MSOT/CT/MR imaging Guided and hypoxia Maneuvered Oxygen self-sufficiency radiotherapy based on One-pot MnO$_2$-mSiO$_2$ @ Au nanoparticle

Supporting Information

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Introduction of photothermal conversion calculation
Figure S1 (a). Elements analysis of MNH₅ (b). TEM images of MNH₅ scale bar from up to down are 500 nm, 200nm and 20 nm. Table1. The element types O, Si, Mn and the atom weight respectively.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>Atom Wt %</th>
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<tbody>
<tr>
<td>O K</td>
<td>54.85</td>
<td>68.23</td>
</tr>
<tr>
<td>Si K</td>
<td>44.51</td>
<td>31.54</td>
</tr>
<tr>
<td>Mn K</td>
<td>0.64</td>
<td>0.23</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
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</table>
Figure S2 (a). Surface area distributed by different pore width of MnO₂-mSiO₂ nanohybrids. (b). Multi-point BET plot of MnO₂-mSiO₂ nanohybrids. Table 2. BET data summary.

<table>
<thead>
<tr>
<th><strong>BET Summary</strong></th>
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<tbody>
<tr>
<td>Slope</td>
<td>5.294 1/g</td>
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<tr>
<td>Intercept</td>
<td>1.289e-01 1/g</td>
</tr>
<tr>
<td>Correlation coefficient, R</td>
<td>0.999715</td>
</tr>
<tr>
<td>C constant</td>
<td>42.056</td>
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<tr>
<td>Surface Area</td>
<td>642.182 m²/g</td>
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</table>
Figure. S3 (a). Cumulative surface area of MnO$_2$-SiO$_2$ nanohybrids. (b) Cumulative pore volume distributed by different pore width of MnO$_2$-SiO$_2$ nanohybrids. Table3. DFT method Summary.

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<tbody>
<tr>
<td>Pore volume</td>
<td>0.989 cc/g</td>
</tr>
<tr>
<td>Surface area</td>
<td>381.083 m$^2$/g</td>
</tr>
<tr>
<td>Lower confidence limit</td>
<td>0.524 nm</td>
</tr>
<tr>
<td>Pore width (Mode(dLog))</td>
<td>16.015 nm</td>
</tr>
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</table>
Figure. S4 (a). $^1$H-NMR spectrum of the unmodified hyaluronic acid (b) $^1$H-NMR spectrum of dopamine (c). $^1$H-NMR spectrum of HA-DN complex.
Figure. S5 Oxygen generation capability of different formulations.

Figure. S6 Photoacoustic imaging for tumor oxygen generation
Figure. S7. CT imaging for formulation distribution in major organs after 24 h injection. The circled sections represent the tumor sites.

Figure. S8 (a). Pharmacokinetic profiles of MnO$_2$-mSiO$_2$@Au-HA nanoparticles following intravenous administration by measuring Au concentrations. (b). Biodistribution in major organs after intravenously injection of MnO$_2$-mSiO$_2$@Au-HA nanoparticles.
Figure S9. T$_2$-weighted MR images of MnO$_2$-mSiO$_2$@Au-HA at varying Mn$^{2+}$ concentrations.

Lower is the linear relationship between the T$_2$ relaxation rate ($1/T_2$) and Mn$^{2+}$ concentrations in MnO$_2$-mSiO$_2$@Au-HA aqueous solutions.
Figure. S10 (a). CT phantom images of Iohexol (upper panel) and MAHNPs (lower panel) at different I or Au concentrations. (b). CT values of MAHNPs and Iohexol with different Au or I concentrations.
The Calculation of the photothermal conversion efficiency was determined by the following steps according to the references[1-3].

Firstly, the aqueous solution of the MnO$_2$-mSiO$_2$@Au-HA nanoparticles (100 ppm) underwent continuous irradiation of 808 nm laser (1.5 W/cm$^2$) until steady state temperature was reached. Then the laser was shut off, and the aqueous solution was naturally cooled to environment temperature. The temperature change of the aqueous solution was recorded (Figure. 2g). The $\eta$ value was calculated as follows:

$$\eta = \frac{hs(T_{\text{Max}} - T_{\text{Surr}}) - Q_s}{I(1 - 10^{-A_{808}})}$$  \hspace{1cm} (1)

Where $h$ is the heat transfer coefficient, $S$ is the surface area of the container, and the value of $hs$ is obtained from the Eq. (4) and Figure 2h. The maximum steady temperature ($T_{\text{Max}}$) was 63.1 °C and environmental temperature ($T_{\text{Surr}}$) was 25.9 °C. The laser power $I$ used in irradiation was 1.5 W/cm$^2$. The absorbance of the MnO$_2$-mSiO$_2$@Au-HA nanoparticles at 808 nm was 0.534. $Q_{\text{Dis}}$ is heat dissipated from the light absorbed by the solvent and container. A dimensionless parameter $\theta$ is calculated as followed:

$$\theta = \frac{T - T_{\text{Surr}}}{T_{\text{Max}} - T_{\text{Surr}}}$$  \hspace{1cm} (2)

A sample system time constant $\tau_s$ can be calculated as Eq. (3)

$$t = -\tau_s \ln(\theta)$$  \hspace{1cm} (3)

According to figure 2g, $\tau_s$ was obtained to be 166.97 s.

$$hs = \frac{m_D C_D}{\tau_s}$$  \hspace{1cm} (4)

In addition, $m_D$ is 0.5 g and $C_D$ is 4.2 J/g·°C in the experiment.
$Q_s$ is heat dissipated from the light absorbed by the container itself, and it was determined independently to be 3.5 mW using a container containing pure water. Thus, substituting according values of each parameters to Eq. 1, the 808 nm laser photothermal conversion efficiency ($\eta$) of the MnO$_2$-mSiO$_2$@Au-HA nanoparticles can be calculated to be 25.38%.

