Synthesis and characterization of core-shell nanomaterials for solar production of hydrogen fuel

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Synthesis and Characterization of Core-Shell Nanomaterials for Solar Production of Hydrogen Fuel

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THESIS

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ABSTRACT OF THESIS

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Abstract

Hydrogen fuel, derived from clean solar energy, easily stored, and free of greenhouse gas emissions, is one part of a multipronged approach to address future global energy shortages. The purpose of this thesis is to investigate metal core/semiconductor shell nanoparticles that can be illuminated with solar light to produce hydrogen fuel by splitting (reducing and oxidizing) water. Metal nanoparticles corrode in water, so a chemically stable shell needs to be placed over metal nanoparticle cores. Nanoscale semiconductors, which are chemically stable in water, have several advantages over bulk semiconductors. First, their bandgaps can be manipulated depending on their size and shape, which is not possible with bulk semiconductors. Secondly, whereas ‘hot’ electrons excited above the bottom edge of the conduction band in bulk semiconductors relax within picoseconds, nanoscale semiconductors have been shown to
exhibit slow electron, cooling which allows time for excited electrons to interact with and split water, producing hydrogen.

Upon illumination with visible light, electrons on the surface of metal nanoparticles exhibit high energy localized surface plasmon resonance (LSPR), increasing the local electric field $10^{14}$-$10^{15}$ times. These hot electrons can tunnel to the shell surface to reduce water and produce $\text{H}_2$. Wide-bandgap semiconductor shells absorb ultraviolet light, and the holes produced upon excitation serve to oxidize water. In this way, metal core/semiconductor shell nanoparticles, along with visible and ultraviolet radiation, can be used to split water and produce hydrogen.

In this work, various nanomaterials were synthesized, including silver core nanoparticles, mixtures of silver and titanium dioxide nanoparticles, Ag/TiO$_2$ core-shell nanoparticles with spherical, onion-like structures, and Ag/TiO$_2$ core-shell nanowires with bristled surfaces. Absorption measurements were made to determine the silver cores’ LSPR energies. Differential pulse voltammetry experiments were performed to determine both semiconductor bandgaps as well as conduction and valence band edges relative to the normal hydrogen electrode (NHE). In order for hydrogen to be produced, the reduction (-0.41 eV vs. NHE) and oxidation (0.82 eV vs. NHE) potentials of water must lie inside the conduction and valence band edges of the semiconductor shell. With differential pulse voltammetry experiments, synthesized nanomaterials were all shown to fulfill that requirement. The optical and electrochemical experiments performed show that the synthesized silver core/metal shell nanomaterials are viable candidates for hydrogen production upon solar illumination.
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Chapter 1

Hydrogen Fuel

1.1 Energy Problems

It is well understood that current energy sources, including oil, coal, and natural gas, are not permanently sustainable. Of the 2,000 billion barrels of known global oil reserves, 875 billion barrels have already been consumed. Additionally, for every 1 billion barrels of oil discovered, we exhaust 4 billion barrels [Kamat 2007]. World energy consumption is projected to grow by 57% from 2002 to 2025. According to the International Energy Outlook 2005, emerging economies account for nearly 66% of the increase in global energy needs, and they will surpass the energy use of mature market economies for the first time in 2020. Growing energy demand in China and India alone is projected to more than double over the forecast period [Asif 2007]. Considering the rapid growth of India, China, and other emerging nations, global energy demands will only increase (see Figure 1.1).

In 2010, 85% of the world’s energy was derived from oil, coal, or natural gas, none of which are limitless in supply. 5% of global energy was from nuclear power plants, and the remaining 10% came from renewables [U.S. Energy Information Administration 2010]. As shown in Figure 1.2, using fossil fuels as our primary source of energy is not a sustainable strategy.
Figure 1.1: World energy consumption is projected to increase by 49% from 2007 to 2035. Total energy demand in emerging market economies, including China & India (non-Organization for Economic Cooperation and Development, or OECD, countries), is set to increase by 84%, compared with an increase of 14% in mature market economies (OECD countries) [U.S. Energy Information Administration 2010].
Figure 1.2: Projection of oil supply and demand through 2050 [Kamat 2007]. The historic trend of growth at 2% per year is not sustainable in the future.
Furthermore, fossil fuels account for 80 to 85% of today’s man-made contribution to greenhouse gases [U.S. Global Change Research Program 2010]. About 335 billion tons of carbon have been released into earth’s atmosphere by humans since 1750, aiding in global climate change. Remarkably, half of this amount has been emitted only since the mid-1970s with atmospheric CO$_2$ levels at 380 ppm as of 2009 [Arndt 2010]. 25% of emitted carbon dioxide is depleted from the atmosphere within 90 years, but 1/8 still remains after 330 years [Siegenthaler 1978]. The long lifetime of carbon dioxide emissions will prevent full recovery of the stratospheric ozone until the latter part of the 21st century [Arndt 2010]. To prevent further depletion of the ozone and mitigate global climate change, a carbon dioxide emission-free energy source must be employed.

Considering the sustainability and environmental concerns surrounding oil, coal, and natural gas, it is clear that alternative sources of energy must be utilized. Today, 13 TW of power is used globally. By the year 2050, that number is expected to increase to 23 TW [Kamat 2007]. Renewable energy can be harvested from wind, solar, ocean tide, and geothermal sources. 2 TW of power can be collected from ocean tides, 2-4 TW are available from wind, and 12 TW can be acquired from geothermal sources on earth. In comparison, 120,000 TW of power from the sun reaches earth [Kamat 2007]. Clearly, solar energy provides the most potential for meeting our future energy demands.

Some problems arise when using alternative energy sources. Biofuels, for ex-
ample, lead to competition with agricultural land for food, driving up food prices. Extraction of geothermal energy must be monitored to avoid local depletion. Sunlight and wind are intermittent energy sources. During winter or rainy months, parts of the world may be under cloud cover for weeks at a time. Wind energy is also sporadic and cannot be stored for days with low winds. Since energy available from solar and wind sources varies depending on the time of day, season, or weather, energy obtained from these sources during very sunny or windy days will need to be stored for use during times of low energy production. A method of storing energy from these fluctuating energy sources is needed.

In order to protect ourselves from future energy shortfalls, we need to utilize the most promising energy source, radiation falling on the earth from the sun, to produce an energy product that can be stored. Hydrogen that can be produced from solar energy and is available for storage is a prime candidate for this application. Furthermore, burning hydrogen fuels does not release any greenhouse gases and thus can serve to alleviate environmental concerns.

Typically, only one end of the production or consumption chain is clean. For example, hydrogen fuel emits no environmentally harmful byproducts when consumed, but its current method of production typically requires the burning of fossil fuels (see Section 1.3). On the other hand, algae are a clean source for biofuels, but these fuels emit harmful byproducts into the atmosphere upon consumption. In contrast, using solar energy to produce hydrogen fuel could lead to a hydrogen production method
that is environmentally friendly to both produce and consume.

1.2 Hydrogen Fuel Uses

Since hydrogen is an energy carrier, it has a wide variety of uses including transportation, heating, and power generation. 450 billion cubic meters of hydrogen is consumed yearly around the world, of which 20% is consumed by the United States [Busby 2005]. A large portion of hydrogen consumption is directed at refining crude oil [Busby 2005]. Hydrogen is also used for the industrial synthesis of ammonia (used mainly for fertilizer and in industry), methanol, and hydrochloric acid, as well as for the cooling of electrical generators. Margarine and other edible fats and oils are solidified using hydrogen. Additionally, hydrogen is used in producing soap, dyes, plastics, vitamins, cleaners, cosmetics, lubricants, and drugs. Fueling spaceships was one of the first uses for hydrogen as a fuel, and today NASA is one of the largest consumers of liquid hydrogen worldwide [Busby 2005]. Automobiles using hydrogen fuel have been produced by Ford, Kia, Honda, Mercedes, General Motors, Audi, BMW, Mazda, Toyota, Hyundai, Jeep, and Volkswagen. Hydrogen-powered ships, motorcycles, trucks, and submarines are also manufactured. Public buses running on hydrogen fuel are being used in Berkeley, California, and other environmentally conscious cities.

