INCREASED VISIBLE-LIGHT PHOTOCATALYTIC ACTIVITY OF TiO $_2$ VIA BAND GAP MANIPULATION

By

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Abstract of Thesis

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Hydrogen gas is a clean burning fuel that has potential applications in stationary and mobile power generation and energy storage, but is commercially produced from nonrenewable fossil natural gas. Using renewable biomass as the hydrocarbon feed instead could provide sustainable and carbon-neutral hydrogen. We focus on photocatalytic oxidation and reforming of methanol over modified titanium dioxide (TiO₂) nanoparticles to produce hydrogen gas. Methanol is used as a model for biomass sugars. By using a photocatalyst, we aim to circumvent the high energy cost of carrying out endothermic reactions at commercial scale.

TiO₂ is a semiconductor metal oxide of particular interest in photocatalysis due to its photoactivity under ultraviolet illumination and its stability under catalytic reaction conditions. However, TiO₂ primarily absorbs ultraviolet light, with little absorption of visible light. While an effective band gap for absorbance of photons from visible light is 1.7 eV, TiO₂ polymorphs rutile and anatase, have band gaps of 3.03 eV and 3.20 eVrespectively, which indicate ultraviolet light. As most of incident solar radiation is visible light, we hypothesize that decreasing the band gap of TiO₂ will increase the efficiency of TiO₂ as a visible-light active photocatalyst. We propose to modify the band gap of TiO₂ by manipulating the catalyst structure and composition via metal nanoparticle deposition and heteroatom doping in order to more efficiently utilize solar radiation. Of the metalmodified Degussa P25 TiO₂ samples (P25), the copper and nickel modified samples, 1%Cu/P25 and 1%Ni/P25 yielded the lowest band gap of 3.05 eV each. A difference of 0.22 eV from the unmodified P25. Under visible light illumination 1%Ni/P25 and 1%Pt/P25 had the highest conversion of methanol of 9.9% and 9.6%, respectively.

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Chapter 1: Introduction

1.1 Hydrogen Gas, Fuel

Hydrogen gas, a zero emissions fuel [1], is a viable alternative to fossil fuels if derived from renewable biomass. Hydrogen's high gross heating value, 33.9 kcal/g, compared to 5.3 kcal/kg for methanol or 11.0 kcal/g for gasoline, increases its desirability as an alternative fuel. Hydrogen production from the photocatalytic reforming of biomass is a net-carbon neutral process. Carbon dioxide (CO₂) produced by the reforming process is considered to be part of nature's CO₂ circle where plants consume CO₂ from the atmosphere upon growth and elute CO₂ upon harvesting and consumption. Research and production of hydrogen fuel cells have been increasing over the last decade. However, one issue that remains is the low energy density of hydrogen gas, 8.4MJ/L, compared to 31.1 MJ/L for gasoline [2]. Running a stationary fuel cell with a large footprint is acceptable, but we will never see widespread acceptance of commercialized hydrogen fuel cell vehicles and home power until we achieve two things: find a way to produce the hydrogen in a renewable and clean manner, and secondarily, find a means to safely store the energy source (hydrogen or precursors) in a smaller volume.

1.2 Semiconductor

There are three basic classifications of solid materials: conductor, semiconductor, and insulator. Unlike conductors, both semiconductors and insulators have a discontinuous electron band. Of these bands the one lower in energy is the valence band (VB); the band higher in energy is known as the conduction band (CB). The difference in energy between the VB and the CB is known as the band gap. The band gap of an insulator is so large that

an electron is not able to be excited from the valence band to the conduction band. In contrast, a semiconductor has a discontinuous electron band with a moderately sized band gap. The band gap is small enough that exposure to a certain amount of energy could excite the electron in the valence band to the conduction band. The energy to excite the electron from the VB to the CB must be at the same, or greater, energy than the band gap. Figure 1 illustrates how a semiconductor can be used in photocatalysis.



Figure 1: Electron-hole Pair Driving Oxidation and Reduction Reactions

As seen in figure 1, the highest occupied molecular orbital (HOMO) of the electron donor (ie. the species being oxidized) must have a higher energy than the valence band of the semiconductor. The donor electron is transferred to the lower energy hole in the semi conductor's valence band. The lowest unoccupied molecular orbital (LUMO) of the electron acceptor (ie. The species being reduced) must be lower in energy than the conduction band of the semiconductor [3]. The valence and conduction band positions of TiO_2 meet these criteria. It is for this reason, among others, that titania based catalysts are studied in this work.

1.3 Titanium Dioxide

Titanium dioxide (TiO₂) is a metal oxide semiconductor photocatalyst that is of particular interest in catalysis due to its photoactivity under ultraviolet illumination, stability under reaction conditions, and high surface area [3]. Photons from ultraviolet sunlight excite electrons in the bulk of the semiconductor. As seen in figure 2, an electron, e^- , is excited from the valence band to the conduction band while simultaneously creating an electron hole, hv^+ , in the valence band [4]. The electron and hole separately diffuse to the surface of the TiO₂ particle and react with adsorbed molecules. On the surface of the particle, the electron hole is the source of the oxidation of methanol, while the electron reduces dioxygen. The oxidized methanol reacts with the reduced dioxygen forming hydrogen gas as the desired product.



Figure 2: Titania Electron-Hole Depiction

The cited electronic band gaps of anatase and rutile are 3.03 eV and 3.20 eV respectively [3], which indicate absorbance of photons from ultraviolet light. An effective band gap for absorbance of photons from visible light is 1.7 eV. As most of incident solar radiation is visible light, we hypothesize that decreasing the band gap of TiO_2 will increase the efficiency of TiO_2 as a visible-light active photocatalyst. In order to more efficiently utilize solar radiation, we propose to modify the band gap of TiO_2 by manipulating the

catalyst structure and composition via metal nanoparticle deposition and heteroatom doping.

