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Supporting info

Size Effect of Gold on Ag-coated Au nanoparticles- embedded silica nanospheres

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Experimental details

1.1 Materials

Tetraethylorthosilicate (TEOS), 3-mercaptopropyl trimethoxysilane (MPTS), (3-aminopropyl)triethoxysilane (APTES), silver nitrate (AgNO₃), Tetrakis(hydroxymethyl)phosphonium chloride (THPC), sodium tri-citrate, 50 mM HCl solution, 50 mM NaOH solution, sodium borohydride (NaBH₄), Gold (III) chloride trihydrate (HAuCl₄), ascorbic acid (AA), 4-aminobenzenethiol (4-ATP),

polyvinylpyrrolidone (PVP), 4-mercaptophenylboronic acid (MPBA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethyl alcohol (EtOH) and aqueous ammonium hydroxide (NH₄OH, 27 %) were purchased from Daejung (Siheung, Korea). All materials were used without further purification.

1.2 Preparation of aminated silica NSs.

Silica nanospheres (NSs) were prepared by the Stöber method.¹ Ammonium hydroxide (28%, 3 mL) and 1.6 mL TEOS were mixed with 40 mL absolute ethanol in a round bottle. The solution was stirred for 20 h at room temperature. The silica NSs were centrifuged at 8500 rpm for 15 min, washed with ethanol several times, dispersed in absolute ethanol and the volume adjusted to obtain a 50 mg mL⁻¹ silica NS solution. To obtain aminated silica NSs, APTES (200 μL) and ammonia solution (40 μL) were added to 4 mL silica NSs in ethanol (50 mg mL⁻¹). The mixture was stirred smoothly for 6 h at room temperature. To enhance the binding of APTES to silica NSs surface, the mixture was heated at 70°C for 1 h with gentle stirring. The aminated silica NSs were obtained by centrifugation at 8500 rpm for 15 min, washed with ethanol several times to remove excess reagents and dispersed in absolute ethanol to obtain a 1 mg mL⁻¹ aminated silica NS solution.

1.3 Preparation of Au NPs of various sizes

1.3.1 Au NPs of 2.5 nm diameter

Gold nanoparticles (Au NPs) of 2.5 nm were prepared by using chloroauric acid (HAuCl₃) and tetrakis(hydroxymethyl) phosphonium chloride (THPC) as a reducing agent. The THPC-capped Au NPs were prepared by a well-established method reported earlier by Duff *et al.*²

with slight modifications. In a round bottle, 47.5 mL of water, 1.5 mL of NaOH (0.2 M) and 12 μ L of THPC (80% in water) were stirred vigorously for 5 min at 25°C. Then, 1 mL of HAuCl₃ (50 mM) was added rapidly to the mixture. The color of mixture changed from yellow to dark brown, indicating the formation of Au NPs. The mixture was further stirred for 30 min. Before use, the reaction mixture was stored at low temperature for 3 days.

1.3.2 Au NPs of 7 nm diameter

Au NPs of 7 nm diameter were prepared by reduction of borohydride according to the well-established method reported by Martin *et al.*³ Briefly, 50 mM HAuCl₄ was prepared in 50 mM HCl (aqueous HAuCl₄ solution). NaBH₄ (50 mM) was prepared in 50 mM NaOH (aqueous NaBH₄ solution). Aqueous NaBH₄ solution (0.1 mL, 50 mM) was added to 10 mL water and stirred vigorously for 1 min at room temperature. Aqueous NaBH₄ solution (0.4 mL, 50 mM) was rapidly added to the solution. The color of the mixture changed from light yellow to red immediately, indicating the formation of Au NPs. Polyvinylpyrrolidone (10.5 mg) was added to the mixture and the pH adjusted to 8.5. Before use, the reaction mixture was stored in a refrigerator for 3 days.

