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Preparation and characterization of a kind of magnetic carbon fibers used as electromagnetic shielding materials

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ABSTRACT

In present work, a new kind of magnetic carbon fiber with nickel/Fe_3O_4 nanoparticles (Ni/Fe_3O_4-NPs) composite coatings was prepared by electrodeposition. Microstructure observation indicated that Fe_3O_4-NPs are homogenously distributed and tightly adhered to the coatings, which guarantee that carbon fiber possess high saturation magnetization and permeability. Electromagnetic interference (EMI) shielding test showed that the prepared magnetic carbon fiber exhibit excellent EMI shielding effectiveness. Based on Schelkunoff electromagnetic shielding theory, the high permeability in the prepared carbon fiber can bring about the co-effect of reflection and absorption mechanisms of radiation and thus obviously improve its EMI shielding effectiveness. Therefore, this magnetic carbon fiber is promising for application in electromagnetic shielding materials.

1. Introduction

Carbon fiber is one of the most advanced and important reinforcements attributed to its high modulus, high strength, low density and low coefficient of thermal expansion [1–3]. These properties make carbon fiber a potential material for heavy duty aircraft, automotive parts, electrical equipment, as well as the field of electromagnetic shielding [4–6]. However, to meet application needs in the field of electromagnetic shielding, the magnetic property of carbon fiber should be improved.

On the other hand, iron oxides, one kind of magnetic material, have gained increasing scientific and industrial interest in recent years [7,8]. Fe_3O_4 has high magnetic properties and electrical conductivity, and its composites show microwave electromagnetic characteristics and absorption properties [9–11]. According to these backgrounds, developing a technique to compound carbon fiber and Fe_3O_4 is a possible way to obtain high-performance magnetic carbon fibers used as electromagnetic shielding materials.

With the development of nanotechnology in recent decades, different kinds of nanoparticles have been co-deposited with metals to obtain high performance nanocomposite coatings, such as ZrO_2, SiC, TiO_2, SiO_2, Al_2O_3 and Fe_2O_3 for wear resistant, lubricity, corrosion resistant and magnetic property [12–18]. At present, there are much more research and reports about nanoparticles composite coatings of metal surfaces. But few studies focuses on composite coatings on fiber.

In present paper, referred to the electrodeposition technique, a new kind of magnetic carbon fiber with nickel/Fe_3O_4 nanoparticle (Ni/Fe_3O_4-NPs) composite coatings was prepared. The surface morphology of the coatings and distribution of Fe_3O_4-NPs have been evaluated. The magnetic property and EMI shielding effectiveness of the prepared carbon fiber were investigated.

2. Experimental

Carbon fiber in present work was in the form of continuous bundle revolving around a bobbin. Each bundle consisted of 12,000 filaments with a diameter of 7 μm stuck together by an organic binder. The size of Fe_3O_4-NPs is 10–15 nm. Before electrodeposition, carbon fiber was heated at 500 °C for half an hour in air to burn out the organic binder. The basic composition of the electrolyte and the plating conditions are shown in Table 1.

The Ni/Fe_3O_4-NPs coated carbon fiber was cut into 2–3 mm and then mixed with ABS (Acrylonitrile Butadiene Styrene) powder in a Brabender Plasti-Corder Torque Rheometer (PLE-330) at 220 °C by a screw speed of 20 rpm. After being compounded, the mixture was hot-pressed molded into composite test sample for measuring the EMI shielding effectiveness. The thickness of the composite was 2 μm, and the content of fiber was 15 wt%.