1.4 Solar Spectrum

Of the solar irradiation that reaches earth's surface only 4% is ultraviolet light (UV), whereas 43% of the solar irradiation is visible light. Finding a photocatalyst that can efficiently use visible light would promote the viability of photocatalytic reactions. Figure 3 [5] illustrates the intensity of the solar irradiation that reaches earth with respect to the wavelength of light. It can be observed that the peak of spectral irradiance is near 500nm.



Figure 3: Wavelength of Solar Irradiation

The visible region (400 nm to 700 nm) is shown via the addition of colors that correspond to each wavelength. Figure 4 [5] depicts the spectral irradiance versus the photon energy. Though photons from UV light have much higher energy, 3.1 eV to 6.2 eV, they are much less abundant than photons from visible light.



Figure 4: Photon Energy of Solar Irradiation

It can be seen that a large percentage of energy derived from solar irradiation is unusable for unaltered TiO₂. Figure 4 also helps to visualize that the electrons in a semiconductor with a band gap of 1.75 eV would be excited by all photons derived from visible and UV light. Decreasing the band gap of the TiO₂ will increase the photocatalytic efficiency of the photocatalyst. It is for this reason that the goal of this thesis project is to shrink the band gap of the TiO₂-based photocatalyst. Band gap modifications will be done via supporting metals (Ag, Cu, Ni, Pd, Pt) on P25, hydrogen treatment and carbon doping of TiO₂.

1.5 Methane Reforming

Currently, a majority of hydrogen gas is produced from steam reforming of natural gas (methane). Figure 5 shows that of the hydrogen produced, 48% is produced by the reforming of natural gas [6, 7]. Of all of the hydrogen currently produced, only 4% is produced renewably.



Figure 5: Sources of Hydrogen Production [6,7]

The synthesis route that this project focuses on pertains to the 0.1% of hydrogen production from other sources. For every mole of methane reacted, either three moles of hydrogen and one mole of CO, or four moles of hydrogen and one mole of CO_2 .

Step 1

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 $\Delta H^{\circ}_R = 206 \text{ kJ/mol}$

Step 2

$$CO + H_2O \rightarrow CO_2 + H_2$$
 $\Delta H^{\circ}_R = -41 \text{ kJ/mol}$

Overall Reaction [8]

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$
 $\Delta H^{\circ}_R = 165 \text{ kJ/mol}$

With a heat of reaction of 165 kJ/mol, methane reforming is a very endothermic process. Due to this high endothermicity, the reaction must be run at high temperatures. Not only is the traditional synthesis of hydrogen gas derived from nonrenewable fossil fuels, it is also energy intensive. Although hydrogen is promoted as a green fuel, the current production is not currently a sustainable process.

1.6 Biomass Conversion

Hydrogen can be sustainably produced via the conversion of biomass, specifically the glucose in biomass. In our process the glucose in the biomass is represented by methanol.



Figure 6: Glucose and Methanol Molecular Structures

Methanol is the simplest model of glucose, as it consists of C-O, O-H, and C-H bonds. Methanol, unlike a more complex model like ethanol, is missing the C-C bond. This work focuses on understanding the photocatalytic conversion of methanol, the simplest biomass model. Future work may study photocatalytic reforming of ethanol and other biomass models.

1.7 Methanol Conversion

Sustainable synthesis of hydrogen via the conversion of methanol, a biomass model, is a green and viable alternative to production of hydrogen from non-renewable, non-sustainable fossil fuels. This work looks at three different reactions in which hydrogen can be produced from methanol: methanol oxidation, methanol steam reforming, and methanol oxidative steam reforming.

1.7.1 Methanol Oxidation

The most studied reaction in my thesis project was the oxidation of methanol. Partial methanol oxidation is an exothermic reaction that stoichiometrically produces two moles of hydrogen for every mole of methanol reacted.

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CO_2 + 2H_2 \qquad \qquad \Delta H^\circ_R = -192.2 \text{ kJ/mol}$$
[9]

Though partial oxidation is a desired reaction, complete oxidation is not. Complete methanol oxidation is also known as combustion. This exothermic reaction produces carbon dioxide and water— not hydrogen.

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2 H_2O \qquad \qquad \Delta H^{\circ}_R = -726 \text{ kJ/mol}$$
[10]

Since no hydrogen is produced, this is an undesired reaction. For this reason the molar ratio of oxygen to hydrogen is always kept below three halves.

1.7.2 Methanol Steam Reforming

An endothermic process, the steam reforming of methanol produces the highest stoichiometric yield of hydrogen from methanol than the other tested reactions.

$$CH_3OH + H_2O \rightarrow CO_2 + 3 H_2$$
 $\Delta H'_R = 49.2 \text{ kJ/mol} [9]$

Much of the methanol steam reforming process will be run by my undergraduate student, Katelyn Dagnall. We will compare the hydrogen yield for methanol oxidation and methanol steam reforming pertaining to each catalyst in order to determine which catalyst is best for each reaction.

1.7.3 Methanol Oxidative Steam Reforming

[9]

Oxidative steam reforming combines the benefits of oxidation and reforming; the overall reaction is exothermic and the stoichiometric yield of hydrogen is higher than that of oxidation.

$$CH_3OH + \frac{1}{2}H_2O + \frac{1}{4}O_2 \rightarrow CO_2 + \frac{5}{2}H_2$$
 $\Delta H^{\circ}_{R} = -71.4 \text{ kJ/mol}$

A future aim of this project is to apply the synthesized catalyst to the oxidative steam reforming of methanol and methane in order to determine what properties of the catalysts make them beneficial for each reaction.

