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Controlling the Growth and Catalytic Activity of Platinum Nanoparticles Using Peptide and Polymer Ligands

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Controlling the Growth and Catalytic Activity of Platinum Nanoparticles Using Peptide and Polymer Ligands

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Chemistry

by

Lauren Marie Forbes

Committee in charge:

Professor Jennifer Cha, Chair
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2013
The Dissertation of Lauren Marie Forbes is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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University of California, San Diego
2013
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ABSTRACT OF THE DISSERTATION

Controlling the Growth and Catalytic Activity of Platinum Nanoparticles Using Peptide and Polymer Ligands

by

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Doctor of Philosophy in Chemistry

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Professor Jennifer Cha, Chair
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Heterogeneous catalysts have widespread industrial applications. Platinum nanomaterials in particular, due to their particularly high electrocatalytic activity and durability, are used to catalyze a wide variety of reactions, including oxygen reduction, which is frequently used as the cathode reaction in fuel cells. As platinum is a very expensive material, a high priority in fuel cell research is the exploration of less expensive, more efficient catalysts for the oxygen reduction reaction (ORR).
We demonstrate here the use of phage display to identify peptides that bind to Pt (100) which were then used to synthesize platinum cubes in solution. However, while the peptides were able to control particle growth, the bio-synthesized Pt particles showed extremely poor activity when tested for ORR. This could be attributed to peptide coverage on the surface or strong interactions between particular amino acids and the metal that are detrimental for catalysis. To investigate this further, we decided to investigate the role of individual amino acids on Pt nanocrystal synthesis and catalysis. For this, we conjugated the R-groups of single amino acids to polyethylene glycol (PEG) chains. Through this work we have determined that the identity of the amino acid R-group is important in both the synthesis and the catalytic activity of the particles. For Pt nanoparticle synthesis, we found that the hydrophobicity of the functional groups affected their ability to interact well with the particles during nucleation and growth, and thus only the hydrophilic functional groups were capable of mediating the synthesis to produce well-defined faceted particles. With respect to ORR, we found distinct trends that showed that the inclusion of certain amino acids could significantly enhance catalysis- even at high polymer loadings. This work presents evidence that counters the common conception that organic capping ligands decrease catalytic activity; in fact activity may actually be improved over bare metal through judicious choice and design of ligands that inhibit Pt oxidation and control chain packing at the Pt surface. Therefore, it may be possible to have ligands on a nanoparticle surface that allow the particles to be well-dispersed on an electrode surface, while simultaneously enhancing catalysis.
CHAPTER 1

Introduction

Fuel cells are electrochemical cells that convert chemical energy stored in fuels to electrical energy. They are advantageous because they can be portable, they are more energy efficient than combustion engines, produce fewer emissions, and they can utilize a wide variety of fuels.\(^1\) One type of fuel cell that is promising is the proton exchange membrane fuel cell or PEMFC. They operate at lower temperature and pressure ranges (50-100°C) than many other types of fuel cells, they can be used as stationary or portable power devices, and they utilize small molecules such as hydrogen, methanol, and formic acid as fuels.\(^2\) In a typical PEMFC oxygen flows through the cathode and is electrochemically reduced while fuel molecules are oxidized at the anode. However, fuel cells are currently too expensive to compete with traditional combustion engines.\(^1-6\) One of the biggest costs involved is the catalyst as the current standard for the cathode catalyst is platinum on carbon (Pt/C). Therefore much research is focused on producing a less expensive, more efficient catalyst for the oxygen reduction reaction (ORR) that occurs at the cathode.

In order to both speed up ORR sufficiently so that it can be used in fuel cells, as it is very slow, and to maximize the reaction efficiency we must look at the conditions at the cathode. The reaction kinetics and the mechanism are very dependent on the nature of the electrode material, the catalyst, and the electrolyte. For maximum energy production, we want a system in which oxygen reduction occurs at a potential
as close as possible to the thermodynamic electrode potential, with high current density and a relatively fast reaction rate.

The potential difference, in volts, between the thermodynamic reduction potential and the potential at which the reduction actually occurs for a half-reaction is known as the overpotential. For an electrolytic cell, such as a fuel cell, this results in a reduced energy output, thus we want to create a cathode with a minimal overpotential. There are five major types of overpotentials for a half-reaction which can be manipulated to reduce the overall overpotential: activation, concentration, resistance. The activation overpotential relates to the activation energy of the reaction, which may include potential reactions that have to occur before electron transfer can occur. The concentration overpotential is due to the depletion of charge-carriers at the surface which can occur under conditions such as slow diffusion or the evolution of a gas that blocks the surface. The resistance overpotential is related to the electrolytic resistivity of the cell due to factors such as electrolyte diffusion and surface polarization. When performing electrochemical experiments to determine the overpotential of a system, we look at the peak potential, which is the potential at which the current is highest (peak current), and the half-wave potential, which is the potential at which the current is equal to one-half the limiting current. The limiting current is the peak current minus the residual current.

Another important measurement in determining the efficiency of a catalyst is mass activity. Mass activity is a measure of the current density of the system per unit of mass. It can be altered by either increasing the surface area of the catalyst and thus
decreasing the mass required to produce a particular current density, or by altering the nature of the cell so that the reaction kinetics are sped up, thereby increasing the current density. The reaction kinetics are dependent on the nature of the reactants, their physical states and concentrations, the temperature, the pressure, and the addition and properties of a catalyst.

The relationship between the current at the electrode and the overpotential of ORR is given by the current-overpotential equation:

\[ I_c = i_{O_2}^0 \left( e^{n_{aO}a_OF\eta_c/RT} - e^{n_{aO}(1-a_O)F\eta_c/RT} \right) \]

where \( I_c \) is the ORR current density, \( i_{O_2}^0 \) is the exchange current density, \( n_{aO} \) is the number of electrons transferred in the rate determining step, \( a_O \) is the electron transfer coefficient, \( \eta_c \) is the overpotential of ORR, \( F \) is the Faraday constant, \( R \) is the ideal gas constant, and \( T \) is the temperature in Kelvin. The exchange current density or background current is defined as the current at zero overpotential. It signifies the intrinsic rates of electron transfer between the analyte and the electrode, and is dependent on the nature of the electrode, the analyte and the electrolyte. The exchange current density represents the reaction rate at equilibrium. For an electrochemical reaction at equilibrium, the rate of the forward reaction is the same as that of the backward reaction, so the net current density of the reaction is zero. The rate of an electrochemical reaction is dependent on the magnitude of the exchange current density. Since we want a system with a high current at a low overpotential, we want the exchange current density to be large, or the factor \( \frac{RT}{a_O n_{aO} F} \) should be small, and
since R, T, and F are constants, we want the product $a_0n_{\text{rt}}$ to be large. The electron transfer coefficient ($a_0$) is linearly dependent on temperature for ORR on Pt, so raising the temperature can increase it. The number of electrons transferred in the rate determining step ($n_{\text{rt}}$) in ORR is highly dependent on the catalyst surface and the nature of the electrolyte.\textsuperscript{7}

In this work we perform our electrochemical measurements using a rotating disk electrode (RDE). A rotating disk electrode is a disk electrode which is rotated at a constant angular velocity ($\omega$) around an axis perpendicular to the disk surface. The rotation of the electrode creates a steady flow of fresh solution over the electrode surface, which is advantageous as it decreases the dependence of the current density on the diffusion rate of the analyte. Under laminar flow conditions the thickness of the diffusion layer is dependent on the electrode angular velocity as

$$\delta = 1.61D^{1/3} \omega^{-1/2}v^{1/6}$$

where $\delta$ is the diffusion layer thickness, $D$ is the diffusion coefficient, $\omega$ is the electrode angular velocity, and $v$ is the kinematic velocity which is equal to the viscosity of the solution divided by the density in cm$^2$/s. Therefore the limiting current $(i_l)$ for a reversible system is given by the Levich equation:

$$i_l = 0.62nFAD^{2/3} \omega^{1/2}v^{-1/6}C$$

where $F$ is the Faraday constant, $A$ is the electrode area and $C$ is the concentration of the dissolved analyte. The disk current density is dependent on the limiting current density as given by the Koutecky-Levich equation:
\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l}
\]

where \(i\) is the disk current density, \(i_k\) is the kinetic current density, and \(i_l\) is the limiting current density. Plotting \(\frac{1}{i_l}\) vs \(\frac{1}{\omega^{1/2}}\) gives a linear graph where the y-intercept is equal to \(\frac{1}{i}\). Dividing \(i\) by the mass of the catalyst on the electrode surface results in the mass activity.\(^8\)

The mechanism for oxygen reduction on Pt has been the most extensively studied of oxygen reduction catalysts. While the details of the reaction are complicated and still being investigated, a simplified diagram is presented in Scheme 1.1.

\[\text{Scheme 1.1. Simplified mechanism for ORR on a Pt catalyst}\]

ORR on Pt is typically a 4-electron process resulting in the generation of water in both acidic and alkaline electrolytes as long as there are no impurities. This reaction can occur either by a direct reduction of \(O_2\) to \(H_2O\) or through two 2-electron steps with \(H_2O_2\) as the intermediate. The reaction can also stop after the first 2-electron transfer with the creation of \(H_2O_2\) which can then desorb off the catalyst surface. Two main
mechanisms, the dissociative mechanism and the associative mechanism, have been proposed for different current densities. The dissociative mechanism for ORR on Pt is considered most likely to occur at low current densities.

\[
\frac{1}{2} O_2 \rightarrow O^{ad}
\]

\[
O^{ad} + H^+ + e^- \rightarrow OH^{ad}
\]

\[
OH^{ad} + H^+ + e^- \rightarrow H_2O
\]

In this mechanism O\(_2\) is adsorbed to an active site on the Pt surface and the bond between the O atoms is broken. The Pt then transfers two electrons to the adsorbed oxygen atom which picks up 2 protons from the surrounding electrolyte, forming water. Hydrogen peroxide is not formed since the oxygen bond is broken before reduction occurs. This process is equivalent to the direct 4 electron pathway. The associative mechanism for ORR on Pt is proposed to happen at high current densities.

\[
O_2 \rightarrow O_2^{ad}
\]

\[
O_2^{ad} + H^+ + e^- \rightarrow HO_2^{ad}
\]

\[
O_2^{ad} + H^+ + e^- \rightarrow H_2O + O^{ad}
\]

\[
O^{ad} + H^+ + e^- \rightarrow OH^{ad}
\]

\[
OH^{ad} + H^+ + e^- \rightarrow H_2O
\]
Although \( \text{H}_2\text{O}_2 \) is not present in this mechanism, it is possible for the \( \text{O}_2 \) bond to not be broken after the second step, creating \( \text{H}_2\text{O}_2 \), which can then be further reduced to water or desorb from the surface. This mechanism is possible for the pathway involving 2 successive 2-electron processes.\(^7\)

Unfortunately, the electrode surface also typically undergoes oxidation to form PtO under reaction conditions, since ORR must be run at high potential.

\[
\text{Pt} + \frac{1}{2} \text{O}_2 \rightarrow \text{PtO}
\]

As the potential is raised the surface becomes increasingly oxidized to PtO. This serves to increase the overpotential through the oxidation at the cathode and reduces the current density due to the reduction in the number of active sites available to oxygen. As the surface composition changes, so does the reaction kinetics, indicating that the ORR mechanism is most likely different on PtO/Pt than on pure Pt.

