Supporting Information for

Electrochemiluminescent detection of cardiac troponin I based on the Au-Ag alloy nanourchins

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Comparison of Analytical performance
As shown in the Table S1, the sensitivity of our H\textsubscript{2}O\textsubscript{2} sensor is competitive with or is better than these of other previous reports.

**Table S1.** Analytical performance comparison of our Au-Ag Alloy NUs modified electrode and other methods.

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>Materials</th>
<th>LDR/μM</th>
<th>LOD/μM</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemistry</td>
<td>Au-Ag Alloy NUs</td>
<td>0.1-200</td>
<td>0.045</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>PtAu/G-CNTs</td>
<td>2-8561</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>AgNP/F-SiO\textsubscript{2}/GO</td>
<td>100-260000</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>OMCN</td>
<td>4-40</td>
<td>1.52</td>
<td>3</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>HRP-Au NCs</td>
<td>0.1-100</td>
<td>0.03</td>
<td>4</td>
</tr>
<tr>
<td>Colorimetry</td>
<td>CoFe-LDHs</td>
<td>1-10</td>
<td>0.6</td>
<td>5</td>
</tr>
</tbody>
</table>
Electrochemical detection of hydrogen peroxide

The CVs of Au-Ag Alloy NUs /GCE modified with different volume of Au-Ag Alloy NUs solution were shown in Fig. S1, and 6 µL is chosen as the optimum volume according to the peak current.

The chitosan film was used for the immobilization of Au-Ag Alloy NUs and fabrication of H$_2$O$_2$ sensor in this system. CVs of Au-Ag alloy/GCE before and after modification of chitosan were shown in Fig. S2, which proved that the chitosan film didn’t affect the electrochemical performances of the sensor obviously in this condition. Moreover, the chitosan film could improve the stability and reproducibility of Au-Ag alloy/GCE. As shown in Fig. S2, the CV of CS/Au-Ag alloy/GCE didn’t change a lot after the disturbance of N$_2$ bubbling in solution, while the reduction current decreased dramatically for the electrode without chitosan modification.

The interference of oxygen reduction was also investigated, and the result shown in Fig. S3 indicated that the oxygen dissolved in solution caused a reduction current at -0.2 to -0.8 V.
In order to determine the optimum potential, the amperometric responses to the successive addition of 10 μM H₂O₂ in PBS at different applied potentials (-0.4 to -0.7 V) were carried out. As shown in Fig. S4, considering the sensitivity and stability, -0.6 V was chosen as the optimum potential.

**Fig. S3** The CV curves of Au-Ag Alloy NUs modified GCE in 0.1 M PBS solution with and without N₂ atmosphere.

**Fig. S4** Amperometric responses to the successive addition of 10 μM H₂O₂ in PBS at different applied potentials (-0.4 to -0.7 V).
Electrochemiluminescent detection of hydrogen peroxide

Before the ECL measurement, the effect of H$_2$O$_2$ concentration was investigated. As shown in Fig. S5, the ECL signal reached the highest when the H$_2$O$_2$ concentration was 8 mM.

**Fig. S5** (a) Amperometric responses to the successive addition of various concentrations of H$_2$O$_2$ at -0.6 V in PBS. The inset shows the partial magnification of current response with the H$_2$O$_2$ concentration ranging from 0.1 to 2 μM. (b) The calibration curve for H$_2$O$_2$ detection. The inset shows a closer look of linear plot of 0.1 to 10 μM.

Electrochemiluminescent detection of hydrogen peroxide

Before the ECL measurement, the effect of H$_2$O$_2$ concentration was investigated. As shown in Fig. S5, the ECL signal reached the highest when the H$_2$O$_2$ concentration was 8 mM.

**Fig. S6** The influence of H$_2$O$_2$ concentration on the ECL intensity of the Au-Ag Alloy NUs modified electrode. All the experiments were carried out in 0.1 M PBS containing 10 μM luminol. Scan rate was 50 mV/s.
As shown in Fig. S6, the electrochemical characterizations, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were carried out step by step in Fe(CN)$_6^{3-/4-}$ solution.

![Fig. S7 CV and EIS at (a) bare GCE, (b) Au-Ag Alloy NUs/GCE, (c) Ab/Au-Ag Alloy NUs/GCE, (d) BSA/Ab/Au-Ag Alloy NUs/GCE, (e) cTnI/BSA/Ab/Au-Ag Alloy NUs/GCE in 0.1 M PBS containing 2.0 mM K$_4$Fe(CN)$_6$. Scan rate: 50 mV/s. EIS: 100 kHz~1 Hz, 5 mV rms, 0.21 V vs SCE.](image)

As shown in Table S2, recovery experiments were also performed by standard addition methods in human serum, and the acceptable recoveries (91.1%-113.0%) were obtained.

**Table S2.** Recovery experiments for cTnI in the human serum by the proposed immunosensor.

<table>
<thead>
<tr>
<th>Serum samples</th>
<th>Added (pg/mL)</th>
<th>Measured (pg/mL)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>455.6</td>
<td>7.8</td>
<td>91.1</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>1133</td>
<td>2.9</td>
<td>113.0</td>
</tr>
<tr>
<td>3</td>
<td>10000</td>
<td>9289</td>
<td>6.8</td>
<td>93.0</td>
</tr>
</tbody>
</table>

**References**