Copper Ion-Induced Fluorescence Band Shift of CdTe Quantum Dots: A Highly Specific Strategy for Visual Detection of Cu\textsuperscript{2+} with a Portable UV Lamp

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1. Reagents and instruments

Tellurium powder, cadmium chloride (CaCl\(_2\cdot2.5\)H\(_2\)O), sodium borohydride (NaBH\(_4\)), copper sulfate (CuSO\(_4\cdot5\)H\(_2\)O), sodium hydroxide and ascorbic acid were obtained from Sinopharm Chemical Reagent (Shanghai, China). Thioglycolic acid (TGA) was purchased from Sigma (USA). Real seawater samples were collected from Beidaihe (Qinghuangdao, China). All other reagents were used as received without further purification.

Amicon Ultra-2 Centrifugal Filter (10 KD) was purchased from Millipore. The thermostat metal bath used for controlling temperature was acquired from BIOER (Hangzhou, China). The fluorescence spectra of CdTe QDs were recorded on a Fluorolog 3-211 fluorescence spectrophotometer (Horiba Jobin-Yvon, France).

2. Synthesis and characterization of CdTe QDs

CdTe QDs stabilized by thioglycolic acid (TGA) were prepared according to the protocols described previously.\(^{S1,S2}\) Briefly, 0.0300 g of tellurium powder and 0.1080 g of sodium borohydride were dissolved in 12 mL ultrapure water deaerated by nitrogen in advance and incubated in ice-bath for about 8 hours under nitrogen atmosphere with magnetic stirring. Then sulfuric acid (22.5 mL, 1 M) was added dropwise into the above mixture to form H\(_2\)Te gas.

Simultaneously, 0.2808 g of CdCl\(_2\) and 120 \(\mu\)L of TGA were dissolved in 180 mL ultrapure water under stirring. Afterward, the pH of the solution was adjusted to 12 by addition of ~ 6 mL NaOH solution (1 M) dropwise. H\(_2\)Te gas was passed through such solution together with nitrogen as a carrier gas. At this stage, CdTe precursors were formed. Subsequently, by refluxing the reaction mixture at 110 °C for ~0.5 hour, the precursors were converted to CdTe QDs with the desirable green emission. To further enhance their fluorescence intensity, the as-prepared CdTe QDs stock solution was exposed to a fluorescent lamp for about 8 days. Finally, the CdTe QDs were purified with ultrafiltration tubes (10 KD, Millipore) to remove the excess reactants and then ready for use for the detection of Cu\(^{2+}\). The size and morphology of the as-synthesized CdTe QDs was characterized on a Tecnai G2 F20 transmission electron microscope, and the typical TEM images of the CdTe QDs were shown in Fig. S1.

Fig. S1. Typical TEM images of the synthesized CdTe QDs.
3. Standard experimental procedures for the detection of Cu²⁺

Typically, 20 μL of the as-synthesized CdTe QDs and 20 μL of ascorbic acid (1 mM) were mixed with different concentrations of Cu²⁺ ions, respectively. Afterward, the mixtures were diluted to 200 μL with ultrapure water and then immediately incubated at 60 ºC for 30 min. All fluorescence photos were taken with a Canon IXUS23OHS digital camera under the irradiation of a 365 nm UV light, and the corresponding fluorescence spectra of the QDs were measured on a Fluorolog 3-211 fluorescence spectrophotometer with the excitation wavelength of 365 nm.

4. XPS results for the Cu²⁺-treated CdTe QDs

Fig. S2 shows the XPS spectra of Cu (2p) in the Cu²⁺-treated CdTe QDs. It is suggested that for Cu (2p), the binding energies of 933 and 952 eV can be ascribed to the Cu (2p3/2) and Cu (2p1/2). According to previous reports, the peaks in the spectra indicate the presence of solely Cu⁺ rather than Cu²⁺ ions.⁵³,⁵⁴

![Fig. S2. XPS spectra of Cu (2p) in the Cu²⁺-treated CdTe QDs.](image)

5. Comparison of different QDs-based assays for the detection of Cu²⁺

Table S1. Comparison of different QDs-based assays for the detection of Cu²⁺.

