Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Toward Selective, Sensitive, and Discriminative Detection of Hg^{2+} and Cd^{2+} via pH-Modulated Surface Chemistry of Glutathione-Capped Gold Nanoclusters

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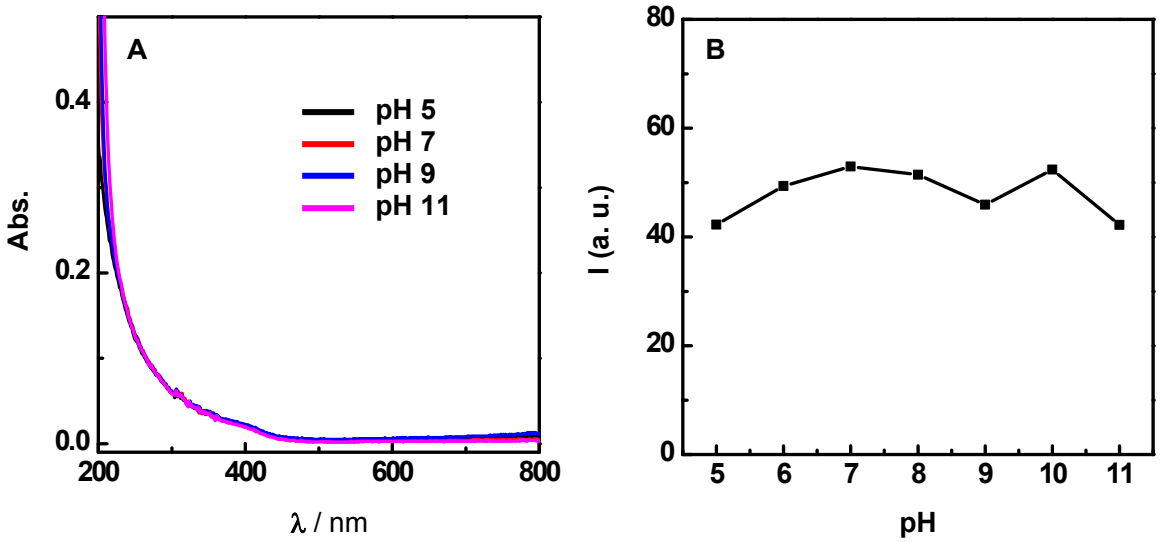


Figure S1. UV-vis absorption spectra (A) and the change of fluorescence intensity (B) of GSH-Au NCs under different pH values.

