Research Article

Synthesis and Microwave Absorption Properties of Core-Shell Structured Co_3O_4 -PANI Nanocomposites

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The core-shell structured Co_3O_4 -PANI nanocomposites have been successfully prepared using an in situ polymerization method, while the core Co_3O_4 nanoparticles were synthesized by carbon-assisted method using degreasing cotton as a template. The obtained samples were characterized by XRD, TEM, FTIR, and XPS. The results indicated that the amorphous PANI was well covered on the surface of the spinel Co_3O_4 and the Co_3O_4 -PANI with core-shell structure was formed with particle size of about 100 nm. The interfacial interaction of the core-shell nanocomposite greatly enhances the microwave absorption properties. The maximum reflection loss of Co_3O_4 -PANI is up to -45.8 dB at 11.7 GHz with a thickness of 2.5 mm and the adsorption bandwidth with the reflection loss below -10 dB reaches 14.1 GHz ranging from 3.9 to 18 GHz when the thickness is between 2 and 5.5 mm. Therefore, the facilely synthesized and low-cost Co_3O_4 -PANI nanocomposite with superior microwave absorption properties can be a promising nanomaterial for high efficient microwave absorption.

1. Introduction

With the wide use of electronic devices, the electromagnetic pollution has been a growing threat to the stable running of electronically controlled systems and more importantly to our healthy life [1, 2]. Considerable attention has been attracted to the study on the high efficient and inexpensive microwave absorbing materials [3, 4]. Of all the discovered microwave absorbing materials, due to its electric conductivity, lightweight, flexibility, stability, and ease of synthesis, polyaniline (PANI), as a traditional practical polymer, has been extensively employed in the synthesis of promising microwave absorbers, for instance, PANI-NiZn, PANI- CoFe_2O_4 , PANI- Fe_3O_4 -graphene, and PANI- Fe_3O_4 -MWCNTs [5–8].

Co_3O_4 is a normal spinel structured crystal with Co^{3+} occupying octahedral sites and Co^{2+} in tetrahedral sites

within the lattice [9]. Co_3O_4 can act as a functional material in various fields, such as catalysts, lithium ion batteries, supercapacitor, and chemical sensors [10–15]. Recent studies have demonstrated that Co_3O_4 can also be used as excellent microwave absorption material. The porous $\text{Co-Co}_3\text{O}_4$ hybrid hollow spheres synthesized by Wu et al. can absorb microwave with maximum reflection loss of -18.5 dB at 6.5 GHz when the thickness is 5.00 mm [16]. The 2D Co_3O_4 @C@PGC fabricated by Wen et al. shows better microwave absorption properties [2]. The maximum reflection loss is -32.3 dB at 11.4 GHz with thickness of 2.3 mm. The CoO_x /CFs composite investigated by Liu et al. exhibits excellent microwave absorption performances [17]. The lowest reflectivity is -45.16 dB at 13.41 GHz with 1.5 mm in thickness. The RGO- Co_3O_4 , PANI-RGO- Co_3O_4 , and PPy-RGO- Co_3O_4 nanocomposites researched by Liu et al. have maximum reflection losses of -43.7 dB at 13.8 GHz (with a thickness

of 3.3 mm), -32.6 dB at 6.3 GHz (with a thickness of 3 mm), and -33.5 dB at 15.8 GHz (with a thickness of 2.5 mm), respectively [18–20].

In this work, we report a core-shell structured Co_3O_4 -PANI nanocomposite with a maximum reflection loss of up to -45.8 dB at 11.7 GHz when its thickness is 2.5 mm. The core-shell Co_3O_4 -PANI was synthesized by a facile, inexpensive, and scalable method and characterized by XRD, TEM, FTIR, and XPS. The behaviors of microwave absorption of Co_3O_4 -PANI were investigated and the microwave absorbing mechanisms were also discussed.

