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Activated carbon fiber/Fe₃O₄ composite with enhanced electromagnetic wave absorption properties

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To obtain a low-density material that is capable of absorbing electromagnetic waves over a wide bandwidth, an activated carbon fiber/Fe₃O₄ composite material (ACF/Fe₃O₄) was prepared using an *in situ* reduction method. Scanning electron microscopy images show that Fe₃O₄ nanoparticles, approximately 10–40 nm in size, were spread uniformly over the surface of the ACF. The resulting composite exhibited superparamagnetic behavior at room temperature. The ability of the ACF and ACF/Fe₃O₄ composite to absorb electromagnetic waves over a frequency range of 8.2–18 GHz was measured using the arch method. The results showed that the maximum reflectivity of an ACF felt was –12.9 dB at 18 GHz, and the effective microwave-absorbing bandwidth ($R < -10$ dB) was 1.9 GHz (16.10–18 GHz). The absorption performance of the ACF was greatly enhanced by being loaded with Fe₃O₄ nanoparticles; the maximum reflectivity of the 2 mm layer of the ACF/Fe₃O₄ composite was –30.07 dB at 16.45 GHz, and the effective bandwidth ($R < -10$ dB) increased to 8.62 GHz (9.38–18 GHz). Coating with nano-Fe₃O₄ magnetic particles can effectively improve the absorption of electromagnetic waves by the ACF, and this technique therefore has great potential for application to the field of electromagnetic shielding.

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Introduction

With the rapid development of electronic technology, electromagnetic interference has become the fourth major type of pollution, after water pollution, atmospheric pollution, and noise pollution, and constitutes a serious threat to human health.^{1–3} Meanwhile, the leakage of electromagnetic waves also affects the normal operation of electronic equipment, resulting in serious losses.⁴ The development of a microwave-absorbing material that is thin while having a low density, as well as having a broad, strong absorption band, would be of great significance to the improvement of the quality of human life and for the industrial production of electromagnetic protection equipment and materials.

In general, magnetic particles such as Fe,⁵ Co,⁶ Ni,⁷ Fe₃O₄,⁸ and carbonyl iron⁹ particles can be used to absorb electromagnetic waves due to their highly complex permeability; however, their high densities and narrow absorption bands limit their applicability.^{10,11} Electromagnetic wave loss is such that the overall loss is determined by both the magnetic and electrical losses. Combining a magnetic material with a dielectric can not only reduce the weight but also achieve better microwave absorption through impedance matching. Carbon

fiber is a type of dielectric-loss material with a carbon content of more than 95%. It offers the advantages of low density and a low coefficient of thermal expansion, as well as good absorbency of electromagnetic waves at high frequencies, relative to magnetic metal materials.^{12,13} However, not every type of carbon fiber can be used as a microwave-absorbing material; this depends on the conductivity of the carbon fiber. An excessively high electrical conductivity causes the carbon fibers to reflect electromagnetic waves, which strongly affects their ability to absorb microwaves. Therefore, only carbon fibers that have been specially treated can be used to absorb microwaves. Wu *et al.*¹⁴ suggested that the use of activated carbon fiber (ACF) is an effective approach to increasing electromagnetic wave absorption because of the multiple reflections and longer propagation distance inside the composite.

In the present study, we prepared a lightweight composite material, capable of absorbing electromagnetic waves over a wide bandwidth, by coating ACF with Fe₃O₄ magnetic particles. The Fe₃O₄ magnetic particles were applied using an *in situ* reduction method, and the reflectivities of the ACF and ACF/Fe₃O₄ felts over a frequency range of 8.2–18 GHz were studied using the arch method.

Experimental

Materials

Viscose fiber felt (Jiangsu Sutong Carbon Fiber Co., Ltd.), phosphoric acid (Nantong Qixiang Biotechnology Co., Ltd.), anhydrous

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ferric chloride (FeCl_3 ; Shanghai Runjie Chemical Reagent Co., Ltd.), and glucose monohydrate ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$; Shanghai Runjie Chemical Reagent Co., Ltd.), all of reagent grade, were purchased and used without any further purification.

Preparation of ACF felt

The viscose fiber felt samples were cleaned by ultrasonication in water for 30 min to remove the textile oiling agent. Phosphoric acid was employed as an activator to prepare the viscose-based ACF. The dried viscose fiber felts were soaked in phosphoric acid solution (2.0 mol L^{-1}) for 2 h and then dried at 60°C . The dried sample was then placed in a vacuum muffle furnace and carbonized under a nitrogen atmosphere. The carbonization temperature was 650°C ; the heating rate was $10^\circ\text{C min}^{-1}$, and the holding time was 1 h. This produced the ACF felt.

