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Research Article

Preparation and Microwave Absorption Properties of Polyaniline and Magnetite Core-Shell-Structured Hybrid

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In this study, polyaniline and Fe_3O_4 (PAN@Fe_3O_4) hybrids are fabricated and their microwave absorption property is studied. PAN@Fe_3O_4 hybrids are fabricated by the in situ aniline polymerization at spherical of Fe_3O_4 which is prepared by the solvothermal process. Fourier-transform infrared spectrophotometer (FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) are applied to confirm the composition of the fabricated PAN@Fe_3O_4 hybrids. The morphologies of PAN@Fe_3O_4 hybrids are studied by scanning electron microscope (SEM) and transmission electron microscopy (TEM). The content of polyaniline in the PAN@Fe_3O_4 hybrids is calculated by thermogravimetric analysis (TGA). The magnetic properties of PAN@Fe_3O_4 hybrids are characterized by vibrating sample magnetometer (VSM). The microwave absorption property of PAN@Fe_3O_4 hybrids are measured on a vector network analyzer. The research show that the microwave absorptions property of the obtained PAN@Fe_3O_4 hybrids can be adjusted by controlling the in situ aniline polymerization at spherical of Fe_3O_4.

1. Introduction

With the expansion use of electric device, including personal computers, mobile phones, microwave oven, and other military equipment and/or space equipment, microwave has become a new pollution to our health [1–6]. The effective way to solve this problem is the development of new microwave absorption materials [7, 8]. The basic requirement of the microwave absorption materials is to show strong microwave absorption, represented by reflection loss [9]. Usually, the microwave absorption materials are to dissipate the incident microwave which includes the dielectric dissipation and magnetic dissipation [10, 11]. Excellent microwave absorption materials also exhibit compatibility between the dielectric dissipation and magnetic dissipation. The magnetic dissipation can be easily achieved by using magnetic materials such as magnetic iron oxide. As a result, magnetite is mostly utilized as microwave absorption materials [12, 13]. The dielectric dissipation can be achieved by introducing the dielectric materials and/or conducting materials [14, 15]. These include phthalocyanine copper and its derivatives [16], the carbon materials including CNT [17], carbon black, and graphene [18], and the conducting polymers such as polyaniline and polythiophene [19]. The conducting polymers that usually combine the low density and excellent conductivity have attracted considerable attention both from the research and the practical application. In the conducting polymers, polyaniline (PAN) can be easily obtained and shows excellent conductivity after doping. Up to now, PAN has been used to prepare composites with polyethylene, poly(vinylidene fluoride), graphene, CNT, and others [20, 21].

With the magnetite as the magnetic dissipation part and PAN as the dielectric dissipation part, PAN and magnetite hybrid materials can be obtained to be used as microwave absorption materials. However, another problem is the compatibility between them due to the inorganic part of magnetite and organic part of PAN. To solve this problem, core-shell-structured hybrid containing magnetite core and PAN shell can be imagined.

In this study, we fabricated hybrid PAN@Fe_3O_4 by the in situ aniline polymerization at the spherical of Fe_3O_4 which is

prepared by the solvothermal process. The PAN@Fe_3O_4 hybrids are characterized by XPS, XRD, TGA, SEM, TEM, FTIR, and VSM. After that, microwave absorption property of the prepared PAN@Fe_3O_4 hybrids is studied in detail.

2. Experimental Section

2.1. Materials. Ethylene glycol (99%), $FeCl_3{\cdot}6H_2O$ (99%), and polyethylene glycol 2000 (99%) were purchased from Kelong Reagents, Chengdu, China. Sodium dodecyl benzene sulfonate (SDBS, 99%), hydrochloric acid (37%), ammonium sulfate (98%), and aniline (99%) were purchased from Changzheng Reagents, Chengdu, China. Other chemicals and reagents were commercial available products, and all of them were used as received.

