

Supporting information

Self-assembly of subwavelength nanostructures with symmetry breaking in solution

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Materials and Methods

Synthesis of Au nanospheres with different diameters. The seed solution was prepared as follows: 100 μl of 1% (w/v) HAuCl_4 was added to 9 ml of 28 mM trisodium citrate (TSC) solution. 300 μl of 100 mM NaBH_4 was added to the above solution under vigorous stirring. The stirring was continued for 30 min and then aged for two hours. The diameter of the seeds was about 3.5 nm. The seed solution can be used to prepare 20 nm Au nanospheres. For example, 214 μl of the 3.5 nm seed solution was diluted to 20 ml. 10 ml of 0.04% (w/v) HAuCl_4 and 10 ml of 0.05% (w/v) ascorbic acid (AA) and 0.025% (w/v) TSC mixture were added separately through a two-channel pump at a speed of 200 $\mu\text{l}/\text{min}$. When the addition finished, the mixture was heated at 120 $^\circ\text{C}$ for one hour, then cooled down to room temperature. The 20 nm Au nanospheres were further used to grow 43 nm Au nanospheres. Then the 43 nm Au nanospheres were used as seeds to grow 86 nm Au nanospheres. Following this way, 120, 160, and 220 nm Au nanospheres were synthesized successively. The concentrations of Au nanoparticles are determined based on the amount of HAuCl_4 used and the diameters of the nanoparticles.

Synthesis of Ag nanocubes with different edge lengths. First, 20 ml of 1, 5-pentanediol was heated for 10 min in an oil bath at 193 $^\circ\text{C}$. Then two precursor solutions were added through a two channel pump with a speed of 250 $\mu\text{l}/\text{min}$. One of the precursor solutions was prepared by dissolving 0.4 g silver nitrate and 0.36 or 0.54 mg Cu_2Cl into 10 ml 1, 5-pentanediol. The other precursor solution was prepared by dissolving 0.2 g of poly(vinylpyrrolidinone) into 10 ml of 1, 5-pentanediol. Ag nanocubes with different sizes were acquired by adjusting the amount of Cu_2Cl and quenching the reaction at different time points. As for the amount of Cu_2Cl fixed at 0.36 mg, 100 nm Ag nanocubes were collected by quenching the reaction once the color of the solution turned into pinkish orange color. 120 nm Ag nanocubes were collected one min later

from the time when the color changed to pinkish orange. 140 and 160 nm Ag nanocubes were synthesized by increasing the amount of Cu_2Cl to 0.54 mg. The Ag nanocubes were isolated through centrifugation and stored in 5 ml ethanol for further use. The concentrations of the Ag nanocubes are determined through ICP-AES.

Coating the Au nanospheres with ultrathin silica shells using MBA as the coupling agent.

In a typical synthesis, 3 ml of 120 nm Au nanospheres was centrifuged once at 3000 rpm for 10 min to remove the supernatant. The sediment was redispersed into 1 ml of 10 μM MBA aqueous solution. The mixture was kept at 60 $^\circ\text{C}$ for 1 h to make the ligand exchange complete. 20 μl of 0.54% sodium silicate solution with pH of 9 was added and kept at 90 $^\circ\text{C}$ for 1 h to grow silica shells with thickness around 1 nm. The silica shells with thickness about 2 nm were coated on the Au nanospheres when the reaction time was extended to 2 hours. The mixture was centrifuged two times at 3000 rpm and dispersed in 0.5 ml ethanol.

Coating the Au nanospheres with ultrathin silica shells using APTES as the coupling agent. 3 ml of 120 nm Au nanospheres was centrifuged once at 3000 rpm for 10 min to remove the supernatant. The sediment was redispersed into 1 ml of 20 μM APTES aqueous solution. The mixture was shook for 10 min at room temperature. Next, 100 μl of 0.54% sodium silicate solution with pH of 9.6 was added and the mixture was kept at 90 $^\circ\text{C}$ for 1 h to grow 4 nm thickness silica shells. 8 nm thickness silica shells was synthesized by adding the 100 μl sodium silicate solution again and kept at 90 $^\circ\text{C}$ for another 1 h. The mixture was centrifuged two times at 3000 rpm and dispersed in 1 ml ethanol.