Preparation of ACF/ Fe_3O_4 felt

The ACF felts were immersed in saturated FeCl_3 solution (1000 mL) at 60°C for 2 h, then 15 g of glucose monohydrate was added, followed by ultrasonication for 1 h. The sample was dried at 60°C , after which it was subjected to a further high-temperature treatment in a vacuum muffle furnace; the treatment temperature was 750°C , the heating rate was $15^\circ\text{C min}^{-1}$, and the holding time was 30 min. This produced ACF/ Fe_3O_4 felts. The preparation process is illustrated in Fig. 1.

Characterization

The surface morphologies of ACF and ACF/ Fe_3O_4 were characterized using field-emission scanning electron microscopy (FESEM; S-4800, Hitachi High-Technologies) with an acceleration voltage of 3 kV.

An X-ray diffraction (XRD) analyzer (D/max-2500 PC, Rigaku) was used to analyze the phase structure of the ACF and ACF/ Fe_3O_4 . The analysis used $\text{Cu K}\alpha$ radiation, a voltage and current of 40 kV and 40 mA respectively, a step length of 0.02° , and a scanning range of $10\text{--}90^\circ$.

The surface chemical compositions of the ACF and ACF/ Fe_3O_4 were analyzed using X-ray photoelectron spectrometry (XPS; ESCALAB-250Xi, Thermo Fisher Scientific). The X-ray source was $\text{Al K}\alpha$, the vacuum level of the test system was $10^{-8}\text{--}10^{-9}$ Pa, and the angle between the electron beam and sample was 45° .

The magnetic properties of ACF/ Fe_3O_4 are presented as a hysteresis loop, measured using a superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM; MPMS3, Quantum Design) at room temperature.

The electromagnetic wave absorption performance was investigated by the arch method. The testing apparatus is schematically illustrated in Fig. 2. The vector network analyzer connected with the receiving and transmitting antennas, one having functions of stimulating and transmitting frequency electromagnetic waves through and the other receiving the reflective signal. According to the feedback signal strength, the size of the samples was $180 \times 180 \text{ mm}$ with 2 mm thickness.

Results and discussion

Phase composition and morphology

The XRD pattern for the ACF is shown in Fig. 3(a). ACF has a typical amorphous structure,¹⁵ with two strong amorphous diffraction peaks at $2\theta = 23^\circ$ and $2\theta = 44^\circ$, corresponding to the (002) and (101) crystal planes, respectively. Fig. 3(b) shows the XRD pattern for ACF/ Fe_3O_4 . New crystals appear at $2\theta = 30.42^\circ$, 35.74° , 40.28° , 43.46° , 53.94° , 57.24° , and 62.90° , which

