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dissertation:

Underpotential Deposition as a Synthetic and
Characterization Tool for Core@Shell Dendrimer-
Encapsulated Nanoparticles

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Underpotential Deposition as a Synthetic and
Characterization Tool for Core@Shell Dendrimer-
Encapsulated Nanoparticles

by

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Dedication

To my family and friends.

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Underpotential Deposition as a Synthetic and Characterization Tool for Core@Shell Dendrimer- Encapsulated Nanoparticles

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The synthesis and characterization of Pt core/ Cu shell (Pt@Cu) dendrimer-encapsulated nanoparticles (DENs) having full and partial Cu shells deposited via electrochemical underpotential deposition (UPD) is described. Pt DENs containing averages of 55, 147, and 225 Pt atoms immobilized on glassy carbon electrodes served as the substrate for the UPD of a Cu monolayer. This results in formation of Pt@Cu DENs. Evidence for this conclusion is based on results from the analysis of cyclic voltammograms (CVs) for the UPD and stripping of Cu on Pt DENs, and from experiments showing that the Pt core DENs catalyze the hydrogen evolution reaction before Cu UPD, but that after Cu UPD this reaction is inhibited. Results obtained by in-situ electrochemical

X-ray absorption spectroscopy (XAS) confirm the core@shell structure.

Calculations from density functional theory (DFT) show that the first portion of the Cu shell deposits onto the (100) facets, while Cu deposits lastly onto the (111) facets. The DFT-calculated energies for Cu deposition on the individual facets are in good agreement with the peaks observed in the CVs of the Cu UPD on the Pt DENs. Finally, structural analysis of Pt DENs having just partial Cu shells by in-situ XAS is consistent with the DFT-calculated model, confirming that the Cu partial shell selectively decorates the (100) facets.

These results are of considerable significance because site-selective Cu deposition has not previously been shown on nanoparticles as small as DENs. In summary, the application of UPD as a synthetic route and characterization tool for core@shell DENs having well defined structures is established.

A study of the degradation mechanism and degradation products of Pd DENs is provided as well. These DENs consisted of an average of 147 atoms per dendrimer. Elemental analysis and UV-vis spectroscopy indicate that there is substantial oxidation of the Pd DENs in air-saturated solutions, less oxidation in N₂-saturated solution, and no detectable oxidation when the DENs are in contact with H₂. Additionally, the stability improves when the DEN solutions are purified by dialysis to remove Pd²⁺-

complexing ligands such as chloride. For the air- and N₂-saturated solutions, most of the oxidized Pd recomplexes to the interiors of the dendrimers, and a lesser percentage escapes into the surrounding solution. The propensity of Pd DENs to oxidize so easily is a likely consequence of their small size and high surface energy.

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Chapter 1. Introduction

1.1 Dendrimer-Encapsulated Nanoparticles

Dendrimer-encapsulated nanoparticles (DENS)¹ are prepared using poly(amidoamine) (PAMAM) dendrimers as a template.² The basic approach for synthesizing DENS within PAMAM dendrimers is comprised of two steps (Illustration 1.1). First, metal ions are mixed with a dendrimer solution. This results in the encapsulation of the metal ions within the dendrimer and the formation of a dendrimer-metal ion complex. Second, a chemical reducing agent such as NaBH_4 is added to this solution resulting in DENS.

The dendrimer templating method offers several significant advantages as a synthetic route. First, the dendrimer stabilizes the nanoparticles and protects them from agglomerating without passivating the nanoparticle surface, which leaves the surface free and available for catalysis.³⁻⁶ Second, the size, composition and structure of the nanoparticles can be controlled by the dendrimer:metal ion ratio and the sequence in which metal ions are loaded into the dendrimers and reduced.¹ Third, the dendrimer templating method allows for the preparation of DENS having less than a few hundred atoms, and clusters of this size can be directly compared to computations.⁷ Fourth, the precise control over the number of atoms in each DEN allows for the synthesis of special sizes of clusters, especially

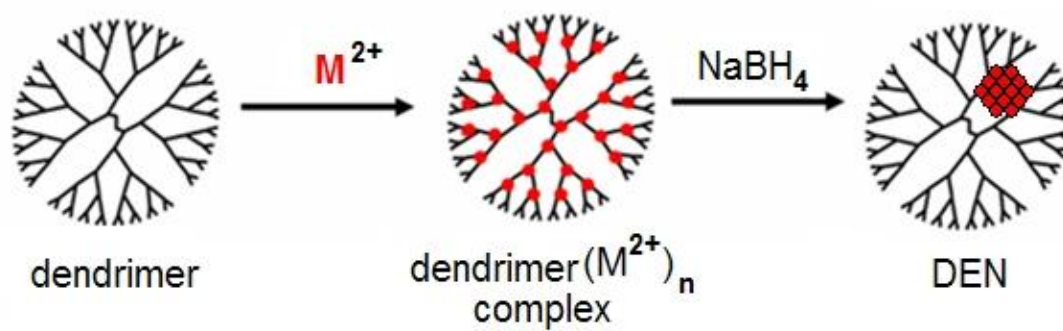


Illustration 1.1.

so-called "magic number" clusters, e.g. cuboctahedra, which are expected to have the most stable geometries due to having closed outer shells.⁸ Fifth, the dendrimer serves as an attachment handle for outfitting surfaces such as glassy carbon (GC) electrodes or carbon nanotubes with DENs, after which, DENs can be applied towards electrocatalysis.^{5, 6, 9} To date, the synthesis and characterization of monometallic Au, Pt, Pd, Cu, Ni, and Fe as well as bimetallic AuAg, PdAu, PtCu, PtAu, PdPt, and CuPd DENs have been reported.^{1, 10-20} Recent research efforts have focused on the synthesis of DENs having complex structures, such as core/shell (core@shell) DENs, the application of DENs in electrochemical catalysis and the effect of nanostructure on catalytic properties, as well as advances in characterization methods and computational studies.²⁰

1.2 Pt DENs

Pt DENs such as those described in this dissertation have been synthesized within sixth generation hydroxyl-terminated PAMAM dendrimers (G6-OH) according to the general scheme shown in Illustration 1.1. Alternate methods for the preparation of Pt DENs such as galvanic exchange have been explored as well.²¹ Pt DENs can be synthesized in both OH- and NH₂- terminated PAMAM dendrimers.^{2, 5, 6, 12} Pt DENs have been immobilized on GC electrodes⁶ as well as multi-walled carbon nanotubes (MWNTs)⁵ and used in the electrocatalysis of the oxygen reduction reaction (ORR).

Synthesis. Hydrolysis of the Pt salt occurs in the first step of the complexation process when 1 H₂O replaces a Cl⁻ ligand, yielding a PtCl₃(H₂O)²⁺ ion. After this initial hydrolysis step, the hydrolyzed Pt²⁺ ions coordinate to tertiary amines within the dendrimer.²² In aqueous solutions at room temperature, the complexation step is complete after about 3 days.²² Ultraviolet-visible (UV-vis) spectra of a solution of K₂PtCl₄ salt and G6-OH dendrimers show that the absorbance of the ligand-metal charge-transfer (LMCT) bands associated with Pt salt decrease over a time period of 3 days, during which there is an increase in the absorbance of the LMCT band corresponding to the formation of a dendrimer/Pt²⁺ complex. Adding a 10-fold excess of NaBH₄ to the complex results in the reduction and coalescence of the encapsulated Pt ions into metallic Pt DENs. The time required for the completion of the reduction process is about 24 hours.²² Following reduction with NaBH₄, the UV-vis absorbance spectrum is dominated by a broad monotonic absorbance typical of metal clusters with diameters smaller than 10 nm.^{22, 23} Some absorbance due to residual unreduced dendrimer/Pt²⁺ complex can still be seen following the reduction step (Figure 1.1).²²

Characterization. The structural characteristics of Pt DENs include their size, crystallinity, and degree of disorder. Transmission electron microscopy (TEM) images show that Pt DENs have the expected sizes according to the nominal number of Pt atoms per DEN.^{3, 22} Analysis of electron diffraction patterns show that Pt DENs exhibit a face-

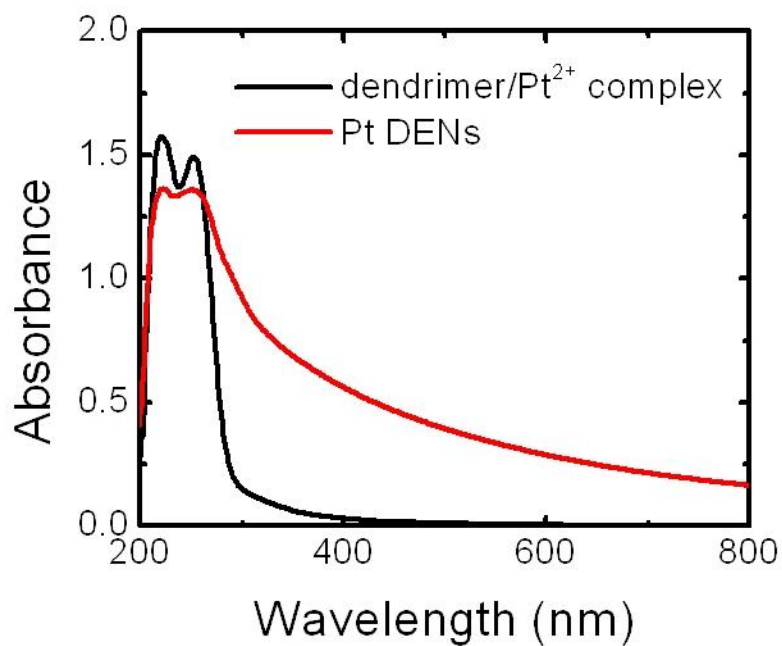


FIGURE 1.1.

UV-vis spectra of the precursor, a dendrimer/Pt²⁺ complex (black line) formed by mixing a 10 μM G6-OH dendrimer solution with 225 equivalents of Pt²⁺ and stirring the solution for 3 days, and the reduced Pt DENs (red line) following the addition of NaBH₄ to the complex and stirring the sealed solutions for 24 h. The instrument was blanked with a 10 μM G6-OH dendrimer solution.

centered cubic (fcc) crystal structure.²²

The small size of DENs precludes structural characterization techniques that require long-range order, such as conventional X-ray diffraction (XRD). However, XRD-pair distribution function (XRD-PDF) and X-ray absorption spectroscopy (XAS) are the most sensitive to short range ordering and therefore they are well suited to the characterization of DENs. XAS provides information about the coordination environment of an absorbing atom, such as the coordination number (CN), type, and bond distances of neighboring atoms. XAS is especially well suited for the structural characterization of DENs because the average CN drops precipitously as nanoparticle size decreases and a larger fraction of the atoms reside on the surface. XRD-PDF measures the distribution of mass in a sample and can be used to determine the atomic structure of both amorphous and crystalline materials.

The analysis of Pt DENs by XRD-PDF suggest that these DENs are at least partially amorphous, that is, short-range order is detected but might not extend throughout the entire nanoparticle.²⁴ Petkov and co-workers characterized DENs consisting of 147 Pt atoms (Pt_{147}) using XRD-PDF.²⁴ Pt_{147} DENs have diameters of about 1.6 nm.¹ However, the peaks in the XRD-PDF, which represent the periodicity of bonds, are broadened and dampened at radial distances beyond about 1.2 nm, indicating increased disorder at the surface. Additionally, it was found that highly ordered fcc structural models could not be used to fit the experimental

data. Reverse Monte Carlo simulations were used to determine structures consistent with the data. These models were then relaxed into more energetically stable configurations by density functional theory (DFT) calculations. The resulting, partially disordered models approximated the data well.

The CNs of Pt DENSs were measured by XAS and then compared to calculated CNs for model structures as an estimate of size.⁸ For example, a cuboctahedral nanoparticle containing 147 Pt atoms would have a Pt-Pt CN of 8.9.⁸ However, XAS measurements made on Pt₁₄₇ DENS indicate that they have a Pt-Pt CN of just 6.3 which is substantially lower than the expected CN for clusters of this size.^{22, 24}.

To obtain a better understanding of the Pt DENS structure, we turned to X-ray photoelectron spectroscopy (XPS) and UV-vis spectroscopy. The results of XPS showed that reduced DENS samples contain some Pt²⁺.²² Taken together with the UV-vis spectra of Pt DENSs following reduction (Figure 1.1), it is clear that some of the Pt²⁺ remains complexed to the dendrimer even after the addition of NaBH₄. The presence of unreduced Pt²⁺ can help explain the low Pt-Pt CNs measured by XAS. Because the XAS signal contains contributions from all of the forms of Pt atoms in the sample, the CN measured by XAS represents the *average* CN over the entire sample. Therefore, the presence of Pt absorbers such as the dendrimer/Pt²⁺ complex in which the Pt-Pt CN = 0, shifts the measured Pt-Pt CN to a number

lower than the one calculated for the model cuboctahedral nanoparticle.

A recent study on Pt DENs that were prepared from Cu DENs via galvanic exchange²¹ provides additional evidence that the presence of some unreduced dendrimer/Pt²⁺ complexes does in fact lower the measured CN. Unlike the Pt DENs described earlier, these DENs were prepared without first forming the dendrimer/Pt²⁺ complex. The XPS of the Pt DENs prepared by galvanic exchange indicates that these DENs are fully reduced and therefore we assume that the samples do not contain any dendrimer/Pt²⁺ complexes. When characterized by XAS, the Pt-Pt CN exactly matched the predicted CN. The only possible explanation that can reconcile all of these results is that Pt DENs prepared by the reduction of dendrimer/Pt²⁺ complexes by NaBH₄ results in a product having a bimodal distribution: within the sample, there are some dendrimers containing fully reduced Pt DENs of the ideal size and others contain only the original precursor dendrimer/Pt²⁺ complex.²²

Electrochemistry. Pt DENs have been immobilized on GC electrodes and MWNTs and used in the catalysis of the ORR.^{5, 6} The attachment of Pt DENs to these surfaces is facilitated by the dendrimer. The immobilization of Pt DENs on GC electrodes is accomplished by applying a positive voltage to the GC electrode, thereby oxidizing it slightly. This most likely changes the solvent interaction at the solution-electrode interface and improves the affinity of the GC

surface for polar moieties such as the OH-termini of G6-OH dendrimers.

The encapsulation of the immobilized Pt DENs is confirmed by selectively protecting the Pt DENs against poisoning by thiols.⁶ After being immobilized on GC electrodes, Pt DENs were exposed to alkanethiols in both polar and nonpolar solvents. In polar solvents, in which G6-OH PAMAM dendrimers are soluble, the alkanethiols bound to the Pt, poisoning the surface to subsequent electrochemical reactions. However, in nonpolar solvents, the dendrimer tightly enfolded the Pt particle, presumably due to the insolubility of the dendrimer, and no poisoning of the Pt surface occurred. The latter result was confirmed by observing ORR on the Pt DENs after they had been exposed to thiols in the nonpolar solvent. The ORR activity after thiol exposure was the same as it was beforehand. It is unlikely the Pt DEN would be so well protected from poisoning if the particle were located to the exterior of the dendrimer.

Stevenson and co-workers outfitted N-doped MWNTs with Pt DENs in NH_2 -terminated dendrimers and used the supported nanoparticles to catalyze the ORR.⁵ Centrifugal separation and UV-vis spectroscopy were used to monitor the decrease in Pt DEN concentration in solution as DENs adsorbed to the MWNTs. Adsorption isotherms reveal that the affinity of the Pt DENs for adsorption increases with increasing edge-plane sites on the MWNTs. This work is of considerable importance to the outfitting of nanomaterial surfaces with DENs.

The surface areas of Pt DENs immobilized on GC electrodes have been measured electrochemically.⁶ By making some reasonable assumptions regarding the roughness of the electrode, the packing of the DENs on the electrode surface, and the projected area of each DEN, it was possible to obtain a theoretical estimate of the DENs surface area. Subsequent electrochemical measurement of the surface area by CO adsorption and H adsorption provided a reasonable reflection of the estimated area, implying that the immobilized Pt DENs have the expected surface area for nanoparticles of the same nominal composition.³

The effect of nanoparticle size on the kinetics and specific activities of ORR catalysis by Pt DENs encapsulated within G6-OH dendrimers (denoted G6-OH(Pt_n) has been studied.³ G6-OH(Pt_n) (n = 55, 100, 147, 200, 240) DENs were immobilized on a rotating disk GC electrode and used to catalyze the ORR. The specific activities of the Pt DENs, measured by rotating disk voltammetry (RDV), decrease with decreasing particle size. Interestingly, the smallest two particles exhibited decreased mass-transfer limited currents. This insinuates that the 2 electron mechanism for ORR, which results in the formation of a byproduct, hydroxide, may be significant for very small particles. The most noteworthy result of this study is the finding that the specific activity of Pt DENs for ORR is sensitive to a change in particle size by less than 50 atoms per nanoparticle.

1.3 Core@Shell DENs

Core@shell nanoparticles are intriguing nanostructures due to the tuning of the electronic properties that results from the interaction between the core and shell metals. Charge transfer occurs in core@shell nanoparticles due to differences in the work function of the component metals.⁷ Lattice mismatch between the core and shell metals imparts a tensile or compressive strain to the shell metal and this also shifts the conduction band center.^{7, 25, 26} Core@shell DENs can be prepared by sequentially reducing the component metals within the dendrimers.^{18, 27, 28} Additionally, the metallic components of some bimetallic alloyed DENs have been shown to segregate into a core@shell configuration.¹⁸

Au@Ag DENs were synthesized by reducing Ag^+ in the form of AgNO_3 onto pre-formed Au DENs comprised of 55 Au atoms.²⁷ The results of UV-vis analysis suggest that the DENs adopt the core@shell configuration. This assumption is based on the finding that increasing the Ag content of the shell increased the characteristic plasmon band in the UV-vis spectrum, but did not shift the position. In contrast, the plasmon observed for AuAg alloy DENs is observed to shift in accordance with changes in the relative amount of Au and Ag present in the alloy.

Au@Pd DENs were prepared in a similar fashion as the Au@Ag DENs described above. Either Pd or Au was used to synthesize a 55-atom DEN to form the core. These were then coated with one or two monolayers of the other metal by adding the metal ions to solution and reducing them using H_2

gas. The catalysis of resazurin to resorufin, which occurs in the presence of small Au nanoparticles (including DENs of this size range) but does not occur on Pd nanoparticles, was also used as a probe of the catalyst surface. When resazurin is added to a solution of the Pd@Au DENs, there is no conversion to resorufin. This also indicates that the Pd is likely on the surface. The core@shell configuration was later confirmed by XAS. The atoms located in the outer shell of DENs are less coordinatively saturated than the atoms in the core and therefore, the CNs of the atoms in shell will be much lower than the CNs of the atoms in the core.

We recently demonstrated that Au@Pt DENs could be prepared electrochemically via underpotential deposition (UPD). DENs containing 147 Au atoms were immobilized on a GC electrode, and this was followed by UPD of a Cu monolayer.²⁹ Galvanic exchange of the Cu monolayer for Pt results in Au@Pt DENs. The surface composition of the DENs was determined by integrating the current under the AuO and PtO reduction waves of a CV recorded using an Au@Pt DENs-modified GC electrode in acidic solution. The Pt shell coverage was calculated as 0.9 by this method. The activity of these core@shell DENs toward the ORR was very close to that of monometallic Pt₁₄₇ DENs.

1.4 Underpotential Deposition

UPD often describes the electrodeposition of atomic monolayers onto foreign metal substrates at potentials that are positive of the bulk potential. The origin of this

phenomenon is a difference between the work function, Φ , of the adatoms (Φ_{Adatom}) and that of the substrate ($\Phi_{\text{Substrate}}$) onto which they deposit.^{30, 31} UPD is favored in conditions where $\Phi_{\text{Substrate}} > \Phi_{\text{Adatom}}$. Due to this difference in Φ , a partial charge transfer from the substrate to the adatom takes place. This charge transfer effectively strengthens the binding energy of the adatoms and makes the interaction with the substrate more attractive and hence energetically favored over the formation of the bulk phase.³² As a result, the first atomic monolayer electrodeposits at more positive potentials than the bulk phase. UPD typically proceeds until a single atomic monolayer has formed, afterwards the deposition of the bulk phase is observed at the bulk reduction potential. The difference in energy between the Nernstian potential and the potential of UPD is called the UPD shift, ΔV_{UPD} .³³ ΔV_{UPD} was first described by Kolb and co-workers in 1974^{30, 31} (Equation 1.1).

$$\Delta V_{\text{UPD}} \approx 0.5(\Phi_{\text{Substrate}} - \Phi_{\text{Adatom}}) \quad (1.1)$$

The solution pH, the presence of competing adsorbates, and kinetic effects also influence ΔV_{UPD} .³³⁻³⁵

1.5 UPD of Cu onto Bulk Pt Electrodes

The voltammetry of Cu UPD on polycrystalline Pt electrodes and on Pt single crystal electrodes of various

orientations has been examined in a variety of acid electrolyte solutions. The structure of the Cu UPD monolayer has been characterized using a suite of techniques including but not limited to electrochemical quartz crystal microbalance (EQCM), infrared spectroscopy (IR), XRD, XPS, XAS, atomic force microscopy (AFM) and scanning probe microscopy (SPM).³⁶

Kinetics. The Cu UPD and Cu stripping waves shift towards negative and positive potentials, respectively, upon increasing the scan rate, indicating that the kinetics of this reaction are slow.³⁶ The amount of Cu deposited also changes as a function of scan rate: Cu monolayer formation is complete under steady state kinetic conditions, but decreases as the scan rate is increased.³⁷ Reversible conditions are usually observed at scan rates in the range of 5-20 mV/s.³⁶⁻³⁹

Effect of Anions. The mechanism and structure of the Cu UPD monolayer depend on the experimental conditions. For example, on Pt(111) in the presence of Cl^- , a single Cu monolayer deposits via UPD in 2 distinct steps with each step corresponding to the deposition of 0.5 atomic monolayers. This 2-step pattern is the result of co-adsorption of Cl^- with Cu during UPD. The deposition of Cu will induce the adsorption of Cl^- on the Pt electrode, resulting in the simultaneous deposition of both Cu and Cl^- in the first step. An incoming Cu atom then kicks out and replaces Cl^- in the second step. In H_2SO_4 solutions that do

not contain halides, a single Cu monolayer on Pt(111) can deposit in a single step.^{36, 39}

Structural Characterization of Cu UPD Monolayers. Cu UPD onto Pt electrodes results in the formations of a commensurate Cu monolayer having the same crystallographic orientation as the underlying Pt surface.³⁶ In-situ XAS studies of Cu UPD onto Pt(111) show that the Cu monolayer assumes the (111) orientation, with Cu residing in the 3-fold hollow positions on the Pt surface.⁴⁰ The samples for XAS analysis were prepared by depositing Cu from solution onto a Pt(111) foil while recording XAS spectra. The XAS spectra were then fit to the XAS equation and variables such as bond length and CNs were extracted. The Cu-Cu CN is a number that represents the average number of Cu atoms that are located in the first coordination shell of each Cu atom in the sample. The Cu-Cu CN was measured as 6, meaning that Cu atoms are, on average, coordinated to 6 other Cu atoms. A Cu-Cu CN of 6 is the expected CN for a (111) oriented Cu monolayer. The Cu-Pt CN was measured as 3, meaning that each Cu atom was coordinated to 3 Pt atoms. A Cu-Pt CN of 3 is the expected CN for a (111) oriented Cu monolayer in which Cu atoms reside in the 3-fold hollow positions on the Pt surface.

Following deposition, a substantial amount of charge transfer occurs between the Pt surface and the Cu adatoms. The effective charge on the Cu atoms in the monolayer on Pt(111) is about +1, which induces the adsorption of

negatively charged anions, such as halides and SO_4^{2-} on top of the Cu monolayer.³⁶

Influence of the Pt Crystal Structure on Cu UPD. The voltammetric profile for Cu UPD on polycrystalline Pt electrodes is noticeably different than for flame annealed Pt single crystal electrodes. The UPD of Cu onto Pt(100) and Pt(111) single crystals in 0.10 M H_2SO_4 under reversible conditions is observed at about 0.6 V and 0.5 V vs. NHE, respectively.³⁷ On polycrystalline Pt electrodes, Cu UPD is shifted negatively to the range of 0.5 V - 0.3 V.^{41, 42} Oxide layers and adsorbates are more stable on polycrystalline Pt, that is, they are removed at more negative potentials compared to Pt single crystal electrodes.⁴³ The surface oxides on Pt(111) single crystal electrodes are less stable and therefore more easily displaced, that is, the surface oxides are reduced between 0.9 and 0.7 V.⁴⁴ This means that surface oxides are more stable on polycrystalline Pt electrodes compared to Pt(111). Because the surface oxides have to be displaced before Cu can undergo UPD, the enhanced stability of the oxide layer on polycrystalline Pt electrodes would shift Cu UPD toward more negative potentials.³²

Cu UPD has also been studied on stepped single crystal electrodes on which more than one crystallographic orientation is present.^{39, 45} The UPD of Cu on Pt(311) electrodes, which have steps and terraces in the (111) and (100) orientations, was compared to Cu UPD on Pt(111) and Pt(100) single crystals by Abruña and co-workers.³⁹ Cu UPD

was carried out in 0.10 M H_2SO_4 that contained 1.0 mM CuSO_4 . Cu UPD onto the Pt(100) single crystal occurred at less negative potentials compared to the Pt(111) single crystal, which suggests that Cu preferentially deposits on the (100) orientation of Pt. The deposition order was reversed on the Pt(311) electrode: Cu preferentially deposited on the Pt(111) step sites of the Pt(311) electrode, meaning Cu UPD occurred first on the (111) steps, followed by the decoration of the (100) terraces at more negative potentials. The interpretation given by the authors was that, due to Pt(311) having narrow 1-2 atom-wide steps and terraces, the adsorbed SO_4^{2-} anions can be more easily displaced from the Pt(111) surface than the Pt(100) surface, and therefore, Cu deposition was preferential on the (111) steps. This is interesting because it implies that the geometry of the electrode, specifically, the area of one region compared to another, may play a role in determining the surface structure on which Cu will preferentially deposit when more than one crystallographic plane is present.

Electrochemical Measurement of the Cu Monolayer Coverage. The Cu coverage, denoted θ_{Cu} , is the ratio of the Cu in the deposited monolayer to the underlying Pt surface atoms. A $\theta_{\text{Cu}} = 1.0$ corresponds to a full, single atomic monolayer. The θ_{Cu} depends on the solution composition and kinetic effects.^{38, 44, 46} For example, at $[\text{Cu}^{2+}] < 100 \text{ } \mu\text{M}$ in acidic solutions, the θ_{Cu} will be less than 1.0 atomic

monolayer, even under reversible conditions.³⁸ At $[\text{Cu}^{2+}] > 100 \text{ }\mu\text{M}$, a θ_{Cu} of 1.0 is normally obtained.³⁸ The deposition of a full Cu monolayer on Pt can also be used to measure the electroactive surface area of Pt electrodes.⁴² For example, the charge density for depositing a full Cu monolayer on Pt(111) is $420 \text{ }\mu\text{C}/\text{cm}^2$, thus the charge due to Cu UPD can be used to determine the Pt surface area.

1.6 UPD onto Nanomaterials

Recently, the UPD of Cu and Pb has been used as a probe for surface structure and also to synthesize precise monolayer shells on nanoparticles and other nanostructured materials.^{25, 26, 47-50} Adzic and co-workers popularized a method for fabricating Pt monolayer shells on metal nanoparticles via Cu UPD onto the metal nanoparticles with subsequent galvanic replacement of the Cu shell by Pt.²⁶ More recently, this method has been applied to the formation of Pt-M mixed monolayers on Pd cores, where $M = \text{Au}, \text{Pd}, \text{Rh}, \text{Ir}, \text{Os}, \text{ or } \text{Re}$.²⁶ UPD, which allows for the controlled, surface-selective deposition of a metal monolayer, is an essential step in the synthesis of these well-defined nanostructures.

Feliu and co-workers have demonstrated how UPD can be regarded as a "voltammetric fingerprint" for the surface morphology of nanorods.⁵⁰ They compared the current trace due to Pb UPD on Au nanorods against that Pb UPD on polycrystalline Au. The current peaks in the voltammogram of Pb UPD onto polycrystalline Au are characteristic of the

different crystallographic domains present on the surface. The voltammogram of Pb UPD onto the Au nanorods displayed several current peaks having the same potentials as the peaks observed in the voltammogram recorded on the polycrystalline Au electrode, thereby confirming the presence of specific crystallographic orientations.

1.7 Research Summary

The studies described herein demonstrate the use of Cu UPD as an electrochemical synthetic route for the synthesis and characterization of core@shell DENs on carbon electrodes. Furthermore, site-selective Cu UPD onto Pt DENs is demonstrated. Prior to this research, the atomic level structure of the surfaces of Pt DENs had not been directly probed due to sample and instrumental limitations. The most significant aspect of these studies is that they provide evidence for the evolution of a faceted surface morphology on Pt DENs within the 1-2 nm size range.

In addition to providing new and valuable insights about the surface structure of Pt DENs, UPD also opens up many new options for core@shell DEN configurations that could not be achieved by standard complexation and chemical reduction steps. It can also be used to produce more complex nanoparticle structures by allowing for partial, selective coverage of certain regions of nanoparticle surfaces.

Chapter 2. Experimental

2.1 Chemicals

All chemicals used in this work are described in the individual chapters.

2.2 Techniques

The preparation of Pt dendrimer-encapsulated nanoparticles (DENs), the DEN-modified glassy-carbon (GC) electrodes and AvCarb carbon paper electrodes followed published procedures and are described in detail in Chapters 3 and 4.^{6, 9, 12, 51} These DENs-modified electrodes served as the substrate on which Cu underpotential deposition (UPD) was studied. The experimental details pertaining to the Cu UPD procedure are also described in Chapters 3 and 4. Elemental analysis by inductively-coupled plasma mass-spectrometry (ICP-MS) of Pd that has leached from Pd DENs is explained in Chapter 5. Characterization methods are also described in the individual chapters.

