Highly Sensitive Glutathione Assay and Intracellular Imaging with Functionalized Semiconductor Quantum Dots

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Fig. S1 Hydrodynamic diameter of QD@SiO$_2$ (A) and QD@SiO$_2$-MnO$_2$ (B) in water and DMEM. Zeta potential of QD@SiO$_2$ (C) and QD@SiO$_2$-MnO$_2$ (D). Inset: corresponding photograph of the particle solution.
Fig. S2 Energy-dispersive X-ray spectroscope (EDS) spectrum of QD@SiO$_2$-MnO$_2$. 
Supporting Information

Fig. S3 Fluorescence excitation (red line) and emission (black line) spectra of QD in toluene (A) and QD@SiO$_2$ in water (B).
Fig. S4 Calculation of relative photoluminescence quantum yields of QD and QD@SiO2 using standard quinine sulfate (QS). Corresponding linear equation: $y_{\text{QD}} = 671117.0619x - 1263.91762$, $R^2 = 0.9986$; $y_{\text{QD@SiO2}} = 321620.65124x - 3917.02263$, $R^2 = 0.9998$; $y_{\text{QS}} = 526928.40956x - 6530.24365$, $R^2 = 0.9938$. 
Fig. S5 UV-vis absorption spectra of aqueous solutions of KMnO$_4$ and MnO$_2$ nanosheets.
Supporting Information

**Fig. S6** UV-vis absorption spectra (A) and zeta potential (B) of QD@SiO$_2$ in the presence of different concentrations of KMnO$_4$ (0, 0.2, 0.4, 0.8, 1.2, 1.6 and 2 mM).
Fig. S7 Fluorescent quenching of the QD@SiO$_2$ by different preparation routes for the nanoprobes. (a) Pristine QD@SiO$_2$. (b) Nanoprobes prepared by physical mixing QD@SiO$_2$ and MnO$_2$. (c) Nanoprobes (QD@SiO$_2$-MnO$_2$) prepared by in-situ growth of MnO$_2$ on the surface of QD@SiO$_2$. The respective concentrations of QD and MnO$_2$ were the same.
Fig. S8 Fluorescence restoration ability of the QD@SiO$_2$-MnO$_2$ toward 500 µM GSH. The nanoprobes were prepared separately using 0.8 and 1.2 mM KMnO$_4$. 

Supporting Information
**Fig. S9** Dynamic reaction between QD@SiO₂-MnO₂ and 500 μM GSH followed by time-dependent fluorescence restoration (A), absorbance variation (B), and ICP-MS (C).
Fig. S10 TEM images of QD@SiO$_2$-MnO$_2$ in the absence (A) and presence (B) of 500 μM GSH.

Scale bar, 50 nm.
**Fig. S11** Confocal images of nanoprobeS or cells. First column: RAW264.7 cells without treatment. Second column: QD@SiO₂-MnO₂ incubated in DMEM without cells for 4 h. Third column: RAW264.7 cells incubated with QD@SiO₂ for 4 h. Scale bar, 7 μm.
**Fig. S12** Variation of intracellular GSH in RAW264.7 cells pretreated with NEM (10 μM) for 20 min. The GSH level was measured using Ellman’s reagents.
**Fig. S13** Intracellular imaging of GSH variation in MCF-7 cells with different treatments by confocal laser scanning microscopy. (A) Untreated cells in the absence of QD@SiO$_2$-MnO$_2$. (B) Cells incubated with QD@SiO$_2$-MnO$_2$. (C) Cells pretreated with NEM (10 μM) for 20 min followed by incubation with QD@SiO$_2$-MnO$_2$. (D) Cells pretreated with LPA (500 μM) for 24 h followed by incubation with QD@SiO$_2$-MnO$_2$. Scale bar, 12 μm.
Table S1 Comparison of different methods for fluorescent assay of GSH.

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<tr>
<th>Methods</th>
<th>Detection limit (μM)</th>
<th>Linear range (μM)</th>
<th>Ref.</th>
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<td>TCF-GSH</td>
<td>0.28</td>
<td>/</td>
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<td>AuNC</td>
<td>0.2</td>
<td>150-1200</td>
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<tr>
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<td>0.2</td>
<td>/</td>
<td>3</td>
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<td>Eu(DPA)₃@Lap-Tris/Cu²⁺ system</td>
<td>0.162</td>
<td>0.5-100</td>
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<td>/</td>
<td>5</td>
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<td>Iridium(III) complex</td>
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<td>1-200</td>
<td>6</td>
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<td>Au-MOF</td>
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<td>0-10000</td>
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<td>CQDs-AuNPs</td>
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<td>QD@SiO₂-MnO₂</td>
<td>0.01</td>
<td>0.01-120</td>
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References


