Synthesis and Microwave Absorption Properties of Core-Shell Structured Co$_3$O$_4$-PANI Nanocomposites

Hongyan Xu,$^1$ Zhenyin Hai,$^2$ Jiagtao Diwu,$^1$ Qiang Zhang,$^2$ Libo Gao,$^2$ Danfeng Cui,$^2$ Junbin Zang,$^2$ Jun Liu,$^2$ and Chenyang Xue$^2$

$^1$School of Materials Science and Engineering, North University of China, Taiyuan, Shanxi 030051, China
$^2$Key Laboratory of Instrumentation and Dynamic Measurement of Ministry of Education, North University of China, Taiyuan, Shanxi 030051, China
$^3$North University of China, Shuozhou, Shanxi 036000, China

Correspondence should be addressed to Chenyang Xue; xuechenyang@foxmail.com

Received 16 May 2015; Accepted 16 August 2015

Academic Editor: Themis Matsoukas

Copyright © 2015 Hongyan Xu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The core-shell structured Co$_3$O$_4$-PANI nanocomposites have been successfully prepared using an in situ polymerization method, while the core Co$_3$O$_4$ 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$_3$O$_4$ and the Co$_3$O$_4$-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$_3$O$_4$-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$_3$O$_4$-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$_2$O$_4$, PANI-Fe$_3$O$_4$-graphene, and PANI-Fe$_3$O$_4$-MWCNTs [5–8].

Co$_3$O$_4$ is a normal spinel structured crystal with Co$^{3+}$ occupying octahedral sites and Co$^{2+}$ in tetrahedral sites within the lattice [9]. Co$_3$O$_4$ 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$_3$O$_4$ can also be used as excellent microwave absorption material. The porous Co-Co$_3$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$_3$O$_4$@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$_3$O$_4$, PANI-RGO-Co$_3$O$_4$, and PPy-RGO-Co$_3$O$_4$ 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\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4}-PANI were investigated and the microwave absorbing mechanisms were also discussed.

2. Experimental

2.1. Preparation of Co\textsubscript{3}O\textsubscript{4}-PANI Nanocomposites. The spinel Co\textsubscript{3}O\textsubscript{4} was synthesized by carbon-assisted method using degreasing cotton as a template. 17.46 g Co(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O was dissolved in 20 mL deionized water with magnetic stirring for 10 min. Then 1.5 g degreasing cotton was immersed in the blood red solution and ultrasonicated for 10 min to disperse the ions on the degreasing cotton homogeneously. Then the treated degreasing 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\textsubscript{3}O\textsubscript{4} nanoparticles.

The core-shell Co\textsubscript{3}O\textsubscript{4}-PANI nanocomposite was prepared by an in situ polymerization method. 0.9 g prepreparred Co\textsubscript{3}O\textsubscript{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 (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{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\textsubscript{3}O\textsubscript{4}-PANI nanocomposite was obtained.

2.2. Characterization. The X-ray powder diffraction (XRD) was carried out using a Bruker D8 with Cu Ka (λ = 1.5406 Å) 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\textsuperscript{-1} on an Avatar 360 spectrometer. X-ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250Xi spectrometer with a standard Al Kα radiation with the binding energies calibrated based on the contaminant carbon (C\textsubscript{1s} = 284.6 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 (Φ\textsubscript{outer} = 7.00 mm and Φ\textsubscript{inner} = 3.04 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\textsubscript{3}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4}-PANI are shown in Figure 1. In the pattern of Co\textsubscript{3}O\textsubscript{4}, it can be observed that the diffraction peaks of Co\textsubscript{3}O\textsubscript{4} at 2θ = 31.3, 36.9, 38.5, 44.8, 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\textsubscript{3}O\textsubscript{4}, respectively, which is in accordance with JCPDS card of the standard spinel cubic Co\textsubscript{3}O\textsubscript{4} (JCPDS number 42-1467) [21]. The crystallite size with respect to (311) peak of Co\textsubscript{3}O\textsubscript{4} has been calculated by the Scherrer relation and is estimated to be 56.6 nm. In the pattern of Co\textsubscript{3}O\textsubscript{4}-PANI, comparing to pure Co\textsubscript{3}O\textsubscript{4}, all peaks of Co\textsubscript{3}O\textsubscript{4} become weaker and the peaks at 2θ = 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\textsubscript{3}O\textsubscript{4}-PANI nanocomposites is due to the presence of Co\textsubscript{3}O\textsubscript{4} which has a great effect on forming PANI during the coating process. The interaction of PANI and Co\textsubscript{3}O\textsubscript{4} in the interface blocks the crystallization of PANI [24]. Both the weakness of Co\textsubscript{3}O\textsubscript{4} peaks and the lack of the PANI peaks in Co\textsubscript{3}O\textsubscript{4}-PANI prove that Co\textsubscript{3}O\textsubscript{4} nanoparticles are well coated by PANI.

