Supporting Information

Tuning the Growth Mode of Pt on AuNRs via Modulating the Competition of Pt Deposition and Oxidative Etching of Au Nanorods

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EXPERIMENTAL SECTION

Materials

All chemicals were used as received without further purification. Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%) was purchased from Alfa Aesar; L-Ascorbic acid (≥ 99%), Hexadecyl trimethyl ammonium Bromide (≥99%) and Cetyltrimethylammonium chloride (≥99%) were purchased from Sigma-Aldrich, Sodium borohydride (99%) was purchased from Sigma-Aldrich, $AgNO_3$ (99.9999%) was purchased from Sigma-Aldrich; Hydrochloric acid was purchased from Sinopharm Chemical Reagent Co., Ltd , Potassium tetrachloroplatinate (II) (K_2PtCl_4) and Potassium bromoplatinite (II) (K_2PtBr_4) were purchased from Aladdin ; Deionized water (resistance > 18.2 MΩ·cm) was used in all reactions. TEM grids were purchased from Beijing Zhongjingkeyi Technology Co., Ltd.

Material characterization

Transmission Electron Microscopy (TEM) images were collected using an HT7700 TEM (100 kV) and a Talos L120C model (120 kV). UV-Vis Spectroscopy: Spectra were recorded on a Lambda 750 UV-Vis spectrophotometer. X-ray Diffraction (XRD) Patterns were measured using a Rigaku Miniflex-600 Advanced Powder diffractometer (Cu Kα radiation, λ = 1.5406 Å), in the 2θ range of 20°–80°, with spin-coated.

Synthesis of monodispersed Au nanorods.

Gold nanorods (AuNRs) was synthesized following a reported method, with the procedure as follows: The seed solution for AuNRs growth was prepared by mixing 5 mL of 0.5 mM $HAuCl_4$ with 5 mL of 0.2 M cetyltrimethylammonium bromide (CTAB) in a 20 mL vial, followed by the injection of 0.6 mL of freshly prepared 0.01 M $NaBH_4$ (diluted to 1 mL with water) under vigorous stirring (1200 rpm). The solution immediately changed from yellow to brownish yellow, and stirring was halted after 2 min. The seed solution was aged at room temperature for 30 min before use. For the growth solution, 0.7 g of CTAB (resulting in a final concentration of 0.037 M) and a specified amount of sodium oleate (NaOL) were dissolved in 25 mL of warm water (~50 °C) in a 100 mL conical flask, which was then cooled to 30 °C prior to the addition of 1.8 mL (or 2.4 mL for AuNRs with higher aspect ratios, tunable up to 6) of 4 mM $AgNO_3$. The mixture was left undisturbed at 30 °C for 15 min, after which 25 mL of 1 mM $HAuCl_4$ was added. Following 90 min of stirring (700 rpm) to form a colorless solution, 0.21 mL (or 0.54 mL for higher aspect ratio AuNRs) of HCl (37 wt.% in water, 12.1 M) was introduced to adjust the pH. After an additional 15 min of slow stirring (400 rpm), 0.125 mL of 0.064 M ascorbic acid (AA) was added, and the solution was vigorously stirred for 30 s, followed by the injection of 0.1 mL (or 0.08 mL for higher aspect ratio AuNRs) of the seed solution. The mixture was stirred for 30 s and then left undisturbed at 30 °C for 12 h to allow nanorod growth. Final products were isolated via centrifugation at 7000 rpm for 30 min, with the supernatant removed.

Synthesis of Au-Pt Hybrid Nanoparticles.

The G-Au-Pt structure

Typically, the as-grown AuNR solution (3 mL) was collected by centrifugation and washing with DI water (3 mL) to remove the excess surfactant. The Au NRs were then redispersed into CTAB solution (0.2 M, 3 mL) in a 5 mL centrifuge tube. The K_2PtCl_4 solution (0.01 M, 165 L) was subsequently added into the Au NR solution under gentle shaking. The DI water (1.835 mL) was sequentially added into the Au NR solution under gentle shaking. The overall volume of the obtained solution was 5 mL with the CTAB concentration of 120 mM. The resultant solution was placed in an oven set at 100 C for 1 h to produce the Au/Pt nanostructures. The product is washed three times with deionized water to remove surfactants and then prepared for TEM characterization.

The E-Au-Pt structure

The E-Au-Pt was synthesized by following the same procedure of the above synthesis of G-Au-Pt structure, only with the variation of the [CTAB] to 10 mM.

Control experiment under Ar atmosphere

The air in the reaction vial was removed by vacuum pumping for 3 min, followed by the purging with Ar for 3 min. This evacuation–Ar purging cycle was repeated three times to minimize the presence of oxygen in the system. Then an Ar balloon was connected to the reaction vial to maintain the Ar atmosphere during the reaction. As a control, one other reaction under ambient air conditions was carried out together. The samples were heated in an oil bath at 100 ℃ for 1 h under otherwise identical conditions.

HER Measurements:

Electrochemical characterization was performed using a standard three-electrode cell connected to a Ivium-n-Stat electrochemical workstation. The working electrode was a Platinum sheet electrode clamp. The graphite rod electrode and Ag/AgCl electrode were used as the counter and reference electrodes respectively. A total of 1 mg of the sample was loaded onto a 1 cm^2 hydrophilic carbon fiber paper. Cyclic voltammetry (CV) activation was performed in a N_2 saturated 1 M KOH electrolyte at a scan rate of 50 mV s^{-1} until the curves were overlapped. Linear sweep voltammetry (LSV) curves were recorded in a N_2 saturated 1 M KOH solution at a scan rate of 5 mV s^{-1}, with iR correction applied. Durability tests were conducted via chronoamperometry using LAND CT3001A electrochemical workstation in 1 M KOH solution, and the test curves were used to evaluate the catalyst stability at a current density of 100 mA cm^{-2}. Electrochemical impedance spectroscopy (EIS) measurements were carried out using Gamry electrochemical workstation (Gamry, Interface 1010E) over a frequency range of 100 kHz to 0.01 Hz with an amplitude of 10 mV.

All the polarization curves (including Pt/C) are recorded under the same condition with automatic iR compensation set to 90%, using the built-in function of the Ivium electrochemical workstation to correct for the solution resistance.

