Supporting Information for

Picomolar Detection of Mercuric Ions by Means of Gold-Silver Core-Shell Nanorod

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Materials and Instrumentation. Malachite green isothiocyanate (MGITC) dye was purchased from Life Technologies. Other chemicals such as $HAuCl_4 \cdot 3H_2O$, $AgNO_3$, HNO_3, ascorbic acid, trisodium citrate, and metallic salts ($CaCl_2$, $Cd(SO_4) \cdot 8H_2O$, $CoCl_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H2O$, $Hg(ClO_4)_2 \cdot 3H_2O$, $MgSO_4$, $Ni(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$) were obtained from major suppliers such as Sigma-Aldrich and Alfa Aesar and were used as received. Distilled water was used throughout the work. The UV-vis spectra were recorded with a Genesys 10s UV-vis spectrophotometer. Raman spectra were recorded at a small portable Raman spectrometer (BWS415, B&W Tek Inc.) with an excitation wavelength of 785 nm, a resolution of 5 cm^{-1}, and a beam diameter of 10 μm. The integration time in each case was typically 20 s. TEM images were obtained by using a JEOL JEM-2010 model at an accelerating voltage of 120 kV. Dynamic light scattering (DLS) were performed on a Zeta Sizer Nano ZS (Malvern Zetasizer 3000HS and He/Ne laser at 632.8 nm at scattering angles of 90 at 25 °C.

Synthesis of Gold Nanorods. Gold nanorods were synthesized using the seed-mediated growth method developed by Murphy *et al*.[1] Briefly, a seed solution of gold nanoparticles with an average diameter of around 4 nm was produced by the reduction of $HAuCl_4 \cdot 3H_2O$ (5 mL, 5 mM) with $NaBH_4$ (0.6 mL, 10 mM) in the presence of a cationic surfactant CTAB (5 mL, 200 mM). The resulting seed nanoparticles were used in the synthesis of gold nanorods. In a typical procedure, to 8 mL of 0.1 M ascorbic acid solution was added 100 mL of 0.10 M CTAB, 2 mL of 25 mM $HAuCl_4$, 1.25 mL of 10 mM $AgNO_3$, and 2 mL of 0.5 M H_2SO_4 under gentle stirring at ambient temperature. Finally, 240 μL of the seed solution was added to the mixture, and the resulting solution was stirred for 1 min and then left undisturbed overnight at room temperature. According to TEM images, the average length, diameter, and aspect ratio of AuNRs were

calculated to be 67 ± 8 nm, 16 ± 3 nm, and 4.2 ± 0.5. The concentration of AuNRs can be calculated by means of their UV-vis spectra and the extinction coefficient at the longitudinal plasmon peak.

Synthesis of Gold-Silver Core-Shell Nanorods. The preparation of Au@AgNRs with various thicknesses of Ag shell was based on the seed-mediated growth method. First, to remove the excess reagents, 2 mL of the as-prepared AuNRs solution (0.25 nM) was centrifuged twice at 10,000 rpm for 5 min. The pellets were redispersed in 1 mL of distilled water. Then, Au@AgNRs were prepared according to the methods developed by Wang *et al.* with slight modifications.[2] Typically, 1 mL of the as-prepared AuNRs solution (0.25 nM) was added to 5 mL of 0.04 M CTAB aqueous solution under vigorous stirring at room temperature. After that, 130 μL of 0.1 M ascorbic acid, various volumes (0 to 400 μL) of $AgNO_3$ (10 mM) and 290 μL of 0.1 M NaOH solution were added to the mixtures sequentially. The color of the solutions changed quickly from light green to brown, indicating the formation of Au@AgNRs with varying thicknesses of Ag shell. To ensure the amount of Au@AgNRs in each sample was the same to that of the initial AuNRs sample (0.25 nM), all the Au@AgNRs samples were concentrated to 1 mL before further use.

Preparation of Raman dye-nanoparticle conjugates. The procedure of preparing MGITC-Au@AgNRs is introduced as follows. Typically, a stock solution of MGITC dye (1 mM, 1 μL) was added into a freshly prepared Au@AgNRs solution (0.25 nM, 1 mL) with vigorous shaking to allow adsorption of Raman dyes to the nanoparticle surfaces. The resulting solution was shaken (600 r/min) in the dark at room temperature for 1 h for sufficient equilibration. The

Raman dye-nanoparticle conjugates were obtained and stored at 4 °C for further use. The amount of Raman dyes per nanoparticle was calculated to be 4000.

Experimental Procedures for Detection of Hg^{2+} using Au@AgNRs. A typical procedure for the detection of Hg^{2+} was performed as follows. A stock solution of Hg^{2+} was serially diluted with distilled water for various folds ranging from 10^{-12} to 10^{-5} M. Aliquots of MGITC (1 mM, 1 μL) were mixed with various concentrations of Hg^{2+} solution (1 mL), and the resulting solutions were allowed to incubate for 10 min at room temperature. Then, the mixtures were incubated with aliquots of the as-prepared Au@AgNR pellets for 1 min, and then the SERS activity for each solution was measured. The eventual concentration of Au@AgNRs was 0.25 nM. Each sample was measured three times.

