Environment-Stable Co$_x$Ni$_y$ Encapsulation in Stacked Porous Carbon Nanosheets for Enhanced Microwave Absorption

Xiaohui Liang$^1$, Zengming Man$^1$, Bin Quan$^1$, Jing Zheng$^2$, Weihua Gu$^1$, Zhu Zhang$^1$, Guangbin Ji$^1$

Guangbin Ji, gbji@nuaa.edu.cn

1 College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 211100, People’s Republic of China
2 Department of Chemistry and Materials Science, College of Science, Nanjing Forestry University, Nanjing 210037, People’s Republic of China

HIGHLIGHTS

- The microwave absorbing performance of alloy@C composites can be controlled through regulating ratio of metal ions.
- Carbon-based alloy@C composites exhibit the potential stability of microwave absorption with almost the whole Ku band for the practical application.

ABSTRACT Magnetic/dielectric@porous carbon composites, derived from metal–organic frameworks (MOFs) with adjustable composition ratio, have attracted wide attention due to their unique magnetoelectric properties. In addition, MOFs-derived porous carbon-based materials can meet the needs of lightweight feature. This paper reports a simple process for synthesizing stacked Co$_x$Ni$_y$@C nanosheets derived from Co$_x$Ni$_y$-MOFs nanosheets with multiple interfaces, which is good to the microwave response. The Co$_x$Ni$_y$@C with controllable composition can be obtained by adjusting the ratio of Co$^{2+}$ and Ni$^{2+}$. It is supposed that the increased Co content is benefit to the dielectric and magnetic loss. Additionally, the bandwidth of CoNi@C nanosheets can take up almost the whole Ku band. Moreover, this composite has better environmental stability in air, which characteristic provides a sustainable potential for the practical application.

KEYWORDS MOFs; Co$_x$Ni$_y$@C nanosheets; Multiple interfaces; Microwave absorption; Environmental stability
1 Introduction

With the rapid expansion of communication technology and increasing electromagnetic radiation, it is necessary to achieve multifunctional absorbers [1–3]. Various strict performance requirements such as thin thickness, light weight, wide frequency band, and strong absorption strength have been proposed [4, 5]. Hence, the study of the composition and structure design of the material has been stimulated [6–8]. Among them, magnetic/dielectric [9–11] composites have received more attention due to the excellent dielectric and magnetic losses. For example, Zhou et al. [12] reported a non-uniform FeCo/ZnO nanosheet that was adjusted by an auxiliary template method to reduce the density and impedance of the composite. By adjusting Ni\(^{2+}\) artificially designed Co\(_x\)Ni\(_y\)@C structure, a strong electromagnetic wave response was obtained by Quan et al. [13]. Che et al. [14] reported CoNi@Air@TiO\(_2\) yolk-shell structure with outstanding microwave absorption property (RL = −58.2 dB). Feng et al. [15] also investigated the CoNi alloy combined with TiO\(_2\) and graphene, and the matching thickness is only 2.0 mm. All of them demonstrated the strong magnetic loss caused by CoNi cores. Therefore, the CoNi alloy could be a candidate for the magnetic loss material.

In addition, the ideal absorber should have the characteristics as follows: strong magnetic loss and sufficient dielectric loss [16, 17]. Porous carbon is considered to be a material with high dielectric loss [18, 19]. Moreover, due to the lightweight property of porous carbon, assembling alloy in carbon materials is a commendable choice. However, the problem is that the process of preparing alloy@porous carbon materials by the conventional template method is complicated [20, 21]. Therefore, with a sample method to prepare alloy nanoparticles embedded in porous carbon is a challenge. Metal/oxide nanoporous carbon composites derived from MOFs have an easy-to-access surface area, diverse structural topologies, and adjustable functions, which is a mature synthesis method developed in recent years [22, 23].

In this study, stacked CoNi-MOFs used as a template deriving Co\(_x\)Ni\(_y\)@C nanosheets have been investigated. It is worth noting that the carbonization process is important for the formation of porous carbon and Co\(_x\)Ni\(_y\) alloys and the stacked structures promote the formation of multiple interfaces. The synthesized Co\(_x\)Ni\(_y\)@C composite has a highly developed porous structure. In the derived porous structure, the carbon layer can protect the metal molecules from oxidation [24]. Moreover, the carbon layer can provide a channel for electron transport, which is good for dielectric loss [25, 26]. In addition, for the CoNi@C (Co\(^{2+}\): Ni\(^{2+}\) = 1:1) nanosheets, the maximum reflection loss value is −43.7 dB, and the lower thickness is 1.7 mm with the filler loading ratio of 20 wt%.

