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Preparation and microwave-absorbing properties of silver-coated strontium ferrite with polyaniline via in situ polymerization

Zheng He, Shuhua Qi *, Xiaolan Zhong, Huan Ma, Pei Wang, Hua Qiu

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

In this contribution, a new type of conductive and magnetic PANI/Ag/$SrFe_{12}O_{19}$ composites were synthesized via three-step method. First, $SrFe_{12}O_{19}$ was synthesized through coprecipitation reaction, then Ag/$SrFe_{12}O_{19}$ particles were prepared via chemical plating method. Finally, PANI/Ag/$SrFe_{12}O_{19}$ composites were obtained by in-situ polymerization in the presence of Ag/$SrFe_{12}O_{19}$. The morphologies and properties of the samples were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), UV–Visible spectrophotometry (UV–Vis) and vibrating sample magnetometry (VSM). Results show that $SrFe_{12}O_{19}$ and Ag/$SrFe_{12}O_{19}$ particles are successfully synthesized. After coating Ag on $SrFe_{12}O_{19}$ surface, the saturation magnetization of particles decrease from 117.22 emu/g to 70.54 emu/g, whereas its conductivity increase to 107 S/cm. Meanwhile, with the introduction of Ag/$SrFe_{12}O_{19}$, the PANI/Ag/$SrFe_{12}O_{19}$ composites exhibit better thermal stability, electric and magnetic properties than pure PANI. Measurements of the reflection loss (R) show that PANI/Ag/$SrFe_{12}O_{19}$ composites have a good microwave absorbing property in the X band, the reflection loss of the composites is below −10 dB between 8.7 GHz and 12.1 GHz, with a minimum loss value of −14.86 at 9.98 GHz.

1. Introduction

With the development of our modern information-filled society, microwave absorption materials have attracted much attention not only because of the military countermeasure to radar detection but also because of the intense demands for reduction of electromagnetic (EM) pollution/radiation and shielding interference in electric communication field [1–3]. Recently, many new techniques have been developed to synthesize microwave absorption materials with combination properties as high absorption rate, light weight, wide absorption band, anti-abrasion and low cost [4–6].

Depending on the absorbing mechanism, materials can be divided into two types, namely: magnetic materials such as ferrite [7]; and electronic materials such as graphite [8]. As a magnetic material with great scientific and technical interest, strontium ferrite ($SrFe_{12}O_{19}$) has been widely used as permanent magnets, magnetic-recording media and absorbing materials. In recent years, $SrFe_{12}O_{19}$ has displayed a promising application in microwave absorption because of its high stability, excellent high-frequency response, large magneto crystalline anisotropy and large magnetization [9–10]. However, $SrFe_{12}O_{19}$ is a non-conductive material, which restricts its universal application requiring electrical conductivity. Coating silver nanoparticles on $SrFe_{12}O_{19}$ (denoted as Ag/$SrFe_{12}O_{19}$) might be a feasible way to solve this problem, through the obtention of an electromagnetic particle. As such, the microwave-absorption property of $SrFe_{12}O_{19}$ could improve significantly [11].

Recently, intrinsically conducting polymers such as polyaniline (PANI), polyacetylene (PA), polypyrrole (PPy) as well as polythiophene (PTH) have been thoroughly investigated for their superior conductivity and light weight [12]. Among the above-mentioned conducting polymers, PANI has been extensively studied due to its easy synthesis, low cost, excellent environmental stability and high electrical conductivity [13–15]. Currently, an increasing number of reports are focusing on synthesizing electromagnetic PANI-based composites, conductive and magnetic materials such as ferrite, carbon nanotubes, graphene and nano-metals are always added in them [16–18]. To the best of our knowledge, there are few reports related to modifying PANI with Ag/$SrFe_{12}O_{19}$.

