Electronic Supplementary Information

Stochastic Electrochemistry with Electrocatalytic Nanoparticles at Inert Ultramicroelectrodes - Theory and Experiments

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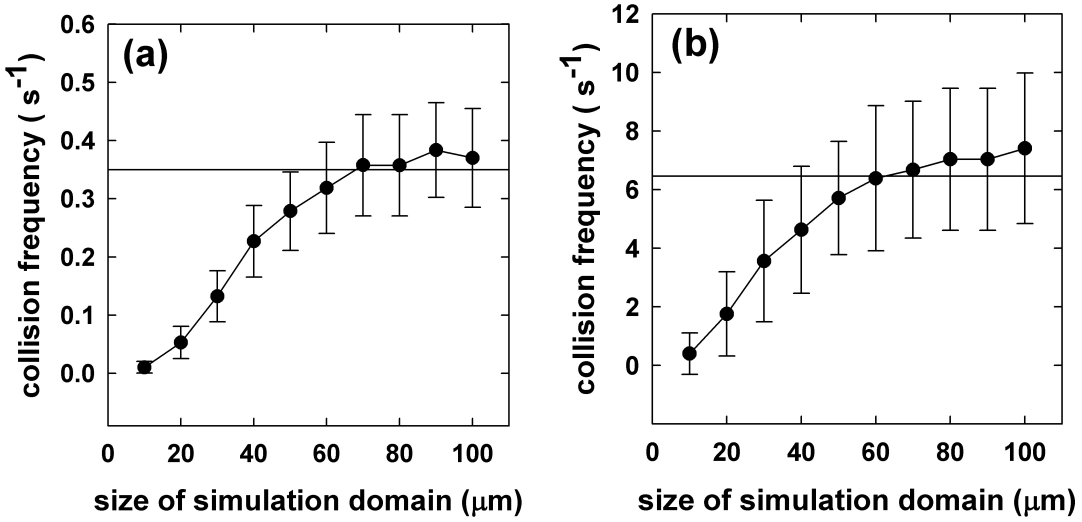

Figure S1. Simulated collision frequency as a function of the size of domain taken for (a) sticking and (b) blip collisions. Particle concentration, 1.6 pM; step period (τ), 1 ms; step length (δ_x), 0.19 μm (consistent with a NP diffusion coefficient, D of 1.75×10^{-7} cm^2/s); radius of UME, 5 μm. Total simulation time was 50 s. The solid line is theoretical value calculated by eqns (a) (1) and (b) (9).

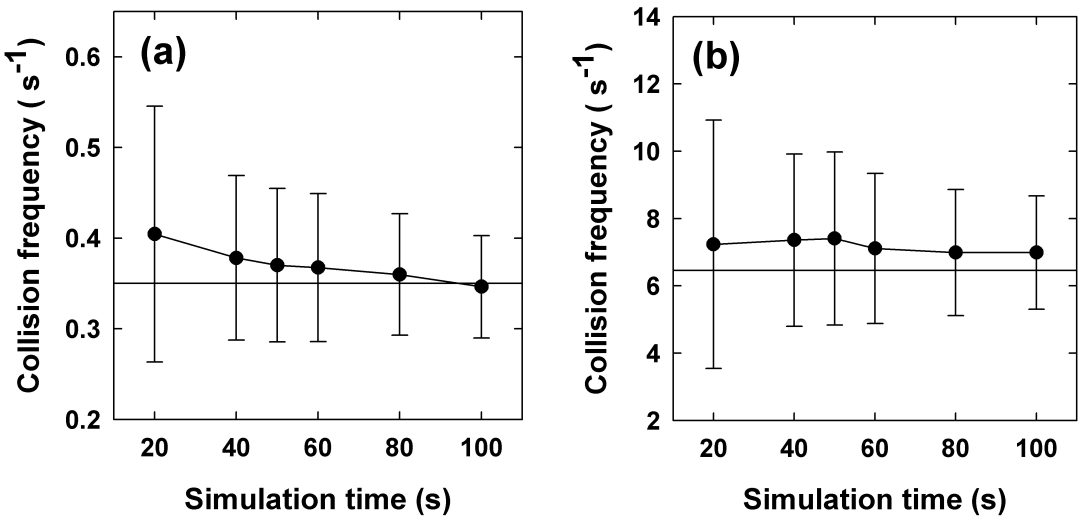

Figure S2. Simulated collision frequency at a various simulation times for (a) sticking and (b) blip collisions. The concentration of particle is 1.6 pM. Particle concentration, 1.6 pM; step period (τ), 1ms; step length (δ_x), 0.19 μm (consistent with a NP diffusion coefficient, D of 1.75×10^{-7} cm^2/s); radius of UME, 5 μm. The size of domain was 100 μm. The solid line is theoretical value calculated by eqns (a) (1) and (b) (9).

