

# Photoelectrochemical Water Splitting

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**Abstract:** To halt the buildup of carbon dioxide (CO<sub>2</sub>), the main greenhouse gas, the development of an alternative energy source to fossil fuels becomes more and more important. Hydrogen (H<sub>2</sub>) has the potential to meet the requirements as a clean non-fossil fuel in the future, if it can be produced using our primary source of energy, the sun, and stored and transported safely. The present article will give a short review on different approaches on semiconductor-based photoelectrochemical water splitting into hydrogen and oxygen (O<sub>2</sub>) using sunlight as the energy input, also generally described as photoelectrolysis.

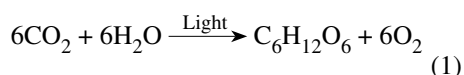
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## Introduction

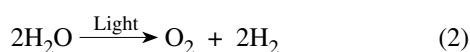
Hydrogen, H<sub>2</sub>, has the potential to meet the requirements as a clean non-fossil fuel in the future, if it can be produced using the world's most abundant energy source, the sun, and stored and transported safely. Research and development (R&D) of an efficient system for solar energy conversion and storage is one of the challenging subjects to solve the global energy problem.<sup>[1,2]</sup> But there is still a large gap between our present global energy consumption (around 13 terawatts, TW), our use of solar energy to supply the world's energy demand (less than 2 %), and the enormous untapped potential of the sun (120'000 TW).<sup>[2]</sup> The realization of a solar hydrogen economy requires solutions to key scientific and technical challenges. One major issue is the need to develop highly efficient photoactive materials capable of harvesting and converting solar energy into stored chemical energy, *i.e.* a clean non-fossil fuel like hydrogen.

In the overall reaction of photosynthesis (Eqn. (1)), plants transform water and carbon dioxide in the presence of light into oxygen and carbohydrates. In effect then,

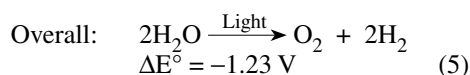
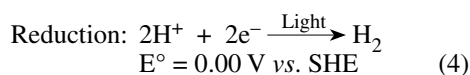
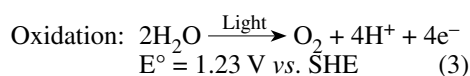
H<sub>2</sub>O is split into O<sub>2</sub> and H<sub>2</sub>, where the hydrogen is not in the gaseous form but bound by carbon.<sup>[3]</sup>



The aim of *artificial photosynthesis* is the light-driven splitting of water into H<sub>2</sub> and O<sub>2</sub> (Eqn. (2)), which has been called a 'holy grail' in chemistry.<sup>[4]</sup> Water represents a plentiful energy resource, which, in a thermodynamically uphill reaction ( $\Delta G \approx 237.2$  kJ/mol), is converted into a clean and storable fuel (H<sub>2</sub>) with sunlight.



The photoelectrochemical (PEC) path to water splitting involves separating the oxidation and reduction processes into half-cell reactions. In Eqns (3) and (4) the half-cell reactions with their corresponding standard reduction potential E° with respect to the standard hydrogen electrode (SHE) are shown. Eqn. (5) shows the overall reaction and the corresponding  $\Delta E^\circ$ . The negative  $\Delta E^\circ$  indicates that water splitting is not a thermodynamically spontaneous process. For the reaction to proceed 1.23 V must be provided externally.



For that purpose, materials are necessary which upon light absorption can drive the water splitting reaction. Three fundamental requirements should be met by any system harvesting and converting solar energy into chemical energy:

- i) the photoresponse of the system must optimally match the solar spectrum;
- ii) photoexcited charges must be separated efficiently to prevent recombination;
- iii) the charges must have sufficient energy to carry out the desired chemical reactions such as water splitting.

Different ways have been chosen to convert solar energy into a chemically stored form as H<sub>2</sub>. One possible approach is semiconductor-based PEC water splitting into H<sub>2</sub> and O<sub>2</sub> using sunlight as the energy input, also generally described as photoelectrolysis.