To test the selectivity of this SERS probe, each metallic ion (Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2}, Ni^{2+}, Pb^{2+} and Zn^{2+}) was prepared in distilled water (1 mL) to afford 10^{-4} M aqueous solution. The stock solutions were diluted to desired concentrations with distilled water when needed. Typically, 1 mL of each metallic salt (10^{-5} M) was incubated with aliquots of MGITC (1 mM, 1 μL) for 10 min. The resulting solutions were mixed with the as-prepared Au@AgNR pellets, after 1 min of incubation, the SERS activity of the resulting solutions was measured. Each sample was measured for three times.

Analysis of Hg^{2+} in River Water and Fish samples. To evaluate the efficiency of this probe in complex samples, we collected river water from the Potomac River near Washington, D.C., and prepared fish samples. Firstly, the obtained river water was filtered by using a PES membrane (filter unit is 22 μm) to remove the insoluble materials and stored at room temperature for further use. Meanwhile, we prepared the fish samples using the similar procedure as reported

previously.[3] Salmon fish was commercial from supermarket and chopped into homogenized tissues, 1 gram of which was dissolved in 10 mL of concentrated HNO_3. The resulting solution was gently stirred at 180 °C for 30 min, and cooled down to room temperature. NaOH (1M) was used to mediate the pH value of the solution to be around 7. Finally, the volume of the fish sample was set to be 100 mL.

To investigate the effects of the sample matrices on the detection, both the river water and fish sample were spiked respectively with different amounts of Hg^{2+} stock solutions to result in final concentrations of Hg^{2+} to be: 0, 10^{-12}, 10^{-11}, 10^{-10}, 10^{-9}, 10^{-8}, 10^{-7}, 10^{-6}, and 10^{-5} M (1 mL of each sample). The spiked samples containing varying concentrations of Hg^{2+} were mixed with aliquots of MGITC (1 mM, 1 μL) for 10 min. Later, the resulting samples were incubated with the freshly prepared Au@AgNR pellets. After 1 min of incubation, the SERS spectra of the samples were collected and analyzed. All the measurements were repeated three times for each sample.

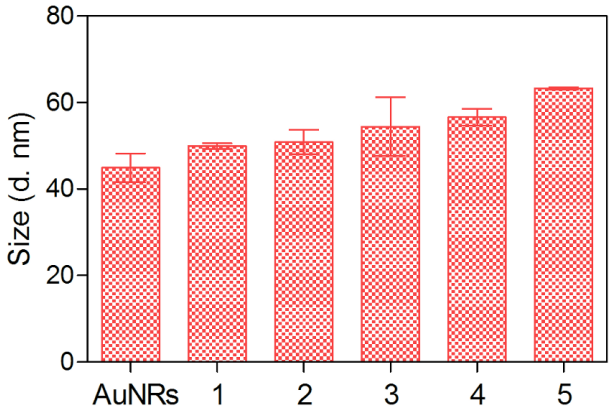

Figure S1. DLS of AuNR sample and the obtained Au@AgNR samples that were treated with increasing volumes of $AgNO_3$ (from left to right). The samples 1-5 were produced from growths with 30, 100, 200, 300, and 400 µL of $AgNO_3$ (10 mM), respectively.

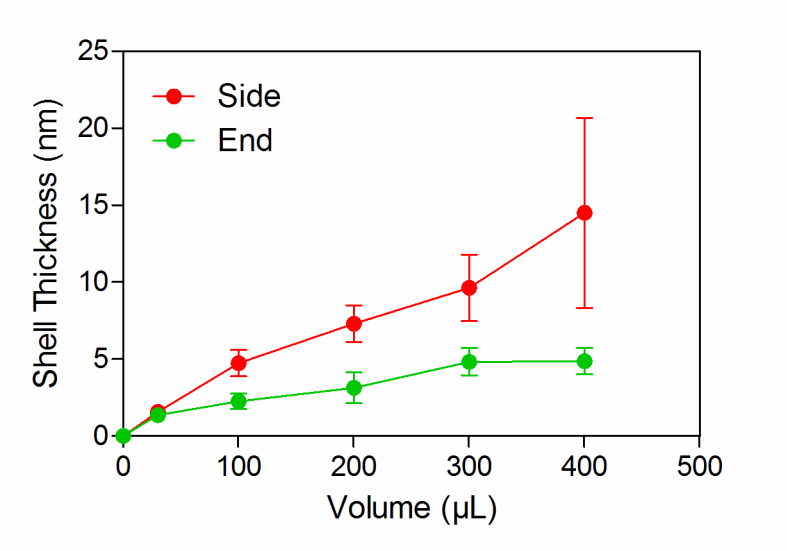

Figure S2. Thicknesses of the Ag shell at the side and ends of the core-shell nanorods versus the volumes of the $AgNO_3$ solutions (10 mM).