1.3.3 Au NPs of 15 nm diameter

Au NPs of 15 nm diameter were prepared by reduction of sodium tri-citrate in water according to the well-established method reported by Turkevich.^{4, 5} Briefly, water (99 mL) and 25 mM HAuCl₄·3H₂O solution (1 mL) were added to an Erlenmeyer flask and stirred vigorously for 5 min at 100 °C. Then, 3.3% sodium tri-citrate solution was added rapidly to the mixture. The reaction mixture was stirred for a further 1 h and cooled to room

temperature. The mixture volume was adjusted to 100 mL. Polyvinylpyrrolidone (100 mg) was added to the mixture and pH was adjusted to 8.5. The solution was stored for 3 days before use.

1.4 Preparation of size dependent Au NPs-embedded silica nanospheres ($\text{SiO}_2\text{@Au}$ NSs)

A volume of 10 mL Au NP solution and 1 mL aminated SiO_2 solution (1 mg mL^{-1}) were mixed, sonicated for 20 min and stored in a shaking incubator overnight. Au NPs-embedded silica NSs were obtained by centrifugation at 8500 rpm for 15 min and washed several times with ethanol to remove unbound Au NPs. The $\text{SiO}_2\text{@Au}$ NSs were dispersed in 1 mL absolute ethanol to obtain an $\text{SiO}_2\text{@Au}$ solution (1 mg mL^{-1}).

1.5 Preparation of Au@Ag NPs-embedded silica NSs ($\text{SiO}_2\text{@Au@Ag}$ NSs)

Au@Ag NPs-embedded silica NSs ($\text{SiO}_2\text{@Au@Ag}$ NSs) were prepared in aqueous solution by reducing silver nitrate on Au NPs by ascorbic acid (AA) in the presence of PVP. Briefly, 0.2 mg of the $\text{SiO}_2\text{@Au}$ NSs was dispersed in 9.8 mL water containing 10 mg PVP and kept still for 30 min. Then, 20 μL of AgNO_3 (10 mM) were added to the mixture, followed by 40 μL of AA (10 mM). The mixture was incubated for 15 min to reduce Ag ion to Ag metal. This process was repeated to obtain AgNO_3 solutions with concentrations of 50, 100, 200, 300, 400 and 500 μM . The $\text{SiO}_2\text{@Au@Ag}$ NSs were centrifuged at 8500 rpm for 15 min and washed several times with ethanol to remove excess reagent. The $\text{SiO}_2\text{@Au@Ag}$ NSs were dispersed in 1.0 mL absolute ethanol to obtain a 0.2 mg mL^{-1} $\text{SiO}_2\text{@Au@Ag}$ NS solution.

1.6 Incorporation of Raman reporter materials into $\text{SiO}_2\text{@Au@Ag}$ NSs

The SiO₂@Au@Ag NSs were modified with 4-ATP as Raman labels. 4-ATP solution (1 mL, 10 mM in EtOH) was added to SiO₂@Au@Ag NPs (0.2 mg). The suspension was stirred vigorously for 2 h at room temperature. The colloids were centrifuged and washed several times with ethanol. The pellet was dispersed in 1 mL ethanol to obtain 0.2 mg SiO₂@Au@Ag NSs modified with 4-ATP.

1.7 Characterization of the SiO₂@Au@Ag NSs

To investigate the morphology and structure of SiO₂@Au@Ag NSs, we performed transmission electron microscope (TEM) measurements using a Libra 120 (Carl Zeiss, Germany) microscope operated at an accelerating voltage of 120 kV. For the optical characterization, UV-vis spectra of the SiO₂@Au@Ag NSs were recorded on an Optizen Pop spectrophotometer (Mecasys, Korea) in the range 300 to 800 nm. Raman measurements were conducted using a Dispersive Raman Microscope (DXR Raman Microscope, Thermo Fisher Scientific).

1.8 UV-vis spectrum measurement

The SiO₂@Au@Ag NSs was dispersed and diluted in ethanol solution to obtain the final concentration of 0.1 mg/mL. Subsequently, the SiO₂@Au@Ag NSs was measured UV-vis spectroscopy in the range of 300 to 800 nm with scanning step of 1 nm/s.