The self-assembly of subwavelength asymmetry nanostructures with gaps below 2 nm. 0.2 ml of purified Ag nanocubes was added to the 0.5 ml of Au@SiO_2 ethanol solution under

ultrasonic bath for 5 min. The assembled product was directly used for TEM characterization without further centrifugation isolation.

The self-assembly of subwavelength asymmetry nanostructures with gaps above 2 nm. 1 ml of 1 mM APTES ethanol solution was added to the 1 ml of Au@SiO₂ ethanol solution and stirred for 24 h at room temperature. The mixture was then centrifuged four times to remove all the free APTES in solution. The Au@SiO₂ modified with APTES was kept in 0.5 ml ethanol, and 0.2 ml of Ag nanocubes was added under ultrasonic bath for 2 min. The assembled product was directly used for TEM characterization without further centrifugation isolation.

Stabilization of Au-Ag nanostructures with thick silica shells. In a typical synthesis, when the self-assembly process was complete, 750 μ l ethanol, 20 μ l TEOS, 160 μ l H₂O, 10 μ l NaOH were added in situ to grow the stabilizing shells. The mixture was kept in an ultrasonic bath for two hours and then centrifuged three times for the optical and structure characterization.

Single-particle scattering spectroscopy correlated with TEM characterization. 5 μ l of the self-assembled nanostructures stabilized with thick silica shells in ethanol was dropped on a support film of a TEM grid with reference. The TEM grid was placed on a piece of quartz glass slide. The illumination light from the lamp passed through a dark-field condenser (NA 0.85) and then focused at the specimen plane. The light from individual single scattering spots was collected with a 63 \times objective (NA 0.7) at the bottom. The scattering spectra were recorded on a confocal Raman spectrograph (inVia Renishaw, UK). To obtain linearly polarized illumination, a linear polarizer was placed between the field diaphragm and the condenser. The polarization direction was changed by rotating the polarizer from 0° to 360° with an increment of 20°. Scattering spectra were corrected and normalized by signal collected from a nearby region

without nanoparticles. Each scattering spot was further characterized by TEM, following the guide of the references of the TEM grid.

