Synthesis of rGO/p-Fe₃O₄@PANI three-phase nanomaterials and electromagnetic wave absorption properties

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Abstract
A novel rGO/p-Fe₃O₄@PANI three-phase nanomaterial was prepared by coating conductive polyaniline (PANI) on reduced graphene oxide (rGO) and porous Fe₃O₄ (p-Fe₃O₄), which can increase the reflection interface of electromagnetic waves and extend the reflection path of electromagnetic waves propagating inside the material, and between them. Three kinds of rGO/p-Fe₃O₄@PANI samples were prepared. The mass percentage of PANI in the samples was established. The mass ratio of rGO to p-Fe₃O₄ was changed to ameliorate the impedance matching and attenuation constant. Compared with rGO/p-Fe₃O₄, rGO/p-Fe₃O₄@PANI exhibits excellent electromagnetic wave absorption performance. When the mass ratio of rGO to p-Fe₃O₄ in the 40 wt% three-phase material is 1:5 and the thickness is 2.5 mm, the minimum RL of rGO/p-Fe₃O₄@PANI is −41.38 dB at 9.75 GHz and the effective absorption bandwidth to electromagnetic wave reaches 3.08 GHz (from 8.40 to 11.48 GHz), indicating that it is a potentially attractive candidate for high efficiency electromagnetic wave absorbers. The combination of the conductive polymer, porous magnetic nanoparticles and rGO improves the impedance matching condition to some extent, and effectively increases the attenuation constant of the material.

1. Introduction

With the rapid development of the modern society, electromagnetic wave has been extensively used in the field of wireless communications, but they have also brought problems such as electromagnetic interference and information leakage [1–6]. In addition, in the military field, there are demands for electromagnetic shielding technology and stealth technology such as in the field of military aircraft [7–9]. These have led to continuous and widespread attention on electromagnetic wave absorbing materials and there is an urgent need to develop an electromagnetic wave absorbing material that is thin in thickness, light in weight, wide in frequency bandwidth and strong in absorption [10, 11].

Carbon nanomaterials represented by graphene and carbon nanotubes are favorable candidates for electromagnetic wave absorbing materials owing to their highly stable and unique structure and high electrical conductivity. Graphene oxide has excellent electromagnetic wave absorption performance owing to its low density, low resistivity, high conduction loss, polarization relaxation of defects and dipole polarization relaxation groups [12–15]. The existence of these dipole polarization relaxation groups is beneficial to the microwave absorption of materials, but these groups may carry a large number of oxygen atoms, which will weaken the polarization and conductivity of graphene oxide, and then affect its polarization/conduction loss as a microwave absorption material [16]. In order to take advantage of the existence of dipolar polarization relaxation groups and avoid the disadvantage of carrying a large number of oxygen atoms, the researchers reduced graphene oxide to rGO, which can reduce the oxygen atom content of rGO. In addition, graphene oxide has high electron mobility, making it difficult to meet the impedance matching of electromagnetic wave
absorption [17]. In order to solve this problem, the researchers have proposed many solutions, but the most effective one is to combine graphene and magnetic particles—Fe₃O₄ [18], Co₃O₄ [19], CoFe₂O₄ [20], NiFe₂O₄ [21] etc.—into a two-phase material.

Among many magnetic materials, Fe₃O₄ is considered to be the most ideal absorbing material in the GHz range owing to its high magnetic permeability, low toxicity, low cost and availability [22, 23]. Wang et al [24] uniformly dispersed 25 nm Fe₃O₄ nanoparticles on the surface of graphene by depositing and annealing in Ar gas. Compared with pure magnetic particles and graphene, the electromagnetic wave absorption properties of the nanocomposite were significantly improved. The material with a thickness of 5 mm has a minimum RL of −40.36 dB, which is a good candidate of lightweight and strong electromagnetic wave absorption. However, conventional Fe₃O₄ for absorbing materials still has some disadvantages such as high density and poor high temperature stability [25, 26]. In view of those, researchers generally attempted to prepare nano-Fe₃O₄ with various microstructures that can enhance the absorption of electromagnetic wave. This means to increase the performance of electromagnetic wave absorbing per unit mass of Fe₃O₄—reduce the amount of Fe₃O₄ [27–29]. At the same time, researchers also tried to design a protective layer on the surface of nano-Fe₃O₄ to form a core–shell structure. The usual methods are in situ polymerization and surface oxidation [30]. In situ polymerization is usually carried out by coating a layer of conductive polymer on the surface of nano-Fe₃O₄, which is stable and helpful to enhance electromagnetic absorption properties, thereby improving the stability and electromagnetic wave absorption properties of nano-Fe₃O₄ [31]. In order to reduce the oxygen content of graphene oxide, we reduced graphene oxide to rGO, and distributed p-Fe₃O₄ with multiple micro-interfaces on the surface of rGO. Finally, PANI was coated on the surface of p-Fe₃O₄, rGO and between them, which was rare to report. When the material absorbs electromagnetic wave, PANI can enhance the absorption and play a role in the smooth transition of dielectric behavior of p-Fe₃O₄ and rGO. At the same time, it can protect p-Fe₃O₄ and rGO from oxidation to some extent.

