Supporting Information

Aperture Control in Polymer-based Composites with Hybrid Core-Shell Spheres for Frequency-Selective Electromagnetic Interference Shielding

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**Fig. S1.** FE-SEM images of PS and PMMA microspheres with average diameters of 200 nm and 20 μm, which were served as core materials for the Graphene@PS and Ni/Au@PMMA core-shell spheres, respectively.

**Fig. S2.** (a–d) HRTEM images and (e) FE-SEM image of the Graphene@PS spheres.
**Fig. S3.** FE-SEM images of Ni@PMMA spheres at different magnifications.

**Fig. S4.** EDS elemental mapping images and composition table of Ni@PMMA spheres showing the distribution of elements (C, O, and Ni).

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt.%</th>
<th>Atomic %</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>7.33</td>
<td>23.43</td>
</tr>
<tr>
<td>O</td>
<td>9.13</td>
<td>21.92</td>
</tr>
<tr>
<td>Ni</td>
<td>83.54</td>
<td>54.65</td>
</tr>
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</table>
**Fig. S5.** EDS elemental mapping images and composition table of Ni/Au@PMMA spheres showing the distribution of elements (C, O, Ni, and Au).

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt.%</th>
<th>Atomic %</th>
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<tbody>
<tr>
<td>C</td>
<td>16.44</td>
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<tr>
<td>O</td>
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<td>9.91</td>
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<tr>
<td>Ni</td>
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<td>40.17</td>
</tr>
<tr>
<td>Au</td>
<td>11.61</td>
<td>2.06</td>
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</table>
Fig. S6. FE-SEM images of Ni/Au@PMMA and Graphene@PS spheres mixed in a weight ratio of 5:2 at different magnifications.

Fig. S7. XPS C1s core-level spectra of PPD-reduced graphene oxide sheets.
**Table S1.** Weight composition, electrical conductivity, and EMI SE of various core-shell sphere composites.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Weight fraction (wt.%)</th>
<th>Electrical conductivity (S/m)</th>
<th>EMI SE (dB)</th>
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<tbody>
<tr>
<td>Graphene</td>
<td>PS</td>
<td>Nickel</td>
<td>Gold</td>
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<tr>
<td>G70</td>
<td>1.43</td>
<td>68.57</td>
<td>0</td>
</tr>
<tr>
<td>M40</td>
<td>0</td>
<td>0</td>
<td>7.61</td>
</tr>
<tr>
<td>M50</td>
<td>0</td>
<td>0</td>
<td>9.52</td>
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<tr>
<td>M60</td>
<td>0</td>
<td>0</td>
<td>11.42</td>
</tr>
<tr>
<td>M70</td>
<td>0</td>
<td>0</td>
<td>13.32</td>
</tr>
<tr>
<td>M10/G60</td>
<td>1.23</td>
<td>58.77</td>
<td>1.90</td>
</tr>
<tr>
<td>M20/G50</td>
<td>1.02</td>
<td>48.98</td>
<td>3.81</td>
</tr>
<tr>
<td>M30/G40</td>
<td>0.82</td>
<td>39.18</td>
<td>5.71</td>
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<tr>
<td>M40/G30</td>
<td>0.61</td>
<td>29.39</td>
<td>7.61</td>
</tr>
<tr>
<td>M50/G20</td>
<td>0.41</td>
<td>19.59</td>
<td>9.52</td>
</tr>
<tr>
<td>M60/G10</td>
<td>0.20</td>
<td>9.80</td>
<td>11.42</td>
</tr>
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</table>

