Journal of Alloys and Compounds 712 (2017) 59–68

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis of sandwich microstructured expanded graphite/barium ferrite connected with carbon nanotube composite and its electromagnetic wave absorbing properties

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ARTICLE INFO

Article history:
Received 25 January 2017
Received in revised form
29 March 2017
Accepted 7 April 2017
Available online 8 April 2017

Keywords:
Expanded graphite
$BaFe_{12}O_{19}$
Carbon nanotube
Sol-gel auto-combustion
Sandwich microstructure
Electromagnetic wave absorbing property

ABSTRACT

The pursuing aim of high reflection loss and broad frequency bandwidth for electromagnetic wave (EMW) absorbing materials is a long-term task and under a close scrutiny. To construct rational microstructures for the absorber have significant impacts on increasing reflection loss and broadening frequency bandwidth. Herein, we presented a sandwich microstructured expand graphite (EG)/$BaFe_{12}O_{19}$ (BF) nanocomposite successfully prepared by *in-situ* sol-gel auto-combustion method. The experimental results showed that EG/BF nanocomposite has better EMW absorbing performance than pure EG and BF, the sandwich microstructured EG/BF connected with carbon nanotubes (CNTs) could further improve the electromagnetic performance effectively. The obtained CNT/EG/BF nanocomposite exhibited a saturation magnetization of 26.5 emu g^{-1} at room temperature and an excellent EMW absorbing performance. The maximum reflection loss of the sandwich microstructured CNT/EG/BF composites with a thickness of 1 mm was up to −45.8 dB and the frequency bandwidth below −10 dB could reach to 4.2 GHz within the frequency range of 2–18 GHz. The research results indicated that the prepared nanocomposite showed great potential as a new type of microwave absorbing material.

1. Introduction

Electromagnetic wave (EMW) absorbing materials have attracted great technical and scientific interests due to their extensive applications in military, civilian areas and so on. With the development of radar technology, stealth aircraft, armor and warship show a strong viability and the invisibility of military equipment puts forward higher requirements on the microwave absorbing materials [1,2]. In addition, in recent years people have witnessed the serious problem of electromagnetic interference due to the multiplication of electronic products and devices in wireless communication tools, local area networks and other communication equipments [3,4]. To solve the electromagnetic interference problem, considerable interest has been attracted to EMW absorbing materials with higher efficiency and wider bandwidth. For a high performance EMW absorbing material, excellent dielectric loss and magnetic loss are two important technical requirements [5]. Especially, carbon materials such as graphite, graphene, expanded graphite (EG), single- or multi-walled carbon nanotubes (SWCNTs, MWCNTs), carbon fibers, conducting polymers have been widely used as EMW absorbing materials due to their lightweight, high conductivity, high stability and good dielectric properties [6–9]. Metal materials such as nickel, iron, cobalt and their oxides and carbonyl iron powder have good magnetism performance and show good magnetic loss than carbon materials [10–12]. However, metal materials have disadvantages, such as heavy weight, poor corrosion resistance and oxidation resistance, which make these materials unsuitable for aircrafts, missile and some special areas. In order to obtain outstanding EMW absorbing performance, carbon and metal composites have attracted significant attention [13–16].

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http://dx.doi.org/10.1016/j.jallcom.2017.04.070
0925-8388/

EG is a kind of graphite compound with low density, large surface, anti-high temperature, oil absorption and excellent electrical conductivity, and it is easy to prepare in low cost. Generally, the graphite sheet spacing of EG is large and up to 1 μm, and it is conducive to the multiple reflection of EMW so that it could increase the EMW absorption loss [17]. EG is a traditional EMW absorbing materials and widely used as a millimeter wave absorbing material with excellent dielectric properties but low magnetic loss. EG which compounded with some magnetic loss materials, such as magnetic metal powder, ferrite material and other oxides, could improve the electromagnetic performance [18,19]. The ferrite is a mature EMW absorber, which has attractive magnetic properties, high magnetic loss, high Curie temperature, excellent chemical stability and low cost. Barium ferrite ($BaFe_{12}O_{19}$, BF) is one of the most versatile hard magnetic material, especially suitable for low-frequency applications with high magnetic coercivity, high electrical resistivity, low eddy current loss and excellent chemical stability, and it has been widely used in the field of EMW absorption [20]. Chen et al. [21] reported that EG/$CoFe_2O_4$ composite was prepared by co-precipitation method. In metal salt solution, the metal oxides are precipitated on the surface of the EG. However, this method is inefficient, and it is difficult to control the metal oxides proportion of the composite. Gairola et al. [22] studied barium ferrite/graphite/polyaniline composites as electromagnetic shielding materials. The EG and barium ferrite were prepared separately, and then EG and barium ferrite mixed in polyaniline precursor solution. The mixture was polymerized and dried to obtain barium ferrite/graphite/polyaniline composites. The method is a simple physical mixing, and the EG and barium ferrite were distributed unevenly. Nowadays, there are several methods available to synthesize $BaFe_{12}O_{19}$ including co-precipitation, ball milling, hydrothermal treatment, auto-combustion method. Typically, sol-gel auto-combustion is a simple, safe and rapid synthesis process. It has many advantages such as energy-saving and time-saving, controllable process and reactants mixed evenly. A certain proportion of metal salt solution containing organic fuel is heated to form oily gel, and the oily gel precursor burns and maintains until the reaction is complete. The process contains an exothermic and self-sustaining chemical reaction between the metal salts gel and a suitable organic fuel. The heat which is necessary to drive the process is primarily provided by the exothermic reaction. Then the product is calcined at high temperature to obtain $BaFe_{12}O_{19}$ [23,24]. Furthermore, it is worth noting that the sol-gel auto-combustion precursor of $BaFe_{12}O_{19}$ is oily gel and EG has large sheet spacing and oil absorption properties [25], which provide a way to prepare sandwich microstructured EG/BF nanocomposite. When the oily gel forms $BFe_{12}O_{19}$, the volume increases rapidly and the secondary expansion of EG would take place. However, to our knowledge, the preparation and EMW absorbing properties of the sandwich microstructured EG/BF nanocomposite has not been reported previously.

