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Achieving tunable electromagnetic absorber via graphene/carbon sphere composites

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ABSTRACT

This article reports on the design and synthesis of tunable electromagnetic absorbers by loading carbon nanospheres on graphene. In this type of composite, carbon spheres with controllable resistivity are employed for achieving tunable electromagnetic absorbers. The resistivity of carbon spheres played a key role in determining the electromagnetic absorbing property. The synthesis of this graphene/carbon nanosphere composite absorber was conducted under wet-chemical conditions. By adjusting the carbonization temperature of carbon nanospheres, the composite absorber could gain its minimum reflection loss value (RL_{min}) at a given frequency region. The electromagnetic attenuation mechanism was also proposed and subsequently proved by control experiments with porous graphene/carbon, graphene oxide/carbon, and graphene/carbon composites.

1. Introduction

Although with the fast growth usage of wireless and electronic devices, aggravating electromagnetic interference problem (EMI) shows a negative role on the nearly electromagnetic devices [1]. To eliminate electromagnetic pollution, electromagnetic absorber has received extremely attention in recent years. Discovery of graphene and the subsequent studies on its physical or chemical feature have revealed that graphene shows huge potential to treat the aggravating electromagnetic interference problem [2,3]. It is well-known that graphene presents good chemical stability, large surface area, high dielectric parameters and low density which is useful to apply in electromagnetic field [4,5]. So, graphene composite has been widely applied in electromagnetic shield field. Batrakov and co-workers have proved that graphene has an optimal shield effect at 30 GHz [6]. Besides, graphene also has been considered to be the good electromagnetic absorber material. For example, the graphene foam reported by Zhang et al. not only achieved a smaller reflection loss value (denoted as RL_{min} value) of −34.0 dB. More importantly, the frequency region (RL_{min} < −10 dB) covered 4–18 GHz. Moreover, at higher frequency region (18–110 GHz), graphene also shows good electromagnetic absorption property [7,8]. Wu et al. revealed the good absorption property of graphene at 125–165 GHz [9].

According to electromagnetic absorption theory, electromagnetic wave can be consumed in multiple forms, like resonance, magnetic domain exchange, eddy current, polarization (electronic, ionic, interface and so on) [10,11]. An ideal reflection loss value was usually achieved since multiple attenuation forms. For instance, $CoNi@SiO_2@TiO_2$ ternary composite prepared by Che et al. got a RL_{min} of −41 dB which was attributed to the synergy effect of interface polarization and eddy current (it usually uses RL_{min} value to represent the attenuation electromagnetic wave intensity [12]. Commonly, the RL_{min} value is related to the attenuation ability. The stronger attenuation ability benefits to a desired RL_{min} value. Only the RL_{min} value less than −10 dB, it has practical application. Similarly, due to the contribution of scattering effect and electron polarization, the RL_{min} value of $Fe_2O_3@CoFe_2O_4$ reported by our

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group was up to −60 dB [13]. Besides, multiple forms of attenuation also happened at other absorbers, liking Co/CoO [14], Co_xFe_y@C [15], porous coin like Fe [16] and ideal RL_{min} values could be gained.

Although more attenuation forms can ensure a lower RL_{min} value, the RL_{min} value corresponded frequency (denoted as optimal absorption frequency) does not to be tunable since the uncontrollable attenuation intensity. It is well-known that the optimal absorption frequency is closely related with the complex part of permeability (μ_r) and permittivity (ε_r). Nevertheless, multiple attenuating mechanisms will lead to uncertain of μ_r and ε_r values and lead to un-adjustable optimal absorption frequency. In fact, most of electronic devices usually work at a specific frequency, it thus useless if the optimal absorption frequency does not fit well these electronic devices. Whereas, it is quite meaningful to develop tunable electromagnetic absorber to satisfy above demands.

Recent researches on graphene have revealed this probability due to its special attenuation theory [17]. It is widely believed that sp^2 hybridization of graphene contains numerous of free electrons [18]. These free electrons are extremely sensitively to the external electromagnetic wave field. Their acts as the medium to allow the electromagnetic energy convert to electric energy and give rise to current [19,20]. The translated electrical energy can be consumed if loading a resistor on graphene, similar to Joule's law.

To ensure a tunable optimal absorption frequency, these loading materials should satisfy two conditions. Firstly, the resistivity of this loading material is easily controllable. Then, the attenuation ability of corresponding graphene composite obeys Joule's lay which other types of attenuation ways are quite weakly and can be neglected. In this case, recent reported graphene composites, like graphene/MnO_2 [21], graphene/Fe_3O_4 [22] graphene/Fe [23] and graphene/$CoFe_2O_4$ [24] were not suitable, due to the exhibition of magnetic loss and polarization effect.