To investigate the morphology and structure of the products, TEM images were taken for Co\textsubscript{3}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4}-PANI and the corresponding results are presented in Figure 2. Figure 2(a) shows that the Co\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{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
4.66 Å which is in line with the (111) interplanar distance of the Co$_3$O$_4$ [12]. The HRTEM analysis shows clear and continuous lattice fringes which further confirm the good crystal structure of prepared Co$_3$O$_4$.

The FTIR spectra of Co$_3$O$_4$ and Co$_3$O$_4$-PANI are shown in Figure 3. The sharp peaks at 572 and 661 cm$^{-1}$ in the spectrum of Co$_3$O$_4$ 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$_3$O$_4$ and Co$_3$O$_4$-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$_3$O$_4$. The peak at 1398 cm$^{-1}$ is corresponding to the stretching vibration of NO$_3^-$, which is due to the residue of Co(NO$_3$)$_3$ [12]. The peaks at 1642 and 3465 cm$^{-1}$ in the spectrum of Co$_3$O$_4$ are assigned to molecular water and O–H [27]. In the spectrum of Co$_3$O$_4$-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$_3$O$_4$-PANI, the very small peaks between 1118 and 1644 cm$^{-1}$ are due to the existence of PANI. The absence of the characteristic peaks of Co$_3$O$_4$...
shows that the PANI is completely coated on the Co$_3$O$_4$ and has an impact on the surface of Co$_3$O$_4$. The analysis above suggests that it is not a simple mix between Co$_3$O$_4$ and PANI but rather an interaction existing at the interfaces of Co$_3$O$_4$ nanoparticles and PANI [30].

The XPS spectra of Co$_3$O$_4$ and Co$_3$O$_4$-PANI nanoparticles are presented in Figure 4. In Figure 4(a), the spectrum of Co$_3$O$_4$ 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 Co$_3$O$_4$, which are characteristic of the Co$_3$O$_4$ phase [31]. The O1s peak centered at 529.8 eV is assigned to the lattice oxygen in the Co$_3$O$_4$ 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 Co$_3$O$_4$-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 Co$_3$O$_4$-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 Co$_3$O$_4$ at 780.4 and 795.4 eV are very weak. It can be inferred that Co$_3$O$_4$ core is well covered by PANI and the core-shell Co$_3$O$_4$-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]:

