

■ Photocatalysis

Getting the Most out of Solar Irradiation:
Efficient Use of Polychromatic Light for Water SplittingÜmit Taştan and Dirk Ziegenbalg^{*[a]}

Abstract: To increase the fraction of utilizable polychromatic light, a new reactor concept was developed and manufactured by using rapid prototyping technologies. Investigation of the prototypes revealed enhancements of the photocurrent by up to one order of magnitude, when TiO₂ was used as the photoanode in combination with commercially available photovoltaic cells. The reported concept is scalable and an easy transfer to technical scale is expected from a techno-

logical as well as an economical perspective. Experimental results underline the conclusion that to achieve efficient overall use of solar irradiation both the material as well as the reactor/process must be considered. Combining these complementary approaches allows largest possible optimization potential. With respect to ongoing research, the concept also breaks ground for the development of catalysts.

Introduction


Energy generation from fossil fuels is a major environmental problem because it is accompanied by emissions of gasses such as carbon dioxide, nitrogen oxides and sulfur oxides, which are either greenhouse gasses or toxic. In addition, the limited long-term availability of fossil fuels requires a strategic change of the energy and resource platforms.^[1] Renewable energy and resource platforms are therefore under intense investigation. In addition to wind and water, solar energy has attracted a lot of attention during the last decades.^[2] Solar irradiation offers the possibility to address both the resource and energy problems. With respect to resources, photons can be used directly to initiate chemical reactions, leading to valuable chemicals or degrade pollutants in wastewater to name just a couple of applications.^[1,3] Currently, energy generation from photons through the use of photovoltaic cells (PV) is even more prominent, because it is the most commercialized solar technology.^[4] An alternative to this approach is water splitting through photocatalytic processes, enabling the direct generation of hydrogen as energy storage as well as reactant.

Although solar irradiation is, in principle, unlimited, the use of photons suffers from two problems: first, solar irradiation is unsteady and second, photons are a highly diluted source of energy.^[5] The first problem is intrinsic for almost all renewable energies and resources. As a consequence, exploitation must be coupled to a storage concept. With regard to photocatalytic water splitting, the generation of hydrogen offers a variety of storage possibilities.^[6–10] From a holistic viewpoint, the “con-

centration” of photons represents a much more significant problem. It imposes either the use of concentration devices or devices with very large irradiated areas. The situation is even more complex when the characteristics of the photocatalysts are considered.

Figure 1 illustrates both the spectral terrestrial photon irradiance and the spectral terrestrial irradiance of a AM 1.5 solar spectrum. Considering photocatalysts, the energy of a photon has to be taken as the relevant parameter. In this way, it is possible to directly correlate the band gap energy of photocatalysts to the utilizable photon irradiance or irradiance. Taking TiO₂ as a prominent example,^[12–14] it can be concluded that only 4% of the total photon irradiance can be utilized for water splitting, when assuming 400 nm as the longest absorbed wavelength. This equals 9% of the irradiance. This means that, under optimal conditions, a maximum of 0.14 mmols^{−1} m^{−2} H₂ can be produced. It can be concluded that, in terms of energy, a power of around 33 W m^{−2} is thermodynamically accessible, when an efficiency of 100% for a fuel cell is assumed. Compared with the absorbable fraction of the irradiance of roughly 93 W m^{−2}, this illustrates that consideration of only the solar irradiance is not appropriate when the utilizable power is to be estimated. In fact, the photon irradiance is an even better suited parameter when the production of chemicals is the target. The low fraction of photons that can be utilized emphasizes the need for catalysts and reactor concepts that are able to use a larger fraction of solar irradiation. Considering once again TiO₂, a significant fraction of 96% of the photon irradiance cannot be used. It is worth mentioning that up to 80% of these photons are reflected.^[15–17] While catalysts are in focus primarily, the development of new reactor concepts has received less attention. Despite this, an improved utilization of photons by means of an improved reactor design would enable the use of smaller and ultimately cheaper devices as well as a reduction of operational costs.

