

## SOLAR PHOTOCATALYTIC HYDROGEN PRODUCTION FROM WATER USING A DUAL BED PHOTOSYSTEM

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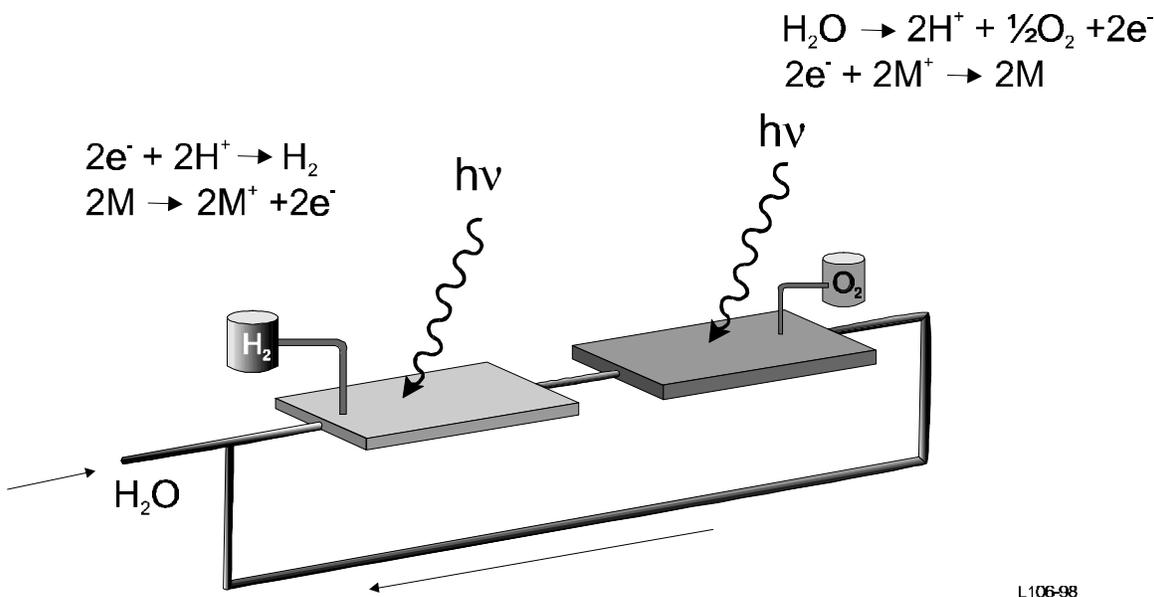
### Abstract

We have been investigating the use of organic pigments as semiconductor photocatalysts in a dual stage water decomposition scheme that would ultimately use solar energy to generate hydrogen from water. We have shown that by employing a combination of simple screening procedures on prospective compounds, such as semiempirical molecular orbital calculations and thin film voltammetry, we can quickly determine whether a compound will be capable of O<sub>2</sub> or H<sub>2</sub> evolution. A number of fused heteroaromatic compounds were identified as possible photocatalysts for O<sub>2</sub> evolution; we subsequently verified that various perylene, indanthrone, and quinacridone compounds do indeed evolve O<sub>2</sub> under Xe lamp illumination. A number of phthalocyanine compounds were shown to evolve H<sub>2</sub>. Using a perylene diimide derivative as the O<sub>2</sub>-evolving photocatalyst and copper phthalocyanine as the H<sub>2</sub>-evolving photocatalyst, respective oxidative and reductive water decomposition was observed using the same IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox electrolyte, demonstrating that continuous closed cycle dual bed photocatalytic water-splitting is feasible.

### Introduction

In this work we are attempting to perform the highly efficient storage of solar energy in the form of H<sub>2</sub> via photocatalytic decomposition of water. While it has been demonstrated that H<sub>2</sub> and O<sub>2</sub> can be evolved from a single vessel containing a single suspended

photocatalyst (Sayama 1994; 1997), we are attempting to perform net water-splitting by using two photocatalysts immobilized in separate containers, or beds. A schematic showing how the device would work is shown in Figure 1.



