Platinum@Hexaniobate Nanopeapods: Sensitized Composite Architectures for Photocatalytic Hydrogen Evolution Under Visible Light Irradiation

Clare Davis-Wheeler Chin
University of New Orleans, cdaviswh@uno.edu

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Platinum@Hexaniobate Nanopeapods: Sensitized Composite Architectures for Photocatalytic Hydrogen Evolution Under Visible Light Irradiation

A Dissertation

Submitted to the Graduate Faculty of the University of New Orleans in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

By

Clare Davis-Wheeler Chin

B.A. Tulane University, 2003

August 2018
To My Parents (in order of appearance):

Mom, Dad, Carol, and Richard

*For everything*

To Micah

*For his wisdom*

To James

*For being my hero*

To Bruce

*In loving memory*

To Jake

*For knowing it all along*
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Abstract

Hydrogen fuel is one of the most important areas of research in the field of renewable energy development and production. Hydrogen gas can be generated by fuel cells, water electrolyzers, and heterogeneous nanoscale catalysts. It can be burned to directly release chemical energy or condensed for storage and transport, providing fuel for combustion devices or storing excess energy generated by renewable sources such as wind turbines and concentrated solar power assemblies. While platinum is the most active catalyst for hydrogen reduction, its high cost significantly deters its utilization in advanced photocatalytic materials. One approach to mitigating this expense is optimizing the morphology and placement of nanostructured platinum catalysts. Highly crystalline, morphologically-controlled platinum nanoparticles (Pt NPs) have been effectively utilized to increase hydrogen generation efficiency in a variety of nanocomposite materials. However, synthesis routes to high-quality Pt NPs can be dangerous and difficult to replicate. Furthermore, utilization of the Pt NPs in nanocomposite materials is hindered by lack of control over catalyst placement.

Nanopeapods are versatile nanocomposites that offer a high degree of control over catalyst placement as well as the potential for interesting new properties arising from the interaction between the catalyst and a semiconductor. Platinum@hexaniobate nanopeapods (Pt@HNB NPPs) consist of linear arrays of Pt NPs encapsulated within the scrolled semiconductor hexaniobate. Pt@HNB NPPs offer significant advantages over similar composites by utilizing the isolated reduction environment of the encapsulated Pt NP arrays to decrease kinetic competition and surface crowding.

This work describes the design, fabrication, and implementation of the new nanocomposite platinum@hexaniobate nanopeapods for sensitized hydrogen production under
visible light irradiation. The following chapters present facile microwave heating syntheses of highly crystalline Pt nanocubes and Pt@HNB NPPs with consistent morphology and high catalyst loading. A detailed study is also presented of the optical properties of the Pt nanocubes, which produced a UV-range absorbance band that indicates the formation of a localized surface plasmon resonance. Most significantly, preliminary results from visible light photolysis indicate that sensitized Pt@HNB NPPs produce hydrogen in quantities comparable to published systems, and that alteration of experimental parameters may result in even greater yields.

**KEY WORDS:** photocatalytic hydrogen generation, photocatalytic nanocomposites, highly crystalline platinum nanocubes, visible light photolysis, Ru(bpy)-sensitized platinum@hexaniobate nanopeapods, microwave synthesis
Chapter 1

Introduction

1.1 Dye-Sensitized Wide Band Gap Semiconductors

The use of dye-sensitized wide band-gap semiconductors for photocatalytic water splitting has been the subject of much recent research. In 1972, Gerischer et. al introduced the first system that produced hydrogen gas (H$_2$) from water by coupling a wide band-gap semiconductor with a photosensitizing dye.\(^1\) Current designs take advantage of the properties of nanoscale semiconductors as well as catalytic nanoparticles to reduce electron transport distances, adsorb sensitizers to greater surface areas, and increase the output of H$_2$ from water splitting. These offer a significant potential contribution to the renewable energy economy, in which photocatalytic H$_2$ generation could be used for H$_2$ fuel cells in cars and other devices.\(^2\)

Various coordinated systems operate under the basic principle of photocatalytic water splitting.\(^2\) A photon with energy greater than 1.23 eV ($\lambda < 1000$ nm) is absorbed and generates an exciton, or pair of photoexcited charge carriers (electrons, e$^-$, and holes, h$^+$). In a semiconductor, the photoexcited electrons are promoted across a gap in energy levels (band gap) from the valence band to the conduction band. The difference in energy between the upper edge of the valence band and the lower edge of the conduction band is known as the band gap energy ($E_g$) and determines the energy of the photon needed to promote photoexcited electrons to the conduction band. The absence of energy levels in the band gap deters direct charge carrier recombination, preventing rapid excited state deactivation and allowing the $e^-$ to migrate to the conduction band while the $h^+$ remain in the valence band. The holes in the valence band perform the oxidation half-reaction (Equation 1.1a), while the electrons that migrate to the conduction

\[ \text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{OH}^- \]
band perform the reduction half-reaction (Equation 1.1b). The overall water splitting equation is shown in Equation 1.1c.

(1.1a) \[ \text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2e^- \]
(1.1b) \[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]
(1.1c) \[ \text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2 \quad \Delta V = 1.23 \text{ eV} \]

Dye-sensitized wide-band gap semiconductor systems are very promising for use in photovoltaic and photoelectrochemical cells, offering very efficient electron injection and transport to catalytic metals that are adsorbed, encapsulated, or otherwise incorporated into the composite catalyst. Although many semiconducting layered metal oxides (LMOs) will undergo this process upon absorbing ultraviolet radiation, a higher output of H$_2$ can be achieved by using a photosensitizing dye to absorb wavelengths in the visible light region of the electromagnetic spectrum. When the photosensitizer is attached to the semiconductor surface, it will inject photoexcited electrons directly into the conduction band of the semiconductor. A catalytic nanoparticle (NP) can attract these electrons for the catalysis of the water reduction reaction. In order to perpetuate the production of H$_2$ and avoid depletion of electrons from the photosensitizer, a sacrificial electron donor is often added to the aqueous solution in which the system is suspended in order to regenerate electrons to the oxidized sensitizer. Figure 1.1 gives a representation of this process based on a published system in which utilizes Ru(bpy)$_3^{2+}$ as the photosensitizer and ethylenediaminetetraacetic acid (EDTA) as the sacrificial electron donor.
1.2 Ruthenium(II) Bipyridine-Based Photosensitizers

One important class of visible light photosensitizers is based on the structure tris(2,2'-bipyridine)ruthenium(II)$^{2+}$, referred to hereafter as Ru(bpy). It is a $d^6$ octahedral coordination complex in which a ruthenium(II) atom is surrounded by three bipyridyl (bpy) ligands (Figure 1.2a) that can be functionalized with various groups. Functionalization of the bpy ligands can include addition of carboxylic acid groups that allow a covalent linkage to semiconductor surfaces. This compound, (4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II)$^{2+}$, will be referred to as Ru(dcbpy) and is shown in Figure 1.2b.

Ru(bpy) complexes possess both singlet and triplet excited states, with a low-energy singlet metal-to-ligand charge transfer ($^1$MLCT) transition that allows for the promotion of electrons from the Ru(II) d-orbitals to the bipyridyl ligands. Those electrons can then be readily

**Figure 1.1.** Injection scheme of electrons from the photoexcited chromophore into the conduction band of the semiconductor, where the electron proceeds to the reduction catalyst to generate $H_2$. The oxidized chromophore is regenerated by the sacrificial electron donor in an irreversible reaction.
injected into a semiconductor with a compatible conduction band energy. Electrons that are not injected undergo intersystem crossing to a $^3$MLCT state, which is a spin-forbidden transition that results in a very slow relaxation to the ground state and thus a very long-lived charge separation from the excited state. Both the long-lived charge separation and the availability of readily-injected excited state electrons make Ru(bpy) complexes ideal for coupling with semiconductors for photocatalytic water splitting.\(^7\)

![Figure 1.2. Visible light sensitizers (a) Ru(bpy) and (b) Ru(dcbpy).](image)

1.3 Layered Metal Oxide Semiconductors
Layered metal oxide (LMO) semiconductors have been extensively used in studies on dye-sensitized photocatalysts due to their stability, wide variation in composition, high efficiency as electron transport mediators, and structural flexibility that can be transformed into a diverse array of morphologies including exfoliated nanosheets, nanotubes, and multiwalled nanoscrolls.\(^8\) LMO semiconductors that are catalytically active usually have very efficient charge-transport pathways that connect the interior to the surface, where water-splitting occurs.\(^9\) Photocatalytic activity of layered niobates, titanates, and tantalates has been liked to crystal structure, with
materials containing a network of corner-sharing octahedral units of metal cations (NbO$_6$, TiO$_6$, and TaO$_6$) showing increased charge-carrier mobility. These layered materials are often classified as perovskites, which consist of infinite two-dimensional octahedral unit layers separated by interlayers of various compositions. The octahedral perovskite units have a general formula ABO$_6$, in which A is an alkali or alkaline earth metal cation and B is a transition metal cation. Figure 1.3a shows the Ruddlesden-Popper perovskite K$_2$La$_2$Ti$_3$O$_{10}$, which is a double-layered perovskite with an interlayer containing K$^+$ cations. Structural modification of the interlayer can be achieved by low temperature (T \leq 500 ºC) topochemical methods such as ion exchange.

1.3.1 $K_4Nb_6O_{17}$

The layered metal oxide semiconductor $K_4Nb_6O_{17}$ has a structure based on a two-dimensional network of edge- and corner-sharing NbO$_6$ octahedra, with a structural asymmetry between the two [Nb$_6$O$_{17}$]$^{4+}$ slabs that creates an interesting dual interlayer structure (Figure 1.3b). Interlayer I is readily permeable, and substitution of the K$^+$ ions with protons (or other cations) is readily achieved via topochemical methods. The other, more sterically hindered interlayer II retains more of its K$^+$ ions even after multiple solvation treatments. When protonation is performed by exposing the host material to HCl, the exchange of K$^+$ for H$_3$O$^+$ ions occurs primarily in interlayer I such that the formula of the protonation product is expressed as H$_x$K$_4$.$x$Nb$_6$O$_{17}$. This leads to a reduction in the interlayer spacing as well as a reduction in band gap, perhaps due to a weakening of the Nb-O bonds to Nb—OH that is expected from the protonation and observed in literature via infrared and Raman spectroscopy. This band gap reduction can have a significant impact on the material’s semiconductor properties, which will be discussed in Chapter 5.
Exfoliation and scrolling of the protonated product $H_xK_{4-x}Nb_6O_{17}$ can be achieved by intercalating a large cation such as tetrabutylammonium (TBA$^+$) into the permeable interlayer.\textsuperscript{14} This forces the sheets apart. Scrolling of the exfoliated sheets can then occur, perhaps in order to relieve the intrinsic mechanical strain from the layer asymmetry or the difference in cation densities on opposite sides of the sheets.\textsuperscript{15} The scrolling process can be carried out by using

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.3}
\caption{Crystal structures of (a) $K_2La_2Ti_3O_{10}$ and (b) $K_4Nb_6O_{17}$. The asymmetry of the octahedral slabs results in the formation of two distinct interlayer types, labeled I and II.}
\end{figure}
several different methods, including aqueous and solvothermal synthesis (see Chapter 5).\textsuperscript{3,17} Nanoscrolls synthesized via solvothermal methods are capped with hydrophobic oleylamine groups, and must undergo surface modification in order to be dispersed in polar solvents.\textsuperscript{18} This process increases the dispersibility of the scrolls in solvents commonly used in photolysis studies, and enables covalent bonding with the carboxylic acid groups on the functionalized complexes (see Chapter 5).

1.3.2 Modifying Layered Metal Oxide Structure and Composition for Catalysis
Interlayer modification can be useful for increasing photocatalytic activity in perovskites and perovskite-like LMOs. The high catalytic activities of some of these layered materials can be attributed to the incorporation of water into the interlayer spacing, which can increase interfacial area and reduce charge transfer distances. Protonation (replacement of alkali or alkaline earth metal cations with hydrogen) can reduce the band gap energy such that compatibility with photosensitizers or co-catalysts is increased. Electronic structure and composition is also an important catalytic factor: studies have shown that only layered metal compounds with $d^0$ (Ti, Zr, Nb, Ta) or $d^{10}$ (Ga, In, Ge, Sn, Sb) ions display activity for water splitting.\textsuperscript{9}

Layered titanates and niobates have been extensively studied for photocatalytic applications due to their high carrier mobility, structural stability, and flexibility for modifications such as exfoliation and scrolling.\textsuperscript{11,19} The Dion-Jacobson perovskite $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ can be protonated, exfoliated, and restacked via acid treatment to produce highly stable colloidal nanosheet suspensions that can then be sensitized with $\text{Ru(bpy)}$ chromophore complexes. These sensitized nanosheets have shown high activity for hydrogen generation under visible light illumination.\textsuperscript{20}

It is well-documented in literature that the conversion of bulk materials to the nanoscale can alter the electronic structure and transitions in semiconductors.\textsuperscript{21} Exfoliation and scrolling of
bulk semiconductors allows the band structure to be tuned to optimize coupling with photosensitizing materials. This technique has been utilized to increase H\textsubscript{2} production in a wide array of photocatalytic systems.\textsuperscript{22} In order for the reduction of water to proceed, the conduction band edge potential (E\textsubscript{CB}) of the semiconductor must exceed the H\textsuperscript{+}/H\textsubscript{2} reduction potential of 0.0 V vs. NHE at pH 0 (-0.41 V vs. NHE at pH 7). The value of E\textsubscript{CB} can be estimated from the band gap potential (E\textsubscript{g}), as seen in Equation 1.2:\textsuperscript{23}

\begin{equation}
E_{CB} \approx 1.23 - \frac{E_g}{2}
\end{equation}

The efficiency of photocatalytic hydrogen generation is subject to the relative rates of the forward and reverse reactions for electron transfer between the photoexcited chromophore and the semiconductor conduction band.\textsuperscript{21} The forward reaction (Equation 1.3a) represents the electron injection process and is initiated via photoexcitation of the ground-state chromophore into its MLCT (metal to ligand charge transfer) excited state, \textsuperscript{\textasteriskcentered}Ru(bpy)\textsubscript{3}\textsuperscript{2+}. The photoexcited chromophore then injects an electron into the semiconductor conduction band, where it may proceed to perform water reduction at the catalyst NP. Equation 1.3b represents the reverse reaction, in which the photoinjected electron recombines with the oxidized chromophore, Ru(bpy)\textsubscript{3}\textsuperscript{3+}.\textsuperscript{24}
The kinetic competition between these two reactions is a main factor in determining H$_2$ output. The rates of both the forward ($k_{inj}$) and reverse ($k_r$) reactions depend on the value of the semiconductor’s conduction band edge $E_{CB}$ with respect to the reduction potentials of the chromophore’s MLCT excited state.$^{24}$ The reduction potentials relevant to electron injection and recombination are those of chromophore’s MLCT excited state, in which either Ru(bpy)$_3^{2+}$ acts as a reductant (with potential $E^{(3+/2+)}$) or Ru(bpy)$_3^{3+}$ acts as an oxidant (with potential $E^{(3+/2+)}$).

Both Ru(bpy) MLCT reduction potentials are well known, and can be used in conjunction with the value of semiconductor $E_{CB}$ to calculate the standard free energy changes for the electron injection and recombination reactions ($\Delta G_{\text{inj}}^0$ and $\Delta G_r^0$, respectively), as seen in Equation 1.4.$^{25}$ The resulting free energy values can then be used to predict and interpret H$_2$ output.
\[(1.4a) \Delta G_{\text{ inj}}^0 = E^{(3^+/2^+)} - E_{\text{CB}}(\text{NScs})\]

\[(1.4b) \Delta G_{\text{ r}}^0 = E_{\text{CB}}(\text{NScs}) - E^{(3^+/2^+)}\]

**Equations 1.4a-b.** Calculation of free energy changes for the forward and reverse reactions of electron transfer from the photoexcited chromophore to the band gap of the semiconductor \((E_{\text{CB}}(\text{NScs}))\). \(\Delta G\) values for (a) electron injection \((\Delta G_{\text{ inj}}^0)\) and (b) recombination \((\Delta G_{\text{ r}}^0)\) reactions can be calculated and compared. Literature values from Ford et al.\(^2\) were used for the reduction potentials of the Ru(bpy) MLCT excited state.

\[(1.4a) E^{(3+/*2+)} = -0.85 \text{ V vs. NHE} \]
\[(1.4b) E^{(3+/2+)} = -1.25 \text{ V vs. NHE} \]

### 1.3.3 Optimizing Photocatalytic Hydrogen Production in Nanoscale Hexaniobate Systems

Photocatalytic hydrogen production by Ru(bpy)-sensitized hexaniobate nanocomposites can be increased by manipulating the electronic band structure of the semiconductor. The protonation of the parent compound \(K_4\text{Nb}_6\text{O}_{17}\) results in a decrease in the band gap energy from 3.7 eV to 3.4 eV. Nanoscale conversion via exfoliation and scrolling further decreases the band gap of hexaniobate to 3.3 eV.\(^2\) This has important implications for photocatalytic hydrogen generation.

<table>
<thead>
<tr>
<th>Material</th>
<th>(E_g) (eV)</th>
<th>(E_{\text{CB}}) (eV)</th>
<th>(\Delta G_{\text{ inj}}^0) (V vs. NHE)</th>
<th>(\Delta G_{\text{ r}}^0) (V vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_4\text{Nb}<em>6\text{O}</em>{17})</td>
<td>3.71</td>
<td>-0.62</td>
<td>-0.22</td>
<td>-1.87</td>
</tr>
<tr>
<td>(H_xK_4-x\text{Nb}<em>6\text{O}</em>{17})</td>
<td>3.42</td>
<td>-0.48</td>
<td>-0.36</td>
<td>-1.73</td>
</tr>
<tr>
<td>Hexaniobate NScs</td>
<td>3.25</td>
<td>-0.39</td>
<td>-0.45</td>
<td>-1.64</td>
</tr>
</tbody>
</table>

**Table 1.1.** Values related to band gap energies for parent \((K_4\text{Nb}_6\text{O}_{17})\), protonated \((H_xK_4-x\text{Nb}_6\text{O}_{17})\), and scrolled hexaniobate semiconductor compounds. Band gap energies \((E_g)\) were calculated via analysis of diffuse reflectance spectra for samples of each compound (see Chapter 5). Conduction band edge potentials \((E_{\text{CB}})\) were calculated using **Equation 1.2**. \(\Delta G^0\) values for the electron injection (forward) and recombination (reverse) reactions were calculated using **Equations 1.3a-b**.
As seen in Table 1.1, decreasing a semiconductor’s band gap energy causes a subsequent decrease in the conduction band edge potential, which results in a more negative free energy change for the forward reaction. In terms of electron transfer kinetics, this can be interpreted as an increase in the driving force for the injection of electrons from the photoexcited chromophore into the conduction band of the semiconductor. Table 1.1 also shows that the $E_{CB}$ trend causes the free energy of the recombination reaction ($\Delta G^0_r$) to become less negative, although the recombination reaction is still kinetically favored. Multiple studies of photosensitized catalyst/semiconductor nanocomposites (including Ru(bpy)/Pt/hexaniobate systems) have concluded that a positive shift of the $E_{CB}$ potential increases the efficiency of electron injection and thus the water reduction reaction.

### 1.4 Platinum Nanoparticles

Platinum nanoparticles (Pt NPs) are highly efficient catalysts for photocatalytic water splitting and the redox reactions of oxygen, hydrogen, methanol, and other fuels. The shape and size of Pt NPs can be controlled to select for specific catalytic reactions, and can also influence interparticle interactions, self-assembly, dielectric properties, and light absorption and scattering. Well-dispersed colloidal Pt NPs offer great flexibility for the construction of catalytic nanoarchitectures, functionalization of oxide and polymer supports, dispersion for photodegradation of organic pollutants, and integration into sensors, fuel cells, and other devices. The use of Pt NPs for plasmonic photocatalysis is an exciting new area of research with promising applications for solar cells, surface-enhanced Raman scattering spectroscopy, molecular sensing, thermal emitters, and a wide variety of other devices for sensing and energy generation. The sensitivity of localized surface plasmon generation to nanoparticle size and
shape exemplifies the need for efficient, high-output synthesis strategies that offer a great deal of control over those factors.\textsuperscript{39-41}

\textbf{1.4.1 Morphology and Dispersibility of Nanoscale Platinum Catalysts}

The synthesis of platinum nanoparticles (Pt NPs) with controlled size and morphology is important in many areas of catalysis, including the development of alternative energy devices that rely on the efficiency of platinum-catalyzed redox reactions.\textsuperscript{35,42} Platinum nanoparticles have been well-established as one of the most efficient materials for a diverse array of catalytic applications, including hydrogen reduction and methanol oxidation reactions, performance in polymer electrolyte and direct methanol fuel cells, many types of hydrocarbon hydrogenation/dehydrogenation reactions, and a wide variety of other photovoltaic and photoelectrochemical systems.\textsuperscript{28,31,43} The importance of nanoscale platinum catalysts is well-documented in literature; the efficiency of catalyzed redox and water-splitting reactions can be greatly increased by the larger surface area offered by Pt NPs over the bulk material. The extremely strong interactions between platinum and hydrogen make nanoscale Pt ideal for hydrogen reduction and hydrogenation catalytic reactions.\textsuperscript{30} In particular, size-controlled Pt NPs are important for the water-splitting reactions found in photoelectrochemical cells. The development of well-dispersed, size-controlled Pt NPs could be an important step in creating an isolated reduction environment for water-splitting nanoarchitectures.

Highly dispersible Pt NPs offer increased flexibility for constructing nanoarchitectures for catalysis, expanding the functional possibilities of the NPs beyond deposition onto a substrate or support and facilitating incorporation of the NPs into more diverse constructs. Dispersible Pt NPs have been incorporated into mesoporous oxide and silica matrices via capillary inclusion and nanoparticle encapsulation methods to make highly efficient heterogeneous catalysts.\textsuperscript{30} More generally, the high loading selectivity enabled by dispersible Pt NPs is ideal for low and
controlled catalyst loadings that significantly impact the durability, cost-effectiveness, and performance of fuel cell designs.\textsuperscript{29} A facile synthesis of highly dispersible Pt NPs offers great potential contributions for the design and function of advanced fuel cells, water-splitting architectures, and other heterogeneous catalyst systems.

\textbf{1.4.2 Formation Mechanism of Platinum Nanoparticles}

While recent literature has reported advances in extremely tunable size and shape for larger Pt nanocrystals, the preparation of well-controlled, highly dispersible Pt NPs at sub-20 nm sizes has been very challenging.\textsuperscript{31} Nanoparticle size ranges of around 10 nm are of particular interest for exploiting the quantum effects such as size-dependent fluorescence and plasmonic resonance.\textsuperscript{41} The ability of platinum as a noble metal to support localized surface plasmons can benefit areas such as field-sensitive optical characterization methods (surface-enhanced Raman scattering, fluorescence and luminescence emission) and sensing applications.\textsuperscript{44} Size tunability is of particular importance for catalysis applications, and shape tunability is also of great importance. Kang et. al published a recent study comparing the catalytic activity of nanoscale Pt cubes vs. octahedra.\textsuperscript{44} While the cubic shape with its dominant \{100\} facet has been shown to have the highest activity for the oxygen reduction reaction, octahedral Pt NPs and their dominant \{111\} facets were shown to have a higher poisoning tolerance in the electrooxidation of formic acid and a lower activation energy for catalyzing liquid-phase electron transfer reactions when compared to cubic Pt NPs (\textbf{Figure 1.4a}).\textsuperscript{29}

Multiple studies of colloidal metal NP synthesis methods have shown that metal NPs produced during cluster formation in solution tend to aggregate, creating large aggregate structures that reduce catalytic activity and decrease flexibility for use in composite nanoarchitectures.\textsuperscript{45} Different types of stabilization methods are employed to prevent agglomeration, including steric stabilization via coordination of sterically-demanding organic
ligands bound to the NP surface to create physical separation from nearby NPs. Mazumber et al. studied the effect of oleylamine (OAm) on colloidal metal NP synthesis, and found that the double bond in OAm may be critical to NP stabilization and growth with narrow size distribution.\(^{46}\) The long hydrophobic chains present on OAm ligands introduce steric hindrance effects to prevent contact between the high-energy surfaces of the growing Pt NPs and thus provide stabilization.\(^{42}\) These adsorptive capping agents decrease excess free energy and prevent further NP growth during the Ostwald ripening phase. However, these studies on OAm indicate that it is necessary to utilize a combination of reducing and shape-control agents, since OAm alone is a weak reducing agent that may cause a prolonged reduction process that produces multinucleation and uneven growth (Figure 1.4b).

The presence of a reducing agent facilitates the decomposition of metal precursor complexes at lower temperatures. In this case, the decomposition temperature of Pt(acac)\(_2\) can be decreased from 140 °C to as low as 100 °C through the addition of a reducing agent.\(^{47}\) Once the precursor complex has decomposed, Pt\(^{2+}\) can be easily reduced to Pt\(^0\) due to its high standard reduction potential.\(^{42}\) Boita et al. recently described a three-step formation process that is useful in describing the process that likely occurs in the microwave heating synthesis of Pt NPs.\(^{48}\) The first step involves a fast and limited nucleation event, which is ignited by the reduction of a platinum salt precursor by ascorbic acid in a scenario consistent with a LaMer nucleation burst.\(^{31}\) This is followed by a diffusion-limited growth phase, also known as “Ostwald ripening,” during which larger NPs grow at the expense of smaller ones. The third step involves the activation of stabilizing or capping agents, which adsorb to the NP surface and provide steric hindrance to halt agglomeration.
1.4.3 Use of Microwave Heating for the Synthesis of Platinum Nanoparticles

Our group has recently published reports of highly tunable rapid topochemical modification of layered metal oxides (LMOs) via microwave synthesis. The success of grafting, intercalation, and exfoliation of multiple LMO hosts suggested that similar results could be achieved not only for the protonated hexaniobate component of NPPs but for an even wider range of inorganic materials. Microwaves have been significant to chemistry applications as diverse as analytical, biochemistry, assembly of catalytic heterostructures, organometallics, polymers, and organic synthesis. Previously, MW syntheses of Pt NPs have been reported, but these have not produced highly crystalline or morphologically selected NPs.

