

Photoelectrochemical Water Splitting

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Abstract: To halt the buildup of carbon dioxide (CO₂), the main greenhouse gas, the development of an alternative energy source to fossil fuels becomes more and more important. Hydrogen (H₂) 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 (O₂) using sunlight as the energy input, also generally described as photoelectrolysis.

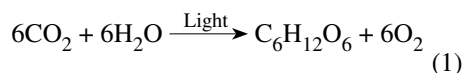
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Introduction

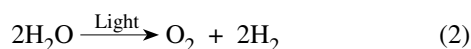
Hydrogen, H₂, has the potential to meet the requirements as a clean non-fossil fuel in the future, if it can be produced using the world's most abundant energy source, the sun, and stored and transported safely. Research and development (R&D) of an efficient system for solar energy conversion and storage is one of the challenging subjects to solve the global energy problem.^[1,2] 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).^[2] 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,

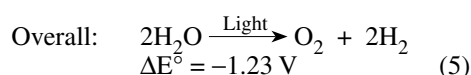
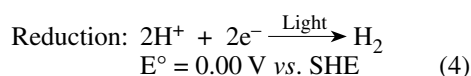
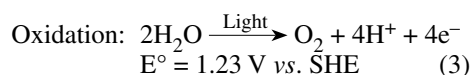
H₂O is split into O₂ and H₂, where the hydrogen is not in the gaseous form but bound by carbon.^[3]



The aim of *artificial photosynthesis* is the light-driven splitting of water into H₂ and O₂ (Eqn. (2)), which has been called a 'holy grail' in chemistry.^[4] 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 (H₂) 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 ΔE° . The negative ΔE° 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 H₂. One possible approach is semiconductor-based PEC water splitting into H₂ and O₂ 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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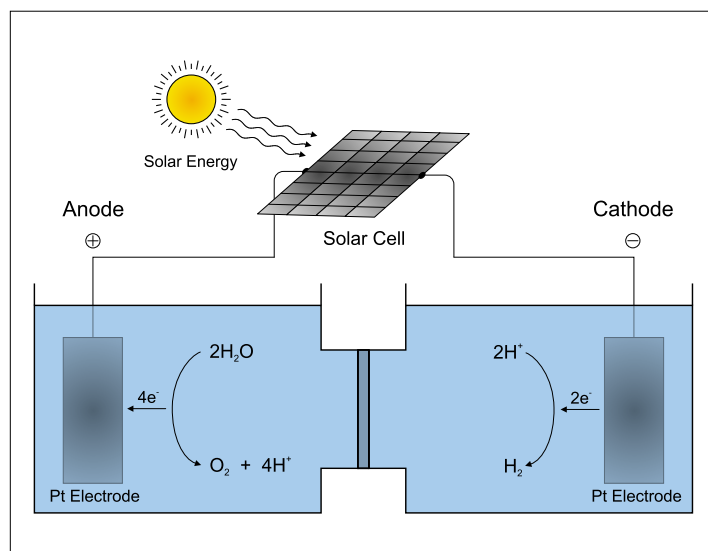


Fig. 1. Schematic representation of a PV approach, where a PV system is coupled to an electrolyzer

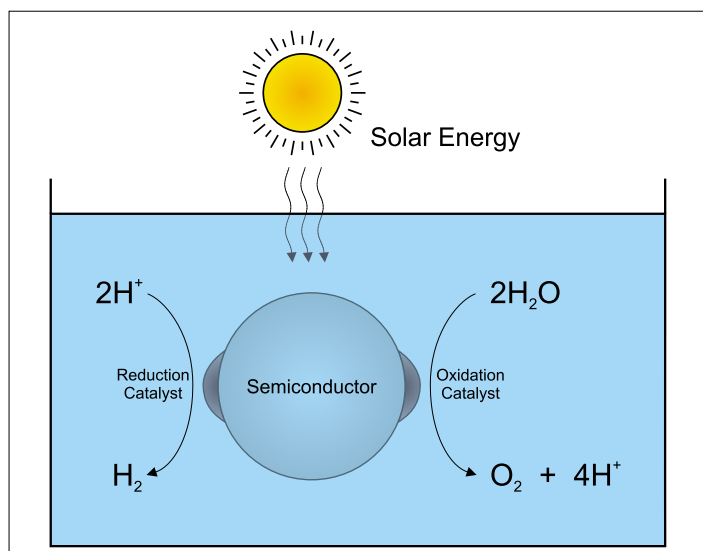


Fig. 2. Schematic representation of a SCLJ approach with one semiconductor loaded with a reduction catalyst and an oxidation catalyst

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.^[5] 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 H₂ and O₂ producing electrodes, like Pt and RuO₂-modified Pt, which act as cathode and anode, respectively.^[6] For example n-p GaInP₂/GaAs,^[7,8] n-p Al_xGa_{1-x}As/Si,^[9] and multiple junction p-i-n amorphous Si^[8,10] cells were used for the photoelectrolysis of water.

