Porous Fe@Fe₃O₄-C Nanocomposite Using Polyvinyl Alcohol Sponge as Template for Microwave Absorption

WENJIN ZHANG,^{1,2} ZIDONG ZHANG,^{1,2,5} YULIANG JIANG,^{1,2}
CHUANXIN HOU,^{4,6} XUEYAN FU,^{1,2} HONGYAN DU,^{1,2} RUI TIAN,^{1,2}
GUOJING ZHAO,^{1,2} SHENGMEI WEI,^{1,2} and RUNHUA FAN^{2,3,7}

1.—School of Materials Science and Engineering, Shandong University, Jinan 250061, China. 2.—Key Laboratory for Liquid–Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, China. 3.—College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai 201306, China. 4.—School of Environment and Material Engineering, Yantai University, Yantai 264005, China. 5.—e-mail: 1986zzd@163.com. 6.—e-mail: 15275319606@163.com. 7.—e-mail: rhfan@shmtu.edu.cn

In order to obtain a material with excellent microwave absorption performance, polyvinyl alcohol (PVA) sponge was employed as the template. The porous structure of the sponge can facilitate faster and more uniform diffusion of the ferric nitrate liquid during the dipping and obtain a uniform distribution of the ferromagnetic particles, which serves as a functional phase to enhance the microwave absorption properties. The Fe@Fe₃O₄-C nanocomposite can then be fabricated through a dipping/carbonization process. The special core–shell structure effectively improves the dielectric and magnetic loss and provides proper impedance matching. The results indicate that the prepared samples show excellent microwave absorption performance, with maximum effective absorption bandwidth up to 7.9 GHz at a thickness of 2.27 mm. The maximum reflection loss can reach −48.36 dB at 9.6 GHz. Therefore, it is feasible to use PVA sponge as a template to fabricate porous Fe@Fe₃O₄-C nanocomposite with excellent microwave absorption performance.

Key words: Microwave absorption, nanocomposite, polymer recycling, electromagnetic pollution

INTRODUCTION

High-performance electromagnetic wave-absorbing materials have drawn widespread attention for their important applications, such as electromagnetic radiation protection.^{1–5} Achieving improved absorption performance usually requires high dielectric loss, high magnetic loss, and optimized impedance matching in materials. Therefore, various kinds of materials have been investigated, including metal oxides,^{6–8} ferromagnetic metals,^{8,9} and multicomponent composites,^{10,11} More importantly, it has been proved that a porous structure greatly improves microwave absorption properties,

not only by enhancing the interfacial polarization, but also by introducing a multiple-reflection-loss mechanism.^{12–16} Chen et al.¹⁶ fabricated a porous graphene micro-flower composite with an effective absorption bandwidth (EAB) of 5.59 GHz and a maximum reflection loss (RL) of −42.59 dB. Hu et al.¹⁵ synthesized porous Fe₂O₃ nanorods with an EAB of 9.2 GHz and a maximum RL of −71.4 dB. These materials have good microwave absorption properties because of their porous skeleton structure, which can increase the number of reflections of electromagnetic waves among different layers. The fabrication of the porous composites, however, usually requires complex and high-cost chemical synthesis processes.

In this paper, a facile method is proposed for preparing porous Fe@Fe₃O₄-C nanocomposites by carbonizing and dipping of recycled polyvinyl

alcohol (PVA) sponge material. As is well known, the PVA sponge can adsorb liquid rapidly and uniformly owing to its internal capillary force, which is proper for the dipping process. In addition, PVA sponge can be obtained by cross-linking foaming of PVA molecular chains using a cross-linking agent, leading to an inherently micron-sized porous structure, which is beneficial to the improvement of the microwave absorption performance. The obtained Fe@Fe₃O₄-C nanocomposites show excellent microwave absorption properties, with a maximum RL of -48.36 dB at 9.6 GHz. Besides, the effective absorption bandwidth is greatly broadened up to 7.9 GHz at a thickness of 2.27 mm, because of the strong magnetic/dielectric coupling loss and good impedance matching.