2 Experimental Section

2.1 Synthesis of Co\(_x\)Ni\(_y\)@C Nanocomposites

CoNi-MOF: 60 mL of DMF (dimethylformamide) dissolved 438 mg Co(NO\(_3\))\(_2\)-6H\(_2\)O and 436 mg Co(NO\(_3\))\(_2\)-6H\(_2\)O (molar ratio = 1:1), 633 mg H\(_3\)BTC (1,3,5-benzenetricarboxylic acid) and 576 mg 4,4′-bipyridine. The supernatant was stirred vigorously for 30 min and then transferred to a Teflon-lined stainless steel autoclave heating at 120 °C for 4 h. Finally, the resulting powder was centrifuged and washed vigorously with DMF and absolute ethanol. The clean powder was dried under vacuum at 80 °C for 12 h. For the Co\(_3\)Ni\(_7\)-MOF and Co\(_7\)Ni\(_3\)-MOF, the molar ratio of Co\(^{3+}\) and Ni\(^{2+}\) is 3:7 and 7:3, respectively, and other conditions are same as the CoNi-MOF. Then, the Co\(_x\)Ni\(_y\)@C-MOF was directly calcinated at 800 °C with heating rate of 2 °C min\(^{-1}\) for 2 h to obtain the Co\(_x\)Ni\(_y\)@C composites under nitrogen atmosphere. In addition, the CoNi@C composites were placed in a sample box covered with a breathable plastic film and left it for 1 year in the natural environment, which is named as CoNi@C-1. Moreover, CoNi-MOFs calcined at 700, 800, and 900 °C with heating rate of 2 °C min\(^{-1}\) were named S-700, S-800, and S-900, respectively.

2.2 Structure Characterization

FESEM (field-emission scanning electron microscopy, JEOL, JSM-7100F) and TEM (transmission electron microscopy, JEOL, JEM-2100F) were used to analyze the morphology and microstructure of the Co\(_x\)Ni\(_y\)@C nanosheets. Raman spectra (Renishaw INVIA micro-Raman...
spectroscopy system) and XRD (D8 Advance X-ray diffractometer, Cu Kα radiation, λ = 1.5418 Å) was used to characterize the structure of the CoₙNiₙ@C nanosheets. X-ray photoelectron spectroscopy (XPS, VGMultiLab 2000) was used to test the chemical states of elements. Adsorption of nitrogen was used to measure Brunauer–Emmett–Teller (BET) surface area using Tristar II 3020 instrument. Agilent PNA N5244A vector network analyzer (VNA) was used to test the electromagnetic parameters in the range of 2–18 GHz with coaxial wire analysis model [27]. Compressing sample and paraffin with 20% filler loading ratio made a ring with inner and outer diameter of 3.04 mm and 7.00 mm to measure.

3 Results and Discussion

3.1 Structure of CoₓNiᵧ-MOFs and CoₓNiᵧ@C Composites

In order to comprehend the formation process of CoₓNiᵧ@C clearly, typical synthesis route is shown in Fig. 1a, b. Stacked precursors with nanosheets morphology were synthesized firstly by hydrothermal method. Then, the precursors were placed in a railboat annealing in the N₂ atmosphere at 800 °C obtained the CoₓNiᵧ@C nanosheets. In fact, the carbonization process is important for the formation of the CoₓNiᵧ alloy and the formation of a porous carbon skeleton, and the stacked nanosheets formed multiple interfaces attenuating microwave. During the calcination process, a partially graphitized carbon layer covered the Co²⁺ and Ni²⁺. At the same time, carbon reduces the metal ions Ni²⁺ and Co²⁺ to Ni⁰ and Co⁰ and then melts them into a CoₓNiᵧ alloy according to the feed ratio. Finally, the derived CoₓNiᵧ alloy nanoparticles were implanted in carbon layer to obtain CoₓNiᵧ/C nanosheets.

Figure 1c, d shows the SEM pictures of CoNi-MOF precursor and CoNi@C nanosheets. Figure 1c exhibits relatively smooth stacked nanosheets morphology with a breadth about 1 μm, and Fig. S1a shows the porous cross profile of the CoNi-MOF precursor. After calcination, the stacked structure became loose and the primary smooth surface became rough (Fig. 1d), emerging more porous structure. In addition, each contact layer forms an interface. Figure S1b, c shows the morphology of Co₃Ni₇@C and Co₇Ni₃@C.
Co$_7$Ni$_3$@C composites, the morphology of Co$_3$Ni$_7$-MOF and Co$_7$Ni$_3$-MOF is inserted, respectively. All of the Co$_x$Ni$_y$@C exhibited loose porous structure, which is good to microwave absorption. Figure 1e, f show TEM and HRTEM images of CoNi@C composite, respectively. It can be clearly seen that the nanosheets are stacked. In addition, the 0.206 nm lattice fringes (obtained from red area in Fig. 1f) can be observed clearly, which is corresponded to (111) plane spacing of the face-centered cubic (fcc) of CoNi crystal [13]. At the edge of CoNi alloy, there is the lattice fringe of the amorphous carbon indicating the presence of carbon layer at the outside of the CoNi alloy. Figure 1e presents the CoNi@C alloy nanoparticles are equably dispersed on the carbon nanosheets, and the selected area electron diffraction insert in Fig. 1e demonstrated the polycrystalline property of the CoNi@C composites. The energy-dispersive X-ray elemental mappings of Co$_x$Ni$_y$@C are displayed in Fig. S1di, showing the distribution of Co and Ni elements. Figures S1d, e show the Co$_3$Ni$_7$@C nanosheets elements mapping, which indicated the content of Co is lower than Ni. Figures S1f, g show the CoNi@C nanosheets elements mapping, which illustrated the content of Co is nearly to Ni. Figures S1h, i show the Co$_3$Ni$_7$@C nanosheets elements mapping, which stated the content of Co is more than Ni. All of results are corresponding to the synthesis progress. In addition, according to the TG analysis in Fig. S2a, the carbon contents in Co$_3$Ni$_7$@C, CoNi@C, and Co$_7$Ni$_3$@C are evaluated to be 8.83%, 9.82%, and 10.28%, respectively. It could be concluded that the weight loss from 0 to 100 °C is water, and the weight loss from 100 to 1000 °C is carbon in the Co$_3$Ni$_7$@C composite [28].

