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DEVELOPMENT OF NEW MATERIALS AND APPROACHES TO PHOTOCATALYTIC SYSTEMS

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Abstract

This work describes our efforts in developing a dual bed photocatalytic system for water-splitting to make H_2. Several potential improvements were investigated: the use of carbonate ion in facilitating the O_2 evolution process, the use of NiO_x as a substitute for Ir on TiO_2, the use of WO_3 as a substitute for TiO_2, and a study of various classes of organic pigments for photocatalytic application. We have also generated some prototype designs for future dual photocatalyst systems that should enable higher efficiencies.

Introduction

We are engaged in a research effort to develop an efficient, affordable, direct photoconversion scheme for generating H_2 from H_2O using sunlight. The approach is to use semiconductors in powdered form in a dual bed configuration, breaking down the energy requirement for water splitting into a 2-photon process, and enabling separate production of H_2 and O_2. A schematic showing how such a system would work is shown in the first row of Figure 1. In this approach, the photocatalytic system would employ two modules, each consisting of a shallow, flat, sealed container, in which micron-sized photocatalytic particles are immobilized. An aqueous solution containing a redox mediator is pumped between the two chambers. Different photoparticles and catalysts are chosen for their respective modules so as to effect oxidative water-splitting in one vessel to evolve oxygen gas, and reductive water-splitting in the other to evolve hydrogen.

The general chemical mechanism for a dual bed concept photosystem would be as follows:

H_2 photoreactor: $4\,H_2O + 4\,M^{\circ} \rightarrow 2\,H_2 + 4\,OH^- + 4\,M^+$

O_2 photoreactor: $\underline{4\,OH^- + 4\,M^+ \rightarrow O_2 + 2\,H_2O + 4\,M^{\circ}}$

net: $2\,H_2O \rightarrow 2\,H_2 + O_2$

M is a "redox mediator", or charge-carrying agent, that shuttles electron equivalents from O_2-evolving photomodule to the H_2 module.

Our inital photocatalysts were TiO_2 in the O_2-evolving bed, and InP in the H_2-evolving bed [Linkous 1996a]. It was soon found that modification with noble metal co-catalysts made for more rapid gas evolution. Iridium was found to facilitate O_2 evolution, and Pt was found to facilitate H_2 evolution. Many candidate redox mediators were screened in order to find the best one [Linkous 1996b]. The alkaline redox couples I^-/IO_3^- and Br^-/BrO_3^- were identified.

Efficiencies were still low because of fundamental limitations with the photocatalysts. The band gap of TiO_2 was too wide (3.0 eV), so that only a small portion of the solar spectrum (in the UV) could be absorbed and utilized. Corrosion was also a problem. H_2 evolution from Pt-InP suspended particulates had slowed considerably after only a few hours of photolysis time. Inspection showed that the originally black powder had become gray, due to oxide formation. It was first thought that photocorrosion was occurring, but subsequently it was found that the InP was reacting with the IO_3^- ion that was forming as a consequence of I^- oxidation.

As a substitute for TiO_2, it was decided to look at WO_3. With a somewhat narrower band gap (2.7 eV), it promised to absorb more of the solar spectrum. The WO_3 became part of an IEA (Internation Energy Agency) collaboration. Dr.'s Jan Augustynski and Martinne Ulmann from the University of Geneva, Switzerland, have been working their own WO_3 preparations as part of a Swiss national collaboration on a tandem photoelectrochemical cell. Their colloidal WO_3 has an effective band gap energy of 2.5 eV, so that it would absorb some 2.5 times as much sunlight as TiO_2 [Augustynski 1996].

The colloids proved to be rather unstable, however. In the presence of a surfactant or other stabilizer, the colloidal state could be maintained, but only at the risk of blocking the surface photochemistry. In the absence of additives, the aqueous colloids could be maintained on their own for several days by continuously stirring in the dark, but the act of performing a photocatalytic evaluation on them accelerated their aggregation. The final material consisted of 1.0 μm particles that were less photoactive than commercial grade WO_3.