2.3 X-ray Absorption Spectroscopy (XAS)

XAS was applied extensively in this work for the structural characterization of Pt@Cu DENs having full and partial Cu shells. XAS is a solid-state X-ray absorption technique used to determine short-range order in materials.⁵²

The X-ray Absorption Spectrum. In a typical XAS experiment, I , the transmitted X-ray intensity, is recorded as a function of X-ray energy (eV).⁵² I is related to μ according Equation 2.1.

$$I = I_0 e^{-\mu t} \quad (2.1)$$

Here, t is the sample thickness and I_0 is the intensity of the incident X-ray beam. As the X-ray energy, E , increases, the X-rays become more penetrating, and so the probability of absorption and thus the X-ray absorption signal decays with approximately a $1/E^3$ dependence.⁵²

Scattering of Monochromatic Synchrotron X-ray Radiation by Condensed Matter. The absorption of monochromatic synchrotron X-ray radiation results in the promotion of a core electron to the continuum. The absorption event occurs when the incident X-ray energy matches the binding energy of the core electrons of an atom in the sample (absorbing species). Following the absorption event, the absorbing species is in the excited state. Relaxation from the excited state occurs as an electron from one of the higher shells fills the vacancy left by the ejected core electron, releasing an X-ray photoelectron in the process. The outgoing photoelectron wave is scattered by the atoms residing in the first coordination shell of the absorbing species. The interference of the outgoing and scattered waves modulates the local dielectric field,

resulting in energy-dependent variations in μ . This effect manifests in the XAS spectrum as energy-dependent oscillations in the X-ray absorption signal, $\mu(E)$. These oscillations are called the extended X-ray absorption fine structure (EXAFS) signal, and contain useful structural information such the position of atoms surrounding the absorber in the sample. The EXAFS signal itself, as function of energy, $\chi(E)$, is calculated from X-ray absorption signal, $\mu(E)$ (Equation 2.2).⁵²

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)} \quad (2.2)$$

Here, $\mu(E)$ is the measured X-ray absorption, $\mu_0(E)$ is the smooth, exponentially decaying background, and $\Delta\mu_0(E)$ is change in the measured absorption intensity at the absorption edge energy, E_0 . Since ultimately, the EXAFS signal is related to the wave behavior of the outgoing photoelectron wave, the X-ray energy, E , is expressed in terms of the spatial frequency or wave-number, k , which has units of 1/distance (Equation 2.3).⁵²

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \quad (2.3)$$

The EXAFS equation (Equation 2.4) thusly expresses the oscillations in X-ray energy absorption intensity as a

function of spatial frequency of the photoelectron, which is related to the scattering of the photoelectron wave by the neighboring atoms that surround the absorbing species.⁵²

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2k R_j + \delta_j(k)] \quad (2.4)$$

Here, N_j is the number of neighboring atoms of kind j , also called the coordination number; R_j is the bond distance to the neighboring atom j ; σ_j^2 is the disorder in the bond distance; $f_j(k)$ and $\delta_j(k)$ are the scattering amplitude and phase-shift to the scattered photoelectron wave.

The absorption signal, $\mu(E)$, can be recorded either as transmission (Equation 2.5) or fluorescence (Equation 2.6).⁵²

$$\mu(E) = \log(I_0/I) \quad (2.5)$$

$$\mu(E) \propto I_f/I_0 \quad (2.6)$$

Here, I_f is the fluorescence intensity, measured at a 90-degree angle from the incident X-ray pathway. After normalizing the data to $\Delta\mu_0(E)$ and subtracting the background, $\mu_0(E)$, the data are fit to the XAS equation using IFEFFIT software, which employs algorithms similar to simulated annealing to locate the approximate global optimum

of the function, $\chi(k)$.⁵³⁻⁵⁵ For the fitting procedure used in this work, scattering paths representing the scattering between the absorber and the neighboring atoms are included in the search space. The path parameters are based on bulk models of structures, but are allowed to "float", meaning these parameters can be varied if a better fit results from the variation.

The studies presented herein employed a special spectra-electrochemical cell that was specifically designed for conducting electrochemical studies in the beam line. A diagram of this cell is provided in Illustration 2.1. The cell is shown in use at the beam line in Illustration 2.2. The use of this cell was first described in a previously published study. The cell was modified slightly by the removal of a detachable interior piece that was used to bubble gases directly into the cell during catalytic studies of CO oxidation.⁹ A more detailed discussion of the use of this cell in this work is provided in Chapters 3 and 4.

2.4 Computational Methods

Calculations of structure from density functional theory, as well as molecular dynamics simulations of the finite element type were performed by collaborators and compared to empirical studies in Chapter 4.

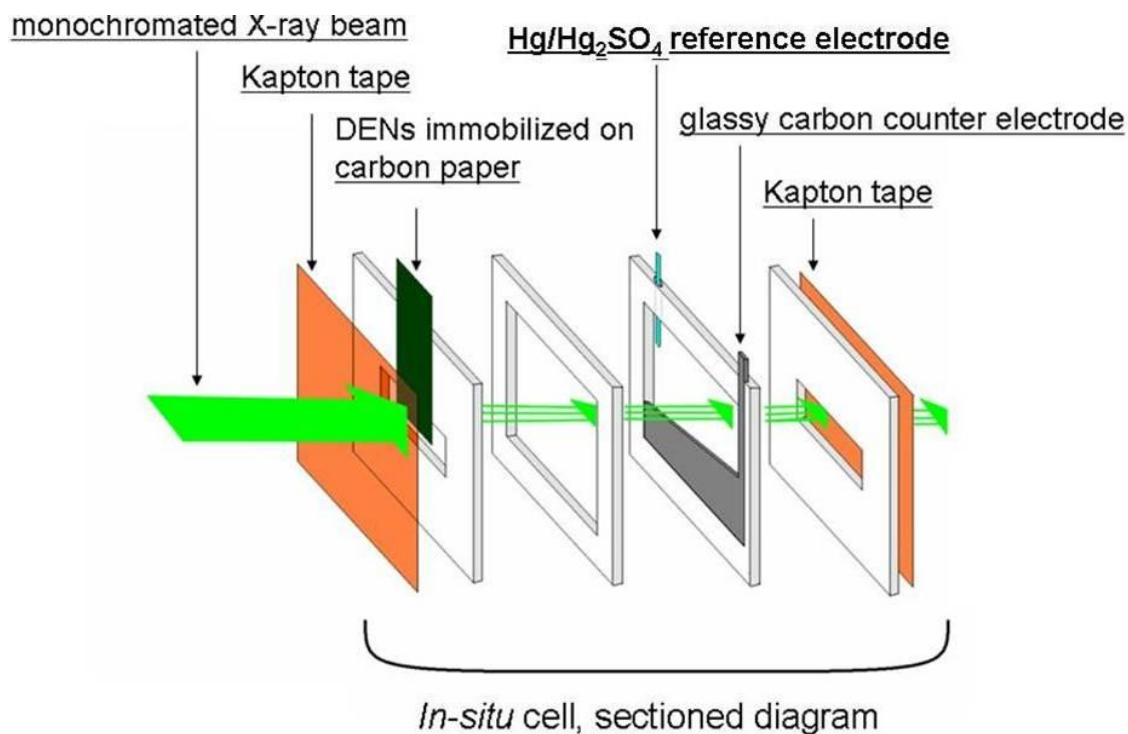


ILLUSTRATION 2.1. Sectioned diagram of the electrochemical cell used in in-situ XAS experiments. The sections of the cell are bolted together around the edges and the internal cavity of the cell is filled with solution from a small hole drilled through the top portion of one of the pieces. The cell is placed in the path of the monochromated X-ray beam (green arrow) so that the beam is incident upon the lower portion of Pt DENS-modified carbon paper working electrode which extends into the solution cavity.

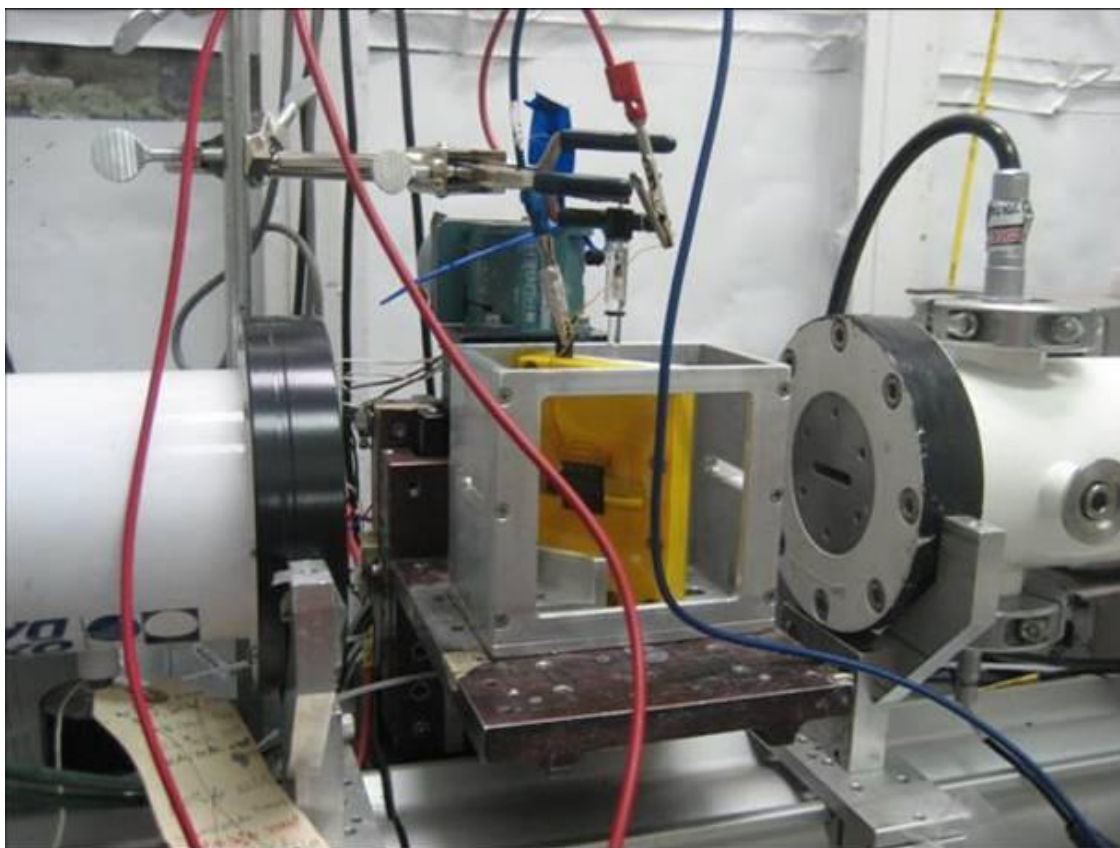


ILLUSTRATION 2.2. A photograph of the in-situ XAS cell in place in the hutch at beam line X-18 B, National Synchrotron Light Source.

Chapter 3: Characterization of Pt@Cu Core@Shell Dendrimer-Encapsulated Nanoparticles Synthesized by Cu Underpotential Deposition

3.1 Introduction and Background

This chapter describes the electrochemical synthesis of Pt core/Cu shell ($\text{Pt}_n\text{@Cu}$, $n = \sim 55, 147, \text{ and } 225$ Pt atoms) dendrimer-encapsulated nanoparticles (DENS).¹ These materials are prepared as shown in Illustration 3.1. First, Pt DENS are synthesized by encapsulating Pt^{2+} within sixth-generation, hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers (G6-OH) to yield a metal/dendrimer complex ($\text{G6-OH}(\text{Pt}^{2+})_n$). Second, the complexes are reduced with BH_4^- . Third, the resulting Pt DENS ($\text{G6-OH}(\text{Pt}_n)$) are purified and immobilized on a glassy carbon (GC) or carbon paper electrode. Finally, a monolayer of Cu is electrodeposited onto the Pt DENS by underpotential deposition (UPD) to yield $\text{G6-OH}(\text{Pt}_n\text{@Cu})$ DENS. Results obtained from voltammetry and in-situ X-ray absorption spectroscopy (XAS) confirm the core@shell structural configuration. The findings reported here are significant for 4 reasons. First, this method for synthesizing bimetallic DENS greatly expands the variety of shell metals that can be incorporated into core@shell DENS. Second, we demonstrate that this method is applicable to nanoparticles having cores containing as few as ~ 55 atoms.

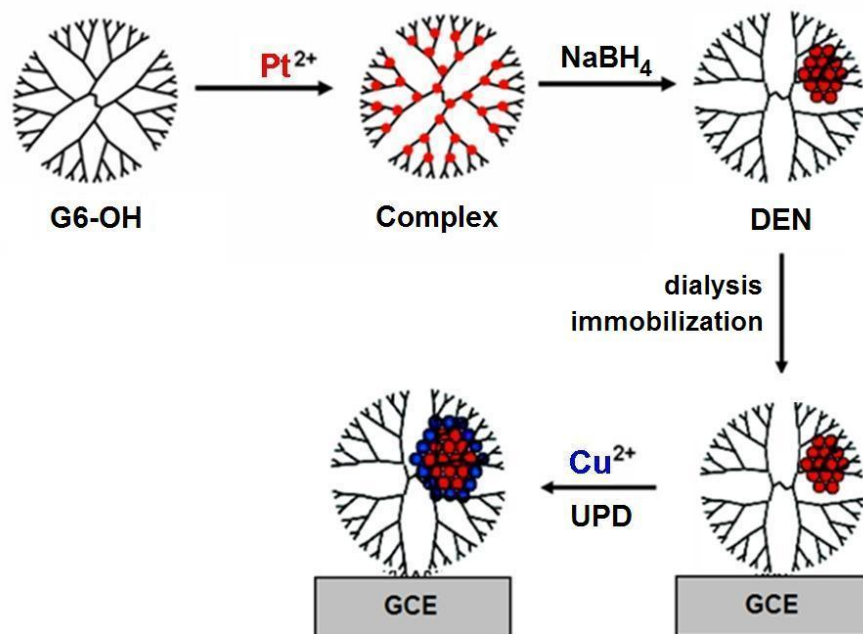


Illustration 3.1.

Third, UPD is a monolayer-specific and potential-dependent process, and therefore the resulting DENs have well-defined structures. Fourth, the UPD process can be used to selectively decorate particular crystallographic facets,^{39, 56, 57} and therefore there is an opportunity in the future to study the catalytic properties of bimetallic DENs having just partial shell coverage.

Near-surface alloys (NSAs), which are two-dimensional analogs of core@shell nanoparticles, have interesting and often unanticipated catalytic properties.⁵⁸⁻⁶¹ Accordingly, we have been interested in developing methods for synthesizing catalytically active core@shell DENs containing a few hundred atoms. Like NSAs, DENs in the 1-2 nm size range are compatible with first-principles calculations,⁷ and thus they provide a means for direct comparison of experimental and theoretical studies of the effect of catalyst structure on reaction rates and selectivity.

We have previously shown that core@shell DENs can be synthesized by the sequential reduction of the component metals.^{27, 28} However, there are some limitations to this method. First, the size monodispersity of DENs synthesized by sequential reduction is generally not as good as that of the monometallic cores.^{27, 28} Second, because the reducing power of chemical reductants is quantized, it is difficult or impossible to strictly control the number of shell atoms deposited on the core. Third, it is impossible to selectively control deposition of the shell metal on particular crystallographic locations of the core. In

contrast, electrochemical methods provide fine energy resolution, and thus a much higher level of control over the shell structure.^{25, 26, 47, 48, 62-67} For example, Adzic and coworkers synthesized Pt-shell nanoparticles by UPD of Cu onto Pd nanoparticles, followed by galvanic exchange of Cu for Pt.²⁶ The average diameter of the resulting Pd@Pt nanoparticles was 4.2 nm. XAS confirmed the core@shell structure and the presence of a single monolayer of Pt. A similar approach was used to synthesize Pt monolayer shells on nanoparticle cores of Au^{57, 63} and Ru.⁵⁷ More recently, this method has been applied to the formation of Pt-M mixed monolayers on Pd cores, where M = Au, Pd, Rh, Ir, Os, or Re.²⁶ UPD, which allows for the controlled, surface-selective deposition of a metal monolayer, is an essential step in the synthesis of these well-defined nanostructures.

We recently presented preliminary results for the synthesis of core@shell Au@Pt DENs synthesized via Cu UPD onto Au DENs, followed by galvanic exchange of the Cu shell for Pt.²⁹ Preliminary measurements of the electrocatalytic activity of these materials for the oxygen reduction reaction were also described.²⁹ In this more comprehensive study, 3 sizes of Pt DENs were prepared and used as substrates for Cu UPD. The results indicate that a single atomic monolayer of Cu is deposited onto Pt DEN cores containing averages of 147 and 225 atoms, while more than one monolayer deposits onto Pt DEN cores containing an average of 55 atoms. Structural analysis of G6-OH(Pt₂₂₅@Cu) DENs by in-situ XAS reveals a Pt-rich core and Pt-Cu and Cu-

Cu bonding that is consistent with the proposed core@shell structure.

3.3 Methodology

Chemicals. G6-OH dendrimers were purchased from Dendritech, Inc. (Midland, MI) as 10.0 wt% solutions in methanol. Prior to use, the methanol was removed under vacuum and the dendrimers were redissolved in sufficient water to yield a 0.10 mM solution. Unless otherwise noted, HPLC-grade water (Fisher Scientific) was used to prepare all aqueous solutions. K_2PtCl_4 , CuSO_4 , LiClO_4 , NaBH_4 , and Ultrex ultrapure H_2SO_4 (18.76 M) were purchased from Sigma-Aldrich (Milwaukee, WI). These reagents were used as received without further purification.

Synthesis of Pt DEN Cores. Pt DENs were prepared according to our previously published procedure.⁶ Briefly, a 0.10 mM aqueous solution of G6-OH was mixed with sufficient aqueous 0.10 M K_2PtCl_4 such that the final Pt^{2+} -to-dendrimer ratios were 55:1, 147:1, or 225:1. The solutions were stirred for 3 days to ensure complete complexation of Pt^{2+} with the interior tertiary amines of the dendrimers.²² The Pt^{2+} /G6-OH complexes resulting from this first synthetic step are denoted as $\text{G6-OH}(\text{Pt}^{2+})_n$ ($n = 55, 147, \text{ and } 225$). The second step of the synthesis involves reduction of $\text{G6-OH}(\text{Pt}^{2+})_n$ with a 10-fold molar excess of 1.0 M NaBH_4 . Immediately following addition of NaBH_4 the reaction vessel was tightly sealed so that H_2 gas, generated by the reaction between BH_4^- and water, was retained. This solution was

stirred for 24.0 h to ensure complete reduction of Pt^{2+} .²² Following the reduction step, but before use in electrochemical experiments, the DENs were dialyzed for 24.0 h in 4.0 L of Millipore water (Milli-Q Gradient PF-06073) to remove salts and other impurities. The water was exchanged midway through the dialysis. After dialysis, but prior to immobilization onto GC electrodes, the DENs solution was mixed with an appropriate volume of aqueous 1.0 M LiClO_4 to yield solutions having final LiClO_4 concentrations of 0.10 M.

Electrochemistry. Both the Au-wire counter electrode and the fritted $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode were purchased from CH Instruments (Austin, TX) and used for all electrochemical experiments unless otherwise specified. All potentials are reported vs. NHE. Several different types of working electrodes were used in this study, including: (1) a 3 mm-diameter, GC disk electrode (CH Instruments, Austin, TX); (2) AvCarb p75 carbon fiber paper (Ballard Materials Products); and (3) a 2 mm-diameter polycrystalline Pt disk electrode (CH Instruments, Austin, TX).

The GC disk electrode was prepared by successive mechanical polishing with 1.0, 0.3, and 0.05 μm alumina, ultrasonication in a 50:50 water-ethanol mixture for 1 min, and finally electrochemical anodizing in 0.10 M NaOH .⁶⁸ The latter process was carried out by stepping the electrode potential from its open circuit value to 1.20 V (vs NHE), and then holding it at this potential for 30 s. The polishing procedure for the Pt disk electrode was the same

as for the GC electrodes. The AvCarb paper electrodes were rendered hydrophilic by cycling their potentials 8 times between 1.64 V and -0.37 V in 0.50 M H₂SO₄.⁹

Pt DENs were immobilized on GC working electrodes by cycling the potential 3 times between 0.24 V and 1.24 V in a solution containing the DENs and 0.10 M LiClO₄.⁶ After Pt DEN immobilization, but before UPD, the DENs were electrochemically cleaned by cycling them 10 times between -0.03 V and 1.34 V in a deoxygenated, aqueous 0.10 M H₂SO₄ solution.⁶⁹ Deoxygenating was accomplished by purging the solution with Ar for 10 min prior to potential cycling. During these scans, waves corresponding to the adsorption and desorption of hydrogen became increasingly more prominent and eventually attained a steady-state shape and magnitude, signaling a clean Pt surface (Figure 3.1).⁶⁹ Immediately after this cleaning procedure, a background cyclic voltammogram (CV) of the Pt DENs was obtained in Cu-free electrolyte solution.

Cu UPD onto the Pt DENs was carried out using the following procedure. First, the electrode potential was stepped from the open-circuit potential (OCP) to 0.64 V for 150 s as a pre-treatment. Similar methods have been used to obtain maximum Cu monolayer coverage on Pt electrodes.^{42, 46} Second, the potential was swept from 0.64 V to 0.84 V, negative to 0.28 V, and then back to 0.84 V. Finally, the DEN-modified electrode was transferred back to the Cu-free solution and a final CV was collected for comparison to the one obtained before exposure to Cu.

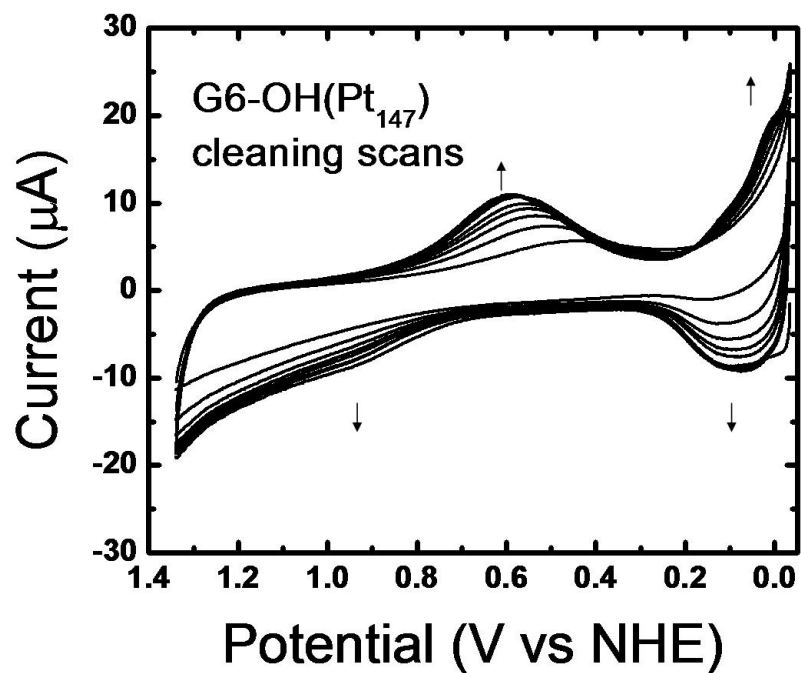


FIGURE 3.1. Cleaning scans in Ar-purged, aqueous 0.10 M H_2SO_4 for a G6-OH(Pt₁₄₇)-modified GC electrode. A total of 10 consecutive CVs were recorded. The CVs were scanned between -0.03 V and 1.34 V at a sweep rate of 100 mV/s.

Electrodes for XAS analysis were prepared by soaking the electrochemically oxidized carbon paper in a solution of dialyzed 10.0 μM G6-OH(Pt₂₂₅) for 24.0 h and then rinsing with water. The immobilized Pt DENs were electrochemically cleaned in 0.10 M H₂SO₄ prior to XAS experiments using the same procedure described for the DEN-modified GC electrodes. Next, a potential step from the OCP to -0.10 V was applied for 15 min to ensure complete reduction of the DENs prior to XAS analysis.⁹ The cell was then filled with a solution containing 0.10 M H₂SO₄ and 0.010 M CuSO₄ and preliminary XAS scans of bare G6-OH(Pt₂₂₅) were collected at OCP prior to depositing Cu. The solutions were not deoxygenated due to constraints imposed by the design of in-situ cell. Care was taken while filling the cell so that it did not contain any air pockets, and the cell remained sealed during the experiments.

Before collecting in-situ XAS spectra, a CV was obtained to determine the potential at which one monolayer of Cu is deposited by UPD (E_{UPD}) (Figure 3.2). E_{UPD} was found to be 0.26 V vs. NHE in the in-situ XAS cell. In-situ XAS data were obtained at two potentials: E_{UPD} and E_{bare} , where E_{bare} = 0.84 V, a potential where no Cu is deposited. The working electrode potential was stepped from the OCP to E_{bare} and held there while XAS data was acquired. Without returning to OCP, the potential was stepped from E_{bare} to E_{UPD} to deposit one monolayer of Cu. After the current due to Cu UPD decreased to a steady-state value close to 0, indicating the completion of the UPD process, the cell was turned off while

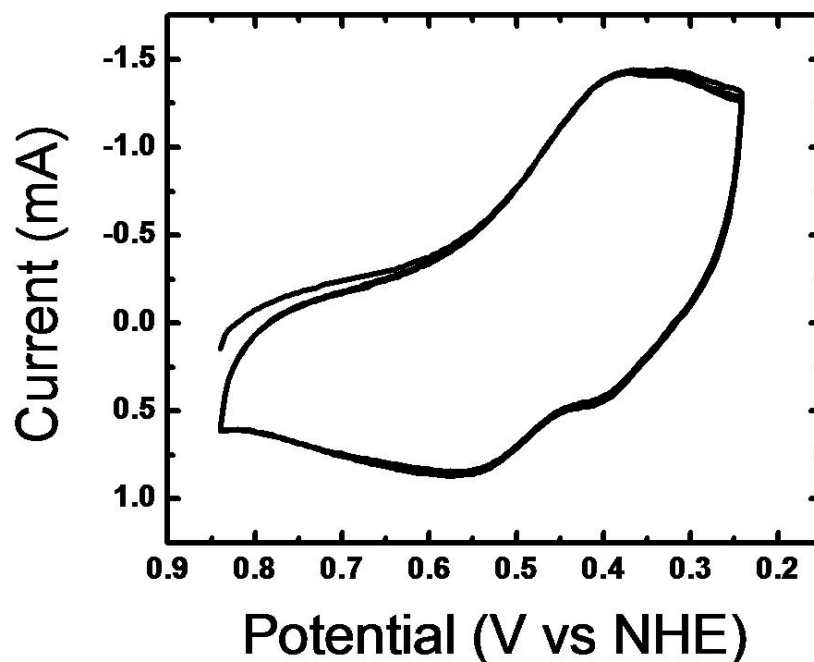


FIGURE 3.2. CVs obtained in the Cu UPD potential region using a G6-OH(Pt₂₂₅)-modified carbon paper electrode and the in-situ XAS cell. Three consecutive CVs are shown. The value of E_{UPD} was found to be 0.26 V. The scans were obtained at a rate of 2 mV/s in an aqueous electrolyte solution containing 0.10 M H₂SO₄ and 0.010 M CuSO₄. The solution was not deoxygenated.

the Cu^{2+} -containing solution was removed and the cell refilled with Cu^{2+} -free 0.10 M H_2SO_4 . The solution exchange process took less than 90 s, after which the cell was reconnected at E_{UPD} . It was prudent to exchange the Cu^{2+} -containing solution for Cu^{2+} -free 0.10 M H_2SO_4 prior to collecting XAS spectra of the Cu-edge, because the X-ray absorption due to free Cu^{2+} in solution would mask the absorption due to Cu atoms on the surface of the DENs. Experiments carried out after the solution exchange confirmed that the full Cu monolayer was retained and also demonstrated the absence of free Cu^{2+} in the solution (Figure 3.3 and 3.4). XAS spectra of G6-OH($\text{Pt}_{225}\text{@Cu}$) were collected once the current at E_{UPD} attained a steady-state value close to 0. The cell potential was held at E_{UPD} during XAS data acquisition. Finally, the Cu shell was stripped by stepping the potential from E_{UPD} to E_{bare} (Figure 3.3) and additional XAS spectra were collected.

Electrochemical measurements obtained using the GC electrodes were made in glass scintillation vials that were triply rinsed with Millipore water prior to use. The experiments using carbon paper electrodes were performed in a Teflon cell that was specifically designed for in-situ XAS experiments (Chapter 2, Illustration 2.1 and 2.2). CVs using GC electrodes were obtained using a CHI 760B potentiostat (CH Instruments). The in-situ XAS experiments were carried out using a WaveNow hand-held Potentiostat (Pine Instruments, Grove City, PA).

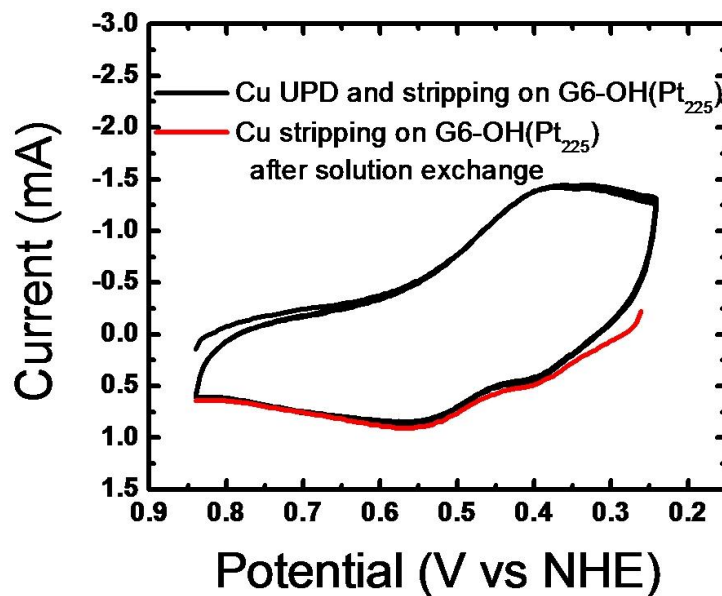


FIGURE 3.3. Voltammetric results obtained before and after the solution exchange procedure described in the main text. The CVs were obtained using a G6-OH(Pt₂₂₅)-modified carbon paper electrode. The black trace was obtained in an electrolyte solution containing 0.10 M H₂SO₄ and 0.010 M CuSO₄ before the solution exchange procedure. The red line was obtained in 0.10 M H₂SO₄ only and corresponds to the Cu stripping profile obtained 12 h after the solution exchange procedure. The red voltammogram was obtained after collecting the in-situ XAS data by sweeping positively from E_{UPD} (0.26 V) to E_{bare} (0.84 V). The observation that the Cu stripping currents are nearly identical before and after solution exchange confirms that the Cu monolayer is retained during the exchange. The solutions were not deoxygenated. The sweep rate = 5 mV/s.

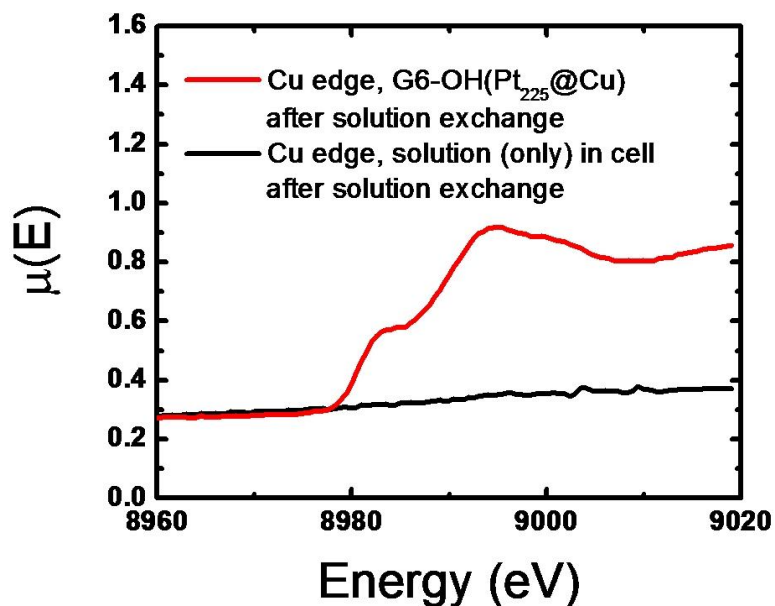


FIGURE 3.4. Red trace: the Cu edge X-ray absorption data for G6-OH(Pt₂₂₅@Cu) DENSs immobilized on a carbon paper electrode immediately following the solution exchange procedure. The electrolyte solution after exchange was 0.10 M H₂SO₄. Black trace: the same data, except after removal of the electrode from the cell (that is, of just the electrolyte solution following exchange). This scan was acquired 12 h after the solution exchange procedure. The results indicate that the solution exchange procedure removes free Cu²⁺ and that the Cu signal measured during in-situ XAS of G6-OH(Pt₂₂₅@Cu) arises exclusively from the Pt@Cu DENSs.

