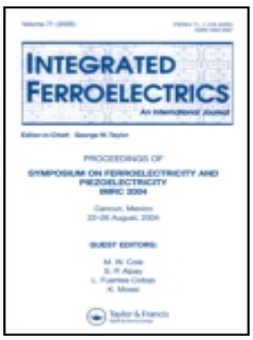

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Bio-template synthesis of hollow Fe_3O_4 fibers and their enhanced microwave absorption performance in Ku-band

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ABSTRACT

A novel kind of microwave absorption composite in Ku-band with low cost, low density and strong absorption was prepared through Bio-template carbonization and solvothermal method. The phase structures and morphologies of the composite had been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The microwave absorption properties of carbonized kapok fibers and Fe_3O_4/kapok fibers were measured by vector network analysis (VNA). When the sample thickness is 1.5 mm, the Fe_3O_4/kapok fibers have an optimal absorption peak value of about −24.1 dB at 17.4 GHz and its effective absorption bandwidth lower than −10 dB reaches 2.4 GHz (from 15.6 to 18.0 GHz). The reflection loss results indicate that the Fe_3O_4/kapok fibers possess higher microwave absorption in the Ku-band. A possible mechanism of the improved microwave absorption performance of the composite was discussed.

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KEYWORDS
Hollow Fe_3O_4 fibers; kapok fibers; bio-template synthesis; microwave absorption

1. Introduction

Recently, there have been an increased number of applications of electromagnetic waves in the Ku-band (12.4–18GHz) for radar, military aircraft and satellite communication and, consequently, much attention has been devoted to microwave absorbing materials in the whole Ku-band[1–5]. However, studies on the absorbent only for Ku-band frequency are very limited[6–9].

As a typical a crucial material for many branches of modern technology, carbonaceous materials, such as graphite (carbon black), graphene, carbon nanotube, carbon nanowire and so on, are relevant to future applications that require environmentally benign and mechanically flexible materials[10, 11]. Currently, most of the carbon based materials are synthesized from fossil fuel precursors such as petroleum, coal, and natural gas, which are non-renewable resources[12]. Biomass is a qualified carbon raw material for the synthesis of valuable carbon materials because it

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is inexpensive, abundant, and renewable. Recently, there have been many reports on the synthesis and characterization of carbonaceous materials[13–15] and their composites[16, 17] from biomass. However, up to now, such studies such as the forming process of carbon microtubes composites and the microwave absorbing performance in Ku-band frequency from biomass are rarely reported.

In this paper, a novel kind of microwave absorption composite in Ku-band with low cost, low density and strong absorption was prepared through Bio-template carbonization and solvothermal method. We investigated the microwave absorbing properties of the Fe_3O_4/kapok fibers. A possible mechanism of the improved microwave absorption performance of the composite was discussed.

2. Experimental

2.1. Preparation of hollow carbon microtubes from kapok fibers

The kapok fibers were collected in Huaibei, China. 20–30 g kapok fibers were first rinsed with deionized water several times and then dried in vacuum at 80°C overnight. Then, the dry kapok fibers were placed at a ceramic boat which was inserted at the entrance of the horizontal quartz tube furnace (40 cm in inner diameter and 100 cm in length, equipped with temperature and gas-flow controller). The carbonization was carried out at 550°C for 4 h in a flowing atmosphere of Ar (100 sccm). The furnace temperature was allowed to cool down to room temperature naturally before the product was taken out. A blackish wool-like product was obtained.

2.2. Synthesis of hollow Fe_3O_4 fibers

$Fe(CO)_5$ was purchased from Jiangsu Tianyi Co. Ltd. All the other reagents used in the experiments were of analytical grade (purchased from Shanghai Chemical Reagent Industrial Company) and used without further purification. In a typical synthesis, 0.1 g NaOH was dissolved into 30 mL ethanolamine under stirring. Then the hollow carbon microtubes (50 mg), 2 ml $Fe(CO)_5$ and 10 ml hydrazine hydrate (85%) were added and sonicated for 10 min. The as-formed brown solution was transformed to a 50 mL Teflon-lined stainless steel autoclave and kept at 180°C for 24 h without stirring. The resulted black powder was washed with distilled water and ethanol three times, respectively, and collected with the aid of a magnet. The washed precipitates were dried in a vacuum oven at 80°C for 8 h.

