

Electronic Supplementary Information

26 March, 2011

Ms. ID: NJ-ART-01-2011-020083

**Synthesis, Characterization, and Electrocatalysis using Pt and
Pd Dendrimer-Encapsulated Nanoparticles Prepared by Galvanic
Exchange**

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7 Pages

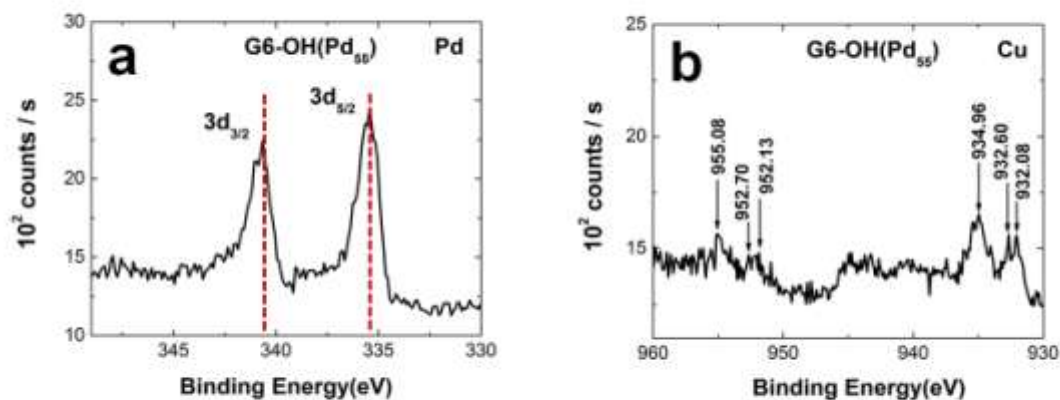


Figure S1. High-resolution XPS spectrum of the (a) Pd(3d) and (b) Cu(2p) regions for G6-OH(Pd₅₅) DENs prepared by galvanic exchange. These spectra were obtained by placing 10.0 μ L of an undialyzed 0.55 mM G6-OH(Pd₅₅) DEN solution onto a Si wafer and drying under H₂ gas to prevent oxidation of the Pd DENs. The spectra were calibrated by using the most intense Cls peak at 284.5 eV. The red dashed lines (Figure S1a) represent the reported peak positions for bulk Pd.

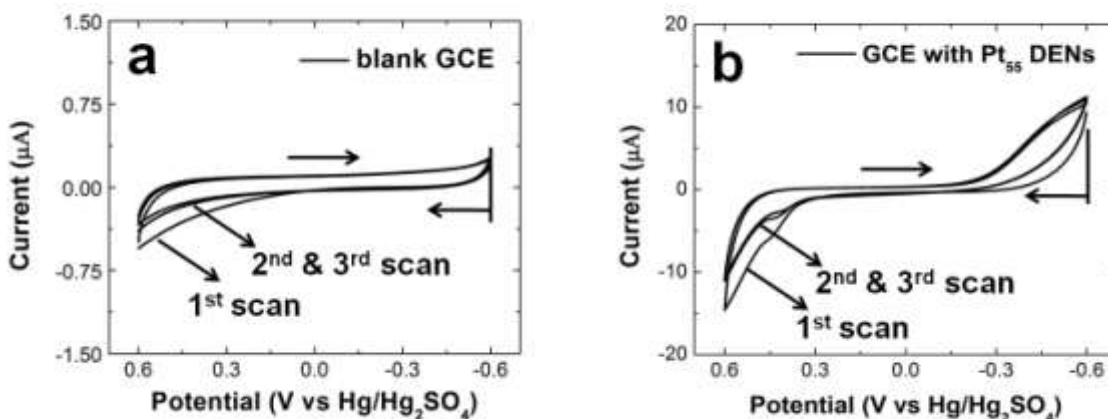


Figure S2. Three consecutive cyclic voltammograms (CVs) obtained using a freshly polished glassy carbon electrode (GCE) in (a) 0.1 M LiClO₄ aqueous electrolyte only and (b) 0.1 M LiClO₄ aqueous electrolyte containing 10.0 μM G6-OH(Pt₅₅) DENs (prepared by galvanic exchange). The scan rate was 10 mV/s.

To study the electrocatalytic activity of Pt DENs toward the oxygen reduction reaction (ORR), the as-synthesized DENs were immobilized on a GCE using our previously reported method.¹ Before immobilization of the metal DENs, the freshly polished GCE was tested in 0.1 M LiClO₄ solution by scanning the potential between -0.6 and 0.6 V. This revealed a small background current during the first scan, which decreased during subsequent scans (Figure S2a). Next, the GCE was polished and placed in a 10.0 μM G6-OH(Pt₅₅) DENs solution containing 0.1 M LiClO₄ and again the potential was scanned from -0.6 to 0.6 V (Figure S2b). The observed faradaic current in these scans (relative to those in Figure S2a) is characteristic of robust immobilization of Pt DENs onto the surface of the GCE.¹ The scan rate was 10 mV/s in all cases.

