**NOVEL CATALYTIC APPROACHES FOR HYDROGEN PRODUCTION
(PHOTOCATALYTIC WATER SPLITTING)**

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ABSTRACT

Efficient hydrogen production via photolysis of water has been the focus of the current study. Water splitting experiments have been performed under visible and ultraviolet irradiation. Experiments under ultraviolet irradiation involved metal-semiconductor photocatalysts and visible irradiation experiments were performed with sensitized photocatalysts.

Pt/TiO₂, Pd/TiO₂ and Rh/TiO₂ based photocatalytic systems were investigated. Pt-TiO₂ photocatalysts were tested and characterized for hydrogen production under UV irradiation for different metal loadings. Pt/TiO₂ showed hydrogen production comparable to literature results. Pd/TiO₂ showed relatively lesser activity towards hydrogen production in comparison with Pt/TiO₂. Rh/TiO₂ however showed no activity towards hydrogen production. Transmission Electron Microscopy, X-ray diffraction and Hydrogen Chemisorption were used to characterize the photocatalysts. A disparity in hydrogen production was observed for different loadings of platinum, when H₂PtCl₆ was used as the precursor. This is attributed to the extent of attack of the support. Interaction of the platinum precursor with the semiconductor support was studied and modeled. pH analysis revealed the support as undergoing attack by the acidic precursor (H₂PtCl₆).

Visible wavelength irradiation experiments were performed using dye sensitized Pt/TiO₂. di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II), bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride, di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II) and Tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate complexes were synthesized and tested for photosensitization ability. Photo-electrochemical characterization, Cyclovoltammetry and UV-VIS Spectrometry were used to determine the electron injection ability and redox potentials of the sensitizer candidates. Visible light irradiation experiments were performed with the metal-semiconductor-sensitizer systems to examine photosensitized water cleavage. None of the sensitizers tested showed activity towards hydrogen production. This inactivity is explained by cyclovoltammetry results which show that the redox potentials of the dyes do not span the redox potentials of water, as is required for successful photolysis of water.

Section 1

Introduction

1.1 Hydrogen - Energy Carrier Of The Future

Hydrogen is an energy carrier with the potential to join electricity as a key component of a sustainable energy system. As an energy carrier and a fuel, its future integration into the energy economy will help make renewable energy sources viable and practical. In the future, it may be produced cost effectively from renewable energy sources. It will be stored and transported for use in home and office heating, generating electricity, industrial processes, and surface and air transportation. It can accomplish this while substituting for and reducing the use of fossil fuels and also preventing pollution.

The benefits of hydrogen make it the ideal component of a renewable and sustainable energy system of the future. It can be produced from water—an abundant supply source—using direct sunlight, renewable electricity, and some biological organisms. When burned directly as a fuel, or converted to electricity, its principal by-product is water, which can be safely returned to the environment or reused to produce more hydrogen. The versatility of hydrogen will enable the rapid expansion of the use of domestic

renewable energy sources, in comparison to electricity alone, resulting in reduced energy imports. Hydrogen energy has the potential for substantially contributing to the reduction of climate-changing emissions and other atmospheric pollutants. Unfortunately, the widespread use of hydrogen energy is not currently feasible because of economic and technological barriers.

1.2 Current Hydrogen Production Technology

Currently, hydrogen is produced on an industrial scale from natural gas by steam reforming. In this process, thermal energy is used to separate hydrogen from the carbon component of natural gas. Hydrogen is also produced as a byproduct of petroleum refining and chemical production processes. Limited quantities of hydrogen are currently produced from the electrolysis of water. This is presently a very expensive process, and is restricted to meeting the limited need for extremely pure hydrogen in manufacturing and space program applications.

Current production prices¹ for hydrogen gas produced by steam reforming range from \$7.00 per giga-joule for a large plant to \$12.00 per gigajoule for a small-capacity plant, assuming a natural gas price of \$2.30 per gigajoule. Production by electrolysis using low-cost, off-peak hydroelectricity

costs between \$10 and \$20 per gigajoule. The current cost of electrolytic production using electricity from renewable energy sources is about \$28 per gigajoule. This cost is expected to be reduced to about \$8 per gigajoule by 2030 with continuing research and development. This reduction in the price of hydrogen is expected to come about by the development of novel hydrogen generation systems.

Hydrogen can be obtained from water by a variety of methods that are currently not feasible for large-scale production, but are the focus of immense research and development activity. These methods include photo-conversion devices/systems involving biological organisms and synthetic materials to split water, and photo-electrochemical processes, which use semiconductors to generate an electric charge to bring about the water splitting.

During the last few years, photo-electrochemical processes at semiconductor-electrolyte interfaces, namely photocatalysis and photosensitization, have attracted interest because of their possible application in the conversion of solar energy into chemical or electrical energy. Research involving photocatalytic and photosensitized splitting of water, although in its infancy could possibly provide the world with a hydrogen energy economy in the future. The remainder of this project work

deals with these processes on TiO_2 based photocatalysts and their application to water splitting.

1.3 Literature Review

Fujishima and Honda² first reported the direct conversion of solar energy into storable chemical energy in the form of hydrogen in 1971. They achieved the production of hydrogen using a photo-electrochemical cell based on a single-crystal n- TiO_2 semiconductor photo-anode. This type of system has subsequently been replaced by particulate systems for photo-production of hydrogen. Particulate systems are attractive because their relative simplicity would result in lower construction and maintenance costs. Moreover, the light absorption efficiency in suspensions can be very high. Since the discovery by Honda et al, several researchers have contributed immensely to the field. Photocatalysis on TiO_2 surfaces has been reviewed in detail by Linsebigler et al³. The review enumerates the various photo-processes that are possible on TiO_2 surfaces and also deals with the physics and electrochemical aspects of photocatalysis on TiO_2 surfaces. Gratzel⁴⁻¹⁸ et al have conducted pioneering research on both metal-semiconductor systems and semiconductor-sensitizer systems for over 20 years. Gratzel et al have studied water splitting properties of Ruthenium tris-bypyridyl complex sensitized TiO_2 systems. The group has also investigated the application of TiO_2 sols and colloidal TiO_2 systems for water cleavage. Nazeeruddin et al^{11,18} have characterized more than 500 dye compounds in terms of spectral

and photo-electrochemical properties to identify suitable sensitizer compounds for successful splitting of water in the visible region. Kalyanasundarm^{8,9,19} has elaborately researched the photo-physical and photochemical properties of polypyridyl and poryphyrin metal complexes. Kamat²⁰⁻²² has extensively reviewed the behavior and properties of semiconductor surfaces in photocatalytic applications. Excellent reviews and articles have been published on the physics and electrochemistry of semiconductor-liquid interfaces by Nozik et al²³ from the National Renewable Energy Lab, Golden, CO. Escudera et al²⁴ have demonstrated the splitting of water on an engineering scale under ultraviolet irradiation of platinized TiO₂ particles. Further, they studied the effect of the method of platination on the hydrogen production. Mills and Porter²⁵ have studied the photo-dissociation of water using platinized TiO₂ and concluded that platinum deposits of more than 0.5% are not only unnecessary but may also be detrimental towards the rate of hydrogen production. Sato et al²⁶⁻²⁸ have studied the photolysis of water on metallized powdered titanium dioxide. The experiments were performed using NaOH adsorbed onto TiO₂. Rhodium, palladium, nickel and platinum were the chief metals employed. They concluded that Rhodium has greatest activity for water splitting. Sato et al²⁸ have also studied the method of photoplatinization as means of platinum deposition on TiO₂ supports.

The latest contributions in the field have been mainly from the National Renewable Energy Laboratory(NREL). Suzanne Ferrere^{30,31} and Turner et al^{29,30,31} have worked extensively on effective sensitizer materials based on iron and copper polypyridyl complexes. Tandem cell technology employing p-n junctions has been the brainchild of NREL under the leadership of John Turner. Tandem cells are the new generation of energy conversion devices and research in the field is being spearheaded by NREL.

1.4. Photo-electrochemical Water Splitting

Figure 1.1 : Solar Spectrum as a function of Photon Energy and Wavelength

A viable light harvesting system for hydrogen production must generate enough voltage to decompose water and the system must be stable

in a water environment. Splitting water into hydrogen and oxygen at 25°C requires a voltage of 1.229V. At current densities for solar applications, typical values of the overvoltage for the hydrogen evolving and oxygen evolving reactions are 50mV and 275mV respectively. This translates to a potential of 1.6V, needed for water splitting when using incident photon energy. This, when compensated for practical single band gap semiconductor systems, would mean a voltage of about 1.8 V to compensate for the internal losses. In other words, the whole visible spectrum could potentially be used for water splitting applications(fig.1.1). The desired reactions to be achieved are:

Metal catalysts would be required on both the hydrogen and oxygen evolving surfaces to speed up the redox reactions and stabilize the semiconductor. An additional requirement is that the semiconductor band edges span both redox potentials of the hydrogen and oxygen evolution reactions. Most well known semiconductors are unsuitable for photo-electrolysis due to several reasons:

- they have too large a band-gap and absorb very little light, leading to low efficiency.

- too small a band-gap and do not generate sufficient voltage.
- Are unstable in a water environment.
- Have band-edges that do not span both the redox potentials of the hydrogen and oxygen evolution reactions

However, several catalytic materials, especially metal oxides, which by nature of their surface properties behave like doped semiconductors, have been found to be very suitable for water splitting.

1.5 Semiconductor Photocatalysis

Figure 1.2 illustrates photocatalytic water splitting. Light of energy equivalent to the band gap, is incident on a semiconductor and causes the generation of electron hole pairs (EHP). The excited state lifetime of the EHP

Figure 1.2: Water Splitting Using Semiconductor Photocatalysis

is large enough to enable charge transfer to adsorbed species. In the case of water splitting, the adsorbed species is water, which exists as H^+ and OH^- . The electron from the EHP can interact with the H^+ ion and the hole can interact with the OH^- ion. This process can go on cyclically if the band edge positions of the semiconductor and the redox potential of the adsorbed species are thermodynamically conducive.

In a heterogeneous semiconductor photocatalytic system, photo-induced molecular reactions take place at the surface of the catalyst. Depending on where the initial excitation occurs, photocatalysis can be generally divided into two classes of processes. When initial photo-excitation occurs in an adsorbate molecule which then interacts with the ground state catalyst substrate, the process is referred to as a catalyzed photoreaction. When the initial excitation takes place in the catalyst substrate and the photoexcited catalyst then transfers an electron or energy, into a ground state molecule, the process is referred to as sensitized photoreaction. The probability and rate of the charge transfer processes for electrons and holes depend upon the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the adsorbate species. The relevant potential level of the acceptor species is thermodynamically required to be below the conduction band potential of the semiconductor. The potential level of the donor, on the other hand, needs to be above the

valence band position of the semiconductor in order to donate an electron to the vacant hole.

Several semiconductors have been identified as candidates (catalysts) for photocatalytic water splitting. The optical band gaps of these materials set the requirement for the nature of light that has to be made incident for successful electron hole pair generation. Different kinds of light sources are currently in use. But the ultimate challenge to researchers today, is the possibility of utilizing sunlight for photocatalysis.

Several criteria are to be considered while choosing a semiconductor for photocatalytic applications.

- The band gap of the semiconductor should be low enough to enable photo-generation of EHPs and the lifetimes of the generated EHPs should be long enough to undergo chemical transfer.
- Since the incident light would heat up the semiconductor, it should be stable and be suitable for operation within a range of 25-100°C.
- Since most photocatalytic applications involve an adsorbed species on the semiconductor surface, the material should be a very porous and capable of adsorbance both in the aqueous and the gaseous phase.
- The positions of the conduction and valence bands with respect to the redox species must also be considered.

- In addition, it should be easy to modify the surface of the semiconductor and alter the photocatalytic properties.

Conventional semiconductors like Silicon and Germanium are not suitable for photocatalysis, primarily because they are not porous and thus cannot be used for solid-fluid applications. Moreover, they tend to corrode in aqueous media. Several semiconductor materials have been identified as potential candidates for photocatalytic applications. Table 1.1 enumerates these semiconductors and their band gaps.

