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Letter

Oxidized electroplating zinc-covered carbon fibers as microwave absorption materials

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ABSTRACT

Zinc oxide nanosheet/zinc-covered carbon fiber composites (ZNSZCFs) were synthesized by annealing the zinc-covered carbon fibers with electroplating in air. The diameter of the ZNSZCFs was about 25 μm. The strongest RL of ZNSZCFs was −32.98 dB at 3.31 GHz. The strong absorption of ZNSZCFs was less than −4 dB (>65%) over the range of 7.54–18 GHz (1.6 mm in thickness) and 5.96–18 GHz (2.0 mm in thickness), respectively. The ZNSZCFs are believed to be ideal microwave absorbing materials.

1. Introduction

The electromagnetic wave in gigahertz range is being widely used in industrial, commercial and military fields, which results in many electromagnetic interference (EMI) problems. In order to properly solve the EMI problems, the microwave absorbing materials have been extensively investigated. In particular, the nanostructure materials and carbon fiber composites have received steady growing interest as microwave radiation absorbing and shielding materials in the high-frequency range due to their fascinating properties [1–4]. Additionally, considerable theoretical and experimental investigations have been focused on the effective microwave absorption materials [5,6]. Zhang et al. [7] indicate that the complex permittivity $\varepsilon_r = \varepsilon' - j\varepsilon''$, the complex permeability $\mu_r = \mu' - j\mu''$, electromagnetic impedance match, and the microstructure of the absorber determine the microwave absorption properties.

Zinc oxide (ZnO), a wide band-gap (3.37 eV) semiconductor at room temperature and large exciton binding energy (60 meV) [8], is a potentially commercial material. Therefore, the preparation, characterization and application of ZnO nanostructures (ZNs) are extensively investigated [9–16]. Recently, Chen et al. [17] reported that EM wave absorption composites, consisting of foam glass, zinc and zinc oxide, were prepared by sintering mixture of foam glass raw material and zinc powder. The results showed that zinc-containing foam glass absorbed efficiently microwaves. Li et al. [18] and Liu et al. [19] reported that the carbon nanotubes/tetrapod – and whisker – shaped ZnO nanstructure composites had excellent absorbing properties, respectively. Additonally, Cao et al. [20] reported the effects of temperature and frequency on the dielectric properties, electromagnetic interference shielding and microwave-absorption of short carbon fiber/silica composites. Results indicated that the composite had good electromagnetic interference shielding property. However, the coating thickness and densities of these microwave absorbing materials were usually quite high that restricted their applications in low density field such as aerospace. Therefore, it was essential to research excellent microwave absorbing materials with wide frequency range, strong absorption, and low density.

In this work, we try to synthesize zinc oxide/zinc-carbon fiber composites (ZNSZCFs) by annealing Zn/CF composites, which are expected to exhibit excellent microwave absorption properties.

2. Experimental details

The carbon fibers used in this study were PAN-based carbon fiber (3 K) and produced by Lan Zhou Activated Carbon Industries of China. The Zn/CF composites were prepared by electroplating process. Fig. 1 shows the FESEM images of carbon fiber and Zn/CF composites. The carbon fibers were cut to 80–100 mm in length before the surface treatment. The electroplating process was achieved at the room temperature. The zinc bath conditions are listed in Table 1. The electroplating time