2. Experimental

2.1. Preparation of Co_3O_4 -PANI Nanocomposites. The spinel Co_3O_4 was synthesized by carbon-assisted method using degrading cotton as a template. 17.46 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL deionized water with magnetic stirring for 10 min. Then 1.5 g degrading cotton was immersed in the blood red solution and ultrasonicated for 10 min to disperse the ions on the degrading cotton homogeneously. Then the treated degrading cotton was transferred into a quartz Petri dish in the tube furnace (OTF-1200X-III, Heifei, China) and calcined at 600°C for 2 h in air to obtain Co_3O_4 nanoparticles.

The core-shell Co_3O_4 -PANI nanocomposite was prepared by an in situ polymerization method. 0.9 g preprepared Co_3O_4 was added into 5 mL of 2 mol/L HCl diluted by 50 mL deionized water and kept for 1 h in an ultrasonic bath. Then 1.6 mL aniline was mixed in the solution and stirred vigorously for 30 min. The aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS, 4.56 g was dissolved in 50 mL deionized water) was slowly added to the above mixture and stirred for 10 h. The obtained precipitate was filtered and washed with HCl, methanol, and deionized water in sequence repeatedly until the precipitate is neutral. Finally, the precipitate was dried at 60°C for 24 h and the Co_3O_4 -PANI nanocomposite was obtained.

2.2. Characterization. The X-ray powder diffraction (XRD) was carried out using a Bruker D8 with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation at 40 eV in the 2θ of 20 – 80° . The morphology was observed by transmission electron microscopy (TEM, JEOL JEM-2011). Fourier transform infrared spectroscopy (FTIR) was recorded from KBr pellets in the range of 500 – 4000 cm^{-1} on an Avatar 360 spectrometer. X-ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250Xi spectrometer with a standard $\text{Al K}\alpha$ radiation with the binding energies calibrated based on the contaminant carbon ($\text{C1s} = 284.6 \text{ eV}$).

In order to measure the electromagnetic parameters, the samples were prepared by uniformly mixing the prepared nanomaterials with a paraffin matrix in the mass ratio of 1:1 and then pressing the mixture into a toroidal shaped compact ($\Phi_{\text{outer}} = 7.00 \text{ mm}$ and $\Phi_{\text{inner}} = 3.04 \text{ mm}$). The electromagnetic parameters of the as-obtained samples were measured in the frequency range of 2.0 – 18.0 GHz by an Agilent HP-8722ES vector network analyzer.

3. Results and Discussions

The XRD patterns of Co_3O_4 and Co_3O_4 -PANI are shown in Figure 1. In the pattern of Co_3O_4 , it can be observed that the diffraction peaks of Co_3O_4 at $2\theta = 31.3, 36.9, 38.5, 44.8,$

FIGURE 1: XRD patterns of Co_3O_4 and Co_3O_4 -PANI.

55.6, 59.3, 65.2, and 77.3 can be assigned to the (220), (311), (222), (400), (422), (511), (440), and (533) planes of Co_3O_4 , respectively, which is in accordance with JCPDS card of the standard spinel cubic Co_3O_4 (JCPDS number 42-1467) [21]. The crystallite size with respect to (311) peak of Co_3O_4 has been calculated by the Scherrer relation and is estimated to be 56.6 nm . In the pattern of Co_3O_4 -PANI, comparing to pure Co_3O_4 , all peaks of Co_3O_4 become weaker and the peaks at $2\theta = 38.5, 55.6,$ and 77.3 are even too weak to be observed, which is on account of the PANI coating. There is a small hump when 2θ is below 30 . This is due to the periodicity parallel and perpendicular to the polymer chains which indicates the polyaniline is amorphous [22, 23]. The absence of the peaks of PANI in Co_3O_4 -PANI nanocomposites is due to the presence of Co_3O_4 which has a great effect on forming PANI during the coating process. The interaction of PANI and Co_3O_4 in the interface blocks the crystallization of PANI [24]. Both the weakness of Co_3O_4 peaks and the lack of the PANI peaks in Co_3O_4 -PANI prove that Co_3O_4 nanoparticles are well coated by PANI.

