Hydrogen from Waterphotolysis

IEA Hydrogen Program | “Annex-20”

Final Report

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“Hydrogen from Waterphotolysis”
Annex-20 of the IEA Hydrogen Program

1. Summary

Annex-20 has been an internationally collaborative research effort conducted over 3 years under the guidance and coordination of the International Energy Agency (IEA) Hydrogen Implementing Agreement (HIA). Similar to its predecessor Annex-14, Annex-20 focused on the development of materials and systems for hydrogen production via photoelectrochemical (PEC) water-splitting. It has been successfully completed at the end of 2007 to make room for a follow-up research and development (R&D) program designed to focus on the complex PEC materials development challenges only. Termed “Annex-26”, this follow-up R&D program will start in the middle of 2008.

Eighteen research groups from Australia, Japan, Korea, The Netherlands, Switzerland and the USA have officially been collaborating under Annex-20 since October 2004. Though significant research progress has been made over the past 3 years in the areas of material science (above all photoelectrode design and deposition techniques, light absorption tailoring, and charge transfer understanding) and systems development (above all concerning two-photon tandem systems, monolithic multi-junction systems, and monomaterial two-step systems), it was found that a much more internationally coherent and comprehensive R&D effort is needed to better integrate the vast pool of knowhow accrued over the past couple of years concerning PEC materials science and hence jointly move toward the development of a winning family of novel, high-performance composite PEC materials for water-splitting. The prototyping of PEC water-splitting devices is understood to be of secondary importance only.

Nevertheless, inspired by the impressive materials science achievements of Annex-20, the ultimate goal of a stable sunlight-to-hydrogen (STH) conversion efficiency of 10% remains well 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. The HIA was one of many international energy cooperation programs established by the IEA. These programs have been 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. As listed in Table-1, the HIA has been undertaking internationally collaborative Research, Development and Demonstration (RD&D) programs through twenty-five specific Annexes (or Tasks). These RD&D efforts of the HIA have always concerned work at the pre-commercial level.

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

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<th>Annexes</th>
<th>Collaborative Work Tasks</th>
<th>Active Period</th>
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* Tasks dedicated fully or in part to photoelectrochemical (PEC) hydrogen production science and technology options.

Since 1979, the IEA-HIA pioneered the joint scientific investigation of direct solar-to-hydrogen (STH) hydrogen production routes based on photoelectrochemical (PEC) water-splitting (Annex-6, Annex-10, Annex-14 and this Annex-20). These efforts have been extended in 1995 to include major fundamental research efforts in biophotolysis of water (Annex-10, Annex-15 and Annex-21).

Theoretical and practical solar hydrogen systems integration and operational studies have also been initiated in 1995, focusing, inter alia, on practical STH 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 (refer to the follow-on R&D program of Annex-26).

### 3. Annex-20

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 as well as a chemical 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).](image)
While the basic feasibility of the PEC water-splitting concept has been experimentally well proven by various research groups and using related but different concepts around the world (first in 1972 by Fujishima & Honda\(^2\)), the issues of high conversion efficiency and long-term device stability remain key challenges that are being researched worldwide.

### 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-20 have been covering work conducted at the interface of fundamental and applied R&D, with an emphasis on materials development and some systems studies.

Material studies through the collaborative Research and Development (R&D) efforts of the IEA-HIA have focussed on the development of tailored semiconductor materials through doping (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 surface morphology adaptations, 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 based on the application of monomaterials that drive a two-step system.

### 3.2. Goals

The ultimate goal of the IEA-HIA photoelectrochemical (PEC) research program is to develop and demonstrate the reliability of PEC systems that can achieve water-splitting with a net sunlight-to-hydrogen (STH) 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 that follow a well-structure and continuous R&D program.

3.3. Participation

Australia, Japan, Korea, The Netherlands, Switzerland and the United States of America (USA) have been the official IEA-HIA member country participants of Annex-20, which combined their respective R&D programs on photoelectrolysis of water.

The following research groups have been active in Annex-20:

- **Australia**: Commonwealth Scientific and Industrial Research Organisation (CSIRO) and University of Queensland (UQLD);
- **Japan**: Tokyo University of Science (TUS) and Japanese National Institute of Advanced Industrial Science and Technology (AIST);
- **Korea**: Pohang University of Science and Technology Korea (POSTECH), Korean Institute of Science and Technology (KIST), Korean Research Institute of Chemical Technology (KRICT), and Korean Institute for Energy Research (KIER);
- **The Netherlands**: Delft University of Technology (TUD) and Leiden University (LEU);
- **Switzerland**: University of Geneva (UGE), University of Bern (UBE), University of Basel (UBS) and Swiss Federal Institute of Technology of Lausanne (EPFL); and
- **USA**: National Renewable Energy Laboratories (NREL), Hawaii Natural Energy Institute (HNEI), Colorado State University (CSU) and University of California (UCal).

During the course of Annex-20, the above listed official IEA-HIA member country expert groups have enjoyed a growing information exchange and/or part-collaboration with additional research groups that have secured funding to start working on PEC water-splitting and that have participated and contributed as observers at expert meetings of Annex-20. The key observer groups included:

- **Australia**: Sustainable Technologies International (STI), University of New South Wales (UNSW) and Australian Nuclear Science and Technology Agency (ANSTO);
- **Austria**: University of Applied Sciences Wels (UASW) and Johannes Kepler University Linz (JKUL);
- **France**: National Centre for Scientific Research (CNRS), the Atomic Energy Research Centre (CEA) and University of Paris South (UPS);
- **Germany**: Gottfried Wilhelm Leibnitz University Hannover (GWLHUH) and University of Applied Sciences Esslingen (UASE);
- **Mexico**: Energy Research Centre of the National University of Mexico (UNAM);
- **The Netherlands**: Energy Research Centre of the Netherlands (ECN);
- **Portugal**: University of Coimbra (UCO);
- **Singapore**: Nanyang Technological University (NTU);
• **Spain**: University of Seville (USE);
• **Sweden**: University of Uppsala (UPU), Chalmers University (CHU);
• **Switzerland**: Greatcell Solar SA (GSA), Solaronix SA (SSA) and University of Applied Sciences Rapperswil (HSR);
• **United Kingdom**: Loughborough University (LOU), University of Bath (UBA), Hydrogen Solar Company Ltd. (HSC) and CERAM Ltd. (CERAM); and
• **USA**: Florida Solar Energy Centre (FSEC) and GE Global Research (GEGR).

### 3.4. Efforts

Overall, the combined levels of effort that have been invested by the eighteen officially participating research groups over the 3-year duration of Annex-20 amounted to an equivalent of around 140 – 150 “man-years”.

### 4. Program Of Work

Following the excellent R&D efforts made under Annex-14 toward proof-of-concept-type material and systems solutions for waterphotolysis, Annex-20 has set out in October 2004 with the following objectives, task approach and subtask work program.

#### 4.1. Objectives

The five key objectives of the three-year follow-on Annex-20 program concerned:

- **Intensification of international collaboration**, making use of extended fields of expertise;
- **Advancement of photoelectrode materials science**, particularly addressing modification (bulk and surface) of low-cost materials and corrosion challenges;
- **Development of engineering solutions**, with a focus on thin-film deposition as well as powder techniques and system integration;
- **Demonstration of the leading concepts**, putting 25-cm² sized PEC devices through 1000-hour test cycles; and
- **Promotion of photolysis of water** through publications, education and outreach programs.
4.2. Approach

The participants of Annex-20 set out to undertake individual and collaborative R&D within the framework of two coordinated Annex subtasks. These have been of common research interest to the individual PEC R&D programs worldwide and have been carried forward, in a more specific and targeted fashion, the achievements of Annex-14.

4.3. Subtasks

The two subtasks of Annex-20 are summarised as follows:

4.3.1. Subtask-A: Material Studies

Subtask-A did have four main groups of activities. They concerned the development and optimisation (doping) of new semiconductor synthesis materials using combinatorial chemistry, the improvement of light absorption through advanced dyes and anions, the studies of interfacial charge transfer under full-spectrum light irradiation, and the development and optimisation of new photocatalysts.

4.3.1.1. Activity A1: Development and optimisation of semiconductors

Recent research brought to light a number of new and promising semiconductor materials (films as well as powders) with appropriate bandgaps for water splitting. With the help of combinatorial chemistry, a broad range of new materials and doping variants can be relatively swiftly screened and performance characterised. Of key interest are semiconductor electrodes based on pure and doped WO$_3$, Fe$_2$O$_3$, TiO$_2$, ZnO, CuInGaSe$_2$ (CIGS), In- & Sn-nitrides, Ta-oxide & Ta-nitride, AgCl, GaInP$_2$N and a-Si. Understanding of the interrelationship between, and properties of, defects have been studied, including defect control mechanisms. As example, a minimum photoanode current of about 7 mA/cm$^2$ is needed to support the 10% performance target (Activity B1) of a well-matched, dye-cell-based multi-junction PEC system.

4.3.1.2. Activity A2: Improvement of solar light absorption

In relation to two-photon water-splitting systems, the latest developments of cumarin and a new series of ‘black’ panchromatic ruthenium(II) sensitisers for anchoring onto TiO$_2$ showed great promise to extend light absorption over the whole visible range and into the near-IR region (up to 920 nm). Au-doped AgCl has been identified as promising light absorber up to about 750 nm while promoters such as NiO$_x$ were found to decidedly improve light absorption of mixed-oxide semiconductors. N-, S- as well as C-doping was identified as interesting new light-absorption option for TiO$_2$. It was aimed to improve light absorption in all photoanodes toward 900 nm in order to match an optimised dye-cell-based multi-junction PEC system.
4.3.1.3. **Activity A3**: Studies of interfacial charge transfer under light irradiation

Metal nanoparticles have proven to be active in catalyzing the charge transfer from semiconductor surfaces to produce hydrogen. Corresponding catalysts for the oxygen formation have therefore to be developed. Particles are also known to be able to interact with light, hereby opening encouraging avenues to utilise novel nanoassemblies for light energy transport and conversion systems. Studies under Annex-20 aimed at the fundamental understanding and resultant development of metal / semiconductor composites that can induce efficient interfacial charge transfer under light irradiation and therefore warrant fundamental investigation. Key questions concerned the speed of electron transfer, the existence of chemical transformation associated with such an electron transfer, and the consequences of electron storage in the metal counterpart.

