

Supporting information

Grain Boundary—A Route to Enhance Electrocatalytic Activity for Hydrogen Evolution Reaction

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Computational Models and Methods

1. Computational Model

High-angle grain boundaries (HAGBs), $\text{Au}\Sigma 6\{2-21\}/[110]$ and $\text{Au}\Sigma 3\{112\}/110$, were modeled according to coincidence site lattice (CSL) theory,^{1,2} as described by the following expression,

$$\Sigma = X^2 + NY^2 \quad (\text{S1})$$

$$\theta = 2\arctan\left(\frac{Y}{X}\sqrt{N}\right) \quad (\text{S2})$$

$$N = h^2 + k^2 + l^2 \quad (\text{S3})$$

where Σ specifies the relation between the two grains unambiguously; $1/\Sigma$ is the proportion of coincidence sites in the crystal lattice. θ indicates the rotation angle for a given facet (hkl) around the rotation axis $[hkl]$ to make sure that $1/\Sigma$ of lattice sites is coincided in an elementary periodic supercell. N denotes the sum of the squares of the indices of a crystal facet (h , k and l); X and Y are two prime numbers with no common factor.

2. Simulation Method

Electronic structure calculations were performed within the DFT framework, as implemented in the Vienna *ab initio* simulation program (VASP). The revised Perdew–Burke–Ernzerhof(RPBE) exchange-correlation functional within the

generalized gradient approximation (GGA) was used with the projector-augmented wave (PAW) pseudopotential. We used a plane-wave cutoff energy of 450 eV and the First order Methfessel-Paxton scheme with a smearing width of 0.2 eV. The Energy minimization criterion was that all forces on free atoms be < 0.05 eV/Å. The changes on various species were derived using a Bader analysis. To model low-index extended Au(110) flat surfaces, we used an elementary surface GB supercell with three-layer slab on the basis of the optimized lattice constants of Au bulk ($a=b=c=4.22$ Å). For structural relaxation and electronic calculation, adsorbate and the uppermost layer were allowed to fully relax in all configurations, while the rest layers were kept fixed during the course of relaxation. A vacuum space of 15 Å perpendicular to the slab surface was used to avoid artificial interactions due to the periodicity boundary condition.

3. Reaction Free Energy:

Binding energy $E_B[\text{H}]$ of hydrogen atom adsorbed on the catalyst surface is defined as:

$$E_B[\text{H}] = E[\text{M} - \text{H}^*] - E[\text{M}] - E[\text{H}] \quad (\text{S4})$$

Where $E[\text{M} - \text{H}^*]$ and $E[\text{M}]$ are the calculated electronic energies of slab with an adsorbed hydrogen atom and bare slab, respectively. $E[\text{H}]$ is referenced to the electronic energy of a hydrogen molecule (H_2).

Gibbs free energies (G) for gaseous and adsorbed hydrogen are calculated at 298.15 K and 101325 Pa, according to the following expressions:

$$G = E_{\text{DFT}} + E_{\text{ZPE}} + \int C_p dT - TS \quad (\text{S5})$$

where E_{DFT} is the electronic energy calculated with VASP; E_{ZPE} is the zero-point energy; $\int C_p dT$ is the enthalpic temperature correction; $-TS$ is the entropy contribution to G . As previously described, for gaseous hydrogen standard ideal gas method was used to calculate E_{DFT} , $\int C_p dT$ and $-TS$ from temperature, pressure, and calculated vibrational energies^[*]. Free energies of adsorbates on the Au surfaces were calculated by treating all $3N$ degrees of freedom of the adsorbate as frustrated harmonic vibrations given that the contribution from the vibrations of the substrate Au

surfaces is negligible. All vibrations were treated in the harmonic oscillator approximation^[*].

The computational hydrogen electrode (CHE) model was employed to determine free energies of reaction intermediates under an applied external potential (U). The Gibbs energy change of $* + (\text{H}^+ + \text{e}^-) \rightarrow \text{H}^*$ is simplified as:

$$\Delta G = \Delta G(\text{H}^*) - G(*) - (\mu[\text{H}_2] - eU) \quad (\text{S6})$$

The chemical potential of a proton-electron pair, $\mu[\text{H}^+ + \text{e}^-]$, is equal to a half of the chemical potential of gaseous hydrogen at $U=0$ vs the reversible hydrogen electrode (RHE), 101325 Pa of H_2 , 298.15 K, and all pH values, $\mu[\text{H}^+ + \text{e}^-] = 0.5\mu[\text{H}_2]$. The limiting potential of proton-electron transfer step is calculated, following $U_L = -\Delta G(\text{H}^*)^{0V}/e$.