This method of preparing microwave absorption material from disused PVA sponge results in excellent microwave absorption performance and will solve the difficulty of PVA sponge degradation, thus providing a new way to solve environmental problems such as electromagnetic pollution and polymer recycling.

EXPERIMENTAL SECTION

Preparation of Fe@Fe₃O₄-C Nanocomposite Material Using Recycled PVA Sponge

As shown in Fig. 1, the recycled sponge was washed with an ultrasonic device in clean water for 2 h, and was then ultrasonically washed in absolute ethanol for 1 h. After that, the sponge was

dried and immersed in solution of ferric nitrate with concentrations of 0.25 mol/L, 0.75 mol/L, and 1.25 mol/L, respectively. The PVA sponge quickly and uniformly absorbed the ferric nitrate solution. Then the sponge was removed after dipping and placed in a dry box at 80°C for 12 h. Finally, the dried sponge was placed in an atmosphere sintering furnace and carbonized in a N₂ atmosphere, with carbonization temperature of 800°C and heating rate of 5°C per min, for 2 h, and the temperature was lowered then to 500°C at a rate of 10°C per min.

Characterization

The morphologies of samples were observed using a field emission scanning electron microscope (FESEM, Hitachi SU-70) and a transmission electron microscope (JEOL JEM-2100). The phase structures were measured by an X-ray diffractometer (Rigaku D/Max-RB). Raman spectra were recorded on a confocal Raman spectroscopic system (Renishaw) with a 532-nm laser. Elemental composition and content were confirmed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi).

Electromagnetic Parameters Measurements

The carbonized sample and paraffin were mixed at a ratio of 3:7 and compressed into a coaxial ring with an inner diameter of 3 mm and outer diameter of 7 mm. The complex permittivity and complex

Fig. 1. Process for preparing microwave-absorbing materials using PVA sponge.

permeability were reversed from S -parameters by the coaxial method.¹⁷

RESULTS AND DISCUSSION

According to Fig. 2a, the PVA sponge contained a large number of micro-pores range from 10 to 50 μm with a high level of connectivity, which is beneficial for immersion in the ferric nitrate solution evenly and rapidly. According to the SEM image of the sample dipped in ferric nitrate solution in Fig. 2b, c, and d, the sponge shrank during the sintering process and the pores became smaller or closed. The surface of the matrix adsorbed elliptical spheres of different sizes, with diameters ranging from several nanometers to several microns. In the transmission electron microscopy (TEM) images shown in Fig. 2e, f, and g, the contrast between the inner and outer part of the spheres is different, which indicates that the spheres are core-shell structures. According to the X-ray diffraction (XRD) spectra in Fig. 3a and XPS spectra in Fig. 4, it can be seen that the core is zerovalent iron and the shell is Fe_3O_4 . As the concentration of the impregnated solution increased, the ellipsoidal objects became denser. But the sponge was also increasingly corroded, and it can be seen that when the concentration of ferric nitrate increased to 1.25 mol/L, the sponge matrix was severely corroded and the pore diameter was larger than 50 μm . The ferric nitrate solution was lost under the action of gravity and could not be stored, so less ferric nitrate reduction products were attached on the matrix.

The phase composition of the samples was analyzed by XRD, shown in Fig. 3a. After the sample was carbonized in a N_2 atmosphere, the ferric nitrate was reduced to iron, and the (110), (200), and (211) diffraction peaks with higher intensity appeared in all three samples. At the same time, it

can be confirmed that the elliptic sphere was covered with a layer of Fe_3O_4 according to Fig. 2b, c, and d, which resulted from the reaction between iron and oxygen elements in the PVA sponge. The Raman spectra of composites dipped in different concentrations of ferric nitrate solution are shown in Fig. 3b. The spectra have two peaks near 1350 cm^{-1} and 1590 cm^{-1} respectively. The D peak is produced by vibrations in graphite crystals, which is not show in the hexagonal lattice. The G peak characterizes the intensity of graphite,^{18,19} and I_D/I_G characterizes the degree of disorder of the material.¹¹ As the concentration of the solution changed, the ratio of I_D/I_G changed from 0.80 to 0.65 and to 1.34. When the concentration of the dipping solution was 1.25 mol/L, the degree of graphitization of the sample was relatively low.