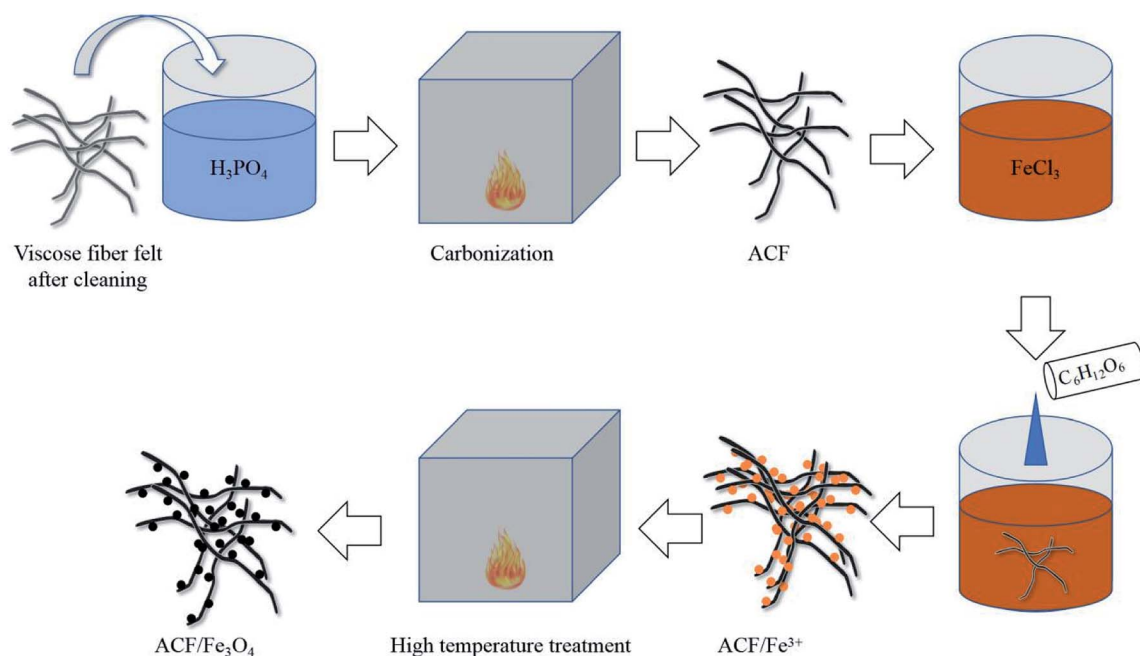


Fig. 1 Preparation of ACF/ Fe_3O_4 .



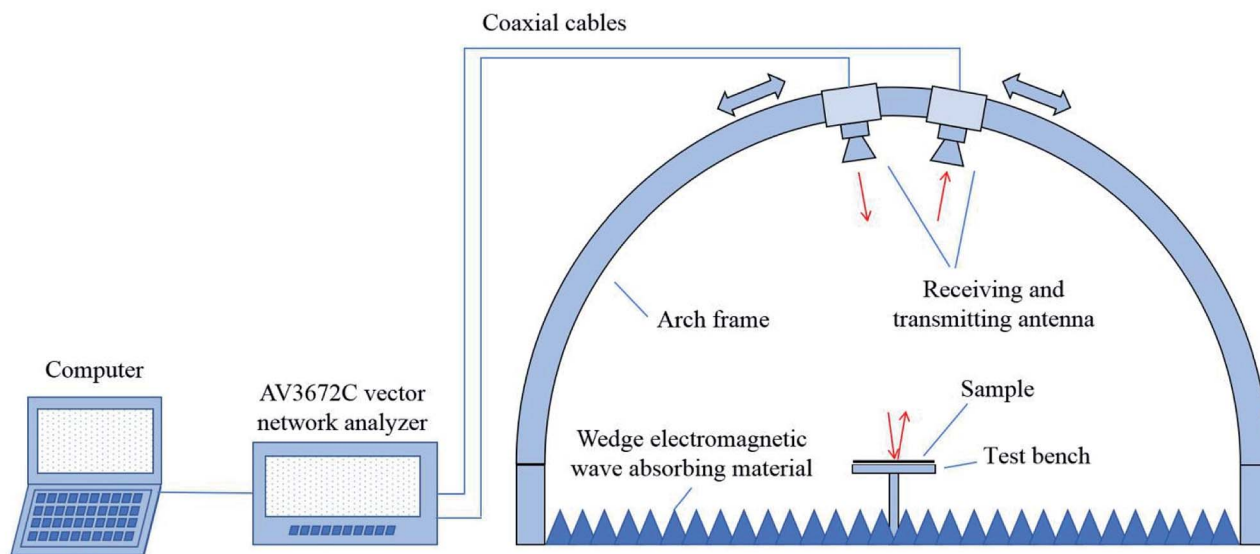


Fig. 2 Arch-method electromagnetic wave absorption test apparatus.

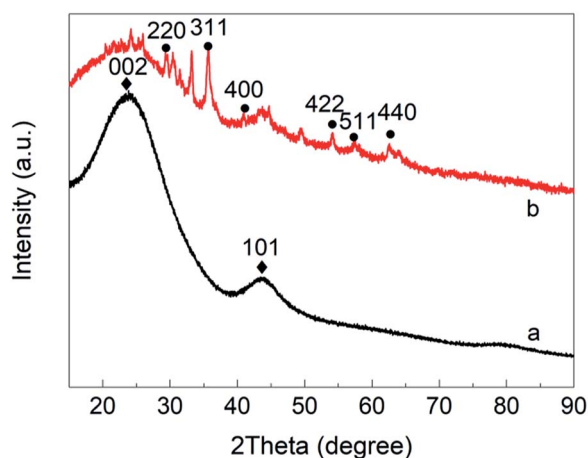


Fig. 3 XRD pattern of (a) ACF and (b) ACF/Fe₃O₄.

correspond, respectively, to the (220), (311), (400), (422), (511), and (400) crystal planes of the face-centered cubic Fe₃O₄ crystals (JCPDS no. 19-0269).¹⁶ It is noted that glucose plays an important role in Fe₃O₄ formation because it can decompose to reductive CO gas, which can fully reduce Fe³⁺ to Fe²⁺. This explains why no Fe₂O₃ signal are found in the XRD pattern. The particle size of Fe₃O₄ at the (311) crystal surface, calculated using the Scherrer equation, is approximately 16.18 nm, indicating that the Fe₃O₄ particles prepared using this method will be nano-sized.