4.3.1.4. **Activity A4**: Development and optimisation of photocatalysts

New families of mixed-oxide catalysts (e.g. with a basis on ZnO, IrO₂, RuO₂, FeNiO₅ or In₀.₉Ni₀.₁Ta₀₄, including layered perovskites such as PbBi₂Nb₂O₉) have been identified as stable photocatalysts with attractive bandgaps of typically 2.5 – 2.6 eV. Various processes (spray pyrolysis and sputtering in particular) have been studied to manufacture suitable nanstructured thin-films of beyond-laboratory-size scale and to produce powder catalysts for applications in suspensions. The aim was to achieve corrosion stability in pH-neutral solutions (pure as well as organically-polluted waters) for at least 2 years.

4.3.2. **Subtask-B: System Studies**

Subtask-B has had four main groups of activities. They targeted the optimisation of multi-junction water splitting systems, the further investigation of two-step reactor systems, the design and demonstration of advanced as well as novel tandem PEC design configurations for water-splitting, and the continuing economic analysis of hydrogen production from PEC systems.

4.3.2.1. **Activity B1: Optimisation of multi-junction systems**

CuInGaSe₂ and a-Si emerged as potential high-performance and/or low-cost semiconductor substrates for integrated multi-junction photovoltaic systems. Using for example AgCl or a-SiC as photoanodes proved to produce the necessary stable catalytic and protective thin films for such systems. Studies indicated that a target-efficiency of 7% (near-term) and of 10% (mid-term) is within reach with optimised oxide-photoanode-based multi-junction systems under stable operation over 2-3 years and beyond.

4.3.2.2. **Activity B2: Investigation of two-step reactor systems**

The latest laboratory efforts have shown great promise for the design of a two-step water-splitting system composed of two different TiO₂ (anatase & rutile) and an iodine-based (I⁻ /IO₃⁻) shuttle redox mediator. Photocurrents of up to 2 mA/cm² have been aimed for, while
VIS light absorption and catalyst (Pt/WO₃ and Pt-SrTiO₃) surface area optimisations were expected to lead to the needed improvements of the quantum efficiency.

4.3.2.3. Activity B3: Demonstration of advanced tandem PEC systems

Recent progress in materials science and systems development indicated that there are at least three major opportunities to demonstrate advanced as well as new tandem PEC systems using either existing large laboratory or else pre-commercial manufacturing equipment. These opportunities comprised (a) CIGS / Fe₂O₃, (b) TiO₂-dye-cell (or a-Si) / AgCl, and (c) an advanced version of TiO₂-dye-cell / Fe₂O₃. In addition, monograin membranes were also understood as a possibility for integration as low-cost substrate for monolithic devices. It was aimed to establish demonstration PEC devices at a scale of up to 25 cm², capable to sustain 1000-hour life-cycle testing programs (similar to PV industry).

4.3.2.4. Activity B4: Preliminary cost analysis of hydrogen production from PEC systems

In order to attain expected cost competitiveness with non-fossil-fuel hydrogen production technologies by 2020, solar hydrogen production is understood to necessitate the achievement of a cost rate of about US$ 10 / GJ of hydrogen. This requires solar photolysis techniques to be simple, technically efficient and reliable. This demanding benchmark would translate into a system-cost (per m² of solar collection area) versus conversion-efficiency ratio requirement of no greater than about 10. This ambitious production cost target is believed to constrain the cost of any renewable source of hydrogen, including PEC water photolysis systems. Preliminary cost analyses were planned to be undertaken as it was understood that they are capable of comparatively assessing and predicting likely performance progress of PEC devices of given structure and materials content, with a view to ascertaining the economics of PEC systems and of hydrogen production cost.

5. Achievements

The following sections provide a series of summary statements about the research achievements that the eighteen research groups of Annex-20 have made over the 3-year period of reporting (October 2004 – October 2007). These statements are presented in chronological order and are grouped according to PEC material and system topics. In addition, some of the PEC water-splitting efforts that have been reported by observers at Annex-20 expert meetings are also summarised. Most of these observer groups have expressed a strong interest to collaborate in the planned follow-on PEC research program termed Annex-26.

It is highly recommended that this summary of research achievements be read in conjunction with the final report of Annex-14³, the predecessor research program to this Annex-20, as the

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Annex-14 report can provide much of the missing contextual understanding concerning this Annex-20 report.

The final report of Annex-14 can be downloaded free of charge at: www.ieahia.org

5.1. Material Studies

5.1.1. Tungsten Trioxide (WO₃)

At the University of Geneva (UGE), improvement of WO₃ thin-film crystallinity by using organic additives ("PEG-300" – polyethylene-glycol) and by annealing at temperatures of up to 550°C has been reported, producing mesoporous particles with diameters of 30 - 50 nm. Crystallinity is also improved by ultrasonic stirring of the precursor solution and by doping with lithium (0.1-0.2 wt%). The films can be reproducibly made and generate photocurrents of about 6 mA/m², albeit for 3 µm WO₃ films and when in 3M H₂SO₄ solutions. Photocurrents of 10 mA/m² have been achieved with organic solutions. Using WO₃ thin-films, seawater (0.5M NaCl) can also be split into H₂ and O₂ (plus a little Cl₂), with expected photocurrent densities of up to 4 mA/cm².

Preliminary studies at Hawaii National Energy Institute (HNEI) involving tungsten oxide and titania have shown that nitrogen doping is an effective way to reduce the bandgap, therefore providing for greater absorption in the visible regime of the solar spectrum. Based on this, a full evaluation of N-doping in sputter-deposited WO₃ films was conducted, with characterizations done jointly at HNEI and the National Renewable Energy Laboratories (NREL) to determine how N₂ incorporation impacts the WO₃ material⁴. N₂ incorporation was achieved as part of the sputtering ambient during deposition. For dilute doping (partial pressure less than 2 mTorr), negligible effects were observed for microstructure and bandgap. However, these small amounts of N₂ incorporation showed significant impact on the PEC performance, with a decrease in PEC efficiency directly correlated with the introduction of N₂. This is attributed to an increase in defects, degrading the carrier transport properties.

At more concentrated levels of N₂-doping, the incorporation of defects into the lattice was found to lead to a breakdown in crystallinity. Figure-2 (a) shows plan-view micrographs for pure WO₃, as well as 2 mTorr N₂, 3mTorr N₂, and 6mTorr N₂ films. Here the evolution in microstructure is clearly observed to shift from large crystals for the pure WO₃ to agglomerates of small nano-sized grains for the 6mTorr N₂ sample. These small grains have an accompanying large concentration of defects that degrade the PEC performance. This decrease in PEC performance is illustrated in Figure-2 (b).

Other characterizations (TEM, XRD) confirmed that the material suffers from a decrease in crystallinity. The conclusion is that although N₂ lowers the bandgap, the resultant effect on microstructure is such that a serious degradation of the electron transport occurs, thereby decreasing the PEC efficiency. Nevertheless, motivated by the results of the N₂-doping experiments, future research to address bandgap and band-edge alignment issues in tungsten-based films will specifically explore quaternary systems where bandgap reduction can be achieved while maintaining good crystallinity. An example of such a quaternary system of particular interest for PEC applications is WₓMo₁₋ₓ(O₂S₁₋y)₃.

Thus far, WO₃ remains the best and most reliably performing photoanode material for tandem-cell PEC water-splitting devices.

5.1.2. Ferric Oxide (Fe₂O₃)

N-type α-Fe₂O₃ remains a most desirable photo-anode material for PEC tandem-cells due to its favourable band-gap as well as position, its corrosion stability in water and its abundance, hence low-cost. However, the inherently short hole diffusion length challenge efficient operation.

At the Swiss Federal Institute of Technology in Lausanne (EPFL), a fast-throughput, thin-film deposition technique (Flash-CVD) for Fe₂O₃ with comparably high yields and reproducibility has been developed. This process is favoured over films made by ultrasonic spray pyrolysis. The photoresponse of the films seem to correlate favourably with the formation of perpendicularly orientated sheet-like crystal structures. Addition of carbonate species, e.g. K₂CO₃, to the electrolyte solution improves the photocurrents by 20 to 30% and shifts the flatband potential. The carbonate species presumably catalyze the oxidation of H₂O.

Building on the above progress, a new fast-throughput deposition technique (PACVD – presurized air chemical vapour deposition) has been perfected at EPFL for the production of re-
liable α-Fe₂O₃ thin-films. Meticulous work has led to one of the long-hoped-for progress leaps. A combination of the “right” process conditions together with Si-doping resulted in a three-fold increase of the photocurrents, almost meeting the target value of 3 mA/cm² (AM 1.5; 1.2 Volt vs. NHE) – refer to Figure-3a. These results will now allow the demonstration of a PEC tandem cell based on α-Fe₂O₃/TiO₂ that achieves stable operation at an expected solar-to-hydrogen (STH) conversion efficiency of around 4.5%, effectively matching the performance of the previous best achievements with WO₃/TiO₂ tandem cells.

