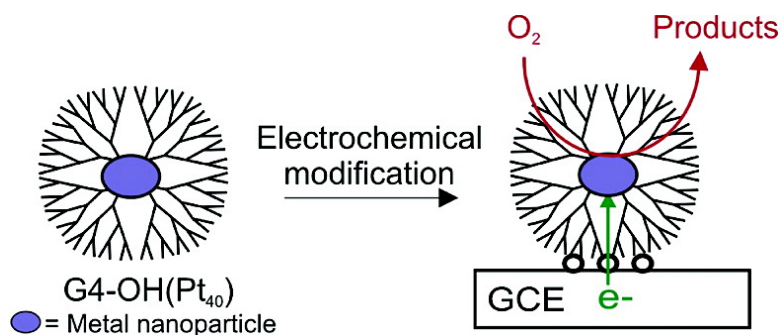


Electrocatalytic O₂ Reduction at Glassy Carbon Electrodes Modified with Dendrimer-Encapsulated Pt Nanoparticles

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J. Am. Chem. Soc., **2005**, 127 (13), 4930-4934 • DOI: 10.1021/ja0435900 • Publication Date (Web): 11 March 2005

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Electrocatalytic O₂ Reduction at Glassy Carbon Electrodes Modified with Dendrimer-Encapsulated Pt Nanoparticles

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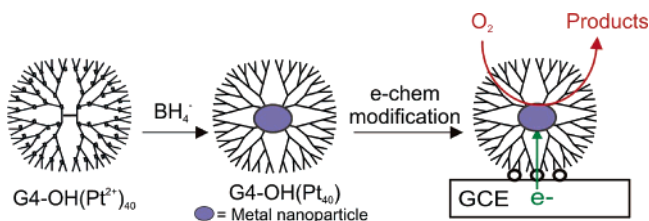
Abstract: Platinum dendrimer-encapsulated nanoparticles (DENs) were prepared within fourth-generation, hydroxyl-terminated, poly(amidoamine) dendrimers and immobilized on glassy carbon electrodes using an electrochemical coupling strategy. X-ray photoelectron spectroscopy, electron microscopy, and electrochemical experiments confirmed that the Pt DENs were about 1.4 nm in diameter and that they remained within the dendrimer following surface immobilization. The resulting Pt DEN films were electrocatalytically active for the oxygen reduction reaction. The films were also robust, surviving up to 50 consecutive cyclic voltammograms and sonication.

Introduction

Here, we show that dendrimer-encapsulated Pt nanoparticles of uniform size can be immobilized on glassy carbon electrodes (GCEs) and that they are electrocatalytically active for the O₂ reduction reaction (ORR) (Scheme 1).¹ This is a significant finding, because there are few alternative methods for immobilizing highly uniform nanoparticle catalysts on electrode surfaces. Therefore, the approach described in this paper will provide a convenient model system for correlating the size, composition, and structure of nanoparticles to their electrocatalytic activity.

Dendrimer-encapsulated nanoparticles (DENs) are prepared by a two-step process.² First, metal ions are extracted into dendrimers where they coordinate in fixed stoichiometries with interior functional groups. Second, the metal-ion/dendrimer composites are reduced to yield encapsulated nanoparticles. This process leads to stable, nearly size-monodisperse, catalytically active nanoparticles composed of Pt,^{3–7} Pd,^{3,5,6,8–16} Au,^{17–20} or

Scheme 1



Cu.²¹ It is also possible to prepare alloy^{22–25} and core/shell^{24,25} bimetallic nanoparticles using a slight variation on this basic synthetic scheme. Monometallic and bimetallic DENs have previously been shown to be catalytically active for homogeneous hydrogenation and carbon–carbon coupling reactions²⁶ as well as for heterogeneous catalytic reactions.^{27,28} We have also shown that it is possible to physisorb DENs onto Au electrodes and use them to electrocatalytically reduce O₂.⁴ However, adhesion of the DENs to the electrode surface was poor, and the catalytic activity was not robust. We attempted to improve stability by covalently linking the terminal amine groups of the dendrimers to an *n*-alkanethiol monolayer having a distal acid group,^{5,6} but the distance between the Pt nano-

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particle and the electrode proved too large for electron tunneling and therefore no electrocatalytic activity was observed.

