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3D Fe$_3$O$_4$ nanocrystals decorating on carbon nanotubes to tune electromagnetic
properties and enhance microwave absorption capacity

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We fabricated a novel dielectric-magnetic nanostructure hybridized by 3D Fe$_3$O$_4$ nanocrystals and
multi-walled carbon nanotubes through a simple co-precipitation route. The 3D Fe$_3$O$_4$-MWCNTs
composites demonstrate enhanced microwave absorption with tunable strong-absorption waveband
in the frequency range of 2-18 GHz. Double-band microwave absorption appears in the investigated
frequency range and various thicknesses. It depends on the loading concentration of 3D
Fe$_3$O$_4$-MWCNTs. Two minimum reflection loss values for 20 wt.% loading can reach -23.0 dB and
-52.8 dB at 4.1 GHz and 12.8 GHz, respectively, which are superior to those of pure MWCNTs as
well as other hybrid of Fe$_3$O$_4$. The improved absorption capacity arises from the synergy of
dielectric loss and magnetic loss, as well as the enhancement of multiple interfaces among 3D
Fe$_3$O$_4$ nanocrystals. All above increase the flexibility of tuning microwave absorption. These results
provide a new strategy to tune electromagnetic properties and enhance capacity for high-efficient
microwave absorber.
High efficiency and lightweight are two key factors for promoting practical application of microwave absorption materials in a wide range of commercial, military, aerospace and healthcare. Carbon materials have been proved a kind of good microwave absorber. Among them, carbon nanotubes,\textsuperscript{1-3} carbon nanocoils\textsuperscript{4,5} and graphene\textsuperscript{6-8} exhibited considerable microwave absorption in reported literature. In particular, carbon nanotubes are promising candidates for high-efficient microwave absorber, due to their lightweight, high conductivity, high aspect ratio, good resistance against corrosion and excellent mechanical properties. However, microwave absorptions of the carbon materials are still needed to be improved. Magnetic materials, including magnetic metal,\textsuperscript{9,10} magnetic oxides\textsuperscript{11-14} etc., are also good microwave absorbers. They exhibit potential microwave absorption, whereas narrow bandwidth prohibits their application. Actually, excellent microwave absorption is usually due to efficient complementarities between the complex permittivity and permeability of materials. Only dielectric loss or magnetic loss in materials generates a weak electromagnetic impedance matches. In recent years, magnetic-dielectric material hybrid, including Fe\textsubscript{3}O\textsubscript{4}-nonmagnetic core-shell microspheres,\textsuperscript{15-17} Fe\textsubscript{3}O\textsubscript{4}-graphene,\textsuperscript{18-21} Fe\textsubscript{3}O\textsubscript{4}-carbon nanotube hybrid,\textsuperscript{22,23} etc.\textsuperscript{24-30} shown enhanced microwave absorption as the optional microwave absorber. However, it remains a great challenge to improve magnetic-dielectric material hybrid for more high-efficient absorption, broader bandwidth, more convenient to tune microwave absorption for application than former ones.

Herein, we synthesized a novel magnetic-dielectric nanostructure hybridized by 3D Fe\textsubscript{3}O\textsubscript{4} nanocrystals and MWCNTs (3D Fe\textsubscript{3}O\textsubscript{4}-MWCNTs). The probable growth process of 3D Fe\textsubscript{3}O\textsubscript{4}-MWCNTs was discussed. Importantly, 3D Fe\textsubscript{3}O\textsubscript{4}-MWCNTs demonstrate more excellent microwave absorption compared to previous work (see Table S1), and the mechanism of enhanced microwave absorption was investigated.
The 3D Fe$_3$O$_4$-MWCNTs nanostructure was fabricated via co-precipitation reaction (see Scheme S1). In order to investigate the possible growth process of 3D Fe$_3$O$_4$-MWCNTs, we got the products of different reaction stages (5 min, 15 min and 30 min reaction time) and named Sample 1, Sample 2 and Sample 3, respectively. Fig. 1 shows the morphology of as-prepared samples. A small amount of Fe$_3$O$_4$ nanocrystals grow on the MWCNTs at first in Fig. 1a and e (Sample 1). Then more and more Fe$_3$O$_4$ nanocrystals grow around the original particles in Fig. 1b and f (Sample 2). These numerous nanocrystals finally form the 3D nanostructure ultimately which is inserted on carbon nanotubes in Fig. 1c and g (Sample 3). The possible growth process of 3D Fe$_3$O$_4$-MWCNTs nanostructure is further illustrated in Scheme S1. Fig. 1d and h show the amplified SEM image and TEM image of the regions of red rectangles, showing the 3D morphology of Fe$_3$O$_4$ nanocrystals.