Note that there are some miscellaneous peaks, which may indicate the presence of FeOOH, FeO, Fe₂C, or Fe(OH)₂. FeOOH and Fe(OH)₂ are likely to be the products of trace amounts of Fe₃O₄ undergoing acid–base reactions; FeO and Fe₂C may be derived from the carbonization reactions, caused by the reaction of Fe₃O₄ with carbon (C) in the raw material or with the cracked gas containing carbon and oxygen.¹⁷

The microstructures of the ACF and ACF/Fe₃O₄ were characterized by FESEM. Fig. 4(a) shows a SEM image of the ACF.

The surface of the ACF is relatively smooth, and there are no particles on the surface that would indicate residual impurities. Fig. 4(b) and (c) shows SEM images of ACF/Fe₃O₄ at different magnifications. Most of the Fe₃O₄ particles are distributed uniformly over the surface of the ACF. The Fe₃O₄ particles are irregular in shape while their sizes are within a range of 15–60 nm, which corresponds to the particle size as calculated from the XRD pattern *via* the Scherrer equation. Fig. 4(d) showed that the as-prepared ACF/Fe₃O₄ felt was easy to bend, indicative of good flexibility after the treatment.

Chemical composition

The elemental compositions and chemical states of the ACF and ACF/Fe₃O₄ were characterized by XPS. Fig. 5(a) shows the XPS survey spectra for the ACF and ACF/Fe₃O₄. There are two distinct peaks in these spectra, corresponding to C 1s and O 1s, respectively. An additional distinct peak appears in the XPS spectrum for ACF/Fe₃O₄, which corresponds to Fe 2p. The high-resolution Fe 2p spectrum is shown in Fig. 5(b); the two peaks at binding energies of 710.9 eV and 724.5 eV correspond to the Fe 2p_{3/2} and Fe 2p_{1/2} spin–orbit peaks, respectively, indicating the formation of Fe₃O₄. Fig. 5(c), (d) shows the O 1s XPS spectra for the ACF and ACF/Fe₃O₄ with peak-fitting curves; three peaks are visible for both the ACF and ACF/Fe₃O₄, at 531.2 eV, 532.3 eV, and 533.2 eV, corresponding to O–C=O, C=O, and C–O, respectively. Meanwhile, the distinct peak at 530.5 eV in the O 1s spectra of ACF/Fe₃O₄ is assigned to the Fe–O bonds in Fe₃O₄, which further demonstrates the existence of Fe₃O₄.

Magnetic and electromagnetic wave absorption properties

Fig. 6 shows the magnetic hysteresis loop for ACF/Fe₃O₄ over a range of –20 000 to 20 000 Oe at room temperature; its shape is a typical S-curve, corresponding to the superparamagnetic behavior. The magnetic properties including the saturation magnetization M_s , magnetic coercivity H_c , and remanent