## Photoelectrolysis

Photoelectrolysis is the general term used to describe semiconductor-based PEC water splitting. Basically, three approaches are possible. Arrangements using either photovoltaic cells (PV approach) or semiconductor-liquid junctions (SCLJ approach), or a combination of the two (PV/SCLJ approach) can be realized. For the sake of simplicity, in the following sections the schematic representations for the different approaches will show single components externally connected. It is evident, that for systems converting solar light into chemical fuel that are cost-effective, economically viable, and meet the efficiency required for practical applications more integrated embodiments have to be used.

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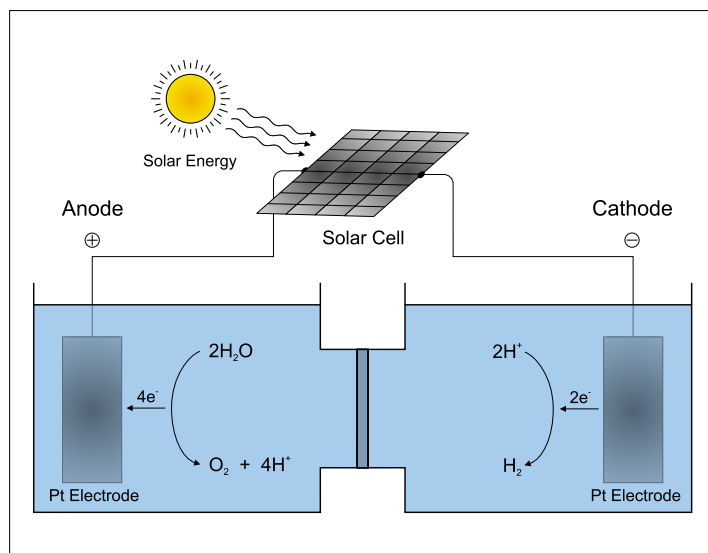


Fig. 1. Schematic representation of a PV approach, where a PV system is coupled to an electrolyzer

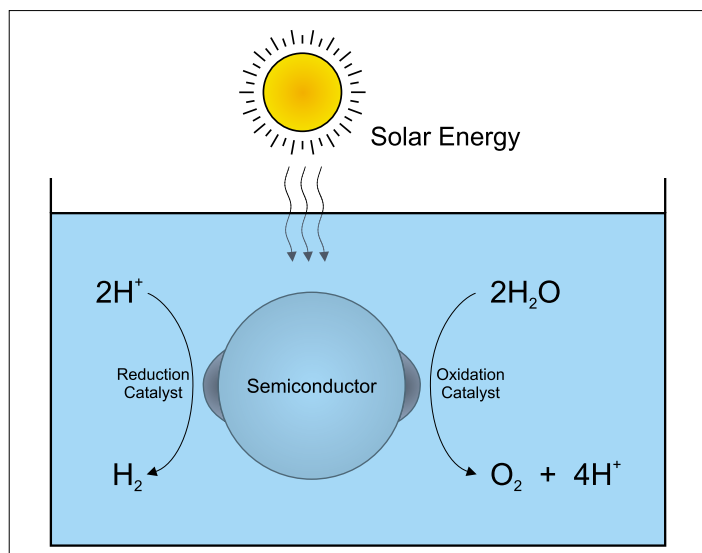


Fig. 2. Schematic representation of a SCLJ approach with one semiconductor loaded with a reduction catalyst and an oxidation catalyst

## Photovoltaic Approach

The approach based on solid-state photovoltaic is to couple a PV system and an electrolyzer into a single system (Fig. 1). An early report described the use of multiple junction semiconductor structures for the conversion of light energy into chemical energy when immersed in an electrolyte and exposed to light.<sup>[5]</sup> Semiconductor layers are connected in series, one behind the other, in a single monolithic device capable of generating the potential needed to split water. These so-called tandem cells or multi-junction cells are modified with or connected to H<sub>2</sub> and O<sub>2</sub> producing electrodes, like Pt and RuO<sub>2</sub>-modified Pt, which act as cathode and anode, respectively.<sup>[6]</sup> For example n-p GaInP<sub>2</sub>/GaAs,<sup>[7,8]</sup> n-p Al<sub>x</sub>Ga<sub>1-x</sub>As/Si,<sup>[9]</sup> and multiple junction p-i-n amorphous Si<sup>[8,10]</sup> cells were used for the photoelectrolysis of water.

