

Triangular AgAu@Pt Core-shell Nanoframes with Dendritic Pt shell and Enhanced
Electrocatalytic Performance toward Methanol Oxidation Reaction

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Experimental section

Chemicals: Silver nitrate (99%), sodium borohydride (99%), trisodium citrate dihydrate (99%), Bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium (BSPP), hydrogen tetrachloroaurate(III) tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), hydroxylamine (HyA), hexadecyltrimethylammonium bromide (CTAB), and ascorbic acid (AA, >99%) were purchased from Sigma-Aldrich and used as received. Ultrapure water (Milli-Q System Millipore, USA) was used for all experiments.

Synthesis of silver nanoparticles: In a typical synthesis, a 250-mL three-neck flask was placed in an ice bath, and ultrapure water (190 mL) was introduced into the flask and bubbled with nitrogen gas for one hour under stirring. Then 1 mL solution of AgNO_3 (20 mM) and 2 mL solution of trisodium citrate (30 mM) were added into the flask. Subsequently 2 mL freshly prepared solution of NaBH_4 (60 mM) was rapidly injected into the solution. Over the next 20 min, 5 drops of the NaBH_4 solution (60 mM) were added into the solution at 2-min interval. Then 0.5 mL solution of NaBH_4 (60 mM) and 0.5 mL solution of BSPP (5 mM) were simultaneously added dropwise into the solution over the next 10 min. The resulting solution was kept stirring for 3 hours in the ice bath and then aged overnight at $\sim 4^\circ\text{C}$ in the dark.

Preparation of silver nanoprisms: The as-prepared solution of silver nanoparticles (20 mL) was irradiated by a 150-W halogen illuminator (MI-150, Fiber-Lite, USA) coupled with an optical bandpass filter centered at 500 ± 20 nm for 1~2 hours and then 600 ± 20 nm for 2~3 hours. The resulting solution exhibited a major extinction bands at ~ 650 nm, indicating the formation of silver nanoprisms.

Synthesis of triangular AgAu@Pt nanoframes: 40 ml of the freshly prepared Ag nanoprisms was

coated with a thin layer of Au by simultaneous infusion of 1 mL of 0.3 mM HAuCl₄ solution and 1 mL of 3 mM HyA solution through two separate tubes on a mechanical syringe pump at an infusion rate of 1.0 mL h⁻¹. The gold coating process was carried out in an ice bath and under vigorous stirring. After Au coating for 1 h, the Ag nanoprism edges were coated with a thin layer of Au, forming Ag@Au-framed nanoprisms. Prior to Pt deposition, the resultant Ag@Au-framed nanoprism solution was heated to 80 °C. After that, 4 mL of 30 mM CTAB solution was injected into the above solution under magnetic stirring, followed by the injection of 50 μL of 10 mM H₂PtCl₆ solution and 0.5 mL of 10 mM AA solution. The reaction mixture was kept at 80 °C for 5 h with vigorous stirring. Finally, the resultant solution was centrifuged and washed three times with deionized water to remove excess reagents.

Morphological, structural, and compositional characterizations: Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2010 at an accelerating voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM) images, high-angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray (EDX) spectra were acquired on a JEOL JEM-2100F at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance equipped with a Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectra (XPS) were investigated on a VG ESCALAB 220I-XL system.

Electrochemical Measurements: The electrochemical measurements were performed in a standard three-electrode cell on an Autolab potentiostat/galvanostat electrochemical workstation. A Pt wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The AgAu@Pt nanoframes modified glassy carbon (GC) electrode (3 mm in diameter, 0.071 cm²) serves as the working electrode. For immobilization of catalysts, 5 μL solution of AgAu@Pt

nanoframes ($C_{Pt} = 183 \text{ g mL}^{-1}$) was dropped onto the GC electrode and dried under ambient condition. Then 5 μL of Nafion solution (1%) was dropped on the AgAu@Pt nanoframes modified GC electrode to prevent erosion of nanocatalysts during electrochemical measurements. The modified substrate was washed with DI water and dried. The electrochemical measurements for methanol oxidation reaction (MOR) were performed in a solution containing of 0.2 M KOH and 1.0 M CH_3OH . Commercial Pt/C catalyst (Alfa Aesar, 10 wt%) was used as the control sample with the same testing conditions.

