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Low material density and high microwave-absorption performance of hollow strontium ferrite nanofibers prepared via coaxial electrospinning

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ABSTRACT

Hollow strontium ferrite ($SrFe_{12}O_{19}$: SrM) nanofibers have been successfully synthesized by coaxial electrospinning with the advantages of low material density and high microwave absorption performance. SrM precursors were used for coaxial electrospinning and annealing at different temperatures (600 °C, 650 °C, 700 °C, and 750 °C). A variety of characterization methods—XRD, TG, SEM, TEM, EDS, VSM and VNA—are used to analyze their particle size, morphology, magnetic response and absorption performance. The outer and inner diameters of hollow nanofibers annealed at 750 °C are 28 and 16 nm, respectively. The hollow structure is clearly visible, and as per calculation results, the material density is nearly 48.5% lower than that of solid fibers with the same diameter. The magnetism properties improve with increasing nanoparticle sizes for the single-domain particles. The saturation magnetization and the coercivity of the hollow nanofibers at 750 °C are 57.8 A m^2 kg^{-1} and 333.9 kA m^{-1}, respectively. When the thickness of the absorber coating was 3.4 mm, the electromagnetic radiation reflection loss reached −12.69 dB at 11.68 GHz. The calculated reflection loss of the hollow sample is better than that of solid fibers; the maximum ratio of structure reduction is 14.5%. Further, the mechanism of SrM formation and the mechanism of the improvement of the microwave absorption properties are discussed.

1. Introduction

With the development of wireless communication, microwave absorbing materials have been applied in the fields of military defense and for reducing the electromagnetic pollution [1–3]. Previous studies on microwave absorption materials have aimed to synthesize light-weight, wide-absorption-band, and high-absorption-rate materials [4,5]. In this regard, the number of studies involving ferrites, metal ultrafine powders, and conductive polymers has been increasing in recent years [6,7].

Hexagonal ferrites with the magnetoplumbite structure, including $SrF_{12}O_{19}$ (SrM) and $BaF_{12}O_{19}$ (BaM), were discovered in the 1950s-1960s by Braun, Smit, and Wijn et al. [8,9]. Because of their high crystal anisotropy, magnetic permeability, saturation magnetization, coercivity, and excellent chemical stability, hexagonal ferrites are used widely to make permanent magnets for a number of high-technology fields. They have also been used to produce microwave-absorbing nanocomposites [10,11] and high-density magnetic recording media [12–14]. Hexagonal ferrites with various structures and morphologies have been studied. Among them, hexagonal ferrite fibers were first fabricated by Pullar et al. in the late 1990s [15–17] and their studies still draw interest owing to the superior performances.

The M-type SrM, one of typical hexagonal ferrites with hard magnetic material, is widely used to prepare absorbing materials because of its high magnetic anisotropy, large magnetization, stability, and low cost [18–20]. However, SrM has a significant disadvantage in that it has a high material density, which limits its applicability. Therefore, the synthesis of one-dimensional fibers can resolve the issue of the high material density.

One-dimensional nanostructures with a large ratio of surface area to volume and a high aspect ratio have been exploited in many fields, e.g., in chemical sensors, filtration media, and microwave absorbing materials [21–23]. In recent years, electrostatic spinning has been developed into one of the primary methods for fabricating fibers [24–27]. Shen et al. [26] prepared $SrFe_{12}O_{19}$ fibers by

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sol–gel-assisted electrospinning and the fabricated fibers exhibited good magnetism properties. Electrospinning is an efficient and easy technique to prepare nanofibers due to high reproducibility and versatility [28,29]. Further, coaxial electrospinning is a simple and low-cost method to fabricate coaxial-structure nanofibers. Moreover, the hollow nanofibers obtained, which selectively removed the core instead of the shell by calcination process fabricated through coaxial electrospinning. Since the surface area of hollow nanofibers is nearly double that of ordinary nanofibers [30–32], hollow nanofibers have a wider application potential in chemical sensors, photocatalysts, and electromagnetic wave absorbing materials [33–35]. Yu et al. [36] prepared Fe_3O_4/Eu(BA)$_3$phen/PVP hollow nanofibers by coaxial electrospinning, and the hollow nanofibers possessed both luminescent and magnetic properties. Some of the common methods of synthesizing hollow fibers are the gel-precursor transformation method [37–39], Ostwald ripening [40] and coaxial electrospinning. Song et al. [37] prepared $Ba_xSr_{1-x}Fe_{12}O_{19}$ (x = 0-1) ferrite hollow fibers via the gel-precursor transformation method, but the preparation process is tedious. Guan et al. [40] prepared hollow $BaFe_{12}O_{19}$ hierarchical fibers as well as arrays of the hollow fibers via Ostwald ripening, and these fibers are suitable for use in microwave absorbers and for magnetic separation. Compared with these methods, coaxial electrospinning is a simple and low-cost technique for producing hollow fibers. However, thus far, coaxial electrospinning has been mainly applied to fabricate single-oxide hollow fibers but rarely used to fabricate composite-oxide hollow fibers [41].

In order to reduce the material density and improve the absorption performance, the fabrication of hollow SrM fibers by coaxial electrospinning is investigated in this study. The synthesis method is straightforward and results in improved performance.