Semiconductor	Band Gap
GaAs	1.4 eV
CdSe	1.7eV
GaP	2.25 eV
CdS	2.5 eV
SiC	3.0 eV
ZnO	3.2 eV
WO ₃	2.7 eV
TiO ₂	3.2 eV

Table 1.1: Semiconductor Candidates

Of these materials TiO₂ has been investigated the most. After the discovery of water splitting by TiO₂ electrodes research efforts have been directed mainly towards altering the spectral response of TiO₂. TiO₂, an insulator ($E_g=3.2\text{eV}$), behaves like an n-type semiconductor due to the

presence of oxygen vacancies on its surface. The reasons for the very high suitability of TiO_2 for photocatalysis are many. TiO_2 has the following unique properties:

- It has a high surface area and can adsorb liquid and gas phase species very well.
- Its surface can be easily modified and its properties can be easily altered.
- It is very stable at higher than room temperatures.
- It is a good catalyst support and does not corrode in aqueous and gaseous media.
- It is very cheap and easy to procure.

In view of the above, TiO_2 has been the most promising photocatalyst but the search is on for alternative materials. The latest technology involving Tandem Cells use GaAs and GaInP_2 cells together²⁹. This technology developed by the National Renewable Energy Lab, Golden, CO, is still in its infancy but its potential has been widely recognized and is expected to bring about the next generation of photo-electric energy conversion devices. Systems involving CdS, ZnO and WO_3 are currently being investigated. WO_3 is also a promising candidate because of its ability to be photo-excited at visible wavelengths. CdS and ZnO coupled systems have also been researched and proven to be good for photocatalytic applications.

1.6 Semiconductor-Water Interface

The semiconductor liquid interface is very much analogous to the semiconductor-semiconductor interfaces, under the condition that the semiconductor is stable in aqueous media. The energetics that occur at the interface are best summarized by the figures 1.3 and 1.4. A p-type semiconductor would cause downward band bending and thus would favor the movement of an electron into the electrolyte while the n-type semiconductor would cause an upward band bending at the interface favoring the quenching of holes in the semiconductor by electrons from the electrolyte.

Figure 1.3: n-type Semiconductor-Water Interface

The development of an accumulation layer followed by a depletion layer in the semiconductor due to the charges in the aqueous medium is clearly depicted in figure 1.3. When a semiconductor comes in contact with an aqueous medium, the ions in the medium will tend to accumulate on the surface of the semiconductor. The nature of the charged particles will depend on whether the semiconductor is n-type or p-type. This will set up an accumulation layer in the semiconductor. As more charges accumulate, interfacial combination occurs leading to a depletion layer in the semiconductor. The analogy between solid contacts and the aqueous contact is thus obvious.

The $\text{H}_2\text{O}/\text{H}_2$ (reaction 1) conversion can be viewed as a set of empty states and the $\text{H}_2\text{O}/\text{O}_2$ (reaction 2) can be considered as a set of filled

Figure 1.4: Band Edge Positions of TiO_2 and Redox States of Water

states (figure 1.4). Thus, electrons could be donated from the filled states to the holes that arise from photonic excitation and electrons could be transferred to the empty states from the conduction band of the semiconductor. The only requirement is that the redox potentials (i.e. the empty and filled states in the aqueous medium) should be positioned such a way that the conduction band edge is energetically above the empty state potential and the valence band edge position is below the filled state potential (figure 1.4). The relative positions of the TiO_2 band edges and the occupied and empty states of the aqueous medium for water splitting are shown below. For an EHP to be created light of energy greater than 3.2 eV needs to be made incident on the TiO_2 particle. Thus, uv-illumination would be required. After excitation, the electron would jump to the conduction band, from where it would drop to the lower potential of the empty states of the aqueous medium and thus cause the evolution of H_2O . The electrons that would exist in the filled states of the aqueous medium would quench the holes in the conduction band. This process could go on cyclically thus bringing about successful splitting of water.

TiO_2 by itself is incapable of successfully splitting water because the EHP recombination rate is very high and there is insufficient driving force for the electrons. However, modified TiO_2 is a highly efficient

photocatalyst. The next section deals with two modifications relevant to water splitting.

Section 2

Semiconductor Modifications

2.1 Types of Modifications

The overall photocatalytic activity of any semiconductor system towards water splitting using visible wavelengths is measured by several factors namely the stability of the semiconductor under illumination, the efficiency of the photocatalytic process, the selectivity of the products, and the wavelength range of response. As mentioned earlier, TiO_2 alone cannot photo-catalyze water-splitting because the electron-hole recombination rate is much larger than electron transfer rate. In addition, although TiO_2 ($E_g=3.2\text{eV}$) is quite stable as a photocatalyst, it is only active in the ultraviolet region which contains only 10 % of the overall solar energy intensity. Modifying the surface of TiO_2 would surmount these limitations. The chief benefits/goals of surface modification of photocatalytic semiconductor systems are:

- a. Inhibition of electron-hole recombination by increasing the charge separation and thus the efficiency of the photocatalytic process.
- b. Increasing the wavelength response range of the system.
- c. Changing the selectivity and or yield of a particular product.

Several modification techniques have been identified and researched over the years. Each of the modifications is aimed at changing a particular aspect of the semiconductor. The chief modifications are as follows:

- Metal Semiconductor Modification
- Surface Sensitization
- Impurity Sensitization
- Composite Semiconductors

Metal-semiconductor modifications are used primarily to inhibit charge recombination and increase the selectivity towards particular products. Surface sensitization has been extensively used to make wide band gap sensitizers spectrally responsive to visible wavelengths. Impurity sensitization is used to alter the n-type or p-type behavior of the semiconductor by introducing dopants. Composite semiconductors employ two or more semiconductors together to bring about material characteristics different from the individual semiconductors. Only the first two modifications are relevant to the current work and will be dealt with in detail in the ensuing sections.

2.2 Metal Semiconductor Modification

The addition of noble metals to a semiconductor surface can change the photocatalytic process by changing the semiconductor surface properties. The metal enhances the yield of particular products and the rate of the photocatalytic

reaction. In this type of modification, a noble metal is impregnated onto the semiconductor particle, leading to the formation of a metal-semiconductor junction (Schottky Contact). The fermi levels in the metal and semiconductor are

Figure 2.1: Metal Semiconductor Modification and Equivalent Circuit

unequal and hence band bending occurs at the interface to bring about equalization of the fermi levels. This causes the electrons, after excitation, to migrate to the metal where it becomes trapped and electron-hole recombination is suppressed. Figure 2.1 illustrates the electron capture at the Schottky barrier of the metal in contact with a semiconductor surface. Figure 2.1 also presents the equivalent circuit of the for the metal-semiconductor-electrolyte system.

Pt has been widely used as the metal for modifying TiO₂ semiconductor particles^{7,24,25,27}. Silver has also been shown to influence charge carrier separation³. The Pt/TiO₂ (figure 2.1) system is the metal-semiconductor system

most commonly studied in water splitting experiments. The addition of Pt to the TiO_2 surface is beneficial for photocatalytic reactions involving gases, especially hydrogen. Platinum is also important because of its own catalytic activity. In effect, Pt modifies the photocatalytic properties of the semiconductor surface by changing the distribution of the electrons. The driving force for the electrons to move into the metal causes a decrease in electron density within the semiconductor, leading to an increase in the hydroxyl group acidity. This in turn affects the photocatalytic process on the semiconductor surface.

The electronic modification of the semiconductor surface via metal deposition can also be observed with other noble metals. Silver has been well researched for surface modification effects. Palladium- TiO_2 and Rhodium- TiO_2 modifications have been investigated by Sato et al²⁷. In the current work, water-splitting experiments have been performed with Pt/ TiO_2 , Pd/ TiO_2 and Rh/ TiO_2 systems. The results are discussed in a later section.

As mentioned earlier, the hydrogen producing step in the water-splitting reaction scheme is a single electron process and the oxygen-producing step is a four electron process. Researchers have studied dual catalyst systems for water splitting. TiO_2 powders with deposited metal particles (Pt) for hydrogen production and metal oxide (RuO_2) particles for oxygen evolution have been employed³. Here the system behaves as a short-circuited micro photo-

electrochemical cell with Pt as the cathode and RuO₂ as the anode. Band gap excitation in the TiO₂ substrate injects negatively charged electrons into the Pt

Figure 2.2: Dual catalyst system employing Pt and RuO₂

particles and positively charged holes into the RuO₂ particles (figure 2.2). Trapped electrons in Pt reduce water to hydrogen and trapped holes in RuO₂ oxidize water to oxygen. The presence of Pt and RuO₂ significantly reduces the over-potential for H₂ and O₂ production, respectively. Pt/TiO₂/RuO₂ systems have been very effective for water splitting experiments under ultraviolet illumination.

2.3 Photosensitization

The use of solid-state materials for efficient conversion of sunlight into electricity has long been a goal of inorganic photochemistry. A molecular approach has been to sensitize wide bandgap semiconductors to visible light with organic or inorganic compounds exhibiting charge transfer excited states.

Figure 2.3: Photosensitization

About 20 years ago, electro-chemists employed this strategy with single-crystal and polycrystalline films of tin oxide and titanium oxide in photo-electrochemical cells. An accepted model for dye sensitization in regenerative photo-electrochemical cells emerged from these studies (figure 2.3). An excited sensitizer state, S^* , injects an electron into the semiconductor with a rate constant

k_2 . The oxidized sensitizer accepts an electron from an external donor present in the electrolyte, with rate constant k_4 . The net process allows light of lower energy than the semiconductor bandgap. The recombination of the injected electron(k_3) and the radiative and non-radiative decay of the excited state(k_{-1}) compete directly with the photocurrent production. If the oxidized donor is reduced at the counter electrode, then the solar cell is regenerative, since no net chemical reaction occurs.

Surface sensitization (coating with a dye) of a wide band-gap semiconductor photocatalyst (TiO_2) via chemisorbed or physisorbed dyes can thus increase the efficiency of the excitation process. The photosensitization process can also expand the wavelength range of the excitation for the photocatalyst, through excitation of the sensitizer followed by charge transfer to the semiconductor. The process of photosensitization is essentially equivalent to the primary photochemical event in natural photosynthesis. It, however, differs from natural photosynthesis due to the fact that the charge separation process is much slower than the charge recombination.

A key ingredient of such photosensitized energy conversion systems is the metal oxide (TiO_2), which plays several important roles. It serves as a high surface area support for the sensitizer, a pathway for injected electron current and a porous medium for the diffusion of the redox-couple. A second and very

important ingredient is the sensitizer, which acts as a photo-driven molecular electron pump. The sensitizer absorbs visible light, pumps an electron into the semiconductor, accepts an electron from the solution redox couple and repeats the cycle. To be useful for solar applications, the sensitizer should meet the following important criteria:

- (i) High stability in the ground and excited states
- (ii) An excited state reduction potential that lies at a more negative potential than the semiconductor conduction band edge
- (iii) A positive ground state oxidation potential to ensure rapid donor-oxidation
- (iv) A strong absorbance of solar energy
- (v) Low cost.

Dye molecule candidates for photosensitization are thus intensely colored, i.e., very responsive in the visible region of the spectrum. Polypyridyl and porphyrinic metal complexes have been identified as ideal for photosensitization applications¹⁹. Since this research work primarily deals with polypyridyl complexes, the following discussion is limited to these dyes.

2.3.1 Polypyridyl Metal Complexes

Transition metals have the characteristic ability to form complexes with a variety of neutral molecules such as carbon monoxide (CO), isocyanides(CNR),

2,2'- bipyridine

1,10- phenanthroline

phosphines(PR_3), pyridine(py), bipyridine(bpy) and phenanthroline(phen). A common feature of all these ligands is the presence of vacant π -orbitals that can accept electrons from the metal ion to form a type of π bonding that supplements the σ bonding arising from the donation of a lone pair of electrons.

Polypyridine complexes of transition metals have been identified as excellent candidates for semiconductor photosensitization due to their intense color and thus high responsivity to visible wavelengths. 2,2'-bipyridine and 1,10-phenanthroline are parent ligands of a broad family of polypyridine/polyimine ligands that have been shown to be capable of complexing with a number of metal ions. Octahedral complexes of the type $[\text{M}(\text{LL})_3]^{2+}$ are easily formed with most metal ions and are very stable.

Absorption spectra of these metal complexes contain several bands corresponding to transitions between several well-defined electronic configurations. While the transitions in the metal are primarily due to d-d transitions, the excited states in the polypyridyl ligand are described as electronic transitions involving electrons of σ or π bonds. It is convenient to describe the transitions in metal complexes in three categories (figure 2.4): those centered primarily on the ligand orbitals, those centered on the metal and charge transfer types involving the electrons of the central metal and the ligands. Conceptually the metal orbital diagram is combined with the ligand orbital diagram to arrive at a composite model for the entire system, as shown in the figure. The metal centered and ligand-centered transitions are not relevant to the current study

1: d-d (MC) 2: π - π^* (LC) 3: d- π^* (MLCT) 4: π -d * (LMCT)

Figure 2.4: Electronic Transitions in Metal-Complexes

and will not be dealt with here.

