

Facile synthesis of uniform interior nanogaps with controllable sizes by using galvanic reaction between Au and Ag

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Experimental Section

Chemicals: Hydrogen tetrachloroaurate solution (HAuCl₄, 30 wt. % in dilute HCl), silver nitrate, sodium citrate dihydrate (>99%), ascorbic acid, ammonia hydroxide, 4-mercaptopyridine, 4-mercaptobenzoic acid, and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich (St Louis, MO) and used without any purification. All the ultrapure water (18.2 MΩ/cm) was prepared from a Millipore water purification system (Milli-Q water system)

Synthesis of spherical Au NPs with 28.9-nm size: A volume of 42.0 μL of HAuCl₄ (30 wt. % in dilute HCl) was added into 200 mL of ultrapure water and heated to boiling under vigorous stirring for 5 min. The solution was kept boiling for another 15 min after the quick injection of sodium citrate solution (1%, 2.8 mL). Finally, a wine red solution was produced and cooled to room temperature for further use.

Synthesis of Au/Ag core/shell NPs with different shell thickness: 10 mL of as-prepared Au NPs were mixed with 1.5 mL of fresh ascorbic acid solution (0.1 M) in a 50 mL tube. The tube was kept shaking by a vortex shaker under a speed of 400 rpm. Then 3 mL of AgNO₃ solution was dropwise added into the tube with a speed of one drop per 20 s. After the addition of AgNO₃, the mixture was kept shaking for another 30 min to complete the reaction. Silver nitrate was reduced by ascorbic acid and the silver was deposited on the surface of Au NPs using the Au NPs as

seeds. The successful coating of Ag on the Au NPs was evidenced by the color change of solution from red to yellow. Ag shell with different thickness was synthesized by varying the Ag concentration (0.33 mM to 4 mM). The as-prepared Au/Ag core/shell NPs were directly used in the following steps as a stock solution without any dilutions and purifications.

Synthesis of uniform nanogaps using the Au/Ag core/shell NPs: 0.5 mL of Au/Ag core/shell NPs were mixed with 0.5 mL of CTAB solution (0.1 M) in a 10 mL glass tube. Then 0.5 mL of H₂AuCl₄ (0.5 - 2.2 mM) solution was dropwise added into the mixture in 30 s under vortexing. The mixture was kept shaking at a speed of 400 rpm for 3 min. The stripping of Ag shell and growth of Au/Ag shell was evidenced by the color change from yellow to orange, and finally to pink. The galvanic reaction was completed in 3 min. After the reaction, the mixture was kept undisturbed at room temperature for at least 5 h, allowing for fully reduction of H₂AuCl₄ by ascorbic acid. The nanoparticles are stable at room temperature for at least three months. Before characterization, 1.0 mL of NPs was centrifuged at 8000 rpm for 4 min and the supernatant was discarded. The reddish precipitate was dispersed in 0.25 mL of ultrapure water.

Characterization by electron microscopy: The sample (2.0 μL) was directly placed on the copper/carbon grids and dried at room temperature for characterization by TEM and HRTEM/STEM. The TEM images were taken by a JEOL electron microscopy (JEOL 1400) operated at an accelerating voltage of 120 kV. The HRTEM/STEM images were recorded by a Tecnai F20 scanning transmission electron microscope operated at an accelerating voltage of 200 kV. The average diameter of NPs was calculated by ImageJ 1.45 (available at <http://rsb.info.nih.gov/ij/>).

Calculation of electromagnetic field: A 3D finite element model was developed to solve time-harmonic Maxwell equations with given boundary condition for the interior nanogap and a single spherical nanoparticle by using a commercial FEM software COMSOL. Linearly (x) polarized plane wave ($\lambda = 633$ nm) was incident on the interior nanogap and a single nanoparticle respectively. Herein, we assume the core and shell are made by pure gold because only a small amount of silver was present in the shell. The empirical dielectric constants of gold was provided by Johnson and Christy with interpolation.

