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Carbon nanotubes modified with ZnO nanoparticles: High-efficiency electromagnetic wave absorption at high-temperatures

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Abstract

Carbon nanotube–ZnO composite powders, which act as high-temperature electromagnetic wave absorbents, are prepared by homogeneous precipitation. Carbon nanotube–ZnO/glass composites are fabricated by pressureless sintering. ZnO nanoparticles are assembled on the surface of carbon nanotubes, which produces heterostructure and enhances polarization at heterogeneous interface. Owing to the consumption of an amorphous carbon layer on the outer surface of carbon nanotubes and the generation of oxygen vacancies in ZnO during sintering, a higher concentration of charge carriers is produced in ZnO, which causes more relaxation polarization and dielectric loss in electromagnetic field. Owing to the shortened relaxation time, and the increase of relaxation polarization, permittivity and dielectric loss increases with the increase in testing temperature. Reflection coefficient of the obtained composite reaches -70 dB. The special integration of multiwalled carbon nanotubes modified with some metal oxide semiconductor nanoparticles provides an effective approach to design high-temperature electromagnetic absorbing materials.

Keywords: Electromagnetic absorbers; Dielectric loss; Permittivity; Reflection coefficient

1. Introduction

With the development of radar, microwave communication technology and especially the need for electromagnetic interference (EMI) shielding coatings and concealing technology, electromagnetic (EM) wave absorbing materials are attracting worldwide attention [1,2]. In recent years, among the candidates for EM absorbent, new types of carbon materials [3–7], carbide [8–13] and metal oxide semiconductor [14–19] have been investigated extensively. Especially, high-temperature EM absorbing and EMI shielding materials have attracted more and more attention because of the requirement for the special applications in high-temperature environment, such as electromagnetic compatibility in harsh environment. Unfortunately, there is very little research on EM absorption properties at high temperature because measurement conditions are harsh, measurement equipments are complicated and conventional matrix cannot meet the requirement. The research on high-temperature EM absorbing material has become the frontier in the field of EM absorbing materials.

The new types of carbon materials, e.g. short carbon fibers (CFs), carbon nanotubes (CNTs) and graphene etc., have attracted extensive interest from various fields including physics, materials, chemistry and biology. The unique electrical, thermal and mechanical properties, which cannot be matched by conventional materials, make carbon materials good candidates in EM absorption applications. The high-temperature complex permittivity and the evolution behavior of CNTs/SiO_2 [20] and CFs/SiO_2 [21] over the temperature range of 30–600 °C in 8.2–12.4 GHz (X-band) are researched. When the sample temperature rises, the increase in real part of the permittivity (ε') is attributed to the shortened relaxation time of electron polarization, and the increase of imaginary part (ε'') is ascribed to the increasing electrical conductivity. SiC is a group IV polar semiconductor, having a wide band gap and many practical and potential applications in EM absorption. The dielectric

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properties and EM absorbing properties of various SiC including SiC matrix composites and SiC/SiBCN composite ceramic [8,9] have been investigated. The considerable increase in EMI shielding effectiveness and EM absorption properties can be attributed to the formation of continuous SiC matrix layer composed of SiC nanocrystals in the porous yttria stabilized zirconia (YSZ) felt, which is beneficial for the production of induced electric current and the enhancement of dielectric loss [8]. Compared with SiC and CNT, the electromagnetic properties of metal oxide semiconductor e.g. β-MnO_2 and ZnO can be adjusted in a wider range by incorporation of dopant and morphology control, which is convenient for the design of materials. The EM attenuation capability of the β-MnO_2 nanorods [22] is evidently enhanced with the increase of temperature. The decrease in ε' would be mainly ascribed to the increase in the disordered degree of orientation alignment of the intrinsic polar moment, and the increase in ε'' may result from the lower resistivity with the increase of temperature. For the Al-doped ZnO/$ZrSiO_4$ composite ceramics [23], permittivity and dielectric loss first increase and then decrease when the testing temperature rises. The increase in permittivity can be attributed to the increase in carrier concentration and conductivity. When the temperature is higher than 400 °C, oxygen vacancy concentration gradually decreases under air atmosphere, which leads to the decrease in conductivity.

