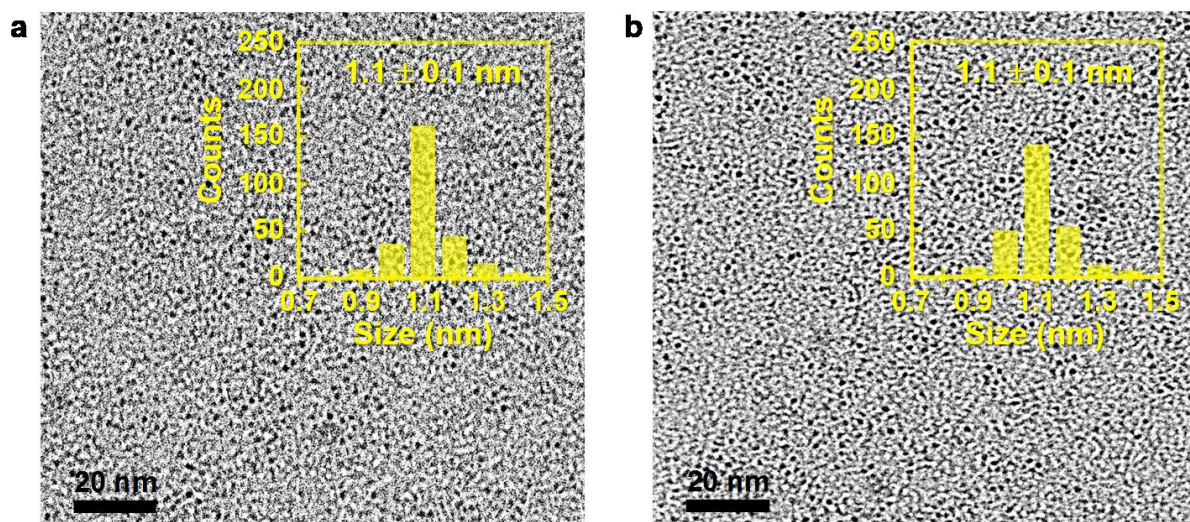
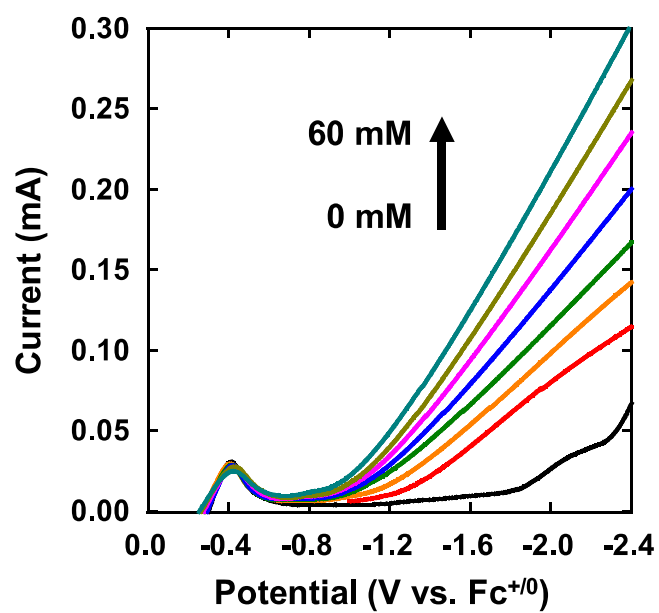
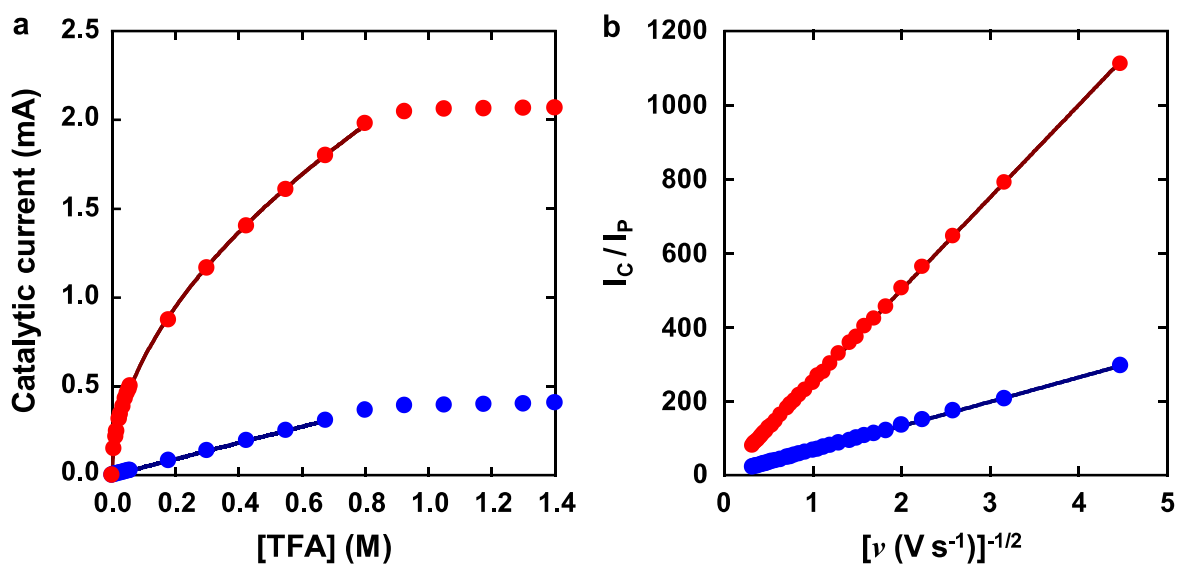