As a representative carbon material, poor graphitization level of amorphous carbon nansphere presents superior advantages. Through adjusting annealing temperature, the resistivity of these carbon nanospheres was adjustable. Besides conductive loss, the polarization loss can be ruled out for the graphene/carbon composite since the identical electronegativity value and less defects on graphene. Graphene/carbon absorber also presents lightweight, high chemical stability features. Thus, development of graphene/carbon composites has been considered to good strategy to prepare tunable electromagnetic absorber.

2. Experimental section

2.1. Materials

Graphene oxide (GO) and graphene were brought from Suzhou NanoTechnology (P. R. China). Methanol, glucose, hydrogen peroxide (H_2O_2), glycol, isopropyl alcohol, ammonia water were purchased from Sinopharm Chemical Reagent Co. (P. R. China) Aminopropyltrimethoxysilane (APS) and melamine was purchased from Aldrich.

2.2. Synthesis of carbon nanospheres with different resistivity (ρ)

A simple solvothermal process has been applied to prepare carbon nanospheres. Typically, 5 g of glucose was added into 25 mL distilled water (DI). Then, 2 mL of ethylene glycol (EG) was dropwise into the above solution. Before transferred to a 50 mL of autoclave and heated at 180 °C for 10 h, this solution was undergo the magnetic stirring for 20 min to form a clear solution. Brown precipitate was obtained by centrifuged and washed with DI for 3–5 times. By further annealing the brown precipitate in the nitrogen gas atmosphere, carbon spheres were achieved. The temperature set as 500, 600, 700 and 800 °C, respectively and corresponding carbon spheres were denoted as CS-500, CS-600, CS-700 and CS-800.

2.3. Preparation of CN/CS composites

Before loading graphene, graphene was treated by 20 mL of HCl (1 M) for 1 h (named as HGN). Synthesis of graphene/carbon composite involves a liquid phase approach. Firstly, 100 mg of as-prepared carbon spheres were dispersed in 100 mL of isopropyl alcohol for ultrasonic treatment 1 h. Then, 2 mL APS was injected into the solution and kept ultrasonic treatment for 10 min, Lastly, 5 mL NH_4OH and 10 mL DI were dropped into the above solution and subsequently dried at 40 °C for 24 h. APS modified carbon sphere (APS/CS) was obtained. Graphene/g-C_3N_4 composite was prepared by a simple liquid phase approach. In brief, 10 mg of HGN was dropped into 50 mL methanol for ultrasonic treatment 1 h. Then, 100 mg APS/CS was added into the solution under another 1 h of ultrasonic treatment.

2.4. Produce porous graphene

The porous graphene was prepared based on Palamiselavm literature [25]: 25 mg of graphene was added into 100 mL H_2O_2 and string at 70 °C for 72 h.

2.5. Characterization

The XRD patterns were recorded on the powder X-ray diffraction (XRD) patterns (Bruker D8 ADVANCE X-ray diffractometer) using Cu Kα radiation (λ = 0.154178 nm with 40 kV scanning voltage, 40 mA scanning current and scanning range from 10 to 80°). Field Emission Scanning Electron Microscopy (FESEM, HITACHI S-4800) and Transmission Electron Microscope (JEM, JEOL 2010) were conducted to observe their structures. The information related to chemical bonds was tested by the Fourier Transform Infrared (FT-IR, Perkin-Elmer IR spectrometer). Raman spectrum was recorded to establish the graphitization degree of carbon nanosphere (Jobin Yvon HR 800 confocal Raman system, wavelength = 514 cm^{-1}).

2.6. Electromagnetic parameters measurement

By the coaxial-line method, S parameters (S11, S12, S21 and S22) were tested by an Agilent PNA N5224A vector network analyzer in which the tested ring was prepared by homogeneously mixing 90 wt% of paraffin wax and 10 wt% GN/CS composite (filled ratio = 1:9) and then pressed into toroidal-shaped samples (Φ_{out}:7.0 mm, Φ_{in}:3.04 mm). Then, a software which has been installed in Agilent PNA was carried out to calculate the ε', ε'', μ', μ'' values. Lastly, the frequency dependence of reflection loss curves were evaluated by the following equations [26–28]:

$$Z_{in} = Z_o(\mu r/\mu r)^{1/2} \tanh\left[j\left(2\pi f d(\mu_r\varepsilon_r)^{1/2}/c\right)\right] \quad (1)$$

$$RL(\mathrm{dB}) = 20\log|(Z_{in} - Z_o)/(Z_{in} + Z_o)| \quad (2)$$

Where Z_{in} means the input impedance of the absorber, Zo accounts for the characteristic impedance of free space (377 Ω). f is the frequency of electromagnetic wave, d is the coating thickness of the absorber while c is the velocity of the light. ε_r ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and μ_r ($\mu_r = \mu' - j\mu''$) are the complex permittivity and permeability of the absorber [29].