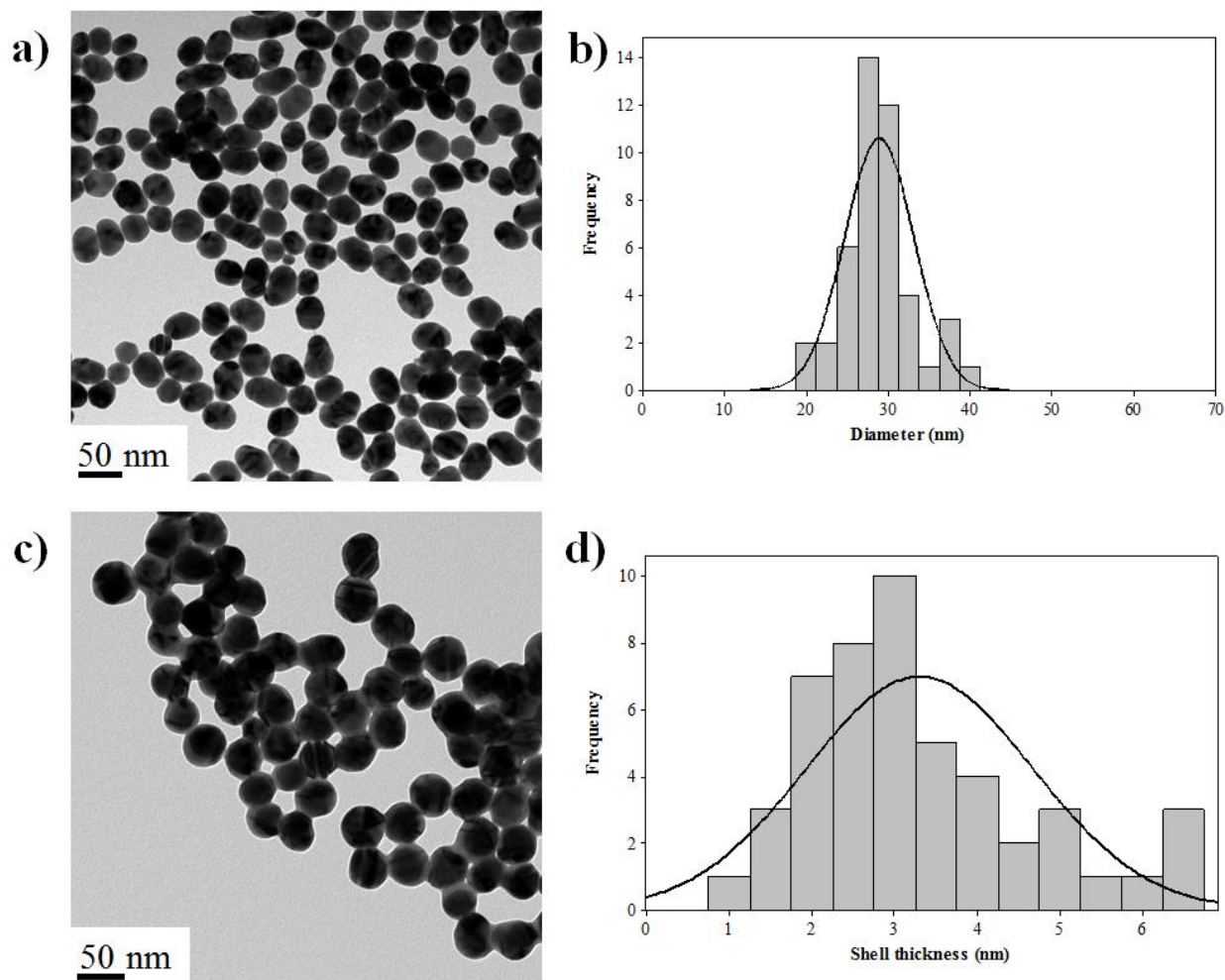
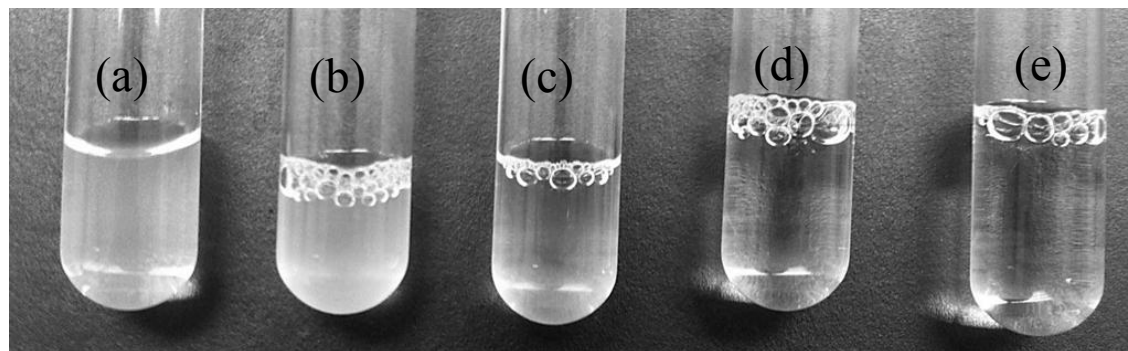