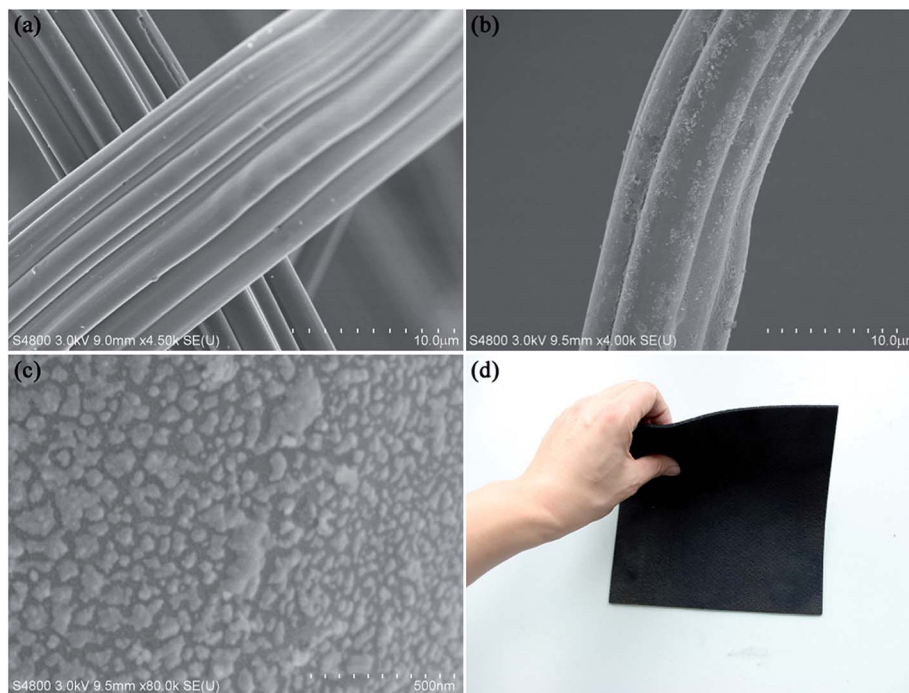


Fig. 4 SEM images of (a) ACF and (b), (c) ACF/Fe₃O₄, and photographic image of (d) ACF/Fe₃O₄.

magnetization M_r are 22 emu g⁻¹, 114 Oe and 3.4 emu g⁻¹, respectively. The M_s of ACF/Fe₃O₄ is lower than that of bulk Fe₃O₄ (ca. 84.5 emu g⁻¹), which can be explained by the small size of the Fe₃O₄ nanoparticles and the addition of ACF, which is in good agreement with the findings of a previous study.¹⁸

The microwave-absorbing properties of the ACF/Fe₃O₄ felt and ACF felt over a frequency range of 8.2–18 GHz are presented

as the reflectivity R , as measured using the arch method. The arch method is a simple and practical method with which the reflectivity of microwave-absorbing materials can be accurately measured without destroying their structure.^{10,13} Fig. 7(a) shows the microwave absorption/reflectivity curve for ACF felt. The maximum reflectivity is -12.9 dB at 18 GHz, and the effective absorption bandwidth ($R < -10$ dB) is 1.9 GHz (16.10–18 GHz).

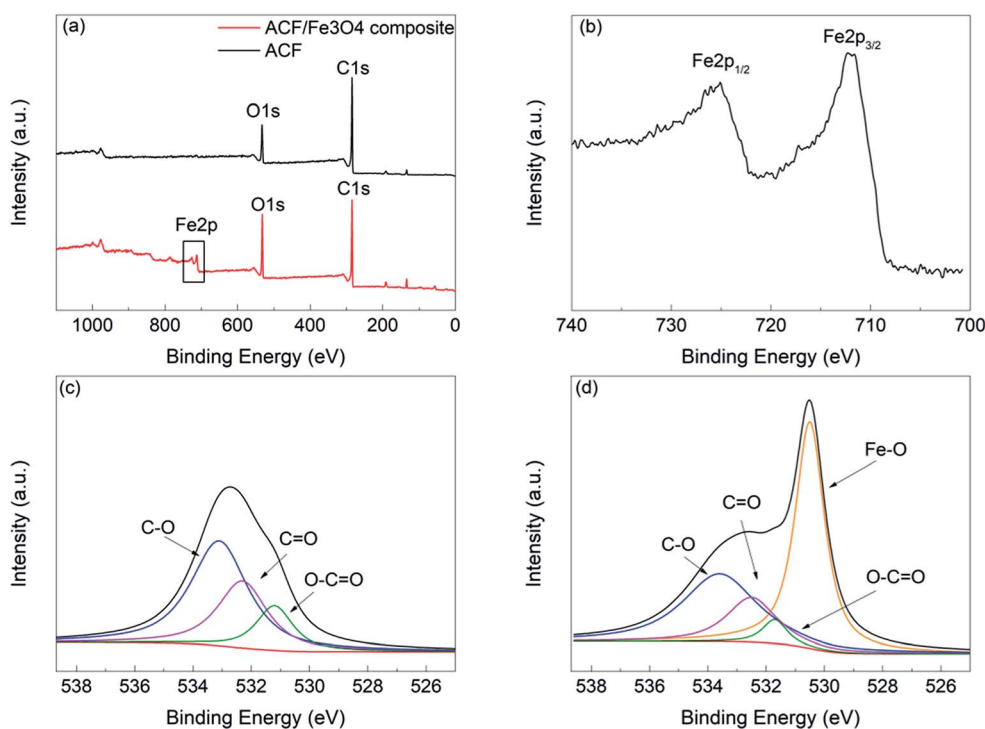


Fig. 5 XPS spectra: (a) survey spectra of ACF and ACF/Fe₃O₄, (b) Fe 2p spectra of ACF/Fe₃O₄, and fitted O 1s spectra of (c) ACF and (d) ACF/Fe₃O₄.