2.2. Preparation of Fe_3O_4. Magnetite was fabricated by the solvothermal process throughout previous literature [8]. $FeCl_3{\cdot}6H_2O$ (10.0 g) and polyethylene glycol 2000 (3.7 g) were mixed with 160 ml ethylene glycol at RT, followed by adding sodium acetate trihydrate (27.0 g). The system was mixed by mechanical agitation as well as ultrasonication for 40 min to form an orange solution. After that, the above-prepared mixture was poured into an autoclave; the whole system was heated at 180°C for 12 h, after that it was cooled down to RT. The product was segregated by a magnet and was purified 3–5 times with purified water and ethanol, respectively. Finally, the product was dried under vacuum at 70°C for 8 h.

2.3. Preparation of Polyaniline and Fe_3O_4 (PAN@Fe_3O_4) Hybrids. The polyaniline and Fe_3O_4 (PAN@Fe_3O_4) hybrids were fabricated by the in situ aniline polymerization at the spherical of Fe_3O_4 with the existence of ammonium sulfate. With the change of the amount of the aniline and ammonium sulfate, polyaniline and Fe_3O_4 hybrids with different contents of polyaniline were obtained. The typical procedure is as follows: 0.25 g Fe_3O_4 was dispersed in 100 ml deionized water with the help of SDBS (25 mg) and mechanical agitation. After that, the system was cooled at 0–5°C through the ice. At the time, aniline (0.25 ml), dissolved in 0.1 mol/l HCl (50 ml), was also cooled at 0–5°C through another ice system. The cooled aniline solution was mixed with the Fe_3O_4 dispersion with vigorous mechanical agitation in the ice bath. The ammonium sulfate (2.5 g) was dissolved in 25 ml purified water at 0–5°C in the third ice bath. After being cooled down, the ammonium sulfate was put dropwise in Fe_3O_4 and aniline mixture. The polymerization was kept on for at least 12 h. In this study, three polyaniline and Fe_3O_4 hybrids named as PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, and PAN@Fe_3O_4-3 were prepared.

2.4. Characterization. The structure of PAN@Fe_3O_4 hybrid materials was characterized by XRD (Rigaku RINT 2400) and XPS (PHI-5300 ESCA). FTIR (8000S) was also utilized to characterize the PAN@Fe_3O_4 hybrids. The content of polyaniline in the PAN@Fe_3O_4 hybrid was calculated by TGA (Q50). The morphologies of PAN@Fe_3O_4 hybrids were studied by SEM (JSM-6490LV) and TEM (H600). The magnetic property of PAN@Fe_3O_4 hybrids was studied by VSM (BHV-525). The electromagnetic property of PAN@Fe_3O_4 hybrids was tested on a vector network analyzer (8720ET) at 0.5–18 GHz. The sample was fabricated through blending PAN@Fe_3O_4 hybrids with wax in a mass ratio of 3 : 1.

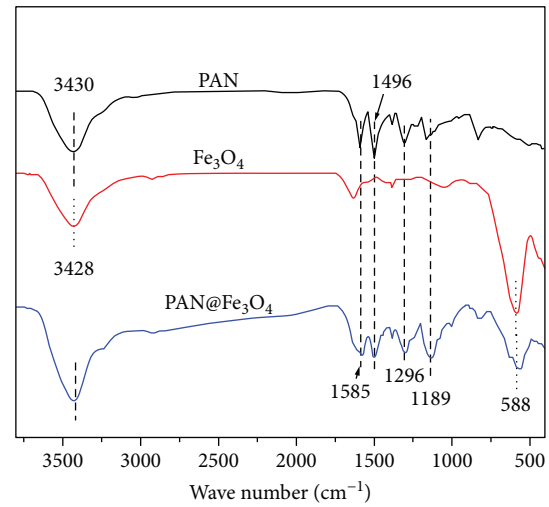


Figure 1: FTIR spectrum of PAN, Fe_3O_4, and PAN@Fe_3O_4-1.