Figure S1. TEM images and size distribution of Au and Au/Ag core/shell NPs: (a) TEM image of gold NPs; (b) size distribution of gold NPs (28.9 ± 3.4 nm) determined by imageJ software; (c) TEM image of Au/Ag core/shell NPs; and (d) size distribution of the Ag shell thickness (3.30 ± 1.34 nm) determined by imageJ software.



Ag:CTAB=0 Ag:CTAB=1:25 Ag:CTAB=1:50 Ag:CTAB=1:75 Ag:CTAB=1:100

Figure S2. Solubility of AgCl in water and CTAB solution. Silver nitrate (2 mM, 1 mL) was mixed with different volumes of CTAB (0.1 M). Then excess NaCl (0.5 mL, 100 mM) was added into the mixture. Molar ratio of Ag NO₃ to CTAB: (a) 0; (b) 1:25; (c) 1:50; (d) 1:75; and (e) 1:100.

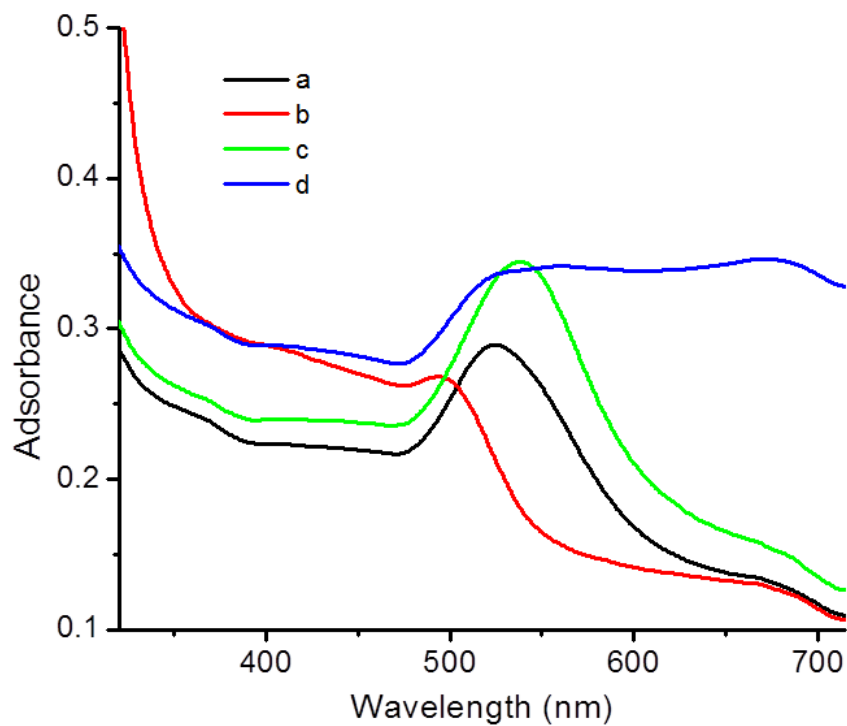


Figure S3. LSPR properties: (a) gold NPs; (b) Au/Ag core/shell NPs; (c) NP with interior nanogap obtained by mixing Au/Ag core/shell NPs with H_{AuCl}₄ in CTAB solution; and (d) NP with huge gap obtained by mixing Au/Ag core/shell NPs with H_{AuCl}₄ in aqueous solution.

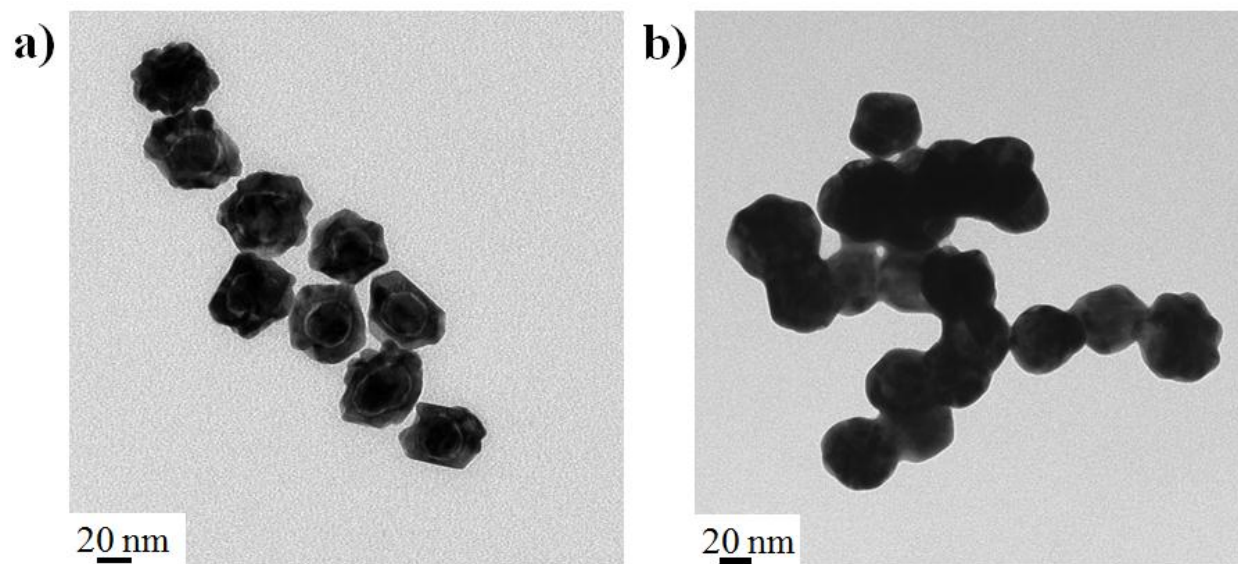


Figure S4. TEM images of Au/Ag core/shell NPs (500 μL) after mixing with 500 μL of HAuCl_4 (1.0 mM) in presence of: (a) 500 μL of CTAB (10 mM) and (b) 500 μL of NH_4OH (25%).