Characterization. UV-vis absorption spectra were collected using a Hewlett-Packard HP8453 UV-vis spectrometer and a quartz cuvette having an optical pathlength of 0.100 cm (Starna Cells, Inc, Atascadero, CA). The DENs spectra were referenced to a solution containing an appropriate concentration of metal-free G6-OH. TEM images were obtained at 200 keV and a magnification of 250,000 in bright-field mode using a JEOL 2010F transmission electron microscope (TEM).

XAS experiments were performed at beam line X18B of the National Synchrotron Light Source at Brookhaven National Laboratory. In-situ data were obtained under potential control using a previously described spectroelectrochemical cell. The XAS spectra were collected in fluorescence mode using an Ar-filled, five-grid Lyttel detector, whereas reference spectra were obtained using Pt and Cu foils and collected in transmission mode. Prior to being fit, the X-ray absorption edges for the in-situ XAS data were aligned in energy with those for the reference foil spectra. XAS data were analyzed using the IFEFFIT6 sixPACK, ATOMS, and Horae software packages.⁵³⁻⁵⁵ This software is available at no charge through the Consortium for Advanced Radiation Sources and is accessible online at <http://cars9.uchicago.edu/ifeffit/Downloads>.

3.4 Results and Discussion

Basic characterization of Pt DENs. The preparation and characterization of Pt DENs containing averages of 55,

147, and 225 atoms encapsulated within G6-OH PAMAM dendrimers followed procedures established in previous reports and briefly described in the Methodology.^{3, 6} These numbers of atoms can form closed-shell cuboctahedra, and for convenience we assume that DENs are close approximations of this ideal structure.⁷⁰ The outermost shell of G6-OH(Pt₅₅) contains 42 Pt atoms and the outermost shell of G6-OH(Pt₁₄₇) contains 92 Pt atoms. The next largest closed-shell cuboctahedron contains a total of 309 atoms, however this is larger than the maximum number of Pt²⁺ ions (254) that can coordinate within a single G6-OH dendrimer; G6-OH PAMAM dendrimers have, on average, 254 internal tertiary amines, and each tertiary amine can coordinate to one Pt²⁺ ion.²⁴ Note that 225 is a magic number for a truncated-octahedron, which has some structural characteristics in common to the cuboctahedron. Specifically, it has a face-centered cubic (fcc) crystal structure, presents (111) and (100) surface facets, and has 140 atoms located within its outermost shell (compared to 162 for a 309-atom cuboctahedron).⁷¹

UV-vis spectra of the G6-OH(Pt²⁺)_n complexes were obtained before and after reduction with NaBH₄ (Figure 3.5) and found to be in accord with previous reports.^{3, 6} TEM measurements and size-distribution histograms (Figure 3.6) were also consistent with previous reports.^{3, 6} Specifically, the G6-OH(Pt_n) DENs, n = 55, 147, and 225, were found to have sizes of 1.5 ± 0.2, 1.9 ± 0.3, and 2.0 ± 0.3 nm, respectively.

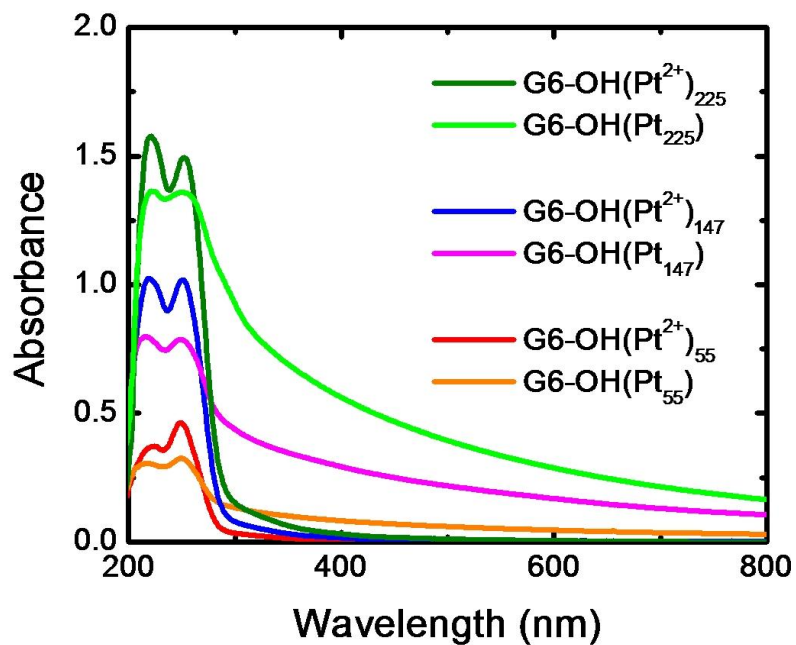


FIGURE 3.5. UV-vis absorbance spectra for Pt DENs and Pt DEN precursors. The optical pathlength was 0.100 cm. The concentration of $\text{G6-OH(Pt}^{2+}\text{)}_n$ and G6-OH(Pt)_n in all solutions was 10.0 μM . The instrument was blanked with a 10.0 μM solution of G6-OH in H_2O .

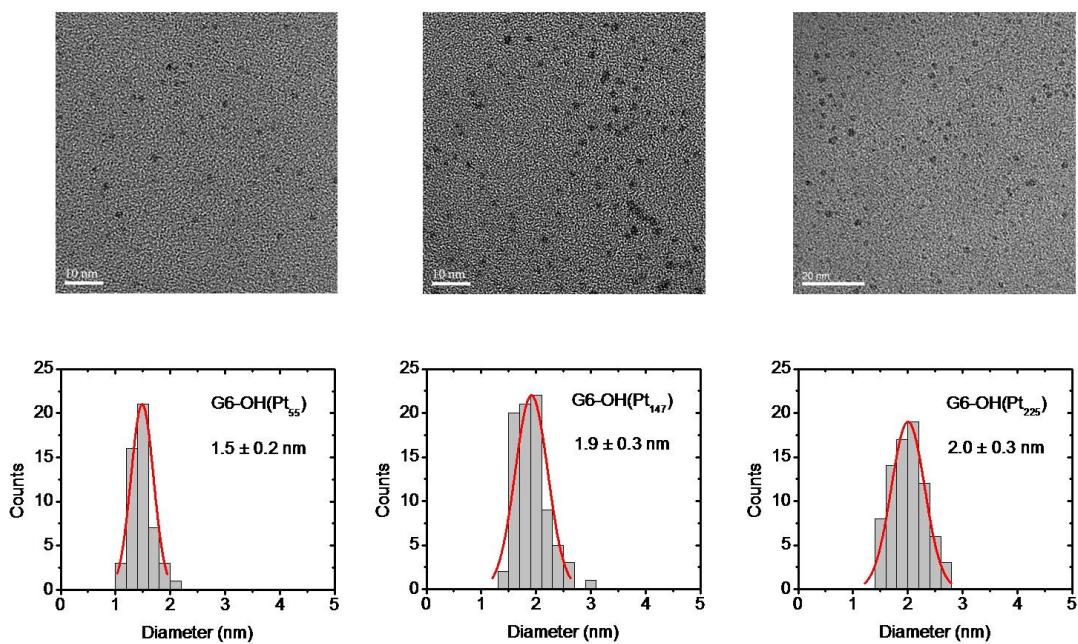


FIGURE 3.6. TEM micrographs and size-distribution histograms for G6-OH(Pt₅₅) (left), G6-OH(Pt₁₄₇) (center), and G6-OH(Pt₂₂₅) (right). The samples were supported on 400-mesh C-coated Au TEM grids. The images were obtained in bright-field mode at 200 keV. The scale bar for G6-OH(Pt₅₅) and G6-OH(Pt₁₄₇) DENs is 10 nm, the scale bar for G6-OH(Pt₂₂₅) is 20 nm.

Measurement of the Pt DEN surface area. Figure 3.7a shows CVs of a G6-OH(Pt₅₅)-modified electrode before (black) UPD of a Cu monolayer, and then after UPD and stripping of Cu (red). Typical features associated with Pt electrochemistry are observed in both scans: Pt oxidation positive of 0.7 V, reduction of the oxide between 0.7 and 0.4 V, and hydrogen adsorption and desorption between 0.2 and 0 V. The near-superposition of the 2 CVs indicates that the Cu UPD process does not significantly affect the electrochemical surface area of the Pt DENs. Figures 3.7b and 3.7c are analogous CVs for GC electrodes modified with G6-OH(Pt₁₄₇) and G6-OH(Pt₂₂₅) DENs, respectively. As the size of the particles increases, the charge associated with Pt oxidation and reduction, as well as that for hydrogen adsorption and desorption, increases.

The total surface area of the three sizes of Pt DENs was determined by measuring the average charge, Q_H , due to hydrogen atom desorption before and after Cu UPD and stripping (between -0.03 V and 0.32 V), and subtracting the capacitive charge (estimated using the current at 0.32 V). The value of Q_H was then converted to surface area using the widely accepted conversion factor of 210 $\mu\text{C}/\text{cm}^2$.⁴³ Note, however, that this latter value is only proven to be appropriate for bulk, polycrystalline Pt, and therefore the surface areas estimated for DENs must be considered with this caveat in mind.⁷² The Pt surface areas determined before and after Cu UPD and stripping for a particular electrode are comparable (Table 3.1). These quantitative

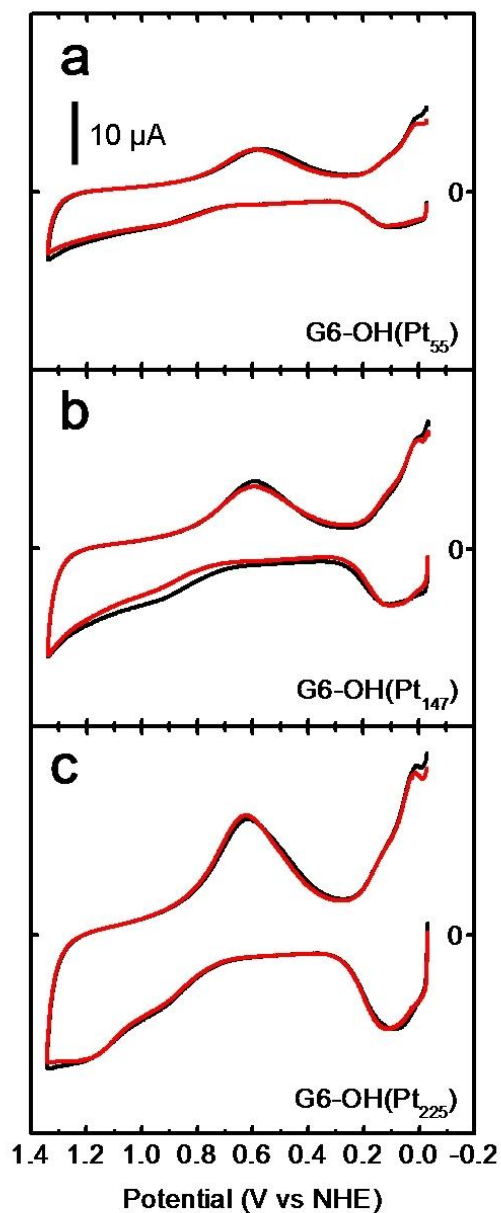


FIGURE 3.7. Cyclic voltammograms obtained using GC electrodes modified with the indicated G6-OH(Pt_n) DENs before (black) and after (red) Cu deposition and stripping. The aqueous 0.10 M H₂SO₄ electrolyte solution was deoxygenated with Ar. The scans started and ended at -0.03 V and were initially swept in the positive direction at a rate of 100 mV/s.

Electrode	Charge from H-des ¹ (μC)		Pt SA ² (cm^2)	Charge from Cu UPD (μC)		θ_{Cu}	Expected θ_{Cu} for complete shell ³
G6-OH(Pt ₅₅)	Pre ⁴	9	0.042	Dep ⁶	20	1.2	2.2
	Post ⁴	9	0.042	Strip ⁶	24		
	Q_{H} ⁵	9	0.042	Q_{Cu} ⁷	22		
G6-OH(Pt ₁₄₇)	Pre	16	0.076	Dep	33	1.0	1.8
	Post	17	0.081	Strip	33		
	Q_{H}	17	0.081	Q_{Cu}	33		
G6-OH(Pt ₂₂₅)	Pre	22	0.10	Dep	44	1.0	1.7
	Post	22	0.10	Strip	44		
	Q_{H}	22	0.10	Q_{Cu}	44		
Polycrystalline Pt disk	Pre	25	0.12	Dep	51	1.0	1.0
	Post	25	0.12	Strip	51		
	Q_{H}	25	0.12	Q_{Cu}	51		

¹ H-des is hydrogen desorption.

² SA is surface area.

³ Expected θ_{Cu} calculated from the number of surface atoms in outer shells of model clusters.

⁴ Pre is the charge due to H-des measured before Cu UPD; Post is the charge due to H-des measured after Cu UPD.

⁵ Q_{H} is the average of the pre and post H-des measurements.

⁶ Dep is the charge due to Cu deposition; Strip is the charge due to Cu stripping.

⁷ Q_{Cu} is the average Cu UPD charge of the dep and strip measurements.

TABLE 3.1. Variables extracted from the voltammetric results shown in Figures 3.7 and 3.8 for G6-OH(Pt_n) DENs and a polycrystalline Pt disk electrode. The charge from H-des was measured in a Ar-purged 0.10 M H₂SO₄ electrolyte solution. The charge arising from Cu-UPD was measured in a Ar-purged 0.10 M H₂SO₄ + 0.010 M CuSO₄ electrolyte solution.

results are in accord with the voltammetry shown in Figure 3.7 and clearly demonstrate that Cu UPD and stripping do not affect the total Pt surface area. The results of a replicate study are also presented (Table 3.2). Although there are some differences in the measured surface areas, due to different numbers of immobilized DENs, the results from the replicate study are consistent with the data in Table 3.1.

The experimentally determined surface areas can be compared to a calculated estimate by making a few assumptions:³³ (1) there is 1 nanoparticle per dendrimer; (2) the nanoparticles are roughly spherical; (3) the projected area of the dendrimer on the electrode surface is 35 nm²; (4) the dendrimers form a nearly close-packed monolayer on the GC electrode; and (5) the roughness factor of the GC electrode is 2.4.³ The Pt surface areas calculated using these assumption are 0.023 cm², 0.043 cm², and 0.065 cm² for immobilized G6-OH(Pt₅₅), G6-OH(Pt₁₄₇), and G6-OH(Pt₂₂₅), respectively. These values can be compared to the experimentally measured surface areas, determined from Q_H (Table 3.1) of 0.042 cm², 0.081 cm², and 0.10 cm², respectively. Given the approximations implicit to both the measured and calculated estimates, these values are in reasonable agreement.

Qualitative analysis of the voltammetry of Cu UPD on Pt DENs. Figure 3.8 displays the results of voltammetry obtained using the same Pt DEN-modified electrodes discussed in the previous section, but in Cu²⁺-free and Cu²⁺-containing

Electrode		Charge from H-des ¹ (μC)	Pt SA ² (cm^2)		Charge from Cu UPD (μC)	θ_{Cu}	Expected θ_{Cu} for complete shell ³
G6-OH(Pt ₅₆)	pre ⁴	10	0.048	dep ⁶	29	1.6	2.2
	post ⁴	9	0.042	strip ⁶	30		
	Q_{H} ⁵	10	0.048	Q_{Cu} ⁷	30		
G6-OH(Pt ₁₄₇)	pre	24	0.11	dep	55	1.1	1.8
	post	29	0.14	strip	60		
	Q_{H}	27	0.13	Q_{Cu}	58		
G6-OH(Pt ₂₂₆)	pre	36	0.17	dep	70	1.0	1.7
	post	34	0.16	strip	68		
	Q_{H}	35	0.17	Q_{Cu}	69		
Polycrystalline Pt disk	pre	25	0.12	dep	51	1.0	1.0
	post	25	0.12	strip	51		
	Q_{H}	25	0.12	Q_{Cu}	51		

¹ H-des is hydrogen desorption.

² SA is surface area.

³ Expected θ_{Cu} calculated from the number of surface atoms in outer shells of model clusters.

⁴ Pre is the charge due to H-des measured before Cu UPD; Post is the charge due to H-des measured after Cu UPD.

⁵ Q_{H} is the average of the pre and post H-des measurements.

⁶ Dep is the charge due to Cu deposition; Strip is the charge due to Cu stripping.

⁷ Q_{Cu} is the average Cu UPD charge of the dep and strip measurements.

TABLE 3.2. Replicate voltammetric data corresponding to the results shown in Table 3.1. The data relating to hydrogen desorption (H-des) was obtained in a Ar-purged 0.10 M H_2SO_4 electrolyte solution. The data relating to Cu UPD was obtained in a Ar-purged 0.10 M H_2SO_4 + 0.010 M CuSO_4 electrolyte solution.

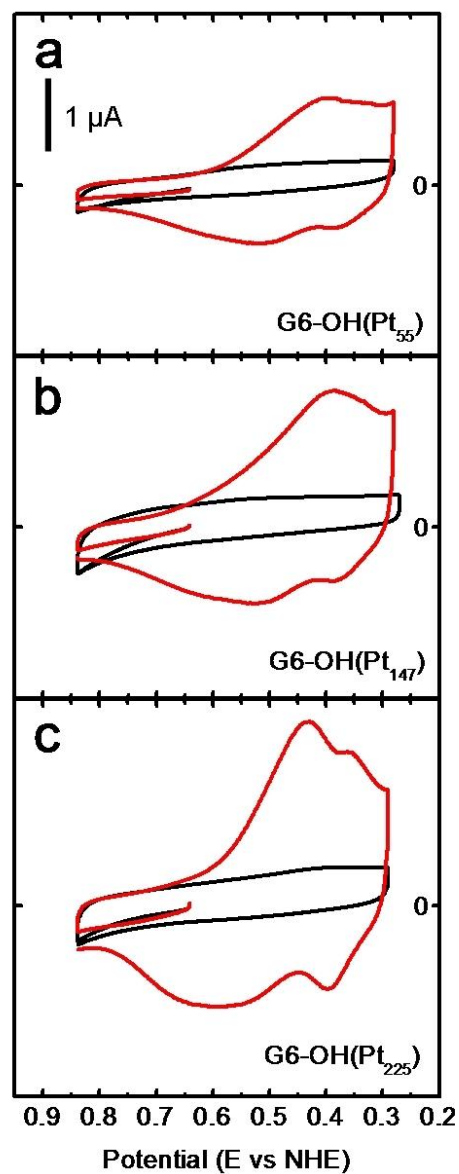


FIGURE 3.8. Cyclic voltammograms obtained using GC electrodes modified with the indicated G6-OH(Pt_n) DENs in aqueous electrolyte solutions containing 0.10 M H₂SO₄ only (black) and 0.10 M H₂SO₄ + 0.010 M CuSO₄ (red). The Cu UPD potential region is shown. The solutions were deoxygenated with Ar. The scans started at 0.64 V and were initially swept in the positive direction at a rate of 10 mV/s.

0.10 M H₂SO₄ solutions. These scans began at 0.64 V, proceeded positive to 0.84 V, reversed to 0.27 V, and then returned to 0.84 V. Others have used similar potential scan programs for Cu UPD onto bulk Pt.^{42, 46} The black line in Figure 3.8a is a CV obtained using a G6-OH(Pt₅₅)-modified electrode in a Cu²⁺-free, 0.10 M H₂SO₄ electrolyte solution. This CV was recorded immediately after the CV shown in black in Figure 3.7a, and it represents the background for the UPD experiment. This CV is featureless and displays only capacitive current. The CV corresponding to the red line in Figure 3.8a was obtained immediately following the background scan using the same electrode, but in the presence of 0.010 M Cu²⁺. The Cu UPD current on G6-OH(Pt₅₅) manifests as a broad reduction wave having a peak potential of 0.40 V. Upon scan reversal, Cu is stripped from the Pt DENs: the first Cu oxidation wave has a peak potential of 0.38 V, and the second is at 0.52 V. The voltammetric profile for Cu UPD on G6-OH(Pt₁₄₇) (red trace, Figure 3.8b) is comparable to the results for G6-OH(Pt₅₅), but with a slight shoulder at more negative energies. The results for Cu UPD onto G6-OH(Pt₂₂₅) are somewhat different. In this case, two distinct reduction waves and two oxidation waves are observed. A bulk, polycrystalline Pt electrode exhibits voltammetry very similar to G6-OH(Pt₂₂₅) (Figure 3.9), and as discussed next the presence of two peaks may signal the evolution of faceting with increases in the size of DENs.

Abruña and coworkers have observed surface-dependent voltammetric signatures for Cu UPD onto a Pt electrode having (111) and (100) facets in 0.10 M H_2SO_4 solution. They found two reduction waves and two oxidation waves, representing Cu UPD onto the two different Pt crystal facets.³⁹ The Cu UPD and stripping peaks on G6-OH(Pt_{225}) DENs also suggest a two-step deposition that we believe may correspond to Cu UPD on different surface features of the DENs. Presumably, these features are not well-enough developed on the smaller particles to exhibit this behavior.

The electrochemical properties of G6-OH(Pt_{225}) DENs with and without a Cu UPD shell were examined by voltammetry in 0.10 M H_2SO_4 (Figure 3.10). The experiment was carried out as follows. First, a G6-OH(Pt_{225})-modified GC electrode was immersed in 0.10 M H_2SO_4 electrolyte solution and the potential was stepped from the OCP to 0.31 V and held there for 10 min before being swept from 0.31 V to -0.01 V and back to 0.31 V at a rate of 10 mV/s. The resulting CV, indicated by the red line in Figure 3.10, is dominated by the onset of the hydrogen-evolution reaction (HER) on the surface of G6-OH(Pt_{225}) DENs. Immediately after recording the CV shown in red the electrode was moved to a solution containing 0.10 M H_2SO_4 + 0.010 M CuSO_4 , and a Cu shell was deposited onto G6-OH(Pt_{225}) DENs by stepping the electrode potential from 0.64 V to 0.31 V and holding it there for 3 min. The electrode was then emersed from solution and immersed in a solution containing only 0.10 M H_2SO_4 under potential control (0.31 V), and then another CV

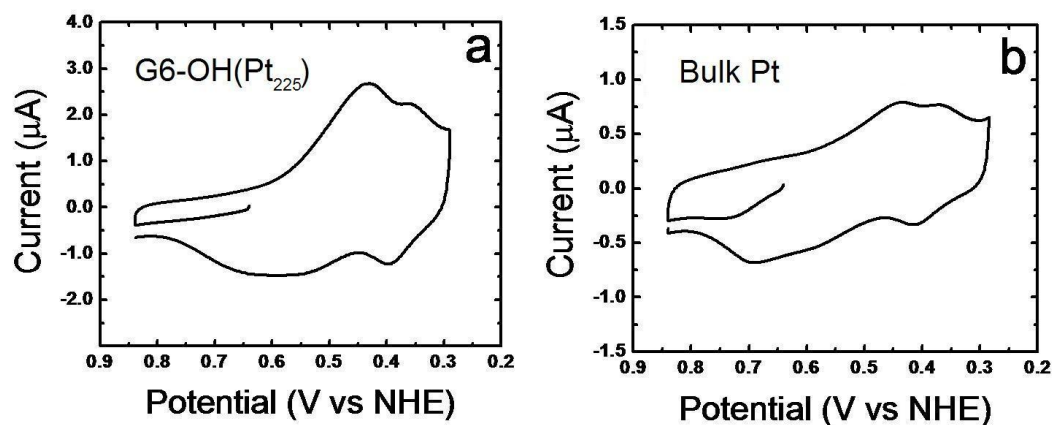


FIGURE 3.9. CVs obtained in the Cu UPD potential region using (a) a G6-OH(Pt_{225}) DEN-modified GC electrode and (b) a 2 mm-diameter bulk Pt polycrystalline disk electrode . The potential scans started at 0.64 V and were initially swept in the positive direction. The CVs were recorded in an electrolyte solution containing 0.10 M H_2SO_4 and 0.010 M CuSO_4 . The sweep rate was 10 mV/s and the solutions were deoxygenated with Ar.

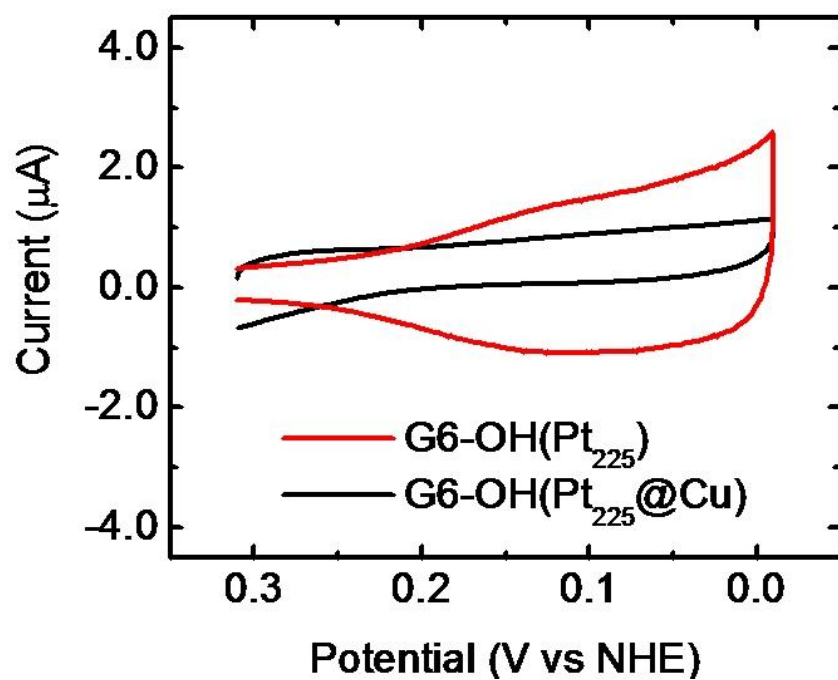


FIGURE 3.10. Cyclic voltammograms of G6-OH(Pt₂₂₅) DENs (red) and G6-OH(Pt₂₂₅@Cu) DENs (black) obtained in aqueous, Ar-purged 0.10 M H₂SO₄ electrolyte solutions. The scans began at 0.31 V and were initially swept in the negative direction at a rate of 10 mV/s.

was recorded. This latter CV, shown by the black line in Figure 3.10, reveals a featureless capacitance in the H adsorption/desorption region, indicating that the Cu shell blocks the HER. As an additional control measure, we also demonstrate that Cu UPD does not occur on GC electrodes modified only with empty (metal-free) G6-OH dendrimers (Figure 3.11).

Quantitative analysis of Cu UPD coverage on Pt DENs. Because the electrodes used for Cu UPD measurements were the same as those used to measure the charge resulting from hydrogen desorption (Figure 3.7 and Table 3.1), the results of these 2 experiments can be directly compared. The charge resulting from Cu UPD and stripping (*Dep* and *Strip*, respectively, in Table 3.1) was estimated from the voltammetric data in Figure 3.8 after subtracting the charge due to the background capacitance. The average charge resulting from Cu UPD and stripping, Q_{Cu} , is also listed in Table 3.1. The coverage of the Cu shell can be expressed as θ_{Cu} in Equation 3.1.

$$\theta_{\text{Cu}} = \frac{N_{\text{Cu}}}{N_{\text{Pt-surf}}} = \frac{Q_{\text{Cu}}}{Q_{\text{H}}} \times \frac{ne_{\text{H}}}{ne_{\text{Cu}}} \quad (3.1)$$

Here, θ_{Cu} is the ratio of Cu atoms in the shell (N_{Cu}) to the number of Pt atoms on the surface of the core ($N_{\text{Pt-surf}}$), Q_{Cu} is the average charge for Cu UPD and stripping (Table 3.1); Q_{H} is the average charge due to desorption of hydrogen atoms

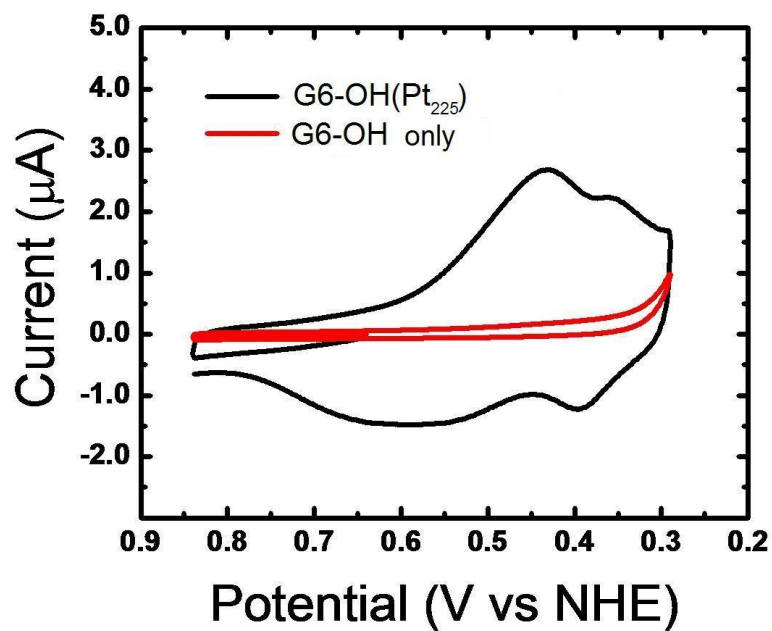


FIGURE 3.11. CVs obtained in the Cu UPD potential region using (red) a G6-OH-modified GC electrode and (black) a G6-OH(Pt₂₂₅) DEN-modified GC electrode. The solution contained Ar-purged 0.10 M H₂SO₄ and 0.010 M CuSO₄. The scans started at 0.64 V and were swept in the positive direction at a rate of 10 mV/s.

from the Pt surface before and after Cu UPD (Table 3.1); $ne_H = 1$ is the number of electrons required for oxidation of one adsorbed hydrogen atom, and $ne_{Cu} = 2$ is the number of electrons required for oxidation of one Cu atom.