Platinum on carbon is the current standard for catalyzing ORR in fuel cells.\(^4\) It is a very catalytically active material and is resistant to corrosion.\(^9\) Unfortunately, platinum is also very expensive, so in order to decrease the costs associated with this catalyst we want to improve the efficiency and decrease the amount of platinum required. Current carbon-supported platinum catalysts do not exhibit any control over particle morphology and so research has typically focused on creating small, monodisperse, shape-controlled particles in order to accomplish this. The size is important to maximize the surface area and minimize Pt mass to reduce costs.\(^10\) Additionally, the size of the Pt particles is important as it can affect the catalytic
activity of the Pt. The shape of the particles can have a significant effect on both the reactivity of the particles and the selectivity toward specific reactions.\textsuperscript{11,12}

Many factors affect the size and shape of Pt nanoparticles. In a typical solution phase process to produce Pt nanoparticles, Pt ions are first reduced to zero-valent metal atoms. Multiple atoms combine to produce small, thermodynamically unstable nuclei. The nuclei either continue to grow and become stable or dissolve back into solution. The excess free energy of the nucleus is

$$
\Delta G_r = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v = 4\pi r^2 \gamma - \frac{4}{3} \pi r^3 \frac{RT \ln S}{V_m}
$$

where

$$
S = \frac{[A]_s}{[A]_{eq}}
$$

where $r$ is the radius of the clusters, $\gamma$ is the surface free energy per unit area, $R$ is the ideal gas constant, $\Delta G_v$ is the change of free energy between solute atoms in solution and in the bulk crystal per unit volume, $T$ is the temperature in Kelvin, $V_m$ is the molar volume of the bulk crystal, and $S$ is the ratio between solute concentrations at saturation $[A]_s$ and at equilibrium $[A]_{eq}$ conditions. When the nuclei reach a critical radius ($r^*$) or overcome a critical free energy barrier ($\Delta G^*$) they become thermodynamically stable. Based on that equation, the number of clusters ($N_r$) can be expressed as a function of radius $r$:

$$
N_r = N_0 e^{-\left(\frac{\Delta G^*}{RT}\right)} = N_A [A]_{eq} S e^{-\left(\frac{\Delta G^*}{RT}\right)}
$$
where $N_0$ is the total number of free solute atoms per unit volume in the system and $N_A$ is Avogadro’s number. So the number of clusters decreases exponentially with increases in the excess free energy $\Delta G_r$.

If $S \leq 1$, the solute is under saturated, $\Delta G_r$ is positive and increases with the growth of nuclei, therefore nucleation is unfavorable. When the solute is supersaturated, $S > 1$, $\Delta G_r$ decreases with the increase in nucleus radius and nuclei become more stable as they grow. When the radius is smaller than a critical value, the free energy of the system is lowered by the nuclei dissolving. The total number of nuclei follows Boltzmann’s distribution and decreases rapidly with the increase of nucleus radius. When nucleus size is greater than the critical radius, free energy is lowered thru nucleus growth. The nucleation rate \( \left( \frac{dN_r}{dt} \right) \) can be determined by

$$r^* = -\frac{2\gamma}{\Delta G_r} = \frac{2\gamma V_m}{RT \ln S}$$

$$\Delta G^* = \frac{16\pi \gamma^3}{3\Delta G_r^2} = \frac{16\pi \gamma^3 V_m^2}{3(RT \ln S)^2}$$

$$N_{r^*} = N_A[A]_{eq} Se^{\left( \frac{-\Delta G^*}{RT} \right)}$$

$$N_{r^*} = N_A[A]_{eq} Se^{\left( \frac{-16\pi \gamma^3 V_m^2}{3(RT)^4(lnS)^2} \right)}$$

$$\frac{dN_{r^*}}{dt} = f_0 N_A[A]_{eq} Se^{\left( \frac{-\Delta G^*}{RT} \right)}$$

$$\frac{dN_{r^*}}{dt} = f_0 N_A[A]_{eq} Se^{\left( \frac{-16\pi \gamma^3 V_m^2}{3(RT)^3(lnS)^2} \right)}$$
where $f_0$ is the ratio of the number of nuclei with critical radius over the total number of nuclei.\textsuperscript{10} The smaller the critical radius and the critical excess free energy, the easier it is to form nuclei. Important parameters that affect nucleation are the surface free energy ($\gamma$), reaction temperature ($T$), and degree of supersaturation ($S$). A large surface free energy leads to a big critical radius, a high free energy, difficulty with nucleation, and a small number of particles. In order to overcome these limitations a high temp and very supersaturated solution can be used. The degree of supersaturation changes throughout the reaction and is a function of the reaction time as seen in LaMer’s plot in Figure 1.1. The separation of the nucleation and growth phases is very important in producing monodisperse, monomorphic nanoparticles. This is frequently accomplished by a very fast reduction of the ions in solution, followed by a slower growth period.\textsuperscript{13}

Figure 1.1. The LaMer mechanism of the nucleation of sulfur showing sulfur concentration as a function of time. Adapted from Ref. [11]
Particle shape is controlled by thermodynamic and kinetic factors which are dictated by intrinsic structural properties of Pt and the reaction systems such as the solvent, capping ligands, and reducing agent. Metal nanoparticles capped by low-index facets to minimize surface energy and total free excess energy. Varying the reaction conditions such as concentration, time, temperature, Pt precursors, reducing agents, and capping ligands can all have a dramatic effect on the size and shape of the particles produced. Some common precursors used in Pt nanoparticle synthesis are hexachloroplatinic acid (H₂PtCl₆), potassium hexachloroplatinate (K₂PtCl₆), potassium tetrachloroplatinate (K₂PtCl₄), and platinum acetylacetonate (Pt(acac)₂). Some common reducing agents used are sodium borohydride (NaBH₄), hydrazine (NH₂NH₂), hydrogen (H₂), citrate, ascorbic acid, heat, polyols, and diols. Pt nanoparticle syntheses can be run in aqueous or non-aqueous solutions. Additionally, using one of many different capping ligands can affect the shape control of the particles. When selecting a ligand for shape-controlled particle synthesis we want the ligands to adsorb to specific facets. Shape control by ligands is accomplished by promoting or inhibiting growth in a specific direction to preserve that crystal facet. Capping agents adsorb selectively due to the different electronic structures and atomic arrangements of different surfaces, making it easier for atoms to add to unprotected surface and increasing growth in that direction. Surfactants, polymers and other organic capping agents largely work by preventing the Pt nuclei from coming in contact with each other thereby stabilizing them. Adsorption of these ligands also decreases the total excess free energy by preventing direct contact between high
energy surfaces of Pt though steric hindrance. This helps to prevent further growth and Ostwald ripening.

The initial study demonstrating shape control over Pt nanoparticles was done by El-Sayed and coworkers\textsuperscript{14,15}. They were able to make cubic and tetrahedral Pt nanoparticles using acrylic acid and polyacrylate at different concentrations. The speed of reduction can also be used to obtain different shaped Pt nanoparticles using the same ligand. One ligand that is commonly used in nanoparticle synthesis is the surfactant cetyltrimethylammonium bromide (CTAB). It adsorbs preferentially to (100) plane of the growing nanocrystals and thus can be used to make cubic, cuboctahedral, and porous Pt particles by varying the reduction rate.\textsuperscript{16,17} Slower reduction (NaBH\textsubscript{4} in alkaline conditions) resulted in cubes, faster reduction (NaBH\textsubscript{4} in acidic conditions) resulted in cuboctahedral particles and ascorbic acid lead to weak reduction which resulted in porous particles. Other ligands which are frequently used in Pt particle synthesis in organic solvents are oleic acid and oleylamine, which can be used to make cubes\textsuperscript{18-20}, tripods, octapods\textsuperscript{21}, rods\textsuperscript{22}, and several other shapes. When choosing a ligand to use, nitrogen is often a preferred functional group because of its favorable interactions with Pt.\textsuperscript{23-25} Additionally, inorganic ions and small molecules are also sometimes used as they can also preferentially adsorb to specific surfaces, and therefore can promote or inhibit growth. For example, Ag species adsorb preferentially on (100) vs. (111), altering their growth rates, so that cubes, cuboctahedra and octahedra have been made with Ag.\textsuperscript{26-28} Pt nanowires have been prepared using trace amounts of Fe(II) and Fe(III) which affect the reduction rates of Pt(IV).\textsuperscript{29-31} The
reduction rate is important as it relates to the separation of nucleation and growth phases, and may prevent the capping agents from working well if it is too fast.\textsuperscript{32}

The shape of the particles determines the facets present on the surface which in turn strongly effects molecular binding on the surface affecting the activity and selectivity of the particles toward specific reactions. For face centered cubic (fcc) Pt crystals, the lowest energy facets are (111), (110), and (100). Certain facets of fcc Pt are known to be more active than others for ORR, although this depends on the electrolyte used as well. In perchloric acid, the activity difference between the different faces is small and increases in the order (100)<(110)<(111). In KOH, the differences are larger but the activity increases in the same order, (100)<(110)<(111). The differences in activity between the facets is even more pronounced in sulfuric acid, and the order is different than in the other electrolytes, (111)<(100)<(110). The differences in activity of the facets in perchloric acid and KOH are likely due to the inhibiting effect of OH\textsubscript{ad}, which is more pronounced on (100) than on (111). In sulfuric acid, the differences largely arise from ability of the sulfate and bisulfate ions to adsorb to the (111) surface, poisoning it.\textsuperscript{33}

Since the particles are synthesized using capping agents, and adsorption of materials on the Pt surface can greatly decrease the activity of the catalyst, collodially synthesized Pt particles must be cleaned before they can be used as catalysts. UV-O\textsubscript{2} cleaning can remove most of the ligands but can oxidize the Pt surface and leave carbon residue.\textsuperscript{34} Solution methods of ligand removal often result in very aggregated particles that do not re-disburse well. Ideally, we would like to use ligands that can
control particle growth, and either have no effect on the particles catalytic activity
toward ORR or even increase it and therefore do not need to be removed.

Although, still not well understood, it is believed that ligands can affect
particle catalytic activity by interacting with the reactants though hydrophobic, steric,
or electrostatic effects, and by affecting the electronic structure of the catalyst surface
by preventing surface oxidation, altering the lattice structure and through partial
electron transfer.35,36 Several groups have begun to investigate the influence of
different ligands on the catalytic activity or selectivity of Pt particles. For example,
calix[4]arene molecules adsorbed onto Pt nanoparticles have been shown to increase
activity for H2 oxidation.37 Because they are large, they sterically hinder O2 adsorption
but do not affect H2 adsorption so that O2 reduction is reduced resulting in selectivity
toward H2 oxidation and improving the activity of the catalyst. Cyanide groups
adsorbed on Pt(111) have been shown to suppress adsorption of SO4^3- and PO4^3-
due to electrostatic repulsion.38-41 This results in a 25 fold increase when ORR is run in
H2SO4 and a 10 fold increase when run in H3PO4. Chen et al. showed increased ORR
activity with increasing electron withdrawing of the para-substituent (–CH3 < -F < -Cl
< -OCF3 < -CF3) by covalently binding aryl substituents to Pt nanoparticles.42 They
speculate that this increase in activity is due to the electron-withdrawing activity of the
ligands, which results in weakened O2 adsorption making it easier for O2 to undergo
reductive elimination. Triphenylphosphine triphosphate (TPPTP)43 has also all been
shown to improve the catalytic activity of Pt nanoparticles.
The benefits of using peptides as ligands for nanoparticle synthesis are that peptides offer a large number of possible sequences of amino acids; therefore there is a high possibility of finding a peptide that binds to a particular material or facet strongly and specifically. Additionally, they can be removed at low temperatures by adding enzymes or changing the pH of the solution, providing a clean surface for catalysis. A popular method to select a peptide which selectively binds a specific crystal face of a material is phage display. It is a combinatorial method that works by incubating peptides bound to bacteriophage with a substrate and selecting the phage with peptides that bind to the substrate. M13 bacteriophage are genetically modified to display a peptide at the end of their p3 protein. A library is created with phage displaying $10^9$ different peptide sequences. This library can then be incubated on a substrate to allow the peptides to bind to it. Following incubation, the substrate is washed with a mild buffer solution to remove the phage that do not bind to the surface or are only weakly bound. The substrate is then washed with an elution buffer, typically low in pH, which disrupts the peptide binding to the surface to remove the bound phage. These phage are next amplified to create a new library enriched in peptides that bind to the substrate. This procedure is repeated 3 or more times and then the DNA of the eluted phage is extracted and sequenced to determine the sequence of the substrate-binding peptide. This method is useful in determining possible biological molecules which can useful as capping agents in nanoparticle synthesis as it provides a way to test the binding of a large volume of different peptides and select the ones that bind.
Figure 1.2. The process of phage display

Phage display has been used to find peptides that bind specifically to a wide variety of materials such as zinc oxide\textsuperscript{45}, gold\textsuperscript{46,47}, silver, silica\textsuperscript{48}, titania, platinum\textsuperscript{32,49,50}, palladium, tin oxide, germanium oxide, and cadmium sulfide\textsuperscript{51}. These material specific peptides have been used to control particle growth in order to create various nanostructures. They have also been used to attach particles to other systems such as viruses or nanotubes and to assemble particles on surfaces. Investigation into the mechanism of peptide binding and control of material growth is ongoing using both experimental and computational methods.\textsuperscript{46-49,52-55} A major difficulty is separating out the effects of the individual amino acids from that of the amino acid order and peptide structure.
Even though phage display offers a useful method of selecting a peptide that can potentially control Pt particle growth, and many ligands have been found to the same purpose, the way in which this control is accomplished is still not well understood. Therefore, we aim to find a peptide that can be used to control Pt nanoparticle synthesis and investigate the mechanisms behind this control. Obtaining a consensus sequence from a peptide library gives some indication of the functionalities that are likely to interact favorably with Pt to obtain shape-controlled particles. This then gives us a starting point to begin investigating the role that specific functional groups have in the synthesis of Pt particles. By separating out functional groups of amino acids present in the consensus sequence of the binding peptides, and attaching them to a macromolecular scaffold for increased stability and particle solubilization, we hope to gain a greater knowledge of how the peptide is able to effect shape control over the growing Pt particles. We additionally investigates the effect these groups have on the catalytic activity of the particles because the shape is only important in that is affects the catalytic activity, and ligands are also known to potentially affect the catalytic activity as well. In sum, this work serves to further the understanding of the role biologically related functional groups have on the synthesis and catalytic activity toward ORR of Pt nanoparticles.