Charge transfer transitions are characterized by their unique spectra and reactivity. Assignments of absorption bands to charge transfer transitions are based on the assumption that the metal and ligand are separate systems that interact weakly. A charge transfer transition is defined as the addition or removal of an electron from a partially filled shell of the metal and a change in the oxidation state by +1 or -1. Charge transfer transitions can be of essentially two types: *ligand to metal charge transfer* (LMCT) and *metal to ligand charge transfer* (MLCT). The latter is likely in metal complexes in which the metal has a small ionization potential and the ligands have an empty π^* orbital. The nature of polypyridyl complexes is thus suitable for these transitions. Most sensitizer compounds used in water splitting and other photochemical applications possess MLCT charge transfer absorption bands that harvest a large fraction of visible light.

2.3.2 Excited States , Ground States and Redox Potentials

The allowed molecular excitation and de-excitation processes in metal complexes of this type are depicted in Figure 2.5. The ground state singlet energy level (S_0) of the molecule is the energy of the molecule at room temperature in solution. The three possible excited states are shown in the

Figure 2.5: Ground and Excited States

figure. S_1 and S_2 represent the singlet excited states and T_1 represents the triplet excited state. The triplet excited state is less energetic than the singlet excited state of the molecule. Absorption of radiation results in the excitation of the molecule from the ground state to one of the excited singlet states. The selection rules for an electronic excitation process require that direct photo-excitation from the singlet ground state to the triplet excited state is spin forbidden.

The absorption of a photon occurs very rapidly, on the order of 10^{-15} s. De-excitation events are much slower. The de-excitation of the excited molecule favors a route, which will minimize the lifetime of the excited state. This de-excitation involves two processes: internal and external conversion. Internal conversions are the result of radiationless transitions to lower excited states

while external conversions are the result of energy transfer to solvent or solute molecules and are usually from the lowest excited states.

Figure 2.6: Correlation of electrochemical redox potential with the energies and redox potentials of the electronically excited state.

Figure 2.7

Figure 2.6 depicts the process of photosensitization with respect to the dye molecule. S represents the ground state of the dye and S^* represents the excited state. The dye can interact either with a donor or an acceptor to bring about chemical reactions. Figure 2.7 shows the series of steps for regenerative

photosensitization for a ruthenium dye sensitizer on TiO_2 , employed in a water splitting system. Here ruthenium, which is initially in the 2^+ ground state, is excited to the $(\text{Ru}^{2+})^*$ state after receiving light energy. It then injects an electron into the TiO_2 support and exists as the $(\text{Ru}^{3+})^*$ excited state. This excited state then undergoes relaxation to the Ru^{3+} ground state, which will in turn accept an electron from the OH^- and the original ground state is regenerated. All these steps however must be energetically favorable for the process to go on cyclically. For the ready transfer of an electron from the excited state into the conduction band of the semiconductor (TiO_2), the excited state reduction potential of the dye must be more negative (or above) the conduction band edge of the semiconductor. Also the ground state oxidation potential of the sensitizer dye must be more positive (or below) than the reduction potential of water (OH^-/O_2).

2.3.3 Polypyridyl Complexes of Ruthenium

As one of the few transition metal complexes with a unique combination of properties such as moderate excited state lifetime, ability to undergo energy and electron transfer processes and chemical stability, $[\text{Ru}(\text{bpy})_3]^{2+}$ has received the attention of many researchers. The most stable oxidation state of Ru is Ru(II). It exhibits visible light absorption band at 452nm and the band is attributed to MLCT $d-\pi^*$ transitions. The MLCT excited state in $[\text{Ru}(\text{bpy})_3]^{2+}$ has three major

decay pathways available: radiative and non-radiative decay to the ground state or cross into nearby thermally accessible d-d states in the metal. Aqueous solutions of $[\text{Ru}(\text{bpy})_3]^{2+}$ are sufficiently photo-inert at ambient temperatures for exploitation as photosensitizers of photoredox and energy transfer processes. Literature values¹⁹ of the redox potentials of $[\text{Ru}(\text{bpy})_3]^{2+}$ are:

$$E_0[\text{Ru}^{3+}/2+] = 1.26 \text{ V}$$

$$E_0[\text{Ru}^{2+}/+] = -1.26 \text{ V}$$

$$E_0[\text{Ru}^{3+}/2+^*] = -0.81 \text{ V}$$

$$E_0[\text{Ru}^{2+^*}/+] = 1.26 \text{ V}$$

2.3.4 Polypyridyl Complexes of Copper

Most of the Copper complexes that can be used for photosensitization do not possess bipyridyl ligands. Phenanthroline and biquinoline ligands form four-coordinated tetrahedral Cu(I) complexes. Biquinoline complexes of Cu(I) show an absorption maximum around 545nm. Thin films of copper-biquinoline complexes have been shown to successfully generate anodic photocurrents in SnO_2 . Supersensitizers employing copper hydroquinone have been shown to produce steady photocurrents.

2.3.5 Polypyridyl Complexes of Iron

Polypyridyl complexes of iron(II) of the type $[\text{Fe}(\text{bpy})_3]^{2+}$ have been subject to detailed analysis. The absorption maximum is around 521nm and excited state lifetimes on the order of 10-20ns have been reported¹⁹. These complexes have characteristics very similar to ruthenium polypyridyl complexes. Mixed ligand complexes of the type $\text{Fe}(\text{bpy})_2(\text{CN})_2$ have shown excited lifetimes of greater than 56ns. The long excited state lifetimes make these compounds excellent candidates for semiconductor sensitization. Redox potentials of $E_0[\text{Fe}^{3+}/2+] = 1.05$ have been reported¹⁹.

2.3.6 Efficiency Parameters

In the previous sections, a few general characteristics and chemical aspects of dye sensitization candidates have been presented. Particulate semiconductor-sensitizer systems have so far not been successful for water splitting and have been found to be very inefficient (<1%). However, new nanostructure materials and films have been shown to be very efficient³². From an experimental viewpoint it is important to evaluate the efficiency of dye sensitized systems when applied to water splitting and energy conversion devices. Researchers employing nanostructured films have been successful in characterizing dye sensitized systems in terms of photocurrents and efficiencies. The same parameters are applicable to photoprocesses in bulk semiconductor-sensitizer

systems but are very difficult to determine using particulate systems. The following is a brief description of the parameters that need to be considered in the evaluation of sensitized systems.

The first step in evaluating the efficiency of a dye is to measure the photocurrent generated on illumination of the dye. The photocurrent is often reported as the incident photon to charge efficiency (IPCE), which is the ratio of electrons measured in the external circuit to the photons incident on the cell. The IPCE measured as a function of the excitation wavelength is called the photo-action spectrum and often resembles the absorption spectrum of the sensitizer. Taking into account the various molecular processes by which photons are converted into an electrical current, the IPCE is the product of three terms: the

$$\text{IPCE} = (\text{LHE})(\varphi)(\eta)$$

light-harvesting efficiency (LHE), the quantum yield for electron injection (φ), and the efficiency (η), with which electrons are collected in the external circuit. The LHE or absorptance is the fraction of light absorbed by the dye sensitizer. An ideal dye-sensitizer will have an LHE of unity at any wavelength. However, for most dye sensitizers, LHE is maximum at the absorption maxima. The LHE can be directly correlated to the molecular extinction coefficient of the sensitizer and the surface coverage. A molecular monolayer of a Ru(II) polypyridyl

sensitizer on flat surface will harvest <1% of the incident light, while the LHE is >99% for the same dye on a nanocrystalline film³² as a result of the high surface area and the long path length afforded by the complex three-dimensional structure of the material. This difference can be seen with the naked eye, since a monolayer of charge transfer sensitizers does not appear colored whereas the sensitized nanocrystalline films are almost opaque.

Electron transfer from the excited state sensitizer to the TiO₂ electrode converts the energy stored in the MLCT excited state to an interfacial charge-separated pair, consisting of an electron in the support and the oxidized sensitizer. The quantum yield for electron transfer from the excited sensitizer to the TiO₂ particle occurs with an efficiency, ϕ . For a broad class of Ruthenium sensitizers with dicarboxylic linkages to TiO₂, $\phi \sim 1$. The electron injection rate constant has been a topic of much debate and is believed to depend on the experimental conditions. An estimate based on time-resolved photoluminescence studies of Ru(II)polypyridyl sensitizers indicates a distribution of electron injection rates with a peak amplitude¹⁹ $\sim 10^9 \text{s}^{-1}$.

Once the electron is in the solid it proceeds through the TiO₂ network to the external circuit with an efficiency of η . Two aspects are important here: back reaction or recombination and forward electron transfer. The rates of these two reactions compete and determine to a great extent whether a particular dye is

successful in photo-sensitization. Since different molecular orbitals are involved in the forward and reverse electron transfer processes, different rates are expected. Electron injection occurs from the π^* levels of the bipyridine ligands, while back electron transfer occurs to the t_{2g} orbitals of the metal center. In sensitized single crystal and bulk semiconductor materials, the back reaction is thought to be inhibited by the electric field region at the semiconductor surface. The semiconductor depletion region sweeps the injected electron toward the bulk and away from the oxidized sensitizer, thereby inhibiting the back reaction. In metal-semiconductor-sensitizer systems, the Schottky barrier that is formed at the metal semiconductor interface causes band bending and thus a driving force from the conduction band electron towards the metal comes into play. Thus, charge separation is greatly enhanced.

A detailed description of the experimental aspects involved in the determination of efficiency for nanostructured systems is given in the experimental section of this report

Section 3

Experimental Section

To study the phenomena associated with the photosensitized and photocatalytic splitting of water, several measurements and experiments were performed. The ensuing sections describe in detail the apparatus and methods used in the current work.

3.1 Experiment Setup for Hydrogen Production

Figure 3.1: Reactor Setup for Hydrogen generation experiments

Figure 3.1 shows the overall reactor setup for carrying out steady state photocatalytic water splitting experiments. The photolysis experiments were carried out in a three-phase (S-L-G) photo-reactor. To facilitate the pick up of the photolysis-product gases, an inert gas (He) is fed continuously to the reaction chamber. Since the product concentrations are very small, a recycle loop is set up as shown to monitor the cumulative concentration over time. In the absence of the recycle loop, the inert gas is continuously fed to the reaction chamber and the actual product concentration is determined. The recycle pump employed was procured from Senior Flexonics Inc (60Hz Model MB21). The inert gas flow to the reactor system was controlled using a mass flow controller. To remove all water vapor from the product gases, the product gas stream was passed through a condenser fitted to the reactor. The coolant used in the condenser was water at room temperature. The effluent stream from the reactor is automatically analyzed by an online gas chromatograph (CARLE series- 400AGC). The cooling water stream serves the dual purpose of condensing water vapor from the effluent stream and simultaneously cooling the lamp jacket.

Reaction Chamber

Figure 3.2 shows a detailed view of the annular reaction vessel. The system was continuous with respect to the gas phase. The reaction vessel is all

glass and has a liquid volume of 750cc and a gas volume of 250 cc. The reaction mixture constitutes of a fixed charge of catalyst/water mixture. The solid phase (photo-catalyst) is suspended in the liquid phase (water) by magnetic stirring.

Figure 3.2: Reaction Vessel

The reaction temperature was monitored by the thermocouple. The catalyst concentrations ranged between 0.5 gm - 1 gm /liter and the inert gas flow rate was maintained at 1-3 cc/min (without recycle).

The energy source for irradiation was a 450W immersion type, medium pressure mercury arc UV lamp procured from Ace Glass Inc. The lamp was continuously cooled by a water jacket supplied with water at room temperature. The temperature inside the reaction vessel was measured by the thermocouple and was found to be 83 ° C. The experimental conditions were kept the same in

all the experiments in order to make comparisons meaningful. The system was purged for an hour with a Helium stream (10 cc/min) before each experiment. Experiments were performed both under UV and visible irradiation. To operate experiments in only the visible range, a sheet filter (Edmund Scientific cutoff 400nm) was wrapped around the chamber holding the lamp. Filtering out specific wavelengths of light is also possible by circulating "filter" solutions instead of water through the cooling jacket of the lamp.

3.2 Materials

Photocatalysts: The photocatalyst employed was TiO_2 (P25). It was obtained from Degussa Corporation. P25 contains both anatase(80%) and rutile(20%) forms of TiO_2 . Anatase is photoactive while rutile is not. XRD analysis of P25 shows two distinct peaks at 2θ values of 25.45 and 27.75 corresponding to the anatase and rutile forms. Surface area of the TiO_2 was determined using the BET technique and was found to be $52\text{m}^2/\text{g}$. The particle sizes are in the range of 25-50nm. More details of the preparation procedure and of the physical and chemical characteristics are described in the product information furnished by Degussa Corporation.