To ensure that we are able to accurately measure θ_{Cu} on Pt DENs, it was also determined for a bulk, polycrystalline Pt electrode (Figure 3.9). The result of this experiment is provided in Table 3.1, and it indicates $\theta_{Cu} = 1.0$ which is the expected result for Cu UPD onto bulk, polycrystalline Pt in 0.10 M H_2SO_4 .³⁶

The values of Q_{Cu} and Q_H for G6-OH(Pt₅₅) are 22 μC and 9 μC , respectively, yielding $\theta_{Cu} = 1.2$ (Table 3.1). The corresponding value of θ_{Cu} for both G6-OH(Pt₁₄₇)- and G6-OH(Pt₂₂₅)-modified electrodes is 1.0. (Table 3.1). This ratio is consistent with our results for Cu UPD on bulk, polycrystalline Pt (Figure 3.9), previously reported measurements of Cu UPD onto Au DENs,²⁹ and literature reports of Cu UPD onto the low-index planes of Pt single crystals and polycrystalline Pt.^{36, 39, 44}

The measured values of θ_{Cu} for Pt DENs merit some comment, because one might envision that θ_{Cu} could be larger. This is because outer shells of nanoparticles in the size range discussed in this project normally contain more atoms than inner shells. For example, a 55-atom cuboctahedral nanoparticle contains 42 atoms in the outermost shell, and the next full shell would contain 92

atoms. Therefore, G6-OH(Pt₅₅) could have a value of $\theta_{\text{Cu}} = 92/42 = 2.2$. The corresponding values of θ_{Cu} for G6-OH(Pt₁₄₇) and G6-OH(Pt₂₂₅) are calculated as $162/92 = 1.8$ and $234/140 = 1.7$, respectively.^{70, 73} We measure corresponding θ_{Cu} values of just 1.2, 1.0, and 1.0, suggesting that Cu UPD does not result in a fully closed outer shell covering the Pt DEN core. This could indicate that shell metals preferentially deposit onto the facets of DENs in a manner that is more characteristic of UPD on bulk single- and polycrystalline Pt, perhaps leaving exposed some high-energy sites such as the edges and vertices of the nanoparticles. It is not clear why coverage on G6-OH(Pt₅₅) is higher than for the other DENs, but more detailed structural studies are underway to address this issue. Finally, we carried out a second set of experiments intended to confirm those provided in Table 3.1. The detailed results are provided in Table 3.2. The values of θ_{Cu} for G6-OH(Pt_n), $n = 55, 147, \text{ and } 225$, were found to be 1.6, 1.1, and 1.0, respectively, in good agreement with those discussed here and presented in Table 3.1.

In-situ XAS analysis of Cu UPD onto Pt DENs. We turned to in-situ electrochemical XAS to confirm some of the preliminary structural conclusions derived from the previously discussed voltammetry experiments.^{18, 19, 28} The experimental methodology for the XAS experiments was discussed earlier, but briefly, dialyzed G6-OH(Pt₂₂₅) DENs were immobilized on carbon paper and the potential of this electrode was controlled during acquisition of XAS data.

Because G6-OH(Pt₂₂₅) DENs are magic number clusters, the coordination numbers (CNs) obtained from the fits to the XAS data can be compared to those calculated for a model structure. The model is based on the quantitative electrochemical results discussed in the previous section. As shown in Illustration 3.2, it consists of a core containing 225 Pt atoms configured in a truncated-octahedron geometry. This structure has 140 Pt surface atoms distributed between eight (111) facets and six (100) facets. The Cu shell atoms are located exclusively on the facets, leaving the edges and vertices naked. Each Pt(111) facet accommodates 18 Cu atoms situated in 3-fold hollow sites, and each Pt(100) facet holds 1 Cu atom in a 4-fold hollow site. The value of θ_{Cu} for this model structure is $150/140 = 1.1$, which is close to θ_{Cu} measured from voltammetric data for G6-OH(Pt₂₂₅) (Table 3.1). CNs can also be calculated for the model shown in Illustration 3.2, and these values are presented alongside the CNs extracted from the fits to the data (*Calculated* and *Extracted*, respectively, in Table 3.3).

The R-space distribution plots for G6-OH(Pt₂₂₅@Cu) DENs, as well as the computed fits, are shown in Figure 3.12a and 3.12b for the Pt L3 and Cu K absorption edges, respectively. These in-situ XAS results were obtained with the DEN-modified electrode held at E_{UPD} (0.26 V), which is the potential of maximum Cu UPD coverage. The corresponding k-space data are provided separately (Figure 3.13).



140 Pt surface atoms

150 Cu shell atoms

$\theta_{\text{Cu}} = 1.1$

● Pt

● Cu

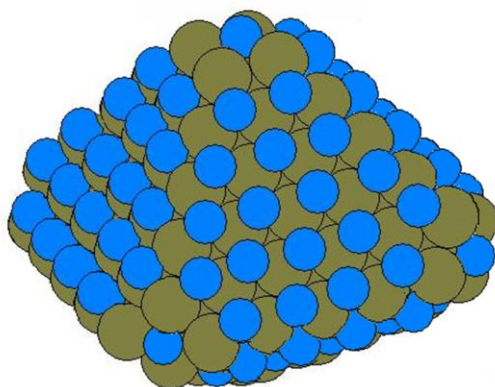


Illustration 3.2.

The structure of the G6-OH(Pt₂₂₅@Cu) DENS is determined by fitting the XAS data, as described in the Experimental Section, and then comparing the extracted CNs to the values calculated for one or more models. The following CNs were extracted from the in-situ spectra: Pt-Pt (n_{PP}), Pt-Cu (n_{PC}), Cu-Pt (n_{CP}), Cu-Cu (n_{CC}), Cu-E (n_{CE}), Pt-m (n_{PM}), and Cu-m (n_{CM}). Here, m is all metal (Pt plus Cu) and E is a low- z nearest neighbor, most likely H₂O, HSO₄⁻ or SO₄²⁻ on the Cu shell.⁷⁴ It was necessary to include the Cu-E scattering path to accurately fit the experimental results, but we did not calculate a CN corresponding to n_{CE} . One final point: the modeling approach assumes $n_{\text{PM}} = n_{\text{PP}} + n_{\text{PC}}$ and $n_{\text{CM}} = n_{\text{CC}} + n_{\text{CP}}$.^{18, 28}

Table 3.3 provides the extracted and calculated (for the model shown in Illustration 3.2) CNs, bond distances, and Debye-Waller factors for G6-OH(Pt₂₂₅@Cu). It is interesting to compare n_{PP} for G6-OH(Pt₂₂₅) at OCP and E_{bare} , before and after Cu UPD (Figure 3.14), with n_{PP} for G6-OH(Pt₂₂₅@Cu) at E_{UPD} . The experimental values for n_{PP} at OCP (CN = 7.0) and E_{bare} (CN = 6.9) underestimate the calculated CN for a 225-atom cluster (CN = 9.5),⁸ but they are close to n_{PP} reported previously (CN = 6.3) for Pt DENS of similar size and under comparable conditions.^{9, 22}

At E_{UPD} , the calculated and extracted values of n_{PP} for G6-OH(Pt₂₂₅) are 9.5 and 9.7, respectively. The extracted CNs for n_{CC} and n_{CP} are also very close to the calculated values (Table 3.3). The extracted n_{PC} is lower than the calculated

CN ¹	Extracted CN ³	Calculated CN ⁴	Bond distance (Å)	Debye-Waller factor
n_{pp}	9.7 ± 1.4	9.5	2.75	0.006 ± 0.0006
n_{pc}	1.3 ± 0.3	2.0	2.57	0.010 ± 0.003
n_{cc}	3.5 ± 1.6	4.2	2.62	0.014 ± 0.006
n_{cp}	3.4 ± 0.2	3.2	2.57	0.010 ± 0.003
n_{ce} ²	1.0 ± 0.4	Not calculated ⁵	1.99	0.006 ± 0.005
n_{pm}	11.0	11.5	N/A ⁶	N/A
n_{cm}	6.9	7.4	N/A	N/A

¹ CN is coordination number.

² n_{ce} represents Cu with a low-Z nearest-neighbor.

³ Extracted CN is extracted from the fit to the data.

⁴ Calculated CN is estimated from the model $Pt_{225}@Cu$ structure with $\theta_{Cu} = 1.1$.

⁵ n_{ce} was not calculated because the concentration of low-Z nearest-neighbors (E) adsorbed to Cu has not been measured on $Pt_{225}@Cu$ structures.

⁶ Not applicable (N/A) to n_{pm} and n_{cm} because these CNs are sums of other CNs and are not variables included in the fit.

TABLE 3.3. Variables extracted from in-situ XAS spectra for G6-OH($Pt_{225}@Cu$). All data were collected with the AvCarb electrode poised at E_{UPD} in a 0.10 M H_2SO_4 solution.

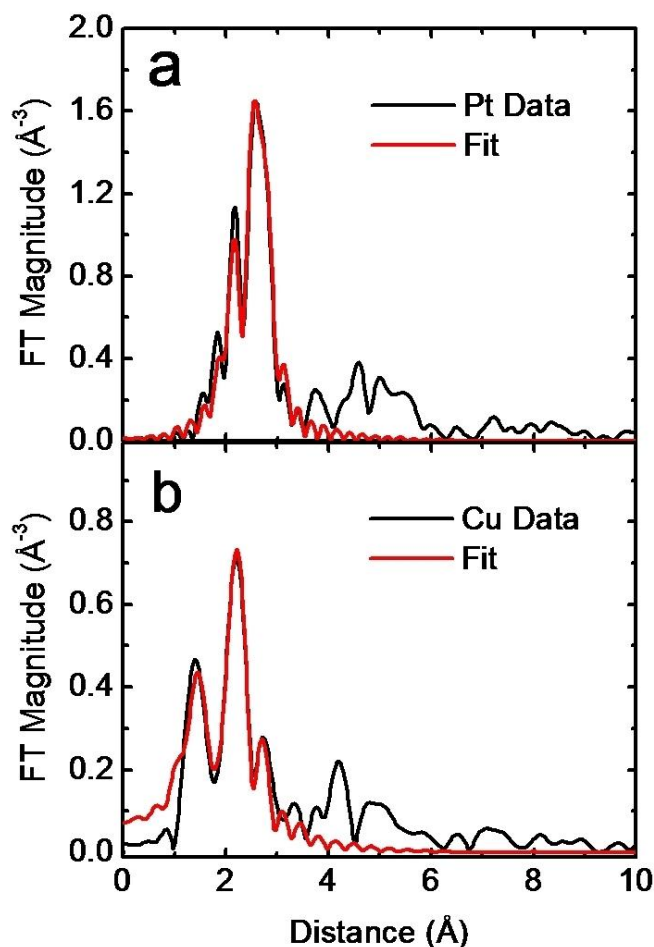


FIGURE 3.12. Radial distribution (R-space) spectra of the in-situ XAS data for G6-OH(Pt₂₂₅@Cu) obtained under potential control in 0.10 M H₂SO₄ at E_{UPD} . The Pt data were fit using a k-space range of 3-15.5 and an R-window of 1.7-3.2. The Cu data were fit using a k-space range of 2-11 and an R-window of 1.2-3.224. Variables, such as the CN, bond distance, and Debye-Waller factors, were extracted from the fits to the data and are presented in Table 3.3.

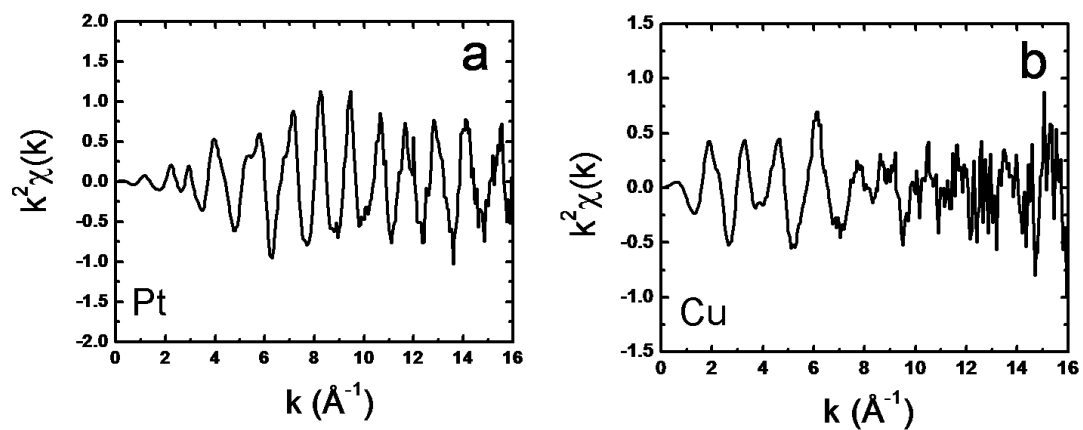


FIGURE 3.13. In-situ XAS k -space data obtained for a G6-OH(Pt₂₂₅@Cu)-modified AvCarb electrode. Data for (a) the Pt L3 edge and (b) the Cu K edge. The data were obtained with the electrode poised at E_{UPD} in a 0.10 M H₂SO₄ solution.

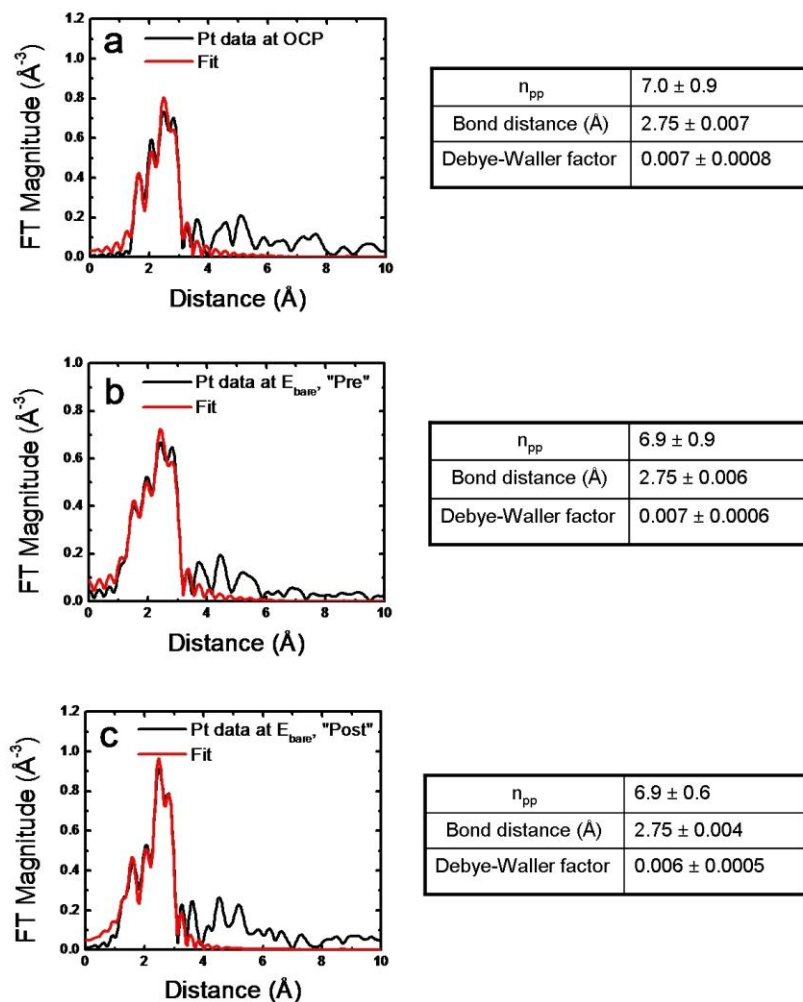


FIGURE 3.14. Radial distribution spectra and variables determined from the fits to the data for the AvCarb electrode modified with bare G6-OH(Pt₂₂₅) DENs at the following potentials: (a) OCP, (b) E_{bare}^{Pre} before Cu UPD ("Pre"), and (c) E_{bare}^{Post} after Cu UPD and subsequent stripping ("Post").

estimate by 0.7. The magnitude of the discrepancy between the calculated and extracted CNs is small and within the uncertainty of the fit. Such discrepancies are not unusual and may be due to disorder.¹⁸ The value of n_{pm} (11.0) is estimated as the sum of n_{pp} and n_{pc} . Likewise, n_{cm} is 6.9. Both n_{pm} and n_{cm} are in good agreement with the corresponding CNs that were calculated from the model: 11.5 and 7.4, respectively (Table 3.3).

From a modeling perspective, there are a few clear trends that distinguish core@shell nanoparticles from random arrangements such as alloys. For example, n_{pp} for G6-OH($\text{Pt}_n\text{@Cu}$) and G6-OH(Pt_n) will be the same if the assumed structure of the former is core@shell. However, if the shell metal partitions into the core phase, n_{pp} will decrease.²⁸ Experimentally, we find that n_{pp} has the value calculated for a 225-atom truncated octahedron after addition of the Cu shell (Table 3.3), which is fully consistent with the proposed core@shell structure. We also know that the value of n_{cm} will be less than n_{pm} for a core@shell particle, because if Cu atoms are confined to the surface of the nanoparticle they will have fewer nearest neighbors than if they are randomly distributed throughout the particle.²⁸ Indeed, consistent with the core@shell structure, we find experimentally that n_{pm} is quite significantly larger than n_{cm} (Table 3.3).

The Debye-Waller factors given in Table 3.3 indicate two-fold greater disorder in the Cu-Cu bonding than for Pt-Pt bonds. However, the Pt-Pt bond disorder for the

core@shell DENs (Table 3.3) is similar to that observed for the monometallic Pt DENs at OCP (Figure 3.14a). This is yet another indication that the core and shell phases of G6-OH(Pt₂₂₅@Cu) DENs are well-segregated. The coordinatively unsaturated atoms of the outer shells of nanoparticles occupy positions of higher energy and tend to exhibit greater disorder than the interior atoms of the nanoparticle, which have full coordination shells.¹⁸

The heterometallic (Pt-Cu) bond distance was determined to be 2.57 Å. We expect the Pt-Cu bond distance to lie between the Pt-Pt bond distance (2.77 Å) and Cu-Cu bond distance (2.55 Å).^{41, 42} Previous in-situ XAS studies of Cu UPD on bulk Pt(111) reported a Pt-Cu bond distance of 2.64 Å.⁴⁰ The difference between the Pt-Cu bond distance reported here and the previously measured Pt-Cu bond distance (on a bulk Pt electrode) could be related to the strain-inducing effects of nanoparticle surface tension.^{46, 47} The Pt-Pt bond distance for G6-OH(Pt₂₂₅@Cu) extracted from the fit is 2.75 Å, which is close to that of Pt atoms in fcc Pt (2.77 Å). The Pt-Pt bond distance for bare G6-OH(Pt₂₂₅) at OCP and E_{bare} is also measured as 2.75 Å. This suggests a slight compression of the core Pt lattice. In contrast, the Cu-Cu bond distance is 2.62 Å, which is considerably larger than that expected for fcc Cu (2.55 Å). The lattice constant for fcc Pt is greater than that of Cu, and thus it is likely that the Cu shell experiences some strain due to lattice mismatch with the underlying lattice of the Pt core.⁷⁵ Indeed, such strain has been observed in Cu overlayers in

previous XAS studies of Cu UPD on bulk Pt(111).^{40, 74} Additionally, the compressive strain of the Pt lattice may be attributed to surface tension.⁷⁶ Nanoparticles exhibit surface tension resulting in lattice compression near the core, and calculations from theory predict a compression of the bond distance of about 1% for Pt nanoparticles having diameters around 2 nm.⁷⁶ The experimentally observed lattice compression for both G6-OH(Pt₂₂₅@Cu) (Table 3.3) and bare G6-OH(Pt₂₂₅) (Figure 3.14) amounts to 0.8%, which is consistent with these calculations.

The results of an independent replicate in-situ XAS experiment returned CNs, bond distances, and Debye-Waller factors that are consistent with the results shown in Table 3.3. These results are provided in Table 3.4.

3.5 Summary and Conclusions

This study was motivated by recent findings that highly structured core@shell nanoparticles can be prepared using electrochemical methods.^{26, 48, 57, 62, 63, 65, 67} We wanted to know if this same general approach could be applied to DENs, which are significantly smaller than previously reported materials. The successful outcome of these experiments provides a general method for synthesizing core@shell model nanoparticles that are sufficiently small and well-defined that their catalytic properties can be compared to first-principles calculations.⁷

CN ¹	Extracted CN ³	Calculated CN ⁴	Bond distance (Å)	Debye-Waller factor
n _{pp}	9.3 ± 0.7	9.5	2.75 Å	0.005 ± 0.0003
n _{pc}	1.1 ± 0.2	2.0	2.57 Å	0.008 ± 0.003
n _{cc}	4.2 ± 1.8	4.2	2.62 Å	0.018 ± 0.005
n _{cp}	2.9 ± 0.2	3.2	2.57 Å	0.008 ± 0.003
n _{ce} ²	1.5 ± 0.3	Not calculated ⁵	1.99 Å	0.008 ± 0.003
n _{pm}	10.4	11.5	N/A ⁶	N/A
n _{cm}	7.1	7.4	N/A	N/A

¹ CN is coordination number.

² n_{ce} represents Cu with a low-Z nearest-neighbor.

³ Extracted CN is extracted from the fit to the data.

⁴ Calculated CN is estimated from the model Pt₂₂₅@Cu structure with $\theta_{Cu} = 1.1$.

⁵ n_{ce} was not calculated because the concentration of low-Z nearest-neighbors (E) adsorbed to Cu has not been measured on Pt₂₂₅@Cu structures.

⁶ Not applicable (N/A) to n_{pm} and n_{cm} because these CNs are sums of other CNs and are not variables included in the fit.

TABLE 3.4. Replicate in-situ XAS data corresponding to the results shown in Table 3.3. The electrode was a G6-OH(Pt₂₂₅@Cu) DEN-modified AvCarb electrode poised at E'_{UPD} . The electrolyte solution contained 0.10 M H₂SO₄.

Chapter 4. Site-Selective Cu Deposition at Pt Dendrimer-Encapsulated Nanoparticles: Correlations Between Theory and Experiment

4.1 Introduction and Background

In this chapter we show that underpotential deposition (UPD) of a Cu shell onto 1.7 nm-diameter Pt dendrimer-encapsulated nanoparticles (DENs)¹ synthesized within sixth-generation, hydroxyl-terminated (G6-OH) poly(amidoamine) (PAMAM) dendrimers occurs via a two-step process corresponding to facet-specific deposition (Illustration 4.1). Specifically, we compared data obtained using first-principles computations with experimental electrochemical and in-situ spectroscopic studies of the deposition and stripping of a Cu shell on Pt DENs consisting of just 147 atoms, denoted G6-OH(Pt₁₄₇). The results indicate that Cu deposits first onto the (100) facets of G6-OH(Pt₁₄₇), followed by deposition onto the (111) facets. These findings are significant for the following two reasons. First, it is remarkable that UPD can be used to preferentially deposit a partial shell of Cu on individual facets consisting of as few as 16 Pt atoms. This level of precision provides a route for directly correlating first-principles calculations to complex, but well-defined nanoparticles consisting of ~200 atoms. Second, we demonstrate that results from density functional theory (DFT) provide mechanistic insights into the UPD

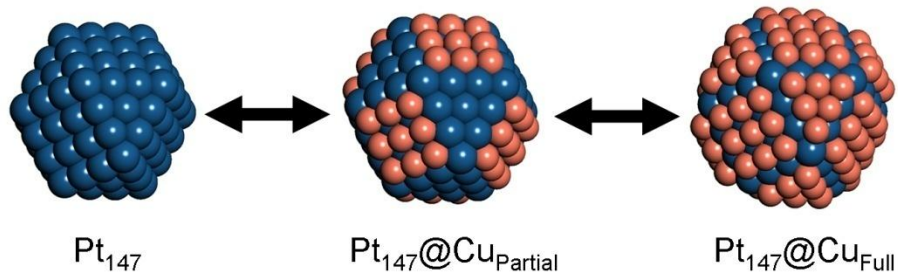


Illustration 4.1.

process that are highly correlated to the shape of cyclic voltammograms (CVs) for Cu UPD onto Pt DENs.

We have previously shown that UPD of Cu onto Au and Pt DENs can be used as a synthetic route to core/shell (core@shell) nanoparticles.^{29, 51} In this approach, monometallic DENs consisting of Au or Pt were synthesized and immobilized onto electrodes, and a Cu shell was deposited via UPD. This resulted in Au-core/Cu-shell (Au@Cu) or Pt@Cu DENs. With regard to the Au@Cu DENs, we found that the Cu shell could be galvanically exchanged for Pt, and that the resulting Au@Pt DENs were electrocatalytically active for the oxygen reduction reaction (ORR).²⁹ In the case of Pt@Cu DENs, we examined UPD of Cu onto three different sizes of Pt DEN cores. CVs for Cu UPD onto the largest of these, a Pt DEN containing 225 Pt atoms (denoted G6-OH(Pt₂₂₅)) revealed two well-defined reduction waves, suggesting that deposition of the Cu shell takes place in two steps.⁵¹ Pt nanoparticles composed of 225 atoms can form closed-shell truncated octahedra, which are face-centered cubic (fcc) crystal structures presenting (100) and (111) facets.⁷⁰ Therefore, we considered that the two voltammetric waves observed during Cu UPD might correspond to discrete deposition onto these two different orientations. This study also suggested that Cu deposition does not occur on edge or corner atoms of the Pt core.⁵¹

A number of studies predating our work have described the UPD of metal shells onto nanoparticles that are substantially larger (4-20 nm)^{25, 26, 48, 57, 62, 63, 67, 77} than the

1.7 nm DENs reported here. For example, Adzic and co-workers deposited full Pt shells onto PdCo nanoparticles having diameters of 4.6 nm. These nanoparticles were synthesized by UPD of Cu onto the PdCo core, followed by galvanic exchange of Cu for Pt. The authors found that the portions of the Pt shell that resided on the (111) orientation of the PdCo core were the most active for the ORR.⁴⁸

Several studies have reported the synthesis of partial (sub-monolayer) shells on nanoparticles using alternate (non-UPD) means of shell deposition. For example, Sanchez-Cortes and co-workers chemically reduced sub-monolayer quantities of Pt onto 15 nm Au nanoparticles and found that the Pt shell preferentially formed sub-monolayer islands oriented in the (111) direction.⁷⁷ Adzic and co-workers have also synthesized Pt sub-monolayers on commercially available 2.5 nm Ru nanoparticles.⁵⁷ In this case, the Pt sub-monolayer was formed via spontaneous electroless deposition of Pt on the surface of the Ru nanoparticles. This resulted in a partial shell constituting approximately 1/9 monolayer of Pt. In this case the location of the partial Pt shell was not reported. Finally, Feliu and co-workers showed that hydroquinone adlayers reversibly adsorb onto the (111) facets of 6 nm Pt nanoparticles, but irreversible adsorption occurs on (100) and (110) facets.⁵⁶

In the present study, we provide experimental and computational evidence that UPD of Cu onto G6-OH(Pt₁₄₇) DENs in a Cu²⁺-containing 0.10 M H₂SO₄ electrolyte occurs in two steps: first onto the (100) and then onto the (111) facets.

Pt@Cu DENs with full and partial Cu shells were prepared via Cu UPD on G6-OH(Pt₁₄₇). The full and partial shell structures were characterized by voltammetry and in-situ X-ray absorbance spectroscopy (XAS), and the experimental results were compared with computational models generated using DFT and molecular dynamics (MD) simulations. We found that DFT-calculated binding energies for Cu on the (100) and (111) surface facets of a "solvated" nanoparticle model, in which SO₄²⁻ anions adsorb to the surface to mimic the solvent-surface interactions used in the experiments, corresponded well with peaks observed in the CVs of Cu UPD onto Pt₁₄₇ DENs. In contrast, the same calculations performed on a naked, SO₄²⁻-free (solvent-free) nanoparticle model did not fit the electrochemical data. Finally, XAS results confirmed that the partial Cu shell is located on the (100) facet, as opposed to the (111) facet, in accordance with the predictions from DFT.

4.2 Methodology

Chemicals and Materials. G6-OH dendrimers were purchased from Dendritech, Inc. (Midland, MI) as 5.0 wt% solutions in methanol. Prior to use, the methanol was removed under vacuum and the dendrimers were redissolved in sufficient water to yield a 0.10 mM solution. Unless otherwise noted, Millipore water (Milli-Q Gradient PF-06073) was used to prepare all aqueous solutions. K₂PtCl₄, CuSO₄, LiClO₄, NaBH₄, and Ultrex ultrapure H₂SO₄ (18.76 M) were purchased from Sigma-Aldrich (Milwaukee, WI). These reagents were used as

received without further purification. Two types of working electrodes were used in this study: (1) a 3 mm-diameter, glassy carbon (GC) disk electrode (CH Instruments, Austin, TX); and (2) AvCarb p75 carbon fiber paper (Ballard Materials Products, Lowell, MA). A Hg/Hg₂SO₄ reference electrode was also purchased from CH Instruments. Compressed Ar gas (Praxair) was purchased and used as received.

Synthesis of Pt@Cu DENs. The precise definitions of full- and partial-shell Cu UPD layers will be discussed in the Results and Discussion section, but for now it is sufficient to say that G6-OH(Pt₁₄₇) DENs having maximum Cu UPD coverage are denoted as G6-OH(Pt₁₄₇@Cu_{Full}) and that DENs having less-than-maximum coverage are denoted as G6-OH(Pt₁₄₇@Cu_{Partial}).

The synthesis of G6-OH(Pt₁₄₇@Cu_{Full}) DENs and subsequent electrochemical measurements using the DENs-modified GC electrodes were made in a polycarbonate flow cell, which enables the exchange of solutions without emersing the electrodes (Figure 4.1). Because the electrodes remain in contact with electrolyte while the solutions are exchanged, the working electrode can be kept under potential control. This is an important provision, because it is necessary to remove free Cu²⁺ ions from the cell following the synthesis of full and partial shells to prevent them from electrodepositing on the electrode during subsequent electrochemical measurements. Emersion of the working electrode during this process could compromise the structure or composition of the Cu shells.

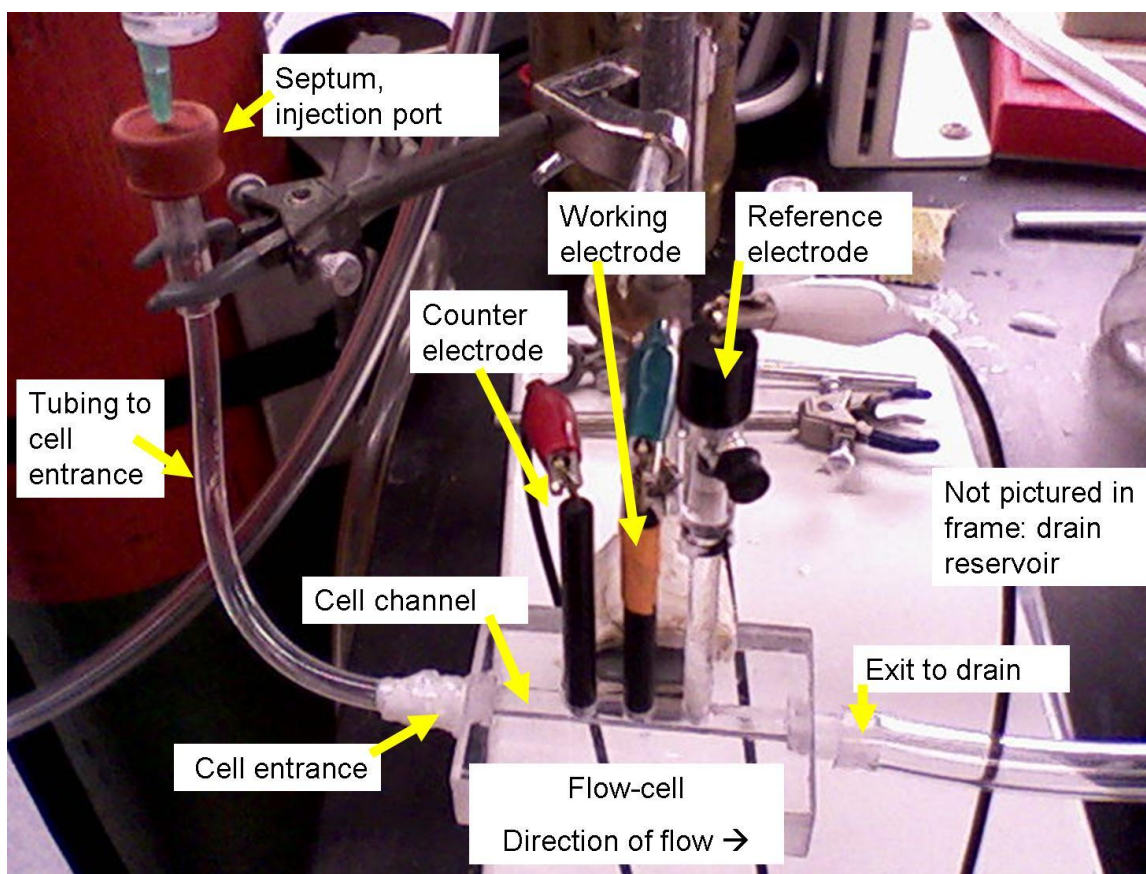


FIGURE 4.1. Picture of the 3-electrode electrochemistry flow cell. The cell has a rectangular cell channel with an internal volume of 1.0 mL, not including the volume of the tubing that attaches the cell entrance to the injection port. The electrodes (GC working, GC counter, and $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference) insert into the channel via holes drilled through the top of the cell. The holes were precisely machined to the diameters of the electrodes so that inserting the electrodes forms an air-tight and water-tight seal. The electrodes are inserted into the cell until they come into alignment with the channel wall facing the solution. The solutions for electrochemistry are injected via a syringe with a 22 gauge needle through a rubber septum at the injection port. The injection port is connected to the entrance to the cell channel by Teflon tubing. The volume of this tubing is ~ 4 mL. All the solutions were purged with Ar for at least 10 min prior to being injected into the cell. The outlet empties into a glass container that is kept continually purged with Ar to prevent backflow of O_2 into the cell.

