Supplementary Information

AuPt Alloy Nanowires via Heterogeneous Doping for Enhanced Ethanol Electrooxidation

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Chemicals

All aqueous solutions were prepared using deionized (DI) water (resistivity > 1 8.25 MΩ·cm^{-1}). Hydrogen tetrachloroaurate (III) ($HAuCl_4 \cdot 3H_2O$, 99.9%, Au 49%o n metals basis, Alfa Aesar), oleylamine (90%, Sigma Aldrich), triisopropylsilane (TIPS, 98%, Sigma Aldrich), hexane (98%, Sigma Aldrich), potassium tetra-chl oroplatinate (K_2PtCl_4, 98%, Sigma Aldrich), potassium hydroxide (KOH, 95%, Alfa Aesar), ethanol (EtOH, analytical grade).

Synthesis of the Au NWs and the Au-Pt alloy NWs

Ultrathin Au NWs were firstly synthesized and purified following the reported methods. Firstly, 20 mg $HAuCl_4 \cdot 3H_2O$ was weighed into a 5 mL glass vial. Then, mix the filtered 330 μL of oleylamine (OAm) and 1.32 μL of hexane evenly, and heat at 40°C for 10 s. Finally, immediately add 500 μL of TIPS and ultrasonicate for 30 s. The mixture was placed in a constant temperature box at 30°C and incubated for 24 h to obtain brown Au NWs. 400 μL of the above-synthesized Au NWs dispersion was carefully transferred above 1 mL of the $CHCl_3$/tetrahydrofuran (THF) (1:4,v/v) mixed solvent and centrifuged at 11,500 rpm for 12 min. The middle brown layer (~400 μL) was collected, the purified Au NWs can be obtained.

The as-purified Au NWs (initially 200 μL) was dispersed in 600 μL THF, followed by the addition of 60 μL K_2PtCl_4 aqueous solution. After the addition of the reductant TIPS, the reaction mixture was mixed thoroughly and incubated undisturbed under ambient condition of 1 h to facilitate the formation of the Au-Pt alloy NWs.

Electrochemical measurements

The total catalyst loading on the glassy carbon electrode is approximately 25 μg $_{metals}$/cm^2. The specific loading method is as follows: 1.2 mg of carbon black (Rohn Superconductor K90) and 0.3 mg metal catalysts were dispersed in 975 μL of a mixture of isopropanol and water to form a uniform suspension. The suspension was then incorporated into a catalyst containing a total of 0.3 mg of metal. Subsequently, the resulting mixture was sonicated in an ice bath for 20 minutes, and a 2.5% Nafion solution was added to the mixture, followed by 50 minutes of ultrasonication. A 6 μL droplet of the prepared catalyst ink were dispensed onto a glassy carbon electrode (GCE) to form the working electrode. The final mass percentage of Pt in the AuPt nanowires catalyst is approximately 14%~18% (with slight variations depending on the composition).

All electrochemical experiments were performed with an electrochemical workstation (CHI 650E) using a conventional three-electrode system at room temperature. Glassy carbon electrode (GCE, Φ=3 mm) was used as working electrode, platinum wire electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. The glassy carbon electrode was polished with Al_2O_3 slurry and washed with ethanol and deionized water in an ultrasonic bath. In this work, all measured potentials are referred to as reversible hydrogen electrode (RHE) potentials.

Ethanol oxidation reaction (EOR) measurements were firstly performed cyclic voltammetry (CV) in N_2-saturated 1.0 M KOH electrolyte to obtain stable voltametric curves to activate the electrode. EOR measurements were performed at room temperature under N_2-saturated 1.0 M KOH +1.0 M ethanol electrolyte. At a scan rate of 50 $mV \cdot s^{-1}$, the CV of EOR was recorded between 0.058 V and 1.457 V relative to RHE. The chronoamperometric curve were recorded at a constant potential of 0.78 V (vs. RHE) for 3,600 s.

The electrochemical active surface area (ECSA) was measured by integrating the hydrogen adsorption charge on CV at a rate of 50 mV s^{-1} in 0.5 M H_2SO_4 saturated with N_2 at room temperature. Assuming that the amount of electricity required per unit area of Pt to adsorb a monolayer of hydrogen is 0.21 mC/cm^2, the hydrogen adsorption/desorption zone is used to calculate the surface area of the catalyst.

Concentration of K_2PtCl_4	Weight(%) Au	Weight(%) Pt	Atomic (Au : Pt)
10mM	31.24	68.76	1:2.22
15mM	26.45	73.55	1:2.82
30mM	13.30	86.70	1:6.56
50mM	8.87	91.13	1:10.36

Table S1 Element compositions of various Au-Pt NWs determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