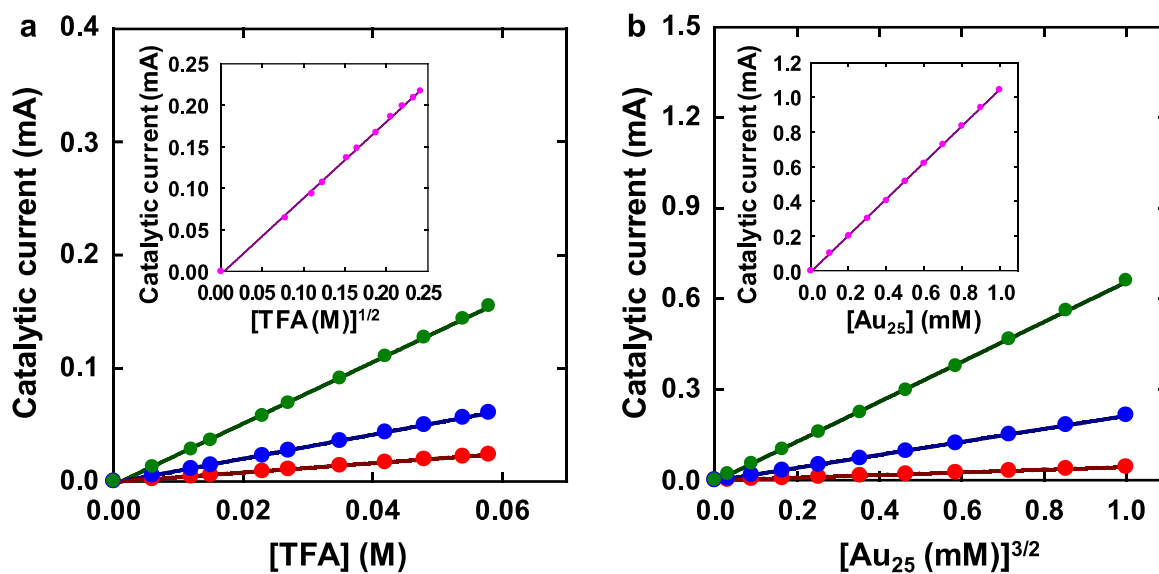
Supplementary Figure 1 | Transmission electron microscopy (TEM) images of metal clusters. TEM images of **a**, Au₂₅ and **b**, PtAu₂₄ clusters. Scale bar for the TEM images is 20 nm and the insets show the histograms of the core size distribution.



