https://doi.org/10.1016/j.matlet.2018.11.171

Unique Electromagnetic Loss Properties of Co-doped ZnONanofiber

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Abstract: In this paper, Co-doped ZnO nanoparticle and nanofiber were prepared by electrospinning method. The results showed that Co-doped ZnO nanofiber performed bead-like fibrous shape and exhibited ferromagnetic properties. The dielectric loss and magnetic loss properties of Co-doped ZnO nanofiber were much better than that of Co-doped ZnO nanoparticle due to the improvement of dipole polarization, interfacial polarization and shape anisotropic. The absorptivity of Co-doped ZnO nanofiber can reach to 70% in the frequency range of 5.3-18 GHz when the coating thickness is 1.5-4.0 mm. It is demonstrated that the bead-like fibrousshape is beneficial to optimize electromagnetic loss and microwave absorption properties of Co-doped ZnO.

Keywords: electronic materials; magnetic materials; zinc oxide; electromagnetic loss

1. Introduction

According to the microwave absorption mechanism, microwave absorption material (MAM) can be generally divided into dielectric loss type and magnetic loss type [1,2]. The dielectric loss type MAM and magnetic loss type MAM are usually compounded to obtain various electromagnetic loss mechanism and then enhance the microwave absorption properties [3-5]. However, it is difficult to develop novel single-component microwave absorber with multiple microwave absorption mechanism [6-8].

As we known, zinc oxide receives extensive attentions due to its advantages of semiconductive properties and piezoelectric features [9, 10]. Recently, it is demonstrated that ferromagnetic properties of ZnO can be caused by defects, metal ions doping, specific morphology and so on [11-14]. Then, multiple dielectric loss and magnetic loss may be co-existed in zinc oxide. As a result, ZnO can be proposed as a novel microwave absorber [15, 16]. The previous studies mainly reported the influences of ions doping on structural, electric and magnetic properties of ZnO. In addition, it is reported that the nanoscale structures, such as nanocapsule, porous spheres and nanoflake heterostructure, are beneficial to improve the microwave absorption properties [17-20]. However, few studies were focused on the effect of 1-D bead-like fibrous shape [21, 22].

Herein, Co-doped ZnO nanofiber and nanoparticle were synthesized through electrospinning method. The morphology and electromagnetic properties were studied. The multiple electromagnetic loss mechanism and the enhanced microwave absorption properties were carried out via tuning the nanoparticle and nanofiber shape.

2. Experimental procedures

Co-doped ZnO nanofiber and nanoparticle were prepared by electrospinning method. The concentration of Co in ZnO is 0.03. Firstly, N,N-Dimetylformamid (DMF) was mixed with ethanol at the ratio of 1:1. Zinc acetate dihydrate and cobalt acetate anhydrous were dissolved in ethanol/DMF solvent to form the metal salt solution. Secondly, Polyvinylpyrrolidone (K-30) was dissolved in ethanol with different concentrations. The concentration of PVP was controlled as 10*wt*% to prepare Co-doped ZnO nanofiber and the concentration of PVP was controlled as 3*wt*% to prepare Co-doped ZnO nanoparticle. Then, the metal salt solution was added into the PVP solution and further magnetically stirred for 4 h to form the spinning solution. Thirdly, the spinning solution was electrospun under the conditions: applied positive voltage with 14 kV, feeding rate with 5 μl/min, collector distance with 12.0 cm. Finally, the as-prepared precursor was dried at 70 °C and then calcined at 600 °C for 3 h in air.

X-ray diffraction patterns were characterized via RigakuD/Max 2500 X-ray diffractometer. Scan electron microscopy was characterized via Hitachi SU8010. The electromagnetic parameters were measured by Network analyzer (Agilent PNA 8363B).The specimens were prepared by mixing 20*wt*% Co-doped ZnO with 80*wt*% paraffin. The mixture was pressed to cylinder-shape with a size of 3 mm (inside) ×7 mm (outside) × 2mm (height).