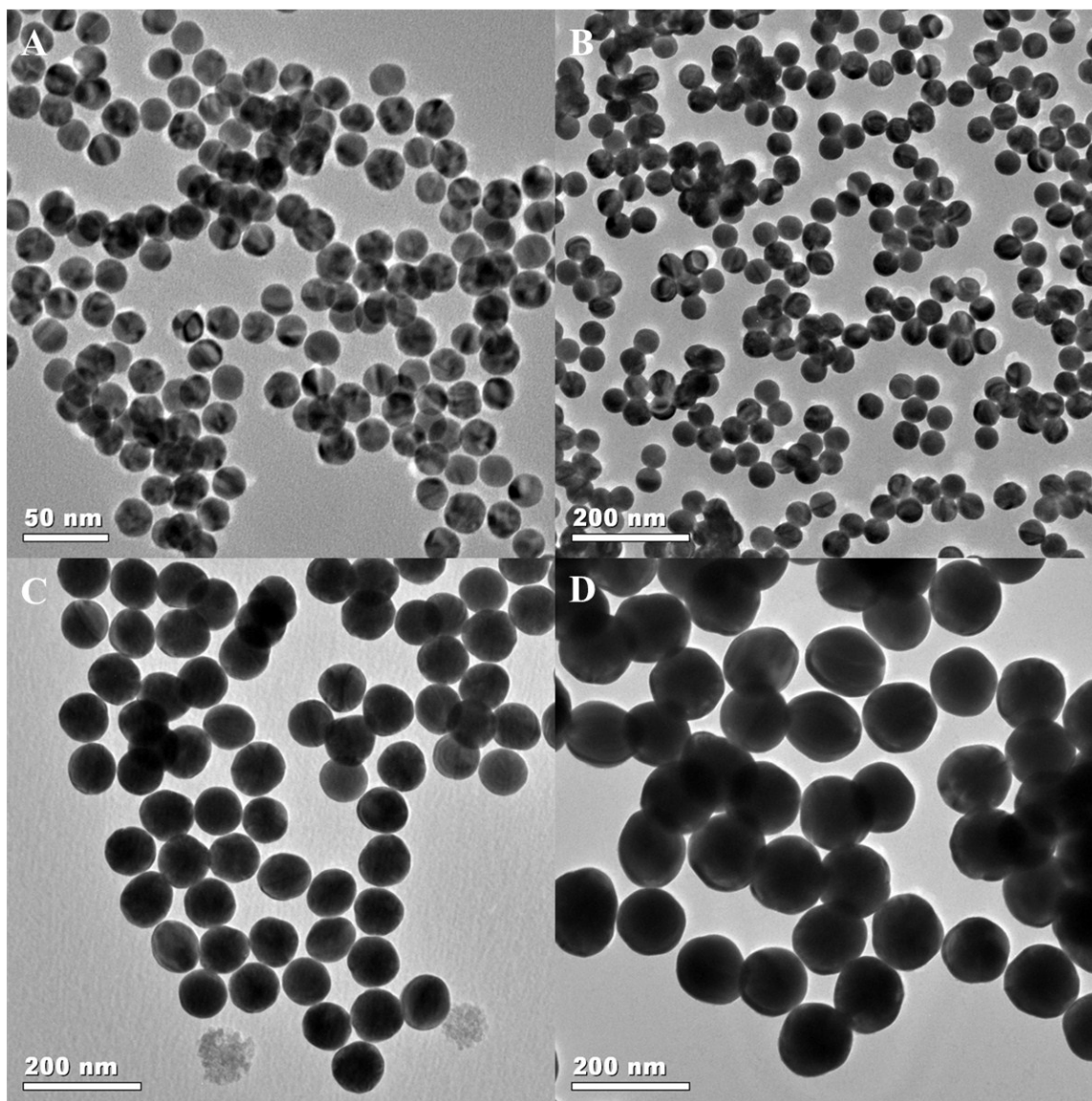


Figure S1. TEM images of Au nanospheres with different diameters: (A) 19 nm, (B) 43 nm, (C) 86 nm, and (D) 128 nm.

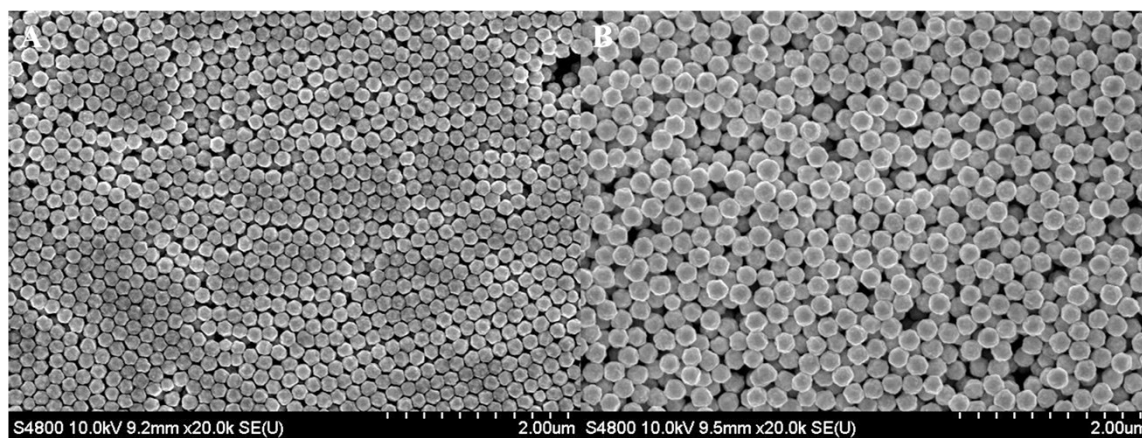


Figure S2. SEM images of Au nanospheres with different diameters: (A) 160 nm, (B) 220 nm.

