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Rice husk based hierarchically porous carbon and magnetic particles composite for highly efficient electromagnetic wave attenuation

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Electronic Supplementary Information

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SI-1: The composition analysis of the synthesized absorbers

The chemical composition of the synthesized absorbers is determined by EDS and TGA technologies as shown in Fig. S1 and S2, respectively. For RHPC, carbon was detected without characteristic peaks of other elements. When RHPC was modified with Fe_3O_4 nanoparticles and further thermally treated, characteristic peaks of Fe and C were observed, which can evidence for the elemental composition of RHPC/Fe. Additionally, when the rice husk and $CoCl_2$ composite was carbonized at 1000 °C, Co and C were detected which gave a basic overview of the chemical composition of RHPC/Co. To further verify the content of Fe and Co in the synthesized absorber RHPC/Fe and RHPC/Co, TGA technology was used as shown in Fig. S2. Under air atmosphere, the weight of RHPC is almost zero upon 800 °C because of the combustion of carbon. However, for RHPC/Fe and RHPC/Co, the residual contents are about 45.3% and 67.1%, respectively. As carbon components can be completely burned in air, the final product will be only Fe₂O₃ and Co₂O₃ for RHPC/Fe and RHPC/Co, respectively. Therefore, the amount of carbon in these composite can be calculated by:

wt % R = (1 - wt % carbon)
$$\frac{M_2O_3}{2M}$$
 (1)

where wt % R is the remaining weight percentage after combustion, wt % carbon is the weight percentage of carbon, and M indicates the molecular weight of the metal (Fe or Co). As deduced from equation 1, the weight percentages of carbon in RHPC/Fe and RHPC/Co composites are 68.3% and 52.3%, respectively.

SI-2: The EM wave absorption performance of RHPC/Fe₃O₄

According to the measured EM parameters of RHPC/Fe₃O₄ (Fig. S8), the EM wave absorption performance of RHPC/Fe₃O₄ was investigated as shown in Fig. S9. RHPC/Fe₃O₄ shows absorption ability for EM wave in the high frequency region. However, the minimum RL is only -18.2 dB at absorber thickness of 1.1 mm. With the increase of the absorber thickness, the EM wave absorption property becomes weak. And the largest EABW is 4.5 GHz at the absorber thickness of 1.2 mm. Therefore, compared with the EM wave attenuation performance of RHPC/Fe and RHPC/Co in the main text, the EM wave absorption property of RHPC/Fe₃O₄ is not satisfactory for the weak RL and

normal EABW. Thus, the attempt in modification of rice husk based carbon with Fe and Co using a pre-modification and post-modification method in this work is an effective way to achieve an excellent EM wave dissipation performance.

SI-3: The EMI shielding performance for RHPC/Fe₃O₄, RHPC/Fe and RHPC/Co

The EM wave interference (EMI) shielding mechanism is the result of reflection from the material surface (SE_R), the absorption of EM energy (SE_A), and the multiple internal reflection of EM radiation (SE_M). From the S parameters (S₁₁ and S₂₁), the power coefficients of reflectivity (R, $R = |S_{11}|^2$), transmissivity (T, $T = |S_{21}|^2$), and absorptivity (A) can be obtained, and their relationship is described as R+A+T=1. The total EM interference SE value of the material (SE_T), SE_R, and SE_A can be respectively calculated as follows:

$$SE_{T} = SE_{A} + SE_{R} + SE_{M}$$
(2)

$$SE_R = -10\log(1 - R) = -10\log(1 - |S_{11}|^2)$$
 (3)

$$SE_{A} = -10\log\left(\frac{T}{1-R}\right) = -10\log\left(\frac{|S_{21}|^{2}}{1-|S_{11}|^{2}}\right)$$
 (4)

where SE_M is the EM multiple internal reflection, which can neither be measured nor be calculated. However, it can be negligible when $SE_T \ge 15$ dB. Then, SE_T can be expressed as: ¹

$$SE_T \approx SE_A + SE_R$$
 (5)

The EMI shielding performance for RHPC/Fe₃O₄, RHPC/Fe and RHPC/Co with the absorber loading of 35% are shown in Fig. S10. With the absorber content of 35%, RHPC/Fe (Fig. S10b) shows a better EMI shielding performance than RHPC/Fe₃O₄ (Fig. S10a) and RHPC/Co (Fig. S10c). Moreover, for these three rice husk based porous carbon and magnetic particles composite absorbers, the values of SE_A are higher than that of SE_R in the whole measured EM wave frequency (2-18 GHz). Therefore, the absorption mechanism contributes the most to the final EM wave attenuation performance of RHPC/Fe₃O₄, RHPC/Fe and RHPC/Co.