In this paper, we report a new strategy for DEN immobilization on GCEs that is simple and that leads to robust, electrocatalytically active DEN monolayers. The approach involves preparation of DENs within hydroxyl-terminated dendrimers and subsequent coupling of the dendrimer to the GCE surface via an electrooxidation reaction. Similar electrochemical immobilization strategies have been reported for the oxidation of amines,²⁹ aryl acetates,³⁰ and alcohols,³¹ as well as for the reduction of aryl diazonium cations.^{32–34} Here, we are particularly interested in prior examples of the electrooxidation of alcohols, because the dendrimers used in this study have multiple hydroxyl groups on their periphery. Specifically, Ohmori and co-workers reported that various alcohols can be electrochemically attached to GCEs via ether bonds in anhydrous alcohol solutions.^{31,35} They also reported that triethylene glycol could be oxidatively coupled to GCEs.³⁶

There are three general approaches for immobilization of electrocatalytic nanoparticles onto electrode surfaces. The first involves two steps: synthesis of the nanoparticles followed by surface immobilization.^{4,37–42} This includes the most common method for preparing electrocatalysts: physical deposition of a mixture of carbon-supported metal nanoparticles and Nafion onto an electrode surface.^{37–40} The dendrimer-based approach reported here also fits into this category. In the second family of methods, nanoparticle formation and immobilization occur simultaneously. This approach includes electrodeposition of metal particles onto electrodes modified with polymer films,^{43–47} vacuum evaporation,⁴⁸ and electrodeless deposition.^{49–51} The third

approach involves immobilization of metal ions, usually within a polymer, and then reduction to metal nanoparticles.^{52–54}

In this paper, we report the preparation of Pt nanoparticles within fourth-generation, hydroxyl-terminated, poly(amido-amine) (PAMAM) dendrimers (G4-OH) and the subsequent electrooxidative coupling of the composite to GCEs in an aqueous 0.1 M LiClO₄ electrolyte solution. The Pt electrocatalysts contain an average of 40 atoms each and have a diameter of 1.4 ± 0.3 nm.^{3,4} Electrodes modified with these Pt DENs are electrocatalytically active for oxygen reduction, implying that the encapsulated Pt nanoparticles are within tunneling distance of the GCE surface. Moreover, the Pt DEN monolayers are robust, surviving up to 50 consecutive electrochemical scans through the O₂ reduction process and sonication for up to 10 min in 0.5 M H₂SO₄ with no significant change in activity.

Experimental Section

Chemicals. G4-OH dendrimers were purchased as a 10–25% methanol solution (Dendritech, Inc., Midland, MI). Prior to use, the methanol was removed under vacuum. K₂PtCl₆ (Strem Chemicals, Inc.), NaBH₄, LiClO₄, CH₂Cl₂, 1-dodecanethiol (The Aldrich Chemical Co.), and H₂SO₄ (EMD Chemicals, Inc.) were used without further purification. 18 MΩ cm Milli-Q deionized water (Millipore, Bedford, MA) was used to prepare aqueous solutions.

