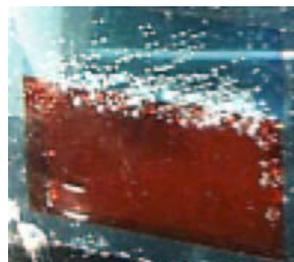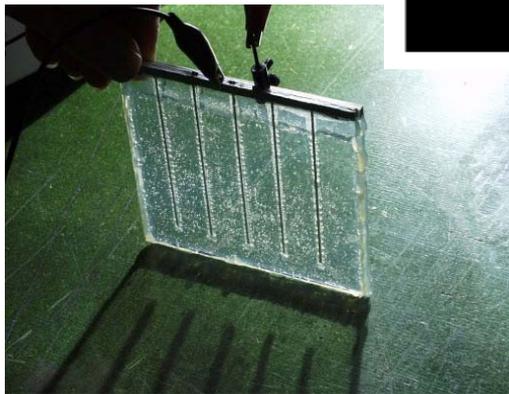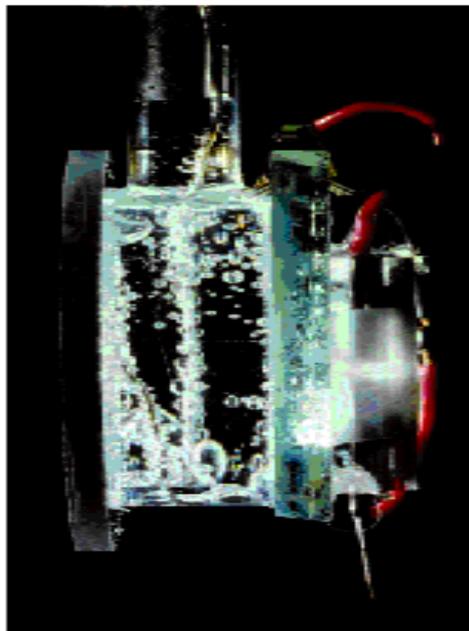**Photoelectrolytic Production of Hydrogen**
Final Report: Annex 14

IEA Agreement on the Production and Utilization of Hydrogen

IEA/H2/TR-02/2004

Photoelectrolytic Production of Hydrogen

IEA Hydrogen Program | **"Annex-14"**

Final Report

Edited by
Andreas Luzzi

Table of Contents

Photoelectrolytic Production of Hydrogen "Annex-14" of the IEA Hydrogen Program

1. Summary

Annex-14 has been an internationally collaborative research effort conducted over 4.5 years under the guidance and coordination of the International Energy Agency (IEA) Hydrogen Implementing Agreement (HIA). Annex-14 focused on the development of materials and systems for the photoelectrochemical (PEC) production of hydrogen. It has been successfully completed toward the very end of 2003 to make room for a new, broader research and development (R&D) program on photoelectrochemical (PEC) hydrogen production. This follow-up R&D Annex is planned to involve many new research groups beyond this Annex-14 and to start in the middle of 2004.

Nine research groups from Japan, Sweden, Switzerland and the USA have been collaborating under Annex-14 since July 1999. Significant research progress has been made over the past 4.5 years in the areas of material science (semiconductor photoelectrodes, light absorption, photocatalyst stability and charge transfer) and systems development (monolithic multi-junction systems, two-photon tandem systems, dual-bed redox systems and monomaterial two-step systems), resulting in the demonstration of various laboratory-scale PEC water-splitting prototype devices.

Although not yet achieved, the ultimate goal of a stable sunlight-to-hydrogen conversion efficiency of 10% is in sight for PEC-based water-splitting technologies.

2. Introduction

Since its inception in 1974 following the first oil crisis, the International Energy Agency (IEA) has operated as an autonomous body within the framework of the Organisation for Economic Cooperation and Development (OECD). The purpose of the IEA is to bring together a broad range of experts in specific technology areas to address energy-related challenges in a collaborative manner with a longer-term global view, and to share the resulting benefits.

The hydrogen program, known as the Hydrogen Implementing Agreement (HIA), of the IEA was established in 1977. This was one of many international IEA energy cooperation programs, which were grouped into fossil fuels, renewable energies (including hydrogen), efficient energy end-use and fusion power. The HIA itself specifically set out to advance hydrogen production, storage and end-use technologies, and to accelerate hydrogen's acceptance and widespread utilisation.

The HIA can look back to an impressive portfolio of fundamental work conducted since 1977[1]. As illustrated in Table-1, the HIA has been undertaking collaborative, pre-commercial Research, Development and Demonstration (RD&D) programs through eighteen specific Annexes (or Tasks).

Table-1: List of current and completed Annexes (or Tasks) by the IEA-HIA.

Annexes	Collaborative Work Tasks	Active Period
Annex-1	Thermochemical Production	1977 – 1988
Annex-2	High-Temperature Reactors	1977 – 1979
Annex-3	Assessment of Potential Future Markets	1977 – 1980
Annex-4	Electrolytic Production	1979 – 1988
Annex-5	Solid-Oxide Water Electrolysis	1979 – 1983
Annex-6 [1]	Photocatalytic Water Electrolysis	1979 – 1988
Annex-7	Storage, Conversion and Safety	1983 – 1992
Annex-8	Technical and Economic Assessment of Hydrogen	1986 – 1990
Annex-9	Hydrogen Production	1988 – 1993
Annex-10 [1]	Photoproduction of Hydrogen	1995 – 1998
Annex-11	Integrated Systems	1995 – 1998
Annex-12	Metal Hydrides for Hydrogen Storage	1995 – 2000
Annex-13	Design and Optimisation of Integrated Systems	1999 – 2001
Annex-14 [1]	Photoelectrolytic Production of Hydrogen	1999 – 2004
Annex-15	Photobiological Production of Hydrogen	1999 – 2004
Annex-16	Hydrogen from Carbon-Containing Materials	2002 – 2004
Annex-17	Solid and Liquid State Hydrogen Storage Materials	2001 – 2005
Annex-18	Integrated Systems Evaluations	2004 – 2006

[1] Tasks dedicated full or in-part to photoelectrochemical (PEC) hydrogen production options.

Since 1979, the IEA-HIA pioneered the joint scientific investigation of direct solar-to-hydrogen production routes based on photoelectrochemical (PEC) water-splitting (Annex-6, Annex-10 and this Annex-14). These efforts have been extended in 1995 to include major fundamental research efforts in biophotolysis of water (Annex-10 and Annex-15).

Theoretical and practical solar hydrogen systems integration and operational studies have also been initiated in 1995, focusing, inter alia, on practical solar-to-hydrogen conversion routes based on the application of conventional photovoltaics (PV) and electrolysis technologies (Annex-11 and Annex-13).

Collaborative, pre-commercial RD&D in solar hydrogen continues to be of core interest to the IEA-HIA program.

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[1] Luzzi A., Bonadio L. and McCann M., **2004**, In pursuit of the future, 25th Anniversary Report of the International Energy Agency Hydrogen Implementing Agreement. This report presents an overview of the varied activities conducted by the HIA and of the main achievements over a quarter of a century.

3. Annex-14

In a photochemical (or photoelectrochemical – PEC) system, a photoactive (semiconductor) material forms a junction when in contact with a liquid (or solid) electrolyte. Because of the junction potential, electron-hole pairs are produced in the photoactive material upon illumination with light. The light-induced electron-hole pairs drive a chemical reduction and an oxidation reaction in the (dominantly aqueous) electrolyte of the PEC system, leading to hydrogen and oxygen evolution (water-splitting). In this situation the photon energy is converted directly into chemical energy rather than into intermediate electrical energy as with solid-state or electrochemical PV cells. The basic function of a PEC hydrogen production cell is illustrated in Figure-1.
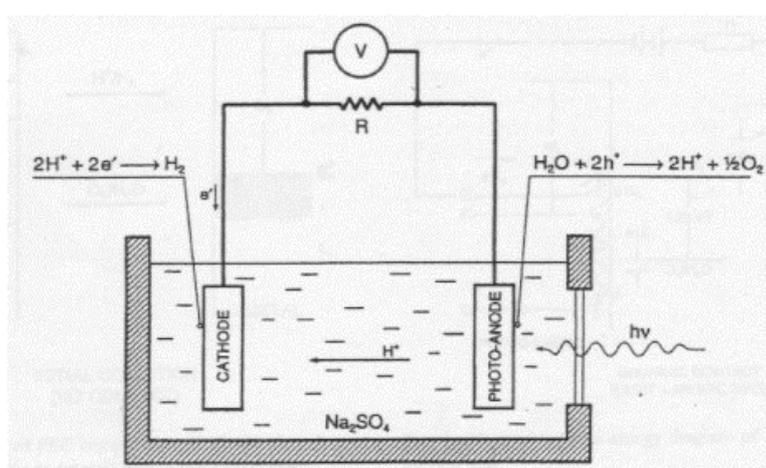

Figure-1: Basic concept of photoelectrochemical hydrogen production from water-splitting (as pioneered by and sourced from Fujishima and Honda, Japan, in 1972).

While the feasibility of the PEC water-splitting concept has been experimentally proven by various research groups around the world (first in 1972 by Fujishima & Honda[2]), the issues of conversion efficiency and device stability remain a research priority.

3.1. Scope

The direct production of hydrogen (H_2) via PEC water-splitting by sunlight requires the use of a light-harvesting device in conjunction with water-splitting catalysts. The necessary semiconductor-based light-sensitive device is similar to a photovoltaic (PV) solar cell, with or without dye sensitisation. The efforts of Annex-14 have been covering work conducted at the interface of fundamental and applied R&D, with an emphasis on material and systems studies.

Material studies through the collaborative Research and Development (R&D) efforts of the IEA-HIA have focussed on developing tailored semiconductor materials through doping

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[2] Fujishima A. and Honda K., *Nature* (London) **1972**, 238, 37-38.

(effecting the photoresponse by bandgap-shifting), improving the light absorption of a variety of wide-bandgap semiconductor materials by techniques such as dye-sensitisation, and developing catalytic and protective layers to safeguard the materials against photocorrosion.

Building on the advancements in materials research, follow-on system studies at the IEA-HIA aimed to maximise the efficiency of multi-junction systems, including combined PV/PEC water-splitting systems, and assess reactor system design options that involve oxygen- and hydrogen-evolving photocatalyst suspensions, including "dual-bed system" concepts.

In addition, the potential of non-oxygen-evolving systems have been evaluated for combining hydrogen production with waste degradation by replacing the photo-oxidation of water with the photo-degradation of the organic waste / pollutants in water.

3.2. Goals

The ultimate goal of the IEA-HIA photoelectrochemical research program is to develop and demonstrate the reliability of PEC systems in achieving water-splitting with a net sunlight-to-hydrogen conversion efficiency of 10%.

The standard 1000-hour test of the PV industry has been adopted as a benchmark for PEC performance and stability testing.

It is understood that the development of practical demonstration systems requires significant scientific and engineering efforts through a comparably medium-term and well-structured R&D program.

3.3. Participation

Japan, Sweden, Switzerland and the United States of America (USA) have been the official IEA-HIA member country participants of Annex-14, which combined their respective R&D programs on photoelectrolysis of water.

The following research groups have been active in Annex-14:

- **Japan**: The Photoreaction Control Research Center (PCRC) of the Japanese National Institute of Advanced Industrial Science and Technology (AIST);

- **Sweden**: The University of Uppsala (UniU);

- **Switzerland**: The University of Geneva (UniG), the University of Bern (UniB) and the Swiss Federal Institute of Technology (EPFL) in Lausanne; and

- **USA**: The National Renewable Energy Laboratories (NREL), the Hawaii Natural Energy Institute (HNEI), the Florida Solar Energy Centre (FSEC) and the University of California (UCal).

Toward the end of Annex-14, these official IEA-HIA member country participants have enjoyed a growing information exchange and/or part-collaboration with additional research groups that have secured funding to work in PEC water-splitting. Particularly since the second half of 2002, some of those non-Annex-14 and/or non-HIA member groups have started to attend Annex-14 expert meetings as observers. The key observer groups included:

- **Australia**: Sustainable Technologies International (STI);

- **France**: The National Centre for Scientific Research (CNRS) and the Atomic Energy Research Centre (CEA);

- **Netherlands**: The University of Delft (UniD) and the Leids Institute for Chemical Investigations (LICO);

- **Mexico**: The Energy Research Centre of the National University of Mexico (UNAM); and

- **United Kingdom**: Hydrogen Solar Company Ltd. (HSC).

3.4. Efforts

Overall, the combined level of efforts invested by the nine participating research groups over the 4.5-year duration of Annex-14 amounted to an equivalent of about 80 – 85 "man-years".

4. Program Of Work

Allowing for the necessary flexibility in the conduct of fundamental R&D work, Annex-14 has set out in July 1999 with the following objectives, task approach and subtask work program.

4.1. Objectives

The overall objective of Annex-14 was to significantly advance the fundamental and applied science in the area of photoelectrochemical (PEC) production of hydrogen over a period of three to five years. More specifically, it aimed to evaluate performance data regarding practical PEC system efficiency and device lifetime. From a scientific point of view, research was focusing on the development of semiconductor materials and structures, on photosensitive dyes, on integrated photovoltaics / electrolysis systems, and on novel single- as well as dual-bed reactor arrangements.

4.2. Approach

To accomplish the above objectives, the participants undertook individual and collaborative research within the framework of two coordinated subtasks, being Material Studies and System Studies. These were of common research interest to the existing photoelectrolysis

programs worldwide and carried forward, in a more specific and targeted fashion, the preliminary work previously address by Annex-10, Subtask A, of the IEA-HIA.

4.3. Subtasks

The two subtasks of Annex-14 are summarised as follows:

4.3.1. Subtask-A: Material Studies

Subtask-A did have two main groups of activities. They concerned the improvement of light absorption of wide-bandgap semiconductor materials such as titanium dioxide and gallium / arsenide by dye-sensitisation and other techniques, and the development of catalytic and protective layers for PEC cells.

Subtask-A has been lead by Switzerland.

4.3.1.1. *Activity-A1*: Improvement of solar light absorption in semiconductors

Semiconductors with wide bandgaps provide the necessary potential for water-splitting, but since they absorb only the most energetic part of the solar spectrum, conversion efficiencies are limited. The light absorption may be improved by modification of the semiconducting materials or by combining them with photo-sensitisers such as dyes that absorb a larger part of the solar spectrum.

