Supplementary Information

3D Fe$_3$O$_4$ nanocrystals decorating on carbon nanotubes to tune electromagnetic properties and enhance microwave absorption capacity

Yi-Hua Chen,$^a$ Zi-Han Huang,$^a$ Ming-Ming Lu,$^a$ Wen-Qiang Cao,$^b$ Jie Yuan,$^{*b}$ De-Qing Zhang$^c$
and Mao-Sheng Cao$^a$

$^a$ School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081.

China, E-mail: caomaosheng@bit.edu.cn

$^b$ School of Information Engineering, Minzu University of China, Beijing 100081, China, E-mail:
yuanjie4000@163.com

$^c$ School of Material Science and Engineering, Qiqihar University, Qiqihar 161006. China, E-mail:
zhdqing@163.com
Experimental section

Materials

All reagents used were of analytical pure grade: multi-walled carbon nanotubes (MWCNTs of 5–15 nm in length and 20–40 nm in diameter) fabricated by the catalytic decomposition of CH\textsubscript{4} was purchased from Shenzhen Nanotech Port Co. Ltd. (China). Ferric ammonium sulfate (NH\textsubscript{4}Fe(SO\textsubscript{4})\textsubscript{2}•12H\textsubscript{2}O) was obtained from Tianjin Fuchen Chemical Reagents Factory. Ferrous ammonium sulfate ((NH\textsubscript{4})\textsubscript{2}Fe(SO\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O), tetrahydrofuran (THF), ammonia water and nitric acid (HNO\textsubscript{3} 65-68 wt. %) was purchased from Beijing Chemical Factory. Anhydrous ethanol was purchased from Beijing Tong Guang Fine Chemicals Company.

Preparation of modified MWCNTs

To obtain modified MWCNTs, 1 g of MWCNTs were refluxed in the mixture including 80 ml of nitric acid and 420 ml of deionized water at 140\degreeC for 24 hours, followed by washing with deionized water until neutral pH value in the washing solution. The acquired neutral solution of the precipitate was treated by ultrasonic cell disruptor for 1 hour. The modified MWCNTs had been prepared.

Preparation of 3D Fe\textsubscript{3}O\textsubscript{4}-MWCNTs

In a typical fabrication experiment, 20 ml of modified MWCNTs (~100 mg) were dispersed in 20 ml of aqueous solution with 1.6 mmol of NH\textsubscript{4}Fe(SO\textsubscript{4})\textsubscript{2}•12H\textsubscript{2}O and 0.8 mmol of (NH\textsubscript{4})\textsubscript{2}Fe(SO\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O. Then 5 ml of NH\textsubscript{3}•H\textsubscript{2}O (25 wt. %) was dropwise added into the suspension. The co-precipitating reaction was maintaining 30 min at 50\degreeC with vigorously mechanical stirring. The resulting suspension was centrifuged and washed with deionized water and anhydrous ethanol. The precipitations was drying in an oven at 80\degreeC. In order to investigate the possible growth process of 3D Fe\textsubscript{3}O\textsubscript{4}-MWCNTs, we get the products of different reaction time (5 min, 15 min and 30 min) and named Sample 1, Sample 2 and Sample 3, respectively.

Characterizations and measurements

The results of X-ray power diffraction (XRD) spectra were performed on an X’Pert PRO system (Cu-K\textsubscript{α}). Raman
spectra were obtained on a HORIBA Jobin Yvon HR800 Raman spectrometer. SEM images were performed on a Hitachi S-4800 SEM system. TEM images were got on a JEM-2100 TEM system, coupled with carbon- or holey carbon-coated copper grids. In order to measure the complex permittivity and permeability, different amounts of 3D Fe$_3$O$_4$-MWCNTs powders (5, 10, 15, 20 and 25 wt. %) and paraffin (95, 90, 85, 80 and 75 wt. %) were dispersed uniformly in the tetrahydrofuran, respectively. After the tetrahydrofuran was completely evaporated, the mixture was cooled to room temperature. A portion of the resulting mixture was pressed into toroidal shape ($\Phi_{\text{out}}$ 7.05 mm; $\Phi_{\text{in}}$ 3.0 mm; Thickness ~1.5mm). The complex permittivity and permeability were measured on an Anritsu 37269D vector network analyzer.

<table>
<thead>
<tr>
<th>Samples in matrices</th>
<th>Wt. %</th>
<th>Min RL [dB]</th>
<th>Effective bandwidth [GHz] (RL $\leq$ -10 dB)</th>
<th>Thickness [mm]</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D Fe$_3$O$_4$-MWCNTs in wax</td>
<td>20</td>
<td>-11.1~-52.8</td>
<td>1.7~3.0</td>
<td>2.0~6.8</td>
<td>This work</td>
</tr>
<tr>
<td>SWCNTs in SCPU</td>
<td>5</td>
<td>-21.9</td>
<td>2.6</td>
<td>2.0</td>
<td>1</td>
</tr>
<tr>
<td>Fe-CNT in epoxy</td>
<td>10</td>
<td>-31.7</td>
<td>2.9</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>$\gamma$-Fe$_3$O$_4$/MWNTs/PBO in wax</td>
<td>12</td>
<td>32.7</td>
<td>2.7</td>
<td>2.7</td>
<td>3</td>
</tr>
<tr>
<td>MWCNT/Fe$_3$O$_4$ nanohybrid in wax</td>
<td>50</td>
<td>-41.6</td>
<td>1.5</td>
<td>3.4</td>
<td>4</td>
</tr>
<tr>
<td>r-GO/Fe$_3$O$_4$ in wax</td>
<td>30</td>
<td>-24.0</td>
<td>4.9</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>GO/CNT-Fe$_3$O$_4$ nanohybrid in wax</td>
<td>30</td>
<td>-37.2</td>
<td>1.0</td>
<td>5.0</td>
<td>6</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@TiO$_2$ microspheres in epoxy</td>
<td>20</td>
<td>-23.3</td>
<td>5.5</td>
<td>2.0</td>
<td>7</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@ZnO nanohybrid in wax</td>
<td>50</td>
<td>-22.7</td>
<td>5.8</td>
<td>3.5</td>
<td>8</td>
</tr>
</tbody>
</table>
Scheme S1. The illustration of the fabrication of 3D Fe₃O₄-MWCNTs

Figure S2. The XRD spectrum of neat MWCNTs and 3D Fe₃O₄-MWCNTs

Figure S3. The Raman spectrum of 3D Fe₃O₄-MWCNTs and neat MWCNTs
Figure S4. The energy dispersive spectroscopy (EDS) analysis of Sample 1 (a), Sample 2 (b) and Sample 3 (c); the mass percent and atom percent is in the inset.

Figure S5. The RL values of Sample 1, Sample 2 and Sample 3.
Figure S6. The RL of 3D Fe$_3$O$_4$-MWCNTs (a) and Fe$_3$O$_4$/MWCNTs blend (b)

Figure S7. Frequency dependence of $\mu''(\mu')^{-2}f^l$ for 3D Fe$_3$O$_4$-MWCNTs

Figure S8. The size distribution histogram of Fe$_3$O$_4$ nanocrystals from the inset
Notes and References