The successful synthesis could be proven by XRD pattern of the obtained Co$_3$Ni$_7$@C composites (Fig. 2a). The (111), (200), and (220) faces peaks of face-centered cubic (fcc) CoNi alloy are matched between 40° and 80° [13], in which the fcc atomic structure diagrams can be seen from Fig. 2b. Additionally, all peak locations are resembled to fcc Ni (JCDPS No. 15-0806) or fcc Co (JCDPS No. 01-1260) [13]. Furthermore, no other impurity peak was found, indicating that only the pure Co$_x$Ni$_y$ alloys were synthesized. In addition, it can be known from the Raman in Fig. 2c, there are carbon layers in the composites. In general, the D-band is relative to the local defects and disorders carbon [29]. The G-band at 1587 cm$^{-1}$ is supported to the $E_{2g}$.
phonon of $sp^2$ bonds of carbon atoms, corresponded to the carbon graphitization degree [30]. As shown in Fig. 2c, with the increase in Co content, the G-band shows higher values, especially for the Co$_7$Ni$_3$@C composites, which indicated existing much graphitic carbon nanostructure in the Co$_7$Ni$_3$@C nanosheets. It is because the Co metal could catalyze the formation of graphitic carbon [31]. Additionally, in order to illustrate the influence of heating treatment temperature on CoNi@C composites, the Raman spectra of CoNi@C is shown in Fig. S2b. It also demonstrated that the $I_G/I_D$ values were increased with the high temperature. It can be inferred that the calcination temperature is conducive to the degree of graphitization of carbon, which will tune the electromagnetic wave loss capability [32]. However, the much graphitic carbon may result in higher conductivity, which prejudice against microwave absorption. In addition, the Co$_7$Ni$_3$@C nanosheets also possess the nanoporous structures. In Fig. 2d, the specific surface areas of all the composites were tested. The BET surface areas of Co$_3$Ni$_7$@C, CoNi@C, and Co$_7$Ni$_3$@C composites are 167.32, 178.69, and 223.74 m$^2$ g$^{-1}$, respectively, which become larger as the Co content increases. From the pores size distribution shown in Fig. S2c, it can be seen the Co$_7$Ni$_3$@C nanosheets appear nanoporous structure, which could provide more contact site for microwave attenuation. The enhanced specific surface areas illustrate the presence of more pore structures with the increasing Co content. Moreover, XPS was used to further analyze the chemical valences and elemental composition. XPS survey spectrum of the CoNi@C nanosheets is presented in Fig. S3a. Obvious peaks of C, Co, and Ni elements were obtained. In addition, the intensity of Co and Ni peaks increases with the increase in Co$^{2+}$ and Ni$^{2+}$ concentration. It is obviously noted that the Co 2$p$ (Fig. 2e) and Ni 2$p$ (Fig. 2f) were all observed in the three samples; moreover, the Co 2$p$ and Ni 2$p$ peaks of CoNi@C in Fig. S3b, c demonstrated the presence of Co and Ni metal [33], which also indicated the successful synthesis of Co$_x$Ni$_y$ alloy. The C 1$s$ in Fig. S3d could also illustrate the formation of C.

3.2 Microwave absorption

In order to explore the electromagnetic wave absorption performance of the composites, reflection loss (RL) values of all samples with 20 wt% filler loading ratios are displayed in Fig. 3a–c. Based on Eqs. 1 and 2 [34, 35]:

$$\text{RL} = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left( \frac{2\pi fd}{c} \sqrt{\frac{\mu_r}{\varepsilon_r}} \right)$$

