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

Jiyong Fang, Yingshuang Shang, Zheng Chen, Wei Wei, Ying Hu, Xigui Yue and Zhenhua Jiang

The key laboratory for high performance polymer of the Ministry Education of China, College of Chemistry, Jilin University, Changchun, Jilin, People’s Republic of China

Electronic Supplementary Information

Table of Contents:

<table>
<thead>
<tr>
<th>Title</th>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI-1</td>
<td>Composition analysis of the synthesized absorbers</td>
<td>Page 1</td>
</tr>
<tr>
<td>SI-2</td>
<td>EM wave absorption performance of RHPC/Fe$_3$O$_4$</td>
<td>Page 1</td>
</tr>
<tr>
<td>SI-3</td>
<td>The shielding performance for RHPC/Fe$_3$O$_4$, RHPC/Fe and RHPC/Co</td>
<td>Page 2</td>
</tr>
<tr>
<td>SI-4</td>
<td>The Cole-Cole semicircle of the synthesized absorbers</td>
<td>Page 2</td>
</tr>
<tr>
<td>SI-5</td>
<td>The pore properties of RHPC/Fe and RHPC/Co</td>
<td>Page 3</td>
</tr>
<tr>
<td>Fig. S1</td>
<td>EDS data for RHPC, RHPC/Fe and RHPC/Co</td>
<td>Page 4</td>
</tr>
<tr>
<td>Fig. S2</td>
<td>TGA curves for RHPC, RHPC/Fe and RHPC/Co</td>
<td>Page 5</td>
</tr>
<tr>
<td>Fig. S3</td>
<td>SEM image of rice husk carbon before etch by HF</td>
<td>Page 5</td>
</tr>
<tr>
<td>Fig. S4</td>
<td>SEM image of RHPC</td>
<td>Page 6</td>
</tr>
<tr>
<td>Fig. S5</td>
<td>SEM image of RHPC/Fe$_3$O$_4$</td>
<td>Page 6</td>
</tr>
<tr>
<td>Fig. S6</td>
<td>SEM image of RHPC/Fe</td>
<td>Page 7</td>
</tr>
<tr>
<td>Fig. S7</td>
<td>SEM image of RHPC/Co</td>
<td>Page 7</td>
</tr>
<tr>
<td>Fig. S8</td>
<td>Permittivity and Permeability of RHPC/Fe$_3$O$_4$</td>
<td>Page 8</td>
</tr>
<tr>
<td>Fig. S9</td>
<td>RL-$t_{nr}$-$Z_{nr}/Z_0$ curves of RHPC/Fe$_3$O$_4$</td>
<td>Page 8</td>
</tr>
<tr>
<td>Fig. S10</td>
<td>The shielding performance for RHPC/Fe$_3$O$_4$, RHPC/Fe and RHPC/Co</td>
<td>Page 9</td>
</tr>
<tr>
<td>Fig. S11</td>
<td>Relationship between $\varepsilon'$ and $\varepsilon''$ of RHPC/Fe$_3$O$_4$</td>
<td>Page 9</td>
</tr>
<tr>
<td>Fig. S12</td>
<td>Relationship between $\varepsilon'$ and $\varepsilon''$ of RHPC/Fe</td>
<td>Page 10</td>
</tr>
<tr>
<td>Fig. S13</td>
<td>Relationship between $\varepsilon'$ and $\varepsilon''$ of RHPC/Co</td>
<td>Page 10</td>
</tr>
<tr>
<td>Fig. S14</td>
<td>The eddy current of RHPC/Fe$_3$O$_4$, RHPC/Fe and RHPC/Co</td>
<td>Page 11</td>
</tr>
<tr>
<td>Fig. S15</td>
<td>The pore properties of RHPC/Fe and RHPC/Co</td>
<td>Page 11</td>
</tr>
</tbody>
</table>
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\(_3\)O\(_4\) 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 Fe\(_2\)O\(_3\) and Co\(_2\)O\(_3\) for RHPC/Fe and RHPC/Co, respectively. Therefore, the amount of carbon in these composite can be calculated by:

\[
\text{wt} \% \ R = (1 - \text{wt} \% \text{carbon}) \frac{\text{M}_2\text{O}_3}{2\text{M}}
\]

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/Fe\(_3\)O\(_4\)

According to the measured EM parameters of RHPC/Fe\(_3\)O\(_4\) (Fig. S8), the EM wave absorption performance of RHPC/Fe\(_3\)O\(_4\) was investigated as shown in Fig. S9. RHPC/Fe\(_3\)O\(_4\) 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/Fe\(_3\)O\(_4\) 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 ($S_{11}$ and $S_{21}$), 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:

$$SE_T = SE_A + SE_R + SE_M \quad (2)$$

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

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

where SE$_M$ is the EM multiple internal reflection, which can neither be measured nor be calculated. However, it can be negligible when SE$_T \geq 15$ dB. Then, SE$_T$ can be expressed as:

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

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 ($\varepsilon_r$) 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 $f$, $\varepsilon_s$, $\varepsilon_\infty$ and $\tau$ are frequency, static permittivity, relative dielectric permittivity at the high-frequency limit, and polarization relaxation time, respectively. Consequently, $\varepsilon'$ and $\varepsilon''$ 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 $\varepsilon'$ and $\varepsilon''$ can be deduced as:

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

(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/Fe$_3$O$_4$, 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 m$^2$/g and 0.399 cm$^3$/g, and those for RHPC/Co are 475 m$^2$/g and 0.237 cm$^3$/g, 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 Fe₃O₄ 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$_3$O$_4$ nanoparticles composite (RHPC/Fe$_3$O$_4$).

Fig. S9. (a) The reflection loss (RL)-Frequency curves of the rice husk based porous carbon and Fe$_3$O$_4$ nanoparticles composite (RHPC/Fe$_3$O$_4$) with the absorber content of 25%; (b) Relationship between simulation thickness and the peak frequency of RHPC/Fe$_3$O$_4$; (c) The relationship between $Z_{in}/Z_0$ and EM wave frequency of RHPC/Fe$_3$O$_4$. 
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 Fe₃O₄ 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: