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GENERATION OF HYDROGEN FROM PHOTOCATALYTIC CLEAVAGE OF WATER

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Abstract

This paper describes the objectives, methods and early results on the US Department of Energy sponsored project to generate hydrogen from splitting of water using photocatalysts. The approach uses organometallic photosensitizers adsorbed onto platinated titania. Platinized titania is a photocatalyst for water splitting, but does not absorb sunlight in the visible range, where most of the sun's energy is contained. Organometallic photosensitizers are synthesized, attached to platinized titania and characterized by UV-Vis spectroscopy, cyclic voltammetry, action spectra and hydrogen generation ability. Thus far, Copper, Iron and Ruthenium catalyst systems have been produced and characterized in this manner. Suitable sensitized systems that have the desriable properties have not yet been found.

Introduction

The cleavage of water to form hydrogen and oxygen would be an ideal source of hydrogen for energy needs. The feedstock, water, is available in virtually inexhaustible supply, and the resulting fuel, hydrogen, burns with no polluting products, the only reaction product being water. The cleavage reaction is endothermic, however, and the energy required to achieve a significant hydrogen production rate is high. Ideally, the energy source must also be available in abundant supply and be nonpolluting. Solar energy meets these requirements, and the use of solar energy to drive the cleavage of water to produce hydrogen is an extremely attractive means to convert solar energy to chemical energy.

There has been extensive investigation of chemical systems that involve the absorption of electromagnetic radiation by chemical agents, followed by reactions leading to the cleavage of water. Photocatalytic cleavage of water by semiconductor photocatalysts is among the most promising techniques since the catalyst is a solid material which is relatively inexpensive, resistant to deactivation, nontoxic and safe to handle. The most promising of these semiconductor systems is a supported catalyst, Pt-RuO_2/TiO_2. The energy of UV light matches the band gap existing in the anatase form of TiO_2. When the surface of the TiO_2 support is illuminated by UV light, electrons in the valence band are excited to the conduction band, leaving an electron hole. The electrons can react with adsorbed water, leading to a sequence of reactions resulting in the production of H_2 and O_2. The Pt and RuO_2 crystallites on the titania surface are believed to catalyze important steps in the subsequent reactions, increasing the rate of product formation.

Despite numerous studies examining this reaction system, the rate of production of hydrogen remains too low for easy commercialization. Significant limiting factors would appear to be (1) the narrow range of wavelengths that are absorbed by titania to initiate the reactions, (2) the difficulty of combining photoaccessibility and reactant accessibility to high surface areas of the photocatalyst, and (3) the efficiency of the subsequent catalytic (versus photocatalytic) steps to form H_2 and O_2. We will investigate novel photocatalytic materials and attempt to alleviate each of the three limitations cited above.

The anatase form of TiO_2 absorbs only a narrow range of solar energy, i.e., wavelengths < 370 nm. More complete utilization of solar energy (to address the first limitation) requires the presence of molecules that will absorb light in the visible wavelength range, i.e., from ~400 to ~850 nm. Among the most efficient are ruthenium complexes such as ruthenium (II) tris-2,2'-bipyridyl cation ($Ru(bpy)_3^{2+}$). These complexes absorb light in the visible wavelength range. The resulting excited complex may lose energy by ejection of an electron if a suitable acceptor is available. The acceptor may be other dyes in the aqueous phase, or the acceptor may be a solid semiconductor, but in either case the acceptor must be located sufficiently close that diffusion to the acceptor is possible within the lifetime of the excited complex (about 300 angstroms for excited $Ru(bpy)_3^{2+}$ in aqueous solution). In this project we plan to explore the binding of photsensitizers to the titania both as a way of isolating the catalyst and, perhaps more importantly, to determine if materials which may have too short an excited lifetime in solution may show activity when bound to the titania directly.

The use of aerogel TiO_2 as the semiconductor support in the Pt-RuO_2 photocatalyst has not been reported. Aerogels have characteristics which address the second limiting factor mentioned above. Aerogels are mesoporous, high specific surface area materials. Mass transfer within the pores of the aerogels is therefore rapid. Because of the very thin pore walls, only a fraction of incident light may be absorbed while the remainder is transmitted. A larger surface area thus may become photocatalytically active. Also because of the structure, a higher fraction of the generated valence electrons and electron holes should react with adsorbed species since the distance to migrate to a solid-liquid interface is very small.

Synthesis of Catalysts/Photosynthesizers

Recent investigations in the laboratories of Grätzel, Ferrere and Meyer (cf. Grätzel and Kalyanasundaram, 1993) indicate that metal complexes with short metal-ligand charge transfer (MLCT) excited state lifetimes are capable of efficient photoinjection of electrons to TiO_2 if covalently bound to the semiconductor surface. Hence we have sought: 1) to prepare iron(II) and copper(I) complexes of substituted diimmine ligands which will allow both modulation of their redox and absorption characteristics and their attachment to TiO_2; and 2) to investigate the ability of the TiO_2-bound complexes to mediate photoinduced water splitting. We have synthesized complexes of the type Fe_2X_2 and CuL_2X (L= -CO_2H and -PO_3H- substituted bipyridyl and biquinoline ligands) in quantities to allow characterization and hydrogen generation experiments. A Ru based complex which has been well studied in solution has also been produced. These are shown in Figure 1. We have also completed the successful adsorption of these sensitizers onto TiO_2 and Pt-TiO_2.

More potential sensitization candidates are to be identified and characterized. Easier and cheaper (e.g. Fe, easier to produce ligands) methods for the synthesis of the selected sensitizer compounds need to be investigated. These second generation complexes in which the photoelectrochemical, redox, and TiO2 absorption properties of the compounds are "tuned" through variation of ligand substituents to improve their capabilities as visible sensitizers. Strategic introduction of electron-withdrawing or electron donating groups on the bipyridyl, phenanthroline and biisoquinoline ligands will shift the redox potentials and the visible absorption maixima of the complexes. The relative efficacy of ionizable substituents (e.g. CO2H, PO3H2, SO3H) for binding the sensitizers to titania will also be assessed. The use of Pt/RuO_2/TiO_2 with the sensitizers will also be examined.

Catalyst Characterization

The responsivity of the sensitizers to different wavelengths of light has been examined through diffuse reflectance UV-VIS measurements of the dry catalyst powders and are shown in Figure 2. It may be seen that these compounds display intense MLCT absorptions in the 500-600 nm region. Experiments to determine the properties (photo-electrical and chemical) of the sensitizers and their electron injection capabilities are to be performed. Experiments need to be conducted to determine the Action spectra and photocurrents in order to characterize the sensitizers in terms of quantum efficiencies. Cyclovoltammetric studies are to be done to quantify the ground state potentials of the sensitizers. Figure 3 illustrates the desirable characteristics for the regenerative oxidation and reduction of a photosensitized system. Figure 4 shows the voltage-current characteristics for the Iron

system, which shows the reduction and oxidation peaks as well as the MLCT peak. Figure 5 shows that the reduction potential is satisfactory but the oxidation potential is not. For this system a sacrificial reductant would need to be used. Figure 6 shows the voltage-current data for the copper system and the absence of a reduction peak suggests that the system undergoes an irreversible oxidation. The nature of attachment of the dye to the TiO_2 photocatalyst and the influence of attachment on the characteristics of the photocatalyst are also to be examined. These may include surface areas, chemisorption and temperature programmed desorption. Comparisons of the characterizations between the fresh and spent catalysts will be made as well as an examination of their longevity.

Investigations of electrochemical, photoelectrochemical, and water splitting photochemical properties will continue with the new sensitizer candidates. As part of this we will obtain action spectra of the sensitizers, including the original set. These characterizations will allow correlation and screening of new materials for effective visible light water splitting.

Hydrogen Generation Measurements

A three-phase continuous photocatalytic reactor for testing the catalysts has been designed and built. It is diagramed in Figure 7. Experiments can be performed both in the ultraviolet and the visible regions and the hydrogen production can be continuously monitored. A provision for filtering out specific wavelengths of light has also been made. Results of other researchers on water splitting experiments under UV illumination have been reproduced for validating the reactor system. The system built can give an accurate picture of catalyst life times and turnover numbers in terms of hydrogen production. The system can also be used to determine the effect of different illumination conditions on the hydrogen production capabilities of the sensitizer/photocatalyst systems. Experimental verification of data from the literature has been made with platinized titantia using UV light as shown in Figure 8.

Experiments involving both ultraviolet and visible regions will be performed and the behavior of the sensitizer under the different illumination conditions will be examined. The effects of the following variables on the hydrogen production will be studied: a. effect of intensity of incident light; b. effect of temperature of the bath; c. effect of sacrificial reductants in the reaction mixture; d. role of pH.

A smaller, non-continuous reaction system will also be fabricated. This will allow in-situ UV-Vis spectra to be obtained to examine the distribution and efficiency of the light spectrum used. Headspace GC analysis will characterize the evolved gas by using a recycle loop.