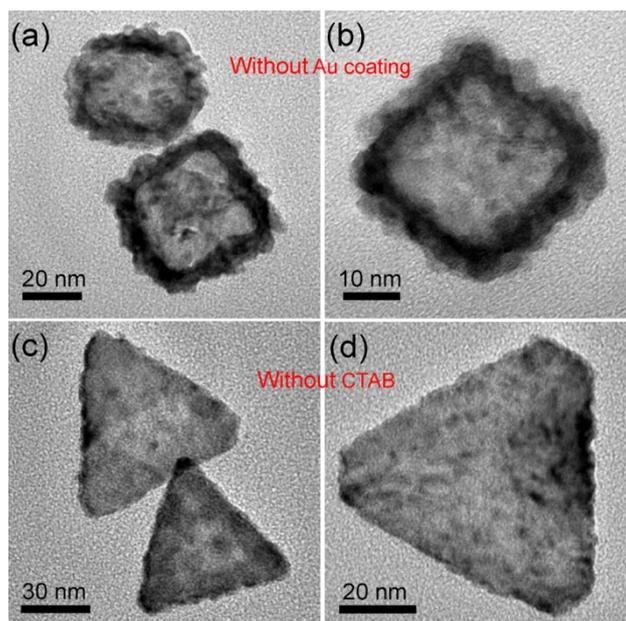


Figure S1 TEM images of the products obtained under different synthetic conditions. (a)-(b) without gold coating process, and (c)-(d) without the involvement of CTAB.

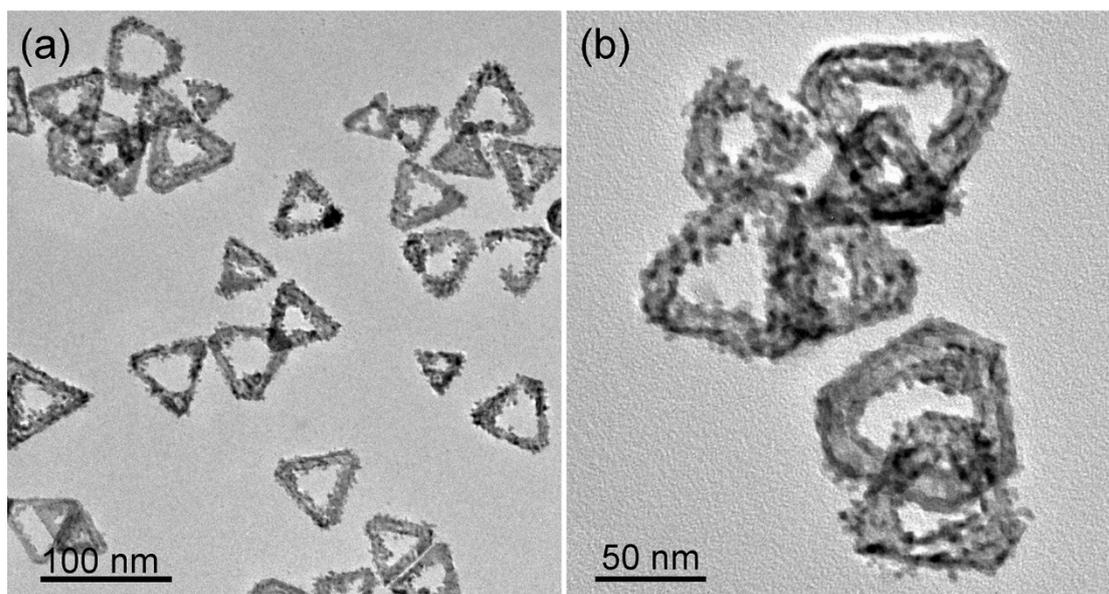


Figure S2 Large area TEM images of the as-prepared AgAu@Pt nanoframes.