4. Exchange Current Density

According to the micro-kinetic model, at equilibrium j_0 can be theoretically computed as an indirect function of ΔG_{H^*} ,

$$j_0 = Fk^0 C_{total} [(1 - \theta)^{1-\alpha} \theta^\alpha] \quad (\text{S7})$$

$$\theta = \frac{\exp\left(-\Delta G_{\text{H}^*}/k_B T\right)}{1 + \exp\left(-\Delta G_{\text{H}^*}/k_B T\right)} \quad (\text{S8})$$

where k^0 is the standard rate constant, α is the transfer coefficient (α is set to be 0.5 in this work), C_{total} is the total number of HER active sites on the surface of catalyst and k_B is the Boltzman constant. Thus a relationship between the j_0 and ΔG_{H^*} can be built.

The current density in one direction at one reaction's equilibrium potential(0V versus the standard electrode (SHE) for HER) can be estimated using Butler-Volmer equation as follows:

$$j = j_{forward} + j_{backward} = j_0 [e^{-\alpha f \eta} - e^{-(1-\alpha) f \eta}] \quad (\text{S9})$$

α is the anodic charge-transfer coefficient ranging from 0 to 1, f is equal to F/RT and η is the overpotential.

5. Turnover Frequency (TOF)

To calculate the Turnover Frequency (TOF) per Au site on Au/CFP, we used the following formula:

$$\text{TOF} = \frac{\# \text{ total hydrogen turnover /cm}^2 \text{ geometric area}}{\# \text{ active sites /cm}^2 \text{ geometric area}} \quad (\text{S10})$$

The total number of hydrogen turnover was calculated from the current density of the electrochemically active surface area-calibrated linear scan voltammetry (Figure 6(a)). For example, when overpotential is 300 mV, the total number of hydrogen turnover is the current density of LSV in this case (Figure 6c).

The upper limit number of the active sites was calculated based on the hypothesis that Au atoms on the Au/CFP surface form the active Au centers, and are accessible to the electrolyte. As shown in Figure S1, the particle sizes of Au/CFP, Au/CFP₃₀₀ and Au/CFP₄₀₀ are approximately the same and evenly distributed. The active site is considered to be the total amount of Au sputtered. According to the quality of CFP before and after sputtering, the number of active sites can be obtained.

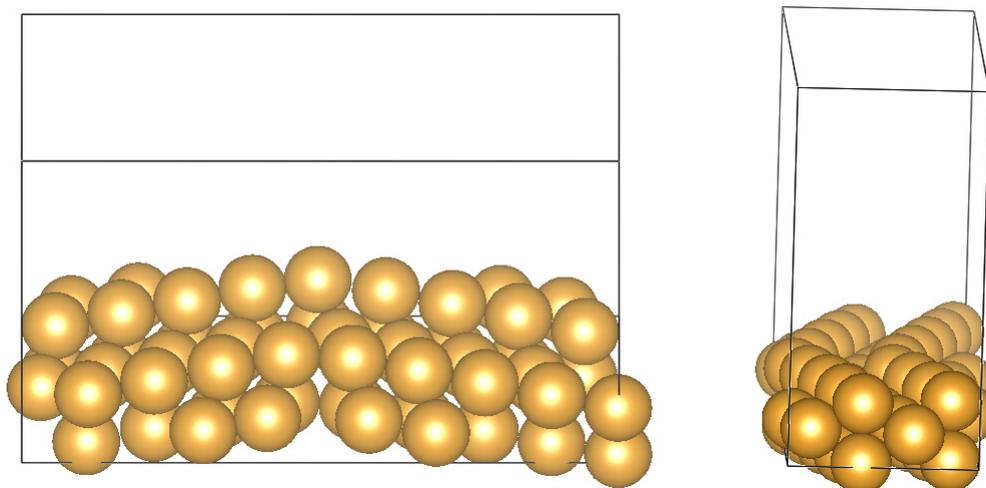


Figure S1. Front and side views of fully relaxed periodic supercells for $\Sigma 6\{2-21\}$ HAGB.