Figure 1.4. Transmission electron micrographs of dispersible platinum nanoparticles. (a) Image of 8-nm cubic Pt NPs displaying {100}-faceted surfaces. Smaller, octahedral Pt NPs with dominant {111} facets can also be seen. (b) Irregularly-shaped Pt NPs show the occurrence of twinned or branched structures, which result from multiple nucleation events. This may have been caused by lack of reducing power or uneven heat distribution in the reaction mixture.
Traditional methods achieve synthesis via conductive heating. Heat is driven into the substance, passing through the walls of the vessel to reach solvents and reactants within.\textsuperscript{53} As such, the rate of heat transfer and equilibrium temperature are significantly affected by the thermal conductivity of the vessel materials. The temperature of the vessel will be greater than that of the reaction mixture until thermal equilibrium is reached, which results in a prolonged reaction time with a restricted amount of control over the heating rate and equilibrium reaction temperature.\textsuperscript{53} For materials such as Pt NPs that are extremely sensitive to heating rate, equilibrium temperature value, and temperature stability, this lack of control offered by conductive heating methods can greatly reduce product quality. In Chapter 2, Pt NPs produced by traditional conductive heating (solvothermal) methods are shown to have significantly inferior morphology compared to those produced via microwave heating.

In microwave reactors designed for materials synthesis, MW with a frequency of 2.45 GHz ($\lambda = 12.25$ cm) are produced by magnetron generators and interact with reaction mixtures through MW-transparent glass or PTFE vessels (\textbf{Figure 1.5}).\textsuperscript{52}

\textbf{Figure 1.5.} (a) Milestone StartSYNTH microwave. (b) Microwave-transparent PTFE vessel configuration used for the synthesis of Pt NPs and Pt@HNB NPPs via microwave heating.
Microwave radiation contains both an electric component, from which dipolar polarization and conduction cause molecular rotation, and a magnetic component, which induces Ohmic heating.\textsuperscript{53} MW radiation couples directly with species in the reaction mixture, inducing instantaneous localized superheating of any reaction species that will respond to either dipole rotation or ionic conduction. If the reaction mixture lacks species that will give sufficiently respond to either, a strongly-absorbing material such as graphite-doped Teflon (Weflon\textsuperscript{TM}) can be inserted into the vessel. These MW susceptors promote MW absorption and heat generation in non-polar reaction mixtures, which results in an even temperature increase during heating, homogeneous energy distribution, and steady maintenance of equilibrium temperature (\textbf{Figure 1.6}).\textsuperscript{50-53}

\textbf{Figure 1.6.} Microwave radiation interacts directly with the reaction mixture and induces instantaneous localized superheating, which leads to an even heat distribution throughout the mixture. For Pt precursors with their shape control and reducing agents, this encourages homogeneous nucleation and leads to the production of monodispersed Pt NPs with a very small size distribution.

Heating rate is an important advantage of MW methods. The timescale of transfer of MW energy to reaction species is much faster than that of kinetic molecular relaxation, effectively transferring energy more quickly than molecules can relax. This results in a non-
equilibrium condition that enhances reaction rates and product yields. Facile reaction control is also achieved through the instant-on/instant off nature of MW reactors. Previous reports on MW heating synthesis of inorganic nanomaterials state that the greatest advantage of MW irradiation is the ability to heat a reaction mixture uniformly. This leads to more homogeneous nucleation and shorter crystallization times, which are beneficial for forming monodispersed metal colloids. The use of MW absorbers or susceptors allows MW to penetrate the reaction mixture to give homogenous and simultaneous rapid heating to quickly reduce metal precursors to their zero-valent state, promoting homogeneous nucleation and growth of metallic NPs (Figure 1.4a). Achieving good size and shape control of metallic NPs is highly dependent on controlling reaction temperatures and heating rates, which govern particle nucleation and growth. The greater degree of control and precision offered by microwave heating methods creates a highly tunable and repeatable strategy for producing high-quality NPs and other nanocomposites.

1.5 Optical and Catalytic Activity of Platinum Nanoparticles
The importance of nanoscale platinum catalysts is well-established for a wide variety of environmental, industrial, and synthetic applications. Pt NPs are highly efficient catalysts for photocatalytic water splitting and the redox reactions of oxygen, hydrogen, methanol, and other fuels. The shape and size of Pt NPs can be controlled to select for specific catalytic reactions, and can also influence interparticle interactions, self-assembly, dielectric properties, and light absorption and scattering. Well-dispersed colloidal Pt NPs offer great flexibility for the construction of catalytic nanoarchitectures, functionalization of oxide and polymer supports, dispersion for photodegradation of organic pollutants, and integration into sensors, fuel cells, and other devices. The use of Pt NPs for plasmonic photocatalysis features promising
applications for solar cells, surface-enhanced Raman scattering spectroscopy, molecular sensing, thermal emitters, and a wide variety of other devices for sensing and energy generation. The sensitivity of localized surface plasmon generation to nanoparticle size and shape exemplifies the need for efficient, high-output synthesis strategies that offer a great deal of control over nanoparticle size and morphology.

The extremely high activity of platinum for the essential redox reactions of photocatalysis has led to a wide and well-established library of data for the catalytic activity of Pt NPs with diverse shapes, sizes, and surface functionalizations. There are several common methods that target the production of colloidal Pt NPs in the desired size range (≤ 10 nm), including colloidal lithography, citrate stabilization, biphasic microemulsions, radiolytic and hydrogen reduction, and wet chemical reduction via solvothermal or high-temperature organic phase techniques. Although the literature for methods that produce morphologically-controlled, highly-crystalline, and well-dispersed Pt NPs includes high-quality catalytic data, two main problems are encountered: optical data is either cursory or completely excluded, and the methods fail to produce dispersible, morphologically consistent Pt NPs when replicated using the published methods.

1.5.1 Studies of Nanoscale Platinum Optical Properties
In contrast to the substantial and self-consistent library of catalytic data for Pt NPs, the available optical data is sparse and inconsistent, even among groups that used the same synthesis method. The widely-cited 1991 study by Creighton and Eadon has been an important source for the optical data of noble metal nanoparticles. The study featured predicted and observed spectra for nanoparticles of 52 different metallic elements, including gold, silver, and platinum. Calculations that have been the standard reference for other noble metal NPs included the prediction that small (10 nm) Pt NPs should produce a well-defined localized surface plasmon
resonance near 200 nm.\textsuperscript{73} Equations derived from Mie theory and the Drude model accounted for such variables as nanoparticle size, solvent refractive index, and the wavelength-dependent complex dielectric constants $\varepsilon_1$ and $\varepsilon_2$. Absorbance cross section (C) and molar absorption coefficient ($\alpha$) could be calculated, allowing Creighton and Eadon to predict a well-defined, plasmonic absorbance peak at 215 nm for 10-nm spherical Pt NPs in an aqueous solvent.\textsuperscript{73}

Localized surface plasmon resonances (LSPR) can concentrate the energy of incoming photons, producing intense electric fields around plasmonic NPs. Small noble metal NPs that produce LSPR are highly sought after for use in composites for many applications, including surface-enhanced Raman spectroscopy, plasmonic waveguides, molecular sensing, thermal emitters, optical antennae, and solar cells.\textsuperscript{68} Chapter 3 contains a detailed analysis of the optical properties of highly crystalline Pt nanocubes, including evidence of a plasmonic absorbance peak at 213 nm. LSPR production by small, highly crystalline Pt NPs offers the advantage of high catalytic activity to current plasmonic nanocomposite materials, which traditionally use Ag and Au NPs.\textsuperscript{68}

Despite the widespread acceptance and accuracy of Creighton and Eadon’s study with respect to the plasmonic properties Ag and Au NPs, the predicted spectrum and plasmonic response of Pt NPs remains widely disputed and inconsistent among detailed optical studies.\textsuperscript{32–34,60,62,74–80} The majority of optical studies on small ($\leq$ 10 nm) Pt NPs report a broad, featureless extinction spectrum over the entire range of 200-800 nm, although there is optical data for colloidal Pt NPs with larger sizes ($> 30$ nm) that shows a well-defined localized surface plasmon resonance (LSPR) peak in both the UV and visible ranges, depending on the size of the particle.\textsuperscript{32–34,60,62,74–80} Detailed optical studies comparing absorbance spectra from Pt NPs produced by various methods suggest that species associated with citrate reduction and the
chloroplatinic acid precursor may interfere with the observation of the LSPR of Pt NPs in the 200-260 nm range. Recent assertions that small Pt NPs hold great promise for improving semiconductor-based photocatalysis have led to a significant increase in the synthesis and utilization of sub-10 nm Pt NPs. Small Pt NPs have been most frequently coupled with TiO$_2$ in various architectures, and the results of these studies consistently show enhanced photocatalytic activity. This enhancement has often been attributed to speculative “Pt plasmons”, but the studies do not provide direct optical evidence that shows the location of an LSPR peak for the Pt NPs. Other groups that have observed photocatalytic enhancement in Pt/semiconductor composites suggest that inter-band excitations within the Pt NPs are responsible. It is clear that understanding the optical properties and plasmonic characteristics of small Pt NPs is essential for continuing to develop Pt/semiconductor photocatalysis. Moreover, the extreme sensitivity of platinum’s plasmonic response to the nanoparticle surface exemplifies the importance of promoting a facile synthesis method for highly crystalline, well-dispersed Pt NPs in the sub-10 nm size range.

1.5.2 Electronic Band Structure of Noble Metal Nanoparticles

In a bulk metal, there is a loss of discrete energy levels and a formation of energy bands. Highest occupied molecular orbitals (HOMOs) become the valence band (VB), while lowest unoccupied molecular orbitals (LUMOs) become the conduction band (CB). In metals, valence band $s$ and $p$ orbitals overlap to form $sp$ bands, whereas the $d$ orbitals have less overlap and form narrower $d$-bands. At absolute zero, all bands in a metal are filled to an energy level known as the Fermi energy ($E_F$), or the maximum energy occupied by an electron at -273 °C. The Pauli exclusion principle dictates that electrons will fill all available levels, such that the top of the VB “sea of electrons” is known as the Fermi level. The population of CB electrons for a metal is a product of the density of CB electron states and the Fermi function.
The density of free CB electrons is one of the most influential factors on the energy at which the LSPR of a metallic NP will occur. When NPs couple resonantly to light, the resonance is dominated by the interaction between photons and free electrons inside the metal’s conduction band. For the purposes of photocatalysis, noble metal nanoparticles are superior to semiconductors for light harvesting due to their low activation barriers that result from a high electron density at the Fermi level. The most commonly used plasmonic metals are Ag and Au, which have optimal band structures and dielectric functions for producing visible-range LSPR. Although Pt is typically considered a noble metal, it does not display LSPR features at visible-range wavelengths.

Comparison between the electronic band structures of Ag, Au, and Pt reveals several critical differences that help explain the deviation of Pt’s optical and plasmonic properties from the Ag and Au. The key difference between their band structures is related to the separation of the valence and conduction bands and the value of each metal’s \( E_F \). Ag and Au both have \( d \)-bands that lie at lower energy levels (below \( E_F \)), while Pt’s \( d \)-bands are at higher energies, crossing and extending 0.5 eV above Pt’s \( E_F \). The position of these unoccupied energy bands provides the final states for optical transitions and determines the absorbance spectrum features of metallic elements. Empty bands at higher energies (above \( E_F \)) give rise to higher-energy optical transitions that produce spectral features in the UV range. Intra-band transitions (crossing the \( E_F \)) increase the imaginary part of the complex dielectric function and cause a broadening and weakening of the plasmon band.

Ag and Au have optical properties that are determined almost exclusively by \( d-d \) transitions within the conduction band. These transitions promote electrons from a single lowest conduction band (CB) energy state: \((n = 5, l = 0)\) and \((n = 6, l = 0)\) for Ag and Au, respectively.
The position of the Ag and Au conduction bands below their respective Fermi levels prevents resonance damping from intraband transitions and gives lower-energy final electronic states that correspond to visible-range LSPR frequencies.\textsuperscript{90,91,94} When the additional benefit of highly-polarizable filled \(d\)-bands is included, optimal conditions for the generation of visible-range LSPR absorbance peaks by Ag and Au NPs are formed.

In contrast, Pt’s absorbance peak includes contributions from intraband transitions that originate from an \(sp\) band near the Fermi level.\textsuperscript{89,91} This plurality of final electronic states for electrons excited at the resonance frequency weakens the plasmonic character of the absorbance of Pt NPs. Additionally, the strong wavelength-dependence of Pt’s dielectric function could weaken the plasmonic character of the band and thus causes a blue shift in its position.\textsuperscript{32} Chapter 3 expands the discussion on the electronic band structure of noble metals, and its impact on their optical properties.

\subsubsection*{1.5.3 Localized Surface Plasmon Resonance on Noble Metal Nanoparticles}

Surface plasmons on noble metal NPs are composed of oscillations of conduction band electrons coupled with an electromagnetic field.\textsuperscript{90} When the frequency of the incident field’s photons is in resonance with the oscillation of the conduction band electrons, the resulting surface plasmon resonance produces an optical absorbance band.\textsuperscript{90} At the nanoscale, boundary and surface effects have increased importance and significantly influence the optical properties of the NPs.\textsuperscript{90} The LSPR frequency depends strongly on NP size, shape, dielectric properties, and interparticle interactions. It is also highly dependent on the local dielectric environment.\textsuperscript{90,95–99}

The complex dielectric function of a metallic nanoparticle consists of the frequency-dependent real and imaginary dielectric constants \(\varepsilon_1\) and \(\varepsilon_2\). Calculations to predict LSPR frequency and intensity utilize these dielectric constants as well as the bulk plasma frequency and the dielectric constant of the surrounding medium, \(\varepsilon_m\).\textsuperscript{74,80,91–93} An ideal plasmonic
resonance occurs when the value of the complex dielectric function reaches a minimum, which requires that 1) the real dielectric constant $\varepsilon_1$ is equal to $-2\varepsilon_m$ and 2) the value of $\varepsilon_2$ is close to zero. The frequency of the resonance condition is determined by the wavelength-dependence of $\varepsilon_1$, while the band width and height are determined by the value of $\varepsilon_2$.\textsuperscript{67,90,100}

As discussed in the previous section, the electronic band structure of Ag and Au prevents resonance damping from intra-band transitions and gives lower-energy final electronic states. Subsequently, their dielectric functions feature low $\varepsilon_2$ values in the visible range, producing distinct LSPR under visible light irradiation.\textsuperscript{101} In contrast, Pt’s absorbance peak includes contributions from intra-band transitions that originate from an $sp$ band near the Fermi level.\textsuperscript{100,105} As a result of these intra-band transitions, Pt possesses very high values for its dielectric constants at visible-range frequencies.\textsuperscript{91} The surface plasmon resonance for Pt should occur at the frequency for which $\varepsilon_1 = -2$, which would correspond to 276 nm using literature values for the dielectric constants.\textsuperscript{32} Other estimations set the resonance condition to occur at a different value varies based on the refractive index of the solvent, the bulk plasma frequency, or the high-frequency contribution to the dielectric constant of Pt.\textsuperscript{32} Sufficient changes in these factors could cause the plasmon resonance condition not to be met, in which case the absorbance bands for Pt NPs would be caused only by inter-band transitions and would be strongly blue-shifted (increasing the difficulty of detection by UV-Vis spectroscopy).

Another factor that can influence the shape and position of the LSPR band is the presence of surface adsorbates such as surfactant molecules.\textsuperscript{33,67,90,100,102–106} Ligand-metal interactions can affect coherent oscillations of conduction band electrons, and ligands can also affect the interaction of light directly with the nanoparticle surface.\textsuperscript{39,90,106} One such effect is the alteration of electron density ($N_e$), which is the factor that determines the number of free electrons
available to form charge density oscillations and thus determines the intensity of the surface plasmon resonance.\textsuperscript{33,90,106} Rivadulla et al. published equations derived from Mie theory in which the LSPR frequency could be predicted based on the plasma frequency of the bulk metal.\textsuperscript{33} Since the bulk plasma frequency varies inversely with the square root of the free electron concentration, adsorbates that increase surface electron density through their attachment to the NP will cause a blue shift in the plasma frequency and thus the LSPR frequency.\textsuperscript{33}

1.5.4 Exploring New Platinum Nanocomposites for Plasmonic Photocatalysis

The basis of plasmonic photocatalysis is that confinement and quantization of conduction band electrons in the small space of a nanoparticle surface causes the enhancement of optical and electrical conductance properties. When the NP diameter is much smaller than the wavelength of the incident radiation, energy is confined to small spatial regions due to the local extinction of LSPRs.\textsuperscript{90} The strong enhancement of the local electric field around excited nanoparticles gives a wide range of potential applications. Excited particles decay either by re-emission of a photon (scattering) or the formation of an electron-hole pair (absorption).\textsuperscript{40} These “hot” electron-hole pairs can be extensively used in photocatalytic applications by utilizing the tunable LSPR frequency to create electrons with energies matching the resonances of other species.\textsuperscript{68}

Despite platinum’s excellent catalytic properties, Pt NPs have been largely excluded from research on advanced photocatalytic and plasmonic materials.\textsuperscript{32,90} However, recent advances in plasmonics suggest that Pt’s higher-energy LSPR bands may introduce advantages such as more efficient degradation of organic pollutants and broader utilization of the solar spectrum (such as UV-range plasmonic effects) when incorporated into composite structures with semiconductors, substrates for enhanced scattering, or sensitizing species.\textsuperscript{82,107–113} Other reports state that UV-range plasmonic responses to NP size and shape are more sensitive than those in the visible
range, allowing greater potential for tunability of frequency selection for different photocatalytic reactions.\textsuperscript{67,68}

Recent studies in the field of plasmonic photocatalysis have recognized that metals such as Rh and Pt hold significant promise for improving advanced catalytic materials.\textsuperscript{68,114} Researchers have recognized many shortcomings of the traditionally-used Ag and Au NPs: lack of durability due to oxidation by air and water of Ag NPs; poor catalytic potential compared to other metals Au NPs.\textsuperscript{68,114} X. Zhang et al. explored the benefits of UV-range LSPR using Rh nanocubes produced via polyol synthesis.\textsuperscript{114} They found that the cubic shape helped focus EM fields, and the UV plasmonic response had excellent potential for applications such as label-free detection of biomolecules and studying UV-light photodegradation of Raman active molecules. They concluded that future studies in advanced plasmonic materials should feature metals with catalytic activity superior to that of Ag and Au.\textsuperscript{32,114,115} N. Zhang et al. observed that small (< 10 nm) Pt NPs can be made to absorb visible light by altering their dielectric environment, using the Pt NPs to absorb light scattered by the dielectric surface of an SiO\textsubscript{2} support as part of a TiO\textsubscript{2}-based nanocomposite.\textsuperscript{68} These studies illustrate that the benefits offered by platinum’s superior catalytic properties for use in plasmonic photocatalytic architectures are numerous, and provide strong support for further research into platinum-catalyzed nanocomposites.

1.6 Photocatalysis via Noble Metal/Semiconductor Nanocomposites

Layered metal oxides are chemically desirable for their stability, biocompatibility, and non-toxicity, and catalytically desirable for their efficiency as an electron transport mediators and photocatalytic activity under UV irradiation.\textsuperscript{116} Layered titanates and layered perovskites including Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}, K\textsubscript{2}Ti\textsubscript{4}O\textsubscript{9}, K\textsubscript{2}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10}, and KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} have been shown to exhibit
intrinsic photocatalytic activity.\textsuperscript{19} In these materials, charge separation occurs in the host layers under UV irradiation and charge carriers migrate to the valence or conduction band to perform oxidation or reduction reactions, respectively. The wide band gap of most LMO semiconductors does limit their functionality in solar-conversion systems, thus they are often coupled with sensitizing dyes and other smaller-band gap materials to make stable, efficient structures for photocatalysis.

Topochemical modification of interlayer structures can induce the conversion of these layered materials from bulk to nanoscale.\textsuperscript{12,19,117} Nanosheets, nanotubes, and nanoscrolls can be produced from multiple LMO hosts. Scrolled inorganic nanostructures are the subject of much current research due to their potential uses in drug delivery, pollutant photodegradation, gas sensing, and a wide range of catalysis applications.\textsuperscript{3,118,119} The hollow cores and extremely large surface areas offered by these scrolled structures invite diverse and extensive functionalization, especially for catalysis applications given the inherently photocatalytic nature of scrolled materials such as $K_4Nb_6O_{17}$ and $TiO_2$.\textsuperscript{2,21,120,121} Nanosheets (NSs) are also widely studied as photocatalysts. Semiconductor NSs are highly anisotropic, with thicknesses of $\sim$1 nm and lateral sizes of 1 μm or more.\textsuperscript{19} This structural aspect has been linked to novel or enhanced photocatalytic properties as compared to the bulk material.

\subsection*{1.6.1 Semiconductor Functionalization with Catalyst Nanoparticles}
Composites featuring wide band-gap semiconductors and noble metal nanoparticles have been extensively studied as materials for artificial photosynthesis.\textsuperscript{3,22} Recent studies have emphasized the importance of hexaniobate-noble metal alloy nanocomposites with excellent visible-region activity for degradation of organic pollutants and preventing the loss of photoactivity during recycling and long-term storage.\textsuperscript{40} The Dion-Jacobson perovskite $HCa_2Nb_3O_{10}$ can undergo exfoliation into NSs via intercalation of bulky tetrabutylammonium (TBA$^+$) cations.\textsuperscript{20}
TBA⁺-capped NSs are restacked into ordered aggregates by the dropwise addition of 0.5 M HCl. Pt NPs are then grown on the surface by irradiating the NSs in an aqueous methanol solution containing the precursor H₂PtCl₆ under UV for 24 hours. This method of platinization is known as *in-situ* photodeposition, and has been widely used to coat nanosheet and nanoscroll surfaces with ultrafine (1-2 nm) Pt NPs that serve as the reduction catalyst for photocatalytic water splitting. This method has been used for the surface deposition of other catalytic NPs, including the study by Hata et al. in which photodeposited Rh₂O₃ NPs were used as an oxidative catalyst.

The photodeposition method is versatile and allows the catalyst NPs to come into direct contact with water for the redox reactions. Studies on hexaniobate NScs loaded with photodeposited ultrafine Pt NPs indicate great potential for increased hydrogen production efficiency, especially when sensitized with Ru(bpy) chromophores. This is due to the very high activity of hexaniobate as an electron-transport mediator, the large surface area for active reduction sites provided by the NScs, and the particular surface charge and composition of hexaniobate that make it exceptionally compatible with Ru(bpy) chromophores. However, despite promising results in earlier studies, hydrogen yields from platinized Ru(bpy)/hexaniobate composites have remained low. One likely cause is surface crowding between adsorbed sensitizers and catalyst Pt NPs (*Figure 1.7*). This reduces potential chromophore loadings and creates kinetic competition for photogenerated electrons, from which the kinetically favored recombination process severely limits hydrogen production. In addition, surface-platinized systems rely on a sacrificial electron donor in order to regenerate the oxidized chromophore, and thus cannot be used for overall water splitting in most practical applications.
1.6.2 Hexaniobate Nanopeapods

Nanopeapods (NPPs) are a unique type of nanoarchitecture that have been reported by our group and offer advanced, precise techniques for engineering the exfoliation, scrolling, and assembly processes. The nanopeapod architecture offers a promising alternative for the placement of the catalytic, magnetic, or other types of NPs. NPPs feature the NPs located within a multi-walled nanoscroll structure and can be formed using a variety of methods, including encapsulation, solvent evaporation, and *in-situ* aqueous synthesis. In the encapsulation method, pre-formed NPs and crystalline hexaniobate are combined, with the hexaniobate scrolling around the NPs to create the NPP structure (Figure 1.8).

Figure 1.7. Scheme showing the photocatalytic reduction of hydrogen by Pt NPs coating the surface of a nanoscroll. Photoexcited electrons are injected from the Ru(II) complex (C) into the conduction band of the semiconductor, in a process that oxidizes the chromophore (C'). Electrons are subject to kinetic competition between the reduction catalyst and the oxidized chromophore. The recombination reaction is energetically favored, which reduces H₂ output.
The ability to selectively place noble metal nanoparticles in various dimensions onto inorganic metal oxide host structures via surface decoration, encapsulation, or in situ growth may allow nanoarchitecture formation for a wide variety of promising applications: biological and chemical sensing, surface-enhanced Raman scattering (SERS), nanoscale optical waveguides, biodiagnosics through selective localized photothermal heating, and heterogeneous catalysis.\textsuperscript{116,126} Semiconductors are especially promising for pairing with noble metal nanoparticles through peapods and other similar nanoarchitectures. By controlling nanoparticle morphology and dielectric environment, LSPR frequency can be tuned for reaction selectivity with different semiconductors and under different types of illumination. These catalytically tailored architectures may offer significant increases in reaction efficiency.\textsuperscript{39,41}

Our group has already reported on a diverse array of NPPs incorporating different metal oxides, magnetic NPs, quantum dots, and plasmonic metals that offer interesting magnetic,
optical, catalytic, and plasmonic properties. Some of our recent publications describe the potential use for nanopeapods for photocatalysis.\textsuperscript{124,125} Hexaniobate was scrolled around well-dispersed pre-formed silver nanoparticles (Ag NPs) in a solvothermal reaction, and gold NPs were grown within pre-formed nanoscrolls in an \textit{in situ} aqueous synthesis. Both types of noble metal NPPs displayed interesting plasmonic effects.

One challenge involving nanopeapods is the optimization of fabrication routes. Key challenges include increasing NPP yield, achieving precise control over pea and pod dimensions, increasing NP filling, and achieving complete hexaniobate exfoliation. Recent studies have shown that microwave heating methods are able to produce large quantities of high-quality NPPs, which will be of great use in developing materials applications for NPPs. In Chapter 5, results of using Ru(bpy)-sensitized platinum@hexaniobate NPPs to produce H\textsubscript{2} via visible light photolysis will be presented.

\textbf{Figure 1.9.} A photoexcited Ru(bpy) chromophore ejects an electron into the conduction band of a platinum@hexaniobate nanopeapod, which offers an isolated reduction environment.
1.7 References


Chapter 2
Rapid Microwave Synthesis and Optical Activity of Highly Crystalline Platinum Nanocubes*

2.1 Introduction

We have developed a novel, facile, and reproducible synthesis of highly crystalline oleylamine-capped colloidal Pt nanocubes by microwave (MW) heating. Use of MW heating decreases reaction times, eliminates the need for dangerous reagents, and gives efficient production of monodispersed 8 nm Pt nanocubes (MW-NPs).