The transmission electron microscope (TEM) image in Fig. 2a further indicates the morphology of 3D Fe$_3$O$_4$-MWCNTs nanostructure. The results of X-ray power diffraction (XRD) spectra for 3D Fe$_3$O$_4$-MWCNTs (Fig. S2) can be typically indexed to the spinel phase of Fe$_3$O$_4$ (JCPDS #88-0866), which conforms to the electron diffraction (SAED) pattern of 3D Fe$_3$O$_4$-MWCNTs, as shown in Fig. 2b. High-resolution transmission electron microscope (HRTEM) images of 3D Fe$_3$O$_4$-MWCNTs in Fig. 2c and d show that Fe$_3$O$_4$ nanocrystals are close deposited on the MWCNTs, and adjacent Fe$_3$O$_4$ nanocrystals tightly grew together. The Raman spectrums of neat MWCNTs and 3D Fe$_3$O$_4$-MWCNTs (Fig. S3) are almost the same, demonstrating that there is no meaningful change for MWCNTs before and after 3D Fe$_3$O$_4$ nanocrystals decorating. Additionally, the content of Fe$_3$O$_4$ in 3D Fe$_3$O$_4$-MWCNTs is characterized by the energy dispersive spectroscopy (EDS) analysis (Fig. S4). The mass percent of Fe$_3$O$_4$ in Sample 1, Sample 2 and Sample 3 is increasing.

Reflection loss (RL) was calculated by using the measured complex permittivity and complex
permeability. In Fig. 3a, under the same condition of 20 wt.% filler loading and a thickness of 6.8 mm, the minimum RL values of both the composites loading with Sample 1 and 3 are much better than that of pure MWCNTs. Meanwhile, the microwave absorption for Sample 3 is the best (Fig. S5). Fig. 3b and c show the RL of 3D Fe₃O₄-MWCNTs composites (loading with Sample 3) with different loading concentration and different thickness. Two minimum RL values of the composites reach -23.0 dB and -52.8 dB with 20 wt.% loading and a thickness of 6.8 mm at 4.08 GHz and 12.8 GHz, respectively. Moreover, the microwave absorption of 3D Fe₃O₄-MWCNTs is proved more excellent than that of Fe₃O₄/MWCNTs blend (Fig. S6). Importantly, by tuning the thickness of 3D Fe₃O₄-MWCNTs composites, considerable microwave absorption appears in different waveband, such as X band, S band, or Ku band, as shown in Fig. 3c.

Fig. 4 shows RL plots of 3D Fe₃O₄-MWCNTs composites with different loading concentration (5 wt.%, 10 wt.%, 20 wt.% and 25 wt.%) versus frequency in the range of 2-18 GHz and thickness in the range of 2-8 mm. In general, materials with RL ≤ -10 dB (red line in Fig. 4) are considered to be suitable for applications. It can be observed that double-band microwave absorption exists in investigated frequency range and various thicknesses, and relies on the loading concentration of 3D Fe₃O₄-MWCNTs as shown in Fig. 4c and d. The minimum RL values of these composites with 10 wt.%, 15 wt.%, 20 wt.% and 25 wt.% loading are -13.1 dB at 15.7 GHz, -23.7 dB at 15.7 GHz, -52.8 dB at 12.8 GHz, -45.2 dB at 6.0 GHz, respectively. The RL plots indicate that 3D Fe₃O₄-MWCNTs could be designed to microwave absorber for different requirements by easily tuning sample thickness and loading concentration of 3D Fe₃O₄-MWCNTs.