Concurrently, at the University of Geneva (UGE) a systematic investigation has been concluded on the effect of dopants upon the photo-electrochemical characteristics of semi-transparent α-Fe₂O₃ and, in particular, the aptitude to perform efficient photo-oxidation of water. The combination of a p-type dopant, Zn(II), and an n-type dopant, Ti(IV), was found to lead to a significant improvement of the photocurrent-voltage characteristic of α-Fe₂O₃ electrodes through both a negative shift of the onset potential and a steeper rise of the photocurrent (refer to Figure-3b). These improvements have been assigned to an increase of the hole diffusion length in the modified α-Fe₂O₃ films.

While the performance enhancing effect of anion doping of hematite (α-Fe₂O₃) films (most importantly using p-type Zn(II) and n-type Ti(IV)) has meanwhile been well proven, it has become clear from detailed further studies at EPFL that such doping has also a major influence on the surface morphology. More specifically, Si-enriched surfaces have shown to lead to higher Incident Photon Current Efficiency (IPCE). However, it remains to be shown whether or not such Si addition constitutes proper lattice-doping or rather a kind of surface coating only. Nevertheless, according to the UOG, Si acts as a structure-directing agent. In addition, dipping the highly nanocrystalline surfaces with noble metals such as Co was found to produce a performance enhancement of between 10-15%.

At EPFL, reliable production of well-performing Fe₂O₃ photoanodes has eventually been re-confirmed. Thin films of Si-doped Fe₂O₃ were deposited by APCVD from Fe(CO)₅ and
TEOS (tetraethoxysilane) on SnO$_2$-coated glass at 415°C. HRSEM revealed a highly developed dendritic nanostructure of 500 nm thickness having a feature size of only 10-20 nm at the surface. Real surface area determination by dye adsorption yields a roughness factor of 21. XRD shows the films to be pure hematite with strong preferential orientation of the (110) axis vertical to the substrate, induced by silicon doping.$^5$ As illustrated in Figure-4 on the following page, the photocatalytic activity of these films with regard to PEC water-splitting is comparably high under sunlight illumination in 1M NaOH. Water is oxidized with an IPCE of 42% at 370 nm, demonstrating a photocurrent of 2.2 mA/cm$^2$ in AM 1.5 sunlight of 1000 W/m$^2$ at 1.23 VRHE. This unprecedented efficiency is in part attributed to the dendritic nanostructure, which minimizes the distance photogenerated holes have to diffuse to reach the Fe$_2$O$_3$/electrolyte interface while still allowing efficient light absorption. Part of the gain in efficiency is obtained by depositing a thin insulating SiO$_2$ interfacial layer between the SnO$_2$ substrate and the Fe$_2$O$_3$ film and a catalytic cobalt monolayer on the Fe$_2$O$_3$ surface. Furthermore, the morphology of the α-Fe$_2$O$_3$ was strongly influenced by the silicon doping, decreasing the feature size of the mesoscopic film. The silicon-doped α-Fe$_2$O$_3$ thin-films show a nano-leaflet-type appearance with a preferred orientation whereby the (001) basal plane is normal to the substrate. Overall, this is thought to enhance the photo response because it renders the feature size commensurate to the diffusion length of holes in hematite crystals.

![Figure-4](image)

**Figure-4**: Current-voltage characteristics and morphology of Si-doped Fe$_2$O$_3$ photoanodes obtained from ultra-sonic spray pyrolysis (USP) and atmospheric pressure chemical vapour deposition (APCVD). Measured in darkness and under simulated sunlight at pH=13.6: a) unmodified APCVD Fe$_2$O$_3$; b) the same electrode after cobalt treatment; c) unmodified USP Fe$_2$O$_3$ (Source: EPFL).

At the Commonwealth Scientific and Industrial Research Organisation (CSIRO), a detailed study has been completed that compared the PEC performance of un-doped, Ti-doped and Si-

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doped $\alpha$-Fe$_2$O$_3$ thin films prepared by magnetron sputtering$^6$. The highest photocurrents, and also the lowest onset potentials as well as resistivity and highest charge carrier concentrations were found for the Ti-doped material (1mA/cm$^2$ at 1.2 VRHE and 80 mW/cm$^2$).

Also at CSIRO, a new vacuum arc technique has been used to produce highly nanocrystalline Fe$_2$O$_3$ thin films. Alternatively, at the Technical University of Delft (TUD), Fe$_2$O$_3$-nanorods have been manufactured by oxidation at around 800ºC. Similarly at TUD, nanorods have also been produced through electrodeposition of Fe on TCO glass substrates, with subsequent oxidation in air at 400ºC only.

As a direct result of the Annex-20 expert meetings in the first part of the research program, specific efforts have been commenced to successfully dope Fe$_2$O$_3$ nanorods, followed by coating with a thin film of noble metals. In addition, comparative in-situ material analyses on photoanode samples received from Annex-20 expert groups have been done at various laboratories, including at the Atomic Energy Commission (CEA), France, and the University of Queensland (UQO), Australia, where advanced PEC material analysis capabilities have been established. Such substrate structures are beneficial for light trapping and electron conduction, most importantly for nanosized photoelectrode material with short diffusion length and fast recombination of electrons and holes – such as with Fe$_2$O$_3$. Efforts have therefore started at various places to attempt to increase the conversion efficiency of Fe$_2$O$_3$ thin-films by depositing such doped or undoped films onto nanostructured substrates. The resulting morphology is understood to be beneficial for light trapping and electron conduction, most importantly for nanosized photoelectrode material with short diffusion length and fast recombination of electrons and holes – such as with Fe$_2$O$_3$. While CSIRO is studying filtered arc deposition (FAD) techniques,$^7$ the Technical University of Delft (TUD) focuses on spray pyrolysis and on electrodeposition techniques of metallic Fe with subsequent thermal oxidation.

Both techniques studied at TUD have the advantage that they can be easily scaled up to larger areas at relatively low cost. To improve the performance of spray pyrolysed Fe$_2$O$_3$, thin SnO$_2$ buffer films were deposited in between the Fe$_2$O$_3$ and the transparent conducting oxide glass (TEC-15). The SnO$_2$ buffer layers have a thickness ranging between 5 and 10 nm and were deposited by spray pyrolysis of a solution of SnCl$_4$ in ethyl acetate. SEM and XRD analyses showed little influence of the SnO$_2$ film on the morphology and structure of the Fe$_2$O$_3$ films. However, the photoresponse of the Fe$_2$O$_3$ changes markedly, as can be seen in Figure-5. Without the buffer layer, back-side illuminated Fe$_2$O$_3$ gives a higher photocurrent, indicating that electron transport is rate limiting. With the buffer layer, front-side illumination gives a higher response, suggesting that hole transport now becomes rate limiting. Furthermore, a negative shift of the photocurrent onset potential of 0.2-0.4 V was found, and the reproducibility of the Fe$_2$O$_3$ photoresponse showed significant improvement. Preliminary results (not shown) suggest that the SnO$_2$ changes the alignment of the energy barriers at the Fe$_2$O$_3$/substrate interface. This may improve the collection efficiency and provides a tentative explanation for the improved photoresponse. Present films of doped Fe$_2$O$_3$ made with spray pyrolysis yield photocurrents of 0.37 mA/cm$^2$ at 1.23 V vs. RHE.

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One of the main challenges for Fe$_2$O$_3$ is to make nanostructured morphologies that can be doped in a controlled manner. Towards this end, at TUD thin metallic Fe films have been deposited with electrodeposition. When oxidizing these films under the right conditions, formation of Fe$_2$O$_3$ nanorods has been reported to occur. Electrodeposition took place in either aqueous FeSO$_4$ solutions, or non-aqueous (DMSO, EC) iron chloride solutions. After deposition, the Fe films were oxidized at 550°C in air. The growth rate during electrodeposition has a pronounced effect on the morphology of the films (refer to Figure-6). The best results so far were obtained in DMSO solutions, yielding photocurrents of ~0.2 mA/cm$^2$ at 1.4 V vs RHE. Addition of Si to the electrodeposition solution resulted in a much smoother morphology of closely packed spheres with an average diameter of ~200 nm, but did not result in higher photocurrents. Current efforts are aimed to obtain nanorods upon oxidation, and to incorporate suitable dopants to improve the photoresponse.

Figure-5: Photocurrent voltammogram of spray pyrolysed Fe$_2$O$_3$ in an aqueous 1M KOH solution under (simulated) AM1.5 illumination (Source: TUD).

Figure-6: SEM electrodeposited iron films on TEC-15 after thermal oxidation at 550°C in air. The current densities chosen for electrodeposition were 1 mA/cm$^2$ (left) and 2 mA/cm$^2$ (right) respectively (Source: TUD).

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During the second part of Annex-20, the significant thin-film synthesis and characterization capabilities of the Loughborough University (LOU) have been put to work for PEC materials development in general and for \( \text{Fe}_2\text{O}_3 \) thin-films in particular. Hydrothermal growth (90°C), thermal oxidation and ultrasonic spray deposition methods are the major techniques that have been applied for PEC material studies during the past couple of months (refer to Figure-7).

Further at LOU Department of Chemistry, PEC \( \text{Fe}_2\text{O}_3 \) thin-films have also been produced successfully by CVD. As an interesting novelty, a mixture of metal-organic precursors has been applied, obtaining new current density records of up to 2.5 mA/cm\(^2\).

Regarding the challenge of doping, at CSIRO a detailed study has been published on the comparison of undoped, Ti-doped and Si-doped \( \alpha\)-\( \text{Fe}_2\text{O}_3 \) thin films prepared by magnetron sputtering. The Ti-doped material had the highest photocurrents and is being investigated further with the aim of identifying the main charge carrier loss processes. Charge transfer models have been developed to describe the experimental data. In an attempt to increase the conversion efficiency, Ti-doped \( \alpha\)-\( \text{Fe}_2\text{O}_3 \) thin films have been deposited onto ZnO nanowire arrays via ITO interlayer (refer to Figure-8).