Nanoscale platinum catalysts are essential components in a wide variety of industrial, environmental, and synthetic applications. Pt NPs have been well-established as one of the most efficient materials for a diverse array of catalytic applications, including performance in polymer electrolyte and direct methanol fuel cells, nonlinear optics, photonics, information storage, and a wide variety of chemical and biological sensing applications.1-5 Nanoscale Pt catalysts also have extremely high activity for redox reactions that include hydrogen and oxygen reduction as well as methanol, carbon monoxide and formic acid oxidation.1,5 This excellent catalytic ability makes nanoscale Pt indispensable for photocatalytic water splitting, C-C hydrogenation and bond formation, and photodegradation of organic pollutants.3,6 The efficiency of catalyzed redox and water-splitting reactions is greatly increased by characteristics intrinsic to nanoscale Pt, such as an increased number of active atoms at edges and corners and an increase in available

*This chapter is based on the publication:
catalytically-active surface area.\textsuperscript{7} The size and shape of Pt NPs can be controlled to select for specific catalytic reactions, and can also influence interparticle interactions, self-assembly, dielectric properties, and light absorption and scattering.\textsuperscript{1,8–10} In particular, small (<10 nm) Pt nanocrystals offer a variety of benefits such as solvent dispersibility, production of a localized surface plasmon resonance, and facet-selective catalytic enhancements.\textsuperscript{4,5,11,12} Those with a cubic morphology are useful for selectively promoting the hydrogen evolution reaction, and show an increased tendency toward self-assembly that may benefit applications in plasmonics and sensing.\textsuperscript{4,5,8,10} Highly dispersible Pt NPs offer increased flexibility for constructing nanoarchitectures for catalysis, expanding the functional possibilities of the NPs beyond deposition onto a substrate and facilitating their incorporation into more diverse constructs.\textsuperscript{2} Colloidal Pt NPs have been incorporated into mesoporous oxide and silica matrices via capillary inclusion and nanoparticle encapsulation methods to make highly efficient heterogeneous catalysts.\textsuperscript{5,8,13,14} The high loading selectivity enabled by these NPs is ideal for controlling and minimizing catalyst loadings, which can significantly impact the durability, cost-effectiveness, and performance of fuel cells.\textsuperscript{4,15}

Despite the widespread use of nanoscale platinum for catalysis, only a few facile synthetic strategies for producing monodispersed Pt NPs have been reported.\textsuperscript{5,13} While high-temperature organic-phase synthesis methods can produce highly crystalline Pt NPs, these methods rely on the toxic Fe(CO)$_5$ to facilitate nucleation and are not consistently repeatable.\textsuperscript{1,12,13,16} Our studies on creating an alternative approach for a safe, facile, and reproducible synthesis found that highly crystalline, shape-controlled, dispersible Pt NPs could be reliably produced using a “one pot” microwave heating method. Microwaves have been significant to chemistry applications as diverse as analytical, biochemistry, assembly of catalytic
heterostructures, organometallics, polymers, and organic synthesis. Microwave methods allow the rapid transfer of energy directly to the reaction, utilizing localized instantaneous superheating to quickly and efficiently heat solvents. This results in a significant reduction in reaction times as well as increased ability to fine-tune reaction parameters. Since it is well-documented that the formation of Pt NPs is extremely sensitive to changes in temperature, the greater degree of control offered by microwave heating allows a much greater tunability of both NP size and shape. Previously, MW syntheses of Pt NPs have been reported, but these have not produced highly crystalline or morphologically selected NPs.

The benefits of a nanoparticle that possesses good size and shape tunability as well as high catalytic activity have motivated increased studies on the synthesis, utilization, and optical properties of sub-10 nm Pt NPs for plasmonic and photocatalytic applications. It is clear that understanding the optical properties and plasmonic characteristics of small Pt NPs is important to the development of advanced catalytic materials. Moreover, the extreme sensitivity of the platinum plasmonic response to the nanoparticle surface exemplifies the importance of promoting a facile synthesis method for highly crystalline, well-dispersed Pt NPs in the sub-10 nm size range. Herein we describe such a facile and reproducible synthesis method for the production of 8-nm Pt nanocubes. A comparison between Pt NPs synthesized by MW, solvothermal, and high-temperature organic synthesis is also presented.

2.2 Experimental

Materials. Oleylamine (OAm) (technical grade, 70%), platinum(II) acetylacetonate (Pt(acac)₂) (97%), L-ascorbic acid (≥99%), and trisodium citrate dihydrate (≥99%) were purchased from Sigma-Aldrich. A dispersion of commercially-produced platinum nanoparticles was also
purchased from Sigma-Aldrich. Toluene (certified ACS, 99.8% anhydrous), hexane (95% anhydrous), and absolute ethanol (200 proof) were purchased from Fisher Scientific.

2.2.1 Synthesis of Platinum Nanoparticles via Microwave Heating

Determination of the optimum parameters for producing 8-nm cubic Pt NPs using microwave heating was conducted by systematically varying reaction time and temperature. Time and temperature parameters were set using the T260 EasyCONTROL software, which provided the user interface to the instrument. Microwave synthesis was performed using a Milestone StartSYNTH Microwave Synthesis Labstation (Milestone Srl, Italy) equipped with a single magnetron generator with a rotating diffuser operating at 2.45 GHz, and a microprocessor-controlled power output of up to 1200 W. Temperature control was achieved by the instrument based on input from a contact-less internal infrared sensor. Reaction temperatures in the range 125-150 °C were examined, with trials for each temperature conducted for 30, 45, and 60 minutes. Maximum power and ramp rate could also be varied through the software, but in our study these were held at constant levels in order to allow focus on the parametric examination of time and temperature effects. For all trials, a maximum power setting of 1200 W and a ramp rate of 3.5 °C/minute was used, with temperature elevation rate controlled via applied power from the instrument. Samples were prepared by inserting a MW-absorbing Weflon™ (graphite-doped Teflon) button and PTFE-coated magnetic stir bar into an empty 15-bar StartSYNTH glass reaction vessel. The Weflon™ button was used in order to serve as a MW susceptor and provide homogeneous heat distribution throughout the reaction mixture. 200 mg Pt(acac)₂ (0.5 mmol), 50 mg L-ascorbic acid (0.28 mmol), 5 mL OAm (15 mmol), and 5 mL toluene (45 mmol) were added to the reaction vessel. The initial mixture was magnetically stirred at 650 rpm for 1 minute prior to insertion into the microwave, after which the reaction vessel was sealed and
secured within the rotor body of the StartSYNTH Microwave Synthesis Labstation. To ensure optimal distribution of heat and chemical species throughout the reaction mixture, magnetic stirring at 650 rpm was set via the T260 EasyCONTROL software and maintained consistently throughout the reaction by the instrument’s internal magnetic rotor. After the reaction, the vessel was cooled to room temperature at 10 °C/minute. **Caution:** One should inspect glass microwave vessels before each reaction; glass defects might lead to hotspots and result in an explosion.

Dark brown Pt NPs were isolated from solution by adding 25 mL EtOH to the product, followed by centrifugation for 10 minutes at 6000 rpm. The light yellow-brown supernatant was discarded and the precipitate was redispersed in toluene. This precipitation-redispersal procedure was repeated three times to obtain OAm-capped Pt NPs. Finally, the Pt NPs were dispersed in 15 mL of toluene and sonicated, then transferred to a glass scintillation vial.

### 2.2.2 Solvothermal Synthesis of Platinum Nanoparticles

Solvothermal synthesis of Pt NPs was carried out using a procedure modified from Cui et al.\textsuperscript{24} with subsequent systematic variations of time, temperature, surfactant, reducing agent, and solvent. In the original procedure, 200 mg Pt(acac)\textsubscript{2} and 100 mg Ni(acac)\textsubscript{2} were combined with 12.5 mL dimethylformamide (DMF) in a PTFE-lined stainless steel autoclave and heated at 120 °C for 42 h. After cooling to room temperature, Pt NPs were isolated via precipitation with EtOH followed by centrifugation for 10 minutes at 6,000 rpm and redispersal in toluene. The NPs were washed with a mixture of acetone, EtOH, and toluene, then centrifuged and redispersed in toluene. After repeating the washing procedure twice, the particles were dispersed in toluene. Production of non-agglomerated Pt NPs was targeted by increasing reaction temperatures in increments of 60 °C from 120-240 °C, and carrying out trials with reaction times of 6 h, 12 h, 18 h, 24 h, and 48 h at each temperature. After identifying 18 h at 180 °C as the
conditions that produced the least amount of aggregation, experiments were performed substituting toluene, benzyl ether, and octadecene as solvent, and OAm, ascorbic acid, tetrabutylammonium bromide (TBAB), and cetyltrimethylammonium bromide (CTAB) as reducing agents.

2.2.3 Ligand Exchange on Commercial Platinum Nanospheres and Microwave-Synthesized Platinum Nanocubes

To carry out the replacement of citrate ligands with OAm ligands on the surface of the commercial Pt NPs, 2 mL of the as-obtained aqueous suspension was centrifuged for 10 minutes at 13,000 rpm. The precipitate was redispersed in EtOH and sonicated 1-2 minutes until fully dispersed. The EtOH suspension was then transferred to a glass scintillation vial and combined with 1 mL OAm and 1 mL hexane. This mixture was sonicated for 2 minutes, then covered with foil and magnetically stirred at 55 °C for 48 h. The ligand-exchanged commercial Pt NPs (LC-NPs) were isolated by adding 15 mL EtOH and centrifuging for 10 minutes at 6,000 rpm. The product was redispersed in hexane via sonication. The process was repeated twice to remove any excess citrate species, after which the product was dried overnight in air. Finally, the LC-NPs were dispersed in EtOH and transferred to a glass scintillation vial.

A similar procedure was used to exchange the amine capping ligands present on the MW-NPs with citrate ligands to produce citrate-capped microwave-synthesized NPs (LMW-NPs). A concentrated aqueous solution of trisodium citrate dihydrate was prepared by adding 3.75 g of the solid to 5 mL of nanopure water and stirring at 45 °C for 1 hour. 2 mL of a toluene suspension of MW-NPs was sonicated to evenly disperse, then combined with 0.5 mL of the concentrated citrate solution and 2 mL of absolute EtOH. The mixture was sonicated again for 2 minutes and then magnetically stirred in a foil-covered glass scintillation vial at 55 °C. Samples were removed after 24 and 48 hours for analysis via Raman spectroscopy to ensure complete
ligand exchange. The removed samples were precipitated via centrifugation for 10 min. at 13,000 rpm. The supernatant was discarded, and the precipitate was washed twice via centrifugation with absolute EtOH and then dried in air overnight.

2.2.4 Characterization

X-ray diffraction (XRD) data was collected on a Philips X’Pert diffractometer utilizing Cu Kα radiation (λ = 1.5418 Å) and a curved graphite monochromator at an accelerating voltage of 45 kV and a current of 40 mA. Peak positions of the Pt NPs diffraction patterns were compared to reference values to confirm elemental Pt composition, and refinement of peak positions and the lattice parameter was performed with ChekCell software using a least-squares method.\(^{25}\) Diffraction patterns were indexed to assign Miller indices and d-spacing values to each peak, and peak broadening was examined by measuring the full-width half maximum (FWHM) of the peak at ~40° 2θ in order to estimate NP size via the Scherrer formula.\(^{26}\)

For transmission electron microscopy (TEM) measurements, Pt NPs were dispersed in toluene, sonicated, and dropcast onto 200-mesh copper grids. Both standard and high-resolution TEM (HR-TEM) images as well as selected area electron diffraction (SAED) patterns were obtained using an FEI G² F30 Tecnai Twin TEM at an accelerating voltage of 300 kV. For SAED imaging, a camera length of 630 mm was used. ImageJ software was used to obtain measurements of nanoparticle average size, size distribution, and standard deviation. The software was also used to analyze the lattice fringes present in HR-TEM images of Pt NPs in order to identify crystal facets.

Confirmation of ligand exchange was conducted via vibrational spectroscopy. Fourier-transform infrared (FTIR) spectroscopy was performed using a Perkin Elmer System 2000 FT-IR spectrometer. A Thermo Scientific DXR dispersive Raman spectrometer was used to collect
measurements with a spectral resolution of 1 cm$^{-1}$ and a value of $\lambda = 532$ nm. Due to differences in activity for the OAm and citrate ligands, the replacement of citrate with OAm (LC-NPs) was examined using FTIR spectroscopy, while the reverse reaction in which OAm was replaced with citrate (LMW-NPs) was examined using Raman spectroscopy.

UV-Visible spectroscopy was used to study the interaction of colloidal NPs over time. UV-Vis absorbance spectra were collected on a Cary 500 UV-Vis/NIR spectrometer in quartz cuvettes containing dilute suspensions of the MW-NPs in hexane.

2.3 Results

2.3.1 Microwave Synthesis of Highly Crystalline Platinum Nanocubes

Microwave syntheses of the Pt(acac)$_2$ precursor in toluene with oleylamine as a stabilizing agent and ascorbic acid as a mild reducing agent readily produced highly dispersible cubic Pt NPs with an average diameter of 8 nm (Figures 2.1a-b). Although octahedral and irregularly-shaped nanoparticles were observed under some conditions, the cubic morphology was predominant in all samples (Figure 2.1c). Optimal reaction conditions were determined by systematically varying reaction time and temperature, and then observing the impacts on NP size and morphology via transmission electron microscopy (TEM). It was determined that a 30-minute reaction at 132 °C was the optimal condition, reliably producing samples with excellent dispersibility in non-polar solvents, a high prevalence of cubic morphology, and a narrow size distribution with an average diameter of 8.2(4) nm (Figure 2.1d).
Systematic temperature variation showed that the lowest temperature (125 °C) produced the smallest Pt NPs, with an average size of 5.1(2) nm (Figure 2.2a). In general, temperatures at or below 130 °C produced morphologically polydispersed samples in which irregular,
polycrystalline NPs were observed among significant increases and decreases of octahedral and cubic morphologies, respectively (Figure 2.2b).

**Figure 2.2.** Transmission electron micrographs showing the effect of time and temperature change on the size and morphology of MW-NPs: (a) lowest temperature (125 °C) produces smallest MW-NPs with wide size and morphological variation; (b) polydispersed morphology including polycrystalline NPs, less cubic and more octahedral NPs produced at 130 °C; (c, d) higher temperatures and 60 minute reaction time produced wide size and morphology distribution with areas of agglomeration.
Studies to optimize the reaction time indicated that the reaction mixture must be held at the desired temperature for no less than 30 minutes to achieve good size and shape consistency throughout. Reaction times below 30 minutes produced a mixture of 2 distinct morphologies: smaller nanocubes and larger octahedra. Increasing the reaction time to 60 minutes at higher temperatures led to wider distributions of both size and morphology, with a greater proportion of irregular polyhedral NPs (Figure 2.2c). These samples also featured prominent areas of agglomerated particles (Figure 2.2d). The effects of reaction time and temperature on MW-NP size are summarized in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3.** (a) Effect of reaction time on MW-NP size, (b) effect of reaction temperature on average size of MW-NPs produced in 30 minute reactions.

### 2.3.2 Characterization of Highly Crystalline Platinum Nanocubes

Characterization of nanoparticle composition and crystallinity was performed via X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution TEM (HR-TEM). Observed peak positions in the XRD patterns of samples were compared to those of a Pt reference pattern\(^{25}\) to confirm the formation of face-centered cubic Pt (Figure 2.4). XRD was
also used to assess the crystallinity of the MW-NPs, and diffraction patterns of MW-NPs were compared to those of C-NPs. In Figure 2.4, the MW-NP pattern shows diffraction peaks that are well-defined and symmetrical, with peak intensities that correspond to a random three-dimensional ordering of polyhedral Pt NPs.\textsuperscript{27} In contrast, the spectra recorded for the C-NPs showed very broad peaks with lower intensities (Figure 2.4), which is consistent with the smaller size and lack of well-defined crystallographic facets in the spherical particles.\textsuperscript{28}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{x-ray-diffraction-pattern.png}
\caption{X-ray diffraction pattern of MW-synthesized 8-nm Pt nanocubes (top) compared to 3.4-nm commercial Pt NPs (middle) and the reference pattern for Pt\textsuperscript{9} (bottom).}
\end{figure}

*Adapted from Ref. 25, \textit{Phys. Rev.}, 1925.*
Morphological characterization and facet identification of the MW-NPs was conducted via HR-TEM and SAED imaging. Highly crystalline samples of Pt NPs are expected to display electron diffraction patterns that contain spectral features associated with the dominant morphological facets; for a small sample of cubic NPs, the dominant {100} facet should produce a bright electron diffraction ring with a radius corresponding to the 0.19 nm d-spacing of the (200) crystallographic plane.\textsuperscript{8,27} Additionally, unidirectional lattice fringes with 0.19 nm interfringe spacing should be observed on Pt nanocube surfaces under HR-TEM.\textsuperscript{8,27} HR-TEM images of the MW-synthesized nanocubes were indexed by measuring the spacing of the lattice fringe (Figure 2.5a).

![Figure 2.5](image)

**Figure 2.5.** (a) High-resolution transmission electron micrograph of a cubic MW-NP showing lattice fringe spacing that corresponds to the (100) surface of Pt, (b) selected area electron diffraction of several cubic MW-NPs with the brightest diffraction ring corresponding to expected (200) spacing. Both measurements support highly crystalline cubic morphology.

As expected, the average lattice spacing of 0.19 nm corresponded to the known value of the {100} facets that comprise the surfaces of cubic MW-NPs.\textsuperscript{8,27} Selected-area electron diffraction (SAED) patterns of small groups of nanocubes were also indexed in order to confirm
the formation of (200) planes in the nanocubes. The measured radii of the diffraction rings were consistent with the 0.23 nm and 0.19 nm spacings of the (111) and (200) planes, respectively (Figure 2.5b).8,27

In order to study interparticle interactions and investigate the formation of the aggregated structures that are expected in colloidal suspensions of Pt NPs over time, UV-Vis spectra were recorded for the same sample of MW-NPs over a period of 3 weeks. Studies on changes in the absorbance spectra of NPs aged over similar time periods have been conducted on Pt NPs synthesized in microemulsions as well as on cadmium and thallium NPs.29 Significant changes in peak position and intensity were observed after 3 weeks, most notably the intensification of spectral features in the region between 225-350 nm (Figure 2.6). Absorbance spectra of samples collected before and after sonication showed no change, suggesting the formation of aggregated clusters of NPs; formation of these clusters was later confirmed by TEM imaging. Spectral features that were observed between 250-300 nm may be the result of interparticle interactions and agglomeration processes, which are known to occur over time due to strong dipole-dipole forces in colloidal Pt NPs and could produce broader, weaker absorbance features at longer wavelengths.29–33 While structure in this region of the spectra was present for as-synthesized MW-NPs, it was significantly less intense and more likely due to self-assembled one- and two-dimensional arrays of NPs as opposed to cluster formation or agglomeration.
2.3.3 Solvothermal Synthesis of Platinum Nanoparticles

Despite using the same reaction species and equivalent time and temperature parameters, solvothermal methods were not effective in the reproducible synthesis of highly dispersible, morphologically-controlled Pt NPs. The effects of increasing reducing agent strength can be seen as a progression from weakest to strongest, beginning with ascorbic acid (Figure 2.7a), moving to tetrabutylammonium bromide (TBAB) (Figure 2.7b), and ending the series with cetyltrimethylammonium bromide (CTAB) (Figure 2.7c). Figures 2.7d-f show variations on a surfactant-free solvothermal approach from Cui et al. that did produce monodispersed Pt-Ni NPs but were still prone to agglomeration. Finally, Figures 2.7g-i show the series of experiments.

![Figure 2.6](image.png)

**Figure 2.6.** UV absorbance spectra showing the effect of aging on formation of aligned or agglomerated structures within the hexane-suspended sample. The increased intensity of the structure between 250-300 nm support formation of clusters or agglomerated regions.
leading to the discovery of the combination of reaction species that was subsequently utilized in the MW-heating synthesis of the high-quality Pt nanocubes that are featured in this work.

Figure 2.7. Effects of reaction conditions on solvothermally synthesized Pt NPs. (a-c) Increasing strength of reducing agent increases agglomeration from ascorbic acid (a), tetrabutylammonium bromide (TBAB) (b), and cetyltrimethylammonium bromide (CTAB). (d-f) Attempts to replicate a surfactant-free method from literature were not successful after multiple trials. (g-i) Effects of time and temperature on Pt NPs morphology at (g) 6h, 240 °C, (h) 9h, 220 °C, and (i) 18h, 180 °C.
XRD spectroscopy was also used to predict Pt NP size, crystallinity, and the possibility of any large areas of agglomeration within samples of Pt NPs from both microwave and solvothermal syntheses. Indexing both reference and experimental XRD patterns gave calculated d-spacing values for the four most intense reflections and assigned \{hkl\} indices to these reflections (Figure 2.8).

![Figure 2.8. X-ray diffraction spectrum of MW-NPs showing d-spacing and Miller indices for the four most prominent peaks.](image)
and MW methods were compared to measurements made from TEM imaging and were found to be sufficiently accurate to secure their use as a prediction tool throughout this study (Figure 2.9).

X-ray diffraction patterns were obtained from multiple samples of Pt NPs produced by solvothermal and microwave methods, ranging from non-agglomerated to highly agglomerated. Diffraction patterns of these samples revealed that the agglomerated samples consistently produced sharper, more intense peaks, whereas non-agglomerated, highly dispersible samples tended to show peaks that were more rounded (Figure 2.9). Particle size estimations made using the Scherrer equation were useful in identifying agglomerated samples due to the significant decrease in peak width.

**Figure 2.9.** XRD spectra demonstrating typical patterns for Pt NPs samples with different levels of aggregation. (a) Highly dispersed Pt nuclei resulting from incomplete growth, NP size ~2 nm. (b) Ideal sample for use in synthesis of Pt@HNB NPPs due to good dispersion of particles with average size of ~8 nm. (c) Highly agglomerated sample, NP size ~30 nm.
2.3.4 Ligand Exchange on Commercial Platinum Nanospheres and Microwave-Synthesized Platinum Nanocubes

Ligand exchange procedures were performed on samples of both as-synthesized MW-NPs and as-obtained C-NPs in order to assess the possible quenching effects of the citrate capping ligands on the appearance of LSPR peaks in the absorbance spectra of the C-NPs. FTIR spectra of LC-NPs show the presence of OAm ligands, with characteristic amine peaks including an NH$_2$ bends at 722 and 1574 cm$^{-1}$ (respectively), asymmetric and symmetric C-H stretches at 2921 and 2852 cm$^{-1}$ (respectively), and a bend of the C-H group near the C=C at 3006 cm$^{-1}$ (Figure 2.10).\textsuperscript{34,35} Figure 2.10 shows consistent similarities between spectra recorded for LC-NPs and for pure OAm, which indicate that the ligand exchange procedure was successful in a nearly complete replacement of the citrate groups with OAm. Furthermore, Figure 2.10 shows significant differences between the FTIR spectra for sodium citrate and the LC-NPs, supporting a thorough ligand exchange.
In Figure 2.11, Raman spectra are displayed showing microwave-synthesized 8-nm Pt nanocubes (LMW-NPs) after ligand exchange to replace OAm capping ligands with citrate capping ligands. Spectra for samples collected after 24 and 48 hours of ligand exchange show very little difference, indicating that 24 hours was sufficient to ensure complete replacement of the OAm ligands with citrate. For comparison, reference samples of pure OAm and trisodium citrate were collected on the same instrument used to collect experimental spectra. Both show good agreement with literature spectra.\textsuperscript{34,35} The strong matching of peaks between the LMW-
NPs and citrate patterns, as well as the absence of characteristic OAm peaks, support a complete ligand exchange. Additionally, solvent dispersal experiments demonstrated that the LMW-NPs dispersed easily in ethanol but were not dispersible in toluene or hexane. This is consistent with expectations for citrate-capped NPs. **Figure 2.11** shows citrate-capped microwave NPs (LMW-NPs).

**Figure 2.11.** Raman spectra of microwave-synthesized 8-nm Pt nanocubes (LMW-NPs) after ligand exchange to replace OAm capping ligands with citrate capping ligands. Spectra for samples collected after 24 and 48 hours are very similar and suggest that complete replacement was achieved after 24 hours.
2.4 Discussion

2.4.1 Microwave Synthesis of Highly Dispersible Platinum Nanocubes

Although the synthesis of colloidal metal NPs has been studied for several decades, only a small number of methods have been developed that reliably yield monodispersed products. The synthesis of highly crystalline, shape-controlled, highly dispersible Pt NPs is usually achieved via high-temperature organic phase methods that rely on an injection of Fe(CO)$_5$ to facilitate a distinct, homogeneous nucleation event.$^1$ When Fe(CO)$_5$ is not used, the Pt NPs produced are shown to be highly agglomerated, with wide distributions of size and shape. Due to the importance of well-controlled, dispersible Pt NPs to applications in catalysis, photonics, and sensing, an efficient and high-output synthesis method that avoids the health, environmental, and safety risks of Fe(CO)$_5$ is highly desirable.

Microwave heating is a versatile and facile method for the production of high quality Pt NPs. Our microwave method eliminates the use of Fe(CO)$_5$ and uses only common, cost-effective reagents to safely and rapidly produce a highly crystalline product. By offering a convenient, economical, large-scale synthesis under mild conditions, MW heating methods may possess great potential for expanding the applications and impact of Pt-based nanomaterials. Our facile, “one-pot” microwave synthesis is a highly reproducible and efficient method with high output capabilities, which may help accelerate the technology readiness of advanced catalytic materials. The greater degree of control and precision offered by microwave heating methods present further advantages for catalytic NPs, since nanoparticle shape and surface structure play important roles in catalytic activity and reaction durability.$^{1,3,5,6,8,12}$

Early studies on the MW heating synthesis of Pt NPs utilized the polyol reduction method and were performed using domestic microwaves.$^{19–21}$ When compared to Pt NPs synthesized
using conventional heating methods, the MW-produced Pt NPs were found to have a much narrower size distribution. This result was attributed to uneven heat conduction to the reaction mixture by the conventional heating methods.\textsuperscript{19–21} While those studies presented a facile and effective method for producing colloidal Pt NPs, the products still lacked crystallinity and shape selectivity. More recent research into the synthesis of morphologically-controlled metallic NPs suggests that the greatest benefit of MW heating comes from the ability of MW irradiation to instantly and uniformly penetrate a reaction vessel.\textsuperscript{16} In the traditional conductive heating methods used in NP synthesis, energy transfer to the reaction mixture may be hindered by differences in the thermal conductivity of the reaction vessel or solvent.\textsuperscript{16–18} In contrast, MW irradiation involves the coupling of microwaves directly with molecules in the reaction mixture through a microwave-transparent reaction vessel. This leads to a much more rapid rise in temperature.\textsuperscript{16–18} This fast and uniform heating promotes the rapid reduction of a metal precursor salt evenly throughout the solution, providing a distinct and homogeneous nucleation event. These conditions are considered essential to the formation of monodispersed colloidal metal NPs.\textsuperscript{3,5}

The observation of two distinct morphologies at lower temperatures (Figures 2.2a-b) may give some insight into the reaction mechanism of platinum nanoparticle synthesis via microwave irradiation. Lower temperatures have been shown to promote the dominance of \{111\} faceted octahedra.\textsuperscript{8,13} Results of a recent study by Kang et al., in which conventional heating methods were used on a reaction mixture very similar to that of the present work, showed that lowering temperature to reduce the reaction rate could be used to reliably select morphology.\textsuperscript{13} The highest reaction temperature produced Pt cubes, while intermediate and lower temperatures produced cuboctahedra and octahedra, respectively. Interestingly, they also
observed that extending reaction times at low temperatures led to a transition from the initial cubic morphology to smaller octahedra. The authors believed this to be a result of an etching and dissolution process of the cubes along the $<111>$ direction. It is possible that a similar phenomenon influenced the morphology of the NPs seen in Figure 2.2a-b, which were produced by one-hour reactions at the lowest temperatures used in this study (125 °C and 130 °C, respectively).