Surface morphology of nanocomposite coatings was examined by a Philips modelMV2300 scanning electron microscope (SEM) operated at 25 kV. Chemical composition of the deposits was determined by energy dispersive X-ray spectroscopy (EDS) system attached to the SEM. The thickness of the composite coatings was measured by means of Olympus-PME3 optical microscopy (OM). Direct images of Fe_3O_4-NPs were obtained by a FEI Tecnai G2 F2 transmission electron microscopy (TEM) at an accelerating voltage of 200 kV in the bright field image mode. Samples were prepared by evaporating a drop of the highly diluted dispersion on a copper grid. The magnetic properties of the carbon fiber with Ni/Fe_3O_4-NPs composite coatings were studied by using a vibrating-sample magnetometer (VSM, FD-MT-A, America) at room temperature. The coaxial transmission line method according to ASTM ES-7-83 was used to measure the EMI shielding effectiveness (SE). The SE was

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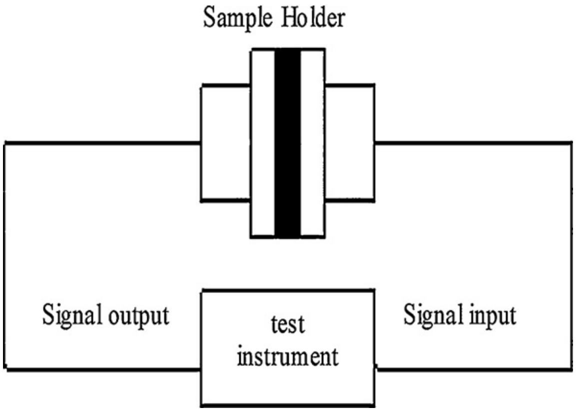

Fig. 1. Set-up for electromagnetic shielding effectiveness measurement.

Table 1
Composition and deposition parameters of the nanocomposite bath.

Deposition parameters	Amount
Nickel sulphate	150 g/L
Ammonium chloride	15 g/L
Boric acid	15 g/L
Dodecyl benzenesulfonic acid, sodium salt	2 g/L
Ferriferrous oxide	60 g/L
Temperature	30 ± 1.5 °C
pH	2.5 ± 0.2
Current density	$1.5 \pm 0.2\ \mathrm{A/dm^2}$
Plating time	10 ± 0.5 min

evaluated by measuring the attenuation or reduction of the electromagnetic wave with the shield in the frequency range from 30 to 1200 MHz, and calculated and expressed in decibels (dB) by using the following equation:

$$\mathrm{SE\ (dB)} = 10\log\frac{P_i}{P_t} = 20\log\frac{E_i}{E_t} = 20\log\frac{H_i}{H_t} \qquad (1)$$

