Supplementary Information

Component Conversion from Pure Au Nanorods to Multiblock Ag-Au-Ag Nanorods Assisted by Pt Nanoframe Templates

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EXPERIMENTAL SECTION

Instrumentation

Field emission scanning electron microscopy (FESEM) images were obtained using a JEOL 7100F and a JEOL 7600F. A JEM-2100F was used to acquire transmission electron microscopy (TEM) images. UV-vis-NIR absorption spectra were acquired using UV-3600(Shimadzu) spectrometers.

Materials

Hydrogen tetrachloroaurate (III) hydrate (HAuCl₄·nH₂O, 99%) and hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆·nH₂O, 99%) were purchased from Kojima. Sodium tetrahydroborate (NaBH₄, 98%) and silver nitrate (AgNO₃, 99.8%) were purchased from Junsei. Sodium iodide (NaI, 99.5%) and L-ascorbic acid (C₆H₈O₆, 99.5%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 98%) was purchased from Samchun and hexadecyltrimethylammonium bromide (CTAB, C₁₉H₄₂BrN, 95%) was supplied by Fluka. All reagents were dissolved in distilled water (18.2 M Ω) that was prepared using a Milli-Q water purification system from Millipore.

Synthetic procedure

Synthesis of Ag-Au-Ag nanorods

Pentagonal Au nanorods were prepared via seed-mediated dropwise addition as reported previously.¹ To synthesize Au@Pt nanorods,² 2 mL of 50 mM CTAB, 1 mL of Au nanorod, 33 μ L of 0.2 mM AgNO₃, and 32 μ L of 0.1 M ascorbic acid were added to a vial in the presence of iodide ions (50 μ M). The solution was heated to 50 °C and kept in an oven to promote the deposition of Ag layers onto the Au nanorods. After 1 hr, 32 μ L of 0.1 M HCl and 45 μ L of 2 mM aqueous H₂PtCl₆ solution were injected into the growth solution. The mixture was kept at 50 °C for approximately 8 hr. After the reaction was complete, we spun the samples in a centrifuge at

4000 rpm for 15 min, and repeated this washing process twice.

To prepare a Au nanoblock@Pt nanoframe, 2 mL of 50 mM CTAB, 500 μ L of 0.2 mM HAuCl₄, and Au@Pt nanorods were combined in the presence of iodide ions (50 μ M). Etching times were controlled as 3, 10, 15 min at 50 °C. After the reaction, samples were centrifuged at 4000 rpm for 15 min, and the washing process was repeated two times.

To prepare Ag-Au-Ag nanorods, 2 mL of 50 mM CTAB, 60 μ l of 2 mM AgNO₃, and 10.28 μ l of 0.1 M NaOH was mixed into a Au nanoblock@Pt Nanoframe solution. Subsequently, 50 μ l of 5.3 mM ascorbic acid was added to the mixture. The mixture was kept at 28 °C for 40 min and the washing process was repeated twice.

Discrete Dipole Approximation (DDA) Calculation.

The source code for DDA calculation was obtained from the webpage of Professor Bruce Draine.³ Johnson and Christy⁴ provided optical constants for Au and Ag. The refractive index dispersion of water was utilized to generate accurate spectra in the short wavelength region. A cylindrically shaped target of a given diameter and length was subdivided with an array of 4 nm cubic cells. The interaction between polarizable point dipoles in the cells and incident light wave was solved iteratively. Cross sections for extinction and scattering were generated from these calculations. The cross sections of a randomly oriented target under nonpolarized light were obtained by averaging the calculations for seven different incident directions and two mutually perpendicular polarization states of the light wave with respect to target frame.



Figure S1. SEM images of Au nanorods (A) and Au@Ag core-shell structure nanorods (B). Without templates, Ag is reduced on Au nanorod in the form of core-shell structure not of multiblock nanorod.



Figure S2. One of the reasons leading to selective etching from the tip of nanorod is whether Pt is edgepreferentially deposited onto Au NRs or homogeneously coated. When optimized amount of Pt is selectively deposited on Au nanorod, selective etching occurs from the tip (A, B). However, when the amount of Pt is larger than optimized condition as much as leading to homogeneous coating, etching randomly occurred (C,D). TEM images (A,C) show morphology of the tip of nanorod and different tendency of etching is observed in SEM images (B,D). 1. Hong, S.; Shuford, K. L.; Park, S., Observation of a Quadrupole Surface Plasmon Mode for Au Nanorods: Effects of Surface Roughness and Crystal Facets. Chem. Asian J. **2013**, 8, 1259-1264.

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