4.3.1.2. *Activity-A2*: Development of catalytic and protective layers

PECs require appropriate catalysts to enhance the water-splitting reactions and to provide electrolyte-resistant layers to protect the semiconducting materials from corrosion. The development and characterisation of such layers has been the prime subject of this subtask.

4.3.2. Subtask-B: System Studies

Subtask-B did have three main groups of activities. They targeted the maximisation of efficiency of multi-junction water-splitting systems and the assessment of reactor system design options for the photoproduction of hydrogen, including the new dual-bed system concept.

Subtask-B has been lead by the USA.

4.3.2.1. *Activity-B1*: Efficiency optimisation of multi-junction systems

Improved device conversion efficiencies can be achieved by application of multi-junction systems, which have already demonstrated encouraging but non-stable efficiencies of the order of 12-14%. Multi-junction systems have been developed and studied with the ultimate

aim of reaching a stabilised target efficiency of 10%. It was aimed to give due consideration to cost effectiveness in the conduct of this R&D work.

4.3.2.2. *Activity-B2*: Investigation of reactor design options

Various conceptual reactor and system designs for the photoelectrolysis of water have previously been proposed, pointing toward the need of fundamental efforts concerning engineering R&D for such solar systems. Collaborative R&D in reactor engineering designs has therefore been conducted. Efforts included:

- Development of mathematical models for reactor designs facilitating photoelectrolysis of water, with the models including calculations of mass transfer, hydrodynamics, and heat balance;

- Development of methods for the measurement of key reactor performance parameters, including hydraulic (dispersion) and gas transfer coefficients, sunlight interception, and hydrogen losses; and

- Comparative evaluations of alternative reactor designs.

4.3.2.3. *Activity-B3*: Assessment of dual-bed systems

A series of particulate semiconductor photo-catalysts for hydrogen as well as for oxygen evolution and mediators for charge transfer have been developed and tested for application in a new, compact and efficient dual-bed reactor system.

5. Achievements

The following sections provide a brief overview of the main areas of materials and systems research that have been covered in a collaboratively manner by the nine research groups of Annex-14 over the past 4.5 years (June 1999 – December 2003). These efforts have not only been building on but did progress the achievements of the previous Annex-10 (1995 – 1998) in a significant manner.

5.1. Material Studies

5.1.1. Semiconductor Electrodes

The thermodynamic potential for splitting water into hydrogen and oxygen at ambient conditions (25°C, ~1 bar) is 1.23 volts. Adding overvoltage losses and some energy to drive the reaction at a reasonable rate, a voltage of about 1.6 – 1.8 volts is required for water decomposition. Current commercial electrolysers operate at between 1.7 and 1.9 volts. Translating the energy of 1.9 eV into a corresponding wavelength of light results in a about 650 nm, which is in the lower energy red portion of the visible light spectrum. This means that the entire visible spectrum has the energy capable of splitting water into hydrogen and

oxygen. The key is to find a light harvesting system that can efficiently collect the energy and direct it towards the water-splitting reaction. In photoelectrochemistry, the light harvesting system is a semiconductor immersed in aqueous solution.

The primary task then is to identify and synthesise the semiconducting material or the semiconductor structure with the properties necessary for direct water-splitting.

The major roadblocks in doing direct photoelectrolysis of water are:

- **Lack of efficient light absorption material** (as presented above, for reasonable solar efficiencies, the semiconductor bandgap must be less than about 2.2 eV, but greater than about 1.6 eV);

- **Corrosion of the semiconductor** (most semiconductors with appropriate bandgaps are thermodynamically unstable in water); and

- **Energetics of the semiconductor** (the matching of the semiconductor bandedge energies with the hydrogen and oxygen evolution reactions).

As part of this Annex-14, a multiplicity of approaches has been taken to discover and design the necessary materials and integration options for a low-cost high-efficiency, stable PEC-based water-splitting system. These various approaches are discussed below.

5.1.1.1. Tungsten Trioxide (WO_3)

With a bandgap of about 2.5 eV and a demonstrated resistance to photocorrosion in aqueous solutions, tungsten trioxide (WO_3) thin-films are well matured for photoanode applications in water-splitting systems. A reliable preparations process for multi-layer WO_3 thin films with an overall thickness of typically about 3 micro-millimeter has been developed, matured and patented at the University of Geneva. The WO_3 films are prepared using precursor colloidal solutions of tungstic acid complemented with various additives.[3] The WO_3 films demonstrate a high transparency (60-80%; light absorption noticeably limited to the blue portion of the sunlight at below ~ 475 nm) and a consistency of a network of preferentially oriented nanocrystals (refer to Figure-2 on the following page). The thin-films demonstrate the ability of this semiconductor to operate as both efficient (photocurrents of up to 6 mA/cm^2 with organic compounds) and stable solar photoanode for oxidation of water and various organic compounds such as methanol. The sufficient resistance of WO_3 against photocorrosion in aqueous solutions has been confirmed over an acidic range of pH, including strongly acidic solutions.

Doped WO_3 – The maximum photocurrents obtained for water-splitting using WO_3 photoanodes under 1-sun AM 1.5 have recently been considerably improved to reach almost 5 mA/cm^2 (refer to Figure-3 on the following page, including a comparison with the former photocurrents of 3.5 mA/cm^2). In parallel, photocurrents as large as 10 mA/cm^2 have been

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[3] Santato C., Odziemkowski M., Ulmann M. and Augustynski J., *J. Am Chem. Soc.* **2001**, 124, 10639-10649.

obtained in the case of the photooxidation (degradation) of various model organic compounds such as alcohols, carboxylic acids or aldehydes (this is due to the combined effects of the favorable kinetics and of the photocurrent doubling phenomenon). These improvements have been achieved through doping of WO_3 as well as a modification in the preparation procedure and are currently the subject of a patent application by the University of Geneva.
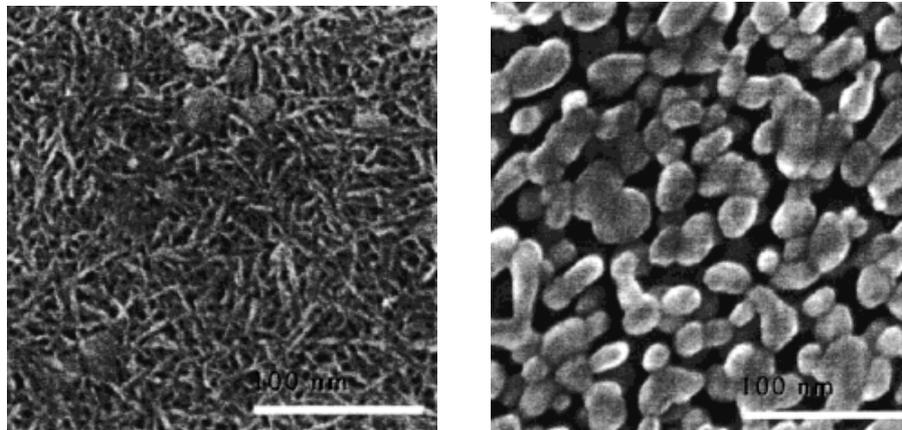

Figure-2: WO_3 thin-films prepared by the deposition of tungstic acid / PEG colloidal solution and 30-min annealing at 400°C and 500°C respectively (Source: Santato, University of Geneva, Switzerland).
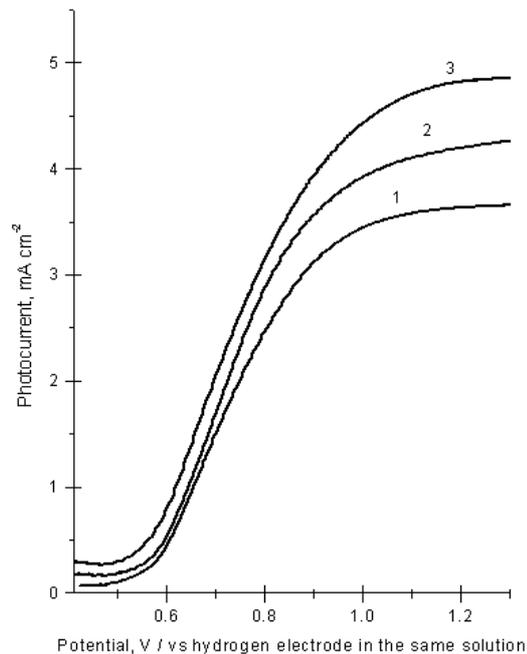

Figure-3: Photocurrent versus applied potential curves for a series of ca 3-micron-thick WO_3 films, recorded in a 3M-H_2SO_4 solution under simulated solar AM-1.5 illumination. The figure illustrates the successive improvements brought about by doping of the precursor (curve 2), augmented by a modification of the preparation procedure (curve 3). Curve 1 is for the film prepared under standard screen-printing conditions (Source: Augustynski, University of Geneva, Switzerland).

At the University of California in Santa Barbara, the necessary R&D infrastructure has been established to rapidly explore, via combinatorial electrochemical methods, the composition-structure-property relationships of a wide range of metal-oxide based solid-state PEC materials for hydrogen production. Material libraries are synthesized and in a first instance screened optically for bandgap definition. Secondary libraries are then created of compositions with solar spectrum absorption. These derivate libraries are subsequently screened for appropriate redox and flatband levels, followed by a final screening for hydrogen production.

A library of WO_3 doped with different transition metals was created using a variety of doping densities with the aim of improving upon the photocatalytic activity of pure WO_3. The first library incorporated Pt, Ru, Ni, Co, Cu, and Zn as dopants within polycrystalline WO_3. The materials were each co-deposited with WO_3 electrochemically from a mixture of 50mM metal chloride solution and a tungsten-peroxo solution prepared by dissolving tungsten metal powder in a 30% hydrogen peroxide solution. Altering the metal-chloride concentrations in the electrolyte, from 0% to 50%, allowed for variation of doping concentrations within the deposited films. The secondary WO_3 library was synthesized with a much smaller variation in doping concentration. The dopant concentration in the electrolyte varied from 0% to 5% versus tungsten, as opposed to the 0% - 50% range used in the primary library. With the greater resolution of this library, Pt and Ru were found to improve upon the photocurrent of WO_3, but only in small concentrations. Since neither of these materials absorb light, adding too much of either most likely reduces photon absorption, and thus leads to lower photocurrent. A small doping density, however, benefits the catalytic properties of the surface without affecting photon capture, and hence, a greater photocurrent compared to pure WO_3 is observed[4].

Tungsten-molybdenum mixed oxides ($W_xMo_{1-x}O_3$, with 0% < x < 100%) of various W:Mo ratios have also been successfully synthesized by combinatorial electrochemical deposition. XRD and Raman spectroscopy were used to observe distinct structural changes within $W_xMo_{1-x}O_3$ for each stoichiometry. Photoactitvity of the mixed oxides were strongly dependent on the composition, and the 50:50 tungsten-molybdenum mixed oxide exhibited optimal photocatalytic activity and electrochromic characteristics of all materials investigated.[5]

Outlook – At the University of Geneva, the development of the WO_3 photoanodes will be continued with a focus on changes in the synthesis as well as the composition of the WO_3 precursor. These efforts are in part related to the extension of the current method of film preparation toward a screen-printing method with subsequent spraying. This combination offers a reduction of the number of precursor applications, leading to a significantly shorter film fabrication procedure and the option to produce large-size PEC thin-films based on conducting glass plates.

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[4] Baeck S., Jaramillo T., Brandli C. and McFarland E., *J. Combi. Chemistry.* **2003**, 4(6), 563-568.
[5] Baeck S., Jaramillo T., Jeong D. and McFarland E., *Chem. Comm.* **2004**, 390-391

5.1.1.2. Ferric Oxide (Fe_2O_3)

Ferric oxide (Fe_2O_3) is considered a very promising, low-cost photoanode material option as alternative to WO_3 when used with two-photon tandem PEC systems. The main material studies of Annex-14 research groups have focused on the fundamental understanding of the relationship between the PEC effectiveness and the structure/morphology of such Fe_2O_3 thin-films. In particular, the effects of new dopants, of new solvents involved in the precursor formation and of a variety of heat treatments were examined.

At the University of Geneva, the standard preparation method of spray pyrolysis (employing a variety of precursors including iron acetylacetonate ($Fe(acac)_3$) type A and iron chloride ($FeCl_3.6H_2O$) type C) has recently been complemented with ultrasonic spray pyrolysis tested at the Swiss Federal Institute of Technology (EPFL). For comparative purposes, tests have also been conducted at the University in Geneva on the formation of Fe_2O_3 films by direct oxidation of the metal in various gas atmospheres. Reactive sputtering and liquid phase chemical vapour deposition (LPCVD) are additional film preparation methods studied at EPFL and at the University of Augsburg (Germany).

The growth rate of hematite (α-Fe_2O_3) the films made at EPFL by ultrasonic spray pyrolysis (USP) was found to be much slower than the growth rate of films commonly made by spray pyrolysis (SP). Because of this, the films obtained by USP were found to be much denser and to contain fewer defects than the films obtained by SP. Therefore, the films made by USP exhibited higher photocurrents (typically 1 mA/cm^2 and higher instead of 50 $microA/cm^2$) and lower onset potential (around 800 mV instead of 1200 mV vs RHE) than films made by SP (refer to Figure-4 on the following page). These thin-films have been deposited in multiple layers on tin-oxide based conducting glass ("TEK-25").

Doped Fe_2O_3 – Different elements are known[6,7] to enhance the photocurrents delivered by α-Fe_2O_3 photoanodes, either by forming mixed oxides when the dopant amount is high, or simply by improving the film conductivity. At the University of Geneva, the effect of doping α-Fe_2O_3 thin-films with the elements Ti, Al, Sn, Pt, Ni, In, Cr and Li has been extensively studied. The importance of prolonged annealing (between 1 to 6 hours) in air at 550°C has generally been confirmed, particularly in relation with Sn, Al and Ti.