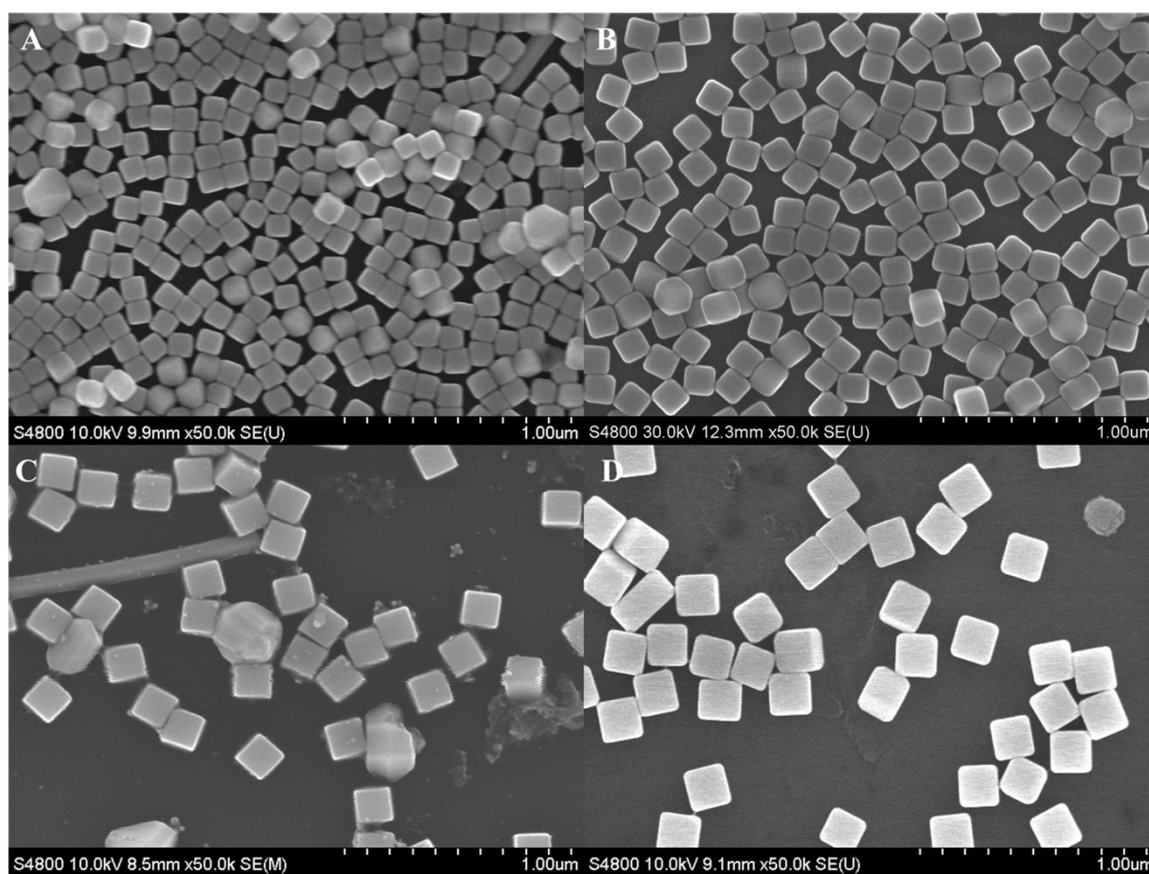


Figure S3. SEM images of Ag nanocubes with different edge lengths: (A) 100 nm, (B) 120 nm, (C) 140 nm, and (D) 160 nm.