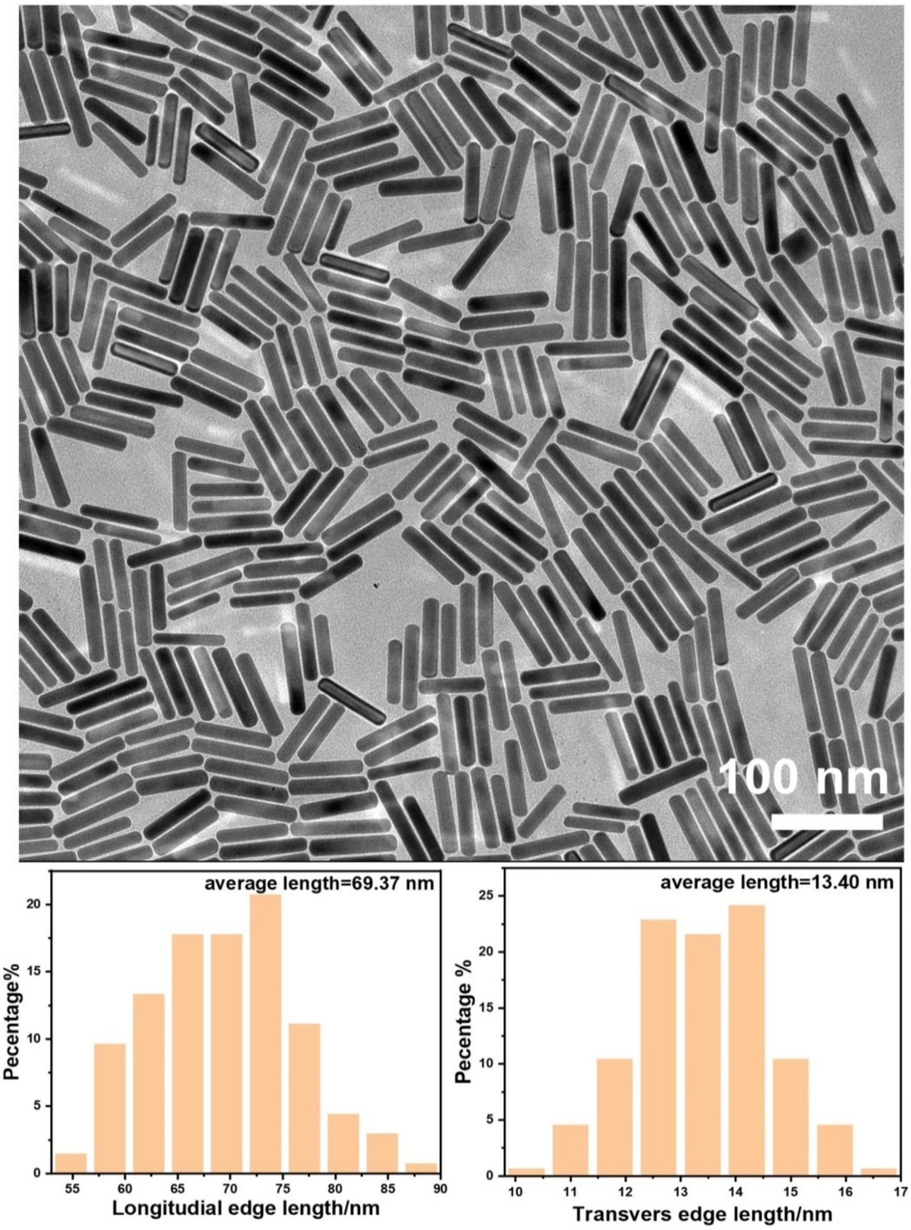

Figure S1. Representative TEM image of AuNRs.

$$\mathbf{AuBr_4^- + 3e^- \leftrightharpoons Au^0 + 4Br^- \quad 0.864V} \qquad \mathbf{1-1}$$

$$\mathbf{AuCl_4^- + 3e^- \leftrightharpoons Au^0 + 4Cl^- \quad 1.002V} \qquad \mathbf{1-2}$$

$$\mathbf{PtCl_4^{2-} + 2e^- \leftrightharpoons Pt^0 + 4Cl^- \quad 0.755V} \qquad \mathbf{1-3}$$

Figure S2. Reduction potentials of the $[AuBr_4]^-/Au$, $[AuCl_4]^-/Au$, and $[PtCl_4]^{2-}/Pt$.