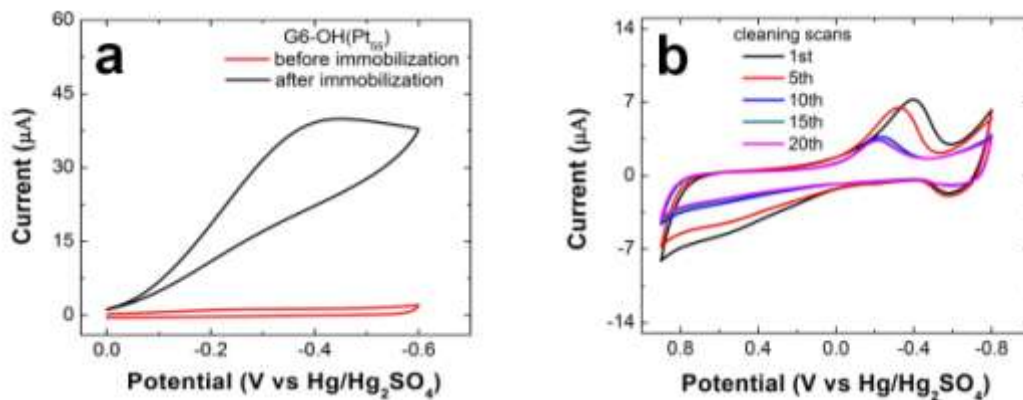


Figure S3. (a) Cyclic voltammograms for the ORR obtained using a GCE before and after immobilization G6-OH(Pt₅₅) DENs. (b) Cleaning scans using a GCE modified with G6-OH(Pt₅₅) DENs (synthesized by galvanic exchange) in a N₂-purged solution. The electrolyte was 0.1 M HClO₄, and the scan rate was (a) 50 mV/s and (b) 100 mV/s.

Figure S3a shows CVs obtained in an O₂-saturated, 0.1 M HClO₄ solution using a GCE working electrode before and after immobilization of G6-OH(Pt₅₅) DENs prepared by galvanic exchange. Before DEN immobilization, there is no significant faradaic current, indicating that the ORR is not catalyzed in the potential range from 0.0 to -0.6 V. However, in the presence of the DENs, an electrocatalytic current is clearly observed with a peak potential at -0.43 V.²

We have previously observed that cleaning scans to more extreme potentials improve the electrocatalytic efficiency of DENs, just as such scans do for bulk Pt electrodes.² Accordingly, after the data represented by the black trace in Figure S3a were obtained, the electrode potential was scanned 20 times between -0.80 V and 0.90 V in N₂-purged 0.1 M HClO₄ (Figure S3b). Following these cleaning scans, the CV represented by the galvanic exchange (O₂) in Figure 6 was obtained under the same

set of conditions used before cleaning (black trace, Figure S3a). After cleaning, the ORR peak potential shifts from -0.43 V to -0.32 V, and the maximum current increases by about 50%. Both of these observations are consistent with a more active Pt surface.³

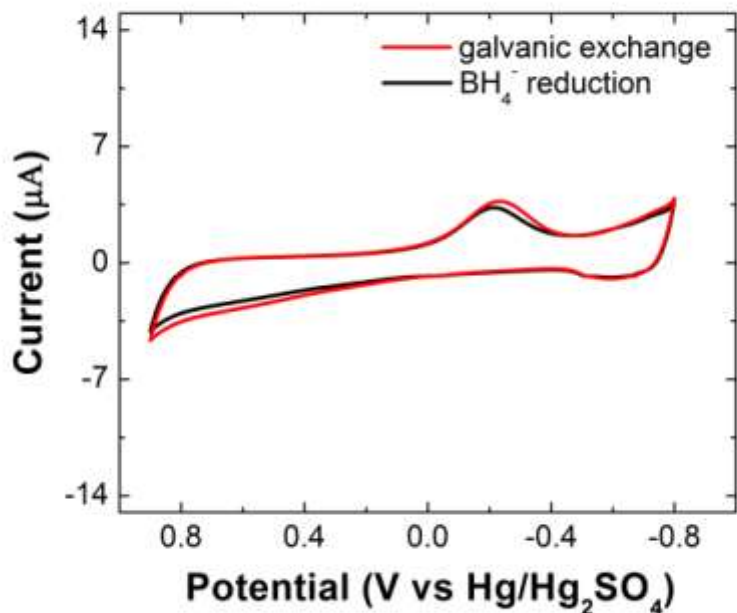


Figure S4. Cyclic voltammograms obtained in the Pt oxidation/reduction and hydrogen adsorption/desorption potential regions. The working electrode was a GCE modified with G6-OH(Pt₅₅) DENs synthesized by galvanic exchange (red trace) or BH₄⁻ reduction (black trace). Integration of the hydrogen desorption peaks in the range -0.43 V and -0.74 V were used to calculate the surface areas of Pt DEN-modified GCEs. The electrolyte was 0.1 M HClO₄ and the scan rate was 100 mV/s. The charge under the hydrogen desorption wave was converted to Pt surface area using the value of 210 µC/cm².^{4,5} Note, however, that this only provides an estimate of the true coverage, because this conversion factor has not been verified for nanoparticles having diameters in the range examined here.

References

1. H. Ye and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 4930-4934.
2. H. Ye, J. A. Crooks and R. M. Crooks, *Langmuir*, 2007, **23**, 11901-11906.
3. G. K. Kiema, M. Aktay and M. T. McDermott, *J. Electroanal. Chem.*, 2003, **540**, 7-15.
4. T. Biegler, D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, 1971, **29**, 269-277.
5. A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini and L. Giorgi, *J. Power Sources*, 2002, **105**, 13-19.