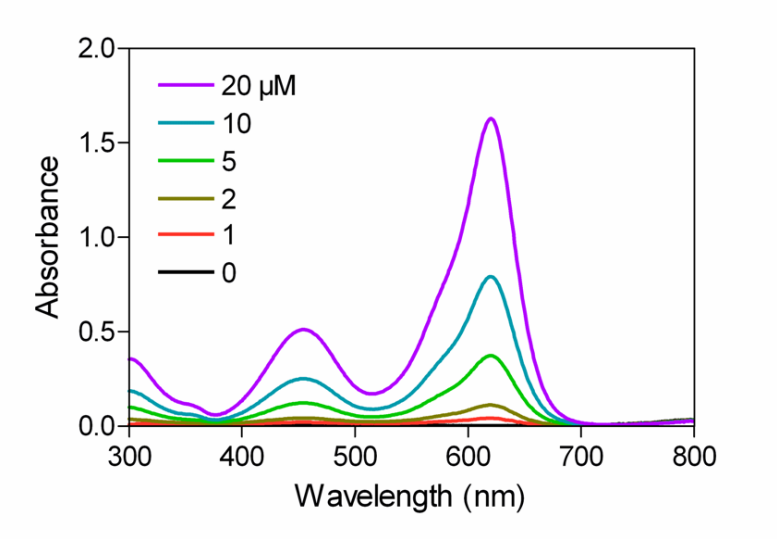

Figure S3. UV-vis spectra of various concentrations (0-20 μM) of free MGITC after incubation with 0.25 nM of Au@AgNRs. The free MGITC in each solution was collected by centrifugation (10000 r/min, 5 min) and the supernatants were measured.

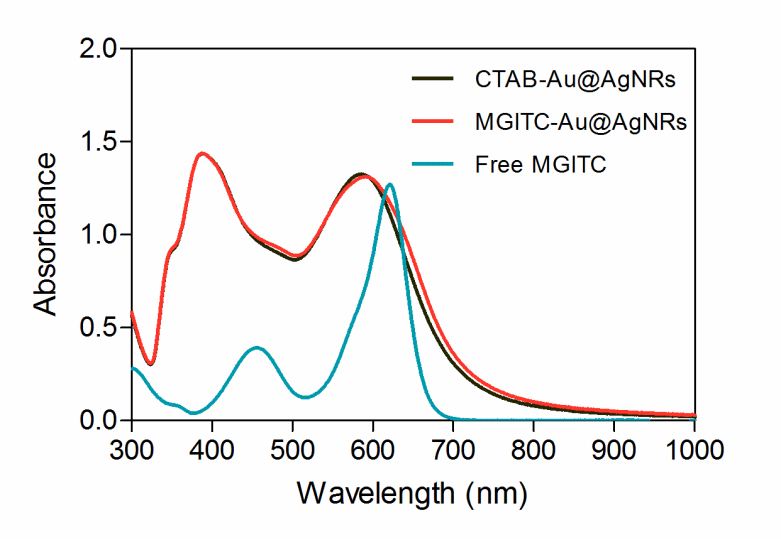

Figure S4. UV-vis spectra of CTAB-coated Au@AgNRs (black line) and MGITC-modified Au@AgNRs (red line) as well as that of free MGITC.

Table S1. Comparison of different advanced methods for Hg^{2+}.

Method	Probe	LOD (μM)	Real Sample	Ref.
Colorimetric	DNA-AuNPs	0.01	Underground water	4
Colorimetric	DNA-AuNPs	0. 1	—	5
Colorimetric	DNA-AuNPs	0.01	Lake water	6
Colorimetric	DNA-AuNPs	1.0	—	7
Colorimetric	QA[a]-AuNPs	0.03	Drinking water	8
Colorimetric	MPA[b]-AuNPs	0.1	—	9
Colorimetric	MUA[c]-AuNCs[d]	5.0×10^{-3}	Pond water	10
Fluorescence	Lysozyme-AuNCs	0.01	—	11
Fluorescence	Lysozyme-AuNCs	3.0×10^{-6}	Seawater	12
Fluorescence	BSA[e]-AuNCs	5.0×10^{-4}	—	13
Fluorescence	R6G-AuNPs	6.0×10^{-5}	River water	14
Fluorescence	RBITC[f]-AuNPs	2.3×10^{-3}	River water	15
RLS[g]	MPA-HCys[h]-AuNPs	0.025	—	16
RLS	Poly-T6[i]-AuNPs	1.0×10^{-3}	Tap and lake water	17
RLS	T-rich DNA/AuNPs	0.1×10^{-3}	—	18
Electrochemical	DNA hairpin	2.5×10^{-3}	Sewage samples	19
Electrochemical	DNA-AuNPs	7.38×10^{-6}	Tap water	20
SPR[j]	DNA-AuNPs	5.0×10^{-3}	—	21
SPR	DNA-AuNPs	1.0×10^{-3}	Tap and pond water	22

[a] Quaternary ammonium. [b] 3-mercaptopropionic acid. [c] 11-Mercaptoundecanoic acid.

[d] Gold nanoclusters. [e] bovine serum albumin. [f] Rhodamine B isothiocyanate.

[g] Resonance light scattering. [h] Homocysteine. [i] 5'-d(T_6)-3'. [j] Surface plasmon resonance.

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