### 2.4.2 Role of Reaction Species in Microwave Synthesis of Platinum Nanocubes

Platinum nanoparticles were synthesized via microwave heating in a wet chemical reduction synthesis, which is also used in solvothermal and high-temperature organic phase methods. According to the wet chemical reduction model, Pt NP formation begins with the reduction of a multivalent ion in a Pt salt to a zero-valent Pt atom. Reducing agents and shape-control agents/surfactants are used to direct NP growth towards the desired size and morphology. When optimizing our reaction mixture for use with MW irradiation, we found that the most precise size and shape control was achieved by utilizing oleylamine and ascorbic acid with toluene as the solvent.

In our system, ascorbic acid was used to reduce Pt$^{2+}$ ions from the precursor to Pt$^{0}$ atoms. Ascorbic acid was chosen as a mild reducing agent that allowed control over the precursor reduction rate during this nucleation period. Stronger reducing agents (CTAB, TBAB) produced agglomerated NPs. The highly monodispersed NPs produced when ascorbic acid was used suggest that a distinct, controlled nucleation period was followed by a period of relatively even nanoparticle growth throughout the reaction mixture. Oleylamine (OAm) was used as a surfactant to achieve shape control during nanoparticle growth. Elemental Pt NPs have a face-centered cubic structure that typically produced low-index facets such as {100}, {110}, and
An important surface-selective capping agent, OAm can promote cubic morphology by adsorbing to the Pt \{100\} surface by bonding with the amine group.\textsuperscript{12,20} Furthermore, OAm’s long hydrophobic chains provide steric hindrance to prevent agglomeration in the growing NPs.\textsuperscript{2} While OAm can be used alone as a mild reducing agent, its weak reducing power can prolong the reduction process and lead to uneven NP growth.\textsuperscript{36} When OAm was combined with ascorbic acid in our system, sufficient reducing power was generated without causing agglomeration. Ascorbic acid facilitated a distinct nucleation burst via reduction of the precursor salt.\textsuperscript{28} When combined with OAm, this provided sufficient reducing power without causing agglomeration. The narrow size and shape distribution of our MW-NPs supports the occurrence of distinct nucleation and growth phases, indicating that MW irradiation effectively replaced Fe(CO)\textsubscript{5} to induce rapid and homogeneous precursor reduction throughout the reaction mixture.

### 2.4.3 Agglomeration and Interparticle Interactions of Platinum Nanoparticles

X-ray diffraction patterns can display characteristic features associated with agglomeration, which can be analyzed with respect to accepted standards from literature and instrument-specific reference patterns. Identification of significant agglomeration within a sample was of critical importance during the earlier phases of developing the synthesis of Pt NPs by microwave heating. Agglomerated samples, which are challenging and time-consuming for TEM analysis, have been well-determined by our group to be unsuitable for use in NPP synthesis due to their inability to be encapsulated by scrolled nanosheets.\textsuperscript{10} As a result, the use of XRD as a screening technique provided a significant increase in the efficiency of Pt NP characterization and synthesis method development.

While MW-synthesized Pt NPs (unlike their solvothermal counterparts) were highly dispersible in non-polar solvents and remained in colloidal suspension for periods exceeding
three months, some agglomeration was observed in two circumstances: within samples synthesized under non-optimal conditions, and after being left uncovered in ambient light conditions for extended periods of time. Once optimal synthesis conditions had been established, the risk of agglomeration was qualitatively assessed by recording the stability of the colloidal NP suspension over a period of no less than 3 weeks. Any visible accumulation of NPs at the bottom or on the sides of the glass scintillation vial, color change, or reduction in the optical scattering depth/opacity of the suspension was interpreted as a decrease in colloidal stability and attributed to the formation of NP clusters or aggregated structures within the suspension. Samples suspected of undergoing post-synthetic aggregation were further analyzed via UV-Vis and TEM. **Figure 2.6** shows the emergence of post-synthetic aggregation as observed by UV-Vis.

### 2.4.4 Solvothermal Synthesis of Platinum Nanoparticles

The solvothermal synthesis method used by our group will reliably produce a range of monodispersed metal and metal oxide NPs and quantum dots, including CeO$_2$, TiO$_2$, CdSe, Fe$_2$O$_3$, and a series of transition metal ferrites MFe$_2$O$_4$ (M = Mn, Co, Ni). After that method repeatedly produced agglomerated Pt NPs, a series of different solvothermal methods were attempted. Solvothermal studies utilizing more powerful reducing agents produced highly agglomerated Pt NPs (**Figure 2.7**). The most successful method utilized a simple reaction mixture with only three species: platinum(II) acetylacetonate (Pt(acac)$_2$), nickel(II) acetylacetonate (Ni(acac)$_2$), and DMF were heated in a stainless steel autoclave for a long (42 h) reaction at the low temperature of 120 °C. In this system, DMF functioned not only as solvent, but also as complexing agent and reducing agent. A high heating rate of 10 °C/minute resulted in a short induction time and high nucleation rate, which generated a large number of small
seeds. The low reaction temperature was designed to benefit nanocrystal faceting during a slow seed growth period, resulting in small particles with a high degree of shape and surface control.\textsuperscript{24} Shape selectivity was controlled by the precursor acetylacetonate ligands, while the initiation of nucleation relied on exothermic heat of mixing effects between the two metal precursors. The initial seeds catalyzed codeposition of Pt and Ni to form alloy NPs.

While this was the most successful solvothermal method and produced one monodispersed, relatively non-agglomerated sample (Figure 2.7a), attempts to replicate it most often produced agglomerated nanoparticles with morphologies that were characteristic of NPs produced in a system with insufficient reducing power (Figure 2.7b-c). This could indicate that the nucleation and/or growth processes deviated from the desired pathways due to contributions from chemical factors, such as uneven reduction throughout the reaction mixture or an imbalance in the precursor supersaturation, or from physical factors, such as uneven heat distribution throughout the autoclave.

\textbf{2.5 Conclusions}

A new, facile synthetic route for the production of highly crystalline and monodispersed Pt NPs has been developed using microwave heating. Our method reduces reaction time, uses common reagents with low safety and environmental risks, and can be used to produce large quantities of high quality Pt NPs that offer excellent versatility for the development of advanced catalytic and plasmonic materials.
2.6 References


Chapter 3
Optical and Catalytic Properties of Highly Crystalline Platinum Nanocubes

3.1 Introduction

Recent interest in the use of platinum nanoparticles (Pt NPs) for advanced applications such as plasmonic photocatalysis encourages a renewed focus on developing reproducible synthetic strategies and conducting detailed optical characterization of high-quality particles. A rapid synthetic route to optically and catalytically active Pt NPs of monodispersed size and morphology has been developed utilizing microwave (MW) heating (see Chapter 2). The optical and catalytic properties of the microwave-synthesized Pt NPs (MW-NPs) were investigated using UV-Visible spectroscopy and cyclic voltammetry. The MW-NPs exhibit high catalytic activity for hydrogen adsorption and methanol oxidation reactions. Absorbance spectra of the 8-nm cubic MW-NPs showed a distinct localized surface plasmon resonance band at 213 nm. Absorbance spectra were also obtained for commercial 3-nm Pt NPs (C-NPs) synthesized via citrate reduction both before and after replacement of the citrate capping ligands with the amine ligands present on the MW-NPs. While the as-obtained citrate capped C-NPs gave featureless absorbance spectra, a distinct peak emerged at 207 nm after the ligand exchange. This observation could provide important insight into the optical behavior of Pt NPs and their potential for use in plasmonic photocatalysis and the development of advanced catalytic materials.

The purpose of this study was to present detailed optical and catalytic data for highly dispersible 8-nm Pt nanocubes. The optical data for our microwave-synthesized Pt nanocubes
strongly supports a plasmonic character for the well-defined absorbance peak we observed at 213 nm. To evaluate the possible role of the citrate capping ligand in quenching optical activity in the microwave-synthesized Pt NPs (MW-NPs), UV absorbance spectra of MW-NPs were compared to those of a sample of commercially produced citrate-capped Pt NPs (C-NPs). Those results support a quenching of the plasmonic resonance by species associated with the citrate ligand. To further study the effects of capping ligands on Pt NP optical properties, a ligand exchange procedure was performed in which the citrate ligands were replaced by oleylamine, the species present on the optically-active MW-NPs. UV-Visible absorbance spectra of the commercial NPs collected after ligand exchange shows the emergence of a strong peak near the predicted LSPR maximum. Confirmation of successful ligand exchange was provided by vibrational spectroscopy.

3.2 Experimental

**Materials.** Oleylamine (OAm) (technical grade, 70%), platinum(II) acetylacetonate (Pt(acac)₂) (97%), L-ascorbic acid (≥ 99%), and trisodium citrate dihydrate (≥ 99%) were purchased from Sigma-Aldrich. A dispersion of commercially-produced platinum nanoparticles (3.4 nm, spherical, 99.99% trace metals basis, dispersed in aqueous citrate buffer) was also purchased from Sigma-Aldrich. Toluene (certified ACS, 99.8% anhydrous), hexane (95% anhydrous), and absolute ethanol (200 proof) were purchased from Fisher Scientific.

3.2.1 *Synthesis of Platinum Nanoparticles via Microwave Heating*

Production of 8-nm Pt nanocubes via microwave heating was carried out using published techniques (see Chapter 2).¹ Briefly, the metal precursor Pt(acac)₂ was combined with the reducing agent ascorbic acid and surfactant oleylamine in a toluene solvent system. The reagents
were magnetically stirred to combine, then heated in a MW-transparent glass vessel for 1 h at 132 °C. The brown product was washed with ethanol and toluene, then separated via centrifugation for 10 minutes at 6,000 rpm. This process was repeated twice, after which the dark brown Pt NPs were dispersed in hexane for characterization and storage.

3.2.2 Ligand Exchange on Commercial Platinum Nanospheres and Microwave-Synthesized Platinum Nanocubes
The replacement of citrate ligands with OAm ligands on the surface of the commercial Pt NPs (C-NPs) was carried out by combining an ethanol suspension of as-obtained C-NPs with OAm and hexane, then stirring at 55 °C for 48 hours. The ligand exchange process was similar for as-synthesized MW-NPs, on which OAm ligands were replaced with citrate ligands. A toluene suspension of the MW-NPs was stirred with a concentrated aqueous solution of trisodium citrate and ethanol for 48 hours at 55 °C. Confirmation of ligand exchange was conducted via vibrational spectroscopy. Please see Chapter 2 for a detailed description of the ligand exchange procedure.

3.2.3 Characterization
Optical and vibrational spectroscopy measurements were collected for as-synthesized MW-NPs, as-obtained C-NPs, and ligand-exchanged LC-NPs. UV-Vis spectra were collected on a Cary 500 UV-Vis/NIR spectrometer in quartz cuvettes containing dilute suspensions either the MW-NPs (in hexane), the C-NPs (both as-obtained in citrate buffer, and after centrifugation and redispersal in DI water), or the LC-NPs (in EtOH). Note: Limitations in sample dispersibility caused by the capping ligands necessitated the use of different solvents in order to obtain high-quality optical data. Solvent effects are accounted for in the Mie theory-based equations that are used for the prediction and analysis of the optical properties of metals, and it has been established that varying solvent characteristics (composition, polarity, refractive index) does not
have a significant effect on the optical spectra of sub-10 nm nanoparticles.\(^2\) Analysis of UV-Vis spectra for Pt NPs was conducted using equations derived from Mie theory.\(^2\)

Catalytic properties of the microwave-synthesized Pt NPs were studied via cyclic voltammetry (CV). Published methods were used to prepare the working electrode via modification of a glassy carbon electrode with Pt NPs.\(^3\)–\(^5\) To prepare the working electrode, a suspension of as-synthesized Pt NPs in hexane was diluted to a concentration of 2 mg/mL, then sonicated for 5 minutes. A micropipettor was used to drop cast 40 μL of the NP suspension onto a mirror-polished glassy carbon electrode with a 3-mm diameter. After drying for 2 hours in air, 20 μL of a 1:100 diluted aqueous solution of Nafion™ perfluorinated resin (5 wt % aliphatic alcohols) was drop cast onto the electrode surface. After drying overnight in air, baseline CV scans were obtained against a Pt wire counter electrode using the unmodified working electrode in the appropriate electrolytes (to minimize dissolved oxygen, all were saturated with N\(_2\) by bubbling through for 10 minutes). Since the presence of oleylamine adsorbed to Pt NP surfaces has been shown to significantly hinder catalytic activity, the NP-modified working electrode was irradiated under UV light with a wavelength of 254 nm to remove the OAm groups from the catalytic surfaces.\(^3\)–\(^5\) To investigate any difference between catalytic activity of the OAm-capped MW-synthesized nanocubes and the citrate-capped nanospheres, a glassy carbon electrode modified with an aqueous suspension of the C-NPs was prepared using the same procedure.

Electrochemical measurements for hydrogen adsorption/desorption (HAD) activity were performed at room temperature (298 K) in a three-electrode cell under constant N\(_2\) bubbling using a VMP-2 potentiostat from Princeton Applied Research. The NP-modified WEs were immersed in aqueous 0.5 M HClO\(_4\) with a Pt wire counter electrode (CE) and an Ag/AgCl
reference electrode (RE). Electrochemical cleaning of the WE was performed by cycling the potential over the entire measured range 20 times, until a steady voltammogram was produced. Cyclic voltammetry (CV) scans for HAD were collected at 100 mV/s with a range of 10 μA by applying a forward (anodic) potential from -0.2 to 1.2 V vs. Ag/AgCl. A reverse (cathodic) potential was then applied over the same range. Resulting CV curves were expressed as current $i$ (μA/cm$^2$) vs. potential $E$ (converted to V vs. NHE) and analyzed for structure in known potential regions for the adsorption and desorption of hydrogen to Pt surfaces.$^{34}$ Electrochemically active surface area (ECSA) measurements were performed by integrating the area under the anodic curve to find the overall surface charge $Q_s$ (μC), and then dividing that value by the standard value of the charge density of a monolayer of Pt-adsorbed hydrogen (210 μC/cm$^2$).$^{34}$

A similar process was used to measure the activity of the MW-NPs and C-NPs for the methanol oxidation reaction (MOR). The same three-electrode system was used, this time immersed in an aqueous electrolytic solution of 0.5 M H$_2$SO$_4$ + 0.5 M MeOH. After electrochemical cleaning and activation of the WE by the method described above, CV scans for MOR were collected at 100 mV/s at a range of 10 μA by applying a forward potential over a range of -0.2 to 1.2 V vs. Ag/AgCl. A reverse potential was applied over the same range. Resulting $i$-E curves (with potential converted to V vs. NHE) were analyzed for MOR activity by finding the peak potential values and comparing peak current densities between the MW-NPs and the C-NPs.
3.3 Results

3.3.1 UV-Visible Spectra and Optical Properties of Platinum Nanoparticles
The optical properties of the Pt NPs were studied with UV-Vis spectroscopy. As a noble metal, nanoscale Pt can be expected to display plasmonic effects. Although calculated spectra for free Pt NPs in the 10-nm size range indicate that localized surface plasmons are not expected to form under visible light irradiation, Mie theory calculations do predict a distinct absorbance peak under UV irradiation at 215 nm for spherical 10-nm Pt NPs in an aqueous solvent. Absorbance spectra collected for the 8-nm cubic MW-NPs in hexane consistently showed a strong peak at 213 nm (Figure 3.1). The use of dilute suspensions of NPs minimized any absorbance due to scattering, so spectral features can be attributed either to UV-range electronic transitions within the NPs or the formation of one- or two-dimensional self-assembled structures.

The data for this study would suggest that the major band at 213 nm is plasmonic in nature, given the agreement of both spectral shape and position with the LSPR band at 215 nm predicted by Mie theory. In contrast, absorbance spectra of the spherical 3.4-nm C-NPs in water did not show any distinct peaks from 200-800 nm, but instead showed a gradual increase over most of the visible range followed by a much steeper increase from 200-250 nm (Figure 3.1). This is consistent with literature spectra for Pt NPs of similar size and morphology produced by the citrate reduction method. The impact of solvent type on optical properties has been shown to be minimal for sub-10 nm nanoparticles.
To assess the possible quenching effects on the appearance of LSPR peaks in absorbance spectra of the C-NPs, UV-Vis spectra of the ligand-exchanged LC-NPs were recorded after replacement of their original citrate capping ligand with OAm (to facilitate comparison with MW-NPs). UV-Vis spectra of the LC-NPs do support a quenching effect from citrate with the emergence of a distinct peak at 207 nm, in contrast to the featureless spectrum of the C-NPs. The OAm-capped MW-NPs show a plasmonic absorbance peak at 213 nm.

Figure 3.1. UV absorbance spectra of 8-nm MW-synthesized Pt nanocubes (MW-NPs), as-obtained 3.4-nm spherical commercial Pt NPs (C-NPs), and ligand-exchanged commercial Pt NPs (LC-NPs). LC-NPs are capped with oleylamine and show emergence of a distinct peak at 207 nm, in contrast to the featureless spectrum of the C-NPs. The OAm-capped MW-NPs show a plasmonic absorbance peak at 213 nm.

To assess the possible quenching effects on the appearance of LSPR peaks in absorbance spectra of the C-NPs, UV-Vis spectra of the ligand-exchanged LC-NPs were recorded after replacement of their original citrate capping ligand with OAm (to facilitate comparison with MW-NPs). UV-Vis spectra of the LC-NPs do support a quenching effect from citrate with the emergence of a distinct peak at 207 nm, which based on its location is likely to be plasmonic in nature (Figure 3.1). This value is slightly blue-shifted with respect to the absorbance peak.
observed at 213 nm for the MW-NPs. This may be due to the smaller size and poorer
crystallinity of the 3.4-nm C-NPs, as supported by XRD measurements (see Chapter 2).

![Figure 3.2. Wavelength-dependent optical constants $n$ (refractive index) and $k$ (extinction
coefficient), plotted over the wavelength range used for UV-Vis observations of Pt NPs. These
values were obtained from literature and used to calculate the complex dielectric constants $\varepsilon_1$
and $\varepsilon_2$ for platinum.](image)

Analysis of the UV-Vis spectra for the Pt NPs was based on Mie theory, which states that
the absorbance spectra of well-separated, colloidal NPs can be calculated based on the
wavelength-dependence of their optical constants (refractive index, $n$, extinction coefficient, $k$,
and optical-frequency relative permittivity, $\varepsilon$).\textsuperscript{13} Widely-referenced literature values of the
optical constants $n$ and $k$ (Figure 3.2) were used to calculate the real and imaginary components of platinum’s complex dielectric function, $\varepsilon_1$ and $\varepsilon_2$ respectively (Table 3.1).

<table>
<thead>
<tr>
<th>Calculating the Complex Dielectric Constants of Platinum</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency-dependent complex dielectric function</td>
<td>$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$</td>
</tr>
<tr>
<td>Real dielectric constant</td>
<td>$\varepsilon_1(\omega) = n^2 - k^2$</td>
</tr>
<tr>
<td>Imaginary dielectric constant</td>
<td>$\varepsilon_2(\omega) = 2nk$</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>$h\nu$ (eV)</th>
<th>Wavelength (nm)</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
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<tr>
<td>6.2</td>
<td>200</td>
<td>0.11</td>
<td>3.7</td>
</tr>
<tr>
<td>6.1</td>
<td>203</td>
<td>0.03</td>
<td>3.8</td>
</tr>
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<td>6.0</td>
<td>207</td>
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</tr>
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</tr>
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<td>4.4</td>
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<tr>
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<tr>
<td>4.8</td>
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</tr>
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<td>-2.12</td>
<td>5.8</td>
</tr>
<tr>
<td>4.2</td>
<td>295</td>
<td>-2.48</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Table 3.1. Equations for calculating the frequency-dependent complex dielectric function $\varepsilon(\omega)$ for Pt, which describes the interaction of the real and complex dielectric constants, $\varepsilon_1$ and $\varepsilon_2$ respectively. Dielectric constant values were then used to calculate values for the optical constants of 8-nm Pt nanocubes in hexane and to predict the location of the LSPR $\lambda_{\text{max}}$. 
The calculated values for ε₁ and ε₂ are shown in Figure 3.3 and are in good agreement with literature\(^{14–16}\). For subsequent calculations of absorption cross-section C and absorption coefficient α, the values used corresponded to the optical constants as measured at the \(\lambda_{\text{max}}\) of 213 nm. The calculated values for C and α were found to be 28.8 \(\text{nm}^2\) and 8.7 \(\times 10^5\) \(\text{cm}^{-1}\), respectively, and were also in good agreement with literature (Table 3.2).\(^{14–16}\)

**Figure 3.3.** Calculated values of the real (ε₁) and imaginary (ε₂) wavelength-dependent dielectric constants for platinum based on literature values for the optical constants \(n\) and \(k\) (refractive index and extinction coefficient, respectively). The calculated values of ε₁ and ε₂ were used to calculate the absorbance coefficient \(\alpha\), absorbance cross-section \(C\), and predicted LSPR \(\lambda_{\text{max}}\) for 8-nm Pt nanocubes in hexane.
### Calculating Absorbance Coefficient, Cross-Section, and LSPR $\lambda_{\text{max}}$

<table>
<thead>
<tr>
<th>Predicted LSPR $\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{max}}^2 = \lambda_c^2 (\varepsilon_0 - 2n_0^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbance coefficient, $\alpha$</td>
<td>$\alpha = \frac{4\pi k}{\lambda_0}$</td>
</tr>
<tr>
<td>Absorbance cross-section, $C$</td>
<td>$C = \frac{18\pi V \varepsilon_2}{\lambda[(\varepsilon_1 + \varepsilon_m)^2 + \varepsilon_2^2]}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$9.7 \times 10^5$ cm$^{-1}$ at 5.8 eV</td>
<td>31</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$8.5 \times 10^5$ cm$^{-1}$ at 6.0 eV</td>
<td>14</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$8.7 \times 10^5$ cm$^{-1}$ at 5.8 eV</td>
<td>This work</td>
</tr>
<tr>
<td>$C$</td>
<td>$28.0$ nm$^2$ for 10-nm Pt NPs at 222 nm</td>
<td>2</td>
</tr>
<tr>
<td>$C$</td>
<td>$27.7$ nm$^2$ for 8-nm Pt NPs at 221 nm</td>
<td>2</td>
</tr>
<tr>
<td>$C$</td>
<td>$28.8$ nm$^2$ for 8-nm Pt NPs at 213 nm</td>
<td>This work</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>310 nm in water</td>
<td>11</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>230 nm in hexane</td>
<td>11</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>213 nm in hexane</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Table 3.2.** Equations for calculating the predicted **LSPR** $\lambda_{\text{max}}$ for a nanoparticle based on the bulk plasma frequency ($\lambda_c$), the high-frequency contribution to platinum’s dielectric constant ($\varepsilon_0$), and the solvent refractive index ($n_0$); the **wavelength-dependent absorption coefficient**, $\alpha$; and the **wavelength-dependent absorption cross-section** ($C$) based on the real and imaginary components of Pt’s dielectric function ($\varepsilon_1$ and $\varepsilon_2$), the dielectric constant of the surrounding medium ($\varepsilon_m$), and the volume of the nanoparticle ($V$). Calculated and observed values for this study are compared to published values.
Calculation of optical coefficients and wavelength-dependent dielectric constants enabled the prediction of an LSPR wavelength of 230 nm for Pt NPs in hexane. The difference between that predicted value and the observed value of 213 nm are most likely due to the effects of cubic morphology and particle size.²,¹⁷⁻²⁰

### 3.3.2 Catalytic Activity of Platinum Nanoparticles via Cyclic Voltammetry

Characterization of MW-NPs’ activity for selected redox reactions related to photocatalysis was carried out via cyclic voltammetry. It was of interest to determine if the MW-NPs displayed comparable activity for the hydrogen adsorption-desorption (HAD) and methanol oxidation (MOR) reactions to published results for highly crystalline Pt nanocubes of roughly the same size.³,⁴,¹³ Many electrocatalytic processes depend upon the surface structure of the catalyst particles, so obtaining CV measurements for the MW-NPs was also used as a secondary characterization method to confirm the predominance of the cubic morphology throughout samples of MW-NPs.¹³ Lastly, analysis of the CV curves obtained from the UV-treated electrodes supported the conclusion that UV irradiation was an effective method for removing oleylamine groups from the surfaces of the as-synthesized particles. Surface-adsorbed OAm ligands are well known to hinder catalytic activity on Pt surfaces.³,⁴

Catalytic activity and structure of the MW-NPs for hydrogen reduction was examined by analyzing their CV curves for HAD and comparing them to those of commercial, 3.4-nm Pt nanospheres (C-NPs) (Figure 3.4). Shape and surface structure of the MW-NPs can be studied by examining the size and relative intensity of two peaks in the 0.15-0.25 V (vs. NHE) region.¹³ The peak at ~0.22 V (vs. NHE) that appears on CV scans of MW-NPs originates from the adsorption and desorption of hydrogen on the Pt {100} facet.⁴ An increased peak intensity results from the fact that more {100} facets are present on the surfaces of the sampled NPs, indicating a predominance of cubic morphology. In addition, the peaks in that region showed an
onset potential that was shifted negatively with respect to those of the C-NPs. This negative shift is consistent with literature values of spherical and octahedral Pt NPs, which is expected from the spherical C-NPs.\(^3\)

**Figure 3.4.** Cyclic voltammatagrams comparing the activity for hydrogen adsorption/desorption (HAD) between 8-nm MW-synthesized Pt nanocubes and 3.4-nm commercially-obtained Pt nanospheres. Scans were performed in aqueous 0.5 M HClO\(_4\) with a rate of 100 mV/s and a range of 10 μA.