The motivation for using hydrogen to fuel these vehicles stems mainly from environmental concerns. Whereas hydrocarbon fossil fuels create harmful carbon
dioxide emissions when they are burned, hydrogen fuels release only water. In a simple hydrogen fuel cell, oxygen is combined with hydrogen, leaving pollutant-free water as the byproduct:

\[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} - \Delta G
\]  

(1.1)

where \( \Delta G = -237.8 \text{ kJ/mol} \) is the Gibbs free energy change, i.e. the energy produced from combining hydrogen with oxygen in a hydrogen fuel cell [Zhang 2008].

In comparison, the chemical reaction and Gibbs free energy energy available for the combustion of propane, the most abundant chemical in automobile gasoline, is:

\[
\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} - \Delta G
\]  

(1.2)

where \( \Delta G = -2073 \text{ kJ/mol} \) is the Gibbs free energy change [Jespersen 1997]. While the Gibbs free energy change for the combustion of propane may be larger than the Gibbs free energy change from combining hydrogen with oxygen, it is important to remember that fossil fuels are not sustainable and will become depleted in the future, and also release greenhouse gases when consumed.

1.3 Current Methods of Hydrogen Production

Today, steam reforming is the most commonly used method for producing hydrogen. In fact, around 95% of hydrogen produced in the United States is done so by steam reforming [Haryanto 2005]. Unfortunately, steam reforming involves the use
of hydrocarbons such as oil or natural gas, reacting them with steam at high temperatures. This process also releases carbon dioxide as a byproduct (see Equations 1.3 through 1.5, Figure 1.3), which is undesirable from an environmental perspective [Jensen 2008], [Schwank 2010].

\[
C_nH_m + n \text{H}_2\text{O} \rightarrow n \text{CO} + \left(n + \frac{1}{2}m\right)\text{H}_2 \quad (1.3)
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (1.4)
\]

\[
C_nH_m + 2n \text{H}_2\text{O} \rightarrow n \text{CO}_2 + \left(2n + \frac{1}{2}m\right)\text{H}_2 \quad (1.5)
\]

Other industrial methods of producing hydrogen include electrolysis of water and coal...
gasification, both of which use mainly fossil fuels as the energy source.

A hydrogen production method that does not use unsustainable fossil fuels is desired. Utilizing solar energy is recommended, since it is by far the most abundant source of renewable energy found on earth (see Section 1.1). Furthermore, the generation of carbon dioxide byproducts during the creation of hydrogen fuels should be avoided. It is clear that an alternative, sustainable, and efficient method of producing hydrogen fuel is needed.
Chapter 2

Nanoparticles as Photocatalysts for Hydrogen Production

2.1 Photocatalytic Water Splitting

Hydrogen may be formed by splitting water, in which case the following reactions must occur:

\[ 4 \text{H}_2\text{O} + 4 e^- \longrightarrow 4 \text{OH}^- + 2 \text{H}_2 \] \hspace{1cm} (2.1) \text{reduction of water}

\[ 4 \text{OH}^- + 4 h^+ \longrightarrow 2 \text{H}_2\text{O} + \text{O}_2 \] \hspace{1cm} (2.2) \text{oxidation of water}

In order to split water, an energy of 1.23 eV must be supplied [van de Krol 2008]. To produce hydrogen from water, an electron donor must provide four electrons (e\(^-\)) with this energy which interact with four water molecules. When this occurs, two molecules of H\(_2\) are produced with 4 OH\(^-\) as a byproduct. This step of the reaction is known as the reduction of water. In order for this reaction to continue over time, the electron donor must also accept electrons from OH\(^-\) in order to fill the hole states. The four holes (h\(^+\)) produced in the donor may interact with 4 OH\(^-\) to yield two molecules of water plus one molecule of oxygen. This half of the reaction is called oxidation. For solar water splitting, a material is needed that can both donate
Figure 2.1: Energy diagram for water splitting. Semiconductor conduction band (CB) must be above the water reduction potential, and the valence band (VB) must be below water’s oxidation potential [Elettra group 2009].

...
produce H₂. This requirement will be tested on synthesized materials in Chapter 6.

2.2 Optimal Nanomaterials for Water Splitting

While the bandgap ($E_g$) of a bulk semiconductor is fixed, the energy levels of nanoscale semiconductors can be engineered and the bandgap is increased compared to their bulk counterparts. In order to change the bandgap of a semiconductor nanoparticle, one may alter the size and shape of the material. Compared to the bandgap for a bulk semiconductor ($E_{g,\text{bulk}}$), the bandgap for a nanoparticle ($E_{g,NP}$) is given by [Gaponenko 1998]:

$$E_{g,NP} \approx E_{g,\text{bulk}} + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m^*_e} + \frac{1}{m^*_h} \right)$$

(2.3)

where $m^*_e$ and $m^*_h$ are the effective masses of the electrons and holes, $R$ is the radius of the nanoparticle, and $\hbar$ is the reduced Planck constant. The second term in the equation is the kinetic energy of localized carriers in the nanoparticle and has a $R^{-2}$ dependence on size; the smaller the nanoparticle, the larger the bandgap.

In bulk semiconductors, hot electrons excited above the bottom edge of the conduction band relax within picoseconds, too quickly for the hot electron to interact with outside materials. However, nanoscale semiconductors have been shown to exhibit slow electron cooling (>1 ns) [Pandey 2008], which allows time for excited electrons to interact with and split water, producing hydrogen.

Titanium dioxide is the most widely investigated material for photocatalytic
water splitting due to its stability over a wide range of pH values and applied potentials, band alignment (see Figure 2.2), low cost, and lack of toxicity. However, the conduction band edge of bulk TiO$_2$ is not at sufficiently negative potential to generate hydrogen at a useful rate, and water splitting in TiO$_2$-based cells can only be accomplished by applying an additional electrical bias [Fujishima 1972]. The large bandgap (3.2 eV) of bulk titanium dioxide allows only a small UV fraction (2-3%) of the solar spectrum to be utilized. Figure 2.3 shows the portion of the solar spectrum that reaches earth’s surface. A small amount of UV light reaches the earth’s surface, but most of the radiation is in the visible and infrared. Much research is focused on attempts to shift the optical absorption of titanium dioxide towards the visible part of the spectrum via doping, with very limited success. The aim of this project is to synthesize materials that utilize the full solar spectrum for water splitting.

Since titanium dioxide is the favored semiconductor material in photocatalytic water splitting research, TiO$_2$ nanoparticles will be studied in this project. To extend the absorption range, metal nanoparticles will be utilized. Metal nanoparticles are known to absorb in the visible and infrared portions of the solar spectrum, depending on their size, shape, and elemental composition. Electrons excited in metal nanoparticles are known to exhibit a phenomenon known as localized surface plasmon resonance (LSPR, see Section 5.2). An incident wave striking a metal nanoparticle will produce a resonant response of the localized surface plasmons (surface conduction electrons), resulting in large electric field enhancements inside and even locally
Figure 2.2: Energy bands for various semiconductors at pH 14 versus reduction and oxidation potentials of water [van de Krol 2008]. Notice the conduction and valence bands of TiO$_2$ lie outside the reduction and oxidation potentials of water, making it a viable candidate for water splitting.
Figure 2.3: The portion of the solar spectrum reaching earth’s surface. The voids are due to absorption in earth’s atmosphere [Lawrence Berkeley National Laboratory 2004].

Outside the nanoparticle [Le Ru 2009].

Upon excitation by visible or infrared light, free electrons on the metal nanoparticle’s surface result in strong surface electromagnetic waves. These surface plasmon energies are measured via absorption measurements described in Section 5.3 of this thesis. Noble metals such as gold, silver, palladium, and platinum may be used. However, gold nanoparticles have lower LSPR energies than silver nanoparticles. While palladium and platinum nanoparticles have larger LSPR energies than silver nanoparticles, their precursor chemicals are 16 times more expensive than silver precursors and therefore would be less cost-effective for industrial, large scale production of hydrogen. Silver nanoparticles were therefore chosen for this projet. Spherical silver
nanoparticles absorb in the visible portion of the solar spectrum, extending the absorption range compared to titanium dioxide nanoparticles, which only absorb UV light.

