Supporting Information

A One-Step Homogeneous Plasmonic Circular Dichroism Detection of Aqueous Mercury Ions using Nucleic Acid Functionalized Gold Nanorods

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EXPERIMENTAL SECTION

Materials

Cetyltrimethylammonium bromide (CTAB, 99%) and sodium borohydride, L-ascorbic acid, hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4$) (99%), and silver nitrate were all purchased from Sigma-Aldrich and used as received. All metal ions were atomic absorption standards. Cu^{2+}, Hg^{2+}, Cr^{6+}, Fe^{2+}, Ag^{+}, Pb^{2+}, and Zn^{2+} (1000 μg/mL in 1% HNO_3 or 5% HCl) were purchased from the National Institute of Metrology P.R China (Beijing, China). All other reagents were available commercially. Milli-Q ultra-pure water (18.2 MΩ) was used in all experiments.

The oligonucleotide was synthesized by Sangon Biotechnology Inc. (Shanghai, P. R. China) with this sequence:

DNA 1: 5'-SH-AAAAAAGTGACCATTTTTGCAGTG-3'

DNA 2: 5'-SH-CACTGCTTTTTTGGTCACAAAAAA-3'

Instrumentation

The size distribution of nanorods was measured using a Zetasizer Nano ZS system (Malvern). A 633 nm laser was used for the DLS characterization. All UV-Vis spectra were acquired on a UNICO 2100 PC UV-Vis spectrophotometer and processed with Origin Lab software. The CD spectra were recorded on a J-710 spectropolarimeter (Jasco, Japan). Transmission electron microscopy (TEM) images and energy dispersive X-ray spectrometry data (EDS) were obtained using a transmission electron microscope JEOL JEM-2100 operating at an acceleration voltage of 200 kV. For the TEM examination, 10 μL of each sample was dried in air and dispersed on to a copper grid coated with a carbon film.

Synthesis of Gold Nanorods

GNRs with an aspect ratio of about 3 were prepared from a slightly modified seed-mediated growth procedure, as described by El-Sayed and Murphy.[29, 30]

Initially, 0.1 mL of a 5 mM $HAuCl_4$ solution was added to 1 mL of 0.20 M CTAB solution, which was kept at a constant temperature of 28.0°C. Immediately, a deep orange color appeared. Then 0.12 mL of freshly prepared 10 mM $NaBH_4$ solution was quickly added to the solution and mixed by inversion. The solution was rapidly stirred for 2 min, and the color of the solution turned pale brown. Upon seed production, the GNRs were formed. 5 mL of 5 mM $HAuCl_4$ was added to 5 mL of 0.2 M CTAB solution and then 4 mL of water was added; this represents the GNR growth solution. To this mixture, 65 µL of 0.1 M ascorbic acid was added, followed by 0.125 mL of 10 mM $AgNO_3$ solution, which was mixed by inversion for about 2 min. The solution became colorless. Finally, 0.05 mL of seed solution was added, with gentle mixing by inversion for about 20 s. The GNRs were used after 4 h.

Preparation of DNA-Functionalized GNRs.

Briefly, 5 µL 1 mM thiolated modified PEG-5000(SH-PEG) solution and 1000 µL 10 nM purified GNR solution were mixed by stirring, then incubated for 8 h whilst shaking. The facets at the ends of the GNRs bound fewer CTAB, so they were able to preferentially conjugate the thiolated modified PEG. The mixture was then collected by centrifugation at 7500 × *g* for 15 min.

Subsequently, 20 µL 100 µM thiolated modified DNA solution was added to 1000 µL 10 nM PEG-thiolated GNR solution, mixed well, and incubated for another 12 h at room temperature. Subsequently, the conjugate was collected by centrifugation at 7500 × g for 15 min. Finally, the DNA-GNR probe was stored in 5 mM CTAB solution at 4°C for the next step. The GNR probes are denoted as GNR-DNA1and GNR-DNA 2.

Determination procedure

Firstly, 50 µL of GNR-DNA-1 was mixed with 50 µL of GNR-DNA-2 solution with gentle shaking for 5 min. To samples of the mixed solution, Hg ion solutions at different concentrations were separately added and mixed well. The concentrations of the Hg ion standard were 0, 0.05, 0.1, 0.5,1, 5 and 10 ng/mL. The solution was then incubated for 1 h at 40 °C to form the assemble structure via the T-Hg^{2+}-T interaction. After reacting, the sample was analyzed by TEM, DLS and CD. A standard curve was established by plotting the CD signal intensity against the concentration

of Hg ion standard. The limit of detection (LOD) was calculated as LOD = 3.3SD/S, where SD is the standard deviation of the response and S is the slope of the calibration curve.