A PV approach was also used in solar-driven water electrolysis at elevated temperatures.^[11] 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 O₂, or the reduction of water into H₂, 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, TiO₂ is very stable in a wide range of pH, but it is active only in the UV region due to its large bandgap. WO₃ is also only active in the short wavelength range of the solar spectrum, but it is less stable in acidic medium. Fe₂O₃ 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.^[12] 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 TiO₂ photoelectrodes.^[13,14] The photoelectrochemical cell consisted of TiO₂ (rutile) as a photoanode

and platinum as a cathode. Illumination of the TiO₂ electrode led to O₂ evolution on the photoanode and H₂ evolution on the cathode. The quantum efficiency increased with an increase in alkalinity in the TiO₂ 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 (ΔpH ~ 13, chemical bias ~ 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^[15] and Ni-doped In-TaO₄,^[16] InNbO₄,^[15] Ln₂Ti₂O₇ (Ln = La, Pr, Nd),^[17] MCo_{1/3}Nb_{2/3}O₃ (M = Ca, Sr, Ba),^[18] RbNdTa₂O₇,^[19] NaTaO₃ doped with La,^[20] La₃TaO₇ and La₃NbO₇,^[21,22] Y₂Ti₂O₇ and Gd₂Ti₂O₇,^[22] and H₂La_{2/3}Ta₂O₇^[23] 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, RuO₂, or NiO. Recently, the oxynitride (Ga_{1-x}Zn_x)(N_{1-x}O_x)^[24] modified with nanoparticles of RuO₂^[25] and with a mixed oxide of rhodium and chromium^[26] was used as a photocatalyst for overall water splitting into H₂ and O₂ with visible light. A solid solution of zinc oxide and germanium nitride (Zn_{1+x}Ge)(N₂O_x) (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 RuO₂ nanoparticles.^[27] Domen and coworkers showed also that β-Ge₃N₄ 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.^[28]

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.^[29] 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.^[30] By combining single crystal p-SiC and nanocrystalline n-TiO₂ water splitting was observed without the used of any external potential, though at a low photocurrent density (0.05 mA/cm²) and low efficiency (0.06%) due to a high recombination of photo-generated electron–hole pairs.^[31] Photocatalytic water splitting was reported with a composite of two semiconductors, Cr-doped Ba₂In₂O₅/In₂O₃, under UV light irradiation.^[32] 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 WO₃ and Pt-loaded SrTiO₃ (doped with Cr, Ta), respectively, were used in an aqueous solution with the IO_3^-/I^- redox pair as mediator.^[33] Photoelectrolysis of water was also demonstrated using Pt-loaded TaON for the H_2 evolution and Pt-loaded WO₃ for the O_2 evolution using the same redox mediator.^[34]

Polycrystalline n-Fe₂O₃ photoanodes have been investigated in a photoelectrochemical cell where the cathode was Zn-doped p-GaP^[35] or p-Cu₂O.^[36] 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 Fe₂O₃ 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 TiO₂ thin film layer on top. The doped TiO₂ 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 TiO₂ 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 TiO₂ surface.^[37] The stability problem of silicon electrodes could be overcome by surface alkylation and metal nano-dot coating.^[38]

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, CuMnO₂^[39] and platinumized CdS^[40] particle suspensions, LaMnO₃/CdS nanocomposites,^[41] Pt-loaded (CuIn)_xZn_{2(1-x)}S₂,^[42] Pt-loaded ZnS-CuInS₂-AgInS₂ solid solutions,^[43] and Cr-doped SrTiO₃^[44] were

