Materials Research Bulletin 51 (2014) 277–286

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Nano-scale and micron-scale manganese dioxide vs corresponding paraffin composites for electromagnetic interference shielding and microwave absorption

Wei-Li Song [a,b], Mao-Sheng Cao [b,*], Bei-Bei Qiao [b], Zhi-Ling Hou [b,c], Ming-Ming Lu [b], Chan-Yuan Wang [d], Jie Yuan [b], Dong-Ni Liu [e], Li-Zhen Fan [a,*]

[a] Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, PR China
[b] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, PR China
[c] School of Science, Beijing University of Chemical Technology, Beijing 100029, PR China
[d] 310 Department, 3rd Institution of China Aerospace Science & Industry, Beijing 100071, PR China
[e] The First Research Institute of Ministry of Public Security, Beijing 100048, PR China

ARTICLE INFO

Article history:
Received 18 August 2013
Received in revised form 15 November 2013
Accepted 16 December 2013
Available online 25 December 2013

Keywords:
A. Composites
A. Oxides
A. Nanostructures
D. Dielectric properties
D. Electrical properties

ABSTRACT

The hydrothermal method was utilized to synthesize beta-manganese dioxide (β-MnO_2) nanorods. Both the neat bulk samples fabricated from the nano-scale β-MnO_2 rods and commercial micron-scale β-MnO_2 particles exhibited similar performance in permittivity, electromagnetic interference shielding and microwave absorption. The wax-based composites embedded with the as-prepared β-MnO_2 nanorods exhibited greater differences in permittivity, electromagnetic interference shielding and microwave absorption, compared to those embedded with the commercial micron-scale MnO_2 particles. The results suggest that neat MnO_2 materials are effective in electromagnetic interference shielding and the composites with β-MnO_2 nanorods present the highest microwave absorption. Electrical conductivity coupled with size effects was considered as the most significant roles in the variations of permittivity, electromagnetic interference shielding and microwave absorption. The related mechanism associated with reflection and absorption has been discussed. The results have provided potential strategies for designing and achieving high-performance electromagnetic interference shielding and microwave absorbing materials.

1. Introduction

Signal interference is one of emerging issues since the advanced progresses have been achieved in current development of electronic and communication technology. Among various solutions, the employment of electromagnetic interference (EMI) shielding materials have caught increasing attention due to their effectiveness in blocking and diminishing interference signals to maintain the stable operation in electronic devices [1–5]. On the other hand, microwave absorbing materials, also known as stealth materials, have also aroused great interesting in the scientific community for their capability in microwave attenuation, and thus have been widely used for signal attenuation and certain communication purposes [6–8].

Recently, polymeric composites with conductive carbonic fillers have been pursued in EMI shielding based on their potentials in electromagnetic absorption and reflection [3–5,9,10]. For example, polymeric composites filled with carbon nanotubes have been found to exhibit superior EMI shielding performance because of their good electrical properties [3–5]. Currently, carbon nanosheets, achieved from exfoliated graphene and reduced graphene oxides, also presented highly effective EMI shielding in the corresponding polymer matrices [9,10]. On the other hand, a variety of explorations have shown that the composites with conductive carbon nanomaterials also exhibited promising performance in microwave absorption [11–14]. For instant, the work by Chen and coworkers have found strong microwave absorption peak in the polyurethane composites embedded with carbon nanotubes [11]. Polymeric composites filled with chemically reduced graphene oxides have also possessed high microwave absorbing capacity due to the unique structure of graphene nanosheets in microwave dissipations and scatterings [12]. Su and coworkers have synthesized Fe-doped SiC powders for studying

* Corresponding authors. Tel.: +86 10 6891 4062; fax: +86 10 6891 4062.
E-mail addresses: caomaosheng@bit.edu.cn (M.-S. Cao), fanlizhen@ustb.edu.cn (L.-Z. Fan).

0025-5408/$ – see front matter.
http://dx.doi.org/10.1016/j.materresbull.2013.12.042

microwave absorption, and the results exhibited highly effective absorption in the investigated region [13].

In addition to the mostly focused carbonic fillers, semiconductive metal compounds have also received emerging concerns [15–18]. Wang and coworkers have prepared CuS nanostructure/poly(vinylidene fluoride) composites, which exhibited effective microwave absorption due to the synergetic effects of the matrices and fillers [15,16]. Duan and coworkers have reported the size effect of FeSi on the microwave absorption of the paraffin wax composites, suggesting that the FeSi particles with smaller size could possess high microwave absorption [17]. Zhang and coworkers have synthesized ZnO micro/nanorod networks, and the as-obtained networks showed a maximum peak up to 37 dB [18]. Recently, manganese dioxides, typical narrow band gap semiconductors (1.3 eV for α-morphology, 0.26 eV for β-morphology and 0.58–0.7 eV for γ-morphology), have attracted typical attention as effective absorbers in microwave absorption [19–21]. Duan and coworkers demonstrated that the α-MnO_2/carbon black composites exhibited wide microwave absorbing properties [19]. Yan and coworkers have studied the microwave absorption of the wax composites filled with manganese oxides with different crystalline phases [20]. Similarly, Wang and coworkers have fabricated MnO_2 of different crystalline phases into wax to evaluate microwave absorption performance [21]. These results suggested promising microwave absorption in the as-achieved wax-composites. On the other hand, as aforementioned, the materials with relatively good electrical properties, such as metals, conducting polymers and conductive carbon-based materials are generally considered as the effective EMI shielding materials [1]. However, very rare work has reported an individual semiconductor as an effective material for EMI shielding, which is mainly due to their unsatisfied electrical properties. Therefore, intrinsic properties based on the narrow band gap in the beta-MnO_2 may afford effective shielding capacitance.