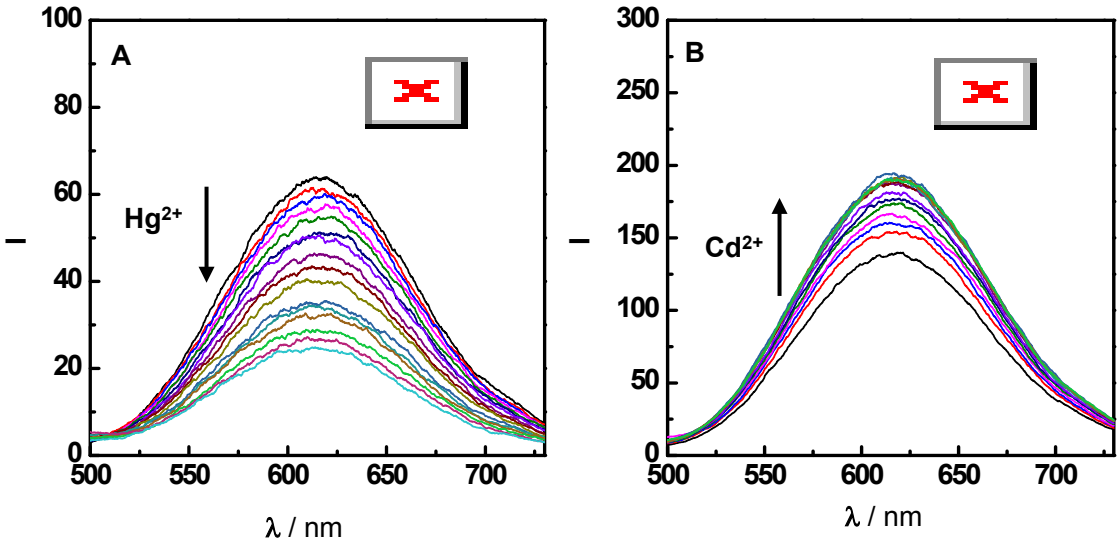


Figure S2. Fluorescence responses of GSH-Au NCs (A) at pH 5 in the presence of Hg^{2+} with the various concentrations from 0 to 1.65 μM and, (B) at pH 11 in the presence of Cd^{2+} with the various concentrations from 0 to 1.4 μM, respectively.