In this paper, we designed and synthesized rGO/p-Fe₃O₄@PANI three-phase nanocomposites. Firstly, p-Fe₃O₄ was prepared by simple hydrothermal method. Secondly, rGO/p-Fe₃O₄ with different mass ratios was prepared by solution mixing and dispersion under ultrasonic stirring. Then, rGO/p-Fe₃O₄ was modified by PANI through in situ polymerization of aniline monomers, resulting that a layer of PANI was coated on the surface of rGO, p-Fe₃O₄ and between them. Finally, rGO/p-Fe₃O₄@PANI nanoparticles were mixed with paraffin to prepare rGO/p-Fe₃O₄@PANI electromagnetic wave absorbing material samples. The structure, morphology, dielectric properties, magnetic properties and electromagnetic wave absorption properties of rGO/p-Fe₃O₄@PANI three-phase nanocomposites were studied.

2. Experimental details

2.1. Materials

Graphene oxide (GO) prepared by Hummers method was purchased from Suzhou Carboniferous Graphene Technology Co., Ltd (China). According to the data provided by the manufacturer about GO, the range of the diameter and number of layers of graphene oxide sheets is 10–50 μm and 1–2 layers. Iron(III) chloride hexahydrate(FeCl₃ ⋅ 6H₂O), ethylene glycol(HOCH₂CH₂OH), sodium acetate trihydrate(CH₃COONa), polyethylene glycol(POOH(CH₂CH₂O)nH), glucose(C₆H₁₂O₆), urea(CH₄N₂O), N,N-Dimethylformamide(DMF, C₃H₇NO), ethanol(C₂H₅OH), and ammonium Hydroxide(NH₃ ⋅ H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd Tetraethyl orthosilicate(TEOS), polyvinyl pyrrolidone(PV), aniline (AN), Hydrochloric acid(HCl), Ammonium persulphate(NH₄)₂S₂O₈ were purchased from Aladdin Reagent. All chemicals used in this work are analytical grade, do not require further purification and are all commercially available. Deionized water is used throughout the experiment.

2.2. Synthesis of magnetic porous Fe₃O₄ microspheres

The magnetic porous Fe₃O₄ in this paper was prepared by the previously reported method [32]. The typical preparation process was as follows: 2.0 g of FeCl₃ ⋅ 6H₂O, 5.4 g of sodium acetate and 1.5 g of polyethylene glycol were added to 60 mL of ethylene glycol and vigorously stirred into a homogeneous solution, and then transferred to a Teflon-lined stainless steel reaction vessel. After reacting at 210 °C for 8 h, it was recovered by magnetic washing and dried to obtain black solid particles. Secondly, 0.69 g of the black solid particles, 1.5 g of glucose, 4.5 g of urea were uniformly dispersed in 60 ml of deionized water by ultrasonic dispersion, and then transferred to a Teflon-lined stainless steel reaction vessel, after reacting at 210 °C for 10 h, it was recovered by washing and dried to obtain black particles.
2.3. Synthesis of rGO/p-Fe₃O₄

The rGO/p-Fe₃O₄ in this paper is given in table 1. Taking No.1 as an example, the preparation process was as follows: firstly, the purchased GO was ultrasonically dispersed into 300 ml of deionized water and transferred to a 500 ml three-necked flask. After magnetic stirring for 20 min, 146 μl of hydrazine hydrate was added, and after reducing for 100 min at 100 °C. After filtration and washing with deionized water and ethanol, then drying in a vacuum oven at 60 °C for 6 h, the rGO was collected. Secondly, ultrasound dispersion of 1.0 g of the black particles prepared in step 2.2 into 50 ml ethanol and 0.2 g rGO into 50 ml DMF were carried out. After ultrasonic dispersion for 30 min, the two were transferred to a 250 ml three-necked flask and mechanically stirred for 2 h. Finally, distillation under reduced pressure was carried out and the ethanol in the system was removed at a temperature of 60 °C. After the ethanol was removed, the temperature was raised to 100 °C to reduce the DMF in the system. A portion of the DMF was left in the three-necked flask for transfer of the product. The remaining mixture was poured into the glass surface dish and dried in a vacuum oven at 100 °C for 5 h to obtain the black granules.