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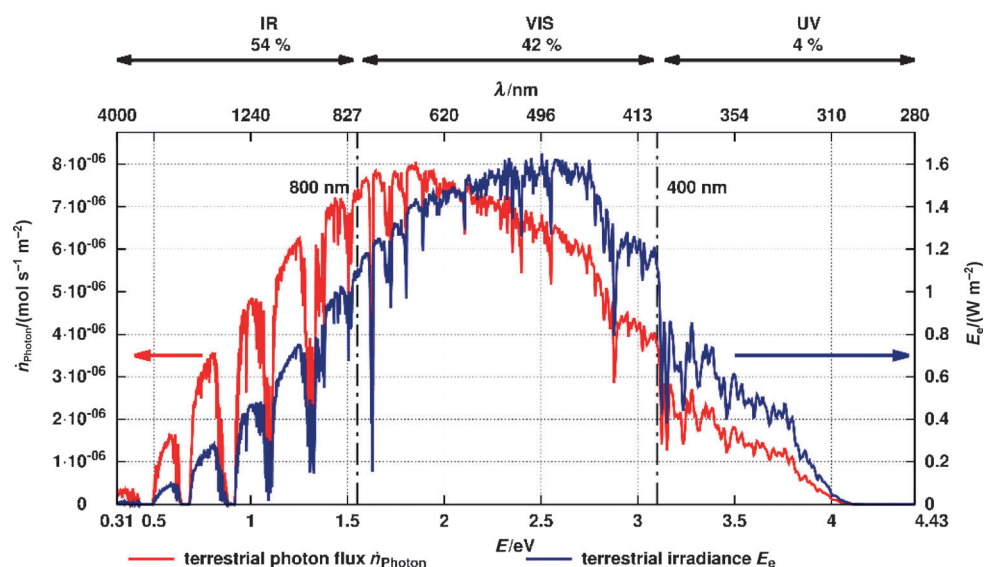


Figure 1. Terrestrial spectral photon irradiance and terrestrial spectral irradiance of a AM 1.5 solar spectrum.^[11]

Furthermore, the use of less active catalysts that can be produced with reasonable manufacturing costs would become more attractive from an economic viewpoint. As pointed out recently by the group of Centi, the development of novel system approaches can also offer a number of advantages and complementary research strategies.^[18]

From a technological viewpoint, reactors for photochemical water splitting can be divided into two types: a) systems utilizing suspended catalysts and b) systems utilizing immobilized catalysts. Suspended catalysts are often more active and the preparation is easier, but their use in a technical reactor is more complex. This stems from the need to ensure a stable suspension, which is most often realized by fast recirculation of water with pumps. Beside the technological problem of providing a stable suspension, the operation of pumps requires additional energy, lowering the overall energy output of a photocatalytic water splitting plant. Additionally, oxygen and water are generated in the same compartment, causing safety issues as well as the need for downstream separation. According to Ampelli et al., the requirements for an optimal photo(electro)-chemical water splitting device can be summarized as 1) production of O₂ and H₂ in separated compartments; 2) continuous operation with easy recovery of products; 3) avoid liquid electrolytes; 4) compact design, with easy scale-up possibilities, and 4) ability to operate at elevated temperatures.

Depending on the proposed use, for example, large-scale centralized production, small-scale, on-site production or production in areas lacking sufficient infrastructures, further requirements including the following can arise:^[19] 1) high productivity per unit of irradiated area; 2) low fixed costs; 3) low operation costs; 4) low maintenance requirements (stability), and 5) tolerance against impurities.

