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Preparation and microwave adsorption properties of core–shell structured barium titanate/polyaniline composite

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ABSTRACT

Nano-$BaTiO_3$ particles were prepared by the sol–gel method. The core–shell structured $BaTiO_3$/polyaniline (PANI) composites were synthesized by in-situ polymerization with as-prepared $BaTiO_3$ nano-particles. The structural, morphology and microwave adsorption properties of the obtained composites were investigated in detail by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and vector network analyzer. The average particle size of the $BaTiO_3$ nanoparticles was measured to be 60 nm and the thickness of shell was 40 nm. The complex permittivity, permeability and reflection loss of the composites were measured at different microwave frequencies in 0–6000 MHz. The effect of the mass ratio of $BaTiO_3$/PANI on the microwave loss properties of the composites was investigated. For the sample obtained by the mass ratio of $BaTiO_3$ to PANI of 4:1, the value of reflection loss peaks is up to −14.5 dB. The width of the −5 and −10 dB is up to 1200 and 750 MHz, respectively. This reveals that the $BaTiO_3$ nanoparticles in the polyaniline matrix affect the microwave absorption properties of the nanocomposites.

1. Introduction

The microwave absorbing materials have been much considered due to the facts that they can absorb energy from microwave and be widely used in the stealth technology of aircraft, television image interference of the tall buildings, and microwave dark-room as well as electromagnetic interference (EMI) [1]. They may be classified as magnetic or dielectric. Actually, these materials have attracted a great attention due to their improved microwave absorption properties, which are relevant to multiform electromagnetic losses based on magnetic and dielectric loss [2]. Recently, The nano inorganic/polymer composite material has been receiving significant interest due to wide range of potential applications of these composites in optoelectronic devices and EMI shielding [3].

Polyaniline (PANI) is a conducting polymer that possesses great advantages, such as various configurations, excellent environmental stability, simply synthesis, easy control of conductivity by changing the oxidation and high levels of electromagnetic shielding performances at microwave frequencies with a low mass by unit of surface [4–7]. The electromagnetic properties of PANI can be modified by the addition of inorganic fillers. The inclusion of magnetic particles may improve the magnetic and dielectric properties of host materials. Therefore, polyaniline combined with magnetic particles provides materials exhibiting novel functionalities [8]. Barium titanate ($BaTiO_3$) is a lead-free ferroelectric and piezoelectric material with a perovskite structure [9]. It exhibits various electrical and magnetic properties, of which the complex permeability and the complex permittivity, in particular, are important in determining their high frequency characteristics [10]. So the hybrid of nano-$BaTiO_3$/PANI is believed to show novel properties due to the molecular level interaction between nano-$BaTiO_3$ and PANI molecular chains. Although some work on such composites has been reported in recent years [11], there seem to be no reports on the complex permittivity and reflection loss of composite absorber in S- and C-band (30–6000 MHz).

In this paper we report the synthesis of core–shell structured $BaTiO_3$/PANI composite. The structure and the morphology of the samples were investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR), and transmission electron microscopy (TEM). The influence of the compound proportion with respect to the microwave adsorption properties of the composites has been investigated. Complex permittivity and permeability of the composites were studied in the 0–6000 MHz using vector network analyzer (PNA).

2. Experimental

2.1. Synthesis of nano-particles

$BaTiO_3$ nano-particles were prepared by the sol–gel method. Some amount of tetrabutyl titanate (the mass ratio of Ti to Ba was

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1:1) was dissolved in the mixture of anhydrous ethanol and acetic acid, which was added into barium acetate (1.2 mol L^{-1}). The entire mixture was stirred at 40 °C for 1 h, and then dried at 80 °C for 5 h. Then the above dried gel was heated in an oven in air atmosphere at 800 °C for 2 h to obtain $BaTiO_3$ nano-particles.

2.2. Synthesis of composite

The core–shell composite of $BaTiO_3$/PANI was prepared by in-situ polymerization. The nano-particles $BaTiO_3$ were dispersed in distilled water, which was added to alcohol–water solution with 1% silane coupling reagent KH 570 for only once, and vigorously stirred in ice–water bath for 0.5 h, producing a fine aqueous dispersion. The subsequent addition (one drop per ten seconds) of aniline and 0.1 mol L^{-1} HCl (volume ratio of aniline:HCl was 1:1) into the $BaTiO_3$–silane coupling reagent–water dispersion was done at room temperature. Then the above mixture was stirred for 0.5 h and cooled to 0 °C with stirring. A hydrochloric acid solution of $(NH_4)_2S_2O_8$ (molar ratio of aniline: $(NH_4)_2S_2O_8$ was 1:1) was added drop wise to initiate the polymerization. The polymerization was carried out at 0 °C for 6 h, with stirring and then the core–shell composite of $BaTiO_3$/PANI was obtained. The composite was isolated by filtration, washed with 1 mol L^{-1} hydrochloric acid solution and distilled water three times and dried at 80 °C for 24 h. The possible reaction procedures in the synthesis of $BaTiO_3$/PANI composite are shown in Fig. 1.