**Figure-7:** SEM micrographs of \( \text{Fe}_2\text{O}_3 \) thin-films produced by hydrothermal growth (left – 5 days at 90°C) and thermal oxidation (right – 5 hours at 800°C) respectively (Source: LOU).

**Figure-8:** ZnO nanowire arrays (A, D) coated with ITO (B, E) and ITO-\( \text{Fe}_2\text{O}_3 \) (C, F) respectively. A, B and C are imaged at 60 degrees, D, E and F are top-views (Source: CSIRO).
Although an overall decrease in the photocurrent was observed (due to band-edge mismatch, imperfect coating etc), the relative response at long wavelengths was enhanced. Nanostructuring was therefore found to change the shape of the IPCE curve. Further work will be done to optimize the coatings on the nano-structured substrates. Interesting is the observation that the barrier model traditionally used to describe semiconductor charge transfer does not fit the IPCE data measured at CSIRO well.

Work at the University of California at Santa Barbara (UCal) on Fe₂O₃ nanorod synthesis have yielded some important results: (1) control over the size and morphology of the nanostructures has been achieved; (2) improved photoelectrochemical performance as compared with spray pyrolysis deposited films has been demonstrated; and (3) single-junction zero-biased STH efficiencies in excess of 1% have been observed using Fe₂O₃ nanorod materials. Of key importance, the developed nanorod synthesis method is applicable to a wide variety of substrate types, and easily adapted to any size substrate. Figure-9 (a) illustrates nanorods of Fe₂O₃ using the newly developed fabrication techniques, and Figure-9 (b) shows PEC photocurrent performance consistent with STH efficiencies exceeding 1% at zero applied bias. Future work will include the reduction of nanorod size to ~6nm to increase the valence band confinement, obtain growth along the [110] axis for improved carrier transport, nanorod-doping by in-situ growth or high-temperature diffusion, exploration of deposition of surface electrocatalysts such as Pt, Ni, Au, and Ru, and integration in multi-junction device configurations.

![Figure-9](image_url)

**Figure-9**: (a) Fe₂O₃ nanorods with diameter of 20 nm and (b) photocurrent versus potential scan of nanorod samples in 0.1 M NaOH under simulated AM1.5G (1-sun) illumination, indicating a STH PEC water-splitting device performance capability of over 1% at zero applied bias (Source: UCal).

Overall, there is a plethora of techniques available to produce Fe₂O₃ thin-films, which allow tuning the surface morphology and hence provide the basics for material optimization. In addition, studies of the photocurrent decay mechanisms of PEC films are most important in order to better understand long-term stability issues. Similarly, the incorporation of effective electrocatalysts into the PEC thin-films is also in need of detailed studies.
Following the benchmark results established at EPFL in the middle of Annex-20 with cobalt derivatized APCVD-Fe\(_2\)O\(_3\) photoanodes (IPEC over 40% at single wavelength of 370 nm and current density of 2.2 mA/cm\(^2\) at 1.23 V\(_{RHE}\) at AM 1.5G), the effects of the underlayer, the substrate and the catalyst on the anode performance have been investigated.

Since a monolayer of SiO\(_2\) deposited on the SnO\(_2\)-substrate by APCVD from TEOS strongly enhances the photocurrent efficiency of APCVD-Fe\(_2\)O\(_3\) films, alternative underlayers where investigated. Underlayer deposition by evaporation or adsorption from solutions of Al(NO\(_3\))\(_3\), Pb(acetate)\(_2\), AgNO\(_3\), NH\(_4\)F and Zr(iOPr)\(_4\) had no effect. APCVD treatment with just ethanol (a component of TEOS) or TFA (trifluoroacetic acid; for surface fluorination of SnO\(_2\)) also gave no improvement. However, APCVD of thin underlayers of TiO\(_2\) or Ta\(_2\)O\(_5\) from Ti(iOPr)\(_4\) or Ta(OEt)\(_5\) yielded photocurrent enhancements equivalent to the SiO\(_2\) underlayer (Ta\(_2\)O\(_5\) is used instead of SiO\(_2\) in nanoscale CMOS devices due to its high dielectric constant). This accords with EPFL’s interpretation that the underlayer acts as a thin insulating layer as in MIS (metal-insulator-semiconductor) junctions, and suggests that further optimization of this important junction will improve electron collection at the SnO\(_2\)-substrate and ultimately the electrode performance.

Furthermore, in order to study the influence of the nature of the substrate on the performance of the hematite photoelectrode, APVCD-Fe\(_2\)O\(_3\) films were deposited on other substrates than SnO\(_2\):F. Pure iron (Armco 99.8+%), steel and silver showed high dark currents (>1 mA/cm\(^2\)) on anodic polarization in 1 M NaOH due to electrochemical oxidation of the substrate, but no discernable photocurrent. Stainless steel, titanium, zirconium, niobium and tantalum yielded low, unstable photocurrents, indicating growth of an insulating oxide layer (passivation). EPFL concluded that non-noble metals are not suitable as substrates, whereas noble metals are expected to make a Schottky-barrier with Fe\(_2\)O\(_3\) due to their high work function. Even different SnO\(_2\):F substrates yield very different photocurrent, the highest ones being obtained so far with TEC-15 which has the lowest haze. Further work will be done under Annex-26.

The reaction of Fe\(_2\)O\(_3\) valence bands with water is notoriously slow, reducing the overall efficiency of water-splitting. Importantly, EPFL has shown that deposition of a cobalt monolayer on the Fe\(_2\)O\(_3\) surface catalyzes the oxidation of water to oxygen, improving the photocurrent by at least 20%. A similar effect has been observed with ruthenium. However, this coating is not stable since it dissolves as RuO\(_4\)\(^2-\) in the basic electrolyte. Another well-known catalyst for oxygen evolution is iridium for which indeed a stable photocurrent enhancement was achieved after deposition of a thin coating from H\(_2\)IrCl\(_6\), although, not better than with the much cheaper cobalt (refer to Figure-10).

At the Technical University of Delft (TUD), efforts toward the end of Annex-20 have focused on synthesizing thin film α-Fe\(_2\)O\(_3\) photoanodes using two methods, being spray pyrolysis and thermal oxidation of electrodeposited Fe films. Both techniques have the advantage that they can be easily scaled up to produce larger areas, at relatively low cost.
Figure-10: Dark and illuminated (AM 1.5G, 100 mW/cm²) current density versus electrode potential plot from APCVD of Fe₂O₃ electrodes as prepared and the effects of adding a catalyst mono-layer of iridium or cobalt (Source: EPFL).

Thin-film hematite Fe₂O₃ photoanodes were deposited on transparent conducting glass substrates by spray pyrolysis using a Fe(AcAc)₃ precursor. By depositing a 5 nm SnO₂ interfacial layer between the Fe₂O₃ films and the transparent conducting substrates, both the reproducibility and the photocurrent can be enhanced. The effects of Si doping and the presence of the SnO₂ interfacial layer were systematically studied. It was shown that the beneficial effect of such an interfacial layer is not limited to the material SiO₂, and that electrons do not need to be able to tunnel through the interfacial layer. In undoped Fe₂O₃ samples, electron transport was found to be rate limiting, whereas hole transport limits the efficiency for Si-doped samples. Mott-Schottky analysis confirmed that Si acts as a donor-type dopant in Fe₂O₃, and by varying the amount of Si in the precursor solution the donor density could be tuned between 10¹⁷ – 10²⁰ cm⁻³. The highest photoresponse was obtained for Fe₂O₃ doped with 0.2% Si, resulting in a photocurrent of 0.37 mA/cm² at 1.23 V vs. reversible hydrogen in a 1.0-M KOH solution under 80 mW/cm² AM1.5 illumination.

To avoid hole transport limitations, TUD aimed to make doped nanostructured Fe₂O₃ films by electrodeposition of thin, alloyed Fe films. Under the right conditions, thermal oxidation of thin Fe films can result in the formation of Fe₂O₃ nanorods. While the formation of nanorods has not yet been observed during preliminary studies, the morphology of the films can be controlled through the growth rate during electro-deposition. The best results so far were obtained in DMSO solutions, using FeCl₂ and TiCl₄ as precursors. Addition of Si to the electro-deposition solution resulted in a much smoother morphology of closely packed spheres with an average diameter of ~200 nm, but did not result in higher photocurrents.

In contrast, Ti doping resulted in a marked increase in the photoresponse. The best results at TUD so far have been obtained using a solution with a Fe:Ti ratio of 90:10, yielding photoanodes that show a photocurrent of 0.24 mA/cm² at 1.23 V vs. reversible hydrogen in a
1.0-M KOH solution under AM1.5 illumination (refer to Figure-11 on the following page). However, this is still a factor of ~10 less than recent results achieved at EPFL for thin Fe₂O₃ films, understood to be the case due to the relatively poor control over the electrodeposition process. Hence, future efforts at TUD, which are planned for during the upcoming Annex-26, are aimed to gain a more detailed understanding of the electrodeposition process and to achieve significantly higher photocurrents.

At Chalmers University (CHU), localized surface plasmon resonances in noble metal nanoparticles have been scrutinized to understand how these improve photocurrent-generation efficiency by decorating TiO₂ and Fe₂O₃ thin-films with arrays of such nanoparticles. It was found that localized surface plasmons in Pt and Pd decay predominantly into electron-hole pairs (as opposed to, for instance, gold and silver, where the decay typically occurs via radiative pathways). Such electron-hole pairs can potentially be used to drive a chemical reaction such as the photoinduced water-splitting.