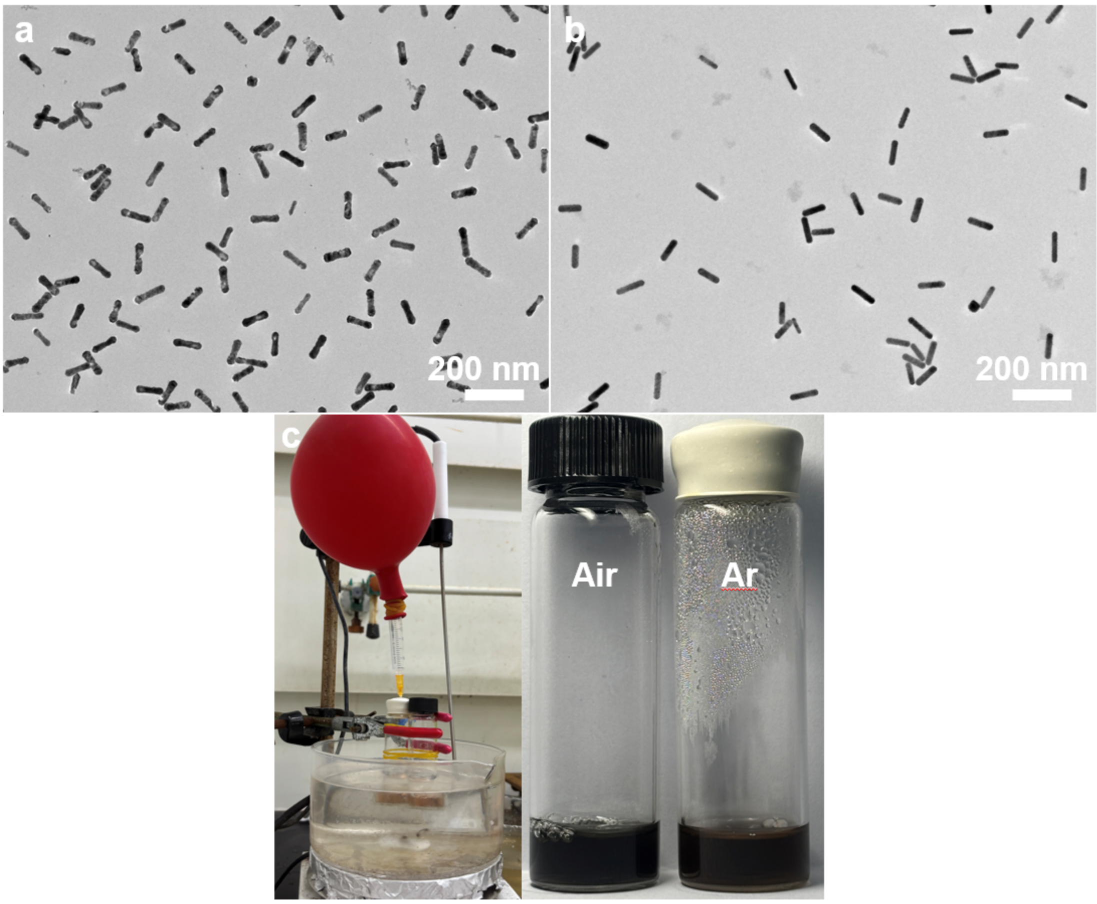

Figure S3. TEM images of the Au-Pt heterostructures obtained under (a) air and (b) Ar atmosphere. (c) The photograph of the reaction system and the color of the sample after reaction.

Table S1. ICP content of the Au-Pt structures in Figure 2

Sample	Au ion concentration (ug/L)
b	2476.47
c	3909.85
d	12018.22
e	17225.99
f	7752.07

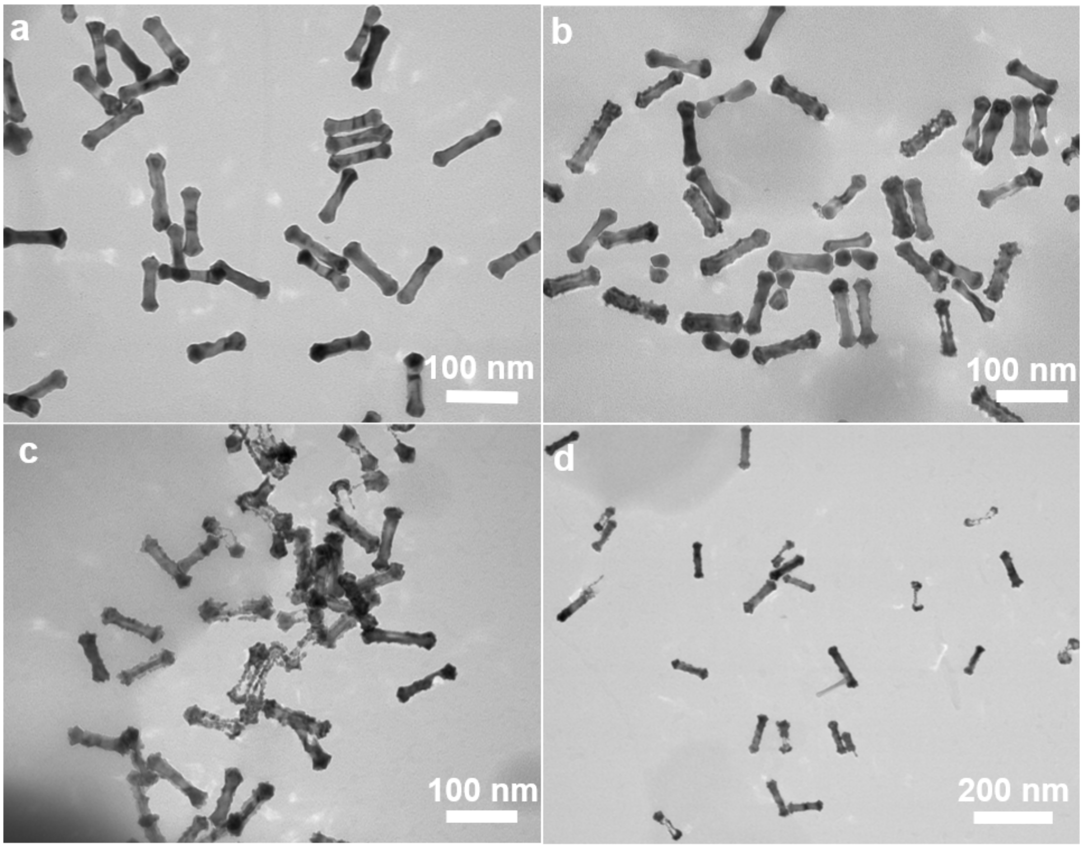

Figure S4. TEM images of the AuNR-Pt heterostructures obtained under different concentrations of CTAC and KI: (a) 5 mM, (b) 10 mM, (c) 15 mM and (d) 25 mM.