1.9 SERS measurement

For SERS measurements, SiO₂@Au@Ag NSs were spread on a glass slide by the drop-cast method. SERS signals were collected in a back-scattering geometry using a ×10 objective lens and detected by a spectrometer equipped with a thermoelectric cooled CCD detector. As a photo-excitation source, a 532 nm diode-pumped solid-state laser (CL532-100-S,

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Crystalaser, USA) was used with a laser power of 10 mW at the sample. The beam size of the spot was $\sim 2 \mu\text{m}$. Single-particles were randomly selected and measured. The acquisition time was 5 s and the scan time was 16 s for each measuring position.

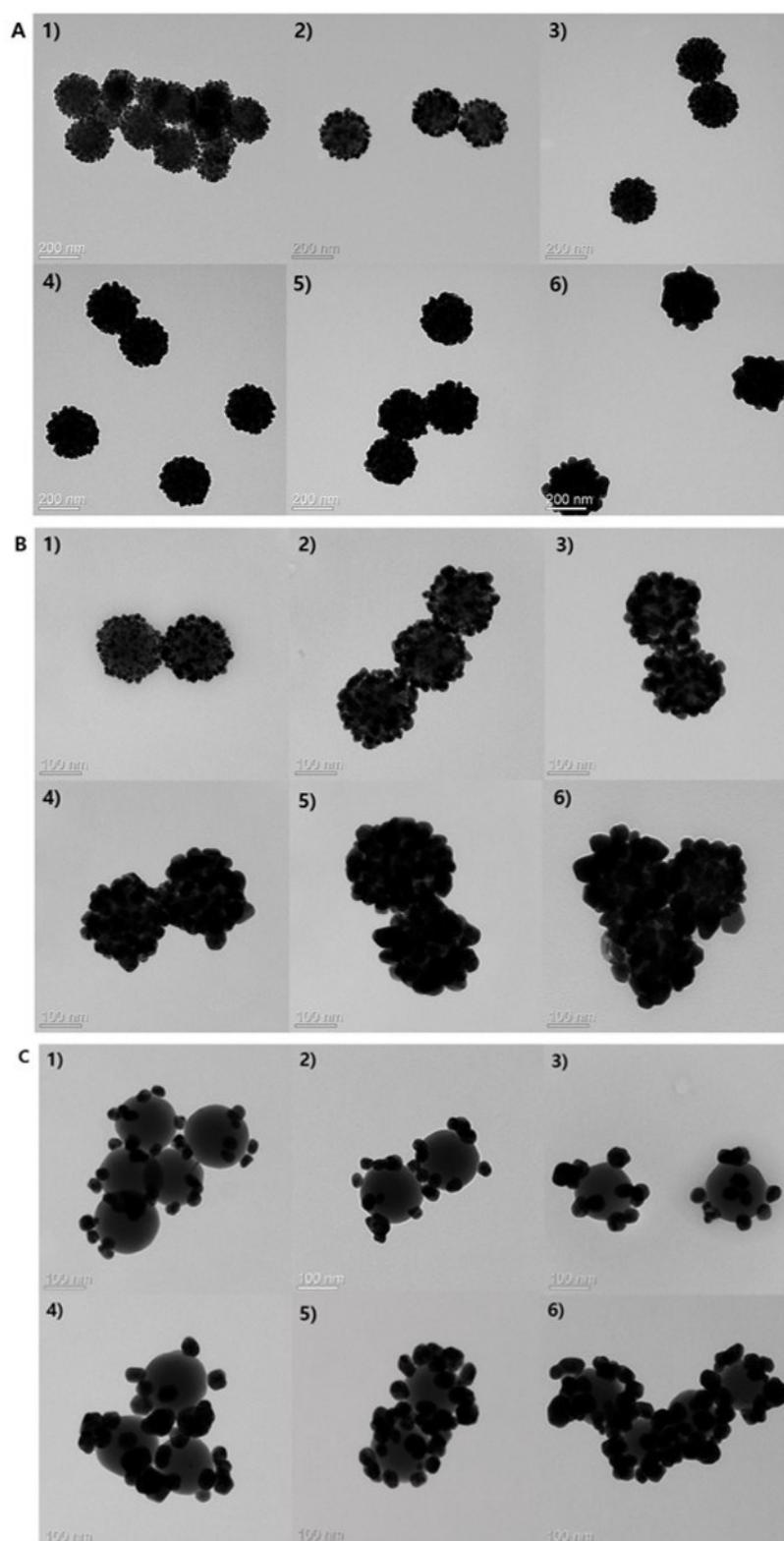


Fig S1. Transmission electron microscopic images (TEM) of the SiO₂@Au@Ag NSs prepared with various concentration of AgNO₃. The Au NPs size is (A) 2.5 nm, (B) 7 nm, (C) 15 nm. AgNO₃ concentration is (1) 50 μM, (2) 100 μM, (3) 200 μM, (4) 300 μM, (5) 400 μM, (6) 500 μM