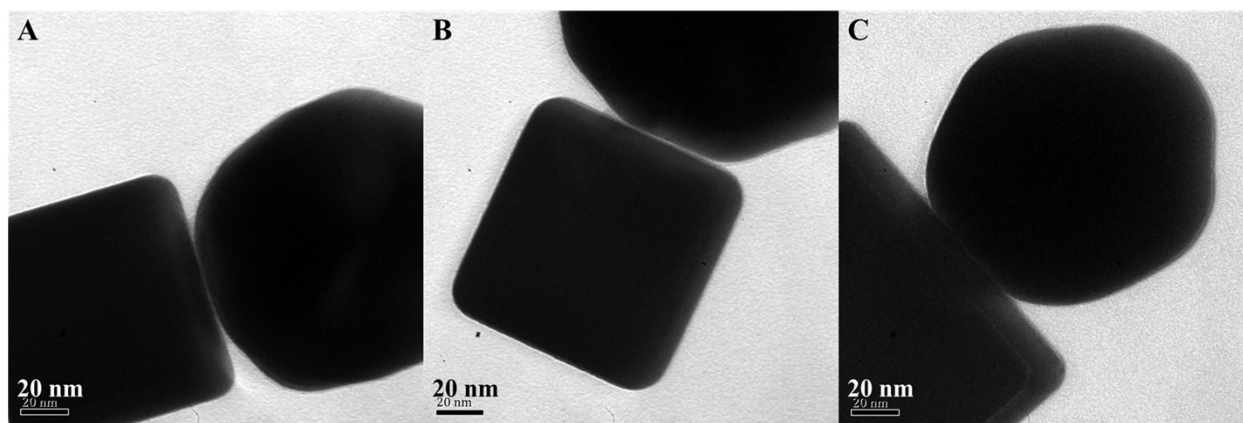


Figure S4. TEM images of the gaps of the samples shown in Figure 2 of the main text. The gaps for all samples are controlled around 1 nm by the ultrathin silica shells. (A) The diameter of the Au nanospheres is about 125 nm, the edge length of the Ag nanocubes is about 100 nm. (B) Au nanospheres: 220 nm, Ag nanocubes: 100 nm. (C) Au nanospheres: 120 nm, Ag nanocubes: 140 nm.

Table S1. The assembly yields for the Au-Ag dimer and Au-(Ag)₂ trimer nanostructures (among 300 nanoparticles)

Types	90 nm Au@100 nm Ag		120 nm Au@100 nm Ag		220 nm Au@100 nm Ag		120 nm Au@140 nm Ag	
Nanostructures	dimer	trimer	dimer	trimer	dimer	trimer	dimer	trimer
Yield (%)	21	1	30	8	24	17	30	5
Total yield (%)	22		38		41		35	

