Supporting information for

Difunctional biogenic Au nanoparticles for colorimetric detection and removal of Hg^{2+}

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EXPERIMENTAL SECTION

Chemicals and bacteria

$HAuCl_4.4H_2O$ was purchased from J&K scientific, Beijing, China. All the other chemicals used were of analytic grade. Metal ion solutions were prepared using corresponded nitrate salts in Milli-Q water (18.2 MΩ/cm). *Cupriavidus metallidurans* SHE was isolated by our lab, and deposited as a patent bacterium in China General Microorganism Culture Center (CGMCC NO. 9266). In this paper, strain SHE was incubated to the mid-log phase using Luria-Bertani (LB) media, which contained peptone 10 g/L, yeast extracts 5 g/L, and NaCl 10 g/L. The resting cells were collected by centrifugation at 8000 × *g* for 10 min, and stored at 4 ^{o}C before use.

Preparation and characterization of biogenic AuNPs

The optical density (OD_{660nm}) of resting cells was adjusted to 2.0 using 0.02 M phosphate buffer solution (PBS). Different concentrations of $HAuCl_4$ (0.5 mM, 1.0 mM, 2.0 mM, 5.0 mM and 10.0 mM) were incubated with the resting cells for 48 h. The purple resting cells were collected by centrifugation at 3000 × *g* for 5 min, and washed 3 times using Milli-Q water. The resuspended resting cells were heated at 121 ^{o}C for 20 min using autoclave sterilizer to release the membrane associated and intracellular AuNPs. Then the colloids were filtered through a 0.22 μm membrane filter and stored at 4 ^{o}C until further use. UV-visible spectra were recorded using spectrophotometer (JASCO V-560, Japan). 1.0 mL sample was placed into a quartz cuvette, and a spectral scan analysis was performed in the 400-800 nm range. TEM images for AuNPs and Au-Hg amalgam were captured using a FEI Tecnai T12 transmission electron microscope operated at 120 kV. The aqueous suspensions of nanoparticles were sonicated for 1 min and a droplet was placed on carbon coated Cu grids and allowed to dry under infrared lamp for 20 min. DLS data of AuNPs and Au-Hg amalgams were obtained by Zetasizer Nano ZS (Marvin instruments, UK). A volume of 0.8 mL of the colloidal AuNPs solution was placed into the specific cuvette and the software give the results of hydrodynamic diameter of nanoparticles. Fourier transformed infrared spectra (FTIR) of crude extracts with and without AuNPs were obtained by using a Shimadzu IRPrestige-21 FTIR spectrophotometer with the wavelength ranging from 400 to 4000 cm^{-1}. The aqueous suspension of AuNPs was centrifuged at 20000 × *g* for 30 min, and the pellet was redispersed for twice using Milli-Q ultrapure water (18.2 MΩ/cm) to remove any unabsorbed biomolecules of the extract. The purified pellet was freeze dried to obtain dry powder. Then KBr was mixed with pellet for FTIR studies.

Hg^{2+} sensing and metal ions selectivity

950 μL aliquot of AuNPs was added into a 1.5 mL eppendorf tube, and then 50 μL Hg^{2+} solution of different final concentration (100 nM to 2 mM) was mixed with the colloid AuNPs, and further incubated for 24 h. Metal ions selectivity was assayed using 1 mM of different metal

ions with AuNPs, and the UV-visible spectra were recorded. The experiments were assayed for 6 times. Residual standard deviation method was applied to calculate the limit of detection (LOD) using formula: LOD= 3.3 σ/S, where σ = residual standard deviation of response, and S = slope of the calibration curve.

Analysis of real water samples

A series of samples were prepared by adding standard solutions of Hg^{2+} into the drinking water with different final concentration (500 μL). Then the same volume of AuNPs was mixed with the samples, and incubated for 24 h before spectra measurement. The samples listed in the Table S1 were: drinking water I (0.2 μM Hg^{2+} without other metal ions), drinking water II (1 μM Hg^{2+} without other metal ions), and drinking water III (0.2 μM Hg^{2+} with 0.2 μM metal ions mixture). The metal ions mixture including Cd^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+}. Each sample was assayed for 3 times.

