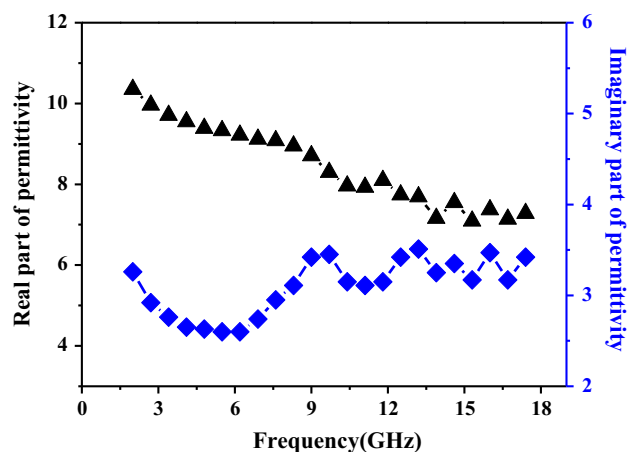


Figure 7 Complex permittivity spectra of MWCNTs/SDBS/Fe₃O₄ in the 2–18 GHz range.

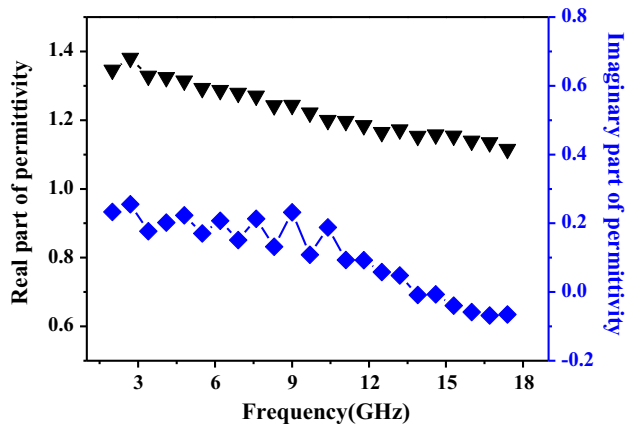


Figure 8 Complex permeability spectra of MWCNTs/SDBS/ Fe_3O_4 in the 2–18 GHz range.

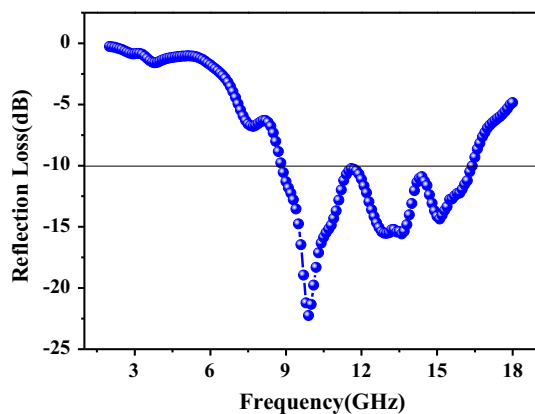


Figure 9 Reflection loss of MWCNTs/SDBS/ Fe_3O_4 in the 2–18 GHz range.

The reflection loss of MWCNTs/SDBS/ Fe_3O_4 is measured in the 2–18 GHz range and is shown in Fig. 9. The sample possesses three absorption peaks at 10, 13.5, and 15 GHz, among which the maximum absorption strength attains to -24 dB, while the absorption bandwidth reaches 8 GHz from 9 to 17 GHz. Peaks at 10 GHz and 15 GHz belong to MWCNTs and Fe_3O_4 , respectively. And the wide peak at 13.5 GHz is attributing to the interaction of electronic transition between MWCNTs and Fe_3O_4 . In MWCNTs/PEDOT: PSS/ Fe_3O_4 , MWCNTs are coated by PEDOT: PSS a conductive polymer which would influence the electronic transition between MWCNTs and Fe_3O_4 directly. While in MWCNTs/SDBS/ Fe_3O_4 , MWCNTs can receive the electronics transition from Fe_3O_4 . The interaction of electronic transitions ensures the nanohybrids absorb more electromagnetic energy and broaden the absorption

bandwidth. Therefore, the nanohybrids show an excellent electromagnetic wave attenuation performance, including high absorption efficiency, strong absorption, and a wide operation frequency bandwidth.

Conclusions

MWCNTs alone exhibited strong absorption, but narrow absorption bandwidth. A newly electrostatic attraction method was applied to fabricate the nanohybrids of MWCNTs/ Fe_3O_4 nanohybrids to enlarge the absorption bandwidth. XRD patterns and TEM images identified that MWCNTs and Fe_3O_4 had been connected together. Their hybrid material exhibited considerable electromagnetic absorbing ability at a frequency of 2–18 GHz. PEDOT: PSS/MWCNTs/ Fe_3O_4 had a reflection loss of -39 dB at 11 GHz and absorption bandwidth up to 4.5 GHz. The maximum absorption strength of MWCNTS-SDBS/ Fe_3O_4 attained to -24 dB, and the absorption bandwidth reached 8 GHz. The interaction of electronic transitions between MWCNTs and Fe_3O_4 can really enlarge the absorption bandwidth. As a result, the hybrids achieved significant microwave absorption. This work further reveals that novel electrostatic attraction method could be efficiently enlarged electromagnetic wave attenuation performance in absorb materials.

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