Acknowledgments

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References

Grätzel, M.and K. Kalyanasundaram, Metal Complexes as Photosensitizers in Photoelectrochemical Cells, in Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, K. Kalyanasundaram and M. Grätzel, Eds, Kluwer Academic Publishers, the Netherlands, 247-271, 1993.

Figure titles

Figure 1 - Sensitizer Complexes.

Figure 2 - UV-Vis Spectra of Sensitized and Unsensitized Titania.

Figure 3 - Band Edge and Ideal Redox Potential Positions.

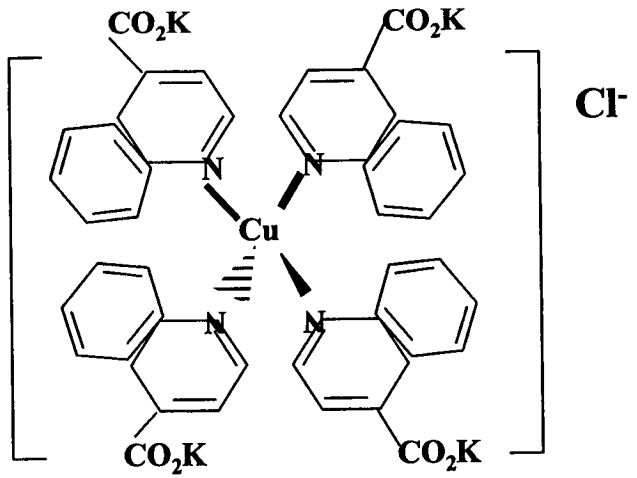
Figure 4 - Cyclic Voltammetry of the Iron Sensitized System.

Figure 5 - Redox Potential Positions of Iron Sensitized System.

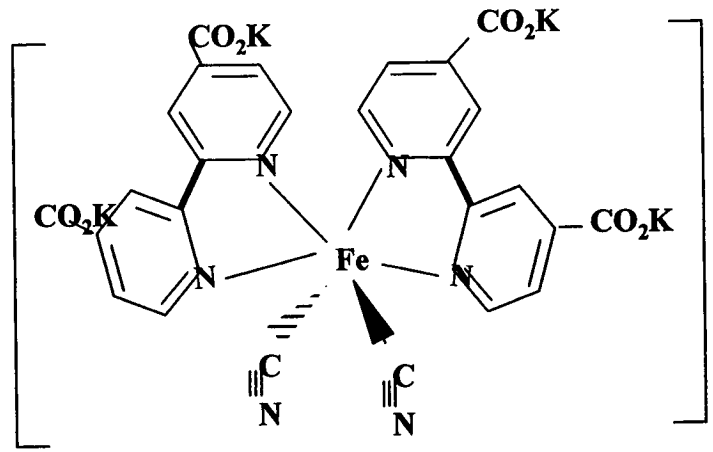
Figure 6 - Cyclic Voltammetry of the Copper Sensitized System.

Figure 7 - Flow Photoreactor System.

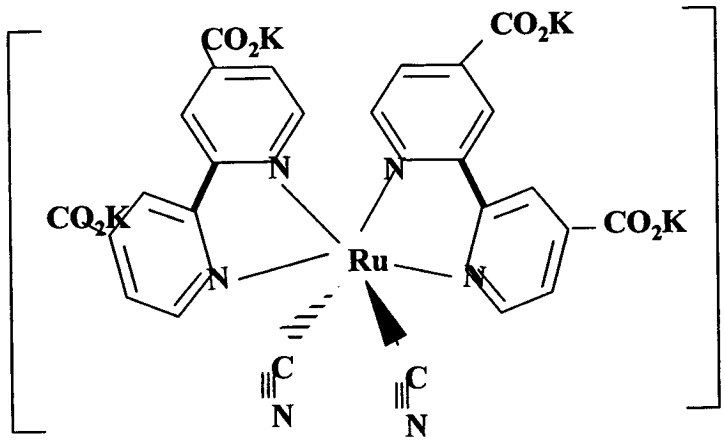
Figure 8 - Comparison of Continuous Hydrogen generation with UV.