3. Results and Discussion

The morphologies of as-prepared nanoparticle and nanofiber were shown in Fig.1. It can be seen from Fig. 1(a) that the as-prepared Co-doped ZnO nanoparticle were aggregated and the particle size was nearly 80 nm. However, as shown in Fig.1(b), the as-prepared Co-doped ZnO nanofiber exhibited bead-like fibrous shape. The particles are connected with each other and there are many interfaces among them. During the formation of Co-doped ZnO nanofiber, PVP acted as the 1-D template when its weight concentration was controlled as 10*wt*%. Then, the lateral chains and backbone of PVP gradually decomposed at 329.7 °C and 393.8 °C, respectively [23]. Moreover, it can be seen from Fig. 1(c) that the mean diameter of Co-doped ZnO nanofiber was around 92.3 nm. The as-prepared samples were characterized by XRD and the results were shown in Fig. 1(d). It can be found that showed that the pure Co-doped ZnO nanofiber and nanoparticle were prepared.

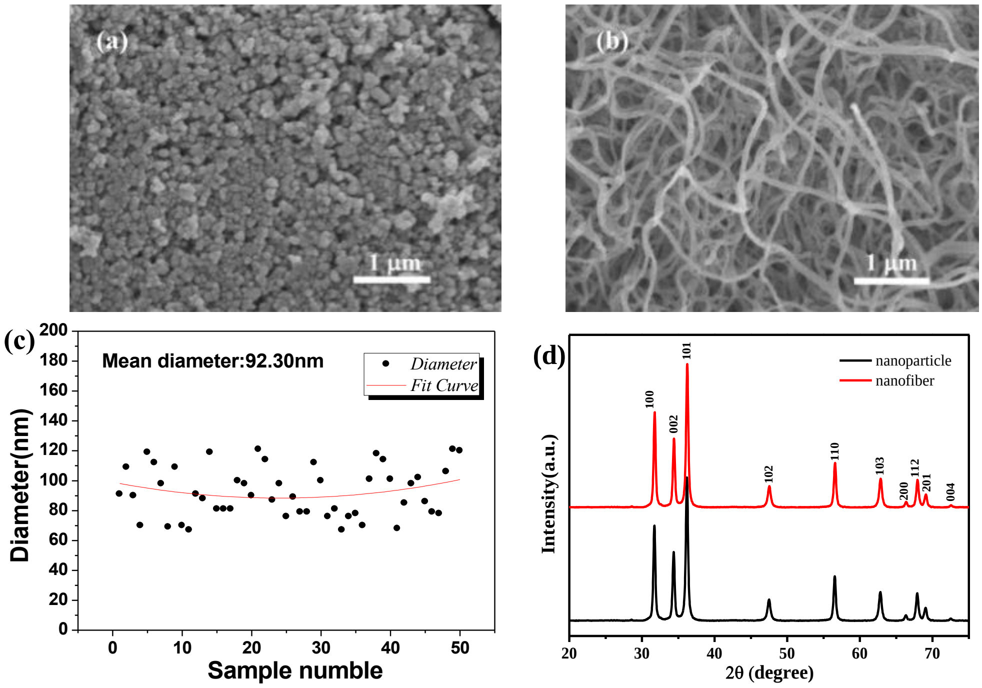

Fig. 1(a) SEM image of nanoparticle, (b) SEM image of nanofiber, (c) the statistical diameters of nanofiber, and (d) XRD patterns of Co-doped ZnO nanoparticle and nanofiber.

Fig. 2 illustrates the hysteresis loop of Co-doped ZnO nanoparticle and nanofiber. As we known, the traditional ZnO performs diamagnetic properties. However, the as-prepared Co-doped ZnO nanofiber exhibits S-shape *M*-*H* curve, indicating ferromagnetic properties. It can be caused by defects in the ZnO after doping metal ion [13, 14]. The saturation magnetization is nearly 0.05 emu/g and the coercivity is about 53.2 Oe. It is beneficial to further obtain the magnetic hysteresis loss of Co-doped ZnO nanofiber.