In this work, $SrFe_{12}O_{19}$ was synthesized using strontium nitrate and ferric nitrate via the co-precipitation method. Ag/$SrFe_{12}O_{19}$ particles were then obtained by chemically coating Ag on the surface of $SrFe_{12}O_{19}$. Finally, PANI/Ag/$SrFe_{12}O_{19}$ composites with satisfactory microwave-absorbing property were prepared via in-situ polymerization. The structures of $SrFe_{12}O_{19}$, Ag/$SrFe_{12}O_{19}$ and

* Corresponding author.

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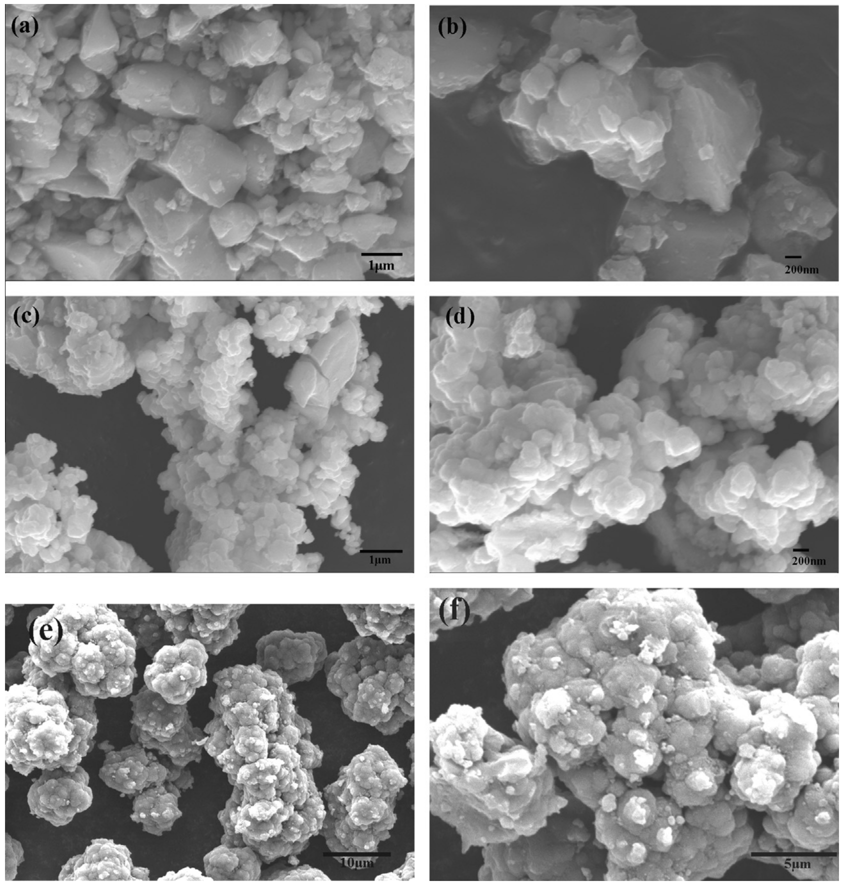

Fig. 1. SEM images of $SrFe_{12}O_{19}$ (a and b), $Ag/SrFe_{12}O_{19}$ (c and d) and $PANI/Ag/SrFe_{12}O_{19}$ (e and f).

$PANI/Ag/SrFe_{12}O_{19}$ were characterized by SEM, EDS, UV–Vis and XRD. Properties such as thermal stability, conductivity, magnetic properties and microwave absorption were also measured in this contribution.

2. Experimental

2.1. Materials

Aniline (AR) was purchased from Sinopharm Chemical Reagent Limited Company and was distilled at reduced pressure before being used. Strontium nitrate ($Sr(NO_3)_2$), sodium dodecyl benzene sulfonate (SDBS), stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$), palladium chloride ($PdCl_2$) and silver nitrate ($AgNO_3$) were purchased from the Chemical Company of Tianjin. Ammonia ($NH_3{\cdot}H_2O$), 36%, ammonium persulphate (APS), ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and formaldehyde were bought from the Chemical Company of Xi'an. Without otherwise specified, the reagents above were used as received.