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



Dicyanobis(2,2'-bipyridine-4,4'-dicarboxylate)iron(II)



dicyanobis (2,2'-bipyridine-4,4'-dicarboxylate) ruthenium (II)

Figure 1

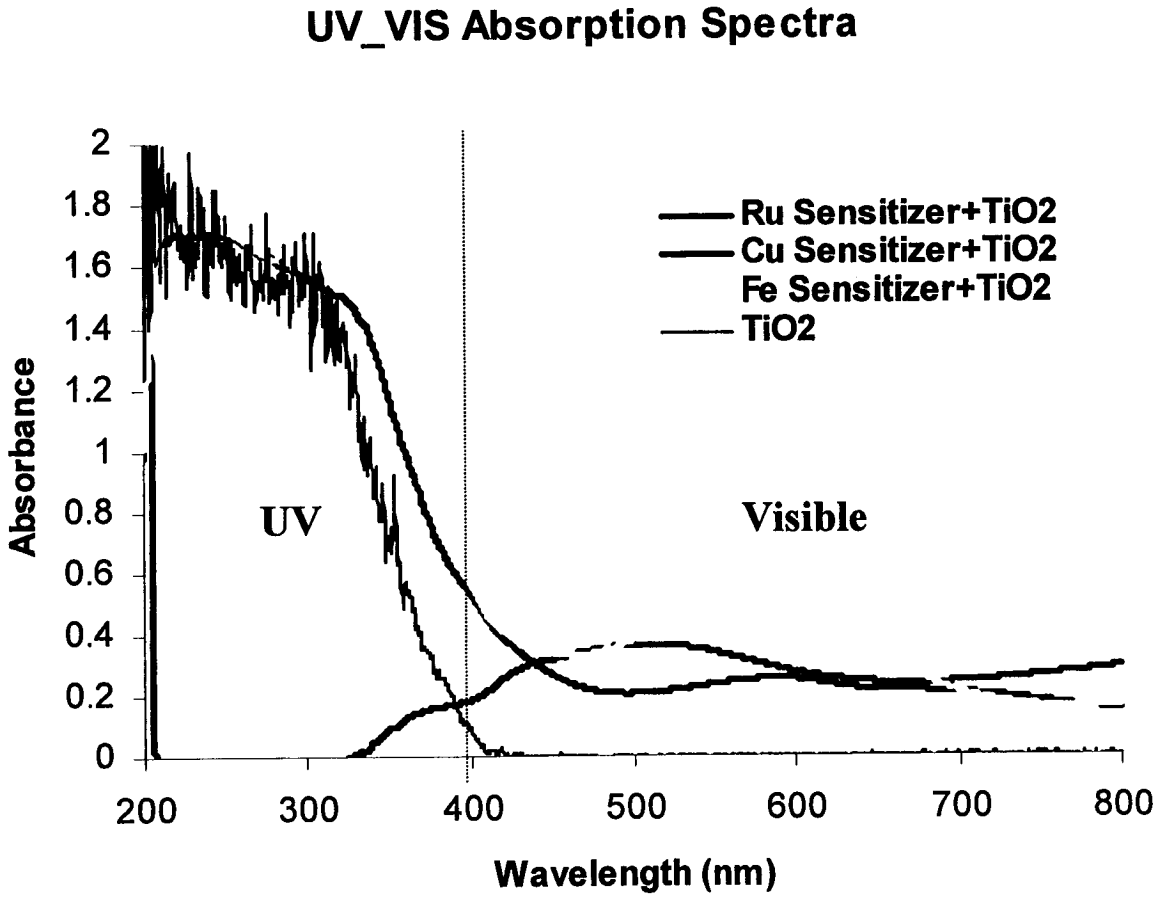
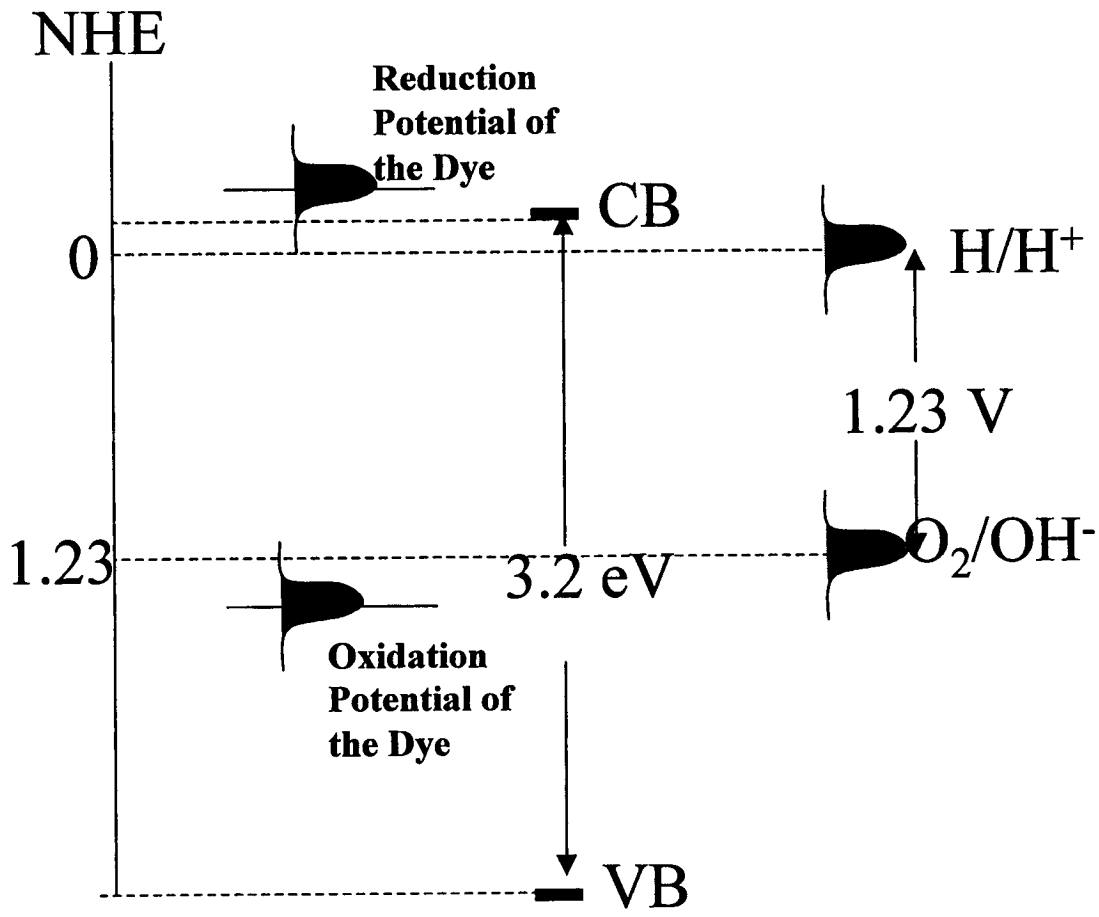