**Figure 1. Schematic of a Dual Bed Photocatalytic Water-Splitting System.**

Two pairs of photocatalytic reactions would occur. In one container, water is reduced to  $H_2$ ; the electron equivalents for the reaction come from a redox mediator,  $M$ . In the second container, water is oxidized to evolve  $O_2$ ; here the oxidized form of the mediator acts as electron acceptor. By circulating the mediator in an aqueous solution between the beds, the transfer of charge equivalents between the two water decomposition half-cell reactions is accomplished. While the maximum quantum efficiency for water-splitting is automatically cut in half, one is now able to utilize lower energy photons to perform less energetically demanding chemical steps, and so achieve better utilization of the solar spectrum.

The direction of reaction is controlled largely by the electronic structure of the photocatalysts. In order to perform  $H_2$  evolution, the conduction band edge of the semiconductor must exceed, or on the electrochemical voltage scale, be more negative than, the electronic energy level for  $H_2$ . The valence band edge must lie below the redox state of the mediator. A similar argument can be made for the  $O_2$ -evolving photocatalyst.

One of the principle advantages of the photocatalytic approach to water-splitting is the module cost. Previous work has shown that photocatalyst dispersions at only a few milligrams per square centimeter can effectively collect the incoming light (Linkous 1995). To scale up the units, one would need  $10 \text{ g photocatalyst/m}^2$ , or  $45 \text{ m}^2/\text{lb}$ . With a projected cost of 10's of dollars per pound, the photocatalyst would have a negligible impact on overall system cost. In a comparative analysis of several semiconductor-

electrolytic H<sub>2</sub>-generating systems (Block 1998), it was estimated that a dual bed reactor operating at 8.0% efficiency would be able to produce H<sub>2</sub> at \$13/Mbtu.

In earlier work on this concept, we tried to identify combinations of redox mediators and photocatalysts that would perform their respective functions. We identified the alkaline IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple as being optically transparent, highly soluble, and active for electron transfer in both Ox and Red states (Linkous 1996). For the O<sub>2</sub>-evolving photocatalyst, we first studied TiO<sub>2</sub>. While it was able to evolve O<sub>2</sub> under a variety of conditions, the 3.0-3.2 eV band gap absorbed too little of the solar spectrum. For the H<sub>2</sub>-evolving photocatalyst, we identified indium phosphide, InP. While initial H<sub>2</sub> yields were good, it proved unstable under illumination in the alkaline solution. Moreover, it was eventually discovered that InP could be attacked by IO<sub>3</sub><sup>-</sup> even in the dark.

That result led us to consider organic pigments as photocatalysts for the respective water-splitting reactions. The number of pigments commercially available is quite large, however, and so we sought to develop a battery of testing methods, both theoretical and experimental, for estimating whether a given compound could effectively absorb visible wavelength light and be able to either photooxidize or photoreduce water. As for a theoretical method, we evaluated several semi-empirical molecular orbital calculation methods and determined that the PM3 method gave the most reliable gas phase ionization potentials for fused ring compounds. The results were not necessarily accurate, but did yield a linear plot by which a correction factor could be obtained. The application of the PM3 method to pigments of interest, plus the development photoelectron and voltammetric methods of testing, are described below.

## Experimental

### Theoretical Calculations

Calculation of the HOMO (highest occupied molecular orbital in the ground state) and LUMO (lowest unoccupied molecular orbital) for each pigment was accomplished using CAChe<sup>®</sup> 3.0 software from Oxford Molecular Group, run on a Pentium II, 233 MHz computer. The molecule was drawn within the program and the valence, hybridization, and initial geometry were corrected using the “beautify” option. After a preliminary geometry optimization by molecular mechanics, MM2, additional optimization was performed using PM3 parameters. The fully optimized molecule was then submitted for PM3 determination of the wavefunctions, including the HOMO and LUMO.

