Supplementary Information

Active Sites on Hydrogen Evolution Photocatalyst

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Free energy calculation method. In proton/electron-transfer reaction, the proton-electron pair is always involved simultaneously in photocatalytic process. In order to obtain the free energy of the each elementary step, when involving $H^+ + e^-$, we consider the reference potential to be that of the standard hydrogen electrode (SHE). Then, one can relate the chemical potential for $H^+ + e^-$ to that of 1/2H₂ in the gas phase.¹ That means that at the condition (pH = 0, $P_{H_2} = 1$, T = 298 K and U = 0 V), the free energy of ($H^+ + e^-$) can be directly replaced with the free energy of half a H₂ molecule. Thus, the free energy of the reaction HA \rightarrow A + H⁺ + e⁻ can be calculated according to the reaction HA \rightarrow A + 1/2H₂.

1. The reaction Gibbs free energy change, $\Delta G_0 = \Delta H - T\Delta S$, is calculated as following: The reaction enthalpy ΔH is usually calculated according to ΔE (from DFT) and Δ (PV). The entropy ΔS can be gotten from the experimental data.

2. We consider the effect of a bias on all states involving an electron in the reaction, by shifting the energy of the state by $\Delta G_U = -eU$, where *U* is the electropotential (at the minimum level of conductor band) with respect to the standard hydrogen electrode.

3. At a pH different from 0, we can correct for the free energy of H⁺ ions by the concentration dependence of the entropy: $\Delta G_{pH} = -k_B T \ln(C_{H^+})$.

Then the reaction free energy is calculated as:

$$\Delta G = \Delta G_0 + \Delta G_U + \Delta G_{pH} + \Delta E_{ZPE}$$

Here, the zero point energy correction of ΔE_{ZPE} is usually a small term in H adsorption suggested in reference² and is neglected in this work. For example, it is only ~0.04 eV for H adsorption on Cu(111) surface.

Derivation of volcano relation

For HER, the generally accepted reaction mechanism is

$$H^{+}_{(aq)} + e^{-} + * \rightarrow H^{*} \qquad (1)$$

$$2H^{*} \rightarrow H_{2} + 2^{*} \qquad (2) \text{ Tafel mechanism}$$

$$H^{*} + H^{+}_{(aq)} + e^{-} \rightarrow H_{2} + * (3) \text{ Heyrovsky mechanism}$$

Within microkinetic framework, considering the reaction rate of Tafel mechanism, namely step (1) and

(2) can be written as:

$$r_{1} = k_{1}C_{H^{+}}\theta(1-Z_{1})$$

$$r_{2} = k_{2}(1-\theta)^{2}(1-Z_{2})$$
(1)
(2)

Where θ is the coverage of surface free site, C_{H^+} is the relative concentration of H^+ in the solution. P_{H_2} is relative partial pressure of H_2 in the gas. Z_1 and Z_2 are the reaction reversibility of step (1) and (2), expressed as:

$$Z_{1} = \frac{(1-\theta)}{C_{H^{*}}\theta K_{eq1}}$$

$$P_{\mu} \theta^{2}$$
(3)
(4)

$$Z_2 = \frac{T_{H_2} \sigma}{(1-\theta)^2 K_{eq2}}$$

In the sequential reaction system, the overall reversibility (Z_{tot}) satisfies:

$$Z_{tot} = Z_1^2 Z_2 = \frac{P_{H_2}}{C_{H^+}^2 K_{eq1}^2 K_{eq2}} = \frac{P_{H_2}}{C_{H^+} K_{eq0}}$$
(5)

Where K_{eq1} and K_{eq2} are the reaction equilibrium constant of step (1) and (2), determined by the adsorption energy of hydrogen E_{ad} and ΔG_0 and can be expressed as:

$$K_{eq1} = \exp(-\frac{\Delta G_1}{L_T}) \tag{6}$$

$$K_{eq2} = \exp(-\frac{\Delta G_2}{k_B T})$$
(7)

$$\Delta G_0 = 2\Delta G_1 + \Delta G_2 \tag{8}$$

Where k_B and h are constants, T is reaction temperature. k_1 and k_2 are the rate constant of reaction step (1) and (2), respectively, which can be determined by the transition state theory:

$$k = \frac{k_B T}{h} \exp(-\frac{\Delta G}{k_B T})$$
(9)