To investigate the morphology and structure of the products, TEM images were taken for Co_3O_4 and Co_3O_4 -PANI and the corresponding results are presented in Figure 2. Figure 2(a) shows that the Co_3O_4 nanoparticles with a relatively small size are obtained. The edges are clear and round. It indicates that the particles are approximately spherical or ellipsoidal. The average size of nanoparticles is about 60 nm , which is consistent with the calculation from XRD mentioned above. From Figure 2(b), we can see that a lot of wrinkled forms cover on the Co_3O_4 dark cores. The edges of particles are quite blur and amorphous, which is attributed to PANI. The formation of amorphous PANI supports the explanation about the lack of PANI peaks in Co_3O_4 -PANI discussed before. After coating with PANI, the particle sizes of the core-shell nanocomposites are around 100 nm . It can be observed in Figures 2(c) and 2(d) that the measured lattice spacing

FIGURE 2: TEM images of Co_3O_4 (a) and Co_3O_4 -PANI (b). HRTEM images of Co_3O_4 (c) and Co_3O_4 -PANI (d).

is 4.66 Å which is in line with the (111) interplanar distance of the Co_3O_4 [12]. The HRTEM analysis shows clear and continuous lattice fringes which further confirm the good crystal structure of prepared Co_3O_4 .

The FTIR spectra of Co_3O_4 and Co_3O_4 -PANI are shown in Figure 3. The sharp peaks at 572 and 661 cm^{-1} in the spectrum of Co_3O_4 are associated with the OB_3 (B represents Co^{3+} in an octahedral hole) and the ABO (A represents the Co^{2+} in a tetrahedral hole) vibrations in the spinel lattice, respectively [25, 26]. Both Co_3O_4 and Co_3O_4 -PANI have two peaks at 1118 and 1398 cm^{-1} . The peak at 1118 cm^{-1} is attributed to the stretching vibrations of C–O and CO_3^{2-} anions. They are introduced by the burn of degreasing cotton during the preparation procedure of Co_3O_4 . The peak at 1398 cm^{-1} is corresponding to the stretching vibration of NO_3^- , which is due to the residue of $\text{Co}(\text{NO}_3)_3$ [12]. The peaks at 1642 and 3465 cm^{-1} in the spectrum of Co_3O_4 are assigned to molecular water and O–H [27]. In the spectrum of Co_3O_4 -PANI, other than the influence of molecular water and O–H, the bands at 1644 and 3446 cm^{-1} are also affected by the quinoid ring and N–H stretching of PANI, separately [24, 28, 29]. In the spectrum of Co_3O_4 -PANI, the very small

FIGURE 3: FT-IR spectra of Co_3O_4 and Co_3O_4 -PANI.

peaks between 1118 and 1644 cm^{-1} are due to the existence of PANI. The absence of the characteristic peaks of Co_3O_4

FIGURE 4: XPS spectra of Co₃O₄ (a) and Co₃O₄-PANI (b).

shows that the PANI is completely coated on the Co₃O₄ and has an impact on the surface of Co₃O₄. The analysis above suggests that it is not a simple mix between Co₃O₄ and PANI but rather an interaction existing at the interfaces of Co₃O₄ nanoparticles and PANI [30].

The XPS spectra of Co₃O₄ and Co₃O₄-PANI nanoparticles are presented in Figure 4. In Figure 4(a), the spectrum of Co₃O₄ samples shows the existence of cobalt, oxygen, and carbon elements at the surface. Two peaks at 780.4 and 795.4 eV correspond to Co2p_{3/2} and Co2p_{1/2} spin-orbit peaks of Co₃O₄, which are characteristic of the Co₃O₄ phase [31]. The O1s peak centered at 529.8 eV is assigned to the lattice oxygen in the Co₃O₄ phase. The relatively small peak Cls at 284.6 eV is ascribed to elemental carbon which results from the insufficient burning of degreasing cotton. In Figure 4(b), it can be observed that there are chlorine, carbon, nitrogen, oxygen, and cobalt elements presented at the surface of Co₃O₄-PANI samples. The Cl2p peak at 198.4 eV indicates the existence of Cl⁻ which is due to the HCl solution used in the synthesis of Co₃O₄-PANI [32]. The Cls and N1s peaks at 285.5 and 400.2 eV are attributed to the C-N and -NH- from the PANI backbone [33, 34]. The O1s peak at 532.4 eV is ascribed to hydroxide ions adsorbed on the surface. The characteristic peaks of Co₃O₄ at 780.4 and 795.4 eV are very weak. It can be inferred that Co₃O₄ core is well covered by PANI and the core-shell Co₃O₄-PANI nanocomposite is well synthesized.