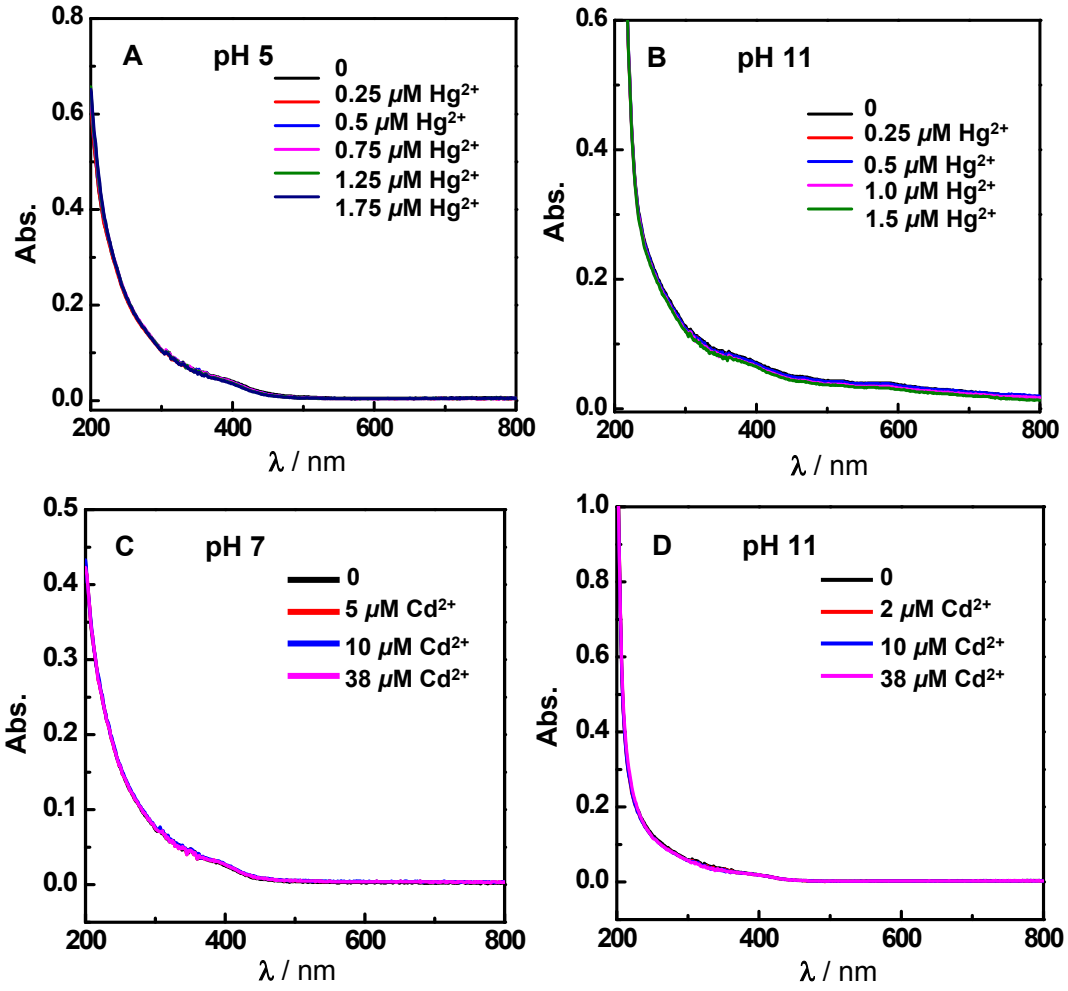


Figure S3. UV-vis absorption spectra of the GSH-Au NCs upon the addition of different concentrations of Hg^{2+} at pH 5 (A) and 11 (B), or Cd^{2+} at pH 7 (C) and 11 (D), respectively.

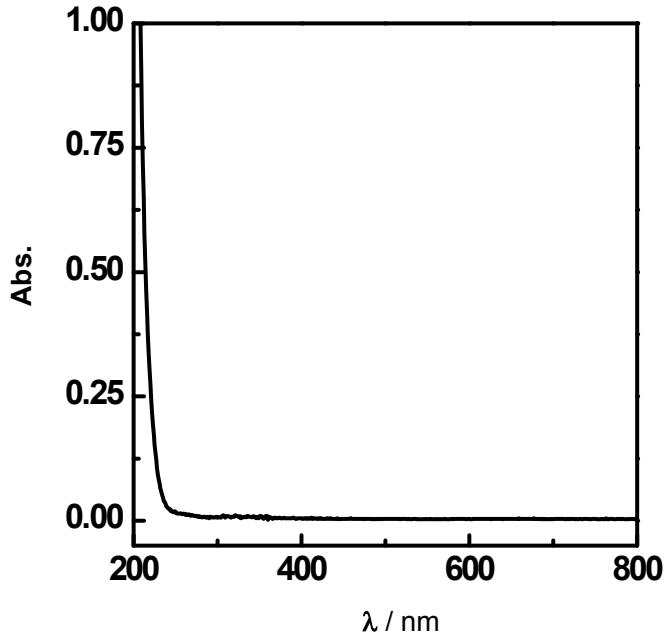


Figure S4. UV-vis absorption spectrum of GSH.