A PV approach was also used in solar-driven water electrolysis at elevated temperatures.<sup>[11]</sup> The basic principle behind is the decrease of the electrochemical water splitting potential with increasing temperature. Solar radiation is used for generating the necessary potential by illuminating photovoltaic cells as well as for the heat source to facilitate water electrolysis. This permits smaller band gap solar cells to drive the water cleavage at sufficiently low temperatures (500 °C) from molten NaOH.

## Semiconductor-Liquid Junction Approach

For arrangements based on semiconductor-liquid junctions, the water splitting potential is generated directly at the semiconductor-liquid interface. The ability of a semiconductor photoelectrode to drive

either the oxidation of water into O<sub>2</sub>, or the reduction of water into H<sub>2</sub>, or the whole water splitting reaction is determined by its band gap and the position of the valence and conduction band edges relative to the water redox reactions. Besides the position of the band edges, there are other requirements that have to be considered for a material to be used for water splitting purpose in a SCLJ approach. The semiconductor has to be active over a broad spectral range, and, upon light absorption, the material should efficiently separate the generated charges. Obviously, this is also valid for the photovoltaic approach. Moreover, the immersed semiconductor has to be stable in the electrolyte and corrosion free.

For example, TiO<sub>2</sub> is very stable in a wide range of pH, but it is active only in the UV region due to its large bandgap. WO<sub>3</sub> is also only active in the short wavelength range of the solar spectrum, but it is less stable in acidic medium. Fe<sub>2</sub>O<sub>3</sub> has a smaller band gap and absorbs in the visible, but it is also not very stable in acidic solutions. Compounds such as CdTe or InP also have smaller band gaps that are better matched to the spectral distribution of sunlight reaching the earth, but these materials either corrode or become inert when used as photoelectrodes in aqueous solution.<sup>[12]</sup> These few examples and the ones mentioned in the following show that every semiconductor has its drawbacks. In search of suitable semiconductors to be used for water oxidation, water reduction, as well as water splitting in semiconductor-liquid junctions, a large number of scientific efforts have been devoted worldwide for several decades.

Fujishima and Honda reported for the first time in 1972 sunlight-assisted electrolysis of water using crystalline TiO<sub>2</sub> photoelectrodes.<sup>[13,14]</sup> The photoelectrochemical cell consisted of TiO<sub>2</sub> (rutile) as a photoanode

and platinum as a cathode. Illumination of the TiO<sub>2</sub> electrode led to O<sub>2</sub> evolution on the photoanode and H<sub>2</sub> evolution on the cathode. The quantum efficiency increased with an increase in alkalinity in the TiO<sub>2</sub> photoanode compartment and in acidity in the Pt cathode compartment. This means that the thermodynamic potential of 1.23 V (Eqn. (5)) required for water splitting was substantially decreased due to the presence of a big pH gradient between the compartments ( $\Delta\text{pH} \sim 13$ , chemical bias  $\sim 0.77$  V).

After the seminal work of Fujishima and Honda, numerous semiconductors have been explored for water cleavage following the SCLJ approach. Many semiconductor materials have been used to drive the water oxidation and the water reduction at the same time. Fig. 2 shows a schematic representation of a SCLJ approach with one semiconductor. Undoped<sup>[15]</sup> and Ni-doped In-TaO<sub>4</sub>,<sup>[16]</sup> InNbO<sub>4</sub>,<sup>[15]</sup> Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (Ln = La, Pr, Nd),<sup>[17]</sup> MCo<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> (M = Ca, Sr, Ba),<sup>[18]</sup> RbNdTa<sub>2</sub>O<sub>7</sub>,<sup>[19]</sup> NaTaO<sub>3</sub> doped with La,<sup>[20]</sup> La<sub>3</sub>TaO<sub>7</sub> and La<sub>3</sub>NbO<sub>7</sub>,<sup>[21,22]</sup> Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>,<sup>[22]</sup> and H<sub>2</sub>La<sub>2/3</sub>Ta<sub>2</sub>O<sub>7</sub><sup>[23]</sup> are examples where photocatalytic water splitting under light irradiation was described. For all these materials, the photocatalytic activity increases significantly when loaded with a reducing and/or oxidizing co-catalyst, such as Pt, RuO<sub>2</sub>, or NiO. Recently, the oxynitride (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>)<sup>[24]</sup> modified with nanoparticles of RuO<sub>2</sub><sup>[25]</sup> and with a mixed oxide of rhodium and chromium<sup>[26]</sup> was used as a photocatalyst for overall water splitting into H<sub>2</sub> and O<sub>2</sub> with visible light. A solid solution of zinc oxide and germanium nitride (Zn<sub>1+x</sub>Ge)(N<sub>2</sub>O<sub>x</sub>) (x = 0.44) was also demonstrated to be an effective photocatalyst for overall water splitting under ultraviolet and visible light when modified by surface loading with RuO<sub>2</sub> nanoparticles.<sup>[27]</sup> Domen and coworkers showed also that  $\beta$ -Ge<sub>3</sub>N<sub>4</sub> exhib-