2.3. Characterization techniques

The phase identification was performed by powder X-ray diffraction (XRD) on a Bruker Advance D8 X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 40 mA, $\lambda = 1.5418$Å) in the range from $2\theta = 10°$ to 80°. The morphologies of

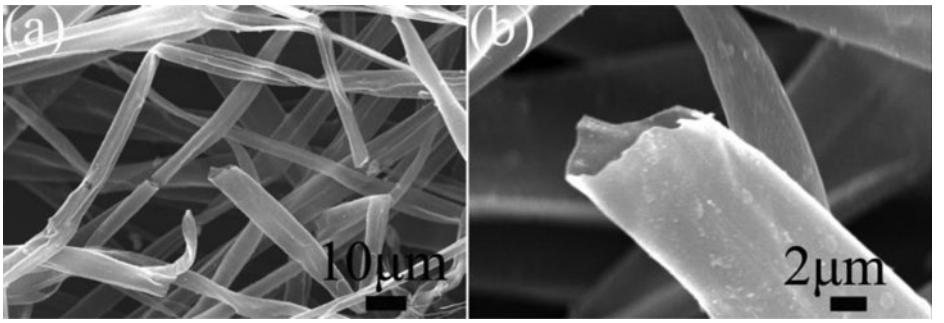

Figure 1. SEM image of carbonized kapok fibers (a) and the high-magnification SEM image (b).

the synthesized products were observed through a JSM-6610LV scanning electron microscopy (SEM). The main constituent elements of typical products were also determined by means of energy-dispersive X-ray spectrometry (EDS, X-Max, Oxford Instruments) attached to the SEM. The complex dielectric permittivity and magnetic permeability were obtained by a vector network analyzer (VNA, AV3629D) using transmission/reflection mode in the frequency range of 2.0–18.0 GHz. The as-prepared composites were mixed uniformly with molten paraffin wax (20 vol. %) and compressed into a cylindrical toroid with an inner diameter of 3.04 mm, an outer diameter of 7.00 mm and a thickness of 2.00 mm. A full one-port calibration was carried out before measurement in order to reduce or remove errors due to the source match, load match, directivity, isolation and frequency response during the microwave measurement. The reflection loss of samples is simulated by the transmission line theory.

3. Results and discussion

3.1. Structural characterization

The morphologies and microstructures of carbonized kapok fibers were observed by SEM. Fig. 1a shows a typical SEM image of the carbonized kapok fibers. It can be found that a large amount of one-dimensional wires with diameter of 5–10 μm and lengths of several hundred μm can be easily observed for the carbonized samples. The high-magnification SEM image (Fig. 1b) indicates that the carbonized kapok fiber possess hollow structures with smooth surface.

Figure 2a shows the XRD patterns of the carbonized kapok fibers. There is a broad diffraction peak at about 25.2°, which approach a d spacing close to 0.34 nm, i.e., d_{002} in graphite. Therefore, the graphite carbon fibers are formed, which is similar to the results reported by Ma YW[13]. In fig. 2b, all the peaks can be indexed as face centered cubic Fe_3O_4 with the lattice constant a = 8.394Å, which is in good agreement with JCPDS card No.85–1436. No evidence of impurities such as α-Fe_2O_3 or γ-Fe_2O_3 is found in the XRD pattern. Therefore, it could be concluded that a kind of magnetite–carbonized kapok fiber composite was formed.

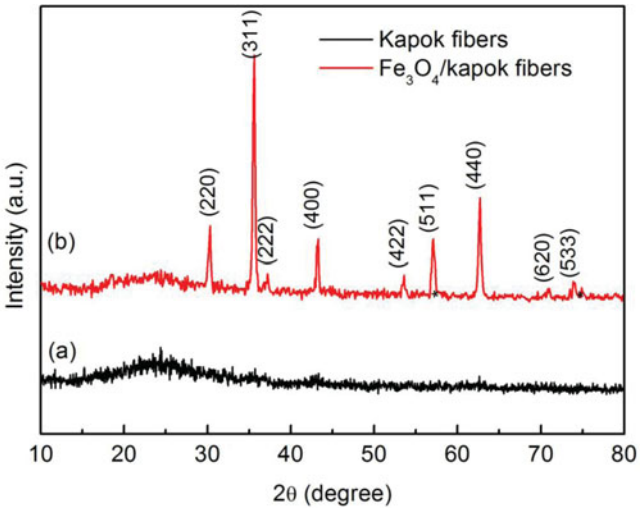

Figure 2. XRD pattern of carbonized kapok fibers (a) and Fe_3O_4/kapok fibers (b).