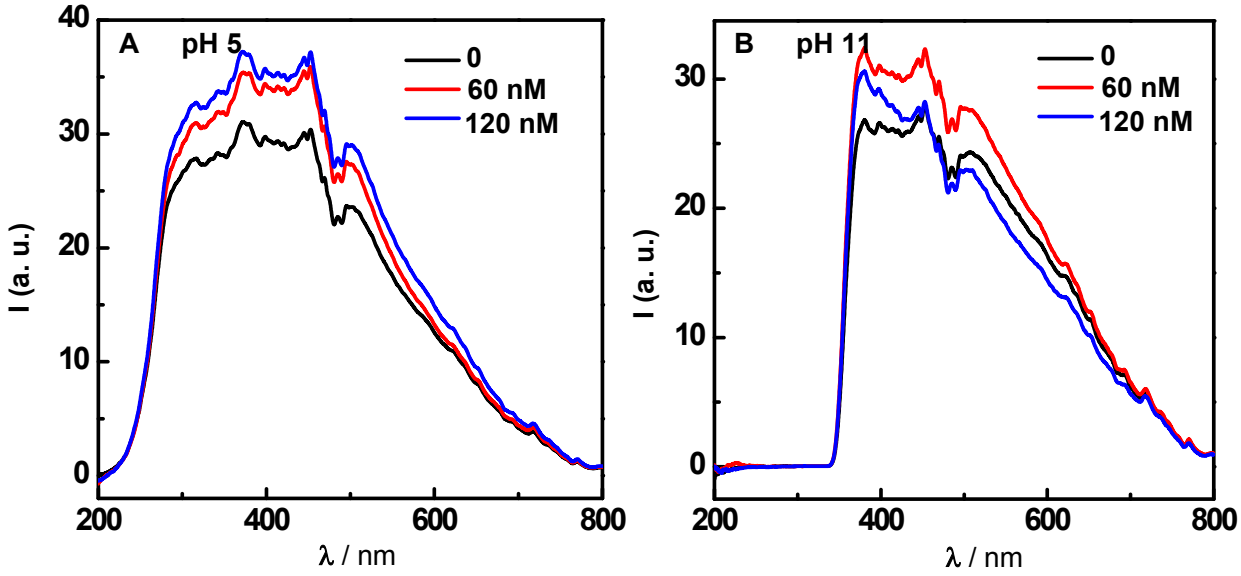


Figure S5. LS spectra of GSH-Au NCs at pH 5 (A) and 11 (B), respectively, upon the addition of different concentrations of Hg^{2+}.

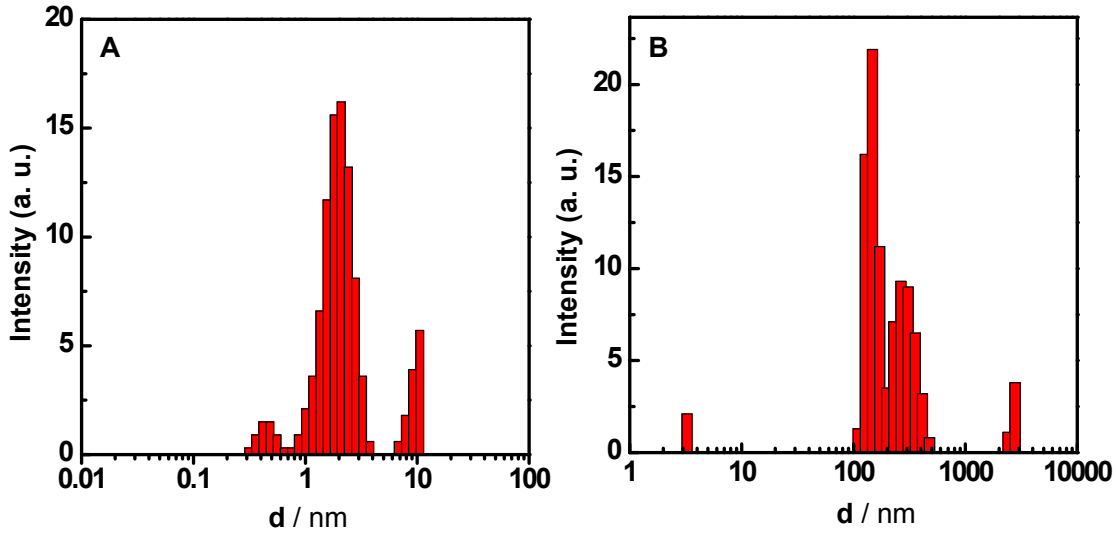


Figure S6. DLS measurements for GSH-Au NCs at pH 5 in the absence (A) and presence (B) of Hg^{2+}.