Chapter 2: Experiments

2.1 Catalyst Synthesis

2.1.1 Calcination Pre-Treatment

The Degussa P25 TiO₂ (P25) was received from Evonik. All P25-based samples were synthesized with P25 calcined in a tube furnace. The pre-cleaned quartz boats were filled two thirds full with titania powder. One to two boats were loaded into a 1 inch outer diameter quartz tube with a thickness and a length of 1/8 inch and 31 inches, respectively. The loaded quartz tube was slid through the furnace opening and supported on each end by ceramic supports. The ends of the tube were fitted with UltraTorr[®] fittings. The upstream side of the tube was connected to the air cylinder, while the downstream side was connected to an air lock. The air purged the quartz tube at 100 ml/min while the furnace heated to 500 °C at a ramp rate of 2 °C per minute. The furnace temperature was maintained at 500 °C for 3 hours. After 3 hours, the furnace cooled to room temperature at a ramp rate of 10 °C per minute under constant air flow. The calcined titania sample was transferred to a glass vial and stored in a desiccator.

2.1.2 Pore Volume Measurement

The calcined P25 was used as a semiconductor support for various metals. All metal modified samples were synthesized via incipient wetness impregnation (IWI). Before beginning IWI, the pore volume of the support relative to the solvent in which the metal salt is dissolved (Water or Toluene) had to be determined. Since P25 is a fumed TiO_2 it has a very low bulk density. Due to this, caution was taken to avoid inhalation of titania particles. In order to check the pore volume, 1.0 gram of support (TiO_2) was weighed. A

capped vial of solvent was weighed and tared. The desired solvent was added drop wise to the support while the support was constantly stirred with a glass rod. This process continued until the incipient wetness point was reached. The incipient wetness point can be identified visually when the support began to glisten, but before the support was completely wet. The difference in weight of the solvent vial after IWI and the beginning measurement gave the mass of solvent to attain the incipient wetness point of the support. The mass of solvent used was converted to volume using the solvent's density. This volume was then divided by the sample mass to attain the pore volume. This process was repeated until an average value of the pore volume, with an acceptable relative standard deviation, RSD < 5.0 %, was measured.

2.1.3 Incipient Wetness Impregnation

Incipient Wetness Impregnation (IWI) is a method used to modify the P25 via supporting metals on the P25 nanoparticles. During IWI, a desired mass of TiO₂ support was measured out. The mass of solvent needed was determined via the calculated pore volume of the support. A vial of the required mass of solvent was prepared. The mass of metal salt needed to achieve the desired loading weight percent was determined via the weight percent of the metal in the salt and the mass of support. The desired amount of the metal salt was added to the solvent vial. Once the metal salt had completely dissolved, the solution was added to the support drop wise under constant stirring until the incipient wetness point was reached. The sample was dried in the oven 24 hours at 110 °C. After 24 hours, the sample was removed from the oven and scraped into a mortar for grinding. The sample was lightly ground with a mortar and pestle until it appeared homogeneous. The ground sample was stored in a vial in the desiccator until calcination.

2.1.4 Reduction and Passivation of Metal-Modified TiO₂

Prior to conducting the methanol conversion reaction, each calcined metalmodified TiO_2 sample was reduced in situ. Each sample was reduced under separate conditions pertaining to the oxophilic nature of the supported metal.

Metal	Temperature (°C)	Time (hours)	$\begin{array}{c} \text{Percent } H_2 \\ \text{in } N_2(\%) \end{array}$	Ramp Rate (°C/min)	Total Flow Rate (ml/min)
Cu	200	2	10	2	50
Ag	200	2	10	2	50
Pd	300	5	5	2	50
Pt	300	5	5	2	50
Ni	500	5	5	2	50

Table 1: Reduction Conditions

Copper modified TiO₂ samples were reduced at 200 °C for 2 hours at a ramp rate of 2 °C per minute under 50 ml/min of 10 % H₂ in N₂ [11]. Silver modified TiO₂ was reduced at 200 °C for 2 hours at a ramp rate of 2 °C per minute under 50 ml/min of 10 % H₂ in N₂. Platinum and Palladium modified TiO₂ samples were reduced at 300 °C for 5 hours at a ramp rate of 2 °C per minute under 50 ml/min of 5 % H₂ in N₂ [12]. Nickel modified TiO₂ samples were reduced at 500 °C for 5 hours at a ramp rate of 2 °C per minute under 50 ml/min of 5 % H₂ in N₂ [12]. After reduction, each metal modified catalyst was passivated in situ under 50 ml/min of 2 % O₂ in N₂ [1111].

2.1.5 Flame Spray Pyrolysis Synthesized TiO₂

The flame-spray pyrolysis synthesized TiO₂ was produced by our collaborators in the Tse Group in the Mechanical and Aerospace Engineering Department at Rutgers. The first round of samples were synthesized by Hadi Halim, Tse group. In the summer of 2015 I was trained to run the synthesis experiments myself. The project focus of my undergraduate student, Rachel Yang, was to help Mustafa Moazel and me in the synthesis and analysis of the flame spray pyrolysis synthesized TiO₂.

Titanium (IV) isopropoxide (TTIP) was the precursor for all flame synthesized materials. A bubbler filled with TTIP was heated to 85 °C. A specific flow rate of hydrogen carrier gas was passed through the bubbler. Dependent on the polymorph of TiO₂ that was desired, various gases were fed into the flame synthesis reaction chamber. The gases were pre-mixed in the reactor before the flame was ignited. Once gases were flowing at steady state into the chamber the flame was ignited and sample was synthesized for 20 minutes. After synthesis the powder from the collection plate and the burner plate were collected and stored in separate vials in the desiccator until use.

2.1.6 Hydrogen Modified TiO₂

Hydrogen modified P25 was produced in our laboratory via collaborations with the Goldman Group in the Chemistry and Chemical Biology Department at Rutgers. My undergraduate student, Robert Lavroff, focused on the synthesis and analysis of all hydrogen modified samples.