its activity for the stoichiometric decomposition of water into  $H_2$  and  $O_2$  under ultraviolet irradiation when loaded with  $RuO_2$  as a co-catalyst. Improving the crystallinity of  $\beta\text{-Ge}_3\text{N}_4$  results in greater photoactivity and markedly reduces the  $N_2$  release due to self-decomposition by photo-generated holes.<sup>[28]</sup>

More promising is a photoelectrolysis cell based on two illuminated semiconductor–liquid junctions. Fig. 3 shows a schematic representation of this approach. A n-type semiconductor is used for the evolution of  $O_2$  and a p-type semiconductor for the evolution of  $H_2$  (Fig. 4). By separating the oxidation and reduction processes into half-cell reactions, one can deal with one reaction at a time. Besides, two semiconductors with smaller band gaps can be utilized since each needs only to provide part of the water splitting potential. The smaller band gap means more absorption in the visible region of the solar spectrum where the sun has a greater photon flux. As a result, the maximum theoretical efficiency is considerably higher.<sup>[29]</sup> The system is contingent on the efficient recombination of electrons formed in the n-type semiconductor (photoanode) with holes formed in the p-type semiconductor (photocathode) *via* back contact connections in both materials. This is theoretically possible only if the valence band of the photocathode lies positive (higher electrochemical potential) with respect to the conduction band of the photoanode. This means, that proper selection of both semiconductor electrode characteristics ensures that the energy necessary for water photoelectrolysis is gathered entirely from the illumination, eliminating the necessity of applying energy from an external source.

In a SCLJ approach with two semiconductors, single crystals of N-doped n-SiC and Al-doped p-SiC were employed as photoelectrodes in a photoelectrochemical

cell.<sup>[30]</sup> By combining single crystal p-SiC and nanocrystalline n-TiO<sub>2</sub> water splitting was observed without the used of any external potential, though at a low photocurrent density (0.05 mA/cm<sup>2</sup>) and low efficiency (0.06%) due to a high recombination of photo-generated electron–hole pairs.<sup>[31]</sup> Photocatalytic water splitting was reported with a composite of two semiconductors, Cr-doped Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>/In<sub>2</sub>O<sub>3</sub>, under UV light irradiation.<sup>[32]</sup> Powders of two different semiconductor photocatalysts were also used for water splitting in the presence of a redox mediator. For the  $O_2$  and  $H_2$  evolution Pt-loaded WO<sub>3</sub> and Pt-loaded SrTiO<sub>3</sub> (doped with Cr, Ta), respectively, were used in an aqueous solution with the  $IO_3^-/I^-$  redox pair as mediator.<sup>[33]</sup> Photoelectrolysis of water was also demonstrated using Pt-loaded TaON for the  $H_2$  evolution and Pt-loaded WO<sub>3</sub> for the  $O_2$  evolution using the same redox mediator.<sup>[34]</sup>

Polycrystalline n-Fe<sub>2</sub>O<sub>3</sub> photoanodes have been investigated in a photoelectrochemical cell where the cathode was Zn-doped p-GaP<sup>[35]</sup> or p-Cu<sub>2</sub>O.<sup>[36]</sup> Spontaneous water splitting under visible light illumination was reported, though the efficiency of the process remained low. In the latter experiment the photoelectrolysis cell had a separate compartment for the Fe<sub>2</sub>O<sub>3</sub> anode and the cathode. The anode compartment had an alkaline electrolyte, whereas for the cathode compartment an acidic electrolyte was used. Consequently, the thermodynamic (theoretical) voltage needed to split water was considerably reduced due to the pH gradient present between the compartments (chemical bias).