### Ultraviolet Photoelectron Spectroscopy

The gas-phase ultraviolet photoelectron spectra were recorded using an instrument and procedures that have previously been described in detail (Westcott 1998). The argon <sup>2</sup>P<sub>3/2</sub> ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy, and the difference between the argon <sup>2</sup>P<sub>3/2</sub> ionization and the methyl iodide <sup>2</sup>E<sub>1/2</sub> ionization at 9.538 eV was used to calibrate the ionization energy scale. During data

collection the instrument resolution (measured using FWHM of the argon  $^{2}P_{3/2}$  peak) was 0.015-0.030 eV. Ionization peak positions are reproducible to  $\pm 0.02$  eV.

## **Voltammetry**

The various pigments were largely intractable in aqueous solution and in most organic solvents as well, so that voltammetric data had to be obtained by casting pigment films directly onto the working electrode and performing the electrolysis on the film in a blank supporting nonaqueous electrolyte. The pigments were solubilized by making a Lewis acid complex with  $AlCl_3$  which could then be subsequently acted on by organic solvents. Even though the pigments could be solubilized in this way, it was still necessary to cast films, because the ligand binding effect shifted the energy levels we were hoping to probe, and the organic solvents employed were electroactive themselves in the anodic potential region.

Solutions were prepared under an inert atmosphere in a glovebox. Using a process recently developed at Xerox (Hsieh 1998), 6 mL of nitromethane and 4 mL of methylene chloride were combined and 0.33 g of aluminum chloride was added. After stirring to dissolve the  $AlCl_3$ , 0.4 mmol of the pigment were added. The flask was stoppered and the solution allowed to stir for 6-18 hours.

The working electrode was a 1.0 cm<sup>2</sup> platinum foil. The electrode was passed through a hydrogen flame and then, under an inert atmosphere, was dipped in the pigment/nitromethane solution 1-7 times to coat, allowing time to dry between coats. After coating, the electrode was removed from the glove box and dipped in deionized water to remove any residual nitromethane, methylene chloride and aluminum chloride. It was then placed in a warm oven at approximately 110 °C until dry.

Voltammetric experiments were run using an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A with data being recorded using a Hewlett Packard 7015B chart recorder. A three electrode, single compartment configuration was used, with a platinum mesh counter electrode, and a  $Ag/AgClO_4$  reference electrode. Solutions were 0.1 M tetraethylammonium perchlorate in DMSO when investigating reduction potentials or 0.1 M  $LiClO_4$  in acetonitrile for oxidation potential studies. The solvents were Aldrich brand anhydrous and were used as received.