Removal of mercury

For mercury removal, 950 μL colloid AuNPs were mixed with 50 μL different concentrations of $Hg(NO_3)_2$ in Milli-Q water, and incubated for 24 h. 200 μL of the supernatant was taken and diluted to 1 mL, then the samples were used for ICP-MS assay. Each sample was determined for 3 times.

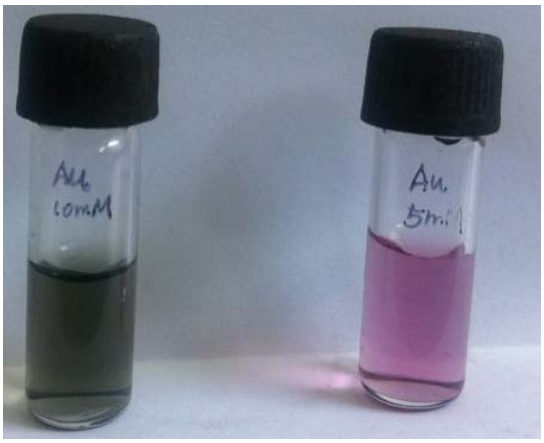


Fig. S1 Digital images of as synthesized $AuNPs_5$ (right) and $AuNPs_{10}$ (left).

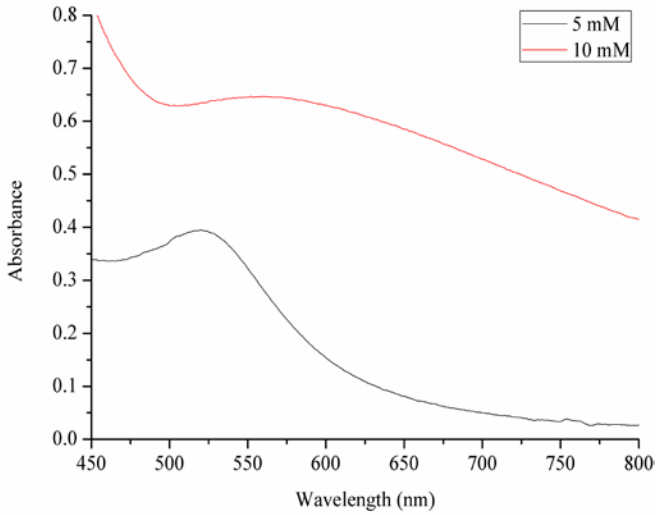
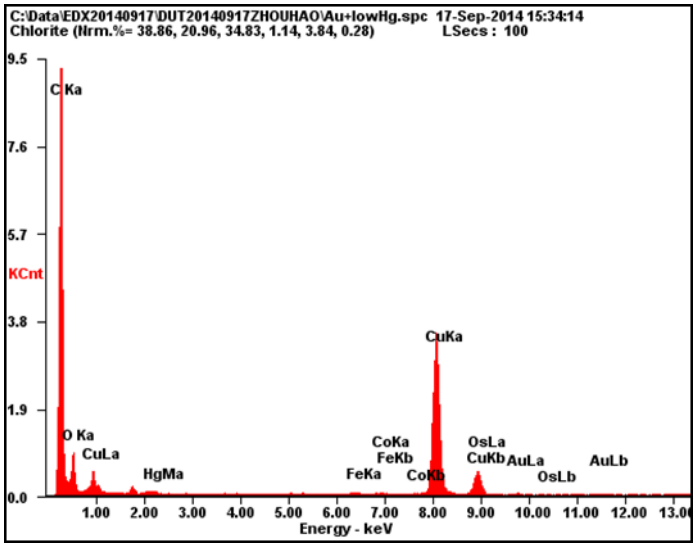
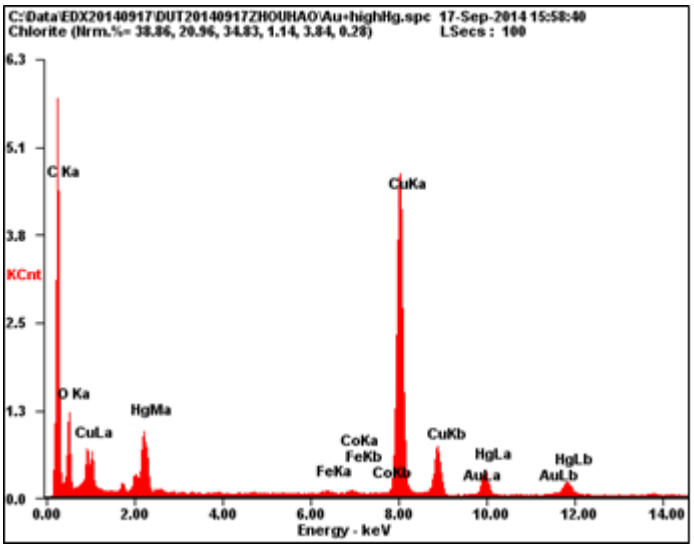