While at the EPFL, Ti-doped Fe_2O_3 films produced photocurrents of around 2 mA/cm^2 under simulated AM-1.5 sunlight using water as electron source, encouraging results were reported by the University of Geneva in relation to Ti/Al-doped Fe_2O_3 thin-films. Photocurrents of typically 5-6 mA/cm^2 have been achieved for 1-μm thin films tested under full output of a 150-Watt xenon (Xe) lamp.

At the National Renewable Energy Laboratories (NREL), in collaboration with the Yerewan State University of Armenia, n-type Fe_2O_3 doped with up to 2% of tantalum (Ta) has been synthesised and studied as photoanode in conjunction with a p-type Cu_2O photocathode.

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[6] Anderman M. and Kennedy J., in Finklea H. (Ed.), *Stud. Phys. Theor. Chem.*, Elsevier, Amsterdam, **1988**, 147.

[7] Kennedy J. and Frese K., *J. Electrochem. Soc.*, **1978**, 125, 709.

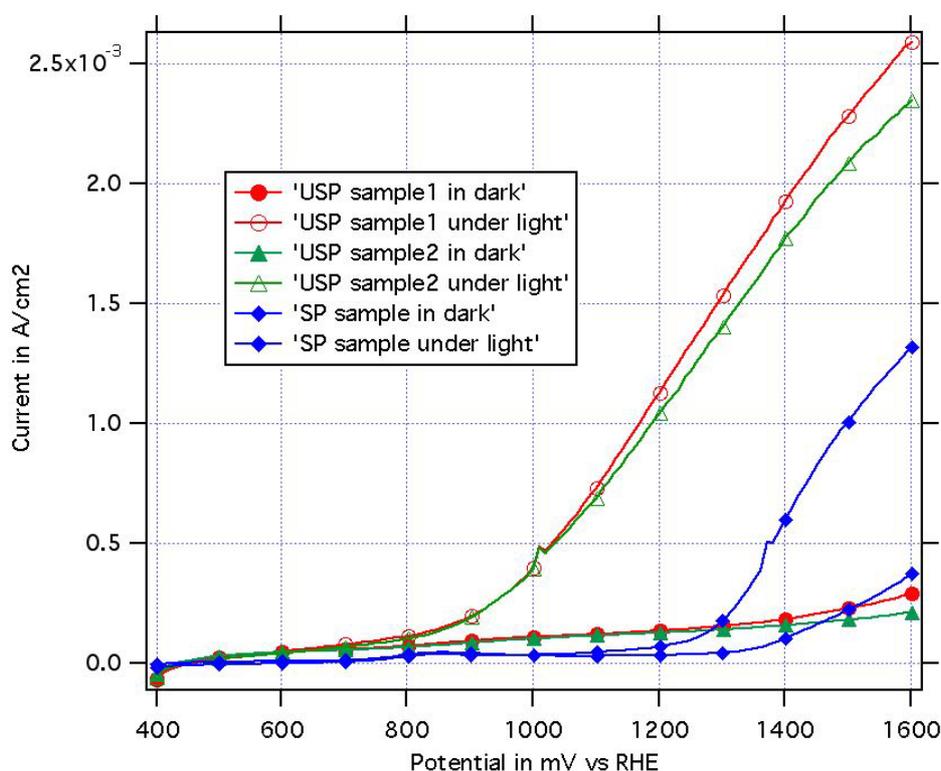Photocurrents of up to 6.4 mA/cm^2 have been measured, indicating successful PEC water-splitting[8].

Figure-4: Current-potential curves of best α-Fe$_2$O$_3$ samples made by ultrasonic spray pyrolysis and spray pyrolysis measured under 1.5-AM in 1M NaOH (Source: Nazeeruddin, Swiss Federal Institute of Technology).

Outlook – Improvements in the morphology and selective doping of the Fe$_2$O$_3$ thin-films are needed to achieve higher photocurrents. The production of homogeneity in particle size of the thin-films and the reproducibility of the results remain additional key challenges on the way to developing ferric oxide as new photoanode material of choice with PEC water-splitting systems.

5.1.1.3. Silver Chloride (AgCl)

Quantum-sized silver, silver-chloride and silver-sulfide clusters (zeolite A composites) have been synthesised and characterised at the University of Bern. Such clusters can be combined with a semiconductor photocathode (eg. Si, SiC, Cu$_2$O, CdS, Ag$_2$S or p-GaInP$_2$) to act as antenna system for the oxygen evolution part in a water-splitting PEC cell[9]. The combination of silver-based zeolite A antenna systems with the TiO$_2$-based "Graetzel"solar cell (DSSC) is

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[8] Aroutiouniana V., Arakelyana V., Shahnazaryana G., Stepanyana G., Turner J. and Khaselev O., *Int. Journal of Hydrogen Energy.* **2002**, 27, 33-38.

[9] Calzaferri G., Brühwiler D., Glaus S., Schürch D., Currao A. and Leiggener C., *J. Imaging Sci. Technol.* **2001**, 45, 331.

envisaged to form a potentially effective water-splitting device. Figure-5 illustrates a van der Waals model of a generic zeolite cluster.
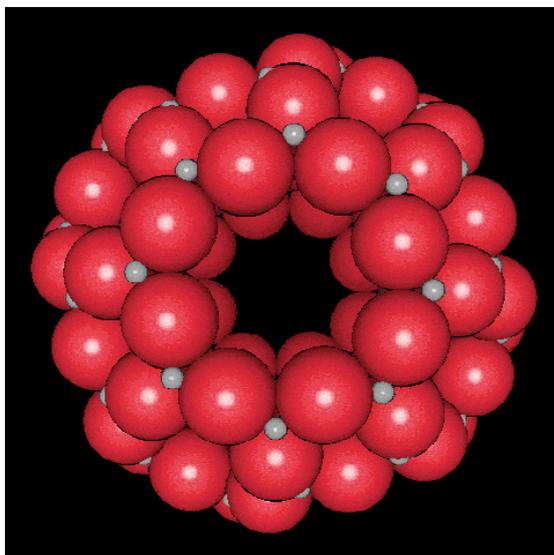

Figure-5: Van der Waals model of a generic zeolite cluster (Source: Currao, University of Bern, Switzerland).

Thin silver chloride (AgCl) layers evolve oxygen under UV/VIS illumination in aqueous solution under appropriate conditions[10]. AgCl deposited on a conducting support such as zeolites photocatalyses the oxidation of water to O_2 in the presence of a small excess of silver ions in solution. The light sensitivity in the visible part of the spectrum is due to self-sensitization caused by the formation of silver species during the photoreaction. Anodic polarisation re-oxidises the reduced silver species. Schürch et al.[11] described the details on the reaction mechanism for the oxidation of water to O_2 with AgCl photoanodes. The water oxidation reaction and the reoxidation of the reduced silver species take place simultaneously, making the system catalytic.

Outlook – It is aimed to improve the activity of AgCl photoanodes and match them with the bias from a TiO_2-based dye-solar-cell for maximum PEC water-splitting.

5.1.1.4. Gallium-Indium-Phosphide (GaInP$_2$)

Although the requirement of a bandgap in the range 1.6 – 2.2 eV is a necessary condition for water-splitting, it is not a sufficient condition. Even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the bandedges may prevent it from doing so. The ability to fully exploit PEC systems for solar energy conversion critically depends on one's ability to understand and control the properties of the semiconductor / electrolyte interface.[12] This is true for GaInP$_2$ (E_g = 1.83 eV), which

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[10] Lanz M., Schürch D. and Calzaferri, G., *J. Photochem. Photobiol. A: Chem.* **1999**, 120, 105.

[11] Schürch D., Currao A., Sarkar S., Hodes G. and Calzaferri G., *J. Phys. Chem. B.* **2002**, 106, 12764.

[12] Bansal A. and Turner J. *Journal of the American Chemical Society.* **2000**, April-9, 6591-6598.

should be able to split water but cannot achieve this due to the bandedge mismatch, a situation that is also true in general for most other semiconductors. The semiconductor bandedges are determined by the chemistry of the semiconductor / electrolyte interface, which is controlled by the composition of the semiconductor, the nature of the surface and the electrolyte composition. Therefore, bandedge engineering becomes a necessary requirement to address these problems by controlling the energetics of the semiconductor bandedges.

Research efforts at the National Renewable Energy Laboratory (NREL) looked at organometallics where it was aimed to combine the bandedge shifting properties of organic compounds and the charge catalysis character of transition metals found in earlier work. In that work, p-GaInP$_2$ surfaces were modified with pthalocyanins, porphyrins and other organic molecules. Based on those results, it was decided to focus on the influence of soluble and insoluble, metallated and unmetallated porphyrins on the bandedges. The initial experiments have been completed in this area, where porphyrins used included nickel(II)-tetra(N-methyl-2-pyridyl) porphyrin chloride [NiTMPyP(2)], Fe(III)TMPyP(2), VO(IV)TMPyP(4) and rhodium(III)-octaethylporphyrin[RhOEP].[13] Treatments were applied by drop-evaporation for water-insoluble compounds and by immersion for water-soluble compounds. The position and movement of GaInP$_2$ bandedges were monitored by capacitance measurements, and shifts of up to 1 volt were observed after some surface treatments. A shift of one volt should in theory be sufficient to effect water-splitting, however, none was observed with these first experimentation. This requires further investigation to determine where the problem lies.

Outlook – Due to its favourable bandgap, GaInP$_2$ remains a very promising material for efficient for PEC water-splitting. Bandedge-shifting, however, is seen as the major challenge to overcome.

5.1.1.5. Titanium Dioxide (TiO$_2$)

Direct-splitting of water into hydrogen (H$_2$) and oxygen (O$_2$) by solar light in PEC cells has received much attention, since hydrogen is considered the fuel of the future[14]. Fujishima and Honda[15] were the first reporting successful PEC splitting of water. They used a semiconductor electrode based on rutile titanium dioxide (TiO$_2$). Since then, both rutile and anatase crystal forms of TiO$_2$ have been largely studied for PEC and photocatalysis applications due to their photoactivity, high corrosion resistance and harmless characteristics[16],[17],[18]. However, there are some disadvantages with TiO$_2$. A major one for solar energy applications is that the bandgap energy, being 3.0 eV for rutile and 3.2 eV for anatase, only allows ultraviolet (UV) absorption. To improve the PEC efficiency of the

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[13] Deutsch T. – **2002**; Leisch J. – **2000**, Warren S. – **2000**, NREL Student Reports. DOE-ERULF Program.

[14] Bak T., Nowotny J., Rekas M. and Sorrell C., *Int. Journal of Hydrogen Energy.* **2002**, *27*, 991-1022.

[15] Fujishima A. and Honda K., *Nature* (London). **1972**, *238*, 37-38.

[16] Grätzel M., *Nature.* **2001**, 414, 338-344.

[17] Mills A. and Le Hunte S., *J. Photochem. Photobio. A: Chemistry.* **1997**, *108*, 1-35.

[18] Fujishima A., Rao T. and Tryk D., *Journal of Photochemistry and Photobiology C: Photochemistry Reviews.* **2000**, 1, 1-21.

material, it is desirable to red-shift the PEC onset to also include the less energetic but more intense visible part of the solar spectrum. Traditionally, this has been achieved by anchoring organic dyes to the surface, and this approach has been successful in dye-sensitised solar cells (DSSC)[19].

Dye-Sensitized TiO$_2$ Solar Cells (DSSC) – A large number of dyes of different kinds have been tested in DSSCs. The most efficient and commonly used in dye-sensitised TiO$_2$ solar cells are based on ruthenium complexes. Different ligands have been tested all in the aim to broaden the absorption spectrum and in this way improve the solar cell efficiency. The efficiency is at best for small cells around 11%, but is for large area cells or modules typically 7%. The DSSC can, as pointed out by Grätzel[20], be utilised in combination with a PEC cell with one (or two) photon adsorbing electrodes to form a quasi tandem cell for (photo)electrochemical electrolysis of water. The DSSC in such a devise simply used to bias the PEC cell.

Artificial Photosynthesis and Water Photoelectrolysis – The so called Artificial Photosynthesis (AF) group in Sweden has adapted a more challenging task. They have for a number of years tried to link a manganese complex to different light absorbing dyes[21] in an attempt to form a complex over which charge can be separated. This "biomimetic" system is inspired by "Photosystem-II" in green plants, in which a manganese complex is the active site producing O$_2$ from water. Copying nature, the aim is that the manganese complex shall, upon adsorption of light in the dye, collect holes and work as a catalyst for oxidation of water, while the excited electrons from the dye shall produce H$_2$. The molecular system that the AF-group is aiming to develop could for instance, if successful, be coupled to a nanostructured TiO$_2$ electrode[22] of the same kind as in the DSSC. This is possible since the same kind of (ruthenium) dye is used as with common DSSCs. However, so far no O$_2$ (and consequently no H$_2$ from potential water-splitting) has been produced by any of the large number of dye-manganese-complexes that the AF-group has studied.

Although a biomimetic system of the kind that the AF-group is aiming for may, at a first glance, look very attractive and innovative, the obstacles to pass before a functioning dye-manganese complex is created seem to be enormous. Already the conventional DSSC using comparatively simple dye-sensitisers experiences challenges concerning efficiency and long-term stability when water is present in the cells. A large dye-manganese-complex will probably not make things easier. Neither is it very likely that a simple linear combination of a light-adsorbing dye and an organic manganese molecule will be able meet the dynamic and energetic conditions necessary to separate the four holes and electrons needed to create one oxygen plus two hydrogen molecules from two water molecules. And if it works, what efficiency can one expect? In this context it should be remembered that the manganese complex used by nature works in an enzymatic environment formed by an extremely complex flexible protein structure. This structure is certainly not there by chance. It has

[19] O'Regan B. and Grätzel M., *Nature.* **1991**, 353, 737-740.
[20] Grätzel M., *Cattech.* **1999**, *3*(1), 4-17.
[21] Magnusson A., Frapart Y., Abrahamsson M., Horner O., Åkermark B., Sun L., Girerd, J., Hammarström L. and Styring S., *J. Am. Chem. Soc.* **1999**, 121, 89-96.
[22] Abrahamsson M., PhD Thesis, Uppsala University **2001**.

most probably, as in all enzymes, a function to lower the activation energy and speed up the oxidation of water to oxygen, which in nature seldom exceeds an efficiency of 1%. To mimic this enzyme part adds further to the complexity of the artificial synthesis task. The success of the AF project as a realistic water-splitting project for hydrogen production by sunlight can therefore be questioned. In addition, whether or not such a chemically and physically vulnerable complex system can in effect lead to superior efficiency and long-term stability than solid state systems remains also questionable.

