Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Composites Science and Technology 66 (2006) 2003–2008
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

Synthesis, magnetic and microwave absorbing properties of core-shell structured $MnFe_2O_4/TiO_2$ nanocomposites

Hong-Mei Xiao [a,b], Xian-Ming Liu [a,b], Shao-Yun Fu [a,*]

[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China*
[b] *Graduate School, Chinese Academy of Sciences, Beijing 100039, PR China*

Received 23 August 2005; received in revised form 27 December 2005; accepted 10 January 2006
Available online 17 February 2006

Abstract

The core-shell $MnFe_2O_4$–TiO_2 nano-composites were prepared by hydrolysis of titanium butoxide precursor in the presence of $MnFe_2O_4$ nanoparticles that were synthesized via the pyrolysis of polyacrylate salt precursor prepared by in situ polymerization of the metal salts and acrylate acid. The magnetic properties of the $MnFe_2O_4$ and $MnFe_2O_4$–TiO_2 composites measured at the maximum magnetic field of 10 kOe and room temperature exhibited a super-paramagnetic behavior. The complex permittivity and permeability of $MnFe_2O_4$ and $MnFe_2O_4$–TiO_2 composites measured in the microwave frequency range of 2–10 GHz showed that the microwave absorption properties of the $MnFe_2O_4$–TiO_2 composites were higher than that of $MnFe_2O_4$.

Keywords: Manganese ferrite; Titanium dioxide; Nanocomposites; Microwave absorbing property; Magnetic property

1. Introduction

Much attention has been paid to microwave absorption materials due to their unique absorbing microwave energy and promising applications in the stealth technology of aircraft, television image interference of high-rise buildings, and microwave dark-room and protection [1–3]. Extensive study has been carried out to develop new microwave absorbing materials with a high magnetic and electric loss [4–9]. To our knowledge, ferrites might be a candidate as the microwave absorbing materials because of their high specific resistance, remarkable flexibility in tailoring the magnetic properties and ease of preparation [2]. In the past decades, the spinel ferrites have been utilized as the most frequent absorbing materials in various forms [3]. Manganese ferrite ($MnFe_2O_4$) is a common spinel ferrite material and has been widely used in microwave and magnetic recording applications [10]. Recently, it has been shown that magnetic nano-composites are useful as microwave absorbing materials due to their advantages in respect to light weight, low cost, design flexibility, and microwave properties over pure ferrites [8,11].

On the other hand, titanium dioxide (TiO_2) is an important inorganic semiconductor and has temperature and environmentally stable dielectric properties [12]. A series of papers dealing with application for the magnetic composites containing TiO_2 nanoparticles have been reported [13–29]. Nonetheless, up to now, most research work has only been focused on the TiO_2-based composites' application for magnetic photo-catalysts [13–23]. There are few articles concerning the microwave absorbing properties of TiO_2-based composites. Soitoh et al. and Ueda et al. reported the mixture of carbonyl iron (FeOH) and TiO_2 in hypolan (chlorosulfonated polyethylene) as the microwave absorber [28,29]. To our best knowledge, the core-shell structured electro-magnetic functional composites are promising as new microwave absorbing materials. However, as we know, no work has been reported on the microwave absorbing properties of core-shell structured TiO_2-based magnetic composites.

* Corresponding author. Tel.: +86 10 62626152; fax: +86 10 62569040.
E-mail addresses: syfu@cl.cryo.ac.cn, syfu@mail.ipc.ac.cn (S.-Y. Fu).

0266-3538/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2006.01.001

Recently, syntheses of ferrite nanoparticles by the thermal decomposition reaction are of great interest in the study and tailoring of specific magnetic properties. Gabal and Ata-Allah [30] synthesized manganese ferrites through the thermal decomposition reaction taking place between the solid-state oxalate mixture of $MnC_2O_4 \cdot 2H_2O$–$FeC_2O_4 \cdot 2H_2O$ in air. However, when the annealing temperature was lower than 1100 °C, there existed impurities such as α-Fe_2O_3 and Mn_2O_3. Compared to the reported methods, there are two advantages of the thermal decomposition of the polyacrylate precursors [31]. It can provide high product yield and highly homogeneous nanocrystalline spinel ferrites at medium calcination temperature.

In this article, the core-shell structured $MnFe_2O_4$–TiO_2 nano-composites were prepared by hydrolysis of titanium butoxide precursor in the presence of $MnFe_2O_4$ nanoparticles in a mixed organic solvent, where $MnFe_2O_4$ was synthesized via the pyrolysis of polyacrylate salt precursors prepared by in situ polymerization of the metal salts and acrylate acid. The crystal structure, magnetic properties of the composites were measured and compared with that of the $MnFe_2O_4$ nanoparticles. The effect of the content of the TiO_2 on the complex permittivity and permeability of the nano-composites at 2–10 GHz frequency have been investigated.