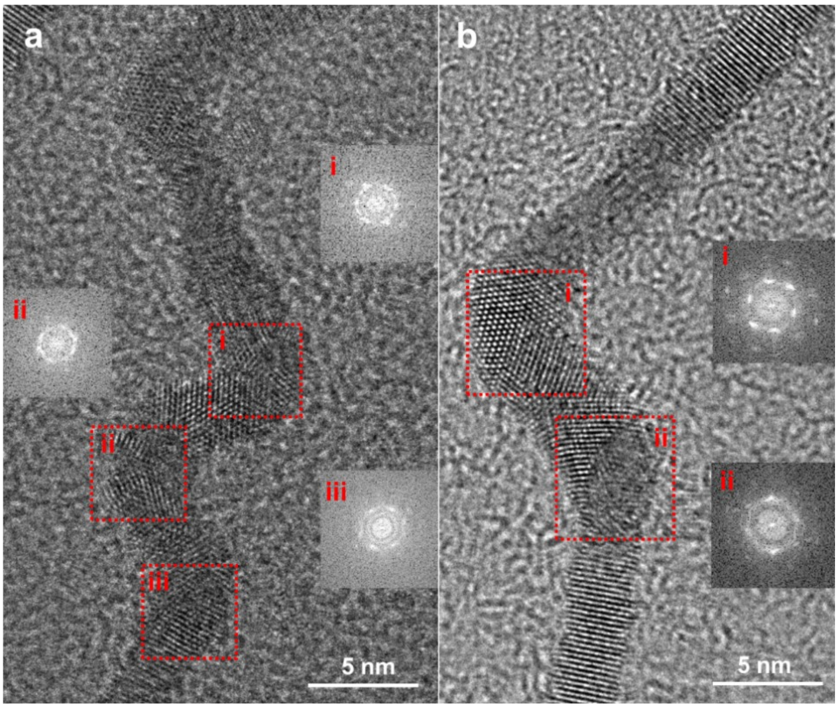

Figure S1 (a-b) HRTEM and FFT images of highly curved regions of AuPt nanowires

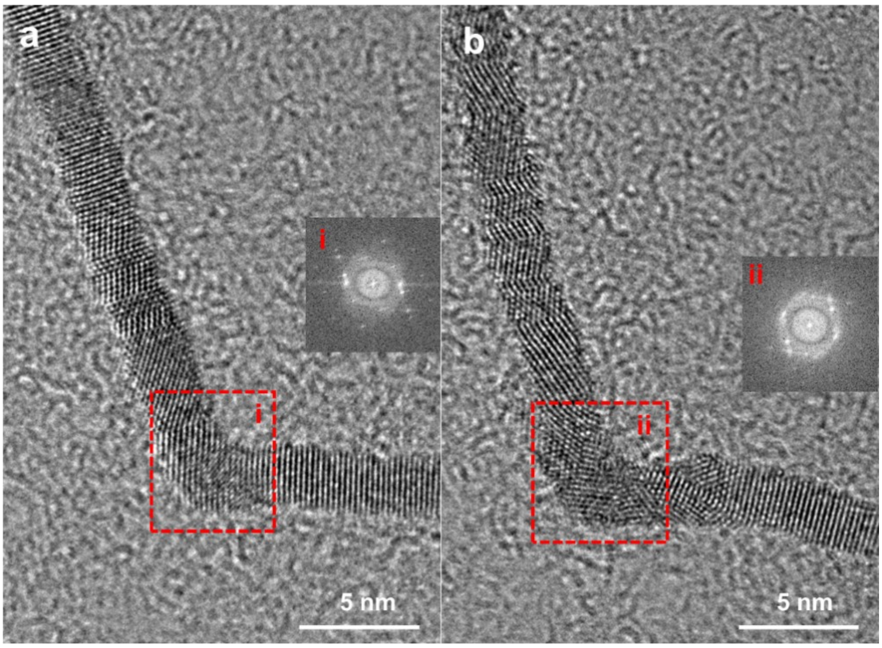

Figure S2 (a-b) HRTEM and FFT images of AuPt nanowires with similar bending angles

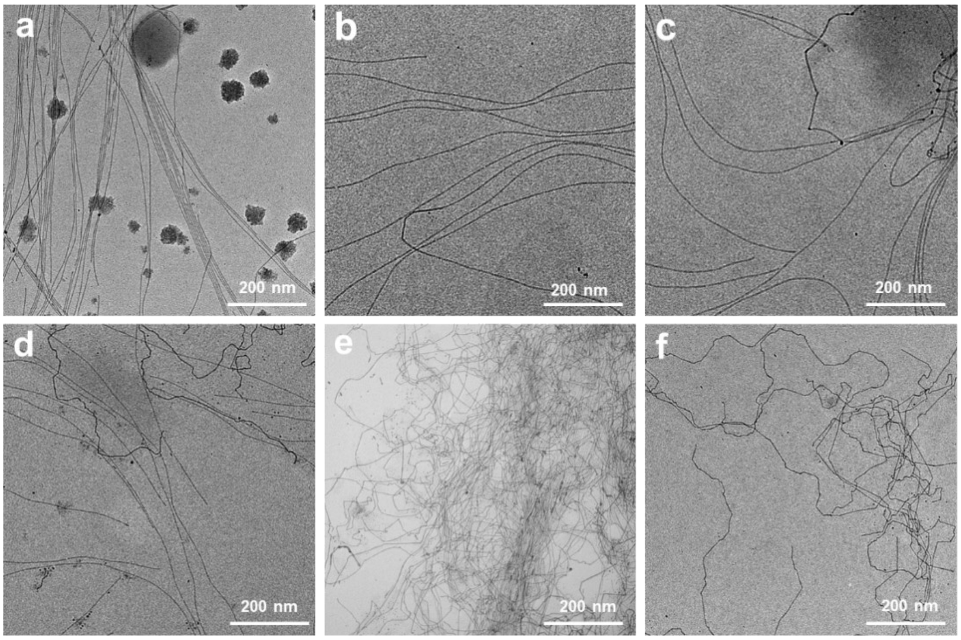

Figure S3 TEM images of Au-$Pt_{6.6}$ NWs collected at different time (a) 0 min (b) 15 min (c) 30 min (d) 40 min (e) 45 min (f) 50 min