Metal Loading: Metal loading was always achieved using the photo-reduction technique. Photo deposition of metals²⁸ from solutions of their salts occurs at

semiconductor surfaces under irradiation with energy greater than the band gap of the semiconductor. Such deposition is based on the photovoltaic effect of semiconducting materials: band-gap illumination creates hole-electron pairs, and electrons are consumed for the reduction of metal ions while holes from the formation of O_2 from water or the oxidation of counterions. Once a small nucleus of metal is deposited on the semiconductor, it would function as a cathode of a short circuited photo-electrochemical cell, and the reduction of metal ions takes place around the metal nucleus.

In the current preparation, the metal precursor (soluble in water) was first added to water. To this precursor solution, TiO_2 was added. The addition of TiO_2 results in a milky white suspension. This suspension was placed in the reaction vessel described earlier. The suspension was then irradiated for a few hours while being magnetically stirred, to form the final catalyst. The precursor undergoes photo-reduction causing the metallization of the support(TiO_2). This technique has been adapted from Escudera et al²⁴. Experiments, to demonstrate the splitting of water using metallized TiO_2 , were performed *in situ* (photoreduction and hydrogen production measurements were performed simultaneously) without any further manipulation of the catalyst. The catalyst was recovered for characterization after the photolysis experiments by evaporation of water from the catalyst-water slurry at 40°C. For photosensitization experiments it was necessary to first metallize the TiO_2 and

then attach the dye sensitizer. In this case the metallization was performed as described above, but the catalyst was recovered by centrifuging the catalyst-water slurry. The exact metal loading was obtained after analysis by Galbraith Laboratories Inc.

Platinum was loaded by photo-reduction of platinic acid and tetra-amine platinum nitrate(TAPN) without any sacrificial agents. Platinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and TAPN were procured from Alfa Aesar. For a Pt loading of 1%, 24 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was added to 75 ml of water and 1gm of TiO_2 . The sample was then irradiated.

Palladium was impregnated similarly using palladium nitrate. Palladium nitrate was obtained from Alfa Aesar. Rhodium chloride, also obtained from Alfa Aesar was used as the precursor for Rh- TiO_2 .

Water: High purity water used as the reaction medium for all the experiments was procured from Fischer Scientific (Optima Grade). Water obtained directly from lab lines was used for cooling.

3.3 Photosensitizer Synthesis

An enumerated list of all the sensitizers synthesized and their properties and the relevant references are provided in the appendix. The following is a brief account of the preparation procedure for three sensitizers tested for

hydrogen production. The synthesis of photo-sensitizers and their attachment to TiO_2 was performed by Billy Davidson under the direction and supervision of Dr. Kenneth Nicholas at the Department of Chemistry, University of Oklahoma.

Preparation of the bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride

0.156 g CuCl (1.58 mmol) was dispensed in a dry box to a 100 mL round-bottom flask equipped with magnetic stirring bar. To this flask, 25.0 mL of dimethylformamide (DMF) solvent was added under nitrogen. A stoichiometric amount consisting of 1.50 g 2,2'-biquinoline-4,4'-dicarboxylate (3.16 μmol) was added while stirring. The 2,2'-biquinoline-4,4'-dicarboxylate was a commercial staple from Aldrich and used without further purification. Within 10 minutes, the solution became dark purple in color. After overnight stirring, the reaction was ended. Ether was added to precipitate a dark purple solid, which was filtered via water aspirator with a 10-15 M glass frit. The product, bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride, was dried in vacuum at 50° C for 3 hours to evaporate residual DMF solvent and yielded 1.53 g of product.

Yield: 92.4%.

Preparation of di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II)

0.030 g of anhydrous FeCl_2 (0.2375 μmol) was added to 10.0 mL of DMF in a 100 mL round-bottom flask equipped with magnetic stirring bar. A stoichiometric amount consisting of 0.116 g 2,2'-bipyridine-4,4'-dicarboxylic acid (0.475 μmol) was then added under nitrogen. The 2,2'-bipyridine-4,4'-dicarboxylic acid was a commercial staple from Aldrich and used without further purification. Within 15 minutes, a dark purple color remained throughout the reaction. After overnight stirring, the reaction was ended. Addition of ether precipitated a purple solid, which was filtered via water aspirator by a 10-15 M glass frit. The product was dried in vacuum at 50°C for 3 hours to evaporate residual DMF solvent and yielded 0.130 g of intermediate product (0.211 mmol), dichlorobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II) (Yield: 89.0 %). This intermediate product was then heated to 100°C for 5 hours with a stoichiometric excess of KCN (0.660 g, 1.01 μmol) in 10.0 mL of DMF within a 100 mL round-bottom flask. After allowing the reaction to cool, ether was added to precipitate the final product, di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II). This product was filtered via water aspirator by a 10-15 μm glass frit and dried in vacuum at 50°C for 3 hours to remove any residual DMF solvent. Yield: 96.7 %.

Preparation of di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II)

The procedure for the synthesis of this dye was slightly modified from literature.^{4,5} Briefly, 0.0803 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.307 μmol) was added to 15.0 mL of DMF solvent while stirring in an inert N_2 atmosphere in a 100 mL round-bottom flask. To this, a stoichiometric amount of ligand, 0.150 g (0.614 μmol) of 2,2'-bipyridine-4,4'-dicarboxylic acid (Aldrich), was added. The mixture was heated to 90°C for 5.0 hours. After allowing the reaction to cool, 75% of the DMF volume was evaporated from the brownish-orange solution by a vacuum pump at elevated temperature. The addition of ether precipitated a brownish-orange solid, dichlorobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium (II), which was filtered via water aspirator with a 30 μm glass frit (0.191 g, 0.2892 μmol). This solid was dried in vacuum at elevated temperature to remove residual DMF. Yield: 94.2%.

To this intermediate product, an excess of KCN was added (0.0904 g, 1.39 μmol), also in 15.0 mL of DMF solvent in a 100 mL round-bottom flask. The reaction was carried out under an N_2 atmosphere with magnetic stirring at 90°C for 6.0 hours. After allowing the reaction mixture to cool, a dark brown precipitate is formed after addition of ether. Filtration via water aspirator with a 10-15 μm glass frit separated the precipitate from the liquid. Drying in vacuum at

elevated temperature produced 0.0631 g of final product, dicyanobis(2,2'-bipyridine-4,4'-dicarboxylate) ruthenium (II). Yield: 36%.

Sensitizer Attachment to TiO₂

All the three photosensitizers are attached to the titania in an identical manner. The attachment process utilizes the coulombic interaction between the negatively-charged carboxylate groups of the dyes and the positively-charged titania surface occurring at a pH of 4-5. The procedure is as follows:

1.0 g of TiO₂ (12.5 μ mol) was dispensed into 200 mL of water at pH 4-5 while magnetically stirring. Distilled water was acidified drop by drop with diluted HCl to increase the acidity to the desired pH. To this milky-white mixture, 5.0×10^{-5} moles of the selected dye is added. All dyes showed strong solubility in water at this pH, as the dissolution of the dye was complete within 5 minutes. Once the dye had dissolved into solution, it quickly adhered to the TiO₂ surface. The mixtures were left to stir overnight. Centrifugation at 6,000 rpm separated the dyed TiO₂ pellet from the colorless supernatant. The samples were then dried under vacuum before testing. This adsorption technique differs from literature techniques in that the de-protonated forms of the dyes are being used rather than the protonated forms. This technique relies on physisorption as opposed to chemisorption of the dye to the TiO₂.

3.4 Characterization Techniques

Cyclovoltammetry³⁹

Cyclic Voltammetry is invariably the first technique employed in any electrochemical investigation of dye materials since it is easy to perform and provides quick and useful information about the system under investigation.

Figure 3.3: Cyclovoltammetry Experimental Setup

The experiment is conducted in a stationary solution (figure 3.3) and thus relies on diffusion for transport of material to the electrode surface. The potential of the working electrode is swept from a value E_1 at which it cannot undergo reduction to a potential E_2 , where the electron transfer is driven rapidly. The applied potential E is a function of the speed at which the potential is swept and the time of sweep. The direction of sweep is then reversed and the electrode potential is scanned back to its original value, E_1 . A typical cyclic voltammogram is shown in the figure 3.4.

The form of the current voltage behavior can be understood by considering the equation in figure 3.4, in which the electrolyte solution contains an electroactive species A, which can undergo

Figure 3.4: A typical Cyclic Voltammogram

reduction to form B. Assuming that the A/B couple has irreversible electrode kinetics, initially no current is passed since the applied potential is not great enough to induce electron transfer. But as the potential is swept to more reducing potentials it reaches values that are capable of inducing reduction of A to B and current starts to establish. The current rise is exponential initially, but as more negative potentials are reached the exponential nature decreases and a maximum is reached. The current flow reflects not only the rate of reduction but also the surface concentration of the electrolyte on the at the electrode. As the potential becomes more negative, although the k_{red} increases the surface concentration of A decreases and is not readily replenished causing the current to drop.

On reaching a value E2 the potential is swept back , oxidizing species B, formed at the electrode during the forward scan, back to species A. A current in

the opposite direction to the forward scan, is observed due to the oxidation. This current increases initially since a high concentration of B is present in the diffusion layer and the kinetics for the conversion of B to A become more favorable as the potential becomes more positive. Gradually, all of the B present in the diffusion layer is reconverted to A and the current drops to zero.

Application

The applicability of Cyclic Voltammetry in studying photosensitizers is enormous. Cyclic voltammetry is the electrochemical analogue to a metal to ligand charge transfer (MLCT). The determination of the oxidation and reduction potentials of the sensitizer substances would provide the relative positions on the standard NHE energy scale, of the semiconductor band edges and the redox potentials. This information tells us if the transfer of electrons from the sensitizer to the semiconductor is energetically feasible. Information on whether the sensitizer can be readily re-oxidized is also obtained. The absence of any of the two redox peaks signifies irreversibility.

In the current work, cyclic voltammetry on the synthesized dyes was performed by Billy Davidson under the guidance of Dr. Ken Nicholas at the Department of Chemistry, University of Oklahoma. Cyclic voltammetry has been performed on the Iron and Copper-based sensitizers. The Fe-based dye

revealed a reversible scan from which the formal reduction potential was calculated. The Copper-based dye was tested in its deprotonated forms and showed an irreversible oxidation to the Cu (II) oxidation state. Due to solubility problems, cyclic voltammetry studies have not been performed on the protonated form of the Ruthenium-based dye. In the experiments conducted, Ag/AgCl electrode was used as the standard electrode($E^0=0.2221\text{V}$ w.r.t. Standard Hydrogen Electrode).

UV-Visible Spectroscopy

Sample Preparation

All photocatalysts were pelletized in a cylindrical sample holder for diffuse reflectance studies. For analysis after reaction, the catalyst slurry from the photocatalytic reactor was centrifuged and the solid residue was dried and analyzed by UV-VIS. The supernate from the centrifuge was also collected for analysis.

Analysis

UV-visible spectrophotometry was used to determine the spectral response of the photo-catalysts. The Spectrophotometer employed was procured from Shimadzu Inc., (Model UV-3001). Photometric studies were performed by

diffuse reflectance on dry catalyst powders.. The sensitizer/photocatalyst is irradiated with different wavelengths of light in the range 200-800 nm. The resulting absorbance spectrum gives the wavelength of light at which there is maximum spectral response i.e., maximum absorption and the relative light harvesting ability of each photocatalyst at a particular wavelength is obtained.

In addition, by performing the UV-VIS analysis on the support and the sensitizer separately, the contribution of the support and the sensitizer to the overall spectral response of the photocatalyst is determined. The red-shifting of the maximum visible absorbance gives insight into the electronic changes involved when TiO_2 attachment to the photosensitizer takes place. To observe any changes in the spectral response of the photocatalyst during photolysis the UV-VIS analysis is done both before and after each experiment.

Transmission Electron Microscopy

Metallized TiO_2 catalysts were studied using Transmission Electron Microscopy(TEM). The photocatalyst were sieved and suspended in iso-propyl alcohol and then transferred onto copper microscopy grids. The grids were than analyzed under an electron microscope at the Department of Microbiology, University of Oklahoma. Appropriate sample sections of the photocatalyst were than photographed. Information about the metal-semiconductor distribution

and the physical nature of the catalysts was obtained. The crystal structure of the catalyst was also examined.

