

Supporting Information

Silica-coated S²⁻-enriched Mn-doped ZnS Quantum Dots as a Photoluminescence Probe for Imaging Intracellular Zn²⁺ Ions

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Table S1. Fitted Decay Lifetime Components for Mn-doped ZnS QDs (QDs-1), SiO₂-S-Mn-ZnS QDs in the Absence (QDs-2) and Presence (QDs-3) of Zn²⁺ ^a

	τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	χ^2	τ_{av} (ms)
QDs-1	0.19±0.04	62.6±8.2	0.65±0.07	32.7±6.0	3.8±0.3	4.7±0.5	1.035	0.51±0.008
QDs-2	0.11±0.01	85.5±17.1	0.55±0.06	13.3±2.2	7.3±1.4	1.2±0.2	0.9816	0.25±0.006
QDs-3	0.13±0.02	72.7±9.4	0.65±0.06	23.5±2.4	4.6±0.4	3.8±0.4	0.9438	0.42±0.005

^a $F(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3}$
The experimental conditions as in Figure 3B.

Table S2. Average Abundance of Common Metal ions in Cells

Element	Concentration	Cells	References
K ⁺	1.2 × 10 ⁵ μM	Pancreatic β-Cells	S1
Na ⁺	2.7 × 10 ⁴ -3.3 × 10 ⁴ μM	70Z/3 cell	S2
Ca ²⁺	0.1-0.145 μM	Glial cell	S3
Mg ²⁺	500 μM	Red blood cell	S4
Cd ²⁺	0.16 ± 0.04 fg cell ⁻¹	HepG2 cells	S5
Cu ²⁺	< 10 ⁻¹² μM	cells	S6
Hg ²⁺	0.80 ± 0.13 fg cell ⁻¹	HepG2 cells	S5

Table S3. Comparison of the Linear Range and Detection Limits of Several Analytical Methods for Zn²⁺

References	Linear range	Detection limit	Detection method
Anal. Chem., 2010 , 82, 3108-3113	0.2-20 μM	40 nM	Ratiometric fluorescent probe
Anal. Chem., 2008 , 80, 8260-8268	5-500 μM	2400 nM	Azamacrocyclic activated QDs
Anal. Chim. Acta, 2011 , 687, 82-88	1.6-35 μM	1200 nM	CdTe QDs-based fluorescent probe
This Method	0.3-15 μM	80 nM	SiO ₂ -S-Mn-ZnS QDs-based fluorescent probe

Table S4. Comparison of the concentrations of Zn in the cell lysis for HepG2 cell, HepG2 cell after incubation with 100 μM Zn²⁺, the Zn-incubated HepG2 cell after imaging test and removing the QD probe

Samples	The concentration of Zn / μM
Sample 1: HepG2 cell	3.4
Sample 2: HepG2 cell after incubation with 100 μM Zn ²⁺	8.4
Sample 3: Sample 2 after imaging test and then removing the QD probe	5.3

Notes: a) The concentration of Zn in the cell lysis was determined by electrothermal atomic absorption spectrometric method (ETAAS); b) The procedures of the samples prepared for ETAAS were the same as for cell imaging; c) The HepG2 cells were harvested by trypsinization (0.5 mL each well). Then, a suspension of HepG2 cells (0.5 mL) was dispersed in 0.5 mL PBS buffer, centrifuged at 1000 rpm for 15 min, washed with PBS buffer three times and resuspended in 0.75 mL of ultrapure water. The HepG2 cells were disrupted by sonication for 30 min at 0 °C and the lysate was filtrated with Amicon Ultra-4 centrifugal Filter Units (10 kDa) by centrifugation at 8000 rpm for 10 min to remove the homogenate of cell debris (or QDs). The obtained HepG2 cell lysis was acidified with HNO₃ for ETAAS detection.

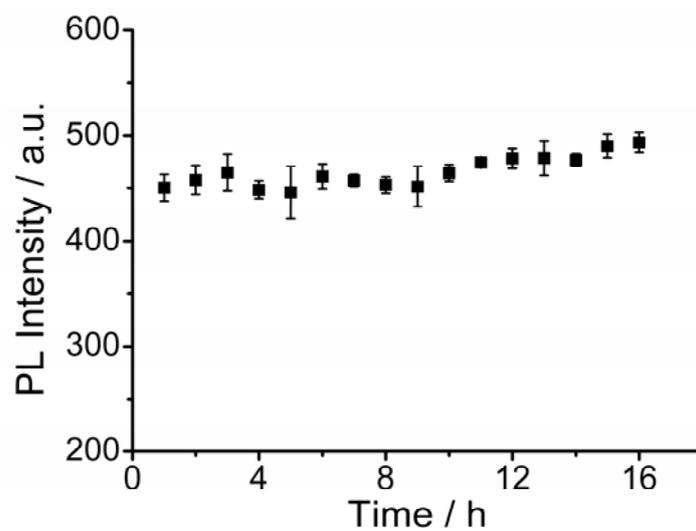


Figure S1. The stability of SiO₂-S-Mn-ZnS QDs (230 mg L⁻¹) in 10 mM Tris-HCl buffer at pH 7.5.

