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Enhanced absorbing properties and structural design of microwave absorbers based on $Ni_{0.8}Co_{0.2}Fe_2O_4$ nanofibers and Ni-C hybrid nanofibers

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ABSTRACT

We have proposed a novel double-layer microwave absorber based on spinel ferrite $Ni_{0.8}Co_{0.2}Fe_2O_4$ nanofibers (NCFO NFs) and Ni-C hybrid NFs prepared via a facile electrospinning method combined with subsequent heat treatment. Electromagnetic and microwave absorption properties of the double-layer microwave absorbers, together with those of the single-layer ones, were systematically investigated in the frequency range of 2–18 GHz. The double-layer absorbers consisting of 50 wt% NCFO NFs/paraffin composite and 5 wt% Ni-C NFs/paraffin composite show superior microwave absorbing performance with stronger absorption and broader bandwidth as compared with the corresponding single-layer ones and many reported double-layer ones. As 1.5 mm thick NCFO NFs composite is used as the matching layer and 0.8 mm thick Ni-C NFs composite is employed as the absorption layer, the optimal reflection loss (RL) of the absorber reaches −84.9 dB at 17.0 GHz with an effective absorption bandwidth below −10 dB of 7.4 GHz ranging from 10.6 to 18 GHz. The enhancement of microwave absorption in the double-layer absorbers should be mainly ascribed to the improvement of impendence matching characteristics due to the efficient coupling and synergistic effect between two layers. These excellent properties demonstrate that our double-layer structures offer a new route to design microwave absorbers with lightweight and high absorption performance over a broad frequency range.

1. Introduction

With the fast development of detection, information and communication technologies in the industrial, commercial and military fields, two serious problems are raised: electromagnetic (EM) interference and EM pollution. They can badly cause electronic equipment interruption, confidential information leakage, and human healthy harm. In order to address these problems, it is essential to employ microwave absorbing materials (MAMs) with strong absorption in a broad frequency range and low mass density [1–8]. Hitherto, various MAMs have been widely investigated. According to the dissipation mechanisms, MAMs are generally classified into two categories: dielectric and magnetic absorbing materials. Dielectric absorbing materials, such as graphene [9], conducting polymers [10], carbon nanotubes [11], carbon fibers [12], $BaTiO_3$ [13] and ZnO [14] possess a large dielectric loss and attenuate EM waves mainly through electronic, ionic, orientation and space charge polarizations. Magnetic absorbing materials include ferrites [15], magnetic metals and alloys [16,17], carbonyl iron [18], etc. They have a high magnetic loss and absorb EM waves usually by hysteresis loss, eddy current loss, natural and exchange resonances [19]. For practical applications, desirable microwave absorbers should possess a number of important features, e.g., lightweight, small thickness, strong absorption capability and wide absorption bandwidth.

Spinel ferrites have been extensively used in the field of EM wave absorption due to their low cost, low toxicity, strong absorption capacity and excellent magnetic properties. Also, spinel ferrites have appropriate permeability and permittivity values,

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which make them possess good impedance matching characteristics and can allow EM waves to efficiently enter into the absorbers and to be attenuated by their high magnetic loss, thus providing a good microwave absorption performance [20–22]. For instance. Zhao et al. [23] prepared Ni-Zn spinel ferrite and Cu-doped, Co-doped Ni-Zn spinel ferrite using a conventional ceramic processing method and found that the single-layer $(Ni_{0.4}Co_{0.2}Zn_{0.4})Fe_2O_4$ absorber with a thickness of 3 mm achieved a reflection loss (RL) below −10 dB at 3.9–11.5 GHz and a minimum RL value of −17.01 dB at 6.1 GHz. Torkian and his coworkers [24] synthesized $Co_xNi_{1-x}Fe_2O_4$ ferrites by a sol-gel auto-combustion method, which exhibited a minimum RL value of −26.3 dB at 9.7 GHz with an absorption bandwidth below −10 dB of 4 GHz through the entire frequency range of X-band (8–12 GHz). But, a large layer thickness and/or a high ferrite loading (above 70 wt%) are usually needed to obtain enough strong microwave absorption and relatively wide bandwidth, which restricts further applications of the ferrite absorbers in the aerobat field that demands lightweight [25].

To overcome the disadvantage of overweight, much effort has been devoted to the improvement of EM parameters and the design of absorber structures. It has been proposed to reduce the weight fraction of absorbents, optimize the EM parameters and enhance the microwave absorbing properties by compositing spinel ferrites with dielectric materials with low density (e.g., carbon materials [26–28]) to form hybrid-type or mixed-type absorbents. The combination of ferrites and dielectric materials can not only improve the EM impedance matching but also generate the high dielectric constant and loss due to effective interface between magnetic and dielectric components. For example, Zhang et al. [29] fabricated Fe_3O_4/carbon composite nanofibers (NFs) by electrospinning followed by stabilization and carbonization and evaluated their microwave absorption properties. It was shown that the minimum RL could reach about −45 dB at 8.0 GHz for a paraffin composite filled with 5 wt% Fe_3O_4/carbon composite NFs. Zhang et al. [30] investigated the microwave absorbing performances of reduced graphene oxide/$MnFe_2O_4$/polyvinylidene fluoride composites. They found that the composites with a filler loading of 5 wt% had a minimum RL of −29 dB at 9.2 GHz and an absorption bandwidth with RL value less than −10 dB of −4.88 GHz over the range of 8.00–12.88 GHz.