3. Results and Discussion

In the study, polyaniline and Fe_3O_4 (PAN@Fe_3O_4) hybrids are fabricated and their microwave absorption property is studied. The PAN@Fe_3O_4 hybrid is fabricated by the in situ aniline polymerization at the spherical of Fe_3O_4 which is prepared by the solvothermal process [8]. Figure 1 shows FTIR spectra of PAN, Fe_3O_4, as well as PAN@Fe_3O_4-1; compared with that of Fe_3O_4, the FTIR curves of PAN@Fe_3O_4-1 show additional absorption peaks at 3430 cm^{-1} (N-H), 1585 and 1496 cm^{-1} (benzene ring), and 1189 cm^{-1} (AR-N) which indicate the existence of polyaniline in the system [19]. In addition, the peak at 588 cm^{-1} (Fe-O) is observed on the spectra curves of Fe_3O_4 and PAN@Fe_3O_4-1.

XPS is also used to characterize the composition of the obtained PAN@Fe_3O_4 hybrids. Figure 2(a) shows the XPS spectra of Fe_3O_4 and PAN@Fe_3O_4-1. On the spectrum of Fe_3O_4, the peaks at 534 eV and 716 eV correspond the O1s and Fe2p, while the peak at 287 eV is resulted from the C1s which might come from the ethylene glycol and polyethylene glycol 2000 used during the solvothermal process. The Fe2p peak can be divided into two peaks at 711 eV and 725 eV which come from Fe2p1/2 and Fe2p3/2 as shown in Figure 2(b); this confirms the existence of Fe_3O_4. In comparison, the XPS spectrum of PAN@Fe_3O_4-1 shows new peak at 405 eV which is attributed to the N1s from the polyaniline at the spherical of PAN@Fe_3O_4-1. Both of the FTIR and the XPS confirm the preparation of polyaniline and Fe_3O_4 hybrids [7].

XRD is a technic to confirm component of prepared new nanocomposites by comparing XRD pattern peaks with the standard card. Figure 3 shows XRD curves of prepared samples. As shown in the picture, six peaks at 30°, 35°, 43°, 54°, 57°, and 63° which match well with (220), (311), (400),

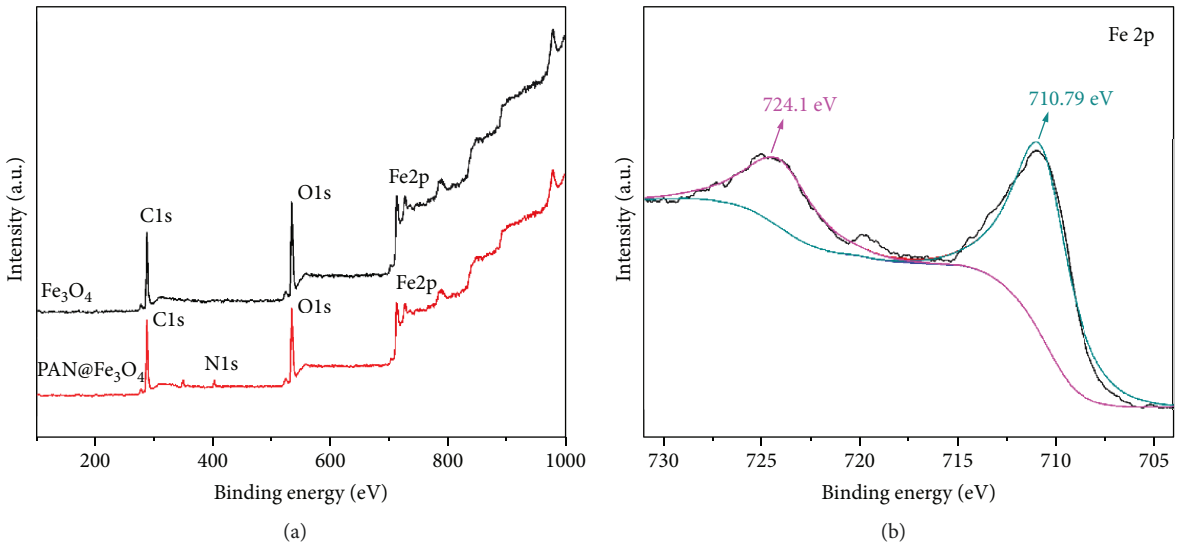


Figure 2: XPS spectra of Fe_3O_4 and PAN@Fe_3O_4-1 (a) and Fe2p peak (b).