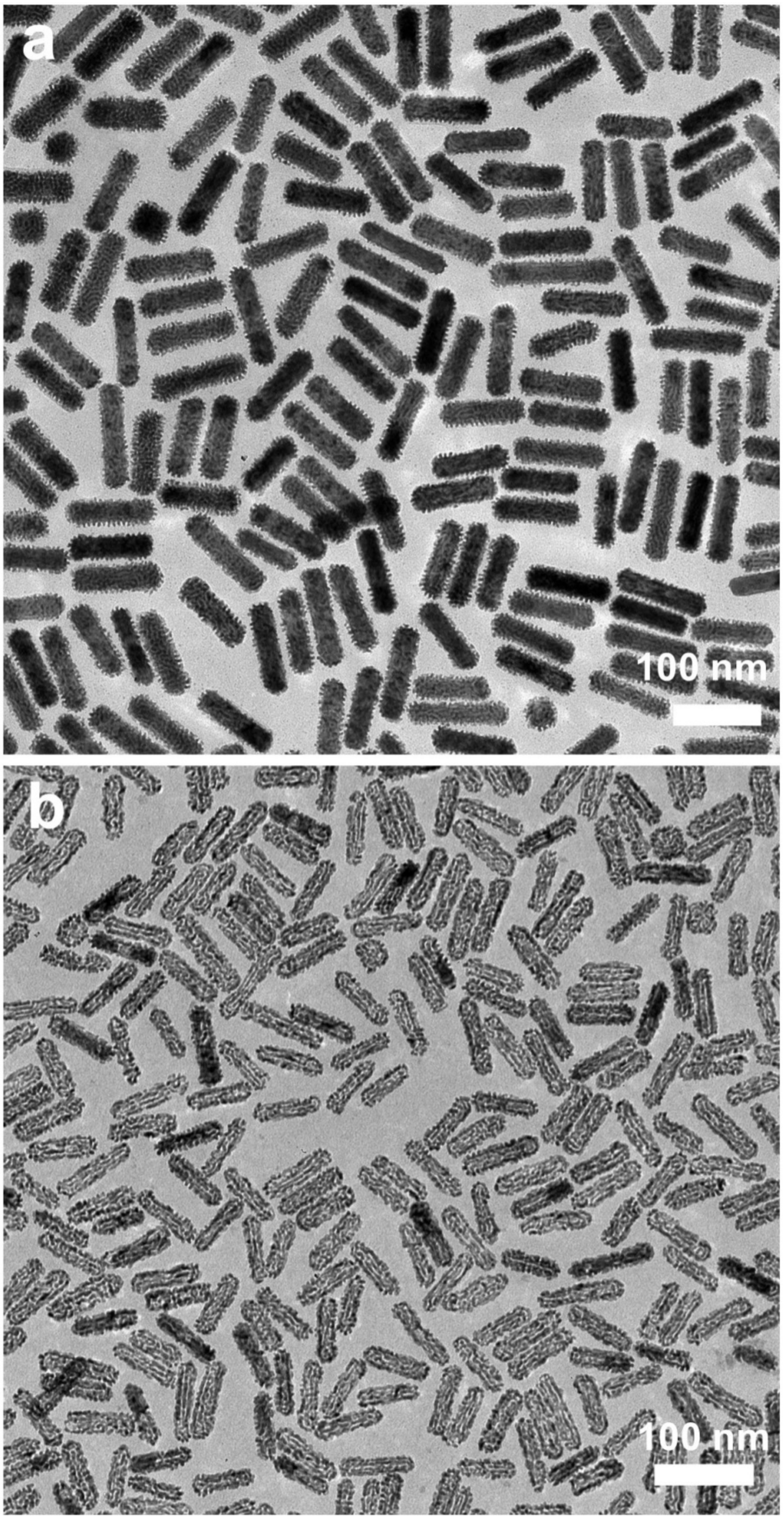

Figure S5. Representative TEM image of (a) G-Au-Pt, (b) Pt nanoframes.

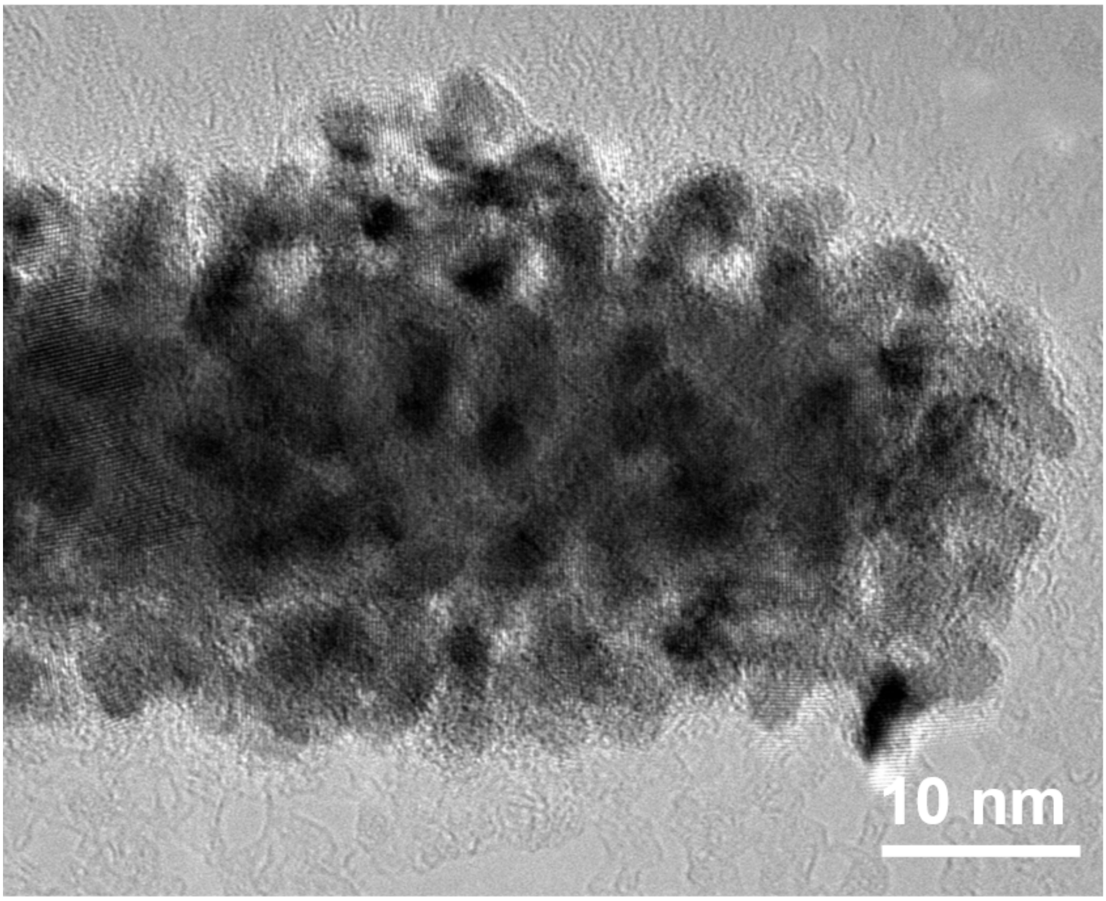

Figure S6. Representative HRTEM image of G-Au-Pt.

