Supporting Information for

Theoretical analysis of the effect of particle size and support on the kinetics of oxygen reduction reaction on platinum nanoparticles

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Reversible potentials for oxygen reduction reaction

Table S1: Reversible potentials for the electrochemical reactions of ORR on (111) and (100) facet

Reaction	Pt(111)	Pt(100)
$H_2O(l) \rightleftharpoons OH^* + H^+_{aq} + e^-$	0.76	0.51
$OH^* \rightleftharpoons O^* + H^+_{aq} + e^-$	0.91	0.87
$O_2(g) + H^+_{aq} + e^- \rightleftharpoons OOH^*$	0.75	0.88

Activation energies for oxygen reduction reaction on (111) facet

Activation energies for oxygen reduction reaction on (100) facet

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Table S2: Activation energies for $H_2O \rightarrow OH + H^+ + e^-$ on (111) facet

Electrode Potential [V]	E_a [eV]
1.3494	0
1.3807	0.0025
1.2807	0.0052
1.1807	0.0194
1.0807	0.0418
0.9807	0.0759
0.8807	0.1289
0.7807	0.1790
0.6807	0.2340
0.5807	0.2936
0.4807	0.3548
0.3807	0.4206
0.2807	0.4943

Table S3: Activation energies for $OH + H^+ + e^- \rightarrow H_2O$ on (111) facet

Electrode Potential [V]	E_a [eV]
0.1948	0
0.3307	0.0179
0.4307	0.0657
0.5307	0.1267
0.6307	0.1422
0.7307	0.1869
0.8307	0.2336
0.9307	0.2806
1.0307	0.3291
1.1307	0.4187
1.2307	0.5080
1.3307	0.5683

Site distribution for supported nanoparticles

We include the site distribution for different sized nanoparticles listed in Table S10:

References

(1) Shao, M.; Peles, A.; Shoemaker, K. *Nano Lett.* **2011**, *11*, 3714–3719.

Table S4: Activation energies for $O + H^+ + e^- \rightarrow OH$ on (111) facet

Electrode Potential [V]	E_a [eV]
-0.1065	0
-0.1146	0.0122
-0.0146	0.0142
0.0854	0.0298
0.1854	0.0504
0.2854	0.0734
0.3854	0.0972
0.4854	0.1209
0.5854	0.1446
0.6854	0.1691
0.7854	0.1952
0.8854	0.2244
0.9854	0.2585
1.0854	0.2994
1.1854	0.3643

Table S5: Activation energies for $OH \rightarrow O + H^+ + e^-$ on (111) facet

Electrode Potential [V]	E_a [eV]
0.0854	0.8561
0.1854	0.7767
0.2854	0.6997
0.3854	0.6235
0.4854	0.5472
0.5854	0.4710
0.6854	0.3954
0.7854	0.3216
0.8854	0.2508
0.9854	0.1850
1.0854	0.1259
1.1854	0.0757
1.2854	0.0366
1.3854	0.0107
1.4854	0.0002
1.5020	0

Table S6: Activation energies for $O_2 + H^+ + e^- \rightarrow OOH$ on (111) facet

Electrode Potential [V]	E_a [eV]
0.5000	0.0185
0.5500	0.0350
0.6000	0.0534
0.6500	0.0775
0.7000	0.1029
0.7500	0.1325
0.8000	0.1630
0.8500	0.1957
0.9000	0.2289
0.9500	0.2640
1.0000	0.2996

Table S7: Activation energies for $OH + H^+ + e^- \rightleftharpoons H_2O$ on (100) facet

Electrode Potential [V]	$E_{a,ox}$ [eV]	$E_{a,red}$ [eV]
0.1000	0.4506	0.0223
0.2000	0.3816	0.0714
0.3000	0.3185	0.1281
0.4000	0.2583	0.1464
0.5000	0.2014	0.1912
0.6000	0.1493	0.2380
0.7000	0.0975	0.2851
0.8000	0.0557	0.3374
0.9000	0.0285	0.4270
1.0000	0.0110	0.5136

Table S8: Activation energies for $O + H^+ + e^- \rightleftharpoons OH$ on (100) facet