*The electrical conductivities of the samples that are not mentioned were <0.0005 S/m.
Fig. S8. Cross-sectional FE-SEM image of the M60/G10 composite. Partially exposed PMMA cores with smooth surfaces and broken metal shells that were separated from the Ni/Au@PMMA spheres could be observed, clearly showing the core-shell structure of the particles. The Graphene@PS spheres were relatively difficult to find in the figure, which indicated that the spheres were well-dispersed among the Ni/Au@PMMA spheres in the epoxy resin.
Fig. S9. DSC thermal cycles for PMMA microspheres. In the first heating process, there were two transitions, while in the subsequent cooling process, there was only one transition at about the same temperature range. The first transition in the first heating curve was identified as the glass transition. In the second heating process, the second transition observed in the first heating curve disappeared. Since PMMA is a typical amorphous polymer, the second transition observed in the first heating curve should be related to the presence of additional chemicals. According to the DSC result of the second thermal cycle, the glass transition temperature ($T_g$) of the PMMA microsphere was determined as 125°C.
**Fig. S10.** Cross-sectional FE-SEM image of the M10/G60 composite. When the composite was compression-molded at 100°C, which is near glass-transition temperature of PS, the Graphene@PS spheres were compressed into clusters, showing deformed structure of hexagonal blocks (white dash) with some protuberances on each block.
Fig. S11. HRTEM images of ultrathin section of M30/G40 composite at different magnifications.

Table S2. Comparison of average reflection, absorption, and transmission fractions of different core-shell sphere composites in the X-band frequency range.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Shielding mechanisms (%)</th>
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<td>Reflection</td>
</tr>
<tr>
<td>G70</td>
<td>12.0</td>
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<tr>
<td>M60</td>
<td>92.3</td>
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<tr>
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<td>92.0</td>
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<tr>
<td>M60/G10</td>
<td>90.2</td>
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Table S3. Frequency-selective EMI shielding properties of various hybrid core-shell sphere composites.

<table>
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<tr>
<th>Composites</th>
<th>$f_c$ (GHz)</th>
<th>$A_{\text{max}}$ (%)</th>
<th>$A_{\text{min}}$ (%)</th>
<th>$\alpha (A_{\text{max}}/A_{\text{min}})$</th>
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</thead>
<tbody>
<tr>
<td>M10/G60</td>
<td>10.65</td>
<td>32.3</td>
<td>16.8</td>
<td>1.92</td>
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<tr>
<td>M20/G50</td>
<td>9.05</td>
<td>24.4</td>
<td>17.2</td>
<td>1.42</td>
</tr>
<tr>
<td>M30/G40</td>
<td>12.05</td>
<td>24.7</td>
<td>15.6</td>
<td>1.58</td>
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<tr>
<td>M40/G30</td>
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<td>22.5</td>
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<td>21.9</td>
<td>9.7</td>
<td>2.26</td>
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<tr>
<td>M60/G10</td>
<td>10.05</td>
<td>18.6</td>
<td>4.1</td>
<td>4.54</td>
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<tr>
<td>M10/G60+G70</td>
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<td>53.5</td>
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<td>2.21</td>
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<tr>
<td>M20/G50+G70</td>
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<tr>
<td>M30/G40+G70</td>
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<td>59.7</td>
<td>32.2</td>
<td>1.85</td>
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<tr>
<td>M40/G30+G70</td>
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Fig. S12. Absorption fraction of the M00/G00 composites as a function of frequency.
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<th>Matrix</th>
<th>Content (wt.%)</th>
<th>EMI SE (dB)</th>
<th>Thickness (mm)</th>
<th>Frequency range (GHz)</th>
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<tr>
<td>Ni/Au (M70)</td>
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<td>WPU</td>
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<td>GO</td>
<td>PMMA</td>
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<td>WPU</td>
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<td>15.5</td>
<td>0.5</td>
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<td>1</td>
<td>1–18</td>
<td>[29]</td>
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<td>Matrix Material</td>
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<td>0.8</td>
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<td>PS</td>
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<td>18</td>
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<td>PVC</td>
<td>7*</td>
<td>34</td>
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<tr>
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<td>PANI</td>
<td>11*</td>
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<td>20</td>
<td>68</td>
<td>57</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
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<td>PS</td>
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<td>50*</td>
<td>67</td>
<td>54</td>
<td>13</td>
<td>2</td>
</tr>
</tbody>
</table>