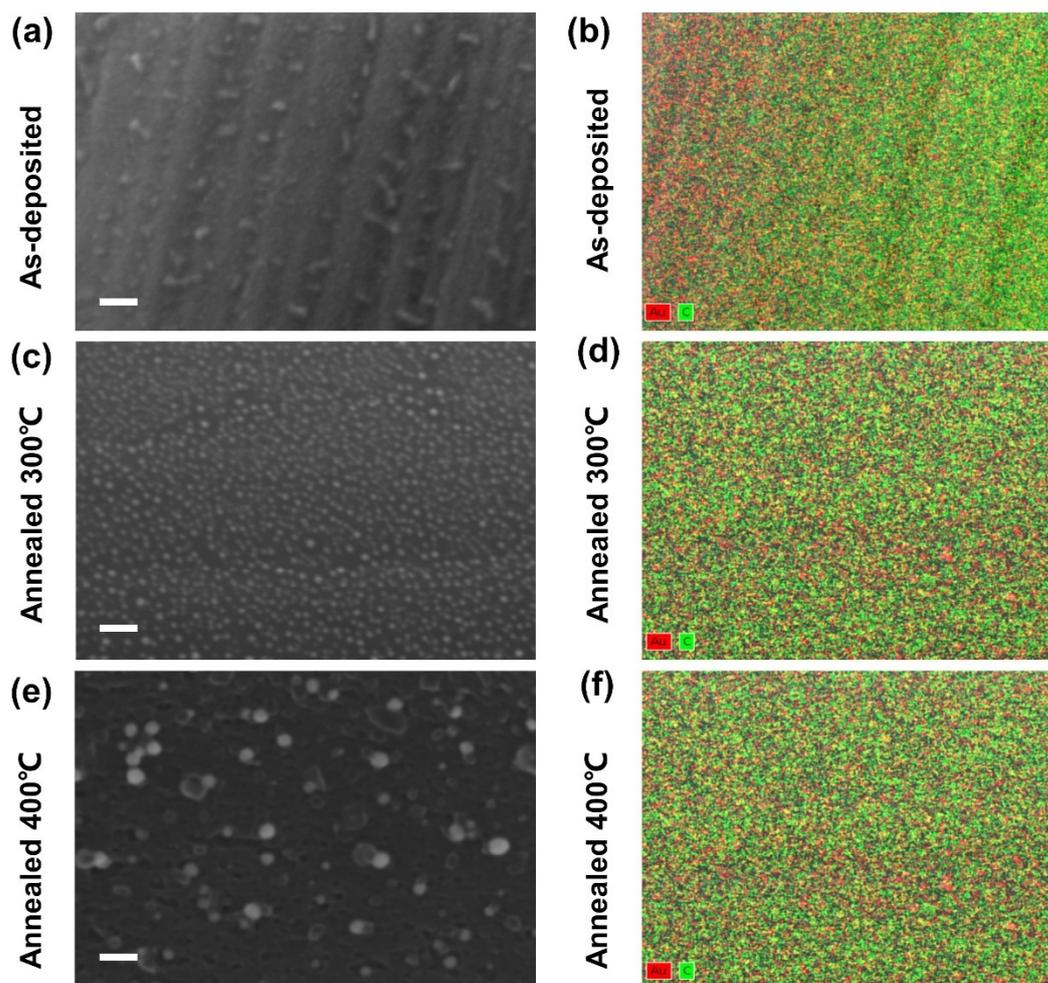


Figure S2. SEM images of as-prepared (a) and annealed Au/CFP electrodes at 300 °C (c) and 400 °C (e), The scale bar represents 100 nm. Compositional maps of as-prepared (b) and annealed Au/CFP electrodes at 300 °C (d) and 400 °C (f), red indicate Au and green indicate carbon.

