Supporting information

SERS Active Gold Nanostar Dimer for Mercury Ion Detection

EXPERIMENTAL SECTIONS

Material

Thiolated DNA oligonucleotides, purified by high performance liquid chromatography (HPLC), were manufactured by Shanghai Sangon Biological Engineering Technology & Services Co. Ltd. (Shanghai, P.R. China). These were dissolved in deionized (DI) water to give a final concentration of 100 μM. Unless stated otherwise, all other chemicals used in this work were purchased from Sigma-Aldrich. DI water from a Milli-Q device (18.2 M Ω, Millipore, Molsheim, France) was used in all experiments. Cu^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+}, Mg^{2+}, and Ca^{2+} (1000 μg mL^{-1} in 1% HNO_3 or 5% HCL) were purchased from the National Institute of Metrology P.R China (Beijing, China).

The detailed sequences of the oligonucleotide are:

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

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

Instrumentation

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 operating at an acceleration voltage of 200 kV. The size distribution of the GNS 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 using a UNICO 2100 PC UV-Vis spectrophotometer and processed with Origin Lab software. Raman spectra were measured using a LabRam-HR800 Micro-Raman spectrometer with Lab-spec 5.0 software attached to a liquid cell. The slit and pinhole were set at 100 and 400 mm, respectively, in the confocal configuration, with a holographic grating (600 g/mm) and an air-cooled He-Ne laser giving 785 nm excitation with a power of ~ 8 mW.

Gold Nanostar synthesis

Gold nanostars were synthesized by a seed-mediated growth method. Initially, the gold seed was prepared by adding 15 mL of 1% citrate solution to 100 mL of boiling 1 mM $HAuCl_4$ solution under vigorous stirring. After cooling to room temperature, 200 µL 1-2 mM $AgNO_3$ (for 50nm GNS is 1mM and 2 mM for 60 nm GNS) and 100 µL 0.1 M ascorbic acid were mixed together quickly into 20 mL of 0.25 mM $HAuCl_4$ with 200 µL seeds, the PH is kept at 3. The colloidal solution was resuspended into 0.05% tween-20 by centrifugation at 3000 rpm for 15 min to prevent further reaction.

Preparation of ssDNA-Functionalized GNS

Briefly, 2 µL 100µM thiolated modified DNA 1 or DNA 2 solution was added to 100 µL of just prepared GNS and incubated for 3h at ambient temperature. Subsequently, 0.05 M NaCl was mixed and then the mixture was incubated for 12 h with constant shaking. The excess DNA was removed by two centrifugations at 3000 rpm for 10 min. The mixtures were denoted as GNS-DNA 1 and GNS-DNA 2.

Synthesis of GNS dimer structure

To prepare 50 nm GNS dimers, 50 nm GNS-DNA 1 and GNS-DNA 2 were mixed with a ratio of 1:1. A similar procedure was used for the 60 nm GNS dimer. The heterodimers were formed by adding equal quantities of 50 nm GNS-DNA 1 to 60 nm GNS-DNA 2. Then, 4-ATP ethanol solution, with a final concentration of 1 µM, was added to all three mixtures and incubated at room temperature overnight. After redispersion in DI water, Hg^{2+} solution, with a final concentration 1 ng mL^{-1}, was mixed with all three samples and shaken for 3 h.

Fabrication of GNS sensors

800 µL 60 nm GNS-DNA 1 and GNS-DNA 2 in the ratio of 1:1 were mixed with 1 µM 4-ATP ethanol solution and incubated for 12 h with constant shaking. This mixture is denoted as the sensor solution. Samples inoculated with different concentrations of Hg^{2+} (0, 0.5, 0.1, 0.05, 0.01,

0.005, 0.002 ng mL^{-1}) were separately added to 100 μL of sensor solution in separate tubes. After reacting for 3 h, the samples were processed by TEM, UV-Visible spectrophotometry and SERS.