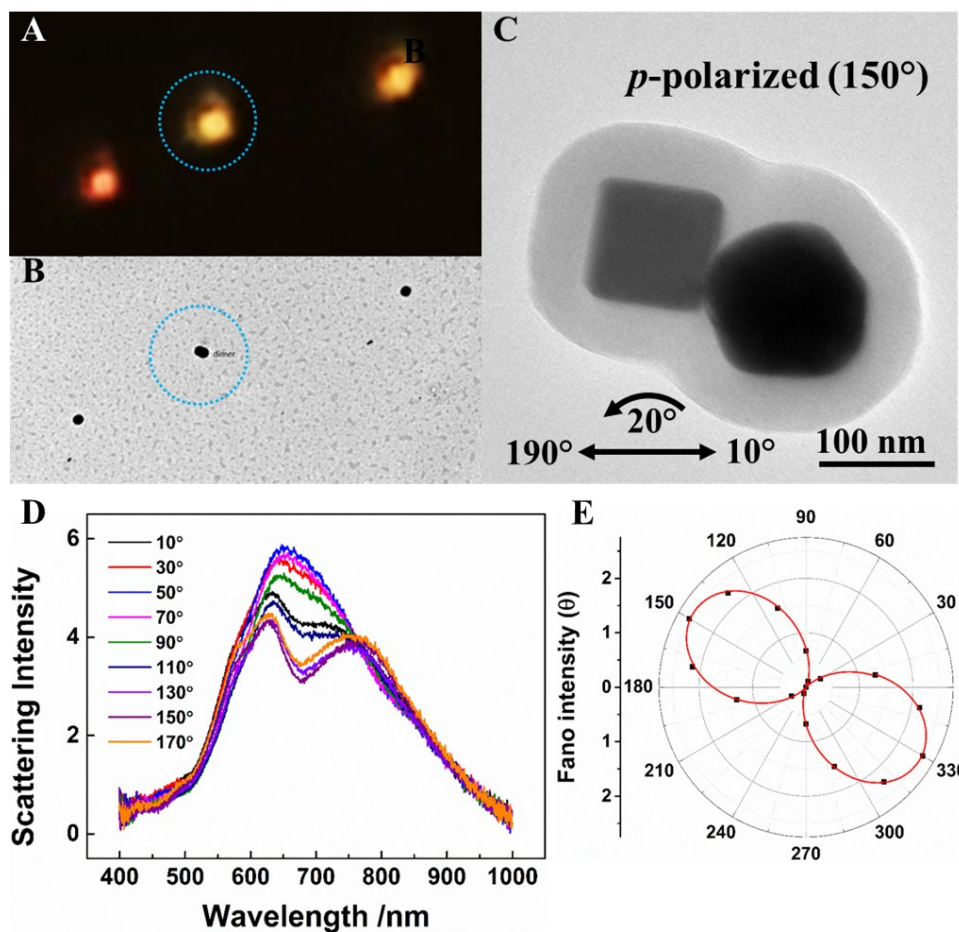


Figure S5. Single-particle scattering spectroscopy of (Au-Ag)SiO₂ dimer. (A) Dark-field image of the nanostructures. (B) The correlated TEM image. (C) High resolution TEM characterization of the dimer. (D) Polarization dependent scattering spectrum of the dimer. Polarization direction is showed in (C). (E) The relationship of the Fano intensity with the polarization angle.

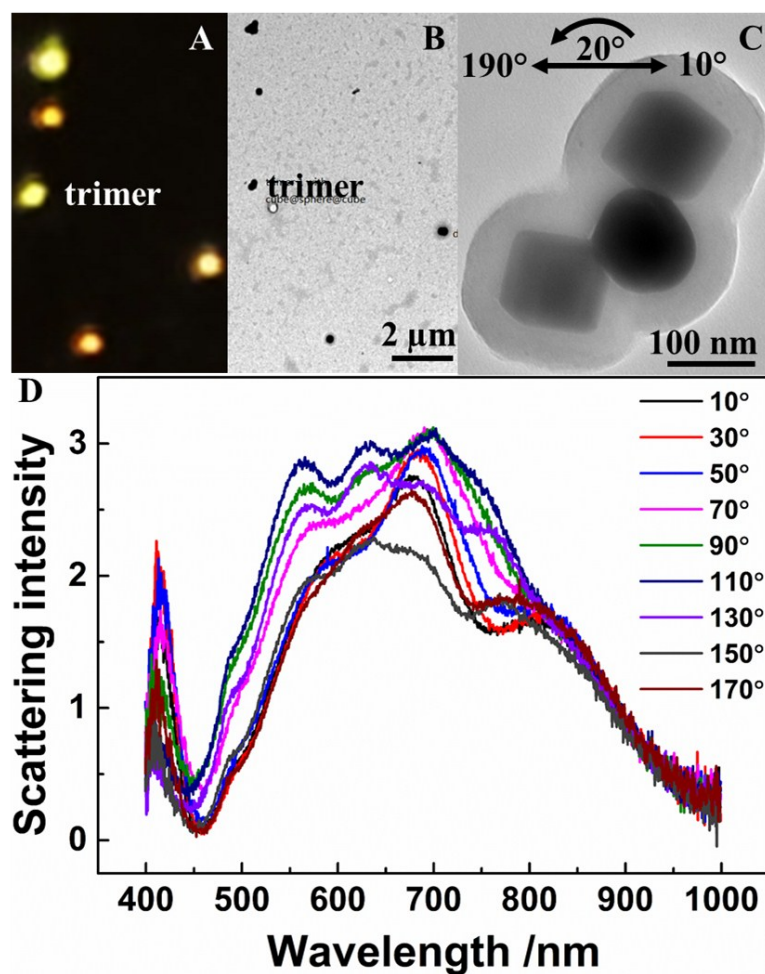


Figure S6. Single-particle scattering spectroscopy of (Ag-Au-Ag)SiO₂ trimer. (A) Dark-field image of the nanostructures. (B) The correlated TEM image. (C) High resolution TEM characterization of the trimer. (D) Polarization dependent scattering spectrum of the trimer. Polarization direction is showed in (C).