where $Z_{in}$ and $Z_0$ are the input impedance of the absorber and impedance of air, $\varepsilon_r$ and $\mu_r$ are normalized complex permittivity and permeability of the absorber, $f$, $d$, and $c$ represent the frequency of incident microwaves, the thickness of absorber, and the velocity of light, respectively. In general, the RL value below $-10$ dB indicates that 90% of the microwave is absorbed and it can be considered as an effective absorption. However, in practical applications, there is a strong requirement for wide bandwidth and thin matching thickness. From reflection loss contour map at different thickness in Fig. 3a–c, it can be seen compared with Co$_7$Ni$_3$@C and Co$_7$Ni$_3$@C composites, and CoNi@C nanosheets could be obtained evident better microwave absorption performance with below 2 mm thickness. In addition, the 3D reflection loss map could more visually present the RL values of the composites. Compared with RL values of Co$_7$Ni$_3$@C (Fig. S4a) and Co$_7$Ni$_3$@C (Fig. S4b) composites, the CoNi@C sample (Fig. 3d) exhibited the strongest microwave absorption performance with $-43.7$ dB at 1.7 mm thickness (Fig. 3e). Furthermore, the effective absorption bandwidth 5.7 GHz of CoNi@C nanosheets in almost whole Ku band could be obtained only with thicknesses of 1.8 mm (Fig. 3f).

In order to verify the fact that the CoNi@C composites obtained at 800 °C possess the best microwave absorption performance, the electromagnetic characteristics of CoNi@C composites with different calcination temperatures are compared in Fig. S5. It can be seen that as the calcination temperature increases, the dielectric constant gradually increases (Fig. S5a, b), and the variety in magnetic permeability (Fig. S5c) is not obvious. The increase in the dielectric constant indicates that the dielectric attenuation characteristics of the composite are enhanced, which is conducive to electromagnetic wave absorption. However, through the comparison of RL, it was found that the reflectance of S-700 (Fig. S5d) and S-900 (Fig. S5e) samples did not reach $-10$ dB, and S-800 (Fig. 3e) showed excellent reflection loss.

To explore the maximum absorption bandwidth below 2 mm thickness, the effective frequency bandwidth of
CoNi@C composites with 1.5-2 mm is shown in Fig. 4a. By comparison, the broadest absorption bandwidth could only be acquired at 1.8 mm thickness. Another method to evaluate the microwave absorption property is performed in Fig. 4b, c and Table S1. SRL$_{mt}$ (RL/matching thickness) (Fig. 4b) and SRL$_{fmt}$ (RL/(filler loading × matching thickness)) of CoNi@C nanosheets were calculated with comparing these values with reported carbon-based nanosheets materials. Obviously, the much higher SRL$_{mt}$ and SRL$_{fmt}$ values of CoNi@C composites outclass the reported composites, which implied the better prospect for CoNi@C as an ultrathin, ultralight, and highly effective microwave absorber. In order to clear the cause of microwave absorption gap with three different samples, the electromagnetic parameters are analyzed in Fig. 4d-f. The values of $\varepsilon'$ (Fig. 4d) and $\varepsilon''$ (Fig. 4e) decreased in the 2–18 GHz range, which exhibited frequency dispersion effect benefited to incident microwave dissipation, conductivity, and dielectric loss. The $\varepsilon'$ and $\varepsilon''$ are increased with the added content of Co, which also illustrate the catalytic effect on graphitized carbon [30]. Although the decline of the $\varepsilon''$ is not good to the dielectric loss, the tangent (tan$\delta_\varepsilon = \varepsilon''/\varepsilon'$) [36] (Fig. 4h) illustrate that the dielectric loss was increased with the addition of Co. At the same time, analogical trends also emerged in complex permeability ($\mu'$ and $\mu''$ in Fig. 4f), which indicated outstanding magnetic loss behavior. The magnetic losses are usually associated with natural resonance, exchange resonance, and eddy current loss [37]. The eddy current loss is determined by $C_0$ ($C_0 = \mu'/(\mu'' - \omega^2)^{-1} = 2\Pi\mu_0\mu_\sigma/\alpha^3$) [38], if the main reason for magnetic loss is the eddy current loss, the $C_0$ values are constant. It is obvious that the $C_0$ value fluctuates and decreases in 2–18 GHz frequency range (Fig. S6b).

Fig. 3 Reflection loss contour map of a Co$_3$Ni$_7$@C, b CoNi@C, and c Co$_7$Ni$_3$@C nanosheets. d 3D RL plots. RL plots with e 1.7 mm and f 1.8 mm thickness of CoNi@C nanosheets.
Therefore, eddy current loss is not the dominant mechanism of magnetic loss, so the exchange resonance and natural resonance should be noticed. The natural resonance usually takes place from 0.1 to 10 GHz [39]. Hence, the peaks of $\mu''$ at 6 GHz (Fig. 4f) are related to the natural resonance. The two peaks of $\mu''$ at 11.5 and 15 GHz (Fig. 4f) are relevant to exchange resonance. In addition, the natural resonance and exchange resonance are all enhanced due to the improved magnetism by Co, in spite of the only enhancement of Co$_7$Ni$_3$@C complex is more obvious. Although the natural and the exchange resonance processes cause a decrease of $\mu'$ and $\mu''$, the magnetic loss still was enhanced with the increase in Co content in Co$_x$Ni$_y$@C composites.

