

## Supporting Information

### Highly Selective and Ultrasensitive Detection of $\text{Hg}^{2+}$ Based on Fluorescence Quenching of Au Nanoclusters by $\text{Hg}^{2+}$ - $\text{Au}^+$ Interactions

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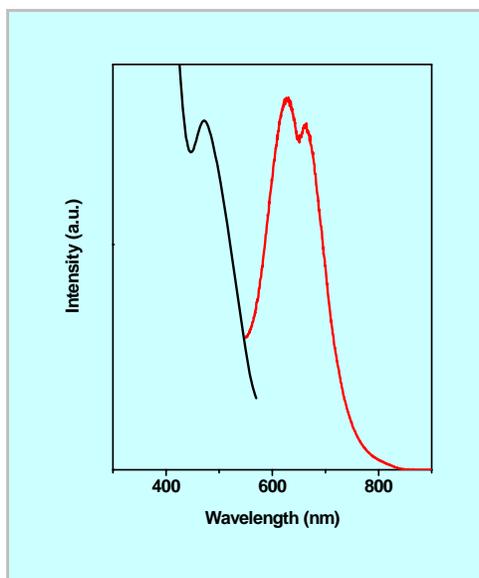
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#### ***Experimental***

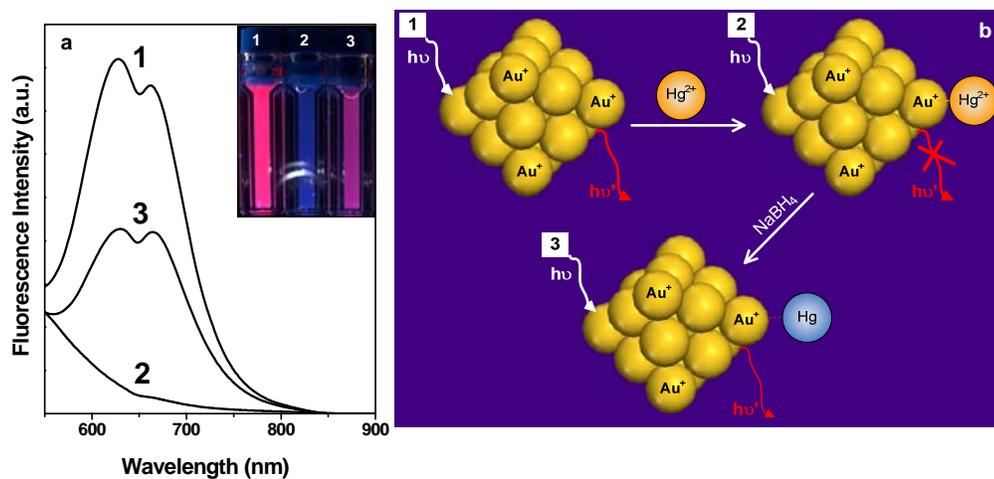
All chemicals were purchased from Sigma-Aldrich and used as-received. Ultrapure Millipore water (18.2 M $\Omega$ ) was used.

***Synthesis of Red Fluorescent Au NCs.*** All glassware was washed with *aqua regia* (HCl/HNO<sub>3</sub> volume ratio = 3:1), and rinsed with ethanol and ultrapure water. (*Caution: aqua regia is a very corrosive oxidizing agent, which should be handled with great care.*) In a typical experiment, aqueous HAuCl<sub>4</sub> solution (5 mL, 10 mM, 37 °C) was added to BSA solution (5 mL, 50 mg/mL, 37 °C) under vigorous stirring. NaOH solution (0.5 mL, 1 M) was introduced 2 min later, and the reaction was allowed to proceed under vigorous stirring at 37 °C for 12 h. The as-synthesized Au NCs (10.5 mL) were dialyzed in membrane tubing with a molecular weight cut-off (MWCO) of 12 kDa (Sigma) against 1 L of continuously stirred ultrapure water at room temperature. After 24 h and 3 changes of water (at 8-h intervals), the tubing contents (Au NCs) were collected, and the solution was concentrated to 10 mL.

