Supporting Information

A robust Mn@FeNi-S/graphene oxide nanocomposite as a high efficiency catalyst for the non-enzymatic electrochemical detection of hydrogen peroxide†

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1. Synthesis of GO
GO was synthesized from the graphite (GR) powder through a modified Hummers method. Typically, 1.0 g GR, 1.0 g NaNO$_3$ and 50 mL conc. H$_2$SO$_4$ were added into a 250 mL beaker and stirred for 30 min in an ice bath. Then, 3.0 g of KMnO$_4$ was added to the mixture and the resultant was transferred to a water bath maintained at 35 ºC. The whole reaction mixture was diluted with 150 mL of distilled water. Afterwards, 10 mL of 30% H$_2$O$_2$ was slowly added and continued for vigorous stirring up to 60 min. The final product was centrifuged and purified by repeated washing with double distilled water until the pH became neutral. Finally, exfoliated GO was obtained by vacuum drying at 65 ºC.

![Graph](image)

Fig. S1. (a) N$_2$-sorption of GO and Mn@FeNi-S/GO and (b) corresponding pore size distribution.
Fig. S2 (a) FE-SEM overlay image of the Mn@FeNi-S particles, and EDX elemental mapping of the Mn@FeNi-S particles showing the presence of (b) S, (c) Mn, (d) Fe, and (e) Ni elements.
Fig. S3 (a) FE-SEM overlay image of the Mn@FeNi-S/GO nanocomposite, and EDX elemental mapping of the Mn@FeNi-S/GO nanocomposite showing the presence of (b) S, (c) C, (d) Ni, (e) Fe, (f) Mn, and (g) O elements.
Fig. S4 (a) FE-TEM image, (b) overlay image of the Mn@FeNi-S, (c) Fe, (d) Ni, (e), S, (f) Mn, and (g) O elements.
Fig. S5. (a,b) HR-TEM Images of the Mn@FeNi-S/GO nanocomposite, and the elemental mapping of (a₁) Fe (green dots); (a₂) Ni (red dots); (a₃) Mn (orange dots); (a₄) S (magenta dots); (a₅) C (yellow dots); and, (a₆) O elements (blue dots); TEM-EDS line scan of
Mn@FeNi-S/GO nanocomposite (b₁) overlay image, line scan profile (b₂), and the corresponding elements lines (b₃-b₉), respectively.

**Fig. S6.** (a) CV curves of FeS/GO, NiS/GO, and MnS/GO electrodes in N₂-saturated 0.1 M PB (pH 7.0) containing 25 µM of H₂O₂ at a scan rate of 50 mV s⁻¹.

**Fig. S7.** (a) CV curves of Mn@FeNi-S/GO electrode in various concentration of H₂O₂ from 25–125 µm, (b) corresponding plot of current (µA) versus concentration of H₂O₂, (c) effect of catalyst
dosage level on GC electrode toward H$_2$O$_2$ sensing, (d) various pH studies of Mn-doped FeNi-S/GO electrode in presence of 25 µM H$_2$O$_2$.

**Fig. S8.** (a) Amperometric (i-t) response of FeNi-S/GO nanocomposite in various successive addition of H$_2$O$_2$, (b) the corresponding plot of current response versus time (seconds).

**Table 1.** Comparison of Mn@FeNi-S/GO modified electrode with other previous reported electrode for H$_2$O$_2$. 

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<table>
<thead>
<tr>
<th>Modified electrode</th>
<th>Material preparation method/Buffer; pH</th>
<th>Linear range (µM)</th>
<th>LOD (nM)</th>
<th>Sensitivity (µA µM⁻¹ cm⁻²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS₂/GCE&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Wet chemical/PB&lt;sup&gt;b&lt;/sup&gt; (0.1 M; pH 7.0)</td>
<td>0.25–9</td>
<td>250</td>
<td>612</td>
<td>S1</td>
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<tr>
<td>ERGO&lt;sup&gt;c&lt;/sup&gt;/AuNPs/GCE</td>
<td>Electrodeposition/PB (0.1 M; pH 6.0)</td>
<td>Upto 100</td>
<td>75</td>
<td>527.8</td>
<td>S2</td>
</tr>
<tr>
<td>NiCo₂S₄/rGO/GCE</td>
<td>Hydrothermal/NaOH (0.1 M)</td>
<td>25–112.5</td>
<td>190</td>
<td>118.5</td>
<td>S3</td>
</tr>
<tr>
<td>NiFe-LDH&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Hydrothermal/PB (0.1 M; pH 7.0)</td>
<td>0.5–840</td>
<td>500</td>
<td>1704</td>
<td>S4</td>
</tr>
<tr>
<td>Fe-MOF&lt;sup&gt;e&lt;/sup&gt;/rGO/CPE</td>
<td>Hydrothermal/PB (0.1 M; pH 7.0)</td>
<td>5.0–945</td>
<td>500</td>
<td>5.17</td>
<td>S5</td>
</tr>
<tr>
<td>Mn₂CuO₄/GCE</td>
<td>Solvothermal/PB (0.05 M; pH 7.0)</td>
<td>0.036–9.3 mM</td>
<td>13</td>
<td>3.107</td>
<td>S6</td>
</tr>
<tr>
<td>AgFeAmaranth/GCE</td>
<td>Stirrer/KOH (0.1 M)</td>
<td>Upto 20 mM</td>
<td>100</td>
<td>1350</td>
<td>S7</td>
</tr>
<tr>
<td>HNONS&lt;sup&gt;f&lt;/sup&gt;@rGO/GCE</td>
<td>Ex-situ/PB (0.1 M; pH 7.0)</td>
<td>0.25–13.1 mM</td>
<td>375</td>
<td>222.16</td>
<td>S8</td>
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<tr>
<td>mSiO₂/GCE</td>
<td>Stirrer/AB (0.1 M; pH 6.8)</td>
<td>4–10 mM</td>
<td>300</td>
<td>–</td>
<td>S9</td>
</tr>
<tr>
<td>FePc-CP&lt;sup&gt;g&lt;/sup&gt;/film</td>
<td>Coupling/PB (0.1 M; pH 7.0)</td>
<td>0.1–1000</td>
<td>17</td>
<td>97.0</td>
<td>S10</td>
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<tr>
<td>FeNi-S/GO/GCE</td>
<td>Heating/PB (0.1 M; pH 7.0)</td>
<td>0.07–123</td>
<td>24.26</td>
<td>2.088</td>
<td>this work</td>
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<tr>
<td>Mn@FeNi-S/GO/GCE</td>
<td>Heating/PB (0.1 M; pH 7.0)</td>
<td>0.055–523</td>
<td>8.84</td>
<td>8.929</td>
<td>this work</td>
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</tbody>
</table>

<sup>a</sup>Glassy carbon electrode. <sup>b</sup>Phosphate buffer. <sup>c</sup>Electrochemically reduced graphene oxide. <sup>d</sup>layered double hydroxides. <sup>e</sup>Metal organic framework. <sup>f</sup>Hexagonal nickel oxide nanosheets. <sup>g</sup>Iron phthalocyanine-conjugated polymer.

Reference