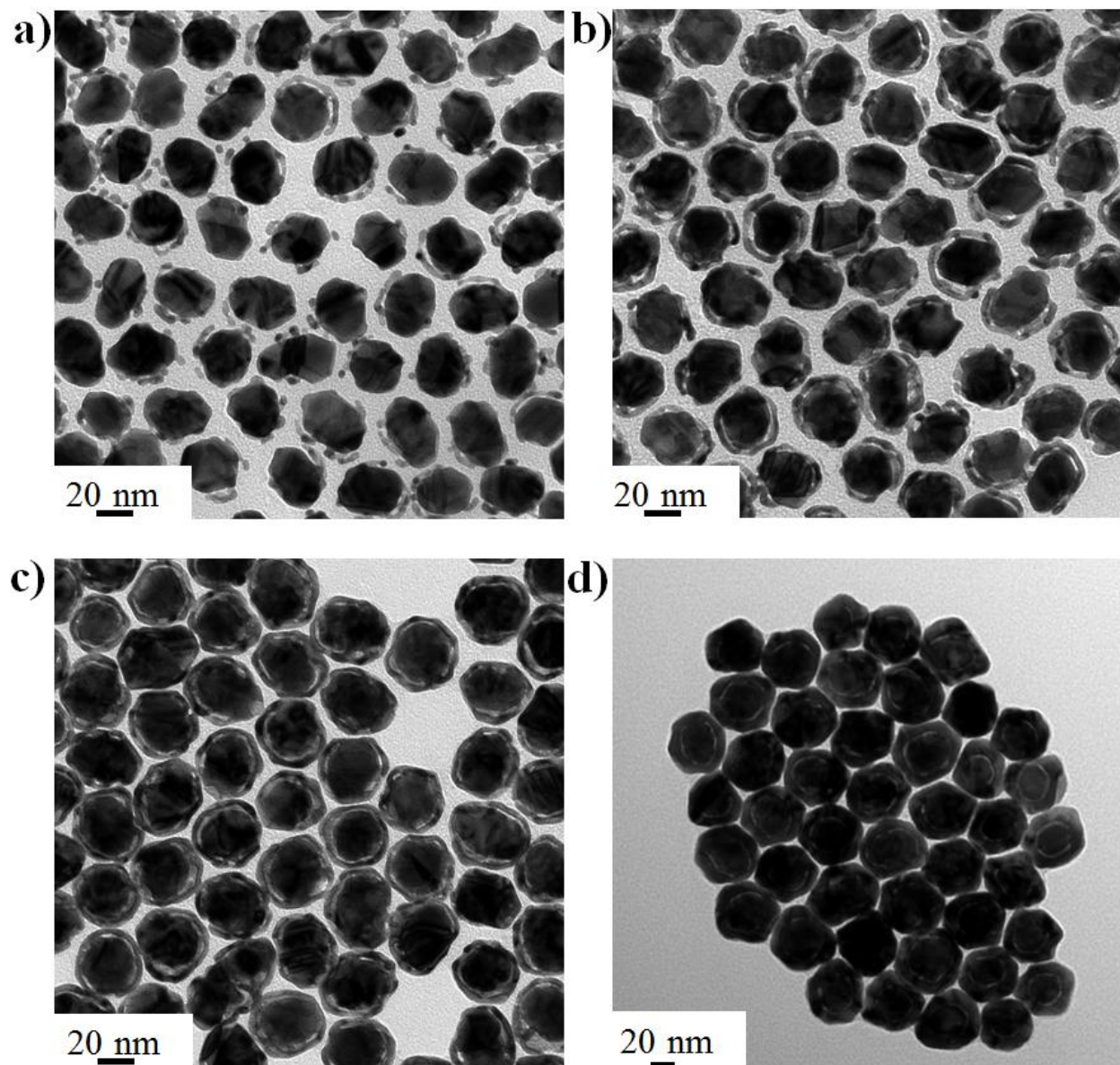


Figure S5. TEM images of Au/Ag core/shell NPs (500 μL) after reacting with different amount of HAuCl_4 (1.0 mM): (a) 30 μL ; (b) 45 μL ; (c) 60 μL ; and (d) 300 μL .