A possible way to make use of the excellent scientific work done by the AF-group could be to integrate their light-harvesting devices (when working) into a living system such as algae. This could eventually solve the problem of durability since the system, if properly fed, would reproduce itself.

Nitrogen-Doped TiO$_{2-x}$N – Back in 1986, Sato[23] already reported about photocatalytic activity in visible light for TiO$_2$ prepared and calcinated with NH$_4$OH. However, it took almost 15 years from then until nitrogen-doped TiO$_2$ again was considered for photocatalytic applications. Asahi et al.[24] and Morikawa et al.[25] reported that nitrogen-doped TiO$_2$ (TiO$_{2-x}$N$_x$) shows a narrower bandgap and a better photocatalytic activity under visible light than the corresponding undoped TiO$_2$. With this approach in mind, Lindgren et al.[26] synthesized nitrogen-doped TiO$_2$ films by means of reactive magnetron direct-current (DC) sputtering. The PEC and optical properties showed that the new bandgap states created by doping indeed improved the photoresponse in the visible region. Highly porous TiO$_2$ thin films of around 700 nm hase been successfully doped with nitrogen, shifting the band-gap down toward 2.3-2.4 eV and showing a photoresponse in the visible light region toward ~550 nm (refer to Figure-6). These results have recently been verified by Burda et al.[27]. Success was reported with the production of TiO$_2$ nanoparticles with a nitrogen dopant concentration up to 8%. The particles were shown to be photocatalytically active, decolouring methylene blue at 540 nm.

The optical and photoelectrochemical properties of nitrogen-doped TiO$_2$ have been further studied by Lindgren et al.[28]. Visible light photooxidation of water was confirmed for DC magnetron sputtered thin-film electrodes based on nitrogen-doped TiO$_2$. It was also shown that in addition to a set of states just above the conduction band, this material also has a wide distribution of states in a range below the conduction band that are related to the N-doping. These states work as centres for electron-hole recombination. They also have a unique property of being able to store photogenerated holes for a long period of time.[29]

[23] Sato S., *Chemical Physics Letters.* **1986**, 123(1,2), 126-128.

[24] Asahi R., Morikawa T., Ohwaki T., Aoki K. and Taga Y., *Science.* **2001**, 293, 269-271.

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[26] Lindgren T., Mwabora J., Avendaño Soto E., Jonsson J., Hoel A., Granqvist C. and Lindquist S., *J. Phys. Chem. B.* **2003**, 107(24), 5709-5716.

[27] Burda C., Lou Y., Chen X., Samia A., Stout J. and Gole J, *Nanolett.* **2003**, 3(8), 1049-1051.

[28] Lindgren T., Mwabora J., Avendaño E., Jonsson J., Hoel A., Granqvist C. and Lindquist S., *J. Phys. Chem. B.* **2003**, 107, 5709-5716.

[29] Lindgren T., **2004**, PhD Thesis #945 University of Uppsala, ISBN 91-554-5892-0.
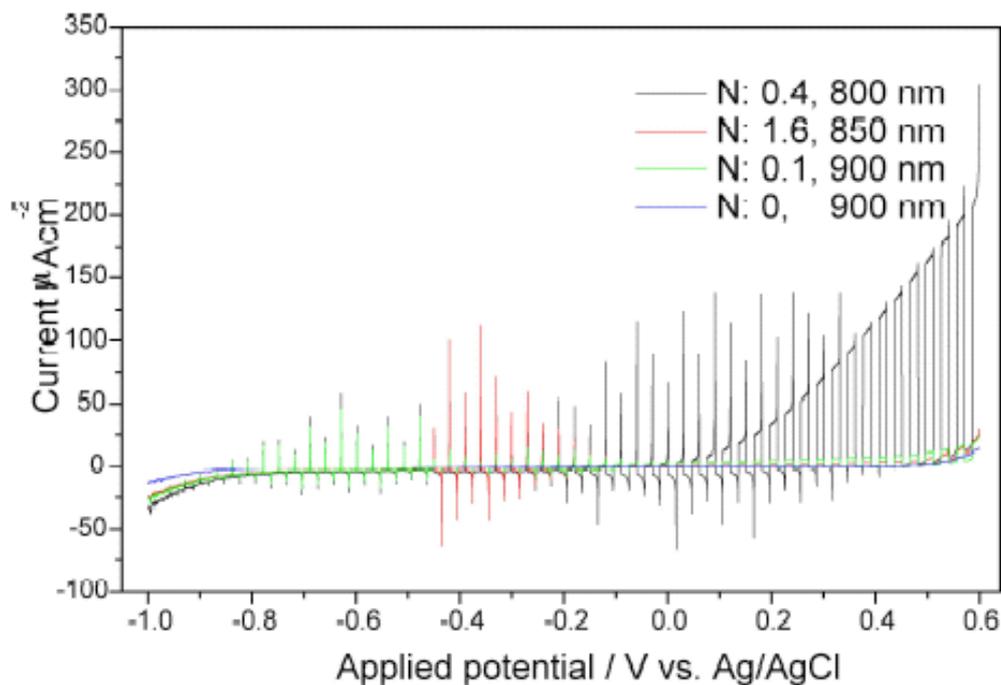
<u>Figure-6</u>: Photocurrent response in visible light (aqueous electrolyte, applied potential) for a series of nitrogen-doped TiO_2 electrodes (Source: Lindgren, University of Uppsala, Sweden).

It is generally accepted that visible light absorption in nitrogen-doped TiO_2 is due to substitutional doping of oxygen, which results in a mix of N^{2p} and O^{2p} states[30]. The nitrogen-generated states are positioned energetically above the valence band (O^{2p}) of TiO_2. At University of Uppsala, this was experimentally shown by measuring the open-circuit potential under irradiation of dye-incorporated samples. Sakthivel and Kisch[31] confirmed similar experimental evidence. Accordingly, the conduction bandedge should remain unchanged by nitrogen doping, and the expected needed bias should be low when $TiO_{2-x}N_x$ is used as water-splitting electrode. Such a material would be of great interest for direct water-splitting or in the TiO_2-based tandem PEC cell.

Other Dopants of TiO_2 – Efficient photocatalytic or photolectrochemical response of TiO_2 doped with other anion materials has been reported. Carbon-modified TiO_2[32], sulfur-doped TiO_2,[33,34] and $TiN_xO_yF_z$[35] are novel and interesting materials, which have shown good photocatalytic response in visible light. Some of these materials, primarily tested as photocatalysts for air and water purification, are potentially also candidates for PEC water oxidation. This is for instance true for the S-doped TiO_2 reported to be photocatalytically active under visible light by Ohno et al. (refer to reference #33).

[30] Irie H., Watanabe Y. and Hashimoto K., *J. Phys. Chem. B.* **2003**, 107(23), 5483-5486.

[31] Sakthivel S. and Kisch H., *ChemPhysChem.* **2003**, 4, 487-490.

[32] Khan S., Al-Shahry M. and Ingler W., *Science.* **2002**, 297, 2243-2245.

[33] Ohno T., Mitsui T. and Matsumua M., *Chemistry Letters.* **2003**, 32(4), 364-365.

[34] Umebayashi T., Yamaki T., Tanaka S. and Asai K., *Chemistry Letters.* **2003**, 32(4), 330-331.

[35] Nukumizu K., Nunoshige J., Takata T., Kondo J., Hara M., Kobayashi H. and Domen K., *Chem. Lett.* **2003**, 32(2), 196-197.

Outlook – As shown with the pioneering work of Fujishima and Honda back in 1972, TiO_2 – in particular anatase – can work as a PEC electrode for hydrogen production from water. But TiO_2 is limited in efficiency since it is absorbing only UV light. The attempts to broaden the spectrum of the inherently very stable TiO_2 photoelectrodes by adding dopants of S, N, C, and/or F are therefore encouraging. Oxygen generation has been proven under visible light absorption at C-doped TiO_2, and lately also at thin film electrodes of N-doped TiO_2. The major challenge in the latter case, which may well turn out to be a very generic problem, is that the dopant also introduces recombination centres. These centres counteract the advantage of visible light absorption. Whether or not the formation of these recombination centres turns out to be an "intrinsic" challenge of all possible TiO_2 dopants, which are designed to broaden the absorption spectrum, remains to be studied.

5.1.1.6. Nitrides (InN and Sn_xN_y)

Indium nitride (InN) and tin nitride films (Sn_XN_Y) have been produced at the University of Uppsala with a reactive DC magnetron sputtering technique.[36] The thin-film semiconductors were optically and photoelectrochemically characterized and the energetic position of their bandedges was determined with respect to the NHE. A spectroscopic bandgap determination of InN showed that the film had an indirect bandgap of 1.4 eV and a direct bandgap of 1.8 eV. The bandgap determination of Sn_XN_Y indicated a bandgap energy of approximately 1.4 eV. All nitride films showed photoresponse in a 0.1M KI (aqueous) electrolyte at an irradiation intensity of 1000 Wm^{-2}. By combining indium and tin nitride in a layer structure it was possible to significantly increase the photoresponse of the electrode.[37]

Outlook – Although research on InN and Sn_XN_Y as thin-film electrodes is still in its infancy, these materials have shown promising bandgaps at around 1.4 eV . In addition, the energetic position of the conduction band in relation to the reduction potential of protons has been found to be not too far from the ideal position. Further research on these materials is understood to be warranted for PEC water-splitting.

5.1.1.7. Copper-Indium-Gallium-Diselenide ($CuInGaSe_2$)

Thin-film $CuInGaSe_2$ (CIGS) devices are well known for their high conversion efficiency even when prepared as polycrystalline thin-films. CIGS thin-films have been successfully prepared from electrodeposited precursors to yield solar energy conversion devices with up to 15.4% efficiency. Electrodeposition is proven as potentially scalable technique for large area thin film fabrication at reduced costs. However, the bandgap of this material is too low to effect the water-splitting reaction.

At the National Renewable Energy Laboratory (NREL), sulfur incorporation has been used in CIGS solar energy materials to increase device performance and provide a graded bandgap

[36] Lindgren,T., Larsson M. and Lindquist S., *Sol. Energy Mat. Sol. Cells.* **2002**, 73, 377-389.

[37] Kebede Z., Lindgren T. and Lindquist S., *J. Sol. Energy Mat. Sol. Cells.* **2004**, Accepted for publication.

structure.[38] The efforts in this area included the incorporation of sulfur throughout the entire film to obtain a higher bandgap material suitable for water-splitting. The combination of lower system manufacturing cost (from electrodeposition) and a high efficiency material represents one of the most important areas of research for hydrogen production systems. In addition, indium in the film may provide some protection against corrosion. In aqueous solution, indium can form a conducting oxide layer that stabilizes the interface and may protect the underlying material, although it is expected that a protective surface film (eg. TiO_2) may ultimately be required. In this initial materials research effort at NREL, $Cu(In,Ga)(Se,S)_2$ semiconducting thin-films were made from electrodeposited $Cu(In,Ga)Se_2$ precursors, followed by physical vapor deposition of In_2S_3, Ga, and Se. The bandgaps of these materials were found to be between 1.6 eV and 2.0 eV (refer to Figure-7), which spans the optimal bandgap necessary for application for the top junction in PV multi-junction devices and unassisted water photolysis.
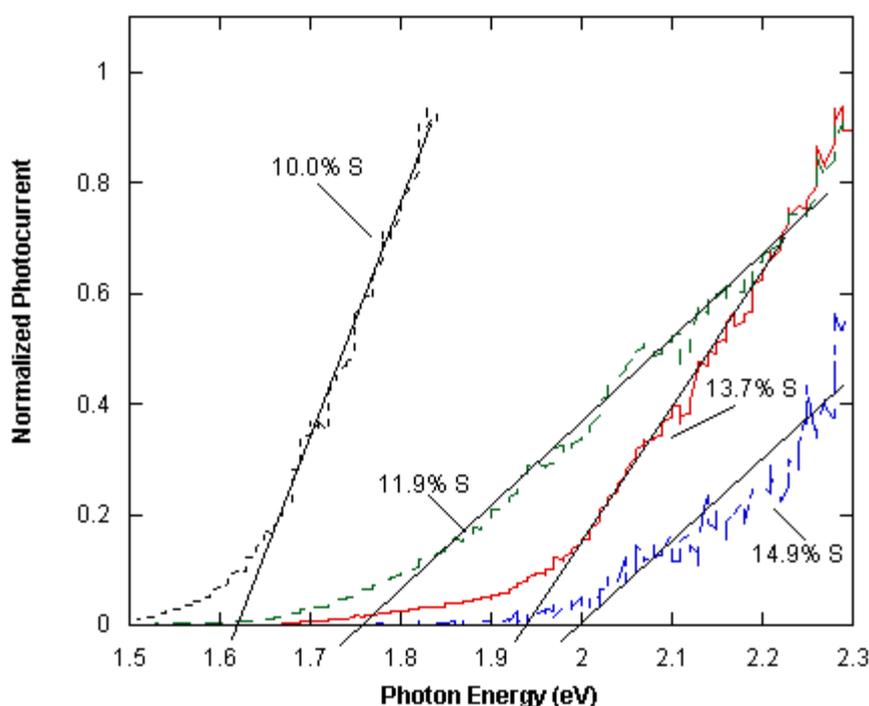

Figure-7: Photoresponse measurements of copper-indium-gallium-diselenide ($CuInGaSe_2$) thin-films with varying composition of bulk-incorporated sulfur (atomic-%) (Source: Turner, National Renewable Energy Laboratory, USA).

Outlook – The promising efforts on SIGS demonstrated the ability to ultimately synthesise materials with a full range of bandgaps from a single material set, encouraging to potentially achieve the "perfect" PEC material for water-splitting. Fundamental materials research work on bandgap engineering is therefore continuing, assisted by fast-screening options available from combinatorial chemistry approaches.

[38] Turner J., Beach J., Deutsch T., EinspahrJ., Leisch J., Menningen K., Kjeldsen L.,, Varner K., Wang H. and Warren S., **2003**, US-DoE FY-2003 Progress Report.