Hydrogen treated samples were synthesized either from uncalcined Anatase (Acrōs Organics) or from calcined P25, lightly ground in order to ensure homogeneity. The desired TiO_2 sample was transferred to a glass sleeve and placed inside a Parr Series 4790 pressure vessel. The vessel was sealed and pressurized to 200 psi with Nitrogen, the vessel was purged. The process was repeated six times in order to ensure no oxygen was present. The reactor was then pressurized with hydrogen to 290 psi. The reactor valve was closed and disconnected from the hydrogen line and connected to a Parr 4838 reactor controller. The

reactor was heated to 200 °C at a ramp rate of 2 °C per minute and held at temperature for 5 days. The reactor temperature was ramped down to room temperature at 2 °C per minute and carefully vented. Once vented, the reactor was purged three times with nitrogen before opening. The hydrogen modified sample was then collected and analyzed.

2.2 Gas Chromatography

2.2.1 Analysis

Gas chromatography is a separations process used for analysis of gaseous reactants and products. The separation of two phases, the stationary bed and the percolating gases, occurs once the mobile phase (sample) is carried through the column by the carrier gas. Each compound will separate along the column based on solubility in the bed at a given temperature. Gas chromatography is known to be an efficient method of analysis due to its ability to detect small amounts of product (ppm scale) and its ability to do so in a short period of time [13].

The gas chromatograph (GC) used in the analysis of the products and reactants of methanol oxidation was an Agilent Technologies 7890B Gas Chromatograph. The GC analysis software was Agilent Technologies ChemStation. The GC method was maintained constant for all reactions. The analysis used both a flame ionization detector (FID) and a thermal conductivity detector (TCD). The front injector, FID, set point temperature was 250 °C with a column flow rate of 4.498 ml/min. The flow rate of H₂ was 40 ml/min, the flow rate of air was 40 ml/min. The carrier gas was N₂ with a flow rate of 25 ml/min. The back injector, TCD, set point temperature was 200 °C with a column flow rate of sample passing through the split vent to the amount of sample passing through the column, was 5:1. The starting temperature of the oven was

50 °C. The final oven temperature was 200 °C. The maximum oven temperature was set to 260 °C. The run time for the GC was 15 minutes plus two minutes equilibration time. Four GC runs were taken per reaction in order to assess steady state projections.

2.2.2 Identification and Calibration

Each of the reactants and expected products for the methanol oxidation and methanol reforming were identified in the GC.

Species	Mw [g/mol]	K [W/m-K]	rt _{FID} [min]	rt _{TCD} [min]
Nitrogen	14.01	0.024	-	-
Oxygen	15.99	0.024	-	4.2
Methanol	32.04	0.212	5.1	13.6
Hydrogen	2.02	0.168	-	3.5
Water	18.02	0.58	-	9.5
Carbon Dioxide	44.01	0.015	-	6.6
Formaldehyde	30.03	0.15	5.20	-
Dimethyl Ether	46.07	0.016	4.9	14.8
Acetaldehyde	44.05	0.18	5.48	-
Formic Acid	46.03		8.9	-
Methane	16.04	0.03	3.43	5.34
Acetic Acid	60.05	0.193	11.6	-
Ethyl Acetate	88.11	0.137	9.4	-

Figure 7: Identified Compounds

Liquid phase compounds were analyzed by manually injecting a known concentration into the front inlet via a syringe. Gas phase compounds were analyzed by flowing a known concentration, diluted with N₂, through the GC injection valve. Identification of each compound was done via analysis of the observed peak and corresponding retention time (rt).

2.3 UV-Visible Spectroscopy

2.3.1 Filling the ex situ Micro Sample Cup

The ex situ micro sample cup (fill volume of 0.022 ml) was weighed and tared. The plastic filling funnel was placed on top of the micro sample cup, and a small amount of catalyst sample was placed in to the funnel. The funnel was held in place while gently tapping the micro sample cup against the lab bench in order to lightly pack the sample. The funnel was then removed from the micro sample cup and the sample was smoothed by scraping off the excess sample and pressing down with the spatula end of the flattening tool. The process was repeated until the sample was smooth and flush to the micro sample cup edge. The excess powder was wiped from the sides and base of the sample cup with a Kimwipe'. The sample cup was weighed and the mass of the sample was calculated and recorded. Dividing the mass of the sample in the micro sample cup by the fill volume yields the bulk density of the catalyst.

2.3.2 Filling the in situ DR Reactor Sample Cup

Firstly, a wire mesh filter was fitted into the reactor bed in order to prevent powder from flowing through the reactor outlet. The plastic reactor filling funnel was placed in a weigh boat; sample is added to the inner edge of the funnel. The boat was then weighed and tared. The funnel was placed on the DR reactor bed. The sample cup was filled by using the spatula end of the flattening tool; the sample was then scraped into the sample cup. Once there was an excess of sample on the sample cup the blunt end of the flattening tool was used to gently pack the sample. Excess sample was scraped from the lip of the sample cup into the funnel. Iterations of this process continued until the sample was flush with the reactor sample cup and smooth. At this point the funnel was carefully removed and placed in the original weigh boat. The sample was weighed again to determine the mass of sample added to the reactor. The reactor dome was secured onto the DR reactor and the DR reactor was gently inserted into the Praying Mantis Diffuse Reflectance Accessory and attached to the apparatus lines.

2.3.3 Calculating Kubelka Munk Units

Both Specular and Diffuse reflectance measure the light reflected from a sample, as opposed to transmitted light. Diffuse reflection is used when the surface consists of small particles that scatter light diffusely, such that the mirror-type reflection seen in specular reflectance [14]. Diffuse reflectance of a sample can be measured either in situ or ex situ in the Praying Mantis Diffuse Reflectance Accessory in the UV-vis Spectrophotometer.