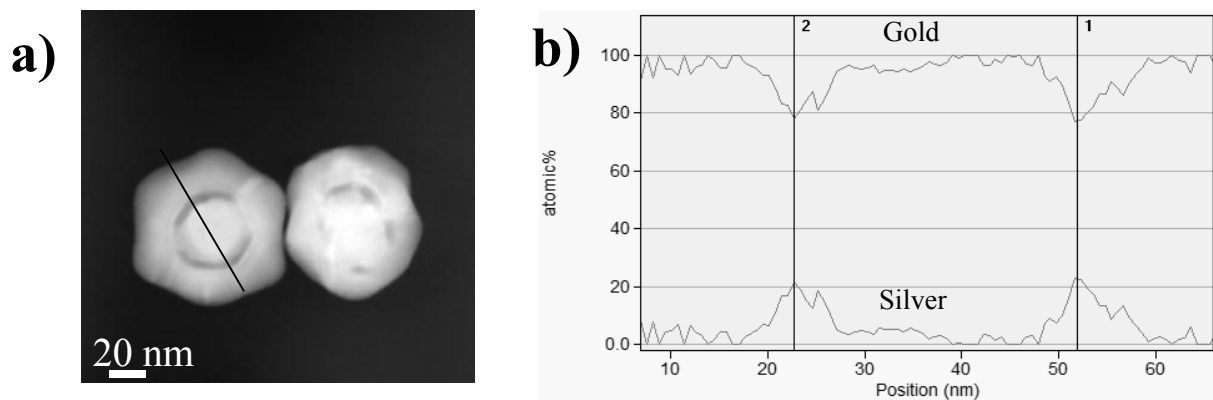


Figure S6. (a) STEM image of typical NPs with interior nanogap; (b) percentage of gold and silver in the NP determined by EDS line scanning.

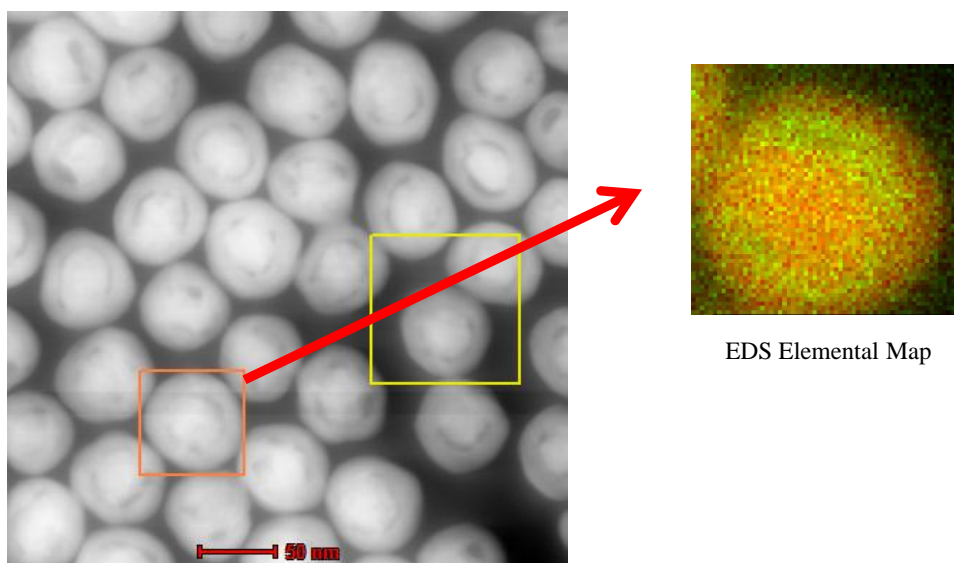


Figure S7. STEM image and EDS elemental map of a single NP with interior nanogap. Green dots and red dots represent silver and gold, respectively. The nanoparticle in yellow frame were used as drift correction for the EDS mapping of the nanoparticle in orange frame.

