

Supporting Information of

The Hydrogen Oxidation Reaction on Platinum Nanoparticles: Understanding the Kinetics of Electrocatalytic Reactions via ‘Nano- Impacts’

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S1 The Calculation of the Coverage of PtNPs

The surface coverage of platinum nanoparticles (PtNPs) can be calculated using the area occupied by all the PtNPs on the substrate electrode divided by that of the electrode and dilution of the stock sample was taken into account. The PtNP suspension was reported, by the manufacturer (nanoComposix, San Diego, CA, U.S.A.), to have a particle concentration of 3.5×10^{13} particles L^{-1} with a 25 nm PtNP radius. The gold macroelectrode was measured to have a radius of 1.01 mm and the volume of each drop cast was 1 μL . DF is the dilution factor of the stock PtNP suspension. Herein,

$$\text{coverage of PtNPs} = 100 \times \left[\pi \times (25 \times 10^{-9})^2 \right] \times (3.5 \times 10^{13}) \times (1 \times 10^{-6}) / \left(DF \times \left[\pi \times (1.01 \times 10^{-3})^2 \right] \right) \quad (S1)$$

In the drop-casting experiments discussed in Figure 8, the amount of PtNPs added to the supporting substrate can be converted to the coverage of PtNPs according to Eq.(S1) and the values are in Table S1.

Table S1. The idealized coverages of PtNPs for the variety of drop-casted electrodes applied in the experiment of Figure 8a.

Dilute factor	Idealized coverages of PtNPs (%)
0.5	4.0
1	2.0
2	1.0
4	0.50
8	0.25
16	0.12
32	0.06
64	0.03

S2 The Kinetic Parameters Applied in the Simulation of Figure 8

For the hydrogen oxidation reaction (HOR) on the drop-casted PtNP clusters, there are four variables determining a voltammogram: the centre-to-centre distance d_{NP} , the

adsorption rate constant k_a , the desorption rate constant k_d and the standard heterogeneous rate constant k_0 . The parameter d_{NP} can be inferred from the experimental data as discussed in S1 and for the HOR where the reaction rates are limited by the slow adsorption process, the parameter k_a can be calculated from the steady-state current. Therefore, only the voltammetric responses of the parameters k_d and k_0 are unclear for HOR on the PtNPs.

Figure S1 shows example voltammograms with various kinetic parameters. The influences of k_d and k_0 are studied with two PtNP coverages (the large PtNP coverage where $d_{NP} = 0.15 \mu\text{m}$ and the small PtNP coverage where $d_{NP} = 5.0 \mu\text{m}$) and two various adsorption rate constants (the fast adsorption process where $k_a = 1 \text{ m s}^{-1}$ and the slow adsorption one where $k_a = 0.001 \text{ m s}^{-1}$). From Figure S1a, S1c, S1e and S1g, it is found that a slow desorption rate constant k_d , corresponding to the process from H(ads) to H_2 , can apparently decrease the backward peak current, especially under a small particle coverage or a slow adsorption process. From Figure S1b, S1d, S1f and S1h, the decrease of the standard heterogeneous rate constant, k_0 , can lead to an observable potential shift in the voltammogram and the peak-to-peak separation increases due to the irreversibility of the electron transfer step. Similarly to the influences caused by k_d , the voltammogram is affected more by k_0 when the PtNP coverage is small or the adsorption process is slow.

As for the drop-casting experiments shown in Figure 8, the voltammogram is nearly reversible when the PtNP coverage is high while it shows a quasi-reversible feature especially under a small PtNP coverage, which indicates the value of k_0 cannot be either too small or too large. The back peaks are observed in all the experimental voltammograms, indicating that the desorption process cannot be ignored in the simulation. As the range of possible k_d and k_0 is found and the value of k_a is determined by the experimental results, for convenience, the same desorption rate constant and standard heterogeneous rate constant are selected in the simulation of Figure 8b.