UV_VIS Absorption Spectra
Absorbance
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
700
800
Wavelength (nm)
UV
Visible
Ru Sensitizer+TiO2
Cu Sensitizer+TiO2
Fe Sensitizer+TiO2
TiO2

Figure 2

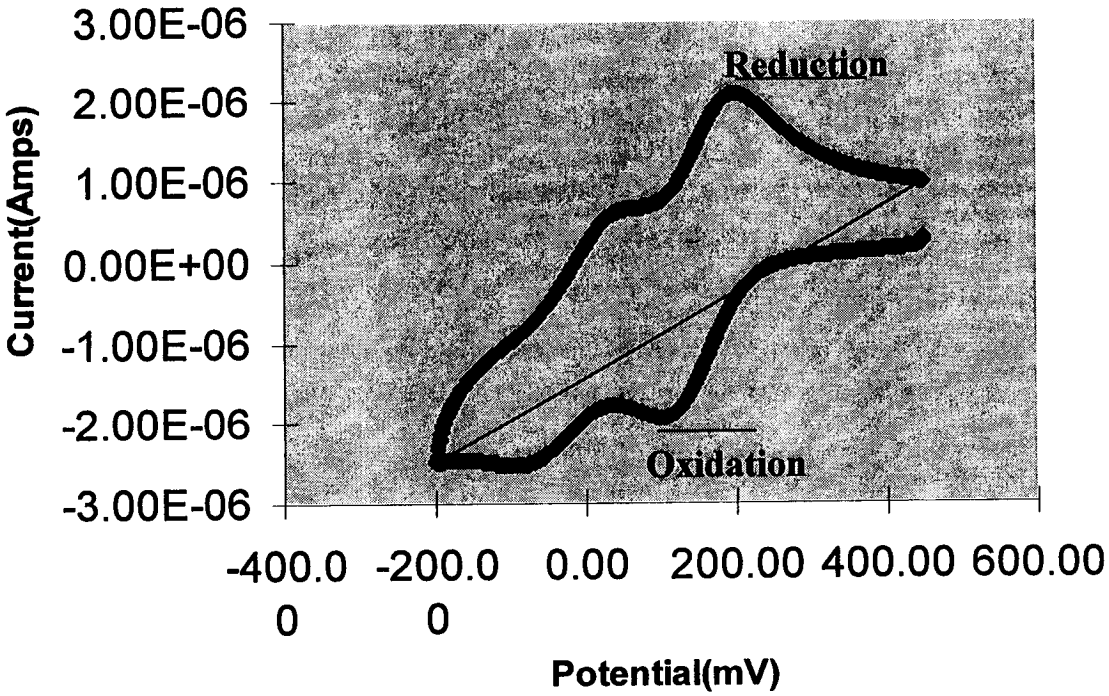
For regenerative photosensitization the ground state oxidation potential of the Sensitizer Dye must be more positive the water oxidation potential (+1.23 V vs NHE)



Ideal Band Edge and Redox Potential Positions for water splitting using dye sensitized semiconductors.