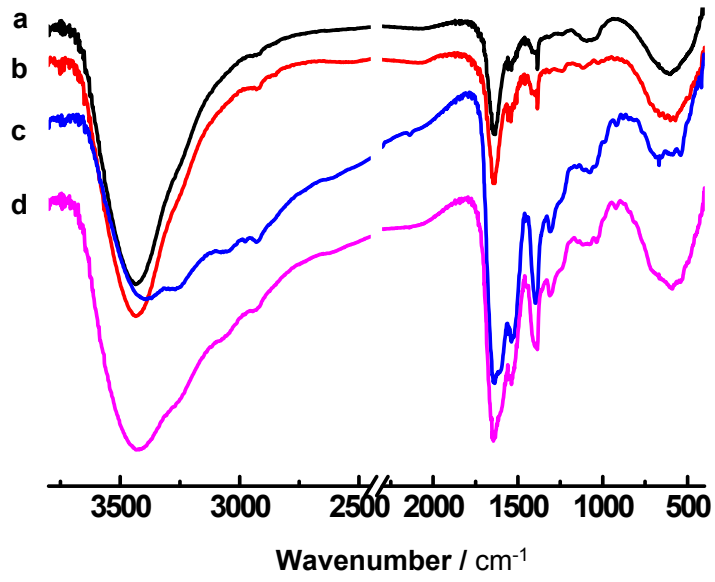


Figure S7. FT-IR spectra of GSH-Au NCs at pH 5 in the absence (a) and presence (b) of Hg^{2+}, and at pH 11 in the absence (c) and presence (d) of Hg^{2+}, respectively. Y axis is transmittance.

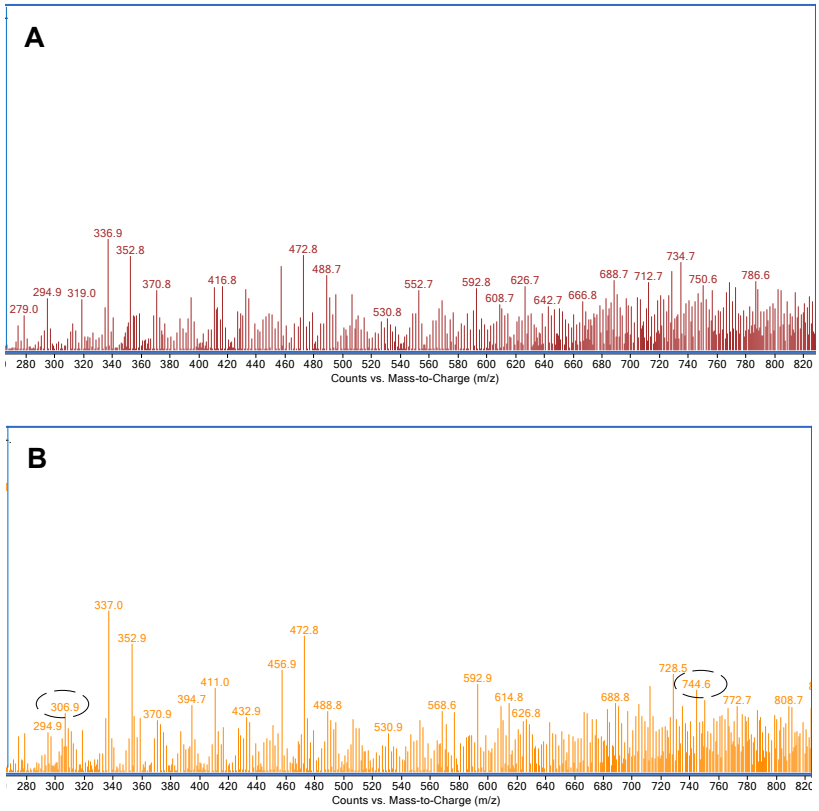


Figure S8. ESI-MS data for GSH-Au NCs at pH 5 in the absence (A) and presence (B) of Hg^{2+}, respectively.