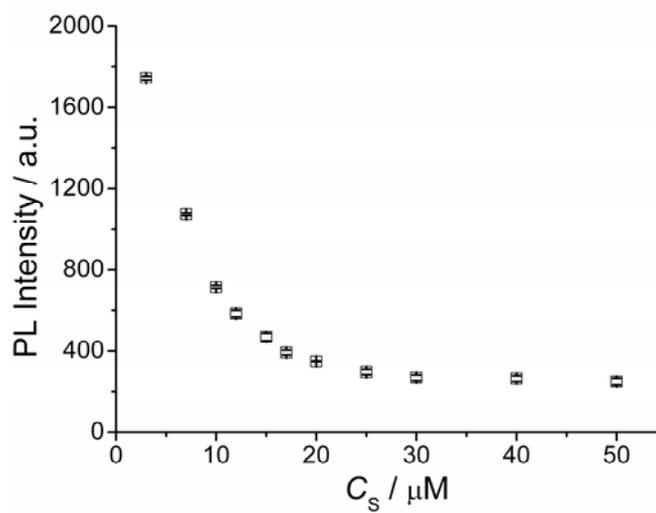


Figure S2. Effect of S²⁻ concentration on the photoluminescence intensity of the Mn-doped ZnS QDs (10 μg mL⁻¹).

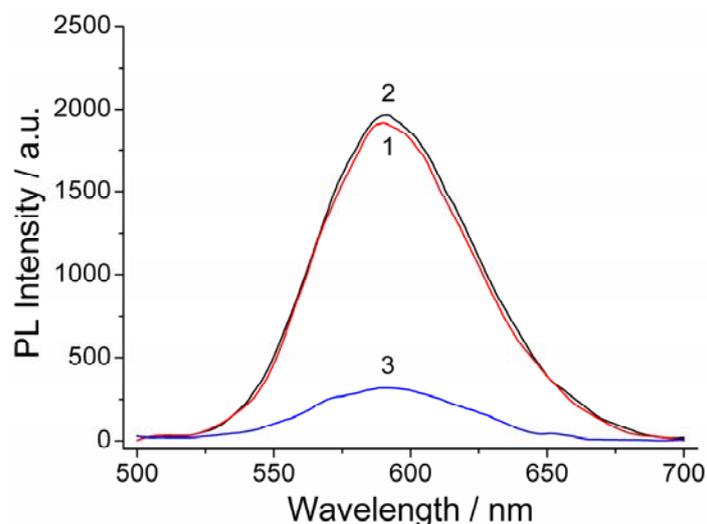


Figure S3. Photoluminescence intensity of the crude Mn-doped ZnS QDs (curve 1), silica coated-QDs without S^{2-} enrichment (curve 2), and SiO_2 -S-Mn-ZnS QDs (165 mg L^{-1} , curve 3) in 10 mM Tris-HCl buffer at pH 7.5.

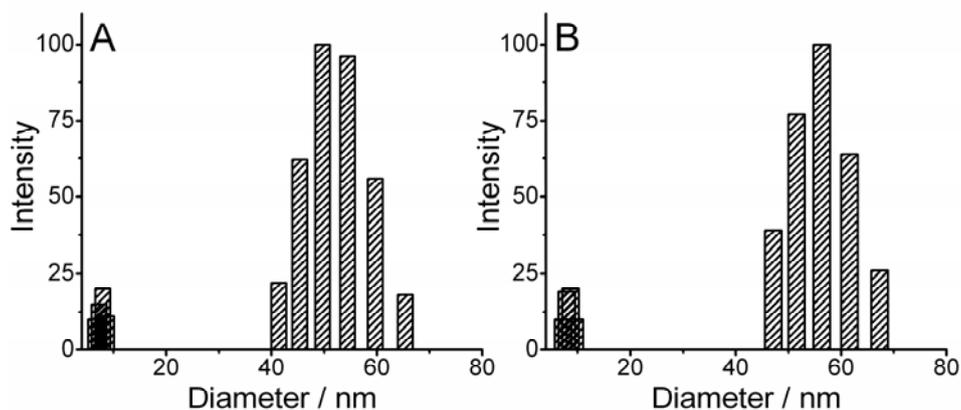


Figure S4. Distribution of the hydrodynamic diameter for (A) SiO_2 -S-Mn-ZnS QDs (1.15 g L^{-1}) and (B) SiO_2 -S-Mn-ZnS QDs added $200 \text{ }\mu\text{M Zn}^{2+}$ in 10 mM Tris-HCl buffer measured by dynamic laser scattering technique (DLS). The measurements were performed at $25 \text{ }^\circ\text{C}$ on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm. The average hydrodynamic diameter of SiO_2 -S-Mn-ZnS QDs and SiO_2 -S-Mn-ZnS QDs added Zn^{2+} is 40.7 nm and 43 nm, respectively.

Reference

- [S1] Arkhammar, P.; Nilsson, T.; Rorsman P.; Berggren, P.-O. *J. Biol. Chem.*, **1987**, *262*, 5448-5454.
- [S2] Stanton, T. H.; Maynard, M.; Bomszyk, K. *J. Biol. Chem.*, **1986**, *261*, 5699-5701.
- [S3] Kudo, Y.; Ozaki, K.; Miyakawa, A.; Amano, T.; Ogura, A. *Japan. J. Pharmacol*, **1986**, *41*, 345-351.
- [S4] Millart, H.; Durlach, V.; Durlach, J. *Magnesium Research*, **1995**, *8*, 65-76.
- [S5] Chen, B. B.; Heng, S. J.; Peng, H. Y.; Hu, B.; Yu, X.; Zhang, Z. L.; Pang, D. W.; Yue X.; Zhu, Y. *J. Anal. At. Spectrom.*, **2010**, *25*, 1931-1938.
- [S6] Rae, T. D.; Schmidt, P. J.; Pufahl, R. A.; Culotta, V. C.; O'Halloran, T. V. *Science*, **1999**, *284*, 805-808.