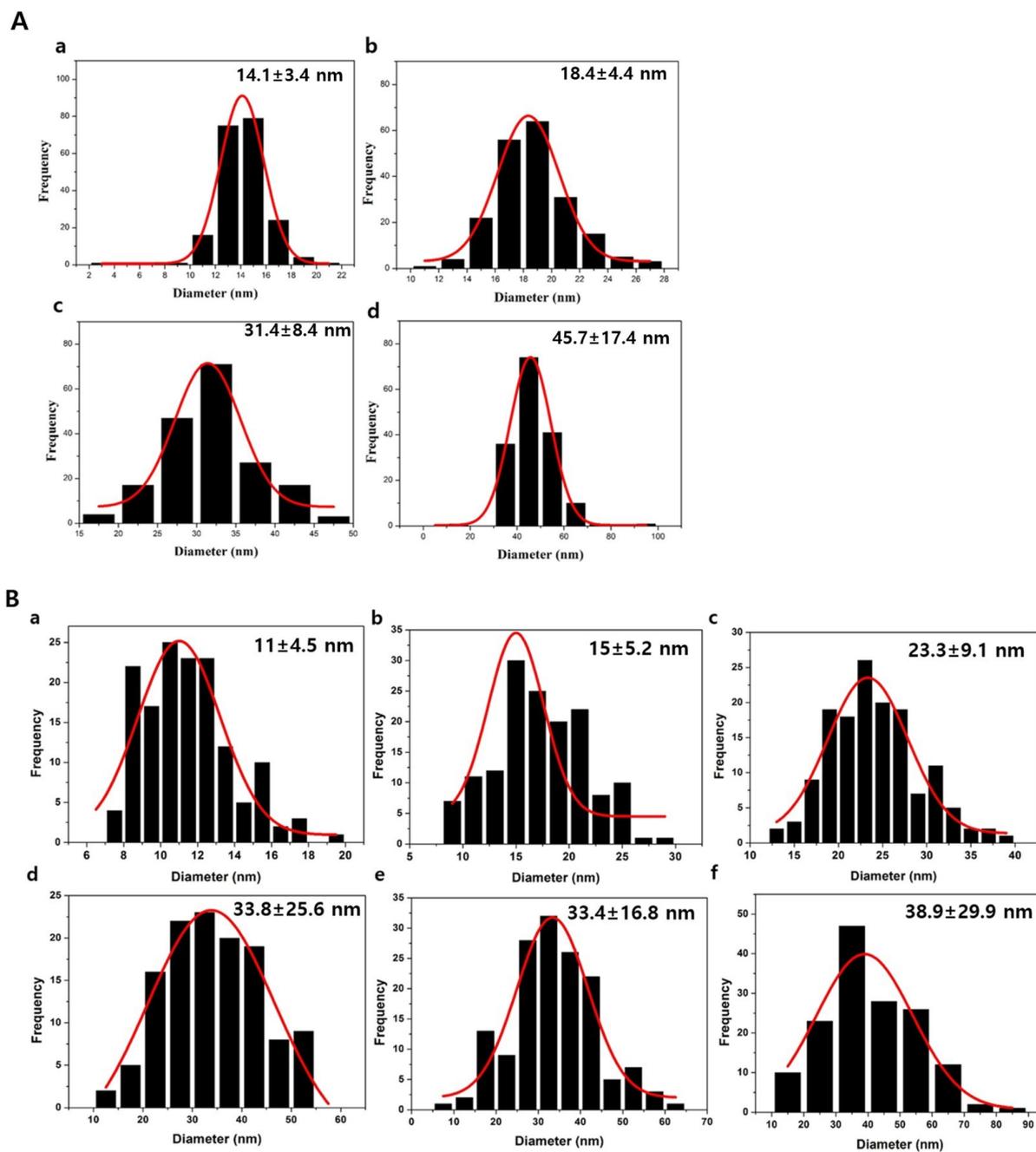


Fig S2. Histograms of the diameters of the Au@Ag NPs on the SiO₂@Au@Ag NSs prepared with various concentration of AgNO₃. The Au NPs size is (A) 2.5nm, (B) 7 nm. AgNO₃ concentration is (a) 50 μM, (b) 100 μM, (c) 200 μM, (d) 300 μM, (e) 400 μM, (f) 500 μM