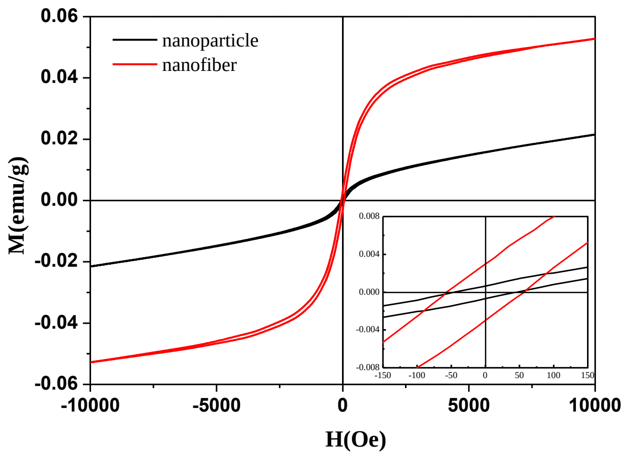

Fig. 2 The hysteresis loop of Co-doped ZnO nanoparticle and nanofiber at room temperature.

The electromagnetic parameters of Co-doped ZnO nanoparticle and nanofiber are measured and the results were shown in Fig. S1. Then, the dielectric loss property and magnetic loss property are calculated and characterized by dielectric loss factor ($\tan\delta_\varepsilon=\varepsilon''/\varepsilon'$) and magnetic loss factor ($\tan\delta_u=\mu''/\mu'$), respectively. The results are illustrated in Fig. 3.

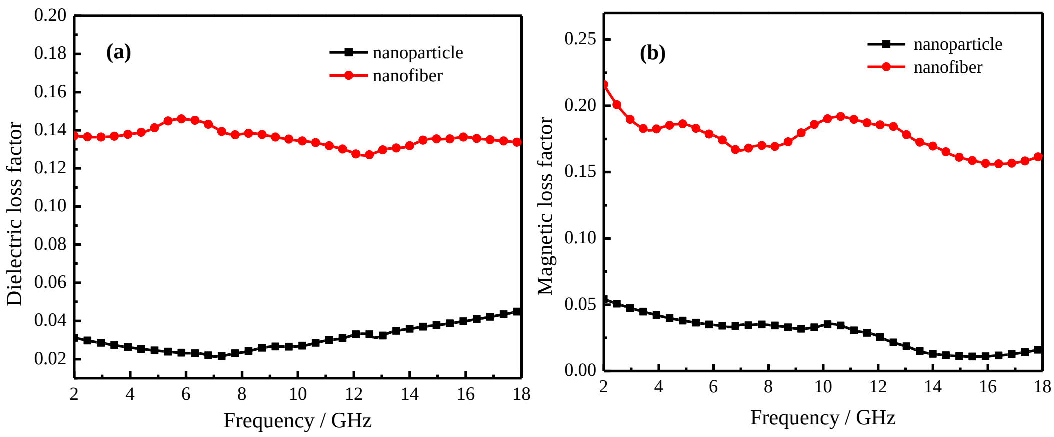

Fig. 3 (a) Dielectric loss factor and (b) magnetic loss factor of Co-doped ZnO nanoparticle and nanofiber.

From Fig. 3(a), the dielectric loss factor of Co-doped ZnO nanoparticle is 0.02-0.04. However, the dielectric loss factor of Co-doped ZnO nanofiber is increased to 0.13-0.14. Firstly, it can be caused by dipole polarization in the Co-doped ZnO nanofiber. The migration between the Co^{2+} and Zn^{2+} ions can induce the intrinsic electric dipole. Secondly, it can be ascribed to orientational polarization. The shape anisotropy of 1-D nanofiber is much larger than that of 0-D nanoparticle. Thirdly, it can be caused by the interfacial polarization because the bead-like shape has more particle interfaces.

From Fig.3(b), it can be seen that the values of magnetic loss factor of Co-doped ZnO nanofiber is also higher than that of Co-doped ZnO nanoparticle. The Co-doped ZnO nanofiber shows stronger magnetic loss property. It may be caused by the enhancement of natural-resonance loss. For the natural-resonance frequency, it can be expressed as: $f_r=(\gamma H_a)/2\pi$, where f_r is natural-resonance frequency, H_a is effective anisotropic field and γ is gyromagnetic ratio. The effective anisotropic field of the Co-doped ZnO nanofiber is improved due to its high length-diameter ratio and remarkable shape anisotropy. Then, it is beneficial to obtain the natural-resonance loss in the GHz frequency band.