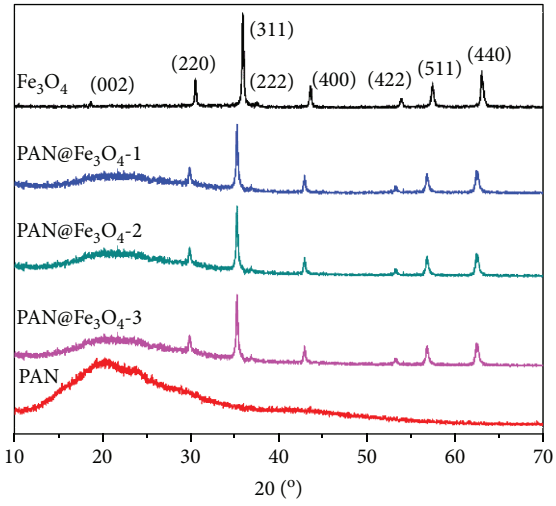


Figure 3: XRD pattern of Fe_3O_4, PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, PAN@Fe_3O_4-3, and PAN.

(422), (511), and (440) planes of the standard XRD of magnetite (JCPDS file no.19-0629) are observed on the curves of Fe_3O_4. While a wide peak at 20° is seen on the curves of PAN. PAN@Fe_3O_4-1 shows peaks combining from PAN and Fe_3O_4, indicating the composition of PAN and Fe_3O_4 in PAN@Fe_3O_4-1. The other samples also show similar XRD patterns which confirm the Fe_3O_4 in the PAN@Fe_3O_4 hybrids [22].

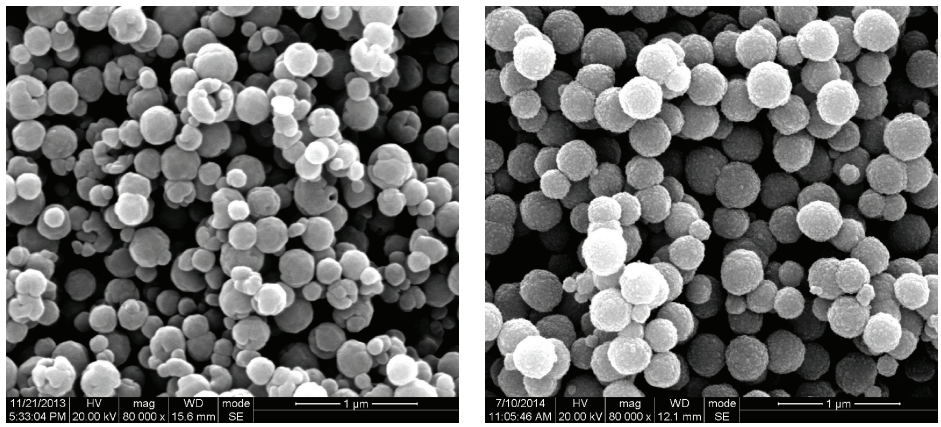
After the characterization of the composition of PAN@Fe_3O_4 hybrids, the micro morphology of them is studied through SEM and TEM. Figure 4 shows SEM micro images of Fe_3O_4 and PAN@Fe_3O_4-1. As shown in the figure, the Fe_3O_4 exhibits smooth surface. In addition, anomalous nanoparticles including spheres, hemispheres, bowls, and open balls are observed for Fe_3O_4. While for PAN@Fe_3O_4-1, its surface becomes coarser indicating the existence of the polyaniline. More importantly, the shape of the PAN@Fe_3O_4-1 becomes regular spheres. The structure change of the PAN@Fe_3O_4-1 from Fe_3O_4 indicates the formation of the core-shell-structured particles.