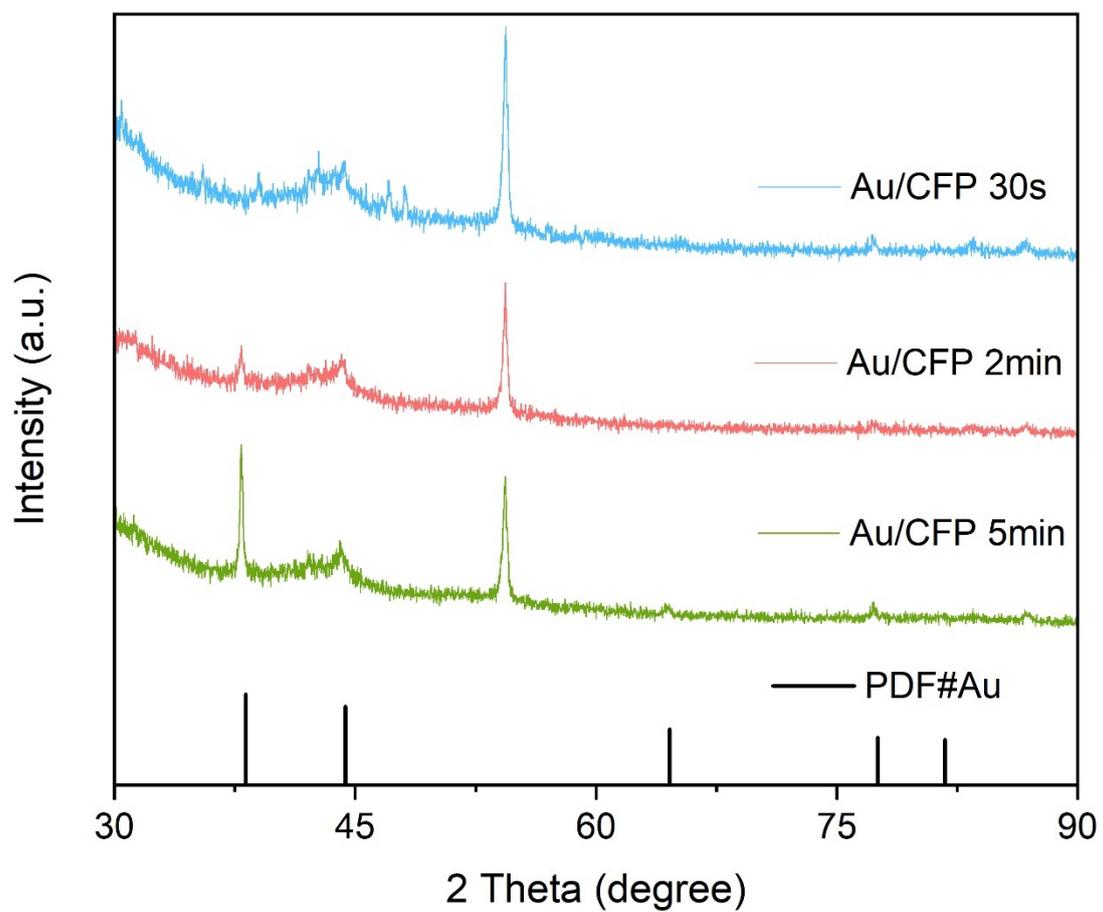


Figure S3. X-ray diffraction patterns of Au/CFP for 30s, 2min and 5min magnetron sputtering.