* - vol.%

RGO: Reduced graphene oxide; PS: Polystyrene; PMMA: Poly(methyl methacrylate); PEI: Poly(ether imide); WPU: Waterborne polyurethane; PEDOT: Poly(3,4-ethylenedioxythiophene); PSS: Poly(styrenesulfone); PP: Polypropylene; PDMS: Polydimethylsilane; PI: Polyimide; MWCNT: Multi-walled carbon nanotube; SWCNT: Single-walled carbon nanotube; PLLA: Poly-L-lactic acid; PC: Polycarbonate; SEBS: Styrene-ethylene-butylene-styrene; PE: Polyethylene; ABS: Acrylonitrile butadiene styrene; CNF: Carbon nanofiber; PVC: Poly(vinyl chloride); PES: Poly(ether sulfone); PANI: Polyaniline; SA: Sodium alginate; PVDF: Poly(vinylidene fluoride).
Note S1: EMI shielding measurements

EMI SE is attenuating ability of materials for incident EM waves, which is defined as the logarithmic ratio of incoming power ($P_I$) to transmitted power ($P_T$) as:

$$SE\ (dB) = 10 \log \left( \frac{P_I}{P_T} \right)$$

(1)

When incident EM waves arrive on shielding materials, they are reflected, absorbed, and/or transmitted. The reflection ($R$), absorption ($A$), and transmission ($T$) coefficients must add up to 1, that is,

$$R + A + T = 1$$

(2)

The total EMI SE ($SE_T$) is the sum of contributions from reflection ($SE_R$), absorption ($SE_A$), and internal multiple reflections ($SE_M$). At higher EMI SE values than 15 dB, the contribution from internal multiple reflection is considered that is merged in the absorption. Thus, the $SE_T$ can be written as:

$$SE_T = SE_R + SE_A$$

(3)

The absorbed EM waves in a material is related to effective absorption coefficient ($A_{eff}$), which can be described as:

$$A_{eff} = \frac{1 - R - T}{1 - R}$$

(4)

And the $SE_T$, $SE_R$, and $SE_A$ are expressed in terms of transmission ($T$), reflection ($R$), and effective absorption ($A_{eff}$) coefficients as:

$$SE_T = 10 \log \left( \frac{1}{T} \right)$$

(5)

$$SE_R = 10 \log \left( \frac{1}{1 - R} \right)$$

(6)

$$SE_A = SE_T - SE_R = 10 \log \left( \frac{1}{1 - A_{eff}} \right) = 10 \log \left( \frac{1 - R}{T} \right)$$

(7)
Note S2: Discussion on EMI shielding mechanism of materials

Some composites have higher SE\textsubscript{A} than SE\textsubscript{R} values despite high reflection coefficient (R). Although they are EM wave-reflecting material, they can be seen to accomplish EMI shielding through absorption with high SE\textsubscript{A} value. For example, the Ni70 composite exhibited higher SE\textsubscript{A} (76.4 dB) than SE\textsubscript{R} (10.9 dB), while it showed lower absorption (A = 0.106) than reflection (R = 0.894), which means that the material absorbed only 10.6% of incident EM waves and reflected 89.4% of them. These confusing data comes from SE\textsubscript{A}, which is calculated with the effective absorption coefficient (A\textsubscript{eff}). The A represents the proportion of absorption for total amount of incident EM waves. On the other hand, the A\textsubscript{eff} represents proportion of absorption for EM waves only inside a material that is not considering reflected EM waves on the surface of material. Hence, simple comparison of SE\textsubscript{A} and SE\textsubscript{R} cannot show the contribution of absorption and reflection, since EM wave-absorbing performance could be overestimated. Instead, for an absorption dominant EMI shielding material, its R and SE\textsubscript{R} can be used as criteria, which should be less than 50% and 3.01 dB, respectively, as following process\textsuperscript{44}:

\[
R = 0.5 = 50\% \quad (A \approx 0.5, \quad T \approx 0 \quad \text{for most EMI shielding materials})
\]
\[
SE\textsubscript{R} = -10 \log (1 - R) = -10 \log (1 - 0.5) = 3.01 \text{ dB}
\]
**Fig. S13.** Digital images of various microspheres in the fabrication process of nickel shells, showing different colors.
Supporting references