If assuming hydrogen adsorption is rate-determining step ($Z_2 = 1$, $Z_I = Z_{tot}^{1/2}$), thus the total reaction rate is

expressed as:

$$r_{tot1} = r_1 = k_1 C_{H^+} \theta (1 - Z_1) = k_1 \frac{C_{H^+} \exp(-\frac{\Delta G_0}{2k_B T}) - P_{H_2}^{1/2}}{\exp(-\frac{\Delta G_0}{2k_B T}) + P_{H_2}^{1/2} \exp(-\frac{\Delta G_1}{k_B T})}$$
(10)

If $\Delta G_1 < 0$, in this case we would expect the rate constant $k_1 = \frac{k_B T}{h}$ and being independent of ΔG_1 , leading

to the following expression:

$$r_{tot1} = \frac{k_B T}{h} \frac{C_{H^+} \exp(-\frac{\Delta G_0}{2k_B T}) - P_{H_2}^{1/2}}{\exp(-\frac{\Delta G_0}{2k_B T}) + P_{H_2}^{1/2} \exp(-\frac{\Delta G_1}{k_B T})}$$
(11)

For the other case where proton adsorption is endothermic $\Delta G_1 > 0$, one can expect that the reaction need to be activated by at least ΔG_1 ; here we assume $k_1 = \frac{k_B T}{h} \exp(-\frac{\Delta G_1}{k_B T})$, and the total reaction rate r_{tot1} can be

expressed as:

$$r_{tot1} = \frac{k_B T}{h} \frac{C_{H^+} - P_{H_2}^{1/2} \exp(\frac{\Delta G_0}{2k_B T})}{\exp(\frac{\Delta G_1}{2k_B T}) + P_{H_2}^{1/2} \exp(\frac{\Delta G_0}{k_B T})}$$
(12)

Similarly, if assuming H₂ desorption is rate-determining step ($Z_1 = 1$, $Z_2 = Z_{tot}$), the total reaction rate is thus expressed as:

$$r_{tor2} = 2r_2 = 2k_2(1-\theta)^2(1-Z_2) = 2k_2 \frac{C_{H^+}^2 - P_{H_2} \exp(\frac{\Delta G_0}{k_B T})}{[C_{H^+} + \exp(\frac{\Delta G_1}{k_B T})]^2}$$
(13)

Under the same assumptions as above, If $\Delta G_2 < 0$, then $k_2 = \frac{k_B T}{h}$

$$r_{tor2} = 2\frac{k_B T}{h} \frac{C_{H^+}^2 - P_{H_2} \exp(\frac{\Delta G_0}{k_B T})}{\left[C_{H^+} + \exp(\frac{\Delta G_1}{k_B T})\right]^2}$$
(14)

If $\Delta G_2 > 0$, then $k_2 = \frac{k_B T}{h} \exp(-\frac{\Delta G_2}{k_B T})$

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$$r_{tot2} = 2\frac{k_B T}{h} \frac{C_{H^+}^2 \exp(-\frac{\Delta G_0}{k_B T}) - P_{H_2}}{[C_{H^+} \exp(-\frac{\Delta G_1}{k_B T}) + 1]^2}$$
(15)

Under the same assumptions and derivations as above, we estimated the reaction rate following the Heyrovsky mechanism, namely step (1) and (3).

If assuming hydrogen adsorption is rate-determining step ($Z_3 = 1$), thus the total reaction rate is expressed as:

If
$$\Delta G_1 < 0$$
, then $k_1 = \frac{k_B T}{h}$

$$r_{tot3} = \frac{k_B T}{h} \frac{C_{H^+}^2 \exp(-\frac{\Delta G_0}{k_B T}) - P_{H_2}}{C_{H^+} \exp(-\frac{\Delta G_0}{k_B T}) + P_{H_2} \exp(-\frac{\Delta G_1}{k_B T})}$$
(16)

If
$$\Delta G_1 > 0$$
, then $k_1 = \frac{k_B T}{h} \exp(-\frac{\Delta G_1}{k_B T})$

$$r_{tot3} = \frac{k_B T}{h} \frac{C_{H^+}^2 - P_{H_2} \exp(\frac{\Delta G_0}{k_B T})}{C_{H^+} \exp(\frac{\Delta G_1}{k_B T}) + P_{H_2} \exp(\frac{\Delta G_0}{k_B T})}$$
(17)

If assuming H_2 desorption is rate-determining step ($Z_1 = 1$), the total reaction rate is expressed as:

If
$$\Delta G_3 < 0$$
, then $k_3 = \frac{k_B T}{h}$
 $r_{tot4} = \frac{k_B T}{h} \frac{C_{H^+}^2 - P_{H_2} \exp(\frac{\Delta G_0}{k_B T})}{C_{H^+} + \exp(\frac{\Delta G_1}{k_B T})}$
(18)