The most recent concept for increasing the photonic efficiency is the tandem solar cell. This type of photoelectrochemical cell (PEC) increases the fraction of utilized photons by combining several light-absorbing materials that are stacked on

each other. Depending on the absorption properties, the photoanode absorbs light up to a certain maximum wavelength. The remaining fraction of the light is transmitted to the underlying materials where it is directly converted into electrical energy. This energy can be applied as an “external” bias to the photoelectrochemical cell. Although this concept indeed increases the fraction of utilized photons, it also suffers from several disadvantages. Manufacturing of tandem cells requires advanced technologies for thin-film processing to realize high efficiencies. Indeed, increasing the complexity of the separate layers by sophisticated engineering offers large potential for further improvements.^[20] Another problem associated with tandem cells is the intrinsic requirement that the tandem cell is exposed to the aqueous electrolyte, resulting in severe problems with corrosion. In an economic context, these two disadvantages lead to high cost for electrode replacement. To reduce the operational costs, the reactor and thus the electrode size might be minimized by utilizing devices that concentrate solar irradiation. However, this would result in an increase of the investment costs.

To approach these challenges, a new reactor concept was developed for efficient use of polychromatic light. Instead of utilizing transmission in a stack, reflection is used to guide the light that was not absorbed to a second part of the reactor. This second part can, for example, consist of a second photoelectrode, a photovoltaic cell or a photoreactor. Accordingly, it is possible to realize a Z-scheme water splitting approach or to apply an “external” bias generated by the photovoltaic cell. As a further benefit, the manufacturing of the electrodes can be simplified.

Results and Discussion

The concept of tandem solar cells can be generalized as a method to split solar irradiation into different fractions, which are utilized separately through different materials opti-

mized to efficiently use a certain fraction of light. From this point, two additional concepts of splitting light into fractions might be used. First, light could be separated by optical components such as dichroitic mirrors. Although this concept is technically feasible, it is not economical. High investment costs are mainly caused by the optical equipment in such a scale that a technical realization within the required scope seems not to be reasonable. The second concept is based on the absorption characteristics of the material. Starting from the same idea as for tandem solar cells, a certain fraction of polychromatic light can be absorbed by a photocatalyst, while the remaining fraction is transmitted. By using a metal support for the photocatalyst, this remaining fraction is not directly passed to a second photocatalytic active part, but reflected back. After passing the photocatalyst for a second time, the not absorbed fraction of the polychromatic light can be guided to a second compartment where it can be used to drive, for example, a photocathode, mimicking a Z-scheme approach, a photovoltaic cell or a photoreaction. Figure 2 illustrates the general concept. This new concept has several advantages compared with the tandem cell approach: The thickness of the photocatalyst can be reduced because light can be absorbed during two passes. This allows more flexibility for the electrode design. Separation of the single components, such as anode and cathode, allows a better individual optimization of the reaction conditions for each reaction. Furthermore, sophisticated thin-film processing is not essentially required and it is possible to implement electrodes that do not require liquid electrolytes.

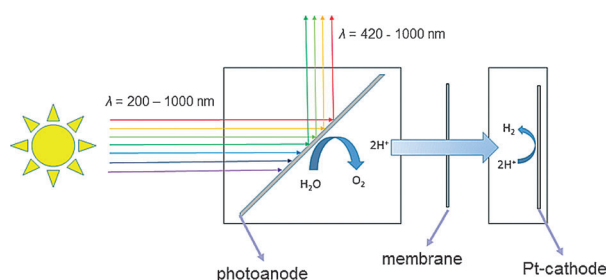


Figure 2. General reactor concept for efficient use of polychromatic light.

Reactor concept 1 enables, at the same time, photocatalytic water splitting and the initiation of photochemical reactions. The concept is shown schematically in Figure 3. With this setup it is possible to convert the fractions of light that cannot be used for water splitting into chemicals. Each reactor component has at least two openings for the exchange of reactants or electrolytes. The reactor compartment for the photoanode is irradiated with polychromatic light and used for the oxygen evolution reaction (OER). The reactor compartment for the hydrogen evolution reaction (HER) is not irradiated. A membrane separates these two parts and allows the exchange of ions. The photoanode is positioned at an angle of 45° to the incident light. Therewith light below a certain wavelength is absorbed, for example, 420 nm when TiO₂ is used. The unabsorbed part of the light is reflected to the reactor compartment for photochemical reactions. This part of the light can be used for the initiation of further photochemical reactions.

