Supporting Information (SI):

Synthesis method

*Au bipyramids.* Citrate stabilized spherical gold nanoparticles are first synthesized at room temperature by adding 0.25 mL of 0.25 mM sodium citrate to 10 mL of a 0.25 mM HAuCl₄ solution followed by a quick injection of 0.3 mL of a fresh (ice cold) 10 mM NaBH₄ solution. The growth solution is made by adding 0.5 mL of 10 mM HAuCl₄, 0.1 mL of 10 mM AgNO₃, 0.2 mL of 1.0 M HCl and 80 µL of L-ascorbic acid to 10 mL of a 0.1 M cethymethylammonium bromide (CTAB) solution. The growth is initiated by injecting a small amount of seed (50 µL typically) into the growth solution and the reaction is performed at 35 °C under gentle stirring. To be cleaned, the core gold bipyramids are cooled for 12 hours at 6 °C and then centrifuged 3 minutes at 2000 g to get rid of the CTAB excess.

*Deposition of Ag onto Au bipyramids.* A quantity of 3 ml of gold bipyramids solution (c = 0.5 mM) was added to 80 mg of PVP (polyvinylpyrrolindone) and stirred for 30 minutes. A chosen volume (25, 50, 100 µL) of 10 mM AgNO₃ was added followed by the addition of a volume (50, 100, 200 µL respectively) of 0.1 M L-ascorbic acid and allowed to mix for 30 minutes. Finally, a dropwise addition of 0.1 M NaOH solution up to pH = 8 was performed in order to gently reduce the silver ions onto the core gold bipyramids. Finally, extinction spectra of colloidal solution are measured using a double beam Varian Cary 5000 spectrometer.

SEM, TEM and electron tomography experiments
HRSEM analysis was performed on a Jeol 6700F electron microscope working at 5 kV accelerating voltage after deposition of the colloidal particles on glass substrate according the reference [28]. HRTEM experiments were conducted on a JEOL 2200 FS electron microscope working at 200 kV equipped with a field emission gun. Before observations, the samples were deposited on a holey carbon membrane copper grid which was previously cleaned using a H₂/Ar plasma gas using a Solarus Plasma Cleaner.

The morphologies for the Au and the Au@Ag bipyramids were investigated by electron tomography with the acquisitions in the STEM-HAADF mode. The acquisitions of the tilt series were performed by tilting the object under study over a range of +/- 70°, with an image recorded every 2.5°. This was done automatically using the tomography software (Digital Micrograph plug-in), which provides an automatic acquisition of the tilted series by controlling the specimen tilt angle by angle and correcting the defocusing and the specimen drift. After the acquisition, the different projections of the tilted series were aligned using the cross-correlation algorithm implemented in the IMOD software. The volume calculation was performed using the algebraic reconstruction techniques, namely the TomoJ macro implemented as a plugin in the ImageJ software using 10 iterations. The 3D visualization of the reconstructed volumes was done using the isosurface rendering method in Slicer 3.3 software.