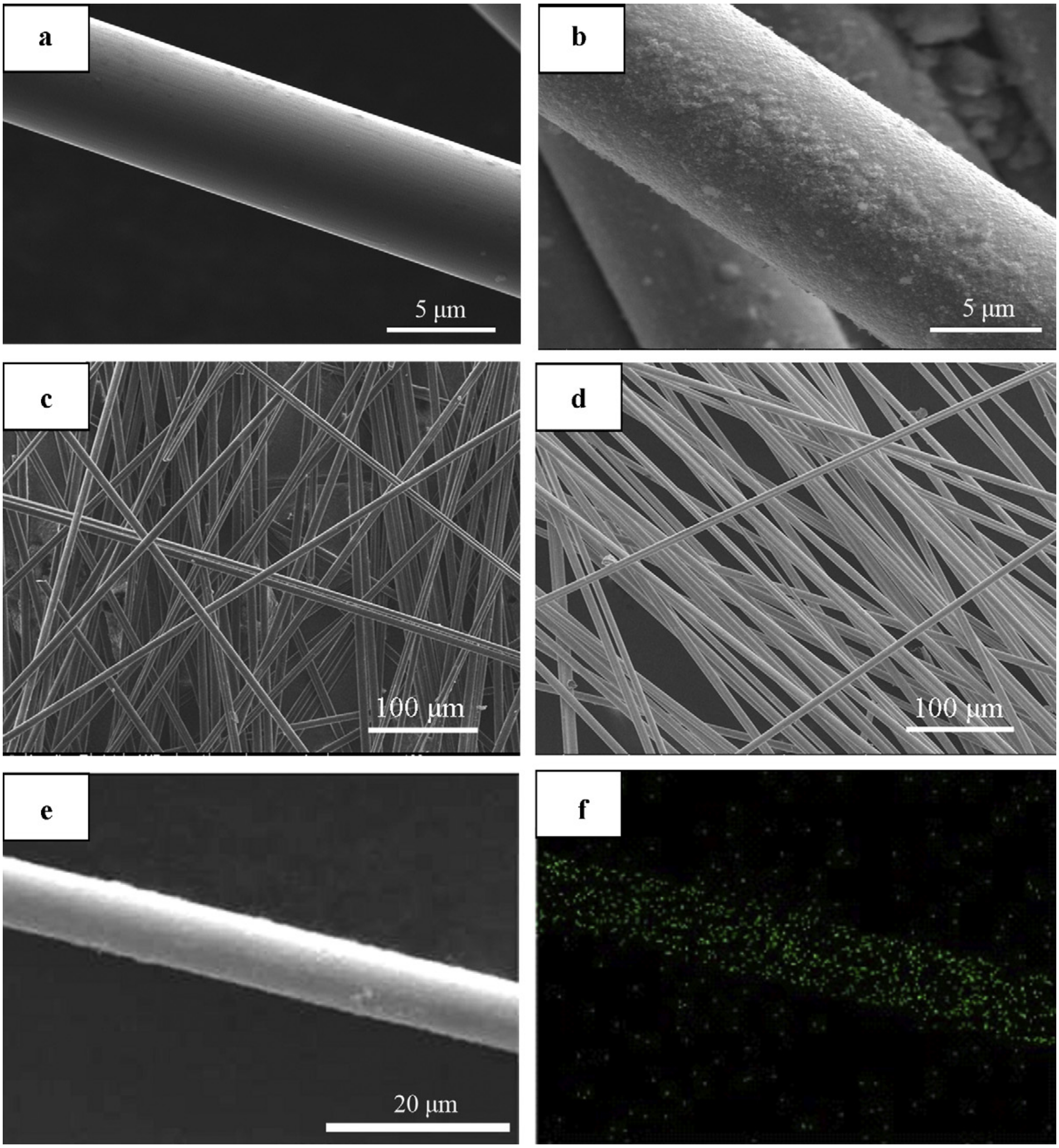

Fig. 2. SEM micrographs of carbon fiber (a), (c), carbon fiber with Ni/Fe_3O_4-NPs composite coatings (b), (d), (e). The corresponding Fe element mapping image of (e) is present (f).

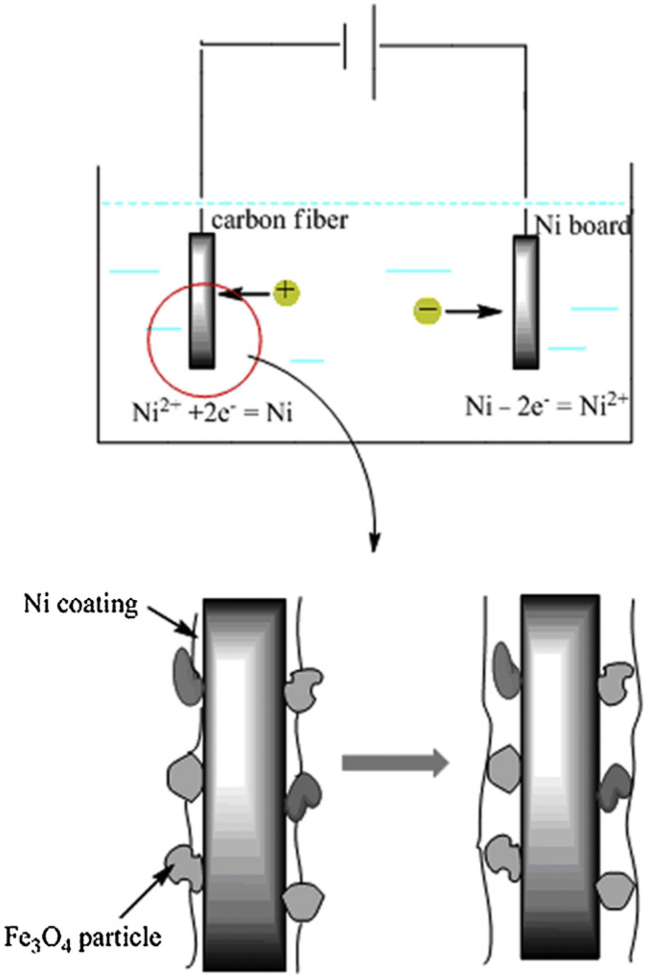

Fig. 3. Schematic diagram of electro-deposition process.