Figure 8: Diffuse Reflectance Schematic

For diffuse reflectance, Kubelka Munk Units (KMU) are analogous to absorbance. The KMU equation, F(R), was calculated by converting percent reflectance spectra obtained from the UV-Visible Spectrophotometer.

$$F(R) = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$

Where R_{∞} is the absolute reflectance. The absolute reflectance is calculated by dividing the percent reflectance of the sample by the percent reflectance of the Spectralon[®] disk.

$$R_{\infty} = \frac{\% R_{Sample}}{\% R_{Spectralon}}$$

The Spectralon[®] disk is an absolute reference for diffuse reflectance and therefore has a diffuse reflectance of unity.

2.3.4 Calculating Band Gap

The band gap of each sample was calculated by converting percent reflectance spectrum attained from an Evolution 300 UV Visible Spectrophotometer to KMU, F(R), which was then converted to the Tauc equation, T(R). The Tauc equation, T(R) is computed by taking the square root of the product of the Kubelka-Munk equation and the energy of each respective wavelength.

$$T(E) = \sqrt{F(R) * E(\lambda)}$$

An analysis of the Tauc equation yields the value of the band gap. First the Tauc equation is plotted (Figure 9a), then the first derivative of the Tauc equation is calculated and plotted, (Figure 9b). Analysis of the maxima of the fist derivative indicates the energy at which the second derivative is equal to zero. The second derivative is then calculated and plotted (Figure 9c). Zooming on the area where the second derivative crosses the y=0 plane (Figure 9d) allows the inflection point of the Tauc equation to be determined more accurately.



Figure 9: Band Gap Calculation

Once the inflection point is determined, the energy, E_i , and y coordinate, T_i , of the inflection point is noted. The slope, *m*, of Tauc plot at the inflection point is determined by the value of the first derivative at the E_i . A line tangent to the inflection point is calculated.

$$T = m_i * E + m_i E_g$$

The band gap, E_g , is the x-intercept of the line tangent to the inflection point. E_g is calculated by dividing the difference between the x and the y coordinate of the inflection point by the slope.

$$E_g = E_i - \frac{T}{m_i}$$

The completed Tauc plot with the tangent line included is shown in figure 10.



Figure 10: Tauc Plot to Determine the Band Gap

The measured band gap of each sample can be visualized as the point that the tangent lines

cross the x-axis, figure 10. Table 2 gives the calculated values numerically.

TiO ₂	Band Gap [eV]
Anatase	3.22
Rutile	2.97

Table 2: Measured Band Gap of TiO₂ Polymorphs

Chapter 3: Results and Discussions

3.1 Effect of TiO₂ Polymorph and Particle Size

P25 is a fumed TiO_2 manufactured as a 3:1 anatase to rutile mixture. X-Ray Diffraction (XRD) analysis of calcined P25, figure 11, indicated that the sample that was used in this experiment had a composition of 86% anatase and 14% rutile, approximately 6:1 anatase to rutile.



Figure 11: XRD of P25 Calcined at 500°C

The XRD analysis suggests that the crystallinity of anatase was less than that of rutile by about 10 % to 20 % and that the crystallinity of the sample is about 1/3 of the crystallinity of near-perfect crystallites.

The measured band gaps of the various TiO_2 polymorphs were compared to values sited in literature, table 3. It is noted that there were small differences between sited and measured values for all three samples. For rutile the difference was - 0.06 eV, for anatase the difference was + 0.02 eV, and for P25 the difference was + 0.17 eV.

TiO ₂	Band Gap [eV]	Literature	
Rutile	2.97	3.03 [15]	
Anatase	3.22	3.20 [15]	
P25	3.27	3.15 [16]	

Table 3: Band Gaps of Various TiO₂ Polymorphs

It is important to note that since P25 is a composite material, changes in its composition could affect the band gap. It is also important to note that many groups which use the Tauc equation to determine the band gap do not calculate the first and second derivative of the Tauc equation. Many other groups identify the inflection point visually. The difference in identification method could lead to experimental error and therefore account for some of the difference between measured and cited values, especially with regards to the P25 sample.

P25 was ground and sieved in order to determine if the macro structure of the fumed sample played an important role in the band gap and absorption properties of P25. Table 4 displays the values of the band gaps of various particle diameters after grinding and sieving. Both the ground samples with macro-cluster particle diameter less than 55 μ m had a band gap of 3.36 eV, whereas the sample containing macro-clusters with diameters greater than 55 μ m had a band gap of 3.26 eV.

TiO ₂	Band Gap [eV]
P25 (ground, $d_p < 45 \mu m$)	3.36
P25 (ground, $45 < d_p < 53 \mu m$)	3.36
P25 (ground, $d_p > 53 \mu m$)	3.26

Table 4: Band Gaps of Various TiO₂ Particle Diameters

It is interesting to note that though the ground sample with $d_p > 53 \mu m$ had a smaller band gap than the two samples with $d_p < 53 \mu m$, it sample a smaller absorbance prenormalization . Figure 12 shows the normalized absorbance of each sample across the wavelengths of interest.



Figure 12: Absorbance of P25 and Ground P25 Samples

In conclusion we note that the P25 which contains all of the particle sizes yields the best photocatalytic properties. Though the band gap of the larger particle size was less than P25 by 0.01 eV, the difference is not enough to justify losing a large percent of absorbance in the UV region. It is for this reason that all of the catalyst modifications are done on P25.

3.2 Effect of Metal Modifications on TiO₂

3.2.1 Bulk Density

The bulk densities of each metal modified catalyst were calculated in order to aid in determining physical properties such as granularity. Table 5 shows the bulk densities of P25 and various modified TiO₂ samples.

