Supplementary Information

Synthesis and Optical Property Characterization of Elongated AuPt and Pt@Au Metal Nanoframes

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Schematic illustration of the elongated Pt@Au nanoframes; Unique surface plasmon features were observed for elongated Pt@Au nanoframes where the short-axis oscillation of surface free electrons is strongly coupled but the long-axis oscillation is not coupled among ridges.

Experimental Section

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 MΩ) that was prepared using a Milli-Q water purification system from Millipore.

Synthetic procedure

Synthesis of elongated Pt@Au nanorod frame

Pentagonal Au nanorods were prepared by a seed-mediated dropwise-addition method as reported previously. To synthesize Au@Pt nanorods, 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 completion of the reaction, we spun the samples in a centrifuge at 4000 rpm for 20min, and repeated this washing process twice.

To prepare elongated AuPt nanoframes and elongated Pt@Au nanoframes, 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 took 40 min at 50 °C. After the reaction, 50 μ L of 5.3 mM ascorbic acid was added to the mixture. The mixture was kept at 28 °C for 30 min and the washing process was repeated twice.

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.

Figures

Au@Pt nanorods	(ppm)	(%)
Ag	0.14	0.3
Au	33.3	75.1
Pt	10.9	24.6

Elongated Pt@Au nanoframes	(ppm)	(%)
Ag	0.26	1.6
Au	13.9	87.9
Pt	1.65	10.4

Table S1. Ag, Au, Pt percentage composition in Au@Pt nanorods and elongated Pt@Au nanoframes analized by Inductively coupled plasma mass spectroscopy (ICP-MS).



Fig.S1 SEM images of Au nanorods(A), Au@Ag core-shell nanorods(B), Au@Pt(edge, i.e. edge-preferential deposition of Pt) nanorods(C), Au@Pt(uni, i.e. uniformly coating of Pt) (D-F) and corresponding UV-vis-NIR spectra(G) showing an important role of Ag layer on edge-preferential deposition of Pt. For Au@Pt(uni) nanorods, the amount of Pt increased from D to F, showing homogeneous coating. In constrast, when the same amount of Pt was applied to Au nanorods with Ag layer, edge-preferential island growth is evident in (C).



Fig.S2 TEM image demonstrating edge-preferential deposition of Pt onto Au nanorod in an island growth mode.



Fig.S3 SEM images (A,B,C) of Au@Pt nanorods and their corresponding TEM images (D,E,F) showing detailed morphology. As the amount of Pt increased (from A to C and D to F), the surface of nanorods is fully coated with Pt, not edge-preferential growth.

Elongated AuPt nanoframe





Element	Weight%	Atomic%
Ag L	0.69	1.24
Pt L	63.94	63.80
Au L	35.38	34.96
Totals	100.00	

Elongated Pt@Au nanoframe



Element	Weight%	Atomic%
Ag L	1.03	1.86
Pt L	16.71	16.70
Au L	82.26	81.44
Totals	100.00	

Fig.S4 EDS data for elongated AuPt nanoframe and elongated Pt@Au nanoframe in terms of composition analysis.



Fig.S5 SEM images of elongated Pt@Au nanoframes before (A) and after (B) O₂ plasma treatment for 6 min.