Metal nanomaterials are not stable in water and will corrode over time [Chuang 2009]. However, we can utilize the extended absorption range of metal nanoparticles due to localized surface plasmon resonance and allow them function for long-term use in water by coating them entirely with a water-stable titanium dioxide shell. This also allows us to take advantage of multiple parts of the solar spectrum; titanium dioxide will absorb ultraviolet light, while the metal core will absorb light from the visible portion of the electromagnetic spectrum. Additionally, Ag/TiO$_2$ core-shell nanoparticles have been shown to exhibit significantly higher photocatalytic activity than TiO$_2$ nanoparticles under illumination with visible light [Chuang 2009].

Reduction of water, governed by Equation 2.1, requires excited electrons for hydrogen production. In our case, these energetic electrons will come from the excitation at visible wavelengths of electrons from the metal core into the conduction band of the titanium dioxide shell. Electron transfer from metal core to semiconductor shell in nanomaterials has been demonstrated in [Furube 2007] and [Du 2009]. These hot electrons with more energy than the lower level of the conduction band in TiO$_2$ are free to interact with surrounding material, such as water in this case. Thus, hot electrons from LSPR excitation of the metal core will provide the energy needed to efficiently reduce water. [Pandey 2010] finds that hot electrons produced
Figure 2.4: Metal core/semiconductor shell nanoparticle reduction of water upon solar illumination [Smolyakov 2009]. (a) shows a metal core surrounded by a semiconductor photocatalyst shell, with reduction and oxidation of water occurring at the surface. In (b), an energy diagram of metal core/semiconductor shell nanoparticles and the reduction and oxidation levels of water are shown, along with the method by which water splitting occurs. The reduction level of water is -0.41 eV vs. NHE while the oxidation level of water is +0.82 eV vs. NHE at pH = 7 [Crabtree 2010]. (NHE = Normal Hydrogen Electrode, see Section 6.1)
in the core of a nanoparticle can indeed tunnel through and be extracted from a semiconductor shell, while [Tisdale 2010] shows that hot electrons in semiconductor nanocrystals can interact with and in fact be donated to an electron acceptor outside the nanoparticle.

The second half of the reaction, oxidation, follows Equation 2.2. In our case, the holes will form upon ultraviolet excitation of the titanium dioxide shell. As seen in Figure 2.2, these holes in the valence band of titanium dioxide will be at sufficiently low potentials to accept electrons and oxidize water. The entire scheme is illustrated in Figure 2.4 and is expected to occur via the following reactions:

\begin{align}
\text{Metal core absorbs visible light to produce excited electrons } e^{-*} \text{ and holes } h^{++} & \quad (2.4a) \\
4 \text{ H}_2\text{O} + 4 e^{-*} & \longrightarrow 4 \text{ OH}^- + 2 \text{ H}_2 & \quad (2.4b) \\
\text{Semiconductor shell absorbs UV light to produce electron-hole pair} & \quad (2.4c) \\
4 \text{ OH}^- + 4 h^+ & \longrightarrow 2 \text{ H}_2\text{O} + \text{O}_2 & \quad (2.4d) \\
4 e^- + 4 h^{++} & \longrightarrow \text{ heat from recombination in metal core} & \quad (2.4e) \\
2 \text{ H}_2\text{O} + 4 h\nu_{vis} + 4 h\nu_{uv} & \longrightarrow 2 \text{ H}_2 + \text{O}_2 & \quad (2.4f)
\end{align}

2.4a describes the absorption of visible light by the metal core to produce hot electron-hole pairs, with the hot electrons traveling to the surface of the semiconductor shell [Furube 2007], [Du 2009]. Recall that these hot electrons in semiconductor nanoparticles have been shown to interact with and be donated to electron acceptors outside
the nanoparticle [Tisdale 2010]. In Equation 2.4b, these hot electrons will interact with water at the surface of the semiconductor shell to reduce water and produce the desired \( \text{H}_2 \). Meanwhile, the semiconductor shell will absorb ultraviolet light, creating electron-hole pairs in the shell as described in 2.4c. These holes will oxidize water on the surface of the shell per Equation 2.4d. The excited electron from the ultraviolet excitation of the semiconductor shell and the hole in the metal core from visible light absorption will combine and let off heat in Equation 2.4e. Equation 2.4f describes this overall reaction.

Synthesis and structural characterization of metal core/semiconductor shell nanoparticles is discussed in Chapter 3. Chapter 4 discusses the measurements of the synthesized nanoparticles’ hydrodynamic sizes. To demonstrate the viability of metal core/semiconductor shell nanoparticles as photocatalysts for water splitting, Chapter 5 introduces absorption data used to determine LSPR energies and bandgap energies of synthesized nanoparticles. The measurements of bandgaps, conduction band edges, and valence band edges of the nanomaterials are discussed in Chapter 6. The results show that the band edges of TiO\(_2\) lie outside the reduction and oxidation potentials of water, making the nanoparticles viable candidates for water splitting. These metal core/semiconductor shell composite nanomaterials allow us to take advantage of the visible and ultraviolet portions of the solar spectrum, as well as use the LSPR phenomenon from the metal core to provide sufficiently energetic electrons for reduction of water. Meanwhile, the core is protected from degradation in water.
by the semiconductor shell, which also provides the holes necessary for oxidation of water.

Optimization of nanoparticles includes finding the balance between creating a thinner outer shell, which would make it easier for excited electrons to travel to the surface and interact with the surrounding water, and making the shell thick enough so that the metal core is thoroughly coated and protected. Bandgaps and LSPR energies can be fine-tuned by altering nanoparticle size and shape. Upon reduction and oxidation of water, H₂ and O₂ will want to combine. Doping of the semiconductor shell with co-catalysts such as RuO₂ could help to physically separate H₂ and O₂. Materials with high surface area are desired in order to maximize the amount of surface excited electrons in contact with surrounding water.
Chapter 3

Nanoparticle Synthesis for Solar Hydrogen Production

3.1 Nanoparticle Synthesis Basics

Nanoparticles are composed of 100 - 1,000 atoms and can take on varying morphologies, including spheres, stars, rods, wires, and cubes. Whereas bulk semiconductors have fixed bandgaps, the size and shape of nanomaterials can be engineered so as to measurably change the bandgap energy. Metal nanoparticles also produce surface plasmons, whose energies can be fine tuned by altering nanoparticle shape and size. Nanoparticles can be synthesized by a variety of mechanisms, including those depicted in Figure 3.1 [Cozzoli 2006]:

- *Growth in templates*, in which electrochemical deposition of desired chemicals in a porous membrane produces nanomaterials

- *Growth promoted by a catalyst*, whereby a solid, rod-like nanocrystal grows out of a catalyst particle

- *Oriented attachment mechanism*, where nanoparticles are first synthesized in solution and then fused along particular crystallographic orientations leading to wires and rods
Figure 3.1: Various approaches to growing nanomaterials [Cozzoli 2006].
• *Growth by selective adhesion*, when precursors elongate along some preferred crystallographic directions into highly anisotropic shapes

• *Growth in the presence of external fields*, whereby electric or magnetic fields promote nanoparticle growth

• *Seeded growth*, in which small spherical nanocrystal seeds (typically metals) are grown into rods and wires upon mixing with precursors and reductants

Core-shell nanomaterials in this study were prepared via the solution chemistry method, whereby precursors are combined in a solvent and heated to produce often spherical nanoparticles. Variables such as heating time, concentration, and temperature can be manipulated to alter resulting nanoparticle size and shape. Precursors in solvent were injected into a glass flask, stirred, heated, and allowed to react. The resulting nanomaterials were then purified by centrifugation, so that the nanoparticles were precipitated upon separation from residual precursors and dispersed in an appropriate solvent. Figure 3.2 shows a simple synthesis setup. a) is a three-neck glass flask, in which the precursors in solution are injected, stirred, and heated. If necessary, condensers to prevent solvent evaporation or gas lines to flow argon or nitrogen to keep the reaction under an inert environment can be connected to the flask. b) is the heating mantle, which applies heat to the flask and is powered by the temperature controller c), which in turn determines temperature from the thermocouple d). e) is the magnetic stir plate which, combined with a magnetic stir bar in the flask, mixes the solution.
Figure 3.2: Typical nanoparticle synthesis setup: a) three-neck glass flask, b) heating mantle, c) temperature controller, d) thermocouple, e) magnetic stir plate. See text for further explanation.
Several different metal core/semiconductor shell syntheses were attempted. By engineering nanoparticles with various metal core/semiconductor shell geometries and sizes, characteristics such as LSPR (discussed in Section 5.2), bandgap, and conduction and valence band energy levels will change. In this way, nanomaterials can be engineered to split water, with the semiconductor conduction and valence bands lying outside the reduction and oxidation levels of water.