References


(44) Bassindale, A. R.; Codina-Barrios, A.; Frascione, N.; Taylor, P. G. Chemical Communications 2007, 0, 2956.


CHAPTER 2

Tunable Size and Shape Control of Platinum Nanocrystals from a Single Peptide Sequence

Nanoscale platinum architectures have been extensively studied as potential materials for applications in catalysis and fuel cells. Due to the high cost of platinum, much of the research has been geared toward developing methods to obtain monodisperse, monomorphic nanocrystals smaller than 10 nm. Peptide-mediated synthesis of inorganic materials is an attractive alternative to colloidal synthesis because it can be performed under ambient conditions and the peptides can be removed from the metal surfaces at mild pH or in the presence of enzymes. As a first step to achieve size and shape-controlled nanocrystals using peptides, we demonstrate here (a) the isolation of peptides that bind to specific crystal planes of platinum and (b) that a single peptide can produce structures ranging from sub-2 nm seed crystals to monodisperse 4 nm platinum polyhedra to 7 to 8 nm platinum cubes simply by changing the rates of metal reduction. This work demonstrates the first steps toward achieving biochemical control of platinum nanocrystal synthesis.

In recent years, the design and synthesis of nanoscale platinum architectures have been explored extensively for applications ranging from heterogeneous catalysis to fuel cells.¹⁵ To obtain homogeneous catalytic activities while minimizing precious metal costs, research has focused on the development of efficient, facile methods to synthesize monodisperse sub-10 nm nanocrystals while exercising accurate shape
Platinum nanocrystals can be synthesized with relatively controlled sizes and morphologies through mediation by a surfactant or polymer. However, the use of ligands that show affinity for specific crystal plane may allow synthesis of more catalytically potent morphologies. Inorganic-binding biomolecules, such as peptides, have excellent potential as a class of morphology-specific ligands due to their variety of available amino acid sequences, but it has proven very difficult to controllably produce monodisperse and monomorphic nanocrystals from peptides with tunable size and shape. We report here the controlled synthesis of platinum nanocrystals with a variety of sizes and morphologies from a single peptide sequence at room temperature. After isolating a peptide designed to bind a specific crystal plane of platinum by phage display, we produced structures ranging from sub-2 nm seed crystals to monodisperse 4 nm platinum polyhedra to 7 to 8 nm platinum cubes using simply the change in the rates of metal reduction. Syntheses with mismatched or no peptide led to ill-defined nanoparticles and bulk aggregates. This work illustrates the first steps toward achieving controlled syntheses of platinum nanocrystals of tunable sizes and morphologies from a single peptide sequence.

Peptides that bind a single crystal plane of platinum were isolated using a variant of phage display, a facile and oft-applied method to find peptides that bind specific substrates. The reason to screen against a single crystal plane of platinum was to obtain homologous sequences that would bind specifically to Pt (100), thereby providing a peptide sequence that would template specifically to this crystal plane. Because combinatorial screening against bulk dispersed heterogeneous powders of
various metals, sputter, or electrodeposited polycrystalline planar substrates would expose the bacteriophage library to multiple metal crystal planes and lead to isolation of peptides with nonspecific binding, phage libraries were screened against Pt (100) alone instead.\textsuperscript{27} Due to the extremely high cost of obtaining single crystal platinum, monodisperse cubic platinum nanocrystals bound by Pt (100) were first prepared using published surfactant-templated colloidal syntheses.\textsuperscript{9} X-ray diffraction (XRD) showed the high crystalline quality, and high-resolution electron microscopy (HRTEM) showed that the cubic nanocrystals were indeed bound by (100) planes (Figure 2.1A,B). Following previously reported procedures, the platinum nanocubes were next dried onto silicon substrates by slow evaporation to create well-ordered packed arrays of platinum nanocrystals and treated with UV/O\textsubscript{2} for 1 h to remove the top layer of capping ligands.\textsuperscript{9} Solutions of the phage library (NEB, Ph.D. 12) composed of $10^9$ different peptide sequences were then carefully dropped onto the cleaned platinum nanocrystal substrates. After incubation for 2 h in a humid environment, unbound phage was removed with a pipet and the platinum surfaces were gently rinsed with Tween 20 solutions. Phage bound to the substrate were eluted at pH 2 and amplified for a second screening against new UV/O\textsubscript{2}-cleaned and oriented platinum nanocrystal films. After three consecutive rounds, the amino acid sequences of the peptides that bound to the Pt (100) platinum nanocrystal substrates were determined through DNA extraction of select phage. As shown in Figure 2.1C, because the starting platinum substrates were highly crystalline and contained mostly a single crystal plane, significant amino acid homology between the sequences was observed, with a
consensus sequence of Pro-Trp-X-X-Gln-Arg-Glu-Leu-Ser-Val (PWxxQRELSV); additional obtained sequences are shown in Table 2.1. While the exact role each amino acid plays on binding platinum is currently being investigated, the generation of a clear consensus sequence indicates binding to a single crystal substrate. The overall isoelectric points of the peptides were close to neutral with values ranging from ~6.7 to 8.5.

Figure 2.1. (A) TEM image of synthetic platinum nanocubes via literature prep. Phages were screened against cleaned thin films of these cubic nanocrystals. (B) Powder XRD pattern of synthesized nanocrystals. (C) Amino acid consensus sequences of peptides obtained after three rounds of screening against the platinum nanocubes.

Next, we explored the ability of the isolated peptides to mediate nanocrystal synthesis. First, the peptide sequence Tyr-Gln-Pro-Trp-Lys-Thr-Gln-Arg-Glu-Leu-Ser-Val (YQPWKTQRELSV) was chosen at random and obtained commercially. The synthesized peptides were terminated with free carboxy and amine ends and provided
as a trifluoroacetic acid (TFA) salt. The calculated pI of the peptide chosen for the studies would, therefore, be ~8.5 and roughly have a net charge of +1 at pH 7.0. Varying concentrations of peptide and Pt$^{2+}$ precursors ($K_2PtCl_4$ or Pt(NH$_3$)$_4$(NO$_3$)$_2$) were incubated in either deionized water or 20 mM Tris buffer for 5-15 min at room temperature with constant stirring, followed by rapid addition of five molar equivalents of sodium borohydride (NaBH$_4$) to Pt$^{2+}$.

Aliquots were removed at time intervals ranging from 10 to 30 min and analyzed by electron microscopy. As shown in Figure 2.2A, in the presence of $K_2PtCl_4$, fast reduction by NaBH$_4$ produced extremely small (1 to 2 nm) platinum nuclei from the soluble platinum-binding peptides with no particles of any defined morphology (Figure 2.2A). These nuclei were obtained almost irrespective of the molar ratio of $K_2PtCl_4$ to peptide (25:1 through 250:1). When smaller molar ratios of $K_2PtCl_4$/peptide were used, the addition of peptide to the platinum solution immediately yielded white precipitates that became a slight tan upon reduction with nothing observable by transmission electron microscopy (TEM). In contrast to the $K_2PtCl_4$ reactions, when the Pt (100) platinum binding peptides were mixed with the less reactive Pt(NH$_3$)$_4$(NO$_3$)$_2$ at 25:1 Pt$^{2+}$/peptide ratios at pH 7 and reduced by NaBH$_4$, well-defined 3 to 4 nm platinum polyhedral nanocrystals were produced (Figure 2.2B). The sizes and shape distributions remained consistent up to 250:1 Pt(NH$_3$)$_4$(NO$_3$)$_2$ to peptide ratios, and the use of either 20 mM Tris buffer (pH 7) or water did not affect particle synthesis. At higher molar ratios of Pt(NH$_3$)$_4$(NO$_3$)$_2$,
particle formation was uncontrolled in both size and morphology and many particles aggregated.

Figure 2.2. (A) 1 to 2 nm platinum nanocrystals synthesized from platinum binding peptides and K$_2$PtCl$_4$ and NaBH$_4$. (B) 4 nm polyhedra platinum nanocrystals synthesized from platinum binding peptides and Pt(NH$_3$)$_4$(NO$_3$)$_2$ and NaBH$_4$. Scale bars in both images are 10 nm.

Using a different inorganic binding peptide, the silver binding NH$_2$-Asn-Pro-Ser-Ser-Leu-Phe-Arg-Tyr-Leu-Pro-Ser-Asp-COOH (NPSSLFRYLPSDL$^{19}$ yielded bulk aggregates with no individual well-defined nanocrystals (Figure 2.3A,B) for both Pt$^{2+}$ sources; these were similar to that observed when no peptides were used at all (Figure 2.3C). The clear discrepancy in nanoparticle sizes obtained when using Pt(NH$_3$)$_4$(NO$_3$)$_2$ instead of K$_2$PtCl$_4$ with the platinum binding peptides implied that the rate of metal reduction might play a key role in controlling the size and morphology of the resultant particles. Rapid nucleation with K$_2$PtCl$_4$ and NaBH$_4$ led to the formation of only small seed nuclei with no subsequent growth. With a less reactive platinum
species such as the ligand stabilized Pt(NH$_3$)$_4$(NO$_3$)$_2$, the slower nucleation led to larger 4 nm particles with narrow size distributions and spherical (polyhedral) shape. Thus, we hypothesized that slowing the rate of metal reduction further would lead to larger particles and different morphologies. To test this, hydrogen gas was used as a slower reductant to decrease the rate of metal reduction even further. Peptide/K$_2$PtCl$_4$ solutions were first purged with nitrogen for 5 min and then hydrogen for another 5 min and then immediately sealed and left to sit overnight with no stirring. Instead of the 1 to 2 nm nuclei obtained previously using K$_2$PtCl$_4$, 7 to 8 nm platinum nanocrystals showing cube and truncated cube morphologies were obtained (Figure 2.4).

Figure 2.3. (A) Bulk platinum precipitates using Pt(NH$_3$)$_4$(NO$_3$)$_2$ and silver binding peptides. (B) Bulk platinum precipitates using Pt(NH$_3$)$_4$(NO$_3$)$_2$ and no peptides. (C) Bulk platinum precipitates using K$_2$PtCl$_4$ and no peptides. All reactions were run using NaBH$_4$ as the reductants.
Figure 2.4. TEM image of 7 to 8 nm truncated cubic and cubic platinum nanocrystals obtained by reacting the platinum(100) binding peptides with $\text{K}_2\text{PtCl}_4$ in hydrogen for 16 h. Inset figure shows the Pt (100) lattice fringes.