2.4. Modified rGO/p-Fe₃O₄

1.0 g of black granules prepared in step 2.3 was added to 20 ml mixed liquids (ethanol: water = 4:1) and mechanically stirred at room temperature for 1 h, then 3 mL of ammonia water and 3 ml of ethyl orthosilicate were added slowly. The mixture was mechanically stirred at room temperature for 12 h, off-white particles were obtained by washing and centrifugation.

2.5. Synthesis of rGO/p-Fe₃O₄@PANI

1.0 g of the off-white particles prepared in step 2.4 and 0.2 g of PVP were added to 50 ml of deionized water and mechanically stirred for 2 h in an ice water bath environment, then hydrochloric acid of 0.6 mol l⁻¹ of 48 ml and 1.0 g aniline was added. After mechanically stirred for 1 h in an ice water bath environment, ammonium persulfate deionized water solution of 0.15 g ml⁻¹ of 40 ml was added slowly. After mechanically stirred in an ice water bath environment for 8 h, the green particles were obtained by washing and centrifugation.

2.6. Characterization

The Fourier-transform infrared (FTIR) spectra of p-Fe₃O₄, rGO/p-Fe₃O₄, modified rGO/p-Fe₃O₄ and rGO/p-Fe₃O₄@PANI were characterized by Fourier-transform infrared spectroscopy (Nicolet 6700). The crystal properties of p-Fe₃O₄, rGO/p-Fe₃O₄ and rGO/p-Fe₃O₄@PANI were characterized by x-ray diffraction (XRD) diffractometer (Bruker D8 Advance, with Cu Kα source, λ = 0.154056 nm). The microscopic morphology and structure of p-Fe₃O₄, rGO/p-Fe₃O₄ and rGO/p-Fe₃O₄@PANI were characterized by scanning electron microscopy (SEM, Zeiss Ultra Plus). The surface functional groups of the product were measured by a x-ray photoelectron spectroscopy (XPS) instrument (Thermo Scientific K-Alpha). The room temperature magnetic properties of the p-Fe₃O₄, rGO/p-Fe₃O₄ and rGO/p-Fe₃O₄@PANI were recorded by a vibrating sample magnetometer (VSM, JDW-2000D) (the external magnetic field was −10000 to 10000 Oe). The electromagnetic parameters of the samples were measured using a vector network analyzer (VNA, Agilent N5247A) at an electromagnetic frequency ranging from 1 to 18 GHz.

### Table 1. The samples prepared with different mass ratios.

| Sample | rGO | p-Fe₃O₄ | rGO:p-Fe₃O₄ |
|--------|-----|---------|-------------|
| 1      | 0.2 g | 1.0 g | 1:5         |
| 2      | 0.1 g | 1.0 g | 1:10        |
| 3      | 0.1 g | 2.0 g | 1:20        |

3. Results and discussion

Figure 1 (a) is the infrared spectrum of p-Fe₃O₄. The absorption peaks of (a)–(d) near 580 cm⁻¹ highlighted by the yellow rectangle are vibration absorption peaks of Fe–O–Fe [33]. Figure 1 (b) is the infrared spectrum of rGO/p-Fe₃O₄. The absorption peak at 3424 cm⁻¹ is the stretching vibration absorption peak of the hydroxyl group of rGO. Figure 1 (c) is the infrared spectrum of TEOS-modified rGO/p-Fe₃O₄. It contains not only the vibration absorption peaks of Fe–O–Fe and hydroxyl groups in figure 1 (b), but also the symmetrical vibration absorption peaks and bending vibration absorption peaks of Si–O bond at 800 cm⁻¹ and 472 cm⁻¹, and the bending vibration absorption peaks of Si–OH at 955 cm⁻¹. The vibration absorption peak of Si–O–Fe is at
1100 cm$^{-1}$, so it can be judged that the SiO$_2$ modified layer has been perfectly coated on the surface of p-Fe$_3$O$_4$ through chemical bonds. Figure 1(d) is the infrared spectrum of rGO/p-Fe$_3$O$_4$@PANI. It contains all the absorption peaks of 1(c). In addition, the peaks at 1580 cm$^{-1}$ and 1500 cm$^{-1}$ belong to the stretching vibration absorption peak of C=C in quinone ring and benzene ring; the peak at 1295 cm$^{-1}$ belongs to the bending vibration absorption peak of C–N in benzene ring; the peak at 948 cm$^{-1}$ corresponds to the vibration absorption peak of C–H, which is belong to the benzene ring after 1, 4 substitution [34, 35]. Those all indicated that the in situ polymerization of polyaniline on TEOS modified rGO/p-Fe$_3$O$_4$ surface was successful.