Synthesized nanoparticles were characterized by transmission electron microscopy (TEM) imaging. Energy-dispersive x-ray spectroscopy (EDS) using the TEM electron beam and Oxford Instruments ISIS software was used to verify elemental composition of the sample.
3.2 Synthesis of Silver Core Nanoparticles

Before core-shell structures could be formed, silver core nanoparticles were produced via a method introduced in [Dadosh 2009]. To synthesize silver nanoparticles, 0.0399 g of sodium citrate (HOC(COONa)(CH₂COONa)₂ · 2 H₂O, Sigma-Aldrich, meets United States Pharmacopeia testing specifications) and 0.0008 g of tannic acid (C₇₆H₅₂O₄₆, Sigma-Aldrich, ACS reagent grade) were added to 20 mL of deionized water. A second solution was made of 0.0101 g of silver nitrate (AgNO₃, Sigma-Aldrich 99+%) and 80 mL of deionized water, resulting in a 0.74 mM aqueous solution. The sodium citrate reduces silver ions in silver nitrate to form neutral silver atoms, which agglomerate to form silver nanoparticles. The tannic acid serves to control the particle size; increasing the tannic acid concentration results in increased nanoparticle
Both solutions were stirred and heated to 60 °C, then combined and allowed to react for 3 minutes. Once the mixture turned yellow, it was brought to a boil at 95 °C for 20 minutes, resulting in silver nanoparticles, as confirmed by elemental analysis in Figure 3.3. It should be noted that the presence of copper and carbon in all EDS spectra arises from the grid on which nanoparticles were placed for imaging. Iron lines are due to vacuum chamber signal. Figure 3.4 shows TEM images of silver nanoparticles. The rightmost TEM image shows a nanoparticle of pentagonal symmetry, which has been observed previously and explained by lattice defect formation in fcc crystals [Dorogin 2010].

3.3 Synthesis of Ag and TiO$_2$ Nanoparticle Mixture

In the first attempt to produce Ag/TiO$_2$ core-shell nanoparticles, a procedure was developed based on a one-pot method presented in [Tom 2003]. Two solutions were prepared, one containing 8.8 mM of silver nitrate (AgNO$_3$, Sigma-Aldrich 99+%) and 13.88 M of deionized water in 15 mL of dimethylformamide (DMF, HCON(CH$_3$)$_2$, Sigma ≥99%), and the other composed of 19.9 mM of titanium(IV) isopropoxide (TIP, Ti[OCH(CH$_3$)$_2$]$_4$, Sigma-Aldrich 99.999%) and 19.9 mM of acetylacetone (CH$_3$COCH$_2$COCH$_3$, Sigma-Aldrich ≥99%) in 40 mL of 2-propanol ((CH$_3$)$_2$CHOH, EMD Chemicals ≥99.5%). The titanium(IV) isopropoxide/acetylacetone/2-propanol and silver nitrate/H$_2$O/DMF solutions were then added together in a 2:1
volumetric ratio and refluxed for 45 minutes while stirring. Once a precipitate was observed, the mixture was cooled to room temperature. The solution was then purified by centrifugation with toluene (C₆H₅CH₃, Burdick & Jackson 99.8%) for 10 minutes at 4,000 rpm two times, with the impurities dissolved in toluene and removed after each centrifugation. The remaining nanoparticles were redispersed in 2-propanol.

DMF serves to reduce the silver ions from silver nitrate, so that silver nanoparticles may form, by the following reaction:

\[
\text{HCONMe}_2 + 2 \text{Ag}^+ + \text{H}_2\text{O} \rightarrow 2 \text{Ag}^0 + \text{Me}_2\text{NCOOH} + 2 \text{H}^+ \quad (3.1)
\]

The titanium dioxide is formed by hydrolysis of the metal oxide precursor:

\[
\text{Ti[OCH(CH}_3\text{)\text{2}]}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4(\text{CH}_3\text{)}_2\text{CHOH} \quad (3.2)
\]

Two different syntheses using variations of the above method were used, altering the order in which the silver and titanium precursors were added together. In the first synthesis, the silver nitrate solution was added dropwise to the TIP solution. TEM images can be seen in Figure 3.5. From the images it is clear that surfactants, likely the viscous acetylacetone, could not be removed from the sample by centrifugation. Individual silver and titanium dioxide nanoparticles can be seen, with the denser silver nanoparticles appearing as larger, darker spheres and the titanium dioxide nanoparticles appearing as smaller, lighter spheres. EDS analysis confirms the presence of silver, titanium, and oxygen (see Figure 3.6). The same results were found when reversing the order in which the precursors were added together; adding
Figure 3.5: TEM images of Ag and TiO$_2$ nanoparticle mixture.
the TIP solution dropwise to the silver nitrate solution yielded similar TEM images and EDS spectra.

3.4 Synthesis of Ag/TiO$_2$ Core-Shell Spherical Nanoparticles

In the second variation of the Tom method, the TIP and silver nitrate solutions were combined dropwise simultaneously. The results are shown in Figures 3.7 and 3.8. This time, core-shell spherical nanoparticles were formed. As in other publications with core-shell spherical nanoparticles [Pastoriza-Santos 2000], [Tom 2003], [Kwon 2007], [Chuang 2009], uniform coating of all core silver nanoparticles with titanium dioxide shells has not been achieved. In fact, images of one or a couple successfully coated nanoparticles are common in literature. TEM images in Figure 3.7 show several silver cores with titanium dioxide shells, along with many uncoated silver nanoparticles.
Figure 3.7: TEM images of Ag core/TiO$_2$ shell spherical nanoparticles.
3.5 Synthesis of Ag/TiO$_2$ Core-Shell Nanowires

As seen in the previous section, silver core nanoparticles could not be uniformly coated with a spherical titanium dioxide shell; some silver nanoparticles were left uncoated which will leave them vulnerable to degradation in water. A more thorough coating of silver by a semiconductor shell was desired, so core-shell nanowires were assembled. Furthermore, a bristled semiconductor surface was created, increasing the surface area as compared to spherical core-shell nanoparticles; the more surface area available for water to interact with, the more efficient hydrogen production will be. To produce more surface area and maintain the core-shell structure vital to this project, silver core/titanium dioxide shell bristled nanowires were synthesized.

In a method adapted from [Du 2006], 0.5 mmol of tetrabutyl titanate (Ti[O(CH$_2$)$_3$CH$_3$]$_4$, Sigma-Aldrich 97%) was added to a solution of 0.5 mmol of silver nitrate (AgNO$_3$, Sigma-Aldrich 99+%) and 6 mL of ethylene glycol (HOCH$_2$CH$_2$OH, Sigma-Aldrich 32...
≥99%). This solution was loaded into a Parr bomb shown in Figure 3.9 and kept closed at 240 °C for 14 hours, then cooled to room temperature. To purify the sample, ethanol (CH₃CH₂OH, Koptec 200 proof) was added to dissolve unwanted synthesis byproducts and the mixture was centrifuged for 5 minutes at 4,000 rpm two times. When ethylene glycol was heated, water plus acetaldehyde were formed:

\[
\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \quad (3.3)
\]

The water then interacted with tetrabutyl titanate to form the titanium dioxide shells:

\[
\text{Ti}[[\text{O(CH}_2)_3\text{CH}_3]_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{CH}_3(\text{CH}_2)_3\text{OH} \quad (3.4)
\]

while water and acetaldehyde helped form the silver cores:
The resulting nanowires with silver cores and titanium dioxide bristled shells can be seen in Figure 3.10. The presence of silver, titanium, and oxygen was confirmed in the EDS spectrum shown in Figure 3.11. Since silver is more dense than titanium dioxide, the silver appears darker on the TEM images than the less dense titanium dioxide. It is therefore clear that a titanium dioxide shell was formed around the metal silver core.

\[ \text{CH}_3\text{CHO} + \text{AgNO}_3 + \text{H}_2\text{O} \rightarrow \text{Ag} + \text{HNO}_3 + \text{CH}_3\text{COOH} \quad (3.5) \]
Figure 3.11: EDS spectrum of Ag core/TiO₂ shell bristled nanowires.
Chapter 4