Statistical analyses of 617 particles from the hydrogen synthesis showed the nanocrystals to be relatively heterogeneous in size and shape, ranging in dimensions from 6 to 8 nm and roughly 20% cubic, 35% truncated cubic, and the rest a mixture of octahedral, tetrahedral, and spherical. For these syntheses, the optimal molar ratio of platinum to peptide appeared to be 1:1; smaller amounts of $\text{K}_2\text{PtCl}_4$ yielded no observable reduced platinum by TEM while larger $\text{K}_2\text{PtCl}_4$/peptide ratios (25:1) caused the formation of larger structures composed of aggregated small particles (Figure 2.5).
When the more stable Pt(NH$_3$)$_4$(NO$_3$)$_2$ was used instead of K$_2$PtCl$_4$ in the hydrogen reactions, no Pt(0) structures of any kind were observed within 16 h. As with previous trials, syntheses without peptide or with silver binding peptide, hydrogen reduction of K$_2$PtCl$_4$ yielded only bulk aggregates (Figure 2.6). Since one of the purposes of screening phage libraries against bare Pt (100) surfaces was to bias the preferential stabilization of the peptides at the (100) face, the successful generation of cubic morphologies enables us to investigate the feasibility of controlling crystal morphology through peptides that interact with specific crystal planes.$^{29}$
This ability to use biomolecular recognition to tune crystal shape would be an exciting advance in nanocrystal synthesis. While the peptide stabilized platinum nanocrystals seemed remarkably stable and well-dispersed for many days and weeks, decreasing the pH of the solutions to 2 caused all of the particles to immediately precipitate and aggregate from solution (Figure 2.7). This most likely is due to disassociation of the peptide from the platinum surfaces at acidic pH, which is consistent with the phage elution process at pH 2. This observation further substantiates the peptides’ involvement in the nanocrystal synthesis as capping ligands. Furthermore, these results show that it is possible to use simple changes in pH to strip surface bound peptides from the platinum nanocatalysts, exposing their active faces. Since proton exchange membrane fuel cells usually require stability at low pH, studies are also currently underway to isolate peptides that can be dissociated from platinum at basic pH.
To obtain optimal catalytic activities in platinum nanocrystals, it is imperative to be able to accurately control the particle size and shape. However, current ligand design limits the potential complexity of what can be synthesized in bulk. This report demonstrates that platinum nanocrystals with specific morphologies and sizes can be controllably synthesized from a rationally isolated single peptide sequence by tuning the rate of metal reduction and nanocrystal nucleation. When the highly reactive precursor K$_2$PtCl$_4$ is rapidly reduced by hydrides, leading to high supersaturation and a large number of initial nuclei, very small seed particles are formed that are quickly stabilized by the peptides. Decreasing the rates of metal reduction through more stable Pt precursors, such as Pt(NH$_3$)$_4$(NO$_3$)$_2$, or less reactive reductants, such as H$_2$, leads to
a smaller number of nucleation seeds and larger particles, generating monodisperse 4 nm platinum polyhedra and 7 to 8 nm cubes, respectively. These results clearly show that the judicious choice of synthesis parameters can lead to the isolation of platinum nanostructures with defined morphologies and sizes from peptides at room temperature and no other metal additives. We plan to expand the power of peptide-mediated synthesis by isolating peptides that bind to other crystal planes of platinum and determine their influence on nanocrystal growth, possibly enabling us to synthesize platinum nanocrystals of complex morphologies that have not yet been made.

**Experimental Section**

**Preparation of Pt Cubes for Phage Screening.** Cubic platinum nanocrystals were prepared using published methods. All of the nanoparticles were analyzed by scanning transmission electron microscopy (STEM), scanning electron microscopy (SEM), TEM, and XRD. To prepare substrates for phage display, 50 μL of a solution of the nanoparticles in 1:1 octane/hexane was slowly evaporated on a clean piece of silicon. The particles were then cleaned by UV/O₂ for 1 h to remove surfactants.

**Phage Display.** Fifty microliters (10 μL of phage library in 40 μL of 0.1% Tris Buffered Saline Tween (TBST)) was placed on a prepared platinum nanocrystal substrate and allowed to incubate for 2 h, after which the drop was removed and discarded. The substrate was washed 6 times with 50 μL of 0.1% TBST. The bound phages were then eluted using 2 consecutive 30 minute rinses with 0.2M glycine and 1
mg/mL BSA (pH 2) solutions. The glycine solutions were then combined and neutralized with 1M Tris (pH 9). Eluted phage were amplified and two more rounds of panning were performed. Bacteriophage DNA was extracted from round 2 and 3 phages for sequencing.

Table 2.1. Additional sequences isolated from Pt (100) binding phage.

<table>
<thead>
<tr>
<th>SHPWNASHVR</th>
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<td>YQPKTQRELSV</td>
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<td>SHPWNASHVR</td>
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**Peptide Mediated Platinum Nanoparticle Synthesis.** For platinum nanocrystal synthesis, peptide solutions (3 x 10^{-5} M) were added to Pt(NH₃)₄(NO₃)₂ or K₂PtCl₄ (7.5 x 10^{-4} to 7.5 x 10^{-3} M) in water or 20 mM Tris buffer (pH 7) in a 1.5 mL Eppendorf tube. The solutions were stirred for 5 min, and then, 5 mol equiv of NaBH₄ relative to platinum were added. The solution is then rapidly stirred for 1 h. Reactions (1-4 μL) were dried on TEM grids for microscopy.

**Peptide Mediated Platinum Nanoparticle Synthesis-Hydrogen Reduction.** Peptide solutions (1.5 x 10^{-5}, 8 x 10^{-6}, and 4 x 10^{-7} M) were added to 10 mL solutions of 1 x 10^{-5} M aged K₂PtCl₄(aq) in water. Nitrogen was bubbled through the solution for 20
min, followed by bubbling hydrogen for 5 min. The flask was sealed and allowed to react for 12 h at room temperature. Reactions (1-4 μL) were dried on TEM grids for microscopy.

Acknowledgments

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Chapter 2, in full, is a reprint of the material as it appears in Chemistry of Materials, 2010. Forbes, Lauren M., Goodwin, Andrew P., Cha, Jennifer N., Chem. Mater., 2010, 22 (24), 6524–6528. The dissertation author was the primary investigator and author of this paper.
References


CHAPTER 3

Polymer end-group mediated synthesis of well-defined catalytically active platinum nanoparticles

Simple, short polyethylene glycol (PEG) chains were found to mediate the synthesis of well-defined 7–8 nm cubic and truncated cubic platinum (Pt) particles that required only mild ligand removal conditions to yield highly active catalysts for the oxygen reduction reaction (ORR). FTIR analyses showed that only the hydroxyl end groups of the PEG chains associate with the platinum particles, which oxidize readily to form carbonyl groups with weaker interactions with the platinum surface. ORR analysis showed a mass activity of 50 μA/μg for the PEG synthesized Pt nanoparticles (NPs), as compared to a mass activity of 45 μA/μg for platinum black. The half-wave potentials of PEG Pt NPs and Pt black were found to be 427 mV and 529 mV, respectively, showing a high catalytic activity of PEG Pt NPs toward ORR. Well-defined particles were also produced from amine -terminated PEG, but as the amines could not be removed by simple acid washing, the ORR activity was greatly diminished. Since short low molecular weight PEG was found to control particle nucleation and growth predominantly through its end groups, this work demonstrates that PEG is a versatile scaffold from which to screen a wide variety of functional moieties, including biomolecules, as templates for complex nanoparticle synthesis.
Introduction

Due to their excellent electrocatalytic activity and resistance to corrosion, nanoscale platinum architectures have been explored extensively for applications ranging from heterogeneous catalysis to fuel cells.\textsuperscript{1-6} Typical synthetic procedures for colloidal particles require strongly adhering capping ligands to control both crystal size and shape.\textsuperscript{7-16} These include polymers,\textsuperscript{17-30} surfactants,\textsuperscript{31-36} and biomolecules.\textsuperscript{37-41} However, strongly-bonding multivalent organic capping agents can inhibit catalytic activity by blocking substrate adsorption. In particular, high molecular weight polymers such as polyvinylpyrrolidone (PVP) and polyethylene-polypropylene-polyethylene must be removed through either high temperature calcination or harsh oxidation, the by-products of which can further poison the platinum surface.\textsuperscript{42-47} In direct contrast, we demonstrate here that very short, low molecular weight polymers of ethylene glycol (PEG200) can moderate the synthesis of well-defined sub-10nm platinum cubes and truncated cubes. While the particles demonstrate decent activity directly after preparation, PEG200 is easily removed with mild acid washing to generate highly active catalysts that show higher mass activities than the standard platinum black for the oxygen reduction reaction (ORR). Both the synthesis and electrocatalytic activity of the particles were found to depend on both the polymer molecular weight and the platinum-binding polymer chain end groups. Surface studies suggest a potential mechanism for polymer desorption and nanoparticle activation.
Materials and reagents

Polyethylene glycol (MW 200), polyethylene glycol (MW 20,000), polyethylene glycol (MW 8,000), polyethylene dimethyl ether (MW 2,000), and potassium platinum tetrachloride (K$_2$PtCl$_4$) were purchased from Sigma-Aldrich and used as received. Methoxypolyethylene glycol-amine (MW 5,000), and methoxypolyethylene glycol-maleimide (MW 10,000) were purchased from Laysan Bio. Hydrogen and nitrogen were purchased from Airgas. Purified water was obtained from a Millipore water purification system and filtered. Fritted midget impingers were obtained from Chemglass Life Sciences.

Platinum nanoparticle synthesis. Polyethylene glycol was added to 10 mL solutions of $10^{-4}$ M K$_2$PtCl$_4$ in a fritted midget impinger. Nitrogen was then bubbled rapidly through the sample for 20 min, followed by rapid bubbling with hydrogen for 5 min. The samples were immediately sealed and allowed to react overnight. The samples were dried on a carbon/formvar TEM grid (Ted Pella) for imaging. The samples were lyophilized to remove the water. Samples were then either weighed, re-dissolved in water and electrochemical measurements were run, or centrifuged washed with DI water and re-lyophilized to run IR measurements.

Characterization. Platinum nanoparticles were characterized by TEM and FTIR. TEM images were collected on a FEI Tecnai G2 Sphera microscope operating at 200 kV. Infrared spectra were obtained by collecting one hundred and twenty-eight scans.
at a resolution of 4.0 cm\(^{-1}\) between 4000 and 600 cm\(^{-1}\) using a Nicolet 6700 FTIR spectrometer equipped with an ATR detector.

**Electrocatalytic characterization.** Electrochemical measurements were performed using a \(\mu\)-Autolab type II (Eco Chemie, Utrecht, Netherlands) and a conventional three-electrode electrochemical cell. Platinum wire was used as a counter electrode while Ag/AgCl (in 1 M KCl) served as a reference electrode. Pt nanoparticle modified glassy carbon was used as a working electrode. Pt nanoparticles (20 \(\mu\)g in water) were cast onto the GCE surface and allowed to dry in ambient air. To secure the Pt nanoparticles onto the GCE, 4 \(\mu\)L 0.05% Nafion in propanol was dropped onto the dried particles until all the solvent had evaporated. Polarization curve was obtained by scanning the potential from 1.0 to 0 V at a scan rate of 10 mV/s in \(\text{O}_2\)-saturated 0.1 M \(\text{H}_2\text{SO}_4\) at a BASi rotating disk electrode (RDE 2). Polarization curves were examined for ORR for rotation rates of 0 to 2000 RPM in increments of 400 rpm.

**Results and discussion**

While high molecular weight polymers and block copolymers such as polyacrylic acid have been used successfully to generate controlled morphologies of nanoscale platinum, their binding strengths with the platinum surfaces often make it difficult for substrate adsorption, hindering catalytic activity. It is therefore of considerable interest to discover molecules that can control the synthesis of platinum structures but can also desorb from the nanoparticles in working conditions. In this report, we demonstrate that simple short linear chains of polyethylene glycol
(PEG200) can be used to synthesize well-defined sub-10nm platinum cubes and truncated cubes. We furthermore show that platinum nanoparticle growth is controlled through the terminal hydroxyl groups on the PEG (HO-PEG-OH) chains that oxidize during or post platinum nanoparticle synthesis. In working electrolytes such as H$_2$SO$_4$ these weak carbonyl-platinum interactions are easily removed, the catalytic properties of which have been characterized using ORR.

Although PEG has been shown to control gold or palladium$^{48}$ crystal growth, results with platinum have yielded mainly small spherical particles.$^{49-51}$ To exert greater control over platinum nanocrystal synthesis from the polymer, different molecular weights of unmodified linear PEG (200, 8000, and 20,000 Da) were reacted at varying molar ratios with N$_2$-purged aged solutions of $1 \times 10^{-4}$ M K$_2$PtCl$_4$ in water and reduced by bubbling H$_2$ through for 5 min and sealing overnight. As shown in Fig. 1A, the shortest PEO (PEG200) chain at 1:1 PEG:Pt molar ratios generated well-defined 6.6 ± 1.0 nm platinum cubes and truncated cubes. As the PEG chain lengths increased (Figure 3.1B, 3.1C), control over both crystal morphology and size appeared to diminish, and using the longest PEG chain (PEG20K) produced largely spherical platinum particles of 4.5 ± 1.1 nm (Figure 3.1C). The longer polymer chains were thought to produce more ill-defined and spherical particles because of the larger effective volume a longer PEG chain would occupy on a growing nanoparticle, which would prevent effective end-group stabilization of a growing particle face.
Figure 3.1. TEM images of platinum nanoparticles synthesized from different molecular weights of PEG: (A) PEG200, (B) PEG8K and (C) PEG20K. Scale bar represents 10 nm.

