Supporting information

Self-enhanced photocathodic matrix based on poly-dopamine sensitized TiO$_2$ mesocrystals for mycotoxin detection assisted by a dual amplificatory nanotag

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**Instruments**

Scanning electron microscopy (SEM) was employed for RTM observation on Hitachi S-4800 microscopy. Transmission electron microscopy (TEM, FEI F20 S-TWIN) and high-resolution TEM (HRTEM) analysis were performed on a JEOL-2100 transmission electron microscope. Open circuit potential-time (OCP), amperometric I-t curves, and electrochemical impedance spectroscopy (EIS) were performed on a CHI 660 electrochemical workstation (Shanghai Chenhua Instrument Co., China) with a three-electrode cell. Ag/AgCl electrode (sat. KCl), a modified GCE (Φ=3 mm), and platinum wire were used as the reference, working and auxiliary electrode, respectively. The pH measurements were performed on a PHS-3C exact digital pH meter (Leici Co. Ltd., Shanghai, China). The excitation source of homogeneous light from xenon lamp (86 mW cm⁻², Beijing, China) was filtered by monochromator before using.

**Synthesis of RTM**

The RTM was synthesized through a simple one-step route. Typically, 0.5 g sodium dodecyl benzene sulfonate (SDBS) was dissolved in 25 mL of 2.2 M HNO₃ solution. After that, the solution was stirred for 15 minutes, and 0.5 mL titanium (IV) isopropoxide was added and maintained at 80 °C for 48 h under continuous stirring. Subsequently, the product was treated by centrifugation, washed with ultrapure water and ethanol for 4-5 times and dried at 60 °C overnight. The final products were achieved by calcining the above sample at 400 °C for 1 h in air to remove the residual organics. The obtained production was dispersed in ultrapure water to prepare 10 mg/mL RTM suspension for future use.

**Synthesis of KIT-6 silica**

High quality mesoporous cubic silica material was synthesized using tetraethoxysilane (TEOS) as the silica source and Pluronic P123 (EO₂₀PO₇₀EO₂₀) as the structure-directing agent. In a typical synthesis, P123 (1.2 mmol, 7.2 g), hydrochloric acid (37%, 13.9 g) and n-butanol (94.5 mmol, 7.0 g) were fed into a 500 mL round-bottom flask and stirred for 1 h. The temperature was kept at 38°C in
synthesis process. TEOS (7.0 g) was added, and the solution was stirred for another 24 h. The solution was transferred to a Teflon-lined stainless steel autoclave at 100°C for 24 h. The mixture liquid was washed with deionized water and filtered several times after the hydrothermal treatment. The sample was dried at 100°C and calcined at 550°C for 5 h to completely eliminate the template. The white mesoporous KIT-6 was obtained.

Nanocasting preparation of mesoporous 3D-Co$_3$O$_4$

Mesoporous Co$_3$O$_4$ was prepared using 3D porous KIT-6 as the hard template with ethanol as the dispersing agent. In a typical synthesis, 3.0 g KIT-6 molecular sieve were added to a Co(NO$_3$)$_2$·6H$_2$O ethanol solution (0.84 mol/L, 30 mL). The samples were evaporated to dryness at 80°C. The products were calcined at 200°C for 6 h. The above steps about casting and evaporating were repeated. Finally, the materials were calcined at 450°C for 6 h. The KIT-6 hard templates were removed using a 2 mol/L NaOH solution. Centrifugal separation was used to eliminate sodium silicate, and the samples were dried at 100°C. The obtained powder was 3D-Co$_3$O$_4$.

Preparation of peanut samples

The fresh peanut was purchased from a local market of agriculture products and ground finely with a laboratory mill. Subsequently, 6 g of sample was placed in a 50 mL centrifuge tube, and 18 mL of methanol/water (80:20, v/v) containing 4% NaCl was added to facilitate the sample to be extracted via vortex mixing. After centrifugation at 4000 rpm for 5 min, 1.2 mL of supernatant was transferred to a 3.0 mL tube and diluted with 1.8 mL of pure water. The resulting solution was used as blank sample for this analytical method.
Optimization conditions of the PEC biosensing platform

Fig. S1 The optimization of this platform of (A) RTM concentration and (B) incubation time of PDA (0.01M) towards the photocurrent density of GCE/RTM/PDA in PBS (pH 7.5). The insets in (A) and (B) were the corresponding line charts.

The modification amounts of RTM was an important factor in affecting the PEC biosensor, and the photocurrent signal of different concentrations of RTM was demonstrated in Fig. S1A. As exhibited, the photocurrent increased until 3 mg/mL RTM was dropped on the electrode surface and then decreased rapidly. It could be explained that more electrons were excited with RTM concentration increasing, causing the enhancement of the photocurrent density. However, the thicker RTM film would gather together, impeding the transfer of the electrons and the effective light harvest, leading to the photocurrent decreased with further increasing.