Figure 5 shows the TEM micro images of Fe_3O_4 and PAN@Fe_3O_4-1. Similar to that of the SEM micro image, the TEM micro image of Fe_3O_4 shows irregular shapes of nanoparticles. In addition, it is clearly that Fe_3O_4 shows hollow structure. As for that of PAN@Fe_3O_4-1, a shell can be observed at the spherical of the nanoparticles. What is more, it seems that the hollow structure of the Fe_3O_4 is filled with something after the polymerization of aniline. Both of the SEM and TEM results indicate the core-shell structure of PAN@Fe_3O_4-1.

After the confirmation of the fabrication of PAN@Fe_3O_4 hybrids, the content of polyaniline in the PAN@Fe_3O_4 hybrids is calculated by the TGA measurement. Figure 6 shows the TGA curves of Fe_3O_4, PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, and PAN@Fe_3O_4-3. Fe_3O_4 shows only 2% weight decrement when the temperature is up to 600°C, which is negligible. As for the PAN@Fe_3O_4 hybrids, obvious weight decrement resulting from the decomposing of polyaniline is observed. The residual mass of PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, and PAN@Fe_3O_4-3 is 90%, 84%, and 77%, respectively. The TGA results mean that the content of polyaniline in PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, and PAN@Fe_3O_4-3 is 10 wt%, 16 wt%, and 23 wt%, respectively.

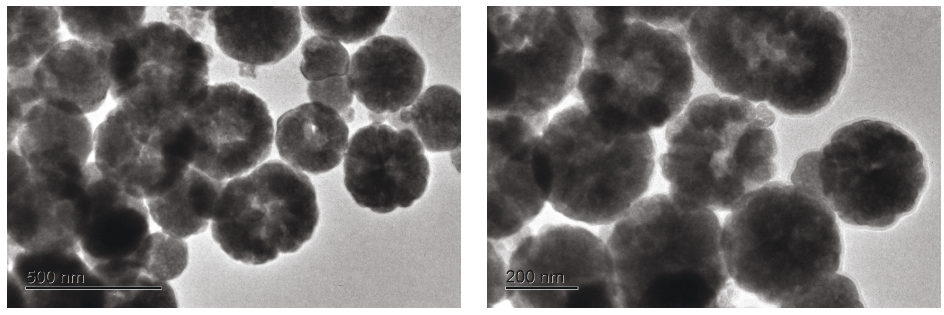
The magnetic property of PAN@Fe_3O_4 hybrid composite was studied by a VSM. Figure 7 shows the saturation magnetization of the samples indicating the magnetic property of the PAN@Fe_3O_4 hybrids. According to the results, the saturation magnetization decreases with the increasing content of polyaniline due to the decrement of content of Fe_3O_4 which contributes the magnetic properties effectively. The saturation magnetization of PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, and PAN@Fe_3O_4-3 is 75.3, 58.9, and 42.1 emu/g, respectively.

With the fabrication and characterization of PAN@Fe_3O_4 hybrids, their microwave absorption property is studied. Permittivity ($\varepsilon = \varepsilon' + i\varepsilon''$) as well as permeability



(a) (b)

Figure 4: SEM micro images of Fe_3O_4 and PAN@Fe_3O_4-1.



(a) (b)

Figure 5: TEM micro images of Fe_3O_4 and PAN@Fe_3O_4-1.

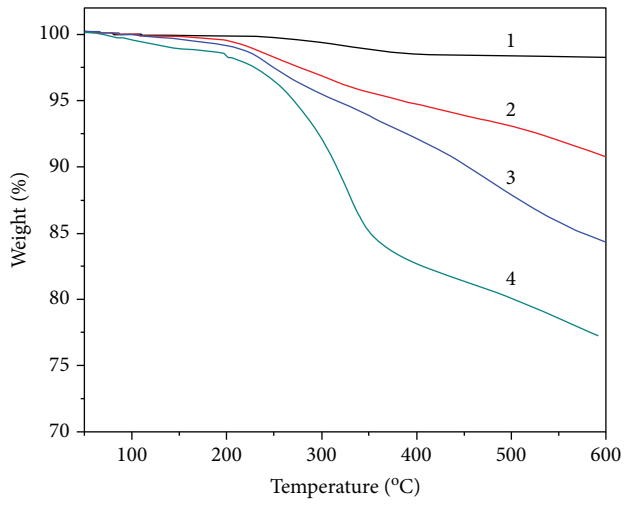


Figure 6: TGA curves of Fe_3O_4 (curve 1), PAN@Fe_3O_4-1 (curve 2), PAN@Fe_3O_4-2 (curve 3), and PAN@Fe_3O_4-3 (curve 4).