To determine the effect different end groups of PEG on platinum synthesis, di-methoxy, methoxy-amine and methoxy-maleimide terminated PEG chains (MW 2,000, 5,000, and 10,000, respectively) were reacted with aged and nitrogen-purged K₂PtCl₄ and reduced in H₂. In the case of the di-methoxy PEG, uncontrolled particle growth and mainly large aggregated clumps were observed, verifying the importance of the end groups on PEG for particle synthesis and ruling out the ethylene oxide backbone as a ligand for synthesis (Figure 3.2A). This was further evidenced by replacing PEG200 with n-butanol that also produced platinum particles with relatively decent control over both morphology and shape (Figure 3.3). In the case of amine terminated PEG (PEG-amine), platinum nanostructures similar to those obtained using PEG200 were obtained, including cubes with size distributions of roughly 8–9 nm (Figure 3.2B). While the maleimide functionalized PEG polymers (PEG-maleimide) demonstrated inferior overall control than either PEG200 or amine-PEG and produced particles of varying morphologies (Figure 3.2C) such as cubes and hexagons, to a large extent particle size was relatively controlled.
Figure 3.2. TEM images of platinum nanostructures synthesized using different end group terminated PEG. (A) Dimethoxy terminated PEG (MW 2000), (B) methoxy-amine terminated PEG (MW 5000) and (C) methoxy-maleimide terminated PEG (MW 10 K).

Figure 3.3. Low and high magnification TEM images of platinum particles synthesized using n-butanol.

The fates of the polymer end groups during particle synthesis were also studied by FTIR. While native PEG200 possesses a strong OH stretch, after synthesis this peak disappeared with the concurrent appearance of a strong carbonyl peak at 1728 cm\(^{-1}\) (Figure 3.4A). The disappearance of the strong OH stretch in the PEG200-Pt
samples indicated that the terminal hydroxyl groups play a significant role in binding to the platinum surface during particle growth. Second, the appearance of a carbonyl unit indicated that the hydroxyl group most likely became oxidized to aldehydes or carboxylic acids during the reaction or post-synthesis. Previous research has shown the use of alcohols as active platinum reductants in the presence of polymers.\textsuperscript{52,53} FTIR analyses further showed that these weak carbonyl-platinum interactions could be dissociated by acids such as the electrolytes used for ORR since simple rinsing of the PEG-Pt particles in 0.5M H\textsubscript{2}SO\textsubscript{4} caused the polymers to wash off (Figure 3.4A, 3.6). While acid washing did cause the particles to aggregate more as seen by TEM, the individual particle morphology and size did not change (Figure 3.5).

![Figure 3.4](image-url)

Figure 3.4. (A) FTIR analyses of PEG200, PEG200-Pt particles and acid washed PEG200-Pt particles. Note that the upper and lower limits of the y-axis of the acid washed particles are 100 and 101.6 (B) FTIR analyses of PEG-amine, PEG-amine particles and acid washed PEG-amine particles. (C) FTIR analyses of PEG-maleimide, PEG-maleimide particles and acid washed PEG-maleimide particles. Note that the upper and lower limits of the y-axis of the acid washed PEG-maleimide particles are 96 and 97. Arrows indicate major peak changes observed between the native polymers alone and the as-synthesized polymer platinum particles.
FTIR analyses of the PEG-amine particles showed the emergence of a new peak at 3391 cm$^{-1}$ indicating that the amines may have oxidized to the N-oxide during or after synthesis (Figure 3.4B).\textsuperscript{54} Although the polymer signals weakened substantially after washing the PEG-amine particles in H$_2$SO$_4$, some polymer still remained behind, indicating that unlike the more labile carbonyl-platinum interactions seen with the PEG200, the oxidized amine-platinum interactions were harder to dissociate. Previous work has also shown that electrochemical oxidation of aliphatic amines causes covalent attachment to platinum surfaces.\textsuperscript{55} FTIR analyses of the PEG-maleimide particles did not provide any peaks different than the polymers alone but the interactions with the platinum surface are presumably through the carbonyl units of the maleimide group, as the carbon-carbon double bond most likely becomes reduced during the platinum synthesis in hydrogen. Acid washing of the PEG-maleimide platinum particles showed that the polymers can be easily washed off.
The activity of the polymer-assisted Pt nanoparticles toward ORR was next tested (Figure 3.7). For this, ORR polarization curves were determined at Pt-modified glassy carbon electrodes (GCE) prepared using nanoparticles synthesized from PEG200, PEG-maleimide, PEG-amine and PEG20K (Figure 3.7 B–E). In all cases, after synthesis the particles were collected by centrifugation and washed three times with 0.1 M H₂SO₄, water and acetone. As a comparison, platinum black was also tested for ORR. The platinum nanoparticles were immobilized onto the GCE through evaporation and confined with 0.05% Nafion. Linear sweep voltammograms were recorded in O₂-saturated 0.1 M H₂SO₄ solution over the 1.0 V to 0.0 V range at 10 mV/s using a rotating disk electrode with rotation speeds of 200, 400, 800, 1200, 1600 and 2000 rpm. The electrochemical reduction of oxygen is observed for all species examined in the potential range of 0.7 V to 0.0 V (vs. Ag/AgCl). For each of the species examined, an increase in current was observed with increasing rotation speed. The values of the peak currents were examined using the Koutecky-Levich equation,
where the inverse of the square root of rotation speed was plotted vs. the inverse of the steady-state current and values for kinetic current were obtained.\textsuperscript{51,56} These values were used to calculate mass activity for each species, which are outlined in Table 1 and clearly show a difference in ORR catalytic activity for the different nanoparticles.

Figure 3.7. ORR polarization curves for Pt Black (a) and platinum particles synthesized from the four different end groups terminated polymer, PEG200 (b), PEG-maleimide (c), PEG-amine (d) and PEG20K (e) in O\textsubscript{2}-saturated 0.1 M H\textsubscript{2}SO\textsubscript{4} over the potential range of 1.0 V to 0.0 V at a scan rate of 10 mV/s.
Table 3.1. Mass activity and half-wave potential of the polymer-capped Pt nanoparticles

<table>
<thead>
<tr>
<th>Platinum Nanoparticles</th>
<th>Mass Activity (μA/μg)</th>
<th>E$_{1/2}$ (mV) (vs. Ag/AgCl)</th>
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</thead>
<tbody>
<tr>
<td>Pt Black</td>
<td>45</td>
<td>529</td>
</tr>
<tr>
<td>PEG200</td>
<td>50</td>
<td>487</td>
</tr>
<tr>
<td>PEG-maleimide</td>
<td>26</td>
<td>568</td>
</tr>
<tr>
<td>PEG-amine</td>
<td>26</td>
<td>421</td>
</tr>
<tr>
<td>PEG20K</td>
<td>22</td>
<td>340</td>
</tr>
</tbody>
</table>

As shown in Figure 3.7B, the PEG200 platinum particles yielded the highest current output of all the polymer-assisted nanoparticles that was also strongly comparable to Pt Black (Figure 3.7A). Table 3.1 also shows a comparable mass activity of PEG200 with Pt black, showing the high surface area of the PEG200 nanoparticles exposed to O$_2$ for ORR. The half-wave potential value shown in Table 3.1 for PEG200 was also relatively high showing a high catalytic ability of this species toward ORR. The PEG-maleimide platinum nanoparticles also performed quite well compared to Pt black with the onset of ORR at a low overpotential (Figure 3.7C) and a half wave potential of 568 mV (Table 3.1). The half-wave potential for the PEG-maleimide particles was actually more positive than that observed for Pt black, showing that these nanoparticles have a high catalytic ability toward ORR. The mass activity for PEG-maleimide, however, was less than that observed for PEG200 and Pt.
black, and this may have been due to two factors: (i) aggregation of the nanoparticles, which would decrease the overall surface area per mass of Pt; (ii) the presence of polymer still at the surface of the nanoparticles which would block active sites from ORR, thus having a similar effect to aggregation. Because the FTIR evidence showed that the PEG-maleimide polymers could be easily removed from the particles by a single acid wash however particle aggregation was more likely the explanation for lower mass activity. As had also been noted earlier, the PEG-maleimide also demonstrated less overall control than either PEG200 or amine-PEG (Figure 3.2C). The catalysis toward ORR was also somewhat diminished for the PEG-amine platinum particles as observed in the voltammetry (Fig. 3.7D), where a significant decrease in peak current was observed as compared to the PEG200 and PEG-maleimide particles and with the onset of reduction of oxygen at a higher overpotential. The half-wave potential was significantly lower than the previous two species, showing a lower catalytic ability toward ORR. The mass activity was also lower than those of Pt Black and PEG200, but comparable to that of PEG-maleimide (Table 3.1). While the lower mass activity of PEG-maleimide may be attributed to aggregation of the particles since FTIR showed facile removal of the polymer from the nanoparticles, since the FTIRs showed that PEG-amine remains behind even after acid washings, the low mass activity in this case may be attributed to the remaining presence of polymer at the Pt surface, thus blocking active sites from ORR. The least favorable catalytic reaction toward ORR proved to be the PEG20K platinum particles (Fig. 3.7E) with a much more negative half-wave potential and a mass activity at 22
μA/μg, lower than that observed for the other platinum particles, in particular, PEG200. With the PEG20K platinum particles, the low ORR activity was most likely due to the fact that the polymer is 100 times larger in molecular weight than PEG200 and cannot therefore wash away from the platinum surfaces and escape through the porous Nafion coating on top, thus hindering ORR almost completely. The stability of the platinum nanoparticles prepared from PEG200 was tested using 1000 repetitive CV cycles over range 0 V to 1.0 V at 50 mV/s in 0.1 M H₂SO₄. After an initial slight decay in current from cycles 1 to 300, the current remained stable thereafter up to 1000 repetitive CV cycles.

**Conclusion**

We demonstrate here that simple linear PEG chains can control the synthesis of well-defined platinum particles but also remain highly active for ORR without any pre-removal of the capping ligands. Because ORR activity is largely dependent on accessible platinum surfaces, the high activity observed with the platinum particles synthesized from unfunctionalized PEG can be correlated to the FTIR analyses. The spectra showed that only the hydroxyl end groups of the PEG chains are associated with the platinum particles. The IR data further showed that the hydroxyl groups oxidized to form weaker and more labile interactions with the platinum surface, enabling easy dissociation in H₂SO₄. When the hydroxyls were replaced with amines, although cubic particles were synthesized ORR activity was greatly diminished and
this was most likely due to the amines being oxidized such that the polymers could not be as easily removed in acid. Therefore, the highest catalytic activity of platinum toward oxygen reduction is observed for particles, whereby the facile dissociation between the oxidized polymer end groups and platinum allow more access to the platinum catalytic surface. The ability to synthesize ORR active sub-10nm particles with controlled morphologies from labile polymer end-groups indicates great promise for fuel cell technologies due to the use of carbon electrodes that can also be degraded in typical organic removal processes, such as thermal treatment or ozonolysis. The work shown also further demonstrates the suitability of using PEG as a macromolecular scaffold as its ability to control particle nucleation and growth is predominantly through its end groups, thereby providing a versatile scaffold from which to test a wide variety of functional groups including biomolecules such as amino acids or RNA for platinum synthesis and catalysis.

**Acknowledgements**

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Chapter 3, in full, is a reprint of the material as it appears in Journal of Materials Chemistry 2011. Forbes, Lauren M., O’Mahony, Aoife M., Sattayasamitsathit, Sirilak, Wang, Joseph, and Cha, Jennifer N., J. Mater. Chem., 2011, 21, 15788-15792. The dissertation author was the primary investigator and author of this paper.