If
$$\Delta G_3 > 0$$
, then $k_3 = \frac{k_B T}{h} \exp(-\frac{\Delta G_3}{k_B T})$

$$r_{tot4} = \frac{k_B T}{h} \frac{C_{H^+}^2 \exp(-\frac{\Delta G_0}{k_B T}) - P_{H_2}}{C_{H^+} \exp(-\frac{\Delta G_1}{k_B T}) + 1}$$
(19)

According to the expressions of the total reaction rate, we can plot the relation of reaction rate varied as Gibbs free energy change of H adsorption (ΔG_1). For the Tafel mechanism, $r_{Tafel} = \min\{r_{tot1}, r_{tot2}\}$; For the Heyrovsky mechanism, $r_{\text{Hey}} = \min\{r_{\text{tot3}}, r_{\text{tot4}}\}$. The corresponding volcano plots were shown in Fig. S6a b. respectively. In real would be limited following and case, r_{tot} $r_{tot} = \max{\min{\{r_{tot1}, r_{tot2}\}}, \min{\{r_{tot3}, r_{tot4}\}}}$, as shown in the Fig. 4a in the main text, where the adsorption (blue line) and desorption (red line) determine the real volcano curve. Such a picture has been suggested before. From Fig. S6b, one can see when $\Delta G_1^{opt} \approx -0.05$ eV, r_{tot} would reach the maximum. According to the equation $\Delta G_1 = E_{ad}^{H} + \frac{1}{2}T\Delta S + eU$, we can get the optimum adsorption strength $E_{ad}^{H,opt} \approx -0.20$ eV. If we assume the desorption of surface H* (reverse reaction of step 1) has an energy barrier of at least 0.30 eV, the peak position in the volcano curve would move toward the left, as demonstrated by the blue dashed line in Fig. S6. Here, we can get the optimum $\Delta G_1^{opt} \approx -0.30 \text{ eV}$, corresponding to $E_{ad}^{H,opt} \approx -0.45$ eV.



Figure S1. XRD pattern of as-prepared anatase TiO₂.



Figure S2. Pt 4f XPS of Pt/TiO₂ sample heat-treated in air condition at 300 °C for 2h. 71.0 and 74.5 eV for Pt⁰, 72.6 and 76.0 eV for Pt²⁺, 74.0 and 77.2 eV for Pt⁴⁺.



Figure S3. Ti 2p, O 1s and Pt 4f XPS spectra of samples Pt/TiO₂-A (black line), Pt/TiO₂-A-CN (red line), Pt/TiO₂-A-CN(used) (blue line). 0, II, IV on the top of panel C denote the valence state of Pt⁰, Pt²⁺, Pt⁴⁺, respectively. It is noticeable that metallic Pt⁰ and oxidized states Pt^{δ +} simultaneously exist in sample Pt/TiO₂-A and Pt⁰ binding energies located at 71.0 and 74.5 eV as the major species present in the

Pt/TiO₂ catalyst. However, the corresponding leaching sample only shows oxidized states $Pt^{\delta+}$ binding energies (72.6 and 76.0 eV for Pt^{2+} , 74.0 and 77.2 eV for Pt^{4+}).



Figure S4. Photocatalytic H_2 evolution rate of Pt/TiO₂ samples with different content of Pt loading. Experiments were conducted in 100 mL 30% methanol aqueous solution containing 10 mg photocatalysts which were carried out under UV-vis light.



Figure S5. Photocatalytic H_2 evolution on TiO_2 and corresponding leached sample. These two samples were loaded 1% Pt by photodeposition method before photocatalytic tests and experiments were carried out under UV-vis light irradiation.



Figure S6. Estimated volcano relation between the total reaction rate and Gibbs free energy of hydrogen adsorption (ΔG_1) following the Tafel mechanism (a) and Heyrovsky mechanism (b).

	Catalyst (mg)	Pt loading (wt %)	H ₂ evolution rate (µmol/h)	$\begin{array}{c} \text{TOF} \times 10^2 \\ (\text{s}^{-1})^{\dagger} \end{array}$	Note
1	20	2	333.5	4.52	ref 3
2	27	1	56.7	1.14	ref 4
3	15	1	110	3.97	ref 5
4	22	1	60	1.48	ref 6
5	20	0.6	200	9.03	ref 7
6	10	1	116	6.28	ref 8
7	200	0.2	680	9.21	ref 9
8	100	0.4	180	2.44	ref 10

Table S1. Turnover frequencies (TOFs) of anatase TiO₂ supported Pt co-catalyst reported in literatures.

[†]The TOFs were calculated based on the Pt metal dispersion. These photocatalytic reactions are all occurred in the methanol aqueous solution.

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