However, the reported ferrite/dielectric materials complex absorbents are usually designed as a single-layer structure and consequently it is hard to simultaneously achieve the requirements of strong EM absorption, broad bandwidth and thin layer. Therefore, double- or multi-layer structures consisting of different absorption layers have been designed and their EM characteristics can be readily tuned and optimized by adjusting the EM parameters and thickness of each layer to obtain good absorption performance over a wide frequency range at a small absorber layer thickness [31,32]. In comparison with the single-layer absorbers, the optimally designed double-layer absorbers with special structures can markedly enhance the EM matching and absorption properties. Firstly, the matching layer can allow more incident EM waves to easily enter into the absorber. Secondly, the interface between the matching layer and the absorbing layer can increase the chance of multi-reflection and scattering, which is in favor of EM wave attenuation [33–35]. For instance, Liu et al. [36] investigated the microwave absorption properties of double-layer absorbers based on $Co_{0.2}Ni_{0.4}Zn_{0.4}Fe_2O_4$ ferrite and reduced graphene oxide composites. The optimal double-layer absorbers exhibited a minimum RL of −49.5 dB at 16.9 GHz as well as an effective bandwidth below −10 dB of as wide as 6.0 GHz from 12 to 18 GHz.

Previous researches on various morphologies of microwave absorbers proved that the size or geometrical morphology of one microwave absorber plays a key role in its microwave absorption properties [37]. One-dimensional (1D) or quasione-dimensional (Q1D) nanostructures can be potentially used for efficient absorbers due to their typical shape anisotropy and dissipation effects for electrons and phonons scattered by the periodical boundary conditions within these nanostructures [13,38]. To date, many spinel ferrites with 1D or Q1D structural feature have been prepared and used as microwave absorbing materials [25,39,40]. Also, among a variety of nanocomposite absorbers, magnetic carbon hybrid NFs have attracted considerable attention because of their lightweight and good microwave absorption properties [41,42]. However, to the best of our knowledge, there has been no related report about the microwave absorbing performance and impedance matching characteristics of double-layer absorbers based on 1D or Q1D spinel ferrite and magnetic carbon hybrid nanocomposites so far. In present work, we have synthesized $Ni_{0.8}Co_{0.2}Fe_2O_4$ nanofibers (NCFO NFs) and Ni-C hybrid NFs through a simple electrospinning process combined with subsequent heat treatment and proposed a novel double-layer microwave absorber based on these two types of NFs. EM characteristics and microwave absorption properties of the double-layer absorbers and the corresponding single-layer ones were systematically investigated in the frequency range of 2–18 GHz. Moreover, the mechanism of enhancement of microwave absorbing performance for the double-layer absorbers has also been discussed in detail.

2. Experimental

2.1. Preparation of NCFO NFs

NCFO NFs were prepared by using sol-gel assisted electrospinning technique which was basically described in our previous work [40]. Briefly, 1.2 g of polyvinylpyrrolidone (PVP, Mw = 1,300,000, Aldrich) was firstly dissolved in a mixed solvent containing 9.12 g of absolute ethanol and 6.08 g of deionized water by magnetically stirring for 1 h at room temperature. Thereafter, 2.7305 g of $Fe(NO_3)_3 \cdot 9H_2O$ (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) 0.1968 g of $Co(NO_3)_2 \cdot 6H_2O$ (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) and 0.6727 g of $Ni(CH_3COO)_2 \cdot 4H_2O$ (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) were added into the above solution and continuously stirred for approximately 6 h at room temperature to form a homogeneous and transparent spinning solution. The electrospinning process was performed on a TL-01 electrospinning apparatus (Shenzhen Tongli Micro/Nano Technology Co., Ltd.) with an applied voltage of 15 kV, a solution feeding rate of 0.5 mL h^{-1} and a receiving distance of 15.0 cm between the needle tip and the collector. Finally, the collected precursor NFs were calcined in air at 800 °C for 2 h with a heating rate of 3 °C/min to yield NCFO NFs with the desired chemical composition.

2.2. Preparation of Ni-C hybrid NFs

The procedure for preparing Ni-C hybrid NFs is similar to that described previously [41]. First, 0.7 g of Polyacrylonitrile (PAN, Mw = 150,000, Aldrich) was dissolved in 8.8 g of *N,N*-dimethylformamide (DMF) by magnetic stirring in a water bath at 50 °C for 2 h. Subsequently, 0.5 g of nickel acetylacetonate (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) was added into the above PAN/DMF solution and continuously stirred for about 12 h at room temperature. The obtained solution was electrospun by using a TL-01 electrospinning machine under the conditions of 15 kV DC voltage, 20 cm receiving distance and 0.5 mL h^{-1} feeding rate. After the spinning process was completed, the collected precursor NFs were stabilized in air at 240 °C for 3 h with a heating rate of 2 °C/min, followed by carbonization at 1000 °C for 1 h with a heating