Figure 3 shows a typical SEM image and EDS of the Fe_3O_4/carbonized kapok fiber composite. It can be found that the surfaces of carbonized kapok fiber become very rough and regular spherical-like Fe_3O_4 particles (shown in Fig. 3b) attach on the inner and outer sides of the carbonized kapok fiber. The EDS pattern of the Fe_3O_4/carbonized kapok fiber composite is presented in Fig. 3c. It is quite obvious that the composite consist of Fe, O and C elements without any detectable contaminant elements. From the inserted photograph in Fig. 3c, we can see that as-synthesized Fe_3O_4/carbonized kapok fiber composite can be easily dispersed in

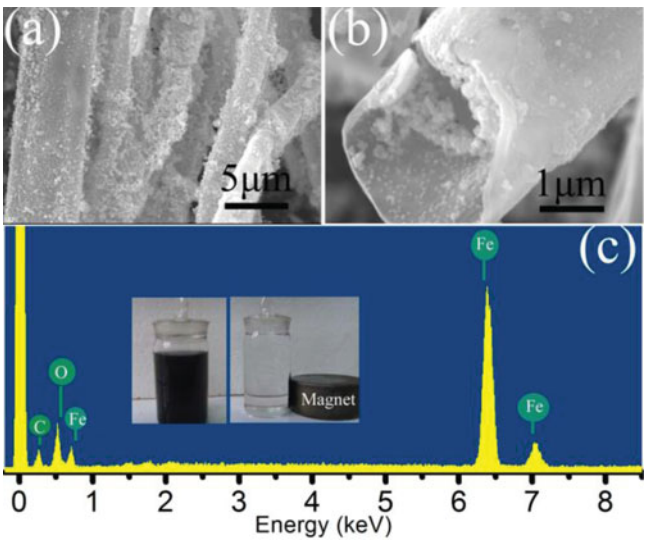

Figure 3. SEM image (a), the high-magnification SEM image (b) and EDS (c) of Fe_3O_4/kapok fibers. (Insert: Photograph of Fe_3O_4/kapok fibers dispersed in ethanol (left) and its response to a magnet (right)).

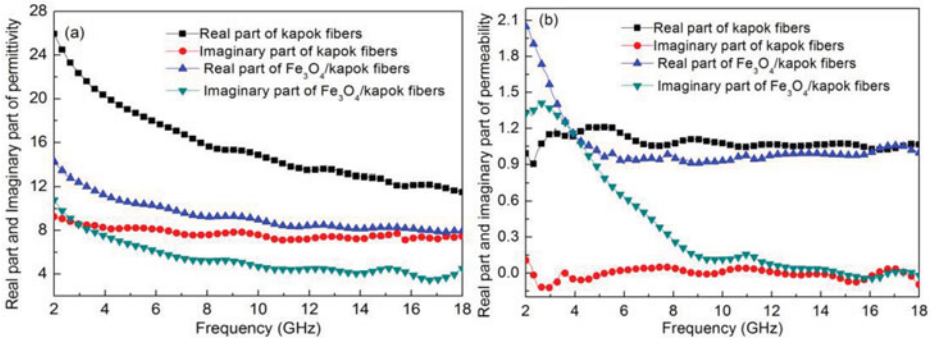

Figure 4. Real part and imaginary part of complex permittivity (a) and Real part and imaginary part of complex permeability (b) of carbonized kapok fibers and Fe_3O_4/kapok fibers.

ethanol and quickly separated from their dispersion by holding the sample close to a commercial magnet.

3.2. Microwave absorption properties

Figure 4a shows real part (ε') and imaginary part (ε'') of the relative complex permittivity of carbonized kapok fibers and Fe_3O_4/kapok fibers in the frequency range of 2.0–18.0 GHz. Both ε' and ε'' values of carbonized kapok fibers and Fe_3O_4/kapok fibers decrease in the frequency range of 2.0–18.0 GHz. Compared the complex permittivity of carbonized kapok fibers and Fe_3O_4/kapok fibers, the ε' value of carbonized kapok fibers is larger than that of Fe_3O_4/kapok fibers. The ε' value of carbonized kapok fibers at 2.0 GHz is about 26.0. However, at the same frequency, the ε' value of Fe_3O_4/kapok fibers is only about 14.0. The imaginary part of permittivity shows a sophisticated change. The ε'' value of carbonized kapok fibers are higher than those of Fe_3O_4/kapok fibers in 2.9–18 GHz frequency range and present an intersecting point at 2.9 GHz. The real part (μ') and imaginary part (μ'') of complex permeability of carbonized kapok fibers and Fe_3O_4/kapok fibers are shown in Fig. 4b. The values of μ' and μ'' of carbonized kapok fibers retains an approximate constant about 1.0 and 0.0, respectively. However, the μ' of Fe_3O_4/kapok fibers exhibits an abrupt decrease from 2.1 to 0.9 in the 2.0–5.0 GHz and retains an approximate constant over 5.0–18.0 GHz, while the μ'' presents a normal natural resonance peak at 2.4 GHz and then decreases with frequency.