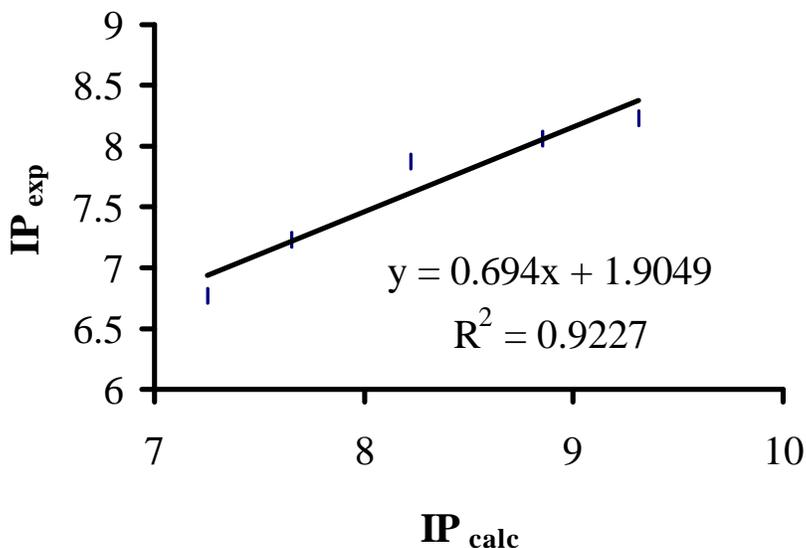
## **Results and Discussion**

### **Semi-Empirical MO Calculations**

As stated in the Introduction, we had shown that one could perform PM3 semi-empirical molecular orbital calculations on organic molecules, derive gas phase ionization potentials based on the calculated HOMO's of the molecules, and then plot these values versus the literature IP values to derive a linear equation containing the correction factor between theory and experiment. However, we soon found that good linear correlations could only

be obtained for structurally analogous series of compounds. The addition of heteroatoms in the fused aromatic rings of many of the more interesting pigments caused energy shifts that warranted a new correction factor. Unfortunately, rather little experimental ionization potential data exists for organic pigments. Plenty of optical spectral data is available, but IP is not recognized as a significant parameter for the dye and pigment industry, even though it undoubtedly correlates with factors of considerable interest, such as lightfastness.

Hence it became necessary to obtain experimental gas phase ionization potential data. This was done via ultraviolet photoelectron spectroscopy (see Experimental section). The values are shown for a number of pigments in Table 1 below. As expected, the experimental values were generally somewhat less than the calculated values. If nothing else, this is due to the fact that the experimental value is an “onset” of ionization, while the calculated value represents the maximum of the thermal Gaussian distribution of energies. It may also be true that PM3 typically overestimates some of the overlap integrals for fused aromatics. A plot of experimental versus theoretical ionization potential for a number of similar compounds (indanthrone, quinacridone, isoviolanthrone, indanthrene gold orange, perylene TCDA, and dimethoxyviolanthrone) are shown in Figure 2. Units are in electron volts (eV). The equation shown is a least squares fitting of the data. Our expectation is that we will now be able to take any prospective fused aromatic quinonoid structure, perform a 20 minute PM3 calculation on it, and then substitute the result into the fitted equation to derive the true ionization potential.



**Figure 2. Plot of experimental versus theoretical ionization potential for photocatalytic pigments.**

**Table 1. Energy Levels of Various Organic Pigments as Determined by PM3 Semi-Empirical MO Calculation, UV-Photoelectron Spectroscopy, Voltammetry, and UV-Visible Spectrophotometry.**

<b>PIGMENT</b>	<b>I.P. theory (eV)</b>	<b>I.P. exp (eV)</b>	<b>E°<sub>ox</sub> (V)*</b>	<b>E°<sub>red</sub> (V)*</b>	<b>λ (nm)</b>	<b>ΔE (eV)</b>
Indanthrone	7.25	6.78	0.99	-0.29	622	1.99
Quinacridone	7.65	7.23	1.39	-1.11	595	2.08
Dimethoxy Violanthrone	7.90	~7.6	1.16	-0.34	706	1.75
Isoviolanthrone	8.22	7.87	1.54	-0.34	712	1.74
Indigo	8.34	7.23	1.19	-0.37	737	1.68
Bis(chlorophenyl) DPP	8.50	7.47	<1.49	-0.70	600	2.06
Pyranthrone	8.54	----	1.39	-0.30	585	2.12
Indanthrene Black	8.83	----	----	----	----	----
Indanthrene Gold Orange	8.84	8.07	1.50	-0.03	562	2.20
Perylene TCDA	9.31	8.22	<2.29	-0.05	604	2.05
Indanthrene Yellow	9.41	----	1.09	----	510	2.43
Perylene Diimide	8.87	----	<2.09	-0.14	652	1.90

\* vs NHE reference electrode

## Voltammetric Studies

While UPS proved useful as a means of acquiring experimental ionization potential data, we also sought to develop an in-house method by which we could make the same determination. The first oxidation and reduction potentials in an electrochemical experiment can approximate the ionization potential and electron affinity, respectively, although a correction involving solvation energies would be necessary for a rigorous determination

