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Double-layer electromagnetic wave absorber based on barium titanate/carbon nanotube nanocomposites

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Abstract

The electromagnetic wave absorption properties of double-layer barium titanate/carbon nanotube (BTO/CNT) nanocomposites were evaluated. The BTO/CNT nanomaterials were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and field emission scanning electron microscopy. The reflection loss (*R.L.*) of the samples was calculated based on the measured complex permittivity and permeability. The minimum *R.L.* of single-layer BTO/CNT 30 wt% nanocomposites sample with a thickness of 1.1 mm reached ~ -30.3 dB (over 99.9% absorption) at 13.8 GHz, and the bandwidth of the reflection loss less than -10 dB (over 90% absorption) was 1.5 GHz. The double-layer composites consist of BTO/CNT 30 wt% (absorption layer) with thickness of 1.0 mm and BTO 30 wt% (matching layer) with thickness of 0.3 mm showed a minimum *R.L.* of ~ -63.7 dB (over 99.9999% absorption) at 13.7 GHz, and the bandwidth of the reflection loss less than -10 dB was 1.7 GHz. Wider response bandwidth, >1.7 GHz also can be achieved with different designs of double-layer absorbers. The *R.L.* significantly improved and wider response bandwidth can be obtained with double-layer composites. The capability to modulate the absorption and bandwidth of these samples to suit various applications in different frequency bands indicates that these nanocomposites could be an excellent electromagnetic wave absorber.

Keywords: B. Nanocomposite; Electromagnetic wave absorber; Carbon nanotube; Barium titanate

1. Introduction

It is essential to design electromagnetic (EM) wave absorber to solve the problem of EM radiation aroused by application of them in communication appliances and electronic tools in scientific, commercial, industrial, and military fields that can harm the health of human beings and pollute the environment [1–14]. EM radiation can cause severe interruption of electronic systems, device malfunction, generate false images, and so on [13,14]. An ideal EM wave absorber material should be lightweight, strongly absorb EM waves, possess tunable absorption frequency, and multifunctionality [1–5]. Thus, nanomaterials are among important candidates for EM wave absorber materials [2–4]. The usage of conducting polymer such as polyaniline [15–18], carbon materials [1,5,9], and dielectric/magnetic materials (iron oxide, barium titanate, carbonyl iron, etc.) [10,11,19,20] has rapidly growing and had been given intense interest as an effective method in the development of EM wave absorber technology. These materials have excellent electrical properties, such as high conductivity and enhanced complex permittivity and permeability behavior (dielectric loss, magnetic loss and relaxation), which is vital in EM wave absorber technology. Furthermore, the exploitation of combination of more than one materials, between the materials mentioned earlier, has been found as a valuable method to realize EM wave absorber material with higher performance [21–24].

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For instance, Tyagi et al. [21] combined carbon nanotubes (CNTs) with ferrite to fabricate nanocomposite for the application of EM wave absorber because single material system cannot meet the demand of high performance absorber. In another study, Bi et al. [22] combined CNTs with alumina, Wang et al. [23] combined carbon black and barium titanate (BTO), and Zhu et al. [24] combined CNTs and BTO, which all have the same aim, to target enhanced EM wave absorbing properties. Additionally, their structure and size also have been deployed to construct excellent EM wave absorber materials.

In recent years, CNTs and BTO have been paid attention as the EM wave absorber materials. High electrical conductivity of the CNTs makes them capable of dissipating electrostatic charges or shielding EM radiation [3,4,15,25]. Meanwhile, BTO (widely used as electric ceramics) perovskite possess high dielectric constant, good ferroelectric properties, and shows occurrence of relaxation at gigahertz frequencies [3,6,7,19,20,23]. The combination of BTO with CNTs can integrate the properties of these two components to form nanocomposites for use as promising EM wave absorber materials.

However, reports on BTO/CNT materials are still very limited. Bi et al. [6] and Huang et al. [7] fabricated BTO/CNT composites and characterized their single-layer EM wave absorption properties. Even though their results showed high reflection loss, *R.L.* (< -20 dB, over 99% absorption), it is worth to notice that certain thickness (2 mm or more) are necessary to obtain those *R.L.* values. Furthermore, it is quite challenging to improve the absorption ability and response bandwidth of single-layer absorbers due to their less variable parameters of design (thickness and weight fraction) and by only incorporating optimized absorbents [9]. In order to gain higher *R.L.*, thin, and possess wide response bandwidth materials, double-layer absorber can be considered as an effective method [9,11,20]. Yuchang et al. [20] reported double-layer absorber consist of carbonyl iron and BTO. In their reports, the samples with thickness under than 2 mm exhibited high *R.L.* and wide response bandwidth.