Sample	Bulk Density [g/ml]
P25 (uncalcined)	0.19
P25 (calcined)	1.06
P25 (calcined) Toluene IWI	0.80
1% Ag/P25	1.11
1% Cu/P25	1.13
1% Ni/P25	1.06
1% Pd/P25	0.68
1% Pt/P25	0.66

Table 5: Bulk Densities

It can be noted that the bulk density of uncalcined P25 was quite small, 0.19 g/ml. Upon calcination at 500 °C for 3 hours the bulk density increased to 1.06 g/ml. All metalmodified samples prepared with water as the IWI solvent maintain this bulk density 1.06 \pm 0.13 g/ml. The calcined P25 sample treated with the toluene IWI method exhibited a smaller bulk density of 0.80 g/ml. It can be noted that the bulk density of the platinum and palladium samples, both synthesized with the toluene IWI method, have a lower bulk density. A possible reason for the low bulk density is that the toluene treated samples are more granular than those treated with water, therefore a larger portion of the micro sample cup contained air for the fumed (uncalcined P25) and granular (toluene treated) samples than for the less granular (water treated) samples.

3.2.2 Energy Level Analysis

It is important to note that all energies presented are on the Absolute Vacuum Scale (AVS) which is defined as the zero energy being the energy of an electron at rest in a vacuum. As opposed to the Standard Hydrogen Electrode Scale, in which the energy of the redox potential of H_2 is set to zero.

As seen in figure 13, the band gap of TiO_2 spans the desired reduction potentials needed for the formation of hydrogen from biomass for the desired reaction.



Figure 13: Energy Levels of Redox Couples and TiO₂ (anatase) Electronic Band Positions [17]

Supporting metal nanoparticles on TiO_2 creates a synergistic effect which helps to both raise the effective position of the valence band, decrease the effective band gap, and increase electron electron-hole charge separation. Absorbance and band gap measurements of each of the metal modified catalysts were taken both ex situ and in situ (postpassivation).

3.2.3 ex situ Absorbance Analysis

The ex situ samples are hypothesized to be a mixture of the metal and metal oxide, where the amount of oxide is related to the oxophilicity of the metal. Post-passivation, the metal nanoparticles have a thin coating of oxide, protecting the metal bulk from oxidizing during reaction. Table 6 gives the valence and conduction band positions of the various metal oxides pertaining to the metals used to modify TiO₂.

Oxide	Valence Band (eV)	Conduction Band (eV)	Band Gap (eV)
PdO	-6.29	-5.29	1.00
CuO	-6.66	-4.96	1.70
Ag ₂ O	-5.89	-4.69	1.20
Cu ₂ O	-6.42	-4.22	2.20
TiO ₂ (anatase)	-7.41	-4.21	3.20
NiO	-7.5	-4.00	3.50

 Table 6: Valence and Conduction Band Positions (AVS) [17]

The positions of the valence and conductions bands of TiO_2 and each supported metal oxide are depicted in figure 14.



Figure 14: Valence and Conduction Bands of Supported Metal Oxides and TiO₂

In order for the metal oxide to be a good co-catalyst it is important that valence band of the supported metal oxide is more positive than that of TiO_2 . This is because the TiO_2 valence band will act as an electron donor to the higher energy metal oxide valence band. The composite oxide will then have a smaller band gap than pure TiO_2 as the difference between

the valence band of the supported metal oxide and the conduction band of the TiO_2 is less than the difference between the valence and conduction band of the TiO_2 . It is also important for certain reactions, such as hydrogen evolution from water, that the conduction band of TiO_2 is less positive than the conduction band of the supported metal oxide, as the electron will be excited to the conduction band with the lower energy. The band gaps of the metal-modified P25, measured post calcination, pre reduction, are given in table 7.

Metal-Modified P25	Band Gap [eV]
1%AgO/P25	3.08
1%Cu ₂ O/P25	3.11
1%NiO/P25	3.07
1%PdO/P25	3.31
1%PtO ₂ /P25	3.37

Table 7: ex situ Band Gaps: Metal Oxides Supported on P25

The ex situ spectra of the metal modified P25 photocatalysts were measured in a UV Visible Spectrophotometer. The percent reflectance was then converted to KMU, figure 15 shows the normalized KMU of each of the metal-modified P25 photocatalysts.



Figure 15: KMU of As-Prepared Metal Modified P25

In the UV region the normalized absorbance of all metal-modified samples is broader than that of P25. It is also interesting to note that the 1%Ag/P25 showed a red-shift and an increased absorbance from 300 nm to 400 nm. In the visible region of the spectra the band gap of copper (II) oxide, 1.7 eV, is seen in the peak that begins at 700 nm. This indicates that pre-reduction the majority of the copper oxide present in the 1%Cu/P25 is CuO.

3.2.4 Post Passivation Absorbance Analysis

Post reduction and Passivation, the decrease in the effective band gap is due to the Fermi level of the supported metal. The effective band gap of the P25 is reduced after metal modification due to the synergistic reaction between the Fermi level of the metal and the valence band of P25. A specific property of each metal, the Fermi level is the energy level at which an electron will rest at an elevated state. Figure 16 depicts the Fermi levels of each supported metals in comparison to the valence and conduction band positions of anatase TiO₂.



Figure 16: Fermi Level with TiO₂ Valence and Conduction Bands [18, 19]

The Fermi level of the supported metal must have a greater energy than the valence band of the TiO_2 support in order to provide the desired synergistic effect. Under these circumstances the electrons have a higher probability or resting at the Fermi level of the metal instead of the valence band of the TiO_2 , thus decreasing the effective band gap of the semiconductor. The band gaps of the metal-modified samples post reduction and passivation were measured in situ and are tabulated in table 8.