To study the microwave absorption properties, reflection loss (R_L) can be used to characterize the microwave absorption capacity, which is affected by morphology, dielectric and magnetic properties, electromagnetic impedance match, and chemical stability of the absorber. R_L is calculated according to the transmission line theory [35]:

$$R_L \text{ (dB)} = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|, \quad (1)$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \left(\frac{2\pi f d}{c} \right) \sqrt{\mu_r \epsilon_r} \right],$$

where Z_{in} is the input impedance of the absorber, Z_0 is the input impedance of air, μ_r and ϵ_r are, respectively, the relative complex permeability and permittivity, f is the frequency of the electromagnetic waves, d is the thickness of the absorber, c is the velocity of electromagnetic waves in free space, and R_L (dB) is the reflection loss of the absorber.

Figure 5 shows the relationship between reflection loss and frequency in different thickness for the obtained samples. In Figure 5(a), it can be observed that the R_L of Co₃O₄ is no more than -6 dB when its thickness ranges from 2 to 5.5 mm, and the maximum R_L is only -6.0 dB at the frequency of 8.3 GHz with a thickness of 5.5 mm. This demonstrates that the Co₃O₄ sample exhibits a very weak ability to absorb microwave. In Figure 5(b), it can be found that the microwave absorption properties of Co₃O₄ are significantly enhanced by PANI coating. The reflection loss of Co₃O₄-PANI is less than -10 dB (90% of microwave absorption) over the frequency range of 3.9–18 GHz when the thickness of sample is between 2 mm and 5.5 mm. The maximum R_L of Co₃O₄-PANI is up to -45.8 dB at 11.7 GHz and the absorption bandwidths corresponding to the R_L values below -10 dB are 5.8 GHz (from 9.6 to 14.4 GHz) when its thickness is 2.5 mm. It is well known that microwave absorption capability relies on the nature shape and size of an absorber [36]. The excellent microwave absorption properties may be due to the special structure and geometrical morphology of the nanocomposite prepared by applying PANI coating on Co₃O₄. Furthermore, the thickness of the samples is another critical factor affecting the intensity and the position of the frequency at the maximum reflection losses [37]. It can be seen that the maximum R_L values obviously shift to the lower frequency as the thickness increases from 2 to 5.5 mm. They also move to the smaller intensity except the maximum R_L value with a thickness of 2.5 mm, which has the maximal intensity of all.

To investigate the microwave absorption mechanism of the Co₃O₄-PANI, the relative complex permittivity, permeability, and loss tangent of Co₃O₄ and Co₃O₄-PANI are

FIGURE 5: Microwave reflection loss of Co_3O_4 (a) and Co_3O_4 -PANI (b).

