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Controlled synthesis and microwave absorption properties of $Ni_{0.6}Zn_{0.4}Fe_2O_4$/PANI composite via an in-situ polymerization process

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ABSTRACT

The binary composites of conducting polyaniline (PANI) and nickle zinc ferrite were synthesized by an in-situ polymerization process, and the electromagnetic absorption properties of the composites were also investigated. The FT-IR spectra present the peaks of PANI (1562, 1481, 1301, 1109, and 799 cm^{-1}) and the bonds of NiZn ferrite (579 and 390 cm^{-1}), indicating the existence of both NiZn ferrite particles and PANI in the composites. With the increasing ratio of nickle zinc ferrite, the composites distributes in irregular compared with pure PANI and $Ni_{0.6}Zn_{0.4}Fe_2O_4$. The TG curves of the pure PANI and PANI/$Ni_{0.6}Zn_{0.4}Fe_2O_4$ composites with different molar ratios clearly show the increase percentage of the ferrite in the composites. Furthermore, we found that the excellent electromagnetic absorption properties and wide absorption bandwidth can be achieved by adjusting proper molar ratios $Ni_{0.6}Zn_{0.4}Fe_2O_4$ to PANI. The maximum reflection loss of $Ni_{0.6}Zn_{0.4}Fe_2O_4$/PANI can reach to −41 dB at 12.8 GHz and the bandwidth exceeding −10 dB can reach to 5 GHz with the absorber thickness of 2.6 mm at the molar ratio of 1:2. This can be attributed to the enhancing magnetic loss and the better impedance matching. Therefore, $Ni_{0.6}Zn_{0.4}Fe_2O_4$/PANI ferrite composites can become a new kind of candidate in the field of the microwave absorbing.

1. Introduction

Among spinel type structure, nickel zinc ferrites have attracted much attention due to its many particular features such as large saturation magnetization, high resistivity, remarkable chemical stability, low dielectric loss, as well as good mechanical hardness [1–3]. These unique properties may meet many requirements in military stealth, high-density magnetic recording media, ferrofluids and so on [4–6]. Peculiarly, nickel zinc ferrites have been extensively studied as microwave absorbing materials due to their strong absorption [7], wide frequency band [8], and high corrosion resistance [9].

However, the microwave absorption properties achieved by single nickel zinc ferrites to date has been far below what is expected, because the materials are suffered from poor stability and high density [10,11]. Previous efforts have focused on constructing nickel zinc ferrites composites with polymers [12], carbon-based materials [13], transition metal oxides [14] etc. For example, Fu et al. prepared a novel composite material of $NiFe_2O_4$ nanorod, which exhibits excellent microwave absorption performance with the minimum reflection loss of −29.2 dB at 16.1 GHz under a thickness of 2.0 mm, as well as the effective absorption frequency (Reflection Loss $R_L < -10$ dB) ranging from 13.6 to 18 GHz [15]. Cao et al. reported the highly effective microwave absorption of ferroferric oxide/multiwalled carbon nanotube vs polyaniline/ferroferric oxide/multiwalled carbon nanotube. It was found that the Fe_3O_4/MWCNT composites demonstrate excellent microwave absorption performance with wide absorption bandwidth due to the combined contribution of dielectric and magnetic loss. And the reflection loss peak achieves up to 40 dB (3 mm in thickness), much more effective than that of naked CNT and ferrite [16].

Compared with the traditional composite component mentioned above, conduction polymers, such as polyaniline (PANI) or polypyrrole (PPy), have drawn considerable interests due to their unique electric properties [17]. The coating on the surface of the ferrites' particles may introduce dielectric loss to the composite. Furthermore, its good electrical conductivity may produce skin effect and additional reflection at the interface between materials and air, which offers effective electromagnetic attenuation, leading to the improvement of compatibility and electromagnetic properties.

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Therefore, the combination of magnetic materials with dielectric materials provides a promising way to achieve high microwave absorption performance [18,19]. Several reports about the composites of the NiZn ferrite/PANI had been reported, for example, the R_L below −10 dB of PANI/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanocomposite prepared by hydrothermal process can up to 5 GHz [20]. Ting et al. [21] synthesized the $NiFe_2O_4$/PANI nanocomposites by situ polymerization of aniline in the presence of different amounts of $NiFe_2O_4$ nanoparticles. The $NiFe_2O_4$/PANI nanocomposites show absorption bands better than that of nickel ferrite with the minimum reflection loss of −21 dB. However, the research on constructing composite of PANI and nickel zinc ferrites for microwave absorption is still lacking and needs further studies. As we know, magnetic performance of nickle zinc ferrite ($Ni_xZn_{1-x}Fe_2O_4$ $0 \le x \le 1$) varies with x, for that Zn^{2+} belongs to nonmagnetic ion. Adding the optimum zinc ions can reduce magnetic anisotropy constant and magnetostriction coefficient, thereby improve the initial permeability and increase saturation magnetization. From our work we found the optimum value of saturation magnetization can be achieved in $x=0.6$. Therefore we choose $Ni_{0.6}Zn_{0.4}Fe_2O_4$ to combine with conductive polymer PANI.

In this work, a simple in-situ polymerization method was adopted to synthesize $Ni_{0.6}Zn_{0.4}Fe_2O_4$/PANI composites, which exhibits improved physiochemical properties and the electromagnetic shielding performance. Moreover, $Ni_{0.6}Zn_{0.4}Fe_2O_4$/PANI composites with different molar ratios (Aniline/$Ni_{0.6}Zn_{0.4}Fe_2O_4$ =3:1, 2:1, 1:1, 1:2, 1:3) were obtained to investigate the influence of the PANI content on the electromagnetic and microwave absorption properties.

