Supporting Information

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Au@Pt Dendrimer Encapsulated Nanoparticles as Model Electrocatalysts for Comparison of Experiment and Theory

David F. Yancey, Liang Zhang, Richard M. Crooks, and Graeme Henkelman

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Calculation of the conversion factor for Pb UPD charge to surface area. An accurate conversion factor between charge and surface area for these small particles does not exist in the literature. Accordingly, values that have been determined for Au single crystal surfaces have been used to calculate a conversion factor for Pb. The charge required to transfer 2 electrons per Au(111) surface atom is 444 μC/cm^2 while the charge needed to transfer 2 electron per Au(100) surface atom is 386 μC/cm^2.[1] A cuboctahedral Au_{147} nanoparticle has 8 Au(111) facets with 6 Pb UPD sites each and 6 Au(100) facets with 9 Pb UPD sites each. That is, 47% of the UPD sites are (100) and 53% of the UPD sites are (111). By combining the conversion factors for the processes on the (100) and (111) facets in the appropriate ratio the conversion factor of 413 μC/cm^2 is determined. This is in good agreement with the previously reported conversion factor for Cu deposition on polycrystalline Au of 405 μC/cm^2 where copper also forms a commensurate layer on the Au surface.[2]

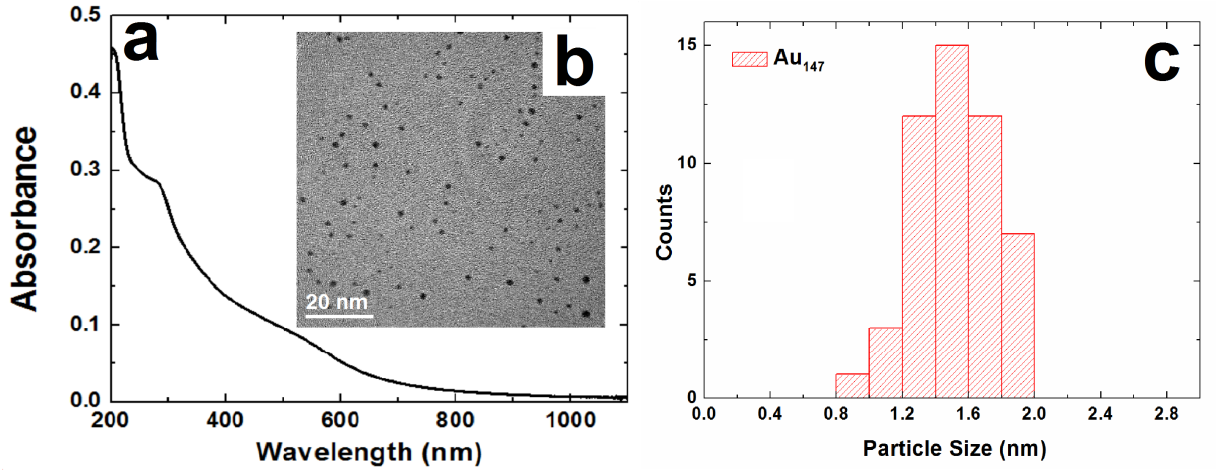

Figure S1. (a) UV-vis spectrum of 2.0 μM G6-NH_2(Au_{147}) DENs (cuvette path-length = 0.200 cm). A weak plasmon band is present at approximately 530 nm, which might arise from a small population of slightly larger particles. There is also a peak in the spectrum at 280 nm that arises from unprotonated tertiary amine groups.[3] (b) Representative TEM micrograph of G6-NH_2(Au_{147}) DENs. (c) Particle size distribution histogram for the Au_{147} DENs used in this study. The average size was found to be 1.5 ± 0.2 nm.

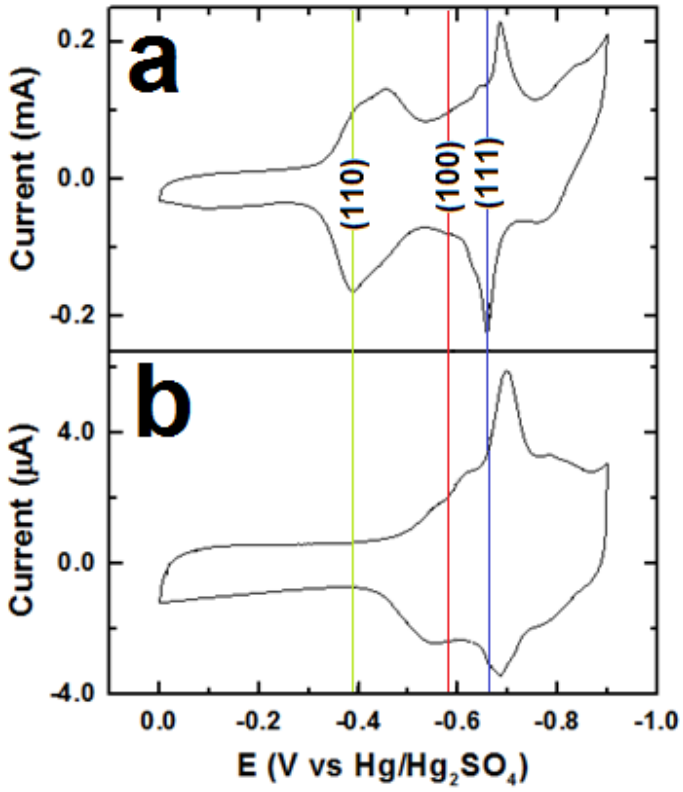

Figure S2. Comparison of Pb UPD voltammetry obtained using (a) a bulk, polycrystalline Au electrode, and (b) a glassy carbon electrode modified with Au_{147} DENs. The CVs were obtained in N_2-saturated 0.10 M $HClO_4$ at scan rates of (a) 100 mV/s and (b) 5 mV/s. The Pb UPD features associated with Au_{147} correlate closely with those observed for the Au(100) and Au(111) facets of bulk polycrystalline Au. Importantly, however, the deposition and stripping peaks associated with Pb UPD on the Au(110) facets of polycrystalline Au are absent on the DEN-modified electrode. This finding is consistent with expectations, because Au(110) facets are absent on Au_{147} DENs.[1] The geometrical electrode areas were (a) 0.196 cm^2 and (b) 0.247 cm^2.

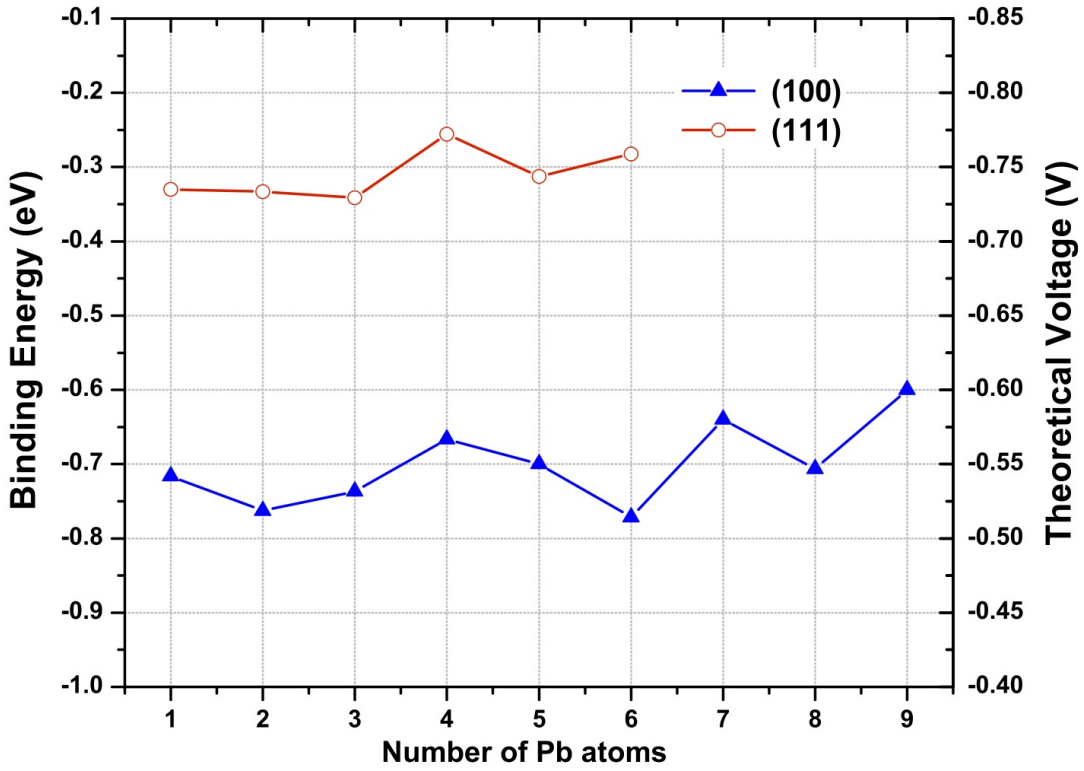

Figure S3. The calculated energies for Pb deposition onto the (100) (blue) and (111) (red) facets of Au_{147} DENs are plotted in terms of binding energy (left y-axis) and theoretical voltage (right y-axis). See eq 3 in the main text for the conversion between binding energy and the theoretical voltage of deposition.