Table 1 summarizes the phase composition, measuring temperature, absorbent content, electromagnetic parameters, optimum thickness, RC and bandwidth of the absorbing materials in the recent literatures. In order to further improve the EM absorption performance, the design of hybrid material is necessary. The suitable heterogeneous interfaces appear to be a key step in the design of artificial nanostructures with high electrical conductivity and dielectric loss [24,25]. In this work, CNT–ZnO composite powders are prepared by urea homogeneous precipitation, which is different from the previous two-step process, where the ZnO powders are first prepared and then the composite powders are fabricated by mixing with CNT dispersant. The fabrication process for the CNT–ZnO/glass composite is shown in Fig. 1. Compared with the two-step process, the homogeneous precipitation employed in this work is more flexible. Moreover, the hybrid structural is more easily accessible in nanoscale. Oxygen atoms of ZnO lattice readily escape to react with the amorphous carbon on the tube wall of CNTs during sintering, which may not only increase the conductivity between CNTs but also lead to the formation of defects in ZnO, leading to the optimization of the EM absorption properties. The effects of filler loading content in composites on dielectric and EM absorption properties at temperatures ranging from room temperature to 400 °C are studied.

2. Experimental procedure

2.1. Preparation of CNT–ZnO powder

CNT–ZnO composite powder was prepared by urea homogeneous precipitation. All the chemicals in our experiments were analytical grade reagents and directly used without further treatment. Preparation of CNT–ZnO composite powder: 0.02 mol zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, purity of 99.0%, Fuchen chemical reagents, Tianjin, China), urea (H_2NCONH_2, purity of 99.0%, Hongyan chemical reagents, Tianjin, China) and 10 g CNT dispersant (mass fraction: 2 wt%, Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences) were added into deionized water at room temperature. The mixture was stirred for 1 h to form a stable solution with a concentration of 0.5 mol/L. After that, the solution was gradually heated to 90 °C in an oil bath under magnetic stirring in open reflux condensation mode, and was kept at 90 °C for 6 h. Finally, the black mixture was collected by vacuum filtration. After washing with adequate deionized water and ethanol to remove any remaining impurity, the CNT–ZnO composite powder was obtained by vacuum drying and annealing at 400 °C in N_2 atmosphere.

2.2. Preparation of CNT–ZnO/glass composite

In this work, borosilicate glass powder (Zhengzhou Longxiang ceramics, Zhengzhou, China) was used as an electrically insulating matrix material. The main ingredients of borosilicate glass powders were SiO_2, B_2O_3 and NaO, the average particle size was 75 μm, and the softening point of borosilicate glass powder was 750 °C. The samples used for dielectric properties measurement were

Table 1
Summary of high-temperature EM absorption properties reported in recent papers.

Phase composition	Measuring temperature (°C)	Absor. content	ε'	ε''	D (mm)	RC_{min} (dB)	Bandwidth (GHz)	Ref.
CNTs/SiO_2	100–500 °C	5 wt%	5–8	2.5–4	3.5	−72.2 dB at 200 °C	4.2 GHz in X-band	[4]
SiC/ZrO_2	20–800	86.9 wt%	6–10	10–11	5	−27 dB at 20 °C	5 GHz in 8–18 GHz	[8]
LAS-SiC/LAS	20–500	10 wt%	–	–	2/2	−42.8 dB at 300 °C	3.9 GHz in X-band	[10]
SiC_f/SiC	25–700	42 vol%	6.3–6.6	0.1–0.4	–	–	–	[11]
SiC	100–500	100 wt%	11–15	1–2	2.1	−16 dB at 500 °C	3.2 GHz in X-band	[12]
T-ZnO/SiO_2	300–700	20 wt%	~2.1	~0.1	–	–	–	[19]
C_f/SiO_2	30–600	20 wt%	19.0–29.4	10.3–14.7	5	−10.2 dB at 30 °C	1.3 GHz in X-band	[21]
β-MnO_2	20–500	100 wt%	8–23	18–34	–	–	–	[22]
ZnO/$ZrSiO_4$	20–650	10 vol%	5.4–7.9	1.2–4.7	2.86	−70 dB at 300 °C	4.2 GHz in X-band	[23]
CNT–ZnO/glass	20–400	3 wt%	6.9–7.2	3.0–3.9	2.72	−70 dB at 20 °C	3.9 GHz	This work
		2 wt%	7.4–8.3	2.6–3.4		−22 dB at 400 °C	3.2 GHz	