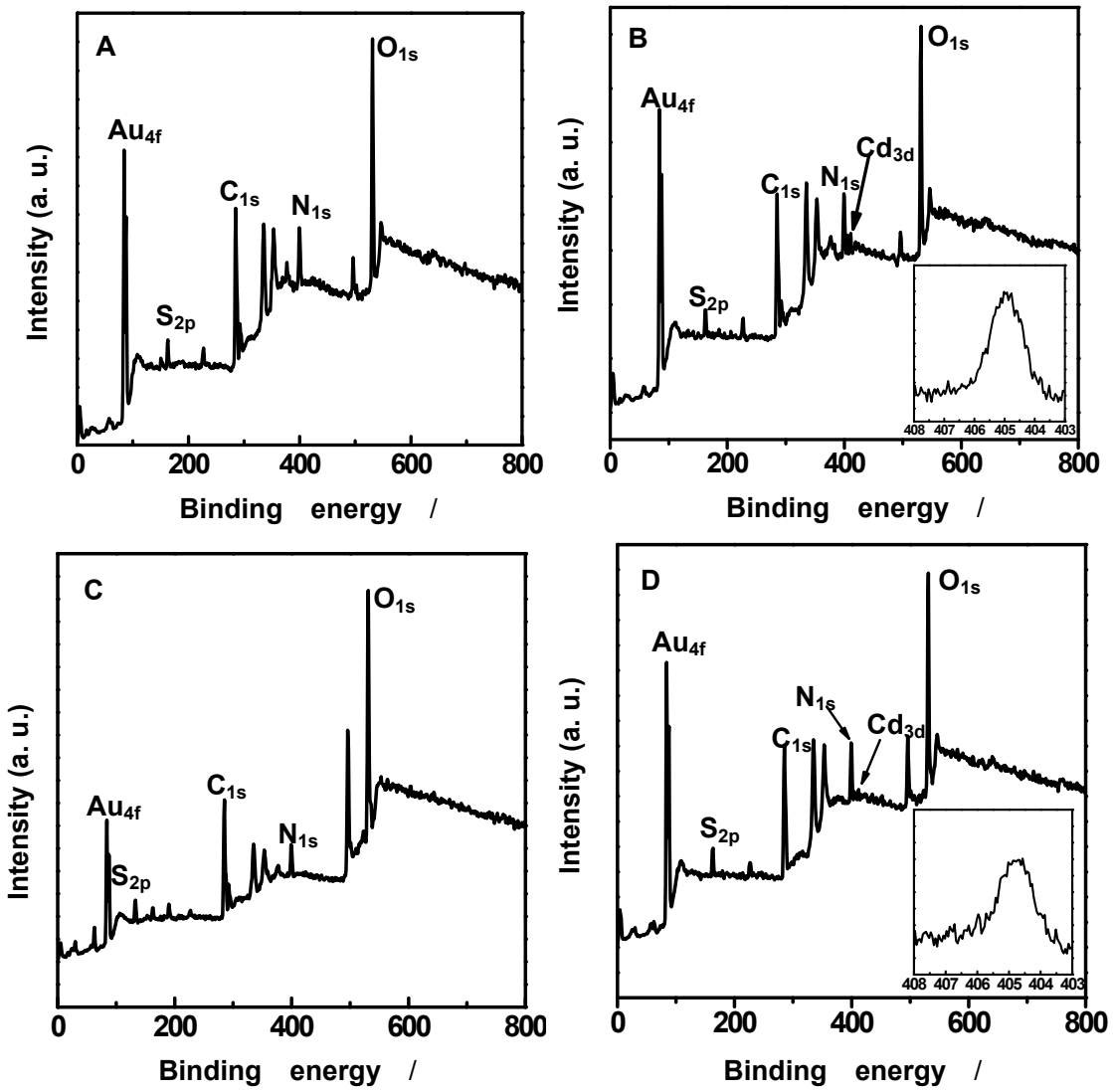


Figure S9. Full-scale XPS spectra of GSH-Au NCs at pH 7 (A, B) and 11 (C, D), respectively, in the absence (left panel) and presence (right panel) of Cd^{2+}. Inset in B and D: Cd 3d high-resolution XPS spectra.