The real permittivity (ε′), imaginary permittivity (ε″), real permeability (μ′) and imaginary permeability (μ″) of 3D Fe₃O₄-MWCNTs were investigated in the frequency range of 2-18 GHz to understand the microwave absorption mechanisms, as shown in Fig. 5. It is obvious that besides
two weak peaks at ~9.9 GHz and ~15.0 GHz of $\varepsilon''$, both the $\varepsilon'$ and $\varepsilon''$ of the composites increase with increasing 3D Fe$_3$O$_4$-MWCNTs loading, changing from 2.8 to 12.0 and 0.02 to 5.06, respectively. They decrease with increasing frequency as shown in Fig. 5a. The resonance peaks are probably associated with the interfaces between MWCNTs and 3D Fe$_3$O$_4$ nanocrystals and the ones among 3D Fe$_3$O$_4$ nanocrystals. According to Debye Theory, there are two important factors account for dielectric loss. One is the combined loss of the dipole polarizations and interfacial polarizations. The former is probably originated from abundant surface functions and defects in the acidified MWCNTs. The latter exists in a large amount of interfaces among 3D Fe$_3$O$_4$ nanocrystals and the interfaces between 3D Fe$_3$O$_4$ nanocrystals and MWCNTs. Another factor is the contribution of conductivity loss originating from the 3D Fe$_3$O$_4$-MWCNTs, which benefits from the excellent conductivity of MWCNTs. Fig. 5b show the frequency dependence of the real part ($\mu'$) and imaginary part ($\mu''$) of complex permeability of 3D Fe$_3$O$_4$-MWCNTs. One slight peaks for $\mu''$ is observed at ~11.0 GHz. In general, the magnetic loss of materials originates mainly from natural resonance, exchange resonance and eddy current loss. The values of $\mu''(\mu')^{2}f^{l}$ are almost constant in 14-18 GHz (Fig. S7). The magnetic loss of 3D Fe$_3$O$_4$-MWCNTs is mainly originated from natural resonance, exchange resonance in 2-14 GHz and eddy current loss in 14-18 GHz. Additionally the scale of Fe$_3$O$_4$ nanocrystals is 10 nm approximately (Fig. S8), which is close to the exchange length and further demonstrates that the exchange resonance was enhanced.

The enhanced microwave absorption capacity with tunable strong-absorption waveband of 3D Fe$_3$O$_4$-MWCNTs nanostructures is attributed to the synergy of dielectric loss and magnetic loss, as well as the enhancement multiple interfaces among 3D nanocrystals. The 3D Fe$_3$O$_4$-MWCNTs processes amounts of interfaces, the contribution of interfacial polarizations to dielectric loss has been greatly improved. Moreover, the 3D Fe$_3$O$_4$ nanostructure probably has less effect on
MWCNTs conductivity pathways for electrons hopping and migrating compared to the other hybrid, in which MWCNTs are coated with Fe$_3$O$_4$ or other magnetic materials. The integrated effect of all advantages mentioned above lead to the enhanced microwave absorption of 3D nanocrystals.

In summary, we fabricated the 3D Fe$_3$O$_4$-MWCNTs nanostructures and investigated its microwave absorption in the frequency range of 2-18 GHz. The results indicate that 3D Fe$_3$O$_4$-MWCNTs demonstrate enhanced tunable microwave absorption. The minimum reflection loss value of 3D Fe$_3$O$_4$-MWCNTs reaches -52.8 dB with 20 wt.% loading at 12.8 GHz. It is convenient to tune microwave absorption by varying the sample thickness and loading concentration of 3D Fe$_3$O$_4$-MWCNTs. The excellent microwave absorption of 3D Fe$_3$O$_4$-MWCNTs is superior to MWCNTs and other generally hybrid of Fe$_3$O$_4$. These findings open up a new pathway to develop outstanding microwave absorbers.

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Notes and References


**Fig. 1** SEM images of Sample 1 (a), Sample 2 (b) and Sample 3 (c); TEM images of Sample 1 (e), Sample 2 (f) and Sample 3 (g); The magnified SEM image and TEM image of the regions of red lines (d and h), respectively.

**Fig. 2** The TEM image of 3D Fe$_3$O$_4$-MWCNTs (a); The SAED pattern of 3D Fe$_3$O$_4$-MWCNTs (b); HRTEM images (c and d) of the regions marked with white circles at (a), respectively.
Fig. 3 Reflection loss of three different samples (a); Reflection loss of 3D Fe$_3$O$_4$-MWCNTs with different loading (b); Reflection loss for 20 wt.% loading with different thickness (c).

Fig. 4 3D RL plots of composites versus frequency in the range of 2-18 GHz and thickness in the range of 2-8 mm loaded with (a) 10 wt.%,(b) 15 wt.%, (c) 20 wt.% and (d) 25 wt.% 3D Fe$_3$O$_4$-MWCNTs.
Fig. 5 Complex permittivity (a) and complex permeability (b) of 3D Fe₃O₄-MWCNTs versus frequency.