Figure 2 shows the XRD spectra of p-Fe$_3$O$_4$, rGO/p-Fe$_3$O$_4$ and rGO/p-Fe$_3$O$_4$@PANI. As shown in figure 2(a), the strong peaks at 30.076$^\circ$, 35.426$^\circ$, 43.053$^\circ$, 56.935$^\circ$ and 62.520$^\circ$ are the characteristic diffraction peaks of Fe$_3$O$_4$, which correspond to (220), (311), (400), (511) and (440) crystal surfaces respectively, and are completely consistent with the standard XRD card data (PDF#99-0073), indicating the existence and good crystallinity of Fe$_3$O$_4$ [36]. As shown in figures 2(b) and (c), a characteristic diffraction peak appears near 2θ = 20$^\circ$–30$^\circ$, which corresponds to the (002) surface of rGO [37]. Characteristic diffraction peaks of Fe$_3$O$_4$ also appear in figures 2(b) and (c), but the intensity of characteristic diffraction peaks of Fe$_3$O$_4$ decreases significantly compared with figure 2(a), especially in figure 2(c). For figure 2(b), the reason why the peak intensity of characteristic diffraction peaks of Fe$_3$O$_4$ decreases is that the mass percentage of p-Fe$_3$O$_4$ decreases when rGO is added. For figure 2(c), because the PANI shell is very thin and amorphous, it has no effect on the composite crystal structure, so there is no obvious characteristic diffraction peaks of PANI. The peak intensity of the characteristic diffraction peak of p-Fe$_3$O$_4$ decreases because the mass percentage of p-Fe$_3$O$_4$ decreases further after the rGO/p-Fe$_3$O$_4$ coating PANI. Consistently, compared with figure 2(b), the peak intensity of the characteristic diffraction peak of rGO near 2θ = 20$^\circ$–30$^\circ$ also decreases. Combining these with Fourier-transform infrared spectra, it can be concluded that rGO/p-Fe$_3$O$_4$@PANI is successfully prepared.
The chemical element composition of the synthesized rGO/p-Fe₃O₄ and rGO/p-Fe₃O₄@PANI complexes was further characterized by XPS. It can be seen from figure 3(a) that the prepared rGO/p-Fe₃O₄ is mainly composed of iron, oxygen, nitrogen and carbon, and the peaks of Cls, N1s, O1s and Fe2p are respectively at 285.08 eV, 399.08 eV, 531.08 eV and ~717 eV. Compared with rGO/p-Fe₃O₄, rGO/p-Fe₃O₄@PANI contains all the peaks of rGO/p-Fe₃O₄, but the intensity of Cls and O1s peaks is improved, especially on O1s. The extra peaks at 103.08 eV and 153.08 eV correspond to the peaks of Si2p and Si1s, which are the result of TEOs modified rGO and p-Fe₃O₄ to some extent. As shown in figure 3(b), the peaks of Fe2p1/2 (723.78 eV) and Fe2p3/2 (709.58 eV) of rGO/p-Fe₃O₄@PANI are weaker than those of rGO/p-Fe₃O₄, which reveals the successful polymerization of PANI and that the existence of PANI reduces the peak intensity of Fe₃O₄. As shown in figure 3(c), the C1s spectrum of rGO/p-Fe₃O₄@PANI contains four main peaks at 284.3 eV, 285.0 eV, 285.6 eV and 286.8 eV, respectively, due to C=C/C=C in the aromatic ring, C=N and C=O (carbonyl group) [38]. As shown in figure 3(d), the N1s spectrum of rGO/p-Fe₃O₄@PANI can be divided into three peaks. The peaks at 398.93 eV and 399.68 eV correspond to quinone diamine (−N=−) and phenylenediamine (−NH−) structure, the peak at 400.38 eV is attributed to the protonated imine (−N⁺=) structure, further demonstrating the successful synthesis of PANI [39].

