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Coaxial double-layer-coated multiwalled carbon nanotubes toward microwave absorption

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ABSTRACT

A novel coaxial double-layer-coated multiwalled carbon nanotube (MWCNTs) was synthesized to obtain excellent electromagnetic-wave-absorbing materials. Hydrochloric-acid-doped polyaniline (PANI) served as the first shell via in situ redox polymerization using $FeCl_3$ as the oxidizing agent. The introduction of PANI effectively solved the problem in which ferroferric oxide (Fe_3O_4)-coated carbon nanotubes had poor integrity and easily fell off in the previous experiment. After the reaction, the oxidizing agent directly provided Fe^{3+} and Fe^{2+} ions for the second Fe_3O_4 shell, which was deposited on the surface of hydrochloric-acid-doped PANI interlayer via coprecipitation. The hybrid fully combined MWCNTs with prominent dielectric properties and Fe_3O_4 with outstanding magnetic properties and showed excellent electromagnetic wave absorption performance with high reflection loss (−15.65 dB at 15.45 GHz) and broad effective bandwidth (←−10 dB) of 3.5 GHz (14–17.5 GHz) at lowest thickness (1.5 mm).

1. Introduction

With the development and use of radio technologies, high-frequency electronic devices in the GHz range have been widely used [1–9]. Therefore, absorbing materials with excellent electromagnetic shielding had been widely favored to avoid serious problems of electromagnetic interference and electromagnetic pollution [10,11]. Light-absorbing materials, such as carbon nanotubes (CNTs), graphene, and carbon spheres are the best choice to satisfy the needs of civilians and military personnel [12]. Zhao et al. [13] used amorphous CNTs (ACNTs) as absorber of electromagnetic waves and determined that the reflection loss (RL) properties of ACNT/PVC composite films can reach −13.2 dB at 12.96 GHz and that the frequency bandwidth ranging below −10 dB covers 3.3 GHz. Their results indicated the advantages of good microwave absorption and wide absorption band of CNTs. To the knowledge, the permeability performance of the materials, such as Fe, Co, Ni, and their oxides, play an important role in the absorption of electromagnetic waves, which can produce magnetic loss and regulate impedance matching [14]. Therefore, introducing magnetic materials into carbon materials to produce a novel absorber combining magnetic and dielectric properties is an excellent idea. Some relevant works show that magnetic materials have an obvious role in promoting electromagnetic-wave-absorbing efficiency, such as ferroferric oxide (Fe_3O_4)@C [15], CNTs/Fe_3O_4 [16], and Fe_3O_4/graphene capsules [17]. Hou et al. [18] utilized the coprecipitation method and prepared multiwalled CNT (MWCNTs)/Fe_3O_4 hybrids, with the maximum RL that can reach −18.22 dB at 12.05 GHz.

Accordingly, the synergistic effects of permittivity and permeability can be widely used in the field of electromagnetic wave absorption [19,20]. In this study, Fe_3O_4/polyaniline (PANI)@MWCNTs coaxial bilayer shell hybrids were prepared via in situ polymerization and coprecipitation method. Extending the dielectric loss by constructing a core–shell structure is an effective approach. PANI not only effectively linked MWCNTs and Fe_3O_4 as a "cross-linking agent" but also improved the coating integrity. PANI provided a two-tier interface and created additional interfacial polarization to improve the dielectric properties. Fe_3O_4 with strong magnetism effectively provided favorable magnetic loss and regulated impedance matching. Furthermore, the results with a maximum RL value of −15.65 dB and broad bandwidth of 3.5 GHz at a minimum thickness of 1.5 mm confirmed that the design ideas were effective.

2. Experimental

The schematic of the Fe_3O_4/PANI@MWCNTs hybrids is shown in Fig. 1. The MWCNTs were dispersed in a solution of H_2O and

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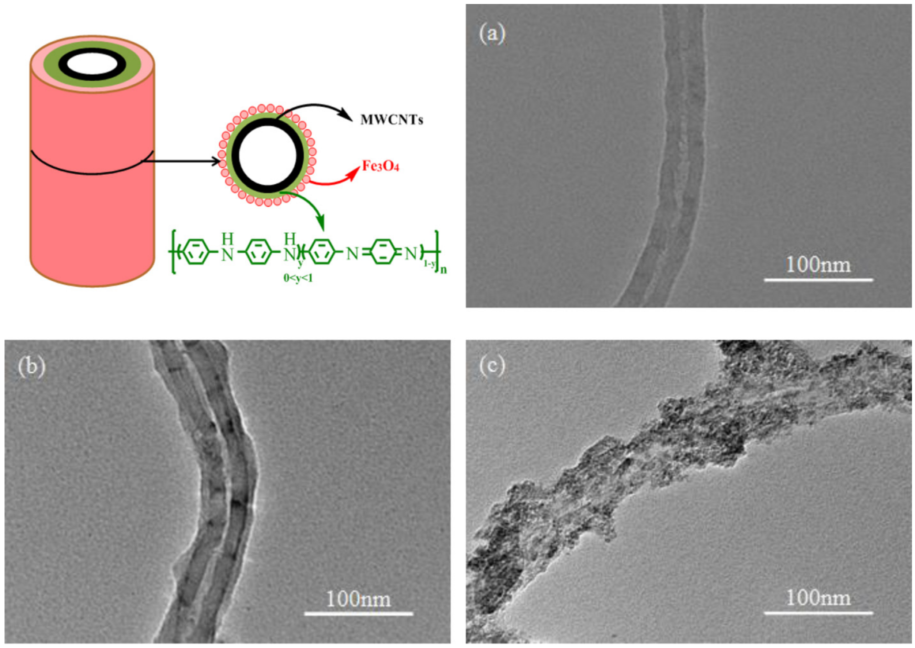

