Supplementary Information for

A new dual-emission fluorescence sensor based on carbon nanodots and gold nanoclusters for the detection of melamine

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Fig. S1 (a) TEM images of GSH@Au NCs. The insets are HRTEM image (top) and size distribution (bottom) of GSH@Au NCs. (b) The UV-vis (black), fluorescence emission (red), and excitation (blue) spectra of GSH@Au NCs. The inset is the photograph of GSH@Au NCs under UV light. (c) Emission spectra of GSH@Au NCs with different excitation wavelengths from 350 to 425 nm.

Fig. S2 XPS spectrum of GSH@AuNCs (a) and the corresponding spectrum of Au4f\textsubscript{7/2} and Au4f\textsubscript{5/2} (b).
**Fig. S3** (a) TEM images of CNDs. The insets are HRTEM image (top) and size distribution (bottom) of CNDs. (b) The UV-vis (black), fluorescence emission (red), and excitation (blue) spectra of CNDs. The inset is the photograph of CNDs under UV light. (c) Emission spectra of CNDs with different excitation wavelengths from 300 to 400 nm; inset is amplified emission spectra of CNDs.

**Fig. S4** XPS spectrum (a), C 1s (b), and O 1s (c) spectra of CNDs.
Fig. S5 FT-IR spectra of GSH@Au NCs (a) and CNDs (b).

Fig. S6 Fluorescence spectra (a) and quenching efficiency (b) of CNDs/GSH@Au NCs in the presence of different concentrations of Hg$^{2+}$. The corresponding photos of the CNDs/GSH@Au NCs (c) and GSH@Au NCs (d) with addition of different concentrations of Hg$^{2+}$ (from left to right: 0, 5, 10, 20, 40, 60 and 80 μM) under a 365 nm UV lamp.
**Fig. S7** The influence of Hg$^{2+}$ on the detection of melamine. The concentration of melamine is 30 μM.

**Fig. S8** Optimization of reaction conditions for detecting melamine based on CNDs/GSH@Au NCs–Hg$^{2+}$ system (a, probe concentration; b, pH value; c, reaction time; d, temperature). The final concentration of Hg$^{2+}$ and melamine are 25 and 30 μM, respectively.
**Fig. S9** Effect of addition order on the fluorescence response to melamine. Order 1: CNDs/GSH@Au NCs are incubated with Hg$^{2+}$ for 20 min without addition of melamine; order 2: CNDs/GSH@Au NCs are pre-incubated with Hg$^{2+}$ for 20 min and then melamine is added; order 3: Hg$^{2+}$, melamine and CNDs/GSH@Au NCs are added together; order 4: pre-incubation of Hg$^{2+}$ with melamine for 1 h and then CNDs/GSH@Au NCs are added. The concentration of Hg$^{2+}$ and melamine are 25 and 30 μM, respectively. Blank is the fluorescence of CNDs/GSH@Au NCs without Hg$^{2+}$ and melamine.

**Fig. S10** Fluorescence spectra of CNDs/GSH@Au NCs in the presence of low concentration of melamine (0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 μM) (a), and corresponding linear range from 0.1 to 5 μM of melamine (b).
**Fig. S11** Fluorescence spectra of GSH@Au NCs–Hg$^{2+}$ system in the presence of different concentrations of melamine (a) and corresponding linear range from 5 to 30 μM of melamine (b). The concentrations of melamine are 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90 and 100 μM, respectively. $I_0$ and $I$ are the maximum fluorescence intensities of GSH@Au NCs–Hg$^{2+}$ system in the absence and presence of melamine, respectively.
**Fig. S12** Fluorescence responses of the ratiometric probe towards various metal ions (a), and the corresponding photographs of CNDs/GSH@Au NCs-metal ions in absence (b) and presence of melamine (c) under UV light. (30 μM melamine; 25 μM Hg^{2+}; 3 mM for Cu^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Cr^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}; 300 μM for Al^{3+}, Pb^{2+}).
**Fig. S13** (a) UV-vis spectra of CNDs/GSH@Au NCs in absence (line a) and presence of melamine (line b), Hg^{2+} (line c), and both Hg^{2+} and melamine (line d); (b) UV-vis spectra of Hg^{2+} (straight line), melamine (dot line), and melamine-Hg^{2+} complex (dash line).