As can be seen from figure 4(a)—the scanning electron microscopy (SEM) of p-Fe₃O₄, the prepared p-Fe₃O₄ exhibits irregular spherical shape and its surface is uneven with errors from top to bottom. Compared with regular spherical shape, the prepared p-Fe₃O₄ has a higher specific surface area that can increase the reflection interface of electromagnetic waves and reveal the reflection path of electromagnetic waves propagating inside the material. It also can be seen that the dispersion of p-Fe₃O₄ is good. The porous structure of p-Fe₃O₄ can be obviously seen from figure 4(b)—the transmission electron microscopy (TEM) of p-Fe₃O₄. As shown in figure 4(c), modified p-Fe₃O₄ dispersed on the surface of rGO sheet does not exhibit a regular spherical shape, but the roughness of the surface and the amplitude of concavity and convexity is lower than that of the single p-Fe₃O₄, but it is still uneven and the structure is still favorable for the in situ polymerization of aniline. In addition, it can be seen from the red region of figure 4(c) that the SiO₂ layer also modified rGO and connected rGO and p-Fe₃O₄ to some extent. As shown in figure 4(d), after in situ polymerization of aniline monomers on the surface of rGO/p-Fe₃O₄, PANI covers the whole p-Fe₃O₄ surface with a very dense coating, which roughens the surface of p-Fe₃O₄ particles and forms a dense core–shell structure of rGO/p-Fe₃O₄@PANI three-phase composite. After PANI is coated on the surface of p-Fe₃O₄, rGO and between them (red region of figure 4(d)), the interfacial relaxation can be increased and the electron polarization can be easily formed under the action of external electric field in the process of transmission, which can improve the dielectric loss of the material to electromagnetic wave, then improve the absorption performance of the material to electromagnetic wave. Figures 4(f)∼(i) shows EDS elemental mapping images of figure 4(e), indicating the uniform distribution of the element of Carbon, Iron, Nitrogen and Oxygen of rGO/p-Fe₃O₄@PANI three-phase nanomaterial.

The magnetic properties of p-Fe₃O₄ (figure 5(a)), rGO/p-Fe₃O₄ (figure 5(b)), rGO/p-Fe₃O₄@PANI (figure 5(c)) were studied by applying the maximum magnetic field of +10 KOe at room temperature using VSM. As shown in figure 5, the saturation magnetization of rGO/p-Fe₃O₄ is reduced from 57.9 emu g⁻¹ to 33.4 emu g⁻¹ and the coercive force is reduced from 120 Oe to 80.4 Oe, compared with pure p-Fe₃O₄. In addition, it is apparent to figure 5(c) that the saturation magnetization of rGO/p-Fe₃O₄@PANI is reduced to...
only 4.46 emu g$^{-1}$ and the coercive force is increased to 130.36 Oe by coating rGO/p-Fe$_3$O$_4$ with PANI. The results show that both rGO/p-Fe$_3$O$_4$ and rGO/p-Fe$_3$O$_4$@PANI exhibit ferromagnetism. Reduced graphene oxide and polyaniline are almost nonmagnetic. The magnetic properties of rGO/p-Fe$_3$O$_4$ and rGO/p-Fe$_3$O$_4$@PANI are attributed to the p-Fe$_3$O$_4$ nanoparticles dispersed on the surface of rGO. The low saturation magnetization of rGO/p-Fe$_3$O$_4$@PANI is attributable to the introduction of non-magnetic PANI shell, which further greatly reduces the effective mass percentage of p-Fe$_3$O$_4$.

In order to characterize and understand the electromagnetic wave absorption mechanism of the prepared materials, the real parts ($\varepsilon'$) of the permittivity, the imaginary parts ($\varepsilon''$) of the permittivity, the real parts ($\mu'$) of the permeability and the imaginary parts ($\mu''$) of the permeability of each rGO/p-Fe$_3$O$_4$@PANI and rGO/p-Fe$_3$O$_4$ samples are measured in the range of the electromagnetic wave frequency of 1-18 GHz and are shown in figures 6(a)–(d).