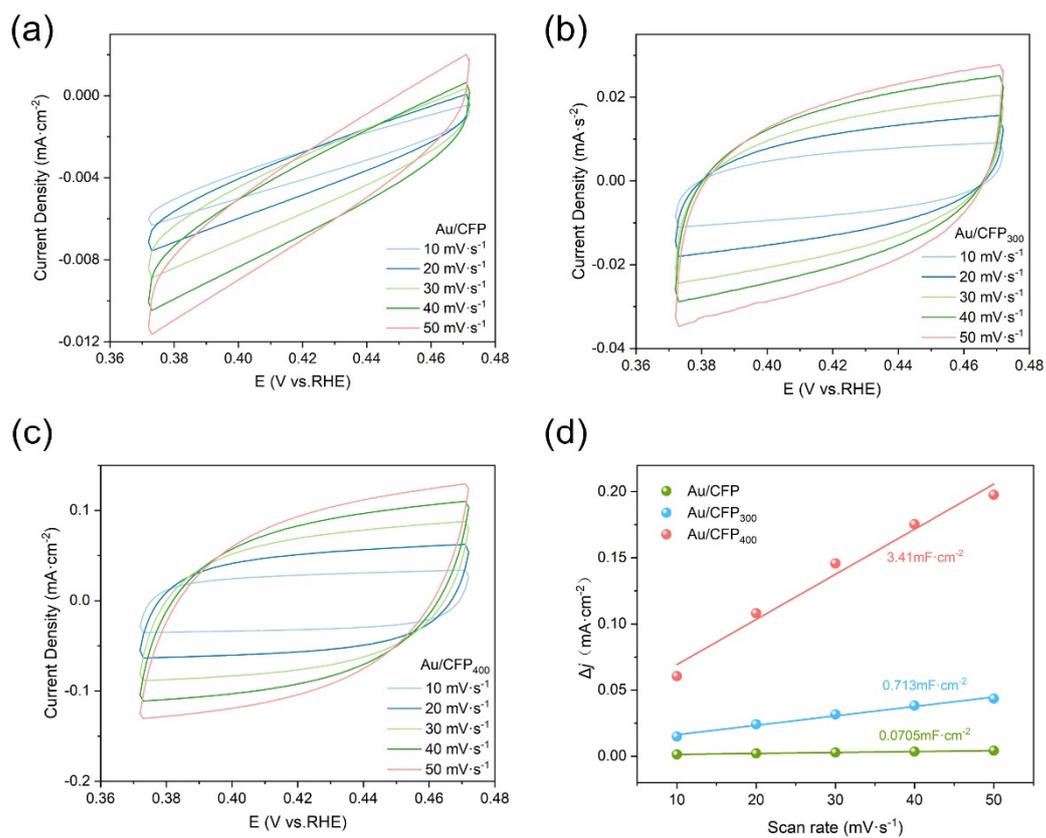


Figure S4. Cyclic voltammograms under different scan rates for (a) Au/CFP, (b) Au/CFP₃₀₀, and (c) Au/CFP₄₀₀. (d) Electrochemically active (EA) surface area derived from the change of charging current density related to scan rate.

Table S1. Calculated values for conversion of electronic energies to free energies. Assumed fugacities for gaseous H₂ are also included.

Species	Fugacity (Pa)	E_{DFT} (eV)	E_{ZPE} (eV)	$\int C_p dT$ (eV)	$-TS$ (eV)
H ₂ (gas)	101325	-7.0425	0.2698	0.0900	-0.4208

Table S2. Calculated values for conversion of electronic energies to free energies on the GBs on Au(110) surface. Assumed fugacities for gaseous species are also included.

Species	E_{DFT} (eV)	E_{ZPE} (eV)	$\int C_p dT$ (eV)	$-TS$ (eV)	$G-E_{\text{elec}}$ (eV)	E_{B} (eV)	G (eV)
H*@Au(110)L	-3.0227	0.1419	0.0383	-0.0965	0.0837	0.4986	0.5822
H*@Au Σ 6(021)/[110]GB_s1	-3.4258	0.1422	0.0355	-0.0900	0.0877	0.0955	0.1832
H*@Au Σ 6(021)/[110]GB_s2	-3.7510	0.1639	0.0118	-0.0181	0.1576	-0.2297	-0.0720
H*@Au Σ 6(021)/[110]GB_s3	-3.7515	0.1649	0.0121	-0.0188	0.1582	-0.2302	-0.0720
H*@Au Σ 6(021)/[110]GB_s4	-3.1817	0.1403	0.0356	-0.0715	0.1043	0.3396	0.4439
H*@Au Σ 6(021)/[110]GB_s5	-3.1861	0.1451	0.0326	-0.0627	0.1151	0.3352	0.4502

*Footnote: $E[\text{H}]$ was referenced to the electronic energies of hydrogen (H₂). $E[\text{H}] = -3.5212$ eV.

Table S3. Calculated values for conversion of electronic energies to free energies of metals on (111) and (211) surface. Assumed fugacities for gaseous species are also included.