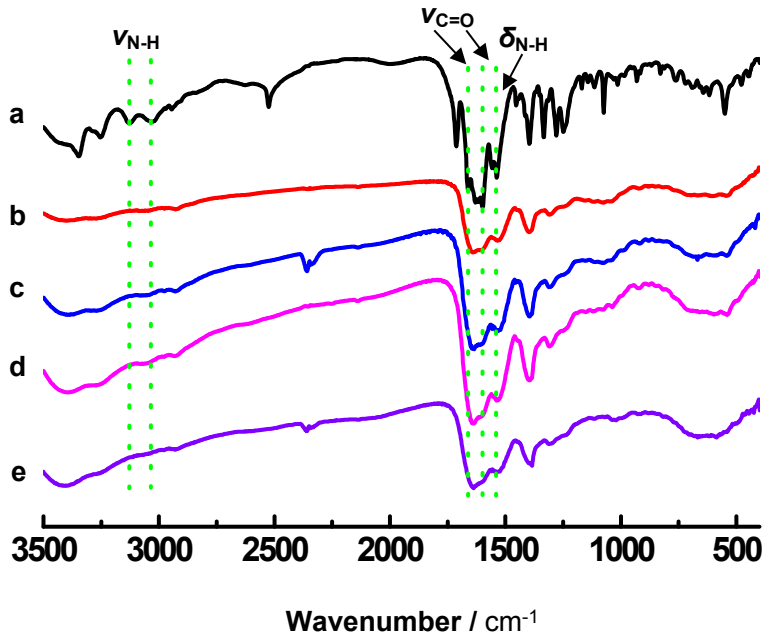


Figure S10. FT-IR spectra of (a) GSH, GSH-Au NCs at pH 7 in the absence (b) and presence (d) of Cd^{2+}, and at pH 11 in the absence (c) and presence (e) of Cd^{2+}, respectively. Y axis is transmittance.

For GSH, peaks at 3126 and 3028, 1660 and 1600, and 1538 cm^{-1} were assigned to the N−H (NH_3^+) stretching band (νN−H), the C=O stretching band of the carboxylic group (νC=O), and the strong absorption peak of N−H deformation of the amide bond (δN−H), respectively.[27,28] Under different pH values (e. g., 7 and 11), GSH has different ionization forms due to the differences of the deprotonation ability of the functional groups mentioned above. For the GSH-Au NCs at pH 7, the peaks of the carboxylic groups shifted to 1643 and 1603 cm^{-1}, and the shape became relatively broad. After the addition of Cd^{2+}, these peaks shifted slightly, indicating in this case, very weak interaction between GSH and Cd^{2+}. For GSH-Au NCs at pH 11, before and after the addition of Cd^{2+}, the peaks of the carboxylic groups shifted as those for GSH-Au NCs at pH 7. However, the peak corresponding to the amide bond became very weak and almost disappeared after adding Cd^{2+}. The similar change also happened for the N−H (NH_3^+) stretching band (νN−H). These results suggest that GSH could strongly coordinate to Cd^{2+} at high pH.