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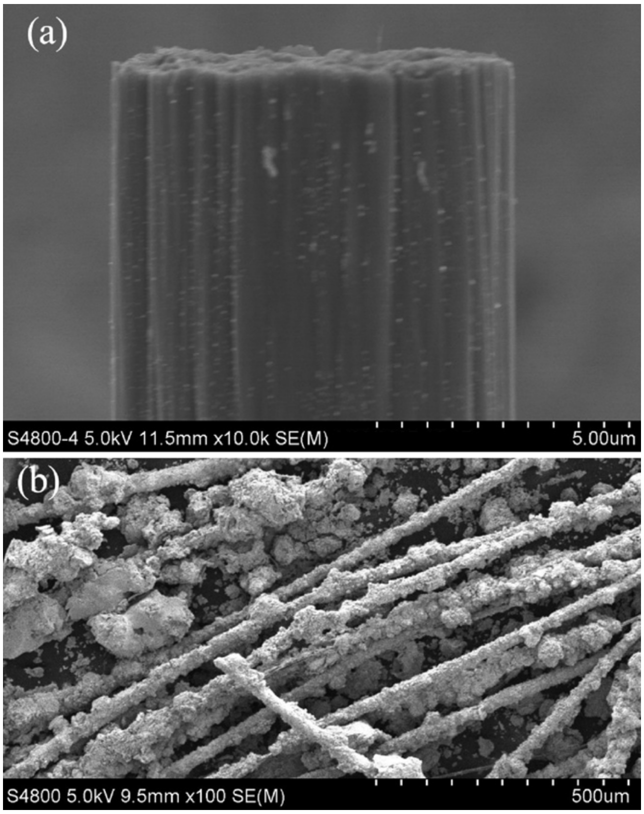

Fig. 1. FESEM images of the carbon fiber (a) and Zn/CF composites (b).

was about 30 min. The current intensity was 20 mA. The Zn/CF composites were washed with distilled water followed by absolute alcohol. The Zn/CF composites were cut to 2–3 mm in length after electroplating carbon fibers. After dried in air, they were annealed at 400 °C for 4 h in air. The heating rate was about 10 °C/min. After cooled down naturally to room temperature, ZNSZCFs were synthesized.

In order to investigate the structure and the morphology, ZNSZCFs were characterized using X-ray diffraction (XRD, X' per pro), and field emission scanning electron microscope (FESEM, S4800).

3. Results and discussion

The XRD pattern is used to analyze the phase of the products. In this work, XRD measurements were carried out using Cu K_α radiation ($\lambda = 1.54056$) from a sealed tube operated at 45 KV and 40 mA. Fig. 2 shows the XRD pattern of ZNSZCFs. It is found that only ZnO (JCPDS: 36-1451) for wurtzite structure and zinc (JCPDS: 04-0831) are observed. Therefore, the ZNSZCFs are obtained.

Fig. 3 shows the different magnification FESEM images of the ZNSZCFs. The result shows that the carbon fibers are coated with ZnO nanosheet after the annealing at 400 °C in air. The nanosheets are aggregated and mingled in each other, which is ascribed to long-range electrostatic interactions among the polar charges of the {0 0 0 1} planes [21]. The diameter of the ZNSZCFs is about 25 μm. It is well known that the ZnO nanosheet is faceted with polar planes ±(0 0 0 1) (the top and bottom surfaces) and nonpolar $\pm(2\,\bar{1}\,\bar{1}\,0)$ (front and end surfaces) and the $\pm(0\,1\,\bar{1}\,0)$ (side surfaces) planes.

Table 1
Bath compositions and operation conditions for electroplating.

Chemical	Concentrations
Zinc chloride	50–70 g/L
Potassium chloride	180–240 g/L
Boracic acid	15–20 ml/L
Saccharin	0.3–0.5 g/L
pH	5–6

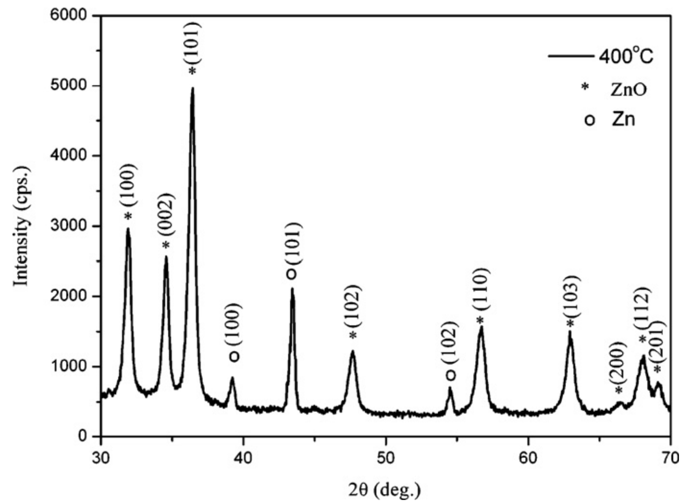

Fig. 2. XRD pattern of ZNSZCFs.