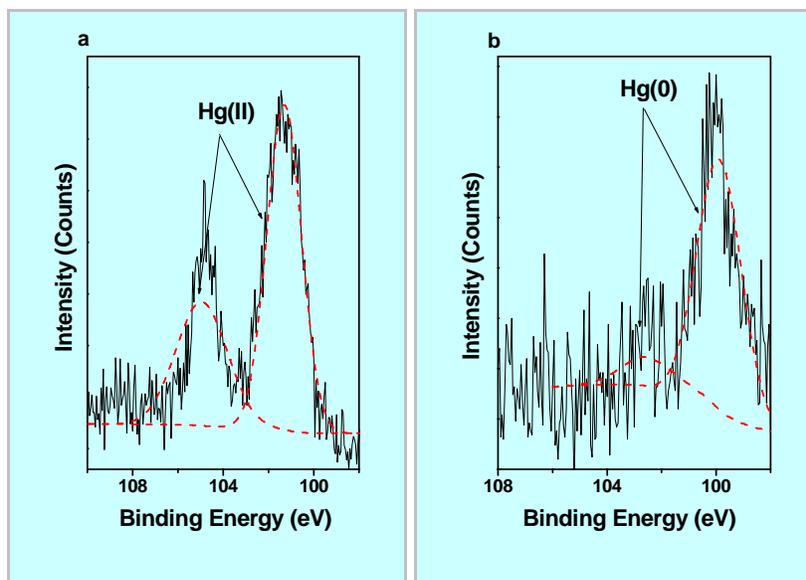
***Synthesis of Au@Ag core-shell NCs.*** In a typical experiment, the as-synthesized Au NCs (10 mL, 5 mM, 37 °C) were mixed with aqueous AgNO<sub>3</sub> solution (2.5 mL, 10 mM, 37 °C), followed by the addition of NaOH solution (25  $\mu$ L, 1 M). The reaction was conducted under vigorous stirring at 37 °C for 24 h. The as-synthesized Au@Ag core-shell NCs were dialyzed in membrane tubing with a MWCO of 12 kDa against 1 L of water. After 24 h and 3 changes of water (at 8-h intervals), the tubing contents (Au@Ag core-shell NCs) were collected, and the solution was concentrated to 10 mL.



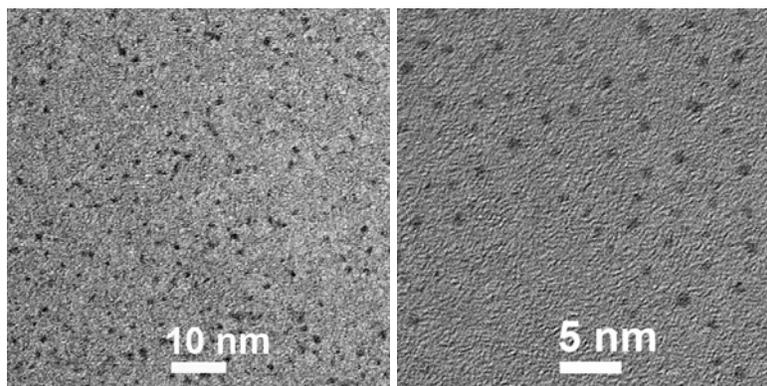
**Fig. S1** Optical excitation (black) and photoemission (red,  $\lambda_{\text{ex}} = 470$  nm) spectra of an aqueous solution of Au NCs.



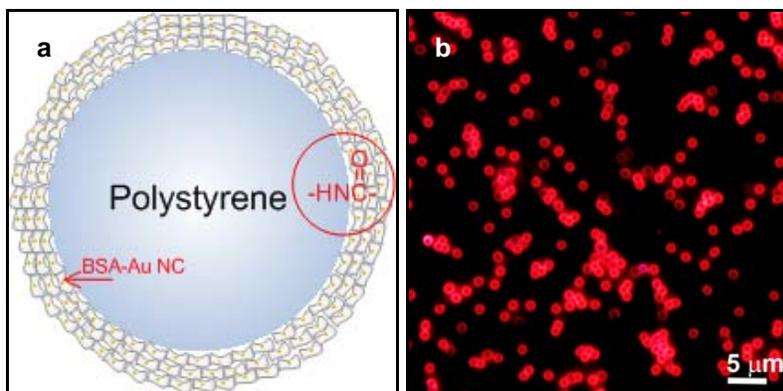
**Fig. S2** (a) Photoemission spectra ( $\lambda_{\text{ex}} = 470$  nm) and (inset) photographs under UV light of Au NCs (20  $\mu\text{M}$ ), and (b) schematic of Au NCs sensing in the (1) absence and (2) presence of  $\text{Hg}^{2+}$  ions (50  $\mu\text{M}$ ), and (3) solution (2) after the addition of aqueous  $\text{NaBH}_4$  (10 mM).



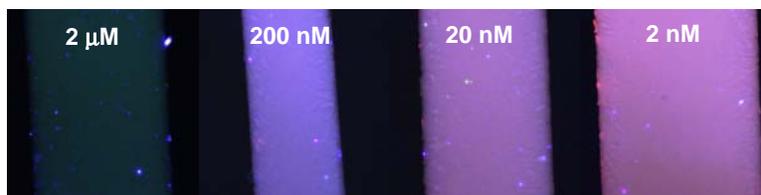
**Fig. S3** XPS Hg 4f spectra of (a) Hg ions sequestered by Au NCs, and (b) sequestered Hg ions reduced by NaBH<sub>4</sub>.