The preparation of G6-OH(Pt₁₄₇@Cu_{Full}) DENs on GC electrodes was carried out as previously described.^{3, 6, 18, 51} Briefly, G6-OH(Pt₁₄₇) DENs were synthesized in water in two steps. First, 147 equivalents of K₂PtCl₄ was mixed with 1.0 equivalent of G6-OH dendrimer to yield a complex, denoted (G6-OH(Pt²⁺)₁₄₇). Second, this complex was reduced using NaBH₄ to yield zerovalent G6-OH(Pt₁₄₇) DENs. The resulting DENs were then purified by dialysis against water for 24 h before being immobilized onto GC electrodes.^{3, 6} The immobilization was carried out in solutions of dialyzed DENs contained in a scintillation vial, after which the DENs-modified GC electrode, bare GC counter electrode, and Hg/Hg₂SO₄ reference electrode were configured in the flow cell. The surface of the DENs was then cleaned by 10 consecutive potential cycles between -0.03 V and 1.34 V in Ar-purged, 0.10 M H₂SO₄ that was injected into the flow cell.⁵¹ All potentials are reported vs. NHE. After electrochemical cleaning, the solution was exchanged for Ar-purged 0.10 M H₂SO₄ that contained 0.010 M CuSO₄ by injecting 12.0 mL of the Cu²⁺-containing solution into the cell.

Cu UPD and stripping experiments using the DENs-modified GC electrode were carried out using the following procedure. First, the electrode potential was stepped from the open circuit potential (OCP) to 0.64 V for 150 s as a pretreatment.⁵¹ Second, the potential was swept from 0.64 V to 0.84 V, negative to 0.29 V, and returned to 0.84 V to record a CV of Cu UPD and Cu stripping. For some additional experiments on the electrochemical properties of G6-

OH(Pt₁₄₇@Cu_{Full}) DENs, we deposited the shell somewhat differently: by stepping, rather than sweeping, the working electrode potential from OCP to 0.29 V, the potential at which a full Cu shell is deposited on the DENs (denoted E_{Full}) and holding the potential there for at least 300 s.⁵¹ Then, while continuing to hold the potential at E_{Full} , free Cu²⁺ in solution was removed by flowing 12.0 mL of Ar-purged, Cu²⁺-free, 0.10 M H₂SO₄ solution through the cell. The removal of Cu²⁺ from the flow cell was confirmed in a separate control experiment (Figure 4.2).

In-situ XAS. The preparation of DENs samples for in-situ XAS analysis is discussed elsewhere.⁵¹ Briefly, however, G6-OH(Pt₁₄₇) DENs were immobilized on AvCarb paper by soaking the AvCarb in solutions of dialyzed G6-OH(Pt₁₄₇) for at least 12 h. The DENs-modified AvCarb electrodes were then configured in a custom designed cell for in-situ XAS experiments, and then they were electrochemically cleaned by 10 consecutive potential cycles between -0.15 and 0.84 V before being used for XAS experiments.^{9, 51}

In-situ XAS data were obtained with the DENs-modified AvCarb electrode poised at one of three potentials: (1) E_{Full} = 0.26 V (in the in-situ cell); (2) E_{Partial} = 0.41 V, which corresponds to a partial Cu UPD monolayer; and (3) E_{Bare} = 0.84 V, a potential at which Cu does not deposit on G6-OH(Pt₁₄₇). These potentials were chosen on the basis of voltammetry corresponding to Cu stripping from G6-OH(Pt₁₄₇@Cu_{Full}) and G6-OH(Pt₁₄₇@Cu_{Partial}) DENs (Figure 4.3). When Cu was stripped from G6-OH(Pt₁₄₇@Cu_{Full}), two peaks were

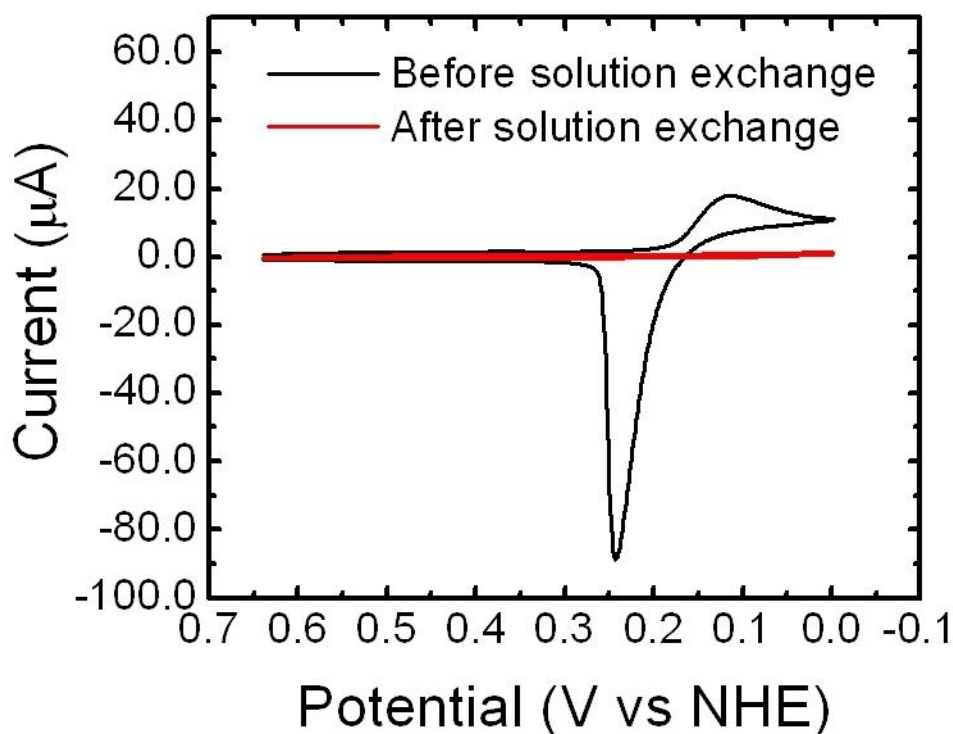


FIGURE 4.2. The results of a control experiment done to demonstrate the successful removal of Cu^{2+} from the flow cell by flushing the cell with 12.0 mL of fresh, Cu^{2+} -free electrolyte. The black CV was recorded using a GC working electrode in a solution of Ar-purged 0.10 M H_2SO_4 + 0.010 M CuSO_4 before flushing the solution and shows current due to the bulk deposition and stripping of Cu. After recording the CV shown by the black line, the Cu^{2+} -containing solution was flushed by injecting 12.0 mL of fresh, Ar-purged Cu^{2+} -free 0.10 M H_2SO_4 into the flow cell. The red CV, which was recorded after the flushing procedure, shows a featureless capacitance, indicating the absence of Cu^{2+} . Both CVs began at 0.64 V and were initially swept in the negative direction at a scan rate of 100 mV/s.

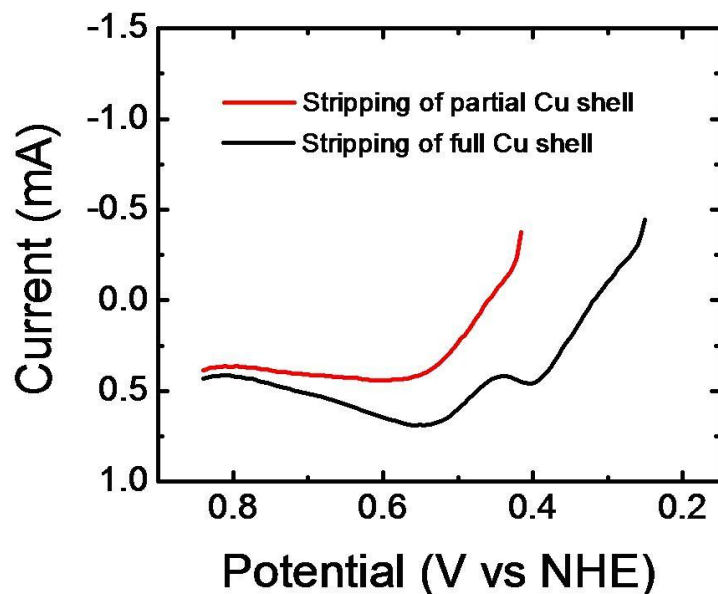


FIGURE 4.3. Cu stripping voltammetry experiments taken in the in-situ XAS cell using G6-OH(Pt₁₄₇) DENs immobilized on AvCarb working electrodes. The current due to the stripping of a partial Cu shell from G6-OH(Pt₁₄₇@Cu_{Partial}) (red) shows only a single stripping wave. The current corresponding to the stripping of a full Cu shell from G6-OH(Pt₁₄₇@Cu_{Full}) (black) exhibits 2 stripping waves. The scan in red started at $E_{\text{Partial}} = 0.41$ V, was held at 0.41 V for 300 s, and was then swept in the positive direction. The scan in black started at $E_{\text{Full}} = 0.26$ V, was held at 0.26 V, and was then swept in the positive direction. The scans were recorded at a scan rate of 2 mV/s in 0.10 M H₂SO₄ + 0.010 M CuSO₄ prior to collecting XAS spectra.

observed in the voltammogram, and we believe these peaks are related to removal of Cu from different Pt facets.

Additional evidence for this conjecture comes from stripping of partial Cu shells. Specifically, when Cu was stripped from G6-OH(Pt₁₄₇@Cu_{Partial}), the resulting voltammetry revealed just one stripping peak.

Some preliminary XAS spectra were collected at E_{Bare} . Next, a full Cu shell was deposited by stepping the electrode potential from E_{Bare} to E_{Full} , after which the solution was exchanged for Cu²⁺-free 0.10 M H₂SO₄ to prevent Cu²⁺ in solution from interfering with the Cu UPD spectrum. Following solution exchange, the cell potential was returned to E_{Full} and held there while XAS spectra were recorded. The solution exchange procedure used for the in-situ XAS studies was described in our previous publication.⁵¹ It requires that the electrode be taken out of potential control for ~ 1 min, but control experiments showed that the full Cu shell remained intact after the solution was exchanged and the potential was reapplied at E_{Full} . After collecting XAS spectra with the electrode poised at E_{Full} , the potential was stepped from E_{Full} to E_{Partial} and held there while collecting additional XAS scans. Finally, the Cu shell was stripped by sweeping the potential from E_{Partial} to E_{Bare} and additional XAS spectra were collected.

Electrochemistry. The GC disk electrodes were prepared by successive mechanical polishing with 1.0, 0.3, and 0.05 μm alumina, ultrasonicing in a 50:50 water-ethanol mixture for 1 min, and finally electrochemical anodizing in 0.10 M

NaOH prior to being used for immobilizing the DENs.^{51, 68} The AvCarb paper electrodes were rendered hydrophilic by cycling their potentials 8 times between 1.64 V and -0.37 V in 0.50 M H₂SO₄ before being soaked in the DENs solutions and used in XAS experiments.^{9, 51}

Following the syntheses of G6-OH(Pt₁₄₇@Cu_{Full}) on GC electrodes via a potential step to E_{Full} , the electrodes were used to record CVs in the hydrogen evolution reaction (HER) potential range. This was carried out as follows.

Immediately after the synthesis and Cu²⁺ removal steps described earlier, and without returning to the OCP, the cell potential was stepped from its resting potential (E_{Full}) to 0.29 V, and then cycled once from 0.29 V to -0.03 V and back to 0.29 V.

The experiments using AvCarb electrodes were performed in the aforementioned spectroelectrochemical cell.^{9, 51} CVs using GC electrodes were obtained using a CHI 760B potentiostat (CH Instruments). The in-situ XAS experiments were carried out using a WaveNow hand-held Potentiostat (Pine Instruments, Grove City, PA).

Characterization. Transmission electron microscope (TEM) images were obtained at 200 keV at a magnification of 200,000 in bright-field mode using a JEOL 2010F TEM. X-ray photoelectron spectroscopy (XPS) studies were obtained using a Kratos Axis Ultra spectrometer equipped with Al K α radiation sources. Spectra were collected at a pass energy of 20 eV and a step size of 0.5 eV.

XAS experiments were performed at beam line X18B of the National Synchrotron Light Source at Brookhaven National Laboratory. In-situ data were obtained while under potential control using a previously described spectroelectrochemical cell.^{9, 51} The XAS spectra were collected in fluorescence mode using an Ar-filled, five-grid Lyttel detector, whereas reference spectra were obtained using Pt and Cu foils and collected in transmission mode. Prior to being fit, the X-ray absorbance edges for the in-situ XAS data were aligned in energy with those for the reference foil spectra. XAS data were analyzed using the IFEFFIT6 sixPACK, ATOMS, and Horae software packages.⁵³⁻⁵⁵ This software is available at no charge through the Consortium for Advanced Radiation Sources and is accessible online at

<http://cars9.uchicago.edu/ifeffit/Downloads>.

Density Functional Theory Calculations. The following models were used to study Cu deposition and stripping on Pt DENs: (1) a bare, cuboctahedral Pt nanoparticle consisting of 147 Pt atoms, denoted $\text{Pt}_{147}^{\text{DFT}}$; (2) a SO_4^{2-} ligand-covered nanoparticle, denoted $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$; (3) a model representing the G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Full}}$) DENs, denoted $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$. The $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$ model contained a total of 48 SO_4^{2-} ions, 3 on each (111) facet and 4 on each (100) facet of $\text{Pt}_{147}^{\text{DFT}}$. The $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$ model contained a total of 102 Cu atoms, 6 on each (111) facet and 9 on each (100) facet of $\text{Pt}_{147}^{\text{DFT}}$. We describe the energy gained from adsorbing a Cu atom on one of these particles, $\text{Pt}_{147}^{\text{DFT}}$ or $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$, as the Cu deposition energy, denoted E_{Deposit} , and the energy required

for desorbing a Cu atom from the $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$ as the Cu stripping energy, denoted E_{Strip} .

The structures of the nanoparticle models were optimized with spin-polarized DFT calculations with the plane-wave Vienna ab-initio simulation package (VASP) code^{78, 79} using the PW91 functional.⁸⁰ The plane wave energy cutoff was 290 eV. The ionic cores were described by the projector augmented-wave (PAW) method.⁷⁹ Nanoparticles were placed on the center of $(28\text{\AA})^3$ cell. A gamma point sampling of the Brillouin zone was appropriate for the isolated particles. The convergence criteria for the electronic structure and the geometry were 10^{-4} eV and 0.02 eV/Å, respectively. We used the Fermi smearing method with a width of 0.2 eV to improve convergence with respect to states near the Fermi level.

Molecular Dynamics Simulations. The final structure of $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$ was released at 350K with NVT MD simulations. The MD simulation was performed with the LAMMPS package and embedded atom method (EAM) many-body potential. The time step was set to 1 fs and structural evolution of the $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$ was monitored for 300 ns.

4.3 Results and Discussion

Cu UPD onto G6-OH(Pt_{147}) DENs. The UPD of Cu onto G6-OH(Pt_{147}) DENs immobilized on GC electrodes results in G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Full}}$) DENs.⁵¹ We chose to use Pt DENs consisting of an average of 147 atoms for this study, because this number can result in a closed shell cuboctahedron. This structure

has 92 Pt atoms on its surface, arranged in 6 (100) facets and 8 (111) facets (Illustration 4.1). Each (100) facet consists of 16 atoms, and each (111) facet consists of 10 atoms, with the edge and corner atoms being shared between the facets. These DENs have a measured diameter of 1.7 ± 0.3 nm (Figure 4.4), which is consistent with previous reports and their calculated diameters (1.6 nm).²²

The red line in Figure 4.5 is a CV, which was recorded in 0.10 M H₂SO₄ containing 0.010 M CuSO₄, showing Cu UPD onto and Cu stripping from G6-OH(Pt₁₄₇) DENs. Two poorly resolved reduction waves are present at 0.41 V and 0.33 V, and these correspond to the deposition of the Cu shell in two steps. The potential difference between the peaks of these waves, denoted $\Delta E_{\text{Dep}}^{\text{Exp}}$, is 0.08 V. Upon scan reversal, two oxidation waves appear at 0.39 V and 0.53 V due to the stripping of Cu from the G6-OH(Pt₁₄₇) core in two steps. These stripping waves, while also broad and convoluted, exhibit a greater degree of peak separation than the deposition waves. The potential difference between these peaks, denoted $\Delta E_{\text{Strip}}^{\text{Exp}}$, is 0.14 V. The background current (black line, Figure 4.5), which is strictly capacitive, was obtained under the same conditions as the UPD scan except in the absence of Cu²⁺.

The electrochemical properties of G6-OH(Pt₁₄₇@Cu_{Full}) and G6-OH(Pt₁₄₇) DENs in the HER potential region were examined in 0.10 M H₂SO₄ (Figure 4.6). Current due to the HER dominated the CV of the G6-OH(Pt₁₄₇)-modified GC electrode, while this reaction was greatly suppressed on the G6-

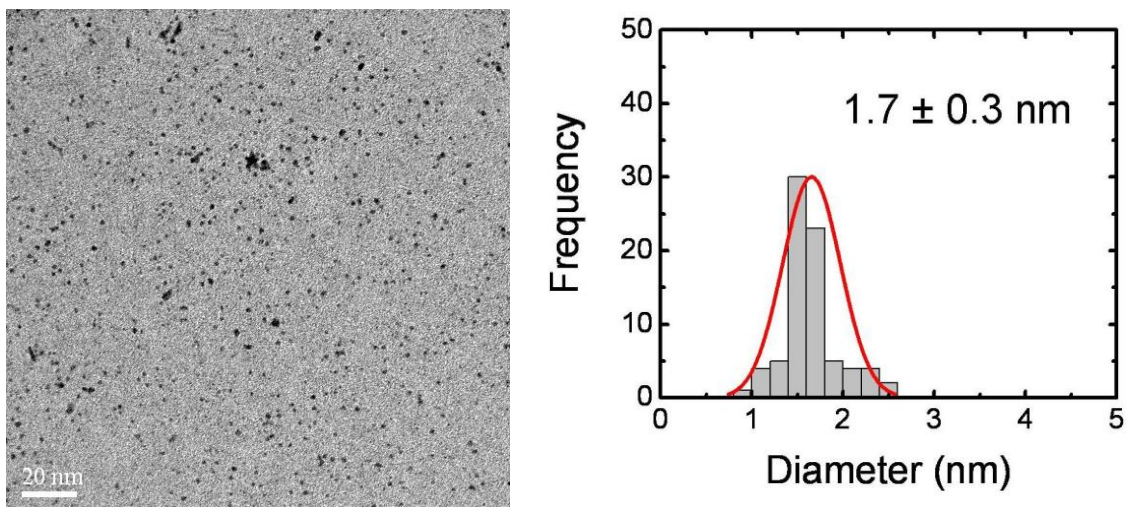


FIGURE 4.4. TEM micrograph of G6-OH(Pt₁₄₇) DENs (left) and the corresponding size distribution histogram.

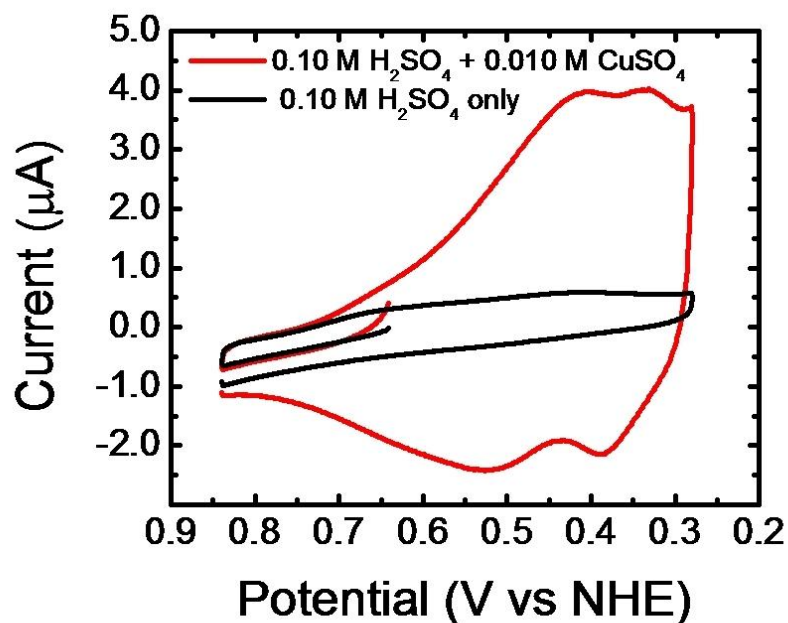


FIGURE 4.5. Voltammetry pertaining to a GC electrode modified with G6-OH(Pt₁₄₇) DENs showing Cu UPD and stripping (red) in 0.10 M H₂SO₄ + 0.010 M CuSO₄ that was deoxygenated with Ar, and the background capacitance (black) in 0.10 M H₂SO₄ only, which was also purged with Ar. Both scans began at 0.64 V and were initially swept in the positive direction at a scan rate of 10 mV/s.

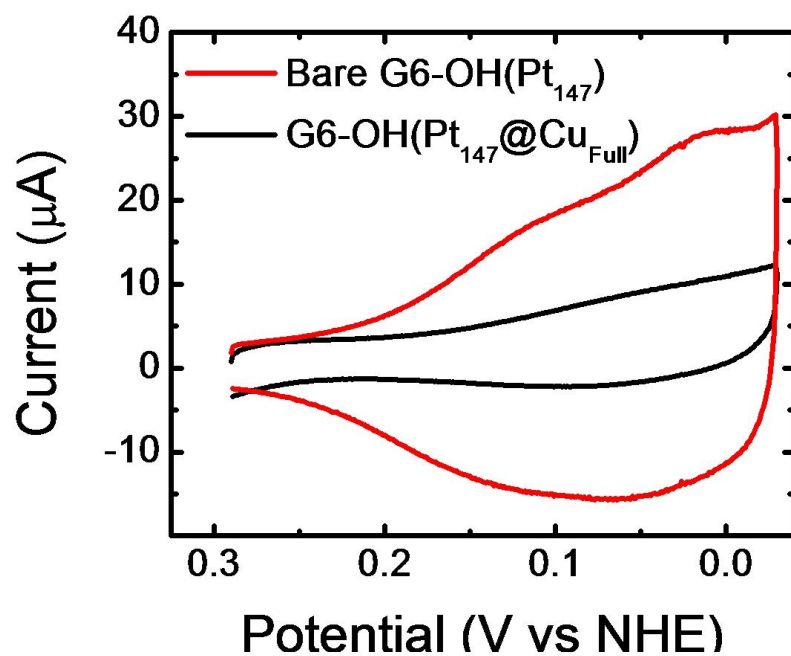


FIGURE 4.6. Cyclic voltammograms of bare G6-OH(Pt₁₄₇) (red) and G6-OH(Pt₁₄₇@Cu_{Full}) (black) obtained in aqueous, Ar-purged 0.10 M H₂SO₄. The scans began at 0.29 V and were initially swept in the negative direction at a scan rate of 100 mV/s.

OH(Pt₁₄₇@Cu_{Full})-modified electrode. We have previously shown that similar results obtain on G6-OH(Pt₂₂₅) DENs with and without a Cu UPD shell.⁵¹ The results in Figure 4.6 suggest that the Cu UPD layer on G6-OH(Pt₁₄₇@Cu_{Full}) assume a well-segregated core@shell structure. This finding will be of particular importance in our later comparison of experimental data with various DFT and MD structural models.

Computational studies of Cu UPD and stripping on Pt DENs. We used DFT to calculate the energies for depositing and stripping Cu atoms (E_{Deposit} and E_{Strip} , respectively) on model nanoparticles and compared these energies to the potentials of the current peaks seen in the CV of Cu UPD onto G6-OH(Pt₁₄₇)DENs (red line, Figure 4.5). We examined the Cu deposition process atom-by-atom using first the Pt₁₄₇^{DFT} model, and then repeated the Cu deposition process using the (SO₄²⁻)Pt₁₄₇^{DFT} model. These models are depicted in Figure 4.7.

The process presented in Figure 4.8 shows that depositing Cu atoms onto all of the (100) facet sites of the Pt₁₄₇^{DFT} model is energetically favorable, meaning the binding energies of the Cu atoms are more negative as compared to Cu atoms on the (111) facets. Therefore Cu UPD would be expected to commence on the (100) facets. Since all the Cu atoms on the (100) facet were deposited at about the same energy ($E_{\text{Deposit}} = -3.71$ eV for the first atom and $E_{\text{Deposit}} = -3.70$ eV for subsequent Cu atoms), we assumed these first few deposition events are the cause of the more positive UPD current peak seen in Figure 4.5.

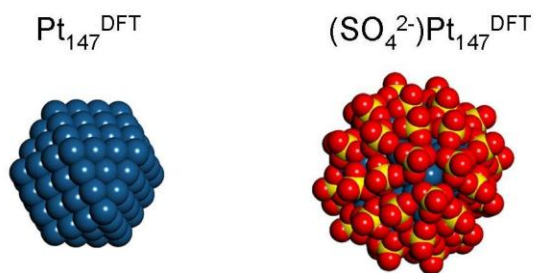


FIGURE 4.7. The DFT-optimized structures of the $\text{Pt}_{147}^{\text{DFT}}$ model (left) and the $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$ model. These models were used in the DFT studies of the Cu deposition process.

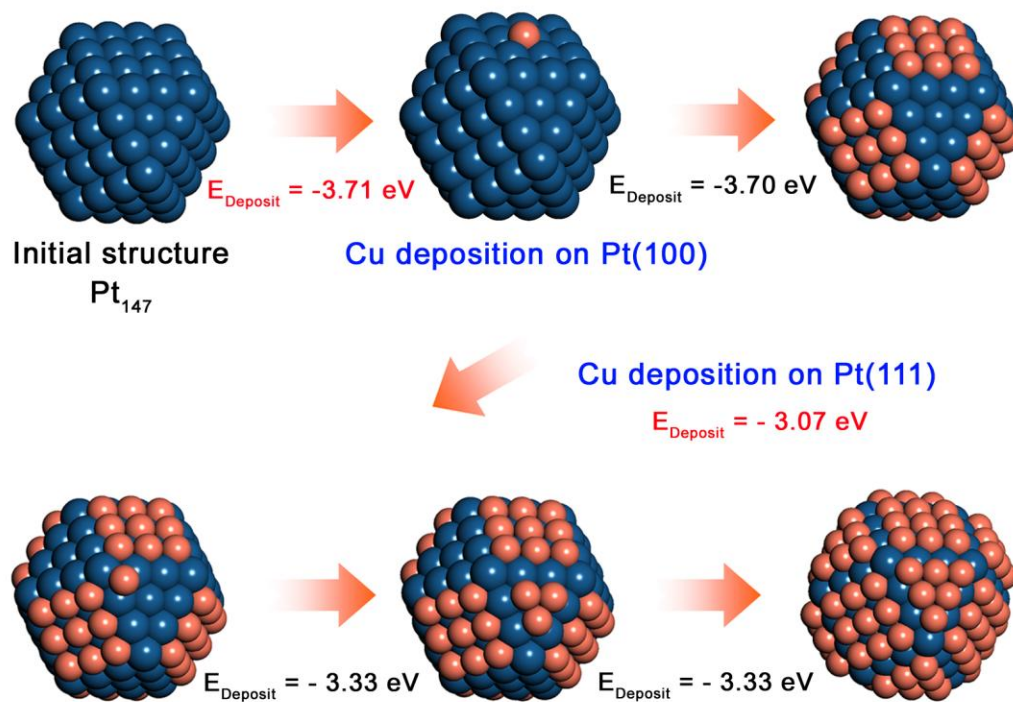


FIGURE 4.8. The Cu deposition process on Pt₁₄₇^{DFT}. The E_{Deposit} values indicated by red text were used to calculate the difference in energy between depositing Cu on different facets, $\Delta E_{\text{Dep}}^{\text{DFT}}$.

Once all of the (100) facets were covered with Cu atoms, Cu was deposited onto the (111) facets. After depositing the first Cu atom on the (111) facet ($E_{\text{Deposit}} = -3.07$ eV) Cu deposition becomes more favorable ($E_{\text{Deposit}} = -3.33$ eV) because of the increasing formation of Cu-Cu bonds. In other words, the first Cu deposition step on the (111) facet is a “peak generating step”, meaning that this step induces spontaneous Cu deposition on the remainder of the facet. We therefore considered the possibility that the E_{Deposit} corresponding to this step may relate to the more negative Cu UPD peak in Figure 4.5.

The difference in E_{Deposit} for Cu on the (100) and (111) facets, denoted $\Delta E_{\text{Dep}}^{\text{DFT}}$, was calculated as the difference in E_{Deposit} corresponding to the first Cu deposition step on the (100) facet and that of the first Cu deposition step on the (111) facet. We found that for the $\text{Pt}_{147}^{\text{DFT}}$ model, $\Delta E_{\text{Dep}}^{\text{DFT}}$ was 0.64 eV. After dividing $\Delta E_{\text{Dep}}^{\text{DFT}}$ by 2, to account for the 2 electrons transferred in the Cu deposition process, we found that $\Delta E_{\text{Dep}}^{\text{DFT}}$ on the $\text{Pt}_{147}^{\text{DFT}}$ model relates to a potential difference between the Cu UPD peaks of 0.32 V. The measured potential difference between the Cu UPD peaks, $\Delta E_{\text{Dep}}^{\text{Exp}}$, is 0.08 V. The error in these DFT calculations is 0.2 eV (0.1 V) and therefore the process shown in Figure 4.8 is not a reliable explanation of the shape of the CV for Cu UPD onto G6-OH(Pt_{147}) DENs. One possible reason for the poor agreement between $\Delta E_{\text{Dep}}^{\text{DFT}}$ and $\Delta E_{\text{Dep}}^{\text{Exp}}$ is that the $\text{Pt}_{147}^{\text{DFT}}$ model is not a suitable structure for comparison to Cu UPD onto G6-OH(Pt_{147})

DENSs under the experimental conditions. Because Cu UPD onto G6-OH(Pt₁₄₇) DENSs takes place in a solution that contains SO₄²⁻ anions, we repeated the DFT calculations using the (SO₄²⁻)Pt₁₄₇^{DFT} model to examine the effects of adsorbed solvent molecules on E_{Deposit} .