2. Experimental section

All chemicals in this work were analytical grade regents and used as raw materials without further purification except aniline. Sodium hydroxide (NaOH), hexadecyl trimethyl ammonium bromide (CTAB), citric acid (CA), ammonium persulfate (APS) were purchased from Nanjing Chemical Reagent Co., Ltd. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_20$), Iron nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) were purchased from Xilong Chemical Co., Ltd. Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) was purchased from Chemical Engineering Technology Research and Development Center of Guangdong province. Aniline (Ani) was purchased from Sinopharm Chemical Reagent Co., Ltd. Moreover, Ani needs to be purified by vacuum distillation before use.

2.1. Synthesis of $Ni_{0.6}Zn_{0.4}Fe_2O_4$

$Ni_{0.6}Zn_{0.4}Fe_2O_4$ was prepared by the common co-precipitation method at room temperature, as reported elsewhere [22]. The typical preparation procedure is as follows: $Ni(NO_3)_2.6H_2O$ (6 mmol), $Zn(NO_3)_2.6H_2O$ (4 mmol), and $Fe(NO_3)_3.9H_2O$ (0.02 mol) were added into 200 mL distilled water to form a clear solution with magnetic stirring. Then surfactant CTAB (0.01 mol) was added into the solution to form a mixture at room temperature for about 30 min. Subsequently, adding 3 mol/L NaOH aqueous solution dropwise to adjust the pH value to 9–11 under vigorous agitation. The solution was then transferred into a 500 mL three-necked round-bottom bottle under mechanical stirring and the temperature maintained at 80 °C for 2 h. The obtained brown precipitate was collected by centrifuging and washing with absolute ethanol and distilled water in sequence for several times thoroughly. Finally, the powders were calcined at 900 °C for 2 h to obtain the spinel phase.

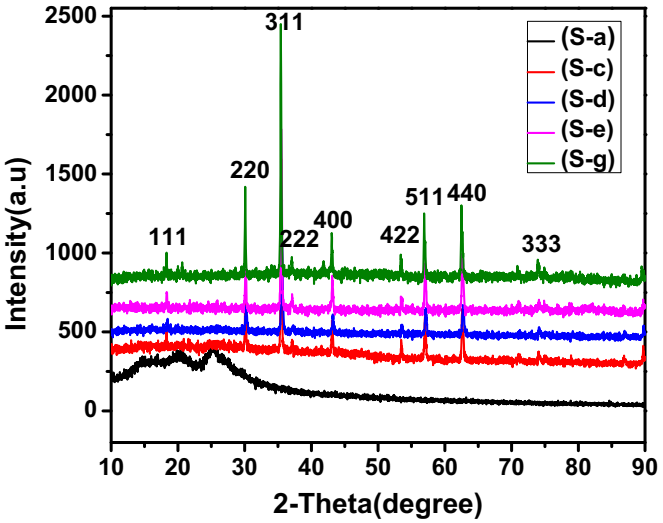

Fig. 1. XRD patterns of PANI (S-a), molar ratios (2:1, 1:1, 1:2) of $Ni_{0.6}Zn_{0.4}Fe_2O_4$/PANI composites (S-c, S-d, S-e) and pure ferrite (S-g).

2.2. Synthesis of $Ni_{0.6}Zn_{0.4}Fe_2O_4$/PANI composites

The powder from the composite of PANI-citric acid (CA) and the $Ni_{0.6}Zn_{0.4}$ ferrite (molar ratio of aniline and ferrite=3:1, 2:1, 1:1, 1:2 and 1:3) was prepared by the situ polymerization method. The detailed processing is described as below. Firstly, a certain amount of CA and Ani (molar ratio CA: Ani=10:1) was put into 200 mL distilled water to form aqueous solution under magnetic stirring. Then proportionate ferrite was added into the solution collected from above, continued with stirring for 30 min to produce a fine aqueous dispersion, simultaneously cooled to 0 °C with stirring. An aqueous solution of $(NH_4)_2S_2O_8$ was added slowly to initiate the polymerization, and ended up in 2 h. The molar ratio of the APS to Ani was 1:1. The polymerization was carried out in the ice-water bath for 12 h with mechanical stirring. Then the obtained product was collected by suction filtration and washed with absolute ethanol and distilled water in sequence for several times thoroughly and finally dried in the oven at 80 °C for 3 h.

The amount of doping acid can affect electrical conductivity of the PANI and the properties of wave-absorbing, which can improve slowly until up to the saturation. In order to obtain good profile and high yield, we prepared the concentration of Ani

Table 1
The compositions, structures, and the experimental conditions of the samples.

Samples	Compositions	Experiment conditions	Structures
S-a	Pure PANI	Ice-water bath 12 h	Close-grained protuberance nanospheres
S-b	n(Ani):n($Ni_{0.6}Zn_{0.4}Fe_2O_4$)=3:1	Ice-water bath 12 h	Lamellar structure with small part of smooth surface
S-c	n(Ani):n($Ni_{0.6}Zn_{0.4}Fe_2O_4$)=2:1	Ice-water bath 12 h	Part of smooth areas become larger
S-d	n(Ani):n($Ni_{0.6}Zn_{0.4}Fe_2O_4$)=1:1	Ice-water bath 12 h	Smooth areas become smaller
S-e	n(Ani):n($Ni_{0.6}Zn_{0.4}Fe_2O_4$)=1:2	Ice-water bath 12 h	Short fibers with uniform rough surface
S-f	n(Ani):n($Ni_{0.6}Zn_{0.4}Fe_2O_4$)=1:3	Ice-water bath 12 h	High uniform spheres with many sheets embedded
S-g	Pure $Ni_{0.6}Zn_{0.4}Fe_2O_4$	900 °C 2 h	Lamellar structure with smooth surface