A multi-junction cell arrangement like in photovoltaic devices was adopted for a SCLJ approach with two semiconductors by using a composite of polycrystalline Si with a doped TiO<sub>2</sub> thin film layer on top. The doped TiO<sub>2</sub> absorbs the short-wavelength part of solar light (blue light,  $\lambda < 500$  nm).

The long wavelength part is absorbed by the polycrystalline Si layer in the back. Upon light absorption, an electron is excited in two steps from a low lying valence band of TiO<sub>2</sub> to a high lying level of the conduction band of Si, which leads to hydrogen evolution on the Pt counter electrode and oxygen evolution on the doped TiO<sub>2</sub> surface.<sup>[37]</sup> The stability problem of silicon electrodes could be overcome by surface alkylation and metal nano-dot coating.<sup>[38]</sup>

### Photovoltaic/Semiconductor–Liquid Junction Approach

In a PV/SCLJ approach for overall water splitting a PV cell is used together with a semiconductor that is in direct electrolyte contact. The PV cell can be combined either with a reduction (photocathode) or with an oxidation (photoanode) photocatalyst. The water splitting reaction involves a two-electron reducing process for the  $H_2$  production (Eqn. (4)) and a four-electron oxidizing process for the  $O_2$  producing part (Eqn. (3)). It is the water oxidation reaction that poses the greatest difficulty in achieving photocatalytic water splitting, mainly because four oxidative equivalents must be accumulated. Therefore, efficient oxygen production at a semiconducting photoanode is the most challenging aspect of PEC water splitting. The additional bias for the hydrogen evolution on a metallic cathode is provided by a solar cell, leading to a PV/SCLJ approach for overall water splitting (Fig. 5).

Nevertheless, different compounds have been explored as reduction photocatalysts for the  $H_2$  evolution from water. For example, CuMnO<sub>2</sub><sup>[39]</sup> and platinumized CdS<sup>[40]</sup> particle suspensions, LaMnO<sub>3</sub>/CdS nanocomposites,<sup>[41]</sup> Pt-loaded (CuIn)<sub>x</sub>Zn<sub>2(1-x)</sub>S<sub>2</sub>,<sup>[42]</sup> Pt-loaded ZnS-CuInS<sub>2</sub>-AgInS<sub>2</sub> solid solutions,<sup>[43]</sup> and Cr-doped SrTiO<sub>3</sub><sup>[44]</sup> were

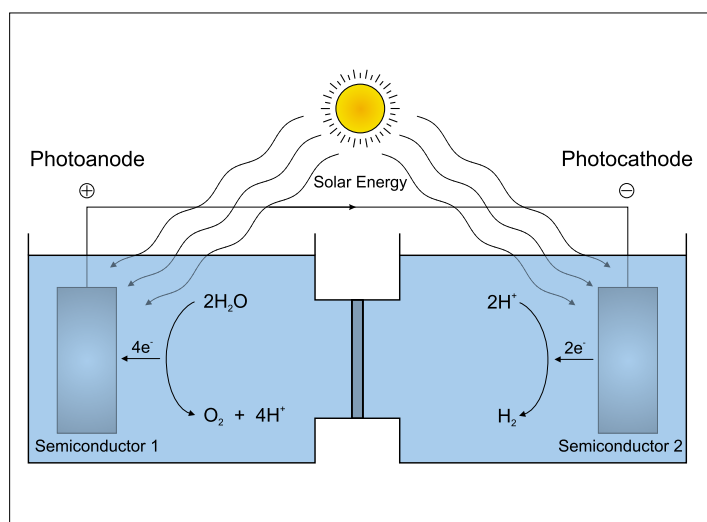


Fig. 3. Schematic representation of a SCLJ approach with two semiconductors used as photoanode and photocathode, respectively