References


CHAPTER 4

Improved Oxygen Reduction Reaction Activities with Amino Acid R Group Functionalized PEG at Platinum Surfaces

Abstract

We demonstrate here that coupling specific amino acid “R” groups to polyethylene glycol (PEG) chains through amide bonds and adsorbing them to platinum (Pt) black improves oxygen reduction reaction (ORR) catalysis over bare metal, even at high polymer loadings. Through our studies, we first show that the presence of PEG on the Pt nanoparticles increases half-wave ($E_{1/2}$) potentials, most likely by preventing Pt oxidation or Pt-OH formation. We also show however that increases in $E_{1/2}$ did not necessarily correlate to gains in mass activities, and that while commercial PEG-OH in fact lowered mass activities, conjugation of PEG to alcohol-containing amino acid R groups connected by amide bonds led to 100-200% gains in reactivity. This work presents evidence that counters the common conception that organic capping ligands decrease catalytic activity; in fact activity may actually be improved over bare metal through judicious choice and design of ligands that inhibit Pt oxidation and control chain packing at the Pt surface. These studies therefore show that it may still be possible to have ligands on a nanoparticle surface that allow the particles to be well-dispersed on an electrode surface while simultaneously enhancing catalysis without further particle treatment. Lastly, at the end of this chapter we show
some of our unpublished efforts of using the amino acid terminated PEG chains for controlling Pt nanoparticle nucleation and growth.

**Introduction**

In recent years, fuel cells have been heavily investigated as potential alternatives to internal combustion engines for producing electricity from a fuel (hydrogen, methanol) and an oxidant (oxygen).\(^1\)\(^-\)\(^6\) Platinum particles on a variety of carbon supports are still one of the most efficient catalysts for fuel cell cathodes. The high cost and low abundance of some of these metals have prompted exploration of economically viable schemes to maximize reagent accessibility to available catalytic sites, which in turn can be increased through the synthesis of smaller, nanoscale metal structures with controlled shapes and sizes. For most of these syntheses, either surfactants or polymers have been used to guide nanocrystal synthesis and highly monodispersed platinum particles of various shapes, such as cubes, cubooctahedra and tetrahedra, have been synthesized from hydroxyl, amine or aromatic organic systems.\(^7\)\(^-\)\(^28\) However, these capping ligands on these nanoparticles must be removed from the metal surfaces by oxidation or heat treatment, which can cause nanoparticle aggregation or damage.\(^8\)\(^,\)\(^29\)\(^-\)\(^33\) As a potential alternate strategy, we demonstrate here that coupling specific amino acid “R” groups to polyethylene glycol (PEG) chains through amide bonds and adsorbing them to platinum (Pt) black can actually improve oxygen reduction reaction (ORR) catalysis over that of bare metal, even at high polymer loadings. Through our studies, we demonstrate that PEG chains provide some
key advantages as capping ligands because of the interactions between the ethylene oxide backbone and water,\textsuperscript{34-36} which can prevent Pt-OH formation and in some cases lead to increases in $E_{1/2}$ relative to Pt black. Furthermore, we show distinct trends in mass activities, where alcohol containing R groups conjugated to PEG chains showed dramatic improvements in ORR versus Pt black bare and with commercial PEG-OH. On the other hand, aromatic, hydrophobic and guanidinium R groups showed significantly reduced mass activities that did not necessarily correlate to decreases in $E_{1/2}$. Through these analyses, we hypothesize that the chemical nature of the amino acid R groups can affect polymer chain packing and interchain associations, which leads to distinct differences in ORR mass activity. We also show that, given the same functional group at the Pt surface, the presence of amide bonds in the polymer chain greatly improves mass activities due to the creation of more “space” between neighboring polymer chains.

**Materials and methods**

**Polymer synthesis.** Different amino acid R groups (Sigma-Aldrich) were attached to polyethylene glycol (PEG) polymers using one of two methods, depending on the hydrophobicity of the R-group. The hydrophilic amines used in the PEG-R syntheses were: ethanolamine (S), amino-2-propanol (T), β-alanine (D), γ-aminobutyric acid (E), histamine (H), cadaverine (K), and agmatine sulfate (R). The synthesis of the polymer using hydrophilic amines was performed by adding 500 μmol of the amine to 5 mL of 0.01 M aqueous solution of methoxypolyethylene glycol-succinimidyl valerate
(mPEG-SVA) (MW=2000 g/mol, Laysan Bio). The solution was heated at 60°C overnight, then cooled and lyophilized. The dry mixtures were dissolved in 5 mL of methylene chloride and vacuum filtered through a Buchner funnel. 1H NMR of the filtrates was taken to confirm purity. Polymer solutions that still contained starting material were dialyzed further. The hydrophobic amines used were: phenethylamine (F), tyramine (Y), tryptamine (W), and isobutylamine (V). The synthesis using hydrophobic amines was done by adding 500 μmol of the amine to 5 mL of 0.01 M solution of methoxypolyethylene glycol-succinimidyl valerate (mPEG-SVA) (MW=2000 g/mol, Laysan Bio) in methylene chloride. The solutions were heated at 40°C overnight. The solutions were then dried and the residues washed with ether. 1H NMR of the precipitates was taken to confirm purity. Polymers that still contained starting material were run on preparatory TLC plates using an 80% methanol/20% methylene chloride solution as the eluent.

**Platinum Particle Synthesis.** PEG-X was added to 10 mL solutions of $10^{-4}$ M $K_2PtCl_4$ in a fritted midget impinger. Nitrogen was then bubbled rapidly through the sample for 20 min, followed by rapid bubbling with hydrogen for 5 min. The samples were immediately sealed and allowed to react overnight. The samples were dried on a carbon/formvar TEM grid (Ted Pella) for imaging. The samples were lyophilized to remove the water. Hydrogen and nitrogen were purchased from Airgas. Purified water was obtained from a Millipore water purification system and filtered. Fritted midget impingers were obtained from Chemglass Life Sciences. Platinum nanoparticles were
characterized by TEM. TEM images were collected on a FEI Tecnai G2 Sphera microscope operating at 200 kV.

**Ligand Adsorption to Pt Black.** The PEG-OH and R-conjugated PEG polymers (PEG-X) polymers were added in water (50, 100, or 500 molar eq) to 1 mL of 1 mg/mL Pt black in water. The solutions were vortexed, sonicated, and allowed to react overnight on a sample shaker. The solutions were then centrifuged at 15,000 rpm for 20 min and the supernatants removed and kept. The solutions were centrifuged again at 15,000 rpm for 20 min and the supernatants removed and added to the previous supernatants. The pellets were washed with DI water, vortexed, sonicated and then re-centrifuged at 15,500 rpm for 20 min. The supernatants were removed and added to the previous samples. The pellets were lyophilized to remove any remaining water. 1D 1H NMR of the lyophilized supernatants was run to determine PEG concentration remaining on the particles. In order to determine mole ratios of PEG-X:Pt, the number of moles of Pt nanoparticles was determined by calculating the molecular weight (g/mol) of spherical Pt particles 2nm in diameter by determining the number of unit cells in the particle, and multiplying that by the total number of Pt atoms times molecular weight of Pt.

**ORR Studies.** Electrochemical measurements were performed using a Q-Autolab type III (Eco Chemie, Utrecht, Netherlands) and a conventional three-electrode electrochemical cell. Platinum wire was used as a counter electrode while Ag/AgCl (in 1 M KCl) served as a reference electrode. A Pt nanoparticle modified glassy carbon rotating disk electrode (GC-RDE, 3 mm dia.) was used as a working electrode. PEG-R
Pt nanoparticles (30 μg in water) were cast onto the GCE surface and allowed to dry in ambient air. The actual mass used for the mass activity calculations does not include the polymer, it is just the mass of the Pt. To secure Pt nanoparticles on GC-RDE, 5 μL 0.05% Nafion in propanol was dropped onto the dried particles until all solvent had evaporated. Polarization curve was obtained by scanning the potential from 1.0 to 0.25 V with the scan rate of 10 mV s\(^{-1}\) in O\(_2\)-saturated 0.1 M H\(_2\)SO\(_4\) at a BASi rotating disk electrode (RDE 2). Polarization curves were examined for ORR for rotation rates of 0 to 2000 RPM in increments of 400. Koutecky-Levich analysis was performed on the oxygen reduction reaction (ORR) studies for increasing rotation rates. A plot of the inverse of square root of rotation speed vs. the inverse of current density was generated. The potential at which the current output was sampled varied between different species. However for any one PEG-Pt-amino acid system (PEG-T), the current was sampled from the same potential for each rotation rate, at the point where the curve becomes steady state. The mass activity was then calculated from the intercept at the y-axis of the resulting plot.

**Results and Discussion**

In this study, individual amino acid R groups were attached to a non-platinum binding macromolecular scaffold to investigate Pt-amino acid interactions at the level of a single amino acid unit. We previously showed that the nonionic polymer polyethylene glycol (PEG) demonstrates very weak binding to platinum surfaces and that only the end-termini are primarily responsible for platinum binding, nanocrystal
growth, and ORR activity. This work focuses on synthesizing PEG chains end-modified with R groups of specific amino acids due to the possibility of encompassing different organic groups in a single study, including acidic or basic residues, aromatic, hydrophobic and alcohols. Furthermore, while biomolecules such as peptides have been used for nanoparticle catalyst synthesis, knowledge of how specific amino acids can affect such synthesis and catalysis is lacking. As an example of this, while we previously showed that Pt (100) binding peptides could yield nanoparticles of defined morphologies ranging from polyhedra to cubes, all of the synthesized peptide-bound particles showed low catalytic activity when subjected to ORR analysis. These extremely low mass activities could be partly attributed to the strong binding affinities of the biomolecular ligands with the platinum surfaces, which could prevent oxygen from adsorbing to the surface. However, it is also possible that some of the amino acids do in fact poison catalytic surface activity.

In order to test the effect of modifying PEG chains with different R groups of amino acids, low molecular weight PEG polymers (MW~2K) terminated with different R-groups (PEG-X) were first synthesized (Scheme 4.1, Figure 4.5). Next, in order to probe the effects of the R group on the ORR, the PEG-R polymers were adsorbed onto commercial Pt black. We examined 11 functional groups corresponding to the R groups of serine (S), threonine (T), histamine (H), arginine (R), lysine (K), phenylalanine (F), tryptophan (W), tyrosine (Y), valine (V), glutamic acid (E), and aspartic acid (D). As a control, commercial PEG-OH (5K) was studied concurrently.
The functionalities were grouped into five categories: alcohols (S, T, PEG-OH), acids (D, E), aromatic (F, W, Y, H), basic (R, K), and hydrophobic (V). For ORR studies, each of the amino acid R group conjugated PEG (PEG-X) polymers were adsorbed onto commercially obtained Pt black; this was accomplished overnight, in water at molar ratios of 100 and 500:1 moles PEG-X: moles Pt particles. At 100:1 PEG-X:Pt reaction ratios very little polymer was lost on all of the PEG-R samples.

Scheme 4.1. Structures of the synthesized PEG-X polymers.
indicating that the polymer coverage was similar for all R groups (Figure 4.6). At 500:1 the final ratios of the PEG-X:Pt particles were approximately 450:1 for all the samples, again indicating similar surface coverage for all of the functional groups (Figure 4.6).

<table>
<thead>
<tr>
<th>POLYMER</th>
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<th>POLYMER</th>
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</table>

Figure 4.1. Polymer Loading for the PEG-X polymers on Pt Black.
Through systematic measurements of ORR, $E_{1/2}$ and mass activities were calculated as a function of R group and polymer coverage. Through loading different amounts of polymer per Pt particle, the effect of PEG chain packing and interchain interactions on ORR was examined.

Figure 4.2. Proposed interchain interactions between PEG-X chains on platinum surfaces.

As with any molecular ligands on a surface, as more polymers are adsorbed onto Pt, interchain associations including hydrogen bonding could also occur depending on the R group used (Figure 4.1). For the ORR studies, lyophilized Pt-PEG-X samples were dissolved in water to a concentration of 5 μg/μL, and 30 μg of each sample were deposited onto a GC-RDE and allowed to dry in air. The GC-RDE
was then coated with 5 μL of 0.05% Nafion to fix the sample onto the GCE surface. ORR measurements were taken using a rotating disk electrode setup with rotation speeds ranging from 0-2000 rpm at 400 rpm intervals. These measurements provided current values for Koutecky-Levich analyses from which mass activities of each sample were determined as outlined in ORR Studies. The half-wave potential for each sample at 1600 rpm was used for comparison of catalytic activity across samples. In the subsequent ORR studies, most of the investigated PEG-X conjugated Pt samples showed a noticeable increase in their half-wave potential (E₁/₂) as compared to Pt black; in some cases, these increases were up to 60 mV greater than Pt-black (Figures 4.2, 4.7).