Figure 4.9 shows the key steps in the Cu deposition process on the (SO₄²⁻)Pt₁₄₇^{DFT} model. The entire process is presented in Figure 4.10. The first step in this process is the desorption of a SO₄²⁻ anion from the (100) facet of (SO₄²⁻)Pt₁₄₇^{DFT} which creates a vacancy (Figure 4.10). After this occurs, Cu deposition commences at the newly formed vacancy on the (100) facet (Figure 4.9, step 1). The E_{Deposit} corresponding to this step was found to be -3.13 eV, which is a much weaker binding energy than the E_{Deposit} observed for Cu deposition on the (100) facet of the naked Pt₁₄₇^{DFT} model (-3.71 eV). After depositing the first Cu atom onto the (100) facet, the deposition of additional Cu atoms onto all of the remaining (100) facet positions was spontaneous (Figure 4.9, step 2), meaning the E_{Deposit} for these steps were found to be more negative than the E_{Deposit} for the initial step (Figure 4.10). Therefore, the deposition of the first Cu atom on the (100) facet is a peak generating step, and the E_{Deposit} for this step can be compared to the more positive Cu UPD peak in Figure 4.5. The E_{Deposit} for depositing the first Cu atom on the (111) facet is -3.04 eV (step 3 in Figure 4.9). This is another peak generating step, meaning that depositing the first Cu atom on the (111) facet induces Cu deposition on the remainder of the (111)

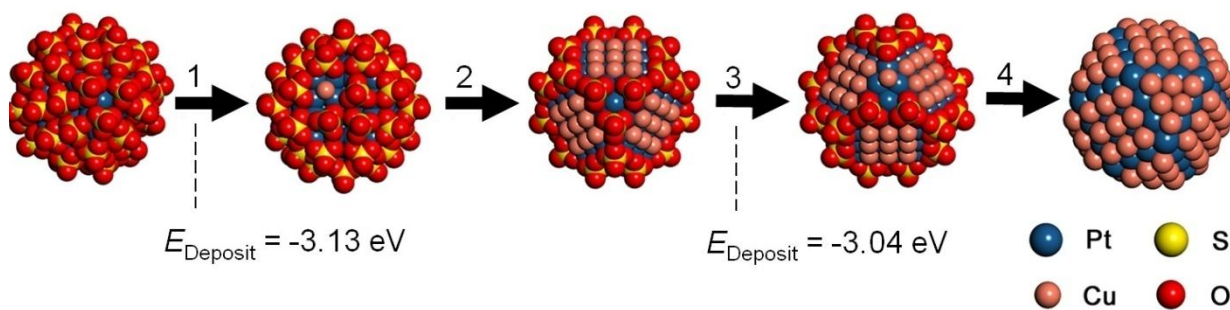


FIGURE 4.9. The Cu deposition process shown on the $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$ model.

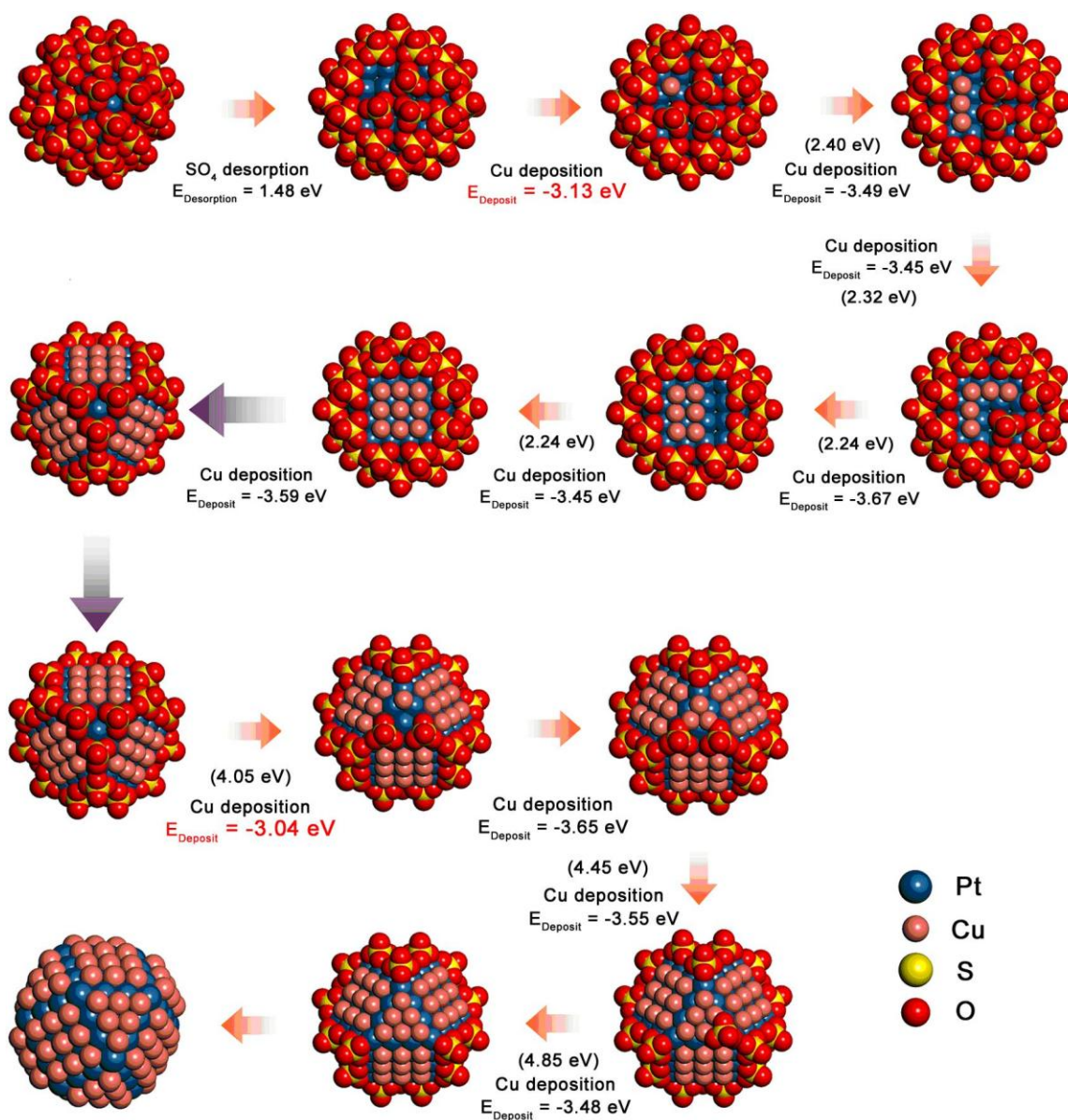


FIGURE 4.10. The complete process for Cu deposition on the $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$ model. The E_{Deposit} values given in red indicate the peak generating steps. The energy of SO_4^{2-} desorption, $E_{\text{Desorption}}$ is given in the parentheses.

facet (step 4 in Figure 4.9). The $\Delta E_{\text{Dep}}^{\text{DFT}}$ was calculated from the difference in energy between the two peak-generated steps. We found that for the $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$ model, $\Delta E_{\text{Dep}}^{\text{DFT}}$ was 0.09 eV. This corresponds to a potential difference of 0.045 V, which is much closer to $\Delta E_{\text{Dep}}^{\text{Exp}}$ (0.08 V), and within the DFT error of 0.1 V.

The E_{Deposit} for the first Cu deposition step on the (100) facet of the $(\text{SO}_4^{2-})\text{Pt}_{147}^{\text{DFT}}$ model (-3.13 eV, Figure 4.10) was shifted towards weaker binding energies compared to the same step calculated on the $\text{Pt}_{147}^{\text{DFT}}$ model (-3.71 eV, Figure 4.8). This shift can be attributed to interactions between adsorbed SO_4^{2-} anions and adjacent Pt atoms, which weakened the E_{Deposit} for depositing the first Cu atom onto the (100) facet. This in turn decreased $\Delta E_{\text{Dep}}^{\text{DFT}}$ from 0.32 V to 0.045 V.

The Cu stripping process was initially modeled by removing Cu atoms from the $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$ model and the key steps in this process are shown in Figure 4.11. The entire process is presented in Figure 4.12. The first step in this process is the removal of the lowest-coordinated Cu adatom from the corner position of (111) facet (step 1 in Figure 4.11). The E_{strip} for this step was calculated as 3.95 eV. This step induces the spontaneous stripping of the remaining Cu atoms from the (111) facet, starting with the Cu atoms located at the corners of the (111) facet (step 2 in Figure 4.11). Therefore, the E_{strip} corresponding to the removal of

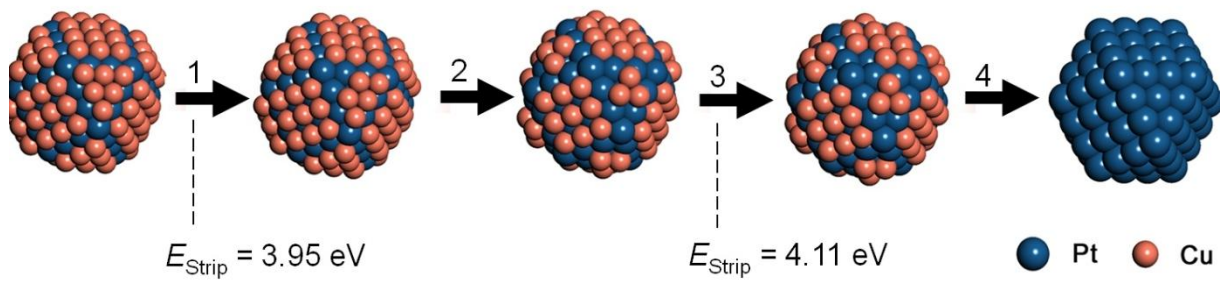


FIGURE 4.11. The Cu stripping process shown on the $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$ model.

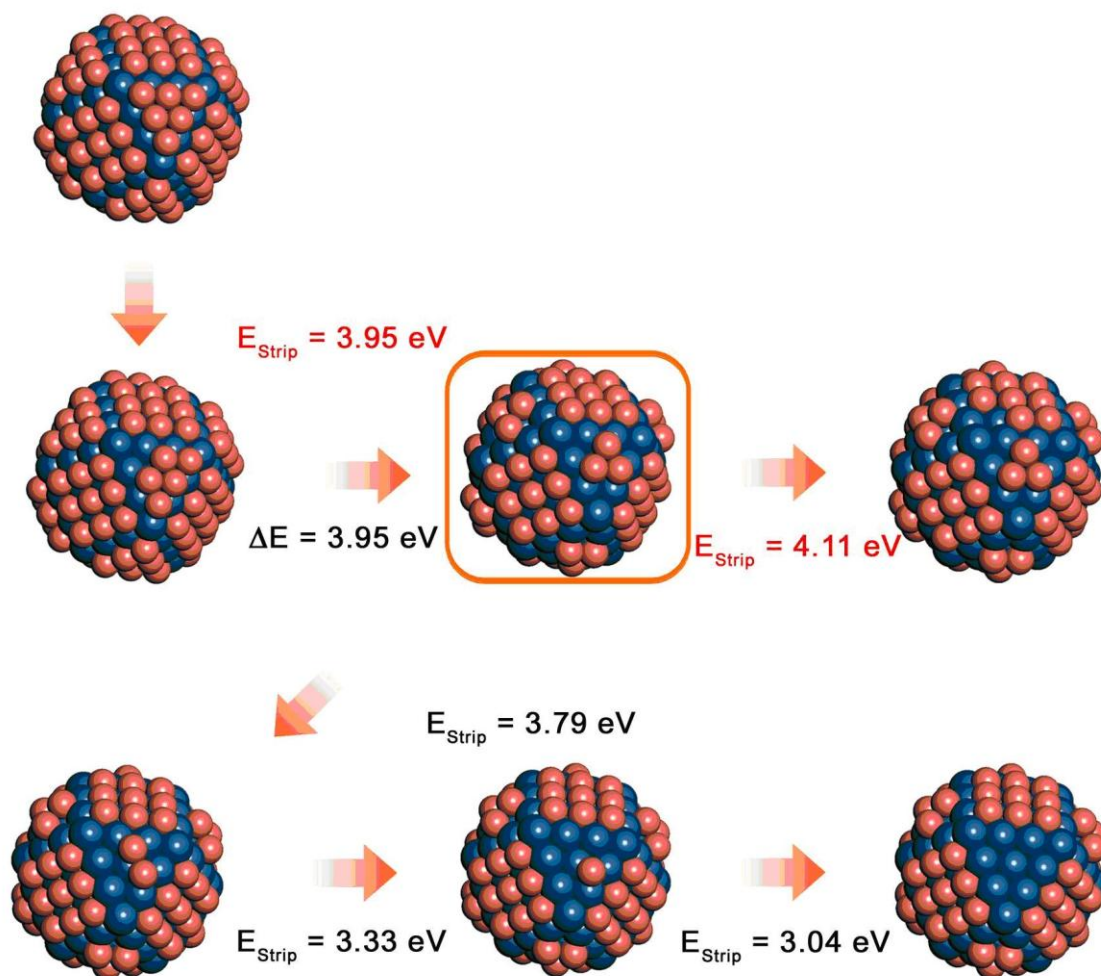


FIGURE 4.12. The detailed Cu stripping process. Once the stripping of Cu has proceeded until the circled structure has been reached, the stripping of Cu from both the (111) and (100) facets is spontaneous.

the first Cu atom relates to the most negative peak in the Cu stripping current (Figure 4.5). Next, Cu atoms were stripped from the (100) facet. The E_{strip} corresponding to removing the first Cu atom from the (100) facet was 4.11 eV. This step is predicted to occur concurrently with the stripping of the last 3 Cu atoms from the (111) facets (step 3 in Figure 4.11). As in the case of Cu stripping from the (111) facet, this initial step induces the spontaneous stripping of the remaining Cu atoms from the (100) facet (step 4 in Figure 4.11). The E_{strip} corresponding to the removal of the first Cu atom from the (100) facet relates to the more positive of the pair of Cu stripping peaks (Figure 4.5). The DFT-calculated difference in energy between the two stripping peaks, $\Delta E_{\text{strip}}^{\text{DFT}}$, was found to be 0.16 eV, corresponding to a potential difference of 0.08 V. This is a close approximation of the experimentally observed difference in potential between the two Cu stripping peaks ($\Delta E_{\text{strip}}^{\text{Exp}}$), 0.14 V, given the DFT error of 0.1 V.

So far, based on these DFT calculations of the Cu UPD and stripping processes, we can reasonable propose that the current peaks at 0.41 V and 0.33 V in the Cu UPD current (Figure 4.5) relate to Cu UPD of the (100) and (111) facets, respectively. We also propose that the peaks in the anodic current seen at 0.39 V and 0.53 V relate to Cu stripping from the (111) and (100) facets, respectively.

Correlation of calculated of Cu binding energies with UPD potentials. We measured the difference between the bulk

Cu reduction potential and the Cu UPD peaks for Cu deposition on G6-OH(Pt₁₄₇) and compared these values to the DFT-calculated energies of bulk Cu deposition and Cu UPD on the facets of the model nanoparticles. The difference between the bulk reduction potential and the potential of UPD is called the UPD shift, ΔV , and is related to the difference in work function between the substrate and the adatoms undergoing UPD.^{30, 31} The ΔV is also influenced by the structure of the electrode-solution interface, such as the adsorption of solvent molecules to the electrode surface.^{33,}

34

Table 4.1 presents the electrochemically measured ΔV along with the -DFT calculated ΔV for Cu deposition. The potential for bulk Cu deposition in 0.10 M H₂SO₄ and 0.010 M CuSO₄ is 0.24 V.⁴² We have also measured the bulk Cu reduction potential and obtained the same result (0.24 V) (Figure 4.2). The bulk deposition potential is denoted V_{Bulk} in Table 4.1. Based on the DFT studies discussed above, we consider the pair of Cu deposition peaks at 0.41 V and 0.33 V in the Cu UPD CV (Figure 4.5) to correspond to Cu UPD onto the (100) and (111) facets of G6-OH(Pt₁₄₇), respectively (V_{100} and V_{111} in Table 4.1). The experimentally measured ΔV corresponding to Cu UPD onto the (100) facet of G6-OH(Pt₁₄₇), ΔV_{100} , is 0.17 V (Table 4.1). This is the

Cu deposition	G6-OH(Pt ₁₄₇)	(SO ₄ ²⁻)Pt ₁₄₇ ^{DFT}	Pt ₁₄₇ ^{DFT}
V ₁₀₀	0.41 V	-1.57 V	-1.85 V
V ₁₁₁	0.33 V	-1.52 V	-1.67 V
V _{Bulk}	0.24 V	-1.39 V	-1.39 V
ΔV ₁₀₀	0.17 V	0.18 V	0.46 V
ΔV ₁₁₁	0.09 V	0.13 V	0.28 V
Cu stripping	G6-OH(Pt ₁₄₇ @Cu _{Full})	(SO ₄ ²⁻) Pt ₁₄₇ @Cu _{Full} ^{DFT}	Pt ₁₄₇ @Cu _{Full} ^{DFT}
V' ₁₀₀	0.53 V	N/A ¹	2.06 V
V' ₁₁₁	0.39 V	N/A	1.95 V
V' _{Bulk} ²	0.24 V	N/A	1.39 V
ΔV' ₁₀₀	0.29 V	N/A	0.67 V
ΔV' ₁₁₁	0.15 V	N/A	0.56 V

¹ Not applicable because we could not determine these data due to computational limitations.

² V'_{Bulk} is also the bulk reduction potential and is listed again using different notation because the sign is reversed for the DFT-calculated values (right column).

TABLE 4.1. Comparison of experimental data with the DFT results.

potential difference between V_{Bulk} and V_{100} . The experimentally measured ΔV for Cu UPD onto the (111) facet of G6-OH(Pt₁₄₇), ΔV_{111} , is 0.09 V, which is the difference between the potentials V_{Bulk} and V_{111} . The DFT-calculated ΔV for Cu deposition onto the (100) and (111) facets of the (SO₄²⁻)Pt₁₄₇^{DFT} model are 0.18 V and 0.13 V, respectively. These DFT-calculated ΔV is in excellent agreement with the electrochemically measured ΔV , given the 0.1 V error in the DFT calculations. We also calculated ΔV for the Pt₁₄₇^{DFT}. For the bare Pt₁₄₇^{DFT} model, ΔV_{100} and ΔV_{111} are 0.46 V and 0.28 V, respectively (Table 4.1). These values do not compare well to the experimental values, and the discrepancy is greater than the error in the DFT calculations (0.1 V). This demonstrates to a first approximation that accounting for solvent molecule interactions in DFT studies produces more realistic models and a better comparison to empirical data.

We also examined the difference between the bulk Cu reduction potential and the Cu stripping potentials, $\Delta V'$. Here, $\Delta V'$ is the difference between the stripping potentials corresponding to the stripping of Cu from the (111) and (100) facets, V'_{111} and V'_{100} , respectively, and the bulk reduction potential. In the case of the two Cu

stripping peaks from G6-OH(Pt₁₄₇), $\Delta V'_{111}$ was measured as 0.15 V, and $\Delta V'_{100}$ was found to be 0.29 V (Table 4.1). The corresponding DFT-calculated values for $\Delta V'_{111}$ and $\Delta V'_{100}$ were found to be 0.56 V and 0.67 V, respectively. The DFT-calculated $\Delta V'$ values are significantly larger (beyond the DFT error of 0.1 V) than the experimental measurements. This implies that there is an unaccounted for error in DFT Cu stripping process shown in Figure 4.11. We believe the source of this error is the absence of solvent interactions in the DFT-modeled stripping process.

Ideally, we would like to model the Cu stripping process on a solvated Pt@Cu nanoparticle model, to best match the Cu deposition process on the (SO₄²⁻)Pt₁₄₇^{DFT} model. However, due to computational limitations, we were not able to model the stripping process on a fully solvated Pt@Cu nanoparticle, as we had done earlier for the Cu deposition process. To address this discrepancy in the best manner possible, we are in the process of running DFT calculations on a solvated hemispherical Pt@Cu nanoparticle. Although this is still not the ideal case, we can make some meaningful observations in effort to explain the poor agreement between the experimentally measured and DFT-calculated $\Delta V'$. The calculations remain in progress at this

time, but we have obtained some preliminary results. First, the presence of adsorbed SO_4^{2-} on the Cu shell increases the Cu-Cu bond length. We speculate that the presence of the SO_4^{2-} will weaken the binding energy of the Cu atoms and shift the DFT-calculated stripping energy toward lower potentials.

In-situ XAS Analysis of $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Full}})$ and $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Partial}})$. We turned to in-situ XAS to characterize the structures of $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Full}})$ and $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Partial}})$ DENs so that these could be compared to the structural models predicted by DFT and MD simulations. In-situ characterization of these structures is necessary because the Cu monolayers and submonolayers are not stable in air or in solution except under potential control for more than a minute and the data for XAS experiments is acquired over around 24 h.

The procedure used to carry out these spectroelectrochemical experiments was discussed in detail in the Methodology Section of this chapter, but, briefly, dialyzed $\text{G6-OH}(\text{Pt}_{147})$ cores were immobilized on an AvCarb carbon-paper electrode and the potential was controlled during XAS data acquisition. The samples were characterized with the electrode poised at two potentials: E_{Full} , which corresponds to a full Cu UPD shell, and E_{Partial} , a potential positive of E_{Full} corresponding to a partial Cu shell. The data obtained at E_{Full} corresponds to $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Full}})$ DENs, and the data taken at E_{Partial} corresponds to $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Partial}})$ DENs.

OH(Pt₁₄₇@Cu_{Partial}) DENs. The CNs obtained from fits to the XAS data can be compared to those calculated different, reasonable structural models, which are shown in Figure 4.13. The CNs calculated for the models are presented alongside the CNs extracted from the fits to the data (calculated and extracted, respectively, in Tables 4.2 and 4.3).

The radial distribution spectra of the XAS data and the computed fits for G6-OH(Pt₁₄₇@Cu_{Full}) are shown in Figure 4.14-a and 4.14-b for the Pt L3 and Cu K absorbance edges, respectively. The R-space distribution and fits for G6-OH(Pt₁₄₇@Cu_{Partial}) are shown in Figure 4.14-c and 4.14-d, and these also show the Pt and Cu edge data. The corresponding k-space data are shown in Figure 4.15. The structure of the G6-OH(Pt₁₄₇@Cu_{Full}) DENs is determined by fitting the XAS data, as described in the Experimental Section, and then comparing the extracted CNs to the CNs calculated for Model F1 and Model F2 (Table 4.2 and Figure 4.13).

The following CNs were extracted from the fits to the in-situ data and compared to CNs calculated for the models: Pt-Pt (n_{PP}), Pt-Cu (n_{PC}), Cu-Pt (n_{CP}), Cu-Cu (n_{CC}), Pt-m (n_{Pm}), and Cu-m (n_{Cm}). Here, m is any metal (Pt or Cu) that is coordinated to Pt or Cu. The modeling approach assumes $n_{Pm} = n_{PP} + n_{PC}$ and $n_{Cm} = n_{CC} + n_{CP}$. The values of n_{Pm} and n_{Cm} essentially represent how coordinatively saturated the Pt and Cu atoms are relative to each other, and these are used to draw conclusions about DEN structure. We additionally extracted another CN, called Cu-E (n_{CE}). Here, E is a low-z

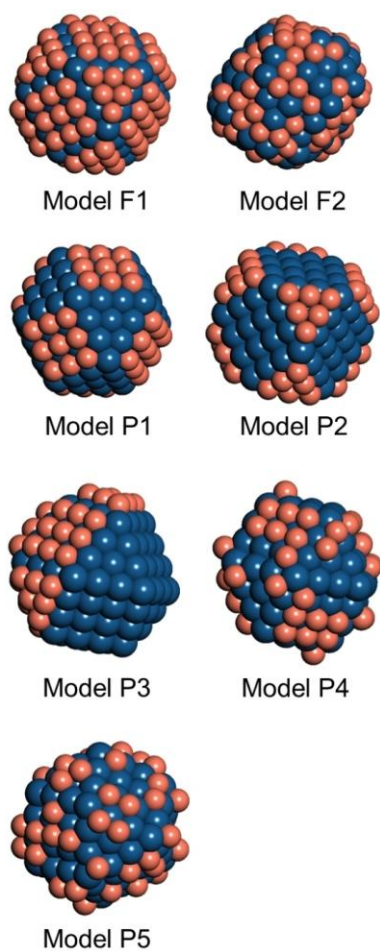


FIGURE 4.13. Structural models calculated by DFT and MD simulations for the purpose of comparing them to values extracted from fits to the XAS spectra of G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Full}}$) and G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Partial}}$).

Coordination number (CN) ¹	Extracted CN ³ (sample)	Calculated CN ⁴ (Model F1)	Calculated CN (Model F2)
n_{PP}	6.7 ± 1.1	8.9	6.9
n_{PC}	2.4 ± 0.8	2.5	2.9
n_{CC}	2.7 ± 3.7	2.8	3.1
n_{CP}	3.9 ± 0.2	3.5	4.1
n_{CE} ²	0.7 ± 0.4	N/A ⁵	N/A
n_{Pm}	9.1	11.4	9.8
n_{Cm}	6.6	6.3	7.2

¹ CN is coordination number.

² n_{CE} represents Cu with a low-Z nearest-neighbor.

³ Extracted CN is extracted from the fit to the data.

⁴ Calculated CN is estimated from the referenced DFT model.

⁵ N/A meaning not applicable because we did not include low-Z neighbors in the referenced models

TABLE 4.2. CNs extracted from in-situ XAS studies of G6-OH(Pt₁₄₇@Cu_{Full}) compared to CNs of model structures.

Coordination number (CN) ¹	Extracted CN ³ (sample)	Calculated CN ⁴ (Model P1)	Calculated CN (Model P2)	Calculated CN (Model P3)	Calculated CN (Model P4)	Calculated CN (Model P5)
n_{PP}	7.5 ± 1.3	8.9	8.9	8.9	8.9	8.9
n_{PC}	1.8 ± 0.7	1.5	1.0	1.2	1.4	1.3
n_{CC}	1.5 ± 0.8	2.7	3.0	2.8	1.9	1.1
n_{CP}	4.9 ± 0.7	4.0	3.0	3.5	3.8	3.6
n_{CE} ²	0.3 ± 2.8	N/A ⁵	N/A	N/A	N/A	N/A
n_{Pm}	9.3	10.4	9.9	10.1	10.3	10.2
n_{Cm}	6.4	6.7	6.0	6.3	5.7	4.7
R-value ⁶	N/A ⁷	3.9	5.7	4.8	3.4	3.7

¹ CN is coordination number.

² n_{CE} represents Cu with a low-Z nearest-neighbor.

³ Extracted CN is extracted from the fit to the data.

⁴ Calculated CNs are estimated from the referenced DFT models.

⁵ n_{CE} was not calculated because the concentration of low-Z nearest-neighbors (E) adsorbed to Cu has not been measured on Pt₁₄₇@Cu structures.

⁶ The R-value describes the correlation between the data and the referenced models

⁷ Not applicable because the R-value only applies to the models.

TABLE 4.3. CNs extracted from in-situ XAS studies of G6-OH(Pt₁₄₇@Cu_{partial}) compared to CNs for model structures.

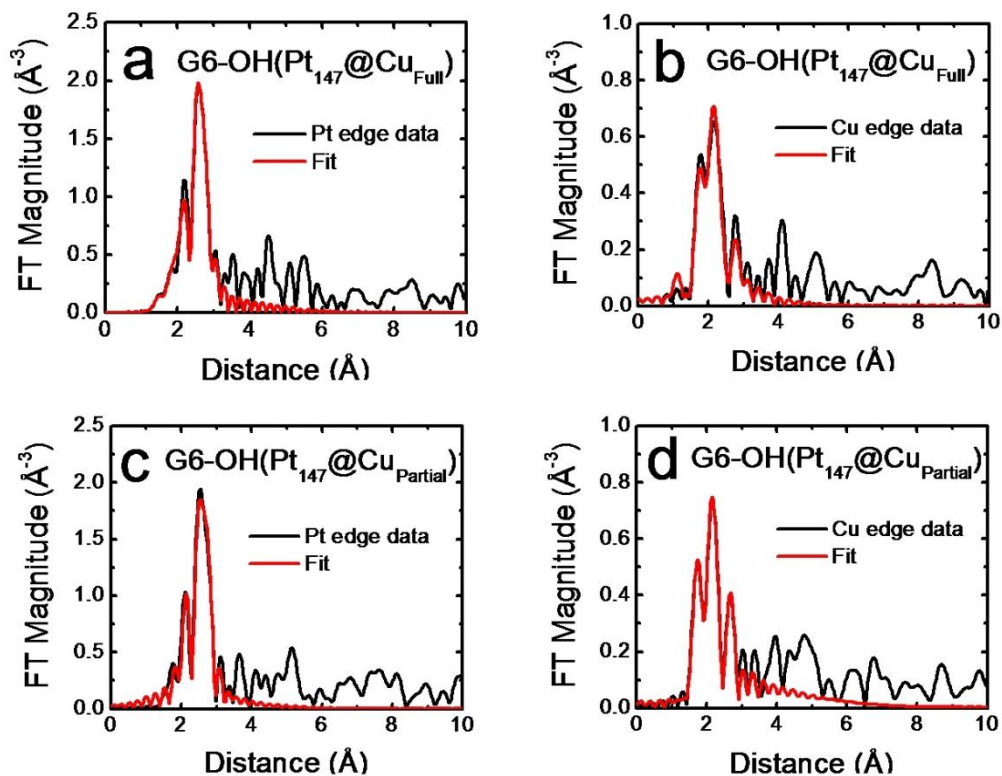


FIGURE 4.14. Radial distribution graphs of the in-situ XAS data (black) and the computed fits (red) for G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Full}}$) (a-b) and G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Partial}}$) (c-d). These data were collected in a solution of 0.10 M H_2SO_4 with the electrode poised at E_{Full} and E_{Partial} for G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Full}}$) and G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Partial}}$), respectively.