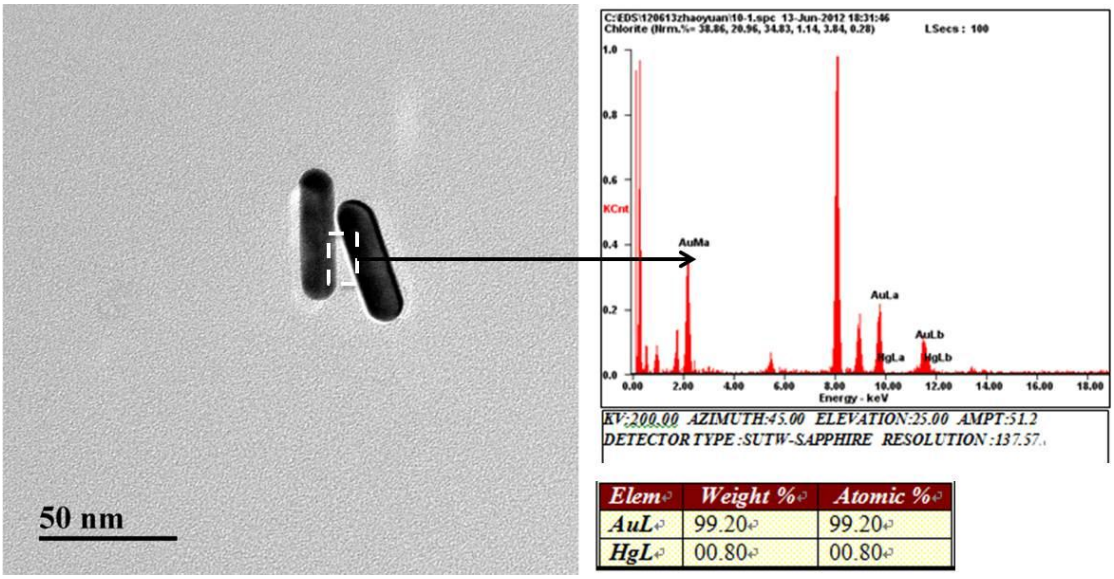

Figure S1. EDS spectrum of the side-by-side assemblies of gold nanorods

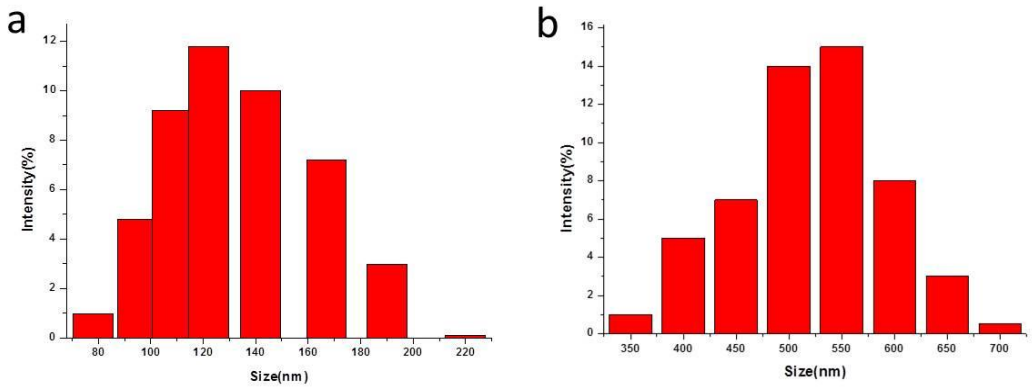

Figure S2. Typical size distributions of side-by-side assembly of gold nanorods (A) without the addition of Hg ion and (B) with the addition of Hg ion at the concentration of 10.0 ng/mL.

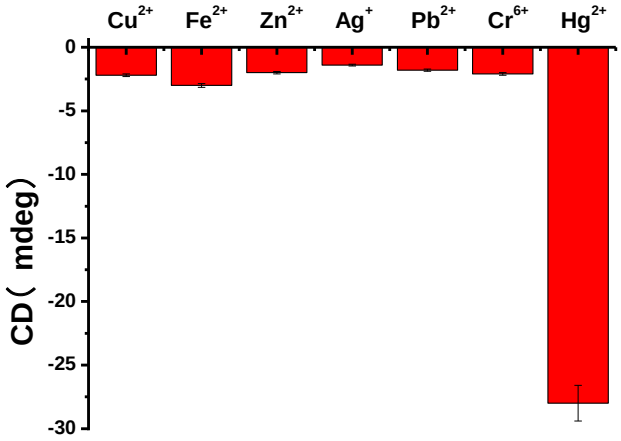

Figure S3. Side-by-side assembly of GNRs in the presence of various heavy metal ions with the concentration of each metal ion was 10ng/mL

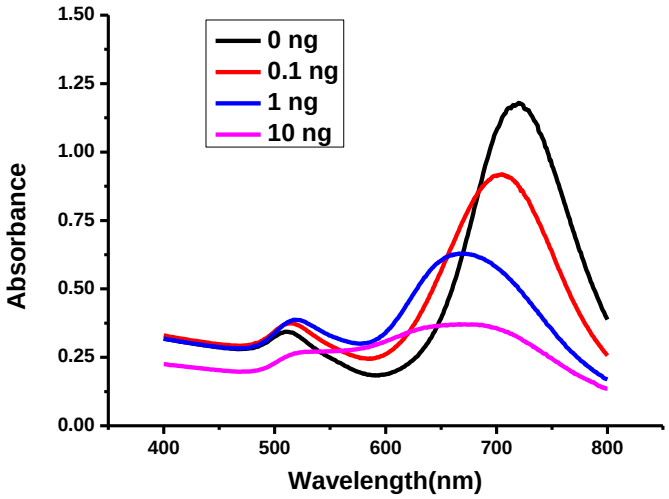

Figure S4. UV/vis spectra of assembly of GNRs in solution with different concentrations of Hg ion

References

29. B. Nikoobakht and M. A. El-Sayed, *Chemistry of Materials*, 2003, **15**, 1957-1962.
30. T. K. Sau and C. J. Murphy, *Langmuir*, 2004, **20**, 6414-6420.