2. Experimental

The chemical reagents, including $Mn(CH_3COO)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, acrylic acid, $(NH_4)_2S_2O_8$, cetyltrimethylammonium bromide (CTAB), titanium tetrabutyloxide, *n*-butanol and ethanol are of analytical grade and were used without further purification.

2.1. Preparation of $MnFe_2O_4$ nanoparticles

Nanocrystalline $MnFe_2O_4$ powders were prepared by a polymer-pyrolysis method using polyacrylates of Mn and Fe as precursor compounds. Measured amounts of $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (molar ratio of Mn:Fe = 1:2) were dissolved in 10 g of acrylic acid aqueous solution (acrylic acid:H_2O = 70:30 wt%) under stirring. Then, a small amount (0.5 g) of 5% $(NH_4)_2S_2O_8$ aqueous solution as the initiator was added to the mixed acrylic acid solution to promote the polymerization. Under heating at 70–90 °C for 2 h, the mixed solution was dried to form the well-distributed polyacrylates of Mn and Fe. After the resulting polyacrylates were dried at 100 °C for 24 h, and calcined at 500 °C for 2 h in air, the $MnFe_2O_4$ nanoparticles were obtained after being slowly cooled to room temperature.

2.2. Preparation of $MnFe_2O_4$–TiO_2 nano-composites

The whole experiment was operated in an ultrasonic pool (100 W, 50 Hz). Titania was coated on $MnFe_2O_4$ nanoparticles by hydrolysis of titanium butoxide precursor. In one experiment, 0.15 g of as-synthesized $MnFe_2O_4$ nanoparticles and 0.15 g of cetyltrimethylammonium bromide (CTAB) were dispersed into 135 mL of *n*-butanol and anhydrous ethanol (8:1 in volume) solution. After sonication for 30 min, a few of drops of nitric acid–water solution (2 wt%) were added to the mixture. Then, 0.12 M titanium tetrabutyloxide in anhydrous ethanol was added by drop-wise into the mixture at room temperature with controlled rhythm. The weight contents of TiO_2 in the composites were 10%, 20%, 50% and 100%, respectively. After the drop-wise addition was over, the reaction mixture was irradiated with ultrasound and the temperature of the reaction mixture rose to 75 °C. This experiment went along for 4 h. The resulting nanoparticles were separated centrifugally. The supernatant was discarded, and the precipitate was washed repeatedly with anhydrous ethanol. Then the precipitate was dried at 100 °C for 24 h in air. The titania-coated $MnFe_2O_4$ nano-composites were obtained after being calcined at 500 °C for 2 h in air.

2.3. Characterization

The dried samples (i.e. $MnFe_2O_4$ and $MnFe_2O_4$–TiO_2 composites) were analyzed for their composition, microstructure, magnetic and microwave properties.

The scanning electron microscopy (SEM) images and EDX were obtained using a HITACHI S-4300 microscope and EMAX Horiba, respectively. XRD analysis was carried out on a Rigaku D/max2500 diffractometer at a voltage of 40 kV and a current of 200 mA with Cu Kα radiation ($\lambda = 1.5406$ Å), employing a scanning rate of $0.02° \ s^{-1}$ in the 2θ ranging from 5 to 70 °C. TEM images and the electron diffraction (ED) patterns were recorded on a Hitachi-600 transmission electron microscope (TEM) at an accelerating voltage of 20 kV. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA) with a maximum magnetic field of 10 kOe.

The samples for measuring microwave properties were prepared by dispersing the $MnFe_2O_4$ and $MnFe_2O_4$–TiO_2 composites powders in paraffin wax, respectively. The volume fraction of the powders is 60%. The powder-wax composites were die-pressed to form cylindrical toroidal specimens with 7.0 mm outer diameter, 3.0 mm inner diameter, and 2 mm thickness. The measurements of complex permittivity, ε, and permeability, μ, for the specimens were carried out using an Agilent E8363B vector network analyzer in the 2–10 GHz ranges.

3. Results and discussion

3.1. Morphology and crystal structures

The panoramic morphology of the representative $MnFe_2O_4$–TiO_2 nano-composite (20%TiO_2) was obtained by SEM as shown in Fig. 1(a), in which the solid sample was mounted on conductive resin with dispersion