We also began to look at organic pigments as alternative photocatalysts. Their high extinction coefficients and good match with the solar spectrum was thought to compensate for comparatively low charge carrier mobilities. Many organic compounds representing the major classes of dyestuffs were evaluated for their suitability as O_2-evolving photocatalysts . Several trends soon emerged. Di- and triarylmethanes, phthalocyanines, polymethines, xanthenes, thioxanthines, and acridines all tended to have insufficiently large ionization potentials. Other classes, such as anthraquinones, perylenes, quinacridones, and pyranthrones reliably gave ionization potentials that should be able to oxidize water. Consideration of water miscibility and light fastness helped narrow the field even further. A field of roughly a dozen structurally related compounds were chosen for experimental evaluation.

Results and Discussion

Effect of CO_3^{2-} on O_2 Evolution

This is another IEA interaction that began only this year. Our collaborators are Dr.'s H. Arakawa and K. Sayama of the National Institute of Materials and Chemical Researach in Tsukuba, Japan. They have observed the stoichiometric, co-evolution of H_2 and O_2 from single pot, photocatalytic powder dispersions of TiO_2 and other photocatalysts in the presence of carbonate ion, CO_3^{2-} [Sayama, 1994]. The presence of carbonate ion had been found to be vital to the O_2 evolution process. Apparently the intermediate surface-adsorbed hydroxyl radicals generated from initial water oxidation are quite reactive, and will oxidize any available redox agent present, even background organic contaminants. The carbonate ion acts as a scavenger for hydroxyl radical, forming a peroxydicarbonate species that ultimately breaks down, releasing O_2[Sayama 1997]. Thus carbonate acts as a catalyst for O_2 evolution.

We decided to see whether the same effect could be observed for the O_2-evolving half of our dual bed system. Accordingly, 250 mg dispersions of various photocatalysts were suspended in 50 ml solution and photolyzed. The relevant data are shown in Table 1. At a 0.5 M CO_3^{2-} concentration, very little improvement was seen; in fact, for the most active Ir-TiO_2 system, a negative effect was apparent. Our interpretation is that the CO_3^{2-} ion adsorbs not only on the TiO_2 surface, but on the co-catalyst as well. For the dual bed approach to work, the redox mediator (IO_3^-) needs open access to the co-catalyst surface. By charge conservation principles, the rate of IO_3^- reduction must match that of O_2 evolution. If the Ir surface is blocked by CO_3^{2-} ion, then any gains made on the TiO_2 surface are lost on the co-catalyst surface. Therefore, in the absence of any kind of favorable preferential adsorption, the use of carbonate ion in directing O_2 evolution in the dual bed system is inadvisable.

Evaluation of NiO_x-TiO_2 Photocatalyst

A black powder consisting of TiO_2 precipitated from $Ti(i\text{-}PrO)_4$ and modified with 3 weight % Ni was given to us by Dr. Arakawa. Part of the agreement was to test the photocatalyst in Florida sunlight. While water-splitting may have occurred, it was at too low a production rate for us to reasonably detect it with our existing gas chromatographic apparatus.

Subsequent testing was done indoors in front of a Xe lamp. In conjunction with our IO_3^- redox mediator, it showed reasonable photoactivity, more than doubling the gas output in comparison to plain TiO_2. On the other hand, Ir-TiO_2 still performs better by an order of magnitude. With an anticipated large scale loading of only 100 mg Ir/m^2, saving money on the cost of the co-catalyst does not justify enlarging the system to accommodate the lower photoactivity level.