The second reactor concept enables the irradiation of two photocatalytic active materials. With this, a Z-scheme approach can be realized and different fractions of light can be used for photocatalytic water oxidation and photocatalytic water reduction. The setup is shown schematically in Figure 4. The reactor for the OER is irradiated with polychromatic light and water can be oxidized by light with energy above the band gap of the photoanode. In addition, light with energy lower than the band gap of the photoanode is reflected to the photocathode where the reduction of the water is initiated.

Commonly used metal oxide catalysts for photocatalytic water splitting often have an unfavorable position of the conduction band for the reduction of water. Therefore, a power source must be connected to a PEC to apply an external voltage. By utilizing reactor concept 3 an additional external bias is generated solely by the reflected light with a photovoltaic cell. With this, the system is independent of other energy sources, similar to the tandem solar cells that are analogues to this approach. Compared with reactor concept 2, the photocathode is replaced by a photovoltaic cell. The photovoltaic cell is connected through an external circuit to the photoanode and, for example, a platinum counter electrode. Figure 5 illustrates the concept.

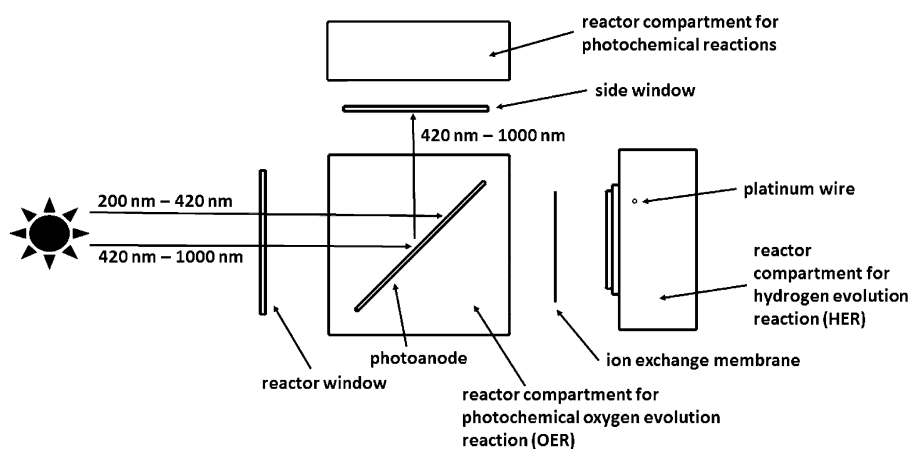


Figure 3. Reactor concept 1: combination of photocatalytic water splitting and photochemical reaction.

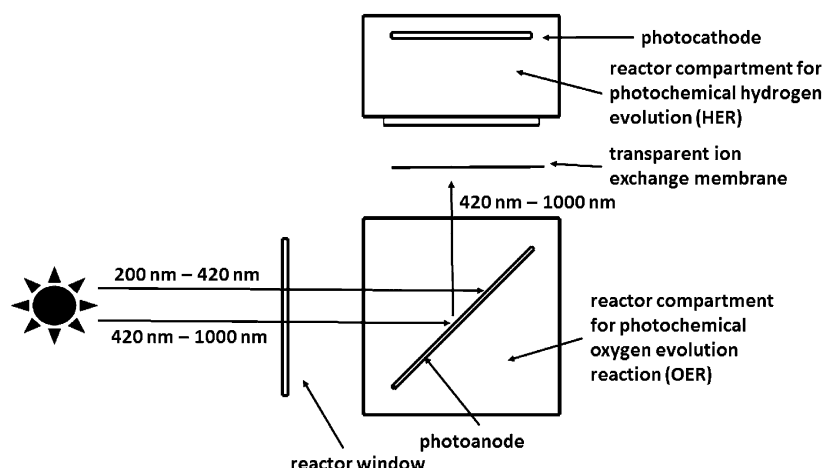


Figure 4. Reactor concept 2: combination of photocatalytic water oxidation and reduction.