where P_i, E_i, and H_i are power, electric field strength and magnetic field strength, respectively, of the incident wave, and P_t, E_t, and H_t are the same properties, respectively, of the transmitted wave [19]. The set-up consisted of a sample holder with its input and output connected to the network analyzer (see Fig. 1).

3. Results and discussion

3.1. SEM analysis

Fig. 2(a)–(d) shows the SEM micrographs of carbon fiber with and without Ni/Fe_3O_4-NPs composite coatings, respectively. It is observed that the Ni/Fe_3O_4-NPs composite coatings on carbon fiber are dense and continuous. Fig. 2(e) shows a carbon fiber with Ni/Fe_3O_4-NPs composite coatings, and Fig. 2(f) presents the distribution of Fe element in corresponding composite coatings on fiber. It is found that Fe_3O_4-NPs are distributed homogeneously in the coatings. As a kind of soft magnetic material, Fe_3O_4-NPs possess excellent saturation magnetization and permeability. The homogeneous distribution of Fe_3O_4 in the coatings could enhance the magnetic property of carbon fiber.

Fig. 3 shows the process of the electro-deposition. As is shown in the diagram, when the circuit switched on, oxidation and reduction reactions occurred in the surface of Ni board and carbon fiber. The chemical reaction made the concentration of Ni^{2+} remain constant and the Ni coatings formed in the surface of carbon fiber continuously. By mechanical agitation, Fe_3O_4 particles dispersed uniformly in the solution. With the Ni^{2+} depositing on the surface of carbon fiber, Fe_3O_4 particles were co-deposited simultaneously.

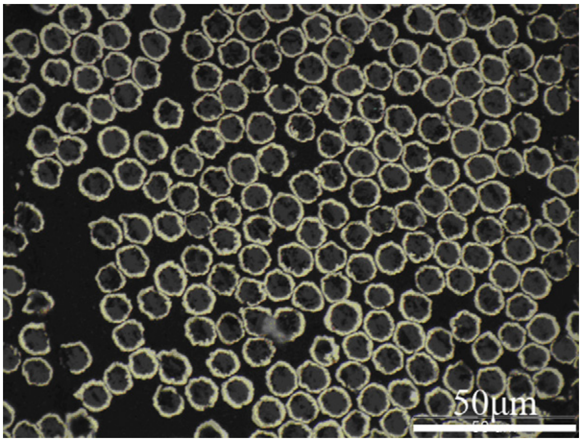

Fig. 4. Optical micrograph of carbon fibers with Ni/Fe_3O_4-NPs composite coatings.

3.2. OM analysis

Fig. 4 shows the cross-section micrograph of carbon fiber with Ni/Fe_3O_4-NPs composite coatings, which is carried out by OM. Centre black parts are carbon fiber while the rings are composite coatings. It is revealed that the coatings were deposited uniformly around each fiber, and the average thickness of the coatings is 1.2 μm.

3.3. TEM analysis

Fig. 5 illustrates the TEM images of the prepared sample. It can be observed that the Fe_3O_4-NPs in the coatings are still in spherical shape with a diameter of 10–15 nm (see Fig. 5a), which is the same as their original state. The result implied that co-electrodeposition technique did not affect the morphology and size of Fe_3O_4-NPs. High-resolution TEM microscopy in Fig. 5b reveals that Fe_3O_4-NPs are tightly adhered to nickel matrix. The TEM diffraction ring (digital diffraction pattern, Fig. 5c) shows that the Fe_3O_4-NPs exhibit a crystalline state, which is consistent with the results reported by Ahmad et al. and Ozkaya et al. [20,21].