![Figure-11: Photocurrent voltammograms of Ti-doped hematite Fe₂O₃ films made by non-aqueous electro-deposition of a Fe-Ti metal alloy, followed by thermal oxidation (Source: TUD).](image)

At the Colorado State University (CSU), encouraging progress was made with the development of the comparably simple, ink-jet-printer based, high-throughput combinatorial method for PEC materials synthesis directly onto conductive glass substrates and subsequent electrochemical analysis. A sample around Fe as precursor is shown in Figure-12. This technique has been prepared for widespread application whereby, if possible, the help of science students worldwide could be employed to develop a systematic, worldwide, web-based PEC materials library. It might be possible for expert groups from Annex-26 to successfully advance this concept worldwide.
Overall, $\alpha$-Fe$_2$O$_3$ remains one of the most promising, low-cost p-type photoanode material for PEC water-splitting. However, a much more structured approach among all R&D expert groups is needed to tackle the yet unknown fundamental material science and associated thin-film manufacturing challenges.

5.1.3. Titanium Dioxide (TiO$_2$)

Due to its very limited spectral response (refer to Figure-13) and despite of over thirty years of intensive research on the material worldwide, studies on TiO$_2$ for PEC water-splitting have only been continued on a comparably small-scale basis by a few Annex-20 expert groups.

**Figure-12**: Example of novel combinatorial PEC materials research approach based on ink-jet-printing of metal oxide precursors onto conductive glass (Source: COU).

**Figure-13**: Comparison of the spectral response of the most widely studied materials worldwide for PEC water-splitting, indicating TiO$_2$’s inherent limitation (Source: EPFL).
Nonetheless, at the University of New South Wales (UNSW) some of the main achievements concerning TiO$_2$ included: (i) the identification of the TiO$_2$ surface active sites for water-splitting, (ii) the identification of the functional properties responsible for water-splitting in addition to the bandgap, (iii) the engineering of chemically induced electric fields for charge separation, and (iv) the derivation of defect disorder diagrams that enable the selection of processing conditions for TiO$_2$-based semiconductors with desired properties. The ceramics experts at UNSW published a review of TiO$_2$ materials for PEC energy conversion.9

At the Delft University of Technology (TUD), unusually high photocurrents have been measured in anatase TiO$_2$ that has been specially prepared by CVD. The process conditions have been selected to result in the deposition of thin-films with a rather rough surface morphology (refer to Figure-14), herewith favouring light-scattering and hence maximizing the path-length of the light through the material while minimizing diffusion distances for photo-generated electrons and holes. Doping with selected transition metal ions, IPCE values of as high as 10% have been reportedly been measured at 500nm. However, as the films were found to be instable in the presence of oxygen, studies have been discontinued.

![Figure-14: Scanning electron micrographs of an unusually fractal TiO$_2$ film (“nano-forest” with average size of around 8-10µm) deposited by chemical vapour deposition (Source: TUD).](image)

In addition to TiO$_2$ thin-film preparation, doping of TiO$_2$ has also been studied by various Annex-20 expert groups.

At the Commonwealth Scientific and Industrial Research Organisation in Sydney (CSIRO) for instance, sulphur-doped TiO$_2$ oxide powders have been successfully synthesized, with the powders achieving high solar radiation absorption in the visible part of the spectrum. However, coating and, more importantly, sintering of the comparably active S-doped TiO$_2$ powders onto conducting substrates without sulphur being lost during the process proved to remain a main challenge.

At TUD, carbon-doped TiO$_2$ (anatase) has also been studied again but showing virtually no visible light response, probably due to the low amount of carbon uptake. The UV photocurrent, however, was found to be 16 times larger than expected based on the absorption coefficient and the depletion layer width. New equipment has meanwhile been developed to study the electrical and optical properties of metal oxide photoelectrodes as a function of

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temperature and partial oxygen pressure in order to better understand and control the defect chemistry of these materials.

Nitrogen-doping of TiO$_2$ using reactive DC magnetron sputtering was studied at University of Uppsala (UPU), whereby nitrogen atoms were confirmed to substitute oxygen atoms.

In support of these doping studies, the first step in the oxidation of water at a metal oxide photoanode surface such as TiO$_2$ has been modelled with quantum transition state theory (QTST) at the Institute of Chemistry of the Leiden University (LEU). Thus far, density functional theory (DFT) has been employed in an attempt to calculate the stability of the various dopants at the surface. This basically aims to indicate whether a certain dopant ion will reside on top of or a little below the surface. Using this information, the experts at LEU aim to successfully apply QTST to investigate the photooxidation of water at the metal oxide surface, which may then contain dopant atoms or ions. By taking an electron out of the highest occupied molecular orbital (the valence band) it is possible to simulate the creation of the hole, and the subsequent reaction with water.

Adding to this, the influence of doping / defects sites on the local microscopic charge carrier mobilities has also been studied at LEU using a Terahertz (THz) Time Domain Spectroscopy set-up. It was found that small amounts of carbon dopant in anatase TiO$_2$ enhance the recombination rate and decrease the number of free charge carriers by a factor of $\sim 3$. For Fe-doped anatase, however, the recombination was found to be even faster ($\sim 50$ ps).

As an additional approach to enhance performance of TiO$_2$, studies of TiO$_2$ surface functionalisation using the help of light sensitized 2Fe-2S-clusters have been conducted at the University of Basel (UBS) during Annex-20, albeit with limited success. Safe anchoring seemed to be difficult, with efforts to electrostatically adsorb Ru(bpy)$_3^{2+}$ on the surface remaining to be a key challenge.

Irrespective of the potential application of TiO$_2$ as photoelectrode material, experts at the University of Geneva (UGE) used various thicknesses of nanocrystalline TiO$_2$ photoanodes to study the effect of electrolyte upon the photocurrent efficiency. As an important finding it was confirmed that it is the mass transport in the electrolyte and not the electron transport across the network of TiO$_2$ particles, which controls the electrode resistance and the amount of the photocurrent. In addition to the diffusional/migrational limitations associated with the transport of the electroactive species, operation of the nanocrystalline TiO$_2$ electrodes was also found being clearly affected by the conductivity of the electrolyte.$^{10}$

Ending with a positive note, with the help of a new high-temperature growth method (including annealing and chemical after-treatment in an inert environment) tested at UGE toward the end of Annex-20, it has been possible to extend the spectral response of n-type rutile TiO$_2$ toward the visible light, up to 430 nm. This resulted in a comparably high incident-photon-to-current efficiency (IPCE) of 30% at 400 nm, potentially putting n-type TiO$_2$ back onto the agenda as a potential low-cost and highly stable photo-anode for PEC water-splitting devices.

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As a further option, mixed oxide TiO$_2$ (eg. titanates with strontium or iron) have been discussed at Annex-20 expert meetings as potential materials research challenge for the new Annex-26. And to finish off, research at TUD toward the end of Annex-20 found that TiO$_2$ nanotubes act as better performing PEC substrates for nanosized PEC materials than nanoparticulate TiO$_2$ due to grain boundary advantages.

5.1.4. Silver Chloride (AgCl)

At the University of Bern (UBE), successful PEC water-splitting has been demonstrated using gold colloids as spectral sensitizers of a AgCl photo-anode in conjunction with a conventional Si solar cell (a-Si:H/Pt) as photocathode. The Au colloids confirmed to improve the photocatalytic capability of the AgCl system in the VIS light spectrum ($\lambda > 420$ nm) by promoting the charge transfer process at the semiconductor/electrolyte interface. For the purpose of performance optimization, the active surface area of the AgCl photoanodes has thereafter been increased through new synthesis procedures. As support for the AgCl, microporous Zeolite A as well as L materials and mesoporous TiO$_2$ nanotubes, WO$_3$ and most importantly Al$_2$O$_3$ membranes have been studied.

While zeolite monolayers worked well as a microporous substrate for AgCl photoanodes with significantly enhanced active surface area, it was also found that the zeolite acted as a buffer for the AgCl ions. For this reason microporous support materials (eg. zeolite A and L – refer to Figure-15) have successfully been tested in combination with mesoporous oxide substrates (TiO$_2$ nanotubes, mesoporous WO$_3$ and Al$_2$O$_3$ membranes). Early results, however, showed that the conductivity between the substrates and the AgCl particles had to be much improved. The conductivity was assessed not to be sufficient to allow fast reoxidation of the reduced silver species that are produced upon illumination of the AgCl.

![Figure-15](image)

**Figure-15**: Cylindrical nanocrystal consisting of donors (empty rectangles) and an acceptor acting as trap at the front and the back of each channel (shaded rectangles). The enlargement shows the microporous tunneling structure of zeolite-L (with dye molecule and its electronic transition moment), which has been employed as ideal substrate with high surface area for AgCl particles to form a high-performance PEC photoanode (Source: UBE).
For these reasons of conductivity limitation, tailored zeolite monolayers have ultimately been prepared on conducting Au-glass and Au-foil surfaces. For the preparation of the monolayers, cubic crystals of zeolite-A (refer to Figure-16) and disc-shaped as well as cylindrical crystals of zeolite-L were used. The zeolites were linked to the Au surface by means of a thiolalkoxysilane as molecular linker. Afterwards, the monolayers were used as back support to the AgCl photoanodes, which demonstrated an increased water oxidation capability. For the modified zeolite-A monolayers, the oxygen signal starts around 600 nmol/h (photocurrent around 10 µA) and decreased to a steady-state of around 400 nmol/h (8 µA).\textsuperscript{11}

![Figure-16: SEM images of photoanode materials based on zeolite-A monolayers without (left) and with AgCl (right) modification (Source: UBE).](image)

Although the research on AgCl photoanodes for water-splitting has generated valuable new insights into the science of solar light sensitisation and ion buffering, the work on AgCl photoanodes is understood not to be continued as a focal area of research in Annex-26.