Furthermore, little literature has reported the relation between EMI shielding and microwave absorption although similar parameters and mechanism in both EMI shielding and microwave absorption could be considered [22,23]. According to the results from EMI shielding and microwave absorbing materials, excellent EMI shielding requires sufficient electrons in the materials [1,2,5]. However, high-performance microwave absorption requires the absorbers to possess moderate electrical conductivity so that electromagnetic waves could largely travel into the absorbing layers to achieve optimal attenuation for electromagnetic energy [23–25]. Apparently, there is still lacking of fundamental understanding on the relationship between microwave absorption and EMI shielding, typically on the rational design of high-performance microwave-absorption materials.

In this work, we have selected β-MnO_2 (E_g = 0.26 eV) for the effective materials in both EMI shielding and microwave absorption. For comparison, nano-scale and micron-scale β-MnO_2 have been employed to investigate the performance differences between their neat bulk materials and corresponding wax-based composites for EMI shielding and microwave absorption separately. Discussion mainly based on the electrical properties has been made to clarify the fundamental mechanism and relationship of EMI shielding and microwave absorption.

2. Experimental

2.1. Materials

Analytical grade manganese sulfate monohydrate, ammonium persulfate powders and commercial manganese dioxide powders were purchased from Beijing Chemical Factory. Paraffin wax was from Shanghai Hualing Mechanical Factory. Ether was provided by Tianjin Tianda Chemical Reagent. Holey carbon-coated copper grids for electron microscopy were from Beijing High-Technology Company. All the chemicals were used without further treatment.

2.2. Measurements

X-ray powder diffraction (XRD) characterizations were applied on an X?Pert PRO system (Cu-Kα). Scanning electron microscopy (SEM) images were achieved on a Hitachi S-4300 field-emission SEM system. Transmission electron microscopy (TEM) images were performed on a JEM-2100 TEM system, coupled with the use of holey carbon-coated copper grids. *S* parameters and complex permittivity were measured on an Anritsu 37269D vector network analyzer (VNA).

2.3. Nanorod preparation

The β-MnO_2 nanorods were prepared by a hydrothermal method with the procedure in our previous work [26]. In a typical preparation, the as-received manganese sulfate monohydrate (8 mmol) and ammonium persulfate (8 mmol) powders were dissolved in de-ionized water (40 ml) under strong stirring to obtain clear aqueous solution. The resulting solution was transferred into a Teflon lined stainless steel autoclave (50 ml). The hydrothermal process was carried out at 140 °C for 12 h. After cooling to temperature, the dark products were rinsed with de-ionized water via centrifuge for several times. The as-precipitated powders were dried in a vacuum oven at 80 °C.

2.4. Testing samples

For preparing neat MnO_2 samples, the as-prepared MnO_2 powders were directly compacted into a sheet with rectangle shape of 22.86 mm × 10.16 mm at a thickness of ~2 mm under 20 MPa. For comparison, the commercial MnO_2 powders were treated by the same process. The *S* parameters and complex permittivity of the as-prepared neat MnO_2 samples were obtained on the VNA with the wave guide method in the frequency range of 8.2–12.4 GHz. In this work, the bulk samples with neat commercial micron-scale MnO_2 and the bulk samples with neat as-prepared β-MnO_2 nanorods were assigned as C-MnO_2 and nano-MnO_2, respectively.

For preparing MnO_2 composite samples, the as-prepared MnO_2 powders (30 wt%) and paraffin wax (70 wt%) were dispersed in an ether solution under vigorous stirring. After the ether was completely evaporated, a portion of the dried mixtures were compacted into a toroidal shape (Φ_{out}, 7.03 mm; Φ_{in}, 3.00 mm) with a thickness of ~2 mm. Similarly, the commercial MnO_2/wax composite samples with 30 wt% MnO_2 loading were fabricated. The *S* parameters and complex permittivity of the as-prepared composite samples were obtained on the VNA with the coaxial method in the frequency of 2–18 GHz. In this work, the resulting wax composites filled with 30 wt% MnO_2 nanorods and the ones with 30 wt% commercial MnO_2 were nominated as MnO_2 nanorods/wax and commercial MnO_2/wax, respectively.

3. Results and discussion

3.1. Characterizations

Fig. 1a demonstrates the XRD patterns of both commercial powders and as-prepared products. The as-prepared products from hydrothermal process were identified to be a pure β-MnO_2 phase (JCPDS no. 24-0735, tetragonal, a = 0.439 nm, c = 0.287 nm). Similar patterns were observed in the commercial powders, also identified to be a β-MnO_2 phase. SEM images suggested that the