Preparation of Pt DENs. Pt DENs were prepared according to a previously published procedure.^{3,4} Briefly, 40 mol equiv of an aqueous 0.1 M K₂PtCl₆ solution was added to a 50 μM aqueous G4-OH solution. The mixture was stirred for 48 h to allow the Pt ions to complex with the interior amines of the dendrimers. Zerovalent Pt DENs (Pt₄₀) were synthesized by slow addition of a 10-fold excess of an aqueous 0.5 M NaBH₄ solution. This Pt DEN solution was allowed to stand in a closed vial for 5 h to ensure complete reduction of Pt. Finally, the solution was dialyzed using a cellulose dialysis sack having a molecular weight cutoff of 12 000 (Sigma Diagnostics, Inc.) to remove impurities.⁹ The resulting Pt DENs were examined by transmission electron microscopy (TEM), which showed that the mean particle size was 1.4 ± 0.3 nm (Figure 1). This result is comparable to our previous results.^{3,4}

Electrode Preparation. Glassy carbon (GC) disks (Bioanalytical Systems, Inc., 3.0 mm diameter) and GC plates (Tokai Carbon Co., grade GC-20), were used as electrodes. GC plates were obtained as 10 cm × 10 cm × 0.3 cm plates and cut into 2 cm × 1 cm × 0.3 cm pieces before use. Both types of GCEs were prepared by polishing with 1.0 and 0.3 μm alumina powder on a polishing cloth (Buehler) followed by sonication in water for 10 min. The electrodes were then rinsed with water and ethanol and dried under flowing N₂ gas. All electrochemical experiments were performed in a single-compartment, glass cell using a standard three-electrode configuration with a Pt-gauze counter electrode and a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, Inc.). Cyclic voltammetry was performed using a Pine AFRDE4 potentiostat configured with an X–Y recorder.

Characterization. X-ray photoelectron spectroscopy (XPS) data were acquired using an Axis His 165 Ultra Kratos instrument (Manchester, UK) with a Mg Kα X-ray source. The XPS positions were referenced to the C(1s) peak at 284.5 eV. TEM images were obtained using a JEOL-2010 TEM having a point-to-point resolution of 0.19 nm. Samples were prepared by placing a drop of solution on a holey-carbon-coated grid and allowing the solvent to evaporate in air. Field-emission scanning electron microscopy (FESEM) images were obtained using a Zeiss VP1530 microscope.

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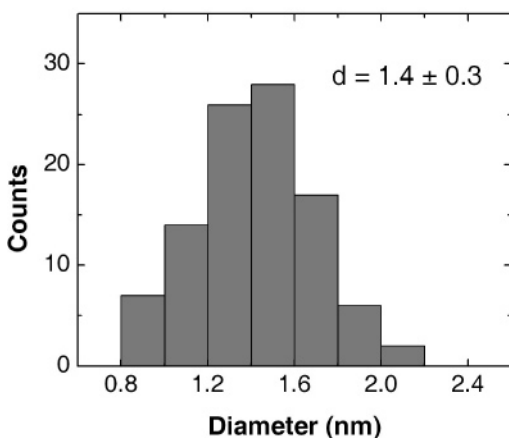
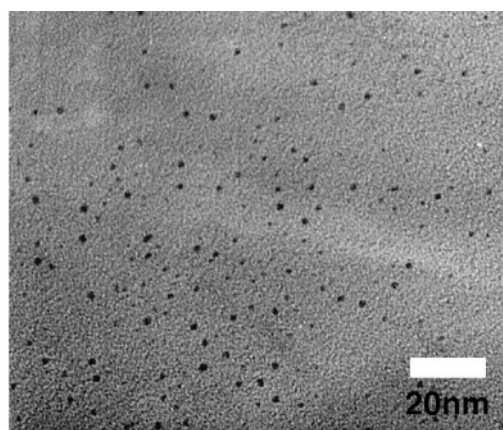


Figure 1. TEM image and particle-size distribution for the G4-OH(Pt₄₀) DENs used in the catalysis experiments. The particle-size distribution is based on 100 randomly selected particles.