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

Specific amounts of $Sr(NO_3)_2$ and $Fe(NO_3)_3{\cdot}9H_2O$ (mole ratio 1:12) were added to a flask under vigorous stirring, and the solution was heated to 30 °C in a water bath. A mixture of the precipitating agent (ammonia solution) and dispersing agent (SDBS) was placed into the solution, and the pH value was adjusted to 9–10. The reaction was carried out at 90 °C for about 3 h with constant stirring. After the reaction was completed, the crude products were washed with deionized water and then dried under vacuum at 80 °C for about 24 h, and finally calcined at 1000 °C for 2 h via a high-temperature tubular oven under the protection of argon. The co-precipitation reaction is as follows:

$$12Fe^{3+} + Sr^{2+} + 38OH^- \rightarrow 12Fe(OH)_3 + Sr(OH)_2 \quad (1)$$

$$12Fe(OH)_3 + Sr(OH)_2 \rightarrow SrFe_{12}O_{19} + 19H_2O \quad (2)$$

2.3. Synthesis of $Ag/SrFe_{12}O_{19}$

The preparation of $Ag/SrFe_{12}O_{19}$ involves an initial pretreatment of $SrFe_{12}O_{19}$ followed by the chemical silver plating on the surface of $SrFe_{12}O_{19}$. First, $SrFe_{12}O_{19}$ was sensitized using 1% $SnCl_2{\cdot}2H_2O$ for about 0.5 h. The sensitized $SrFe_{12}O_{19}$ was then activated using $PdCl_2$ to enhance the adhesion force between the silver coating and $SrFe_{12}O_{19}$. The reaction of $SnCl_2{\cdot}2H_2O$ and $PdCl_2$ is shown as:

$$Sn^{2+} + Pd^{2+} = Sn^{4+} + Pd \quad (3)$$

After the above initial steps, $SrFe_{12}O_{19}$ (1 g) was immersed in the solution of $Ag(NH_3)_2OH$ (0.5 mol/L, 100 mL), while adding HCHO solution (2.15 mL) dropwise using a syringe. The mixture was then stirred for 0.5 h at room temperature. $Ag/SrFe_{12}O_{19}$ was obtained after washing and drying. The reaction is as follows:

$$HCHO + 4[Ag(NH_3)_2]OH \rightarrow 4Ag\downarrow + 6NH_3 + (NH_4)_2CO_3 + 2H_2O \quad (4)$$

2.4. Synthesis of $PANI/Ag/SrFe_{12}O_{19}$

$PANI/Ag/SrFe_{12}O_{19}$ composites were prepared via in situ polymerization. $Ag/SrFe_{12}O_{19}$ (0.3 g) and a mixture of ethanol, distilled water and HCl solution were placed into a flask under stirring. Aniline (0.01 mol, 0.931 g) was then added into the flask. After bringing the temperature of the mixture down to 0 °C, APS (0.01 mol, 2.482 g) was added dropwise to the mixture. The reaction was carried out at 0 °C for 6 h. The resulting precipitate was filtered, washed several times with distilled water, and then dried in a vacuum at 60 °C for about 24 h.

2.5. Characterization of $SrFe_{12}O_{19}$, $Ag/SrFe_{12}O_{19}$ and $PANI/Ag/SrFe_{12}O_{19}$

The surface morphologies and chemistry analysis of $SrFe_{12}O_{19}$, $Ag/SrFe_{12}O_{19}$ and $PANI/Ag/SrFe_{12}O_{19}$ were characterized via scanning electron microscopy (SEM; JSM-6390, HITACHI, Japan), energy dispersive spectroscopy (EDS; INCAX-ACT, Oxford Instruments Inc.), 56MCUV – Visible spectrophotometry (UV–Vis, Ruili, China) and X-ray diffraction (XRD; PANalytical, Holland).