5.1.1.8. Tantalum Oxide (TaO)

New photocatalysts such as transition metal (M) doped $In_{0.8}M_{0.2}TaO_4$ (M = Mn, Fe, Co, Ni, Cu) were synthesized and tested as photocatalysts for water-splitting at the Photoreaction Control Research Center (PCRC) of the Japanese National Institute of Advanced Industrial Science and Technology (AIST)[39]. The rate of H_2-evolution from aqueous methanol solution under UV irradiation significantly changed with the variation of doping atoms, and $In_{0.8}Ni_{0.2}TaO_4$ showed the highest activity. Under visible light irradiation (>420 nm), H_2 and O_2 evolved from an aqueous methanol and silver nitrate solution, respectively, using the photocatalysts $In_{0.8}M_{0.2}TaO_4$ (M = Mn, Fe, Co, Ni, Cu). An optimization of Ni-doping of $In_{1-x}Ni_xTaO_4$ powders was conducted and found that $In_{0.9}Ni_{0.1}TaO_4$ was the best photocatalyst for water-splitting. The bandgap of the highly crystalline nanoparticles of $In_{0.9}Ni_{0.1}TaO_4$ is 2.3 eV, and particles with sizes in the range of 300–500 nm were observed by TEM measurements. 1.0-wt% partially oxidized nickel was loaded as electron-trapping and H_2-evolution sites onto the $In_{0.9}Ni_{0.1}TaO_4$ surface from an aqueous $Ni(NO_3)_2$ solution. The TEM measurements showed that nearly spherical nano NiOx particles with a size of about 15 nm are distributed on the surface of $In_{0.9}Ni_{0.1}TaO_4$. Stoichiometric amounts of O_2 and H_2 were evolved under visible-light irradiation using NiOx/ $In_{0.9}Ni_{0.1}TaO_4$ with a quantum yield of about 0.66%. This system behaves as s short-circuited microphotoelectrochemical cell. The surface of NiOx is the cathode and the surface of $In_{0.9}Ni_{0.1}TaO_4$ is the anode. Work is ongoing and aims at improving the conversion efficiency by surface modification and by increasing the specific surface area of the catalyst particles from ~1 m^2/g toward 10-15 m^2/g.

5.1.1.9. Zinc Oxide (ZnO)

At the University of California (UCal) in Santa Barbara, ZnO has been deposited from a DMSO-based electrolyte to produce high quality, crystalline ZnO films that do not require post-deposition processing. For the automated testing system at UCal, traditional synthesis has been modified by the addition of 0.5M $LiNO_3$, which greatly improves solution conductivity and reduces the mass transport limits of the electrochemical cell. Several hundred samples of different ZnO-based materials have been synthesized and screened for photocurrent. All materials were binary systems consisting of ZnO and a single other element – typically a transition metal – and a range of dopant concentrations (~ 0.1% - 10%) was explored for each element. The aim of doping ZnO is to improve the photocatalytic activity under visible illumination and to increase the stability of the material.

Table-2 on the following page has been constructed to qualitatively indicate the impact of the dopants on the material properties in comparison with pure ZnO ("very poor", "poor", "average", "good", and "excellent"). Cobalt showed the greatest improvements in terms of visible light photocurrent, and the cerium-doped samples proved to be the most stable ones. Iron, nickel, ruthenium, and manganese doped samples also showed improvements versus pure ZnO. After having explored 24 different binary ZnO systems, of multiple doping densities, the research team at UCal is now looking forward to focusing on the best materials to begin investigation of ternary and quaternary libraries.

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[39] Zou Z., Ye J. and Arakawa H., *J. Phys. Chem. B (letters)* **2002**, 106, 13098-13101.

Table-2: Qualitative impact (excellent, good, average, poor, very poor) of 24 different elements when co-deposited with ZnO as compared to pure ZnO.

Co-Deposited Species with ZnO	Visible Photocurrent	UV-VIS Photocurrent	Stability
Ag	Poor	Poor	Average
Al	Good	Average	Good
Au	Poor	Poor	Average
Ce	Average	Average	Excellent
Cd	Poor	Poor	Average
Co	Excellent	Poor	Good
Cr	Poor	Poor	Average
Cu	Poor	Poor	Average
Eu	Poor	Poor	Average
Fe	Good	Good	Average
Mn	Average	Average	Good
Mo	Poor	Poor	Poor
Ni	Excellent	Excellent	Average
Nb	Poor	Average	Good
Pd	Very Poor	Very Poor	N/A
Pt	Poor	Poor	Poor
Rh	Poor	Poor	Average
Ru	Excellent	Excellent	Average
Sb	Poor	Poor	Average
Sn	Average	Average	Good
Ti	Very Poor	Very Poor	N/A
V	Poor	Poor	Average
Zr	Average	Average	

5.1.1.10. Nanostructured Electrode Synthesis by Combinatorial Electrodeposition

A general method has been developed at the University of California in Santa Barbara for the synthesis of high-surface-area mesoporous films using electrochemically driven self-assembly of surfactants at solid-liquid interfaces. Mesoporous WO_3, ZnO and TiO_2 have been successfully electrodeposited by controlling synthesis conditions. Nanophases were controlled by changing the deposition potential, which directly affects the surface charge densities of the electrode and, therefore, the surface assembly patterns of the inorganic-surfactant aggregates. The photoresponse of the mesoporous tungsten oxide or zinc oxide film was higher than that of the nonporous control film, consistent with an increased surface area and the different surface morphologies.[40,41] Templates and synthesis strategies will be varied, in order to fabricate new materials with optimisation of solar conversion efficiency.

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[40] Baeck S., Choi K., Jaramillo T., Stucky G. and McFarland E., *Adv. Mater.* **2003**, 15(15), 1269-1273

[41] Jaramillo T., Baeck S., Kleiman-Shwarsctein A. and McFarland E., *Macromol. Rapid Commun* **2004**, 25, 297–301.

Means for depositing nanoparticulate pure metals (Pt, Au, Pd), alloys (Pt-Au, Pt-Ru) and metal oxides (WO_3) by pulsed electrodeposition have been developed at UCal, which have been incorporated into automated synthesis and screening systems. Particle size and density is controlled by varying pulse parameters. Nanoparticualte Pt/WO_3, which was prepared by pulsed electrodeposition, was found to be active for methanol oxidation and resistant to carbon monoxide (CO) poisoning.[42]

5.1.2. Light Absorption

Light absorption of photo-sensitive electrodes is often insufficient or inappropriate to match with the (electric) current needs of integrated counter-electrodes or photovoltaic bias in PEC systems. A variety of methods to improve light absorption have been developed throughout the course of Annex-14 and being summarised in the following section.

5.1.2.1. Ruthenium(Ru)-Based Dye Sensitisers

Back in 2001, novel ruthenium-based (Ru) sensitisers have been developed at the Swiss Federal Institute of Technology (EPFL), which show enhanced spectral response and molar extinction coefficients compared to the standard Ru-dye code-named "N719". The photocurrent action spectra of the new tetradentate ligand based Ru dyes (code-named "K8") show broad features covering a large part of the visible spectrum and delivering a photocurrent density of around 18 mA/cm^2 under standard global AM 1.5. These dyes have two broad absorption spectrum bands in the visible light region (around 428nm and 555nm), which are due to metal-to-ligand charge-transfer (MLCT) transitions. The incident monochromatic photon-to-current conversion efficiency (IPCE) of K8 shows a consistently high value of over 70% in the plateau region and still an excellent 65% at 700 nm (refer to Figure-8 on the following page).

The K8-type dyes have opened up opportunities to optimise the performance of sensitisers with respect to dye-uptake solution concentration, solvents for dye-uptake solutions, TiO_2 layer thickness and electrolyte composition. However, driven by the promise of WO_3-based photoanode films with photocurrents of around 5 mA/cm^2, the light absorption spectra of functionalized tetradentate ligand dyes according to K8 had to be further increased toward 800nm – 900 nm. Based on ruthenium-II quadrapyridyl complexes, such K8-type dyes have therefore been successfully further developed and long-term performance tested using dye-sensitized TiO_2 solar cells[43]. The dyes achieve incident photon-to-current efficiencies (IPCE) of around 70% – 80% in the light spectrum between 400 nm and 800 nm and they have shown to lead to back-electrode currents of up to 20 mA/cm^2 (refer to Figure-9 on the following page). This increased performance facilitates the design of simple, efficient two-photon tandem PEC systems based on DSSC.

[42] Baeck S., Jaramillo T. and McFarland E., *Abs. Pap. Am. Chem. Soc.* **2002**, 224: 062-FUEL Part 1.

[43] Zubavichus Y., Slovokhotov Y., Nazeeruddin M., Zakeeruddin S., Grätzel M. and Shklover V., *Chem. Mater* **2002**, 14, 3556-3563.
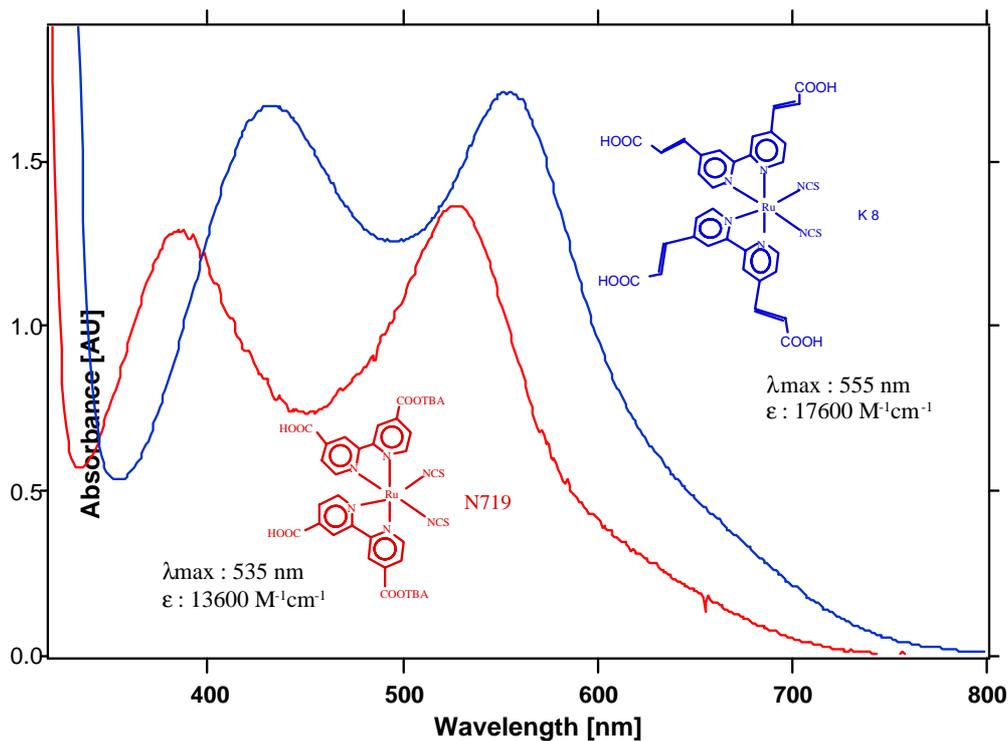
Figure-8: Comparison of the absorption spectra of the new ruthenium complex ("K8") with the standard Ru-dye "N719" used with dye-sensitised solar cells (DSSC) (Source: Nazeeruddin, Swiss Federal Institute of Technology).
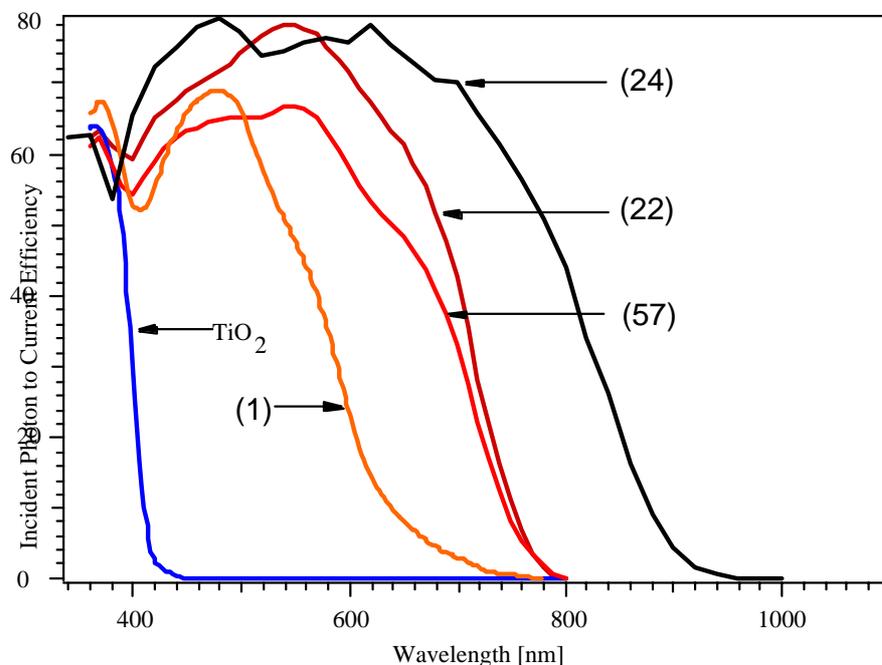

Figure-9: Photocurrent action spectra of bare nanocrystalline TiO_2 film compared to improved Ru-based sensitizers $[Ru(dcbpyH_2)_2(NCS)_2]$ adsorbed on TiO_2 films. The incident photon-to-current conversion efficiency (IPHE) is plotted as a function of wavelength (Source: Nazeeruddin, Swiss Federal Institute of Technology).

In association with the development of high-performance dyes for the TiO_2-based tandem PEC system, novel redox mediators based on Co(II)/Co(III) polypyridyl complexes have also been synthesised and tested at EPFL in TiO_2–based DSSC[44]. These cells showed higher open-circuit potential compared to the standard iodide/triioide redox couple of DSSC while maintaining excellent photocurrents. The new redox system reduces the risk of corrosion of the silver-based current collectors that have to be employed in practical PEC water-splitting devices where the size of the PEC device exceeds a few square centimetres.