Results and Discussion

Immobilization of Pt DENs on GCEs. The immobilization of Pt DENs on GCEs was carried out using a procedure similar to that reported by Ohmori and co-workers for the modification of GCEs with alcohols.^{31,35} A freshly polished GCE was placed in an aqueous 20 μ M G4-OH(Pt₄₀) solution containing 0.1 M LiClO₄, and then the potential of the electrode was scanned three times between 0 and 1.0 V (vs Ag/AgCl, 3 M NaCl). This resulted in robust immobilization of the Pt DENs. Figure 2a shows three cyclic voltametric background scans obtained in a DEN-free electrolyte solution. Only a small background current is observed. The data in Figure 2b were obtained under the same conditions as Figure 2a, but in the presence of Pt DENs. An irreversible oxidation wave appears at potentials >0.6 V. For alcohols, the current associated with this wave has previously been attributed to electrochemical oxidation of the GCE, which is followed by nucleophilic attack on hydroxyl groups.^{31,55} However, this mechanism is speculative and the details remain to be worked out. After the first scan, the current decreases and then remains approximately constant for the third scan. We believe the decrease in the oxidation wave is mainly attributable to the irreversible immobilization of Pt DENs onto the GCE after the first scan.

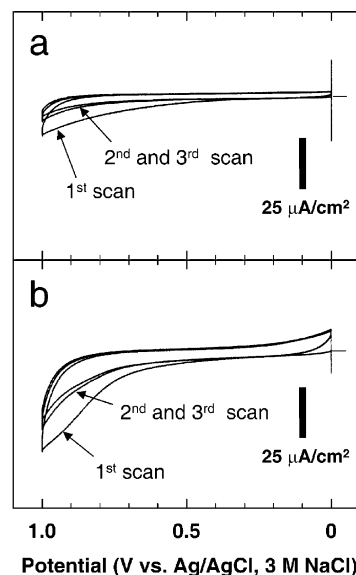


Figure 2. Three consecutive cyclic voltammograms obtained using a freshly polished GCE in (a) electrolyte solution only, and (b) electrolyte solution plus 20 μ M G4-OH(Pt₄₀). The aqueous electrolyte solution contained 0.1 M LiClO₄. The scan rate was 10 mV/s.

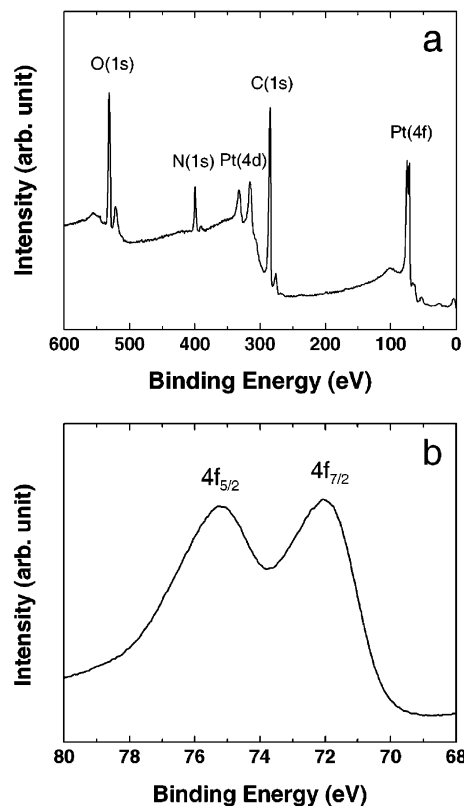


Figure 3. (a) An XPS spectrum of a G4-OH(Pt₄₀) film electrochemically immobilized on a GCE. (b) A high-resolution XPS spectrum in the Pt(4f) region for the same film. The electrode was cut from a sheet of glassy carbon, as described in the Experimental Section.