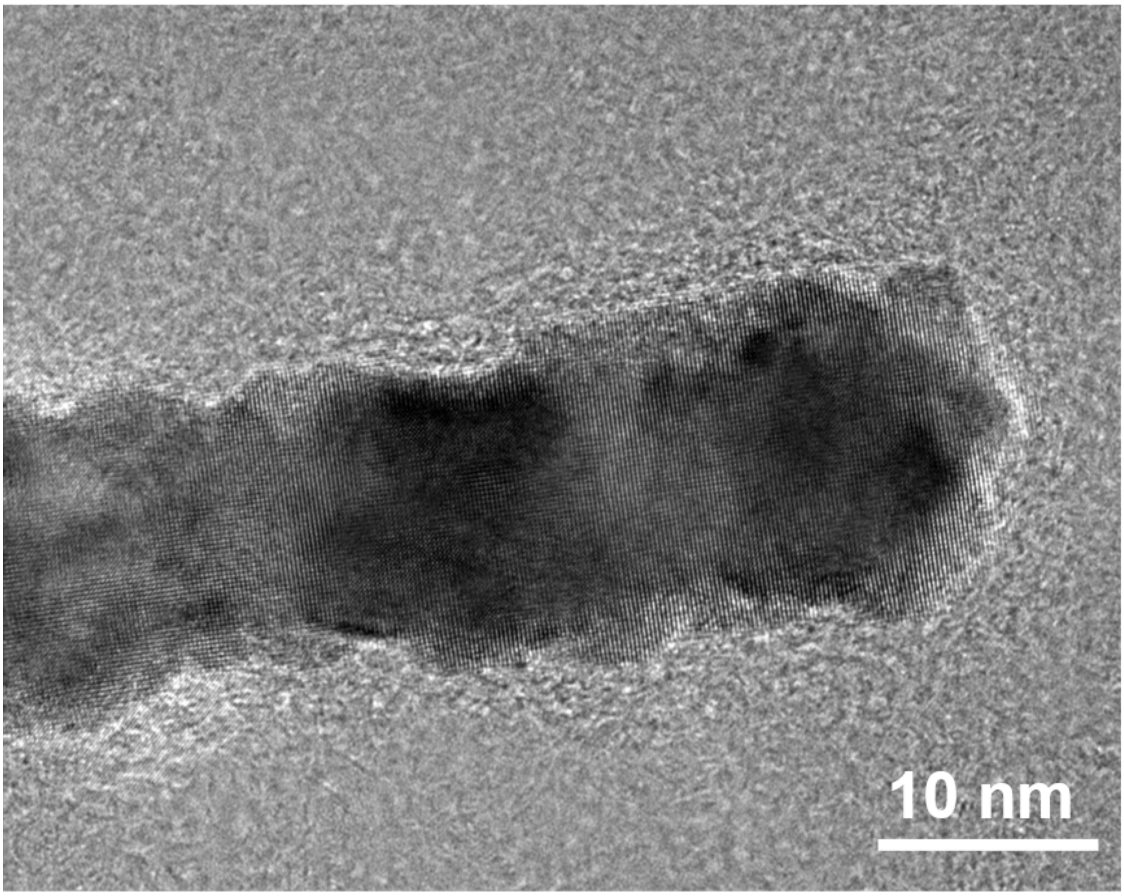

Figure S7. Representative HRTEM image of E-Au-Pt.

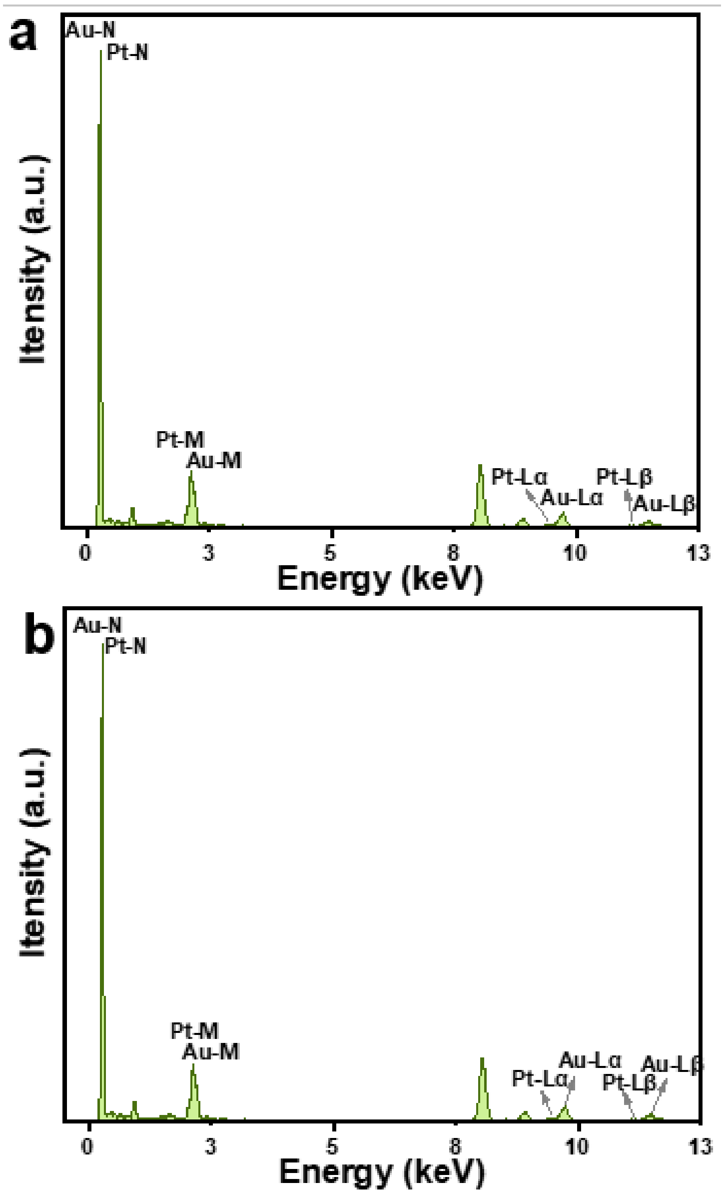

Figure S8. EDS spectrum of a representative (a) G-Au-Pt, (b) E-Au-Pt nanostructure.