Combined with above results, the carbon fiber with Ni/Fe_3O_4 nanocomposite coatings possesses excellent microstructure. It indicates that electrodeposition in a nickel-plating bath is a feasible and convenient method for the preparation of Ni/Fe_3O_4 nanocomposite coatings on the carbon fiber. The dense, continuous Ni matrix with homogenous distributed Fe_3O_4-NPs also guarantees that the coated carbon fiber in present work would exhibit outstanding magnetic property and electromagnetic shielding property.

3.4. Analysis of magnetic and EMI shielding properties

The magnetic property of carbon fiber with Ni/Fe_3O_4-NPs composite coatings was investigated. As a reference, the magnetic property of carbon fiber with Ni coatings was also measured. The room-temperature magnetic hysteresis loops are present in the inset of Fig. 6. The curves indicate that carbon fiber with Ni coatings and Ni/Fe_3O_4-NPs composite coatings both are soft magnetic material for its moderately high saturation magnetization and low coercivity. The permeability of soft magnetic material can be expressed as $\mu = M/H$, where M is the magnetization and H is the external magnetic field. Thus, the permeability of soft magnetic materials mainly depends on their magnetization. Due to the effect of Fe_3O_4-NPs, carbon fiber with Ni/Fe_3O_4-NPs composite coatings

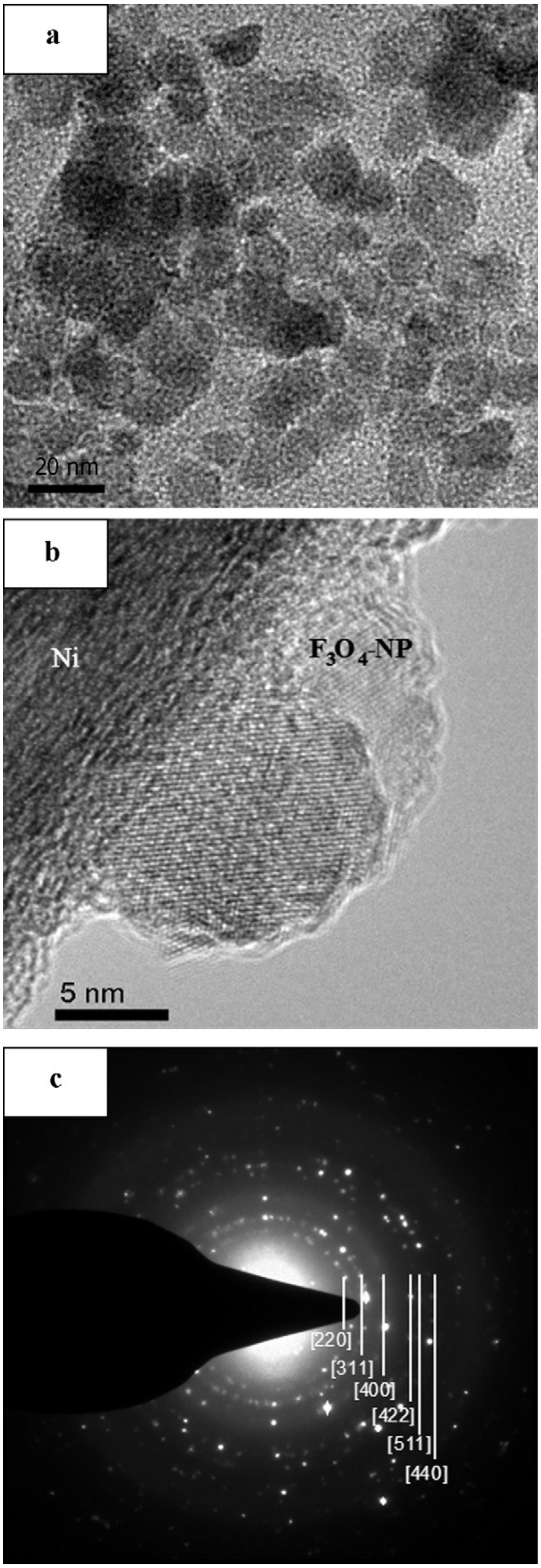

Fig. 5. TEM images (a), (b), and electron diffraction pattern for Fe_3O_4-NPs (c).