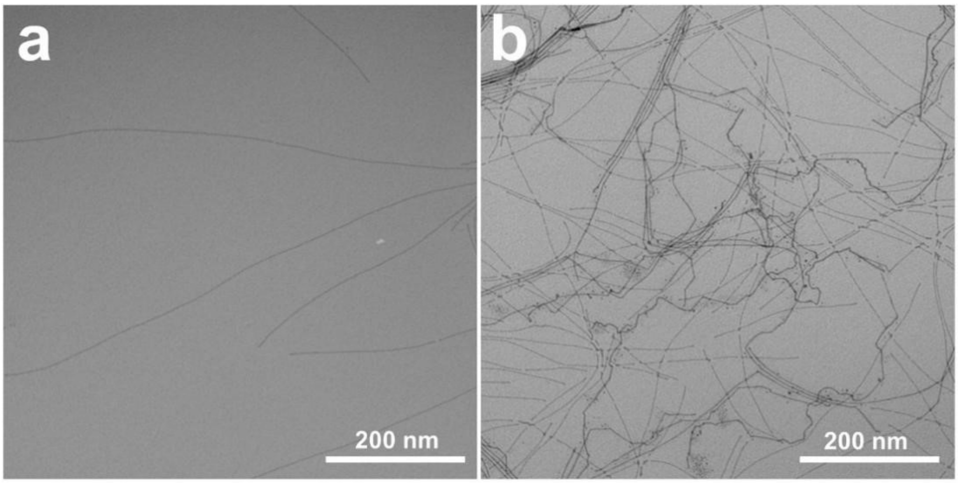

Figure S4 TEM images of Au-Pt NWs formed with (a) 11.45 mM and (b) 13.25 mM of K_2PtCl_4.

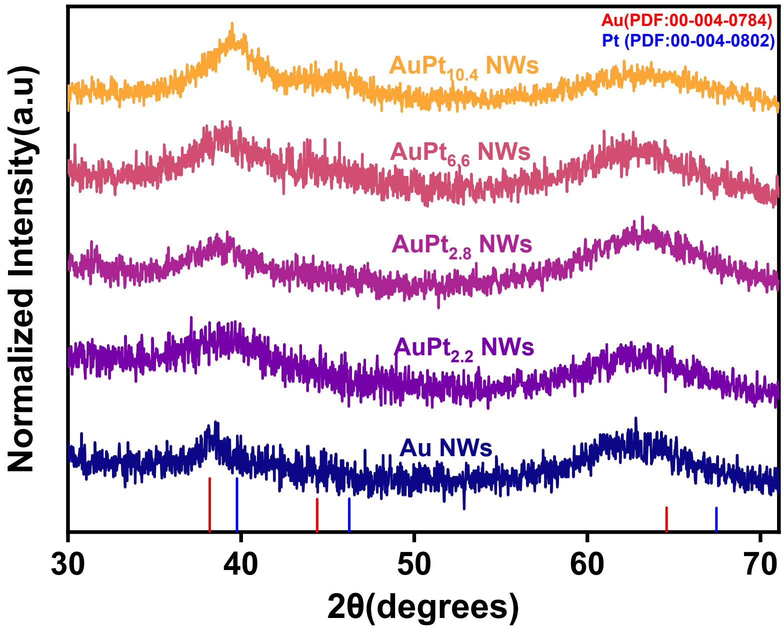

Figure S5 XRD spectra of different AuPt NWs.

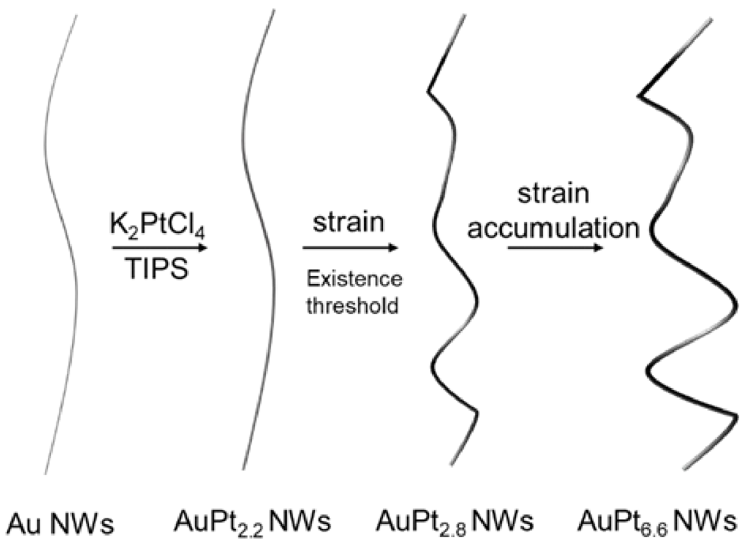

Figure S6 Schematics illustrating the transformation from Au to bent AuPt NWs.

