Supporting Information for:

## Drop-cast Gold Nanoparticles are not Always Electrocatalytically Active for the Borohydride Oxidation Reaction

Lachlan F. Gaudin<sup>a</sup>, Alison M. Funston<sup>a,b</sup>, and Cameron L. Bentley<sup>a,\*</sup>

<sup>a</sup>School of Chemistry, Monash University, Clayton, 3800 VIC, Australia

<sup>b</sup>ARC Centre of Excellence in Exciton Science, Monash University, Clayton, 3800 VIC, Australia

\*Corresponding author: <a href="mailto:cameron.bentley@monash.edu">cameron.bentley@monash.edu</a>

## Contents

Section S1. Characterisation of AuNP@HOPG electrode	3
Section S2. Supplementary Data for the SECCM Scan	4
Section S3. Supplementary Statistical Evaluations	7
Section S4. Movie captions	.18

Section S1. Characterisation of AuNP@HOPG electrode

**Table S1.1.** NP counts, spatial densities, and nearest neighbour distances (NND) for a collection often sampled regions of the AuNP@HOPG surface. Images were collected via SEM, with an area of $\sim 1150 \ \mu m^2$ .

Image	NP Count	Spatial Density	NND	NND	NND
Number		(µm <sup>-2</sup> )	(µm)	standard	%RSD
				deviation	
1	15	0.0130	4.95	116.0	23.4
2	18	0.0157	3.66	112.3	30.7
3	33	0.0287	2.31	81.5	35.2
4	19	0.0165	2.57	113.8	44.2
5	33	0.0287	1.80	91.0	50.6
6	52	0.0452	1.14	57.5	50.5
7	41	0.0357	1.74	74.7	42.8
8	41	0.0357	1.29	53.5	41.3
9	41	0.0357	1.47	67.3	45.7
10	35	0.0304	1.60	75.1	46.8

 Table S1.2. Totalled/Averaged results from Table S1.1

	Total NP count	Average Spatial Density	Average NND	Average NND standard deviation	Average NND %RSD
Totals /Averages	328	0.0285	2.26	84.3	41.12



**Figure S1.1.** Distribution of NP diameters from a selection of 50 NPs on the AuNP@HOPG electrode.



**Figure S1.2.** 10 CV cycles of electrochemical pre-treatment conducted on the AuNP@HOPG electrode in 0.1 M NaOH with a Pt counter electrode and a leakless Ag/AgCl reference electrode, performed at a scan rate of 0.5 Vs<sup>-1</sup>.

Section S2. Supplementary Data for the SECCM Scan

Number of NPs at location (total #)	Classification	Count (% in cluster size)
	Normal	27 (15.1)
Single NPs (178)	Abnormal	31 (17.4)
	Inactive	120 (67.4)
	Normal	15 (30.6)
2 (49)	Abnormal	12 (24.5)
	Inactive	22 (44.9)
	Normal	9 (32.1)
3 (28)	Abnormal	9 (32.1)
	Inactive	10 (35.7)
	Normal	4 (40.0)
4 (10)	Abnormal	3 (30.0)
	Inactive	3 (30.0)
	Normal	1 (33.3)
5 (3)	Abnormal	2 (66.6)
	Inactive	0 (0.00)

 Table S2.1. Total numbers and classifications of nanoparticle "type" from the SECCM scan featured in this work.



Figure S2.1. Diagrams of potential causes for particle abnormality and inactivity, a) particle detachment from surface, b) particle passivation by adsorbates, c) particle-substrate contact disruption, and d) intrinsically inactive particle.



Figure S2.2 Comparison of sweep rate on macroscopic BOR activity. CVs were collected on a AuNP@GC macrodisk (3 mm diameter) following the exact drop casting procedure as for the HOPG sample. CVs were collected in 0.1 M NaOH containing 5 mM NaBH<sub>4</sub> purged with N<sub>2</sub> using a Pt wire counter electrode and a leakless Ag/AgCl reference electrode, later calibrated against an SCE reference. The 2000 mV/s CVs were collected one at a time, with electrolyte agitation (stirring) conducted between scans to simulate a pseudo-steady-state response, as generated in the SECCM experiment.





Figure S3.1. Calculated Moran's I and Monte Carlo Simulations for each of the four classifications of NP in the SECCM scan used in this work. Red line indicates the calculated value for the actual particle distributions. Monte Carlo simulations were performed with 100,000 randomly-generated permutations of the same size as the actual dataset.