Fig. S2 SPR adsorption of AuNPs obtained at 5 mM and 10 mM $HAuCl_4$.



(a)



(b)

Fig. S3 EDX spectra of AuNPs with (a) 20 μM and (b) 1 mM Hg^{2+}.

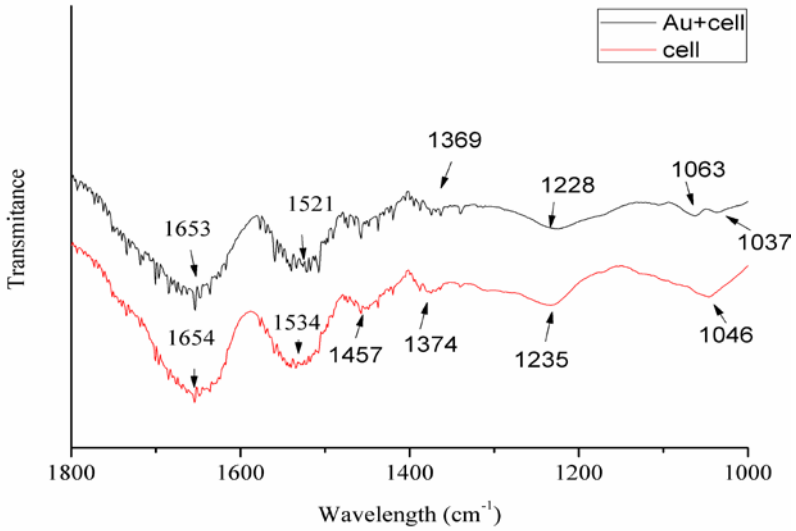


Fig. S4 FTIR spectra of cell crudes with and without AuNPs

Table S1 Comparison of detection Hg^{2+} using AuNPs or AgNPs

Nanoparticle	Linear range	LOD	RSD	Reference
Biogenic-AgNPs	10 μM to 100 μM	2.2 μM	2.2%	1
L-tyrosine-AuNPs	33 nM to 300 nM	53 nM	NR	2
Biogenic-AuNPs	1 nM to 1μM	2.6 nM	NR	3
DNA-AuNPs	0 μM to 5 μM	0.5 μM	NR	4
Biogenic-AuNPs	100 nM to 100 μM	13.2 nM	2.4%*	This work

* n=3

Table S2 Determination of Hg^{2+} ions in drinking water

Sample	Added (μM)	Determined by Au NPs (μM) (Mean±E, n=3)	Determined by ICP-MS (μM)
Drinking water I	0.20	0.22±0.03	0.24
Drinking water II	1.0	1.08±0.05	1.16
Drinking water III	0.20	0.29±0.06	0.27

*Drinking water I: (0.2 μM Hg^{2+} without other adding metal ions), drinking water II (1 μM Hg^{2+} without other adding metal ions), and drinking water III (0.2 μM Hg^{2+} with 0.2 μM metal ions mixture)

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