Electrochemically active surface area (ECSA) for the MW-NPs was calculated by finding the area under the curve for the known potential regions of hydrogen adsorption and desorption (**Figure 3.4**). The value of that integral gave the overall surface charge of the Pt NPs, \(Q_s\) (μC), which was then used to find ECSA by dividing by the known maximum surface charge for Pt
Experimental values for surface charge and ECSA had an average value of 48.9 μC and 0.232 cm² Pt, respectively, which are in good agreement to literature values for nanocubes of similar sizes.⁷

Activity for the methanol oxidation reaction (MOR) was measured for MW-NPs and C-NPs in an aqueous solution of 0.5 M H₂SO₄ + 0.5 M MeOH (Figure 3.5). Adzic et al. established that the onset and peak potentials, peak magnitude, and peak shape observed for the MOR can be used to characterize the morphology of Pt NPs.²¹ The {100} facet is expected to produce well-defined peaks at 0.8 V and 0.64 V (vs. NHE) in the anodic (forward) and cathodic (reverse) scans for methanol oxidation, respectively.⁷ The anodic peak should also show a forward shift in its onset potential of ≈0.7 V vs. NHE in the presence of predominantly (100) surfaces. As seen in Figure 3.5, peak potentials of the MW-NPs correspond closely to those expected values. The significantly greater current densities of those peaks for the MW-NPs as compared to the C-NPs are expected due to the lack of {100} facets in the spherical C-NPs.
The peak intensities of both HAD and MOR CV scans for the MW-NPs indicate that the OAm surfactant groups had been successfully removed from the catalytic surfaces by the UV treatment (Figures 3.4 and 3.5). The presence of OAm on the surfaces of Pt NPs would result in featureless curves due to a lack of any significant catalytic activity.  

**Figure 3.5.** Cyclic voltammatagrams comparing the activity for the methanol oxidation reaction (MOR) between 8-nm MW-synthesized Pt nanocubes and 3.4-nm commercially obtained Pt nanospheres. Scans were performed in aqueous 0.5 M H$_2$SO$_4$ + 0.5 M MeOH with a scan rate of 100 mV/s and a range of 10 μA.

The peak intensities of both HAD and MOR CV scans for the MW-NPs indicate that the OAm surfactant groups had been successfully removed from the catalytic surfaces by the UV treatment (Figures 3.4 and 3.5). The presence of OAm on the surfaces of Pt NPs would result in featureless curves due to a lack of any significant catalytic activity.
3.4 Discussion

A major obstacle in the development of Pt NPs for photocatalytic applications has been the lack of cohesive data that includes reproducible synthetic strategies along with morphological, optical, and catalytic characterization. Typically, studies that produce highly crystalline, well-dispersed Pt NPs provide consistent structural and catalytic data but do not include optical data, while detailed studies on the optical properties of Pt NPs exclude catalytic data and often utilize particles that are aggregated, polydispersed, or have low crystallinity. This may be due to the difficulty in achieving good morphological and size control, the widespread use of Pt NPs in the context of supported structures that do not require dispersibility or high crystallinity, or the extremely sensitive nature of platinum’s optical response.21–32 The great potential benefits offered by Pt NPs to the field of photocatalysis research demand both reliable, efficient synthetic methods and consistent data on platinum’s most important features. The following data is discussed with the goal of meeting that demand and generating interest in the increased inclusion of high-quality Pt NPs in research for photocatalytic applications.

3.4.1 Catalytic Properties of Microwave-Synthesized Platinum Nanocubes

Achieving a well-controlled synthesis of highly crystalline Pt NPs is critical for correlating morphological properties with performance for the redox reactions associated with photocatalysis.13 Producing size-controlled Pt nanocubes with defect-free, uniform faceting is thus very desirable for achieving high efficiency for the hydrogen reduction reaction of photocatalytic water splitting.33 It is established that different facets of Pt NPs have distinctive potential regions and intensities due to differences in each facet’s ability to absorb reagent species or reaction intermediates.30 The {100} facet that is dominant in the cubic MW-synthesized Pt NPs is known to have the highest binding strength to intermediates, although once
activated via the oxidation of the intermediates they show the highest activity and produce the
most intense peaks for both the HAD and MOR reactions. Kinetic differences between the
\{100\} and \{111\} planes are due to the adsorption strength of intermediate hydroxyl or COH
species, and the resulting electrochemical data can be used to characterize and confirm
nanoparticle morphology.\textsuperscript{30} Since intermediate species bind most strongly to the \{100\} surfaces
and least strongly to the \{111\} surfaces of Pt NPs, peaks associated with the \{100\} surface may
take longer to activate and subsequently may not appear until after those associated with the
\{111\} surface. Due to this phenomenon, at least twenty cycles of electrochemical cleaning were
run before each set of CV measurements was collected.

Cyclic voltammetry (CV) is useful for studying the morphology and activity of Pt NPs
for various redox processes associated with photocatalysis.\textsuperscript{34} CV scans measure the current or
current density in response to a cycled forward (anodic) and reverse (cathodic) applied potential.
Features of interest in cyclic voltammograms include the ratio of peak currents from the anodic
and cathodic scans as well as the separation and position of peak potentials. Deviation of peak
current ratios from unity indicates homogeneous kinetics or other problems with the reversible
process coupling. Peak potential positions can give information on the identity and
predominance of crystalline facets in the system.\textsuperscript{34}

The Pt working electrode can oxidize water to produce oxygen at positive potentials or
reduce water to produce hydrogen at negative potentials. The adsorption of hydrogen occurs at
less negative potentials compared to hydrogen evolution. Cyclic voltammograms collected in
acidic solution by large (mm-scale) Pt WEs exhibit characteristic pairs of peaks corresponding to
the adsorption/desorption of hydrogen-containing species. The electrode’s electrocatalytically
active surface area (ECSA) can also be obtained from HAD CV scans by comparing it to the
standard value of the charge density of a monolayer of Pt-adsorbed hydrogen (210 μC/cm²).³⁴

For MW-NPs CV scans for hydrogen underpotential deposition and HAD gave shape profiles that strongly indicated the predominance of {100} surfaces (Figure 3.4). This is supported both by the peak at ~0.2 V vs. NHE that indicates desorption of hydrogen from the {100} face and the negatively-shifted onset and increased intensity of the oxidation potential peaks in the surface hydroxyl formation region seen in the reverse scan.³,¹³

CV scans of the methanol oxidation reaction for the MW-synthesized Pt NPs also support the prevalence of cubic morphology. Well-established behavior of the {100} face for MOR, including an onset potential of 0.7 V and a peak current density at 0.8 V in the anodic current, was consistently seen for the MW-NPs (Figure 3.5).²¹ Peaks observed in the cathodic current were also consistent with values expected for the {100} face, with a peak at 0.64 V (all values vs. NHE).²¹,³⁴,³⁵ For both the HAD and the MOR measurements, very significant differences were observed between the 3.4-nm commercial NPs and the 8-nm MW-NPs. The spherical commercial NPs were not expected to give strong peaks for either the {100} or {111} surfaces. Observed catalytic activity for the commercial NPs was lower than that of the C-NPs. This is most likely due to the lack of {100} facets as a result of the C-NPs spherical morphology and polycrystalline nature. Highly faceted surfaces have been well-established to provide superior catalytic activity on Pt NPs for the reactions tested.³,⁴,⁶,¹³,²¹,³⁶

3.4.2 Effect of Synthesis Method on the Optical Properties of Platinum Nanoparticles
The lack of reproducible data and a persistent disagreement on the character and properties of Pt’s absorbance features have warranted detailed optical studies on our MW-synthesized Pt NPs. The following discussion of previous optical studies of Pt NPs, followed by a brief examination of LSPR formation and the resulting optical properties of noble metal NPs, is presented here as support for the plasmonic nature of the absorbance features reported in this work.
Synthesis of colloidal Pt NPs via reduction of chloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6}) in aqueous solvents using citrate stabilizing agents is one of the most popular methods, and is used in many of the detailed optical studies of Pt NPs.\textsuperscript{9,10,12,37–41} A quenching effect associated with the species used in this method could explain the disagreement between calculated spectra that predict a distinct LSPR and the widely-reproduced featureless absorbance spectra for citrate-stabilized Pt NPs.\textsuperscript{9,10,12,37–41} Although some groups report the production of monodispersed particles with good size control using this method, citrate-stabilized Pt NPs are typically not highly crystalline and lack absorption spectrum features.\textsuperscript{9–12,37,41}

In 1984, Furlong et al. published their use of the citrate reduction method to produce Pt NPs.\textsuperscript{26} The UV-Vis spectra recorded for all samples were consistent with the current literature, showing a smoothly increasing absorbance as wavelength decreased but no spectral peaks over the entire 200-800 nm range. Furlong states that the electronic properties of colloidal Pt sols are not known, and cites unsuccessful attempts by other groups to calculate spectra or reconcile experimental data with the accepted standard spectrum produced by Mie theory calculations.\textsuperscript{2,10} The UV-Vis spectra for the agglomerated samples presented in their study set a still-followed precedent for much of the optical data available for Pt NPs: broad, featureless extinction curves that rise with a slope proportional to the degree of aggregation in the sample and reaching a maximum at 200 nm.

Henglein et al. compared absorbance spectra for Pt NPs synthesized via citrate reduction to those produced by radiolytic and hydrogen-reduction methods.\textsuperscript{12} Only the citrate-stabilized Pt NPs showed a featureless absorbance spectrum while the hydrogen-reduced and radiolytic Pt colloids gave the first observation of Creighton and Eadon’s predicted LSPR band at 215 nm. The weakness of Pt’s absorbance (compared to Ag or Au) led these researchers to believe that
the peak could be hidden by substances present in the colloidal solution that absorb near the same region. The citrate reduction method (along with the popular polyol reduction with polyvinylpyrrolidone stabilization) uses precursors $\text{H}_2\text{PtCl}_6$ and $\text{A}_2\text{PtCl}_4$ ($\text{A} = \text{Na}, \text{K}$) that are known to form species that absorb in same region as the predicted LSPR $\lambda_{\text{max}}$ for small Pt NPs.\textsuperscript{2,42–45} Bigall et al. were able to see a plasmonic response in the extinction spectra of citrate-stabilized Pt NPs, but only for those with diameters of 30 nm and above.\textsuperscript{37}

### 3.4.3 Formation and Characteristics of LSPR on Noble Metal Nanoparticles

Comparison between the electronic band structures of Ag, Au, and Pt reveals several critical differences that help explain the deviation of Pt’s dielectric function and optical properties from the other noble metals.\textsuperscript{14,15,31} The complex dielectric function of a metallic nanoparticle consists of the frequency-dependent real and imaginary dielectric constants $\varepsilon_1$ and $\varepsilon_2$. Calculations to predict LSPR frequency and intensity utilize these dielectric constants as well as the bulk plasma frequency and the dielectric constant of the surrounding medium, $\varepsilon_m$ (Table 3.1).\textsuperscript{14,15,31} Experimental values for the frequency of LSPR absorbance bands produced by small colloidal NPs depends strongly on NP size, shape, dielectric properties, and interparticle interactions. It is also highly dependent on the local dielectric environment.\textsuperscript{46}

Both Ag and Au have conduction bands located below the Fermi level, which prevents resonance damping from intra-band transitions and gives lower-energy final electronic states. Subsequently, their dielectric functions feature low $\varepsilon_2$ values in the visible range, producing distinct LSPR under visible light irradiation. In contrast, Pt’s absorbance peak includes contributions from intra-band transitions that originate from an $s\rho$ band near the Fermi level.\textsuperscript{15} As a result of these intra-band transitions, Pt possesses very high values for its dielectric constants at visible-range frequencies.\textsuperscript{14,15} The surface plasmon resonance for Pt should occur at the frequency for which $\varepsilon_1 = -2$, which would correspond to 276 nm using literature values for
the dielectric constants. Other estimations set the resonance condition to occur at a different value varies based on the refractive index of the solvent, the bulk plasma frequency, or the high-frequency contribution to the dielectric constant of Pt. Sufficient changes in these factors could cause the plasmon resonance condition not to be met, in which case the absorbance bands for Pt NPs would be caused only by inter-band transitions and would be strongly blue-shifted (increasing the difficulty of detection by UV-Vis spectroscopy).

Another factor that can influence the shape and position of the LSPR band is the presence of surface adsorbates such as surfactant molecules. Adsorbates are usually stabilizing agents used in synthesis to prevent particle aggregation. In the present work, OAm was used as a stabilizer as well as a shape-control agent to target the production of \{100\} facet-terminated nanocubes. The critical role of adsorbate species in nearly all of the most common Pt NP syntheses demonstrates the need to understand the possible effects that these species have on LSPR formation and the optical properties of Pt NPs. Absorbance features and LSPR generation can be influenced by adsorbates through chemical interface damping, in which surface plasmon energy is transferred to the excitation modes of a surface metal-adsorbate complex. A recent study by Romann et al. of OAm-capped silver nanocubes stated that ligands could cause a significant broadening and shifting of the LSPR band by 1) altering the effective optical index and dielectric environment and 2) affecting coherent conduction band oscillations in the NPs. Other studies have modified the typical optical property equations by adding a term to account for chemical interface damping, or by treating the NP/adsorbate system as a core/shell particle. Influence from surface-adsorbed oleylamine could explain the deviation of the calculated LSPR for 8-nm Pt nanocubes in hexane from 230 nm (predicted) to 213 nm (observed). The various significant impacts of adsorbed ligands on LSPR generation and
observation are sufficient to warrant serious investigation into the possible quenching effects of citrate ligands on Pt NPs, and may help to explain some of the discrepancies between calculated and observed spectra in many studies. In this work, spectra were collected amine-stabilized MW-NPs and ligand-exchanged C-NPs (LC-NPs) and compared to spectra collected for as-obtained citrate-stabilized C-NPs. The emergence of distinct peaks on the absorbance spectra of LC-NP samples, which gave featureless spectra prior to ligand exchange, supports a suppressive effect from the citrate species in solution or adsorbed to the surface of the NPs.

3.4.4 Optical Properties of Microwave-Synthesized Platinum Nanocubes

It is of interest to differentiate between the bands that result from plasmonic resonance and those that represent interaction with an adsorbed species, neighboring particle, or aggregated structure. It is also important to examine the difference between spectral changes caused by the formation of aggregated NP clusters and those caused by a one dimensional assembled array of NPs. The absorption bands of Pt NPs are known to be sensitive both to the electronic structure of the Pt atoms and the interactions between the nanoparticles, including self-assembly and aggregation. Interaction with a surrounding dielectric environment consisting of capping agents, nanocomposite components, or a solvent could also change the spectrum. Borodko et al. observed distinct bands that were attributed to plasmonic resonance as well as bands that represented charge transfer between carbonyl groups in an adsorbed capping agent molecule to vacant d-orbitals in the Pt NPs. The data for this study would suggest that the major band at 213 nm is plasmonic in nature, given the agreement of both spectral shape and position with the LSPR band at 215 nm predicted by Mie theory (Figure 3.4).
3.5 Conclusions

Detailed optical studies of highly crystalline 8-nm MW-synthesized Pt NPs show the repeatable production of a distinct plasmonic resonance absorbance peak at a wavelength consistent with well-established calculated literature values. The plasmonic nature of this absorbance peak is supported by its location at the predicted LSPR $\lambda_{\text{max}}$ for small ($\leq$10 nm) Pt NPs, as well as its increased intensity and decreased width as compared to literature spectra reported for spherical Pt NPs produced by other methods. Quenching by adsorbate species, lack of crystallographic faceting, and other surface effects associated with spherical NPs would produce a broader, lower intensity LSPR absorbance band. The suppressive effect of the citrate capping groups most commonly found on Pt NPs in previously reported optical studies was supported by the appearance of distinct peaks near the predicted LSPR $\lambda_{\text{max}}$ after ligand exchange on the C-NPs. The appearance of well-defined absorbance peaks occurred after the citrate capping ligands present on the commercially-obtained C-NPs were replaced with OAm ligands (which are present on the as-synthesized MW-NPs that give the plasmonic absorbance at 213 nm). The blue shift of the absorbance for the LC-NPs is likely the result of their smaller size, and the peak at 207 nm is also likely to be plasmonic in nature. Production of an LSPR by small, highly crystalline Pt NPs offers significant benefits for applications in plasmonic photocatalysis.
3.6 References


Chapter 4

Platinum@Hexaniobate Nanopeapods Synthesized via Facile Microwave Method

4.1 Introduction

Platinum@hexaniobate nanopeapods (Pt@HNB NPPs) are new nanocomposites that are formed by encapsulating dispersible Pt NPs into ordered one-dimensional arrays inside the scrolled nanosheets of the wide band-gap semiconductor $\text{H}_x\text{K}_{4-x}\text{Nb}_6\text{O}_{17}$. Pt@HNB NPPs offer an isolated environment for catalysis by the highly crystalline Pt nanocubes that have been recently reported by our group (see Chapter 2).\(^1\) We have developed a novel, facile, and reproducible synthesis method for Pt@HNB NPPs using microwave heating. This method utilizes common, cost-effective reagents, features reduced reaction times and, and gives very high yields of up to 200 mg per synthesis (compared to 10-20 mg yields from other methods). Pt@HNB NPPs produced via MW synthesis show superior morphology to those produced by alternative methods.

Composite nanostructures that combine nanoscale sheets or scrolls of wide band-gap semiconductors with metal or metal oxide nanoparticles have been the subject of much recent research for applications in photocatalysis and energy production and storage.\(^2-4\) Scrolled nanoscale semiconductors feature hollow cores and greatly increased surface areas that invite diverse and extensive functionalization for catalysis applications.\(^5-9\) The layered metal oxide semiconductor $\text{H}_x\text{K}_{4-x}\text{Nb}_6\text{O}_{17}$ (“hexaniobate”) is chemically desirable for its stability and unique structural features that can be used to produce exfoliated and scrolled morphologies.\(^10,11\) Hexaniobate is of catalytic interest for its efficiency as an active generator and transport mediator of photoexcited charge carriers under UV irradiation.\(^2-4\) Due to its wide band gap, hexaniobate
is often coupled with sensitizing dyes, metal or metal oxide nanoparticles, and other smaller-band gap materials to make stable, efficient composite nanostructures for visible-range photocatalysis. Sensitizing dyes such as Ru(bpy) offer versatile functionalization and facile adsorption to the hexaniobate surface. However, this chemical anchoring has been shown to be not completely stable in aqueous solution, and these systems require a cocatalyst such as Pt or IrO₃ to achieve efficient water splitting.³

Dopants can also be used to shift the onset of hexaniobate’s photocatalytic activity into the visible region. Pian et al. synthesized the TiO₂/Bi-doped hexaniobate compound TiO₂/BiₓNb₆₋ₓO₁₇, which performed the degradation of methylene blue under visible light irradiation.³⁻¹² Doped hexaniobate photocatalysts offer diverse composition and structural options, but can involve complex synthesis methods that are challenging to reproduce. One very promising application for photocatalytic water splitting involves a nanocomposite architecture with Ru(bpy)-sensitized hexaniobate nanoscrolls that were coated in ultrafine Pt NPs via UV-photodeposition methods.⁹ Other studies have involved the functionalization of hexaniobate with cocatalysts such as cadmium selenide quantum dots for efficient visible-light harvesting.⁵⁻⁷,⁹

Although these Pt NP/hexaniobate nanocomposites have been well-established in literature as promising systems for photocatalytic water splitting, there is a lack of published synthetic strategies that give good control over placement of the platinum catalyst.³,⁹ Platinum@hexaniobate nanopeapods (Pt@HNB NPPs) are new nanocomposites that are formed by encapsulating dispersible Pt NPs into ordered one-dimensional arrays inside scrolled hexaniobate nanosheets (Figure 4.1). Pt@HNB NPPs offer a high degree of catalyst placement control, along with flexibility of surface functionalization for adsorption of photosensitizer molecules or even oxidative catalysts for overall water-splitting systems. The NPP architecture
creates an isolated environment for the reduction of H₂ from water via linear arrays of high-surface area Pt nanocubes. Utilizing the hollow inner core of the scrolled semiconductor for water reduction creates greatly increased outer surface space on the Pt@HNB NPPs, which reduces surface crowding from adsorbed photosensitizers and decreases or eliminates kinetic competition for electrons between the Pt NPs and the oxidized sensitizer. This will be covered in detail in Chapter 5.

**Figure 4.1** Platinum@hexaniobate nanopeapod. A linear array of 8-nm Pt nanocubes are encapsulated within scrolled sheets of the semiconductor H₃K₄₋ₓNbₓO₁₇ (hexaniobate).

The immense potential of well-dispersed, morphologically selected Pt NPs and well-formed Pt@HNB NPPs for advanced optical and catalytic applications demonstrates the need for efficient, reliable, and high-output synthetic strategies. Nanopeapods can be formed using a variety of methods, including encapsulation, solvent evaporation, and *in-situ* aqueous synthesis.⁹,¹¹,¹³ In the encapsulation method, pre-formed NPs and crystalline hexaniobate are combined, with exfoliated sheets of hexaniobate scrolling around linear arrays of NPs to create the NPP structure.
One approach to achieving a safe, facile, and reproducible encapsulation method for the production of Pt@HNB NPPs may be found in the use of microwave heating. Microwave (MW) heating involves the rapid transfer of energy directly to the reaction, utilizing localized instantaneous superheating to quickly and efficiently heat solvents. This results in a significant reduction in reaction times as well as increased ability to fine-tune reaction parameters. Synthesis via MW heating, in as little as 1.5 hours, produced Pt@HNB NPPs with morphology and loading superior to those produced via solvothermal (6-18 hours) and solvent evaporation (3-7 days) techniques. Details on the synthesis and morphological characterization of the MW-synthesized Pt@HNB NPPs will be presented.

4.2 Experimental

Materials. K$_2$CO$_3$ (99%) and Nb$_2$O$_5$ (99%) were acquired from Alfa Aesar. Oleylamine (OAm) (technical grade, 70%) and tetrabutylammonium hydroxide (TBAOH) 30-hydrate were purchased from Sigma-Aldrich. Toluene (certified ACS, 99.8% anhydrous), hexane (95% anhydrous), and absolute ethanol (200 proof) were purchased from Fisher Scientific.

4.2.1 Synthesis of K$_4$Nb$_6$O$_{17}$
Crystalline samples of the layered metal oxide K$_4$Nb$_6$O$_{17}$ were prepared via a high-temperature ceramic method. Nb$_2$O$_5$ was dried for 1 hour at 900 °C and stored under argon. K$_2$CO$_3$ and Nb$_2$O$_5$ (molar ratio 1.4:1) were ground using a ball-milling apparatus and placed in an alumina crucible. An initial 10% molar excess of K$_2$CO$_3$ was included to compensate for volatilization during the high-temperature synthesis. The mixture was heated at 900 °C for 1 hour. After cooling to 700 °C in the oven and to room temperature in the open air, a further 10% excess of K$_2$CO$_3$ was added to prevent the formation of potassium-deficient phases; this mixture was
ground via ball-milling again. The sample was then heated for 2 days at 1050 °C, followed by 1 hour at 1100° C. After cooling to room temperature, the sample was washed via centrifugation with de-ionized water and acetone and dried overnight at 75 °C.

4.2.2 Protonation of Host to $H_3K_{4-x}Nb_6O_{17}$
Protonation was performed by placing 8 mL of 6 M HCl and 1 g of $K_4Nb_6O_{17}$ in a 23 mL capacity PTFE liner within a stainless steel autoclave (Parr model 4749A) and heating at 90 °C for 2 d. The product was washed via centrifugation with de-ionized water and acetone and then dried overnight at 75 °C.

4.2.3 Synthesis of Platinum@Hexaniobate Nanopeapods via Microwave Heating
Nanopeapods were synthesized using crystalline $H_3K_{4-x}Nb_6O_{17}$ and pre-formed microwave-synthesized Pt NPs (MW-NPs), which were synthesized via published method (Chapter 2). Time and temperature parameters were set using the T260 EasyCONTROL software that pairs with the Milestone StartSYNTH Microwave Synthesis Labstation (Milestone Srl, Italy), which contains a single magnetron generator with a rotating diffuser operating at 2.45 GHz, and a microprocessor-controlled power output of up to 1200 W. A contact-less internal infrared sensor was used in temperature control. The microwave-absorbing Weflon™ button and PTFE-coated stir bar were added to the 15-bar StartSYNTH reaction vessel, followed by 100 mg of $H_3K_{4-x}Nb_6O_{17}$, 200 mg TBAOH, 5 mL OAm, and 2 mL toluene. A toluene suspension of OAm-capped MWNPs (20 mg/mL) was briefly sonicated, after which 5 mL (100 mg NPs) were extracted to add to the mixture in the glass reaction vessel. The mixture was sealed, magnetically stirred briefly, and secured in the rotor body of the StartSYNTH Microwave Synthesis Labstation. Reaction conditions were varied to determine optimum parameters, utilizing ramp rates of 3.5 °C/minute, reaction times of 60, 75, 90, or 105 minutes, and reaction temperatures ranging from 125-145 °C. After cooling to room temperature at 10 °C/minute, the
silvery-brown product was washed with a mixture of 25 mL EtOH and 15 mL toluene before being isolated via centrifugation. **Caution:** One should inspect glass MW vessels before each reaction; glass defects might lead to hotspots and result in an explosion. To isolate the peapods and remove any residual free Pt NPs, the product was redispersed in 25 mL hexane and centrifuged further for 1 minute. The supernatant was discarded, and a process consisting of shaking/gently centrifuging the heaviest parts of the product in 5 mL of hexane was repeated 3-5 times until NPPs were separated from the unencapsulated NPs and unscrolled hexaniobate nanosheets. TEM samples were prepared after 3-5 rounds of separation; the top and bottom of the remaining product were transferred onto separate TEM grids to determine the degree of scrolling and encapsulation in the different regions. The top and bottom samples were dispersed separately in hexane for storage.

### 4.2.4 Synthesis of Platinum@Hexaniobate Nanopeapods via Solvothermal and Solvent Encapsulation Methods

Solvothermal synthesis of Pt@HNB NPPs was performed using a method from Adireddy et al.\(^\text{10}\) 100 mg H\(_4\)K\(_{4-x}\)Nb\(_6\)O\(_{17}\), 200 mg TBAOH, and 5 mL OAm were combined and magnetically stirred at room temperature for 2 h. 8 mL of a toluene suspension of MW-NPs was sonicated for 1 minute to disperse, then added to the hexaniobate mixture to stir briefly until well-combined (5 minutes). The mixture was then transferred to a 23 mL Teflon-lined stainless steel autoclave (Parr, model 4749, 1800 psig). The sealed autoclave was heated at 220 °C for 6 h and then cooled to room temperature. The precipitate was washed with a mixture of 15 mL of toluene and 30 mL of EtOH before being isolated via centrifugation. The product was then redispersed in 35 mL of toluene and further centrifugation was carried out to isolate the NPPs and remove any residual free NPs. Reaction parameters were systematically varied to study the formation
mechanism of NPPs, with temperatures ranging from 180-240 °C and times ranging from 6 to 12 h. Washing and purification steps were the same as those used in the MW synthesis.