Figure 3

Fe[2,2'-bipyridine-4,4'-dicarboxylate)$_2$(CN)$_2$]



Ag/AgCl Reference

- **Peak at 200mV and the peak at 100mV correspond to the reduction and oxidation potentials of the Dye.**
- **The peak at 25 mV and the trough at -75 mV be attributed to the Metal to Ligand Charge Transfer (MLCT).**
- **The dye may be suitable for systems employing a sacrificial reductant.**

Figure 4

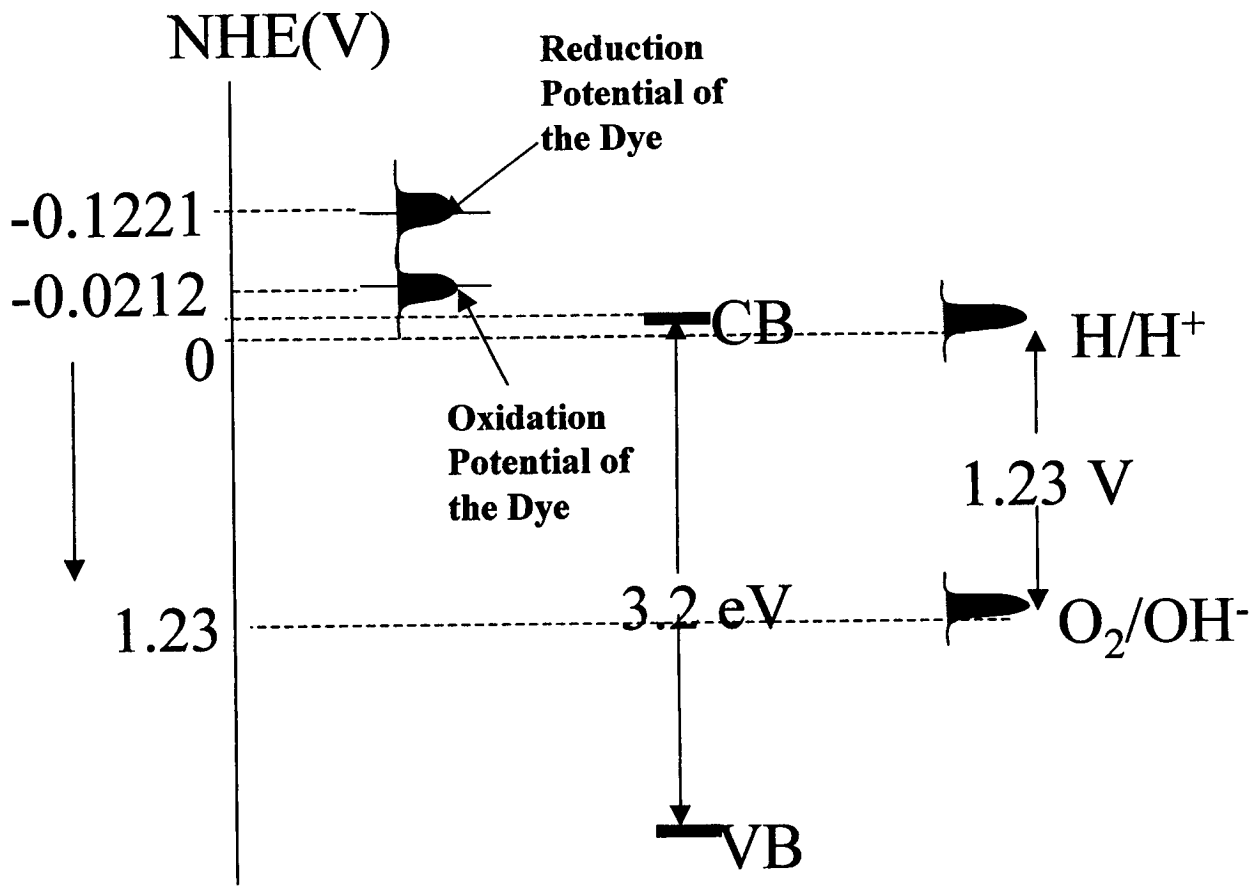
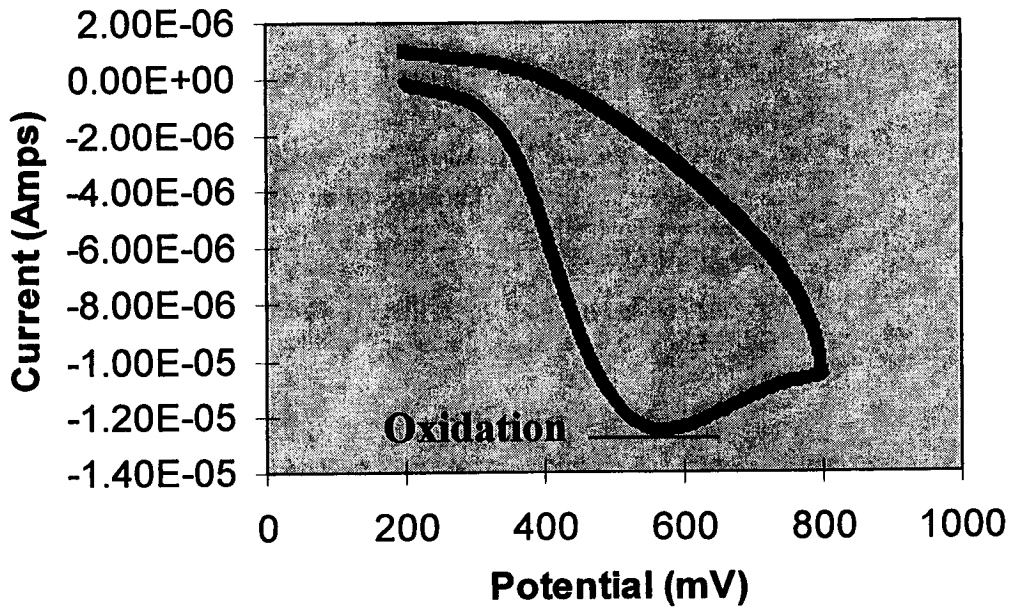