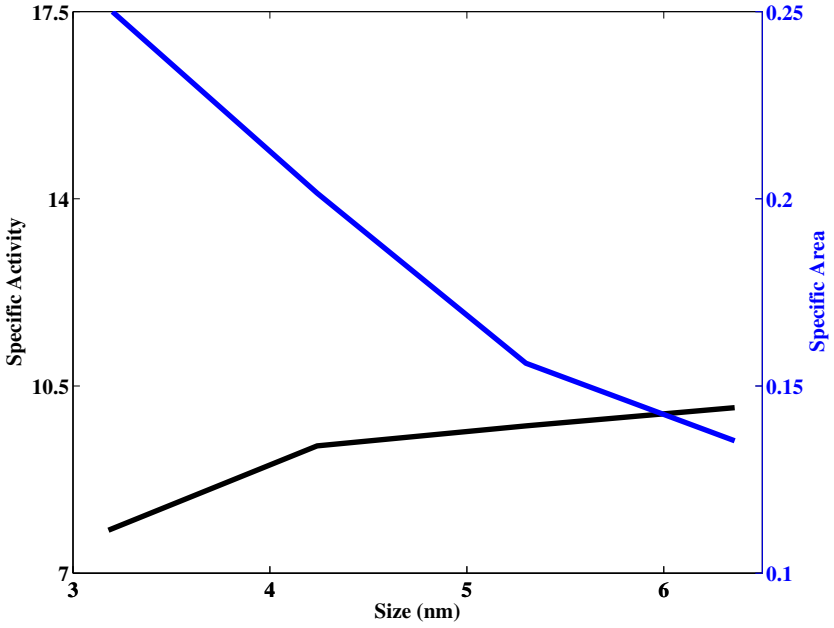
Electrode Potential [V]	$E_{a,ox}$ [eV]	$E_{a,red}$ [eV]
0.1000	0.8127	0.0410
0.2000	0.7347	0.0630
0.3000	0.6581	0.0864
0.4000	0.5818	0.1101
0.5000	0.5056	0.1338
0.6000	0.4297	0.1580
0.7000	0.3551	0.1834
0.8000	0.2829	0.2111
0.9000	0.2149	0.2430
1.0000	0.1527	0.2808

Table S9: Activation energies for $O_2 + H^+ + e^- \rightarrow$ OOH on (100) facet

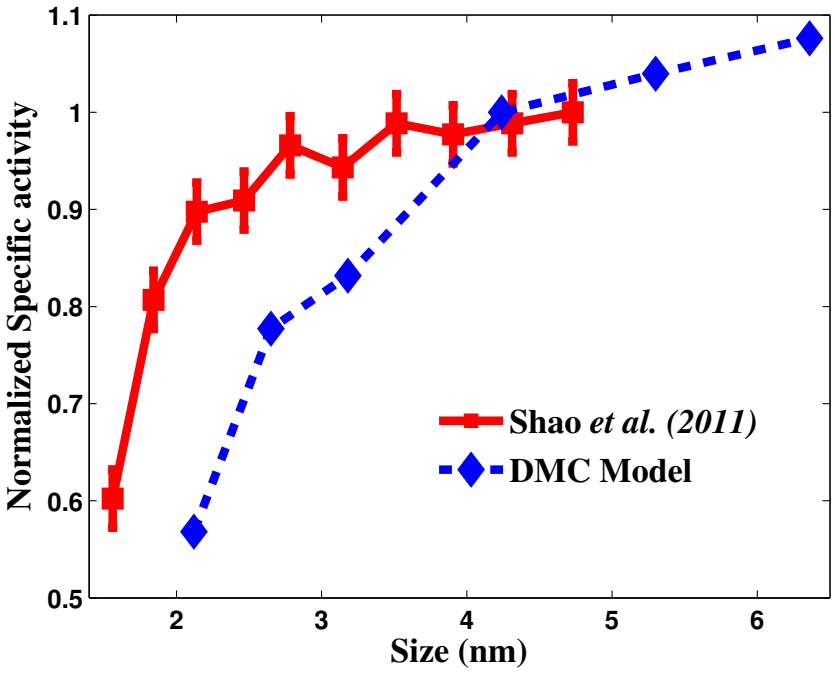
Electrode Potential [V]	E_a [eV]
0.5000	0.0016
0.5500	0.0073
0.6000	0.0153
0.6500	0.0277
0.7000	0.0461
0.7500	0.0674
0.8000	0.0927
0.8500	0.1203
0.9000	0.1508
0.9500	0.1825
1.0000	0.2156

Table S10: Site distribution of the supported nanoparticle for varying metal-support interaction

	$\gamma^* = -0.5$	$\gamma^* = -0.25$	$\gamma^* = 0$	$\gamma^* = 0.25$
$n_{perimeter}/n_{tot}$	0.13	0.09	0.06	0.05
n_{111}/n_{tot}	0.68	0.72	0.78	0.81



(a)



(b)

Figure S1: A plot of the (a) calculated specific activity and specific surface area (blue) are shown as a function of the particle size and (b) comparison of the calculated specific activity with the experiments of Shao *et al.*[1] The normalized mass activity from the model is matched to the experimental results at a size of 4.8 nm. This size is chosen to examine at the maximum particle size so as to examine the saturation effects of the specific activity.