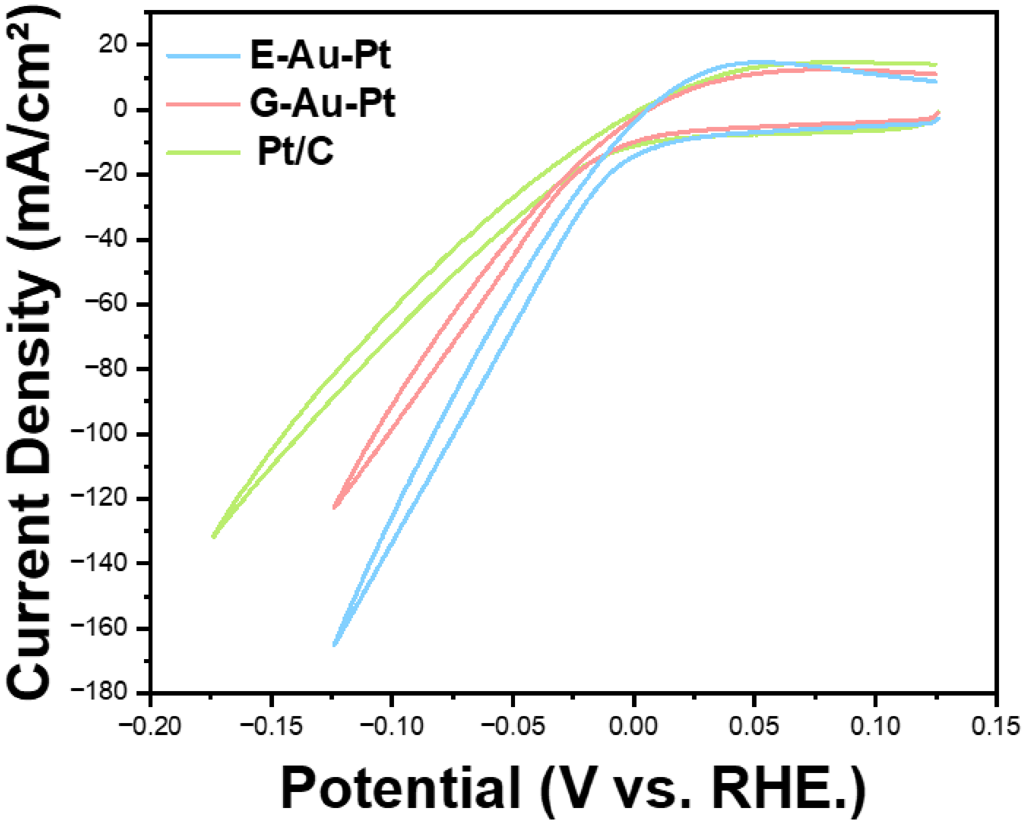

Figure S9. CV of the E-Au-Pt, G-Au-Pt heterostructure catalysts and commercial Pt/C catalysts in 1 M KOH.

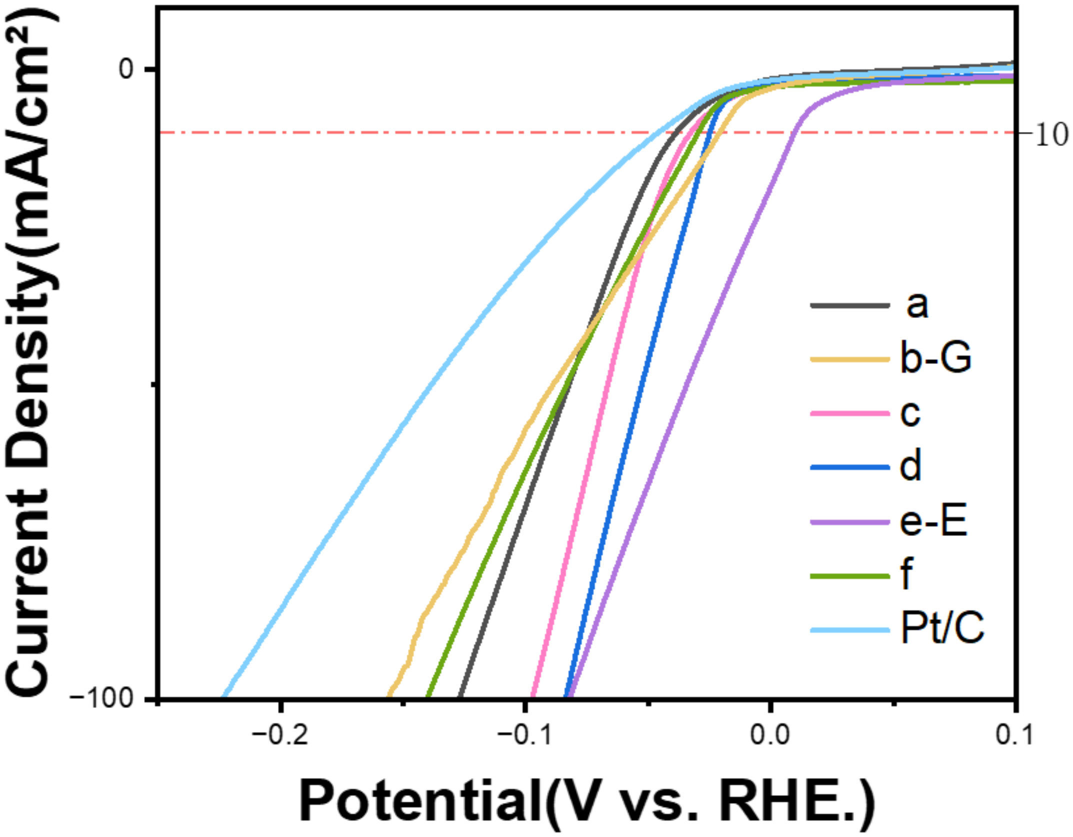

Figure S10. LSV of the Au-Pt heterostructures in Figure 2 in the main text in 1 M KOH at 100 mA cm^{-2} without iR compensation.