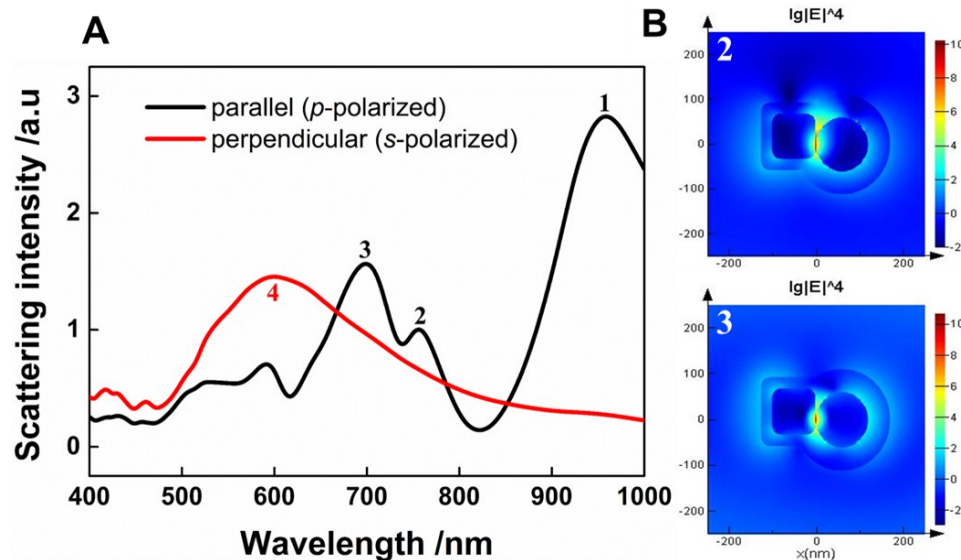


Figure S7. (A) The scattering spectra of the No.2 dimer under electric polarization parallel (black line) and perpendicular (red line) to the dimer axis; (B) The electric field distributions of the No.2 dimer at the peaks labeled as 2 and 3 in the scattering spectrum.

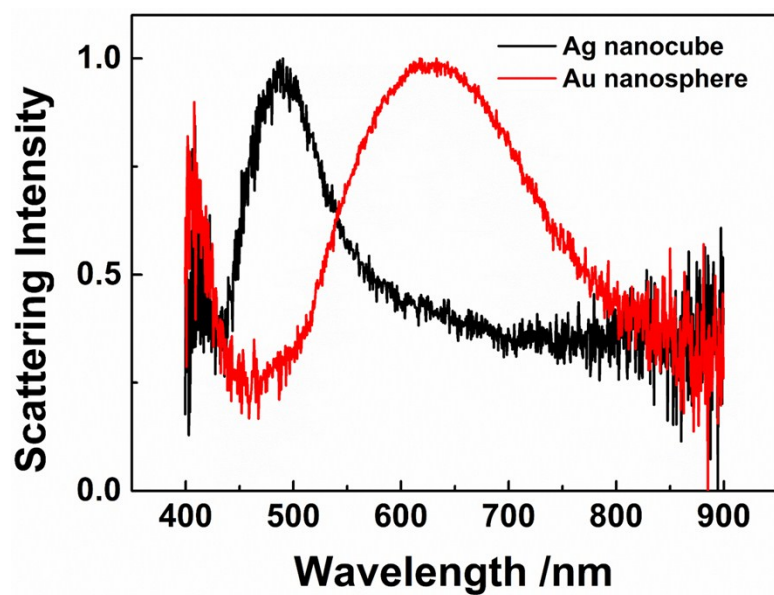


Figure S8. The experimental scattering spectra of single Ag nanocube (black line) and single Ag nanosphere (red line).