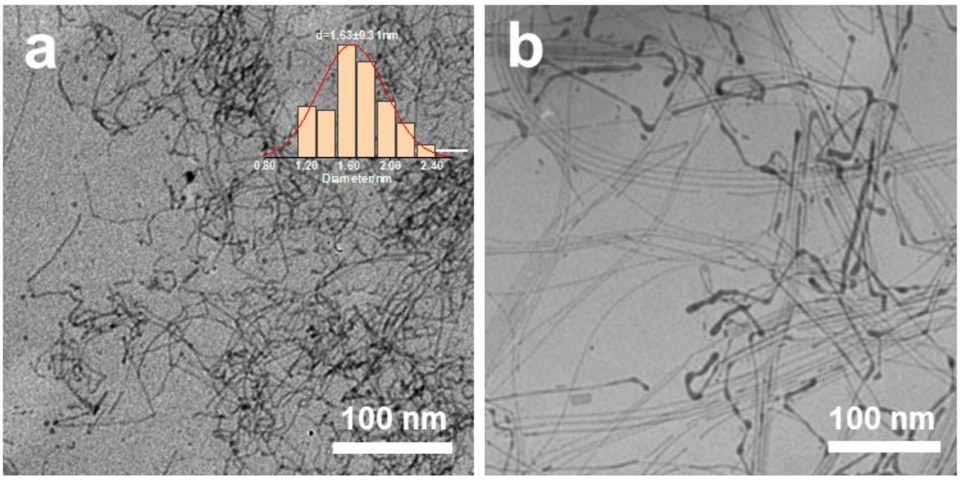

Figure S7 TEM images of Au/Au-Pt NWs formed with (a) 2 mM $NaBH_4$ reduction and (b) in absence of reductants.

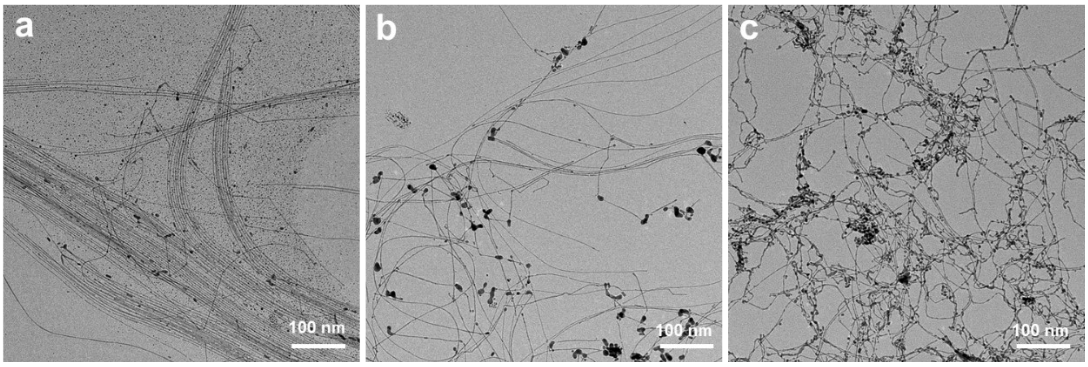

Figure S8 TEM images of the Au/AuPt nanowires/nanostructures formed with 5 mM of (a) hydroquinone, (b) L-ascorbic acid and (c) sodium triethoxyborohydride as the reductant.

