Supplementary Material (ESI) for Chemical Communications

Supporting Information

Mercury(II) detection by SERS based on a single gold microshell

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EXPERIMENTAL SECTION

Materials and reagents. Thiolated tetramethylrhodamine (TAMRA)-tagged DNA oligomer was purchased from BIONEER Corporation (Daejeon, Korea). The sequence of this modified oligomer was 5'-HS-$(CH_2)_6$-CTT GTT TCT CCC CCC TGT TTC TTG -TAMRA-3', containing a thiol at 5' and tetramethylrhodamine at 3'. Amine-terminated polystyrene bead (PS-NH_2) was procured from Bangs Laboratories, Inc. (Fishers, IN, USA) and used as received. Absolute ethanol was purchased from Merck Chemicals (Darmstadt, Germany). Mercury perchlorate, other metal perchlorate salts, Tris-(2-carboxyethyl) phosphine hydrochloride (TCEP), sodium phosphate monobasic, formaldehyde, Tetrakis(hydroxymethyl)phosphonium chloride (THPC), hydrogen tetrachloroaurate (III) trihydrate were obtained from Aldrich (Milwaukee, WI, USA). Sulfuric acid and hydrogen peroxide were purchased from J. T. Baker (Phillipsburg, NJ,

USA) and used without further purification. Deionized double distilled water was used to prepare all the solutions.

Preparation of gold microshells.

Gold nanoparticle synthesis. AuNPs were synthesized by following a procedure reported previously.[1] Sodium hydroxide (0.5 mL, 1 M) in water and 1 mL of THPC solution (prepared by adding 12 μL of 80% THPC in water) were added to 45 mL of deionized H_2O and stirred. Next, $HAuCl_4$ trihydrate (2.0 mL, 27 mmol) in water was added quickly to the solution and was stirred for 5 min. The color of the solution changed from colorless to brown. The resulting brown solution was stored in refrigerator at 4°C when not used immediately.

Attachment of AuNP seed layers to amine-terminated polystyrene beads (PS-NH_2).[2] 0.5 mL of PS-NH_2 solution and 5 mL water were mixed in a centrifuge tube. The mixture was centrifuged at 2000 rpm for 5 min and redispersed in water after the supernatant was removed. The PS-NH_2 solution was washed three more times and then redispersed in 5 mL water. After drying overnight in a vacuum oven, the PS-NH_2 (0.05 g) and 0.5 mL water were mixed in a centrifuge tube to prepare 10% PS-NH_2 dispersed in water. The PS-NH_2 solution was sonicated until PS-NH_2 was well dispersed in water. And then, 5 mL of colloidal AuNPs were added to the PS-NH_2 solution. The centrifuge tube was shaken gently for a few minutes and then kept quiescent for 2 h. The mixture solution was centrifuged at 2000 rpm for 5 min and the supernatant was decanted before 5 mL water was added. The sequential processes of centrifugation, decanting, and adding water were repeated several times. Finally the slightly red particles (PS-NH_2/AuNP) were dispersed again in 5 mL water. The solution was stored in refrigerator at 4°C,

when not used immediately.

Preparation of electroless Au plating solution. Potassium carbonate (250 mg, 0.018 mmol) was dissolved in 1000 mL of water in a reaction bottle. To an aqueous solution of potassium carbonate was added 15 mL of 1% $HAuCl_4$ under stirring. The color of the solution changed from pale yellow to colorless. This colorless solution was used in the electroless plating steps for gold microshells formation.

Functionalization of gold microshells with ss-DNA. 1 mg gold microshell was dispersed in 1 mL of 10% ethanol aqueous buffer solution (10 mM PBS, pH 7.4). For the preparation of DNA-modified gold microshell, the ss-DNA was incubated for 1 h in 1 mM TCEP to reduce disulfide bound oligomer. DNA-modified gold microshells were synthesized by incubating 100 μM of ss-DNA in 1 mL of the gold microshell solution. The final concentration of oligonucleotide was 3 μM. After standing for 48 h at room temperature, the samples were centrifuged and dispersed in 1 mL of 10% ethanol aqueous buffer solution (10 mM PBS, pH 7.4).

Trapping a DNA-modified single gold microshell at the tip of the micropipette and manipulation. Micropipettes were fabricated by heating and pulling borosilicate glass capillaries (Harvard Apparatus Inc., GC150F-10) in a laser-based micropipette puller device (Sutter Instruments Inc., P-2000) and stored in a petri dish on the top of an adhesive tape. At first, a DNA-modified single gold microshell placed on a slide glass. It follows that the DNA-modified single gold microshell on the slide glass was trapped at the end of a micropipette by pulling gently and released into a small drop of Hg^{2+} ion solution. SERS spectra of the DNA-modified gold microshell were obtained by

focusing the Raman laser probe through an optical microscope.

Instruments. SERS spectra were obtained using a homemade Ramboss Micro-Raman system spectrometer with a 632.8 nm line from a 20 mW He/Ne laser (Model LGK7665) as the excitation source. The homemade Ramboss Micro-Raman system spectrometer was equipped with a TE cooled (-50 °C) charged-coupled device (CCD) camera (1024×128 pixels). The laser beam was focused on a spot approximately 2 μm in diameter through an objective lens of ×100 magnification. The grating (1200 grooves mm^{-1}) and the slit provided a spectral resolution of 4 cm^{-1}. Calibration of the spectrometer was conducted using the Raman band of a silicon wafer at 520 cm^{-1}, with which the peak intensities of the adsorbates on gold microshells were normalized. Field Emission-Scanning Electron Microscopy (FE-SEM) measurements were made using a Hitachi S-4800 at an accelerating voltage of 15 kV.

References.

1. T. Pham, J. B. Jackson, N. J. Halas and T. R. Lee, *Langmuir*, 2002, **18**, 4915-4920.
2. S. L. Westcott, S. J. Oldenburg, T. R. Lee and N. J. Halas, *Langmuir*, 1998, **14**, 5396-5401.

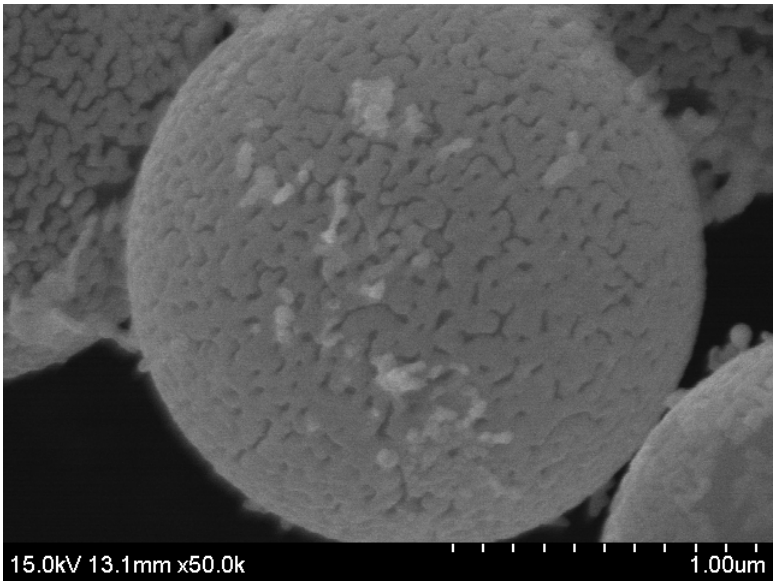

Fig. S1 Scanning electron microscopy (SEM) image of gold microshells composed of (PS-NH_2/AuNPs) with the diameter of 2 μm.