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

where $Z_{in}$ is the input impedance of the absorber, $Z_0$ is the input impedance of air, $\mu_r$ and $\varepsilon_r$ 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 Co$_3$O$_4$ 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 Co$_3$O$_4$ sample exhibits a very weak ability to absorb microwave. In Figure 5(b), it can be found that the microwave absorption properties of Co$_3$O$_4$ are significantly enhanced by PANI coating. The reflection loss of Co$_3$O$_4$-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 Co$_3$O$_4$-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 Co$_3$O$_4$. 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 Co$_3$O$_4$-PANI, the relative complex permittivity, permeability, and loss tangent of Co$_3$O$_4$ and Co$_3$O$_4$-PANI are
presented in Figure 6 to characterize dielectric loss and magnetic loss properties of absorbers. In Figure 6(a), the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of relative permittivity of Co$_3$O$_4$ 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$_3$O$_4$ [38]. Comparing to Co$_3$O$_4$, Co$_3$O$_4$-PANI has much higher and more unstable $\varepsilon'$ and $\varepsilon''$ 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$_3$O$_4$ core has a great effect on the permittivity, which is attributed to a large number of interfacial polarization charges [2, 40]. Both the $\varepsilon'$ and $\varepsilon''$ values decrease rapidly with frequency increasing from 2 to 6 GHz. $\varepsilon'$ keeps declining until the frequency reaches 18 GHz, but $\varepsilon''$ 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$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$-PANI nanocomposite. The real ($\mu'$) and imaginary ($\mu''$) parts of relative permeability of Co$_3$O$_4$ are slightly above 1.0 and below 0.1, respectively. Being almost identical to those of Co$_3$O$_4$, the real and imaginary parts of relative permittivity of Co$_3$O$_4$-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$_3$O$_4$ and Co$_3$O$_4$-PANI show a very weak magnetic loss.

Figures 6(e) and 6(f) show the loss tangent of Co$_3$O$_4$ and Co$_3$O$_4$-PANI. Apparently, the dielectric loss tangent ($\tan \delta_\varepsilon = \varepsilon''/\varepsilon'$) is much larger than the magnetic loss tangent ($\tan \delta_\mu = \mu''/\mu'$) for both Co$_3$O$_4$-PANI and Co$_3$O$_4$. This indicates that the main absorption mechanism of Co$_3$O$_4$-PANI and Co$_3$O$_4$ is dielectric loss. The dielectric loss of Co$_3$O$_4$-PANI is nearly four times as high as that of Co$_3$O$_4$. The interfacial interaction between the Co$_3$O$_4$ cores and PANI shells greatly affects the dielectric loss of Co$_3$O$_4$-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$_3$O$_4$-PANI.

4. Conclusion

The Co$_3$O$_4$ 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$_3$O$_4$ nanoparticle prepared is the spinel structure with average size of around 60 nm and the Co$_3$O$_4$-PANI nanocomposite is the core-shell structure with particle size of about 100 nm. Comparing to Co$_3$O$_4$, the core-shell structured Co$_3$O$_4$-PANI exhibits greatly enhanced microwave absorption properties. The optimal absorption peak of Co$_3$O$_4$-PANI
Figure 6: The complex relative permittivity of Co₃O₄ (a) and Co₃O₄-PANI (b), the complex relative permeability of Co₃O₄ (c) and Co₃O₄-PANI (d), and the loss tangent of Co₃O₄ (e) and Co₃O₄-PANI (f).
reaches $-45.8\text{ dB}$ at $11.7\text{ GHz}$ with a thickness of $2.5\text{ mm}$ and the adsorption bandwidth corresponding to the reflection loss below $-10\text{ dB}$ is $14.1\text{ GHz}$ (from $3.9$ to $18\text{ GHz}$) when the thickness is between $2$ and $5.5\text{ mm}$. This is believed to be due to the interfacial interaction of the core-shell structure. The microwave absorption properties of $\text{Co}_3\text{O}_4$-PANI may be further optimized by varying the ratio of $\text{Co}_3\text{O}_4$ core and PANI shell during the synthesis process in the future work. The superior microwave absorption properties demonstrate that the core-shell structured $\text{Co}_3\text{O}_4$-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.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China for Distinguished Young Scholar (Grant no. 51225504) and the National High-Tech Research and Development (863) Program of China (Grant no. 2015AA042600).

References


[34] L. Yan, J. Wang, X. Han, Y. Ren, Q. Liu, and F. Li, "Enhanced microwave absorption of Fe nanoflakes after coating with SiO$_2$ nanoshell," *Nanotechnology*, vol. 21, no. 9, Article ID 095708, 2010.


Submit your manuscripts at http://www.hindawi.com