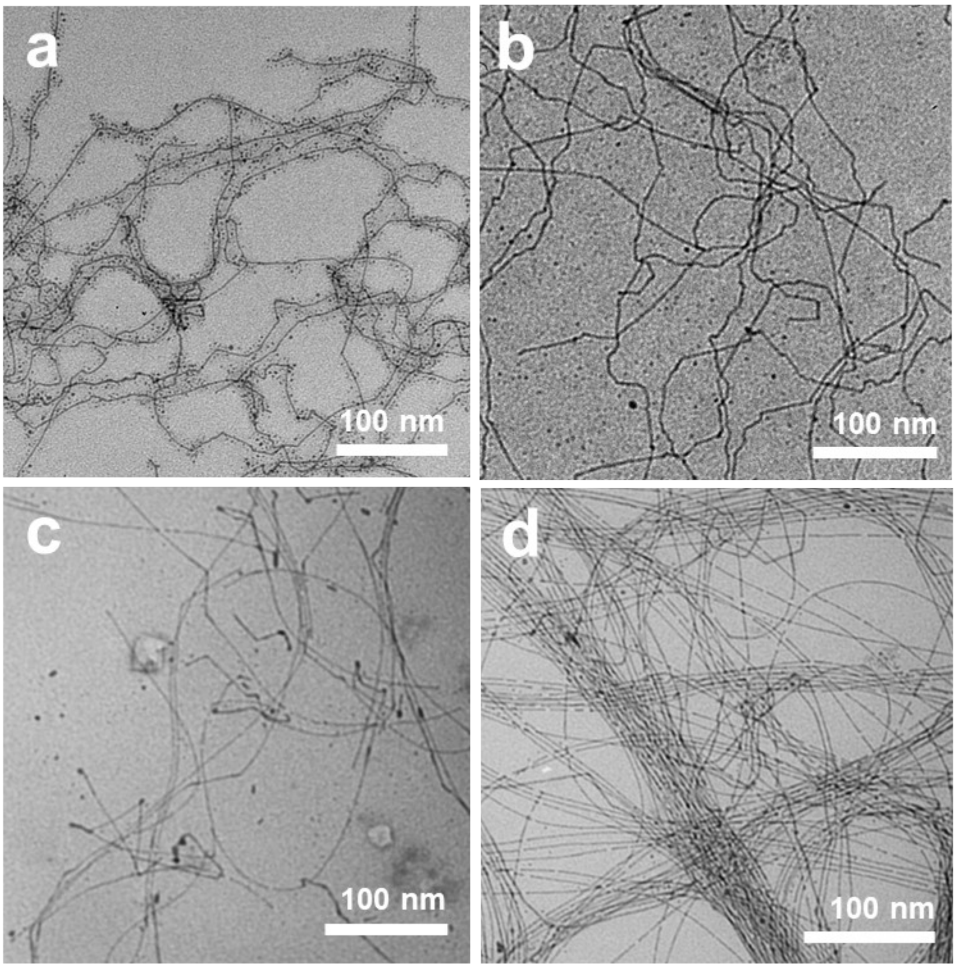

Figure S9 TEM images of the AuPt NWs obtained with (a) 100 μL, (b) 30 μL, (c) 10 μL and (d) 5 μL of TIPs as reductant.

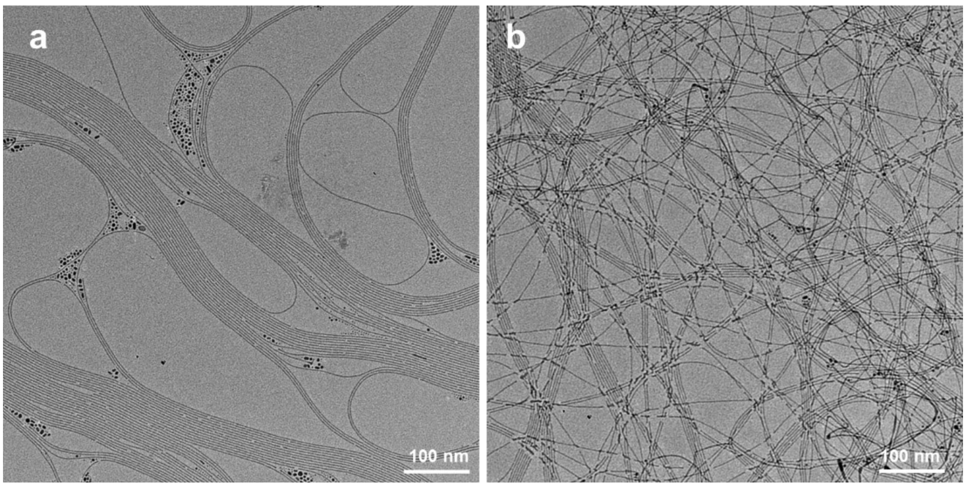

Figure S10 Figure R10 and S10. TEM images of (a) of Au NWs and (b) Au NWs incubated in TIPS for 50 min.

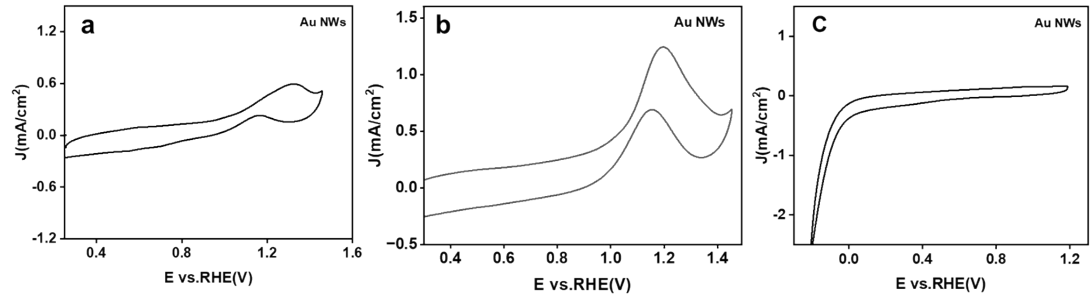

Figure S11 Cyclic voltammetry curves of Au NWs in (a) 1 M KOH + 1 M ethanol, (b) 1 M KOH + 1 M acetaldehyde, and (c) 1 M KOH + 1 M acetic acid.