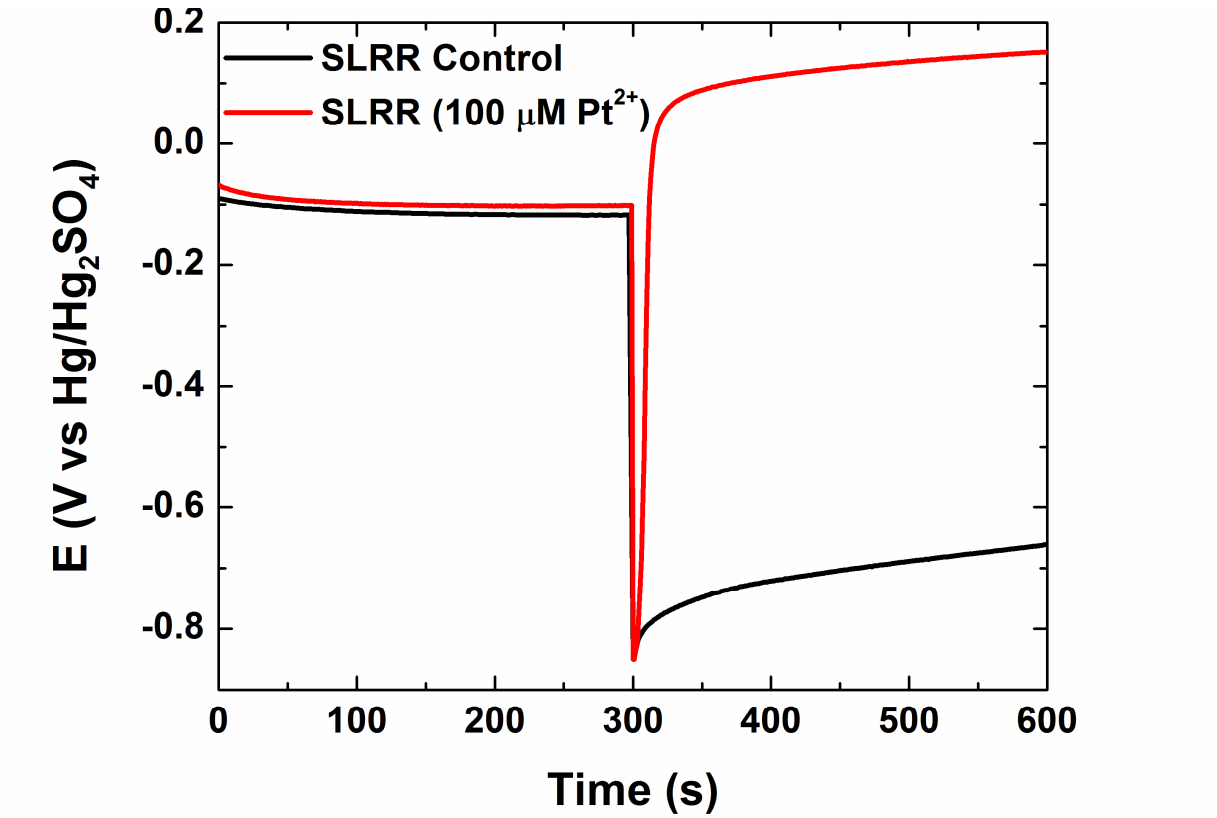

Figure S4. The open circuit potential (OCP) of Au_{147}-modified glassy carbon electrodes during the electrosynthesis of $Au_{147}@Pt_{102}$ DENs: The OCP was monitored for 300 s in an aqueous solution containing 1.0 mM $Pb(NO_3)_2$ and 0.10 M $HClO_4$. At t = 300 s, a pulse to -850 mV (vs Hg/Hg_2SO_4) was applied for 3 s to deposit a full monolayer of Pb onto the Au_{147} DENs. Immediately thereafter, the circuit was opened again and the OCP was measured for another 300 s as a function of time. The red trace shows the result when Pt^{2+} was added immediately after opening the circuit following Pb UPD. The black trace is a control experiment showing the time evolution of the OCP when no Pt^{2+} was added to the electrolyte solution after Pb UPD. The electrode was rotated at 1600 RPM throughout the deposition and galvanic exchange process to ensure a high electrolyte flux to the surface of the electrode.

References

1. Hernández, J.; Solla-Gullón, J.; Herrero, E.; Feliu, J. M.; Aldaz, A. *J. Nanosci. Nanotechnol.* **2009**, *9*, 2256-2273.
2. Santos, M. C.; Mascaro, L. H.; Machado, S. A. S. *Electrochimica Acta* **1998**, *43*, 2263-2272.
3. Pande, S.; Crooks, R. M. *Langmuir* **2011**, *27*, 9609-9613.