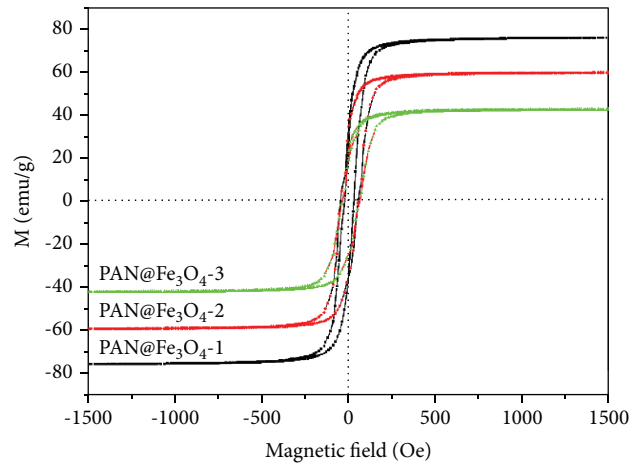


Figure 7: Magnetization curves of PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, and PAN@Fe_3O_4-3.

($\mu = \mu' + j\mu''$) were measured from 0.5–18 GHz for Fe_3O_4 and PAN@Fe_3O_4 hybrids. By using the obtained permittivity and permeability, PAN@Fe_3O_4 hybrids' microwave absorption properties are calculated by using transmit line theory [23, 24]. Figure 8(a) exhibits reflection loss (RL) of Fe_3O_4; the minimum RL is −15.3, −12.7, −15.5, and −17.2 dB at 1.0, 1.5, 2.0, and 2.5 mm, respectively. Usually, the reflection loss below −10 dB indicates that 90% microwave energy is dissipated and the reflection loss below −20 dB means that 99% microwave energy is being dissipated. As the minimum reflection loss of Fe_3O_4 is higher than −20 dB, it is not good enough to be used directly.

Figures 8(b) and 8(c) show the RL of PAN@Fe_3O_4-1 and PAN@Fe_3O_4-2. The outcome shows both RL of PAN@Fe_3O_4-1 and PAN@Fe_3O_4-2 are worse than that of Fe_3O_4,