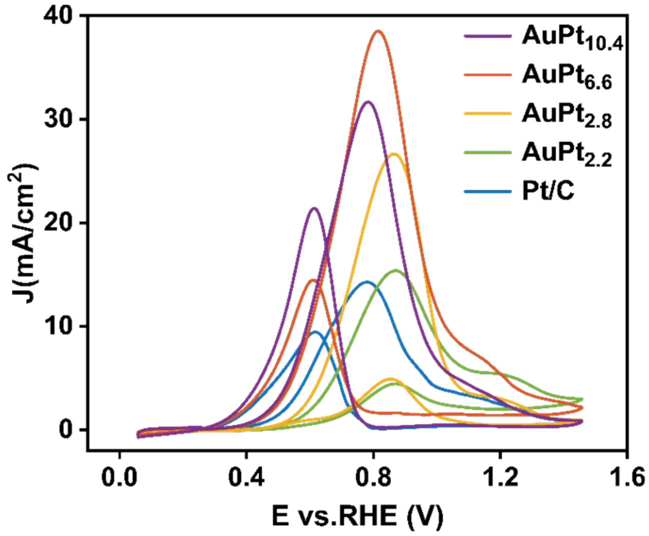

Figure S12 CV curves of Au-Pt NWs and commercial Pt/C

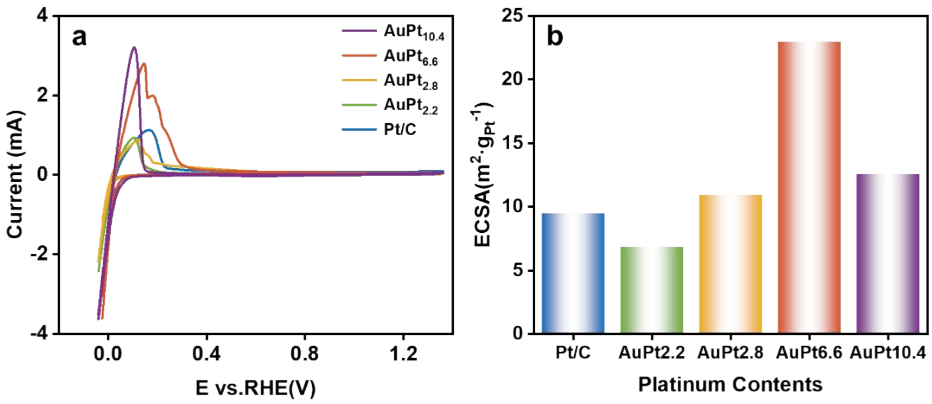

Figure S13 (a) CV curves of commercial Pt/C and AuPt NWs were recorded in 0.5 M H_2SO_4 aqueous solution at room temperature at scan rate of 50 mV/s (b) The calculated ECSAs of the Au-Pt alloy NWs and Pt/C.

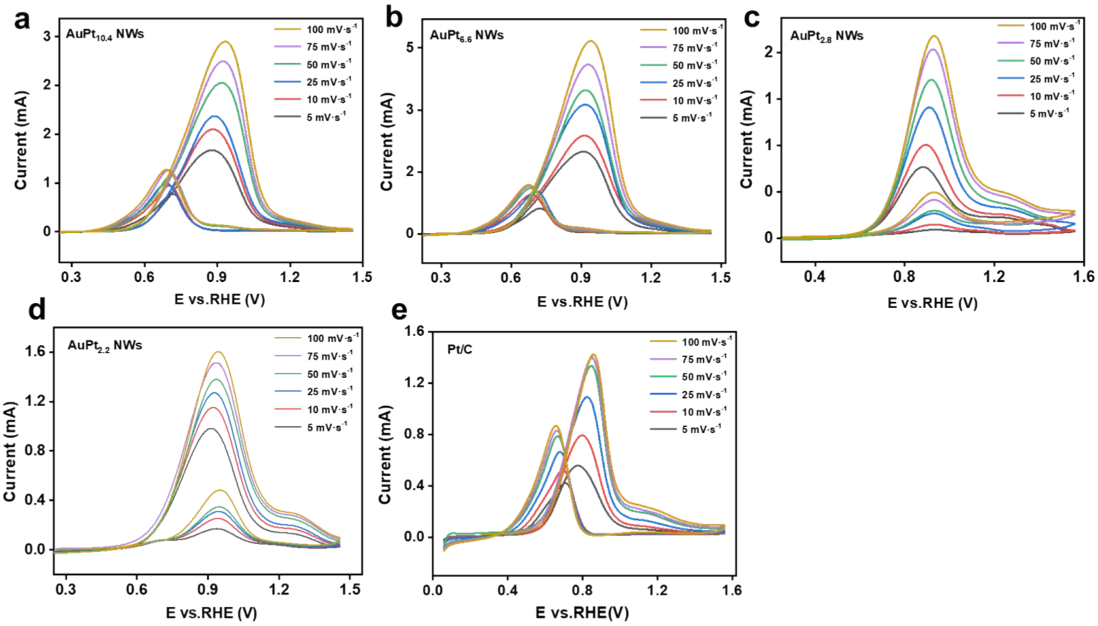

Figure S14 Cyclic voltammetry curves of different AuPt nanowires at various scan rates (a) $AuPt_{10.4}$ NWs (b) $AuPt_{6.6}$ NWs (c) $AuPt_{2.8}$ NWs (d) $AuPt_{2.2}$ NWs (e) Pt/C