XPS measurements confirmed the presence of both the dendrimer and Pt on the GCE after electrochemical immobilization of the DENs. Figure 3a shows the XPS spectrum of a Pt DEN-modified GCE electrode. The N(1s) peak at 399.8 eV confirms the presence of the PAMAM dendrimers, while the Pt(4d) and Pt(4f) peaks confirm the presence of Pt. The Pt(4f_{5/2}) and Pt(4f_{7/2}) peaks are present at 75.3 and 72.1 eV, respectively,

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which is slightly higher than would be observed for bulk Pt (71.2 eV for Pt(4f_{7/2})). However, this result agrees with previous XPS investigations of Pt DENs and is probably a consequence of the small size of these nanoparticles and the presence of the dendrimeric ligands.^{56–58}

To confirm that the Pt DENs described in the previous paragraph are not just physisorbed to the electrode surface, we performed a control experiment in which a GCE was soaked in a Pt DEN solution for 15 min but with no potential applied. The GCE prepared using this method also revealed the presence of Pt and N peaks in the XPS spectra (Supporting Information), but they were substantially lower (31% and 42%, respectively) than those obtained using electrochemically modified GCEs. This is the anticipated result, because PAMAM dendrimers physisorb to nearly all surfaces including Au,^{4,59} mica,⁶⁰ and highly oriented pyrolytic graphite (HOPG).⁶⁰ We also examined a GCE modified exactly as described for Figure 3, except in this case only the dendrimer was immobilized (no Pt DEN). The resulting XPS spectrum (Supporting Information) indicated the presence of N and the absence of Pt. Interestingly, the peak intensity of N was only 50% as intense as that shown in Figure 3a. This might suggest that the encapsulated Pt nanoparticles catalyze linking of the dendrimer onto the GCE surface.⁶¹

The size of the immobilized DENs was examined by TEM and FESEM. TEM micrographs were obtained by scraping Pt DENs off the electrode surface and examining the powder. The results indicated that the particle size was 1.6 ± 0.4 nm (Supporting Information), which is just slightly larger than the diameter of the DENs prior to immobilization (1.4 ± 0.3 nm). FESEM has a resolution of 2.1 nm, and there were no observable differences between micrographs obtained from unmodified (naked) GCEs and GCEs modified with Pt DENs. This indicates that there are no Pt aggregates $> \sim 10$ nm in diameter present on the GCE surface (Supporting Information).

Electrocatalytic O₂ Reduction. Figure 4 shows cyclic voltammograms (CVs) for the reduction of O₂ at a naked GCE, a GCE modified with Pt-free G4-OH dendrimers, and a GCE modified with G4-OH(Pt₄₀) DENs. All three CVs were obtained in an O₂-saturated aqueous electrolyte solution containing 0.5 M H₂SO₄. Reduction at the naked GCE begins at a potential of about -0.1 V, and there is a well-defined peak at -0.39 V attributable to O₂ reduction. The electrochemical behavior at a GCE modified with G4-OH (but no Pt DENs) is similar to the naked GCE. However, the G4-OH(Pt₄₀)-modified GCE exhibits an onset current of about 0.5 V and a well-defined peak at 0.22 V. The ~ 600 mV positive shift in the O₂ reduction peak for the Pt DENs indicates a significant electrocatalytic effect. It also demonstrates that the Pt DENs are within electron tunneling distance of the GCE surface and that O₂ is able to penetrate the G4-OH dendrimer, encounter the encapsulated Pt nanoparticle, and that the product of the reaction is able to escape the dendrimer interior.

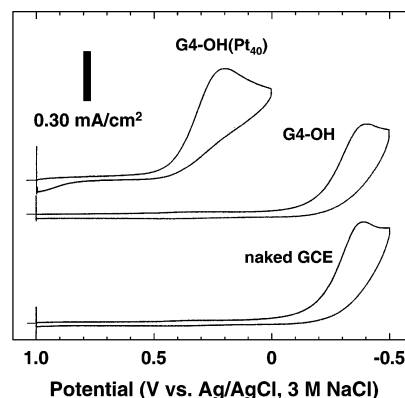


Figure 4. CVs for the reduction of O₂ using (top to bottom) a GCE modified with G4-OH(Pt₄₀) DENs, a GCE modified with Pt-free G4-OH dendrimers, and a naked GCE. The data were obtained in an aqueous 0.5 M H₂SO₄ electrolyte solution saturated with O₂. The scan rate was 50 mV/s.

