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Constructing flower-like porous $Bi_{0.9}La_{0.1}FeO_3$ microspheres for excellent electromagnetic wave absorption performances

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ABSTRACT

Uniform flower-like porous $Bi_{0.9}La_{0.1}FeO_3$ microspheres etched for 30, 60 and 90 min (named as pBLFO-30, pBLFO-60 and pBLFO-90, respectively) have been successfully constructed by a facile chemical etching process based on $Bi_{0.9}La_{0.1}FeO_3$ particles (BLFO) as precursors. In particular, Sample pBLFO-60 has the largest specific surface area of 75.09 m^2 g^{-1}, which leads to the most outstanding electromagnetic wave attenuation performance. The optimal reflection loss (RL) value reaches −57.9 dB when the matching thickness is 2.9 mm at 6.9 GHz and the effective absorption bandwidth (RL < −10 dB) is 2.7 GHz (6.1−8.9 GHz). The three-dimensional porous architecture and enhanced magnetic loss make great contribution to the electromagnetic wave absorption performance, among which the porous microstructure ensures multiple scattering and enhances the magnetic loss contributing to better impedance matching. Meanwhile, the electromagnetic wave absorption performance of porous BLFO microspheres are superior to those of most porous electromagnetic wave absorbers, implying their potential application as novel electromagnetic wave absorbing materials.

1. Introduction

Recently, porous or hollow microstructures with large surface area and adjustable pore size have drawn tremendous attention in various aspects such as catalysis [1,2], supercapacitors [3,4], battery anodes [5] and electromagnetic wave absorption materials [6–8] owing to the unique structure with numerous pores. Notably, electromagnetic (EM) wave absorption materials have been urgently required to eliminate the expanded EM wave that could interrupt the normal operation of electronic equipment as well as pose a threat to human health [9–11]. Thus, it is imperative to explore ideal EM wave absorption materials, which possess strong absorption performance, broad absorption bandwidth, and more importantly, light weight and thin coating thickness [12–15].

Varieties of absorbing materials have been exploited, which present the potential application in the EM wave absorption field. As traditional EM wave absorption materials, Fe_3O_4, Fe_2O_3 and other magnetic metal materials exhibit excellent EM wave absorption performance [16,17]. Especially for ferrites, magnetic materials are demonstrated to have both strong EM wave absorption performance and broad absorption frequency bandwidth by virtue of their large magnetic permeability [18,19]. Nonetheless, most of magnetic materials have large densities, which hinders their practical application.

It is well known that the microstructures of absorbers play a key role in the EM wave absorption performance [20,21]. The porous or hollow structured materials with light weight are supposed to be a hopeful candidate for EM wave absorption performance [22–28]. Zhou et al. reported a new strategy of in-situ polymerization to prepare ordered mesoporous carbon and the maximum RL value was −27 dB with the matching thickness of 2 mm [24]. Sun et al. fabricated the porous Fe_3O_4@ZnO sphere decorated graphene with uniform pore size and the minimal RL value could reach almost −40 dB with a broad absorption bandwidth up to −11.4 GHz [25]. Zhao et al. synthesized 3D honeycomb-like SnO_2 foams by using 322 nm polystyrene spheres as sacrificial template and the optimal RL was −37.6 dB with an absorber thickness of 2 mm [26]. Yang et al. designed silica coated mesoporous Fe (Fe@SiO_2) microcubes and the RL value of −54 dB could be obtained at a matching thickness of 4.5 mm, in which the mesoporous iron microcubes reduced the thickness of silica resin composites [27]. Xu et al. prepared mesoporous carbon hollow microspheres with designable mesoporous shell (pore size 4.7 nm) and interior void by a facile in-situ stöber templating approach and a polysis-etching

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process and the composite exhibited outstanding EM wave absorption performance [28]. Therefore, it can be concluded that the mesoporous or hollow microstructures are conducive to the EM wave absorption performance based on the reported work.

In this work, porous BLFO microspheres with light weight can be synthesized by utilizing BLFO particles obtained from a molten-salt approach as precursors and subsequently a facile chemical etching process. The ferric (III) of partial BLFO crystals are reduced to the ferric (II) with the action of hydrazine and the ferric (II) subsequently coordinated with methyl mercaptoacetate to construct flower-like porous BLFO microspheres. The evolution of microstructures in BLFO can be easily controlled by adjusting the etching time. Remarkably, the porosity and specific surface area of porous BLFO microspheres are enhanced significantly. A succession of gradient experiments related to etching times were also performed. Particularly, Sample pBLFO-60 exhibits the most superior EM wave absorption property, in which the optimal RL value reaches −57.9 dB at 6.9 GHz with an absorber thickness of 2.9 mm and the effective absorption bandwidth is 2.7 GHz, ranging from 6.1 GHz to 8.9 GHz. The given merits of porous BLFO microspheres, such as strong absorption, broad responding bandwidth, easy preparation and fairly low density, can bring them a promising prospect in the EM wave absorption field.

2. Experimental

Reagents including Bi_2O_3, La_2O_3, Fe_2O_3 (starting materials) and NaCl-KCl (molten salts system) were purchased from Sinopharm Group. DimethyFormamide (DMF), hydrazine (a reducing agent) and methyl mercaptoacetate (a complexing agent) were also obtained from Sinopharm Group. All the chemicals were of analytical grade.

