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Electromagnetic wave absorption properties of barium titanate/carbon nanotube hybrid nanocomposites

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ABSTRACT

Barium titanate/carbon nanotube (BTO/CNT) hybrid nanocomposites were fabricated by sol–gel method. The BTO/CNT hybrid nanomaterials were characterized using X-ray diffraction, transmission electron microscopy, field emission scanning electron microscopy, Raman and X-ray photoelectron spectroscopy. The BTO/CNT hybrid nanomaterials were then loaded in paraffin wax with different weight percentage, and pressed into toroidal shape with thickness of 1.0 mm to evaluate their complex permittivity and complex permeability using vector network analyzer. The reflection loss of the samples was calculated according to their measured complex permittivity and permeability. The minimum reflection loss of the BTO/CNT 60 wt.% hybrid nanocomposites sample with a thickness of 1.0 mm reached 29.6 dB (over 99.9% absorption) at 13.6 GHz, and also exhibited a wide response bandwidth where the frequency bandwidth of the reflection loss of less than −10 dB (over 90% absorption) was from 12.1 to 13.8 GHz. The BTO/CNT 60 wt.% hybrid nanocomposites with thickness of 1.1 mm showed a minimum reflection loss of ~−56.5 dB (over 99.999% absorption) at 13.2 GHz and was the best absorber when compared with the other samples of different thickness. The reflection loss peak shifted to lower frequency and wider response bandwidth can be obtained as the thickness of the samples increased. The capability to modulate the absorption band of these samples to suit various applications in different frequency bands simply by manipulating their weight percentage and thickness indicates that these hybrid nanocomposites could be a promising electromagnetic wave absorber.

1. Introduction

In recent years, the development of communication appliances and electronic tools in scientific, commercial, industrial, and military fields, such as navigation systems, computers, mobile phones, radar technology and wireless network systems is progressing fast [1–8]. Although these technologies are convenient, electromagnetic (EM) radiation has restricted their advancement and is becoming a serious crisis. EM radiation can harm the health of human beings, especially expectant mothers and children and pollute the environment [2,4,5,7–10]. Thus, it is essential to defend human beings and electronic devices from excessive exposure to EM radiation. Therefore, the demand for EM wave absorber materials have increased and received much attention to effectively solve the problem of exposure to EM radiation. An ideal EM wave absorber material should be lightweight, strongly absorb EM waves, possess tunable absorption frequency, and multifunctionality [1,5,10].

Nanomaterials are among important candidates for EM wave absorber materials [5,9,11]. The relative density of nanomaterials is lower and their specific surface area is larger than those of the corresponding bulk materials. As a result, there are a large number of active atoms at the nanomaterials surface, which has a large interfacial dielectric loss induced by interface polarization [10]. Carbon nanotubes (CNTs) are light, possess a high aspect ratio and unique magnetic properties, and exhibit favorable mechanical, chemical and electric properties that have attracted considerable attention [1,5–8,12]. Their high electrical conductivity makes CNTs capable of dissipating electrostatic charges or shielding EM radiation [5–8,12]. The ability to absorb EM wave can be optimized by synthesizing nanocomposites which includes the CNTs. Barium titanate (BTO) is one of the widely used materials for electric ceramics and has been applied for various of applications [2,3,13–15]. BTO perovskite possess high dielectric constant, good

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ferroelectric properties, and shows occurrence of relaxation at gigahertz frequencies [2,3,7,8,11,13–19], thus a good candidate for the development of nanocomposites EM wave absorber. The combination of BTO with CNTs can integrate the properties of these two components to form hybrid nanocomposites for use as EM wave absorber materials.

Reports on BTO/CNT hybrid materials as the EM wave absorbers are very limited. Bi et al. [6,7] and Huang et al. [8] synthesized BTO/CNT compound by a solvothermal method and investigated their EM wave absorption properties. In their reports, the CNTs were oxidized with modification using strong acids treatment, which used harsh solvents and a time consuming process. In contrast, a mild hydrothermal treatment that is environment friendly, fast, efficient, and allows for easy modification has been performed [20]. No harsh organic or aqueous solvents were used in this process and it is thus a less destructive modification route. This treatment leads to the introduction of carboxyl and hydroxyl groups to the surface of the CNTs, which allows them to be highly dispersed in polar solvents and prevent agglomeration caused by strong intrinsic van der Waals attraction between the CNTs. Meanwhile, Wang et al. [14] fabricated BTO and carbon black compound via sol–gel method and also investigated the EM wave absorption properties. Sol–gel method is a widely used and classical fabrication approach, which offer a lot of inherent merits such as high purity, better homogeneity, lower temperature of preparation, and low manufacturing cost [17–19]. To the best of our knowledge, the evaluation of EM wave absorption properties of BTO/CNT hybrid nanocomposites, where the CNTs were mild hydrothermally treated, prepared using sol–gel method has not been examined.

In this study, we prepare BTO nanoparticles and graft them onto the surface of CNTs by using sol–gel method. We then evaluate the ability of these materials to absorb EM waves by measuring their dielectric and magnetic losses when penetrated by an EM wave. The complex permittivity and complex permeability of these hybrid nanocomposites are measured and their reflection loss is also calculated.

