

Supporting information for

A Theoretical Consideration on the Surface Structure and Nanoparticle Size Effects of Pt in Hydrogen Electrocatalysis

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Outline

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1. Derivation of the volcano relations

According to the Brønsted-Evans-Polanyi (BEP) principle^{1, 2}, the forward and backward activation free energy for Heyrovsky and Volmer reaction at any θ^0 values can be related to the equalized forward and backward activation free energy at θ^0 value of 0.5 ($\Delta G_x^{0\neq}$) as the following equations.

$$\Delta G_{\text{heyrovsky}}^{+0\neq}(\theta^0) = \Delta G_{\text{heyrovsky}}^0 + \alpha_{\text{heyrovsky}} \Delta G_{\text{H}}(\theta^0) \quad (\text{s1})$$

$$\Delta G_{\text{heyrovsky}}^{-0\neq}(\theta^0) = \Delta G_{\text{heyrovsky}}^0 - (1 - \alpha_{\text{heyrovsky}}) \Delta G_{\text{H}}(\theta^0) \quad (\text{s2})$$

$$\Delta G_{\text{volmer}}^{+0\neq}(\theta^0) = \Delta G_{\text{volmer}}^0 - (1 - \alpha_{\text{volmer}}) \Delta G_{\text{H}}(\theta^0) \quad (\text{s3})$$

$$\Delta G_{\text{volmer}}^{-0\neq}(\theta^0) = \Delta G_{\text{volmer}}^0 + \alpha_{\text{volmer}} \Delta G_{\text{H}}(\theta^0) \quad (\text{s4})$$

where α_x are constants called symmetric factor (or transfer coefficient), x represents “volmer” or “heyrovsky” and “+” and “-” refer to the forward and backward reaction respectively. According to the transition-state theory, $k_x^{\pm 0} = (k_B T / h) \exp(-\Delta G_x^{\pm 0\neq}(\theta^0) / k_B T)$, we therefore have the following

relations for various rate constants.

$$k_{\text{heyrovsky}}^{+0} = k_{\text{heyrovsky}}^0 \exp\left(-\frac{\alpha_{\text{heyrovsky}} \Delta G_H(\theta^0)}{k_B T}\right) \quad (\text{s5})$$

$$k_{\text{heyrovsky}}^{-0} = k_{\text{heyrovsky}}^0 \exp\left(\frac{(1-\alpha_{\text{heyrovsky}}) \Delta G_H(\theta^0)}{k_B T}\right) \quad (\text{s6})$$

$$k_{\text{volmer}}^{+0} = k_{\text{volmer}}^0 \exp\left(\frac{(1-\alpha_{\text{volmer}}) \Delta G_H(\theta^0)}{k_B T}\right) \quad (\text{s7})$$

$$k_{\text{volmer}}^{-0} = k_{\text{volmer}}^0 \exp\left(-\frac{\alpha_{\text{volmer}} \Delta G_H(\theta^0)}{k_B T}\right) \quad (\text{s8})$$

where k_x^0 refers to the equalized rate constant for the forward and backward processes in each reaction as $\theta^0=0.5$. Since all the elementary reaction steps are in equilibrium at equilibrium potential, we have $\Delta G_H(\theta^0) + k_B T \ln \frac{\theta^0}{(1-\theta^0)} = 0$. Therefore, we can also express eq s5 to 8 as,

$$k_{\text{heyrovsky}}^{+0} = k_{\text{heyrovsky}}^0 \left(\frac{\theta^0}{1-\theta^0}\right)^\alpha \quad (\text{s9})$$

$$k_{\text{heyrovsky}}^{-0} = k_{\text{heyrovsky}}^0 \left(\frac{\theta^0}{1-\theta^0}\right)^{-(1-\alpha)} \quad (\text{s10})$$

$$k_{\text{volmer}}^{+0} = k_{\text{volmer}}^0 \left(\frac{\theta^0}{1-\theta^0}\right)^{-(1-\alpha)} \quad (\text{s11})$$

$$k_{\text{volmer}}^{-0} = k_{\text{volmer}}^0 \left(\frac{\theta^0}{1-\theta^0}\right)^\alpha \quad (\text{s12})$$

The exchange current density j^0 can be expressed by eq s13 (Tafel-Volmer mechanism) or eq s14 (Heyrovsky-Volmer mechanism).

$$j^0 = F k_{\text{volmer}}^{+0} \theta^0 = F k_{\text{volmer}}^{-0} (1-\theta^0) \quad (\text{s13})$$

$$j^0 = F \left(k_{\text{heyrovsky}}^{+0} (1-\theta^0) + k_{\text{volmer}}^{+0} \theta^0 \right) = F \left(k_{\text{heyrovsky}}^{-0} \theta^0 + k_{\text{volmer}}^{-0} (1-\theta^0) \right) \quad (\text{s14})$$

Substituting eq s13 and s14 with eq s9 to 12 will lead to the following j^0 expressions for the Tafel-Volmer and the Heyrovsky -Volmer reaction mechanisms respectively,

$$j^0 = F k_{\text{volmer}}^0 (\theta^0)^\alpha (1-\theta^0)^{1-\alpha} \quad (\text{s13})$$

$$j^0 = F (k_{\text{heyrovsky}}^0 + k_{\text{volmer}}^0) (\theta^0)^\alpha (1-\theta^0)^{1-\alpha} \quad (\text{s14})$$

If we use k^0 to replace k_{volmer}^0 in Eq. s13 and $(k_{\text{heyrovsky}}^0 + k_{\text{volmer}}^0)$ in eq s14, we will arrive in the

following universal expression for j^0 .