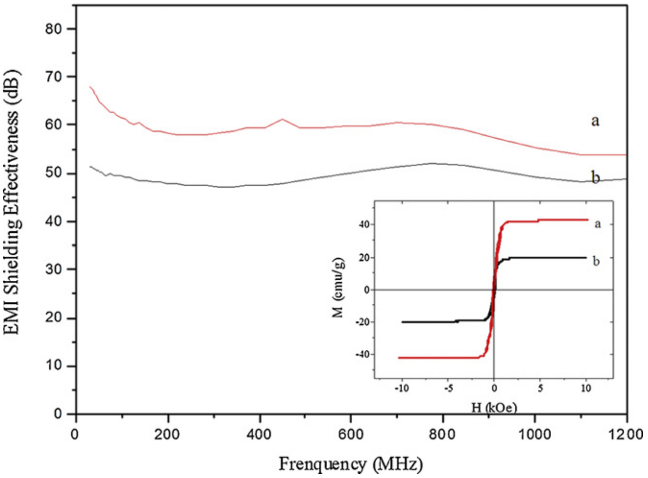

Fig. 6. EMI shielding effectiveness of carbon fibers (a) and carbon fibers with Ni coatings (b) (the inset is magnetization curves obtained by VSM of Fe_3O_4 nanoparticle (a) carbon fibers with Ni/Fe_3O_4-NPs composite coatings (b) at room temperature).

had higher saturation magnetization (47.6 emu/g) than carbon fiber with Ni coatings (19.8 emu/g), and carbon fiber with Ni/Fe_3O_4-NPs composite coatings had higher permeability than carbon fiber with Ni coatings. In the case of electromagnetic interference shielding materials, high permeability will increase the absorption mechanism in the shielding process, and improve the EMI shielding effectiveness ultimately. It was reported that Fe_3O_4 possessed good microwave absorbing ability due to its excellent magnetic property [22–24]. Therefore, carbon fiber with Ni/Fe_3O_4-NPs composite coatings is promising for application in electromagnetic shielding and absorbing materials.

Fig. 6 shows the EMI shielding effectiveness of carbon fiber with Ni/Fe_3O_4-NPs composite coatings and carbon fiber with Ni coatings. The EMI shielding effectiveness of carbon fiber with Ni coatings is around 50 dB, while the EMI shielding effectiveness of carbon fiber with Ni/Fe_3O_4-NPs composite coatings is around 58 dB, much higher than that of carbon fiber with Ni coatings (see Fig. 6).

According to Schelkunoff electromagnetic shielding theory, there are three different attenuation mechanisms to the surface of electromagnetic wave shielding material: reflection, absorption and multiple reflections [25]. Based on the characteristics of metal, it is concluded that the traditional metal EMI shielding material mainly behave according to reflective mechanisms. However, relying solely on reflection mechanism is not sufficient. Iron oxides, such as Fe_3O_4 and other soft magnetic materials, possesses good microwave absorbing ability originating from their high value of the magnetic permeability, which could enhance the effect of absorption mechanism in the shielding materials. In Ni/Fe_3O_4-NPs composite coatings, Fe_3O_4-NPs were distributed homogeneously in the nickel matrix, which could result in the co-effect of reflection and absorption mechanisms of radiation and finally lead to the higher EMI shielding effectiveness.

4. Conclusions

In summary, we prepared and characterized a new kind of magnetic fiber coated with Ni/Fe_3O_4-NPs composite coatings. The EMI shielding effectiveness of this material is investigated. It is found that the prepared magnetic carbon fiber exhibits excellent EMI shielding effectiveness. The high permeability in the prepared carbon fiber can bring about the co-effect of reflection and absorption mechanisms of radiation and thus obviously improve their EMI shielding effectiveness. Based on the present work, combining conductive material with magnetic material is a feasible method to enhance the EMI shielding effectiveness of shielding material. It is hoped that the present study could lay a foundation for the future research on EMI shielding materials.

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