Dynamic Light Scattering Measurements

4.1 Determination of Hydrodynamic Size

Dynamic light scattering (DLS) is effective at measuring the hydrodynamic size of particles if their diameter is smaller than the wavelength of incident light, such as for core-shell nanoparticles synthesized in this thesis. The DLS software calculates the nanoparticle radius through measurements of scattered light intensity changes between small times \( t \) and \( t + \tau \). For DLS measurements to determine nanoparticle size, polarized light is incident upon the nanoparticles in solution and the scattered light of a specific polarization is analyzed. The intensity of the scattered light is time-dependent and this time-correlated intensity is what the DLS system measures. The intensities \( I \) of light measured at times \( t \) and \( t + \tau \), where \( \tau \) is small, are correlated. A measure of this similarity between the two measurements of light intensity at close times \( t \) and \( t + \tau \) is the autocorrelation function given by [Berne 2000]:

\[
\langle I(0)I(\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T I(t)I(t + \tau)dt
\]  

(4.1)

Through analysis of this autocorrelation function, particle size can be determined. First, consider the second order correlation function:
\[ g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} \]  

(4.2)

For a monodisperse sample, the correlation function can be represented by [Wyatt Technology 2011]:

\[ g^{(2)}(\tau) = B + \beta e^{-2\Gamma \tau} \]  

(4.3)

where \( B \) is the baseline of the correlation function at infinite delay, \( \beta \) is the correlation function amplitude at zero delay \((\tau = 0)\), and \( \Gamma \) is the decay rate. The ASTRA V software used in this experiment uses a nonlinear least squares fitting algorithm to fit the measured correlation function to Equation 4.3 to retrieve \( \Gamma \). The decay rate can then be converted to the diffusion constant for the particle \( D \) by the relation:

\[ D = \frac{\Gamma}{q^2} \]  

(4.4)

where \( q \) is the magnitude of the scattering vector given by:

\[ q = \frac{4\pi n_0}{\lambda_0} \sin \left( \frac{\Theta}{2} \right) \]  

(4.5)

with \( n_0 \) being the index of refraction of the solvent containing the nanoparticles, \( \lambda_0 \) being the wavelength of incident light, and \( \Theta \) being the scattering angle between the incident light and detector [Wyatt Technology 2011]. Finally, to determine nanoparticle size, \( D \) can be related to the hydrodynamic radius \( r_h \) of a diffusing sphere by the Stokes-Einstein equation [Wyatt Technology 2011]:
$r_h = \frac{kT}{6\pi \eta D}$  \hspace{1cm} (4.6)

where $k$ is Boltzmann’s constant, $T$ is the temperature in K, and $\eta$ is the solvent viscosity. In this way, the hydrodynamic radius is calculated by the DLS software through measurements of intensity changes between small times $t$ and $t + \tau$.

4.2 Dynamic Light Scattering Data

When possible, dynamic light scattering (DLS) measurements, taken with Wyatt Technology’s DynaPro DLS, were used to determine hydrodynamic size for nanoparticles with approximately spherical geometries. The DLS setup is shown in Figure 4.1: Dynamic light scattering setup. The laser is incident through the sample cuvette at point a) and exits at b) to be analyzed.
4.1.

Since the silver nanoparticles are roughly spherical, DLS could be used to measure their size. As shown in Figure 4.2, typical hydrodynamic size of silver nanoparticles is between 10 and 20 nm, which agrees with TEM images (Figure 3.4).

DLS measurements of Ag/TiO$_2$ core-shell spherical nanoparticles were taken. As shown in Figure 4.3, particles were measured to be roughly 30 nm in diameter, with a large spread in values. This is in agreement with sizes seen in TEM images, and the wide spread in particle size can also be confirmed from Figure 3.7.
Figure 4.3: DLS data for Ag core/TiO$_2$ shell spherical nanoparticles. Average particle size is 30 nm in diameter, with large spread.
Due to their non-spherical geometry, DLS could not be used to determine the size of core-shell nanowires or the silver and titanium dioxide mixture surrounded by residual surfactant. However, such information can be determined from TEM images. Figure 3.10 shows core-shell nanowires hundreds of nanometers long and roughly 100 nm in diameter.
Chapter 5

Optical Measurements

5.1 Determination of Semiconductor Nanoparticle Bandgap

A spectrophotometer was used to detect the bandgap of semiconductor nanoparticle shells. Information about absorption coefficient versus the wavelength of incident light for our nanoparticles was collected. Planck’s equation can be used to provide a rough estimate of the bandgap energy $E_g$ by relating it to the wavelength $\lambda_{\text{max}}$ at which the absorption has a maximum:

$$E_g = h \nu$$  \hspace{1cm} (5.1)

where $h$ is Planck’s constant, and $\nu = c/\lambda_{\text{max}}$. Using the proper unit conversions, the Planck equation can be rewritten in the following form, most useful for direct application:

$$E_g \text{ (eV)} = \frac{1240}{\lambda_{\text{max}} \text{ (nm)}}$$  \hspace{1cm} (5.2)

The absorption peak, and thus the bandgap of semiconductor nanoparticles, is highly dependent on the shape and size of the nanomaterial. A broad bandgap absorption peak shows a large distribution of nanoparticle sizes and/or shapes, whereas a narrow
absorption peak implies a monodisperse sample.

5.2 Determination of Localized Surface Plasmon Resonance (LSPR) Energies in Metal Nanoparticles

A spectrophotometer was also used to determine localized surface plasmon resonance (LSPR) energies of electrons near the surface of the metal nanoparticle cores. Upon excitation by radiation, the electric field causes free electrons on the metal nanoparticle’s surface to oscillate. The resultant electric field near a silver nanoparticle can be enhanced as much as $10^{14} - 10^{15}$ times [Bahadory 2008]. It should be noted that this response is not seen in bulk metals, but only in metal nanomaterials. The displacement of the surface electrons from the nucleus is counteracted by the Coulomb attractive force. This push-pull from the effects of the incident radiation and the Coulomb force on the surface electrons results in coherent electron oscillations on the surface, called the dipole plasmon resonance. Because nanoparticles are smaller than the wavelength of light, the electric field of light can be considered constant and the problem becomes quasi-electrostatic, since the dielectric constant of the materials is still dependent on the wavelength of incident light.

A spectrophotometer and its software gives information about the wavelength, or energy (by Equation 5.2), of the surface plasmons upon measuring the light transmitted by the sample. The Laplace equation:
\[ \nabla^2 \Phi = 0 \quad (5.3) \]

where \( \Phi \) is the electric potential connected to the electric field by \( \mathbf{E} = -\nabla \Phi \), solved with the boundary conditions that the electric potential is continuous at the nanoparticle surface and the normal portion of the electric displacement \( \mathbf{D} = \epsilon \mathbf{E} \) is also continuous, gives a description of the enhanced electric field outside of the nanoparticle [Kelly 2003]:

\[ \mathbf{E}_{\text{out}} = \mathbf{E}_0 \hat{x} - a \mathbf{E}_0 \left( \frac{\hat{x}}{r^3} - \frac{3{x}}{r^5}(x\hat{x} + y\hat{y} + z\hat{z}) \right) \quad (5.4) \]

where \( \mathbf{E}_{\text{out}} \) is the electric field outside the nanoparticle, \( \mathbf{E}_0 \) is the electric field of the incident light, \( r \) is the distance from the center of the spherical nanoparticle, and \( a \) is the polarizability of the nanoparticle. The incident electric field is enhanced by the second term in the above equation, which is the induced dipole field with induced dipole moment \( a \mathbf{E}_0 \). The polarizability of a metal nanoparticle can be related to its dielectric constant:

\[ a = b^3 \left( \frac{\epsilon_N - \epsilon_M}{\epsilon_N + 2\epsilon_M} \right) \quad (5.5) \]

where \( \epsilon_N \) is the dielectric constant of the nanoparticle, \( \epsilon_M \) is the dielectric constant of its surrounding medium, and \( b \) is the magnitude of the nanoparticle radius.