Metal-Modified P25	Band Gap [eV]
1%Ag/P25	3.08
1%Cu/P25	3.05
1%Ni/P25	3.08
1%Pd/P25	3.27
1%Pt/P25	3.38

Table 8: in situ Band Gaps: Metal supported on P25

The observed band gaps of platinum and palladium modified P25 are too large to harness visible light. It was therefore hypothesized that the platinum and palladium catalysts would not show increased activity under visible illumination when compared to the no illumination condition.

The in situ spectra of the reduced and passivated metal-modified P25 photocatalysts were measured under 100 ml/min N_2 flow in a UV Visible Spectrophotometer. The percent reflectance of the in situ sample was then converted to KMU, figure 17 shows the normalized KMU of each of the metal-modified P25 photocatalysts post reduction and passivation.



Figure 17: KMU of Reduced and Passivated Metal Modified P25

In the UV region, pre-normalization the Pt/P25 KMU showed a two-fold increase in absorbance UV region, as well as a small increased absorbance in the visible region. Post normalization the Pt/P25 shows a broader absorbance in the UV region than the P25. This indicates that we have made a better photocatalyst, however have not made a visiblelight active photocatalyst. All metal modified catalysts have an increase in normalized absorbance in the visible region, with palladium and platinum being the lowest. The plasmonic resonances of silver and copper metal nanoparticles are seen in the peaks of absorbance at 500 nm and 560 nm, respectively.

3.3 Flame Synthesized TiO₂

Synthesized as a byproduct during the flame synthesis of various carbon-doped TiO₂ polymorphs, a black, heavily carbon doped anatase, FS C-A (as prepared), became of interest due to its color. The band gap of the as prepared sample was 2.75 eV (Table 9) however it was hypothesized that the sample was so heavily carbon doped that the color and band gap was in part due to carbon coating the surface of the TiO₂. Since carbon would block the active sites, this would indicate that the as prepared sample was calcined at 700 °C for 3 hours with a ramp rate of 2 °C/min. During this calcination process carbon was burned off and monitored both by gas chromatography and mass spectrophotometry. The carbon loss was visually confirmed by a change in color from black to dark gray. Due to the high temperature and long calcination time it is assumed that all of the surface carbon was burned off, and therefore, the remaining carbon was doped into the sample.

TiO ₂	Band Gap [eV]
Flame Synthesized C-Anatase (as prepared)	2.75
Flame Synthesized C-Anatase (calcined)	2.96
1%Cu/ Flame Synthesized C-Anatase (calcined)	2.78

Table 9: Band Gap of Modified Flame Synthesized Carbon Doped Anatase

Post calcination, the FS C-A sample had a band gap of 2.96 eV, this increase was expected since much of the black color— and therefore some of the absorbance— was due to the existential carbon. In an effort to decrease the band gap of the material the metal that had had the greatest effect on the band gap of P25 was supported on calcined FS C-A. The 1%Cu/FS C-A was calcined post synthesis, as all metal modified samples were. Post

calcination the 1%Cu/FS C-A was blue-gray in color and had a band gap of 2.78 eV. It is hypothesized that this catalyst will be photoactive under both UV and Visible illumination.



Figure 18: KMU of Modified Flame Synthesized TiO₂

The absorbance of 1% Copper supported on the Flame Synthesized Carbon doped anatase (1%Cu/FS C-A) in the visible spectrum was greater than P25 and calcined FS C-A which indicates that 1%Cu/FS C-A could potentially be a good visible-light-active photocatalyst.

3.4 Hydrogen Modification of Anatase

Hydrogen modification of anatase TiO_2 (H-Anatase) following the protocol outlined by Mao [20] yielded a gray sample. No noticeable changes were seen in the KMU or band gap of the synthesized catalyst after 4 days of exposure to atmosphere. Table 10 shows the measured band gaps of hydrogen modified anatase compared to as-purchased anatase.

TiO ₂	Band Gap [eV]
Anatase	3.22
H-Anatase (2 day)	3.28
H-Anatase (2 day) + air exposure	3.29
H-Anatase (5 day)	3.17
H-Anatase (5 day) + air exposure	3.17
H-1%Cu(O)/Anatase (5 day)	3.07

Table 10: Hydrogen Modified Anatase Band Gaps

The band gap of the H-Anatase (5 day) sample was smaller than that of anatase by 0.05 eV. After 5 days in the Parr reactor, hydrogen modified 1%Cu(O)/Anatase (5 day) was blue-gray in color and exhibited a band gap of 3.07 eV. Figure 19 shows the absorbance of anatase and H-Anatase synthesized under hydrogen at 20 bar and 200 °C for either 2 or 5 days. Both the hydrogen modified anatase and the hydrogen modified copper anatase samples showed both greater absorbance in the parts of the UV region (200 nm-375 nm) and the visible region (550 nm-800 nm). The absorbance of the hydrogen modified copper anatase, H-1%Cu(O)/Anatase, was greater than both anatase and hydrogen modified anatase, figure 19.



Figure 19: KMU of Hydrogen Modified Anatase

XRD analysis of the 5-day H-Anatase indicated that the sample was 99 % anatase and 1 % rutile. The starting material was only guaranteed to 98 % purity, so the 1 % rutile is presumed to come from the as-purchased anatase. XRD also suggested that the diameter of the anatase crystallite was 91.8nm, about 4 times larger than pre-modified anatase.

Methanol oxidation over H-Anatase yielded a high initial conversion of methanol, however, the catalyst deactivated quickly. For both the no illumination condition and the UV illumination condition, conversion reached zero at 40 minutes. The activity under visible light decreased noticeably throughout the hour-long reaction, however, conversion was maintained above 20 % as seen in figure 20.