The three types of planes are the most stable facets for wurtzite structured ZnO [21–23]. Additionally, Kong and Wang [23] reported that the morphologies of nanostructure ZnO by thermal evaporation were dominated by the polar-surface. They indicated that the (0 0 0 1) plane of wurtzite structured ZnO could be terminated with Zn [(0 0 0 1)-Zn] or oxygen $[(0\,0\,0\,\bar{1})$-O], leading to positively and negatively changed top and bottom surfaces. In this work, the ZnO nanosheet for wurtzite structure and Zn are obtained (Fig. 2). The

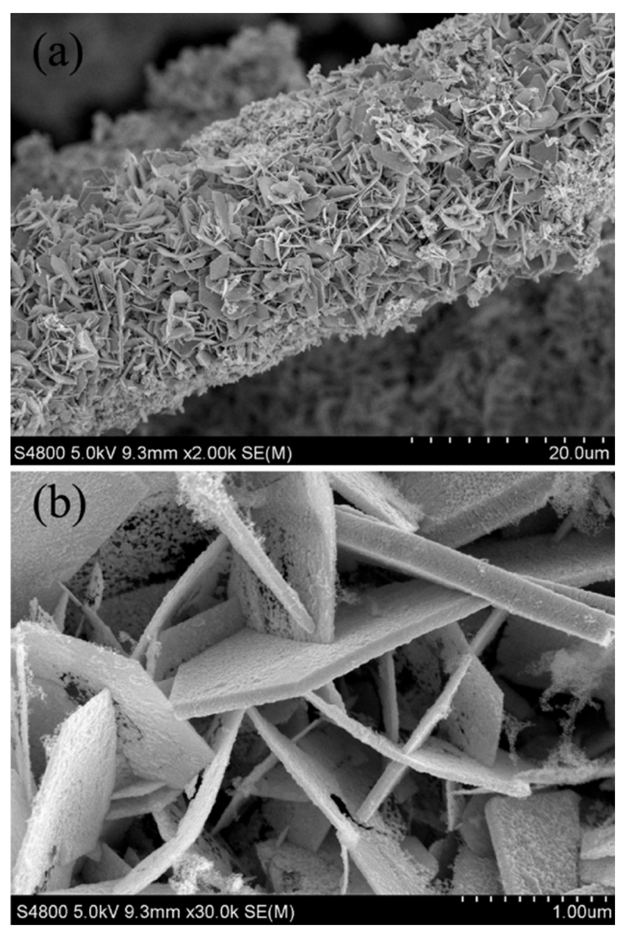

Fig. 3. The different magnification FESEM images of ZNSZCFs (a) low magnification and (b) high magnification.