As shown in figure 6(a), The value of $\varepsilon'$ of rGO/p-Fe$_3$O$_4$(1:20)@PANI, rGO/p-Fe$_3$O$_4$(1:10)@PANI, rGO/p-Fe$_3$O$_4$(1:5)@PANI, rGO/p-Fe$_3$O$_4$(1:3)@PANI and rGO/p-Fe$_3$O$_4$(1:5)@PANI decreased from 7.36 to 5.46, 9.59 to 7.40, 11.32 to 8.39 and 12.83 to 7.90, respectively. For the rGO/p-Fe$_3$O$_4$@PANI samples, as the mass percentage of rGO increases, $\varepsilon'$ of the samples shows an increasing tendency, which is attributed to the introduction of PANI and the high conductivity rGO and the synergistic effect of rGO and PANI. For rGO/p-Fe$_3$O$_4$(1:5)@PANI and rGO/p-Fe$_3$O$_4$(1:5), although $\varepsilon'$ of the former is slightly smaller than the latter, the variation with frequency of $\varepsilon'$ of the former is significantly smaller than the latter. The cause is that PANI is polymerized with rGO/p-Fe$_3$O$_4$ at a mass ratio of 1:1. The conductivity of PANI is not as good as rGO, so the $\varepsilon'$ of rGO/p-Fe$_3$O$_4$(1:5)@PANI is smaller than that of rGO/p-Fe$_3$O$_4$(1:5). However, after introducing conductive PANI into rGO/p-Fe$_3$O$_4$ system, PANI can play a role in coordinating the interface between rGO and p-Fe$_3$O$_4$ resulting in improving the $\varepsilon'$ of rGO/p-Fe$_3$O$_4$(1:5)@PANI to some extent. So the $\varepsilon'$ of rGO/p-Fe$_3$O$_4$(1:5)@PANI is only slightly smaller.
than rGO/p-Fe3O4(1:5) and the variation with frequency of $\varepsilon''$ of rGO/p-Fe3O4(1:5)@PANI is smaller than rGO/p-Fe3O4(1:5).

As shown in figure 6(b), the value of $\varepsilon''$ of rGO/p-Fe3O4(1:20)@PANI, rGO/p-Fe3O4(1:10)@PANI, rGO/p-Fe3O4(1:5)@PANI, rGO/p-Fe3O4(1:5) decreased from 2.11 to 2.60, 2.65 to 3.39, 2.80 to 4.28 and 2.60 to 3.91, respectively. For rGO/p-Fe3O4@PANI samples, the change tendency and cause of $\varepsilon''$ of samples are approximately same as $\varepsilon'$ of samples. However, the $\varepsilon''$ of rGO/p-Fe3O4(1:5)@PANI is significantly higher than that of rGO/p-Fe3O4(1:5). The $\varepsilon''$ of rGO/p-Fe3O4(1:5) is approximately similar to that of rGO/p-Fe3O4(1:10)@PANI. The reason may be that even if rGO has a greater loss to electromagnetic waves than PANI, the mass percentage of PANI in rGO/p-Fe3O4@PANI system is significantly larger than that of rGO and the role of coordinating system of PANI, the loss to electromagnetic wave can be improved and the value of $\varepsilon''$ increases, but the effect of these is still limited.

As shown in figures 6(c) and (d), for rGO/p-Fe3O4@PANI samples, since the mass percentage change of p-Fe3O4 is small, their values of $\mu'$ and $\mu''$ are not much different and increase with frequency varies. The variation range of the $\mu'$ and $\mu''$ values of rGO/p-Fe3O4@PANI are less than rGO/p-Fe3O4, mainly due to the introduction of PANI on the surface of p-Fe3O4, which reduces and stabilizes the magnetic properties of p-Fe3O4 to a certain extent. In general, the values of $\mu'$ and $\mu''$ of all samples were similar and no significant change occurred.
As shown in figure 6(c), the dielectric loss tangent of rGO/p-Fe₃O₄@PANI is larger than that of rGO/p-Fe₃O₄ on the whole. Although the dielectric loss tangent of two kinds of sample change with the frequency in the same trend, the change amplitude of the dielectric loss tangent of rGO/p-Fe₃O₄@PANI with the frequency is obviously smaller than that of rGO/p-Fe₃O₄, which also shows that the introduction of PANI into the rGO/p-Fe₃O₄ system can not only increase the dielectric loss to electromagnetic wave to some extent, but also stabilize the dielectric loss of material to electromagnetic wave within frequency of 1–18 GHz. The reason is that PANI is coated on the surface of p-Fe₃O₄, rGO and between them, which can play a coordination and transition role between p-Fe₃O₄ and rGO. For rGO/p-Fe₃O₄@PANI samples, with the decrease of the mass percentage of rGO (i.e., the increase of the mass percentage of p-Fe₃O₄), the dielectric loss tangent of rGO/p-Fe₃O₄@PANI samples to electromagnetic wave has no significant change, probably because the mass percentage of rGO is relatively small to PANI, even if the mass percentage of rGO changes, the dielectric loss tangent of material to electromagnetic wave has no significant change. As shown in figure 6(f), for rGO/p-Fe₃O₄@PANI, because the mass percentage change of p-Fe₃O₄ is small, their magnetic loss tangent values have no significant difference. The change range of magnetic loss tangent of rGO/p-Fe₃O₄@PANI is smaller than that of rGO/p-Fe₃O₄, mainly because of the introduction of PANI, which reduces and stabilizes the magnetism of p-Fe₃O₄ to some extent.