Figure 20: Conversion of Methanol Oxidation over H-Anatase

The high initial conversion of methanol was coupled with a high selectivity. Though hydrogen was not produced during any of the reactions, only one product was observed. This product, with a retention time in the FID of 6.31 min was also seen as a byproduct of methanol oxidation reactions over all of the modified TiO₂ catalysts. The process of identifying this compound is underway and will be completed once the system is connected to the Mass Spectrophotometer.

3.5 Photocatalytic Methanol Oxidation

Methanol oxidation was carried out at 200 °C under three conditions: no illumination, UV illumination, and visible-light illumination. The mass of each metal sample was roughly 0.02 g. the flow rate was 100 ml/min of consisting of 8.5 % air (1.7 % O_2) and 3 % methanol in N_2 .

Though the measured band gaps (table 8) of the various samples post passivation would indicate that the silver, copper, and nickel modified catalysts will be photocatalytically active under visible light, while Palladium and Platinum modified samples would not. Figure 21, however, shows that all metal-modified samples had a higher activity in the visible-light region than P25, and that the activity of all of the metal modified samples had a higher activity under visible light than under no illumination. This indicates that though the effect of the Fermi level may not be seen in the band gap measurement, it does aid to effectively decrease the band gap allowing the metal-modified P25 to absorb energy from visible light. It is also notably that all metal-modified P25 samples were still more active under UV illumination conditions than under visible-light illumination conditions.



Figure 21: Conversion of Methanol over Metal-Modified P25

Of the metal-modified P25, the copper, nickel, and platinum modified samples, have the highest conversion of methanol under visible light irradiation. The 1%Cu/P25 and 1%Ni/P25 yielded the lowest band gap of 3.05 eV each— a difference of 0.22 eV from the

unmodified P25. The highest photocatalytic conversion of methanol was observed over 1%Cu/P25 under UV Illumination.

Once the conversion of methanol was determined the rate of production of hydrogen and selectivity of hydrogen was measured. At 200 °C, only the platinum and palladium supported metals produced hydrogen gas from methanol oxidation, figure 22.



Figure 22: Rate of Hydrogen Production (mmol/g-hr) Over Metal-Modified P25

Overall, the rate of production of hydrogen over platinum modified P25 was the highest across all three illumination conditions. Of all three illumination conditions, palladium modified P25 had the highest rate of production under visible light illumination, 6.9 mmol/g-hr, which is promising for future work on visible-light active photocatalysts.

The results indicate that at 200 °C platinum modified P25 is the best photocatalyst for hydrogen production. All metal-modified P25, however, produced hydrogen when the reaction temperature was raised to 250 °C. It is possible that the same analysis at a higher

Chapter 4: Project Summary and Future Objectives

4.1 Project Summary

The work done in this thesis has shown that metal modification effectively decreases the band gap of the TiO₂-based catalyst and also increases the catalytic ability of the titanium dioxide catalyst for methanol oxidation.

Of the metal-modified Degussa P25 TiO₂ samples (P25), the copper and nickel modified samples, 1%Cu/P25 and 1%Ni/P25 yielded the lowest band gap of 3.05 eV each. This is a decrease of 0.22 eV from the unmodified P25, 3.27 eV. The highest photocatalytic conversion of methanol was observed over 1%Cu/P25 under UV Illumination, and under visible light illumination 1%Ni/P25 and 1%Pt/P25 had the highest conversion of methanol. Hydrogen production, however, was only seen for 1%Pd/P25 and 1%Pt/P25 during the methanol oxidation at 200 °C. The copper, nickel, and silver modified P25 did produce hydrogen from methanol oxidation at 250 °C.

A future aim of this work is to repeat these experiments at a higher temperature to compare methanol conversion and hydrogen yield across all metal modified catalysts. Of the various metals that have been supported on P25, platinum, copper, and nickel are the most promising for future work due their high photocatalytic activity, the low band gap for copper and nickel, and the hydrogen production under platinum modified P25.

4.2 Future Objectives

As previously mentioned, the objective of this project was to increase the photocatalytic activity via band gap manipulations of TiO_2 nanoparticles. The photocatalytic activity was tested under methanol oxidation and methanol reforming.

The immediate future aims of this project focus on identifying the selectivity of the various metal-modified TiO_2 catalysts for all reactions and reaction conditions detailed above. This will aid in determining which catalyst is the best for each reaction when taking separation processes into account. This will involve identifying all observed byproducts for each reaction and running calibrations on the GC for each compound.

This project has branched out into four projects that will be studied during my PhD. Firstly, the photocatalytic steam reforming of methane and the photocatalytic oxidative steam reforming methanol will be analyzed in in greater detail for all synthesized catalysts, with the primary focus on the metal-modified catalysts.

Secondly, the collaboration with the Tse group will continue. Various flame synthesized, carbon-dopes TiO_2 nanoparticles will synthesized. Both materials characterization and photocatalytic properties will be analyzed. The Flame synthesized Carbon-Doped Anatase that is synthesized via this collaboration will be tested in photocatalytic conversion of methanol and methane in order to determine the activity of photocatalyst in visible light.

Thirdly, the hydrogen modification process will be expanded to include modification of the metal-modified TiO_2 nanoparticles. Hydrogen modification of these samples will be done before or after incipient wetness impregnation in order to determine the best synthesis method. The photoactivity and selectivity of these photocatalysts will be tested for the reactions described in this project.

Fourthly, nitrogen-doped TiO₂ nanoparticles will be synthesized via a collaboration with the Feldman group in the Department of Materials Science Engineering at Rutgers University. The photoactivity and selectivity of these photocatalysts will be tested under the reaction conditions described in this project.

All future objectives of this project are centered on the sustainable photocatalytic production of hydrogen gas from biomass. Sustainable, green catalysis will remain a cornerstone focus of the Celik Catalysis Group.

Chapter 5: References

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