Finally, the wavelength \( \lambda \) (or energy) of the surface plasmons is given by its relation to the extinction and Rayleigh scattering efficiencies, \( Q_{\text{ext}} \) and \( Q_{\text{sc}} \), of the
nanoparticle [Kelly 2003]:

\[ Q_{\text{ext}} = 4x \Im \left( \frac{\epsilon_N - \epsilon_M}{\epsilon_N + 2\epsilon_M} \right) \]  
\[ Q_{\text{sc}} = \frac{8}{3} x^4 \left| \left( \frac{\epsilon_N - \epsilon_M}{\epsilon_N + 2\epsilon_M} \right) \right|^2 \]

where

\[ x = \frac{2\pi b \sqrt{\epsilon_M}}{\lambda} \]  

A similar calculation can be carried out for the quadrupole plasmon resonance. The wavelengths of the surface plasmons in Equation 5.7 are the absorption peaks found from the spectrophotometer. LSPR due to excitation of silver nanoparticles, for example, is centered around 410 nm (Figure 5.2). Using Equation 5.2, this corresponds to energy of 3.02 eV.

5.3 Absorption Data

To determine semiconductor bandgaps and LSPR energies from the metal cores, nanoparticles were characterized using ultraviolet-visible absorption measurements with Varian’s Cary 5000 UV-Vis-NIR spectrophotometer shown in Figure 5.1. Light is incident upon the nanoparticle solution through c) and the intensity of the transmitted light is measured at d). First, the absorption profile of the solvent in which the nanoparticles are dispersed is measured. The results of this measurement are then subtracted from the second measurement of absorption of nanoparticle in solvent, giving the absorption due to the nanoparticles only.
Figure 5.1: Varian’s Cary 5000 UV-Vis-NIR spectrophotometer. a) is the sample vial in which the nanoparticles in solvent to be studied are placed, while b) is a reference vial in which the solvent only is placed. Absorption from the solvent only will be subtracted from the absorption measured from the nanoparticles plus solvent, to arrive at the LSPR peak from the nanoparticles only. c) is where the laser beam enters the sample and the transmitted light is detected at d).
The blue absorption (LSPR) peak in Figure 5.2 is around 410 nm, as is expected for silver nanoparticles [Chuang 2009]. As discussed in the previous section, this corresponds to surface plasmon energies of 3.02 eV. The absorption peak is relatively narrow, implying a relatively monodisperse sample, as confirmed in Figures 3.4 and 4.2.

The green absorption curve for the silver and titanium dioxide nanoparticle mixture is shown in Figure 5.3. The bandgap absorption peak discussed in Section 4.1 is around 435 nm. Using Equation 5.2, the bandgap of the titanium dioxide shell is found to be approximately 2.85 eV, though the metal core is interfering with direct measurements of the semiconductor bandgap.
The Ag/TiO$_2$ core-shell spherical nanoparticles, produced by simultaneously injecting the silver precursor and the titanium precursor dropwise, yield the red absorption data in Figure 5.4, which shows an absorption peak around 440 nm. This peak is redshifted from the silver nanoparticle absorption peak of 410 nm (Figure 5.2), and confirms successful coating of silver cores with a titanium dioxide shell [Du 2006], [Chuang 2009]. This absorption peak corresponds to a bandgap of 2.82 eV, neglecting the certain interference of the metal cores in the measurement. The absorption peak is very broad, implying a large spread in nanoparticle sizes, as confirmed in Figures 3.7 and 4.3.

Analysis of the Ag/TiO$_2$ core-shell nanowires' purple absorption curve (Figure 5.5) shows a first peak at 310 nm, followed by a second peak near 560 nm attributed
Figure 5.4: Absorption of Ag/TiO$_2$ core-shell spherical nanoparticles.

Figure 5.5: Absorption of Ag/TiO$_2$ core-shell bristled nanowires.
to the transverse surface plasmon resonance from the silver nanowire core, with high absorption throughout the visible spectrum as reported by [Du 2006]. The two bands of plasmon absorption correspond to the oscillation of the free electrons along and perpendicular to the long axis of the rods. The first peak at 310 nm corresponds to a bandgap of 4.00 eV, while the second peak at 560 nm corresponds to a bandgap of 2.21 eV. Electrochemical methods in Chapter 6 will shed more light on which peak corresponds to the true bandgap of the core-shell nanowires.
Chapter 6

Electrochemical Measurements

6.1 Voltammetry Background

While optical absorption measurements provide information about the bandgap of semiconductor nanoparticles, electrochemical measurements can be used to confirm their bandgaps, as well as to detect the positions of their conduction and valence band edges to determine if the synthesized nanomaterials will be have the proper band alignment to split water. As discussed in Section 2.2 and demonstrated in Figure 2.4, if the conduction band edge of the titanium dioxide nanoparticle shell is higher (more negative) than the reduction potential of water at pH=7 (-0.41 eV vs. NHE, normal hydrogen electrode), then the semiconductor nanomaterial is suitable for water splitting. The valence band edge of the semiconductor must also be below (more positive than) the oxidation potential of water at pH=7 (+0.82 eV vs. NHE). Thus, the conduction and valence bands of the nanomaterials must lie outside the reduction and oxidation potentials of water in order to produce H₂. Additionally, even if the conduction bands of the nanomaterials are slightly below the reduction level of water, recall that ‘hot’ electrons excited to energies above the bottom edge of the conduction band could still interact with outside material [Pandey 2010], [Tisdale 2010] and reduce water.
Voltammetry is the branch of electrochemistry that can be used in analysis of nanoparticles. A potential that varies over time is applied to an electrode, while the resulting current flowing through the electrochemical cell containing the nanomaterials is measured. A typical electrochemistry experiment involves the material of interest in solution along with an electrochemical cell, working electrode, reference electrode, counter electrode (also referred to as the auxiliary electrode), potentiostat, and a computer for data acquisition and analysis (see Figures 6.1 and 6.2).

The electrochemical cell is a glass vessel that contains the nanomaterials in solution. The working electrode is the surface at which the reactions of interest and measurements occur. The reference electrode is a standard, to which all electrochemical measurements can be compared. One of the most common reference electrodes in electrochemistry is the normal hydrogen electrode (NHE). One can use any number
Figure 6.2: Illustration of a three-electrode cell [Bard 2001]. Note that the working electrode is in the center. In these experiments, the cell was not placed under vacuum but rather argon gas for deoxygenation.
of other reference electrodes, and the potentials measured can be converted to the standard NHE scale (see Figure 6.3). The NHE scale can then be converted to the vacuum level, often used in physics, by the following relation:

\[
V \text{ vs. NHE (V)} = \left( \frac{-4.5eV - E_{\text{vac}}}{e} \right)
\]

(6.1)

where the left hand side is the electrode potential vs. NHE, \( E_{\text{vac}} \) (eV) is the energy of electrons in vacuum, and \( e \) is the charge of an electron [Bae 2005]. However, all reduction and oxidation levels will be considered relative to NHE in the following experiments.

The third electrode in the electrochemical cell is the counter (auxiliary) electrode. An electrical current is allowed to flow through the counter electrode and it, along with the working electrode, provides a circuit through which current and the potential difference between the working and reference electrodes are measured. Finally, the potentiostat is the device which applies controlled voltage to the system as well as measures the current and voltage. The potentiostat is connected directly to the electrodes in the electrochemical cell, as well as to the computer where information about current and potential is sent to be analyzed.

At the working electrode surface, nanoparticles will be reduced or oxidized at the appropriate applied potential. As the potential at the electrode becomes negative, an electron can be injected into the conduction band of the nanoparticle at its reduction potential, producing a measurable current. Conversely, as the potential at
Figure 6.3: Potentials of various reference electrodes vs. NHE (normal hydrogen electrode) and SCE (saturated calomel electrode) [Bard 2001]. Experiments were performed using a saturated Ag/AgCl electrode, whose potential is shown to be 197 mV vs. NHE.
the electrode becomes positive, the nanoparticle can donate an electron to the electrode, leaving a hole in the valence band of the nanoparticle at its oxidation potential as in Figure 6.4, producing a measurable current [Bae 2005]. In this way, as the potentiostat alters the applied potential and the detected current is seen to increase at specific potentials, the conduction and valence bands of the nanoparticles can be identified.

The electrochemical voltammetry experiments performed are known as differential pulse voltammetry (DPV), in which the applied potential is scanned with a series of fixed, small amplitude pulses. The current is measured just prior to and just
after each pulse is applied [Settle 1997], and the difference between the two currents is plotted against the voltage applied. Differential pulse voltammetry is often used to obtain good signal over background [Bae 2005].