Table S2. ICP contents of G-Au-Pt and E-Au-Pt

	Au (at.%)	Pt (at.%)
G-Au-Pt	46.56	54.44
E-Au-Pt	26.0	74.0

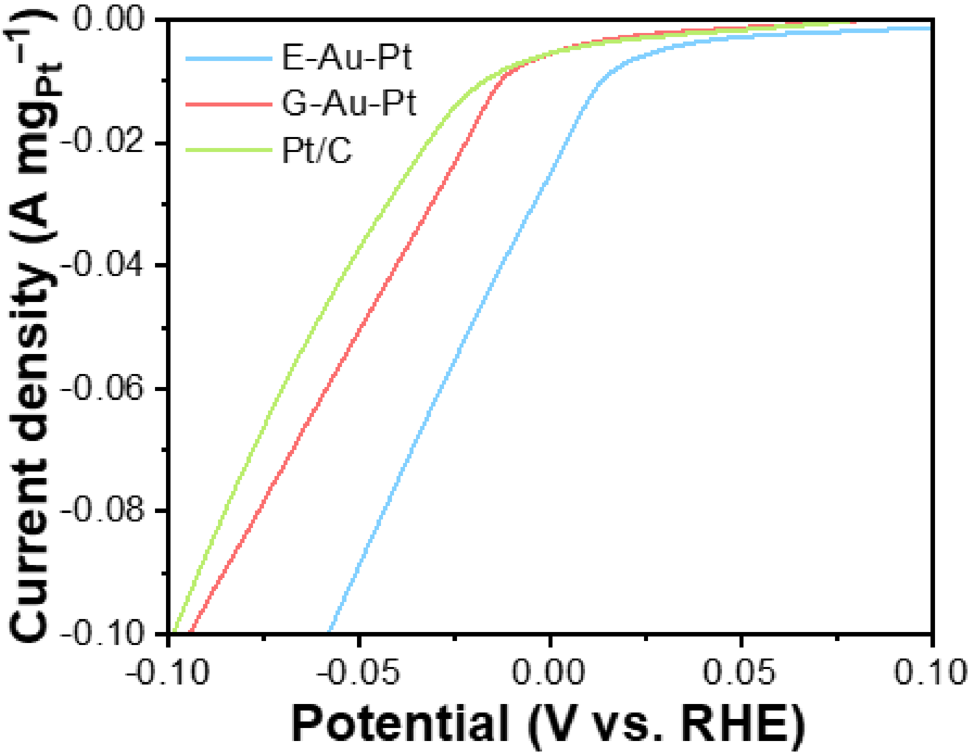

Figure S11. The mass activity of E-Au-Pt, G-Au-Pt and the commercial Pt/C catalysts by normalizing the current density to the loading mass of the Pt.

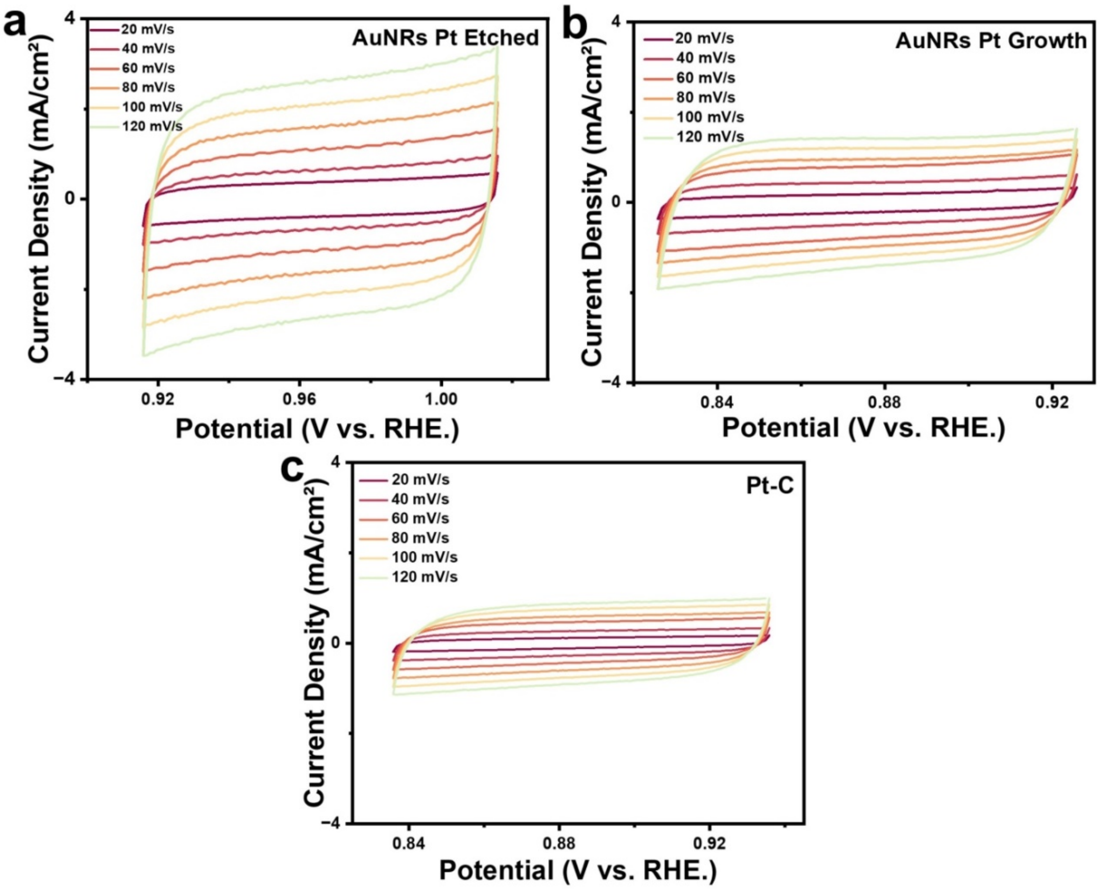

Figure S12. CV curves of (a) E-Au-Pt, (b) G-Au-Pt and (c) Pt/C in the double layer region at scan rates of 20, 40, 60, 80 ,100 and 120 mV s^{-1} in 1M KOH.

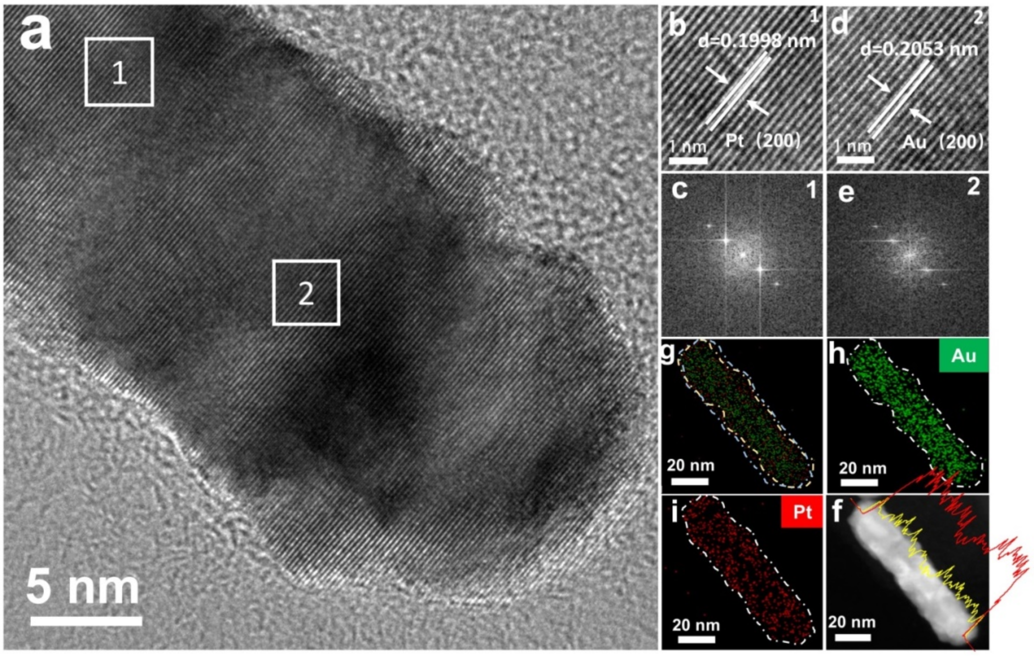

Figure S13. (a, b, d) HRTEM images, (c, e) fast Fourier transform (FFT) of the squared regions in (b, d), (g-f) EDS mapping of an individual E-Au-Pt particle after testing the stability.