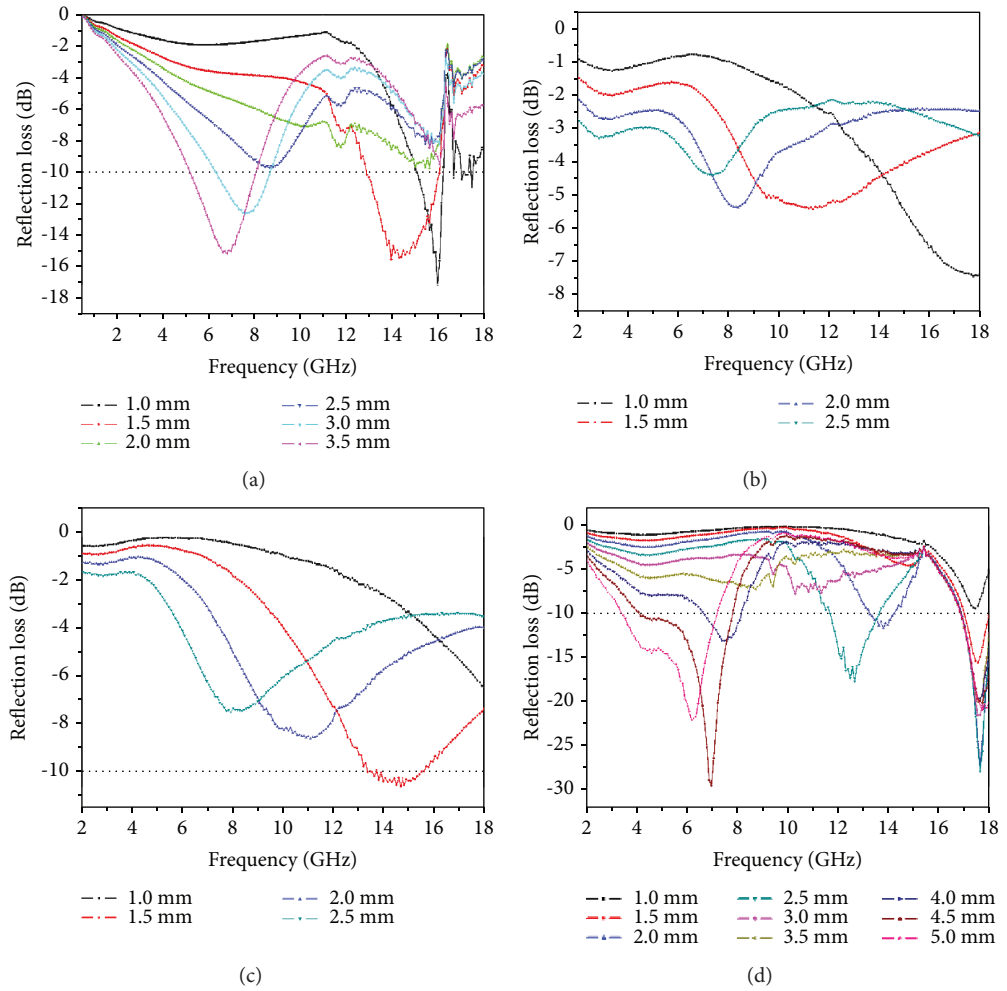


Figure 8: Reflection loss of Fe_3O_4 (a), PAN@Fe_3O_4-1 (b), PAN@Fe_3O_4-2 (c), and PAN@Fe_3O_4-3 (d).

which might be contributed to the mismatching of impedance between Fe_3O_4 and polyaniline. While for PAN@-Fe_3O_4-3, excellent microwave absorption property is obtained. As can be seen through Figure 8(d), the minimum RL of PAN@Fe_3O_4-3 is as low as −29.3 dB. The low reflection loss of PAN@Fe_3O_4-3 is due to the changeable content of polyaniline through the aniline polymerization at the spherical of Fe_3O_4. As a result, controlling the in situ aniline polymerization at the spherical of Fe_3O_4 can adjust the microwave absorption property of the obtained PAN@-Fe_3O_4 hybrids.

4. Conclusions

In conclusion, a series of polyaniline and Fe_3O_4 (PAN@-Fe_3O_4) hybrids was prepared to study their microwave absorption properties. PAN@Fe_3O_4 was fabricated by the in situ aniline polymerization at the spherical of Fe_3O_4. FTIR, XPS, and XRD measurements showed the composition of polyaniline and Fe_3O_4 in the prepared PAN@Fe_3O_4 hybrids. SEM and TEM micro images indicated the core-shell structure of the PAN@Fe_3O_4 hybrids. The TGA results suggested that the content of polyaniline in PAN@Fe_3O_4-1, PAN@Fe_3O_4-2, and PAN@Fe_3O_4-3 is 10 wt%, 16 wt%, and 23 wt%, respectively. The saturation magnetization of the PAN@Fe_3O_4 decreased with the increment of PAN content in the hybrids. The minimum reflection loss of PAN@-Fe_3O_4-3 was as low as −29.3 dB which is much better than the other samples. Controlling the in situ aniline polymerization at the spherical of Fe_3O_4 can adjust the microwave absorption of the obtained PAN@Fe_3O_4 hybrids.

Data Availability

The data used to support the findings of this study are included within the article. The funding statement will be provided in the coming revised version.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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