6.2 Differential Pulse Voltammetry Data

All differential pulse voltammetry data were taken with a Gamry Reference 600 potentiostat, Gamry’s electrochemical cell, a saturated Ag/AgCl reference electrode submerged in 0.1 molar tetrabutylammonium perchlorate solution (a conducting liquid of pH=7.3) in a bridge tube, a 3 mm diameter platinum disk working electrode, and a 150 mm platinum wire counter electrode. Data was analyzed with Gamry’s Echem Analyst software. Immediately before data acquisition, the nanoparticle solutions were deoxygenated with argon gas for a minimum of 15 minutes, and during the voltammetry experiments argon gas was allowed to flow over the surface of the solution, blanketing the cell. This ensured that oxygen did not contaminate the data, since oxygen can be reduced, interfering with electrochemical measurements. A typical DPV experimental setup is shown in Figure 6.5. Experimental parameters are shown in Figure 6.6. Pulse size of the applied potential was 25 mV and the step size was 2 mV. The sample period was 1 s and the pulse time was 0.1 s.

Potentials were measured against a saturated Ag/AgCl reference electrode. As can be seen in Figure 6.3, the conversion from a potential vs. Ag/AgCl to a potential vs. NHE (the standard scale in electrochemistry) is given by:
Figure 6.5: Voltammetry setup. a) is the electrochemical cell, containing the nanoparticle in solution and magnetic stir bar. b) is the potentiostat. c) is a septum containing a small platinum wire as the counter electrode. d) is the working 3mm platinum electrode and e) is a bridge tube containing the saturated Ag/AgCl reference electrode and a solution of 0.1 M tetrabutylammonium perchlorate as a conducting salt in the nanoparticle solvent. The argon gas flow hose is at f) and allows the entire experiment to be done oxygen-free. g) is a pierced septum top to allow pressure to escape, and h) is the magnetic stir plate which, along with the magnetic stir bar in the electrochemical cell, mixes the nanoparticle solution. The clips pictured connect the potentiostat to the electrodes, and one clip serves to ground the cell.
V vs. Ag/AgCl \( (V) + 0.197 = V \) vs. NHE \( (V) \) \hspace{1cm} (6.2)\\

For analysis of the silver and titanium dioxide nanoparticle mixture (images in Figure 3.5), 0.1 M tetrabutylammonium perchlorate (a conducting salt) was added to the nanoparticle solution. Differential pulse voltammograms are shown in Figure 6.7. The first scan was made from 0.0 V to 3.0 V vs. Ag/AgCl in search of the semiconductor nanoparticles’ valence band edge. An anodic, or oxidation, peak is seen at +2.36 V vs. Ag/AgCl, corresponding to the valence band edge of the nanoparticle. From Equation 6.2, this corresponds to a valence band at +2.56 V vs. NHE. The second scan was made from 0.0 V to -3.0 V in search of the conduction band edge of the semiconductor nanoparticles. A clear cathodic, or reduction, peak was found at...
-0.67 V vs. Ag/AgCl, corresponding to -0.47 V vs. NHE. The bandgap is therefore 3.03 eV, the difference between the conduction and valence band edge energies.

Figure 6.7: Differential pulse voltammogram of silver and titanium dioxide nanoparticle mixture, under fluorescent lighting (laboratory overhead lights on).

The silver and titanium dioxide nanoparticle mixture has a conduction band edge at -0.473 eV vs. NHE, more negative than the reduction potential of water at -0.41 eV vs. NHE (see Figure 2.4), as is necessary to donate electrons to reduce water.
The valence band edge at +2.56 eV vs. NHE is also more positive than the oxidation potential of water (+0.82 eV vs. NHE), and is therefore capable of accepting electrons to oxidize water. As is desired (see Figure 2.1), the reduction and oxidation potentials of water lie between the conduction and valence band edges of the nanoparticles.

To study the Ag/TiO$_2$ core-shell nanoparticles shown in Figure 3.7, 0.1 M tetrabutyl ammonium perchlorate was added to the nanoparticle solution and the potential was scanned from 0.0 V to 3.0 V vs. Ag/AgCl electrode in search of the valence band edge. As can be seen in Figure 6.8, a clear anodic peak was found at +2.08 V vs. Ag/AgCl, corresponding to +2.28 V vs. NHE from Equation 6.2. The scan in the negative potential direction from 0.0 V to -3.0 V vs. Ag/AgCl showed a clear cathodic peak at -0.66 V vs. Ag/AgCl (-0.46 V vs. NHE). The bandgap, or the energy gap between the conduction and valence bands, was found to be 2.74 eV. As with the previous nanomaterial, the core-shell nanoparticles’ conduction and valence bands edges lie outside the reduction and oxidation potentials of water, making them viable water splitting candidates.

Ag/TiO$_2$ core-shell bristled nanowires with 0.1 M tetrabutyl ammonium perchlorate salt were analyzed in differential pulse voltammograms seen in Figure 6.9. To search for the valence band edge of the nanoparticles, the potential was scanned from 0.0 V to 3.0 V vs. Ag/AgCl. A clear anodic peak is seen at +1.91 V vs. Ag/AgCl (+2.11 V vs. NHE). A reverse scan from 0.0 V to -0.8 V vs. Ag/AgCl shows the first cathodic peak at -0.68 V vs. Ag/AgCl (-0.48 V vs. NHE), corresponding to
the conduction band edge of the nanoparticles. The energy difference between the
conduction and valence band edges of the core-shell nanowires results in a bandgap
of 2.59 eV. Again, these nanoparticles are promising candidates for the production of
solar hydrogen as their conduction and valence band edges lie outside the reduction
and oxidation levels of water.

Further studies were done on the Ag/TiO$_2$ core-shell nanowires, since they were
the most thoroughly coated nanomaterials and therefore would be most likely to be
used for water splitting. The nanoparticles were tested both in the dark and under
illumination with a 115 W halogen lamp and a UV cutoff filter, which was passing
the light above the 397 nm wavelength. Differential pulse voltammetry was performed
by scanning in the positive potential direction. The results are shown in Figure 6.10.
Compared to the DPV experiment performed on nanowires in the dark (top), it is
clear the oxidation peak has shifted from 1.91 V to 2.04 V vs. Ag/AgCl, and there is
new activity in the bandgap between 0.2 V and 1.16 V vs. Ag/AgCl. This new activity
could be attributed to electrons excited from the metal core upon visible illumination,
or it could also be attributed to defect states. According to [Pacchioni 2008], these
may be due to oxygen defects (TiO$_{2-x}$) or titanium interstitials (Ti$_{1+x}$O$_2$).
Figure 6.8: Differential pulse voltammogram of Ag/TiO$_2$ core-shell nanoparticles, under fluorescent lighting (laboratory overhead lights on).
Figure 6.9: Differential pulse voltammogram of Ag/TiO₂ core-shell bristled nanowires, under fluorescent lighting (laboratory overhead lights on).
Figure 6.10: Differential pulse voltammetry of Ag/TiO$_2$ core-shell nanowires (top) in the dark, and (bottom) illuminated with a halogen lamp filtered through a 397 nm long-pass filter.
Chapter 7

Conclusions

7.1 Summary of Findings

Hydrogen fuel, derived from clean solar energy, easily stored, and free of greenhouse gas emissions, is one part of a multipronged approach to address future global energy shortages. Solar hydrogen can be both produced and consumed without carbon emissions. Utilizing the hot LSPR electrons seen in metal nanoparticles upon illumination with visible light, metal core-semiconductor shell nanoparticles can be used to split water. Silver core nanoparticles were successfully synthesized. Based on a procedure from [Tom 2003], several attempts were made to synthesize Ag/TiO$_2$ core-shell nanoparticles, with variations in the order precursors were added together. During the first coating attempt, the titanium precursor was added dropwise to the silver precursor, while in the second attempt the order was reversed. Both syntheses resulted in a mixture of silver and titanium dioxide nanoparticles.