In this study, we prepared BTO nanoparticles by using sol–gel method and then grafted them onto the surface of CNTs. Then, the complex permittivity and permeability of these nanocomposites are measured and their *R.L.* is calculated. Their performance as a double-layer EM wave absorber was also investigated to achieve thin sample with high absorption ability and wide response bandwidth.

2. Materials and methods

2.1. Fabrication of BTO/CNT nanocomposites

Multi-walled CNTs (Wako Pure Chemical Industries Ltd., Japan, $d=20$–30 nm) were functionalized by mild hydrothermal treatment, as we reported in Refs. [3,26,27], with some modifications. BTO nanoparticles were prepared by sol–gel method as reported in Ref. [3], with some modifications, and functionalized CNTs were added to fabricate BTO/CNT nanocomposites. Barium acetate $Ba(CH_3COO)_2$, titanium tetraisopropoxide $Ti[(CH_3)_2CHO]_4$, acetic acid, ethanol, and pure water were obtained from Wako Pure Chemical Industries Ltd., Japan.

$Ba(CH_3COO)_2$ was dissolved in mixed solution of 20 ml ethanol and 3 ml acetic acid (solution A), stirred in water bath at 60 °C for 0.5 h. In the same time, $Ti[(CH_3)_2CHO]_4$ was mixed in 10 ml ethanol (solution B). Solution A and B were combined and 1 ml pure water was added to perform hydrolysis. Then these two solutions were stirred at 60 °C for 2.0 h to form a sol, which contained Ba/Ti molar ratio 1:1. Next 0.15 g functionalized CNTs were added to the final solution, sonicated for 1 h, and stirred furthermore for about 1.5–2 h, 80 °C until gel was formed. The black color gel was then dried at 100 °C for 24 h to make a xerogel. Finally, the product was calcined at 800 °C for 2 h under the presence of Argon gas. Samples for BTO were prepared using same process excluding the addition of CNTs.

Samples for the complex permittivity and permeability measurement were prepared by loading the BTO/CNT in polyurethane (PU) with a weight fraction of 30 wt%. For comparison, the samples of BTO 30 wt% and CNT 3 wt% were also fabricated with the same process. The thickness of all of the samples was 1 mm. The samples for this measurement are denoted as BTO/CNT, BTO, and CNT hereafter.

2.2. Characterization method

The crystal structure of prepared nanomaterials was analyzed by using X-ray diffraction (XRD; Rigaku Rotaflex, Japan) with Cu Kα radiation ($\lambda=0.15406$ nm). X-ray photoelectron spectroscopy (XPS; Kratos Axis Ultra DLD) was performed with a standard Mg Kα (1256.6 eV) X-ray source operating at 10 mA and 15 kV to characterize the elemental composition and chemical states of the samples. The morphology was characterized using transmission electron microscopy (TEM; JEM-2100, JOEL, Japan) and field emission scanning electron microscopy (FE-SEM; Hitachi S-5000, Japan) with an accelerating voltage of 200 kV and 20 kV, respectively.

The complex permittivity and permeability were measured using a vector network analyzer (37247D, Anritsu Co. Ltd.) within the frequency range of 0.5–13.8 GHz. The samples were cut into a toroidal shape with an outer diameter of 7.0 mm, inner diameter of 3.0 mm. The reflection loss of single- and double-layer was calculated from the measured complex permittivity and permeability of the samples.

3. Results and discussion

3.1. Structure and morphology of BTO/CNT nanocomposites

XRD patterns of the CNTs and BTO/CNT are shown in Fig. 1 (a). All peaks of the BTO/CNT can be assigned to the cubic perovskite structure (JCPDS no. 31-0174) [3,7,17,19]. Strong intensity of (110) peak can be observed from BTO/CNT at $2\theta=31.8°$. The CNTs showed typical multi-walled CNTs (002) broad peak at 22° [3,28] which overlapped with the (100) peak of BTO/CNT. Even though the peak for CNTs in the BTO/CNT was overlapped, their existence was confirmed from the XPS spectra.