X-ray Diffraction

Information about the crystallinity of the photocatalysts was obtained using X-ray diffraction. The equipment used was a powder diffractometer. The ratio of rutile to anatase forms of TiO_2 in the photocatalysts was also obtained using x-ray diffraction.

Chemisorption

Metal dispersion on the support(TiO_2) was obtained by chemisorption experiments. Chemisorption of hydrogen was performed on Pt- TiO_2 for different loadings of platinum. The catalyst were pre-treated in Hydrogen at 200°C for two hours. Then the sample was heated in vacuum(10^{-6} torr) for 1hr and cooled down. Hydrogen adsorption was then performed at room temperature.

pH Analysis

The pH of the precursor solutions was measured using a Corning pH meter. Due to the differences in specific rates of hydrogen production with different precursors for platinization, it was suspected that the acidity of the

precursor solutions may have an affect on the support. The evolution of pH with time after the addition of TiO_2 to the precursor solutions gives the nature of the interaction between the support and the precursor. The evolution of pH when H_2PtCl_6 precursor solutions were contacted with TiO_2 was measured for different initial pH of the precursor solutions

Photo-Electrochemical Analysis

Thin Films

Thin films of TiO_2 were made on conducting glass (resistance $8\text{ohm}/\text{cm}^2$),

Figure 3.5 Process of Film Making

using the technique of Naseeruddin et al¹¹. These films were then soaked overnight in the dye solutions. The glass is conductive on only one side and it is onto this side that the TiO_2 /Sensitizer film is deposited. The films are about 1sq

cm in area. The film thickness is in the order of 5-10 micrometers. The TiO_2 /Sensitizer film on the conductive glass forms the working electrode. The counter electrode is also made using the conductive glass. Platinum metal is electrochemically deposited on conductive glass. The electrolyte used is platinic acid solution(1N) at a pH of 1-1.5. Silver electrode is used as the reference. A voltage of -0.7 V is applied across a piece of platinum wire and the conductive glass piece.

Figure 3.6: Measurement of Short Circuit Current and Open Circuit Voltage

The Platinum coated glass and the TiO_2 coated glass form the cathode and anode respectively. These are connected as shown and placed in the path of a light beam. The currents thus generated give a measure of the electron injecting capabilities of the dye. Spectroscopic analysis with the UV-VIS is performed before and after illumination and thus any degradation of the dye

upon illumination can be easily observed. Before illumination an electrolyte is added in such a way that it is sandwiched between the two electrodes. The electrodes are connected to leads which are connected to the potentiometer, which measures the zero current voltage and zero voltage current. The photocurrent generated by the dye upon illumination is a direct measure of the readiness with which injection of electrons from the dye to the semiconductor occurs. An accurate picture of the efficiency of electron injection of a dye cannot be based solely on the photocurrent, but should be drawn only from quantum yield calculations with the help of an Action Spectra and the Absorption Spectrum. The light harvesting ability of the dye, the photon flux at any particular wavelength and the photo-current at that wavelength together quantify the quantum efficiency.

The Action Spectrum of the dye is measured using the above described electrode set up and a monochromator. The monochromator varies the wavelength of the light incident on the semiconductor electrode from 400-700 nm and corresponding photocurrents are processed by a potentiostat and a final curve is generated.

The UV-VIS absorption spectrum of the dye and the action spectrum of the dye together can yield the quantum efficiency of the dye. By knowing the intensity of the incident photons, their wavelength and the photocurrent

generated, one can estimate the number of electrons generated per photon incident. The quantum efficiency of photochemical processes are usually on the order of 5-10%.

Section 4

Results and Discussion

The photo-assisted splitting of water using the photocatalysts described in the previous sections has been studied. Most water photolysis experiments involving aqueous suspensions of photocatalysts described in literature, have been carried out in small batch reactors. These devices only allow the study of the system in the non-steady state and hence the dynamic behavior of the photocatalytic system cannot be studied. The photocatalytic reactor setup used in the current work was a three-phase slurry batch reactor with a continuous gas phase. A detailed description of the apparatus and the experimental setup is given in the experimental section of the report.

4.1 Ultra Violet Experiments

The experimental setup and the reactor allowed the continuous monitoring of the hydrogen production over the photocatalysts. All the experiments under UV irradiation were performed on metal modified semiconductor materials. The chief metals employed were Platinum, Palladium and Rhodium. The semiconductor material was always TiO_2 . Characterization on the catalysts was done to gain insight into the nature of interaction of the metal with the semiconductor.

In order to make comparisons meaningful for different catalysts the specific rate of hydrogen production has been defined as the μmols of hydrogen produced over the entire experiment per gram of catalyst, expressed on a per hour basis.

As a first step the photocatalytic activity of TiO_2 was tested. It was observed that after four hours of irradiation there was no evidence of hydrogen evolution. Escudero et al²⁴ have performed similar experiments and have concluded that TiO_2 , by itself is not active towards photocatalytic water splitting under uv-irradiation.

4.1.1 Pt- TiO_2

Preliminary studies were performed using Pt- TiO_2 photocatalyst for water splitting under uv irradiation. A large reactor (1000 ml volume) with 800 ml of water was used and 1 gm of TiO_2 was added to it. Enough platonic acid precursor was added to achieve a platinum loading of 2%. Platinization and water splitting were carried out *in situ* and simultaneously. The reactor temperature was constant at 80°C. The photon flux in the UV range was calculated using the lamp specifications, spectra and reactor dimensions and was found to be 1.5×10^{20} photons/sq.cm-sec. The hydrogen production (figure 4.1) increased steadily during an induction period and then remained almost

constant with time. Low purge gas (He) flow rate and dead volume of the tubing carrying the sample to the GC, cause the initial delay in the appearance of hydrogen production. The subsequent induction period can be attributed to the process of photo-platinization. Considerable oxygen evolution was also observed. The molar ratio of hydrogen to oxygen evolution was 2.3. This is higher than the stoichiometric ratio of 2. Similar observations have been reported in the literature^{25,28}. The lower oxygen evolution is attributed to the fact that the oxygen evolution reaction (hole scavenging process) is a four-electron process while the hydrogen production step is a single electron process. In addition, some of the oxygen evolved is used to fill vacancies on the TiO_2 surface.

Fig. 4.1 Water Splitting

The lamp was switched off after 16 hrs and the reactor was allowed to cool off. The lamp was switched back on after 4 hrs and the figure shows the evolution of photo-products on second illumination. The photocatalyst under second illumination behaves similar to the fresh catalyst except that the hydrogen production maximum is reached faster. Here, again the initial delay in the appearance of hydrogen production is due to the lag time caused by the low purge gas flow rate through the dead volume of the tubing. The activity of the catalyst appears to remain unchanged. Escudera et al²⁴ have reported that TiO₂ does not deactivate even after prolonged exposure to uv irradiation. The specific rate of hydrogen production was about 23 $\mu\text{mols/hr-gm cat.}$ The

recovered catalyst was studied by diffuse reflectance UV-Vis spectroscopy. The absorption spectra are shown in the figure 4.2. The absorption spectrum shows an increase in the intensity of absorption under visible and near uv wavelengths,

but does not show any new maxima. It is evident that the absorption characteristics of the TiO_2 are not significantly altered by platinization.

The large volume reactor was cumbersome, prone to leaks and had a large gas volume. Due to these problems with the large volume reactor, a similar but

smaller reactor (150ml vol.) was built and all further experiments were conducted in it. The photon flux in the small reactor was estimated to be 3.4×10^{19} photons/sec. It was our intent to study the effect of platinum loading on the hydrogen production capabilities of the photocatalyst. Three different catalyst samples of Pt-TiO₂ with platinum loading 0.1%, 0.5% and 1% (wt %) were tested for hydrogen production. The amount of TiO₂ was 500mg and the catalyst was suspended in 75ml of water, in all cases. Platinic Acid($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was used

as the precursor for platinization. The method for catalyst preparation was photo-platinization. The platinization of TiO_2 and the photo product measurements were done *in situ*. Figure 4.3 shows the evolution of hydrogen with illumination time using the three catalysts. The illumination was carried out for 12 hours. The initial delay in the appearance of hydrogen is due to the lag time mentioned earlier. Each of the catalysts shows an induction period for hydrogen production, which can be attributed to the fact that hydrogen production is not establish fully until platinum deposition is completed.

The 0.5%Pt- TiO_2 catalyst showed highest activity. Strangely, The 0.1% and the 1% Pt- TiO_2 showed similar lower activity. Moreover, none of the catalysts showed activity similar to the catalyst in the large reactor. It is also important to note that the catalyst used in the large reactor had a higher platinum loading (2%). The specific rates of the respective catalysts are given in table 4.1. The higher activity of the 0.5% Pt- TiO_2 suggests an optimum platinum loading value for maximum hydrogen production in the smaller reactor.

Table 4.1

Catalyst	Specific Rate ($\mu\text{mols/hr-gm catalyst}$)
0.1 % Pt- TiO_2	7.7208
0.5 % Pt- TiO_2	14.6548
1.0 % Pt- TiO_2	6.5504
2.0% Pt- TiO_2 (large reactor)	23.5015

Mills and Porter²⁵ have reported that hydrogen production using platinized TiO₂ suspensions is maximized at an optimum loading of 0.5%. They further suggest that Pt deposit levels >0.5% are unnecessary and may be detrimental towards the rate of H₂ production. However, they do not speculate on the possible reasons for the optimum platinum loading. In the current work, we have attempted to establish possible reasons for the above behavior of platinized TiO₂ systems. Experiments were also performed using Pt-TiO₂, using tetra amine platinum nitrate (TAPN) as the platinum source. The method of platinization was again photo-platinization. The loading levels of platinum were 0.5% and 1%. The Hydrogen evolution with irradiation time is plotted in figure 4.4. In this case, the hydrogen production with the 1% platinum loading was much more than the 0.5% platinum loading. The specific rates of 0.5% and 0.1% Pt-TiO₂ were 4.6 and 8.9 $\mu\text{mols/hr-gm catalyst}$ respectively. From the results it is clear that the precursor for platinization does have an effect on the activity of Pt-TiO₂ towards hydrogen production via water splitting.

Fig. 4.4 Hydrogen production with Pt/TiO₂ under UV

The catalysts were characterized using X-ray diffraction and Transmission electron microscopy. XRD data revealed no metal peaks, due to the low loading of the metal (figure 4.5). However, a characteristic drop in the anatase peak intensity with increased platinum loading was observed. The rutile peak on the other hand showed no change. The rutile/anatase ratios in the photocatalysts tested are tabulated in table 4.2.

Catalyst	Rutile/Anatase
0.1 % Pt-TiO ₂	0.159248
0.5 % Pt-TiO ₂	0.179516
1.0 % Pt-TiO ₂	0.282656
0.5% Pt-TiO ₂ + HCl	0.219282

Table 4.2

The loss in peak intensity suggests a loss of crystallinity. This could be possible only if the precursor (platinic acid) was in some way attacking the TiO₂. This type of acid attack has been proposed by Santacesaria et al⁴⁵ for the

impregnation of Platinum using H_2PtCl_6 precursor on Al_2O_3 . It has been suggested that the acid attack may not only involve the partial dissolution of the support, but also a subsequent re-deposition during subsequent evaporation of the solution for analysis of the catalyst.

The amounts of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ used are 12.5 mgs and 25 mgs per gram of TiO_2 , for 0.5% and 1% loading, respectively. The pH of platinumic acid solution before the addition of TiO_2 is about 3.43 for the platinum loading of 0.5% and the pH of the solution for 1% loading is about 3.14. The isoelectric point of TiO_2 occurs at a pH of 4. Hence, it is reasonable to expect that the platinumic acid (PtCl_6) may attack the TiO_2 . Figure 4.6 shows the hydrogen production when HCl was added to Platinumic acid solution with pH 3.43 (for Pt loading 0.5%) to make the pH to 3.14 (equivalent for 1% loading). In this case hydrogen production rapidly

decreases. XRD analysis of the catalyst showed a drastic decrease in the anatase peak intensity (fig 4.5). The peak intensity of the 1%Pt-TiO₂ was comparable to the peak intensity of the 0.5%Pt-TiO₂+HCl.