The solvent evaporation approach to synthesizing Pt@HNB NPPs was modified from Rostamzadeh et al.11 First, empty hexaniobate nanoscrolls (NScs) were synthesized solvothermally using the method of Adireddy et al.10 1.5 mL of a toluene suspension MW-NPs (~20 mg) and 10 mg hexaniobate NScs were combined, sonicated for 1 minute, and dispersed in a small glass scintillation vial. The vial was placed under a fume hood, uncovered, and stirred at room temperature until the solvent had completely evaporated (~3 d). Pt@HNB NPPs were then separated from the free particles by adding 5 mL toluene, sonicating to disperse, and then briefly centrifuging. The supernatant was discarded and the precipitate was dispersed in toluene.

4.2.5 Characterization
For transmission electron microscopy (TEM) measurements, Pt@HNB NPPs were dispersed in hexane and dropcast onto 200-mesh copper grids. Images were obtained using an FEI G2 F30 Tecnai Twin TEM at an accelerating voltage of 300 kV. TEM images of Pt@HNB NPPs were analyzed with the ImageJ software to find interlayer spacing values of the multiwalled NPPs, determine inner and outer NPP diameters, and calculate filling fractions for the NPPs. X-ray diffraction (XRD) data was collected for the host and protonated hexaniobate compounds on a Philips X’Pert diffractometer utilizing Cu Kα radiation (λ = 1.5418 Å) and a curved graphite monochromator at a voltage of 45 kV and a current of 40 mA.
4.3 Results

4.3.1 Formation and Morphology of Platinum@Hexaniobate Nanopeapods

The MW synthetic route was used to produce platinum@hexaniobate nanopeapods (MW-NPPs) with good morphology and nanoparticle loading (Figure 4.2). Characterization of MW-NPPs was conducted through TEM imaging and analysis for a variety of goals, including the construction of a general morphological model, the optimization of MW reaction conditions to produce maximum loading and structural uniformity, and the exploration of the MW formation mechanism. Key morphological data collected from TEM images of Pt@HNB NPPs included average NPP length, outer and inner diameter, scroll wall and interlayer structure, and interparticle distance between encapsulated NPs.

Examination of 300 Pt@HNB NPPs via TEM showed lengths ranging from 70-900 nm, with an average length of 300 nm. Host nanoscrolls were found to have between 2 and 6 layers, with a very consistent interlayer spacing of 2.2 nm, which corresponds to the size of the OAm molecule and is consistent with other NPP architectures synthesized by our group (Figure 4.2e). This distance is also the same as the interparticle distance observed between Pt NPs both assembled on unscrolled HNB surfaces and encapsulated into NPPs. Interdigitation of the long aliphatic chains may be favorable to nanoparticle assembly and its subsequent encapsulation into NPPs.\(^\text{16}\)

Outer diameters ranged from 20-50 nm, depending on number of layers and size of encapsulated NPs, while inner diameters for NPPs with good morphology and loading gave an average of 12 nm (Figure 4.2d). Previous nanopeapod studies by our group have shown that, for mid-sized NPs (~7-10 nm), the inner diameter of the NPP is dictated by the captured NPs and that below 12 nm is consistently seen to be the lower limit for inner diameter size, even when the
encapsulated NPs are significantly smaller.\textsuperscript{10} This may be due to an intrinsic limit on the curvature imposed by limits in the local \( \text{Nb--O--Nb} \) bond angles between adjacent \( \text{NbO}_6 \) octahedra in the hexaniobate sheets.\textsuperscript{10}

**Figure 4.2.** (a-c) MW-NPPs with good morphological uniformity and high loading; (d) average inner diameter of MW-NPPs; (e) average interlayer spacing of MW-NPPs.
Control experiments to determine the optimal MW reaction conditions for morphologically uniform Pt@HNB NPPs with high rates of NSc conversion and NP loading were performed by systematically varying reaction time and temperature. Similar control experiments by our group with solvothermal synthesis methods determined that reaction temperatures below 200 °C did not produce significant encapsulation. It was found that a minimum microwave reaction temperature of 130 °C was needed to produce MW-NPPs with high filling loads and consistent, rigid morphology (Figure 4.2a-c); temperatures below 130 °C produced mostly empty NScs. Reaction times of at least 1 h were also needed to produce high levels of scrolling and encapsulation. Table 4.1 summarizes the morphological data.

<table>
<thead>
<tr>
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<th>Average (nm)</th>
<th>Range (nm)</th>
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<tbody>
<tr>
<td>Length</td>
<td>300</td>
<td>70-900</td>
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<tr>
<td>Outer diameter</td>
<td>34</td>
<td>30-45</td>
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<tr>
<td>Inner diameter</td>
<td>12</td>
<td>7.1-21</td>
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Table 4.1. Morphological characteristics of a sample of 300 MW-synthesized Pt@HNB NPPs observed in TEM micrographs.

Figure 4.3 presents data on the size of NPs encapsulated within the NPPs, and illustrates the phenomenon of NP assembly formation on the exterior of the NPPs. TEM images showed that successfully encapsulated MW-NPs had an average diameter of 7.8 nm (Figure 4.3a). MW-synthesized Pt@HNB NPPs generally demonstrated selectivity toward encapsulation of smaller NPs compared to the average size of encapsulated NPs seen in systems such as Fe$_3$O$_4$@HNB (~9 nm).$^{10}$ Although a few very large (~13 nm) and very small (~5 nm) Pt NPs were seen to be encapsulated, the majority of encapsulated NPs (80%) were close to the measured average. The
TEM micrograph of MW-NPPs shown in Figure 4.3b demonstrates that unencapsulated NPs often formed assemblies on the exterior of NPPs with various degrees of NP filling, although free NPs can also be observed in the same sample. Optimization of MW-NPP synthesis reduced the occurrence of the free NPs and “decorated NPPs” that are seen in Figure 4.3b.

The examination of 300 MW-NPPs via TEM imaging was also used to evaluate NP loading. Figure 4.3c shows that even samples with overall high loading percentages contain a few less-filled NPPs, although experiments to optimize MW synthesis parameters have decreased the incidence of these less-filled NPPs. Results of the TEM image analysis showed that over 70% of the MW-NPPs had filling levels of 50% or greater, while only 7% of the observed MW-NPPs had less than 25% filling (Figure 4.3d). Loading percentages for the MW-Pt NPPs can be increased by tuning the microwave reaction conditions and using hexaniobate that has the lowest possible remaining K⁺ composition.¹⁷
Figure 4.3 (a) Table of comparing sizes of MW-NPs that were encapsulated by MW-NPPs vs. unencapsulated, free MW-NPs; (b) TEM image of MW-NPPs showing both encapsulated and free MW-NPs; (c) TEM image showing typical high- and low-loading MW-NPPs; (d) filling percentages of 300 MW-NPPs.
4.3.2 Comparison of Platinum@Hexaniobate Nanopeapods Produced via Microwave, Solvent Evaporation, and Solvothermal Methods

Solvothermal and solvent evaporation methods were also evaluated for the reproducible synthesis of Pt@HNB NPPs. Comparison of the morphologies and loading percentages between NPPs produced by the three methods clearly shows that MW synthesis gives peapods with the most complete scrolling, highest loading, and greatest morphological uniformity. Between the other two methods, solvent evaporation produced superior NPPs. In the solvent evaporation method, hexaniobate NScs were first synthesized using the same experimental conditions as solvothermally-synthesized NPPs, except that no Pt NPs were added. Preformed hexaniobate NScs were combined with MWNPs in toluene and the solvent was allowed to slowly evaporate to dryness over a period of 3 d. Peapod structures are created as the removal of the solvent creates capillary forces that draw some of the NPs into the interior of the NScs. Figure 4.4a-b shows TEM images of Pt@HNB NPPs produced via solvent evaporation.

The same solvothermal synthesis method used for reproducible synthesis of Fe₃O₄@HNB, CeO₂@HNB, and several other types of morphologically uniform, high-loading NPPs by our group was not successful at producing Pt@HNB NPPs. Attempts to synthesize Pt@HNB NPPs using a variety of solvothermal parameters failed to produce structures with any significant encapsulation of NPs. Figure 4.4c-d shows typical results from solvothermal synthesis attempts.
Figure 4.4. Comparison of Pt@HNB NPPs produced by different synthesis methods. (a-b) NPPs from solvent evaporation (SE-NPPs). Notable features include (a) smaller size of encapsulated NPs (compared to MW-NPPs) and (b) multiple rows of encapsulated NPs. (c-d) NPPs from solvothermal methods (ST-NPPs). Features include (c) linear arrays of NPs on hexaniobate surfaces and (d) loose scrolling with irregular morphology.
4.4 Discussion

The new nanocomposite platinum@hexaniobate nanopeapods have been repeatedly produced in quantities of up to 200 mg per synthesis via a new, efficient method utilizing microwave heating. The following discussion addresses the possible Pt@HNB NPP formation mechanism, which factors may contribute to incomplete NPP formation, and results from the MW synthesis method compared to solvothermal and solvent evaporation methods.

4.4.1 Nanopeapod Formation Mechanism

The nanopeapod architecture offers significant benefits by combining scrolled semiconductor nanosheets with catalytic nanoparticles. The act of scrolling can be utilized by nanoscale mechanical devices or to capture specific guest species for the production of new materials with enhanced properties. Systematic variation of reaction conditions produced a variety of effects that were observed in TEM images of the MW-NPPs, which provided an opportunity to investigate the formation mechanism. TEM images (obtained from the current study as well as our group’s previous NPP investigations) support a 3-step mechanism of “alignment → encapsulation → detachment.” These images also suggest that imbalances or deviations at each point of the process can hinder or even prevent the formation of NPPs.

According to the proposed 3-step formation mechanism, delamination of the hexaniobate crystallite occurs as exfoliated nanosheets begin to break at certain crystallographic planes and convolve into nanoscrolls. Pre-aligned nanoparticles are captured by the scrolling process and subsequently encapsulated within the peapod before it detaches from the bulk hexaniobate. The exact size and morphology of the NPP depends on structural defects in the nanosheets, rate of scrolling, nanoparticle size and alignment geometry, and reaction factors such as time and temperature. The effects of those factors on NPP size and morphology will be briefly discussed.
Results from the MW synthesis of Pt@HNB NPPs are in agreement with previous studies of solvothermal NPP production with respect to the effect of reaction time and temperature. Excessively high temperatures can induce rapid exfoliation of hexaniobate nanosheets such that nearby NPs are unable to strongly adhere to the sheets or align before detachment occurs. This produces poorly filled or empty scrolls and, when Pt NPs are used, formations of agglomerated NPs on the scroll exteriors. For MW synthesis, reaction temperatures above 145 °C should not be used due to product quality and safety concerns. At more optimal temperatures (around 130 °C for MW), scroll formation is favored due to the rapid exfoliation that can occur under those conditions. Free NPs are readily captured within the scrolls and do not adhere as strongly to the outer surface.16

Conversely, lower temperatures delay exfoliation and allow the flat topologies of the unexfoliated sheets to accumulate much more extensive NP surface assembly.16 Reactions carried out at lower MW temperatures (T ≤ 125 °C) produced large areas of unexfoliated hexaniobate crystallites “decorated” with a surface coating of NPs, or nearly-formed NPP structures that had undergone some scrolling but had not detached from the crystallite surface (see Figure 4.5). The formation of such composites suggests that lower reaction temperatures promote slower exfoliation and delamination, and produce decorated hexaniobate surfaces as a result of scrolling being hindered by attached NPs.
In addition to lower temperatures, shorter reaction times were also found to increase incidences of excessive NP accumulation and incomplete nanoscroll detachment. A study by our group on silver@hexaniobate nanocomposites showed that both reaction temperature and time

Figure 4.5. MW-NPPs showing deviations from ideal morphology and loading. (a) Extensive pre-organized NP assemblies on unscrolled hexaniobate surfaces that probably prevented NPP formation; (b) failure of NPPs to detach from bulk hexaniobate crystalline; (c) one- and two-dimensional NP arrays interfering with complete encapsulation; (d) bi-directional scrolling rather than complete NPP formation.

In addition to lower temperatures, shorter reaction times were also found to increase incidences of excessive NP accumulation and incomplete nanoscroll detachment. A study by our group on silver@hexaniobate nanocomposites showed that both reaction temperature and time
must be sufficiently high to avoid production of decorated nanosheets or nanoscrolls instead of complete NPPs. Increasing temperature led to improved scroll conversion and detachment, but encapsulation to form NPPs only occurred over a certain time and temperature threshold. Other studies conducted by our group found that high degrees of pre-organization on certain areas of the hexaniobate crystallite significantly hindered scrolling and detachment of the NPPs, and were more prevalent with shorter reaction times. Excessive pre-organization was previously seen on Fe₃O₄ NP chains assembled on hexaniobate for encapsulation, which probably resulted from the dipolar interaction between the magnetic NPs. Strong dipole-dipole interactions between Pt NPs are known to facilitate assembly into one-dimensional arrays, which would also be aided by the morphological uniformity of the MW-synthesized Pt nanocubes. As such, reaction time and temperature must be carefully controlled to ensure the correct amount of pre-organization to form Pt@HNB NPPs.

In low-yield Pt@HNB NPP samples, two phenomena were consistently observed: the presence of extensive preorganized NP assemblies on the hexaniobate crystallite surfaces, and a lack of exfoliation and detachment of scrolled structures from the surface of the large crystallites (Figure 4.5). Figures 4.5a,c show a large number of cubic Pt NPs assembled in both linear and two-dimensional grouped arrays on the hexaniobate surface. Figure 4.5d shows bi-directional scrolling on a pre-exfoliated nanosheet. 1D chains can be seen on opposite sides of the exfoliated sheet, while the edges of the HNB sheet appear to have already formed one complete (empty) nanoscroll. Since these hexaniobate sheets possess a morphology that is normally conducive to scrolling and were successfully exfoliated from the larger crystallite, it is likely that the formation of multiple NP arrays occurred on the sheets after exfoliation and were the main factor in preventing the formation of NPPs.
In this study, optimal conditions for Pt@HNB NPPs with high NP loading and good morphology were found to be a reaction temperature of 135 °C and reaction time (including ramp) of 1 hour and 45 minutes (Figure 4.2). More precise control over the concentration of Pt NPs and their interaction with the hexaniobate was also necessary for optimizing the Pt@HNB NPP synthesis protocol. Due to its flexibility and precision, the use of MW heating has been crucial to the successful formation of Pt@HNB NPPs. Typical MW yields range from 100-200 mg NPPs per synthesis, which is a significant improvement over the 10-50 mg produced by other methods. The quick reaction times, high yields, and reproducibility of both Pt NPs and Pt@HNB NPPs suggest that the MW heating method is ideal for large-scale production of high-quality platinum nanocomposites.

### 4.4.2 Incomplete Scrolling and Conversion from Hexaniobate

In addition to non-optimal reaction conditions, another factor that may deter conversion into peapods is the quality of hexaniobate used: crystallinity, phase purity, and degree of protonation. Figure 4.6 shows the effect of hexaniobate quality on MW-NPP morphology. The more rigid and uniform MW-NPPs (Fig. 4.6a) are contrasted with the morphologically polydispersed, loosely-scrolled MW-NPPs shown in Figure 4.6b. The two different batches of protonated hexaniobate were synthesized using the same method, but came from different samples of parent compound $K_4\text{Nb}_6\text{O}_{17}$. 
X-ray diffraction patterns of the two $\text{H}_x\text{K}_{4-x}\text{Nb}_6\text{O}_{17}$ samples are presented in Figure 4.7. Figure 4.7a shows the pattern for the hexaniobate used in the synthesis of the high-quality NPPs seen in Figure 4.6a. Notable features include a sharp, intense [040] peak at 11.2º two theta, with no other peaks of significant intensity, indicating high phase purity and good crystallinity. In contrast, the large number of extra peaks in pattern Figure 4.7b suggest the presence of multiple crystalline phases, possibly due to formation of potassium-deficient products during the synthesis of the parent compound. Figure 4.7b, which was the hexaniobate used to synthesize the lower-quality NPPs in Figure 4.6b, also displays a [040] peak at 11.0º two theta that is more broad and significantly lower intensity with respect to the equivalent peak in Figure 4.7a. Overall, the features seen in Figure 4.7b indicate decreased crystallinity, low phase purity, and a lower degree of ion exchange. Previous research by our group has indicated that these hexaniobate characteristics are strongly associated with the production of lower-quality NPPs.
4.4.3 Solvothermal and Solvent Evaporation Methods of Platinum@Hexaniobate Nanopeapod Synthesis

Comparison of the morphologies and loading percentages between NPPs produced by the three methods (microwave, solvothermal, and solvent evaporation) clearly shows that MW synthesis gives peapods with the most complete scrolling, highest loading, and greatest morphological uniformity. Solvent evaporation methods produced superior Pt@HNP NPPs compared to solvothermal methods. In the solvent evaporation method, empty hexaniobate NScs were first
solvothermally synthesized. The preformed hexaniobate NScs were then combined with MWNPs in toluene and the solvent was allowed to slowly evaporate to dryness over a period of 3 d. Peapod structures are created as the removal of the solvent creates capillary forces that draw some of the NPs into the interior of the NScs.\(^{11}\) **Figure 4.4a-b** show TEM images of Pt@HNB NPPs produced via solvent evaporation (SE-NPPs), in which significant differences from MW-NPPs are seen. **Figure 4.4a** shows that SE-NPPs favor smaller Pt NPs (with an average size of 6.8 nm) for selective encapsulation as compared to MW-NPPs (average NP size of 7.8 nm). **Figure 4.4b** shows the increased incidence of multiple encapsulated chains within SE-NPPs, which may be due to the decreased average NP size. Additionally, while solvent evaporation produced NPPs with loading percentages comparable to MW-synthesized NPPs, morphological uniformity among the solvent evaporation products was significantly lower.

Attempts to synthesize Pt@HNB NPPs using a variety of solvothermal parameters failed to produce structures with any significant encapsulation of NPs. Interestingly, repeated trials of the same solvothermal method used by our group for the highly reproducible synthesis of Fe\(_3\)O\(_4\)@HNB, CeO\(_2\)@HNB, and other types of morphologically uniform, high-loading NPPs did not successfully produce good-quality Pt@HNB NPPs.\(^{17}\) Attempts to improve the products by systematically varying time and temperature were also unsuccessful. **Figure 4.4c-d** shows typical results from solvothermal synthesis attempts. As seen in **Figure 4.4c**, the solvothermal method published by our group resulted in the formation of 1D arrays on partially-exfoliated nanosheets and hexaniobate crystallites. These results are similar to those produced by solvothermal synthesis of Ag@HNB NPPs at low temperatures and short reaction times.\(^{16}\) **Figure 4.4d** shows a typical result of an attempt to improve the morphology and loading of solvothermally-synthesized Pt@HNB NPPs (ST-NPPs) by increasing time and/or temperature.
The ST-NPPs seen in Figure 4.4d demonstrate that increased reaction times still produced loosely-scrolled products with low-level encapsulation of NPs. While it may be possible to produce high-quality Pt@HNB NPPs via solvothermal or solvent encapsulation methods, they still include challenges such as longer reaction times and more complex procedures.

4.5 Conclusions

There is a great deal of interest in the use of Pt NPs in nanocomposites for photocatalysis, but it is almost always reported for supported Pt nanostructures rather than particles that are dispersed in solution or contained in an ordered assembly. Supported noble metal nanostructures and other PGM NP/semiconductor nanocomposites, which are fabricated via colloidal lithography or deposition of pre-made particles onto substrates, form the basic structures for this type of photocatalysis. The use of Pt@HNB NPPs not only offers the benefits of ordered arrays of plamonic NPs in direct contact with a semiconductor, but also offers an isolated reduction environment that could dramatically improve the efficiency of H₂ produced from photocatalytic water splitting. The fast, efficient, high-yield production of Pt@HNB NPPs offered by microwave synthesis methods facilitates the investigation into these promising new applications. Photolysis studies on the production of hydrogen by Pt@HNB NPPs will be presented in Chapter 5.
4.6 References


Chapter 5
Hydrogen Production via Visible Light Photolysis by Sensitized Platinum@Hexaniobate Nanopeapods

5.1 Introduction

Increased awareness about the economic and environmental costs of fossil fuel dependence has resulted in the prioritization of developing advanced materials for clean, renewable energy production. Artificial photosynthesis has emerged as a promising aspect of this “green energy” technology.\(^1\) Catalytic generation of hydrogen from water, driven by sunlight, can be used to produce high-purity, energy-dense fuel that produces no carbon emissions when burned, and is free from the harmful effects of drilling or mining for fossil fuels.\(^2\)

Dye-sensitized wide-band gap semiconductor/catalyst nanocomposites have been extensively studied as materials for artificial photosynthesis.\(^1,3\) Previous studies on the semiconductor \(\text{H}_x\text{K}_{4-x}\text{Nb}_6\text{O}_{17}\) (“hexaniobate”) have described its electronic and morphological advantages for photocatalytic hydrogen generation, especially when sensitized with polypyridyl ruthenium (Ru(bpy)) chromophore complexes.\(^4-6\) Catalytic platinum nanoparticles (Pt NPs), which are added to the outer surfaces of the nanoscrolls via *in situ* photodeposition, provide sites for hydrogen evolution.\(^7\)

Despite promising results in earlier studies, hydrogen yields from platinized Ru(bpy)/hexaniobate composites have remained low. One contributing factor is surface crowding between adsorbed sensitizers and catalyst Pt NPs, which reduces potential chromophore loading.\(^8\) Direct photocatalytic water splitting is thermodynamically uphill, and charge recombination reactions are energetically favorable.\(^9\) This creates kinetic competition
between the oxidized chromophore and the reduction catalyst for photogenerated electrons, from which the kinetically favored recombination process severely limits hydrogen production. Surface-adsorbed Pt NPs can also directly catalyze the recombination reaction and further decrease H$_2$ output.\textsuperscript{4}

To counteract the effects of kinetic competition, it is possible to increase electron input for water reduction through the use of reductive quenching agents such as trimethylamine, sodium ascorbate, and methyl viologen. Reductive quenchers act as intermediary species by accepting an electron from the chromophore’s photoexcited state and transferring it to the reduction catalyst. This effectively extends the excited state lifetime of the chromophore and theoretically provides a greater quantity of electrons for the water reduction reaction.\textsuperscript{10} However, the use of quenching agents does not address one key limitation of existing Ru(bpy)/Pt/semiconductor nanocomposites: inability to perform overall water splitting.

It is well established in literature that a key challenge of photocatalysis for overall water-splitting is the separation of oxidative and reductive environments.\textsuperscript{8} Due to limitations in catalyst placement and lack of accessible reaction sites for a complete photolysis cell, existing systems are only capable of performing reduction half-reactions through the use of sacrificial electron donors. This limits their usefulness in practical applications for photolytic materials, since materials such as hydrogen fuel cells and low-temperature water electrolyzers provide separate oxidative and reductive environments and can thus perform overall water splitting.\textsuperscript{11} The need for sacrificial electron donors also severely limits the efficiency of hydrogen production by photolytic half-cell systems. Electron transfer from the sacrificial electron donor to the oxidized chromophore was found to be the slowest step in H$_2$ production.\textsuperscript{4} According to
Maeda et al., the sacrificial donor could be replaced with a non-sacrificial donor if the Pt catalyst could be compartmentalized to eliminate the back reaction with H₂.⁸

A unique nanoarchitecture can be used to address these issues and promote significantly increased hydrogen yields. Previous studies by our group have described “nanopeapods,” a composite in which nanoparticles are captured by scrolling hexaniobate to form linear assemblies in the hollow inner core.¹²,¹³ This study presents the nanocomposite platinum@hexaniobate nanopeapods (Pt@HNB NPPs), which feature one-dimensional arrays of encapsulated platinum nanocubes (see Chapter 4). This creates an isolated environment for the catalytic evolution of H₂ on platinum, significantly reducing or even eliminating kinetic competition for photogenerated electrons. Ru(bpy) chromophore molecules can also be adsorbed in higher loadings on the catalyst-free surface. Initial photolysis results show that the NPP-based system produced much greater quantities of H₂ than control groups under identical conditions. Experiments targeting the optimization of experimental parameters such as Ru(bpy) complex functionalization and semiconductor adsorption, solvent dispersibility, and quenching species indicate that Ru(bpy)/Pt@HNB NPPs may be able to produce significant quantities of hydrogen.

Pt@HNB NPPs offer a high degree of control over the catalyst location, isolating water reduction to the encapsulated inner array of Pt NPs and making the large surface area of the high-quality hexaniobate nanoscrolls available for other uses. This may grant Pt@HNB NPPs the flexibility to replace the sacrificial electron donor with an oxidation catalyst or other non-sacrificial donor. In fact, as-synthesized solvothermal Pt@NPPs have adsorbed amine surface groups that could be used to donate electrons to the oxidized chromophore, serving as non-sacrificial electron donors. The system could then be used to target overall water splitting.
This work presents a study on the use of Ru(bpy)-sensitized Pt@HNB NPPs for the production of H₂ via visible-light photolysis. The preparation of NPPs for photolysis via surface functionalization, adsorption of different Ru(bpy)-based chromophore molecules to the NPPs surface, and preparation of the materials for H₂ production will be presented. Structural, optical, and surface group characterization will be described, along with the results of analysis by steady-state and time-resolved luminescence spectroscopy and gas chromatography.

5.2 Experimental

Materials. K₂CO₃ (99%) and Nb₂O₅ (99%) were acquired from Alfa Aesar. Oleylamine (OAm) (technical grade, 70%) and tetrabutylammonium hydroxide (TBAOH) 30-hydrate were purchased from Sigma-Aldrich. Toluene (certified ACS, 99.8% anhydrous), hexane (95% anhydrous), and absolute ethanol (200 proof) were purchased from Fisher Scientific.

5.2.1 Synthesis of K₄Nb₆O₁₇
Crystalline samples of the layered metal oxide K₄Nb₆O₁₇ were prepared via a high-temperature ceramic method.⁵ Nb₂O₅ was dried for 1 hour at 900 °C and stored under argon. K₂CO₃ and Nb₂O₅ (molar ratio 1.4:1) were ground using a ball-milling apparatus and placed in an alumina crucible. An initial 10% molar excess of K₂CO₃ was included to compensate for volatilization during the high-temperature synthesis. The mixture was heated at 900 °C for 1 hour. After cooling to 700 °C in the oven and to room temperature in the open air, a further 10% excess of K₂CO₃ was added to prevent the formation of potassium-deficient phases; this mixture was ground via ball-milling again. The sample was then heated for 2 days at 1050 °C, followed by 1 hour at 1100° C. After cooling to room temperature, the sample was washed via centrifugation with de-ionized water and acetone and dried overnight at 75 °C.
5.2.2 Protonation of Host to $H_xK_{4-x}Nb_6O_{17}$
Protonation was performed by placing 8 mL of 6 M HCl and 1 g of $K_4Nb_6O_{17}$ in a 23 mL capacity PTFE liner within a stainless steel autoclave (Parr model 4749A) and heating at 90 °C for 2 d. The product was washed via centrifugation with de-ionized water and acetone and then dried overnight at 75 °C.