The difficulty of preparing samples that would yield voltammetric data is described in the Experimental section. Even so, once the Lewis acid pigment solubilization technique was mastered, voltammetric data for nearly all the prospective organic photocatalysts could be obtained. These results are also shown in Table 1. In general, there was fair agreement between the  $\Delta V$  value, based on the difference between the  $E_{\text{ox}}$  and  $E_{\text{red}}$  measurements, and the  $\Delta E$  value based on spectroscopy. Sometimes the voltammetric wave was irreversible, so that the measured redox potential was more of an upper bound than the actual value. While the correlation between calculation and experiment was less than with the UPS measurements, it should be noted that the electrochemical experiment better reflects the solid state energy levels that would participate in the photocatalytic reaction. It is also true that there is no limitation having to do with structural analogues; the voltammetric waves are unambiguous indications of the energies where charge transfer would be expected from a given compound. Certainly the general trend of calculated HOMO increasing with  $E_{\text{ox}}$  was observed, especially for the perylenes.

## O<sub>2</sub> Evolution Studies

Having established a number of methods for estimating the available oxidation potential of a photocatalyst, it was time to see whether water could indeed be oxidatively decomposed to evolve O<sub>2</sub>. Accordingly, the prospective photocatalysts were suspended with 2.0 weight percent co-catalyst in a dichloroethane solution and deposited by painting onto an acrylic substrate.

This represented something of a departure from past methods. Formerly, we had made co-catalyst modifications of the primary photocatalysts by a number of methods, such as photoreduction or direct borohydride reduction of a noble metal salt. The direct chemical reduction method has been found to be difficult and counterproductive with the organic pigments. The reducing effect of the BH<sub>4</sub><sup>-</sup> ion often served to irreversibly reduce and discolor the pigment.

Consequently, we have been directly physically mixing the photocatalyst and co-catalyst powders. While this does not make for as intimate a mixture as the aforementioned methods, nevertheless, related studies in photocatalytic detoxification studies with similarly intractable materials has shown that positive effects can indeed be observed by direct blending of the photocatalyst and co-catalyst powders (Linkous, 2000).

The O<sub>2</sub> evolution data from the photocatalytic experiments is shown in Table 2. Each value represents a 6-hour photolysis with a Xe lamp using iodate ion as electron acceptor in 1.0 M NaOH solution. The co-catalyst was iridium black.

**Table 2. Volume of O<sub>2</sub> Evolved in Water-Splitting Experiments using Organic Pigments**

Photocatalyst	O <sub>2</sub> Evolved (ml)
Perylene Diimide	4.4
bis(p-chlorophenyl) DPP	3.6
Indanthrone	3.3
Perylene TCDA	3.2
Pigment Red 177	2.6
Indanthrene Yellow	2.0
Quinacridone	1.8
Isoviolanthrone	1.5
Acrylic blank	1.5
Indigo	1.4
Dimethoxyviolanthrone	1.3
TiO <sub>2</sub>	1.3
Indanthrene gold orange	0.9
Indanthrene Black	0.7

Most of the pigments performed better than TiO<sub>2</sub> tested under the same conditions. The value obtained for the acrylic blank (which also included Ir co-catalyst) may represent a UV background effect that should be subtracted out. Even so, despite the modest yields of O<sub>2</sub>, it is apparent that we have accomplished our goal in finding more active O<sub>2</sub>-evolving photocatalysts than TiO<sub>2</sub>.

### Photocatalytic H<sub>2</sub> Evolution

Having achieved some measure of success with the O<sub>2</sub>-evolving photocatalysts, it was time to turn our attention toward H<sub>2</sub>-evolving photocatalysts. From the literature and

from our PM3 calculations, it was apparent that the phthalocyanine (Pc) family of compounds could serve as photocatalysts in this regard (Kearns 1961; Giraudeau 1980). A number of phthalocyanine compounds were acquired and submitted to testing in the same manner as the O<sub>2</sub>-evolving photocatalysts above, except that the electrolyte contained 0.2 M iodide ion to serve as electron donor, and the co-catalyst was 2.0 weight percent platinum black.