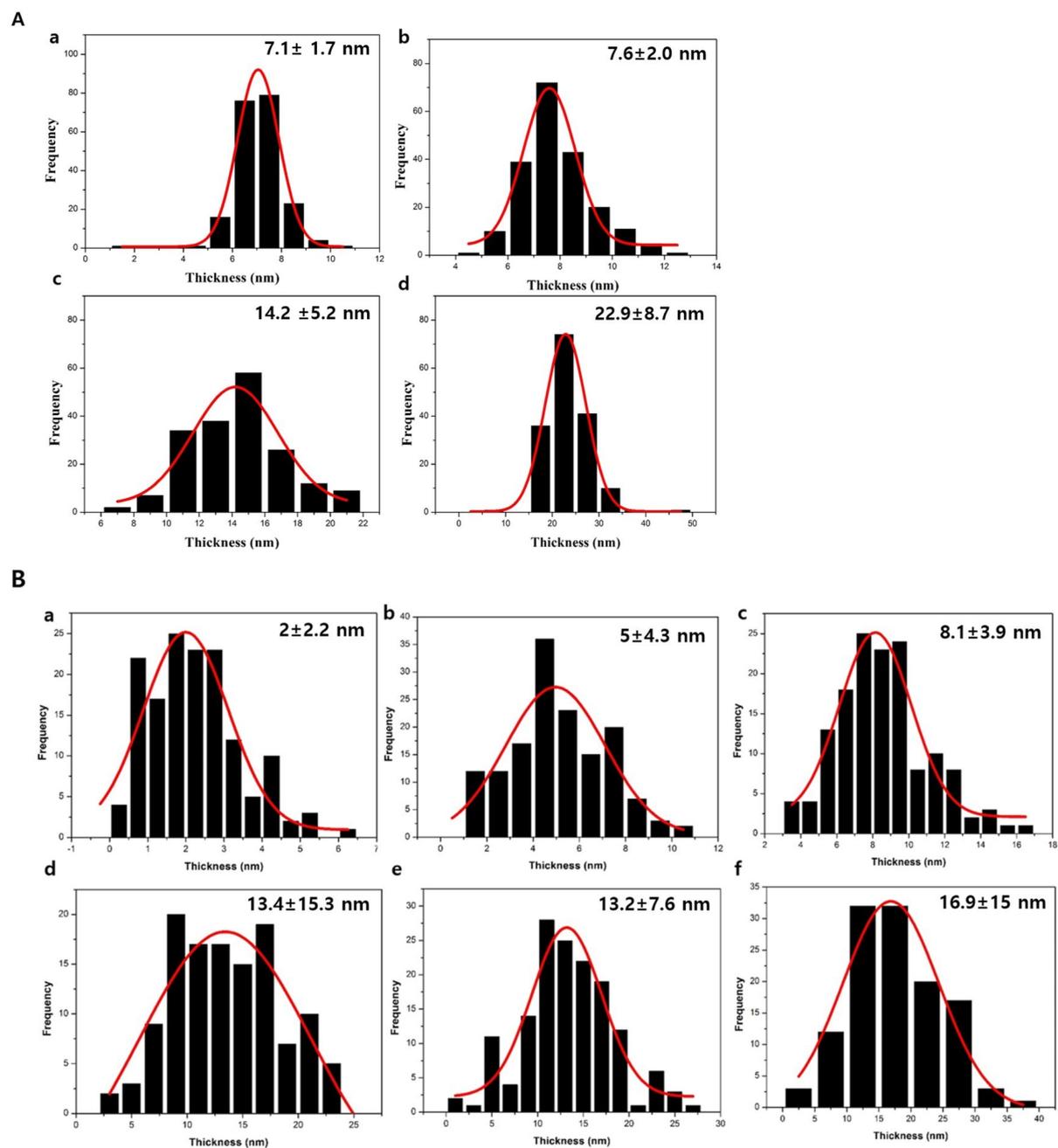


Fig S3. Histograms of the Ag shell thickness on SiO₂@Au@Ag NSs prepared with various concentration of AgNO₃. The Au NPs size is (A) 2.5 nm, (B) 7 nm. AgNO₃ concentration is (a) 50 μM, (b) 100 μM, (c) 200 μM, (d) 300 μM, (e) 400 μM, (f) 500 μM.