Table 1. Evaluation of NiO_x-TiO_2 as Alkaline O_2-Evolution Photocatalyst: Carbonate Effect

All solutions were 1.0 M NaOH

photocatalyst	light source	$[CO_3^{2-}]$	$[IO_3^-]$	O_2 evolved (ml)
NiO_x-TiO_2	sun	0	0	< 0.02
NiO_x-TiO_2	sun	0.5 M	0	< 0.02
NiO_x-TiO_2	Xe	0	0.2 M	0.98
NiO_x-TiO_2	Xe	0.5 M	0.2 M	0.93
TiO_2	Xe	0	0.2 M	0.40
Ir-TiO_2	Xe	0	0.2 M	11.7
Ir-TiO_2	Xe	0.5 M	0.2 M	3.93

Evaluation of Sol/Gel-Deposited WO_3 Photocatalyst

Because of our difficulties in maintaining the colloidal particle size of WO_3 obtained via ion exchange, our Swiss collaborators sent us their own preparations that had been immobilized via sol/gel techniques on ITO. Since their photocatalysts had been painted on a surface and lightly sintered before testing, the original particle size could be preserved. The porous dispersion consisted of 15-30 nm particulates.

We put together a special cell that could hold the WO_3/ITO samples nearly perpendicular to the direction of irradiation while being surrounded by the redox mediator solution. Gas evolution into the head space was analyzed for O_2 via gas chromatography. Data for the photocatalytic behavior of these samples are shown in Table 2. As a comparison, a dispersion of Ir-TiO_2 was cast onto glass and tested in alkaline IO_3^- solution under the same conditions.

Because of the acid/base properties of WO_3, the solutions were made 1.0 M in H_2SO_4. It was seen that only modest concentrations of ferric ion are optimum; the 1.0×10^{-3} M solution actually generated more O_2 than the 0.1 M solution. This is due to an optical absorption effect: the 0.1 M solution was decidedly orange in color, and so absorbed much of the light that the WO_3 could have used. Co-catalysts did not improve the O_2 evolution rate. The iodate ion actually did rather well in the acidic solution, even though the risk of darkening the solution with triiodide at this pH was great. Rather than colorize the solution, there was some evidence that solid I_2 was precipitating onto the WO_3 surface. While from a practical device point of view this would be a prohibitive development, for a short batch photolysis experiment it did not significantly change the results.

Table 2. Evaluation of Sol/Gel-Deposited WO_3 on ITO as an O_2-Evolution Photocatalyst

Solution composition: $[Fe^{3+}] = 0.001$ M, or $[IO_3] = 0.2$ M; 1.0 M H_2SO_4

photocatalyst	mediator	O_2-evolved (ml)
WO_3	Fe^{3+}	0.04, <0.02[b]
Pt-WO_3	Fe^{3+}	0.03
Ir-WO_3	Fe^{3+}	0.02
WO_3	IO_3^-	0.4
WO_3 (Fisher)	Fe^{3+}	<0.02
Ir-TiO_2 (film)[a]	IO_3^-	2.3

[a] solution was 1.0 M NaOH; [b] $[Fe^{3+}] = 0.1$ M

The Ir-TiO_2 film was by far the most photoactive. Thus despite the inherent advantages of WO_3 in terms of solar absorption, it still lags TiO_2 in terms of overall photoactivity.

Electronic Structure of Quinacridone and Other Organic Pigments

This year came the business of actually locating and working with some of the pigments we had done calculations on earlier. Not all of them were commercially available. Also, other promising substances were subsequently identified. Ultimately, some 12 structurally related pigments were acquired.

The first step was to characterize their electronic structure. This was attempted electrochemically, but proved to be difficult because the pigments were poorly soluble and resisted sulfonation. Instead, we are going to try and obtain direct ionization potential data to compare to our calculations. The effort now is focused on identifying an apparatus that can work with these involatile, high molecular weight compounds.

Meanwhile, electronic structure information is also available via solid phase spectra. Most of the compounds were amenable to vacuum sublimation, and so solid films on glass could be prepared in this manner. It was intended to derive the effective energy gap of each material from the onset of absorption of its lowest energy transition. Some of the spectra were too broad and diffuse to identify a clear onset of absorption, so sometimes we had to simply mark the peak maximum. A few were soluble in organic solvent, yielding clear absorption maxima.

In Table 3, effective band gap data are given for the 12 organic pigments that we have acquired and tested. A general correlation is seen between the size of the band gap and the magnitude of the calculated ionization potential.