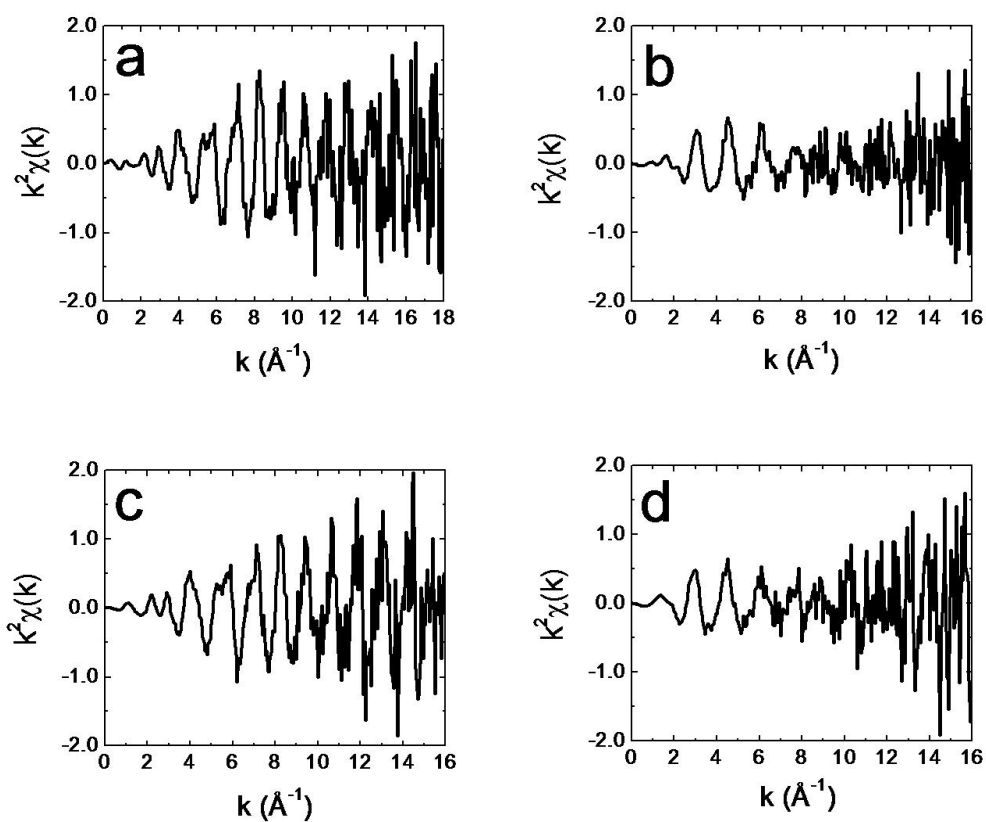


FIGURE 4.15. k -space data pertaining to the R -space distributions shown in Figure 4.14 for XAS data obtained from (a) the Pt edge of the G6-OH(Pt₁₄₇@Cu_{Full}) DENs (b) the Cu edge of the G6-OH(Pt₁₄₇@Cu_{Full}) DENs (c) the Pt edge of the G6-OH(Pt₁₄₇@Cu_{Partial}) DENs (d) the Cu edge of the G6-OH(Pt₁₄₇@Cu_{Partial}) DENs.

nearest neighbor, most likely H_2O , HSO_4^- , or SO_4^{2-} , on the Cu shell.⁷⁴ It was necessary to include the Cu-E scattering path to accurately fit the experimental data, however we did not calculate a CN corresponding to n_{CE} because low- z neighbors were not included in the models.

Table 4.2 provides the extracted CNs for G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Full}}$), as well as the calculated CNs for 2 full shell models: Model F1 and Model F2 (Figure 4.13). Model F1 is the previously described $\text{Pt}_{147}@\text{Cu}_{\text{Full}}^{\text{DFT}}$ model, in which Cu resides on the facet locations. The structure represented by Model F2 was constructed by performing MD simulations on Model F1, and shows the partial mixing of the Cu shell atoms with the Pt core.

The experimental value for n_{PP} (Table 4.2) was extracted from the data taken with the electrode poised at E_{Full} and represents the average Pt-Pt CN for G6-OH($\text{Pt}_{147}@\text{Cu}_{\text{Full}}$). We found that the extracted value for n_{PP} (CN = 6.7 ± 1.1) is significantly lower than the calculated n_{PP} of Model F1, (CN = 8.9). A Pt-Pt CN of 8.9 is the ideal CN for a 147-atom Pt cluster.⁸ Although the extracted n_{PP} underestimate the ideal value for the 147-atom Pt core, it is the same as n_{PP} reported previously for Pt DENS of this size.^{9, 22} There are several possible explanations for the discrepancy between the extracted and modeled n_{PP} . First, we have previously shown that some Pt^{2+} remains within the dendrimer after reduction, and this will result in a lower-than-expected value for n_{PP} .²² Because n_{PP} represents the ensemble average Pt-Pt CN for the entire sample, it will

include contributions from both Pt atoms in the DENs, and unreduced Pt^{2+} , which has no nearest neighbors ($\text{CN} = 0$). To determine if this was the case in this study, we carried out XPS measurements on the Pt DENs used for the XAS analysis. The results of XPS measurements on the $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Full}})$ are shown in Figure 4.16 and verify the presence of unreduced Pt^{2+} in addition to zero-valent Pt DENs.

A second possible cause for the lower-than-expected n_{pp} value could be partial alloying of some of the Cu shell atoms with the Pt atoms directly beneath them, as shown in Model F2. As Cu atoms partition into the core, they displace some of the Pt atoms that reside in the first coordination shell of other Pt atoms, and therefore, on average, the Pt atoms in the DENs have fewer Pt nearest neighbors. Hence, n_{pp} could be decreased as a result of partial alloying. However, we have made some observations which make it seem unlikely that Model F2 is a viable representation of the actual DENs. Specifically, we noted earlier that the full Cu shell blocks the HER (Figure 4.6), which is not expected in the case of PtCu alloyed nanoparticles which have both Pt and Cu on their surfaces. For example, the groups of Strasser et al.⁸¹ and Stevenson et al.⁸² have shown that the HER does in fact occur on PtCu alloy nanoparticles due to the presence of some Pt atoms on the surface. Therefore, we believe that the blocking of the HER on the $\text{G6-OH}(\text{Pt}_{147}@\text{Cu}_{\text{Full}})$ DENs provides evidence that the Pt atoms in our DENs remain beneath the Cu shell and do not partition to the surface as depicted in Model F2.

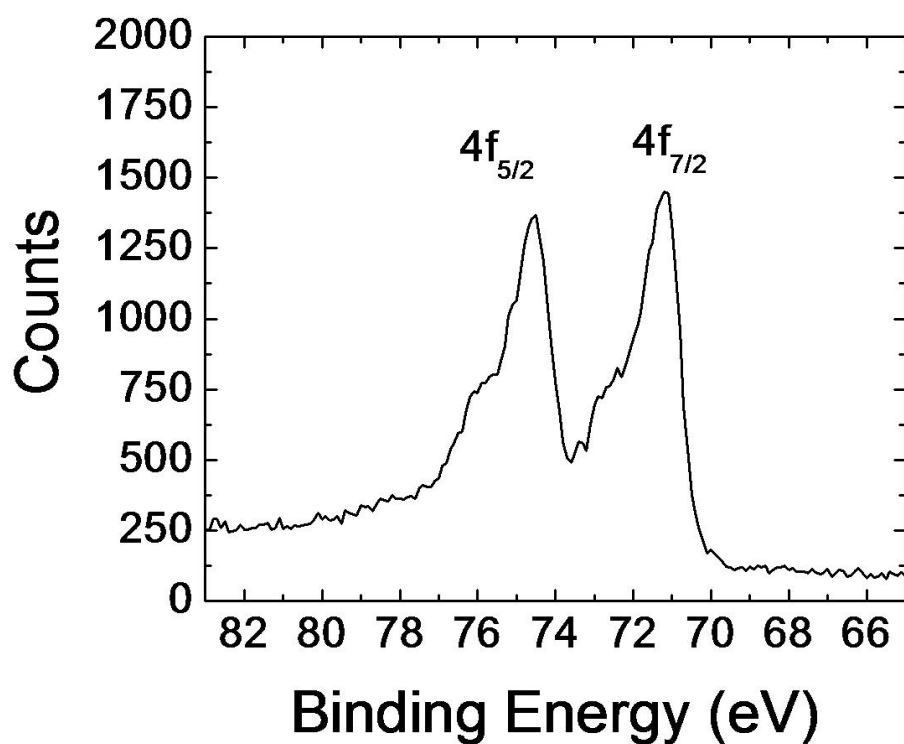


FIGURE 4.16. XPS data obtained on G6-OH(Pt₁₄₇) on AvCarb paper. The Pt 4f peaks are indicated for zero-valent Pt at 71.0 and 74.5 eV, approximately. The apparent shoulders at more positive binding energies, 72.5 and 76.0 eV, are due to the presence of some Pt²⁺.

The extracted CNs for n_{PC} , n_{CP} , and n_{CC} are all in reasonable agreement with the values predicted from both of the model clusters, and are consistent with trends for core@shell structures as well. From a modeling perspective, there are a few clear trends that distinguish core@shell nanoparticles from random arrangements such as alloys. For example, the combined values of n_{cm} will be less than n_{pm} for a core@shell particle, because if Cu atoms are confined to the surface of the nanoparticle they will have fewer nearest neighbors than if they occupy coordinatively saturated positions in the core.²⁸ Indeed, consistent with the core@shell structure, we find that n_{pm} is larger than n_{cm} experimentally and for both models (Table 4.2). Therefore, we postulate that the true structure of G6-OH(Pt₁₄₇@Cu_{Full}) has a Pt rich core and a Cu-rich shell.

The Debye-Waller factors and bond distances for G6-OH(Pt₁₄₇@Cu_{Full}) are provided in Table 4.4. The Debye-Waller factors indicate greater disorder in all of the Cu-M bond pairs (n_{CC} , n_{CP}) compared to Pt-Pt bonds. This is indicative of segregation of the core and shell phases of G6-OH(Pt₁₄₇@Cu_{Full}), because the atoms on the surface are considered to occupy high energy defect positions and tend to exhibit greater disorder than the coordinatively saturated atoms nearer the core.^{22, 51} The average Pt-Pt bond distance (2.74 Å) is shorter than that of bulk Pt (2.77 Å). The contractile straining of the core phase may be attributed to surface tension.⁷⁵ The Cu-Cu bond distance (2.68 Å) exhibits a tensile strain due to lattice mismatch

Coordination number (CN) ¹	Bond distance (Å)	Debye-Waller factor
n_{PP}	2.74	0.004 ± 0.0007
n_{PC}	2.65	0.023 ± 0.019
n_{CC}	2.68	0.005 ± 0.003
n_{CP}	2.65	0.023 ± 0.019
n_{CE} ²	1.98	0.06 ± 0.07
n_{Pm}	N/A ³	N/A
n_{Cm}	N/A	N/A

¹ CN is coordination number.

² n_{CE} represents Cu with a low-Z nearest-neighbor.

³ Not applicable (N/A) to n_{Pm} and n_{Cm} because these CNs are sums of other CNs and are not variables included in the fit.

TABLE 4.4. The bond distances and Debye-Waller factors extracted from the fit to the XAS data for G6-OH(Pt₁₄₇@Cu_{Full}).

with the underlying Pt lattice. Cu monolayers on Pt will template the underlying Pt lattice, which has a larger lattice constant, and so the Cu-Cu bond distance is expanded.

The CNs extracted from the fits to the XAS data for G6-OH(Pt₁₄₇@Cu_{Partial}) are presented in Table 4.3 alongside the CNs for the partial shell model structures depicted in Figure 4.13. The bond lengths and Debye-Waller factors are provided in Table 4.5. The CN for n_{pp} is comparable to n_{pp} measured for G6-OH(Pt₁₄₇@Cu_{Full}), meaning that the Pt core does not change significantly upon removing Cu atoms from the surface. The calculated CNs for the model structures can be compared to the extracted CNs for the sample, G6-OH(Pt₁₄₇@Cu_{Partial}) DENs. Model P1 is the most likely partial shell model according to the results of DFT calculations in which Cu shell atoms are preferentially located on the (100) facets. Model P2 illustrates the opposite case, in which Cu decorates the Pt(111) facets. Model P3 is a partial shell model in which the Cu shell exhibits Janus-like coverage. Given the experimental data and DFT calculations presented earlier, it is unlikely that Models P2 and P3 would be the result of Cu UPD onto G6-OH(Pt₁₄₇) DENs, however, we decided to include them in our analysis for the sake of comparison.

Model P4 was constructed from Model P1 by removing a few of the Cu atoms from the (100) facets and placing them on (111) facets. This could be a viable structure, because the peaks in the CVs of Cu UPD and stripping on the DENs

Coordination number (CN) ¹	Bond Distance (Å)	Debye-Waller factor
n_{PP}	2.73	0.004 ± 0.0006
n_{PC}	2.56	0.010 ± 0.004
n_{CC}	2.63	0.019 ± 0.018
n_{CP}	2.56	0.010 ± 0.003
n_{CE} ²	1.98	0.004 ± 0.004
n_{Pm}	N/A ³	N/A
n_{Cm}	N/A	N/A

¹ CN is coordination number.

² n_{CE} represents Cu with a low-Z nearest-neighbor.

³ Not applicable (N/A) to n_{Pm} and n_{Cm} because these CNs are sums of other CNs and are not variables included in the fit.

TABLE 4.5. The bond distances and Debye-Waller factors extracted from the fit to the XAS data for G6-OH(Pt₁₄₇@Cu_{partial}).

(Figure 4.5, red line) are overlapping, signifying that the stripping of the Cu atoms from one facet might not be complete before stripping from the other facet commences. In other words, some Cu atoms would still remain on the (111) facet, having yet to be stripped, when Cu atoms commence in stripping from the (100) facet, and this is illustrated by Model P4. Model P5 is a partial shell model in which the Cu atoms are randomly distributed on the surface with no preference for one facet over another. This model is an unlikely candidate, because it is incompatible with the results of our DFT studies, yet it was also included for comparison.

To determine which models provided the most favorable comparisons to our data, we calculated a correlation factor based on the calculated and extracted CNs, and expressed this as the R-value in Table 4.3. The R-value, which is the sum of the magnitude of differences between the extracted and calculated CNs, is used to compare the models to the data, and to each other to determine which model most closely approaches the experimentally characterized structure. The R-value was calculated according to Equation 4.1.

$$\text{R-value} = \sum_{\text{CN}} \sqrt{(\text{CN}_{\text{Extracted}} - \text{CN}_{\text{Model}})^2} \quad (4.1)$$

Here, $\text{CN}_{\text{Extracted}}$ are CNs that were extracted from the fit to the data (n_{pp} , n_{pc} , n_{cc} , and n_{cp}) ("extracted" in Table 4.3)

and CN_{Model} are the corresponding CNs for the model structures. A lower correlation factor means a lesser overall magnitude of difference across all the CNs of the sample and the model and thus a better overall fit. The R-value for Model P4 (3.44) (Table 4.3) was the lowest and therefore Model P4 provides the best structural comparison to the experimental data. This model (P4) is in good agreement with our DFT studies, which showed that the stripping of the Cu from the (100) facet did, in fact, commence before all of the of the Cu had stripped from the (111), and thus it is highly likely that this model could be close to the structure of the G6-OH(Pt₁₄₇@Cu_{Partial}) that was characterized by in-situ XAS.

4.4 Summary and Conclusions

This study was motivated by findings of interesting, facet-specific properties on nanoparticles. Accordingly, we sought to determine whether such properties could be detected on Pt DENs. The agreement between the experimental observations from DFT, XAS, and electrochemical studies confirm to a first approximation that SO₄²⁻ anion-mediated Cu deposition and direct Cu stripping process that was modeled using DFT calculations can explain the voltammetric fingerprint for Cu UPD on G6-OH(Pt₁₄₇) DENs. Perhaps the most meaningful result of these DFT studies was the finding that adsorbing SO₄²⁻ solvent anions to the surface of the model Pt nanoparticle produced results that compared more favorably

to empirical data than those for the DFT model in which solvent molecule interactions were not considered.

We are now turning our attention to the application of core@shell DENs in catalysis. By decorating particular crystallographic orientations of DENs electrocatalysts, we will be able to individually address the catalytic activity of particular locations on nanoparticles and obtain new, atomic-scale knowledge of the structure-property relationship.

Chapter 5. Quantitative Analysis of the Stability of Pd Dendrimer-Encapsulated Nanoparticles

5.1. Introduction and Background

In this chapter we report on the stability of aqueous solutions of Pd dendrimer-encapsulated nanoparticles (DENs) under oxygen containing (air saturated), inert (N_2 saturated), and reducing (H_2 saturated) conditions. The results indicate that Pd DENs are not fully stable in the presence of air or N_2 , but that they do retain their integrity under reducing conditions. Additionally, the presence of coordinating anions, such as Cl^- , accelerate the oxidation of DENs. These findings are consistent with previous results indicating that Pd nanoparticles of many types degrade over time in oxidizing⁸³ and catalytic environments.⁸⁴⁻⁸⁷ The presence of degradation products makes it difficult to identify the active species in nanoparticle-based catalytic reactions. For example, it has been found that metal atoms or ions dissociated from nanoparticles catalyze carbon-carbon coupling reactions.^{85, 86, 88} Accordingly, this quantitative study of Pd DEN stability is significant.

An interesting aspect of the DEN architecture, which distinguishes it from other forms of stabilized Pd nanoparticles, is the ability of the dendrimer to retain Pd^{2+} resulting from oxidation of the metallic nanoparticle

component.⁸³ Accordingly, we use the terms "retained" to refer to Pd²⁺ that remains within the dendrimer following DEN oxidation and "leached" to refer to Pd²⁺ that escapes from the dendrimer template into the solution. Unless otherwise indicated, all ionic forms of Pd are denoted here as Pd²⁺, but it is understood that this includes various hydrolyzed and unhydrolyzed complexes of Pd²⁺ with Cl⁻.

DENs are synthesized in a two-step process. First, metal ions are extracted from solution into the dendrimers via complexation with internal tertiary amines. Second, the metal ions are reduced, usually using BH₄⁻, and subsequently coalesce to form zerovalent metallic nanoparticles within the dendrimer templates. Monometallic Au, Pt, Pd, Cu, Ni, and Fe, as well as bimetallic AuAg, PdAu, PtCu, PtAu, PdPt, and CuPd DENs have been synthesized using this basic procedure.^{1, 10, 12, 15-17, 83, 89-94} DENs are stabilized by the dendrimer framework and therefore do not aggregate into larger particles. However, small molecules are able to penetrate the dendrimer and access the surfaces of the encapsulated nanoparticles, and therefore DENs are good models for homogeneous,^{90, 95, 96} heterogeneous,⁹⁵ and electrochemical^{17, 89, 94} catalysts. Specifically, DENs have been shown to be catalytically active for olefin and alkene hydrogenation,^{96, 97} oxygen reduction,^{89, 94} carbon monoxide oxidation,¹⁷ and carbon-coupling reactions.

We have previously shown that aqueous solutions of Pd DENs oxidize in the presence of air when Pd²⁺-coordinating ligands, such as Cl⁻, are present.⁸³ However, UV-vis

spectroscopic data indicated that the stability of Pd DENs improved when such ligands were removed by dialysis and DEN solutions were maintained under an inert gas atmosphere. The susceptibility of Pd DENs to oxidation was demonstrated by alternately bubbling aqueous DEN solutions with O₂ and H₂. In the presence of O₂, a ligand-to-metal charge-transfer (LMCT) band emerged in the UV-vis spectrum, indicating oxidation of the Pd DEN and complexation of the resulting Pd²⁺ ions with the tertiary amines of the dendrimer.⁸³ Subsequent exposure to H₂ gas eliminated the LMCT band, indicating re-reduction of the retained Pd²⁺. We have also observed that the size of Pd DEN catalysts increases following the Stille coupling reaction.⁸⁷ This likely occurs because of oxidative degradation of the Pd DENs followed by redeposition of zerovalent Pd atoms, or very small clusters of atoms, onto other DEN catalysts present in solution. This result suggests that in at least some cases Pd²⁺ leaches from within the dendrimer host.

If a nanoparticle undergoes an undesirable reaction, such as oxidation, agglomeration, or precipitation, the lifetime of the catalyst is reduced. Hence, it is important to determine the stability of the catalyst during reaction.^{85, 86, 95, 98} For example, Astruc and co-workers used Pd DENs, Pd dendrimer-stabilized nanoparticles (DSNs), and Pd monolayer-protected clusters (MPCs) that were extracted from DENs to catalyze the Suzuki coupling reaction.⁸⁵ They found that the concentration of leached Pd increased when reaction kinetics were fast, and this finding correlated

with the observation of an increased presence of aggregated Pd black. The other important finding in this study was that Suzuki coupling substrates add oxidatively to Pd nanoparticles during catalysis, resulting in leaching. These findings are important, because increased concentrations of leached Pd resulted in agglomeration and precipitation and this effectively quenched the active catalyst.

Rothenberg and co-workers have monitored leaching from tetraoctylammonium glycolate-stabilized Pd nanoparticles during Heck and Suzuki coupling reactions in deoxygenated water.⁸⁶ For these studies, a reactor having two compartments separated by a nanoporous alumina membrane was used. Catalytic Pd nanoparticles, having diameters ranging from 11-20 nm, and the necessary reactants were placed into one of the chambers. If the nanoparticles were stable during reaction, then they would remain within this chamber. However, catalyst degradation would lead to formation of ions and perhaps smaller metal clusters, and these would be able to diffuse into the second chamber through the 5 nm membrane pores. Elemental analysis of the solution in the second chamber revealed that the concentration of Pd increased as a function of time, indicating poor catalyst stability. Indeed, even in the absence of the active reactants, the Pd nanoparticles oxidized and Pd was observed in the second chamber.

In the present study, Pd DENs consisting of an average of 147 atoms were prepared within sixth-generation, hydroxyl-terminated, poly(amidoamine) (PAMAM) dendrimers

(G6-OH(Pd₁₄₇)), and their stability was evaluated in the presence of aqueous solutions saturated with air, N₂, and H₂. The results indicate that Pd DENs partially oxidize in air- and N₂-saturated solution, but that the amount of oxidized Pd is small (typically less than 10% of the total zerovalent Pd initially present) after 12.0 h. Typically, about half of the oxidized Pd is retained within the dendrimer and half leaches into the solution. Oxidation is accelerated in the presence of coordinating ligands such as Cl⁻. In H₂-saturated water, G6-OH(Pd₁₄₇) DENs are stable.

5.2. Methodology

Synthesis of Pd DENs. Sixth-generation, hydroxyl-terminated PAMAM dendrimers (G6-OH) were obtained from Sigma-Aldrich as a 4.49 wt% solution in methanol. Prior to use, the methanol was removed under vacuum and the dendrimers were redissolved in HPLC-grade, submicron-filtered water (Fisher Scientific) to make a 10.0 μM stock solution. K₂PdCl₄ and NaBH₄ were purchased from Sigma-Aldrich and used as received. Pd DENs were prepared by the chemical reduction of a precursor dendrimer-Pd ion complex, denoted as G6-OH(Pd²⁺)₁₄₇. A 2.00 μM solution of G6-OH(Pd²⁺)₁₄₇ was prepared by mixing 200 μL of a 100 μM G6-OH dendrimer solution in 9.48 mL of HPLC-grade water, followed by the slow addition of 294 μL of a 10.0 mM solution of K₂PdCl₄ while stirring. The solution was stirred for an additional

30 min, which is the time required for all of the Pd^{2+} ions to complex to the interior tertiary amines of the dendrimer.⁸³ The formation of the $\text{G6-OH(Pd}^{2+}\text{)}_{147}$ complex was confirmed by UV-vis spectroscopy, which reveals a characteristic ligand-to-metal charge transfer (LMCT) band at 224 nm.⁸³ Next, 30.0 μL of a freshly prepared 1.00 M aqueous solution of NaBH_4 was added to the complex. The solution was stirred for 30 min and then a second UV-vis spectrum was obtained to confirm that the precursor complex was completely reduced to form $\text{G6-OH(Pd}^{2+}\text{)}_{147}$ DENs.⁸³

Purification. Purification of DENs was performed by dialysis. Dialysis sacks having a nominal mass weight limit (NMWL) of 12 kDa were purchased from Sigma Diagnostics. 40.0 mL of a 2.00 μM DENs solution was prepared and dialyzed for 24.0 h against 4.0 L of HPLC-grade water. To prevent oxidation of Pd DENs during purification, the dialysis water was purged with H_2 for 30 min prior to, and also during, dialysis. Additionally, the dialysis was carried out in a glove bag purged with H_2 gas. The dialysis water was exchanged for 4.0 L of fresh HPLC-grade water after 12.0 h.

Characterization. UV-vis absorbance spectra were obtained using a Hewlett-Packard HP 8453 UV-Vis spectrometer. Quartz cuvettes having an optical path length of 0.20 cm were used. An aqueous 2.00 μM solution of G6-OH was used as a blank for all UV-vis measurements.

TEM images were obtained using an JEOL 2010F TEM. Samples were prepared for analysis by dropwise addition of a

G6-OH(Pd₁₄₇) solution onto 400 mesh Cu TEM grids coated with a thin layer of carbon (EM Sciences). Prior to analysis, the grids were allowed to dry overnight in a desiccator.

Separation of leached Pd by centrifugal filtration.
Leached Pd was quantitatively separated from solutions of DENs by centrifugal filtration through a cellulose membrane having a nominal molecular weight limit (NMWL) of 10 kDa. Amicon Ultra Centrifugal Filtration Devices with an Ultracel 10 kDa NMWL membrane were purchased from Millipore (Billerica, MA). The membrane material is constructed from regenerated cellulose. Prior to use, the filters were rinsed with HPLC water and the lower vials used to collect the filtrate were cleaned in 4.0 M HNO₃. One hour was required for all of the solvent in 2.0 mL aliquots of aqueous 2.0 μ M G6-OH(Pd₁₄₇) to pass through filter when solutions were centrifuged at an acceleration of 5000 g, where g is the free-fall acceleration in units of m·s⁻². Sample aliquots were removed by the procedure described in the previous paragraph. Centrifugation was carried using a Fisher Scientific AccuSpin 400 fixed-rotor centrifuge.

Elemental analysis of leached samples. The amount of leached Pd was evaluated using inductively coupled plasma-mass spectrometry (ICP-MS). Following centrifugal filtration, 900 μ L of filtrate containing the leached Pd, along with an internal standard, was added to volumetric flasks and made to volume in a 1.00 wt% solution of Ultra Trace HNO₃ (Fisher Scientific). All volumetric glassware was acid washed in a 4.0 M HNO₃ bath overnight and then rinsed

with deionized water prior to sample preparation. Indium was used as the internal standard to correct for drift. An aliquot from a 100 ppm stock solution of indium in 2.00 wt% HNO₃ (Fisher Scientific) was added to all samples and calibration standards such that the final In concentration was 1.00 ppm. Quantitative analysis of leached Pd was performed on a GBC Optimass 8000 ICP-TOF-MS, using a pneumatic nebulizer and cyclonic spray chamber, with a peristaltic pump sample uptake manifold. Calibration standards containing 5.00, 10.0, 25.0, 50.0, 100, 300, and 500 ppb Pd were prepared from a 110 μ M K₂PdCl₄ stock solution. A 1.00 wt% solution of UltraTrace HNO₃ (Fisher Scientific) containing 1.00 ppm In served as a blank.

5.3 Results and Discussion

Synthesis and characterization of Pd DENs. Pd DENs were synthesized in a two-step process. First, Pd²⁺ ions were complexed to the interior amines of G6-OH PAMAM dendrimers, and then the G6-OH(Pd²⁺)₁₄₇ complex was reduced with BH₄⁻ to yield G6-OH(Pd₁₄₇) DENs. Figure 5.1 provides UV-vis spectra of G6-OH(Pd²⁺)₁₄₇ and G6-OH(Pd₁₄₇) before and after dialysis. Prior to reduction, the G6-OH(Pd²⁺)₁₄₇ spectrum (black line) reveals a strong ligand-to-metal charge-transfer (LMCT) band centered at 224 nm, which confirms complexation of Pd²⁺ to G6-OH.⁸³ After reduction (G6-OH(Pd₁₄₇), red line), the sharp LMCT band is replaced by a broad absorbance characteristic of small metal nanoparticles.²³ TEM image analysis indicates that the Pd

DENs are 1.5 ± 0.3 nm in diameter (Figure 5.2), which is consistent with previous reports and the calculated size of 1.6 nm for cuboctahedral Pd clusters containing 147 atoms.⁹⁶ An XPS spectrum was obtained from undialyzed G6-OH(Pd₁₄₇) (Figure 5.3). The features present at 335.7 and 341.0 eV correspond to the 3d_{5/2} peaks of Pd(0), and the splitting between them (5.3 eV) is also consistent with zero-valent Pd (5.26 eV).^{99,100} That only these two peaks are observed confirms that Pd is primarily in the reduced form following the reduction step.

Dialysis of G6-OH(Pd₁₄₇). The main point of this paper is to compare the stability of Pd DENs in air-, N₂-, and H₂-saturated aqueous solutions both before and after dialysis. However, this requires that the nanoparticles remain stable during dialysis. Therefore, to prevent oxidation of Pd DENs during dialysis, the dialysis water was purged with H₂ for 30 min prior to and during dialysis. Additionally, the dialysis was carried out in a glove bag purged with H₂ gas.

Figure 5.1 compares UV-vis spectra obtained before and after the dialysis of 2.00 μ M G6-OH(Pd₁₄₇) in H₂-saturated water. That the red spectrum (before dialysis) and the green spectrum (after dialysis) are nearly identical indicates that the composition and concentration of the DENs are unchanged by the purification process. TEM size-distribution data (Figure 5.2) before and after dialysis are also consistent with this conclusion.

We confirmed that there is no detectable loss of Pd during dialysis by elemental analysis. Specifically, ICP-MS

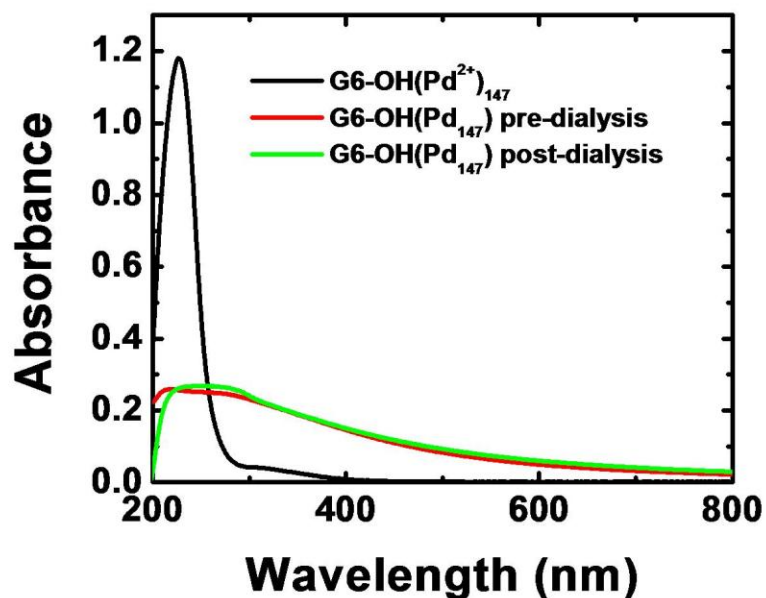


FIGURE 5.1. UV-vis absorbance spectra of aqueous 2.00 μM solutions of G6-OH(Pd₁₄₇) before and after reduction. The prominent band at 224 nm in the spectrum of G6-OH(Pd²⁺)₁₄₇ corresponds to the LMCT band associated with complexation between Pd²⁺ and the tertiary amines of the dendrimer.