Species	E_{DFT} (eV)	E_{ZPE} (eV)	$\int C_p dT$ (eV)	$-TS$ (eV)	$G-E_{\text{elec}}$ (eV)	E_{B} (eV)	G (eV)
H*@Ag(111)	-4.4726	0.1496	0.0146	-0.0239	0.1403	-0.9513	-0.8109
H*@Ag(211)	-3.3845	0.1352	0.0253	-0.0761	0.0844	0.1368	0.2212
H*@Au(111)	-2.9566	0.1518	0.0278	-0.0478	0.1318	0.5647	0.6965
H*@Au(211)	-3.2689	0.1554	0.0290	-0.0529	0.1314	0.2524	0.3838
H*@Cu(111)	-2.9865	0.1465	0.0206	-0.0320	0.1352	0.5348	0.6699
H*@Cu(211)	-3.5826	0.1635	0.0053	-0.0067	0.1622	-0.0613	0.1009
H*@Ni(111)	-3.3682	0.1557	0.0221	-0.0350	0.1428	0.1531	0.2959
H*@Ni(211)	-3.2252	0.1478	0.0295	-0.0640	0.1134	0.2961	0.4094
H*@Pb(111)	-2.5786	0.1178	0.0272	-0.0461	0.0988	0.9427	1.0415
H*@Pb(211)	-2.8413	0.1669	0.0236	-0.0382	0.1523	0.6800	0.8323
H*@Pt(111)	-3.7965	0.1891	0.0171	-0.0254	0.1808	-0.2752	-0.0943
H*@Pt(211)	-3.9701	0.1805	0.0195	-0.0298	0.1702	-0.4488	-0.2785
H*@Ir (111)	-3.8209	0.1885	0.0147	-0.0212	0.1821	-0.2996	-0.1176
H*@Ir (211)	-4.0331	0.1773	0.0191	-0.0290	0.1674	-0.5118	-0.3445
H*@Mo(111)	-3.4441	0.1328	0.0303	-0.0545	0.1085	0.0772	0.1858
H*@Mo(211)	-4.2310	0.1792	0.0098	-0.0144	0.1746	-0.7097	-0.5351
H*@Pd(111)	-3.3392	0.1346	0.0432	-0.1098	0.0680	0.1821	0.2501
H*@Pd(211)	-3.3874	0.1439	0.0337	-0.0648	0.1129	0.1339	0.2468
H*@Ti(111)	-3.1398	0.1628	0.0053	-0.0066	0.1615	0.3815	0.5430
H*@Ti(211)	-4.2410	0.1014	0.0263	-0.0066	0.1210	-0.7197	-0.5987
H*@W(111)	-3.6307	0.1489	0.0234	-0.0377	0.1346	-0.1094	0.0252
H*@W(211)	-4.4016	0.1922	0.0077	-0.0108	0.1891	-0.8803	-0.6912

*Footnote: $E[\text{H}]$ was referenced to the electronic energies of hydrogen (H_2).

$E[\text{H}] = -3.5212$ eV.

Table S4. Calculated values for conversion of electronic energies to free energies of metals on (100) and (110) surface. Assumed fugacities for gaseous species are also included.

Species	E_{DFT} (eV)	E_{ZPE} (eV)	$\int C_p dT$ (eV)	$-TS$ (eV)	$G-E_{\text{elec}}$ (eV)	E_{B} (eV)	G (eV)
H*@Ag(100)	-2.4630	0.1356	0.0244	-0.0399	0.1201	1.0583	1.1784
H*@Ag(110)	-2.4134	0.1428	0.0217	-0.0360	0.1285	1.1079	1.2364
H*@Au(100)	-3.0023	0.1505	0.0311	-0.0568	0.1248	0.5190	0.6438
H*@Au(110)	-3.0227	0.1419	0.0383	-0.0965	0.0837	0.4986	0.5822
H*@Cu(100)	-2.7237	0.1551	0.0183	-0.0275	0.1459	0.7976	0.9434
H*@Cu(110)	-3.4455	0.1757	0.0137	-0.0227	0.1667	0.0758	0.2424
H*@Ni(100)	-3.9672	0.1376	0.0080	-0.0102	0.1354	-0.4459	-0.3105
H*@Ni(110)	-3.2029	0.1566	0.0233	-0.0390	0.1409	0.3184	0.4593
H*@Pb(100)	-1.1464	0.0582	0.0345	-0.0591	0.0337	2.3749	2.4085
H*@Pb(110)	-2.5535	0.1011	0.0413	-0.0965	0.0459	0.9678	1.0136
H*@Pd(100)	-5.7785	0.1691	0.0274	-0.0469	0.1496	-2.2572	-2.1077
H*@Pd(110)	-6.0441	0.1855	0.0180	-0.0272	0.1763	-2.5228	-2.3465
H*@Pt(100)	-3.8156	0.1677	0.0285	-0.0499	0.1463	-0.2943	-0.1480
H*@Pt(110)	-4.1087	0.1869	0.0173	-0.0259	0.1783	-0.5874	-0.4091

*Footnote: $E[\text{H}]$ was referenced to the electronic energies of hydrogen (H_2).

$E[\text{H}] = -3.5212$ eV.

Table S5. The flat surface and grain boundaries active sites on Au(110). The coordination numbers and band centers are given.

Facet/site	$\overline{\text{CN}}^d$	ε_d/eV
Au(110)	7.00	-4.05
AuGB_s1	5.61	-3.38
AuGB_s2	5.66	-3.08
AuGB_s3	6.18	-3.21
AuGB_s4	6.79	-3.47
AuGB_s5	6.79	-3.47