### 5.1.5. III-V Nitrides (eg. GaInPN)

At the National Renewable Energy Laboratories (NREL) in Golden, III-V nitrides (above all GaP\textsubscript{1-x}N\textsubscript{x} and GaInPN) options have been developed and extensively studied as potential photoanodes for new monolithic PEC device designs on Si-tandem devices with Zn-doped GaInPN intermediate films (similar to PV for back surface field creation – refer to Figure-17).\textsuperscript{12} Regarding corrosion stability, SiN and SiC coatings are also being developed for multi-junction PEC cells.


5.1.6. Copper-Chalcopyrites (eg. CIGS)

Based on their successful utilization in PV devices and the availability of widebandgap compositions, the Annex-20 expert group at the Hawaii Natural Energy Institute (HNEI) initiated an evaluation of copper chalcopyrite films for use as photoelectrode material. In particular CuGaSe$_2$ (CGS) and CuInGaSe$_2$ (CIGS) in the bandgap range of 1.3 eV – 1.65 eV were studied. Such films grown in a physical vapor deposition process exhibit p-type behavior and would thus be employed as photocathodes, facilitating the H$_2$-evolution reaction. Using a vacuum deposition chamber dedicated to the synthesis of PV-quality copper chalcopyrite materials, thin-films were deposited by thermal co-evaporation of elemental Cu, In, Ga and Se onto heated substrates. From a twin set of CIGS (Eg~1.30 eV) samples, both a solid-state solar cell and a photoelectrode were fabricated. Initial PEC testing in 0.5M H$_2$SO$_4$ showed stability at cathodic potentials and high photocurrents, which are on par with those of solid-state solar cells. As can be seen in Figure-18, the 1-sun saturation photocurrent of the photoelectrode was almost identical to the short-circuit current of the solar cell (28 mA/cm$^2$). However, a large cathodic bias needs to be supplied, suggesting unfavorable valence band edge alignment with the water oxidation redox potential and kinetic barriers for H$_2$-evolution reaction on the bare electrode surface.

![Concept of PEC tandem-cell employing GaInPN on Si (Source: NREL).](image1)

**Figure-17:** Concept of PEC tandem-cell employing GaInPN on Si (Source: NREL).

![Photocurrent versus potential scan of CIGS electrode in 0.5M H$_2$SO$_4$ and (b) current voltage behavior of solid state CIGS solar cell, both under simulated AM1.5G (1-sun) illumination (Source: HNEI).](image2)

**Figure-18:** (a) Photocurrent versus potential scan of CIGS electrode in 0.5M H$_2$SO$_4$ and (b) current voltage behavior of solid state CIGS solar cell, both under simulated AM1.5G (1-sun) illumination (Source: HNEI).
Based on the non-ideal band edge alignment and various loss mechanisms, a tandem device scheme is seen as necessary for the employment of such chalcopyrite films into PEC water-splitting devices. Semitransparent films are therefore necessary in order to allow some light to pass through to a bottom PV junction. Thick (2 micron) and thin (0.9 micron) semitransparent CGS samples have been produced at HNEI to evaluate the optical properties and the amount of photocurrent generated as a function of thickness. The photocurrent of 10 mA/cm² for the thin device is not much less than that of the thick device (15 mA/cm²). These findings show that, in principle, device engineering is possible to current-match a CGS electrode film with a supplemental PV junction to form an integrated PEC water-splitting device. Future work under the auspices of Annex-26 will include surface modification to lower the valence band maximum position, and noble metal island depositions to improve the catalytic properties of the electrode surface.

At the Energy Research Centre of the National University of Mexico (UNAM), most recent PEC research has also focused on the development of CuInSe₂ photoelectrodes via sequential electrodeposition on Mo-foil substrates, with matrix-incorporation of Ga proving to increase the band-gap to 1.6eV. Results confirmed that p-type CIGS has the potential as a reliable option for a CIGS/H₂SO₄-based PEC system.

At the University of Applied Sciences Wels, Austria (UASW), previous work on CuInSe₂ monograin membranes with catalytic micro-islands has been revisited during Annex-20 as potentially promising approach to water-splitting. Photocurrent scanning tunneling microscopy shows that nanosized metal contacts allow the reduction of overvoltage through barrier height control via size and distance. In particular, 100 nm gold or Pt-coated gold particles improve H₂ production at GaAs electrodes. The reduction of overvoltage is considered essential for achieving high efficiencies in excess of 10 – 15%.

Overall, valence band shifting, bandgap widening and corrosion stabilisation are some of the most imminent challenges to tackle for PEC water-splitting using Cu-chalcopyrites. In addition, CuInGaSSe₂ is of particular interest as thin PEC film in combination with Si.

5.1.7. Mixed-Metal Oxides (eg. InVO₄, BiVO₄, NaBiO₃)

At the beginning of Annex-20, orthorhombic InVO₄ has been studied intensively at the Technical University of Delft (TUD) for its potential as one of the promising new complex-metal photo-electrode material in PEC devices. Films prepared by spray-pyrolysis have resulted in the material to have a comparably large band-gap of between 3.3±0.3eV, albeit with a sub-band-gap absorption at around 600nm of ~ 1.6eV and a photocurrent on-set at 450nm (~ 2.75eV). Doping with Cu and/or Ni, however, proved to be inefficient as the doping centres were found to act as efficient recombination centres. Although treatment with silver ions has shown to improve performance slightly, it was concluded from the intensive synthesis and characterization efforts undertaken at TUD that orthorhombic InVO₄ is less promising as new photoelectrode material than anticipated and research has therefore been discontinued.

At the Advanced Industrial Science and Technology (AIST), however, research on complex-metal-oxyde photoelectrodes (produced via metal-organic deposition MOD method; 6
layers of ~100nm each) showed that BiVO$_4$ electrodes demonstrate excellent solar energy conversion efficiency under visible-light irradiation. H$_2$ and O$_2$ evolved in a 2:1 ratio from a Na$_2$SO$_4$ aqueous solution with an external bias. The band structure of BiVO$_4$ was investigated by open-circuit potential, flat-band potential, XPS, and by DFT calculations. The top of the valence-band potential of BiVO$_4$ was shifted negatively compared to the potentials of the conventional oxide semiconductors without Bi. The hybridization between the O-2p and Bi-6s orbitals might contribute to the negative shift of the BiVO$_4$ valence band that has been observed (PS: CB of BiVO$_4$ is similar to WO$_3$ at around 2.4eV). Treatment with an aqueous pH=6 solution of AgNO$_3$ improved the photocurrent significantly. The maximum IPCE at 420 nm was 44% (refer to Figure-19) and a STH of about 0.2% was measured without external bias, which indicates that a STH of about 2.8% can be expected with external bias in a PEC tandem-cell arrangement. AgNO$_3$ treatment also improved the stability of the photocurrent. The Ag$^+$ ion in/on the BiVO$_4$ catalyzed the intrinsic O$_2$ formation with the holes.\textsuperscript{13}

![Figure-19: IPCE spectra of BiVO$_4$ photoelectrodes (Source: AIST).](image)

As a further variant of mixed-metal oxides, sodium bismuthoxide (NaBiO$_3$) powder has been studied at the Tokyo University of Science (TUS). This materials was been confirmed to act as O$_2$-evolution photocatalyst from NaIO$_3$ aqueous solution under VIS light irradiation ($\lambda$ > 420nm), hence working well as part of a 2-step water-splitting system using an I-/IO$_3$- redox mediator and a coumarine-derivative dye-sensitized TiO$_2$ photocatalyst for H$_2$-evolution. The NaBiO$_3$ powder material is being characterized and optimized for water-splitting.

Experts at the National Institute of Advanced Industrial Science and Technology (AIST) in Japan inaugurated a versatile high-throughput facility to conduct combinatorial material screening for PEC water-splitting applications\textsuperscript{14}. Initial work on iron binary oxides such as Fe-Ti, Fe-Nb and Fe-V, all synthesized on n-type Fe$_2$O$_3$, resulted in the identification of FeVO$_4$ as promising new PEC material. Following on from this work, ternary iron oxides have been evaluated in a preliminary manner at 700ºC, indicating that Fe-Ti-Zr has excellent photocurrent, with peak photocurrents observed at Fe/Ti/Zr = 60:10:30. Its photocurrent is higher than TiO$_2$ under Xe lamp irradiation, even without a filter (refer to Figure-20). Further work is being scheduled as part of the upcoming Annex-26.


\textsuperscript{14} Arai T., Konishi Y., Iwasaki Y., Sugihara H. and Sayama K., J Comb Chem 2007, 9, 574-581.
Figure-20: The photocurrent for various metal ratios of Fe–Ti–Zr ternary oxide photoelectrodes (fired at 700°C) under visible light (left) and full-arc irradiation (right) (Source: AIST).

In a similar investigation at AIST, CuBi$_2$O$_4$ was reconfirmed to also have a high cathodic photocurrent, hence being a promising VIS light p-type semiconductor. AIST has commissioned an automatic semiconductor synthesis system based on the application of conducting glass substrates for the evaluation of the visible light responsibility of photo-electrode materials (composition, structure and photo-electrochemical properties).

As an additional metal oxide example, novel Mo-Co alloy thin-films have been developed and tested for H$_2$-evolution at the Korea Institute of Science and Technology (KIST). These films are showing good activity and, above all, high stability in strong alkaline electrolytes when combined with FeNiO$_x$ films for O$_2$-evolution (films have O$_2$ deficiency on surface). However, the FeNiO$_x$ films themselves did indeed decrease the overpotential for oxygen-evolution but did not show high stability inside its electrolyte.