In addition, the reflection loss (RL) is calculated to evaluate the microwave absorption properties via transmission line theory:

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

$$Z_{in} = Z_0\left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2}\tanh\left[\left(j\frac{2\pi fd}{c}\right)(\mu_r\varepsilon_r)^{1/2}\right]$$

where Z_{in} and Z_0 are impedance of the absorber and free space, respectively. *f* is the frequency, *d* is the coating thickness and *c* is the velocity of light. The calculated RL of Co-doped ZnO nanoparticle and nanofiber with different coating thickness are shown in Fig. 4.

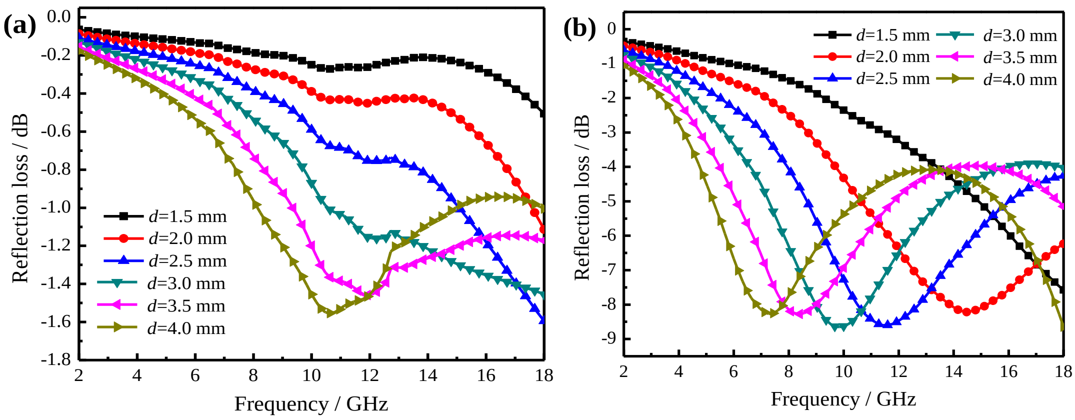

Fig. 4 Reflection loss of Co-doped ZnO with different thickness, (a) nanoparticle, (b) nanofiber.

It can be seen that the RL of nanoparticle even not reach to -2 dB in 2-18 GHz. It means that the microwave absorption properties of Co-doped ZnO nanoparticle are not obvious. However, the RL of Co-doped ZnO nanofiber is less than -5.2 dB in 5.3-18 GHz when coating thickness is 1.5-4.0 mm. That is to say, the absorptivity of Co-doped ZnO nanofiber can reach to 70% in 5.3-18 GHz. The as-prepared Co-doped ZnO nanofiber exhibited excellent microwave absorption properties.

4. Conclusions

Co-doped ZnO nanoparticle and nanofiber with pure hexagonal wurtzite phase were successfully synthesized by electrospinning method. The Co-doped ZnO nanofiber exhibited unique bead-like shape and behaved as the ferromagnetic property. The dielectric loss and magnetic loss properties of Co-doped ZnOnanofiber were stronger than that of Co-doped ZnO nanoparticle. The microwave absorption properties of Co-doped ZnO nanoparticle were weak. However, the absorptivity of Co-doped ZnO nanofiber reached to 70% in the frequency range of 5.3-18 GHz when the coating thickness is 1.5-4.0 mm, performing much better electromagnetic loss properties. The as-prepared bead-like Co-doped ZnO nanofiber can be potentially used as lightweight microwave absorption material.

Acknowledgements

This work is supported by the Hong Kong Scholars Program 2016 under Grant No. G-YZ0G, the Natural Science Foundation of Jiangsu Province (BK20180091), the National Natural Science Foundation of China (51402154) and the Six Major Talent Peak Expert (Grant No. R2016L08).

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Figure captions

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