5.1.2.2. Bromium(Br)- and Gold(Au)-Based Sensitisers

AgCl photoanodes can be combined with a semiconductor photocathode to act as antenna system for light harvesting as well as transport in the oxygen evolution part of a water-splitting PEC cell.[45] At the University of Bern, a two-compartment PEC has been operated using a nanostructured silver chloride layer as photocatalytic anode in combination with platinised silicon or $GaInP_2$ as counter electrode. Br- and Au-sensitisation resulted in encouraging performance improvements.

Sensitisation with Br – Considerable improvement of sensitivity, and consequently O_2 production, has been observed with Br^--sensitised AgCl photoanodes. Water-splitting capability tests were also carried out where the AgCl photoanode was combined with hydrogen-producing semiconductors, such as a platinised silicon solar cell and platinised p-$GaInP_2$. AgCl layers were employed in the anodic part and the H_2 evolving semiconductors in the cathodic part of a PEC cell for light-assisted water-splitting.[46] Maximum hydrogen evolution was observed in the pH range of between 4 and 6. The photoactivity of the AgCl extends from the UV into the VIS light region in a process known as self-sensitisation.

Sensitisation using colloids – To increase the absorptivity of the AgCl photoanodes, the addition of sensitizing agents, chemical species that have a high absorptivity in the visible light spectrum, has recently also been tested. Silver chloride electrodes sensitised with Au colloids show an increased O_2 production compared to normal AgCl layers under the same photoelectrochemical reaction conditions.[47] These results show the sensitising approach with colloids to be a promising one, and encourage further investigation of the sensitisation concept with different nanoparticles.

Three-dye antennae systems – Using a three-dye antenna on a zeolite-L structure, light harvesting over the whole visible spectrum with subsequent energy transport leading to fluorescence at the cylindrical zeolite-L ends has been demonstrated at the University of Bern (refer to Figure-10 on the following page).[48]

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[44] Nusbaumer H., Moser J., Zakeeruddin S., Nazeeruddin M. and Grätzel M., *J. Phys. Chem. B.* **2001**, 105, 10461-10464.

[45] Calzaferri G., Brühwiler D., Glaus S., Schürch D. and Currao A., *J. Imag. Sci. and Technology.* **2001**, 45.

[46] Schürch D. and Currao A., *Chimia.* **2003**, 57, 204.

[47] Currao A., Reddy V. and Calzaferri G., *ChemPhysChem.* **2004**, in press.

[48] Calzaferri G., Huber S., Maas H. and Minkowski C., *Angew. Chem. Int. Ed. Engl.* **2003**, 42, 3732.
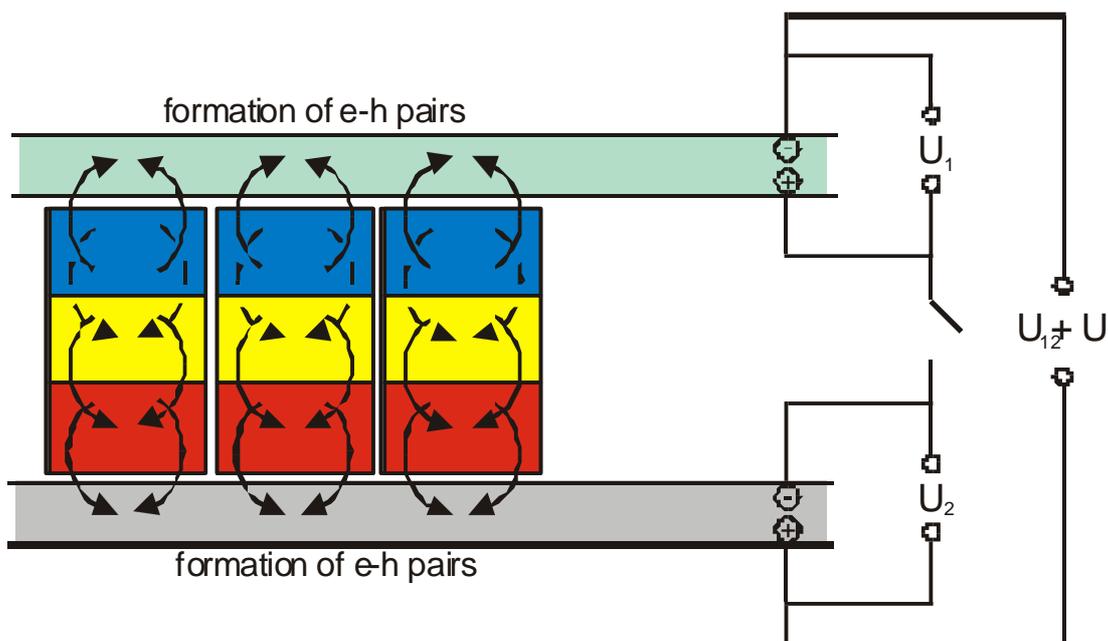
Figure-10: Tandem solar cell where mono-directional antenna systems with blue, yellow and red dyes are put between two n-type semiconductors with different bandgaps (Source: Calzaferri, University of Bern, Switzerland).

In natural photosynthesis, light is absorbed by photonic antenna systems consisting of a few hundred chlorophyll molecules. These devices allow fast energy transfer from an electronically excited molecule to an unexcited neighbour molecule in such a way that the excitation energy reaches the reaction centre with high probability. Trapping occurs there. The anisotropic arrangement of the chlorophyll molecules is important for efficient energy migration. In natural antennae the formation of aggregates is prevented by fencing the chlorophyll molecules in polypeptide cages. A similar approach is possible by enclosing dyes inside a microporous material and by choosing conditions such that the cavities are able to uptake only monomers but not aggregates. At the University of Bern, such experiments have been using zeolite-L as a host as it was found to be very versatile. Its crystals consist of an extended one-dimensional tube system and can be prepared in a wide range of sizes. The individual tubes have been filled with successive chains of different dye molecules. It was shown that photonic antenna materials can be prepared, not only for light harvesting within the volume, but also for radiation-free transport of electronic excitation energy to a target molecule fixed at the ends of the nanochannels as well as with an injector molecule fixed at their „entrances". The molecule, which has been excited by absorbing an incident photon, transfers its electronic excitation to another one. After a series of such steps the electronic excitation reaches a luminescent trap. The energy migration is in competition with spontaneous emission, radiation-free decay, quenching, and photochemically induced degradation. Fast energy migration is therefore crucial if a trap should be reached before other processes can take place.

The supramolecular organization of the dyes inside the channels is a first stage of organisation. It allows light harvesting within a certain volume of a dye-loaded nano-crystalline zeolite and radiation-free transport to both ends of the cylinder or from the ends to

the centre. The second stage of organisation is the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite-L channels, which can trap or inject electronic excitation energy. The third stage of organisation is the coupling to an external device via a stopcock intermediate. The wide-ranging tunability of these highly organised materials offers fascinating new possibilities for exploring excitation energy transfer phenomena and challenges for developing new photonic devices for solar energy conversion and storage.[49,50,51] This includes the development of a novel thin-layer solar cell in which light absorption and the creation of an electron-hole pair are spatially separated, rendering itself well for PEC applications.

5.1.3. Photocatalyst Stability

The most stable semiconductors in aqueous solution are oxides. But their bandgaps are either too large for efficient light absorption or their semiconductor characteristics are poor. Semiconductors with better solid-state characteristics are typically thermodynamically unstable with respect to oxidation. This however has to been seen against the fact that p-type semiconductors generally offer some protection against photocorrision because the surface is cathodically protected under illumination. Lowering the bandgap of the stable oxide-based semiconductors is therefore an important area of work, in combination with the need to identify protective coatings for those materials with ideal solar absorption, but poor stability in a PEC system.

5.1.3.1. Indium-Nickel-Tantalum-Oxide ($InNiTaO_4$)

$In_{0.9}Ni_{0.1}TaO_4$ showed to be a stable photocatalyst for photoelectrochemical water-splitting. More than 7.2 mmol of gases (4.8 mmol of H_2 and 2.4 mmol of O_2) evolved during the course of a first, 400-hour continuous visible light irradiation experiment. The photocatalyst samples remained unchanged during the course of the reaction.

5.1.3.2. Copper-Oxide / Titanium-Dioxide (Cu_2O/TiO_2)

Heterojunction structures based on copper and titanium oxide (Cu_2O/TiO_2) have been synthesised and screened for photocatalytic activity at the University of California.[52] Cu_2O is a photocatalyst that benefits from a small bandgap (2.0 eV), which allows for excellent solar absorption. It is limited, however, by photocorrosion, which degrades the material rapidly. TiO_2, on the other hand, is a robust photocatalyst that is stable for long periods of time (ca. thousands of hours). It is, however, limited by poor visible photon absorption (bandgap 3.0 eV). By creating a heterojunction of Cu_2O covered with TiO_2, a photocatalytic system (which operates as a photocathode) resulted, which absorbed more visible light than pure Cu_2O and was as stable as pure TiO_2.

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[49] Yatskou M., Pfenniger M., Meyer M., Huber S. and Calzaferri G., *ChemPhysChem,* **2003**, 4, 567.
[50] Huber S. and Calzaferri G., *ChemPhysChem,* **2004**, 5, 239.
[51] Maas H. and Calzaferri G., *The Spectrum*, **2003**, 13(3), 18.
[52] Siripala W., Ivanovskaya A., Jaramillo T., Baeck S. and McFarland E., *Solar Energy Materials & Solar Cells.* **2003**, 77(3), 229-237.

5.2. System Studies

5.2.1. Monolithic Multi-Junction Systems

Solid-state multi-junction devices can deliver the energy required for hydrogen production from water while accessing a large fraction of the solar spectrum, providing high efficiency. Monolithic multi-junction cell technology connects photovoltaic layers (pn-junctions) with different semiconductor bandgaps in series, one behind the other, in a single monolithic cascade device. In a tandem device for example, the top semiconductor junction would absorb the visible light spectra, and the bottom junction would absorb the near-infrared portion of the spectrum. Since the cells are in series, the voltage generated by the device is the sum of the individual voltages. But it requires two photons of light to generate one electron in the external circuit. This configuration offers a greater utilisation of the solar spectrum, providing the highest theoretical conversion efficiency for any photoconversion system. The monolithic structure also minimises the amount of active area needed for specific power applications. While single-gap electrodes have a solar conversion efficiency limit of 32%, tandem-junction devices have an efficiency limit of 42%. Figure-11 shows the efficiency gains for one particular set of materials, GaInP$_2$ / GaAs / Ge. With a view to the goal of practical future applications, higher system efficiency reduces the amount of land area that must be covered and while simultaneously also decreasing the amount of semiconductor material that must be applied for a particular amount of solar-produced hydrogen. This decreases the final cost of the produced hydrogen.
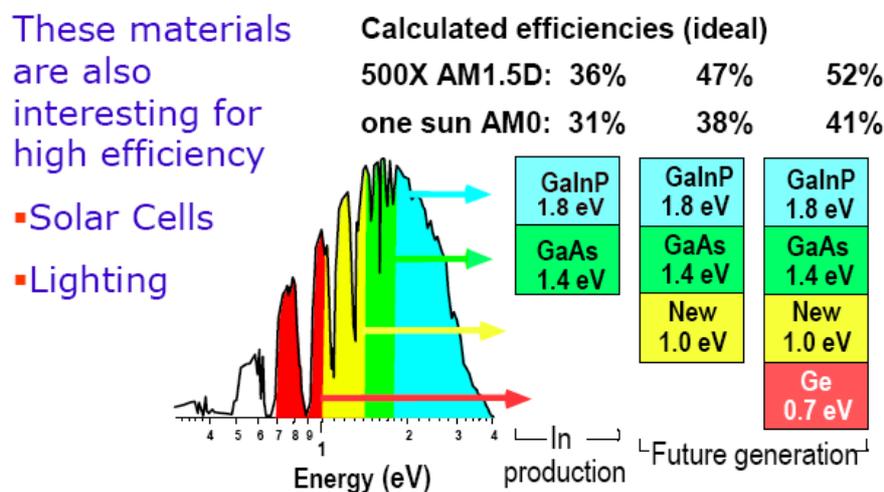

Figure-11: Ideal, theoretical solar energy conversion efficiencies of tandem-junction devices (Source: Turner, National Renewable Energy Laboratory, USA).

In addition to the increased efficiency of these systems, the opportunity here also includes the possible use of an unstable (in aqueous solution) material as the bottom junction and a stable and protective top junction. The combination of specific materials can lead to an efficient water-splitting system, where the individual materials would be unsuitable on their own. The difficulty in this approach is matching the light absorption characteristics of the two materials. For maximum efficiency, the solar spectrum must be split equally between all the

junctions in the PEC water-splitting device. This presents quite a challenge when using very different materials for such devices.

5.2.1.1. Gallium-Indium-Phosphide (GaInP$_2$)

WO$_3$ – GaInP$_2$ Systems – Preliminary tests in 2003, in which a GaInP$_2$ photocathode sample provided by NREL was placed behind a semitransparent WO$_3$ photoanode film prepared by the University of Geneva, showed that the photoelectrolysis of water started already in the absence of any external bias. These results allow one to envisage efficient operation of such a PEC cell, illuminated with solar light, under a modest 0.4-0.5 V bias. Absorbing the green and red part of the solar spectrum and having a bandgap energy of 1.7 eV, GaInP$_2$ is perfectly complementary to WO$_3$ (2.5 eV), which captures the blue part of the spectrum.

It was found that the performance and stability of the photoanode and the photocathode are strongly affected by the nature of the electrolyte. While it is well established that the pH of the latter should not exceed 2, the choice of the electrolyte anion remains open. In particular, the use of an electrolyte containing chloride ions is to be examined, including the direct use of sea water (corresponding roughly to a 0.5M solution of NaCl). For electrolytes containing moderate amounts of chloride ions, it appears that the proportion of chlorine produced together with oxygen at the photoanode remains low enough to be subsequently absorbed by washing with water to form hypochloric acid. Tandem PEC cell demonstrator systems with an active surface area of 4-cm^2 are being constructed, including the combination of WO$_3$ or ferric oxide (Fe$_2$O$_3$) photoanodes with GaInP$_2$, twin amorphous silicon (Si) or a-silicon (a-Si) / germanium (Ge) PV cells / photocathodes.