2. Materials and methods

2.1. Modification of CNTs

Multi-walled CNTs (Wako Pure Chemical Industries Ltd., Japan, d = 20–30 nm) were functionalized by mild hydrothermal treatment, as reported by our research group in Ref. [20], with some modifications. Pure water, potassium hydroxide (KOH), and potassium persulfate (KPS) were used in the treatment and they were also obtained from Wako Pure Chemical Industries Ltd., Japan.

CNTs were added to the aqueous solution of KOH and ultrasonically mixed in a stainless steel reaction autoclave with a polytetrafluoroethylene liner. KPS was added to the aqueous solution and ultrasonically mixed as a next step. The autoclave was then sealed and heated at 160 °C for 2.0 h. Finally, the solutions were filtered and rinsed with pure water and ethanol for several times. The products were dried overnight in vacuum at 50 °C. The mild hydrothermally treated CNTs were denoted as modified CNTs hereafter.

2.2. Preparation of BTO/CNT hybrid nanocomposites

BTO nanoparticles were prepared by sol–gel method and modified CNTs were mixed to prepare BTO/CNT hybrid 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.

Barium acetate 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, titanium tetraisopropoxide 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 modified CNTs were added to the final solution, sonicated for 1.0 h, and stirred furthermore for 1.0 h. The mixture was then aged for 2 days and a black color gel was obtained. The gel was dried at at 100 °C for 1.0 h to make a xerogel. Finally, the product was calcined at 800 °C for 2.0 h. Samples for BTO were prepared using same process excluding the addition of modified CNTs.

2.3. Characterization method

The crystal structure of prepared powders was analyzed by using X-ray diffraction (XRD; Rigaku Rotaflex, Japan) with Cu Kα radiation (λ = 0.15406 nm). 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. Raman spectroscopy measurements were performed on a Raman spectrometer (HoloLab series 5000, Kaiser Optical Systems) with 532 nm laser excitation. Lorentzian fitting was conducted for the low Raman shift range. 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 real and imaginary parts of complex permittivity ε ($\varepsilon = \varepsilon' - j\varepsilon''$) and permeability μ ($\mu = \mu' - j\mu''$) were measured by scattering parameters measurement method in reflection mode using a vector network analyzer (37247D, Anritsu Co. Ltd.) within the frequency range of 0.5–13.8 GHz. Samples for these measurements were prepared by loading the BTO/CNT hybrid nanocomposites in paraffin wax with a weight fraction of BTO/CNT hybrid nanocomposites of 40, 50, and 60 wt.%. The powder-wax composites were pressed into a toroidal shape using a mold designed with an outer diameter of 7.0 mm, inner diameter of 3.0 mm, and thickness of 1.0 mm. The reflection loss was calculated from the measured complex permittivity and permeability of the samples. For comparison, the samples of BTO 60 wt.% and modified CNTs 20 wt.% were also fabricated with the same process.

3. Results and discussion

3.1. Structure and morphology of BTO/CNT hybrid nanocomposites

XRD patterns of the modified CNTs and BTO/CNT hybrid nanocomposites are shown in Fig. 1. All peaks of the BTO/CNT can be assigned to the cubic perovskite structure (JCPDS No. 31-0174) [8,11,13], and no split peak was observed around 2θ = 45° [3,14]. Strong intensity of (110) peak can be observed from BTO/CNT hybrid nanocomposites at 2θ = 31.6°. The modified CNTs showed typical multi-walled CNTs (002) peak at 22° [21,22] which overlapped with the (100) peak of BTO/CNT. Similar pattern of the modified CNTs also can be observed from the pristine CNTs sample (not shown in the figure). Even though the peak for CNTs in the BTO/CNT is not clear (overlapped), their existence was confirmed

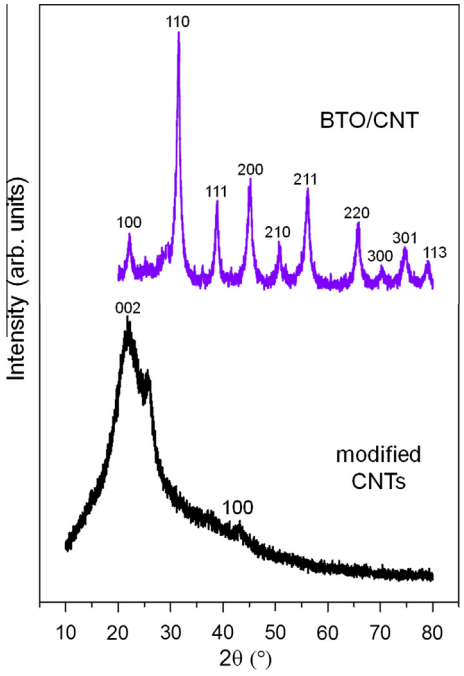

Fig. 1. XRD patterns of the modified CNTs and the BTO/CNT hybrid nanocomposites.