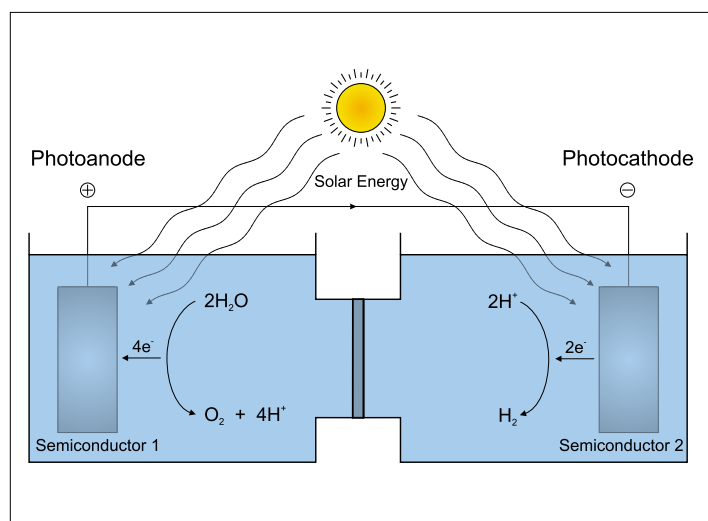


Fig. 3. Schematic representation of a SCLJ approach with two semiconductors used as photoanode and photocathode, respectively

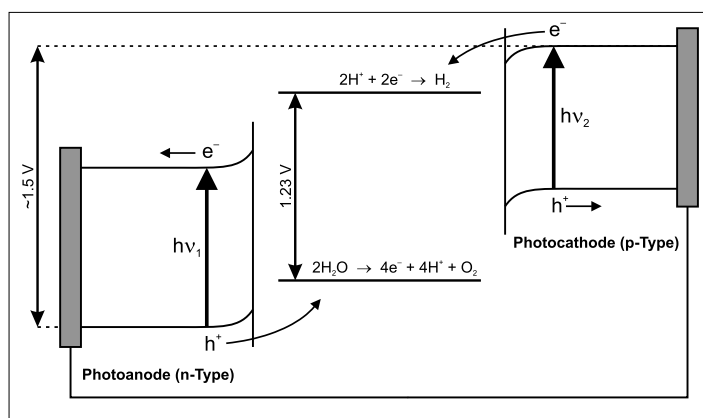


Fig. 4. Scheme of a photoelectrolysis cell based on two semiconductor–liquid junctions. A n-type semiconductor is used for water oxidation into O_2 (photoanode) and a p-type semiconductor for H^+ reduction into H_2 (photocathode). The thermodynamic potential for water splitting is 1.23 V. If overpotentials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

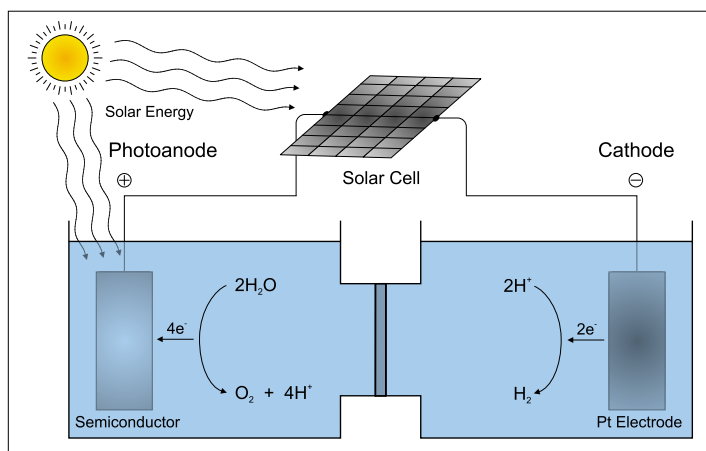


Fig. 5. Schematic representation of a PV/SCLJ approach with a semiconductor photoanode and a Pt cathode

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.^[45] 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 photo-generation 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 .^[46] Sacrificial agents were also used in separate water reduction and oxidation experiments with the same oxide semiconductor. For $Ln_2Ti_2S_2O_5$ ($Ln = \text{lanthanoid}$),^[47] $MCrO_4$ ($M = Sr, Ba$),^[48] $Bi_2W_2O_9$, Ag_2WO_4 , and $AgBiW_2O_8$ ^[49] 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 ,^[50] iridium oxide clusters coupled to single Cr centers in mesoporous silica,^[51] or with Bi_2MoO_6 ^[52] in the presence of a sacrificial electron acceptor. Carbon-^[14,53] or nitrogen-doped TiO_2 ,^[54] undoped,^[55] carbon-,^[56] or nitrogen-doped TiO_2 nanotubes,^[57] undoped^[58] or Mg-doped WO_3 ,^[59] Ta-,^[36] Ti-, Al-,^[60] Si-,^[61] or Sn-doped Fe_2O_3 ,^[62] solid solutions of $Fe_2O_3-Nb_2O_5$,^[63] and $BiVO_4$ ^[64] 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.^[65] Experiments carried out with gold^[66,67] and silver^[68] 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.^[69]

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.^[70] 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.^[71] 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. Conversion 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.^[72] 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.^[73] 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 .^[67]

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).^[74] 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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