Analysis of the XPS spectrum can accurately determine the elemental composition. Figure 4 shows the XPS spectrum of samples impregnated with different concentrations of ferric nitrate. The survey spectrum in Fig. 4a indicates the existence of C, Fe, and O elements in the three samples. It can be seen that the content of iron gradually increased, while the content of carbon gradually decreased, which was caused by the change in the concentration of ferric nitrate. In addition, when the concentration reached 1.25 mol/L, the PVA matrix was seriously corroded. Therefore, the content of carbon element decreased after carbonization, which was consistent with the morphology observed by SEM. The $\text{Fe}2p$ spectrum is shown in Fig. 4b. According to the literature,²⁰ the positions of $\text{Fe}2p^{1/2}$ and $\text{Fe}2p^{3/2}$ correspond to Fe_3O_4 , which is consistent with the XRD spectrum. In addition, the peak of zerovalent iron is very weak, because it is covered with a layer of Fe_3O_4 shell. Due to the limitation of the surface depth of XPS detection, the signal on the $\text{Fe}2p$

Fig. 2. (a) SEM image of the PVA sponge. (b)–(d) SEM images of PVA sponge dipped in 0.25 mol/L, 0.75 mol/L, and 1.25 mol/L ferric nitrate solution, respectively. (e)–(g) TEM images of PVA sponge dipped in 0.25 mol/L, 0.75 mol/L, and 1.25 mol/L ferric nitrate solution, respectively.

Fig. 3. XRD pattern (a) and Raman spectra (b) of samples dipped in different concentrations of ferric nitrate.

spectrum is relatively weak. The O1s spectrum in Fig. 4c has been separated into three peaks, corresponding to Fe–O, H–O, and C–O bonds, respectively. It is because the samples adsorbed oxygen, water, and carbon dioxide in the air. The peak on the C1s spectrum in Fig. 4d has been split into three peaks by deconvolution, corresponding to C=C, C–C, and C–O–C, which indicated that the main component of the PVA sponge after carbonization is carbon.

Microwave absorption properties are highly associated with electromagnetic parameters (including relative complex permittivity and permeability). The relative complex relative permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) and relative permeability ($\mu_r = \mu' - j\mu''$) can be obtained by Eqs. 1 and 2:²¹

$$\frac{\mu_r}{\epsilon_r} = \left(\frac{1 + \Gamma}{1 - \Gamma} \right)^2 \quad (1)$$

$$\mu_r \epsilon_r = - \left[\frac{c}{\omega d} \ln \left(\frac{1}{T} \right) \right]^2 \quad (2)$$

where Γ is reflection coefficient, T is transmission coefficient, ω is angular frequency, c is the speed of light in free space, and d is the thickness of the coaxial ring. The real part (ϵ' and μ') represents the storage ability of electric and magnetic energy, and the imaginary part (ϵ'' and μ'') represents the loss ability of electric and magnetic energy.²²

Figure 5a and b show the ϵ' and ϵ'' with different ferric nitrate solutions. It can be seen in Fig. 5a that the dielectric real part of the sample with the dipping concentration of 0.25 mol/L has a fluctuation range of more than 5 from 2 to 18 GHz, and the dielectric fluctuation range of the sample with the dipping concentration of 0.75 mol/L is above 2; the ϵ' of the dipping concentration of the 1.25-mol/L sample is about 6. This is owing to the corrosion of the matrix by the high concentration of ferric nitrate, resulting in carbon content decrease in the sample. Thus, the dielectric sensitivity is weakened in the 2–18-GHz band. It can be found that the sample with a dipping concentration of 0.25 mol/L has a maximum imaginary value around 14 GHz in Fig. 5b, and the sample with a dipping concentration of 0.75 mol/L has a maximum imaginary value around 11 GHz. The value of samples with dipping concentration of 1.5 mol/L is < 1 . According to the free electron theory:²³

$$\epsilon'' = \frac{\sigma}{\omega} \quad (3)$$

where σ represents electrical conductivity, and ω is angular frequency. As the dipping concentration was increased, the conductive phase components also increased forthwith, and likely the conductivity increased and the imaginary part of the dielectric constant decreased. Therefore, the sample dipped in 0.25 mol/L ferric nitrate has higher dielectric loss and better microwave absorption performance.