Figure 4.3. Plots of mass activity (mA/mg) versus half wave potential (E₁/₂) for PEG-X coated Pt black at (left) 100:1 molar ratios of PEG-X:Pt and at (right) 500:1 molar ratios of PEG-X:Pt

In addition, several of these, including PEG-X polymers corresponding to the amino acids serine (PEG-S), threonine (PEG-T), aspartic acid (PEG-D) and glutamic acid (PEG-E) showed increases in mass activities with the highest value observed for PEG-T at 68 mA/mg with 500:1 polymer:Pt loading. These substantial increases in
either $E_{1/2}$ or mass activities with the polymer coating were surprising since typically an increase of blockage of the Pt surface results in a decrease in either $E_{1/2}$ or mass activities. While significant decreases in potential or activity were observed at all polymer loadings with the PEG-X chains corresponding to arginine (PEG-R) and valine (PEG-V), all the other PEG-X systems demonstrated either an increase in $E_{1/2}$ or mass activities and in some cases both. Since commercial PEG-OH coated Pt black also showed higher $E_{1/2}$ values (Figure 4.2, 4.7) compared with Pt black alone, it can be assumed that one possible reason for the observed higher $E_{1/2}$ values may be that the interaction between PEG and water\textsuperscript{34-36} helps prevent platinum oxidation or the formation of Pt-OH.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>MASS ACTIVITY (mA/mg)</th>
<th>$E_{1/2}$ (V)</th>
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<td>PEG-OH</td>
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Figure 4.4. ORR data for the PEG-X:Pt Black samples at 100:1, 500:1 and 1000:1.
Noticeable differences in the relationship between $E_{1/2}$ and mass activity were also observed in some of the other Pt-PEG-X samples, indicating that the R group could also play a significant role in influencing either Pt black dispersibility in solution or accessibility for oxygen to bind and undergo reduction at the Pt surface. In the case of the aromatic R groups, such as PEG-W, PEG-F and PEG-H, while higher polymer loadings caused the $E_{1/2}$ numbers to increase to values as high as 0.60 V, the mass activities greatly decreased with respect to Pt black. One potential reason for these seemingly disparate results is that the aromatic PEG chains may be close packed
on the Pt surface through H-bonding (Histidine-Histidine) or π-π interactions (Tryptophan-Tryptophan, Phenylalanine-Phenylalanine), which would also lead to increased H-bonding between the amide bonds in each PEG polymer. In the case of PEG-Y, the electron withdrawing –OH group weakens the π-π interactions, leading to weaker inter-chain interactions and enabling greater ORR activities as compared to the other PEG chains that contain aromatics. In contrast to the aromatic R group conjugated polymers, Pt black coated with PEG chains modified with hydroxyl R groups, including PEG-S, PEG-T, and PEG-Y, showed significant gains in both $E_{1/2}$ and mass activities relative to Pt black. As shown in Figure 4.2, 4.7, PEG-S coated Pt black showed mass activities of 63.0 mA/mg with 100:1 PEG-S:Pt loadings while PEG-T showed mass activities of 68.0 mA/mg with 500:1 PEG-T:Pt loadings. However, as PEG-S loadings increased further to 500:1, the mass activities dropped from 63.0 mA/mg to 40.8 mA/mg. Similarly, as PEG-T increased from 500:1 to 1000:1, the mass activity dropped from 68.0 mA/mg to 27.8 mA/mg. In contrast to the hydroxyl amino acid PEG chains, when commercial PEG-OH was used, the mass activities were significantly lower than those of Pt black with increasing $E_{1/2}$ values for all polymer loadings. One way to explain the difference in mass activities seen between PEG-S and PEG-T versus PEG-OH is that although PEG-OH does yield high $E_{1/2}$ values which consequently increase with higher polymer loadings, interchain associations between the close-packed PEG-OH chains prevent or inhibit fast oxygen diffusion to the Pt surface. On the other hand, due to the existence of the amide bonds in the PEG-S and PEG-T chains, even at relatively high polymer loadings, small gaps
remain within the polymer coatings enabling oxygen to diffuse through them (Figure 4.1). In the case of PEG-T, the extra methyl group at the α-carbon would further prevent complete chain packing enabling the highest mass activities to be observed at a value of approximately 70 mA/mg. However, as PEG-T was further increased to 1000:1 polymer:Pt loading, the sheer amount of polymer at the Pt surface prevented oxygen from adsorbing to the Pt surface and the mass activity dropped to 27.8 mA/mg (Figure 4.7). A sample of the ORR output for the PEG-T coated Pt black is presented in Figure 4.3.

Figure 4.5: (A) LSV polarization curves for ORR at PEG-T (100:1) in O$_2$-saturated 0.1 M H$_2$SO$_4$ at scan rate 10 mV s$^{-1}$ for 400 to 2000 rpm. (B) Koutecky-Levich plot of polarizations curves of PEG-T (100:1) from data outlined in (A). (C) LSV polarization curves of 30 μg Pt loading for ORR at PEG-T (500:1, solid), PEG-T (100:1, dashed) and Pt black (dotted) in conditions outlined in (A).

Figure 4.3A shows the ORR polarization curve for 100:1 PEG-T:Pt at rotation speeds of 400, 800, 1200, 1600, and 2000 rpm. The voltammetry displays a clear, steady-state reduction signal for oxygen reduction onset at potential 0.6 V vs. Ag/AgCl. The signal increases with increasing rotation speed and the half-wave potential (E$_{1/2}$) was calculated from the wave for 1600 rpm. Figure 4.3B shows the Koutecky-Levich plot of the inverse of the square root of rotation speed vs. the inverse of the current density. The data were fit to a linear plot, the intercept of which was
used to calculate the mass activity of the species. This same analysis was performed for all of the PEG-X Pt samples and mass activities and half-wave potentials were noted. Figure 4.3C outlines a comparison between PEG-T (100:1, dashed line), PEG-T (500:1, solid line) and Pt black (dotted line). It is clear that the E_{1/2} and current output of the PEG-T (100:1) is improved compared to that of Pt black, and this is attributed to the presence of the PEG-T groups. With higher loading of PEG-T (500:1), the current output and E_{1/2} improved further. This could be attributed to the extra methyl group at the α-carbon of threonine reducing the ability of the ligands to close-pack on the Pt surface. With the 500:1 PEG-T Pt samples, we also observed a deviation from the steady-state diffusion seen for the 100:1 samples to that of quasi steady-state. With respect to the basic and acidic R groups, while PEG-D showed mild improvements in both E_{1/2} and mass activity and was similar in performance to PEG-K coated Pt black, PEG-E showed only increases in E_{1/2} (Figure 4.2, 4.7). The lower mass activity observed with PEG-E vs PEG-D may be due to the extra methylene group in glutamic acid which hinders or slows O_{2} diffusion to the surface. Similarly, while PEG-K did show better E_{1/2} values overall than either PEG-D or PEG-E, there was no corresponding increase in mass activity. This may be attributed to the dual effect of having a 5 carbon alkyl carbon chain in between the amide bond and the primary amine in the case of PEG-K which could potentially lower the rate of diffusion of oxygen to the Pt surface due to its hydrophobic nature. In contrast to PEG-K however, the other basic amino acid, arginine-conjugated PEG (PEG-R) showed very low E_{1/2} and mass activity values. One reason a guanidinium-conjugated PEG polymer could
lower E$_{1/2}$ and subsequently mass activity is due to the strong interactions between neighboring guanidinium (Guan$^+$-Guan$^+$) which has been observed in molecular simulation studies.$^{39-40}$ As opposed to neighboring primary amines, such as those contained in the amino acid lysine, homo-ion pair formation between arginine-arginine units has been measured and has been proposed to be due to both solvent exclusion and dispersion interactions between the two ions. The lowering of both E$_{1/2}$ and mass activities with PEG-R is also similar to that observed with PEG-V (Figure 4.2) which may be due to both groups causing solvent exclusion or solvent reordering at the Pt surface. On the other hand, lysine conjugated PEG (PEG-K) first does not cause water exclusion and the interchain interactions between neighboring PEG-K is weaker due to electrostatic repulsion, thereby explaining why PEG-R showed both low E$_{1/2}$ and mass activities but PEG-K did not (Figure 4.1). Finally, since addition of PEG-T improved ORR catalytic activity compared to Pt black, a 2000-scan cyclic voltammetry study was undertaken to measure the stability of PEG-T to extended ORR reactivity.

Figure 4.6: Stability study of PEG-T (500:1) for 2000 cyclic voltammetric sweeps in O$_2$-saturated 0.1 M H$_2$SO$_4$ for scan rate 100 mV s$^{-1}$
Figure 4.4 shows CVs acquired of PEG-T at 500:1 loading after 10, 100, 250, 500, 1000, 1500, and 2000 scans. The reductive wave for oxygen was stable up to approximately 500 scans; however, the current output and the potentials deteriorated between 500 and 1000 scans and continued to do so up to the final 2000th scan. The signal appeared to split into two separate signals, which may be due to different adsorbed species on the Pt surface. Since previous studies have shown that Pt black is stable for up to 10,000 scans, the observed deviation in ORR signal can be attributed to the deterioration of the PEG-T units rather than Pt. Future studies of this system will examine the stability of different amino acid loadings of the PEG-X-Pt system, as well as different types of amino acids to generate more stable yet highly catalytic materials toward ORR.

In addition to ORR studies, we also tested the modified PEG polymers on platinum nanoparticle synthesis to probe the effect of each amino acid. Since the backbone of PEG was shown to impart little influence on nanocrystal size or morphology (Chapter 3), the PEG-X systems allowed investigating nanoparticle synthesis at the amino acid level. For this, each of the PEG-X polymers was mixed with K$_2$PtCl$_4$ in water at a 1:1 mol ratio and reduced in H$_2$. The solutions were sealed and reacted at room temperature overnight to allow particle growth to occur. The samples were then imaged by TEM to determine the morphologies of the particles. Samples were synthesized using PEG-OH, PEG-COOH, PEG-Q, PEG-S, PEG-T, PEG-Y, PEG-H, PEG-F, and PEG-W. First, platinum particles were synthesized using commercially obtained PEG-OH and synthesized PEG-S to determine what effect, if
any, the amide group in PEG-S had on the particle synthesis. It was determined that the inclusion of amide units had a negligible effect on the synthesis as both PEG-OH and PEG-S produced cubic and truncated cubic Pt particles as seen in Figure 4.1. The morphology of the Pt particles is highly dependent on the hydrophobicity of the functional group used in the synthesis (Figure 4.2). The particles synthesized using the hydrophilic PEG-X samples (OH, S, T, COOH, Q) were well-defined shapes capped by specific facets. Within the hydrophilic groups, PEG-OH, PEG-S, PEG-COOH, resulted in mainly cubic particles, whereas PEG-T and PEG-Q resulted in largely cuboctahedral particles. On the other hand, the particles synthesized using the aromatic PEG-X polymers (W, Y, H, F) showed poor control over crystal growth and morphology, yielding mainly misshapen structures or aggregates. This may have been caused in part by the relative low solubility of some of these aromatic amino acids in water which may have driven the formation of polymer aggregates or assemblies and prevented the amino acids from binding to Pt.

**Conclusion**

Pt black bound by amino acid R group-terminated PEG showed significantly higher ORR activities depending on the identity of the end functional group. In particular, alcohol-containing R groups showed near 100% and ~270% increases in mass activities over that of Pt black and commercial PEG-OH bound Pt respectively. While the PEG polymer itself could help increase $E_{1/2}$ by presumably preventing Pt–OH formation, the difference between commercial PEG-OH and PEG-S or PEG-T can
only be accounted for when considering the role of the amide bonds within the PEG-X chains. Although hydrogen bonding can occur between the amide bonds of neighboring PEG-X chains, the presence of amide bonds in the polymer backbone would also enable larger gaps to exist within the polymer layer, preventing the chains from packing too tightly on the Pt surface and allowing for oxygen diffusivity. When strong R group associations occurred on the Pt surface due to either π-π interactions, hydrogen bonding or hydrophobicity, the PEG-X coated Pt black showed poor mass activities which could be due to strong inter-chain associations lowering the accessibility of oxygen for the surface. The work shown here demonstrates the possibility of developing capping ligands for Pt nanoparticle catalysts that can still stabilize particles, allow for particle dispersibility both in solution and on electrodes while providing high ORR activities, in some cases above that of bare metal.