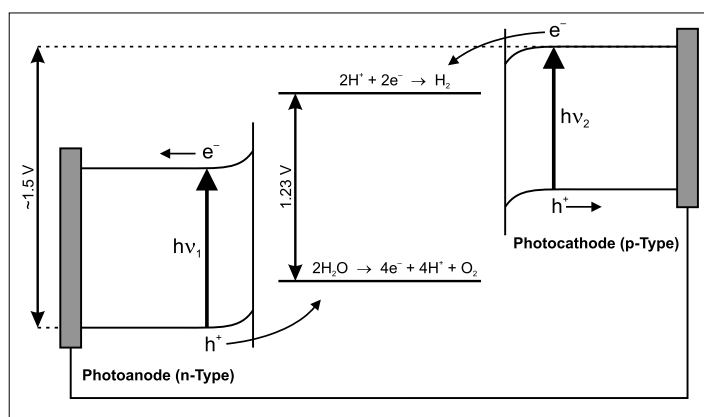


Fig. 4. Scheme of a photoelectrolysis cell based on two semiconductor–liquid junctions. A n-type semiconductor is used for water oxidation into  $O_2$  (photoanode) and a p-type semiconductor for  $H^+$  reduction into  $H_2$  (photocathode). The thermodynamic potential for water splitting is 1.23 V. If overpotentials are considered, around 1.5 V have to be generated by illumination to drive the reaction.

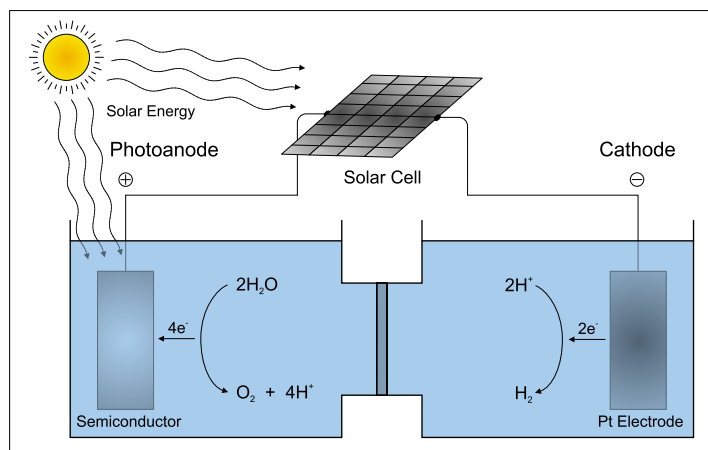


Fig. 5. Schematic representation of a PV/SCLJ approach with a semiconductor photoanode and a Pt cathode

reported to evolve  $H_2$  without any external bias in the presence of hole scavengers under illumination. Transition metal loaded  $WS_2$  showed photocatalytic  $H_2$  production in the presence of a photosensitizer, an electron relay, and a sacrificial agent.<sup>[45]</sup> A CuO incorporated  $TiO_2$  catalyst was found to be an active photocatalyst for the reduction of  $H_2O$  under sacrificial conditions. The catalytic activity originates from the photogeneration of excited electrons in the conduction bands of both semiconductors,  $TiO_2$  and CuO, resulting in a build-up of excess electrons in the conduction band of CuO.<sup>[46]</sup> Sacrificial agents were also used in separate water reduction and oxidation experiments with the same oxide semiconductor. For  $Ln_2Ti_2S_2O_5$  ( $Ln = \text{lanthanoid}$ ),<sup>[47]</sup>  $MCrO_4$  ( $M = \text{Sr, Ba}$ ),<sup>[48]</sup>  $Bi_2W_2O_9$ ,  $Ag_2WO_4$ , and  $AgBiW_2O_8$ <sup>[49]</sup>  $H_2$  production was reported in the presence of sacrificial electron donors or  $O_2$  production when sacrificial electron acceptors were present in solution.