The RL curves at given frequency and the matching absorber thickness are calculated as follow[18, 19]:

$$RL\,(dB) = 20\ \log\left|\frac{Z_{in}-Z_0}{Z_{in}+Z_0}\right| \tag{1}$$

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

Where μ_r and ε_r are the relative permeability and permittivity respectively, f is the frequency of incident electromagnetic wave, d is the absorber thickness, c is the velocity of light, Z_0 is the impedance of free space (376.7 Ω), and Z_{in} is the input

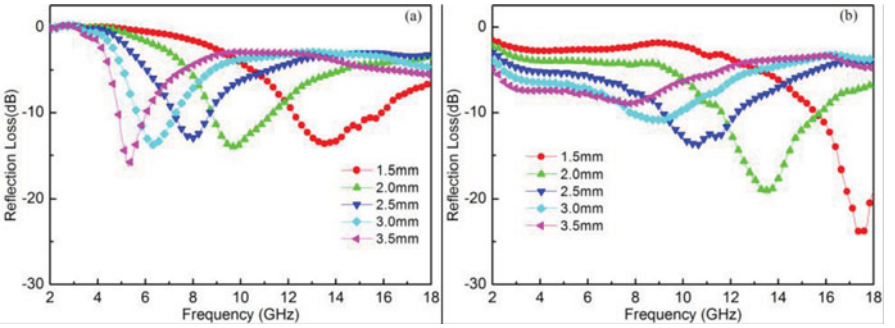

Figure 5. Reflection loss with different thicknesses of carbonized kapok fibers (a) and Fe_3O_4/kapok fibers (b).

impedance of absorber. From relations (1) and (2), it can be concluded that the microwave absorption of the composites is mainly determined by the combination of six parameters (ε', ε'', μ', μ'', f and d), and the minimum reflection of incident plane wave happens when Z_{in} is close to the constant Z_0.

Figure 5 shows the simulation of reflection loss (RL) versus frequency at different thickness of the carbonized kapok fibers and Fe_3O_4/kapok fibers. It is clearly found that the absorption peaks of two samples moves toward lower frequency band with the increasing thickness from 1.5 to 3.5 mm. For the carbonized kapok fibers, despite its thickness, it all has absorption peaks that lower than −10 dB. When the thickness is 3.5 mm, it has an optimal absorption peak value of about −16.2 dB at 5.2 GHz and its effective absorption bandwidth lower than −10 dB reaches 1.2 GHz (from 4.8 to 6.0 GHz). For the Fe_3O_4/kapok fibers, when the thickness is 1.5 mm, it has an optimal absorption peak value of about −24.1 dB at 17.4 GHz and its effective absorption bandwidth lower than −10 dB reaches 2.4 GHz (from 15.6 to 18.0 GHz). The reflection loss results indicated that the Fe_3O_4/kapok fibers possess higher microwave absorption in the Ku-band and the carbonized kapok fibers possess higher microwave absorption in the C-band. Obviously, the introduction of Fe_3O_4 in the carbonized kapok fibers is critical to the absorption in the Ku-band. Generally speaking, the improvement of microwave absorption obviously originates from two key factors: the impedance matching and electromagnetic wave attenuation[4, 20]. It can be noticed from relations (1) and (2) that the combinations of six parameters mainly determined the microwave absorption of the composites, and the minimizing reflection of incident plane wave can happen when Z_{in} is close to the constant Z_0. For our as-prepared Fe_3O_4/kapok fibers, the two factors are affected by electromagnetic parameters. On one hand, with the introduction of the magnetic Fe_3O_4 particles, the conductivity decreases and the impedance matching performance is improved. On the other hand, a natural resonance at about 2.4 GHz results a magnetic loss mechanism.

4. Conclusion

In summary, the hollow Fe_3O_4/kapok fibers composite has been prepared conveniently through biomass kapok fibers carbonization and subsequently

solvothermal method. The excellent microwave absorption properties in Ku-band have been obtained due to proper combination of the complex permeability and permittivity resulting from the magnetic Fe_3O_4 particles and dielectric hollow carbon microtubes. For the most excellent microwave absorption properties in Ku-band, it has an optimal absorption peak value of about −24.1 dB at 17.4 GHz and its effective absorption bandwidth lower than −10 dB reaches 2.4 GHz (from 15.6 to 18.0 GHz) when the thickness is 1.5 mm. The improvement in absorbing property can be ascribed to the better magnetic loss and matched characteristic impedance. It is believed that hollow Fe_3O_4/kapok fibers composite is an ideal microwave absorption material with lighter weight, stronger and wider frequency microwave absorption in Ku-band.

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