These results are shown in Table 3 below. The chloro-aluminum Pc was chosen as a representative trivalent metal center. Earlier work had shown that these MPc-X's could perform well as electrode materials in a photoelectrochemical cell (Klofta 1985). Because of its above-plane central moiety, the vanadyl Pc has a unique crystal structure and optical spectrum, and so was of interest for this application (Griffiths 1976). As it turned out, the more common copper Pc evolved the most H<sub>2</sub>. This may correlate with its superior extinction coefficient in the solid state (Moser 1963).

**Table 3. Volume of H<sub>2</sub> Evolved in Water-Splitting Experiments using Phthalocyanine Organic Pigments**

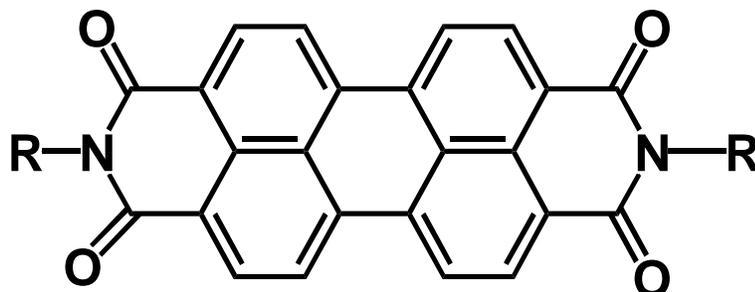
photocatalyst	H <sub>2</sub> evolved (μl)
CuPc	113.0
VOPc	25.6
AlPc-Cl	16.0
NiPc	22.6

While the amounts of gas evolved are considerably less than with the O<sub>2</sub>-evolving photocatalysts, we are confident better photocatalysts will be identified with time. The challenge to date has been to identify organic materials whose HOMO was sufficiently positive on the voltage scale to oxidize water, but whose LUMO was also sufficiently positive so that the band gap energy could be surmounted using visible wavelength light. More often than not, LUMO levels for organic pigments are energetically capable of performing water reduction, and so with time more favorable materials will be found.

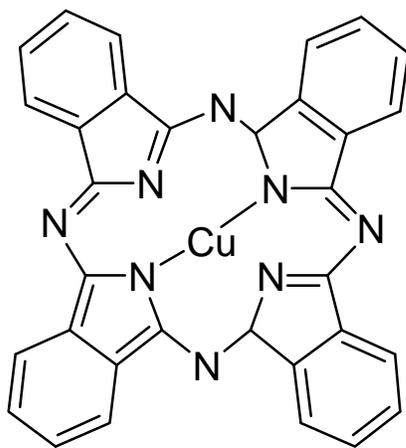
### **Proof of Concept Operation**

Having found organic pigments that would support O<sub>2</sub> evolution and H<sub>2</sub> evolution, it was time for proof of concept, i.e., to show that the separate photocatalytic systems could evolve their respective gas using the same redox electrolyte. Our best O<sub>2</sub>-evolving photocatalyst was the ditridecyl perylene diimide and our best H<sub>2</sub>-evolving photocatalyst was copper phthalocyanine. Their structures are shown in Figures 3 and 4. The two photocatalysts were tested as before, except that instead of using entirely Ox or Red forms of the redox mediator, the experiment was begun at equal parts IO<sub>3</sub><sup>-</sup> and I<sup>-</sup>. In each case,

the respective gas was obtained in ~80% of the amount obtained with 100% of Ox or Red, respectively, thus showing that net water-splitting would occur in closed cycle operation.



