Supporting Information

The facile one-step aqueous synthesis of near-infrared emitting Cu\(^{+}\) doped CdS quantum dots as fluorescence bioimaging probes with high quantum yield and low cytotoxicity

Ting-Ting Sun\(^a,1\), Ming Wu\(^b,c,1\), Xi-Wen He\(^a\), Wen-You Li\(^a,\ast\), Xi-Zeng Feng\(^b,\ast\)

\(^a\) College of Chemistry, Research Center for Analytical Sciences, State Key Laboratory of Medicinal Chemical Biology (Nankai University), Tianjin Key Laboratory of Molecular Recognition and Biosensing, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, 94 Weijin Road, Tianjin 300071, China. E-mail: wyli@nankai.edu.cn

\(^b\) State Key Laboratory of Medicinal Chemical Biology (Nankai University), College of Life Science, Nankai University, 94 Weijin Road, Tianjin 300071, China. E-mail: xzfeng@nankai.edu.cn

\(^c\) College of Life Sciences, Qufu Normal University, 57 Jingxuan West Road, Qufu 273165, China. E-mail: wumingqufu@163.com

\(^1\)These authors contributed equally to this work.

(CB = Conduction Band)

(CD = Conducting Band)

(VB = Valence Band)
Fig. S1 Scheme of the mechanism for Cu dopant emission.

Table S1 Previous Cu:CdS QDs properties.

<table>
<thead>
<tr>
<th>Sulfur source</th>
<th>Heating atmosphere</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Cu$^+$ or Cu$^{2+}$</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>QY%</th>
<th>Cell imaging</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td>N$_2$</td>
<td>aqueous</td>
<td>100</td>
<td>Cu$^+$</td>
<td>586</td>
<td>21.86</td>
<td>KB</td>
<td>1</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>Air</td>
<td>aqueous</td>
<td>100</td>
<td>Cu$^{2+}$</td>
<td>722</td>
<td>&lt;10</td>
<td>HeLa</td>
<td>2</td>
</tr>
<tr>
<td>Sulfur powder</td>
<td>Air</td>
<td>aqueous</td>
<td>100</td>
<td>Cu$^+$</td>
<td>680</td>
<td>20-30</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Dodecanethiol</td>
<td>Air</td>
<td>organic</td>
<td>200</td>
<td>Cu$^+$</td>
<td>707</td>
<td>15.8</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>H$_2$S gas</td>
<td>Air</td>
<td>organic</td>
<td>100</td>
<td>Cu$^{2+}$</td>
<td>680</td>
<td>-</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Sulfur powder</td>
<td>Air</td>
<td>organic</td>
<td>220</td>
<td>Cu$^{2+}$</td>
<td>710</td>
<td>65</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>Thiourea</td>
<td>Air</td>
<td>aqueous</td>
<td>95</td>
<td>Cu$^+$</td>
<td>466-612</td>
<td>20</td>
<td>-</td>
<td>25</td>
</tr>
</tbody>
</table>
SI. 1
The photoluminescence quantum yield (PLQY) of as-prepared Cu\(^{\text{+}}\):CdS QDs was counted by FLS 920 fluorescence spectrophotometer (Edinburgh, Britain) inherent calculator using the formula as:

\[
Q_{\text{Y,QDs}} = \int \frac{L_{\text{emission}}}{E_{\text{slovent}}} - \int E_{\text{sample}}
\]

where \( L_{\text{emission}} = \) Sample emission
\( E_{\text{slovent}} = \) Solvent excitation
\( E_{\text{sample}} = \) Sample excitation

The consequence was almost the same with the F-4500 fluorescence spectrophotometer (Hitachi, Japan) which was calculated by manual computation expression as follows:

\[
Q_{\text{Y,QDs}} = Q_{\text{Y,dye}} \times \frac{A_{\text{QDs}}}{A_{\text{dye}}} \times \left( \frac{n_{\text{QDs}}}{n_{\text{dye}}} \right)^2 \times \frac{1 - 10^{-D_{\text{dye}}}}{1 - 10^{-D_{\text{QDs}}}}
\]

where A was the integrated area, n was the refractive index, and D was the optical density of QDs and dye. Moreover, the integral method was accurate and simple comparing to the traditional process.

Fig. S2 Synthesis of water soluble Cu\(^{\text{+}}\) doped CdS quantum dots via one-step method.
Fig. S3 (a) The emission wavelength and PL intensity of the Cu\(^{2+}\):CdS QDs synthesized with different Cu dopants amount. (b) Influence of pH on the emission wavelength and PL intensity of the Cu\(^{2+}\):CdS QDs. (c) The emission wavelength and PL intensity of the Cu\(^{2+}\):CdS QDs with different concentration of L-Cys. (d) The emission wavelength and PL intensity of the Cu\(^{2+}\):CdS QDs with different ratios of Na\(_2\)S: Cd\(^{2+}\). (e) Influence of reflux time on the emission wavelength and PL intensity of the Cu\(^{2+}\):CdS QDs.
Fig. S4 XPS spectra of the Cu\(^{2+}\):CdS QDs.

Fig. S5 The PL spectra of the Cu\(^{2+}\):CdS QDs synthesized in the optimal conditions in N\(_2\) atmosphere after 0, 3, 6, 12, 48 hours.
Fig. S6 The effects of pH on the fluorescence properties of the as-prepared Cu\textsuperscript{2+}:CdS QDs.

Fig. S7 Fluorescence images of 3T3 cells. (a) Bright field image, (b) fluorescent image and (c) merged image cells incubated for 4 hours with 20 μg/mL Cu:CdS QDs synthesized at optimal conditions in air atmosphere.
Fig. S8 Effect of the d-dots prepared in air atmosphere on the viability of HeLa cells. The viability of HeLa cells in vitro measured by MTT assay. The HeLa cells were incubated for 1, 2, 4, 6 hours with different concentrations (0, 5, 10, 20, 50 μg/mL) of the Cu:CdS QDs prepared in air atmosphere.