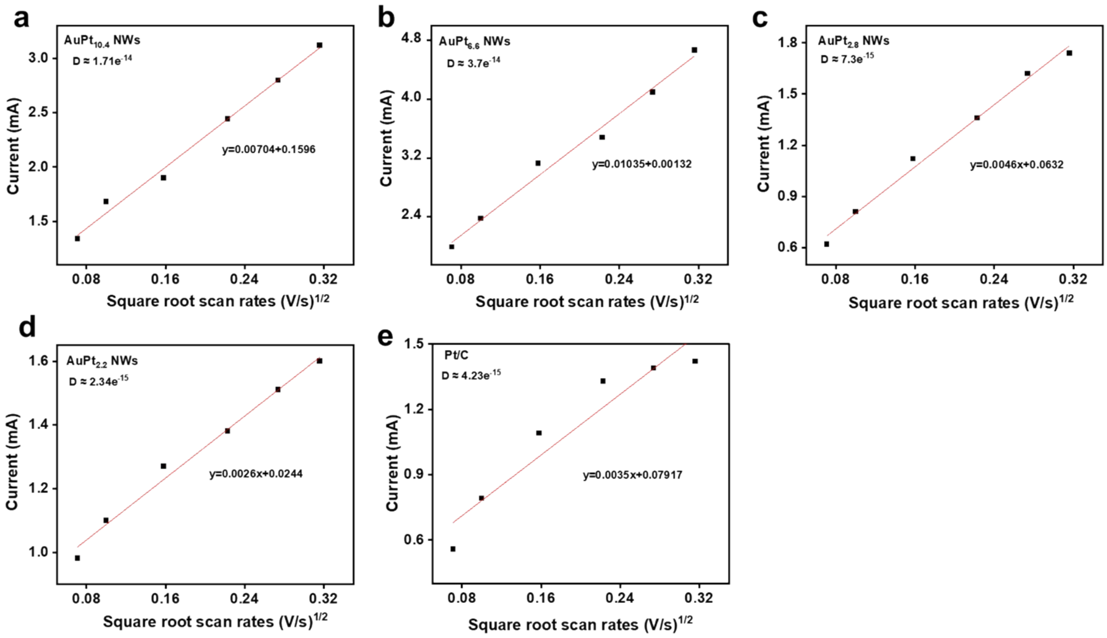

Figure S15 Relationship between peak current density and $v^{1/2}$ for different AuPt nanowires at various scan rates (a) $AuPt_{10.4}$ NWs (b) $AuPt_{6.6}$ NWs (c) $AuPt_{2.8}$ NWs (d) $AuPt_{2.2}$ NWs (e) Pt/C (D represents the mass transfer coefficient)

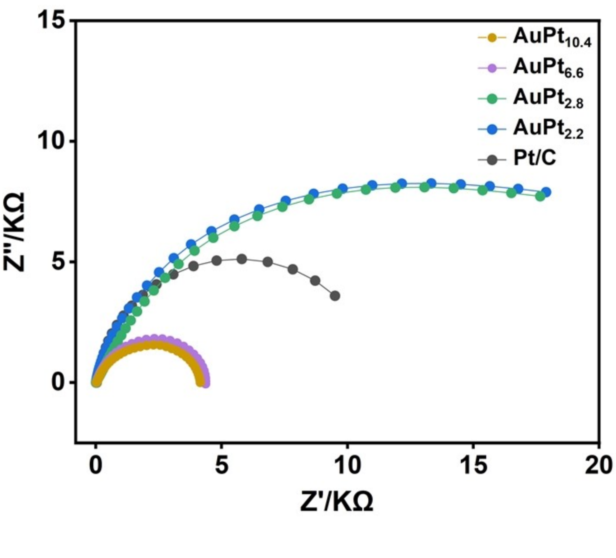

Figure S16 Electrochemical impedance spectroscopy (EIS) analysis of Pt/C and different AuPt alloy NWs.

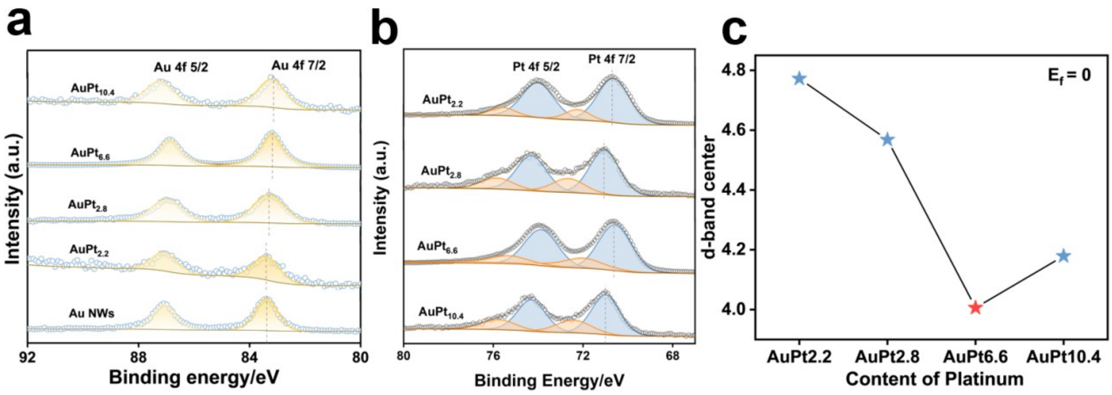

Figure S17 (a) Au 4f XPS spectra of the synthesized Au NW and Au-Pt alloy NWs (b) Pt 4f XPS spectra of the Au-Pt alloy NWs (c) The position of the d-band center relative to the Fermi Level (E_f=0) for Pt with various Pt content.