step period, τ (ms)	step length, δ_x (μm)	Concentration of NP (pM)	radius of electrode (μm)	number of collision	
				Staircase (/s)	Blip (/s)
0.1	0.059	1.6	5	0.4038	22.9648
1	0.19	1.6	5	0.3702	7.4076
10	0.59	1.6	5	0.3646	2.4128
100	1.9	1.6	5	0.2982	0.7336
1	0.19	0.16	5	0.035	0.8052
1	0.19	0.8	5	0.195	3.4134
1	0.19	3.2	5	0.7594	14.7718
1	0.19	16	5	3.722	71.6312
1	0.19	1.6	1.25	0.0596	0.3088
1	0.19	1.6	2.5	0.1670	1.8554
1	0.19	1.6	10	0.8432	29.5298
1	0.19	1.6	15	1.405	65.4142

Table S1. Simulation results at various conditions. In all cases, diffusion coefficient, D is 1.75×10^{-7} cm^2/s. The total simulation time and the size of domain are 50 s and 100 μm.

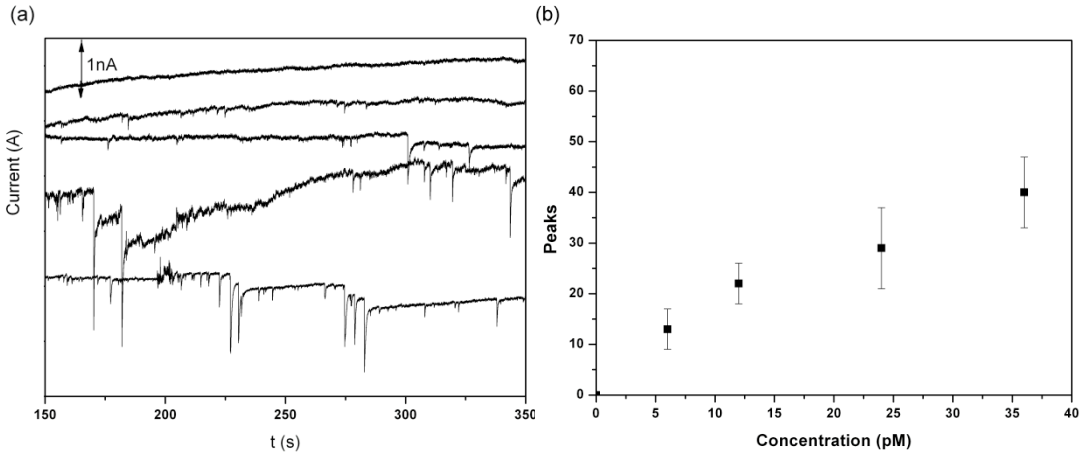

Figure S3. Au NP/PtO_x UME/borohydride oxidation system. (a) The *i-t* curves on a pre-oxidized Pt UME (5 μm in radius) at 0 V in the presence of different concentrations of Au NPs, from top to bottom, 0, 6, 12, 24 and 36 pM. (b) Peaks in a time interval of 200 s at different NP concentrations; electrolyte, 10 mM $NaBH_4$; 0.1 M NaOH.

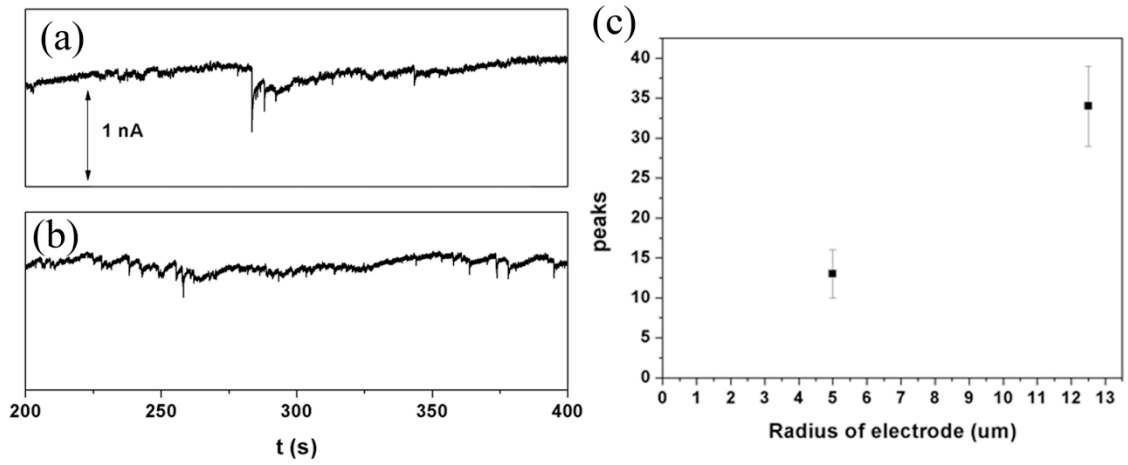

Figure S4. Au NP/PtO_x UME/borohydride oxidation system. (a) and (b), *i-t* curves recorded on different sized pre-oxidized Pt UMEs (5 μm and 12.5 μm in radius) at 0 V in the presence of 6 pM Au NPs. (c) Peaks in the time interval of 200 s on different sized electrodes; electrolyte, 10 mM $NaBH_4$; 0.1 M NaOH.