2. Experimental

2.1. Materials

All reagents were used as received without further purification. Poly(vinyl pyrrolidone) (PVP, $Mw = 1300000$) was purchased from Sigma-Aldrich, USA. Strontium nitrate ($Sr(NO_3)_2$) was from bought Chengdu Chemical Reagent Co. Ltd., China. Ferric nitrate ($Fe(NO_3)_3\cdot 9H_2O$) was obtained from Xilong Chemical Co. Ltd., China. *N*,*N*-dimethylformamide (DMF) was provided by Beijing Chemical Reagent Co. Ltd., China.

2.2. Synthesis of hollow $SrFe_{12}O_{19}$ nanofibers

The shell precursor solution was prepared using 0.1 mmol $Sr(NO_3)_2$, 0.012 mmol $Fe(NO_3)_3\cdot 9H_2O$, and 0.6 g PVP dissolved in 5.4 mL DMF under continuous stirring by a magnetic stirrer for 12 h. To prepare the core precursor solution, 0.6 g PVP was dissolved in 5.4 mL DMF under magnetic stirring for 12 h at 25 °C.

Subsequently, PVP@PVP/[$Sr(NO_3)_2$+$Fe(NO_3)_3\cdot 9H_2O$] was transferred into the coaxial electrospinning apparatus. The shell solution and the core solution were loaded into the outer and the inner plastic syringe, respectively. The coaxial needle was composed of a truncated 16# stainless steel needle as the outer one and a truncated 8# stainless steel needle as the inner one. The fibers collector was placed 15 cm away from the spinneret. The solutions were electrospun at 30 °C under a positive high voltage of 15 kV at a feed rate of 0.50 mL h^{-1} and pumped by a syringe pump. PVP@PVP/[$Sr(NO_3)_2$ + $Fe(NO_3)_3\cdot 9H_2O$] core-shell composite nanofibers were obtained in the collector. The preparation process is shown in Fig. 1.

The as-prepared electrospun nanofibers were first dried in a vacuum chamber at 50 °C for 6 h. The composite nanofibers were sintered at different temperatures (600, 650, 700, 750 °C) at a heating rate of 1 °C min^{-1} for 3 h in an air atmosphere.

In addition, solid nanofibers were also prepared via single-needle electrospinning for comparison. The single nozzle was a truncated 8# stainless steel needle. Other conditions and processes, including preparation and calcination, were consistent with coaxial electrospinning.

2.3. Measurements

The thermal stabilities of the composite nanofibers were analyzed by thermal gravimetry analysis (TG/DTA, STA 499 F3, Netzsch). Structure analysis was performed via X-ray diffraction (XRD, D/max2500, Japan) using Cu/Kα radiation (λ = 1.54056 Å). The morphology of the hollow $SrFe_{12}O_{19}$ nanofibers was analyzed by scanning electron microscopy (SEM, Hitachi S-4800, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS). In addition, transmission electron microscopy (TEM, JEM 1200EX, Japan) images were also obtained. Magnetic measurement was performed using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA). The impedance matching condition was analyzed using a vector network analyzer (VNA, PNA 8363B, Agilent) in the frequency range of 2–18 GHz.

3. Results and discussion

3.1. TG and DTA

TG-DTA curves of electrospun composite nanofibers are shown in Fig. 2. The TG curve shows a minor weight loss (~5.78%) below 230 °C, which was mainly related to the loss of DMF in the system. In addition, there is a steep weight loss (~69.70%) between 230 °C and 380 °C, which can be attributed to the decomposition of PVP. On the DTA curve, a main exothermic peak is observed at 276.3 °C, which is also due to the combustion of PVP. Moreover, a slow weight loss (~5.94%) in the range of 380 °C–450 °C can be attributed to the intramolecular decomposition of PVP [41] and the decomposition of Sr and Fe nitrates. No weight loss above 450 °C indicates the formation of the decomposition products of the SrM (i.e., γ-Fe_2O_3 and $SrCO_3$).

3.2. XRD

The calcination temperature plays a vital role in the formation of SrM. Fig. 3 shows the XRD patterns of hollow SrM nanofibers annealed at different temperatures. When the composite nanofibers were annealed at 600 °C, the minor peaks of γ-Fe_2O_3 (PDF#39-1346) are visible but the peaks of $SrCO_3$ are not evident due to the low concentration. It can be concluded that γ-Fe_2O_3 is one of the products in the synthesis of SrM and 600 °C is lower than the temperature for SrM formation. When the temperature is increased to 650 °C, it can be seen that γ-Fe_2O_3 and $SrCO_3$ transform to SrM (PDF#33-1340) as the characteristic peaks of hollow SrM nanofibers are visible at 2θ = 32.35° and 34.18°, which correspond to the (107) plane and the (114) plane, respectively. If the temperature is further increased, the peaks of SrM increase. This phenomenon can be explained by the improvement in the SrM crystallinity with the temperature. Moreover, the peak intensity at 35.63° weakened, indicating the impurities of γ-Fe_2O_3 decreased. The classical Debye-Scherrer equation is used to calculate the sample powder diffraction peak.

$$D = 0.89\lambda/(\beta \cos\theta) \quad (1)$$

λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ is the Bragg's angle. The average crystallite size (D)