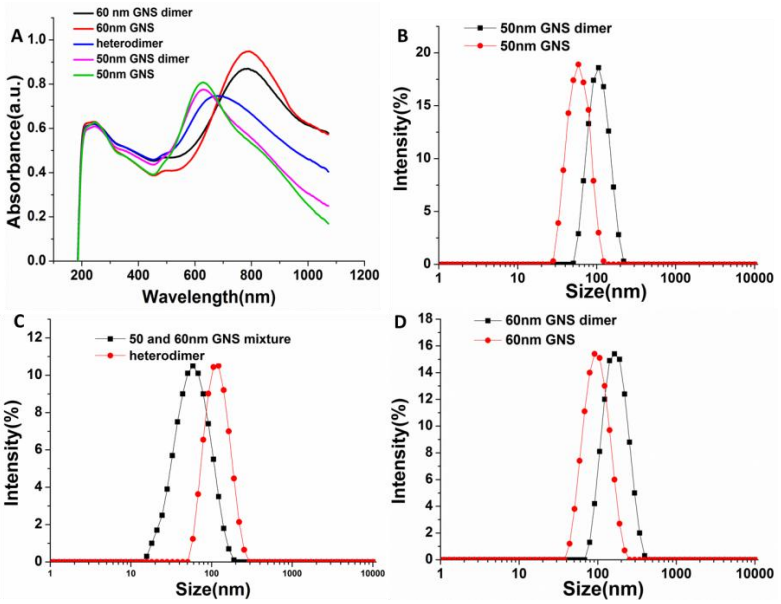

Figure S1. Uv-vis spectrum of different GNS dimers and particles (A), DLS of 50, heterodimer, 60 nm GNS sensor before and after addition 1 ng mL^{-1} Hg^{2+} (B, C, D).

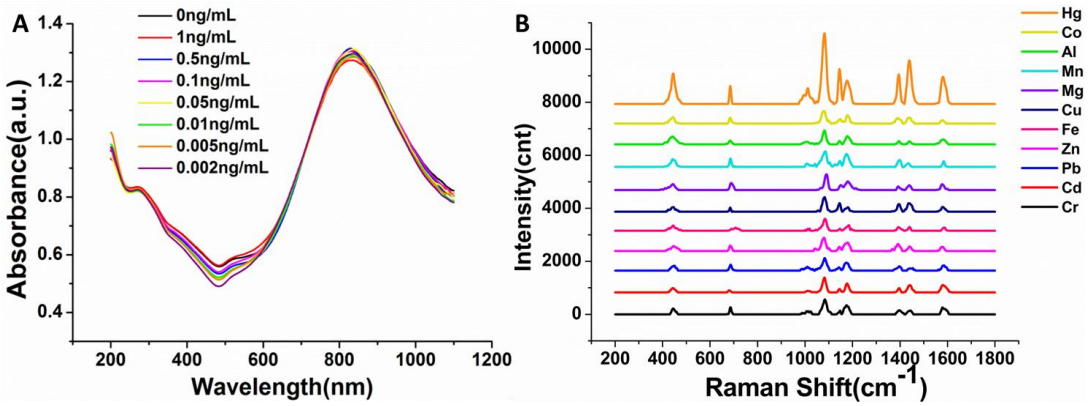

Figure S2. Uv-vis spectrum of 60 nm GNS dimer sensors in diverse Hg^{2+} samples (A), SERS intensity of different heavy metal irons based on 60 nm GNS dimer sensor(B)

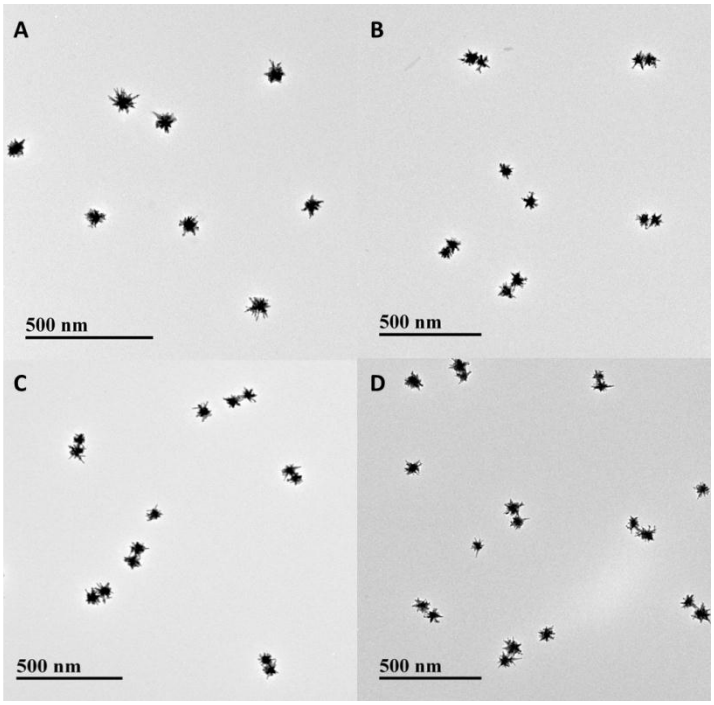

Figure S3. Lower magnification images of GNS dimer sensor with different Hg^{2+} addition (A) 0 ng mL^{-1}, (B)0.005 ng mL^{-1}, (C)0.01 ng mL^{-1}, (D)0.05 ng mL^{-1}