Formaldehyde sensing based on the catalytic reaction of
$\beta$-HgS nanocrystals

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**Fig. S1** TEM images of $\alpha$ (a)- and $\beta$ (b)-HgS nanocrystals.

**Fig. S2** Typical photographs of TMB solution in the irradiation of room light (a), and photographs of OPD solution illuminated by 365 nm UV lamp in dark (b) in the presence of a series of metal sulfide nanomaterials. Experimental conditions: (a) $[\text{TMB}] = 0.5$ mM; metal sulfide nanomaterials concentration was set to be 0.333 mg·mL$^{-1}$; reaction temperature of 37 $^\circ$C; reaction time of 30 min. (b) $[\text{OPD}] = 0.25$ mM; metal sulfide nanomaterials was set to be 0.125 mg·mL$^{-1}$; reaction temperature of 65 $^\circ$C; reaction time of 60 min.
Fig. S3 The comparison of TMB-β-HgS nanocrystals solution in the presence (1) and absence (2) of dissolved oxygen, in the absence of room light (3). Experimental condition: [TMB] = 0.5 mM; β-HgS nanocrystals concentration was set to be 0.333 mg·mL⁻¹; reaction temperature of 37 °C; 0.2 M HOAc-NaOAc buffer solution of pH 4.2; reaction time of 30 min.

Fig. S4 The comparisons of OPD-β-HgS nanocrystals solution in the presence (1) and absence (2) of dissolved oxygen, in the absence of room light (3). Experimental conditions: [OPD] =0.25 mM; β-HgS nanocrystals concentration was set to be 0.125 mg·mL⁻¹; reaction temperature of 65 °C; 50 mM Tris-HCl buffer solution of pH 7.4; reaction time of 60 min.
**Fig. S5** CV curves of $\alpha$- (black line) and $\beta$- (red line) HgS nanocrystals in N$_2$-saturated 50 mM Tris-HCl solution of pH 7.4. Scanning rate was 30 mV. s$^{-1}$.

**Fig. S6** CV curve of OPD in N$_2$-saturated 50 mM Tris-HCl solution of pH 7.4. Scanning rate was 30 mV. s$^{-1}$. 
**Fig. S7** pH-dependent oxidase-like activity of β-HgS nanocrystals towards TMB. Experimental conditions: [TMB] = 0.5 mM; β-HgS nanocrystals concentration was set to be 0.333 mg·mL⁻¹; reaction temperature of 37 °C; reaction time of 30 min.

**Fig. S8** Temperature-dependent oxidase-like activity of β-HgS nanocrystals towards TMB. Experimental conditions: [TMB] = 0.5 mM; β-HgS nanocrystals concentration was set to be 0.333 mg·mL⁻¹; 0.2 M NaOAc-HOAc buffer solution of pH 4.2; reaction time of 30 min.
The relationship between Abs @ 652 nm and TMB concentration. Experimental conditions: β-HgS nanocrystals concentration was set to be 0.333 mg·mL\(^{-1}\); reaction temperature of 37°C; 0.2 M NaOAc-HOAc buffer solution of pH 4.2; reaction time of 30 min.

The relationship between Abs @ 652 nm and β-HgS nanocrystals concentration. Experimental conditions: [TMB] = 0.5 mM; reaction temperature of 37 °C; 0.1 M NaOAc-HOAc buffer solution of pH 4.2; reaction time of 30 min.
Fig. S11 Steady-state kinetic analysis of the oxidation reaction of TMB catalyzed by β-HgS nanocrystals on the basis of the Michaelis–Menten model.

**Table S1** Kinetic parameters of the β-HgS nanocrystals –TMB system

<table>
<thead>
<tr>
<th><a href="mg%C2%B7mL%E2%81%BB%C2%B9">E</a>ᵃ</th>
<th>(K_m) (mM)</th>
<th>(V_{\text{max}}) (M min⁻¹)</th>
<th>(K_{\text{cat}}) (min⁻¹)</th>
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<tr>
<td>0.333</td>
<td>0.146</td>
<td>(1.132 \times 10^{-6})</td>
<td>(7.92 \times 10^{-4})</td>
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</table>

ᵃ β-HgS nanocrystals concentration of 0.333 mg·mL⁻¹ was equalled to be \(1.43 \times 10^{-3}\) M, referred to Hg molar concentration.
Fig. S12 $^1$H NMR spectrum (500 MHz) of purified the oxidation product in DMSO-$d_6$ of OPD catalyzed by $\beta$-HgS nanocrystals. The marked "*" peaks are unknown peaks.
Fig. S13 The ESI-MS result of the extracted solution of the $\beta$-HgS nanocrystals- TMB catalytic reaction system by chloroform.
**Fig. S14** The ESI-MS result of reaction product of OPD and formaldehyde.

**Table S2** Recovery experiments of formaldehyde spiked in sleeve-fish and Chinese cabbage samples*.

<table>
<thead>
<tr>
<th></th>
<th>Sleeve-fish sample</th>
<th></th>
<th></th>
<th>Chinese cabbage sample</th>
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</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Spiked/×10⁻⁵ M</td>
<td>Measured/×10⁻⁵ M</td>
<td>Recoveries/%</td>
<td>No.</td>
<td>Spiked/×10⁻⁵ M</td>
<td>Measured/×10⁻⁵ M</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>-0.26 ± 0.07</td>
<td></td>
<td>1</td>
<td>0</td>
<td>0.23 ± 0.14</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>1.10 ± 0.19</td>
<td>113.4</td>
<td>2</td>
<td>1.2</td>
<td>1.32 ± 0.18</td>
</tr>
<tr>
<td>3</td>
<td>2.4</td>
<td>2.35 ± 0.09</td>
<td>108.6</td>
<td>3</td>
<td>2.4</td>
<td>2.48 ± 0.20</td>
</tr>
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</table>

* The errors were obtained by measuring three parallel samples.