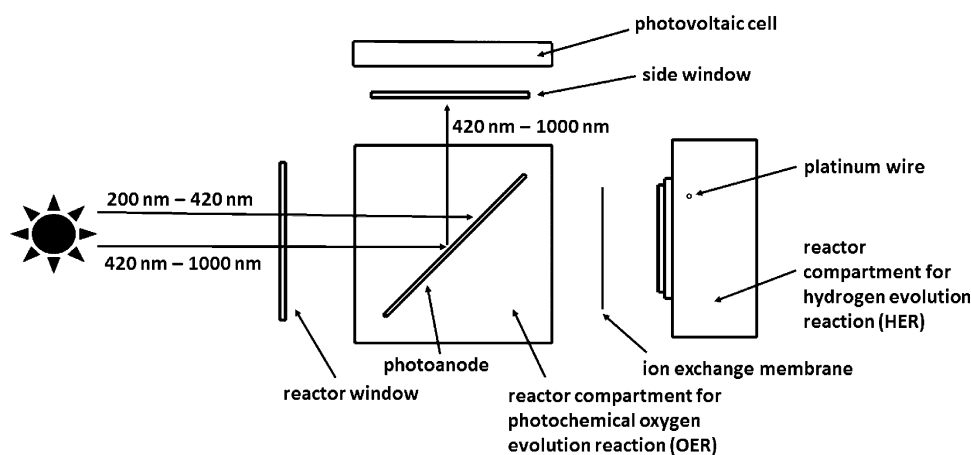


Figure 5. Reactor concept 3: applying an "external" bias solely generated from incident light through combining a photovoltaic cell with the PEC.

To enable an even larger flexibility for the development of photoelectrode materials and utilize more than two spectral ranges, it is possible to position the photoelectrodes in angles α smaller than 45° to the light beam. With this, additional reactors for utilizing reflected light can be installed and operated simultaneously. Furthermore, the surface geometry of the photoanode is not limited to a flat surface, but can also be, for example, parabolic, to focus the light and thus enable a smaller overall reactor volume. To demonstrate the feasibility of the general concept, two prototype reactors were developed and manufactured. By following the requirement of low investment costs, rapid prototyping technologies were chosen for manufacturing. The prototypes were built from polypropylene (PP) through selective laser sintering. PP offers sufficient chemical resistance and is easily available. The chosen manufacturing method allows minimization of the number of required sealings, with only the fluidic connections, the windows, and the electrode inserts needing to be sealed. Prototype A had an internal volume of 150 mL at the photoanode side and 60 mL at the cathode side (see Figure 6). The irradiated areas of the photoanode and the side window were 12.5 cm^2 . Due to the

rather large internal volumes, a second prototype (B) with reduced dimensions and an internal volume of 25 mL at the photoanode side and 15 mL at the cathode side was developed. The irradiated area of the photoanode was 1.76 cm^2 and the side window had an area of 2.25 cm^2 . TiO_2 on a Ti sheet was used as a photoanode. Given the large band gap, TiO_2 is the ideal test material for the developed reactor concept. As pointed out previously, light below 400 nm cannot be used to initiate water oxidation. Hence, light with energy lower than the band gap energy is lost. By implication, this raises a large optimization potential if the visible part of solar irradiation could be used.

Therefore, reactor A and B were equipped with photovoltaic cells to mimic the tandem solar cell approach. By using reactor A, it could be shown that the photocurrent is independent of the angle between the light beam and the photoanode (Figure 7), proving that angling the electrode does not reduce the amount of absorbed photons.