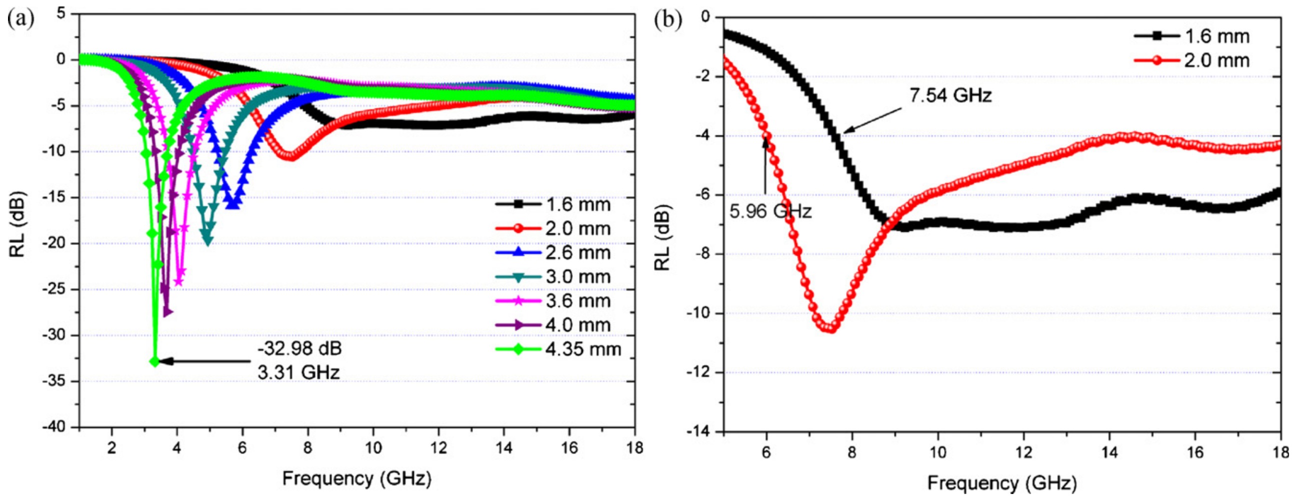

Fig. 4. RL curves of different thickness of ZNSZCFs.