The M-H loop [40] of Co$_x$Ni$_y$@C nanosheets variation up with increased content of Co is shown in Fig. 4g to further prove the increased magnetic property. The saturation magnetization value (Fig. 4g) was much lower than pure Co$_x$Ni$_y$ alloy, which is because the dielectric carbon layer wrapped outside of the Co$_x$Ni$_y$ alloy. It is general to know the magnetic tangent ($\tan \delta = \mu''/\mu'$) [36] are dominant criterion for evaluating magnetic loss. With the increased content of Co, the magnetic loss (Fig. 4i) was increased. Therefore, the increase of Co content improved dielectric and magnetic loss at the same time, which also enhanced the impedance matching ($Z_r = Z_{in}/Z_0$). $Z_r$ value close to 1 indicates better impedance matching. From Fig. S6a, one can find that the
CoNi@C composites achieved the best impedance matching. Therefore, it illustrates that appropriate ratio of Co and Ni content was good for dielectric loss, while a superfluous was against the impedance matching, resulting in the miserable microwave absorbing performance.

Furthermore, in order to illustrate the microwave absorption stability of the Co,Ni$_x$@C composites, the CoNi@C samples as representative were exposed in air for 1 year later to test the microwave absorption. All the measured values of $\varepsilon'$, $\varepsilon''$, and $\mu'$ of CoNi@C and CoNi@C-1(Fig. 5a, b) shown declined a little bit after exposing in air for 1 year later. Additionally, the RL values (Fig. 5c) and effective bandwidth (Fig. 5d) of CoNi@C-1 composites further proved the stability. Although the decline of the permittivity and permeability unavoidably weakens the attenuation ability for microwave, the CoNi@C-1 composites still appeared better RL loss of $-35$ dB with 1.85 mm thickness (Fig. 5c). Broadband effective absorption bandwidths could be successfully reached 5.1 GHz with thickness of 2.15 mm. Therefore, the CoNi@C composites can keep better stability in air for 1 year or longer time with strong microwave response.

In addition to the mechanism of microwave attenuation described above, the conduction loss is another important factor to consume electromagnetic energy. Figure 6a presents atomic structure diagrams of the fcc Co and fcc Ni forming fcc CoNi alloy, which structure increased the stability of the CoNi alloy particles. Moreover, the Co amount affecting the dielectric properties is also proved by density functional theory (DFT) calculations [41]. Because of the increased Co content, the strong conductive loss was good to microwave attenuation. The mechanism of electromagnetic energy conversion in this study can be well revealed, based on the original work
reported by Cao and his co-workers that electron transport and dipole polarization do competitive synergy on electromagnetic attenuation [7]. In Fig. 6b, the mechanism of microwave absorption is presented comprehensively, including electron transmission conduction loss, stacked porous nanosheets providing more contact site for microwave, dipole polarization between the CoNi alloy and carbon layer, and dielectric and magnetic loss. Among them, electron transmission conduction loss mainly come from the carbon nanosheets, and the modes of electron transmission could be explained by Yuan et al. [42, 43]. Both electron transport and dipole polarization have great impact on high-performance electromagnetic attenuation, which can be well explained by their competitive synergy originally reported by Cao et al. [44, 45]. Additionally, the stacked nanosheets could also form interlayer interfaces and the CoNi$_x$@C nanoparticles could provide multiple interfaces, when electromagnetic waves enter different interfaces, the attenuation degree of loss is different; therefore, multiple interfaces allow electromagnetic waves to be attenuated to a greater extent.

4 Conclusion

In summary, the stacked Co$_x$Ni$_y$@C nanosheets were successfully synthesized by adding CoNi-MOF derived changing with Co$^{2+}$ and Ni$^{2+}$. The microwave absorption loss mechanism included interfaces attenuation brought by stacked structure, conduction loss induced by electron transport, dielectric loss created by carbon, magnetic loss, natural and exchange resonance caused by CoNi$_x$ alloy, and dipole polarization brought by defective carbon and Co$_x$Ni$_y$@C nanoparticles. Microwave absorption performance with a minimum RL value of $-43.7$ dB with 1.7 mm thin thickness and an effective absorption bandwidth of 5.7 GHz with 1.8 mm thickness could be achieved with a lower filler loading ratio of 20 wt%. Benefiting from the abrasive porous nanosheets structure, it can provide more exposure site for microwave scattering. Therefore, stacked CoNi-MOF-derived multiple interfaces Co$_x$Ni$_y$@C nanosheets provided new ideas for the synthesis of alloy@C composites and increase applications in the microwave absorption field.

5 Supplementary Material

SEM, TG, Raman, pore size distribution, XPS, RL permittivity, permeability, $Z_r$, and $C_0$ curves of the composites, microwave absorption property comparisons of reported literature and this work.