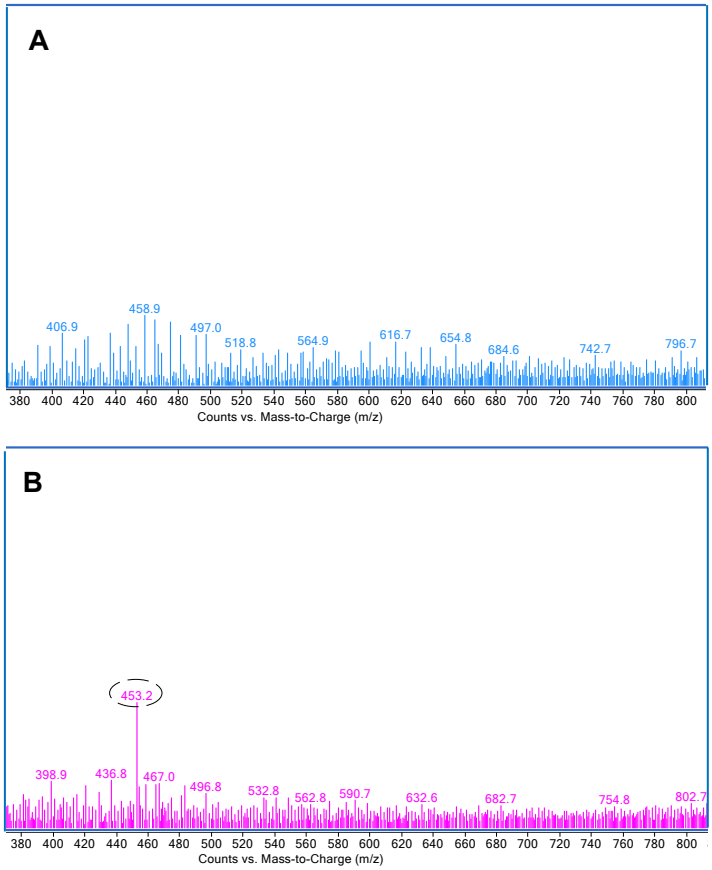


Figure S11. ESI-MS data for GSH-Au NCs at pH 11 in the absence (A) and presence (B) of Cd^{2+}, respectively.

Table S1. QYs and Zeta Potentials of GSH-Au NCs at pH 7 and 11 in the Absence and Presence of Cd^{2+}

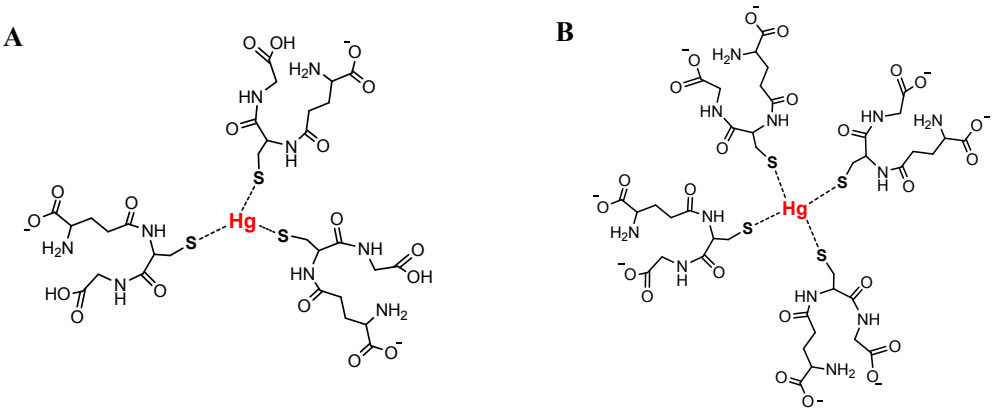
Sample	QY(%)	Zeta potential (mV)
GSH-Au NCs (pH 7)	0.22	-9.78
GSH-Au NCs (pH 7)+Cd^{2+}	0.24	-9.26
GSH-Au NCs (pH 11)	0.15	-40.90
GSH-Au NCs (pH 11)+Cd^{2+}	0.24	-32.87

Table S2. Binding Energies Corresponding to the Deconvoluted Peaks of C 1s, O 1s, and N 1s of GSH-Au NCs at pH 11 in the Absence and Presence of Cd^{2+}

Sample	BE[a] C1s (eV)			BE O1s (eV)		BE N1s (eV)	
	C–C	C–O	C=O	O=C–O*[b]	[c]*O=C–O	CO–NH[d]	[e]N–H
GSH-Au NCs	284.74	285.64	288.00	532.16	530.86	399.59	401.07
GSH-Au NCs +Cd^{2+}	284.63	285.73	287.76	532.42	530.87	399.38	400.66

[a]Binding energy. [b]Hydroxyl O in the carboxylic group. [c]Carbonyl O in the carboxylic group. [d]Amidic N in the peptide linkage between the cysteinyl and glycyl residuals. [e]Amino N.

Scheme S1. Proposed Structures of Hg-GSH Complexes at pH 5 (A) and 11 (B)



Scheme S2. Proposed Structures of Cd-GSH Complexes at pH 7 (A) and 11 (B) on Au Surface