Fig. 4. XPS spectra of samples dipped in different concentrations of ferric nitrate solution. (a) Survey spectrum, (b) Fe2p, (c) O1s, and (d) C1s.

Debye polarization relaxation is an important mechanism for analyzing the microwave absorption performance. The relative complex permittivity can be expressed as below:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j2\pi f\tau} \quad (4)$$

where ε_∞ is relative permittivity at the high-frequency limit, ε_s is the static permittivity, and τ represents the polarization relaxation time.

Then,

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (2\pi f)^2\tau^2} \quad (5)$$

Fig. 5. (a), (b) The real and imaginary parts of the relative complex permittivity. (c), (d) The real and imaginary parts of the relative complex permeability.

$$\varepsilon'' = \varepsilon_{\infty} + \frac{2\pi f \tau (\varepsilon_s - \varepsilon_{\infty})}{1 + (2\pi f)^2 \tau^2} \quad (6)$$

Thus, the relationship between the real part and the imaginary part of the complex permittivity satisfies Eq. 5.²⁴:

$$\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_{\infty}}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_s - \varepsilon_{\infty}}{2}\right)^2 \quad (7)$$

Therefore, the relationship between ε' and ε'' is represented by a curve of a circular shape. For a ε' - ε'' curve, each semicircle corresponds to a Debye dipole relaxation.²⁵ Each semicircle is usually called a Cole-Cole semicircle.^{26,27} In other words, the greater the number of semicircles, the greater the Debye dipole relaxation effect, and the greater the contribution to the absorbing properties of the material.^{26,28,29} As shown in Fig. 6, when the concentration is 0.25 mol/L and 0.75 mol/L, there are 2–3 semicircles on the Cole-Cole semicircle diagram. When the concentration is 1.25 mol/L, there is no semicircle, and there is, therefore, almost no relaxation effect. It has been mentioned above that high concentration of ferric nitrate corrodes the PVA sponge matrix, resulting in loss of amorphous carbon in the composite, so no relaxation polarization can be observed from the Cole-Cole semicircle diagram.

The reflection loss (RL) value was used to evaluate the microwave absorption properties.^{29–31} The reflection curve of the sample is shown in Fig. 7. The RL values of different thickness were calculated based on the transmission line theory³²:

$$Z_{in} = Z_0 \sqrt{\mu_r/\varepsilon_r} \cdot \tanh\left[j(\omega d/c) \sqrt{\mu_r/\varepsilon_r}\right] \quad (8)$$

$$RL \text{ (dB)} = 20 \times \log |(Z_{in} - Z_0)/(Z_{in} + Z_0)| \quad (9)$$

where Z_{in} is input impedance of the absorber, and z_0 is impedance of free space. Z_{in}/Z_0 represents the ability of an electromagnetic wave to enter the materials. There is no electromagnetic wave reflection on the air-absorbent interface if the value of Z_{in}/Z_0 is equal to 1. Z_{in}/Z_0 values for all samples are shown in Fig. 7. Among the three absorbers, the sample with an immersion concentration of 0.25 mol/L exhibited the optimal impedance matching. The optimal impedance and strong dielectric loss ability led to excellent reflection loss.

In order to meet the criteria for practical application, the RL value should be less than -10 dB, which means more than 90% of the electromagnetic waves are attenuated. The bandwidth of $RL < 10$ dB was called the effective absorption bandwidth (EAB).^{33–35} As shown in Fig. 7, the reflection loss curve of different samples changes with the thickness, with (a)–(c) corresponding to the concentrations of 0.25 mol/L, 0.75 mol/L, and 1.25 mol/L,

Fig. 6. Cole–Cole semicircular curve of samples dipped in different concentrations of ferric nitrate solution. (a) 0.25 mol/L, (b) 0.75 mol/L, and (c) 1.25 mol/L.