5.2.3 Synthesis of Nanoscrolls
NOTE: In order to optimize procedures for the loading of chromophore molecules onto Pt@HNB NPPs without wasting expensive Pt materials, empty nanoscrolls (NScs) were utilized in their place. NScs were synthesized via solvothermal and aqueous methods as described below. The morphological features and surface chemistry of the NScs were assumed to be equivalent to those of NPPs; this was confirmed by repeating the optimized procedures with NPPs and observing equivalent results. Empty NScs were also used as a control group for studying hydrogen generation via visible-light photolysis by NPPs.

Aqueous Synthesis of Nanoscrolls (ANS)
ANS were synthesized by the method of Saupe et al.\textsuperscript{14} 0.1 g of $H_xK_{4-x}Nb_6O_{17}$ and 1.5 g of tetrabutylammonium hydroxide were combined in 1.5 mL DI water. The mixture was placed in a glass scintillation vial and magnetically stirred at 45 °C for 7 d. The white product was separated via centrifugation for 10 minutes at 6000 rpm in 25 mL ethanol and 15 mL acetone. The supernatant was discarded and the precipitate was centrifuged again, then dispersed in ethanol.

Solvothermal Synthesis of Multiwalled Intercalated Nanoscrolls (INS)
Multi-walled nanoscrolls were synthesized by the method of Adireddy et al.\textsuperscript{15} by combining 0.1 g of $H_xK_{4-x}Nb_6O_{17}$, 5 mL OAm, 0.15 g TBAOH, and 8 mL toluene in a PTFE liner and stirring at
room temperature for 1 h. The PTFE liner was then placed inside a stainless steel autoclave and heated at 220 °C for 6 h. After cooling to room temperature, the product was washed by dispersion in 5 mL hexane and sonication for 2 minutes to form a uniform suspension. 15 mL of ethanol were added and the mixture was centrifuged for 10 minutes at 6000 rpm. After discarding the supernatant, 25 mL of EtOH and 15 mL of acetone were added and the product was sonicated for 2 minutes and then centrifuged for 10 minutes at 6000 rpm.

5.2.4 Synthesis of Platinum Nanoparticles and Platinum@Hexaniobate Nanopeapods via Microwave Heating

Platinum@hexaniobate nanopeapods (Pt@HNB NPPs) were synthesized from crystalline hexaniobate and pre-formed platinum nanoparticles (Pt NPs) via microwave heating method (see Chapters 2 and 4 for detailed descriptions of Pt NPs and Pt@HNB NPPs synthesis, respectively). Briefly, 6 mL of a toluene suspension of Pt NPs was combined with 0.1 g HxK4-xNb6O17, 0.15 g TBAOH, and 5 mL OAm. The mixture was heated while stirring at 135 ºC for 1 hour and 45 minutes, then washed and separated via centrifugation with hexane and ethanol. The dark brown NPPs were isolated via centrifugation and redispersal, repeated 3-5 times to ensure removal of free Pt NPs and unscrolled hexaniobate.

5.2.5 Surface Modification via Ligand Exchange and UV Irradiation

Two surface modification methods were used to make as-synthesized Pt@HNB NPPs dispersible in polar solvents: solution-phase ligand exchange and UV irradiation. A concentrated TBAOH solution was made by dissolving 1 g TBAOH in 2 mL absolute ethanol and stirring for 1 h at 70 ºC. 50 mg of as-synthesized Pt@HNB NPPs were dispersed in the solution and sonicated for 1 minute. The mixture was then stirred for 3 days at 50 ºC to produce hydrophilic TBA⁺-capped NPPs, which were washed in DI water and ethanol, and then centrifuged at 6000 rpm for 10 minutes. The white precipitate was dried at 70 ºC overnight. The dried TBA⁺-capped NPPs
were redispersed in 0.5 mL HCl and stirred overnight. The product was washed and isolated via centrifugation in ethanol and acetone. The proton-capped NPPs were then dried and used for Ru(bpy) adsorption and photolysis.

To remove amine ligands via the irradiation method, 50 mg of as-synthesized Pt@HNB NPPs were added to 5 mL ethanol and sonicated to disperse (~1 min.).

The suspension was placed on a stir plate next to a UV lamp with a wavelength of 254 nm, which were then covered. The NPPs were stirred under UV irradiation at room temperature for 1 hour. The UV-treated NPPs were centrifuged in ethanol and then dried for use in chromophore adsorption and photolysis.

5.2.6 Synthesis of Ru(II) Bipyridyl Chromophore Complexes

In this study, three different ruthenium(II) bipyridyl compounds were used to sensitize Pt@HNB NPPs for visible light absorption. Tris(2,2’-bipyridine)ruthenium(II)\(^{2+}\) was used as both dichloride and phosphorous hexafluoride salts: Ru(bpy)\(_3\)Cl\(_2\) and [Ru(bpy)\(_3\)](PF\(_6\))\(_2\), respectively. By convention, both will be referred to in discussion as Ru(bpy). The phosphorous hexafluoride salt of (4,4’-dicarboxy-2,2’-bipyridine)ruthenium(II)\(^{2+}\) will be referred to as Ru(dcbpy). The Ru(bpy) and Ru(dcbpy) complexes were synthesized according to Paris et al. and Spritschnick et al., respectively, by Patricia R. Fontenot and Rebecca E. Adams of Tulane University from Russell Schmehl’s research group. Characterization was conducted via nuclear magnetic resonance (NMR) spectroscopy.

5.2.7 Adsorption of Ru(bpy) and Ru(dcbpy) onto Nanoscrolls and Nanopeapods

The adsorption of the Ru(bpy) and Ru(dcbpy) complexes onto the nanostructure surfaces was adapted from Maeda et al. Stock solutions of Ru(bpy) and Ru(dcbpy) with concentrations ranging from 50-200 μM were prepared by combining 3-10 mg of the appropriate complex with 100 mL of absolute ethanol, then stirring for 1 hour at 50 °C. Adjustments to the pH were made.
by adding 1 M HCl dropwise. The stock solution was then combined with the dried substrate (NScs or NPPs) in a ratio of 2.5 mL:7.5 mg, sonicated briefly, covered and stirred at room temperature for 1 hour to establish an adsorption-desorption equilibrium. After separation via centrifugation at 13,000 rpm for 10 minutes, the supernatant was collected for UV-Vis examination. To prevent absorbance due to scattering by suspended particles, the supernatant was filtered using a PTFE syringe filter with a pore size of 0.22 μm. The orange precipitate was dried overnight at 70 ºC. The amount of Ru(bpy)/Ru(dcbpy) chromophore adsorbed onto the given substrate was estimated by using an equation from Maeda et al. (Equation 5.1):

\[
\text{Adsorbed chromopore (\(\mu\text{mol g}^{-1}\))} = \left[ \frac{A_{\text{before}} - A_{\text{after}}}{A_{\text{before}}} \right] \left[ C \left( \frac{\mu\text{mol L}^{-1}}{L} \right) \times (2.5 \times 10^{-3} \text{ L}) \right] \left[ \frac{7.5 \times 10^{-3} \text{ g}}{7.5 \times 10^{-3} \text{ g}} \right]
\]

in which \(A_{\text{before}}\) and \(A_{\text{after}}\) represent the absorbance of the chromophore in a test solution at the MLCT maximum wavelength before and after the adsorption procedure, and \(C\) represents the concentration of the chromophore in solution before adsorption. 

5.2.8 Photolysis and Gas Chromatography to Study \(H_2\) Evolution by Sensitized Platinum@Hexaniobate Nanopeapods

Samples of Pt NPs, empty NScs, and Pt@HNB NPPs (“catalysts”) were dried overnight at 70 ºC and measured into portions of ~5 mg. NPPs were used both as-synthesized and after undergoing various surface modification procedures (ligand exchange or UV irradiation). A mixture containing the catalyst, an electron donor, the chromophore, and a quencher was placed in a glass irradiation vial with a self-healing PTFE septum and sonicated briefly. Two different systems were studied, utilizing either water or acetonitrile as the solvent and containing an appropriate electron donor, quencher, and chromophore salt. The system components and concentrations
were based on literature, in order to provide a basis for comparison of the H$_2$ evolution from each.\textsuperscript{8,10} The aqueous system consisted of 0.1 M methyl viologen (MV) as the quencher and 0.01 M ethylenediaminetetraacetic acid (EDTA) as the electron donor in 4 mL of DI water. The acetonitrile system utilized 0.4 M trimethylaniline (TMA) as the quencher and 0.05 M triethylamine (TEA) as the electron donor. DI water (2.5-10\%) was added to the acetonitrile solution for a total volume of 4 mL. The chromophore (Ru(bpy) or Ru(dcbpy)) was used in a 260 $\mu$M concentration for all systems, with the chloride salt used for the aqueous system and the PF$_6$ salt used for the acetonitrile system.

After sonication, small stir bars were added to the samples, which were then degassed under Ar for 10 minutes and placed on a large stir plate. The samples were then stirred and irradiated in a custom photolysis chamber, which consisted of a 500 W Hg-Xe arc lamp with a 450 $\pm$ 50 nm interference filter (overall incident power = 2.3 mW) wrapped with blue LED lights. The irradiation wavelength was centered around the MLCT absorbance band of Ru(bpy) at 450 nm. Evolved gases were analyzed by gas chromatography at regular intervals.

\textbf{5.2.9 Characterization}

X-ray powder diffraction was performed using a Philips X’Pert X-Ray Diffractometer equipped with Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å) and a curved graphite monochromator at an accelerating voltage of 45 kV and a current of 40 mA. UV-Visible absorbance and diffuse reflectance spectroscopy were collected on a Cary 500 UV-Vis/NIR dual-beam spectrometer with an internal diffuse reflectance accessory and PTFE reflectance standards. Absorbance spectra were collected in EtOH using plastic cuvettes over a range of 350-600 nm and analyzed using equations derived from Beers Law. Diffuse reflectance spectra were collected using powdered samples mounted on quartz slides and analyzed by transforming the data via the Kubelka-Munk function, creating a Tauc plot by plotting $h\nu$ vs. $(h\nu(F(R)))^{1/2}$, and calculating the band gap and
conduction band potential.\textsuperscript{8,19} Fourier-transform infrared (FTIR) spectroscopy was conducted using a Perkin-Elmer 2000 FTIR spectrometer. Transmission electron microscopy (TEM) were performed on an FEI G\textsuperscript{2} F30 Tecnai Twin TEM at an accelerating voltage of 300 kV (Tulane University).

Steady state luminescence spectroscopy was conducted using PIL luminescence spectrometer on dilute EtOH or toluene suspensions of the sample in quartz cuvettes. Samples were degassed under Ar for 10 minutes, after which spectra were collected at an excitation wavelength of 450 nm (Ru(bpy)) or 475 nm (Ru(dcbpy)) and a 1 nm s\textsuperscript{-1} scan rate (Tulane University). Time-resolved luminescence spectroscopy was performed on solid samples by Rebecca E. Adams of the Schmehl Group at Tulane University using a transient absorbance spectrometer with a nanosecond Nd:YAG laser.

Visible light photolysis was conducted using an LED illumination chamber centered around the metal to ligand charge transfer (MLCT) band of Ru(bpy) at 450 nm. Evolved gases were analyzed by injecting 50 μL of the head space from each irradiation vial into a Gow-Mac TCD 400 Series gas chromatograph, which was equipped with a thermal conductivity detector and a molecular sieve column (Tulane University). Microlab software was used to analyze the time change between detection of the Ar carrier gas and the sample based on the difference in the thermal conductivity of Ar and H\textsubscript{2} gas. Moles of hydrogen produced were found by integrating the area under the peak for H\textsubscript{2}, which occurs 65 seconds after injection, and applying a series of equations to transform the data from area to H\textsubscript{2} volume (μL) to moles via the ideal gas law. Time course, turnover number, and quantum yield for each sample could then be calculated from the H\textsubscript{2} generation data.
5.3 Results

5.3.1 Synthesis of Nanoscrolls

Figure 5.1 shows the results of nanoscrolls made by solvothermal and aqueous methods (Figures 5.1a-b and 5.1c, respectively). In Figure 5.1d, the results of solution-phase ligand exchange on as-synthesized solvothermal NScs can be seen to experience no significant damage during the surface treatment. The solvothermally-synthesized intercalated multiwalled nanoscrolls (INS) possess higher morphological consistency, with rigid structures and consistent interlayer spacings, inner and outer diameters. Due to these features, INS are expected to have greater available surface area and higher chromophore adsorption potential with respect to NScs synthesized via the traditional aqueous method (ANS). As seen in Figure 5.1c, ANS are scrolled more loosely and possess a wider range of length and diameter variation. Results from chromophore loading experiments performed in this study support the greater availability of adsorption sites on the solvothermally-synthesized NScs.
5.3.2 Synthesis of Platinum@Hexaniobate Nanopeapods via Microwave Heating

Transmission electron microscopy (TEM) was used to evaluate NPP samples for potential use in photolysis. Pt@HNB NPPs were synthesized via microwave synthesis (see Chapter 4) and are expected to display consistent, well-formed morphology with high loading of Pt NPs. **Figure 5.2** presents typical results, along with one unusual result that is included here due to its use as
one of the photolysis samples. While Figures 5.2a-c show highly regular scrolls with ordered linear assemblies of cubic Pt NPs in consistently-sized interior spaces, Figure 5.2d shows encapsulation of seed-like Pt NPs (~2 nm) that were a result of decreased power during MW synthesis. It is of interest that the inner diameter of the NPPs in Figure 5.2d is relatively consistent with those in Figures 5.2a-c, and that while comparatively few NPs are encapsulated within the central inner space, the seed-like NPs can be seen intercalated within the multiple walls of the NScs as well as forming assemblies around the outside of the NPPs. As expected due to its lower Pt loading, this sample produced less H₂ during photolysis.
5.3.3 Surface Modification via Ligand Exchange and UV Irradiation

In order to optimize dispersibility of NPPs in a variety of polar solvents, it was necessary to remove or replace the hydrophobic amine capping groups on the as-synthesized Pt@HNB NPPs. To determine which method produced the most highly-dispersible NPPs with the least amount of
impact on peapod morphology and filling, two different synthesis routes were explored. The first method was based on the solution-phase ligand exchange method published by Wu et al.\(^{20}\) In order to optimize the NPPs surface for Ru(bpy) adsorption, it is necessary to replace the TBA\(^+\) capping molecules with H\(^+\), and so the method includes two steps in which OAm groups are first replaced by TBA\(^+\), after which the TBA\(^+\) groups are replaced by H\(^+\) via acid treatment. Characterization by TEM and FTIR was performed after each step. The second method involved short term (1 h) UV irradiation at room temperature.\(^{16}\)

**Figure 5.3** displays the FTIR results of the solution-phase ligand exchange on the surface chemistry of NPPs. In **Figure 5.3a**, the presence of OAm ligands on the surface of the as-synthesized NPPs is represented by characteristic amine peaks including NH\(_2\) bends at 722 and 1574 cm\(^{-1}\) (respectively), asymmetric and symmetric C-H stretches at 2921 and 2852 cm\(^{-1}\) (respectively), and a bend of the C-H group near the C=C at 3006 cm\(^{-1}\).\(^{21,22}\) The strong asymmetric and symmetric C-H stretches at 2921 and 2852 cm\(^{-1}\) can still be seen after the first part of the solution-phase treatment in **Figure 5.3b**, although in this case those features are produced by the TBA\(^+\) groups that have replaced the OAm. The absence of features associated with the C=C bond found in OAm suggest that the first phase of ligand exchange was successful. **Figure 5.3b** also shows evidence of hydroxyl groups with the appearance of a broad band near 3500 cm\(^{-1}\), which was accepted as evidence of ligand exchange in literature.\(^{23}\) In **Figure 5.3c**, the prominent C-H stretch is no longer present while the hydroxyl peak is stronger. This indicates that the TBA\(^+\) group has been removed from the NPP surface.
Due to the long reaction time and potential damage to the NPPs associated with the solution-phase surface modification method, an alternate route was explored. Because oleylamine is well known to inhibit the catalytic performance of highly crystalline Pt NPs by blocking the reactive surfaces, several groups have studied which methods of removing or replacing OAm produced the most complete exchange with the least structural impact.\textsuperscript{16,24} Multiple studies identified UV irradiation as the most effective and least harmful technique.\textsuperscript{16,24} Solvent-based and thermal annealing methods were also explored, but found to be ineffective or damaging. \textbf{Figure 5.4} shows the results of both solution-phase and UV irradiation methods of surface modification, with \textbf{Figure 5.4a} showing the sample before any treatment was applied.

\textbf{Figure 5.3.} FTIR spectra of Pt@HNB NPPs after different methods of surface modification.
Figures 5.4b-c show the intermediate and final phases of the solution-phase method. Although no significant morphological impacts are seen after the TBAOH/EtOH treatment in Figure 5.4b, severe damage to both NPPs morphology and loading can be observed after the HCl treatment in Figure 5.4c. It seems that even low concentrations of acid have a destructive effect on the NPPs, as can be seen in the disordered, unscrolled hexaniobate and greatly reduced NPP loading.

Figure 5.4d shows the results of the UV treatment, which are negligible with respect to both morphology and loading. The UV irradiation method produced superior results in a far shorter reaction time (1 hour as opposed to 3-7 days), and was the method chosen to treat the NPPs used for photolysis.
5.3.4 Diffuse Reflectance Spectra of Semiconductors

Figure 5.5a shows initial percent reflectance spectra for the parent compound, protonated phase, and scrolled hexaniobate semiconductor collected using the diffuse reflectance accessory on the UV-Vis spectrometer. In Figure 5.5b, a Tauc plot has been constructed by converting the...
percent reflectance spectra of $K_4Nb_6O_{17}$, $H_xK_{4-x}Nb_6O_{17}$, and hexaniobate NScs via the Kubelka-Munk function, $F(R)$ and plotting $(hvF(R))^{1/2}$ vs $hv$. Band gap values ($E_g$) were estimated by finding the inflection point in the first derivative of the Tauc plot curve. Results for $E_g$ were in good agreement with literature values as well as the predicted trend of decreasing as the parent compound $K_4Nb_6O_{17}$ underwent protonation and scrolling. $E_g$ values for $K_4Nb_6O_{17}$, $H_xK_{4-x}Nb_6O_{17}$, and hexaniobate nanoscrolls (NScs) were found to be 3.7, 3.4, and 3.3 eV, respectively.

![Image](image.png)

**Figure 5.5.** UV-Visible diffuse reflectance data for parent, protonated, and scrolled hexaniobate. (a) Percent reflectance data was transformed via the Kubelka-Munk function. (b) Tauc plot of transformed percent reflectance data with $E_g$ values for each compound determined using the inflection point method.

### 5.3.5 Adsorption of Ru(bpy) and Ru(dcbpy) onto Nanoscrolls and Nanopeapods

Multiple trials were performed to attach Ru(bpy)/Ru(dcbpy) complexes to NScs and NPPs of different structures and surface functionalizations. The sensitizer loading was calculated based on Equation 5.1. To find the optimal parameters for adsorption, different chromophore stock solutions were prepared with variations of Ru complex type, pH, and chromophore concentration. The stock solution was added to 5-mg dried samples of the substrate and stirred, after which the supernatant was separated by centrifugation and analyzed via UV-Vis absorbance.
spectroscopy. The amount of adsorbed chromophore was calculated according to **Equation 5.1** from the UV-Vis absorbance spectra, using Beer’s Law to calculate an experimental molar absorptivity coefficient for each chromophore solution. Pre-adsorption test solutions were expected to give absorbance values ranging from 0.5 – 1.5, based on chromophore concentration. The very low absorbance values for the post-adsorption solutions were expected as a result of the chromophore coming out of solution onto the substrate surface.

A comparison of the UV-Vis spectra from before and after each adsorption procedure is shown in **Figures 5.6 – 5.8**, in which different adsorption parameters are evaluated to find which produced the highest chromophore loading onto the substrate. A slight instability in the adsorption of the chromophore to the hexaniobate surface is anticipated, but comparison of the loading values given by this method is effective for optimizing the sensitization protocol.
Figure 5.6 displays the effect of chromophore functionalization on adsorption. It has been repeatedly demonstrated in literature that the electrostatic linkages resulting from the interaction of the cationic Ru(bpy) complex result in lower chromophore loadings than the covalent interaction provided by the CO₂H-functionalized Ru(dcbpy).\textsuperscript{8,28–30} This is supported by the data in Figure 5.6, in which the difference between stock and supernatant intensity is significantly greater for the Ru(dcbpy) sample than for the Ru(bpy) sample.

Figure 5.6. UV-Visible absorbance spectra showing the effect of chromophore functionalization on substrate loading. The red and blue arrows represent the loading onto NScs of Ru(bpy) and Ru(dcbpy), respectively. The Ru(dcbpy) sample shows higher chromophore loading.
Figure 5.7 shows the effect of increasing chromophore concentration: under identical reaction conditions, the adsorption of the more concentrated Ru(dcbpy) solution resulted in higher loadings compared to the less concentrated solution. Analysis of the absorbance data using Equation 5.1 gave loading values of 29.9 and 39.1 μmol g⁻¹ for the 50 and 100 μM solutions, respectively.

![UV-Vis absorbance spectra](image)

**Figure 5.7.** UV-Visible absorbance spectra showing the effect of chromophore stock solution concentration on substrate loading. The red and blue arrows indicate loading values for the 50 and 100 μM solutions, respectively. The 100 μM solution produced higher chromophore loadings onto the NScs.
In Figure 5.8, the effects of chromophore stock solution pH are examined for both aqueous-method and solvothermally-produced NScs. Over the tested range of pH values (1-5), the solvothermal SENS show significantly greater chromophore loadings. This may be due to difference in surface functionalization between the two NSc types, or a greater available surface area on the solvothermally-synthesized SENS. With the pH 1 solution in Figure 5.8a, the ANS and SENS were found to have loadings of 11.0 and 23.3 μmol g⁻¹, respectively. Figure 5.8b demonstrates that higher loading occurred for both types of samples as pH became less acidic (pH 3 was the value used for the chromophore solutions by Maeda et al.⁸) The pH 3 solution produced loadings of 19.1 and 39.1 μmol g⁻¹ for the ANS and SENS, respectively. The pH 5 chromophore solution gave the highest loadings onto both types of NScs, with ANS and SENS loading values of 30.2 and 55.9 μmol g⁻¹, respectively. It is of interest to observe the difference in the shape of the absorbance curve at pH 5 (Figure 5.8c), which may be due to differences in energy level splitting in the MLCT band resulting from changes in protonation of the carboxy groups in the less acidic environment.²⁸
X-ray diffraction was performed in order to determine if Ru(bpy) complexes had intercalated into the scroll interiors, or had adsorbed to the outside of the scroll (Figure 5.9). In order to confirm that the sensitizer was being loaded only onto the substrate surface and not being intercalated into the interlayers of the hexaniobate substrates, the diffraction patterns of NScs before and after chromophore adsorption were examined. Low angle reflections in the

Figure 5.8. UV-Visible absorbance spectra showing the effect of chromophore stock solution pH on chromophore loading. As the pH of the solution became less acidic, loading values of chromophore onto both types of NScs increased.
diffraction patterns of the NScs before and after chromophore adsorption were unchanged, indicating that the large complexes did not intercalate into the hexaniobate interior. Expansion of the interlayer to incorporate the chromophore complexes would have been observed as a shift to lower values in the reflections below 10 degrees 20.25

**Figure 5.9.** X-ray diffraction spectra of NScs before and after chromophore adsorption. The lack of shift in peak positions indicates that the chromophore was not adsorbed into the inner structure of the NScs.
5.3.6 Steady State Luminescence Spectroscopy

Steady-state luminescence spectroscopy was conducted to evaluate quenching efficiency, which relates to the efficiency of electron injection from the chromophore excited state into the conduction band of the semiconductor. Samples with Ru(bpy) or Ru(dcbpy) adsorbed onto either ANS or SENS surfaces demonstrated a decrease in luminescence intensity with respect to that of the stock chromophore solution. This decrease is due to quenching of the chromophore MLCT excited state via electron injection into the semiconductor conduction band. A larger difference between the intensity of the chromophore stock solution and that of the Ru/NScs samples indicates higher (more efficient) quenching and would be expected to yield higher H₂ output.

Figure 5.10 displays the decrease in the intensity of the steady state luminescence spectra from pre-adsorption Ru(bpy) and Ru(dcbpy) chromophore solutions to post-adsorption supernatant solutions. Chromophore concentration was recorded by quantifying the UV-Vis absorbance decrease via Equation 5.1, with supernatant from higher-loading samples displaying a decrease in both absorbance and luminescence intensity. According to Figure 5.10, the Ru(dcbpy)/SENS sample shows significantly higher quenching efficiency than the Ru(dcbpy)/ANS sample, as expected based on increased chromophore adsorption and more efficient electron injection via the covalent linkage with the NScs surface. Steady-state luminescence spectra were also used to find the emission maximum wavelength, which is then used as the excitation wavelength for time-resolved luminescence spectroscopy. For Ru(dcbpy)/ANS and Ru(dcbpy)/SENS samples, the emission maximum wavelength was found to be 661 and 664 nm, respectively (Figure 5.10).
5.3.7 Time-Resolved Luminescence Spectroscopy

In Figure 5.11, excited state decay curves for Ru(dcbpy) adsorbed onto an insulator (SiO$_2$) and two different samples of NScs are shown. As expected, the Ru(dcbpy)/SiO$_2$ sample fit a monoexponential decay pattern. Both NSc samples fit a biexponential pattern, although a significant increase in the steepness of the decay curve for the Ru(dcbpy)/SENS sample can be observed relative to the curve of the Ru(dcbpy)/ANS sample.
Visible light photolysis was performed on ~5 mg samples of Pt NPs, empty NScs, and Pt@HNB NPPs. Two main systems of species and sample preparation were used: an aqueous system that used methyl viologen (MV) as a reductive quencher and EDTA as a sacrificial electron donor, and an acetonitrile-based system in which TMA was the reductive quencher and TEA was the sacrificial electron donor. DI water was added to the acetonitrile system in quantities varying

**Figure 5.11.** Time-resolved transient absorbance spectra of Ru(dcbpy) adsorbed onto an insulator (SiO₂) vs. two types of semiconductor NScs.