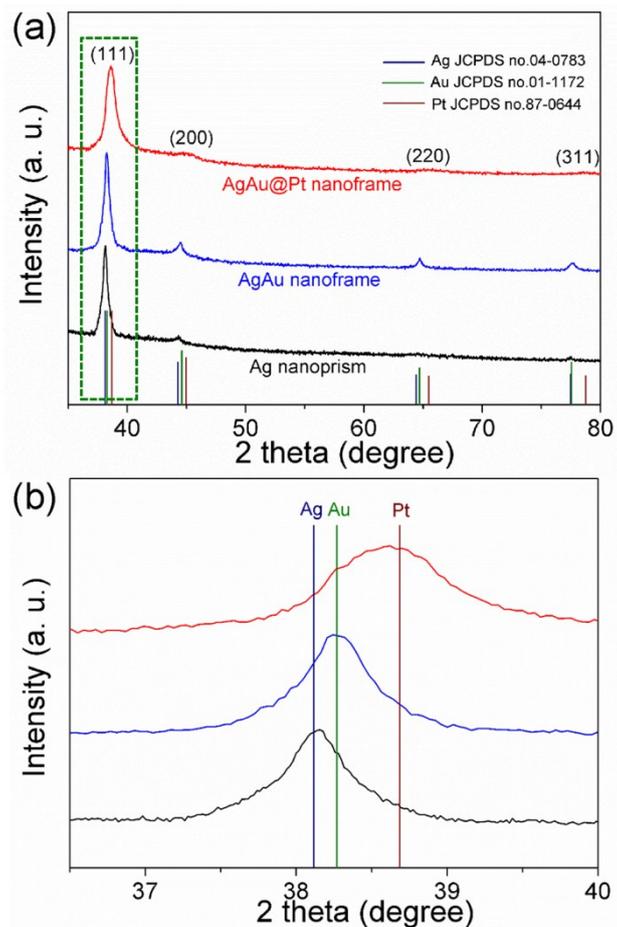


Figure S3 (a) XRD patterns of the resultant Ag nanoprisms, AgAu nanoframes, and AgAu@Pt nanoframes. (b) Magnified region marked in panel (a).

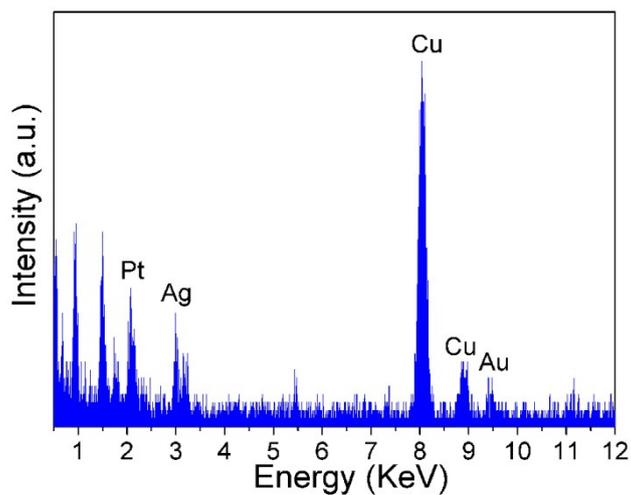


Figure S4 EDS spectrum of the triangular AgAu@Pt nanoframes. The peaks of Cu were originated from the carbon-coated copper grid.

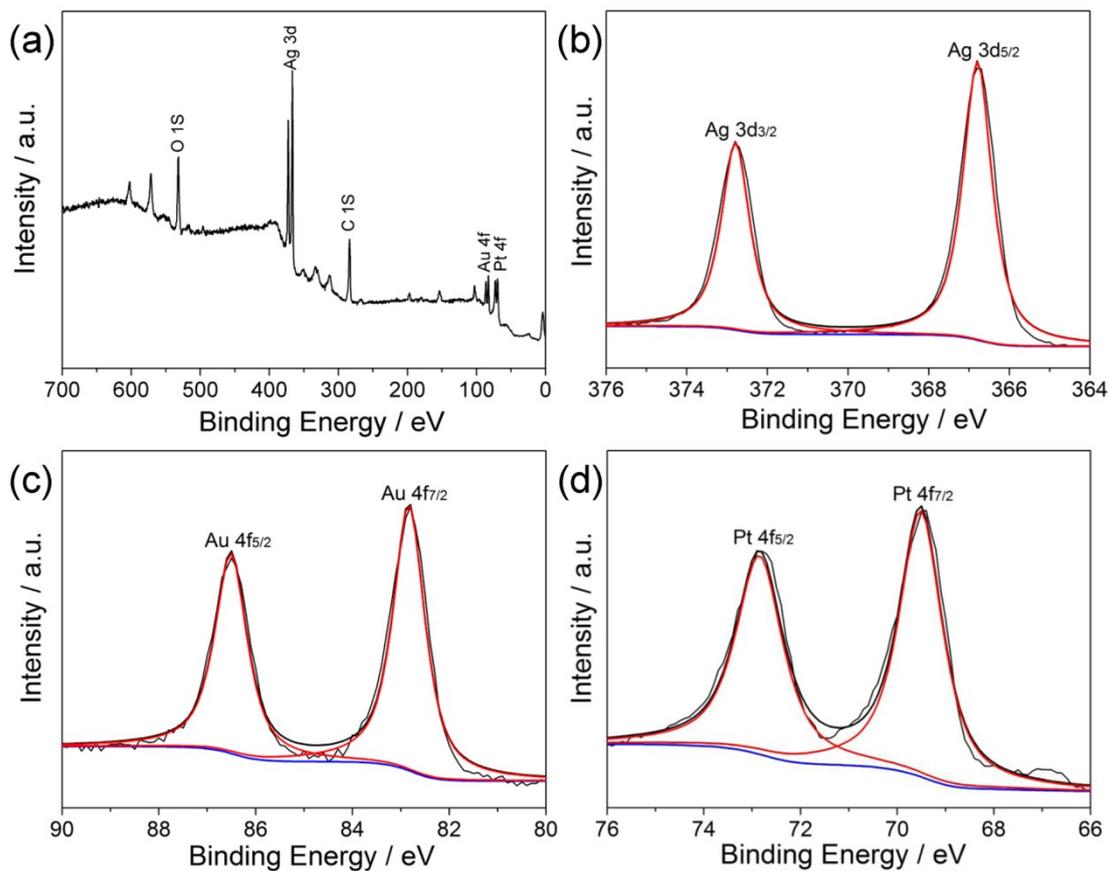


Figure S5 XPS spectra of the triangular AgAu@Pt nanoframes. (a) Survey scan spectrum, (b) Ag 3d region, (c) Au 4f region, and (d) Pt 4f region.