Numerous compounds have been explored as oxidation photocatalysts for the  $O_2$  evolution from water. Increased photochemical water oxidation was observed with ruthenium complexes used as sensitizers adsorbed on  $RuO_2$ ,<sup>[50]</sup> iridium oxide clusters coupled to single Cr centers in mesoporous silica,<sup>[51]</sup> or with  $Bi_2MoO_6$ <sup>[52]</sup> in the presence of a sacrificial electron acceptor. Carbon-<sup>[14,53]</sup> or nitrogen-doped  $TiO_2$ ,<sup>[54]</sup> undoped,<sup>[55]</sup> carbon-,<sup>[56]</sup> or nitrogen-doped  $TiO_2$  nanotubes,<sup>[57]</sup> undoped<sup>[58]</sup> or Mg-doped  $WO_3$ ,<sup>[59]</sup> Ta-,<sup>[36]</sup> Ti-, Al-,<sup>[60]</sup> Si-,<sup>[61]</sup> or Sn-doped  $Fe_2O_3$ ,<sup>[62]</sup> solid solutions of  $Fe_2O_3-Nb_2O_5$ ,<sup>[63]</sup> and  $BiVO_4$ <sup>[64]</sup> are all semiconductors able to oxidize water when an external potential is applied. Thin silver chloride layers also evolve oxygen under UV/Vis illumination in aqueous solution under suitable conditions.<sup>[65]</sup> Experiments carried out with gold<sup>[66,67]</sup> and silver<sup>[68]</sup> colloids sedimented on AgCl layers, as well as AgCl photoanodes modified with zeolite A and zeolite L monolayers as back support showed an increased photoelectrochemical activity for water oxidation.<sup>[69]</sup>

A PV/SCLJ approach was employed for the photoelectrolysis of water by connect-

ing in series tungsten trioxide ( $WO_3$ ) or iron oxide ( $Fe_2O_3$ ) photoanodes with a nanocrystalline dye-sensitized  $TiO_2$  solar cell.<sup>[70]</sup> The short wavelength portion of the solar spectrum is absorbed by the photoanode. A nanocrystalline dye-sensitized  $TiO_2$  solar cell is placed behind the transparent photoanode, capturing the long wavelength portion of the solar spectrum. The photovoltage generated by the second photosystem enables the generation of  $H_2$  at a platinum cathode.  $WO_3$  was also used as photoanode material for the oxygen evolution in an integrated thin film device with an amorphous silicon-based PV cell and a suitable catalyst film for the hydrogen evolution. The device exhibited a stable solar to hydrogen conversion efficiency around 3% in acidic solution.<sup>[71]</sup> A triple junction amorphous Si solar cell coated with indium-tin-oxide (ITO) and connected to a Pt cathode showed also the potential to split water. Conversions efficiencies around 5% were reported, though long-term stability of the ITO layer was an issue. The photoanode has to be protected from corrosion by e.g. a fluorinated tin oxide ( $SnO_2:F$ ) layer.<sup>[72]</sup>  $TiO_2$  films prepared by anodic oxidation of titanium sheet were used in a PV/SCLJ approach by combining the photoanode with a silicon-based PV cell and a Pt cathode.<sup>[73]</sup> A AgCl photoanode was combined with a single junction amorphous silicon solar cell connected to a platinum cathode. The AgCl layer was employed in the anodic part and the platinum electrode in the cathodic part of a setup for water photoelectrolysis consisting of two separate compartments connected through a salt bridge. Illumination of both the AgCl photoanode and the amorphous Si solar cell led to photoelectrochemical water splitting into  $O_2$  and  $H_2$ .<sup>[67]</sup>

## Conclusions

Systems converting solar light into chemical fuel are required to be cost-effective, economically viable, and they should meet the efficiency required for applications on medium and large scales. The components

employed should also be environmentally safe and abundant. The few examples mentioned above show that a large amount of scientific efforts is devoted worldwide to semiconductor-based PEC water splitting. All three approaches for water photoelectrolysis have their advantages and disadvantages, inherent to the approach itself and/or to the semiconductors used. Many leading researchers in photoelectrochemistry agree that research should now be focused on the most promising approach for water splitting, being a PV cell combined with a semiconductor-based PEC cell (PV/SCLJ approach).<sup>[74]</sup> Depending on the reaction taking place at the semiconductor-liquid junction, that is either hydrogen or oxygen evolution, the PEC cell consists of a photocathode and an anode, or a photoanode and a cathode, respectively. It is the water oxidation reaction that poses the greatest difficulty in achieving photocatalytic water splitting. Therefore, efficient oxygen production at a semiconducting photoanode is the most challenging aspect of PEC water splitting. Different research groups worldwide have set project objectives to develop an efficient semiconductor photoanode for the oxygen evolution. The additional bias for the hydrogen evolution on a metallic cathode is provided by a solar cell, leading to a PV/SCLJ approach for overall water splitting. Hence, the goal of the PV/SCLJ approach is to combine *the best of both worlds* for a sustainable and renewable  $H_2$  production.

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