**PEG-S** – 1H NMR (400 MHz, CDCl3) δ: 3.63 (s, 182H), 3.54 (m, 2H), 3.49 (t, J = 5.8 Hz, 2H), 3.36 (s, 3H), 2.26 (t, J = 7.2 Hz, 2H), 1.74 (p, J = 6.9 Hz, 2H), 1.60 (m, 2H)

**PEG-T** – 1H NMR (400 MHz, CDCl3) δ: 3.90 – 3.84 (m, 1H), 3.67 – 3.58 (s, 182H), 3.53 (t, J = 3.7 Hz, 2H), 3.41 (dd, J = 6.6, 2.8 Hz, 1H), 3.36 (s, 3H), 3.00 (ddd, J = 13.6, 8.1, 5.2 Hz, 1H), 2.26 (t, J = 7.2 Hz, 2H), 1.72 (ddt, J = 10.3, 7.0, 3.8 Hz, 2H), 1.61 (q, J = 6.1 Hz, 2H), 1.14 (d, J = 6.3 Hz, 3H)

**PEG-D** – 1H NMR (400 MHz, CDCl3) δ: 3.63 (s, 182H), 3.53 (m, 2H), 3.44 (d, J = 5.5 Hz, 2H), 3.36 (s, 3H), 2.43 (t, J = 5.9 Hz, 2H), 2.19 (t, J = 7.0 Hz, 2H), 1.66 (m, 2H), 1.57 (m, 2H)

**PEG-E** – 1H NMR (400 MHz, CDCl3) δ: 3.63 (s, 182H), 3.53 (m, 2H), 3.36 (s, 3H), 3.27 (q, 2H), 2.34 (t, J = 6.8 Hz, 2H), 2.21 (t, J = 7.2 Hz, 2H), 1.81 (m, 2H), 1.69 (m, 2H), 1.59 (m, 2H)

**PEG-R** – 1H NMR (400 MHz, CDCl3) δ: 3.63 (s, 182H), 3.53 (m, 4H), 3.47 (m, 2H), 3.36 (s, 3H), 2.33 (t, J = 7.2 Hz, 2H), 1.65 (m, 6H), 1.57 (s, 2H)

**PEG-K** – 1H NMR (400 MHz, CDCl3) δ: 3.64 (s, 182H), 3.55 (m, 2H), 3.38 (s, 3H), 3.25 (q, J = 5.9 Hz, 2H), 2.95 (m, 2H), 2.88 (s, 2H), 2.25 (t, J = 6.8 Hz, 2H), 1.66 (m, 2H), 1.54 (m, 2H), 1.47 (m, 2H)

Figure 4.7. 1H NMRs of Synthesized PEG-X Polymers
PEG-F – 1H NMR (400 MHz, CDCl3) δ: 7.29 (m, 2H), 7.21 (t, J = 6.5 Hz, 3H), 3.64 (s, 182H), 3.55 (m, 2H), 3.47 (t, J = 7.0 Hz, 2H), 3.38 (s, 3H), 2.80 (t, J = 7.1 Hz, 2H), 2.18 (t, J = 7.3 Hz, 2H), 1.67 (m, 2H), 1.58 (m, 2H)

PEG-Y – 1H NMR (400 MHz, CDCl3) δ: 6.98 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 3.60 (s, 182H), 3.52 (m, 2H), 3.41 (m, 2H), 3.35 (s, 3H), 2.69 (t, J = 6.9 Hz, 2H), 2.13 (m, 2H), 1.63 (p, J = 7.0 Hz, 2H), 1.51 (p, J = 7.2, 6.6 Hz, 2H).

PEG-W – 1H NMR (400 MHz, CDCl3) δ: 7.60 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 6.9 Hz, 1H), 7.02 (s, 1H), 3.63 (s, 182H), 3.55 (m, 2H), 3.40 (t, J = 6.3 Hz, 2H), 3.38 (s, 3H), 2.97 (t, J = 6.6 Hz, 2H), 2.13 (t, J = 7.2 Hz, 2H), 1.64 (m, 2H), 1.55 (m, 2H).

PEG-V – 1H NMR (400 MHz, CDCl3) δ: 3.61 (s, 182H), 3.46 (t, J = 6.1 Hz, 2H), 3.35 (s, 3H), 3.03 (m, 2H), 2.19 (t, J = 7.3 Hz, 2H), 1.72 (m, 3H), 1.58 (m, 2H), 0.88 (d, J = 6.7 Hz, 6H)

PEG-H – 1H NMR (400 MHz, CDCl3) δ: 7.53 (s, 1H), 6.78 (s, 1H), 3.61 (s, 182H), 3.49 (d, J = 6.0 Hz, 2H), 3.41 (m, 2H), 3.35 (s, 3H), 2.77 (t, J = 6.4 Hz, 2H), 2.17 (t, J = 7.3 Hz, 2H), 1.65 (m, 2H), 1.49 (m, 2H)

Figure 4.7. ¹H NMRs of Synthesized PEG-X Polymers, continued.

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Chapter 4, in part, is a reprint of the material as it appears in Journal of Materials Chemistry, A 2013. Forbes, Lauren M., Sattayasamitsathit, Sirilak, Xu, Phyllis, O’Mahony, Aoife, Samek, Izabela A., Kaufmann, Kevin, Wang, Joseph, Cha, Jennifer N., J. Mater. Chem. A, 2013, DOI: 10.1039/C3TA12133J. The dissertation author was the primary investigator and author of this paper.

Appendix. Proton NMR Spectra of PEG-X Polymers

$^1$H NMR of synthesized PEG-R
$^1$H NMR of synthesized PEG-S

$^1$H NMR of synthesized PEG-T
1H NMR of synthesized PEG-D

1H NMR of synthesized PEG-E
$^1$H NMR of synthesized PEG-H

$^1$H NMR of synthesized PEG-W
$^1$H NMR of synthesized PEG-K

$^1$H NMR of synthesized PEG-Y
$^1$H NMR of synthesized PEG-F

$^1$H NMR of synthesized PEG-V
References


CHAPTER 5

In addition to ORR studies of PEG-X coated Pt black (Chapter 4), we are investigating the role that various amino acid side groups have on the catalytic activity of faceted Pt particles. Polyethylene glycol (PEG) chains were modified with functional groups related to the R-groups of different amino acids and adsorbed to collodially synthesized Pt cubes, cuboctahedra, and tetrahedral through ligand exchange methods. We are currently measuring the catalytic activity of the PEG-X coated Pt particles toward ORR to determine if there are differences in the effect of the amino acid R-groups on ORR between Pt particles capped with different facets. These differences will give us greater insight into the roles that different types of functional groups play in ORR on Pt particles.

Materials and Methods

Polymer synthesis. Different amino acid R groups were attached to polyethylene glycol (PEG) polymers using one of two methods depending on the hydrophobicity of the R-group. The hydrophilic amines used in the PEG-R syntheses were: ethanolamine (S), amino-2-propanol (T), β-alanine (D), γ-aminobutyric acid (E), histamine (H), cadaverine (K) and agmatine sulfate (R). The hydrophobic amines used were: phenethylamine (F), tyramine (Y), tryptamine (W) and isobutylamine (V). All amines were purchased from Sigma-Aldrich. The synthesis of the polymer using hydrophilic amines was done by adding 500 μmol of the amine to 5 mL of 0.01 M aqueous
solution of methoxypolyethylene glycol-succinimidyl valerate (mPEG-SVA) (MW=2000 g/mol, Laysan Bio). The solution was heated at 60°C overnight, then cooled and lyophilized. The dry mixtures were dissolved in 5 mL of methylene chloride and vacuum filtered through a Buchner funnel. $^1$H NMR of the filtrates was taken to confirm purity. Polymer solutions that still contained starting material were dialyzed further. The synthesis using hydrophobic amines was done by adding 500 μmol of the amine to 5 mL of 0.01 M solution of methoxypolyethylene glycol-succinimidyl valerate (mPEG-SVA) (MW=2000 g/mol, Laysan Bio) in methylene chloride. The solutions were heated at 40°C overnight. The solutions were then dried and the residues washed with ether. $^1$H NMR of the precipitates was taken to confirm purity. Polymers that still contained starting material were run on analytical TLC plates using an 80% methanol/20% methylene chloride solution as the eluent.

**Nanoparticle Synthesis.** Cubes were synthesized following the published procedure by Sun et. al.$^1$, with nucleation being induced at 120°C. Cuboctahedral particles were synthesized using as published by Yang, et. al.$^2$ Tetrahedral particles were synthesized as published by Zaera et.al.$^3$ All chemicals were obtained from Sigma-Aldrich.

**Ligand Exchange.** The dried particles were suspended in 5 mL pyridine and refluxed at 100 °C for 3 hours. The temperature was then reduced to 65 °C and the solution was stirred overnight. The particles were crashed out with hexane and centrifuged for 10 minutes at 10,000 rpm. The pyridine-coated particles were then dispersed in water (1 mg/mL) and separated into 1 mL aliquots. 1000 equivalents of PEG-X were added to each aliquot and shaken for about 12 hours. The samples were then centrifuged for 5
minutes at 14,500 rpm, the supernatant removed and retained. The samples were washed with 100 μL of water and centrifuged again for 5 minutes at 14,500 rpm. The supernatant was again removed and combined with previous supernatant. The samples were allowed to air-dry at room temperature and the supernatants were lyophilized.

**TEM Analysis.** The particles were characterized by TEM on a Philips CM 100 TEM and a FEI Tecnai 12-Spirit BioTwin. For the cube particles suspended in hexane, a carbon-formvar grid was dipped in the solution and then allowed to dry. For the other nanoparticle solutions in water, a 3 μL sample was removed from the solution and dropped carefully onto the grids. The drop was allowed to dry under ambient conditions. Average size was determined by randomly measuring 100 particles.

**1H Solution NMR.** NMRs of the supernatants were run by dissolving the sample in 500 μL of D₂O spiked with 0.01 M DMF and running for 512 scans. NMRs of Pt nanoparticle samples were prepared by adding 500 μL of D₂O to the dried nanoparticle samples and sonicating the solutions to suspend the particles. The solutions were then transferred to NMR tubes and sonicated 30 minutes immediately followed by running NMRs of the samples for 512 scans. All spectra were collected on a 400 MHz Bruker Avance-III Spectrometer.

**Results and Discussion**

Functional groups corresponding to the R-groups of amino acids were attached to 2000 MW PEG polymers in order to investigate the effects amino acid side chains can have on the catalytic activity of faceted Pt particles. The PEG
polymer acts as a non-Pt binding macromolecular scaffold, allowing for the investigation of single amino acid units. We have demonstrated previously that polyethylene glycol interacts very weakly with platinum surfaces and that the end-termini are primarily responsible for platinum binding, nanoparticle growth, and ORR activity. This system allows us to study many different amino acid R-groups including acidic, basic, aromatic, hydrophobic and hydroxyl groups. The variety of groups examined can hopefully give us clues into the interactions ligands can have with the surface of a Pt nanoparticle. We have also previously adsorbed these PEG-X polymers to Pt black and shown that the identity of the end group is important in the catalytic activity of the PEG-X-Pt particles toward ORR.

We have now expanded our investigation from small irregularly shaped Pt black particles to collodially synthesized faceted Pt particles, in order to gain greater insight into the interactions of the different functional groups on different Pt surfaces and the effect they have on the catalytic activity of the particles toward ORR.

Figure 5.1. Collodially prepared Pt a) cubes b) cuboctahedra and c) tetrahedral
Cubic, cuboctahedral, and tetrahedral Pt particles were synthesized by published colloidal methods\textsuperscript{1-3}. The samples were imaged by TEM to confirm particle shapes and sizes. Figure 5.1 shows TEM images of the particles. The particles then underwent ligand exchange using pyridine as an intermediate in order to obtain Pt particles capped by the PEG-X polymers. 1D \textsuperscript{1}H NMRs were taken to confirm ligand exchange. The washed PEG-X-capped particles were allowed to air-dry to prevent aggregation that was seen with lyophilization as seen in Figure 5.2.

![TEM images of the particles](image)

Figure 5.2. PEG-S-Pt cubes a) lyophilized and b) air-dried

We are currently running experiments to measure the catalytic activity of the PEG-X coated particles toward ORR. We hope to see differences in the effect specific functional groups have on the catalytic activity based on the particle shape.
References