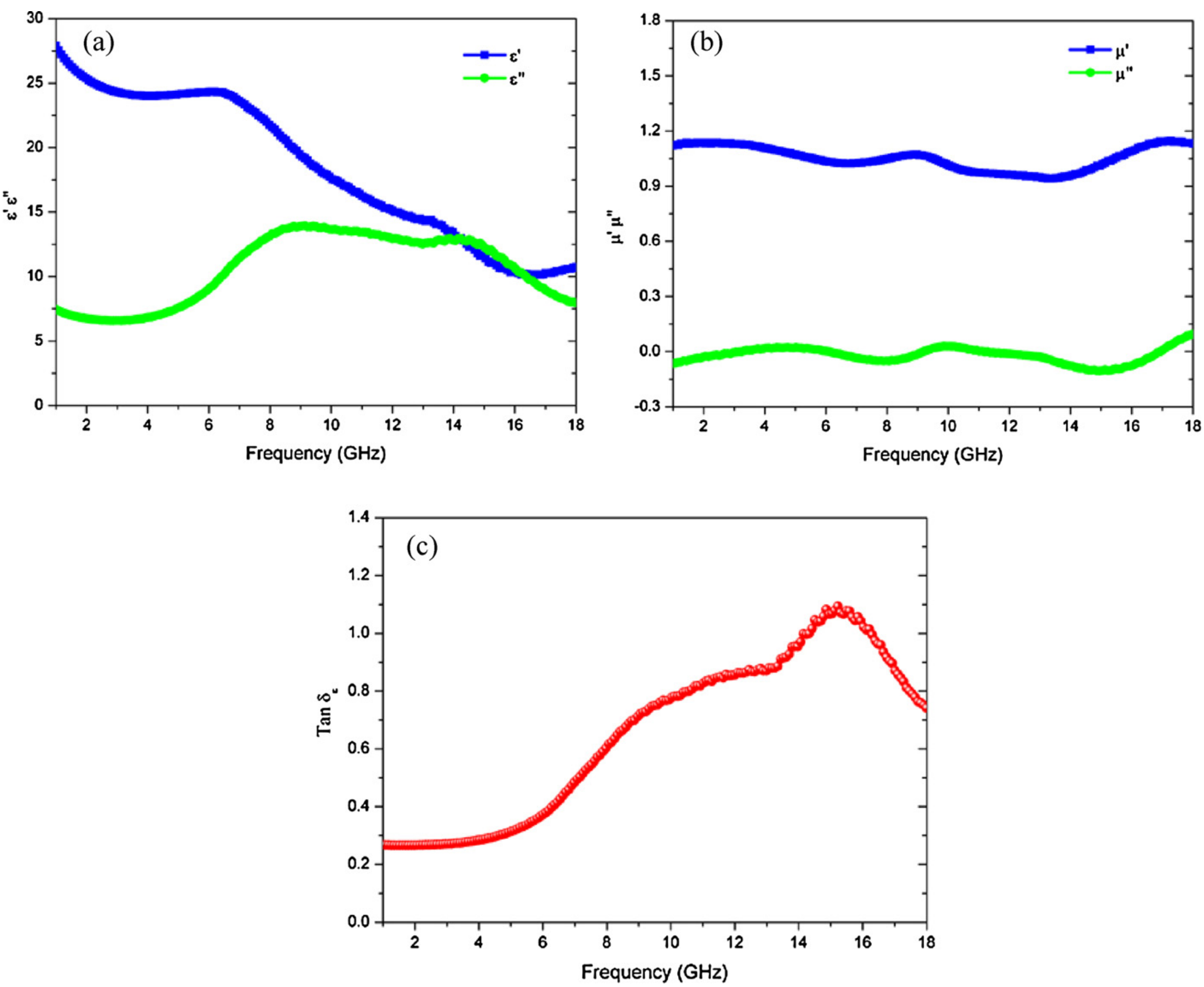

Fig. 5. The complex permittivity, the complex permeability and dielectric dissipation factors of ZNSZCFs: (a) ε' and ε''; (b) μ' and μ''; (c) $\tan\delta_\varepsilon$.

top surfaces of the sheets are not totally smooth, and some particles or hillocks are exhibited (Fig. 3b). Therefore, we indicated that the growth of ZnO along [0 0 0 1] direction was restricted and on the other planes were favored that resulted in the appearing of the nanosheets. Further investigation of its growth mechanism is still needed.

Agilent E8363B PNA vector network analyzer was used to measure microwave absorption coefficient of ZNSZCFs. The ZNSZCFs were homogeneously dispersed into acetone solution of paraffin by ultrasonic method until acetone solution was vaporized completely. Then they were pressed to a ring (external diameter 7 mm, internal diameter 3 mm) at 350 MPa. The weight fraction of ZNSZCFs was 60%. Fig. 4 shows the frequency dependences of the RL of different thickness ZNSZCFs. It can be found that the absorption frequency decreases with the thickness increasing. The strongest RL of ZNSZCFs is −32.98 dB at 3.31 GHz. The strong absorption of ZNSZCFs is less than −4 dB (>65%) over the range of 7.54–18 GHz and 5.96–18 GHz, and the corresponding thickness is only 1.6 mm and 2.0 mm, respectively. The ZNSZCFs are believed to be ideal for making lightweight, strong absorption and wide-frequency microwave absorbing materials.

It was well known that the microwave enhancement absorption of microwave absorbers resulted mainly from dielectric loss and magnetic loss. In order to investigate the intrinsic reasons for microwave absorption properties, the four parameters (ε', ε'', μ' and μ'') of ZNSZCFs were measured directly by the coaxial line method using the Agilent E8363B PNA vector network analyzer at the 1–18 GHz range (Fig. 5a and b). The results show that the ε' and ε'' of ZNSZCFs are 27.80–10.03 and 7.37–10.11, respectively. The μ' and μ'' of ZNSZCFs are 0.93–1.15 and −0.06 to 0.95. Therefore, the microwave enhancement absorption of ZNSZCFs results mainly from dielectric loss in this paper. Additionally, the ε'' shows a wide peak when the frequency ranges are 2.79–18 GHz. The dielectric dissipation factors ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) based on the permittivity of composites are calculated (Fig. 5c). The $\tan\delta_\varepsilon$ of ZNSZCFs increases from 0.27 to 1.09, and presents an width peak in the 1–18 GHz. These results indicate strong absorption and wide range microwave absorption of ZNSZCFs.

4. Conclusions

In this letter, ZNSZCFs were synthesized by annealing electroplating Zn/CF composites at 400 °C for 4 h in air. The FESEM result shows that the diameter of the ZNSZCFs is about 25 μm. Interestingly, the strongest RL of ZNSZCFs is −32.98 dB at 3.31 GHz. The strong absorption of ZNSZCFs is less than −4 dB (>65%) over the range of 7.54–18 GHz (1.6 mm in thickness) and 5.96–18 GHz (2.0 mm in thickness), respectively. The ZNSZCFs are believed to be ideal for making lightweight, strong absorption and wide-frequency microwave absorbing materials.

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