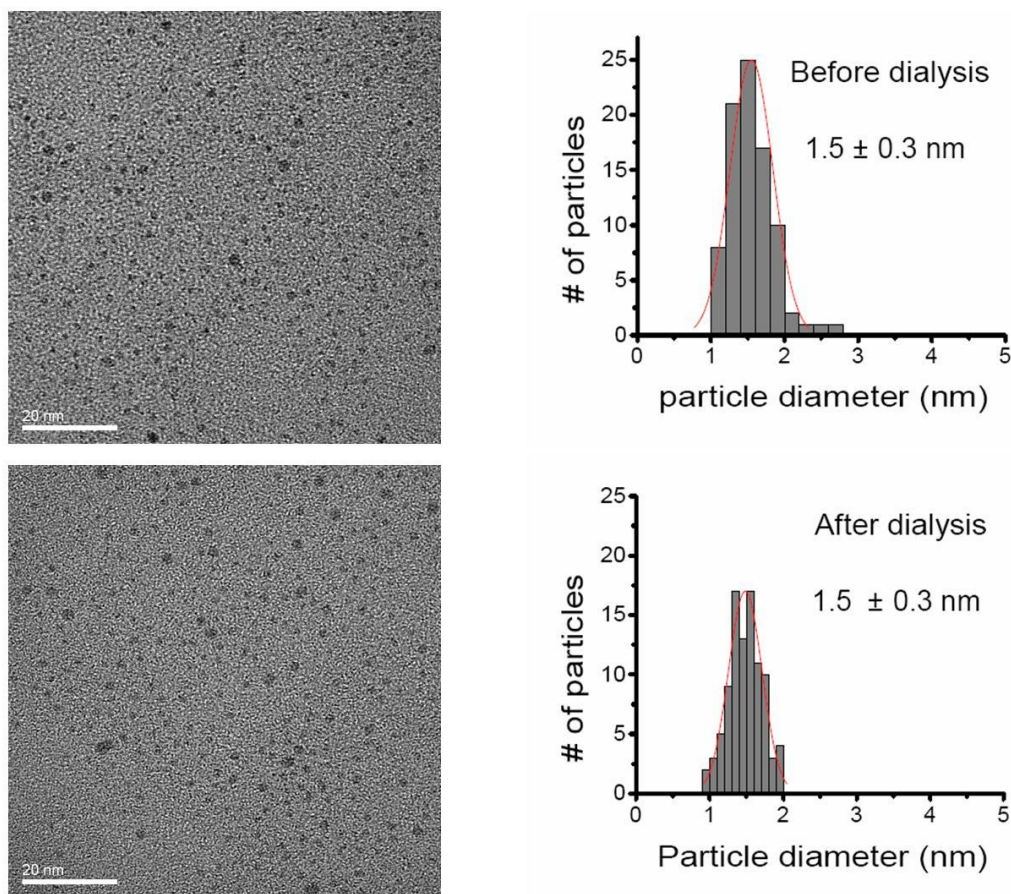


FIGURE 5.2. TEM images and size-distribution histograms for Pd DENs before and after dialysis. TEM grids were prepared as described in the experimental section. Particle diameters were measured manually using Digital Micrograph software and a histogram was constructed from the tabulated values of 100 particles using Microcal Origin.

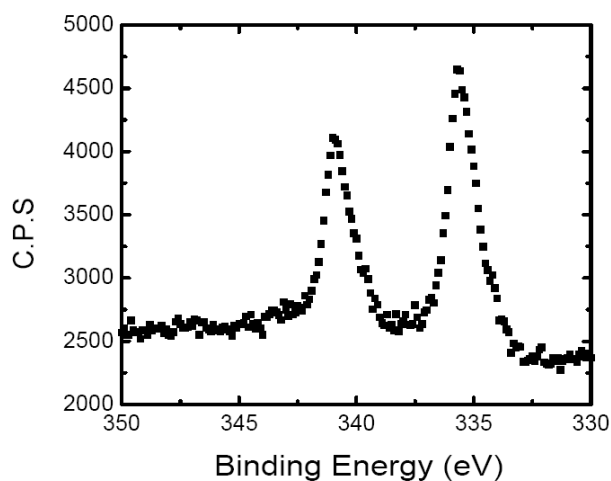


FIGURE 5.3. An X-ray photoelectron spectrrum (XPS) spectrum of freshly prepared G6-OH(Pd₁₄₇) DENs. The peaks at 335.7 and 341.0 eV correspond to the 3d_{5/2} peaks of Pd(0). XPS of freshly prepared 2.00 μ M G6-OH(Pd₁₄₇) was performed using a Kratos Axis Ultra DLD spectrometer having a monochromatic Al K α X-ray source. The spectrum was obtained in charge-compensation mode at a pass energy of 20 eV, a resolution of 0.1 eV, and a dwell time of 1.00 s. The samples were prepared by drop-casting a freshly prepared 2.00 μ M Pd DEN solution onto Au-coated Si wafers. The wafers were dried under vacuum. To correct for charging, peak locations were referenced to the most intense carbon peak, assumed to be the C-N bond of the dendrimer, which is present at 286.0 eV.^{99, 100}

analysis of DEN solutions obtained before and after dialysis yielded Pd concentrations of 291.7 μM and 293.8 μM , respectively. These values can be compared to 294 μM , which is the expected concentration of Pd in a 2.00 μM DEN solution. The error in the expected concentration was calculated by propagation of errors and found to be 1.3%, or 3.3 μM .

To ensure that dialysis removes Cl^- , and presumably other ions introduced to the DENs solution during synthesis, a simple, qualitative test for the presence of Cl^- was carried out. Specifically, an excess of Ag^+ in the form of an aqueous AgNO_3 solution was added to an aqueous $\text{G6-OH(Pd}_{147})$ solution before and after dialysis. Figure 5.4 shows that an easily detectable quantity of AgCl precipitate forms in the DENs solution prior to dialysis, but that no precipitate is observed after dialysis. If we assume that the maximum possible concentration of Cl^- initially present in solution is 1.18 mM (from K_2PdCl_4), then a simple equilibrium calculation suggests that the lowest concentration of Cl^- needed to generate a precipitate is 13.4 μM . This confirms that nearly 100% of the Cl^- is removed by dialysis.

UV-vis spectroscopic analysis of DEN stability. 2.00 μM $\text{G6-OH(Pd}_{147})$ aqueous DEN solutions were placed in vials and immediately sealed with septum caps after completion of the reduction and dialysis steps described in the previous sections. Next, water-saturated air, N_2 , or H_2 was bubbled into the vials via a syringe inserted through the septums



FIGURE 5.4. The results of the addition of AgNO_3 to solutions containing dialyzed DENs (left), undialyzed DENs (center), and the KCl control (right) are shown. The calculated concentration of Cl^- in undialyzed $2.0 \mu\text{M}$ $\text{G6-OH(Pd}_{147})$ DENs, introduced as K_2PdCl_4 in the starting material, is 1.18 mM . The KCl control contained 1.18 mM of KCl in water. A ten-fold excess of Ag^+ , with respect to this concentration of Cl^- , was added in the form of AgNO_3 to each solution. The minimum detectable amount of Cl^- was determined from the solubility product of AgCl as $13.4 \mu\text{M}$ using the following equilibrium equation, where K_{sp} is the solubility product for solid AgCl (1.8×10^{-10}).

for 12 h. Gas purging of the vials was performed with stirring and within a glove bag that was purged with N₂. Aliquots for spectroscopic analysis were periodically removed from the vials using a syringe.

Spectra of undialyzed G6-OH(Pd₁₄₇) DENs stirred in the presence of air are provided in Figure 5.5a. The initial spectrum ($t = 0$) is consistent with the red and green spectra in Figure 5.1 and confirms that the Pd DENs are initially completely reduced. After 1.0 h of exposure to air, peaks at 218 and 280 nm emerge. The sharp increase in the absorbance of the LMCT band at $\lambda_{\text{max}} = 218$ nm indicates partial oxidation of the encapsulated Pd DENs and subsequent recomplexation of Pd²⁺ to the interior tertiary amines of the G6-OH dendrimers (note that the exact position of the LMCT peak ranges from 218–224 nm due to convolution of the peak with the baseline). UV-vis measurements of the undialyzed G6-OH(Pd₁₄₇) solution at times ranging from 2.0 – 12.0 h indicate that the absorbance of the LMCT band continues to increase, while the continuum absorbance at longer wavelengths decreases. The latter is consistent with the presence of fewer or smaller DENs. Although it is difficult to judge the baseline underlying the LMCT peak, the percentage of oxidized Pd can be estimated from the spectroscopic data. For example, taking into account the rising baseline, the absorbance of the peak at 218 nm corresponding to 12.0 h of exposure to air is about 0.18. This can be compared to the absorbance of the same peak for the G6-OH(Pd²⁺)₁₄₇ precursor (black line, Figure 5.1) of 1.2,

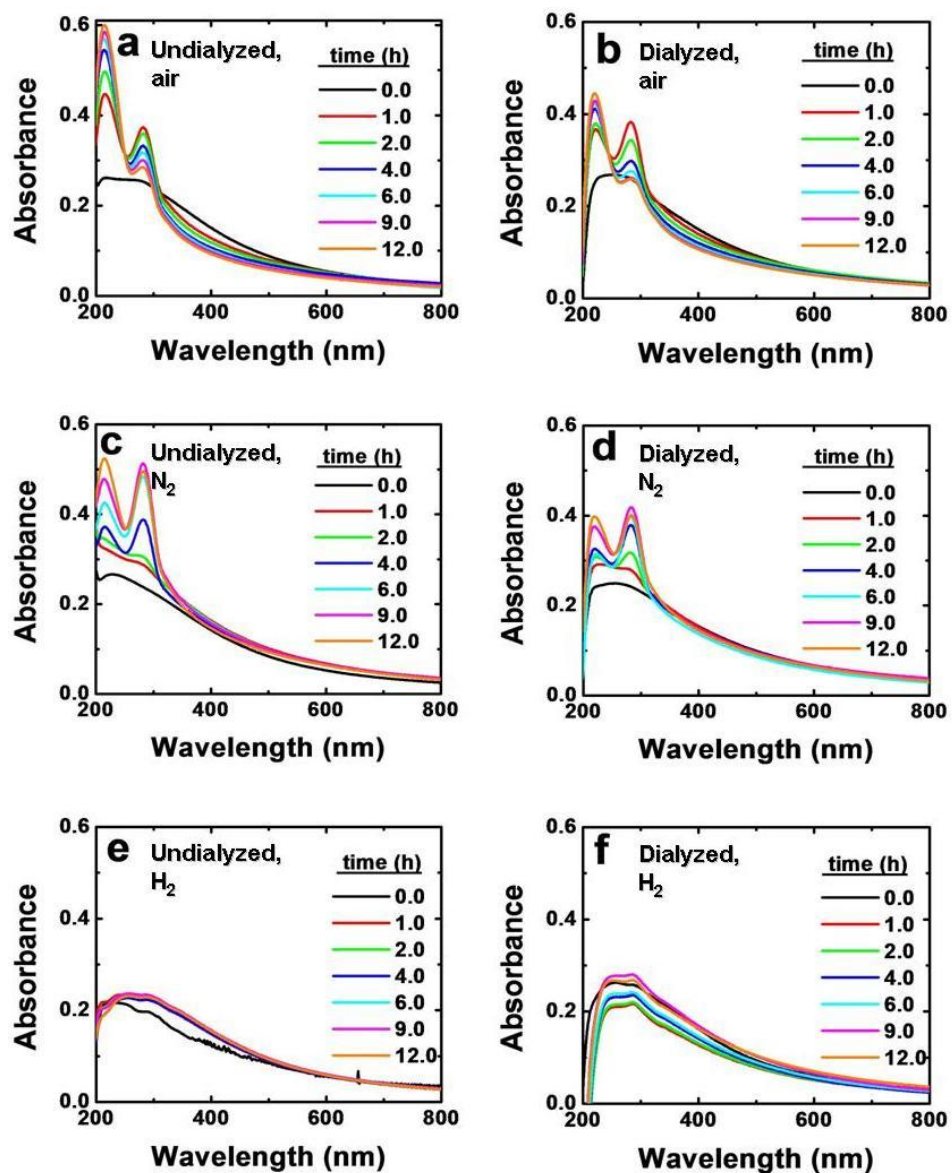


FIGURE 5.5. Time-resolved UV-vis absorbance spectra obtained before (left) and after (right) dialysis of G6-OH(Pd₁₄₇) DEN solutions. The aqueous DEN solutions were purged with: (a) and (b) air; (c) and (d) N₂; and (e) and (f) H₂.

which corresponds to the absorbance when 100% of the Pd is complexed to the dendrimer. To a first approximation, therefore, the extent of oxidation is about 15%.

Figure 5.6a is a plot of the absorbance of the LMCT band at $\lambda_{\text{max}} = 218 \text{ nm}$ vs. time that corresponds to the spectra in Figure 2a. It is clear that a significant amount of oxidation takes place initially, but that the rate slows at longer times. Two additional points merit mention. First, the origin of the peak at 280 nm is uncertain, but we⁹³ and others^{101, 102} have previously correlated it to partial degradation of PAMAM dendrimers. The presence of this peak is inconvenient because it complicates determination of the baseline for the LMCT band corresponding to the dendrimer-Pd complex, but otherwise it (and the species that it corresponds to) appears to be benign. Second, the LMCT band arises only from Pd^{2+} that is complexed to the dendrimer. However, it is possible that other Pd^{2+} species resulting from DEN oxidation, but which do not yield a distinct absorbance between 200 and 800 nm, are present in solution. This point will be discussed in more detail later, but for now it is only important to keep in mind that the LMCT peak corresponds to one particular type of Pd^{2+} .

Spectra G6-OH(Pd_{147}) DENs dialyzed under H_2 and then exposed to air for times up to 12.0 h are provided in Figure 5.5b. This family of spectra is quite similar to that just discussed (Figure 5.5a). Specifically, a LMCT band corresponding to oxidation of Pd DENs and subsequent

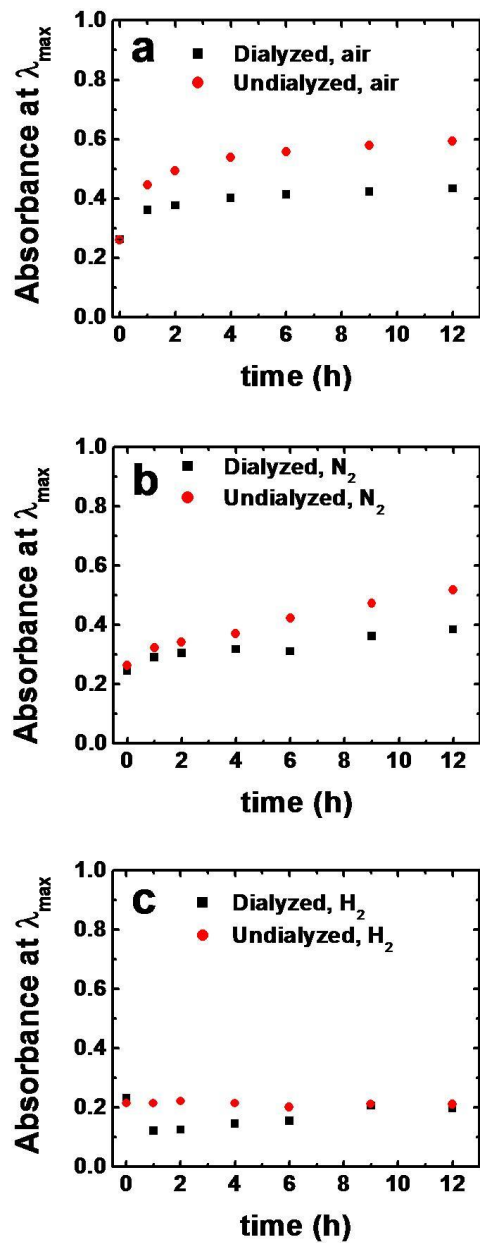


FIGURE 5.6. Absorbance of the LMCT band at $\lambda_{\max}$ vs. time for G6-OH(Pd₁₄₇) DENs purged with: (a) air; (b) N₂; and (c) H₂. Because of the convolution of this peak with the rising baseline, $\lambda_{\max}$ varied within the range 218 – 224 nm. recomplexation to the dendrimers is present at $\lambda_{\max} = 222$ nm.

This peak increases in magnitude as a function of time (Figure 5.6a), and the absorbances at longer wavelengths decrease. This result indicates that removal of Cl^- and other complexing ligands from the aqueous DEN solution does not fully stabilize the DENs against air oxidation. Note, however, that the magnitude of the LMCT band is smaller after dialysis, which indicates that reformation of $\text{G6-OH(Pd}^{2+})_n$ complex upon exposure to air is less extensive after the removal of coordinating anions. However, the presence of the dendrimer degradation peaks at 280 nm in parts a and b of Figure 5.5 makes it difficult to construct the baseline required to quantify the relative rates of $\text{G6-OH(Pd}^{2+})_n$ reformation.

Spectra of aqueous solutions of undialyzed and dialyzed $\text{G6-OH(Pd}_{147})$ stirred in the presence of N_2 are provided in Figure 5.5c and 5.5d, respectively. The trend is the same as that observed when the DENs are present in air-saturated water: growth of the LMCT band at $\lambda_{\text{max}} = 218$ and 223 nm for the undialyzed and dialyzed solutions, respectively. Because of the presence of the dendrimer degradation peak at 280 nm, it is not possible to quantitatively measure the rate of increase in these peaks, and hence the rate of DEN oxidation. However, the growth rate of this peak in the N_2 -saturated solutions (Figure 5.6b) appears qualitatively slower than in air-saturated water (Figure 5.6a). At this point in the study, it appears that the presence of O_2 is a contributing factor to the oxidation of Pd DENs, but that either water or the dendrimer itself can also serve as a

sufficiently powerful oxidant to convert Pd DENs to Pd²⁺ in the presence or absence of complexing ligands. Note, however, that unlike the spectroscopic results for air-saturated Pd DEN solutions there is no measurable decrease in the absorbance of the N₂-saturated DENs solutions at wavelengths >350 nm. We will have more to say about the stability of Pd DENs exposed to N₂-saturated water later.

The spectra of undialyzed and dialyzed aqueous solutions of G6-OH(Pd₁₄₇) exposed to H₂ are shown in Figures 5.5e and 5.5f, respectively, and the evolution of the LMCT band at $\lambda_{\text{max}} = 224$ nm as a function of time is provided in Figure 5.6c. There are clear differences between these spectra and those obtained from Pd DENs in air- and N₂-saturated water. First, the LMCT band is absent in all of these spectra, indicating no detectable oxidation of Pd. Recall, however, that this band only correlates to Pd²⁺ that is complexed to the tertiary amines of the dendrimer. Pd that is oxidized, but not recomplexed to the dendrimer, will not be observed spectroscopically. However, we will show later that there is no evidence for any form of Pd in these solutions other than as Pd DENs. Also notice that the peak at 280 nm, which we tentatively assign to a degradation product of the dendrimer is also absent in the presence of H₂. This observation suggests that the 280 nm peak might be correlated to an oxidizable intermediate species of Pd or to an unidentified byproduct. Taken together, the results shown in Figures 5.5 and 5.6 indicate that the presence of a H₂ eliminates the conversion of G6-OH(Pd₁₄₇) to dendrimers

encapsulating both zerovalent Pd and Pd^{2+} ($\text{G6-OH}(\text{Pd}_{147-n}\text{Pd}_n^{2+})$), but that when H_2 is absent, as is the case in the presence of O_2 and even N_2 , mixed valence materials are resultant. We conclude that the degradation of the zero-valent Pd DENs in the air and in O_2 -free N_2 is due to corrosion of a galvanic nature. To maintain charge balance, something in solution must become reduced in order for Pd to become oxidized to Pd^{2+} as was observed in Figure 5.5 a-b and 5.6 a-b. It makes the most sense that the galvanic half-cell reaction which is coupled to the Pd oxidation half-cell would have to be the autocatalytic reduction of protons to form H_2 gas. Thus, when the Pd DENs solutions are saturated with H_2 , one of the half-cell reactions, the reduction of protons to H_2 , is blocked and this precludes the other half cell reaction, Pd oxidation, from occurring.

In the next section we explore the presence of forms of Pd^{2+} that might be present in the solution outside of the dendrimer. That is, forms of Pd^{2+} other than $\text{G6-OH}(\text{Pd}_{147-n}\text{Pd}_n^{2+})$.

Centrifugal filtration and analysis of $\text{G6-OH}(\text{Pd}^{2+})_{147}$ solutions. The just-discussed spectroscopic study indicates that a fraction of the atoms in Pd DENs oxidize and recomplex with the dendrimer unless they are maintained within a H_2 saturated environment. However, these data do not provide information about the fate of Pd species that escape from the dendrimer and into the solution. Accordingly, we devised the following experiment to separate and quantify leached Pd (in any form) from Pd^{2+} bound to the

dendrimer. Specifically, centrifugal filtration membranes, which are designed to retain solutes having masses greater than 10 kDa, were used to separate the G6-OH dendrimers (MW = 58.3 kDa), and any forms of Pd they contain, from all forms of solution-phase Pd. The filtrates resulting from these experiments were then analyzed for Pd by ICP-MS.

The viability of this approach was confirmed by the following control experiment. We know from prior experience that air-saturated, aqueous $\text{G6-OH(Pd}^{2+}\text{)}_{147}$ solutions are highly stable, even after long-term dialysis against pure water. Accordingly, we prepared a 2.00 μM solution of $\text{G6-OH(Pd}^{2+}\text{)}_{147}$, immediately filtered a portion of it, and then analyzed the filtrate for Pd by ICP-MS. A second aliquot of this solution was stirred in air-saturated water for 12.0 h, filtered, and analyzed for Pd. These experiments were carried out in triplicate. The average concentration of Pd recovered from these six experiments was $5.5 \pm 1.7 \mu\text{M}$, which can be compared to the 294 μM initial concentration of Pd^{2+} present in the 2.00 μM solution of $\text{G6-OH(Pd}^{2+}\text{)}_{147}$.

We draw several conclusions from this experiment. First, because just under 2% of the Pd initially present in the $\text{G6-OH(Pd}^{2+}\text{)}_{147}$ solution passes into the filtrate, it is clear that the dendrimer, and any Pd it carries, is retained by the filter. Second, the amount of Pd in the filtrates of the aged solutions was no higher than in those that were freshly prepared. Accordingly, it seems likely that the small amount of Pd found in the filtrate was not initially

complexed by the dendrimer. Third, dendrimer fragments, resulting from degradation reactions of the type that might be responsible for the peak at 280 nm (Figure 5.5) and that are small enough to pass through the filter, are apparently not present to a significant degree. Fourth, Pd^{2+} that forms and recomplexes with the dendrimer after exposure of the DENs to air- or N_2 -saturated water is strongly retained within the dendrimer. Fifth, the filtration process itself does not destabilize the dendrimers and cause them to release Pd.

Centrifugal filtration and analysis of $\text{G6-OH}(\text{Pd}_{147})$ solutions. Experiments intended to quantify the extent of leaching from $\text{G6-OH}(\text{Pd}_{147})$ DENs were carried out as follows. First, triplicate 1.00 mL aliquots were obtained from the same dialyzed and undialyzed 2.00 μM $\text{G6-OH}(\text{Pd}_{147})$ solutions used to obtain the spectroscopic data shown in Figures 5.5 and 5.6. Second, these samples were filtered to separate the parent DENs from their solutions. Third, the filtrates were analyzed by ICP-MS to determine the extent of Pd leaching from the dendrimers. The results from these experiments are plotted in Figure 5.7. Figure 5.7a is a plot of the concentration of leached Pd found in the filtrates of dialyzed and undialyzed aqueous 2.00 μM $\text{G6-OH}(\text{Pd}_{147})$ solutions that were air-saturated for times ranging up to 12.0 h. The key points derived from these data are as follows. First, there is a higher extent of leaching in the undialyzed DEN solutions. Second, leaching is rather rapid initially and then it slows.

However, it is not clear from these results whether or not the extent of leaching achieves equilibrium after 12.0 h. Third, the concentration of leached Pd is surprisingly small. After 12.0 h, the percentages of leached Pd are 6.2% and 4.0% for the undialyzed and dialyzed DENs, respectively. These values can be compared to ~2.0%, which is the percentage of Pd passing into the filtrate in the control experiments described in the previous section. Similar conclusions can be drawn from the results presented for the Pd DENs exposed to N₂-saturated aqueous solutions (Figures 5.7b), except here the extent of leaching is lower: 5.3% and 2.0% for the undialyzed and dialyzed DENs, respectively. The results obtained for leaching in the H₂-saturated aqueous solutions are quite different, however. Whether the solutions were dialyzed or not, the amount of Pd found in the filtrates of these solutions was considerably less than 2.0% of the original concentration of Pd in the G6-OH(Pd₁₄₇) DENs. We conclude that Pd DENs kept under H₂ are fully stable.

5.4. Summary and Conclusions

This study was prompted by numerous recent findings suggesting that reactions thought to be catalyzed by Pd nanoparticles may actually be catalyzed by nanoparticle fragments or oxidation products.^{85, 86} Accordingly, we sought to learn more about the stability of Pd DENs in oxidizing (air), inert (N₂), and reducing (H₂) aqueous environments. The results indicate that in air- and N₂-saturated aqueous

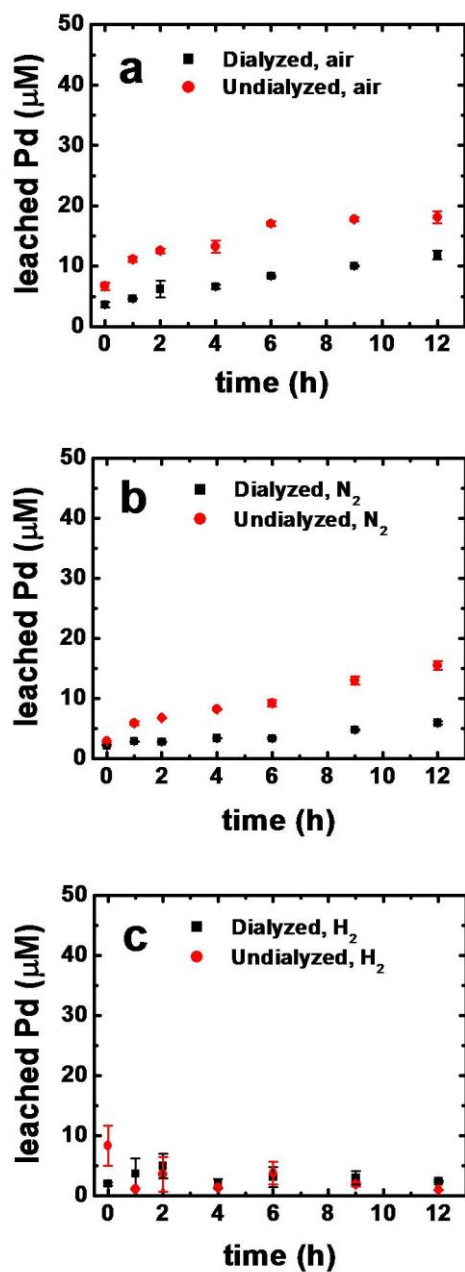


FIGURE 5.7. Plots of the concentration of leached Pd in filtered aqueous solutions vs. time. The G6-OH(Pd₁₄₇) DENs solutions were purged with: (a) air; (b) N₂; and (c) H₂.

solutions DENs are not fully stable. In the worst case (undialyzed, air-saturated), about 15% of the Pd atoms in a 147-atom DEN oxidize and recomplex with the dendrimer after 12.0 h. A smaller percentage (up to ~6%) of Pd escapes from the dendrimer and is found in the surrounding aqueous solution. At present we do not know the form of these extra-dendrimer species. In the best case (dialyzed, N₂-saturated), < ~4% of the Pd atoms oxidize and recomplex with the dendrimer after 12.0 h and about 2% is found in the aqueous solution. Pd DENs are fully stable in H₂-saturated aqueous solution.

The underlying reason for the oxidative instability of Pd nanoparticles likely relates to their oxidation potentials being shifted negative compared to bulk Pd. It seems likely that the observed decreased stability of Pd DENs in the presence of complexing ligands has the same origin: a ligand-induced negative shift in the oxidation potential of the metal. To the best of our knowledge these size-dependent redox potentials have not been determined, but clearly such measurements would be of tremendous value. Importantly, the redox potentials of nanoparticles are intrinsic, and therefore these size-dependent shifts may provide a significant barrier to the use of DENs and related nanoparticles for certain types of catalyses.

Summary and Outlook

This dissertation described the development of Cu underpotential deposition (UPD) on dendrimer-encapsulated nanoparticles (DENs) as a synthetic route to core@shell Pt@Cu DENs and as a characterization tool for the assessment of surface morphology and quantitative analysis of composition. The UPD of Cu onto Pt DENs was shown to result in nanoparticles having the core@shell configuration, and the selectivity of Cu for particular crystallographic facets on Pt DENs was also demonstrated. In short, by controlling the electrode potential, the site-specific decoration of the surface of a Pt DEN with a Cu shell is achieved.

Prior to these studies, very little was understood about the surface structure of DENs. Due to their small size and the presence of the dendrimer, the surface of DENs cannot be accessed by conventional characterization techniques for studying surface structure, such as scanning probe methods. This dissertation shows that UPD can be used as a probe for the surface morphology of DENs. Perhaps the most remarkable finding reported here is that Cu UPD onto Pt DENs containing as few as 147 atoms provides evidence of faceting of a faceted surface morphology.

The nanoparticles prepared by Cu UPD onto Pt DENs have structures that are consistent with models in which the shell metal decorates only the planar facets but not the edges or corners that adjoin the facets. One can envision

that these DENs could be used as bifunctional nanoparticle catalysts, in which different steps of the reaction are carried out on separate and well defined regions of the nanoparticle. To the best of our knowledge, core@shell DENs prepared by the methods laid out in this dissertation^{29, 51} are the first example of this unique structure.

Some preliminary calculations performed on Pt@Cu DENs show that these nanoparticles could be active catalysts for the oxidation of CO to CO₂. The model of CO oxidation on Pt@Cu DENs show that the substrates, CO and O₂ molecules, bind to different regions of the Pt@Cu surface. CO molecules bind to the partially exposed Pt atoms along the edges and corners, while O₂ molecules prefer the Cu shell atop the facets, therefore, the 2 substrates would not be competing for space to adsorb onto the catalyst surface.

It remains to be seen if Pt@Cu DENs will be stable during the catalysis of the CO oxidation reaction. The Cu shell is only stable within a limited potential window: the Cu begins to strip away from the Pt core at potentials positive of 0.2 V. Preliminary calculations predict the Cu shell will be stable during CO oxidation. However, it remains to be seen whether interactions of solvent or adsorbate molecules with the surface of the nanoparticle will change the stability of the Pt@Cu DENs during the reaction. Using calculations from density functional theory, we showed that adsorbed solvent molecules play a significant role in the stability of the Cu shell. Because we know that that solvent and adsorbate interactions, as well as

nanoscale effects such as the size of the crystal domains on the electrode can influence the stability of UPD monolayers, it will be an interesting and worthwhile to determine whether Pt@Cu DENs are stable during the catalysis of CO oxidation. If they are stable, the kinetics of the CO oxidation reaction on Pt@Cu DENs can be studied and compared to computational studies.

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