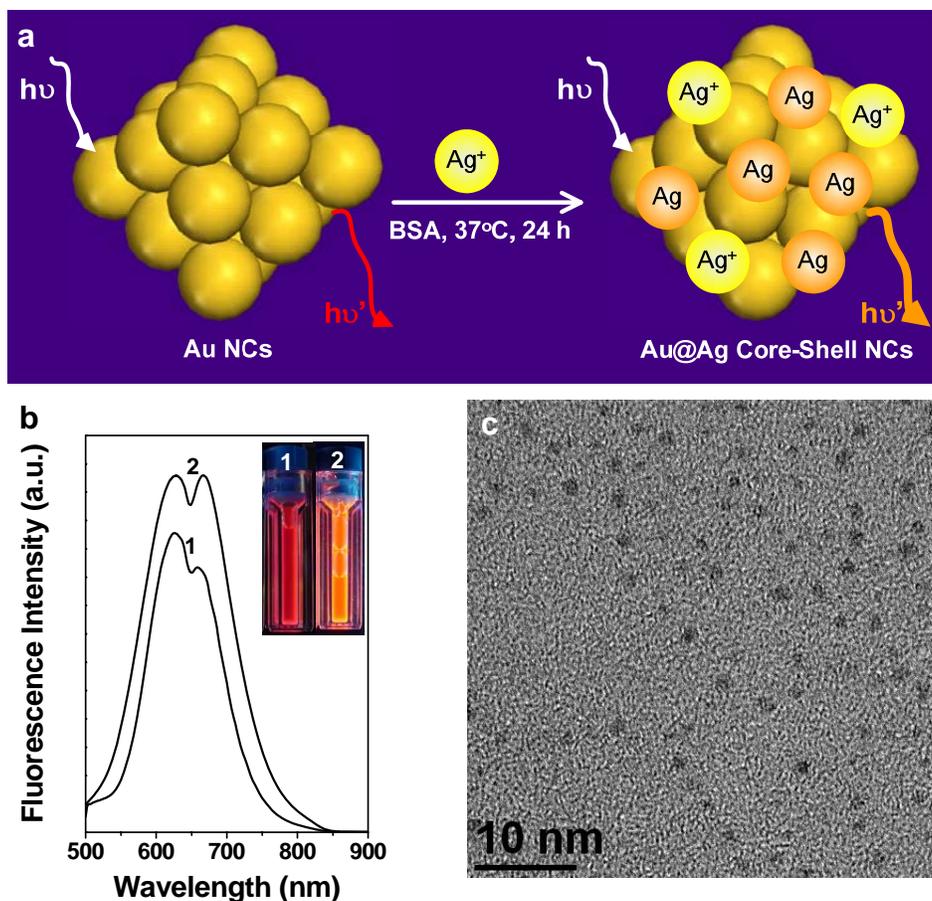
**Fig. S4** Representative TEM images of Au NCs in the presence of Hg<sup>2+</sup> ions, indicating a cluster size of ~0.8 nm.



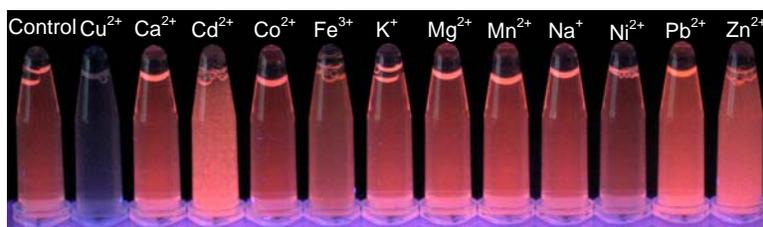
**Fig. S5** (a) Schematic of Au NCs conjugated to polystyrene beads (1  $\mu\text{m}$ ) through 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide (EDC) method. (b) A representative fluorescence image of polystyrene–Au NCs.



**Fig. S6** Photographs under UV light of test strips that have been dipped in solutions of  $\text{Hg}^{2+}$  ions of the specified concentrations.



**Fig. S7** (a) Schematic of the formation of Au@Ag core-shell NCs. (b) Photoemission spectra ( $\lambda_{\text{ex}} = 470 \text{ nm}$ ) and (inset) photographs under UV light of (1) Au NCs and (2) Au@Ag core-shell NCs. (c) Representative TEM image of Au@Ag core-shell NCs, indicating a cluster size of  $\sim 1.2 \text{ nm}$ .



**Fig. S8** Photographs under UV light of aqueous Au@Ag core-shell NCs solutions (20  $\mu\text{M}$ ) in the presence of 50  $\mu\text{M}$  of various metal ions.