It has been reported by Resasco et al⁴⁴ that the interactions between the metal precursor species and the support (TiO₂) during impregnation processes, may play a decisive role in determining the resulting properties of the catalysts. Several possible types of interactions have been identified. First, there is adsorption of the metal precursor species on the oxide support. The adsorbed species may then undergo subsequent surface reaction with the support. Finally, when the impregnating solution is acidic, the surface of the support may be attacked causing partial dissolution of the support itself. Resasco et al⁴⁴ have studied the interaction of RuCl₃ precursors on TiO₂ and propose that the adsorbed species undergo a ligand exchange reaction on the surface by which some chloro ligands are exchanged by surface OH groups. It is plausible that an interaction similar to the one suggested by Resasco et al occurs in the current H₂PtCl₆/TiO₂ system. The proposed interaction mechanism is as follows:

(a) Anion Adsorption

(b) Ligand exchange reaction

The above scheme suggests the variation of pH of the impregnating solution during the deposition process. Initially, as the anion adsorption proceeds, the pH should increase since H^+ are consumed from the solution. Once the ligand exchange reaction sets in, H^+ ions are evolved into the solution and hence the pH should decrease. This is indeed observed to be the case. The evolution of pH with time after the addition of TiO_2 to the H_2PtCl_6 solution has been monitored for three different starting pH values. As shown in figure 4.7, the pH increased rapidly from the initial value reaching a maximum in a few seconds and then decreased gradually. The continued decrease of the pH with increase in contact time of the TiO_2 with the solution is attributed to the attack of the surface.

figure 4.7 pH variation with different initial pH

In the current study, the pH variation and the phenomena involved in the above behavior of TiO₂ in H₂PtCl₆ solutions has been modeled using kinetic rate expressions. The following reactions have been assumed to occur:

(1) *H⁺ and ML⁻ Equilibrium*

(2) *Anion Adsorption*

(3) *Ligand Exchange*

(4) *HL Equilibrium*

(5) *Surface Attack*

The rate expressions for each of the reactions are also shown. Ti-OH is considered as the surface site (S). The total surface site concentration (C_T) is the sum of vacant site concentration (C_S), the concentration of the complex TiOHML_x (C_{HMLS}) and the concentration of the complex TiOHML_{x-1}OTi

(C_{HMLSS}). The rate of the surface attack is assumed dependent only on the concentration of HL (C_{HL}) as the amount of TiO_2 is in large excess. The concentration of H^+ (C_H) contributes directly to the pH of the solution. All the rate constants were taken to be of the form:

$$k = k_o e^{\alpha t + \beta}$$

The concentrations of the various species were calculated using the following expressions.

$$\begin{aligned} \frac{dC_H}{dt} &= -r_1 + r_4 & \frac{dC_{HML}}{dt} &= r_1 - r_2 & \frac{dC_{ML}}{dt} &= -r_1 \\ \frac{dC_{HML.S}}{dt} &= r_2 - r_3 & \frac{dC_{S.HML.S}}{dt} &= r_3 & \frac{dC_{HL}}{dt} &= r_3 - r_4 - r_5 \\ \frac{dC_L}{dt} &= r_4 & \frac{dC_{TiO_2}}{dt} &= -r_5 & C_S &= C_T - C_{HML.S} - C_{S.HML.S} \end{aligned}$$

Least squares minimization technique was employed to fit the theoretical model to the experimental data. Microsoft Excel was used to compute the model.

Table 4.3

R1		R2		R3		R4		R5	
$\alpha 1f$	-14.2924	$\alpha 2f$	-0.66212	$\alpha 3f$	-1.17832	$\alpha 4f$	-1.015	$\alpha 5f$	0
$\beta 1f$	6.549147	$\beta 2f$	2.520147	$\beta 3f$	4.609277	$\beta 4f$	3.13524	$\beta 5f$	2
$\alpha 1b$	-6.39061	$\alpha 2b$	-1.06019	$\alpha 3b$	-1	$\alpha 4b$	-0.9996	$\alpha 5b$	0
$\beta 1b$	2.579936	$\beta 2b$	4.003615	$\beta 3b$	3	$\beta 4b$	3.00037	$\beta 5b$	0

The rate constants determined through the model are shown in the table 4.3.

The experimental values and the values determined by the model are

Fig 4.8 Model and Experimental pH values

Fig 4.9 Model and Experimental pH values

plotted in figures 4.8,4.9 and 4.10. All the rate constants are the same for all the plots. The initial H^+ ion concentration and the equilibrium values of C_{ML} (metal-ligand complex concentration) and C_{HML} ($H^+ML_x^-$ concentration) are the only values different in each of the plots. The variation of concentration with time for the various species in the reactions for an initial pH of 3.15 is shown in figures 4.11-4.17.

Fig 4.10 Model and Experimental pH values

Fig 4.11 Hydrogen Ion Concentration

The hydrogen ion concentration first decreases and then increases and agrees with the predictions of the model. The site concentration steadily decreases with time while the concentration of the complex $TiOH-ML_{x-1}-O-Ti$ increases with time. The concentration of the intermediate complex $TiOH-ML_x$ first increases and then decreases, as it is consumed to form $TiOH-ML_{x-1}-O-Ti$.

The excellent agreement between the model and the experimental values supports the conclusion that the attack of the support (TiO_2) by the precursor

Fig 4.12 Site Concentration

Fig 4.13 H+ ML-

Fig 4.14 Ti-OH-HMLx-O-Ti

(H_2PtCl_6). The apparent differences in the activity of the Pt-TiO₂ photocatalysts may be due to the fact that the attack of the support is more pronounced at higher metal loadings due to lower pH levels. It is, however, unclear why the anatase form of TiO₂ is preferentially attacked over the rutile form.

4.1.2 Chemisorption

Chemisorption studies were performed on the Pt-TiO₂ catalysts. All the catalysts were pretreated with hydrogen at 200°C for 1.5 hrs. The catalysts were then heated under vacuum for 2 hrs at 200°C. The system was then cooled down to room temperature and H₂ adsorption was performed. Table 4.4 shows the dispersion of platinum on TiO₂ for three different loadings.

Catalyst	H/Pt
1%Pt/TiO ₂ (0.31gr) H ₂ PtCl ₆ precursor	0.24
0.5%Pt/TiO ₂ (0.392gr) H ₂ PtCl ₆ precursor	0.34
1%Pt/TiO ₂ (0.300gr) TAPN precursor	0.12

Table 4.4

The results show that the platinum dispersion is higher for the 0.5%Pt-TiO₂ catalyst than for the 1% Pt-TiO₂ when H₂PtCl₆ is used as the precursor. However, when 1%Pt-TiO₂ is prepared using TAPN as the precursor, the dispersion is much lower. The higher dispersion could explain in part the higher

activity of the 0.5%Pt-TiO₂. Escudera et al²⁴ have concluded that the higher the dispersion of the metal on the support the higher the activity of the catalyst towards hydrogen production via water splitting.

4.1.3 TEM Analysis

Transmission Electron Microscopy was performed on the Pt-TiO₂ photocatalysts (precursor H₂PtCl₆). Fig 4.18 shows the TEM pictograph of 0.5%Pt-TiO₂ photocatalyst. The pictograph shows the lack of a planar structure of the TiO₂. The surface of the TiO₂ appears to be covered by deposits. It is possible that the surface deposits in Pt-TiO₂ are due to the surface attack of the precursor and subsequent "re-deposition" of TiO₂.

The metal particles appear well dispersed and confirm the dispersion values obtained by chemisorption. Some of the metal particles are covered by the TiO_2 . Fig 4.19 shows the TEM pictograph of TiO_2 alone under the same magnification of Fig 4.18. Here, the TiO_2 particles show planar structure and no

deposits can be seen. The particle size also appears to be smaller. The differences in the two pictures also suggest that attack of the TiO_2 occurs with H_2PtCl_6 precursors.

4.1.4 Pd-TiO₂ and Rh-TiO₂

Pd-TiO₂ and Rh-TiO₂ were tested in experiments similar to the experiments with Pt-TiO₂. The precursor used for Rh-TiO₂ was RhCl₃. Rh-TiO₂ showed no activity towards hydrogen production. RhCl₃ is known to attack TiO₂ (Resasco et al)⁴⁴ and this has been observed by the XRD study of the Rh-TiO₂ catalyst. Figure 4.20 shows the anatase peak intensities for TiO₂ and 0.5%Rh-TiO₂. The severe drop in peak intensity and due to the loss of crystallinity may be the primary reason of the inactivity of Rh-TiO₂ towards hydrogen production. The activity of Rh-TiO₂ towards water splitting could however be evaluated using a different precursor. Sato et al²⁷ reported that Rh based photocatalysts are more active than Pt-based catalysts. More studies need to be performed on Rh-TiO₂ using alternative precursors to determine the intrinsic activity towards water splitting.

Pd-TiO₂ was made using PdNO₃ as the precursor. Hydrogen production experiments were conducted on 0.1%, 0.6% and 1.5% Pd-TiO₂. The 1.5% Pd-TiO₂ showed no activity towards hydrogen production. The hydrogen production when 0.6% and 0.1% Pd-TiO₂ were used is shown in figure 4.21. The activity of the 0.1% Pd-TiO₂ was higher than the activity of the 0.6%Pd-TiO₂. However, the activity of the palladium catalysts was much lower than the platinum-TiO₂ catalysts. The different rates of hydrogen dissociation on platinum and palladium may be the reason for the disparity in the activity⁴⁸.

4.1.5 Conclusions

The pH analysis experiments and modeling complemented by the Transmission Electron microscopy results, all suggest that when TiO₂ is placed in contact with H₂PtCl₆ precursor solutions, several phenomena occur leading to the attack of the TiO₂ surface. This interaction between the precursor and support may adversely affect the activity of the catalyst.

Catalyst	Specific Rate (μ mols/hr-gm catalyst)
0.1 % Pt-TiO ₂	7.7208
0.5 % Pt-TiO ₂	14.6548
1.0 % Pt-TiO ₂	6.5504
0.5% Pt-TiO ₂ (TAPN)	4.6194
1% Pt-TiO ₂ (TAPN)	8.9014
2.0% Pt-TiO ₂	23.5015

Table 4.5

In the current work, different specific rates of hydrogen production via water splitting for different loadings of platinum have been observed(Table 4.5). This may be due to the fact that the support is attacked to a greater extent at a higher loading (more precursor)leading to lower pH and hence is less active. The increase in the specific rate with platinum loading, when TAPN (a neutral precursor) is used in place of H_2PtCl_6 supports a conclusion that the disparity in specific rates has more to do with the "activity" of the support than the platinum loading when H_2PtCl_6 is used as a precursor. In the large volume reactor the pH of the precursor solution is very low even though platinum loading is higher. This would lead to a lower extent of attack of the catalyst and hence better activity.

4.2 Visible Light Experiments

The main goal of all the experiments under visible irradiation was to address the various issues pertaining to the applicability of dye sensitization of wide band gap semiconductors (TiO_2) for the purpose of hydrogen generation via water splitting. Several researchers have been investigating the application of polypyridyl metal complexes as photosensitizers. However, most of these efforts have dealt primarily with Ruthenium polypyridyl complexes and their analogues. Ruthenium complexes, although highly efficient, are very expensive. The School of Chemical Engineering and Material Science and the Department of Chemistry at the University of Oklahoma, have embarked on a research effort to evaluate alternative cheaper photosensitizers for the purpose of water splitting using visible light.

Iron and Copper are much cheaper materials when compared to Ruthenium. The objective was to synthesize and test polypyridyl complexes of iron and copper and test their feasibility in water splitting experiments. Preliminary work involved synthesis of iron and copper based dyes, their testing for hydrogen production and determination of redox potentials of the dyes. Other work involved the modification of these dyes and characterization of their electrochemical behavior.

4.2.1 Photosensitizer Synthesis

Photosensitizer synthesis was an important part of the research. Efforts were directed towards the synthesis of Iron and Copper complexes analogous to the Ruthenium polypyridyl and biquinoline complexes. Ruthenium complexes have been widely characterized for photophysical and photochemical properties and served as the basis for the synthesis of the iron and copper complexes. Some of the synthesis procedures employed originated in our labs while other have been adapted from literature. The information on the complexes that have been synthesized have been tabulated in the appendix.

The literature references containing the sensitizer synthesis are given in the appendix and the modifications to any of the procedures are also mentioned. After testing of the above three sensitizers was completed, it was evident that none of them showed any activity for of hydrogen production via water splitting under the conditions examined in this study. The analysis of these dyes, to determine the reason for the in-activity are dealt with in a separate section.