### 5.3.8 Hydrogen Production via Visible Light Photolysis by Sensitized Platinum@Hexaniobate Nanopeapods

Visible light photolysis was performed on ~5 mg samples of Pt NPs, empty NScs, and Pt@HNB NPPs. Two main systems of species and sample preparation were used: an aqueous system that used methyl viologen (MV) as a reductive quencher and EDTA as a sacrificial electron donor, and an acetonitrile-based system in which TMA was the reductive quencher and TEA was the sacrificial electron donor. DI water was added to the acetonitrile system in quantities varying
from 2.5-10% of the total solution volume. Pt NPs and empty NScs served as control groups to ensure that any observed hydrogen was being generated by the NPPs. No H\textsubscript{2} was observed from any of the NSc samples, and only one sample of Pt NPs produced any H\textsubscript{2}, in a very small quantity compared to the NPPs. It is therefore assumed that any significant quantity of H\textsubscript{2} was generated by visible light driven photolysis by the sensitized Pt@HNB NPPs.

**Figure 5.12** shows the general range of H\textsubscript{2} production from sensitized Pt@HNB NPPs under irradiation at 450 ± 50 nm by a 500 W Hg-Xe arc lamp wrapped with blue LED lights (overall incident power = 2.3 mW). Samples were irradiated for a total of 60-90 minutes, with analysis of the product’s thermal conductivity via gas chromatography of 50 μL of head space from the photolyzed samples occurring at regular intervals. Quantities of H\textsubscript{2} produced ranged from 0.4-3.4 μmol, and seem to be most significantly affected by the accessibility of the chromophore to the NPPs in solution. Studies of surface-platinized Ru(bpy)/Pt/hexaniobate NScs systems report H\textsubscript{2} output values of ~3 μmol over the same time period.\textsuperscript{9} Platinized hexaniobate NScs onto which a phosphonated ruthenium(II) complex was pre-adsorbed reported higher H\textsubscript{2} outputs (~12 μmol) over the same time period.\textsuperscript{8} In this study, the largest quantity of H\textsubscript{2} was evolved by a sample that did not undergo pre-adsorption (5.12e) and interacted with the chromophore via the reductive quencher TMA. Since the authors of the cited work state that the strong covalent linkage between the pre-adsorbed phosphonated chromophore was the most important factor in determining H\textsubscript{2} output, it is expected that pre-adsorption of the carboxy-functionalized Ru(dcbpy) complex onto Pt@HNB NPPs will result in a significant increase in H\textsubscript{2} production under optimized photolysis conditions.
Samples in equivalent systems under the same photolysis conditions gave very similar results across multiple trials, indicating that the experiments are reproducible. Pt@HNB NPPs were either pre-adsorbed with the chromophore or dispersed in a 260 μM chromophore solution. Photolysis systems were either aqueous or acetonitrile-based, with corresponding changes in electron donor (EDTA or TEA) and reductive quencher (MV or TMA). Other experimental parameters varied include method of NPP surface treatment and chromophore type (Ru(bpy) vs. Ru(dcbpy)). In general, quality and surface conditions of the Pt@HNB NPPs seemed to have the greatest influence over H₂ output. Samples with higher Pt loadings that retained morphological

**Figure 5.12.** Hydrogen production (μmol) under visible light irradiation by Pt@HNB NPPs under a variety of experimental conditions.
integrity after surface modification gave the highest H$_2$ yields, while samples with poor
dispersibility due to solvent miscibility or that had been severely degraded by surface treatment
gave the lowest H$_2$ yields. Superior yields were given by samples in which the NPPs had
undergone surface modification via UV irradiation prior to photolysis and utilized the carboxy-
functionalized Ru(dcbpy) chromophore.

5.4 Discussion

5.4.1 Semiconductor Morphology and Composition
Nanoscroll morphology and quality is extremely important to the efficiency of H$_2$ generation,
most notably since the increased surface area offered by nanoscrolls over the bulk material
allows a greater number of sites for sensitizer adsorption and reduces competition for surface
sites between sensitizers, electron donors, and other system components.$^{15}$ Electrostatic
attraction is one driving force for chromophore adsorption. This is an advantage for the
interaction between cationic Ru(bpy) complexes and the surface of hexaniobate NScs, which
retain their negative charge over a wide range of pH values.$^8$

In literature, the significantly higher activity of NScs as compared to nanosheets (NSs)
has been attributed to the higher affinity of the NScs for Ru(bpy). Higher adsorption onto NScs
results in a higher quantum yield of charge injection from the MLCT of Ru(bpy), leading to a
higher H$_2$ evolution rate.$^9$ Maeda et al. attributed this to the fact that the electron transfer
pathway is in the plane of a single sheet for NScs, as opposed to the electron tunneling that must
occur between NSs in order to interact with the catalyst.$^9$ The multiwalled structure of our NPPs
may induce some loss of electron transfer efficiency from that same phenomenon, although
further characterization in that area is needed.
Protonation also plays an important role in several aspects of Ru(bpy)/hexaniobate systems. Examples include the reduced interlayer distance that can lead to improved interlayer electron conductivity\(^6\), the conversion of bonds from Nb=O to Nb—OH and subsequent opportunities for beneficial covalent sensitizer linkages\(^3^1\), and the observed band gap reduction in the protonated material that may result from that conversion of Nb-O to weaker Nb—OH bonds.\(^2^6\)

### 5.4.2 Semiconductor Optical and Electronic Properties

UV-Visible diffuse reflectance spectroscopy was used to examine the electronic band structure of the hexaniobate semiconductor. The conduction band potential of a semiconductor is an important parameter for the efficient production of H\(_2\) in dye-sensitized systems. In their study on layered metal oxide nanosheets, Maeda et al. found that NSs with a more negative conduction band potential were preferable for dye-sensitized H\(_2\) evolution.\(^3\) In the preparation of the scrolled semiconductor component of the NPPs, the crystalline layered metal oxide K\(_4\)Nb\(_6\)O\(_{17}\) undergoes protonation via ion exchange to form H\(_x\)K\(_{4-x}\)Nb\(_6\)O\(_{17}\). Previous studies have shown that protonated hexaniobate displays significant changes in optical and electronic properties, including a decrease in band gap size.\(^2^6,2^7,3^2\) Scrolling of the hexaniobate further reduces the band gap to 3.3 eV.\(^2^7\)

The driving force behind the injection of photogenerated charge carriers from a photosensitizing complex into the conduction band of an adsorbed semiconductor is the difference in reduction potentials between the semiconductor and the desired reaction. The decrease in scrolled hexaniobate conduction band energy causes a subsequent change in its conduction band edge, with its potential becoming more favorable for the water reduction reaction that would occur at the Pt NPs.\(^2^7,3^3\) Analysis of diffuse reflectance spectra of parent, protonated, and scrolled hexaniobate in this study are in good agreement with the literature trend,
with band gap energies decreasing from 3.7 eV to 3.3 eV (parent and scrolled compound, respectively) (Figure 5.5). These band gap values were used to calculate the conduction band edge of the NScs according to equations from Matsumoto. The values were found to be -0.435 eV, which is sufficiently negative compared to the H+/H2 reduction potential of -0.41 eV (at pH 7) to promote efficient electron injection into the hexaniobate conduction band and subsequent water reduction to H2.

UV-Visible absorbance spectroscopy was used to study the adsorption of Ru(bpy) and Ru(dcbpy) chromophore complexes onto the surface of one interesting effect observed during the trials on pH variation was the change of the shape of the Ru(dcbpy) curve when the pH was increased to 5. Spectra recorded at pH values 1 and 3 show that the curve retains a distinct shape that includes two local maxima between 400-500 nm (Figure 5.8a-b). However, the shape of the curve observed at pH 5 displays only a single, higher-intensity maximum in the same wavelength range (Figure 5.8c). This may be due to changes in band splitting that result from having two carboxy groups located on one of the bipyridyl ligands, while the other two bipyridyl ligands remain non-functionalized. When the groups are both fully protonated, MLCT band splitting occurs due to the existence of two distinct, stabilized excited state transitions that represent electron transfer from the Ru(II) atom to either the carboxy-functionalized (ccb) or non-functionalized (bpy) bipyridyl ligands. However, when the carboxyl groups become deprotonated as the pH becomes more basic, the transitions become increasingly delocalized as the Ru(II) → ccb-π* transition loses stability. Additionally, the presence of two deprotonated COO− groups on the same bipyridyl ligand significantly increases the dipole moment, which results in a blue shift in the remaining absorbance maximum. Both phenomena can be seen in the absorbance spectra of the samples at pH 5 (Figure 5.8c).
5.4.3 Examination of Electron Kinetics via Luminescence Spectroscopy

Steady state luminescence can be used to examine the efficiency of electron injection from the photoexcited chromophore into the semiconductor conduction band. Maeda et al. found that a decrease in steady state luminescence intensity of the MLCT band of Ru(bpy) occurred when the chromophore was adsorbed to semiconductor surfaces, indicating excited state quenching of the chromophore by electron injection into the semiconductor conduction band. Examination of luminescence intensity for the same complex adsorbed onto an insulator (SiO$_2$) showed no significant intensity decrease, as expected from a lack of electron injection. Maeda et al. also observed differences in quenching efficiency with hexaniobate NScs based on the functionalization of the adsorbed chromophore, with the electrostatically bound Ru(bpy)/NScs complexes showing 50% quenching efficiency as opposed to 88% from the covalently-bound Ru(dcbpy)/NScs. Our results are in good agreement with these findings, with Ru(bpy)/NScs showing 70% quenching efficiency. Higher quenching efficiency indicates more rapid electron injection.

Time-resolved measurements were made via transient absorbance (TA) spectroscopy, in which a Nd:YAG laser pulses made on a nanosecond timescale produce excitation irradiation at a wavelength selected by the monochromator. This wavelength is determined via steady-state luminescence spectroscopy, and the pulse produces a population of photoexcited electrons that decay over time based on the decay pathways available to them. Possible decay pathways include radiative decay (phosphorescence), non-radiative decay (thermal relaxation), and electron transfer, if a species with a compatible band structure is adsorbed or coordinated to the chromophore. TA spectra can be fitted to monoexponential or biexponential decay curves, depending on which pathways are present. Radiative and non-radiative decay are considered “concentration” or “self” quenching and comprise the “long” lifetime component, which is the
only excited state decay process that occurs for samples in which there is no electron transfer. If 
electron transfer does occur, a “short” lifetime component will also be calculated to represent 
electron injection into the conduction band of the semiconductor.\textsuperscript{37} Each component includes a 
value for excited state lifetime (τ) as well as a prefactor (A) that represents the relative 
contribution of that component to the overall excited state decay curve.

The value of τ is defined as the amount of time it takes for the concentration of excited 
states to decay to 1/e of the initial value.\textsuperscript{6} Prefactor values are derived from the mono- or bi-
exponential decay curves which are fit to the data. For data fitted to a biexponential curve, the 
ratio of the prefactors A\textsubscript{1} and A\textsubscript{2} is used to assess the efficiency of electron injection. The 
dominance of a prefactor is interpreted as the dominance of that component to the overall excited 
state decay of that sample: in samples with very efficient electron injection, the “short lifetime” 
prefactor would have a much higher value than that of the “long lifetime” prefactor.\textsuperscript{27} Prefactor 
and lifetime data for the samples is summarized in Table 5.1.

In Table 5.1, it can be seen that both lifetime components are significantly shorter and 
the A\textsubscript{1}/A\textsubscript{2} ratio is much higher for the Ru(dcbpy)/SENS samples as compared to the 
Ru(dcbpy)/ANS samples. The fact that A\textsubscript{1}/A\textsubscript{2} > 1 for both samples indicates that electron 
transfer is the dominant excited state decay component for both, but the difference in the 
magnitude of the values suggests that electron injection occurs much more efficiently into the 
SENS conduction band. The superior scrolling of solvothermal nanoscrolls, improvements in 
surface-exchange techniques, and the efficiency of adsorption testing and sample collection are 
most likely the cause of the significant increase in electron injection efficiency from Ru(dcbpy) 
into SENS samples.
5.4.4 Hydrogen Production via Visible Light Photolysis by Sensitized Platinum@Hexaniobate Nanopeapods

The first NPP photolysis trials conducted used low-quality NPPs with low Pt loading (**Figure 5.2d**) in the acetonitrile system with 10% H₂O, and produced 0.4 μmol H₂ (**Figure 5.12a**). Replicating those conditions using much higher quality NPPs with good Pt loading as seen in **Figure 5.2b** produced 0.5 μmol H₂, representing a slight increase in H₂ production (**Figure 5.12b**). When pre-adsorption of the Ru(dcbpy) chromophore was conducted, lower-quality NPPs that had been damaged by surface modification (**Figure 5.4c**) were able to produce a significantly increased quantity of H₂, 0.9 μmol (**Figure 5.12c**). This may indicate that, while NPP quality does have some effect on H₂ production, having good coordination with the chromophore is much more important for producing high H₂ yields.

### Table 5.1.

Transient absorbance data for Ru(dcbpy) adsorbed onto an insulator (SiO₂) and two types of NScs: aqueous (ANS) and surface-exchanged solvothermal (SENS). For the NScs samples, the A₁ and A₂ prefactor values represent the relative contribution of each component (electron transfer and self-quenching, respectively) to the overall excited state lifetime. The time value of each component is expressed as τ₁ or τ₂ (ns). Since the excited state lifetime decay of Ru(dcbpy) on an insulator has only one component, it is expressed as τ₁.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>A₁</th>
<th>τ₁ (ns)</th>
<th>A₂</th>
<th>τ₂ (ns)</th>
<th>A₁/A₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂-1</td>
<td>0.0643</td>
<td>460</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SiO₂-2</td>
<td>0.0337</td>
<td>570</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>ANS-1</td>
<td>0.2318</td>
<td>24</td>
<td>0.0257</td>
<td>408</td>
<td>9</td>
</tr>
<tr>
<td>ANS-2</td>
<td>0.2415</td>
<td>22</td>
<td>0.0225</td>
<td>410</td>
<td>10</td>
</tr>
<tr>
<td>SENS-1</td>
<td>0.6594</td>
<td>4.5</td>
<td>0.0037</td>
<td>102</td>
<td>180</td>
</tr>
<tr>
<td>SENS-2</td>
<td>5.109</td>
<td>3.3</td>
<td>0.0092</td>
<td>130</td>
<td>550</td>
</tr>
</tbody>
</table>
Parameters including percent H$_2$O, NPP surface treatment, chromophore functionalization, and solvent were varied in order to optimize H$_2$ production, with results summarized in Table 5.2. For NPPs that did not undergo surface modification before photolysis, altering the percent H$_2$O had significant effects on H$_2$ production. Two samples used in the acetonitrile system successfully generated H$_2$ with 10% H$_2$O, but failed to produce any H$_2$ when the water content was increased to 20-40%. As-synthesized (OAm-capped) NPP samples were also tested in the aqueous system, but not one of 8 samples produced any H$_2$. This is most likely due to the lack of dispersibility caused by the hydrophobic surface groups and a corresponding inability to interact with the chromophore. Different samples were tested for pre-adsorption as

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Solvent</th>
<th>% H$_2$O</th>
<th>Chromophore</th>
<th>Surface Modification</th>
<th>μmol H$_2$</th>
</tr>
</thead>
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<tr>
<td>5.12a</td>
<td>MeCN</td>
<td>10</td>
<td>Ru(bpy)</td>
<td>None</td>
<td>0.4</td>
</tr>
<tr>
<td>5.12a</td>
<td>MeCN</td>
<td>40</td>
<td>Ru(bpy)</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>5.12b</td>
<td>MeCN</td>
<td>10</td>
<td>Ru(bpy)</td>
<td>None</td>
<td>0.5</td>
</tr>
<tr>
<td>5.12b</td>
<td>MeCN</td>
<td>20</td>
<td>Ru(bpy)</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>5.12c</td>
<td>MeCN</td>
<td>10</td>
<td>Ru(dcbpy)</td>
<td>Ligand exchange, pre-adsorption</td>
<td>0.9</td>
</tr>
<tr>
<td>5.12d</td>
<td>MeCN</td>
<td>10</td>
<td>Ru(dcbpy)</td>
<td>UV irradiation, pre-adsorption</td>
<td>0.9</td>
</tr>
<tr>
<td>5.12e</td>
<td>MeCN</td>
<td>10</td>
<td>Ru(dcbpy)</td>
<td>UV irradiation</td>
<td>3.4</td>
</tr>
<tr>
<td>5.12f</td>
<td>H$_2$O</td>
<td>100</td>
<td>Ru(dcbpy)</td>
<td>UV irradiation</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 5.2. Data for hydrogen production via visible light photolysis (λ = 450 nm) from Pt@HNB NPPs in a variety of experimental conditions. The sample names listed in this table are used in Figures 5.12, 5.13, and 5.14.
well as with the chromophore in solution, but none showed any H₂ production. However, NPPs that underwent surface modification via UV irradiation were able to successfully interact with the chromophore in an aqueous environment both via pre-adsorption and in solution during photolysis (Figure 5.13).

![Graph showing H₂ production over irradiation time for different samples](image)

**Figure 5.13.** Hydrogen production (µmol) by Pt@HNB NPP samples with different types of surface modification (see Table 5.2).

Of all samples tested so far, the highest H₂ yield was produced by a sample that underwent UV irradiation before photolysis, and was then dispersed in the acetonitrile system with Ru(dcbpy) and 10% H₂O. **Figure 5.14** shows H₂ production by that sample (labeled 5.12e) next to a sample of the same NPPs tested under identical conditions (labeled 5.12d) except
having undergone pre-adsorption with Ru(dcbpy) before photolysis. Both samples contained Ru(dcbpy) dissolved in solution. The significant difference in H₂ yield may be attributable to competition between the pre-adsorbed chromophore on the high-yield sample in Figure 5.14 and the reductive quencher TMA for photogenerated electrons from the reduced chromophore in solution.

**Figure 5.14.** Difference in hydrogen production (μmol) by Pt@HNB NPP samples under identical conditions, differing only in having undergone chromophore pre-adsorption (5.12d) vs. no pre-adsorbed chromophore (5.12e). See Table 5.2.
Challenges of optimizing the photolysis system for NPPs include adapting dispersibility to aqueous and other polar solvents (to replicate and compare literature results), which requires some sort of surface modification since the as-synthesized NPPs are hydrophobic due to their surface amine groups. The possible adsorption of other reaction species or intermediates may block contact with the sensitizer, which further emphasizes the need for greater understanding and control of NPPs surface chemistry. Purifying samples to exclude any free nanoparticles, which could catalyze the recombination reaction and decrease H\(_2\) production, is also important. Previous studies have observed that H\(_2\) generation was greatly decreased or even prevented if any part of the system (semiconductor, chromophore, electron donor) was missing.\(^9\) This was also the case in our study, as control groups of sensitized Pt NPs and empty NScs either produced very small quantities of H\(_2\) (Ru/Pt NPs) or no H\(_2\) at all (Ru/NScs).

Maeda et al. studied the photocatalytic activity for H\(_2\) production from Ru(bpy) complexes adsorbed to hexaniobate nanoscrolls via electrostatic attraction. Their results showed activity for H\(_2\) production to be \(\sim 3 \, \mu\text{mol h}^{-1}\), which is similar to the amount of H\(_2\) produced in a one-hour time period by the best-performing sample in this study.\(^9\) The only significant difference between the experimental conditions used by Maeda at al. and those of the current study is the interaction between the chromophore and the semiconductor surface. Maeda et al. used hexaniobate NScs with a pre-adsorbed Ru(bpy) chromophore, as opposed to our study, in which the highest H\(_2\) yields were produced by samples in which chromophore was dispersed in solution and interacted indirectly with hexaniobate NScs via the reductive quencher TMA (Figure 5.14).\(^9\)

Subsequent studies by Maeda at al. utilized a covalent linkage between the semiconductor and chromophore via phosphonic acid groups on the chromophore’s bipyridyl
ligands. The significant increase in H₂ production by the covalently-bonded Ru(bpy)₂(4,4′- (PO₃H₂)₂bpy)²⁺ was attributed to the increased efficiency of electron transfer enabled by the covalent linkage. Multiple studies have subsequently demonstrated that one of the most important requirements for efficient H₂ production by dye-sensitized semiconductors is strong adsorption of chromophore molecules onto the surface of the semiconductor.

5.5 Conclusions

The data from current results suggests that Pt@HNB NPPs are a viable system for visible light photolysis. Pt@HNB NPPs reproducibly generated H₂ from visible light photolysis under a variety of conditions, with the highest yields comparable to those seen from similar systems in literature. Optimization of experimental parameters is still continuing, and future results are expected to surpass current yields. The isolated reduction environment, large available surface area for chromophore adsorption, and flexibility for functionalization with oxidative catalysts are important and unique features of this system.

Future work could involve continuing to optimize reaction parameters for H₂ production. In particular, studies involving pre-adsorbed Ru(dcbpy) complexes with no reductive quencher in solution are expected to produce high H₂ yields. One further area of interest is the possibility of functionalizing the outer NPP surface with an oxidative catalyst or non-sacrificial electron donor in order to pursue a unified system for overall water splitting. Amine groups present on the NPPs may be suitable for replacing the sacrificial electron donor. A system that utilized amines or photodeposited iridium oxide NPs for the oxidation half-reaction and Pt NPs for the reduction half-reaction would be an exciting step in developing functional nanoscale structures for overall water splitting.
5.6 References


Chapter 6
Conclusions

This dissertation contains details on the research leading up to the production of hydrogen under visible light irradiation by sensitized platinum@hexaniobate nanopeapods. This work was based on previous syntheses by our group of hexaniobate nanopeapods containing catalytic nanoparticles. Au@HNB and Ag@HNB NPPs were produced by solvothermal, solvent encapsulation, or in-situ growth, and displayed optical properties that suggested their potential applications for photocatalysis. The synthesis of NPPs containing a highly active reduction catalyst had not been conducted, so the first parts of this study address the synthesis and characterization of both the catalyst and semiconductor components of Pt@HNB NPPs.

Typical synthesis methods for producing highly crystalline, dispersible Pt NPs presented challenges in the form of reproducibility and accessibility. High-temperature organic phase and solvothermal synthesis methods, conducted under a wide range of experimental parameters and utilizing various reducing and shape control agents, did not produce Pt NPs that could be easily encapsulated within scrolled hexaniobate sheets. Platinum precursors are extremely dependent on having homogeneous energy and precursor dispersion throughout the reaction solution. Microwave heating proved to be useful for providing that environment with a high degree of control over reaction rate and real-time monitoring of equilibrium temperature. Microwave-transparent reaction vessels were able to sustain thorough energy distributions and promoted homogeneous nucleation and growth of NPs throughout the reaction mixture. Because it is not necessary to externally induce nucleation when using microwave heating methods, the dangerous reagent Fe(CO)₅ was eliminated from the procedure, creating a more facile strategy with fewer
health and environmental risks. The microwave synthesis method utilizes only common and readily available reaction species to accompany the Pt precursor. This method can promote larger-scale production of high quality Pt NPs for photocatalytic applications.

The highly crystalline Pt NPs produced by the microwave method displayed interesting optical properties, including the production of a localized surface plasmon resonance with a distinct and intense peak at 213 nm. Previously reported optical studies utilized polycrystalline nanospheres that were typically produced by the citrate reduction method, and were associated with a lack of LSPR response at the predicted wavelength of 215 nm. It was discovered that the citrate method and the morphology of these NPs were likely suppressing LSPR production when commercially obtained 3.4-nm Pt nanospheres underwent a procedure to replace their citrate capping ligands with oleylamine, which is present on the MW-synthesized Pt NPs. While the as-obtained commercial nanospheres did not show any absorbance features across the UV and visible spectrum, the ligand-exchanged amine-capped nanospheres produced a distinct absorbance peak at 207 nm. The blue shift of this peak with respect to the predicted value is most likely due to the smaller size of the NPs, as the calculations that predicted an LSPR at 215 nm utilized spherical 10-nm Pt NPs.

The efficient and readily reproducible MW synthesis method provided large quantities of Pt NPs to target the formation of the new nanocomposite platinum@hexaniobate nanopeapods. It was discovered that solvothermal and solvent evaporation methods, which had been repeatedly used by our group to synthesize high-quality NPPs containing a wide variety of NPs, were not able to produce Pt@HNB NPPs with high NP loading or consistent morphology. However, we were again able to utilize MW heating to produce high-quality inorganic nanomaterials in the form of tightly scrolled, morphologically uniform, highly loaded Pt@HNB NPPs. This facile
and readily reproducible method produces much higher yields (200 mg vs. 10-20 mg per synthesis) compared to solvothermal and solvent evaporation methods.

Pt@HNB NPPs were developed with a specific purpose in mind: photocatalytic water splitting to generate H₂ under visible light irradiation. The unique nanopeapod architecture offers an isolated reduction environment that was successfully utilized to produce quantities of H₂ that are comparable to reported methods. Preliminary trials on optimizing the preparation and environment for photolysis via Pt@HNB NPPs have established that surface treatment and coordination to the chromophore are very important in determining H₂ output. The hydrophobic amine groups that are present on the surface of as-synthesized Pt @HNB NPPs needed to be removed so that the NPPs could interact with the chromophore and with water. Short term (1 h) UV irradiation was found to be the superior method for surface modification, as solution-based methods dealt serious morphological damage to the NPPs. Initial photolysis trials demonstrated that dispersibility is crucial, and that slightly altering the surface properties of the NPPs or the species and quantities of photolysis reagents can greatly increase or hinder H₂ production.

Based on current photolysis results, it is anticipated that an optimized method will produce significant quantities of H₂. Pre-adsorption of a carboxy-functionalized Ru(II) bipyridine chromophore to the surface of UV-treated Pt@HNB NPPs is predicted to be an optimal configuration, and it is reasonable to predict that it will be able to exceed (perhaps significantly) previously reported hydrogen generation results due to its isolated reduction environment and high surface area for chromophore loading. It is also possible that the Pt@HNB NPPs’ unique architecture for overall water splitting by utilizing the free surface space to adsorb an oxidative catalyst.
Vita

Clare Davis-Wheeler Chin was born in San Francisco, California to Dr. David L. Wheeler and Rev. Betty J. Davis. She spent her childhood in Overland Park/Kansas City, KS with her younger brother Micah, her parents, and her step-parents, Bruce Lacoss and Carol Wheeler. She obtained a Bachelor of Arts with a double major in Environmental Studies and English from Tulane University in New Orleans, Louisiana in 2003. After receiving her teaching certification through the Teach Greater New Orleans program at the University of New Orleans, she taught science at Medard H. Nelson UNO Charter Middle School from 2005-2006. In the fall of 2006, she joined the faculty of Benjamin Franklin High School in New Orleans to start their AP Environmental Science program. In 2013, she was awarded the Louisiana Board of Regents Graduate Fellowship to study Chemistry at the University of New Orleans. She was accepted by the Wiley Research Group in spring 2014 to study nanopeapods for photocatalytic applications. In 2017, she married James Frederick Chin. That same year, she served in a Collaborative Appointment at the National Renewable Energy Laboratory in Golden, Colorado. She is glad that her doctoral studies confirmed that it is indeed a good idea to put metal in the microwave.