Acknowledgements Financial supports from the National Nature Science Foundation of China (No. 51971111) and the foundation of Jiangsu Provincial Key Laboratory of Bionic Functional Materials are gratefully acknowledged.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence.
References

1. J.H. Luo, K. Zhang, M.L. Cheng, M.M. Gu, X.K. Sun, MoS2 spheres decorated on hollow porous ZnO microspheres with strong wideband microwave absorption. Chem. Eng. J. 380, 122625 (2020). https://doi.org/10.1016/j.cej.2019.122625

2. M. Jahan, R.O. Inakpenu, K. Li, G.L. Zhao, Enhancing the mechanical strength for a microwave absorption composite based on graphene nanoplatelet/epoxy with carbon fibers. Sci. Res. 9, 230 (2019). https://doi.org/10.4236/ sjcm.2019.92013

3. X.H. Liang, B. Quan, Z.M. Man, B.C. Cao, N. Li, C.H. Wang, G.B. Ji, T. Yu, Self-assembly three-dimensional porous carbon networks for efficient dielectric attenuation. ACS Appl. Mater. Interfaces 11, 30228–30233 (2019). https://doi.org/10.1021/acsami.9b08365

4. L.X. Huang, Y.P. Duan, X.H. Dai, Y.S. Zeng, G.J. Ma, Y. Liu, S.H. Gao, W.P. Zhang, Bioinspired metamaterials: multibands electromagnetic wave adaptability and hydrophobic characteristics. Small 15, 1902730 (2019). https://doi.org/10.1002/smll.201902730

5. O. Balci, E.O. Polat, N. Kakenov, C. Kocabas, Graphene-enabled electrically switchable radar-absorbing surfaces. Nat. Commun. 6, 1–10 (2015). https://doi.org/10.1038/ncomms7628

6. X.L. Li, X.W. Yin, C.Q. Song, M.K. Han, H.L. Xu, W.Y. Duan, L.F. Cheng, L.T. Zhang, Self-assembly core-shell graphene-bridged hollow MXenes spheres 3D foam with ultrahigh specific EM absorption performance. Adv. Funct. Mater. 28, 1803938 (2018). https://doi.org/10.1002/adfm.201803938

7. M.S. Cao, X.X. Wang, W.Q. Cao, X.Y. Fang, B. Wen, J. Yuan, Thermally driven transport and relaxation switching self-powered electromagnetic energy conversion. Small 14, 1800987 (2018). https://doi.org/10.1002/smll.201800987

8. J.C. Shu, X.Y. Yang, X.R. Zhang, X.Y. Huang, M.S. Cao, L. Li, H.J. Yang, W.Q. Cao, Tailoring MOF-based materials to tune electromagnetic property for great microwave absorbers and devices. Carbon 162, 157–171 (2020). https://doi.org/10.1016/j.carbon.2020.02.047

9. W. Liu, L. Liu, G.B. Ji, D.R. Li, Y.N. Zhang, J.N. Ma, Y.W. Du, Composition design and structural characterization of MOF-derived composites with controllable electromagnetic properties. ACS Sustain. Chem. Eng. 5, 7961–7971 (2017). https://doi.org/10.1021/acssuschemeng.7b01514

10. X. Bai, Y.H. Zhai, Y. Zhang, Green approach to prepare graphene-based composites with high microwave absorption capacity. J. Phys. Chem. C 115, 11673–11677 (2011). https://doi.org/10.1021/jp202475m

11. H.T. Guan, H.Y. Wang, Y.L. Zhang, C.J. Dong, G. Chen, Y.D. Wang, J.B. Xie. Microwave absorption performance of Ni(OH)2 decorating biomass carbon composites from jackfruit peel. Appl. Surf. Sci. 447, 261–268 (2018). https://doi.org/10.1016/j.apsusc.2018.03.225

12. C.H. Zhou, C. Wu, M.A. Yan, Versatile strategy towards magnetic/dielectric porous heterostructure with confinement effect for lightweight and broadband electromagnetic wave absorption. Chem. Eng. J. 370, 988–996 (2019). https://doi.org/10.1016/j.cej.2019.03.295

13. B. Quan, X.H. Liang, G.B. Ji, Y.N. Zhang, G.Y. Xu, Y.W. Du, Cross-linking-derived synthesis of porous CoNi/C nanocomposites for excellent electromagnetic behaviors. ACS Appl. Mater. Interfaces 9, 38814–38823 (2017). https://doi.org/10.1021/acsami.7b13411

14. Q.H. Liu, Q. Cao, H. Bi, C.Y. Liang, K.P. Yuan, W. She, Y.J. Yang, R.C. Che, CoNi@SiO2@TiO2 and CoNi@Air@TiO2 microspheres with strong wideband microwave absorption. Adv. Mater. 28, 486–490 (2016). https://doi.org/10.1002/adma.201503149

15. J. Feng, F.Z. Pu, Z.X. Li, X.H. Li, X.Y. Hu, J.T. Bai, Interfacial interactions and synergistic effect of CoNi nanocrystals and nitrogen-doped graphene in a composite microwave absorber. Carbon 104, 214–225 (2016). https://doi.org/10.1016/j.carbon.2016.04.006