BLFO particles were synthesized via a molten salt method. Bi_2O_3, La_2O_3, Fe_2O_3 and NaCl-KCl were mixed, with a molar ratio of [Bi]/[La] = 9:1 and a molar ratio of BLFO/NaCl-KCl = 1:10. The mixture was ground in ethanol for 4 h. The mixture was transferred to a crucible after drying, and then loaded into a furnace. The phase of BLFO can be obtained after heating the mixture at 750 °C for 2 h and washing the mixture several times with deionized water to remove the NaCl-KCl salt.

Porous BLFO microspheres were prepared via a one-step etching method. A certain amount of BLFO particles were dispersed ultrasonically into a solution of DMF, heated in a water-bath at 80 °C, and hydrazine and methyl mercaptoacetate were then added. $N_2$was used to prevent the reaction between methyl mercaptoacetate and O_2. The reaction was terminated by cold ethanol after etching for different times (30, 60, 90 min). The black powders were ultimately obtained after washing by deionized water and ethanol five times and drying in vacuum for 12 h.

The phase structure of all the samples was identified by an X-ray diffractometer with Cu-Kα radiation (Rigaku D/MAX-2400, Japan). Raman spectra were collected using a microscopic Laser-Raman spectrometer (Renishaw-invia, England) with a 514 nm radiation. The morphological characterizations of all the samples were obtained using scanning electron microscopy (Hitachi S-4800, Japan) and transmission electron microscope (FEI Tecnai G2 F20, America). The surface areas of porous BLFO microspheres were determined using a Brunauer-Emmett-Teller (BET) surface analyzer (ASAP2460, Micromeritics Instrument Corp, USA) and the pore size distribution was estimated according to Horvaih-Kawazoe (HK) theory. X-ray photoelectron spectroscopy (XPS, recorded on an AXIS SUPRA X-ray photoelectron spectrometer, UK) spectra were measured by using an ultrahigh vacuum VG Scientific Corp MK-II electron spectrometer. The magnetic hysteresis loops of porous BLFO microspheres were measured by a vibrating sample magnetometer (VSM, Lake Shore 7410, USA).

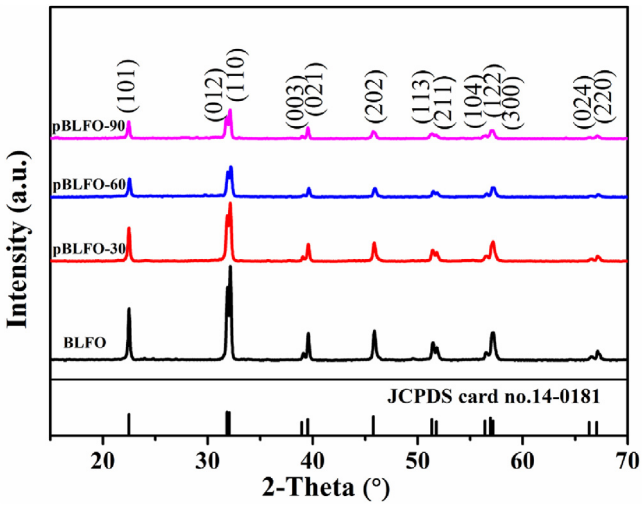

Fig. 1. XRD patterns of BLFO particles prepared by molten salt method and porous BLFO microspheres etched for different times.

The EM wave absorption performances of the obtained absorbers were also investigated. The paraffin was selected as the matrix and the mixture of paraffin and 60 vol% porous BLFO microspheres were heated, mixed and then molded into rings, with an outer diameter of 7 mm, an inner diameter of 3 mm and a height of about 3 mm for EM measurement. The complex permittivity (ε', ε'') and permeability (μ', μ'') were tested with the system composed of a vector network analyzer (VNA) (HP8720ES) and a coaxial fixture.

3. Results and discussion

The XRD patterns of all the samples are shown in Fig. 1. It is found that the as-prepared BLFO synthesized by the molten salt route are highly crystallized as a single phase and no other phases such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ could be detected, which is in agreement with JCPDS card No.14-0181, pertaining to the composition of $Bi_{0.93}La_{0.07}FeO_3$. Meanwhile, the calculated lattice parameters of BLFO are a = b = 5.58 Å and c = 13.81 Å, which coincides with the literature result [29]. The XRD patterns of porous BLFO

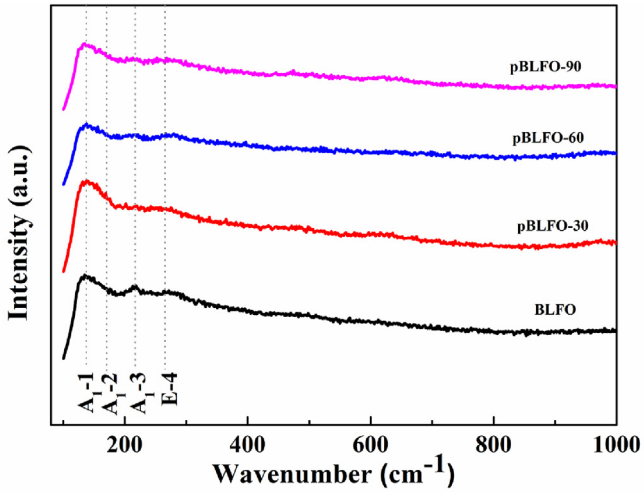

Fig. 2. Raman spectra of BLFO particles and porous BLFO microspheres with different etching times.