To optimize the amounts of PDA, different incubation times were explored to fabricate the GCE/RTM/PDA electrode. As illustrated in Fig. S1B, with the incubation time increasing, the more visible light was absorbed and more photo-generated electrons were driven to electrode surface due to that more PDA enhanced the stability of the PEC biosensor. Nevertheless, a deterioration of the photocurrent density was obtained with a further enhancement of the incubation time, attributing to the thicker PDA film would impede the transfer of the electrons from the electrode to the outside layer, leading to the photocurrent responses descended. For the sake of a significant photocurrent signal and higher sensitivity, 30 min was chosen as the optimized time for the signal recording in the following experiments.
Optimization of Detection Conditions

Fig. S2 The optimization of the experimental conditions of (A) anti-ZEN, (B) ZEN incubation time, (C) pH value and (D) applied potential.

In this sandwich-like assay, incubation time of anti-ZEN and ZEN greatly affected the sensitivity of the fabricated sensor and optimization results were shown in Fig. S2A and Fig. S2B. The photocurrent response on the PEC biosensor declined upon the increasing immersion time in 3 mg/mL anti-ZEN from 10 min to 30 min, and then the photoresponse remained stable. Therefore, considering the optimal analytical performance, the incubation time of 30 min was selected in the future study. Besides, the recognize time between anti-ZEN and ZEN also influence the sensitivity of the sensor. As demonstrated in Fig. S2B, the photocurrent density reached nearly a plateau until 30 min, indicating that abundant ZEN couldn’t be absorbed in the electrode. The pH value and applied potential were important factors relevant to the photo-current response. As shown in Fig. S2C, the sensors were tested in a series of PBS with pH ranging from 6.5-8.5, the maximum photocurrent response appeared at pH of 7.5. Therefore, in order to ensure the large current density, pH 7.5 PBS was selected in following measurements. The applied potential was another key
parameter that could influence the overall PEC signal, and it was also supposed to be optimized. With an increase of potential from 0 to -0.4 V, the photocurrent gently improved (Fig. S2D) and the photocurrent at -0.4 V shows the maximal response for the PEC detection of PSA. Owing to the low applied potential was beneficial to the elimination of interference from other reductive species that coexisted in the real samples. Therefore, -0.1V was selected as the applied potential for the determination of ZEN, and this bias voltage also satisfied the detection requirement.
**Fig. S3.** The photocurrent response of GCE/RTM/PDA/Ab$_2$/ZEN (a) in PBS (pH 7.5) as well as the GCE/RTM/PDA/Ab$_2$/ZEN/Ab$_2$@OMCO in PBS (pH 7.5) without (b) and with (c) deaerated by pure nitrogen for 15 min.

As exhibited in Figure S3, the GCE/RTM/PDA/Ab$_2$/ZEN/Ab$_2$@OMCO in air-saturated solution (b) exhibited larger photocurrent than that in nitrogen-saturated solution (c), implying the positive effect of dissolved oxygen and the production of cathode photocurrent in this PEC process. Compared to curve a, curve b showed lower photocurrent owing to the steric hindrance effects of Ab$_2$@OMCO. From this experiment, we found that the steric hindrance of Ab$_2$@OMCO could hinder the oxygen reacting and impede the electron transfer between electrode and electrolyte.
**Table S1** Comparison with various methods of the ZEN detection

<table>
<thead>
<tr>
<th>Methods</th>
<th>Linear Range (ng/mL)</th>
<th>LOD (ng/mL)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Surface-enhanced Raman scattering</td>
<td>10^{-3}-1.0</td>
<td>10^{-3}</td>
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<tr>
<td>Chromatographic assay</td>
<td>0.125-10</td>
<td>0.0625</td>
<td>5</td>
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<tr>
<td>Fluorescence (FL)</td>
<td>0.019-0.422</td>
<td>7×10^{-3}</td>
<td>6</td>
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<tr>
<td>Electrochemical (EC)</td>
<td>0.005 - 15</td>
<td>1.7×10^{-3}</td>
<td>7</td>
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<tr>
<td>PEC</td>
<td>10^{-6}-20</td>
<td>3.3×10^{-7}</td>
<td>This Work</td>
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Table S2 Recovery measurements of ZEN in peanuts (n=5) \(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZEN (ng/mL)</th>
<th>Added ZEN (ng/mL)</th>
<th>Measured ZEN (ng/mL)</th>
<th>Recovery (%)</th>
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<tr>
<td></td>
<td>1.0×10(^{-4})</td>
<td>1.043×10(^{-4})</td>
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<td>Peanuts</td>
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<td></td>
<td>1.0×10(^{-2})</td>
<td>1.021×10(^{-2})</td>
<td>102.0</td>
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</table>
References