In order to study that the three-phase nanocomposite material may have better electromagnetic wave absorption performance than the two-phase composite material, the reflection loss (RL) of each rGO/p-Fe₃O₄@PANI and rGO/p-Fe₃O₄ (1:5) is according to the transmission line [40]:

\[
RL = 20 \log_{10} \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|
\]  

(1)

\[
Z_{in} = Z_0 \frac{\mu_r}{\epsilon_r} \tanh \left( \frac{j2\pi fd\mu_r\epsilon_r}{c} \right)
\]  

(2)

Among them, \(Z_{in}\) is the characteristic input impedance of the absorbing material, \(Z_0 \approx 377 \Omega\) is the characteristic impedance of free-space, \(f\) is the frequency of electromagnetic wave, \(c\) is the speed of light, \(d\) is the thickness of the samples of absorbing material and \(\epsilon_r\) and \(\mu_r\) is the complex relative permittivity and permeability, respectively. Since the thickness of the sample has a significant influence on the attenuation characteristics of the electromagnetic wave, the RL of each rGO/p-Fe₃O₄@PANI three-phase and rGO/p-Fe₃O₄ (1:5) two-phase composites of different thicknesses (2 to 3.5 mm) were compared and shown in figure 7. Generally, a material has an RL value which is less than ~10 dB (90% of electromagnetic waves are absorbed) is considered to be an effective electromagnetic wave absorbing material. As shown in figure 7, as the thickness increases, the reflection peak gradually moves toward the lower frequency, satisfying the quarter-wavelength model [41].

As shown in figure 7(a), rGO/p-Fe₃O₄ (1:20)@PANI has a minimum RL of ~27.75 dB at 13.07 GHz and effective absorption bandwidth to electromagnetic wave reaches 5.40 GHz (from 10.7 to 16.1 GHz) when the thickness is 2.5 mm. As shown in figure 7(b), rGO/p-Fe₃O₄ (1:10)@PANI exhibits a minimum RL of ~30.94 dB at 10.86 GHz, and an effective absorption bandwidth to electromagnetic waves of 3.56 GHz (from 9.35 to 12.91 GHz) when the thickness is 2.5 mm. As shown in figure 7(c), rGO/p-Fe₃O₄ (1:5)@PANI has a minimum RL of ~41.38 dB at
9.75 GHz, an effective absorption bandwidth to electromagnetic waves of 3.08 GHz (from 8.40 to 11.48 GHz) when the thickness is 2.5 mm. For each rGO/p-Fe₃O₄@PANI sample, with rGO mass percentage increases, the performance of electromagnetic wave absorbing of rGO/p-Fe₃O₄@PANI has been improved, the effective absorption bandwidth to electromagnetic wave shows a narrowing trend and moves toward the low frequency trend. As shown in figure 7(d), rGO/p-Fe₃O₄ (1:5) exhibits a minimum RL of −31.50 dB at 9.84 GHz and an effective absorption bandwidth to electromagnetic wave of 3.17 GHz (from 8.39 to 11.56 GHz) when the thickness is 2.5 mm. Comparing the RL of rGO/p-Fe₃O₄ (1:5) with rGO/p-Fe₃O₄ (1:5)@PANI, the minimum RL of rGO/p-Fe₃O₄ (1:5)@PANI is greater than rGO/p-Fe₃O₄ (1:5), their effective absorption bandwidth to electromagnetic wave and its distribution are about equal, that is, after introducing PANI into the rGO/p-Fe₃O₄ dual-phase composite system, RL of the material can be improved under the condition of ensuring the effective absorption band of the electromagnetic wave. The electromagnetic wave absorption property of the material is enhanced.

Figure 6. (a) The real and (b) imaginary parts of the permittivity of the samples; (c) the real and (d) imaginary parts of the permeability of the samples; (e) dielectric and (f) magnetic loss tangent of the samples.
An electromagnetic wave absorbing material with excellent performance needs to meet two basic requirements: when electromagnetic waves are projected onto the surface of the material, the electromagnetic wave should enter the material as much as possible, thereby there is a need to minimize direct reflection of electromagnetic wave as much as possible when electromagnetic waves are projected onto the surface of the material [42]. To achieve this goal, it is necessary to match the wave impedance of the composite sample to that of free-space. According to equation (1), the input impedance $Z_{in}$ is required to be equal to the free-space wave impedance $Z_0$ (377 $\Omega$), that is, the imaginary part of $Z_{in}$ is close to zero and the real part of $Z_{in}$ is close to 377 $\Omega$.