Fig. 1. Coating mechanism of Fe_3O_4/PANI@MWCNTs and TEM images of (a) pristine MWCNTs, (b) PANI@MWCNTs, and (c) Fe_3O_4/PANI@MWCNTs.

ethanol (Beijing Chemical Works) mixed with aniline (J&K Company) and hydrochloric acid (purity of 36%; Beijing Chemical Works). The MWCNTs (outer diameter of 30–50 nm, length of 10–20 μm, and purity of >98%) were bought from Chengdu Organic Chemicals Co., Ltd. After ultrasonic dispersion for 2 h, the oxidizer ($FeCl_3$; Alfa Aesar (China) Chemicals Co., Ltd.) was dropwise added to the previously mentioned solution. The entire reaction mixture was constantly stirred for 16 h in an ice bath under the protection of argon. The Fe^{3+} and Fe^{2+} ions in the original solution were used to prepare Fe_3O_4 by coprecipitation. Finally, the final product (i.e., Fe_3O_4/PANI@MWCNTs) was obtained after suction filtration, washing, and drying. The hybrids were observed using transmission electron microscopy (TEM, Tecnai $G^2$20) and X-ray diffraction (XRD, D/MAX2500VB2+/PC, Japan) respectively. The vibration sample magnetometer (VSM, Squid-VSM, Quantum Design) was applied to obtain the magnetic performance. The vector network analyzer (HP-8277ES Agilent) was used to measure the electromagnetic parameters. The MWCNTs powder was blended with paraffin wax (weight ratio = 6:4) to obtain test sample.

3. Results and discussion

Fig. 1 shows the TEM images of the intuitive morphology and microstructure of pure MWCNTs and Fe_3O_4/PANI@MWCNTs. As shown in Fig. 1(a), the pure MWCNTs had a regular appearance and smooth surface. Fig. 1(b) shows the first cladding, that is, hydrochloric-acid-doped PANI with approximately 5 nm thickness coated on the surface of the MWCNTs (PANI@MWCNTs). Hydrochloric-acid-doped PANI as a "crosslinker" provided the necessary conditions for the deposition of the inorganic nanoparticle layer through coprecipitation. The TEM image of Fe_3O_4/PANI@MWCNTs is shown in Fig. 1(c). The Fe_3O_4 particles were evenly covered on the surface of PANI@MWCNTs. XRD analysis of the material was performed, as shown in Fig. 2(a), to confirm the composition of the deposits on the surface. The position $2\theta = 26.8°$ corresponds to the standard crystal plane (0 0 2) of the MWCNTs. The analysis showed that 2θ = 35.4°, 43.9°, 52.9°, 56.8°, and 62.9° correspond to the (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) crystal faces of the standard structure Fe_3O_4 (JCPDS19-0629) [21], respectively, indicating the presence of Fe_3O_4. However, in this experiment, a large noise was detected in the XRD spectrum, indicating that the surface coating was not pure Fe_3O_4 and that doping of iron oxide impurities occurred.

Hysteresis loop tests and magnet adsorption experiments were performed to prove the magnetic properties of the hybrids (Fig. 2 (b)). The hysteresis loop was characterized in the range of ±5000 Oe at room temperature. Two important parameters of the magnetic hybrids were saturation magnetization (Ms) and residual magnetization (Mr), with values of 3.11 emu/g and 0.37 emu/g, respectively. The values of these parameters were lower than those reported in other documents mainly because of the presence of MWCNTs, PANI, and small impurities in the hybrids. However, the high coercive force (Hc; 68 Oe) would improve the natural resonance frequency of Fe_3O_4, which would ensure superior absorption performance. In further proving that the material possessed magnetic properties, the most intuitive experiment was intentionally prepared and conducted, as illustrated in Fig. 2(b); when the magnets was closed to the hybrids, the hybrids were completely biased toward the magnet. Two test experiments confirmed the existence of Fe_3O_4.

A good absorber is based on two basic conditions. First, the absorber must exhibit impedance matching, such that electromagnetic waves can enter the material without reflection as much as possible. Second, the absorber must exhibit attenuation matching, such that the electromagnetic wave can be consumed as much as possible and has close contact with the complex permittivity ($\varepsilon_r = \varepsilon' - i\varepsilon''$) and complex permeability ($\mu_r = \mu' - i\mu''$). Among them, the real parts (ε' and μ') represent the electric and magnetic storage capabilities, respectively, whereas the imaginary parts (ε'' and μ'') represent the wastage capability. As shown in Fig. 3(a), the excellent dielectric properties ε' and ε'' reached up to 13.7 and 2.62 at 1 GHz, respectively, which can be mainly attributed to the contribution of MWCNTs and the interfacial polarization from the double-layer core–shell structure. Differently, the hybrids exhibited weak complex permeability (μ'_{max}, 1.03; μ''_{max}, 0.1) compared with complex permittivity in Fig. 3(b), which mainly resulted from non-magnetic substances, such as MWCNTs and