Table 3. Energy Gap and Ionization Potential Data for Organic Pigments

name	band gap energy (eV)	calculated IP (eV)
dimethoxy-violanthrone	2.08^e	6.93
indanthrene Gold Orange	2.4^p	7.96
Cromophtal Red 3B	2.2^s	7.27
isoviolanthrone	$2.5, 2.0, 1.9^s$	7.26
indanthrene Yellow GCN	3.2^s	8.56
indanthrene Black BBN	1.9^s	7.93
bis-(p-chlorophenyl) DPP	$2.17^p, 1.98^e$	7.02
indigo	1.84^p	7.42
pyranthrone	2.6^s	7.62
quinacridone	$2.16^p, 1.98^e$	6.67
indanthrone	1.89^p	6.24
perylene TCDA	2.20^p	8.45

^{s}solution; ^{p}peak; ^{e}edge

"Tandemizing" the Dual Bed Configuration

Utilization of two photocatalytic beds automatically cuts the overall quantum efficiency in half. This may be considered a negative attribute, but perhaps more accurately it should be thought of as a trade-off between quantum efficiency and the need to make effective use of the solar spectrum. While net water decomposition to H_2 and O_2 has been observed in single component photocatalytic suspensions [Sayama, 1996], the photocatalyst employ typically possessed a band gap energy of > 3.0 eV. Less than 10% of the solar spectrum can be utilized by such materials.

The general strategy of fabricating devices consisting of two or more small band gap materials connected in series for effective absorption of sunlight while generating enough driving force for water splitting has been employed in a number of configurations. Principal among these is the "tandem" cell approach, where two dissimilar materials with different band gap energies are deposited onto one another. The material with the wider band gap is placed forwardmost to the direction of irradiation, so that light of longer wavelength passing through it can be absorbed by the narrower band gap material.

The dual bed photocatalytic system can be "tandemized" by essentially folding the second bed underneath the first one, as shown in Figure 1. If scattering losses in the uppermost module can be minimized, and complementary photocatalysts are employed, then one can achieve the tandem effect, that is, have high energy photons absorbed in the first semiconductor layer, and lower energy photons absorbed in the second layer. The circulating redox electrolyte would then flow from left to right across the top module and right to left across the lower one. The single unit would be tilted slightly so that evolved gases would percolate to a head space at the upper corner. Materials cost savings would also accrue, since the module area is basically cut in half, and the photocatalysts would be immobilized on either side of the same transparent membrane.

Another development in the evolution of the dual bed configuration has to do with the motion of the redox mediator working fluid. It is projected that an efficiency increase may be had by perforating the membrane or transparent support. In this embodiment, the redox mediator effuses through microperforations in the photocatalyst support to reach the other immobilized photocatalyst dispersion. This feature eliminates the need to include a pump to move the redox solution across the surface of the photocatalyst; instead, a hopper supplying make-up water will suffice.

In the various tandem concepts, the photocatalysts are dispersed in layers on either side of a transparent membrane. One then has at least three laminates combining to form a single sheet. It has been demonstrated that the individual particles in each layer can communicate with each other, or in other words, an electron-hole pair generated well within a photocatalyst layer can migrate via particle-particle contact to the working fluid interface and perform redox chemistry. One can then speculate that if the photocatalyst laminates are thickened until they contact each other, there could be charge carrier flow across the membrane to the opposite interface. The optimum thickness of the photocatalyst layers at this point is uncertain, since it would be a trade-off between the penetration depth of the light each layer is expected to absorb, the diffusion lengths of the photogenerated charge carriers, and the mechanical strength of the photocatalyst bilayer.

If the two photocatalyst layers could electronically communicate with each other, then the need for a redox mediator would be obviated. The perforation feature would still have value; instead of having the mediator diffuse through the pores, the protons resulting from water oxidation (assuming acidic media) would be the mobile species. The pores could then be filled with a proton-conducting ionomer or other medium that would be selective toward the solvated species of interest. This would eliminate much of the parasitic gas intermingling that would occur through an open, perforated structure.