Figure 8 presents the complex input impedance of each rGO/p-Fe$_3$O$_4$@PANI three-phase composite and rGO/p-Fe$_3$O$_4$ (1:5) two-phase composite at a thickness of 2.5 mm.

It can be seen from figure 8 that the imaginary part of $Z_{in}$ of rGO/p-Fe$_3$O$_4$(1:20)@PANI sample is 4.10 $\Omega$ at 12.9 GHz and the real part of $Z_{in}$ is 411.0 $\Omega$; the imaginary part of $Z_{in}$ of rGO/p-Fe$_3$O$_4$(1:10)@PANI sample is 5.03 $\Omega$ at 10.775 GHz, the real part of $Z_{in}$ is 401.8 $\Omega$; the imaginary part of $Z_{in}$ of rGO/p-Fe$_3$O$_4$(1:5)@PANI sample is −1.47 $\Omega$ at 12.815 GHz, the real part of $Z_{in}$ is 302.3 $\Omega$; the imaginary part of $Z_{in}$ of rGO/p-Fe$_3$O$_4$(1:5) sample is 4.11 $\Omega$ at 12.815 GHz and the real part of $Z_{in}$ is 418.59 $\Omega$. It can be seen that the rGO/p-Fe$_3$O$_4$(1:10)@PANI sample have the best impedance matching and impedance matching performance of the rGO/p-Fe$_3$O$_4$(1:5)@PANI is relatively good. Therefore, introducing PANI and adjusting the mass percentage of rGO can improve the impedance matching performance of electromagnetic wave absorbing of material need not only satisfy the impedance matching.

On the other hand, its electromagnetic energy should be attenuated through dielectric loss and magnetic loss mechanism of material when the electromagnetic wave propagating inside the material. A material having excellent performance of electromagnetic wave absorbing needs to prevent electromagnetic wave leaking out due to incomplete attenuation, resulting in affecting the performance of electromagnetic wave absorbing of the material. The absorption performance is given by the attenuation constant $\alpha$, which can be determined as [43]:

![Figure 7. Reflection loss curves of (a) rGO/p-Fe$_3$O$_4$(1:20)@PANI, (b) rGO/p-Fe$_3$O$_4$(1:10)@PANI, (c) rGO/p-Fe$_3$O$_4$(1:5)@PANI, (d) rGO/p-Fe$_3$O$_4$(1:5) samples with different thicknesses.](image-url)
Figure 9 shows the attenuation constant of each rGO/p-Fe₃O₄/PANI three-phase composite and rGO/p-Fe₃O₄ (1:5) two-phase composite at a thickness of 2.5 mm. The attenuation constant of rGO/p-Fe₃O₄/PANI composites increases with the increase of the mass percentage of rGO. The attenuation constant of rGO/p-Fe₃O₄ (1:10)@PANI is similar to rGO/p-Fe₃O₄ (1:5), but all are smaller than rGO/p-Fe₃O₄ (1:5)@PANI. Therefore, PANI, introduced into rGO/p-Fe₃O₄ system, can improve the attenuation constant of materials. Therefore, rGO/p-Fe₃O₄ (1:5)@PANI has the best performance of electromagnetic wave absorbing, which is a consequence of relatively good impedance matching and excellent attenuation constant.

4. Conclusions

In summary, rGO/p-Fe₃O₄@PANI was successfully synthesized by three steps. The impedance matching and attenuation constant of the samples were adjusted by changing the mass percentage of rGO and p-Fe₃O₄ in rGO/p-Fe₃O₄@PANI. Compared with rGO/p-Fe₃O₄, rGO/p-Fe₃O₄@PANI exhibits excellent electromagnetic wave absorption performance. When the mass ratio of rGO to p-Fe₃O₄ in the 40 wt% three-phase material is 1:5 and the thickness is 2.5 mm, the minimum RL of rGO/p-Fe₃O₄@PANI is −41.38 dB at 9.75 GHz and the

$$\alpha = \frac{\pi f}{c} \sqrt{2(\mu'' \varepsilon'' - \mu' \varepsilon') + \sqrt{(\mu''^2 + \mu'^2)(\varepsilon''^2 + \varepsilon'^2)}}$$  

(3)
effective absorption bandwidth to electromagnetic wave reaches 3.08 GHz (from 8.40 to 11.48 GHz). This result proves that rGO/p-Fe3O4@PANI can be used as an excellent electromagnetic wave absorbing material.

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