5.2.1.2. Amorphous Silicone (a-Si)

With monolithic multi-junction PEC devices, the surface areas of the PV cell and the electrolyser are identical. Triple-junction amorphous silicon PV cells have been integrated with an alkaline (2-M KOH) electrolyser.[53] Based on short-circuit current, a solar-to-hydrogen conversion efficiencies of 7.8% was achieved with this low-cost silicon-based system. However, the a-Si-based multi-junction system suffered from surface oxidation. This was markedly reduced through the use of single- as well as multi-layer a-Si / a-SiC systems studied at the UNAM.[54] SiC possesses good stability in alkaline as well as acidic solutions. A solar-to-hydrogen conversion effciency of the order of 7% has been realised with such multi-layer a-Si / a-SiC PEC cells. The major disadvantage of a-SiC however is its large bandgap (> 3 eV). But, this limitation may be overcome by sensitisation of SiC with synthetic dyes as well as narrow bandgap semiconductors.

At the Hawaii Natural Energy Institute (NHEI), a novel hybrid-junction photoelectrode configuration is being developed, incorporating a low-cost, highly-stable, wide-bandgap PEC film (Fe$_2$O$_3$) deposited on top of an optically-tailored, current-matched, "high-voltage" solid-

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[53] Khaselev O., Bansal A. and Turner J., *Int. J. of Hydrogen Energy.* **2001**, 26, 127-132.

[54] Sebastian J., Mathews N., Mathew X., Pttabi M. and Turner J., *Int. J. of Hydrogen Energy.* **2001**, 26, 123-125.

state junction (a-Si:Ge) to generate the bias for water-splitting (refer to Figure-12). Compared to solid-state designs, the hybrid configuration allows the lateral current collection loss to be eliminated, the front surface over-potential loss to be reduced, and the geometry to be greatly simplified, hence easing fabrication and reducing costs. Initial tests of such a hybrid Fe_2O_3 photoelectrode demonstrated sustained hydrogen currents of about 3 mA/cm^2 under concentrated irradiance (about 2 suns) applying a 1.0 Volt bias.[55]
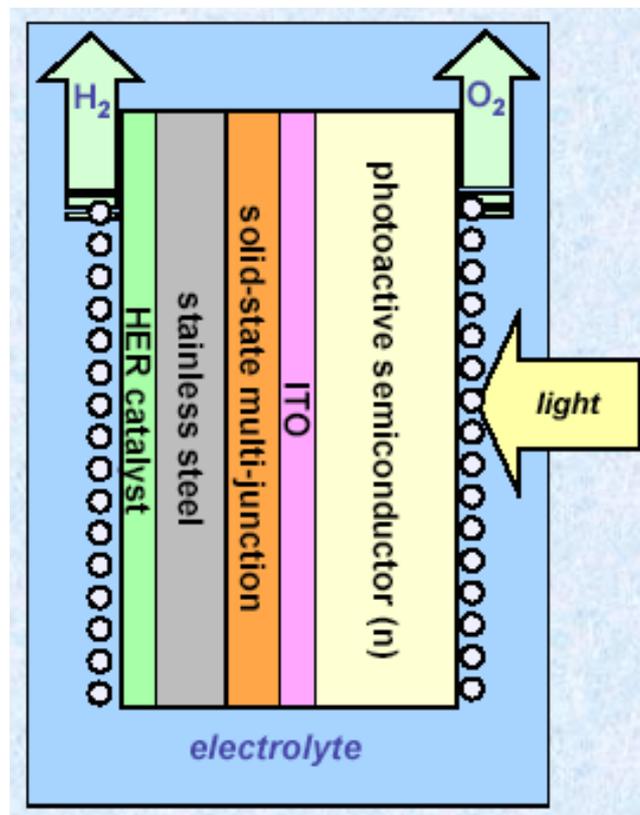

Figure-12: Conceptual design of a hybrid-junction photoelectrode for water-splitting (Source: Miller, Hawaii Natural Energy Institute, Hawaii).

5.2.2. Two-Photon Tandem Systems

The two-photon tandem PEC system concept was pioneered jointly by expert groups at three Universities in Switzerland (Augustynski & Courvoisier – University of Geneva; Graetzel – Swiss Federal Institute of Technology; and Calzaferri – University of Bern).[56] It focuses on the development of a water photolysis device combining two mesoscopic semiconductor oxide films. In order to optimise the performance and efficiency of such two-photon tandem PEC devices, it is desirable that the optical responses of the two chosen oxides complement each other in the visible wavelength range of the solar spectrum.

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[55] Miller E., Rocheleau R. and Deng X., *International Journal of Hydrogen Energy*, **2003**, 28(6), 615-623.
[56] Augustynski J., Calzaferri G., Courvoisier J. and Grätzel M., Proc. Of 11th WHEC, **1996**, Vol.3, 2379-2387.

5.2.2.1.   Tungsten-Oxide (WO_3) / Titanium-Dioxide (TiO_2)

In the tungsten trioxide (WO_3) based tandem PEC concept, nanocrystalline WO_3 serves as photoanode (oxygen-evolution) in the system, capturing photons from the blue part of the solar emission spectrum. A TiO_2-based Graetzel dye-solar-cell uses the complementary part of the VIS light and generates the necessary bias for hydrogen-evolution via conventional platinum counter-electrode (refer to Figure-13).
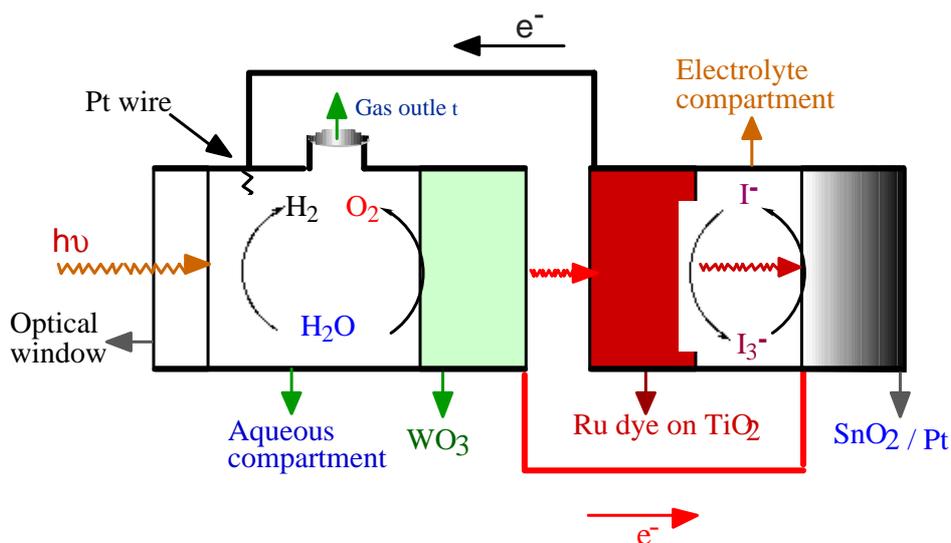

Figure-13: Circuit diagram of the two-step, two-photon PEC cell for water-splitting using a WO_3 photoanode and a photoelectrochemical PV cell (TiO_2-based dye-sensitized solar "Graetzel" cell") with platinum counter electrode (Source: Graetzel, Swiss Federal Institute of Technology).

The role of the photoanode is to generate oxygen from water directly, hence without resorting to an additional electrode or redox catalyst. The oxidation process is initiated by the light-induced electron-hole pair separation in the WO_3 (Equation-1), thin-film, followed by the reaction of valence band holes with water (Equation-2).

$$h\upsilon \ + \ WO_3 \ \longrightarrow \ WO_3\,(\,h^+ + e^-\,) \qquad (1)$$

$$4h^+ + \ 2H_2O \ \longrightarrow \ O_2 \ + \ 4h^+ \qquad (2)$$

The most advanced water photolysis system employs a translucent WO_3 film, which is superimposed on the nanocrystalline dye-injection solar cell (dye-sensitised solar cell – DSSC – or "Graetzel" solar cell). The DSSC absorbs the light in the green and red spectral region, which is transmitted by the tungsten trioxide[57]. The DSSC serves as a photo-driven

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[57] Nazeeruddin M., Péchy P.,. Renouard T., Zakeeruddin S., Humphry-Baker R., Comte P., Liska P. Cevey L., Costa E., Shklover V., Spiccia L., Deacon G., Bignozzi C. and Grätzel M., *J. Am. Chem. Soc.* **2001**, 123, 1613.

bias increasing the electrochemical potential of the photoelectrons produced by bandgap excitation of the WO_3 to render reduction of water to hydrogen feasible (Equation-3).

$$2e^- \ + \ 2H^+ \ \longrightarrow \ H_2 \qquad (3)$$
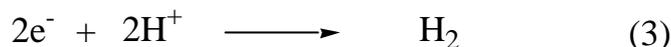
The light harvesting of the WO_3 film employed in the currently most advanced two-photon tandem PEC cell configuration is limited to wavelengths below 475 nm. The optimal conversion efficiency with such PEC devices, however, requires a bandgap of about 1.4 eV for the dye solar cell, and 1.8 eV for the photoanode. While the spectral onset of the black dye predominantly used in the DSSC corresponds nicely to 1.4 eV, the onset of the WO_3 is too high, being at around 2.5 eV.

5.2.3.   Dual-Bed Redox Systems

The feasibility of photocatalytically decomposing water into its constituent elements using a dual bed, or modular photosystem, under solar radiation was investigated at the Florida Solar Energy Centre (FSEC). The system involved two modules, each consisting of a shallow, flat, sealed container, in which microscopic, photocatalytic particles are immobilized (refer to Figure-14). The photocatalysts absorb light, generating free electrons as well as lattice vacancy holes, which are capable of performing reductive and oxidative chemistry, respectively. The photocatalysts were chosen as to whether they specifically promote H_2 or O_2 evolution in their respective containers. An aqueous solution containing a redox mediator is pumped between the two chambers in order to transfer electron equivalents from one reaction to the other.
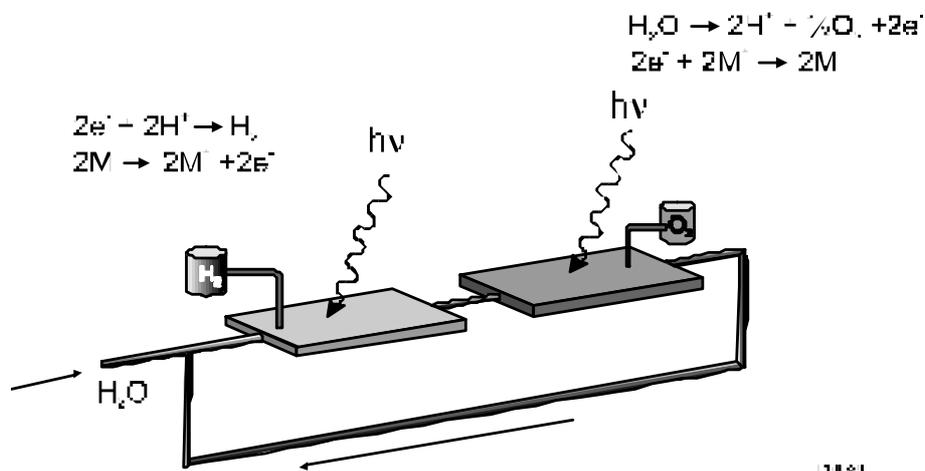

Figure-14: Schematic of a dual-bed photocatalytic water-splitting system (Source: Linkous, Forida Solar Energy Centre, USA).

The dual-bed redox PEC water-splitting system was designed to feature (a) separate evolution of H_2 and O_2, (b) potentially higher utilisation of the solar spectrum, since the two light-absorbing modules are able to use more abundant, lower energy photons, and (c) cheap reagents, photocatalysts, and construction materials, plus minimal processing result in a low cost module.

The early work on this project concentrated on traditional inorganic semiconductor powders as photocatalysts such as TiO_2 and InP. While H_2 and O_2 evolution was observed, it was realised that these materials could not reach the original 8% efficiency objective of the project. With a bandgap energy of 3.0 eV, TiO_2 did not absorb enough of the solar spectrum. While InP had a better-suited bandgap energy of 1.3 eV, it was subject to corrosion in the alkaline electrolyte.

It was decided at that point to consider organic semiconductors. While limited photoconductivity in the solid state was a definite weakness of the pigments, it was thought that it could be overcome with their high extinction coefficients in the visible range, plus being able to utilize the synthetic opportunities of organic dyestuff chemistry. A combination of molecular orbital calculations, voltammetric wave analysis, and gas phase ultraviolet photoelectron analysis enabled the definition of what molecular structures would make the best photocatalysts. A number of compounds have subsequently been designed, synthesized, and tested that appeared to have optimum characteristics. The absorption spectra of the pigments plus their abilities to oxidise or reduce water went together to make complementary pairings that would absorb most of the visible spectrum while performing net water-splitting.

The best pairing was made from an alkyl chain derivative of perylene diimide as an O_2-evolving photocatalyst and copper phthalocyanine as the H_2-evolving photocatalyst. The perylene was modified with an Ir co-catalyst, while the phthalocyanine was modified with a 1% dispersion of Pt. The basic criterion of dual bed function was satisfied, for example visible light ($\lambda > 400$ nm) illumination of the perylene dispersion evolved O_2, while the copper phthalocyanine dispersion evolved H_2. However, the yields were quite low, on order of 10's of microliters in a 6-hour experiment. It was decided that using the pigments as dye sensitisers may be the best way to employ their good light-absorbing characteristics.

Another limitation observed was that O_2 evolution could only be driven if the redox mediator was predominately present in the reduced form, while H_2 evolution could only be observed when the oxidized form was the majority species. In order for dual-bed systems to operate properly in a cyclical manner, the Ox/Red ratio in the circulating fluid should fall as it passes through the O_2-evolving chamber, and rise as it passes through the H_2-evolving chamber. It was exceedingly difficult to measure significant gas evolution in systems where the Ox/Red ration was unity.