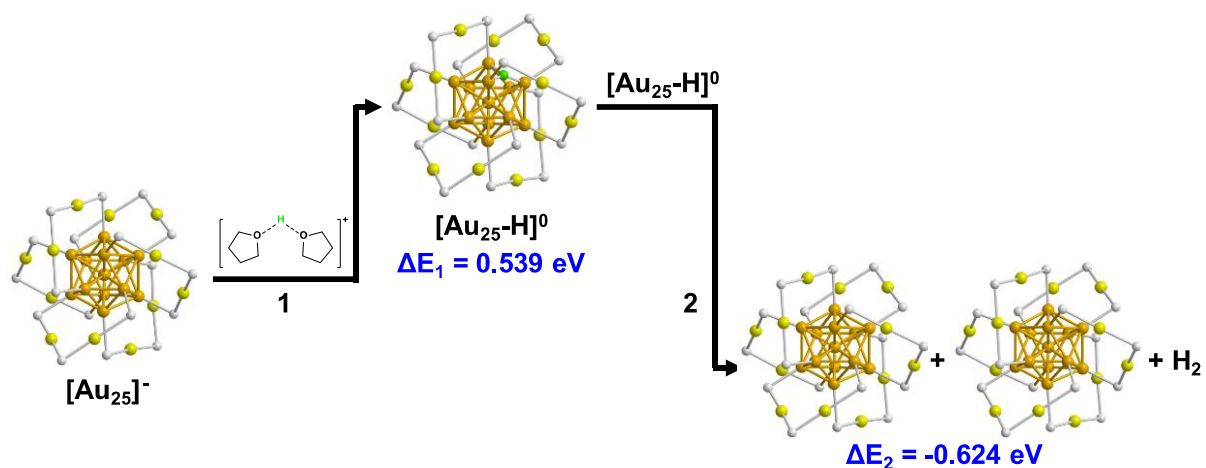
Supplementary Figure 2 | TFA dependent HER catalyzed by Au₂₅. LSVs of Au₂₅ (1 mM) in THF containing 0.1 M Bu₄NPF₆ at 50 mVs⁻¹ in the presence of 0, 4, 8, 12, 21, 34, 45, and 60 mM of TFA.



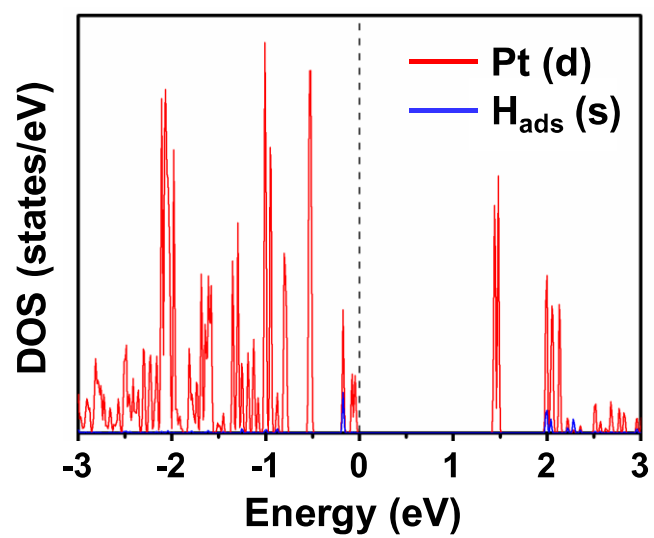
Supplementary Figure 3 | Determination of k_{obs} values. **a**, Dependence of the catalytic current on the concentration of TFA in the presence of 1 mM PtAu₂₄ (red) and 1 mM Au₂₅ (blue) at -1.5 V. **b**, Plots of I_c/I_p versus $v^{-1/2}$ ($v = 0.05 - 10 \text{ V s}^{-1}$) for a THF (0.1 M Bu₄NPF₆) solution containing 1.0 M TFA in the presence of 1 mM PtAu₂₄ (red) and 1 mM Au₂₅ (blue) at -1.5 V.