16. B. Quan, W.H. Shi, S.J.H. Ong, X.C. Lu, P.L.Y. Wang et al., Defect engineering in two common types of dielectric materials for electromagnetic absorption applications. Adv. Funct. Mater. 29, 1901236 (2019). https://doi.org/10.1002/adfm.201901236

17. H.Q. Zhao, Y. Cheng, W. Liu, L.J. Yang, B.S. Zhang, L.Y.P. Wang, G.B. Ji, Z.C.J. Xu, Biomass-derived porous carbon-based nanostructures for microwave absorption. Nano-Micro Lett. 11, 24 (2019). https://doi.org/10.1007/s40820-019-0255-3

18. G. Li, T. Xie, S. Yang, J.H. Jin, J.M. Jiang. Microwave absorption enhancement of porous carbon fibers compared with carbon nanofibers. J. Phys. Chem. C 116, 9196–9201 (2012). https://doi.org/10.1021/jp300505u

19. X. Qiu, L. Wang, H. Zhu, Y.K. Guan, Q.T. Zhang. Lightweight and efficient microwave absorbing materials based on walnut shell-derived nano-porous carbon. Nanoscale 9, 7408–7418 (2017). https://doi.org/10.1039/C7NR02628E

20. Y. Liang, R. Fu, D. Wu, Reactive template-induced self-assembly to ordered mesoporous polymeric and carbonaceous materials. ACS Nano 7, 1748–1754 (2013). https://doi.org/10.1021/nn305841e

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s40820-020-00432-2) contains supplementary material, which is available to authorized users.
21. Z. Wu, Q. Li, D. Feng, P. Webley, D. Zhao, Ordered mesoporous crystalline γ-Al2O3 with variable architecture porosity from a single hard template. J. Am. Chem. Soc. 132, 12042–12050 (2010). https://doi.org/10.1021/ja104379a

22. C.W. Abney, K.M.L. Taylor-Pashow, S.R. Russell, Y. Chen, R. Samantaray, J.V. Lockard, W.B. Lin, Topotactic transformations of metal-organic frameworks to highly porous and stable inorganic sorbents for efficient radionuclide sequestration. Chem. Mater. 26, 5231–5243 (2014). https://doi.org/10.1021/cm501894h

23. P. Falcaro, R. Ricco, C.M. Doherty, K. Liang, A.J. Hillb. M.I. Styles, MOF positioning technology and device fabrication. Chem. Soc. Rev. 43, 5513–5560 (2014). https://doi.org/10.1039/C4CS00089G

24. X.M. Zhang, G.B. Ji, W. Liu, B. Quan, X.H. Liang, C.M. Shang, Y. Cheng, Y.W. Du, Thermal conversion of an Fe3O4@metal-organic framework: a new method for an efficient Fe-Co/nanoporous carbon microwave absorbing material. Nanoscale 7, 12932–12942 (2015). https://doi.org/10.1039/C5NR03176A

25. J.C. Shu, M.S. Cao, M. Zhang, X.X. Wang, W.Q. Cao, X.Y. Fang, The electrochemical performance of coin-shaped lithium batteries prepared from dendritic nickel and their practical applications in aqueous electrolytes. Electrochim. Acta 246, 558–565 (2017). https://doi.org/10.1016/j.electacta.2017.07.156

26. M.S. Cao, X.X. Wang, M. Zhang, W.Q. Cao, X.Y. Fang, J. Yuan, Variable-temperature electron transport and dipole polarization turning flexible multifunctional microsensor beyond electrical and optical energy. Adv. Mater. (2020). https://doi.org/10.1002/adfm.201908299

27. Y.F. Wang, D.L. Chen, X. Yin, P. Xu, F. Wu, M. He, Hybrid of MoS2 and reduced graphene oxide: a lightweight and broadband electromagnetic wave absorber. ACS Appl. Mater. Interfaces 7, 26226–26234 (2015). https://doi.org/10.1021/acsami.5b08410

28. J.P. Xie, Y.Q. Zhu, N. Zhuang, H. Lei, W.L. Zhu et al., Rational design of metal organic framework derived Fe5S2 hollow nanocages@reduced graphene oxide for K-ion storage. Nanoscale 10, 17092–17098 (2018). https://doi.org/10.1039/c8nr05239e

29. Z.M. Man, P. Li, D. Zhou, R. Zang, S.J. Wang et al., High-performance lithium-organic batteries by achieving 16 lithium storage in poly (imine-anthraquinone). J. Mater. Chem. A 7, 2368–2375 (2019). https://doi.org/10.1039/C8TA11230D

30. R. Kuchi, H.M. Nguyen, V. Dongquoc, P.C. Van, S. Surabhi, S.G. Yoon, D. Kim, J.R. Jeong, In-situ Co-arc discharge synthesis of Fe3O4/SWCNT composites for highly effective microwave absorption. Phys. Status Solidi A 215, 1700989 (2018). https://doi.org/10.1002/pssa.201700989

