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# Microwave absorbing properties of barium hexa-ferrite/polyaniline core-shell nano-composites with controlled shell thickness

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## HIGHLIGHTS

- Electromagnetic properties of nano-composites were tuned by the shell thickness.
- The proper core/shell thick made contributions to refining impendence match.
- Optimized nano-composite exhibited a broad −10 dB absorption bandwidth of 3.8 GHz.

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## ABSTRACT

Barium hexa-ferrite ($BaFe_{12}O_{19}$)/polyaniline (PANI) core–shell nano-composites have been fabricated by an in situ polymerization and the shell thickness of PANI layers were tuned by increasing the content of the starting monomer and evaluated by combination TG and TEM results. Based on these, the influences of the shell thicknesses on the properties of the as-synthesized nano-composites have been investigated. The results indicated that the electric and magnetic characteristics of the synthesized nano-composites have been tuned by altering the shell thickness. With refining impedance match and taking advantages of conductance loss, magnetic resonance loss and interfacial loss, the microwave absorbing properties of the synthesized composites have been enhanced. Both the microwave absorbing efficiency and frequency range changed as the shell thickness increased. The optimized core–shell nano-composites with the shell layer of 30–40 nm demonstrated the best microwave absorbing properties with the maximum absorption −28 dB at 12.8 GHz and the −10 dB absorption bandwidth of 3.8 GHz (11.8 GHz–15.6 GHz) as the thickness of the absorbing layer was as thin as 2.0 mm.



## 1. Introduction

With the wide use of various electronic devices, increasingly serious electromagnetic (EM) wave pollution and EM interference have attracted more and more attention [1,2]. To solve these problems, high performance EM wave absorbing materials with high absorption efficiency, wide absorption frequency range, small thickness and light weight are always expected and struggled for [2]. Based on the magnetic or dielectric loss, a variety of EM wave absorbing materials have been designed and developed such as ferrites, conducting polymers and so on [3–6].

Nowadays, it is believed to be a potential and feasible way to promote the EM wave absorbing properties further to meet the requirement of the actual applications by compositing technique [2]. Among them, various composites based on the magnetic ferrites and conducting polymers have aroused great research interest for the effective combination of the magnetic loss and dielectric loss as well as the interfacial loss, which may provide a good choice to enhance the absorption efficiency or broaden the absorption frequency range [7–15].

As a relatively early attempt, a core–shell composite with the continuous coverage of polyaniline (PANI) on the surface of barium ferrite particles was successfully fabricated, which demonstrated the maximum refection loss at higher frequency [11]. Instead of PANI, poly(3,4-ethylenedioxy thiophene) (PEDOT) was used as the conducting polymer shell and composited with barium ferrite. The resulted nano-composites approached high microwave absorption value of 22.5 dB due to the high dielectric and magnetic loss [12].

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Focusing on the modification of magnetic core to improve the EM absorbing properties, high quality (Co,Ti)-doped barium ferrite nano powders have been synthesized by surfactant-assisted solvothermal route and composited with PANI. The reflection loss of the ferrite-conducting polymer composites increased owing to organic-inorganic composite technique and proper heteroatom substitution [13]. A wider absorption frequency range could be obtained by adding different polyaniline contents in barium ferrite [14]. In order to refine the impedance match, various magnetic ferrite components such as $NiCoFe_2O_4$ [15], MnZn ferrite [16], NiZn ferrite [17] have been explored. Actually, it was realized that the interfacial loss and matching impedance must be the important factors to enhance the EM absorbing properties of the ferrite-conducting polymer composites. A deep insight into microwave absorption of $Fe_3O_4$/PANI composites was preceded by controlling shell thickness. The results indicated that the introduction of dielectric loss, interfacial loss, and the improved matching impedance together made contributions to the enhancement of the synthesized composites in microwave absorption properties [18]. The case may become more complicated as using the complex oxides like ferrites as the magnetic core instead of the simple iron oxide due to their irregular particle shapes, easy magnetic agglomeration and complicated magnetic properties. However, the tunable magnetic properties of the ferrites retained more possibilities to improve the synthetic EM absorbing properties of the final composites; therefore it is very necessary to probe into the interfacial loss and matching impedance of the ferrite core and conducting polymer shell. Nevertheless, to our knowledge, there were still seldom reports on clarifying the interfacial effect by quantitatively controlling the match of core–shell thickness till now [14, 18, 19].

Herein, barium hexa-ferrite ($BaFe_{12}O_{19}$)/polyaniline (PANI) core–shell nano-composites with controlled shell thickness have been synthesized by an in-situ polymerization route and the shell thickness was semi-quantitatively evaluated by the thermal gravimetric analysis (TGA) and transmission electronic microcopy (TEM). Based on these, the effects of interfacial structures and the match core–shell thickness on the microwave absorbing properties have been investigated.