$$j^0 = Fk^0(\theta^0)^\alpha(1-\theta^0)^{1-\alpha} \quad (\text{s15})$$

Substituting eq s15 with the relation between $\Delta G(\theta^0)$ and θ^0 lead to the following relation.

$$j^0 = Fk^0 \exp(-\alpha\Delta G_H(\theta^0)/k_B T) / (1 + \exp(-\Delta G_H(\theta^0)/k_B T)) \quad (\text{s15a})$$

2. Details for DFT Calculations.

The spin-polarized DFT calculations are performed on periodic supercells under the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE), as implemented with PWSCF code contained in the Quantum ESPRESSO distribution.³ The Kohn-Sham one-electron wave functions are expanded on the basis of plane waves with a kinetic energy cutoff of 30 Ry and a charge-density cutoff of 300 Ry. Ultrasoft pseudopotentials are employed for nuclei and core electrons. Four-layer slabs of a variety of sizes, (3×3), $(2\sqrt{3} \times 2\sqrt{3})$ and (4×4) respectively, are used to model Pt single crystal surfaces. The equilibrium lattice constant of 3.993 Å is used for Pt unit cells. In the calculations, the topmost two layers of the slabs are allowed to relax with the adsorbed species, whereas the remaining layers were fixed in their bulk positions. A vacuum layer 15 Å in thickness is added above the top layer of slabs. Sampling of the Brillouin zones is achieved by summation over Monkhorst-pack meshes with dimensions of $(6 \times 6 \times 1)$. The accuracy of this structure is tested using a five-layer slab with its uppermost two layers relaxed and shows that the change of adsorption energy is negligible. Structural optimization was performed until the Cartesian force components acting on each atom are brought below 10^{-3} Ry/Bohr and the total energy is converged to within 10^{-5} Ry. The value of E_{H_2} is computed by placing a single H₂ molecule in a cubic cell with length of 20 Å.

3. Supporting Figures

Figure s1. The plots of the calculated $\Delta E_H(\theta)$ values (points) as a function of θ for H adsorption on Pt (111), Pt(100) and Pt(110) surfaces. The lines are the linear-fit to the calculated data.

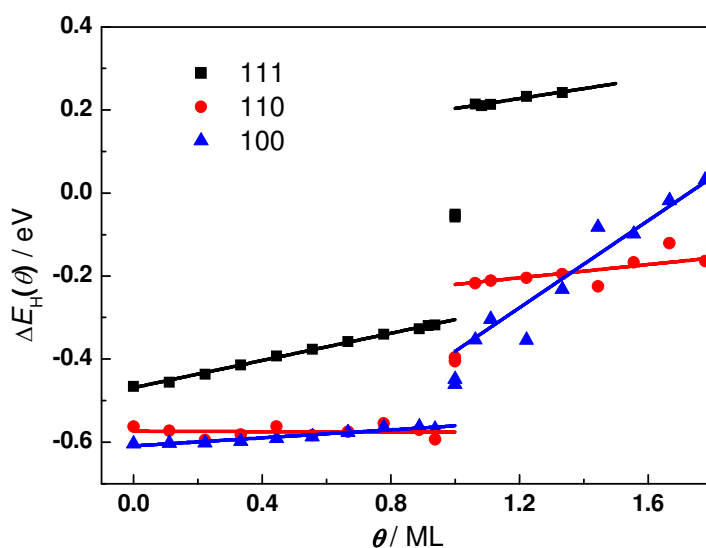
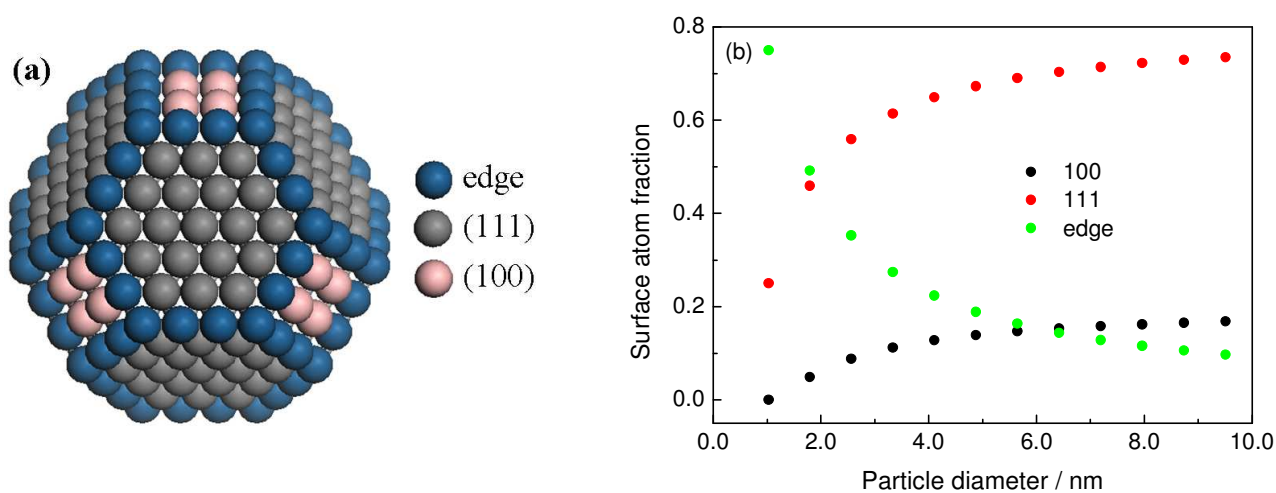


Figure s2 (a) The schematic diagram of a cuboctahedral nanoparticle; (b) The percentage of different types of atoms on the surface as a function of particle size.



4. References

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