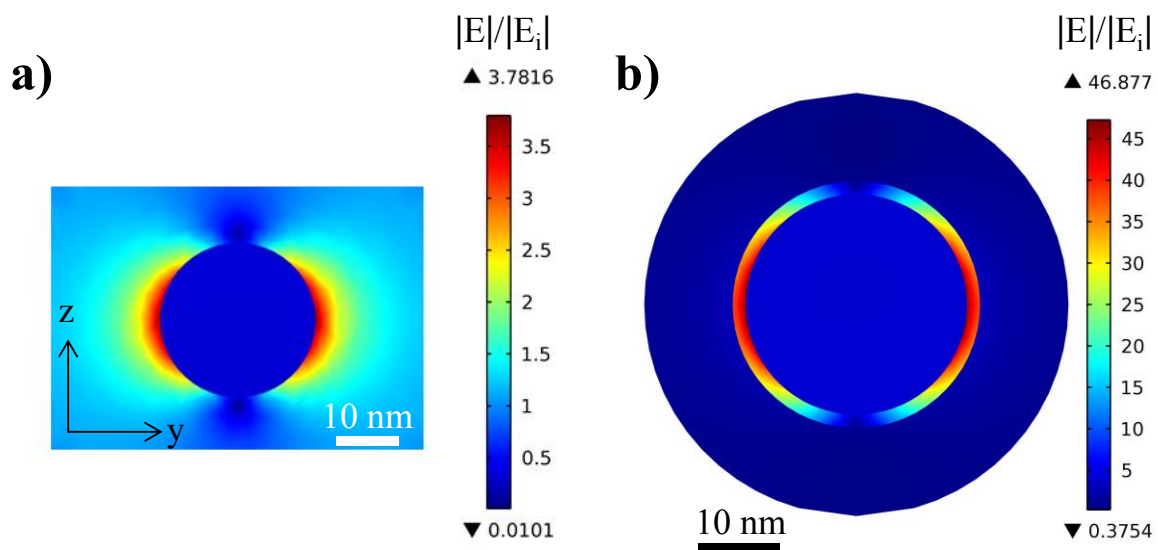
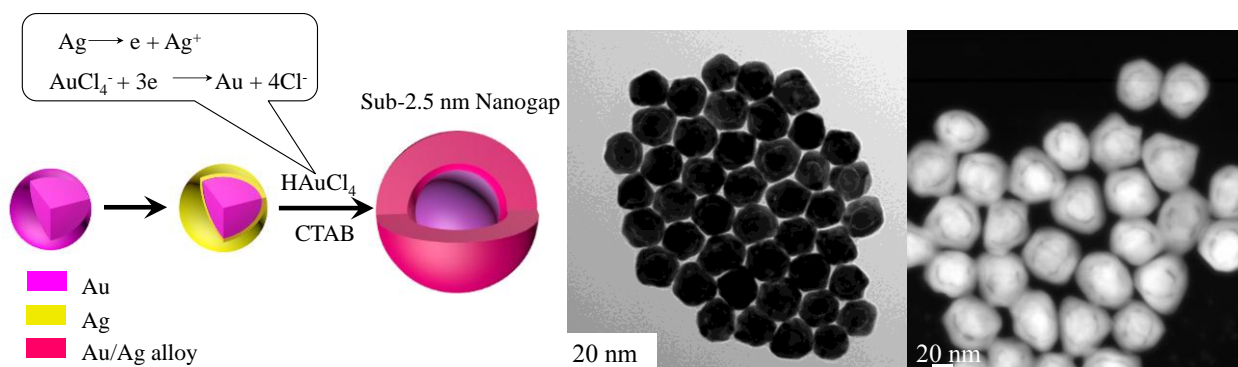


Figure S8. Electromagnetic field of a single nanoparticle (25 nm) and the nanogap (1.5 nm) between a 25-nm core and 10-nm shell nanoparticle.

Graphic Abstract



Uniform sub-2.5 nm nanogaps with controllable size were fabricated based on the galvanic reaction of HAuCl_4 and Ag shell of Au/Ag core/shell NPs in presence of CTAB. The size of nanogap (0.9 -2.5 nm) could be easily tuned by varying the shell thickness of Au/Ag core/shell precursor. This is the first study about fabrication of interior nanogaps with controllable sizes.