31. W.H. Gu, B. Quan, X.H. Liang, W. Liu, G.B. Ji, Y.W. Du, Composition and structure design of Co3O4 nanowires network by nickel foam with effective electromagnetic performance in C and X Band. ACS Sustain. Chem. Eng. 7, 5543–5552 (2019). https://doi.org/10.1021/acsacschemeng.9b00017

32. X. Yang, Y.P. Duan, Y.S. Zeng, H.F. Pang, G.J. Ma, X.H. Dai, Experimental and theoretical evidence for temperature driving an electric-magnetic complementary effect in magnetic microwave absorbing materials. J. Mater. Chem. C 8, 1583–1590 (2020). https://doi.org/10.1039/c9tc06551b

33. L.L. Song, Y.P. Duan, J. Liu, H.F. Pang, Transformation between nanosheets and nanowires structure in MnO2 upon providing Co2+ ions and applications for microwave absorption. Nano Res. 13, 95–104 (2020). https://doi.org/10.1007/s12274-019-2578-2

34. X.J. Zhang, J.Q. Zhu, P.G. Yin, A.P. Guo, A.P. Huang, L. Guo, G.S. Wang, Tunable high-performance microwave absorption of Co1−xS hollow spheres constructed by nanosheets within ultralow filler loading. Adv. Funct. Mater. 28, 1800761 (2018). https://doi.org/10.1002/adfm.201800761

35. S. Yun, A. Kirakosyan, S. Surabhi, J.R. Jeong, J. Choi, Controlled morphology of MWCNTs driven by polymer-grafted nanoparticles for enhanced microwave absorption. J. Mater. Chem. C 5, 8436–8443 (2017). https://doi.org/10.1039/C7TC02892J

36. X.F. Zhang, X.L. Dong, H. Huang, B. Lv, J.P. Lei, C.J. Choi, Microstructure and microwave absorption properties of carbon-coated iron nanocapsules. J. Phys. D: Appl. Phys. 40, 5383–5387 (2007). https://doi.org/10.1088/0022-3727/40/17/056

37. J. Ma, J.G. Li, X. Ni, X.D. Zhang, J.J. Huang, Microwave resonance in Fe/SiO2 nanocomposite. Appl. Phys. Lett. 95, 102505 (2009). https://doi.org/10.1063/1.3224883

38. H.Q. Cui, X.H. Liang, W. Liu, W.H. Gu, Y.B. Ji, Y.W. Du, Stable microwave absorber derived from 1D customized heterogeneous structures of Fe5N@C. Chem. Eng. J. 381, 122589 (2020). https://doi.org/10.1016/j.cej.2019.122589

39. Z.G. An, S.L. Pan, J.J. Zhang, Facile preparation and electromagnetic properties of core-shell composite spheres composed of aloe-like nickel flowers assembled on hollow glass spheres. J. Phys. Chem. C 113, 2715–2721 (2009). https://doi.org/10.1021/jp809199s

40. B.H. An, B.C. Park, H.A. Yassi, J.S. Lee, J.R. Park, Y.K. Kim, J.E. Ryu, D.S. Choi, Fabrication of grapheminate multi-granule nanocluster composites for microwave absorption application. J. Compos. Mater. 53, 28–30 (2019). https://doi.org/10.1177/0021998319835032

41. J.S. Deng, X. Zhang, B. Zhao, Z.Y. Bai, S.M. Wen et al., Fluffy microrods to heighten the microwave absorption properties through tuning the electronic state of Co/CoO. J. Mater. Chem. C 6, 7128–7140 (2018). https://doi.org/10.1039/C8TC02520G

42. M.S. Cao, W.L. Song, Z.L. Hou, B. Wen, J. Yuan, The effects of temperature and frequency on the dielectric properties, electromagnetic interference shielding and microwave-absorption of short carbon fiber/silica composites. Carbon 48, 788–796 (2010). https://doi.org/10.1016/j.carbon.2009.10.028

43. B. Wen, M.S. Cao, Z.L. Hou, W.L. Song, L. Zhang et al., Temperature dependent microwave attenuation behavior for carbon-nanotube/silica composites. Carbon 65, 124–139 (2013). https://doi.org/10.1016/j.carbon.2013.07.110
44. W.Q. Cao, X.X. Wang, J. Yuan, W.Z. Wang, M.S. Cao, Temperature dependent microwave absorption of ultrathin graphene composites. J. Mater. Chem. C 3, 10017–10022 (2015). https://doi.org/10.1039/c5tc02185e

45. B. Wen, M.S. Cao, M.M. Lu, W.Q. Cao, H.L. Shi et al., Reduced graphene oxides: light-weight and high-efficiency electromagnetic interference shielding at elevated temperatures. Adv. Mater. 26, 3484–3489 (2014). https://doi.org/10.1002/adma.201400108