The electrocatalytic properties of GCEs modified with physisorbed Pt DENs (no electrochemical linking to the GCE) were also examined. These surfaces were found to be less catalytically active than the electrochemically linked films (Supporting Information). For example, the O₂ reduction peak had a poorly defined shape and was shifted 140 mV negative as compared to the uppermost CV shown in Figure 4. Control experiments corresponding to the three CVs in Figure 4, but carried out in O₂-free electrolyte solutions, were also performed. They revealed only a small background current (Supporting Information). This result confirms our contention that the peaks in Figure 4 arise from O₂ reduction.

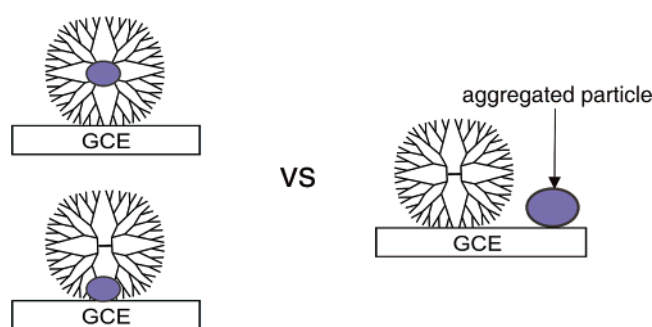
Stability of G4-OH(Pt₄₀)-Modified GCEs. The stability of the G4-OH(Pt₄₀) films on GCEs was tested by repetitive cycling between 1.0 and 0 V. Even after 50 scans, no significant change in the O₂ reduction peak current or position was observed (Supporting Information). As a further test of stability, a G4-OH(Pt₄₀)-modified GCE was sonicated in a 0.5 M H₂SO₄ solution for 10 min, and afterward the resulting voltammetry indicated no significant change of the O₂ reduction peak current or position as compared to a CV obtained prior to sonication (Supporting Information). XPS measurements were also performed to verify the presence of the dendrimer and Pt after both of these stability tests. The resulting XPS spectra showed no significant change of the N and Pt bands as compared to the freshly prepared G4-OH(Pt₄₀) films. These results support the presence of a robust link between the dendrimer and the GCE, and an equally durable attachment of the Pt nanoparticle within the dendrimers.

Location of the Pt Nanoparticles. Thus far, we have assumed that the Pt nanoparticles remain within the dendrimers during immobilization. However, the data presented up to this point do not exclude the possibility that the Pt DENs are somehow extracted from within the dendrimers and present as naked nanoparticles, possibly as aggregates having diameters below the resolution of FESEM (~ 10 nm), sorbed to the GCE surface (Scheme 2). While we view this scenario as unlikely, it is fundamental to the central claim of this paper (Scheme 1) and therefore needs to be addressed.

To verify that the Pt nanoparticles remain within the dendrimers during the electrochemical immobilization procedure, we performed a selective Pt DEN poisoning experiment

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Scheme 2



using 1-dodecanethiol (C12SH) dissolved in either ethanol or CH_2Cl_2 . Because ethanol is a good solvent for PAMAM dendrimers, we hypothesized that the dendrimer would have an open structure in ethanol. Therefore, C12SH should easily penetrate the outer branches of the dendrimer, adsorb to the surface of the encapsulated Pt nanoparticle, and reduce its subsequent electrocatalytic activity.^{62,63} In contrast, we reasoned that the dendrimer would collapse around the Pt nanoparticles in CH_2Cl_2 , which is a poor solvent for PAMAM dendrimers, and thereby protect the encapsulated DENs from C12SH adsorption. This hypothesis is based on existing literature demonstrating that the dendrimer branches can act as selective gates that modulate substrate access to DENs.⁸ Additionally, it has previously been shown that in air, which of course is a very poor solvent for PAMAM dendrimers, the dendrimeric branches completely collapse around DENs and render them totally inaccessible to substrates.^{27,64}