4.2.3 Photo-Response of the Dyes

Fig. 4.22 UV_VIS Absorption Spectra

The chief physical behavior considered in the choice of dye materials is their responsivity to visible light. UV-VIS spectrometric studies of the dyes synthesized all show strong absorption in the visible region. As mentioned earlier, the strong absorbance is due to metal to ligand charge transfer in the dye complexes. On attachment to TiO_2 (no spectral response in the visible), the spectral response of the TiO_2 -dye system is greatly enhanced in the visible region. It is this increased response that makes these systems attractive for solar applications. Figure 4.22 shows the UV-VIS spectra of the dyes synthesized. The di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II) complex shows exceptional absorption in the visible range and is better than the di-cyanobis(2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II) sensitizer in

terms of light harvesting capability. The absorption and light harvesting capabilities of bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride seem to be similar to those of the ruthenium complex. The respective absorption maxima are summarized in table 4.6.

Table 4.6 Sensitizer	Wavelength of Maximum Absorption
di-cyanobis(2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II)	496nm
bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride	558nm
di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II)	542nm
Tris(2,2'-bipyridine)ruthenium(II) dihexafluorophosphate	448nm

From the UV-VIS spectra (Figure 4.22) and table 4.6, it is evident that the absorption maxima undergo a shift to higher wavelengths after the attachment of the dye to TiO₂. di-cyanobis(2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II) has an absorption maximum of 496 , but this maximum is at about 510nm after attachment to TiO₂. Similar, shifts can be observed with the iron and copper based sensitizers. This shift is known as the red shift and has been reviewed extensively^{7,20}.

4.2.4 Hydrogen Production

The following four sensitizers were the only ones tested for hydrogen production:

di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II)

bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride

di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II)

Tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate

All the above dyes were attached to TiO_2 (P25) in the form obtained from Degussa Corporation. This attachment technique differs from literature techniques in that the de-protonated forms of the dyes are being used rather than the protonated forms. This technique relies on physisorption as opposed to chemisorption of the dye to the TiO_2 . A discussion of the attachment is presented later.

None of the above sensitizers- TiO_2 shows activity towards water splitting when used without any sacrificial agents. One experiment was performed using EDTA as a sacrificial agent. di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II) was employed as the sensitizer. The hydrogen production in this case is shown in figure 4.23. Hydrogen production was not observed until after 3hrs of irradiation.

It is important to note that the TiO₂ material used differs from the materials in most of the research articles in the area⁴⁻¹⁸. Most researchers in the area employ either single crystalline, colloidal or nano-crystalline materials. The particle sizes of TiO₂ in the current study are of the order of 25nm and are much larger than typical sizes employed. Gratzel et al⁴ have reported the sustained production of hydrogen using TiO₂ sols and tris-ruthenium bipyridyl complex. A similar sol was prepared and the tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate complex was used as sensitizer. However, the hydrogen production could not be reproduced in our lab.

It must be mentioned here that the system employed by Gratzel et al¹⁴ involved the use of flocculating agents and surfactants in the reaction mixture. The tests performed in our laboratory did not include these agents

as it is possible that the decomposition of the agents themselves may result in hydrogen production thereby masking production (or lack of production) due to water splitting. The different results obtained in this study may be due to the lack of flocculating agents and surfactants.

Several reasons can be cited for the lack of activity towards hydrogen production in the Pt-TiO₂/Sensitizer systems. Relative positions of the redox potentials, TiO₂ particle-size and mode of sensitizer-semiconductor attachment are the most important. Each of these aspects is addressed in the ensuing sections.

4.2.5 Relative Redox Potentials

Figure 4.24: Ideal relative position of dye redox potentials, semiconductor band edges and water redox potentials

By far the most important criteria in determining the applicability of a dye complex to water splitting is the relative position of dye redox potentials with respect to the semiconductor band edges and the redox potentials of water. As was mentioned earlier, the conduction band edge of the semiconductor and the oxidation potential of water must be more positive than the reduction potential of the dye sensitizer. In addition, the reduction potential of the water must be more negative than the oxidation potential of the dye sensitizer. This ideal setting is illustrated in the figure 4.24. It is obvious that the redox potentials of the dye must span the redox potentials of water.

The most widely used means for the determination of the redox potentials of sensitizer complexes is cyclic voltammetry. Cyclic voltammetry has been performed on the dyes whenever solubility was not a problem. All cyclovoltammograms in the current study have been referenced to the Ag^+/AgCl electrode.

Figure 4.25 shows the cyclic voltammogram of bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride. As can be seen from the

cyclic voltammogram, the complex exhibits only one peak (reverse peak) corresponding to the anodic peak potential of 575mV(0.7971V vs. NHE). The lack of a corresponding cathodic peak suggests irreversibility of the oxidation process. This characteristic behavior of the dye could be the primary explanation for the inactivity of $\text{TiO}_2\text{-Pt/Cu}$ complex system towards hydrogen production via water splitting. One *possible* reason for the apparent electrochemical irreversibility of the Cu(I) complexes tested by CV is that Cu(II) can either be 4, 5, or even 6 coordinate in the excited state. In order to open up a fifth or sixth coordination site, the pseudotetrahedral conformation must 'twist', allowing for another ligand to be attached. Possible ligands may

include the chloride anion (which is present) or even solvent molecules such as DMF (N, N-dimethylformamide) or H₂O (water can serve as a ligand). The twisting minimizes the role of steric hindrance in the prevention of additional ligand attachment. Whether or not such twisting of the Cu(I) complexes occurs when the sensitizer is bound to TiO₂ is unknown. Attempts to perform CV with dyed TiO₂ have been unsuccessful (Gerald Meyer at Johns Hopkins)³³. It is important to note that CV results apply only to the free sensitizer that remains dissolved in solution, not TiO₂-bound sensitizer. CV with TiO₂-bound sensitizer would be the ideal experimental observation, as TiO₂-bound sensitizer is the photocatalyst that is actually used in the photolysis experiments.

Successful and cyclic splitting of water would require a sensitizer that will undergo oxidation and reduction with equal ease. bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride obviously does not meet this requirement and hence cannot be employed in the water splitting reaction scheme. In addition, the oxidation potential of the dye (0.7971V) is more negative than the O₂/H₂O potential(1.23V). This means that the donation of electrons from O₂/H₂O filled states to the copper ion is not thermodynamically feasible. Irreversibility and the oxidation potential of the copper sensitizer complexes remain the chief areas of research focus with respect to water splitting applications.

The cyclic voltammogram of the Tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate sensitizer is shown in figure 4.26. The curves shown excellent symmetry and distinct cathodic and anodic peaks suggesting reversible redox characteristics. The anodic peak potential is 1325mV(1.5771V vs. NHE) and the cathodic peak potential is 1125mV(1.3571V vs. NHE). The anodic peak potential i.e., oxidation potential of the complex is more positive than the O_2/H_2O potential and thus meets one criterion for successful application in water splitting processes. However, the cathodic peak potential i.e., the reduction potential is below (more positive than) the TiO_2 conduction band edge($E_{cb} \sim 0V$). This implies that the injection of electrons from the dye excited state into the semiconductor is unfavorable. It must be noted here that the true dye reduction potential associated with the electron injection process is the excited state reduction potential. Techniques to

Figure 4.26 Ruthenium^{II}(2,2'-bipyridine)₃(PF₆)₂

determine excited state potentials are complicated and have not been employed in the current study. Tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate has been extensively studied^{9,19} and has been proven to be extremely efficient for electron injection in nanocrystalline systems. With the advent of a new generation of sandwich cell type energy conversion devices, the application of Tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate for solar to electricity conversion is being extensively investigated³².

Fig 4.27 $\text{Fe}[\text{2,2'-bipyridine-4,4'-dicarboxylate}]_2(\text{CN})_2$

The cyclic voltammogram for the di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II) complex is shown in the figure 4.27. Figure 4.27 shows two sets of peaks. The distinct peaks are at 200mV(0.4221V vs. NHE) and

100mV(0.3221V vs. NHE) correspond to the reduction and oxidation potentials of the dye complex. The peaks at -25 mV and -75 mV are attributed to Metal to Ligand Charge Transfer (MLCT). The observance of both oxidation and reduction peaks suggests a reversible oxidation process. But the relative positions of the potentials of the dye with respect to the redox potentials of water do not meet the requirements. However, the dye could be used in systems using a sacrificial oxidant.

In summary, it is evident that the cyclovoltammogram studies have revealed possible causes for the lack of activity of the $\text{TiO}_2\text{-Pt/sensitizer}$

Fig 4.28 Relative redox potentials of the dye candidates

systems studied here towards hydrogen production via water splitting. The di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II) complex could not be studied using cyclovotammetry due to solubility problems. The

relative positions of the redox potentials, TiO_2 band edges and water redox potentials are summarized in the figure 4.28.

4.2.6 Photocurrent Measurements using Sandwich Cells

In evaluating the capabilities of a dye complex and a dye- TiO_2 system it is important to analyze the magnitude of photocurrents and efficiencies of the dye-sensitizer systems. In this study, preliminary experiments to evaluate the sensitizer systems have been performed using sandwich cells. All the cells employed nanocrystalline TiO_2 deposited on ITO conductive glass. The current to photon flux characteristics were determined using a

Figure 4.29: IPCE and Photocurrent Density for Cu complex/ TiO_2

calibrated solar cell (1 sun = 135 mW/cm^2), a monochromator and a potentiostat.

The current density was determined and the incident photon to current efficiency (IPCE) was evaluated using the expression:

$$\text{IPCE}(\%) = \frac{1.25 \times 10^3 \times \text{photocurrent density } (\mu\text{A} / \text{cm}^2)}{\text{wavelength (nm)} \times \text{photon flux } (\text{W} / \text{cm}^2)} \times 100\%$$

The figures 4.29,4.30 and 4.31 show plots of the photocurrent and the

Figure 4.30: IPCE and Photocurrent Density for Fe complex/TiO₂

IPCE values against the wavelength of incident light for the di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II)/TiO₂, bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride/TiO₂ and di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) iron(II)/ TiO₂ systems against a platinum counter electrode and an iodide electrolyte.

Figure 4.31: IPCE and Photocurrent Density for Ru complex/TiO₂

The current densities and IPCE values are relatively low for the iron and copper sensitizer systems. The ruthenium system, on the other hand, is efficient especially at wavelengths around the wavelength of maximum absorption (495nm). All the systems show higher efficiencies and higher current densities at wavelengths close to 400nm. This is probably due to direct band gap excitation of TiO₂. At these near uv-wavelengths, direct band gap excitation dominates the electron injection process. The high current densities and IPCE values of the ruthenium sensitizer, in comparison to the iron and the copper sensitizers, is the primary reason for its widespread use as a photosensitizer. The IPCE and current density spectra of ruthenium complexes reported in literature¹¹ differ from the ones obtained in this study. Reasons for the discrepancy have not yet been identified.

4.2.7 Attachment Issues

All the three photosensitizers are attached to the titania in an identical manner. The attachment process utilizes the coulombic interaction between the negatively charged carboxylate groups of the dyes and the positively-charged titania surface occurring at a pH of 4-5. The procedure for dye attachment has been described in the experimental section of this report. This adsorption technique differs from literature techniques¹¹ in that the deprotonated forms of the dyes are being used rather than the protonated forms. This technique relies on physisorption as opposed to chemisorption of the dye to the TiO_2 .

Electronic excited states of most metal complexes and organic dyes are

Figure 4.32 Sensitizer Attachment to TiO_2

short lived (few hundred nanoseconds) and the charge injection process becomes efficient only for those dye molecules that are in the immediate vicinity of the semiconductor electrodes. In the case of the polypyridine complexes of Ru(II), the diffusion length of the excited state is about 250 angstroms for an excited state lifetime of 500ns. Thus, dyes are either adsorbed or chemically bound to the surface by some form of derivatization. Several studies by Gratzel et al⁹ have shown that the presence of carboxyl groups at 4,4'-positions of the bipyridine ligand promotes the interaction of the sensitizer with the oxide semiconductor. Spectroscopic studies^{20,32,21} by researchers have revealed that the presence of carboxylic groups on the sensitizer brings about the formation of C-O-Ti bonds. The carboxylate group serves therefore as an interlocking group enhancing electronic coupling between the π^* orbitals of the bipyridine ligand and the Ti(3d) orbital manifold of the semiconductor. The mechanism of the coupling is illustrated in the figure 4.31. In di-cyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium(II), ruthenium exhibits octahedral coordination, so six possible ligands can be attached. The 2,2'-bipyridine-4,4'-dicarboxylic acid ligand is an aromatic, bidentate ligand. Aromatic ligands are necessary to provide an electron pathway between the ruthenium (via MLCT) and the TiO₂ surface (via electron injection). With two of these dicarboxylated bipyridine ligands placed on the ruthenium, the possibility that one or more of the carboxyl groups can attach to the TiO₂ surface is increased. When the

two bipyridine ligands are arranged in a cis conformation, a maximum of three carboxyl groups can attach to the TiO_2 surface. The remaining two coordination sites on the ruthenium atom are occupied by the electron-dense cyanide ligands. The high electronic density of these cyanide ligands provides additional electronic character to the central ruthenium atom. The addition of electron-withdrawing carboxyl groups onto the bipyridine ligands pulls electronic character away from the ruthenium. The donation of electronic character by the cyanide ligands back to the ruthenium is believed to stabilize the entire sensitizer complex. The rationale behind the selection of the iron (II) (2,2'-bipyridine-4,4'-dicarboxylic acid) $_2(\text{CN})_2$ sensitizer was that the dye is analogous to the standard ruthenium(II) sensitizer, with the notable exception of the center metal atom. The attachment chemistry of this dye is similar to the ruthenium sensitizer. In the case of the bis(2,2'-biquinoline-4,4'-dicarboxylate) copper (I) chloride sensitizer, the ligand (2,2'-biquinoline-4,4'-dicarboxylate, dipotassium salt) is also an aromatic bidentate ligand with two carboxyl groups that can serve to covalently bond the sensitizer to the TiO_2 .