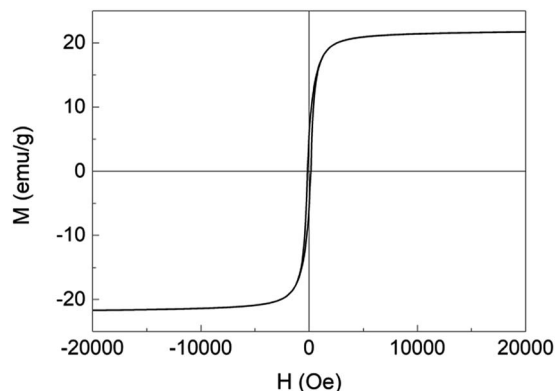


Fig. 6 Magnetic hysteresis loop of ACF/Fe₃O₄ at room temperature.

Since ACF is a nonmetallic conductive fiber material with relative high resistance, it can be regarded as a harmonic oscillator in the electromagnetic field, which resonates with incident electromagnetic waves to form a dissipative current. Such generated photocurrent is finally consumed in the material system. ACFs can also be regarded as a dipole under the action of an electromagnetic field. The surface polarization of ACFs further dissipates and decays the photocurrent, converting the electromagnetic energy to other forms of energy under the action of the surrounding matrix.¹⁹ Fig. 7(b) shows the absorption–reflectivity curve of ACF/Fe₃O₄. The absorption properties of ACF felt are greatly enhanced after loading with Fe₃O₄ nanoparticles, with the maximum reflectivity reaching -30.7 dB at 16.4 GHz, and the effective absorption bandwidth ($R < -10$ dB) is 8.2 GHz (9.8–18 GHz). Such enhanced properties are mainly due to the unique electromagnetic properties of nano Fe₃O₄. The attached Fe₃O₄ have functions of hysteresis loss, natural resonance and exchange resonance toward electromagnetic wave, resulting in significant attenuation of electromagnetic wave. Besides, magnetic nanoparticles increases the effective contact interface to electromagnetic wave, greatly enhancing the interfacial polarization effect. Thus, the enhanced absorbing property of the composite is owing to the synergistic effect of the electric loss ACF and the magnetic loss Fe₃O₄.^{20,21}

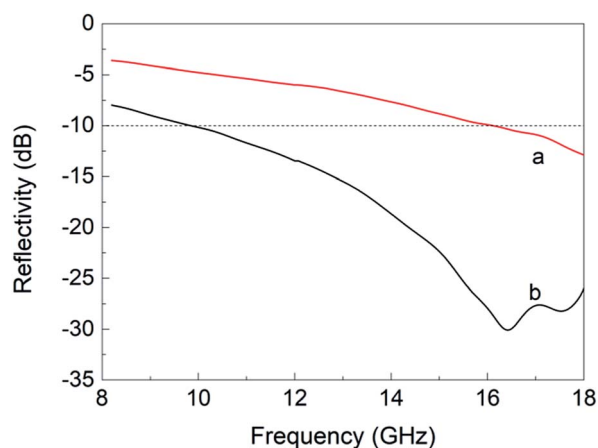


Fig. 7 Reflectivity curves of (a) ACF and (b) ACF/Fe₃O₄.

Conclusion

In summary, an ACF/Fe₃O₄ composite was successfully prepared using an *in situ* reduction method. The Fe₃O₄ was in the form of nanoparticles that are uniformly dispersed over the surface of the ACF and which exhibit superparamagnetism at room temperature. The maximum reflectivity of the ACF reached -12.9 dB at 18 GHz, while the effective absorption bandwidth ($R < -10$ dB) was 1.9 GHz. The ACF/Fe₃O₄ felt exhibits greatly improved microwave absorption relative to the ACF felt, with a maximum reflectivity of -30.7 dB at 16.4 GHz and an effective absorption bandwidth ($R < -10$ dB) of 8.2 GHz, for a thickness of 2 mm. Together, these properties indicate that ACF/Fe₃O₄ offers the promise of wide-ranging applicability in the fields of absorbing materials and electromagnetic shielding.

Conflicts of interest

There are no conflicts to declare.

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