5.1.8. Zinc-Oxide (ZnO)

At University of California (UCal) Santa Barbara, the photoelectrochemical production of hydrogen is studied using a combinatorial approach. An automated system has been designed and commissioned for synthesis and high-throughput characterization of photoelectrodes. Automated characterization techniques include electrochemical screening, chemo-optical H$_2$ detection, and UV-VIS spectroscopy. A case study on Zn$_{1-x}$Co$_x$O showed that an increasing amount of cobalt improves the visible light absorption, but reduces the charge transport efficiency. Meso-structured TiO$_2$ and ZnO were fabricated by surface-templated electrodeposition. Using high-throughput photoelectrochemical screening, the optimum concentration of the structure-directing agent was identified.

Very preliminary work on ZnO-based photoanode thin-films was conducted at NREL to evaluate its performance as a top-junction material for multi-junction PEC systems. ZnO has a large bandgap (3.2 eV), and therefore to have merit in PEC application, this bandgap must be reduced. N-doping was evaluated, and is shown to effectively incorporate into ZnO films to reduce the bandgap. The fabricated films to date have shown poor crystallinity (related to the low-temperature of the deposition methods chosen). Future efforts will therefore revolve around improving the growth process and quality of the films. In addition to the synthesis
work, theoretical calculations have been conducted that show that doping of group-1B transition metals (Cu, Ag) will result in bandgap reduction for ZnO. Cu was incorporated into the ZnO films with mixed results. While the bandgap reduction was successful with Cu found at Zn sites for select films, the measured photocurrents, however, were comparably low. Future efforts at NREL will also focus on improving material properties through growth process optimization.

5.1.9. Ferro-Electrics (eg. Perovskites)

During early work under Annex-20 at the Pohang University of Science and Technology Korea (POSTECH), layered metal-doped perovskites and composite photocatalyst powders have shown to achieve UV quantum efficiencies of up to 50%. La$_2$Ti$_2$O$_7$–based powders with cation (Cr) dopants and Sr$_2$Nb$_2$O$_7$–based powders with anion dopants (N, C, S) have been studied for splitting of organics under VIS light. Cation-doped perovskites, however, suffered from recombination, while anion-doping lead to stability problems. In both cases, only a limited amount of dopants could be incorporated before the parent structure started to change.

Following on from this work at POSTECH, photocatalytic nanodiode (PCD) configurations, particularly n-CdS nano-particles deposited on the bulk of p-Ag$_2$GaS$_2$ particles, have then been developed, showing good activity for H$_2$-evolution under VIS light from water containing Na$_2$S/NaSO$_3$ or H$_2$S dissolved into alkali-containing water.

Toward the end of Annex-20, at POSTECH a new configuration with a conducting ohmic layer between p- and n-type semiconductors was fabricated (WO$_3$/W/PbBi$_2$Nb$_{1.9}$Ti$_{0.1}$O$_9$) by depositing the W-clusters over p-type perovskite base material, and later oxidizing the surfaces of these clusters to obtain n-type WO$_3$ overlayers. With further adaptation, the development of photocatalytic p-n nanodiode composites involved n-type PbBi$_2$Nb$_{1.9}$W$_{0.1}$O$_9$ (perovskite – via solid-state reaction methods) in combination with solgel produced p-type WO$_3$ or CaFe$_2$O$_4$ (calcium ferrite) – refer to Figure-21. Reactions were made in aqueous methanol solutions (30ml methanol plus distilled water 170ml) or in an aqueous AgNO$_3$ solution (0.05mol/l and 200ml).

![Figure-21](image)

**Figure-21:** Development of photocatalytic p-n nanodiode composites for PEC water-splitting, using n-type PbBi$_2$Nb$_{1.9}$W$_{0.1}$O$_9$ (or Ti instead of W) and p-type WO$_3$ or p-type CaFe$_2$O$_4$ (Source: POSTECH).
5.1.10. Oxi-Nitrates & Nano-Sulfides (eg. \( \text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x \) & \( \text{CdIn}_2\text{S}_4 \))

At the Korea Research Institute of Chemical Technology (KRICT), materials research efforts focused on the development of oxynitrides (\( \text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x \), Pt/\( \text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x \), as well as \( \text{RuO}_2/\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x \)) and nano-sulfides (band gap for cubic spinel nanostructure \( \text{CdIn}_2\text{S}_4 \): \( \text{Eg} = 2.19\text{eV} \) at 570nm) as novel PEC water-splitting materials, the latter ones demonstrating quantum yields of around 12-17% at 500nm (refer to Figure-22).

![Figure-22: SEM of nanostructured CdIn_2S_4 as potential new photocatalyst material, showing the 3-5µm Marigold (left) and a nanotube versions (right, size 25nm x 780nm) (Source: KRICT).](image)

5.1.11. Silicon-Carbide (a-SiC)

The integration of an “all-silicon” multi-junction PEC water-splitting device remains an attractive concept due to its straightforward fabrication process and the abundance of the raw material. Based on theory, a PEC junction of amorphous silicon carbide (a-SiC) films in the bandgap range of 1.9-2.2 eV could be supported by an amorphous silicon (a-Si) solid-state tandem junction.

Various a-SiC films with a bandgap of ~2.0 eV have therefore been evaluated at HNEI for PEC performance and stability. These 2\textsuperscript{nd} generation p-type a-SiC photocathodes demonstrated photocurrents in excess of 8 mA/cm\(^2\), a dramatic improvement over previous work. However, stability remains an area of concern as partial delamination has been observed for several samples. Moreover, the amount of cathodic bias required, though improved over earlier generation films, is still excessive for practical PEC applications. Future work will include identification of corrosion mechanisms, quantification of the energetic and kinetic parts of the high cathodic potential requirement, and metal island catalyst depositions to improve the kinetics of the \( \text{H}_2 \) evolution reaction.

5.2. System Studies

As research by the various groups of Annex-20 experts around the world progressed, only a limited number of system studies have been undertaken. The focus of work was rather put on PEC materials development and assessment as this area benefited from advances in scientific understanding and from new combinatorial tools becoming available (refer to Section 5.1).
5.2.1. Monolithic Multi-Junction Systems

At Hawaii Natural Energy Institute (HNEI), new multi-junction planar photoelectrode concepts have been studied using Mo-doped sputtered WO₃ films in conjunction with a-Si:Ge or a-Si tandem systems. 5% efficient systems have been identified as achievable in the near future based on the preliminary developments conducted under Annex-20.

5.2.2. Two-Photon Tandem Systems

The development of two-photon tandem PEC demonstration devices has received particular attention by Annex-20 members over the past couple of years, including the pre-commercial development efforts of the British Hydrogen Solar Company Inc. (HSC).

Two new PEC demonstration cells have been developed at Tokyo University of Science (TUS), namely: (i) a S-doped TiO₂ film photoanode and Pt cathode (steady-state photocurrent of 5 µA/cm² obtained from NaOH aqueous solution under VIS light), and (ii) a TiO₂ (anatase) photoanode with 2 black-dye TiO₂ solar cells as tandem PEC cell (2 series-connected DSC solar cells with $\eta=6.3\%$, Voc=1.4V, Jsc=8.2mA/cm², ff=0.53, active cell area 2 x 5mm wide and 25mm long). The latter one resulted in a STH energy conversion efficiency of 1.2%, which demonstrates a new record for a stable, all-TiO₂-based PEC water-splitting device.

At the University of Applied Sciences Rapperswil (HSR), a simple PEC water-splitting cell benchtop kit has been assembled for educational demonstration purposes. The cell comprised an almost square-shaped multi-layered WO₃ photoanode on a TEC-15 substrate with an actively illuminated area of 5 cm² (supplied by the University of Geneva) and a Pt-film cathode with an active area of 6 cm² (supplied by the University of Bern). The Pt-film was sputtered onto a glass substrate in the form of a “picture frame” and therefore did not obstruct the lightpath to the WO₃ photoanode when assembled back-to-back with the anode. The cell was biased by two monocrystalline Si PV cells of 1 cm² each, which have been connected in series (refer to Figure-23). Outdoors, a peak STH conversion efficiency of around 1.8% has been measured under sunlight conditions of close to AM 1.5. Main operational drawbacks included high ohmic resistance due to imperfect electrical connections and corrosion stability of the films.

![Figure-23](image-url): Simple benchtop WO₃-Pt-Si tandem device (operated in 1M-H₂SO₄) to demonstrate PEC water-splitting for educational purposes using artificial as well as real sunlight (Source: HSR).
At Korea Institute of Science & Technology (KIST), two integrated PV-electrolysis lab-scale devices have been fabricated and successfully demonstrated toward the end of Annex-20. While the first one was using a conventional monocrystalline Si-PV-cell in combination with a nickel ferrite (FeNiO\textsubscript{x}) photoanode thin-film for O\textsubscript{2}-evolution and a Pt mesh as cathode (1M-NaOH), the second option was applying a 17% efficient CIS PV-cell (divided into 3 series-connected subcells). Using a halogen light source, results for the Si-based PEC device and an illumination of around 100 mW/cm\textsuperscript{2} indicated a STH conversion efficiency of 9.3%, while the CIS-based PEC device achieved a STH efficiency of close to 10%, albeit under an illumination of a 50 W/cm\textsuperscript{2}. The stability of the FeNiO\textsubscript{x} thin-film is being further investigated during Annex-26.

At HSC, prototype PEC water-splitting tandem-cells at scales of up to 25cm x 25cm have been demonstrated. The main issues encountered herewith concern sheet resistance of transparent conducting substrates, long-term stability of photoelectrodes and light trapping of the PEC cells. Figure-24 illustrates some of HSC’s scale-up steps of PEC water-splitting device developments based on the WO\textsubscript{3}-Pt-DSC tandem-cell concept (DSC – TiO\textsubscript{2}-based Dye Solar Cells), which has been patented by the Swiss Federal Institute of Technology in Lausanne (EPFL), on behalf of EPFL and the University of Geneva.