**Fig. S14** Fluorescence lifetimes of free CNDs/GSH@Au NCs (straight line) and CNDs/GSH@Au NCs in the presence of Hg^{2+} (dash dot line), and both Hg^{2+} and melamine (dash line).
<table>
<thead>
<tr>
<th>Methods</th>
<th>Probes</th>
<th>Linear range ($\mu$M)</th>
<th>LOD ($\mu$M)</th>
<th>References</th>
</tr>
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<tr>
<td>GC/MS</td>
<td>-</td>
<td>0.396-1.59</td>
<td>0.0793</td>
<td>1</td>
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<tr>
<td>GC-MS</td>
<td>-</td>
<td>0.396-0.8</td>
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<td>Molecular imprinting</td>
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<td>0.1-3.1</td>
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<td>Colorimetric</td>
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<td>Colorimetry</td>
<td>Fe$_3$O$_4$ nanoparticles–H$_2$O$_2$–ABTS</td>
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<td>5</td>
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<td>Fluorescence</td>
<td>DNA–Ag nanoclusters</td>
<td>0.2-4.0</td>
<td>0.1</td>
<td>6</td>
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<tr>
<td>Fluorescence</td>
<td>Au nanoclusters</td>
<td>0.5-10</td>
<td>0.15</td>
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<tr>
<td>Fluorescence</td>
<td>polymer-capped CdTe quantum dots</td>
<td>2.0-35</td>
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<tr>
<td>Fluorescence</td>
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<td>Fluorescence</td>
<td>CNDs/GSH@Au NCs – Hg$^{2+}$ system</td>
<td>0.1-30</td>
<td>0.0293</td>
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</table>
Table S2 Detection of melamine in raw milk, infant formula and cat food based on CNDs/GSH@Au NCs–Hg^{2+} system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of melamine (μM)</th>
<th>Recovery (%)</th>
<th>RSD (n=3, %)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Amount added</td>
<td>Amount found</td>
<td></td>
</tr>
<tr>
<td>Raw milk 1</td>
<td>0</td>
<td>not found</td>
<td>-</td>
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<tr>
<td>Raw milk 2</td>
<td>5</td>
<td>4.91 ± 0.01</td>
<td>98.2</td>
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<tr>
<td>Raw milk 3</td>
<td>15</td>
<td>15.02 ± 0.01</td>
<td>100.1</td>
</tr>
<tr>
<td>Raw milk 4</td>
<td>30</td>
<td>29.34 ± 0.02</td>
<td>98.47</td>
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<tr>
<td>Infant formula 1</td>
<td>0</td>
<td>not found</td>
<td>-</td>
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<tr>
<td>Infant formula 2</td>
<td>5</td>
<td>5.09 ± 0.006</td>
<td>101.8</td>
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<tr>
<td>Infant formula 3</td>
<td>15</td>
<td>14.88 ± 0.01</td>
<td>99.2</td>
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<td>Infant formula 4</td>
<td>30</td>
<td>29.92 ± 0.03</td>
<td>99.7</td>
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<tr>
<td>Cat food 1</td>
<td>0</td>
<td>not found</td>
<td>-</td>
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<tr>
<td>Cat food 2</td>
<td>5</td>
<td>4.93 ± 0.003</td>
<td>98.6</td>
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<tr>
<td>Cat food 3</td>
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<td>14.82 ± 0.01</td>
<td>98.8</td>
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<td>Cat food 4</td>
<td>30</td>
<td>29.47 ± 0.007</td>
<td>98.2</td>
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</table>

References