 Table S3.1 In-depth definitions of the shorthand for the electrochemical CV parameters used in the text.

Shorthand	1 Definition		
E <sub>onset</sub>	Potential at which the current value reaches 4% of the maximum current		
i <sub>onset</sub>	Current value at the E <sub>onset</sub>		
E <sub>a1</sub>	Potential of the first forward peak (a <sub>1</sub> )		
I <sub>a1</sub>	Peak current of the first forward peak (a <sub>1</sub> )		
E <sub>a2</sub>	Potential of the second forward peak $(a_2)$		
I <sub>a2</sub>	Peak current of the second forward peak (a <sub>2</sub> )		
E <sub>off, forward</sub>	Potential at which the current is at a local minimum after the a <sub>2</sub> peak		
E <sub>c1</sub>	Potential of the first reverse peak $(c_1)$		

I <sub>c1</sub>	Peak current of the first reverse peak $(c_1)$		
E <sub>off, reverse</sub>	Potential at which the current returns to the i <sub>onset</sub> value		
Qforward	Area under the CV on the forward sweep		
Qreverse	Area under the CV on the reverse sweep		

Figure S3.3. Results of the analysis of variance conducted on NP-containing locations with cluster

```
size = 2.
```





Figure S3.4. Indicative characteristics of the BOR CV as a function of particle cluster size, for the third CV cycle



**Figure S3.5.** Pearson Coefficient heatmap for the 1<sup>st</sup> CV cycle of single particle locations. Empty columns and rows here represent lack of values due to the lack of the first BOR peak in the first cycle.



Figure S3.6. Pearson Coefficient heatmap for the 2<sup>nd</sup> CV cycle of single particle locations



Figure S3.7. Pearson Coefficient heatmap for the 3<sup>rd</sup> CV cycle of single particle locations



Figure S3.8. Pearson Coefficient heatmap for the 1<sup>st</sup> CV cycle of particle locations of cluster size 2. Empty columns and rows here represent lack of values due to the lack of the first BOR peak in the first cycle.



**Figure S3.9.** Pearson Coefficient heatmap for the 2<sup>nd</sup> CV cycle of single particle locations of cluster size 2.



Figure S3.10. Pearson Coefficient heatmap for the 3<sup>rd</sup> CV cycle of single particle locations of cluster size 2



Figure S3.12. Pearson Coefficient heatmap for the 1<sup>st</sup> CV cycle of particle locations of cluster size 3. Empty columns and rows here represent lack of values due to the lack of the first BOR peak in the first cycle.



**Figure S3.13.** Pearson Coefficient heatmap for the 2<sup>nd</sup> CV cycle of single particle locations of cluster size 3.



Figure S3.14. Pearson Coefficient heatmap for the 3<sup>rd</sup> CV cycle of single particle locations of cluster



Figure S3.15. Pearson Coefficient heatmap for the 1<sup>st</sup> CV cycle of particle locations of cluster size 4. Empty columns and rows here represent lack of values due to the lack of the first BOR peak in the first cycle.



**Figure S3.16.** Pearson Coefficient heatmap for the 2<sup>nd</sup> CV cycle of single particle locations of cluster size 4.



Figure S3.17. Pearson Coefficient heatmap for the 3<sup>rd</sup> CV cycle of single particle locations of cluster size 4

Section S4. Movie captions

**Movie S1**. Spatially-resolved electrochemical movie (1444 pixels over a  $190 \times 190 \ \mu\text{m}^2$  scan area) obtained with the voltammetric hopping mode SECCM protocol, visualizing electrochemical activity at scan area 1 on the AuNP@HOPG sample. Experimental parameters were as follows: cyclic voltammogram (CV) waveform with a voltammetric scan rate ( $\upsilon$ ) = 2 V s<sup>-1</sup>, approach voltage (E<sub>a</sub>) = 0 V vs Ag/AgCl QRCE, initial potential (E<sub>i</sub>) = -0.75 V vs Ag/AgCl QRCE and final potential (E<sub>f</sub>) = 1.00 V vs Ag/AgCl vs QRCE (correction to SCE = +72 mV). The data shown is from the third CV cycle. The data presented are not interpolated. The data contained in this movie were used to construct all figures in the text.