**Figure-24:** Succession of demonstrator PEC water-splitting devices based on the WO\textsubscript{3}-Pt-DSC tandem-cell concept, showing from left to right: Individual 10cm x 10cm device (2004); individual 30cm x 30cm device (2005); electrochemically and fluiddynamically fully integrated, 10cm x 10cm PEC water-splitting device modules demonstrated in 2006 (Sources: HSC).

### 5.2.3. Bio-Promoted Systems

At Korea Institute of Energy Research (KIER), a novel bio-promoted PEC water-splitting concept has been developed experimentally as part of the national Korean PEC R&D program and in conjunction with Annex-20. As a basic concept of bio-promoted PEC water-splitting, proton-producing hydrogenase enzymes are being employed in conjunction with a solid-state photoanode and an ion bridge (refer to Figure-25) or with a suitable nanofiltration membrane (see Figure-26).
As a further design evolution toward the very end of Annex-20, experts at KIER have shown that it is possible to omit the use of the ion bridge when employing a nanorod-based TiON/Ti electrode, designed as an anodized tubular TiO$_2$ electrode (ATTE) on a titanium foil (refer to Figure-26).

Anodizing of the ATTE (at 20 and 30V; bath temperature 5 and 25°C; anodizing time 1 and 17 hours) followed by annealing (350°C – 850°C for 1 and 5 hours) in an O$_2$ atmosphere of Ti foils led to the formation of a tube-shaped (20V) or sponge-like (30V) TiO$_2$ film on the Ti foils. The samples were proven based on methylene blue (MB) discoloration and Cr(VI) reduction to be photocatalytically active. In addition, the electrical and physical properties, including the current density, open-circuit voltage, morphology and crystalline structure, of the ATTE were correlated with the H$_2$ production rate in an enzymatic PEC system. The ATTE samples showing the highest evolution rate were composed of both anatase and rutile.
esting is the fact that increasing the light intensity caused a considerable enhancement in the rate of H₂ production from 71 to 153 µmol/(hr×cm²) with the Pyrococcus furiosus (Pfu) enzyme amount optimized at 10.98 units. This system configuration led to the stoichiometric 2:1 evolution of H₂ and O₂. It was assessed that the STH efficiency of this bio-promoted PEC water-splitting concept at AM 1.5 amounts to between 6.3% and up to 9.0%.

Additional studies have been made at KIER on the immobilization of the hydrogenase on the cathode and the selection of the cathode in a material aspect. First experiments indicated that the anodized Ti foil could also replace a Pt cathode successfully. Further work is ongoing.

6. Economics

At the Hydrogen Solar Company Ltd (HSC) in the UK, 7% efficient WO₃-Pt-DSC photoelectrochemical tandem cells have been demonstrated in a pre-commercial effort, supporting an estimate of possible hydrogen production costs of between 15 – 25 US$/GJ hydrogen. This was estimated to be two to three times cheaper than the projected costs for generating hydrogen via the conventional photovoltaic + electrolysis route, indicating that direct photoelectrolysis might be a promising and credible route towards H₂ production. Considering the climate of Los Angeles for example, a 7m x 7m array of photoelectrochemical cells has been predicted to generate enough hydrogen to drive a Mercedes A-Class “NECAR” fuel cell based hydrogen car for a distance of around 17'500 km per year (refer to Figure-27).

![Figure-27](image)

*Figure-27:* Artists impression of a 49 m² residential PEC water-splitting system producing enough hydrogen to power a family-size fuel cell car over 17'500 km per year in Los Angeles (Source: HSC).

7. Conclusions

Looking back to 3 years of internationally collaborative, pre-commercial R&D efforts facilitated by Annex-20, it has become clear that the “ideal” photoelectrode material is not “readily available”. Success will rather be the result of major concerted efforts on the development of novel composite materials and associated thin-film production techniques capable of large-scale manufacture. This will be the task of a follow-up Annex-26.
Nevertheless, some of the major achievements can be summarised as follows (listed in no order of priority and including important contributions by Annex-20 observer groups, too):

- **Threefold performance improvement** of $\alpha$-$\text{Fe}_2\text{O}_3$ thin-film photoanodes, delivering photocurrents of up to $2.8\, \text{mA/cm}^2$ (at AM 1.5 and 1.2 Volt vs. NHE), which allows for $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$ based PEC tandem cells to achieve stable operation at an expected solar-to-hydrogen (STH) conversion efficiency of around 4.5% – Switzerland;

- Significant **enhancement of corrosion stability** of III-V semiconductors upon nitriding when applied with PEC water-splitting – USA;

- **Discovery** of n-type ternary iron oxide (Fe-Ti-Zr as 60-10-30), demonstrating higher photocurrents under Xe-lamp irradiation than TiO$_2$ – Japan;

- Demonstration of **novel photocatalytic p-n nanodiode perovskite composite powders** for PEC water-splitting, using n-type PbBi$_2$Nb$_{1.5}$W$_{0.1}$O$_9$ (or Ti instead of W) and p-type WO$_3$ or p-type CaFe$_2$O$_4$ – Korea;

- Scientific confirmation that **nanostructuring of photoelectrodes changes the shape of the IPCE curve** and that the barrier model traditionally used to describe semiconductor charge transfer needs revision – Australia;

- Development of a simple, ink-jet-printer based, very-high-throughput **combinatorial method** for PEC materials synthesis directly onto conductive glass substrates – USA;

- First-time **modelling of water oxidation at metal oxide photoanode surfaces** such as TiO$_2$ using **quantum transition state theory** and density functional theory to calculate the stability of dopants at the surface – The Netherlands;

- Confirmation that Cu-chalcopyrites are principally capable to form stable PEC water-splitting devices with good STH conversion efficiency of **around 10%** once current-matched with a supplemental PV junction to form an integrated, monolithic PEC water-splitting device – USA;

- Development of **novel bio-promoted concept** for enzymatic PEC water-splitting – Korea;

- Establishment of **efficiency benchmarking** of PEC water-splitting using semiconductor electrodes – Australia;\(^{15}\)

- **World-record STH energy conversion efficiency** of **1.2%** for a stable, all-TiO$_2$-based PEC water-splitting device using a TiO$_2$ (anatase) photoanode in tandem with two black-dye TiO$_2$ solar cells – Japan; and

- **World-first** demonstration of electrochemically and fluidodynamically **fully integrated modules for PEC water-splitting**, using 10cm x 10cm WO$_3$-Pt-DSC tandem devices – UK.

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Toward the end of Annex-20, experts from the Netherlands have published a comprehensive compendium of PEC water-splitting knowledge.\(^\text{16}\)

### 8. Outlook

Considering the historic aim of many PEC R&D expert groups and governmental support programs around the world, namely to work toward a stable, 10%-efficient PEC water-splitting system producing hydrogen at US$ 10/GJ, significant materials science and engineering progress is needed.

However, what would the investment cost target need to be for a stable, 10%-efficient PEC water-splitting system to achieve this aim of solar hydrogen production at US$ 10/GJ – and would such a cost target be realistic at all?

As indicated in Figure-28, a complete 10%-efficient PEC water-splitting system operating reliably over 20 years in the climate of Southern Spain or of Southern California could cost around US$ 120/m\(^2\). Very simplistically, this assumes a net worth of hydrogen production throughout the entire life of the water-splitting system of 15 GJ/m\(^2\) and cumulative operation and maintenance costs of US$ 30/m\(^2\) only.

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**Figure-28**: Idealistic comparison of the US$ 10/GJ cost target for the production of hydrogen from PEC water-splitting with the crude oil spot price of US$ 60/barrel and with today’s manufacturing costs of related technologies such as 2\(^\text{nd}\) generation thin-film solar photovoltaics or flat-plat solar hot water using highly solar-selective surfaces (Source: Luzzi).

Though such a cost target is very low, particularly since the costs for hydrogen storage and handling are not accounted for, today’s manufacturing costs of related technologies for instance such as 2\(^\text{nd}\) generation thin-film solar photovoltaics or flat-plat solar hot water using

highly solar-selective surfaces are already at or below such a price target. Theoretically, this indicates that the price target of US$ 10/GJ for a PEC water-splitting system is highly challenging but not totally impossible when abundant PEC materials and smart manufacturing techniques can be employed.

In addition, considering that US$ 10/GJ equates to a crude oil price of around US$ 60/barrel, this cost target of US$/GJ of hydrogen is highly debatable.

9. Appendix

Table-2 lists the total of eight expert meetings and briefings, which have been conducted at the start, during and just after the official Annex-20 program.

Table-3: List of expert meetings & briefings conducted as part of Annex-20 (incl. follow-up meeting toward Annex-26).

<table>
<thead>
<tr>
<th>Meeting</th>
<th>Date</th>
<th>Venue</th>
<th>Attendance</th>
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<tbody>
<tr>
<td>Kick-off meeting</td>
<td>27-28 September 2004</td>
<td>TUD, Delft, Netherlands</td>
<td>19+2</td>
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<tr>
<td>1st expert meeting</td>
<td>9 August 2005</td>
<td>Rosen Centre Hotel, Orlando, USA</td>
<td>5+8</td>
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<tr>
<td>1st expert briefing</td>
<td>25 October 2005</td>
<td>Focus Abengoa F., Sevilla, Spain</td>
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<tr>
<td>2nd expert briefing</td>
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<td>2nd expert meeting</td>
<td>2+5 July 2006</td>
<td>G-Hotel Höman, Uppsala, Sweden</td>
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<tr>
<td>3rd expert briefing</td>
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<tr>
<td>3rd expert meeting</td>
<td>7-8 May 2007</td>
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<tr>
<td>Follow-up meeting</td>
<td>16 May 2008</td>
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