presented in Figure 6 to characterize dielectric loss and magnetic loss properties of absorbers. In Figure 6(a), the real (ϵ') and imaginary (ϵ'') parts of relative permittivity of Co_3O_4 are around 3.5 and 0.5, respectively, and both of the two parameters change slowly as the frequency increases. They decrease relatively fast when frequency increases from 2 to 6 GHz and then tend to stabilize with some fluctuations. The fluctuations are related to the resonance behavior caused by the charge polarization of Co_3O_4 [38]. Comparing to Co_3O_4 , Co_3O_4 -PANI has much higher and more unstable ϵ' and ϵ'' values (Figure 6(b)). The high values are partially due to the strong polarization in PANI generated from polaron/bipolaron and other bound charges [3]. But PANI itself cannot improve the permittivity that much [30, 39]. The interfacial interaction between the PANI and Co_3O_4 core has a great effect on the permittivity, which is attributed to a large number of interfacial polarization charges [2, 40]. Both the ϵ' and ϵ'' values decrease rapidly with frequency increasing from 2 to 6 GHz. ϵ' keeps declining until the frequency reaches 18 GHz, but ϵ'' stops decreasing at the frequency of 12 GHz and then has a slight rise. The variation of permittivity with frequency can be explained by the interfacial relaxation between Co_3O_4 cores and PANI shells, as well as the Debye relaxation of PANI [3, 41]. As the applied field alters, the charges redistribute alternatively between Co_3O_4 cores and PANI shells, and the dipoles in nanocomposites cannot reorient themselves along with the field.

By comparing the relative permeability of Figures 6(c) and 6(d), it is clearly shown that PANI coating almost has no influence on the permeability of Co_3O_4 -PANI nanocomposite. The real (μ') and imaginary (μ'') parts of relative permittivity of Co_3O_4 are slightly above 1.0 and below 0.1,

respectively. Being almost identical to those of Co_3O_4 , the real and imaginary parts of relative permittivity of Co_3O_4 -PANI fluctuate around 1.0 and 0.1, separately. The small difference may be caused by the interfacial interaction where the motion of charges produces an induced magnetic field. The small values indicate that both Co_3O_4 and Co_3O_4 -PANI show a very weak magnetic loss.

Figures 6(e) and 6(f) show the loss tangent of Co_3O_4 and Co_3O_4 -PANI. Apparently, the dielectric loss tangent ($\tan \delta_\epsilon = \epsilon''/\epsilon'$) is much larger than the magnetic loss tangent ($\tan \delta_\mu = \mu''/\mu'$) for both Co_3O_4 -PANI and Co_3O_4 . This indicates that the main absorption mechanism of Co_3O_4 -PANI and Co_3O_4 is dielectric loss. The dielectric loss of Co_3O_4 -PANI is nearly four times as high as that of Co_3O_4 . The interfacial interaction between the Co_3O_4 cores and PANI shells greatly affects the dielectric loss of Co_3O_4 -PANI as discussed above. So it can be concluded that the core-shell structure makes a major contribution to the excellent microwave absorption properties of Co_3O_4 -PANI.

4. Conclusion

The Co_3O_4 nanoparticle has been synthesized by carbon-assisted method using degreasing cotton as a template and coated with PANI using an in situ polymerization method. The XRD, TEM, FTIR, and XPS characterizations show that the Co_3O_4 nanoparticle prepared is the spinel structure with average size of around 60 nm and the Co_3O_4 -PANI nanocomposite is the core-shell structure with particle size of about 100 nm. Comparing to Co_3O_4 , the core-shell structured Co_3O_4 -PANI exhibits greatly enhanced microwave absorption properties. The optimal absorption peak of Co_3O_4 -PANI

FIGURE 6: The complex relative permittivity of Co_3O_4 (a) and $\text{Co}_3\text{O}_4\text{-PANI}$ (b), the complex relative permeability of Co_3O_4 (c) and $\text{Co}_3\text{O}_4\text{-PANI}$ (d), and the loss tangent of Co_3O_4 (e) and $\text{Co}_3\text{O}_4\text{-PANI}$ (f).

reaches -45.8 dB at 11.7 GHz with a thickness of 2.5 mm and the adsorption bandwidth corresponding to the reflection loss below -10 dB is 14.1 GHz (from 3.9 to 18 GHz) when the thickness is between 2 and 5.5 mm. This is believed to be due to the interfacial interaction of the core-shell structure. The microwave absorption properties of Co_3O_4 -PANI may be further optimized by varying the ratio of Co_3O_4 core and PANI shell during the synthesis process in the future work. The superior microwave absorption properties demonstrate that the core-shell structured Co_3O_4 -PANI nanocomposite can be a promising nanomaterial for high efficient microwave absorption.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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