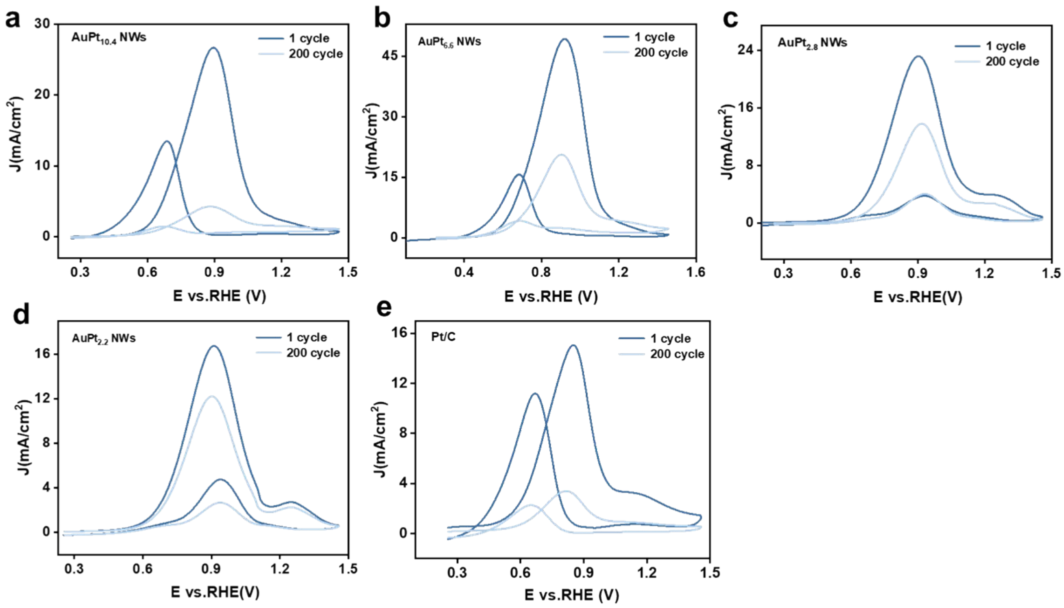

Figure S18 Cyclic voltammetry plots showing the durability of different AuPt nanowires (a) $AuPt_{10.4}$ NWs (b) $AuPt_{6.6}$ NWs (c) $AuPt_{2.8}$ NWs (d) $AuPt_{2.2}$ NWs (e) Pt/C.

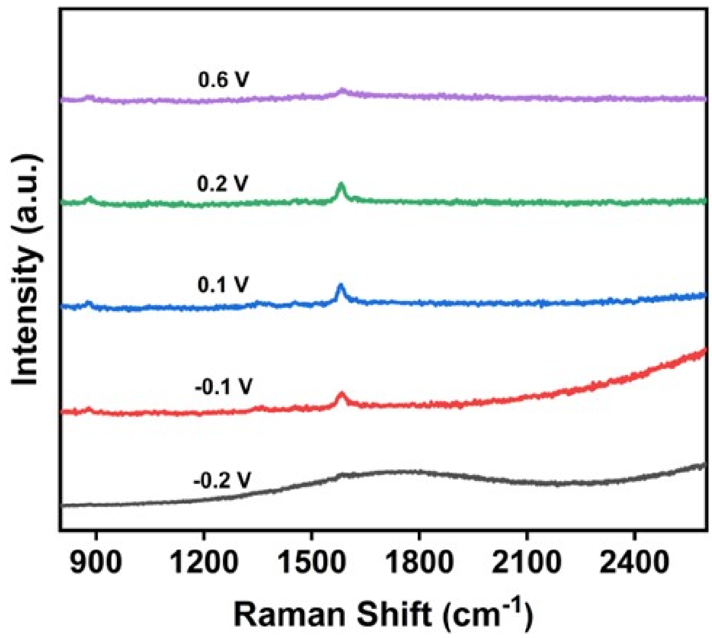

Figure S19 *In-situ* Raman spectra of the EOR process with $AuPt_{6.6}$ NWs as the catalysts.

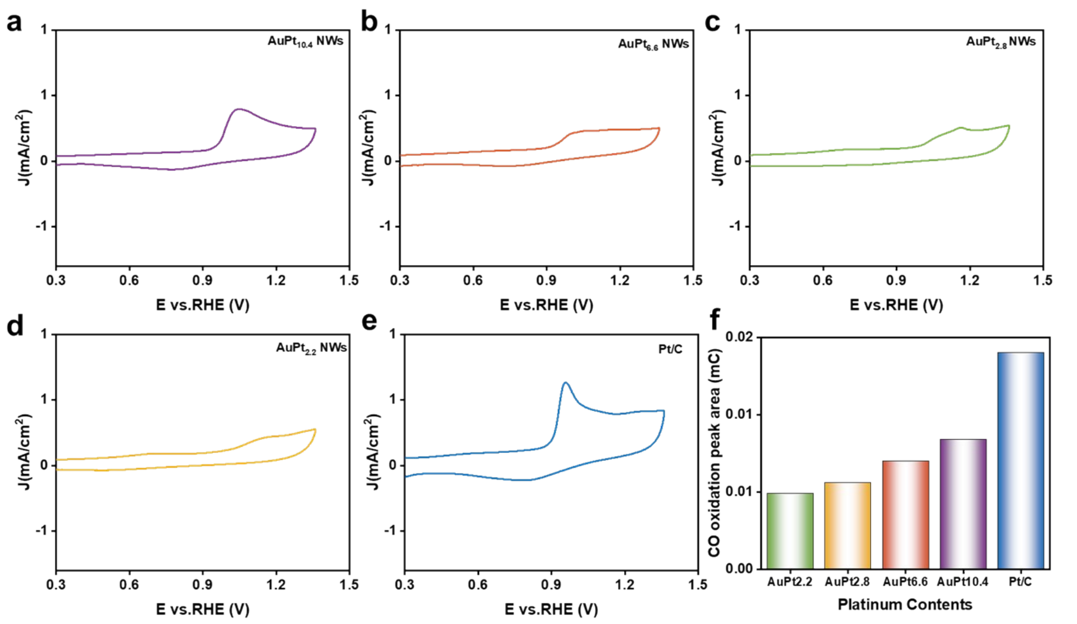

Figure S20 CO stripping voltammetry of (a) $AuPt_{10.4}$ NWs (b) $AuPt_{6.6}$ NWs (c) $AuPt_{2.8}$ NWs (d) $AuPt_{2.2}$ NWs (e) Pt/C (f) Statistical chart of CO oxidation peak area integrals.