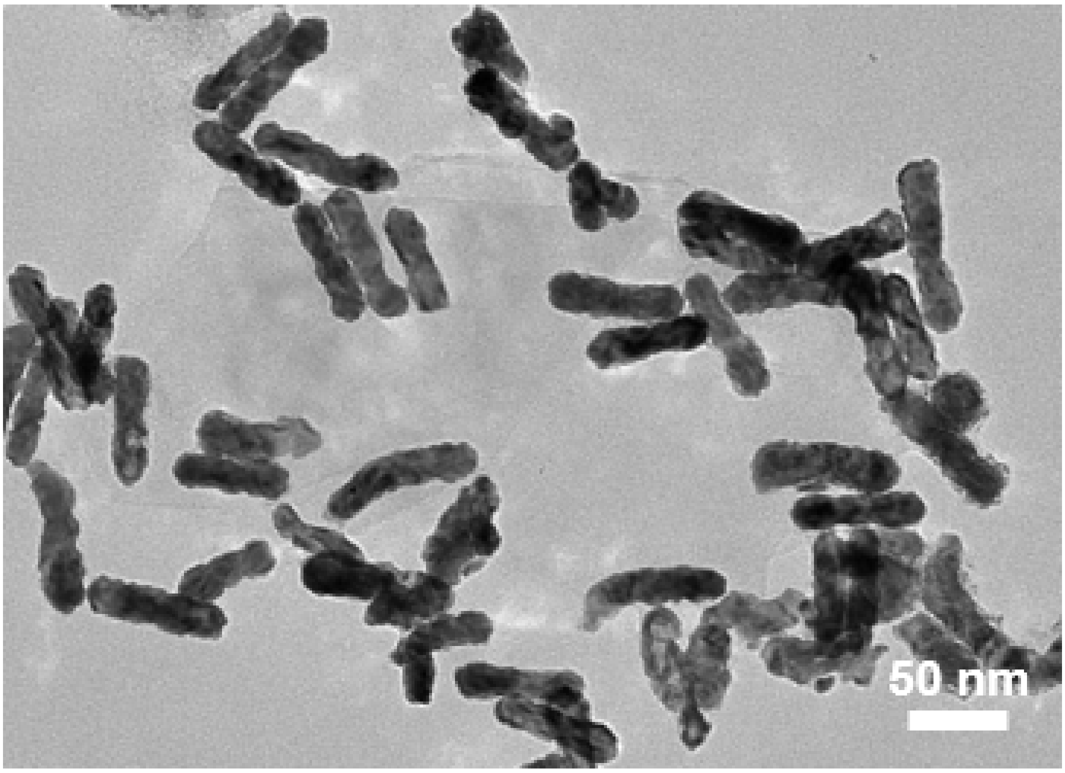

Figure S14. Representative TEM image of E-Au-Pt after testing the stability.

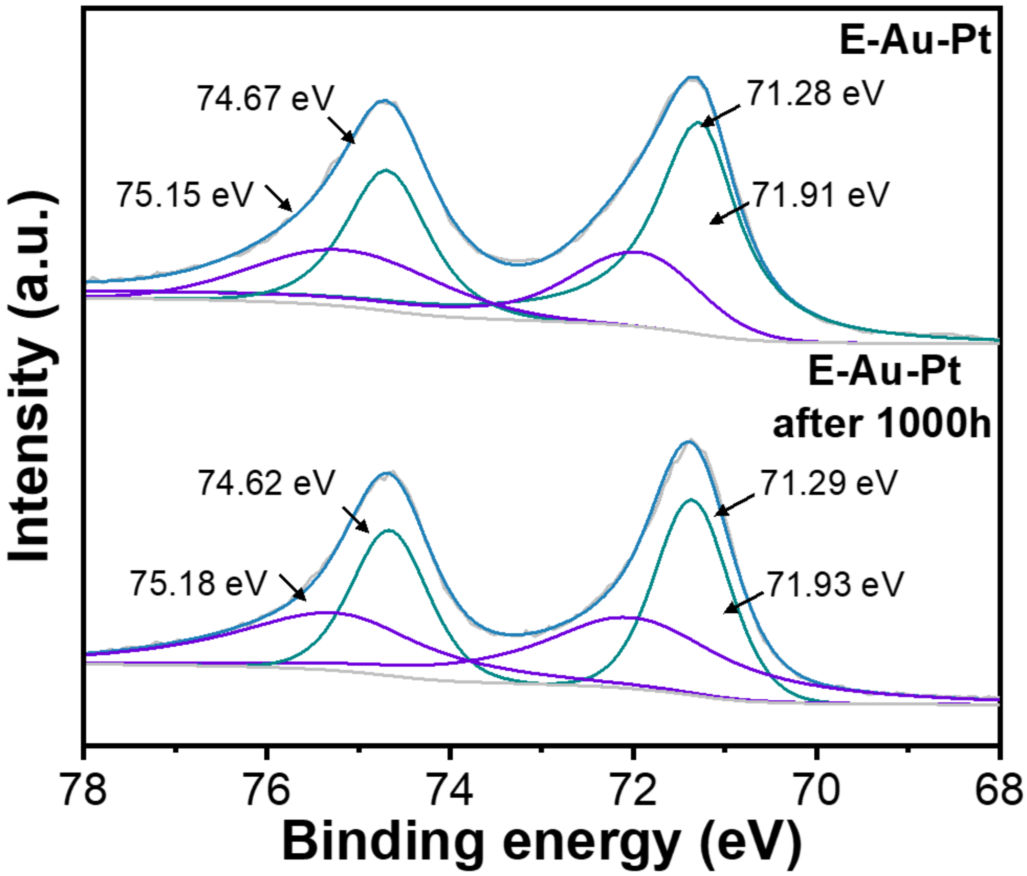

Figure S15. XPS spectra of E-Au-Pt after testing the stability.