## 2. Experimental

### 2.1. Synthesis of $BaFe_{12}O_{19}$/PANI core-shell nano-composites

The core–shell structured $BaFe_{12}O_{19}$/PANI nano-composites were synthesized by an in-situ polymerization method. The typical experimental procedure was described as follows: firstly, the flake-shaped $BaFe_{12}O_{19}$ nano powder with their average dimensions of 300 nm in diameter and 50 nm in thickness prepared by sol–gel auto-combustion method [20] were weighted and ultrasonically dispersed in the diluted hydrochloric acid (HCl) solution (1 mol/L) for 30 min. Subsequently, the resulted mixture was transferred into a three-necked flask and mechanically stirred in an ice-water bath. The aniline monomer with the designed ratios of aniline and $BaFe_{12}O_{19}$ ranging from 3:10 to 8:10 and ammonium persulfate (APS) aqueous solution with the molar ratio of aniline to APS of 1:1.2 were pre-cooled and pumped into the flask one by one. After oxidative polymerization for 20 h, the polymerized products were collected by filtration and washed by the ethanol/water solution till the filtrate became colorless. Then, the final products were obtained after drying in a vacuum drying oven at 50 °C for 12 h. The final samples were denoted as $S_1$, $S_2$, $S_3$, $S_4$, $S_5$, and $S_6$ according to the designated weight ratios of $BaFe_{12}O_{19}$ and aniline at 10:3, 10:4, 10:5, 10:6, 10:7 and 10:8, respectively.

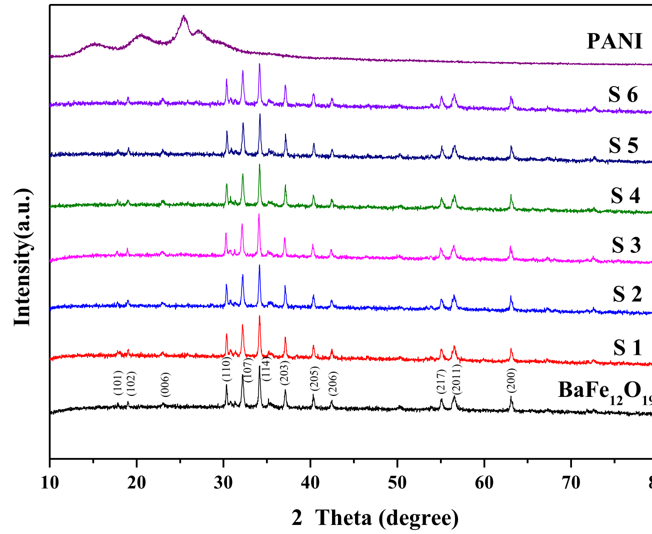


**Fig. 1.** The XRD patterns of the as-synthesized $BaFe_{12}O_{19}$/PANI nano-composites including those of pure $BaFe_{12}O_{19}$ and PANI for comparison.

### 2.2. Characterization

The phase compositions of the as-synthesized composites were analyzed by X-ray diffraction technique with $CuK_\alpha$ radiation (XRD, Bruker D8 advance) and their Fourier transformation infrared (FT-IR) spectra were scanned by a Bruker Tensor 27 FT-IR spectrophotometer over the range of 400–4000 $cm^{-1}$ with a 4 $cm^{-1}$ resolution. The morphologies of the as-synthesized composites were observed by transmission electron microscope (TEM, Philips, Tecnai 12) and the thermo-gravimetric analysis (TGA) was carried out on a PerKinElmer-Pyris 1 in the temperature range of room temperature (R.T.) to 800 °C at a heating rate of 5 °C/min. The magnetic properties were measured by using a vibrating sample magnetometer (VSM, ADE-EV7). The electric/magnetic parameters including complex permittivity and complex permeability were measured by the vector network analyzer (VNA, Aglient N5242A) based on the co-axial transmission line method. The ring samples with the external diameter of 7 mm, internal diameter of 3 mm and thickness of about 2 mm were prepared by mixing the synthesized

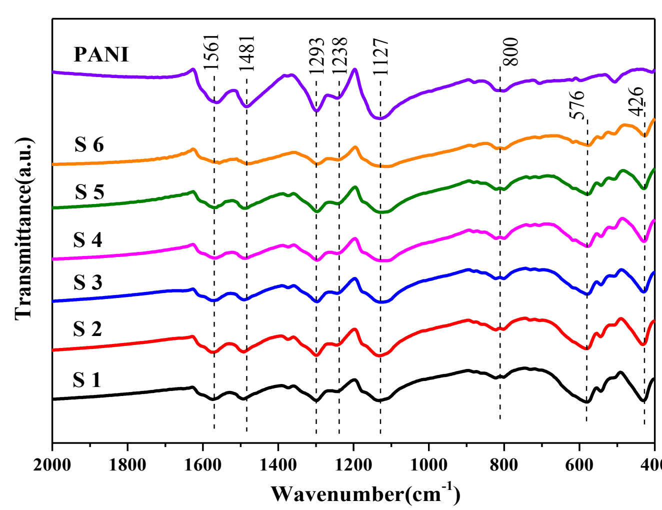


**Fig. 2.** The FT-IR curves of the as-synthesized $BaFe_{12}O_{19}$/PANI nano-composites including that of pure PANI for comparison.