SI-4: The Cole-Cole semicircle of the synthesized absorbers

According to the electromagnetic theory, it is known that the dielectric loss of the carbon materials

may be attributed to natural resonance, electron polarization relaxation and Debye dipolar relaxation and so on. As for the Debye dipolar relaxation, the relative complex permittivity (ε_r) can be expressed by the following equation (6):

$$\varepsilon_{r} = \varepsilon_{\infty} + \frac{\varepsilon_{s} - \varepsilon_{\infty}}{1 + j2\pi f\tau} = \varepsilon' - j\varepsilon''$$
(6)

where f, ε_s , ε_{∞} and τ are frequency, static permittivity, relative dielectric permittivity at the highfrequency limit, and polarization relaxation time, respectively. Consequently, ε' and ε'' can be described by the following equation (7) and (8):

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_{s} - \varepsilon_{\infty}}{1 + (2\pi f)^{2} \tau^{2}}$$
(7)

$$\varepsilon'' = \frac{2\pi f \tau (\varepsilon_s - \varepsilon_\infty)}{1 + (2\pi f)^2 \tau^2}$$
(8)

According to the above equation (7) and (8), the relationship between ε' and ε'' can be deduced as:

$$\left(\varepsilon' - \frac{\varepsilon_{\rm s} + \varepsilon_{\infty}}{2}\right)^2 + \left(\varepsilon''\right)^2 = \left(\frac{\varepsilon_{\rm s} - \varepsilon_{\infty}}{2}\right)^2 \tag{9}$$

Thus, the plot of $\varepsilon' vs. \varepsilon''$ would be a single semicircle, generally denoted as the Cole-Cole semicircle. Each semicircle corresponds to one Debye relaxation process. The Cole-Cole semicircle of RHPC/Fe₃O₄, RHPC/Fe and RHPC/Co are shown in Fig. S11-13, respectively.

SI-5: The pore properties of RHPC/Fe and RHPC/Co

The pore properties of RHPC/Fe and RHPC/Co were investigated by nitrogen adsorption and desorption experiment. As shown in Fig. S15, RHPC/Fe and RHPC/Co have a porous structure which is consistent with the SEM observations. And as determined by nitrogen adsorption-desorption measurements, the BET surface area and the pore volume for RHPC/Fe are 533 m²g⁻¹ and 0.399 cm³g⁻¹, and those for RHPC/Co are 475 m²g⁻¹ and 0.237 cm³g⁻¹, respectively. And as shown in Fig. S15b, RHPC/Fe and RHPC/Co have a hierarchical porous structure consisting of micro, meso and macro pores.



Fig. S1. (a) EDS elemental data for the rice husk based porous carbon (RHPC), (b) EDS elemental data for the rice husk based porous carbon and Fe particles composite (RHPC/Fe) and (c) EDS elemental data for the rice husk based porous carbon and Co particles composite (RHPC/Co).



Fig. S2. The TGA curves of the rice husk based porous carbon (RHPC), the rice husk based porous carbon and Fe particles composite (RHPC/Fe) and the rice husk based porous carbon and Co particles composite absorber (RHPC/Co).



Fig. S3. The SEM image of the rice husk based carbon before etch by HF.



Fig. S4. The SEM image of the rice husk based porous carbon (RHPC).



Fig. S5. The SEM image of the rice husk based porous carbon and Fe_3O_4 nanoparticles composite (RHPC/Fe₃O₄).



Fig. S6. The SEM image of the rice husk based porous carbon and Fe particles composite absorber (RHPC/Fe).



Fig. S7. The SEM image of the rice husk based porous carbon and Co particles composite absorber (RHPC/Co).



Fig. S8. The relative complex permittivity and permeability of the rice husk based porous carbon and Fe_3O_4 nanoparticles composite (RHPC/Fe₃O₄).



Fig. S9. (a) The reflection loss (RL)-Frequency curves of the rice husk based porous carbon and Fe_3O_4 nanoparticles composite (RHPC/Fe₃O₄) with the absorber content of 25%; (b) Relationship between simulation thickness and the peak frequency of RHPC/Fe₃O₄; (c) The relationship between Z_{in}/Z_0 and EM wave frequency of RHPC/Fe₃O₄.



Fig. S10. (a) The EMI shielding performance for RHPC/Fe₃O₄; (b) the EMI shielding performance for RHPC/Fe and (c) the EMI shielding performance for RHPC/Co.



Fig. S11. The relationship between the real part and the imaginary part of the permittivity for the rice husk based porous carbon and Fe_3O_4 nanoparticles composite (RHPC/Fe₃O₄).



Fig. S12. The relationship between the real part and the imaginary part of the permittivity for the rice husk based porous carbon and Fe particles composite (RHPC/Fe).



Fig. S13. The relationship between the real part and the imaginary part of the permittivity for the rice husk based porous carbon and Co particles composite (RHPC/Co).



Fig. S14. The value of the eddy current $(C_0, \mu''(\mu')^{-2}f^{-1})$ for RHPC/Fe and RHPC/Co vs. EM wave frequency in 2-18 GHz.



Fig. S15. (a) The nitrogen sorption isotherms of RHPC/Fe and RHPC/Co and (b) the pore size distribution of RHPC/Fe and RHPC/Co.

Reference:

1. B. Shen, Y. Li, W. T. Zhai and W. G. Zheng, ACS Appl. Mater. Interfaces, 2016, 8, 8050-8057.