Supplementary information

N-doped TiO₂ based Visible Light Activated Label-free Photoelectrochemical Biosensor for Detection of Hg²⁺ through Quenching of Photogenerated Electrons

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1. Preparation of the N-doped TiO$_2$ powder and film

2.0 g urea and 30 mL ethanol were mixed thoroughly by stirring at room temperature, then 4 mL tetrabutyl titanate was slowly added into the mixture. After stirring for 30 min, 0.5 mL water was slowly dropped into the above solution and stirred for another 2 h to hydrolyze the titanate completely. After that, the solution was heated at 60 °C to evaporate the water and following annealed at 600 °C for 2 h with a heating rate of 5 °C per min. The N-doped TiO$_2$ was obtained as pale yellow powder.

FTO glass was cleaned by ultrasonic for 15 min with acetone and ethanol respectively. 3 g ethyl cellulose (EC) was added in 20 g terpineol and the mixture was kept at 50 °C to dissolve EC. 0.2 g N-doped TiO$_2$ powder and 1.6 g above viscous solution were added into a mortar and grinded for around 30 min. After that, the TiO$_2$ paste was cast onto the cleaning FTO glass by doctor blade method with 3M tape as spacer. The result N-doped TiO$_2$ film was dried at 50 °C and was annealed at 450 °C for 2 h.

2. Morphology and X-ray diffraction patterns of the N-doped TiO$_2$

SEM was used to observe the morphology of the N-doped TiO$_2$. As shown in Fig. S1, the morphologies of the undoped TiO$_2$ (Fig. S1A) and N-doped TiO$_2$ (Fig. S1B) were both spheres except the difference of the sizes. The diameters of the undoped TiO$_2$ spheres were from 200 to 500 nm, while the N-doped TiO$_2$ showed an aggressive performance and larger diameters around 1 μm. From the XRD spectra of Fig. S1C, there were two similar diffraction curves of undoped TiO$_2$ and N-doped TiO$_2$, which matched well with the diffraction peaks of the anatase TiO$_2$ (JCPDS 21-1272) without any detectable dopant-related peaks. However, the enlarge image of the peaks showed a slight shift of the XRD patterns, indicating an obvious moving from 25.6° to lower angle 25.4°. This phenomenon confirmed that the N atom replaced the O atom in the lattice of TiO$_2$, because the larger atomic radius of N led to the increase
of cell parameters, which was important for the improvement of visible light absorption.

![SEM images of TiO$_2$ and N-doped TiO$_2$](image)

**Fig. S1.** SEM images of the TiO$_2$ (A) and N-doped TiO$_2$ (B); (C) XRD patterns of TiO$_2$ and N-doped TiO$_2$. The insert was the enlarge image of the main peaks.

3. **The photocurrent responses for the fabrication process of the biosensor**

The photocurrent responses of the different states in the fabrication process of the biosensor were presented as Fig. S2. The pure FTO (F doped SnO$_2$) glass had no obvious photoelectrical signal under light illumination. With the coating of N-doped TiO$_2$ layer, the electrode showed a reasonable photocurrent around 180 nA. After that, the QT1 chain was immobilized onto the film by APTES and GA, and the photocurrent was slight decreased by the thin layer of poor conductive DNA bases. At last, the fabricated PEC biosensor could detect Hg$^{2+}$ with a substantial decline in photocurrent.
**Fig. S2.** Photocurrent responses of the FTO, the N-doped TiO$_2$, the QT1 immobilized N-doped TiO$_2$ electrode and the QT1 immobilized N-doped TiO$_2$ electrode adding 6 µM Hg$^{2+}$.

4. The detection of the real samples.

The detection of real samples could extend the application of our PEC biosensor in the environmental analysis. First, the concentrations of Hg$^{2+}$ in the river water were detected by ICP-AES, and no Hg$^{2+}$ was found in the samples. So we applied the standard addition method for the study. The river water samples were centrifuged and the solution was taken for the test. The results were listed in Table S1, indicating a reasonable recovery of Hg$^{2+}$.

**Table S1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hg$^{2+}$ added (µM)</th>
<th>Hg$^{2+}$ found (µM)</th>
<th>Recovery (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.661</td>
<td>83.0</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>4.003</td>
<td>100.1</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>4.877</td>
<td>97.5</td>
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