Supplementary Figure 4 | Charge-state dependent electrochemical HER mechanisms catalyzed by Au_{25} . Dependence of the catalytic current, I_c , **a**, on the concentrations of TFA in the presence of Au_{25} (1 mM) and **b**, on the concentration of Au_{25} in TFA (1.0 M) solution at -1.0 (red), -1.3 (blue), and -1.8 (green) V. Insets show plots for dependence of the I_c on the concentrations of **a**, TFA and **b**, Au_{25} at -2.2 V. The data are fitted by first-order linear functions (solid lines).



Supplementary Figure 5 | Reaction pathway for the production of H₂ from the reaction of [Au₂₅]⁻ with TFA. In step 1, a solvated proton is transferred from THF molecules to [Au₂₅]⁻ to form [H-Au₂₅]⁰; in step 2, an adsorbed H in one [H-Au₂₅]⁰ reacts with a second adsorbed H in a second [H-Au₂₅]⁰ to form H₂. The calculations are at the DFT-TPSS level; besides the two explicit solvent molecules, an implicit solvent model is also included for the whole system.



Supplementary Figure 6 | The orbital-projected density of states on Pt in PtAu₂₄ and the adsorbed H atom. The Fermi level is set as zero.

Supplementary Note 1. Synthesis of Au₂₅(SC₆H₁₃)₁₈ and PtAu₂₄(SC₆H₁₃)₁₈. The Au₂₅ and Pt-doped clusters were synthesized according to the procedures reported elsewhere (ref. 34). The syntheses were very reproducible and the purity of the synthesized clusters was confirmed by mass spectrometry and absorption spectrometry.

Supplementary Note 2. Chemicals. Potassium chloride (KCl, >99%), tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, >99%), trifluoroacetic acid (TFA, >99%), Nafion® (5 wt% solution), and carbon black (Vulcan XC-72) were purchased from Sigma-Aldrich. Britton-Robinson aqueous universal buffer solution was prepared from phosphoric acid (H₃PO₄, 85%), boric acid (H₃BO₃, >98.5%), acetic acid (CH₃COOH, 99.5%), and sodium hydroxide (NaOH, 98%). Extrapure grade dichloromethane (CH₂Cl₂) and tetrahydrofuran (THF) were used. Water was purified using a Millipore Milli-Q system (18.2 MΩ·cm). All the chemicals were used as received without further purification.

Supplementary Note 3. Characterization of metal clusters. Matrix-assisted laser desorption ionization (MALDI) mass spectra were acquired using an AB Sciex MALDI-TOF mass spectrometer (4800 plus) equipped with a standard UV nitrogen laser (337 nm). The accelerating voltage was held at 15 kV and the spectrum was collected in a linear-positive ion mode. Sample solution in CH₂Cl₂ (0.7 mM) was mixed with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as a matrix (saturated in CH₂Cl₂) and then applied to the sample plate and air-dried. Absorption spectra were obtained from a Shimadzu UV-vis-NIR spectrophotometer (UV-3600) using freshly prepared cluster solutions in tetrachloroethylene. Transmission electron microscopy (TEM) images were recorded with a JEOL transmission electron microscope (JEOL 2100F). Samples for TEM were prepared by drop-casting CH₂Cl₂ solution of clusters (0.5 mg/mL) on a 400 mesh Formvar/carbon-coated copper grid (01814-F, Ted Pella) and drying for 1 h at room temperature before imaging.