<table>
<thead>
<tr>
<th>Detection Strategy</th>
<th>Sensing materials</th>
<th>Detection limit</th>
<th>Dynamic range</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence quenching</td>
<td>Branched poly(ethyleneimine)-functionalized carbon QDs</td>
<td>6 nM</td>
<td>0.01~1.1 μM</td>
<td>S5</td>
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<tr>
<td>Fluorescence quenching</td>
<td>Fe₃O₄@C@CdTe core/shell microspheres</td>
<td>Not Available</td>
<td>1~10 μM</td>
<td>S6</td>
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<tr>
<td>Fluorescence quenching</td>
<td>CTAB-modified CdSe/ZnS QDs in the presence of thiosulfate</td>
<td>0.15 nM</td>
<td>0.03~0.6 μM</td>
<td>S4</td>
</tr>
<tr>
<td>Fluorescence quenching</td>
<td>L-cysteine-capped ZnS QDs</td>
<td>7.1 μM</td>
<td>20~260 μM</td>
<td>S7</td>
</tr>
<tr>
<td>Fluorescence quenching</td>
<td>Thioglycerol-capped CdS QDs</td>
<td>0.1 μM</td>
<td>1~1200 μM</td>
<td>S8</td>
</tr>
<tr>
<td>Fluorescence quenching</td>
<td>Type-II core/shell CdTe/CdSe QDs</td>
<td>20 nM</td>
<td>0.05–50 μM</td>
<td>S9</td>
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<tr>
<td>Fluorescence quenching</td>
<td>CdTe QDs coated by octamercaptopropyl polyhedral oligomeric silsesquioxane</td>
<td>2.3 nM</td>
<td>0.01–1 μM</td>
<td>S10</td>
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<tr>
<td>Fluorescence quenching</td>
<td>CdSe/CdS core/shell QDs modified with a polymer of MAO-mPEG</td>
<td>16 nM</td>
<td>0.01–0.5 μM</td>
<td>S11</td>
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<td>Fluorescence quenching</td>
<td>Size dependent quenching of CdTe QDs</td>
<td>0.02 μM</td>
<td>0.05–4 μM</td>
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<td>Fluorescence quenching</td>
<td>Mercaptopropionic acid (MPA)-capped CuInS$_2$ ternary QDs</td>
<td>0.037 μM</td>
<td>0.1–10 μM</td>
<td>S13</td>
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<td>Fluorescence quenching</td>
<td>Silica-coated ZnS:Mn QDs</td>
<td>7.3 nM</td>
<td>0.2–4 μM</td>
<td>S14</td>
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<tr>
<td>Fluorescence quenching</td>
<td>Gemini surfactant C$_{12-4-12}$-coated CdSe/ZnS QDs</td>
<td>1.1 μM</td>
<td>20–500 μM</td>
<td>S15</td>
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<td>Fluorescence quenching</td>
<td>16-mercaptophexadecanoic acid (16-MHA)-capped CdSe QDs</td>
<td>5 nM</td>
<td>0–100 μM</td>
<td>S16</td>
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<td>Fluorescence quenching</td>
<td>Peptide-coated CdS QDs</td>
<td>0.5 μM</td>
<td>0–2 μM</td>
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<td>Fluorescence quenching</td>
<td>Amino TPEA-modified carbon QDs</td>
<td>10 nM</td>
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<tr>
<td>Fluorescence band shift</td>
<td>Thioglycolic acid (TGA)-capped CdTe QDs</td>
<td>0.1 μM</td>
<td>0.1–20 μM</td>
<td>This work</td>
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</table>

6. The effect of coexisting quenching ions on the detection of Cu$^{2+}$

**Fig. S3.** Investigation of the effect of coexisting quenching ions on the detection of Cu$^{2+}$. (a) the results of the proposed sensing system treated with water samples spiked with individual metal ions (2 μM each), respectively; (b) the results of the proposed sensing system treated with water samples spiked with Cu$^{2+}$ or the mixture of Cu$^{2+}$ and a certain quenching ion (2 μM each), respectively. The samples in the photos (from left to the right): no spiked metal ions, Cu$^{2+}$, Pb$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Fe$^{3+}$ for images in Fig. S3a and no spiked metal ions, Cu$^{2+}$, Cu$^{2+}$/Pb$^{2+}$, Cu$^{2+}$/Co$^{2+}$, Cu$^{2+}$/Ni$^{2+}$ and Cu$^{2+}$/Fe$^{3+}$ for images in Fig. S3b.

**References:**