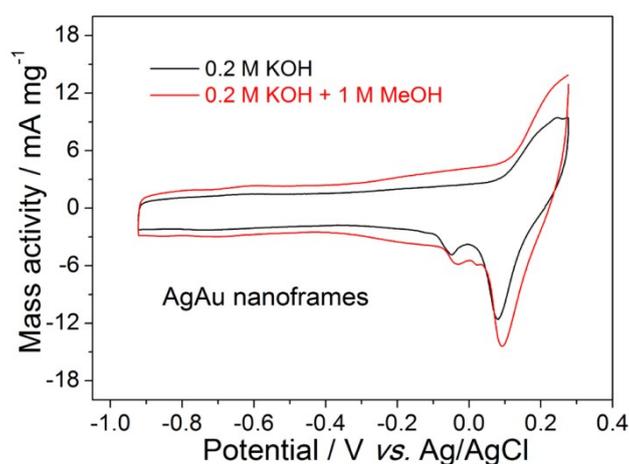


Figure S6 CV curves of AgAu nanoframes performed in N_2 -saturated 0.2 M KOH + 1 M CH_3OH solution with a sweep rate of 50 mV s^{-1} , respectively.

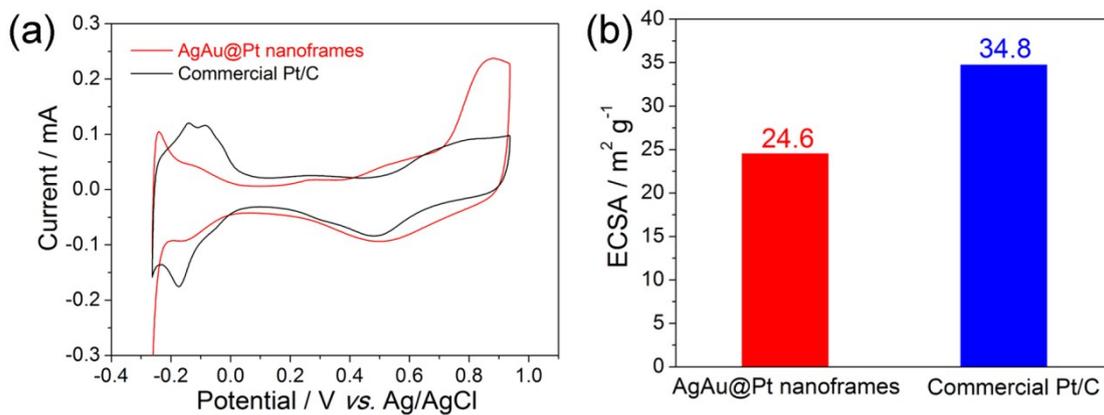


Figure S7 (a) Typical CV curves of triangular AgAu@Pt nanoframes and commercial Pt/C catalyst performed in N₂-saturated 0.5 M H₂SO₄ solution with a sweep rate of 50 mV s⁻¹. (b) ESCAs of the AgAu@Pt nanoframes and commercial Pt/C catalyst.

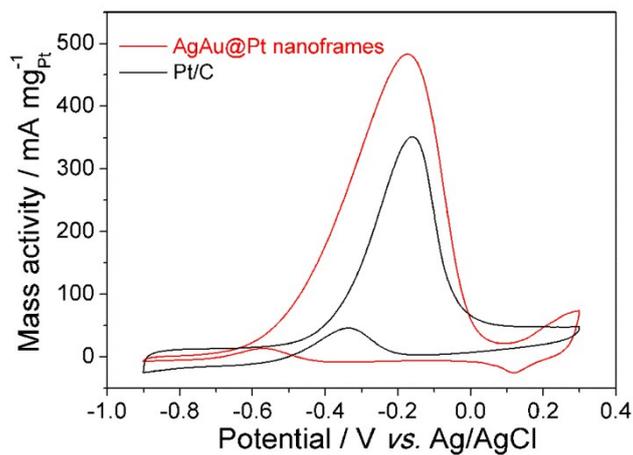


Figure S8 Mass activities of triangular AgAu@Pt nanoframes and commercial Pt/C catalyst.