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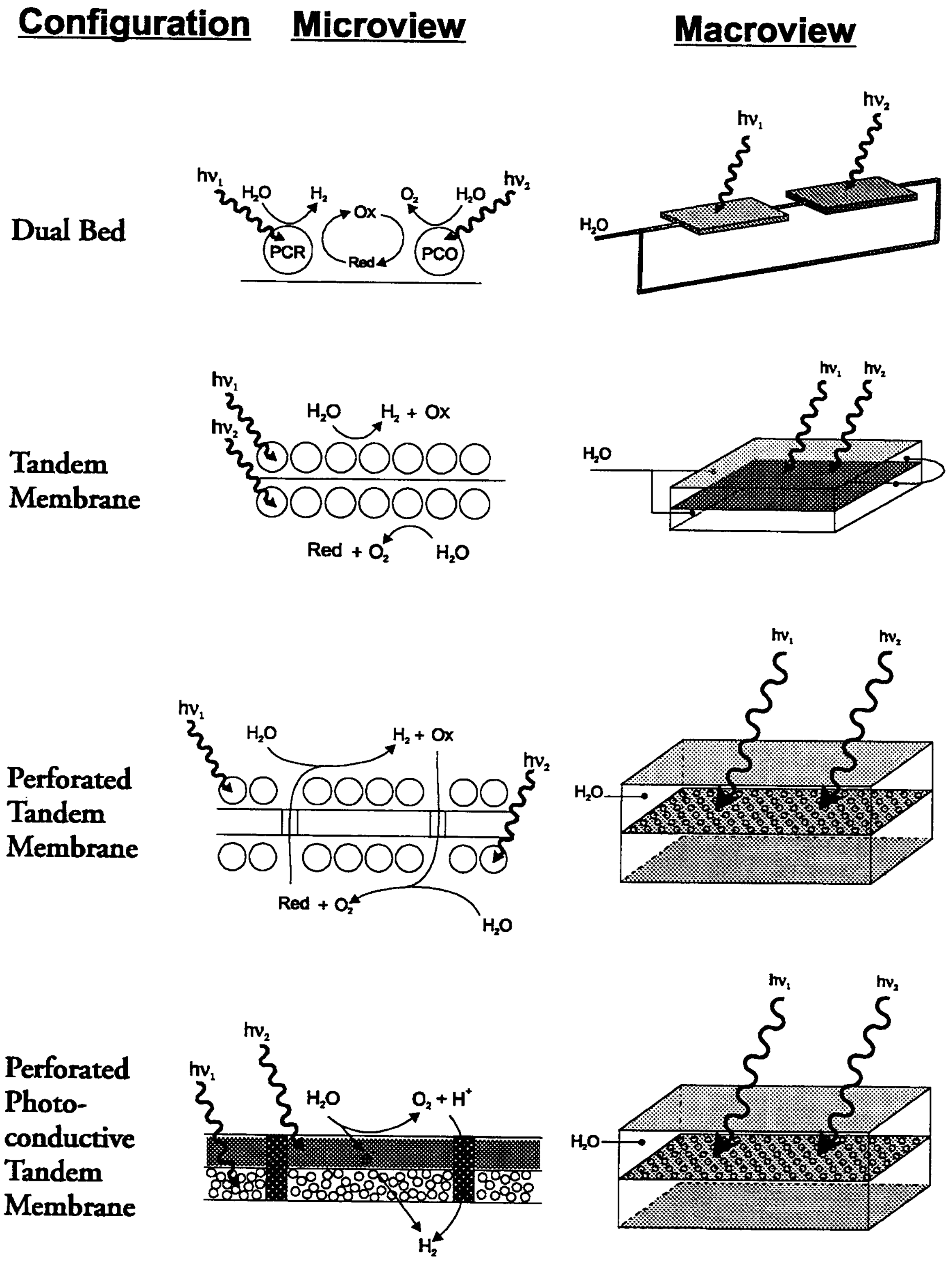

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Figure 1. Evolution of Dual Bed Photocatalytic Water-Splitting Systems