Fig. 7. Impedance Z_{in}/Z_0 for Fe@Fe₃O₄-C nanocomposites at different dipping concentrations. (a) 0.25 mol/L, (b) 0.75 mol/L, and (c) 1.25 mol/L.

respectively. In the space coordinate system, the corresponding reflection loss is less than -10 dB, except for the red area in the three-dimensional surface. The effective absorption bandwidth can be seen through the bottom surface mapping corresponding to different thicknesses. We can learn that the dipping of 0.25 mol/L ferric nitrate solution has better microwave absorption performance, and the sample dipped in 1.25 mol/L solution has poor absorbing properties in the 2–18-GHz band. When the concentration is 0.25 mol/L, the sample with a

thickness of 2.71 mm has the best absorption performance, which can reach -48.36 dB at 9.6 GHz. Figure 8b shows that the sample with a dipping concentration of 0.25 mol/L has the widest EAB in the 2–18-GHz band, which is 7.9 GHz, and thickness is 2.27 mm.

CONCLUSION

In summary, we fabricated Fe@Fe₃O₄-C nanocomposites for microwave absorption using recycled PVA sponge impregnated with ferric

Fig. 8. Reflection loss corresponding to different concentrations. (a), (b) 0.25 mol/L; (c), (d) 0.75 mol/L; (e), (f) 1.25 mol/L.

nitrate. Compared with the concentrations of 1.25 mol/L and 0.75 mol/L of ferric nitrate, samples dipped in 0.25 mol/L ferric nitrate solution showed better microwave absorption properties. The optimal reflection loss is -48.36 dB when the sample thickness is 2.71 mm at 9.6 GHz, and the optimal

effective bandwidth is approximately 7.9 GHz when the sample thickness is 2.27 mm. The best absorption performance is mainly owing to a favorable dielectric loss, magnetic loss, good impedance, and thickness matching. Therefore, the idea of using disused PVA sponge to fabricate Fe@Fe₃O₄-C

nanocomposites for microwave absorption proposed herein is feasible.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 51601105), China Postdoctoral Science Foundation (Grant Nos. 2017M622199, 2018T110687), Young Elite Scientists Sponsorship Program by CAST (Grant No. 2017QNR001), and Innovation Program of Shanghai Municipal Education Commission (Grant No. 2019-01-07-00-10-E00053).