The third attempt at producing Ag/TiO$_2$ core-shell nanoparticles involved the simultaneous addition of the TIP solution to the silver solution. This resulted in spherical, onion structures with silver cores and titanium dioxide shells. However, coating was not uniform and some silver nanoparticles remained uncoated, which is consistent with literature [Pastoriza-Santos 2000], [Tom 2003], [Kwon 2007], [Chuang
These metal core/semiconductor shell nanoparticles are good candidates for water splitting; because of metal nanoparticles’ LSPR phenomenon they use no energy input other than solar irradiation. Unassisted water splitting is feasible and indeed the ultimate goal of this project. A titanium dioxide shell serves to protect the metal core from corroding in water. Titanium dioxide also serves as the surface at which all reactions take place, with visible light-excited electrons ejected from the metal core into the semiconductor shell reducing water, as well as holes from ultraviolet excitation of the semiconductor being used to oxidize water. The titanium dioxide nanoparticles absorb UV light while the silver nanoparticles extend the absorption to include visible light, allowing much of the solar spectrum to be utilized.

Ag/TiO\textsubscript{2} core-shell nanowires with bristled surfaces were also synthesized. According to data from [Du 2006] as well as from LSPR data in Figure 5.5, these materials have high absorption across much of the solar spectrum. More thorough and uniform coating of the metal core has been demonstrated in these nanowires, as compared to spherical core-shell nanoparticles. This will help protect the silver core, which is not stable in water over time. Bristled nanowires also have the advantage of having a higher surface area on which water molecules can react with excited electrons to produce hydrogen.

Other metal cores could be synthesized, including palladium, platinum, and gold. For example, Au/TiO\textsubscript{2} core-shell spherical nanoparticles can be synthesized using the [Tom 2003] method, but it should be noted that gold core/titanium dioxide
shell nanoparticles are not as promising candidates for water splitting compared to silver core/titanium dioxide shell nanoparticles, since their surface plasmon resonance should peak around 523 nm [Kwon 2007]. The energy of the Au/TiO$_2$ surface excited electrons is thus 2.37 eV (Equation 5.2), lower than Ag/TiO$_2$ spherical core-shell nanoparticles with bandgap energies of 2.82 eV. Since Ag/TiO$_2$ core-shell spherical nanoparticles provide surface electrons with higher energies than Au/TiO$_2$ core-shell spherical nanoparticles, and thus more energy to reduce water, silver nanoparticles are a more desirable choice. While palladium and platinum nanoparticles provide higher energy electrons from their LSPR, coating of these materials with a titanium dioxide shell is presently more difficult. Additionally, the precursors for palladium and platinum are 16 times more expensive than silver precursors and therefore would be less cost-effective for industrial, large scale production of hydrogen.

Absorption measurements were made to determine silver LSPR energies, found to be 3.02 eV, as well as semiconductor bandgaps. Differential pulse voltammetry measurements were made to determine both semiconductor bandgaps as well as conduction and valence band edges, as in [Bae 2005]. Table 7.1 summarizes these results.

The silver and titanium dioxide nanoparticle mixture provides the largest bandgap from both optical and electrochemical measurements. The bandgap found from electrochemical measurements (3.03 eV) is greater than that found from optical absorption measurements (2.85 eV). The Ag/TiO$_2$ core-shell spherical nanoparticles were found to have bandgaps of 2.82 eV from optical measurements and 2.74 eV from elec-
Table 7.1: Bandgaps, conduction band edges, and valence band edges of synthesized nanomaterials. $E_{g,\text{abs}}$ is the bandgap detected from optical absorption measurements in Chapter 5. $E_{g,\text{DPV}}$ is the bandgap determined from differential pulse voltammograms in Chapter 6. $E_{\text{CB,DPV}}$ and $E_{\text{VB,DPV}}$ are the conduction and valence band edges of the nanomaterials found from differential pulse voltammograms in Chapter 6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{g,\text{abs}}$ (ev)</th>
<th>$E_{g,\text{DPV}}$ (ev)</th>
<th>$E_{\text{CB,DPV}}$ (eV vs. NHE)</th>
<th>$E_{\text{VB,DPV}}$ (eV vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag &amp; TiO$_2$ NP mixture</td>
<td>2.85</td>
<td>3.03</td>
<td>-0.47</td>
<td>2.56</td>
</tr>
<tr>
<td>Ag/TiO$_2$ core-shell spherical NPs</td>
<td>2.82</td>
<td>2.74</td>
<td>-0.46</td>
<td>2.28</td>
</tr>
<tr>
<td>Ag/TiO$_2$ core-shell nanowires</td>
<td>2.21</td>
<td>2.59</td>
<td>-0.48</td>
<td>2.11</td>
</tr>
</tbody>
</table>
trochemical differential pulse voltammetry experiments. Finally, the Ag/TiO$_2$ core-shell nanowires were found to have the smallest bandgap both from electrochemical (2.59 eV) and optical (2.21 eV) studies. The difference in the bandgaps found optically, as described in [Bae 2005], with those found electrochemically could be due to the method being approximate. There have been several methods other than the one used in this thesis to determine bandgap from absorption data, such as in [Reddy 2003] and [Meier 2007], where bandgap is determined by linear extrapolation of plots of photon energy vs. $(\alpha \omega)^{\frac{1}{2}}$, where $\alpha$ is the absorption coefficient and $\omega = 2\pi \nu$. Perhaps one of the methods used in these and other papers is more accurate. Also, LSPR from metal cores likely interfered with optical bandgap measurements. The bandgaps determined both electrochemically and optically do, however, follow the same trends with the mixture of silver and titanium dioxide nanoparticles displaying the largest bandgap and the Ag/TiO$_2$ core-shell nanowires having the smallest bandgap.

Recall from Chapter 2 and Figure 2.1 that for hydrogen to be produced from water, the conduction and valence bands of the photocatalyst must lie outside the reduction (-0.41 eV vs. NHE) and oxidation (+0.82 eV vs. NHE) potentials of water:

$$E_{CB} < -0.41 \text{ eV} < +0.82 \text{ eV} < E_{VB}$$

(7.1)

It is clear from experimental results that these three nanomaterials all fulfill that requirement; all semiconductor valence band edges are at appropriate energies to oxidize water, and conduction band edges are slightly above the reduction potential
of water. Ag/TiO$_2$ core-shell nanowires show the most thorough coating of the metal core, and display the most negative conduction band edge, making them most suitable for water splitting.

Differential pulse voltammograms of core-shell nanowires irradiated with a 397-2400 nm, 115 W halogen lamp (Figure 6.10) showed electron activity between the nanowires and working electrode in the bandgap, between 0.2 V and 1.16 V vs. Ag/AgCl, not seen in nanowires under no illumination (in the dark). This new activity could be due to electrons excited from the metal core upon visible illumination. It might also be explained by defect states in the shell, such as titanium interstitials or oxygen defects.

7.2 Further Research

The next step in this project would be water splitting experiments using gas chromatography to confirm H$_2$ and O$_2$ production upon exposure of the nanoparticles in water to solar radiation. A detector on the gas chromatograph sensitive enough to detect low levels of H$_2$ and O$_2$ will be needed in order to prove unassisted splitting of water. Additional future experiments include:

- Tailoring of band edges by altering nanoparticle size and shape
- Analysis of electron carrier processes between core and shell with femtosecond pulse laser experiments
- Doping of the titanium dioxide shells with co-catalysts such as RuO$_2$
- Experiments to check the porosity of semiconductor shells

- Adding a magnetic element, such as NiAg, to the core so that nanoparticles can easily be reclaimed from water with a magnet

- Confirming the reduction potential of the nanomaterials using dyes with known redox potentials

- Analyzing absorption data to determine bandgap using various other methods, such as those found in [Reddy 2003] or [Meier 2007]

- Creating a separation membrane for O$_2$ and H$_2$

Synthesizing nanowires with smooth surfaces might make it easier for hot electrons from the metal core to travel to their surface and interact with water, compared to bristled nanowires synthesized in this project. Additionally, altering the metal core’s shape could allow for infrared absorption.

This thesis has shown that silver core/titanium dioxide shell nanomaterials are viable candidates for unassisted hydrogen production upon solar illumination. Electron transfer from metal core to semiconductor shell has been demonstrated by [Furrube 2007] and [Du 2009], while hot electrons excited above the lower level of the conduction band in semiconductor nanoparticles have been shown to interact with and be donated to electron acceptors (such as water) outside the nanoparticle [Tisdale 2010]. Furthermore, the conduction and valence band edges of the nanomaterials have been demonstrated to be sufficient to reduce and oxidize water to produce hydrogen.
Bibliography