Herein, the sandwich microstructured EG/BF nanocomposite was successfully prepared through *in-situ* sol-gel auto-combustion method. The EG/BF nnaocomposite significantly enhanced EMW absorbing performance compared to pure EG and pure $BaFe_{12}O_{19}$. To obtain excellent EMW absorbing performance, CNTs were added to the sandwich microstructured EG/BF nanocomposite to improve its dielectric constant. The addition of CNTs made the separated sandwich EG/BF interconnected and formed a three-dimensional conductive network, and it was benefit to electrical conductivity of the nanocomposite and increase dielectric performance [26,27].

2. Experimental section

2.1. Preparation of EG

EG was prepared through the rapid expansion of natural flake graphite intercalated compound at 800 °C. First, the natural flake graphite which was mixed with the mixture of H_2SO_4 and HNO_3 was stirred at room temperature for 1 h. Then added $KMnO_4$ to the mixture and kept stirring for 2 h. The products were washed several times with deionized water until pH = 7 and dried them in a vacuum oven to form graphite intercalated compound. Final, the graphite intercalated compound was rapidly expanded at 800 °C to obtain EG Ref. [28]. The oxygen-containing groups intercalated between graphite sheet layers instantly decomposed into gas at high temperatures, and the spacing of graphite sheet layers and atomic layers were expanded.

2.2. *In-situ* synthesis of sandwich microstructured EG/BFand CNT/EG/BF nnaocomposite

The sandwich microstructured EG/BF nanocomposites were synthesized by *in-situ* sol-gel auto-combustion method and the schematic diagram is shown in Fig. 1. A certain amount of $Fe(NO)_3 \cdot 9H_2O$ and $Ba(NO)_2$ and citric acid were used as raw materials. First, $Fe(NO)_3 \cdot 9H_2O$ and $Ba(NO)_2$ were dissolved in deionized water and the mole ratio of Fe^{3+} to Ba^{2+} is 12:1. The citric acid was dissolved into the aqueous solution, and then mixed with the nitrate solution acquired above. The mole ratio of citric acid to total

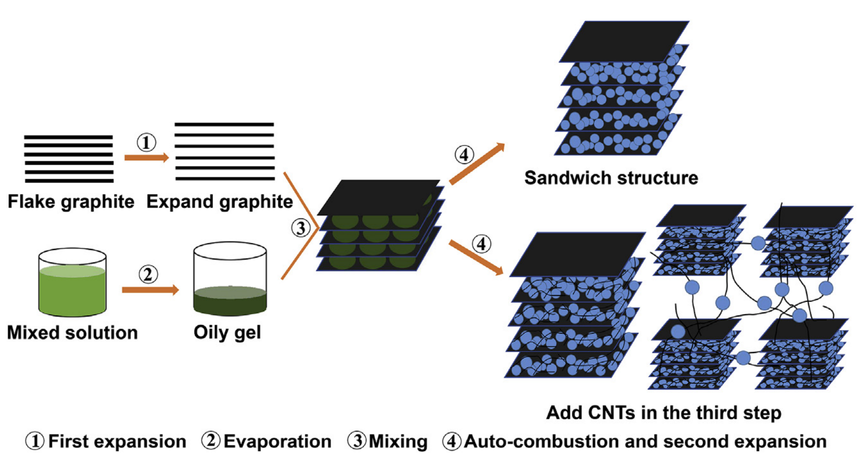

Fig. 1. The synthesis schematic diagram of sandwich microstructured EG/BF and CNT/EG/BF nanocomposite.