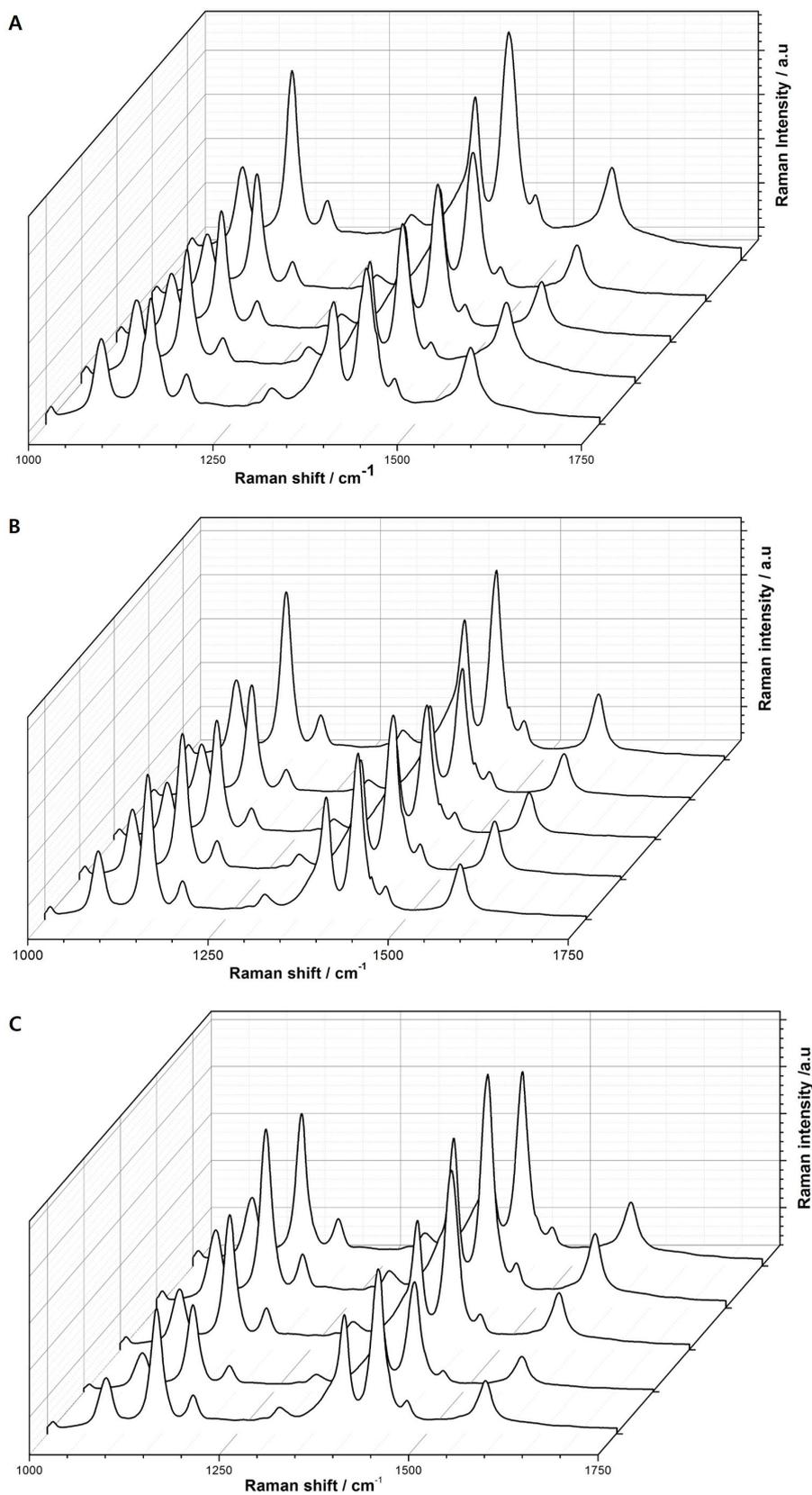


Fig S4. SERS spectra of 4-ATP according to the 300 μM (A), 400 μM (B, C) of AgNO_3 concentration of the $\text{SiO}_2@\text{Au}@\text{Ag}$ NSs prepared from 2.5 nm (A), 7 nm (B) and 15 nm (C) Au NPs. The spectral range of 1000-1750 cm^{-1} .