On the other hand Tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate, which does not have any carboxylic groups is not linked to the sensitizer through an ester type linkage. In this case the sensitizer (soluble in water) is physically adsorbed onto the TiO_2 surface.

The interaction between the sensitizer and the semiconductor controls the rate of heterogeneous electron transfer. The greater the proximity of the sensitizer to the TiO_2 , the greater the efficiency of electron injection. Several different types of attachments have been proposed by substituting specific ligands at specific positions.

4.2.8 Future Work

The previous sections outline the results of preliminary investigations into dye sensitizer/ TiO_2 systems. This research has focussed on establishing experimental and analysis procedures. Several new approaches to

Figure 4.33: Two Sensitizer Systems

photosensitization may be explored. Among them, two sensitizer systems and some new attachment issues are described below.

From an extensive literature review and practical testing of sensitizers, the redox potentials of the sensitizer materials must span the water redox potentials for regenerative photosensitized water splitting. This however, is extremely difficult to obtain in practical sensitizer systems. It should be much easier to synthesize dye complexes, which have either their oxidation potential or reduction potential meeting the criteria for regenerative photosensitization. With this in mind we suggest an alternative approach employing a dual sensitizer/ TiO_2 system may be suggested. Figure 4.33 shows the relative electrochemical potentials and the electron pathways of such a process. M_1 and M_2 are the transition metal atoms of two sensitizer complexes. Each of the sensitizers should be able to undergo excitation under visible light irradiation. The excited state of one system (M_1) will be responsible for the injection of electrons into the conduction band of the TiO_2 , which will bring about the H/H^+ reaction. The excited state of the second sensitizer (M_2) quenches the electron deficient M_1 . M_2 , which is electron deficient, can be quenched by electrons from the filled states of O_2/OH^- . This process can go on cyclically bringing out successful water splitting.

The motivation to try sensitizers based on iron and copper as opposed to the use of ruthenium is that iron costs about 1% of the cost of ruthenium. Since the synthesis of that first copper(I) sensitizer, much knowledge has been gained about the potential for tuning of the copper(I) sensitizer properties. Ligand tuning is accomplished by the addition of specific substituent groups in specific locations on the ligand in order to generate the desired sensitizer properties. The base ligand chosen for the ligand tuning experiments was 1,10-phenanthroline. This ligand is often used in the spectrophotometric determination of copper and iron because of its high affinity for those metals. There are also many examples in literature about substituted 1,10-phenanthrolines, which makes the synthetic planning much easier.

The key positions on 1,10-phenanthroline appear to be the 2, 4, 7, and 9 positions. Addition of methyl or phenyl groups at the 2 and 9 positions increases the excited state lifetimes of the Cu(I) complexes into the ns region (2,9-dimethyl: 90 ns; 2,9-diphenyl: 310 ns)³. The addition of electron-withdrawing groups (nitro or carboxylic acid groups) at the 5 or 6 positions increases the formal reduction potential. A Cu(I) phenanthroline complex with a nitro group at the 5 position has been synthesized (copper (I) bis(5-nitro-1,10-phenanthroline) chloride). While the formal reduction potential is increased with this sensitizer, it is reduced irreversibly. A 4,7-dicarboxylated phenanthroline ligand may both increase the formal reduction potential, have

reversibility as well as allow covalent attachment of the sensitizer onto the TiO₂ surface. The "ideal" phenanthroline ligand might have an electron withdrawing group at the 5 position (to increase E^o), a "linker" at the 4 and 7 positions (to attach to the TiO₂), and either an alkyl or a phenyl group at the 2 and 9 positions (to increase τ , the excited state lifetime). It would be electrochemically reversible with a formal reduction potential of at least +1.23 V vs. NHE.

Several additional sensitizers have been synthesized and preliminarily tested in an attempt to alter specific photochemical and electrochemical properties, which may affect the water splitting capabilities of the dyes. These dyes and their absorption maxima are given in the table 4.7.

Table 4.7 Sensitizer	Absorption Maximum
Bis(cyano)bis(1,10-phenanthroline)iron(II)	555nm
Bis(bathocuproinedisulfonic acid) copper (I) chloride	485nm
Bis(5-nitro-1,10-phenanthroline) copper (I) chloride	452nm
Bis(cyano) bis(2,2'-biquinoline-4,4'-dicarboxylic acid)ruthenium(II)	496nm

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APPENDIX

Sensitizer Name	Bis(cyano)-bis(2,2'-bipyridine-4,4'-dicarboxylic acid) ruthenium (II)
Ligand	bipyridine
Attached Groups	2 carboxylic acid groups (in deprotonated forms)
UV_VIS	
Maximum Absorbance Wavelength	496 ± 2 nm in the visible
Cyclovoltammetry	
Oxidation Potential	
Reduction Potential	
Reversibility	Yes (0.90 V vs. SCE) (ref. 1)
Color	Brown
Stable pH	4.0 – 9.0 in the deprotonated form
Solubility	Water (4.0 < pH < 9.0)
IPCE	yes
Possible Attachment Mode	Ester linkage with TiO ₂ surface-bound hydroxyl groups.
Comments	Synthetic procedure: Heimer, T. A.; Bignozzi, C. A.; Meyer, G.J. <i>J. Phys. Chem.</i> 1993, 97, 11987.

Figure 1: Ru^{II}(bipyridine-dicarboxylic acid)₂(CN)₂

Sensitizer Name	Bis(cyano)-bis(2,2'-bipyridine-4,4'-dicarboxylic acid) iron (II)
Ligand	2 bipyridines
Attached Groups	2 carboxylic acid groups
UV_VIS	
Maximum Absorbance Wavelength	542 ± 2 nm in visible
Cyclovoltammetry	
Oxidation Potential(G.S.)	0.313 ± 0.005 V vs. Ag/AgCl reference electrode
Reduction Potential(G.S.)	0.233 ± 0.005 V vs. Ag/AgCl reference electrode
Reversibility	Yes
Color	Bluish-purple
Stable pH	4.0 – 9.0
Solubility	Water at the right pH
IPCE	yes
Possible Attachment Mode	Ester linkage with TiO ₂ surface-bound hydroxyl groups.
Comments	Adapted from Schilt, <i>J.A.C.S.</i> 1960, 82, 3000.

Figure 2: Fe^{II}(bipyridine-dicarboxylic acid)₂(CN)₂

Sensitizer Name	Tris(2,2'-bipyridine) ruthenium (II) dihexafluorophosphate
Ligand	3 bipyridines
Attached Groups	None
UV_VIS	
Maximum Absorbance Wavelength	448 ± 2 nm
Cyclovoltammetry	
Oxidation Potential	
Reduction Potential	
Reversibility	Yes; 1.24 V vs. NHE (reference 2)
Color	Brown
Stable pH	2.0 – 13.0
Solubility	Water, DMF
IPCE	No
Possible Attachment Mode	None provided; this is a free sensitizer.
Comments	Synthetic procedure: <i>J.A.C.S.</i> 1982, 104, 7519-7526.

Figure 3: Ru^{II}(bipyridine)₃(PF₆)₂

Sensitizer Name	Bis(cyano)bis(1,10-phenanthroline)iron(II)
Ligand	2 phenanthrolines
Attached Groups	None
UV_VIS	
Maximum Absorbance Wavelength	555 ± 2 nm in visible
Cyclovoltammetry	
Oxidation Potential(G.S.)	0.80 ± 0.05 V vs. Ag/AgCl reference
Reduction Potential(G.S.)	0.70 ± 0.05 V vs. Ag/AgCl reference
Reversibility	Yes
Color	purple
Stable pH	2.0 – 13.0
Solubility	Water
IPCE	No
Possible Attachment Mode	None provided; this is a free sensitizer.
Comments	Synthetic reference: Schilt. <i>J.A.C.S.</i> 1960, 82, 3000. Weak but discernible CV peaks.

Figure 4: $\text{Fe}^{\text{II}}(\text{phenanthroline})_2(\text{CN})_2$

Sensitizer Name	Bis(bathocuproinedisulfonic acid) copper (I) chloride
Ligand	2 bathocuproinedisulfonic acid (parent ligand: 1,10-phenanthroline)
Attached Groups	Sulfonic acid groups
UV_VIS	
Maximum Absorbance Wavelength	485 ± 5 nm
Cyclovoltammetry	
Oxidation Potential	1.10 V vs. Ag/AgCl reference
Reduction Potential	
Reversibility	No
Color	Reddish-brown
Stable pH	2.0 - 9.0
Solubility	Water at right pH
IPCE	Yes
Possible Attachment Mode	Sulfonate ester with TiO ₂ surface-bound hydroxyl groups.
Comments	Synthetic procedure: <i>Archives of Biochemistry and Biophysics</i> . 322(1) 1995, 127-134.

Figure 5: Cu^I(bathocuproinedisulfonic acid)₂Cl

Sensitizer Name	Bis(2,2'-biquinoline-4,4'-dicarboxylic acid) copper(I) chloride
Ligand	2 biquinolines
Attached Groups	2 carboxylic groups for each ligand
UV_VIS	
Maximum Absorbance Wavelength	558 ± 2 nm in visible
Cyclovoltammetry	
Oxidation Potential(G.S.)	0.600 V ± 0.050 V vs. Ag/AgCl
Reduction Potential	
Reversibility	No
Color	Purple
Stable pH	4.5 - 9.0
Solubility	Water
IPCE	Yes
Possible Attachment Mode	Ester linkage with TiO ₂ surface-bound hydroxyl groups.
Comments	2,2'-biquinoline-4,4'-dicarboxylate is the most inexpensive commercial ligand available.

Figure 6: Cu^I(biquinoline-dicarboxylic acid)₂Cl

Sensitizer Name	Bis(5-nitro-1,10-phenanthroline) copper (I) chloride
Ligand	1,10-phenanthroline
Attached Groups	NO ₂ at the 5 position
UV_VIS	
Maximum Absorbance Wavelength	452 ± 2 nm
Cyclovoltammetry	
Oxidation Potential	0.593 ± 0.005 V vs. SCE (reference 3)
Reduction Potential	
Reversibility	No
Color	Brown
Stable pH	Unknown
Solubility	Water, DMF
IPCE	No
Possible Attachment Mode	None provided; this is a free sensitizer.
Comments	Preliminary compound in ligand tuning experiments. The addition of the nitro group does increase the oxidation potential as desired, but in an electrochemically irreversible manner.

Figure 7: Cu^I(5-nitrophenanthroline)₂Cl

Sensitizer Name	Bis(cyano)bis(2,2'-biquinoline-4,4'-dicarboxylic acid) ruthenium (II)
Ligand	2 biquinolines
Attached Groups	2 carboxylic acid groups for each ligand
UV_VIS	
Maximum Absorbance Wavelength	496 ± 2 nm
Cyclovoltammetry	
Oxidation Potential	1.0 V vs. Ag/AgCl reference
Reduction Potential	None (possibly at 0.25 V vs. Ag/AgCl)
Reversibility	No
Color	Brown
Stable pH	4.5 – 9.0
Solubility	Water
IPCE	No
	Ester linkage with TiO ₂ surface-bound hydroxyl groups
Possible Attachment Mode	
Comments	Synthetic procedure: Adapted from <i>J. Chem. Soc., Faraday Trans. 2</i> , 1987, 83(12), 2295-2306.

Figure 8: Ru^{II}(biquinoline-dicarboxylic acid)₂(CN)₂

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