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Y. Zhang, Y. Huang, T. Zhang, H. Chang, P. Xiao, H. Chen, Z. Huang, and Y. Chen, *Adv. Mater.* **27**, 2049 (2015).
2. W.-L. Song, X.-T. Guan, L.-Z. Fan, Y.-B. Zhao, W.-Q. Cao, C.-Y. Wang, and M.-S. Cao, *Carbon* **100**, 109 (2016).
3. Q. Liu, Q. Cao, H. Bi, C. Liang, K. Yuan, W. She, Y. Yang, and R. Che, *Adv. Mater.* **28**, 486 (2016).
4. X. Zhang, Y. Rao, J. Guo, and G. Qin, *Carbon* **96**, 972 (2016).
5. K. Bi, D. Yang, J. Chen, Q. Wang, W. Hongya, C. Lan, and Y. Yang, *Photon. Res.* **7**, 457 (2019).
6. P. Bhattacharya and C.K. Das, *J. Mater. Sci. Mater. Electron.* **24**, 1927 (2013).
7. Y. Wang, C. Wöll, *Chem. Soc. Rev.* **46** (2017).
8. J. Liu, J. Cheng, R. Che, J. Xu, M. Liu, and Z. Liu, *ACS Appl. Mater. Interfaces* **5**, 2503 (2013).
9. K. Singh, A. Ohlan, A.K. Bakhshi, S.K. Dhawan, *Phys. Mater. Chem. Phys.* **119**, 201 (2009).
10. F. Qin and C. Brosseau, *J. Appl. Phys.* **111**, 224 (2012).
11. Y. Du, W. Liu, R. Qiang, Y. Wang, X. Han, J. Ma, and P. Xu, *ACS Appl. Mater. Interfaces* **6**, 12997 (2014).
12. V.K. Singh, S. Anuj, M.K. Patra, S. Lokesh, R.K. Jani, S.R. Vadera, K. Narendra, *Carbon* **50**, 2202 (2012).
13. G. Li, T. Xie, S. Yang, J. Jin, and J. Jiang, *J. Phys. Chem. C* **116**, 9196 (2012).
14. H.L. Zhu, Y.J. Bai, R. Liu, N. Lun, Y.X. Qi, F.D. Han, J.Q. Bi, *J. Mater. Chem. C* **21**, 13581 (2011).
15. H. Qi, X. Qi, H. Cai, R. Xie, L. Long, Z. Bai, Y. Jiang, S. Qin, W. Zhong, and D. Youwei, *Sci. Rep.* **7**, 11213 (2017).
16. C. Chen, J. Xi, E. Zhou, P. Li, Z. Chen, and G. Chao, *Nano-Micro Lett.* **10**, 26 (2018).
17. M.A. Stuchly and S.S. Stuchly, *IEEE Trans. Instrum. Meas.* **29**, 176 (1980).
18. X.F. Zhang, X.L. Dong, H. Huang, B. Lv, J.P. Lei, and C.J. Choi, *J. Phys. D Appl. Phys.* **40**, 5383 (2007).
19. Y. Bai, S. Qin, W. Nie, J. Li, J. Li, H. Wang, L. Qiao, and D. Guo, *Ceram. Int.* **44**, 8236 (2018).
20. T. Yamashita and P. Hayes, *Appl. Surf. Sci.* **254**, 2441 (2008).
21. A.M. Nicolson and G.F. Ross, *IEEE Trans. Instrum. Meas.* **19**, 377 (1970).
22. P. Xie, Z. Wang, Z. Zhang, R. Fan, C. Cheng, H. Liu, L. Yao, T. Li, Y. Chao, and W. Ning, *J. Mater. Chem. C* **10**, 1039 (2018).
23. X.F. Zhang, X.L. Dong, H. Huang, Y.Y. Liu, W.N. Wang, X.G. Zhu, B. Lv, J.P. Lei, and C.G. Lee, *Appl. Phys. Lett.* **89**, 1679 (2006).
24. G. Li, L. Sheng, Y. Liming, K. An, W. Ren, and X. Zhao, *Mater. Sci. Eng. B* **193**, 153 (2015).
25. K. Zhang, X. Gao, Q. Zhang, and X. Chen, *J. Mater. Sci. Mater. Electron.* **29**, 3401 (2018).
26. S. Xin, J. He, G. Li, T. Jing, and H. Xue, *J. Mater. Chem. C* **1**, 765 (2012).
27. N. Sun, D. Baosheng, F. Liu, P. Si, M. Zhao, X. Zhang, and G. Shi, *J. Alloys Compd.* **577**, 533 (2013).
28. X. Liu, S.W. Or, S.L. Ho, C.C. Cheung, C.M. Leung, Z. Han, D. Geng, Z. Zhang, *J. Alloys Compd.* **509**, 9071 (2011).
29. J. Zou, Z. Wang, M. Yan, and B. Hong, *J. Phys. D Appl. Phys.* **47**, 994 (2014).
30. Y.H. Zou, H.-B. Liu, L. Yang, Z.-Z. Chen, *J. Magn. Magn. Mater.* **302**, 343 (2006).
31. Y. Tong Liu, P. Zhu, and S. Kobayashi, *Nanoscale* **6**, 2447 (2014).
32. C. Caloz, T. Itoh, *Electromagn. Metamater. Transm. Line Theory Microw. Appl. Eng. Approach* **133** (2005).
33. B. Zhao, X. Guo, W. Zhao, J. Deng, and R. Zhang, *ACS Appl. Mater. Interfaces* **8**, 28917 (2016).
34. M. Zhou, X. Zhang, L. Wang, J.M. Wei, L. Wang, K.W. Zhu, and B.X. Feng, *Mater. Chem. Phys.* **130**, 1191 (2011).
35. K.S. Zhou, J.-J. Deng, L.-S. Yin, S. Ma, S. Gao, *Trans. Nonferrous Metals Soc. China* **17**, 947 (2007).

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.