2.3. Characterization

Fourier transform infrared (FT-IR, IR-8400S, Shim, Japan) spectrometer was used for monitoring the structure changes of the product from 400 to 4000 cm^{-1}. Phase formation of the as-synthesized product was identified by X-ray diffraction (XRD, D/max-rA, Rigaku, Japan) using Cu Kα radiation (λ=0.15418 nm) with a scanning rate 0.04°/min in the 2θ range of 5°–75°. The microstructure of the PANI and PANI/ $BaTiO_3$ particles was analyzed by transmission electron microscope (TEM, H-800, Hitachi, Japan) operated at 150 kV. The measurements of microwave adsorption properties for the specimens were carried out using vector network analyzer (PNA, Nanjing PNA Instruments, China) in the 0–6000 MHz ranges. The samples were prepared by dispersing the $BaTiO_3$/PANI 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 mm outer diameter, 3 mm inner diameter, and 3 mm thickness.

3. Results and discussions

3.1. Structure and morphology study

The XRD patterns of $BaTiO_3$ nanoparticles, PANI and $BaTiO_3$/PANI composite are shown in Fig. 2. It shows the synthesized powders of $BaTiO_3$ to be pure tetragonal perovskite structures (see Fig. 2a) [14]. A typical XRD pattern of polyaniline shows one

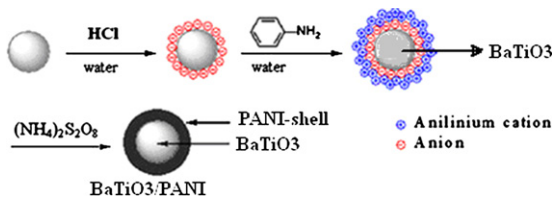

Fig. 1. The possible reaction procedure in the synthesis of $BaTiO_3$/PANI composite.

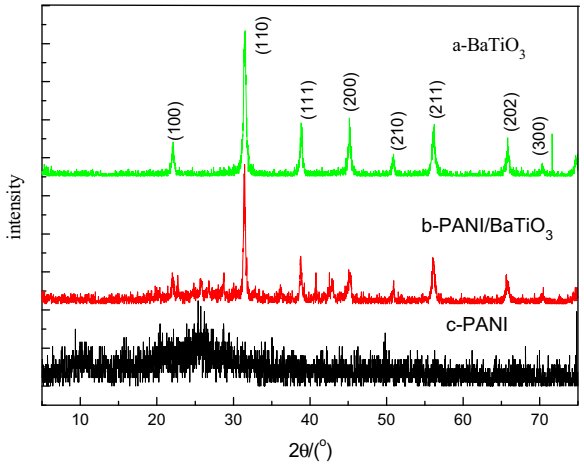

Fig. 2. XRD patterns of a-$BaTiO_3$ particles, b-PANI/ $BaTiO_3$ composite, c-PANI.

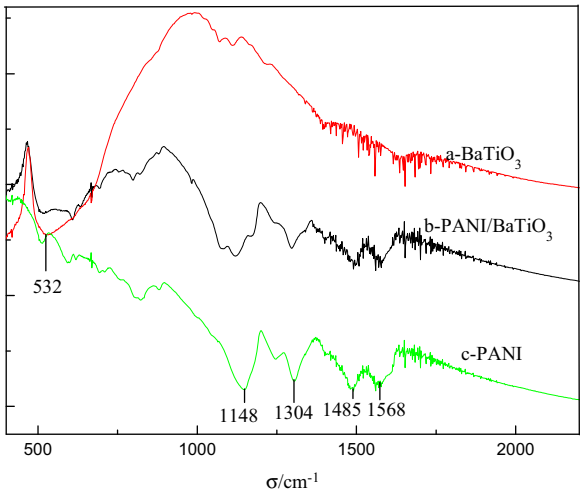

Fig. 3. FTIR spectra of a-$BaTiO_3$ particles, b-PANI/ $BaTiO_3$ composite, and c-PANI composite.

broad diffraction peak centered at 2θ=25.51° (see Fig. 2c), which can be ascribed to the periodicity parallel and is perpendicular to the polymer chains [15]. Fig. 2b shows the values of the $BaTiO_3$/PANI composite, which contains the characteristic peaks of PANI and $BaTiO_3$, including the peaks at 2θ=22.02°, 25.64°, 31.44°, 38.8°, 45.06°, 50.92°, 56.02° and 65.68°. These results indicated that the structure of the core materials is a perovskite structure, and the $BaTiO_3$/PANI core–shell composites were obtained.

The FTIR spectra of the $BaTiO_3$ nanoparticles, PANI and $BaTiO_3$/PANI composite are shown in Fig. 3. It is observed in Fig. 3a that there is a peak at 532 cm^{-1}, corresponding to stretching mode of TiO_6 octahedra in $BaTiO_3$ [16]. The characteristic peaks of PANI occur at 1148, 1244, 1304, 1485, 1565 and 805 cm^{-1}. The peaks at 1565 and 1485 cm^{-1} are attributed to the characteristic C=C stretching of the quinoid and benzenoid rings, and the peaks at 1304 and 1244 cm^{-1} correspond to N–H bending and asymmetric C–N stretching modes of the benzenoid ring, which are also observed in each curve of Fig. 3c. The peak near 1148 cm^{-1} is associated with vibrational modes of N=Q=N (Q refers to the quinonic-type rings), indicating that PANI was formed in our sample. The peak at around 805 cm^{-1} is attributed to the out-of-plane bending of C–H in the substituted benzenoid ring [17,18]. On the other hand, both absorption peaks of PANI and $BaTiO_3$ appear in Fig. 3b that clearly demonstrates the successful encapsulation of $BaTiO_3$ nanoparticles with PANI.