As a result, systems studies were performed. An electrochemical equivalent of a dual-bed cell was constructed and tested using a dual channel power supply and twin interdigitated nickel wire networks. Redox mediators representing a range of electrochemical reversibilities (potassium ferro/ferricyanide as a reversible couple, potassium iodate/iodide as a quasi-reversible couple, and benzhydroquinone/benzoquinone as an irreversible couple) were tested. The coulombic efficiency of the system (H_2 gas evolved in comparison to integrated current, or charge) was found to fall for the reversible couple as the Ox form of the mediator rose with time, while it remained high for the irreversible system. This work pointed out the need to develop more sophisticated redox mediators, which would possess characteristics that would discourage back-reaction.

5.2.4. One-Pot / Two-Step Systems

It is challenging to develop and design the necessary photocatalysts for overall water-splitting into H_2 and O_2 under visible light irradiation. Nevertheless, in natural photosynthesis, water is split into O_2 and H^+:e to form carbohydrates from CO_2 through the so-called Z-scheme reaction which comprises two photo-excitation sites and many redox mediators under visible light irradiation. To achieve PEC water-splitting into H_2 and O_2 stoichiometrically under VIS light, a one-pot and two-step photocatalytic system that mimics the Z-scheme is feasible. A single system can represent the combination of two different visible light responding photocatalysts, which produce H_2 and O_2 respectively, and a redox mediator reagent.

5.2.4.1. Pt-WO$_3$ / Pt-Sr-TiO$_3$ Two-Step System

At the Photoreaction Control Research Center (PCRC) of the Japanese National Institute of Advanced Industrial Science & Technology (AIST), water-splitting into H_2 and O_2 using two different semiconductor photocatalysts and a redox mediator, mimicking the Z-scheme of photosynthesis, were studied (refer to Figure-15). H_2-evolution was measured on a Pt/SrTiO$_3$ (Cr-Ta-doped) photocatalyst using an I^- electron donor under visible light irradiation (>420 nm). Simultaneously, O_2-evolution was established with a Pt/WO$_3$ photocatalyst using an IO_3^- electron acceptor. Both H_2 and O_2 gases evolved in the stoichiometric ratio ($H_2/O_2 = 2$) for more than 250 h under VIS light irradiation using a mixture of said Pt/WO$_3$ and the Pt/SrTiO$_3$ (Cr-Ta-doped) powders suspended in NaI aqueous solution. The quantum efficiency of the PEC water-splitting was calculated to be about 0.1% at 420.7 nm.[58]
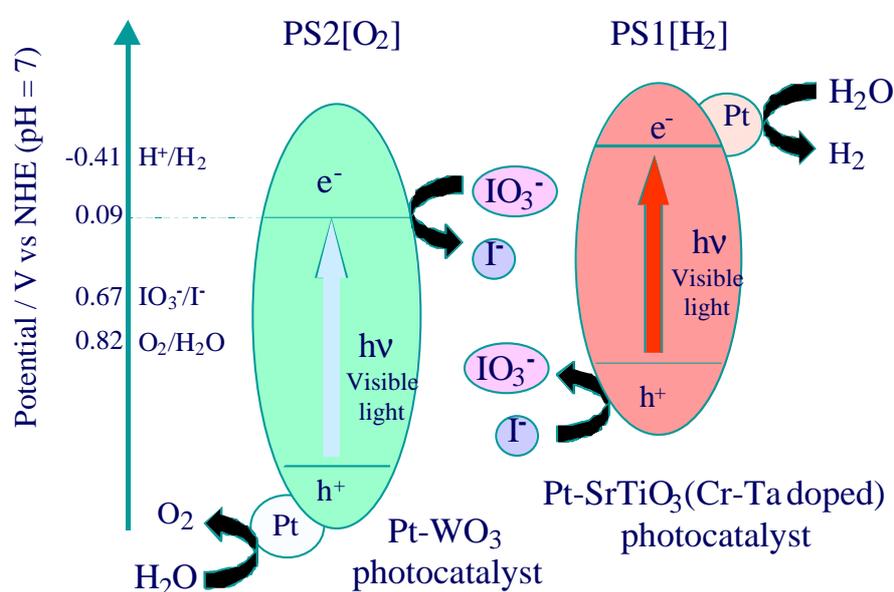

Figure-15: Reaction mechanism for two-step photocatalytic water-splitting system using powder catalyst in suspension. The system mimics the Z-scheme in natural photosynthesis (Source: Arakawa, Photoreaction Control Research Centre, AIST, Japan).

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[58] Sayama K., Mukasab K., Abea R., Abeb Y. and Arakawa H., *J. of Photochemistry and Photobiology A: Chemistry.* **2002**, 148, 71–77.

6. Economics

Encouraged by world-record performance results in 1998 at the National Renewable Energy Laboratory (NREL)[59], whereby a monolithic multi-junction PV (pn-GaAs) / PEC (GaInP$_2$) laboratory device with platinum counter-electrode achieved a 12.4% solar-to-hydrogen conversion efficiency, an advanced PEC system design has been developed and subsequently costed.[60] Figure-16 shows the conceptual design used for this cost estimation. It is based on a GaInP$_2$ multi-junction PEC water-splitting system design that employs light concentration for current-matching between anode and cathode.
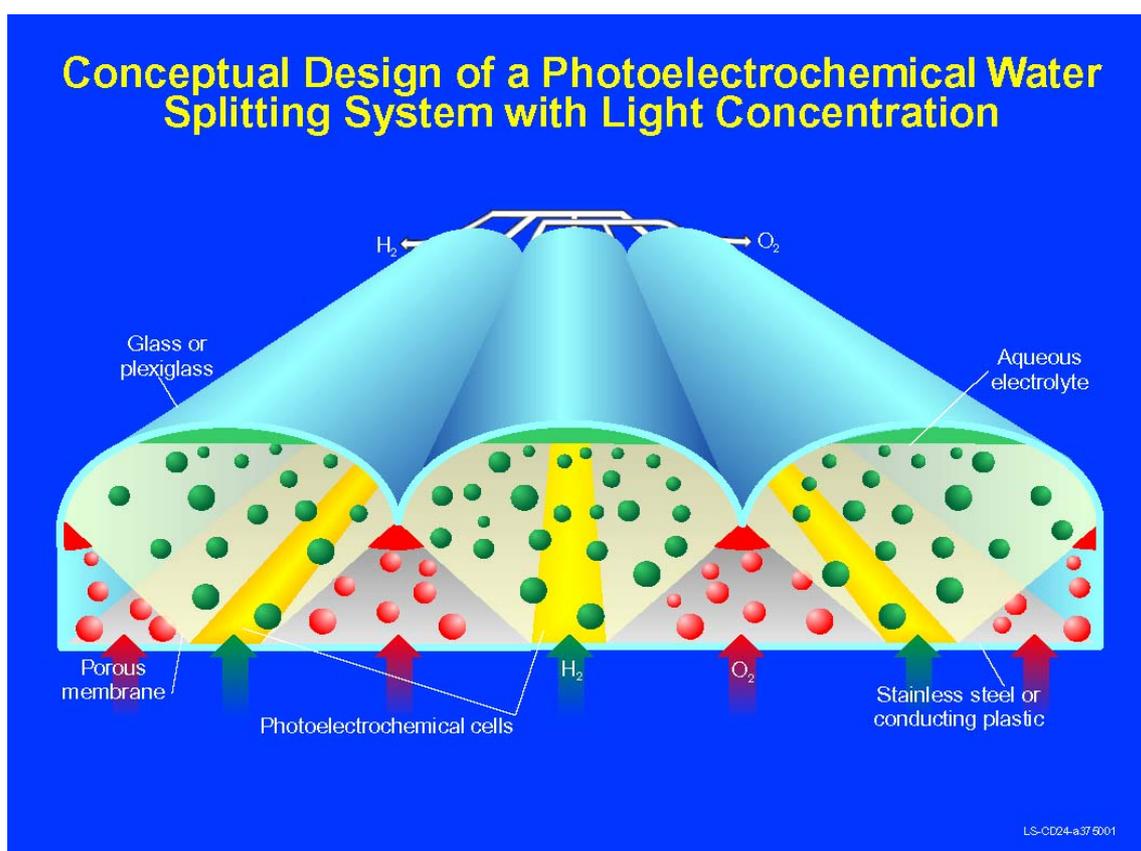

Figure-16: Conceptual design of a multi-junction photoelectrochemical water-splitting system with light concentration. This design has been used as the basis for a detailed PEC hydrogen production costing study (Source: Turner, National Renewable Energy Laboratory, USA).

The risk assessment that supported this PEC solar hydrogen production cost analysis resulted, for example, in the finding that there is an 80% certainty for hydrogen produced with such a PEC system to costs less than US$ 41.3 per Gigajoule.

This is understood to be a factor of four higher than the **long-term cost target** of **US$ 10 per GJ of hydrogen** set by the US Department of Energy (DoE).

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[59] Khaselev O. and Turner J., *Science*, **1998**, 2, 42-427.
[60] Mann M. **1999**, Milestone Report US-DoE Hydrogen Program, November.

7. Conclusions

Some of the major highlights achieved throughout the 4.5 years of collaborative R&D in Annex-14 can be summarised as follows (provided in no order of priority and including important contributions by some of the above mentioned Annex-14 observer groups):

- **World-first water-splitting catalyst powder** $(In_{0.9}Ni_{0.1}TaO_4)$ developed for operation under VIS light – Japan;

- Encouraging **photoelectrode performance enhancement results** from successful transition-metal-oxide (TiO_2), metal-oxide (ZnO) and III-IV compound (GaN, GaInP) doping using either N or C – the Netherlands, Sweden, Switzerland, the USA;

- Strong engineering **progress** with the **preparation and characterization of photoanode thin-films** (WO_3, Fe_2O_3), including doping (Ti, Al, Ni, Sn) using ultrasonic spray-pyrolysis, sputtering or sol-gel – Australia, the Netherlands, Sweden, Switzerland, the USA;

- Promising conceptual development of **novel planar, multi-junction PEC water-splitting cells** – the USA;

- Completion of deposition and characterisation equipment for **ultra-fast screening of new electrochemical materials** (combinatorial chemistry) – the USA;

- Development of **modelling capability of photo-oxidation** based on quantum transition theory – the Netherlands; and

- Pioneering manufacture of 100mm x 100mm **demonstrator PEC water-splitting tandem cells** (WO_3/TiO_2), with scale-up program toward 300mm x 300mm devices – Switzerland and the UK.

8. Outlook

The key challenges to advance PEC cell innovation toward the market concern the progress needed in material science and engineering. The development of highly efficient corrosion-resistant photoelectrode materials and their processing technologies are most important. As no "ideal" photoelectrode material for water-splitting (eg. optimal bandgap and energetic position) exists commercially, new materials have to be engineered and synthesised. Combinatorial chemistry approaches offer fast-tracking options for the associated necessary material screening. In addition, fundamental research on doping for bandgap shifting and surface chemistry modification is required, including studies on the associated effects on surface as well as bulk semiconducting properties (eg. light absorption, interfacial charge transfers including Schottky and Helmholtz barrier, flat-band potential, etc.).

From a systems integration point of view and to optimise the techno-economic performance of PEC water-splitting systems, current-matching between anode and cathode and ohmic resistance minimisation deserve considerable materials design and engineering attention.

Ultimately, in a post-fossil-fuel era, the sun will re-emerge as the total driving force to fully sustain life on earth, most likely with electricity and hydrogen as the two key energy carriers. As presented in Figure-17, they are predicted to define a future energy triangle that builds on the science, technology and engineering "sister" components of photovoltaics (PV), fuel cells (FC) and photoelectrochemical (PEC) cells.
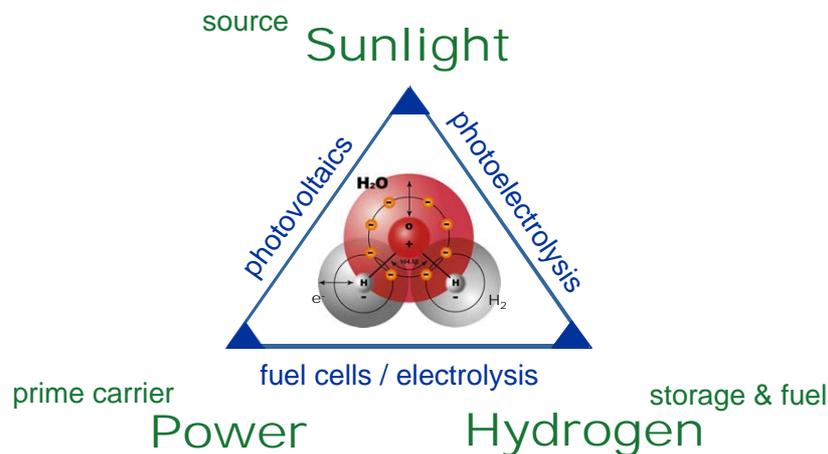

Figure-17: A possible future energy triangle based on solar energy, electricity and hydrogen, with photovoltaics, fuel cells and photoelectrochemical cells as enabling technologies (Source: Luzzi).

Integrated PEC devices offer great potential for simplicity, thin-film-based mass production, application of environmentally benign and abundant materials, and therefore cost reduction compared to alternative solar-driven hydrogen production options. The materials science and engineering needs and long-term potential of photoelectrolytic water-splitting cells are strongly related to the ones of fuel cells and photovoltaics, indicating that PEC systems have the capability of becoming a prime technology innovation building block of the hypothetical energy triangle of the post-fossil-fuel era shown above.

9. Appendix

Table-3 lists the six expert meetings that have been conducted during the Annex-14 program.

Table-3: List of expert meetings conducted as part of Annex-14 (incl. planned follow-up meeting).

Meeting	Date	Venue	Attendance
Kick-off meeting	7-9 October 1998	NREL, Golden, USA	9
1st expert meeting	14-15 March 2000	ANU, Canberra, Australia	7
2nd expert meeting	1-3 November 2000	EPFL, Lausanne, Switzerland	17
3rd expert meeting	10-12 September 2001	Angström Centre, Uppsala, Sweden	10
4th expert meeting	3-4 August 2002	Hokkaido University, Sapporo, Japan	11
5th expert meeting	27-28 April 2003	Accueil Ass. Ranleigh, Paris, France	21
Follow-up meeting	27-28 September 2004	Delft University, Delft, Netherlands	19