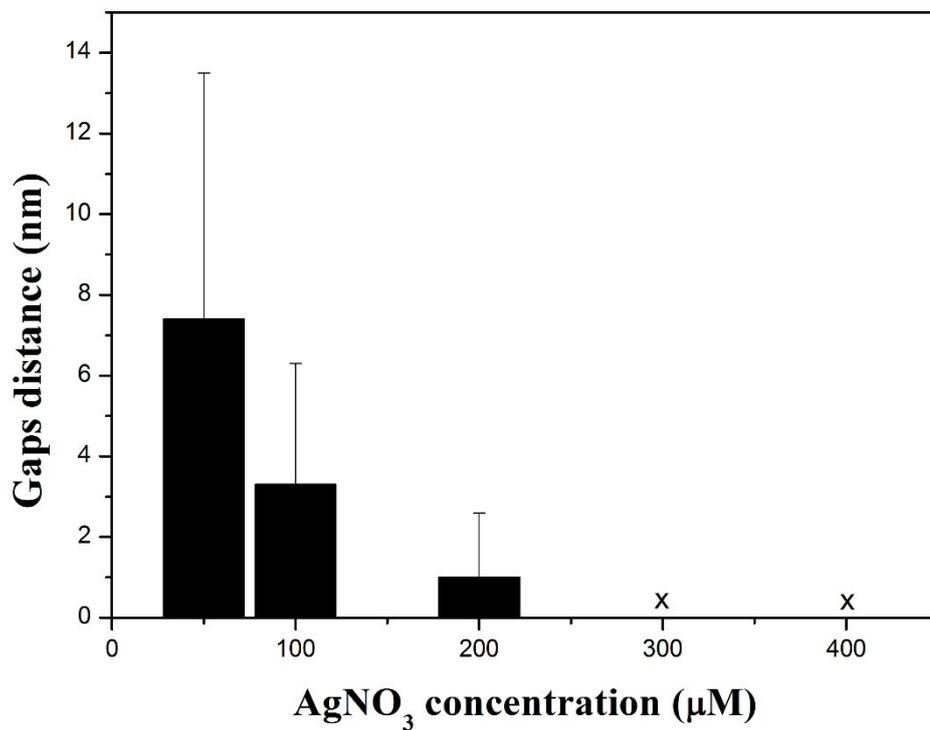


Figure S5. Effect of AgNO₃ concentration on the gaps distance between two Au@Ag NPs on the surface of the SiO₂@Au@Ag NSs prepared from 2.5 nm Au NPs.

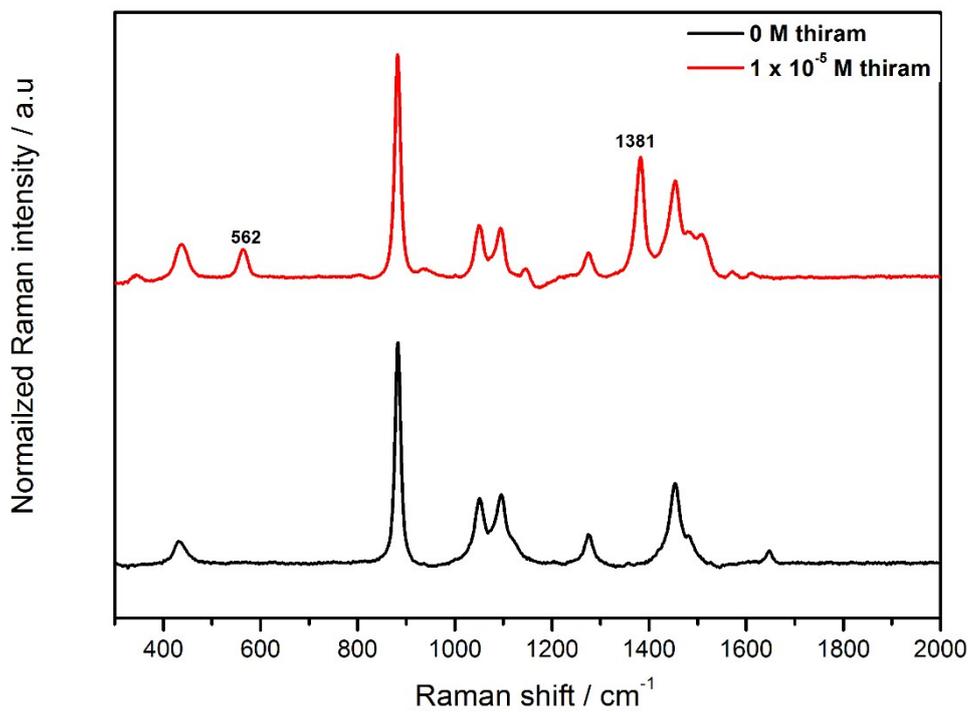


Fig S6. Detection of thiram using the $\text{SiO}_2@\text{Au}@\text{Ag}$ NSs prepared from 7 nm Au NPs.

Reference

1. I. A. Ibrahim, A. Zikry and M. A. Sharaf, *J. Am. Sci*, 2010, 6, 985-989.
2. D. G. Duff, A. Baiker and P. P. Edwards, *Langmuir*, 1993, 9, 2301-2309.
3. M. N. Martin, J. I. Basham, P. Chando and S.-K. Eah, *Langmuir*, 2010, 26, 7410-7417.
4. G. Frens, *Nature*, 1973, 241, 20-22.
5. J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot and A. Plech, *The Journal of Physical Chemistry B*, 2006, 110, 15700-15707.