NHE(V)
Reduction Potential of the Dye
-0.1221
-0.0212
0
CB
H/H+
Oxidation Potential of the Dye
1.23 V
1.23
3.2 eV
O2/OH-
VB

Figure 5

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



Ag/AgCl Reference

- **The trough at 550 mV corresponds to the oxidation potential of the Dye.**
- **The absence of a reduction potential peak suggests an irreversible oxidation process**

Figure 6

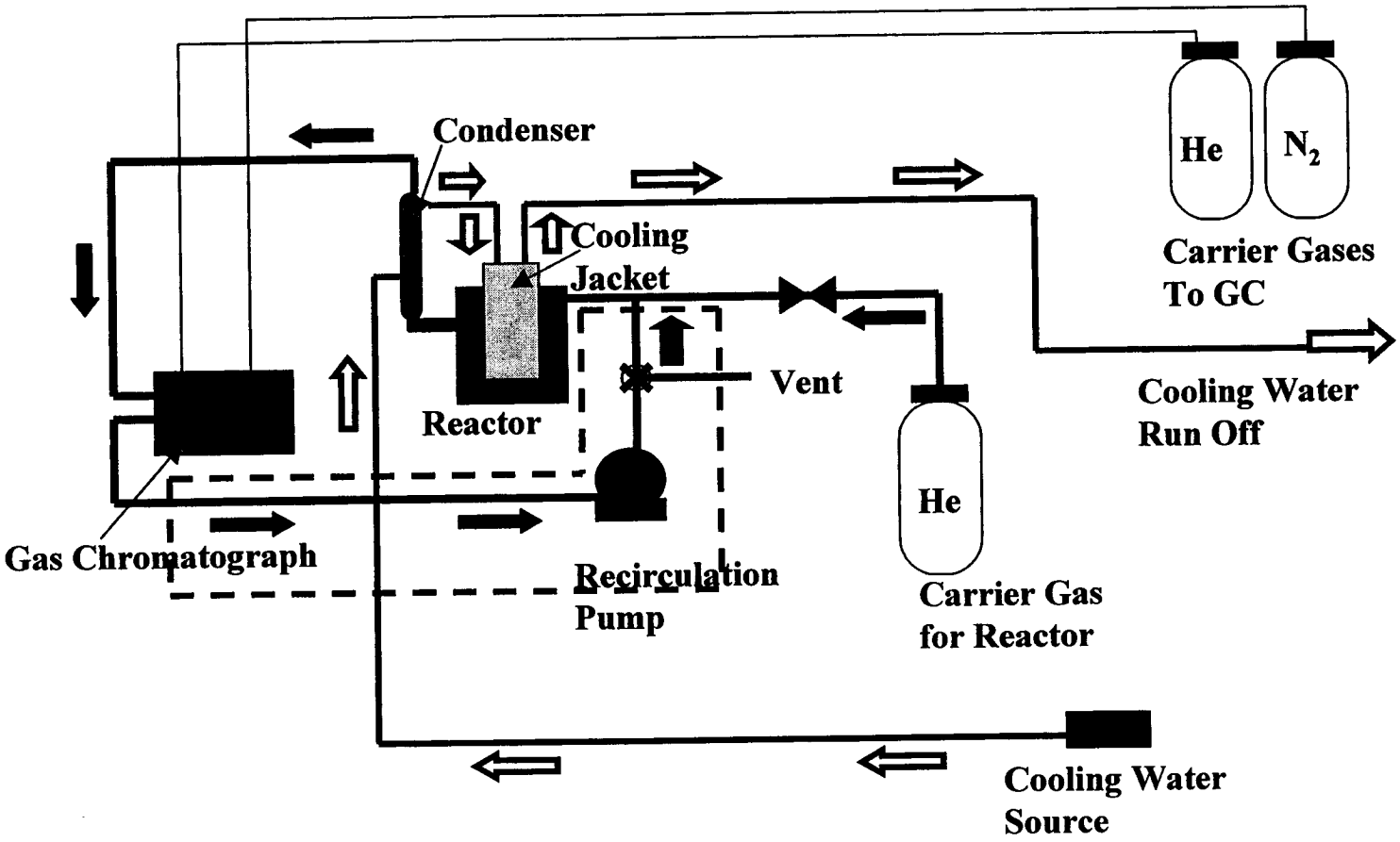
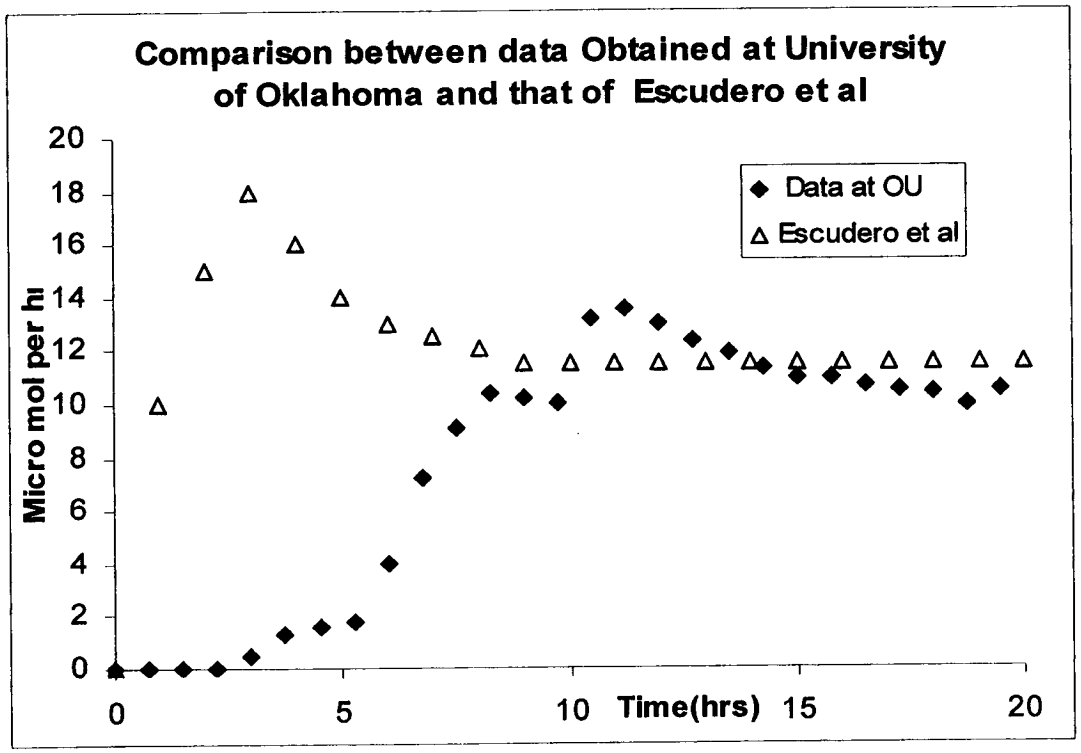

Condenser
Cooling
Jacket
Reactor
Vent
He
N_2
Carrier Gases
To GC
Cooling Water
Run Off
He
Carrier Gas
for Reactor
Gas Chromatograph
Recirculation
Pump
Cooling Water
Source

Figure 7



TiO_2-Pt (1 gm) Photocatalyst under UV irradiation

Figure 8