After exposing Pt DEN-modified GCEs to 3 mM C12SH solutions in either ethanol or CH_2Cl_2 for 20 min and then rinsing in solvent and water, the CVs shown in Figure 5 were obtained in an O_2 -saturated electrolyte solution. The top CV corresponds to C12SH treatment in CH_2Cl_2 . This CV is only slightly changed as compared to the corresponding CV shown in Figure 4, suggesting that during exposure to C12SH the dendrimer protected the nanoparticle against poisoning. In contrast, when the poisoning experiment was carried out in ethanol, the subsequent CV indicated extensive surface passivation of the Pt DENs. No change in electrocatalytic activity was observed for Pt DEN-films exposed to ethanol or CH_2Cl_2 in the absence of C12SH, which indicates that the differences in the two CVs shown in Figure 5 are not attributable to solvent (ethanol or CH_2Cl_2) poisoning. On the basis of these results, we concluded that Pt nanoparticles are present within the dendrimers (left side of Scheme 2) even after the electrochemical immobilization process. Otherwise, there would be no effect of solvent on the accessibility of the naked Pt surface toward C12SH. Taken together with the microscopy results discussed earlier, which showed no evidence of metal aggregation, we are confident in concluding that the model of an intact, surface-immobilized Pt DEN catalyst is correct.

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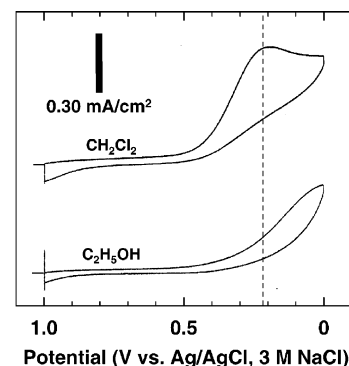


Figure 5. CVs obtained using G4-OH(Pt_{40})-modified GCEs. Prior to obtaining the CVs, the modified electrodes were exposed to C12SH dissolved in either CH_2Cl_2 (top) or ethanol (bottom) for 20 min. The CVs were obtained in an aqueous 0.5 M H_2SO_4 electrolyte solution saturated with O_2 . The dashed line shows the position of the O_2 reduction peak before the modified electrodes were exposed to C12SH solution. The scan rate was 50 mV/s.

Summary and Conclusions

We have shown that Pt DENs prepared within hydroxyl-terminated PAMAM dendrimers can be immobilized on GCEs using an electrochemical attachment method. The resulting films are electrocatalytically active for O_2 reduction, and they are remarkably stable, retaining their electrocatalytic properties even after 50 consecutive cyclic voltammetric scans through the O_2 reduction wave. Selective thiol poisoning experiments demonstrate that the Pt nanoparticles are retained within the dendrimers after electrochemical immobilization. Future studies will involve the use of electrochemical generation-collection experiments to quantitatively assess the electrocatalytic activity of the metal nanoparticles,^{37,38} including alloy and core-shell bimetallic DENs,²⁵ as a function of the size and elemental composition of the DENs.⁴⁰

Acknowledgment. We acknowledge the U.S. Department of Energy, DOE-BES Catalysis Science grant no. DE-FG02-03ER15471, and the Robert A. Welch Foundation for financial support of this work. The FESEM acquisition was supported by the National Science Foundation under Grant No. DBI-0116835. We thank Dr. William Lackowski and Yulia Vasilyeva of the TAMU Materials Characterization Facility for assistance in obtaining the XPS data, and Dr. Zhiping Luo and Tom Stephens of the TAMU Microscopy and Imaging Center for assistance with the microscopy.

Supporting Information Available: TEM images and particle-size distributions for G4-OH(Pt_{40}) after electrochemical immobilization; FESEM images confirming the absence of Pt aggregates on the GCE surface; CVs of modified and unmodified GCEs in N_2 -saturated electrolyte solutions; voltammetry illustrating the stability of G4-OH(Pt_{40})-modified GCEs; XPS spectra and voltammetry confirming electrochemical linking of dendrimers to the GCE surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0435900