**Figure 3. Structure of O<sub>2</sub>-Evolving Photocatalyst N,N'-Ditridecyl-3,4,9,10-Perylene Tetracarboxylic Diimide.**



**Figure 4. Structure of Copper Phthalocyanine.**

In future work, modifications of the existing configuration will be attempted to increase system efficiency. We will attempt this objective in several ways. One is to demonstrate tandemized versions of the dual bed system using organic pigments and polymer membrane technology. Subsequently, we will introduce porosity or microperforations into the photocatalytic membranes. Finally, we will try to prevent back reaction by developing controlled conformation redox mediator complexes.

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## References

Block, D.L. 1998. "Comparative Costs of Hydrogen Produced from Photovoltaic Electrolysis and from Photoelectrochemical Processes," In *Proceedings of the 12<sup>th</sup> World Hydrogen Energy Conference*, vol 1:185-194. Buenos Aires, Argentina: International Association for Hydrogen Energy.

Giraudeau, A., F.-R.F. Fan, and A.J. Bard. 1980. "Semiconductor Electrodes. 30. Spectral Sensitization of the Semiconductors n-TiO<sub>2</sub> and n-WO<sub>3</sub> with Metal Phthalocyanines," *J. Am. Chem. Soc.* 102:5137-5141.

Griffiths, C.H., M.S. Walker, and P. Goldstein,. 1976. *Mol Cryst. Liq. Cryst.* 33:149.

Hsieh, B.R., and A.R. Melnyk. 1998. *Chem. Mater.* 10:2313-2316.

Kearns, D.R., and M. Calvin. 1961. "Solid State Ionization Potentials of Some Aromatic Organic Compounds," *J. Chem. Phys.* 34: 2026-2030.

Klofta, T.J., P.C. Rieke, C.A. Linkous, W.J. Buttner, A. Nanthakumar, T.D. Mewborn, and N.R. Armstrong, "Tri- and Tetravalent Phthalocyanine Thin Film Electrodes: Comparison with Other Metal and Demetallated Phthalocyanine Systems," *J. Electrochem. Soc.* 132: 2134-2144.

Linkous, C.A., N.Z. Muradov, and S.N. Ramser. 1995, "Consideration of Reactor Design for Solar Hydrogen Production from Hydrogen Sulfide Using Semiconductor Particulates," *Int. J. Hydrogen Energy*, 20:701-710.

Linkous, C.A., D.K. Slattery, A.J.A. Ouelette, G.T. McKaige, and B.C.N. Austin. 1996. "Solar Photocatalytic H<sub>2</sub> from Water Using a Dual Bed Photosystem." In *Hydrogen Energy Progress XI: Proceedings of the 11th World Hydrogen Energy Conference*, vol. 3, 2545-2550.

Linkous, C.A., G.J. Carter, D.B. Locuson, A.J. Ouelette, D.K. Slattery, and L.A. Smitha. 2000. "Photocatalytic Inhibition of Algae Growth Using TiO<sub>2</sub>, WO<sub>3</sub>, and Co-catalyst Modifications," submitted to *Env. Sci. Technol.*

Moser, F.H., and A.L. Thomas. *Phthalocyanine Compounds*. New York:Reinhold Publishers.

Sayama, K., and H. Arakawa. 1994. "Effect of Na<sub>2</sub>CO<sub>3</sub> Addition on Photocatalytic Decomposition of Liquid Water over Various Semiconductor Catalysts." *J. Photochem. Photobiol. A: Chem.*, 77: 243-247.

Sayama, K. and H. Arakawa. 1997. "Effect of Carbonate Salt Addition on the Photocatalytic Decomposition of Liquid Water over Pt-TiO<sub>2</sub> Catalyst." *J. Chem Soc., Faraday Trans.*, 93: 1647-1654.

Westcott, B.L., N.E. Gruhn, and J.H.J. Enemark. 1998. *J. Am. Chem. Soc.* 120:3382-3386.

**Figure 1. Schematic of a dual bed water-splitting system.**

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