To test the combination with photovoltaic cells, two commercially available low-cost photovoltaic cells with cell potentials of 1 and 4 V were purchased for less than 10 € each.

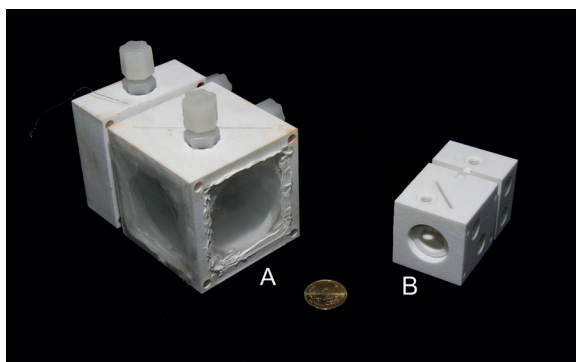


Figure 6. Images of PEC A and B. The prototypes were constructed by using selective laser sintering.

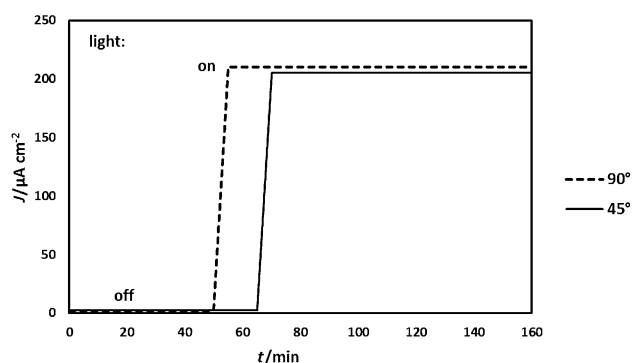


Figure 7. Photocurrent measurements with TiO_2 as a photoanode and Pt as a cathode, during irradiation with a 300 W xenon lamp without filter and without applying an external bias for different angles between the anode and the incident light.

These kinds of photovoltaic cells were chosen to stick to the idea of a simple and inexpensive reactor setup. By utilizing photovoltaic cells, the activity of the photoelectrochemical cell can significantly be improved (Figure 8). When only deionized water was used as electrolyte, no photocatalytic activity was observed, which is in accordance with the band positions of titanium dioxide. When additionally a 1 V PV was connected, a photocatalytic activity of about $5 \mu\text{A cm}^{-2}$ was measured. Utilizing a 4 V PV to apply a bias increased the photocurrent to about $20 \mu\text{A cm}^{-2}$. To simulate sea water as an electrolyte, measurements were carried out with a 3.5% NaCl solution. Even higher photocurrents were registered, although the pH value of solution did not change. This is attributed to the increased conductivity. The photocatalytic activity without PV is roughly $5 \mu\text{A cm}^{-2}$ and increases to about $20 \mu\text{A cm}^{-2}$ with a 1 V PV and to approximately $80 \mu\text{A cm}^{-2}$ with a 4 V PV. This corresponds to an increase of the photonic efficiency by a factor of 4 or 16, respectively. The highest photocatalytic activity could be achieved by applying an additional chemical bias by using two different electrolytes at the anode side (1 M NaOH) and the cathode side (1 M HCl). The applied chemical bias with a pH difference of 14 and the additional photopotential is sufficient to drive water splitting. For these conditions a photocatalytic activity of about $20 \mu\text{A cm}^{-2}$ without PV, approximately $30 \mu\text{A cm}^{-2}$ with a 1 V PV and around $250 \mu\text{A cm}^{-2}$ with a 4 V PV could be achieved. An improvement of the photonic efficiency by a factor of 1.5 and 12.5 is possible by using this technically very simply setup.

To validate the generic applicability of the concept, the PEC was furthermore operated only with the bias generate by solely irradiating the PV cell. Under these conditions, the cell operates as an electrolysis cell. The results are shown for both

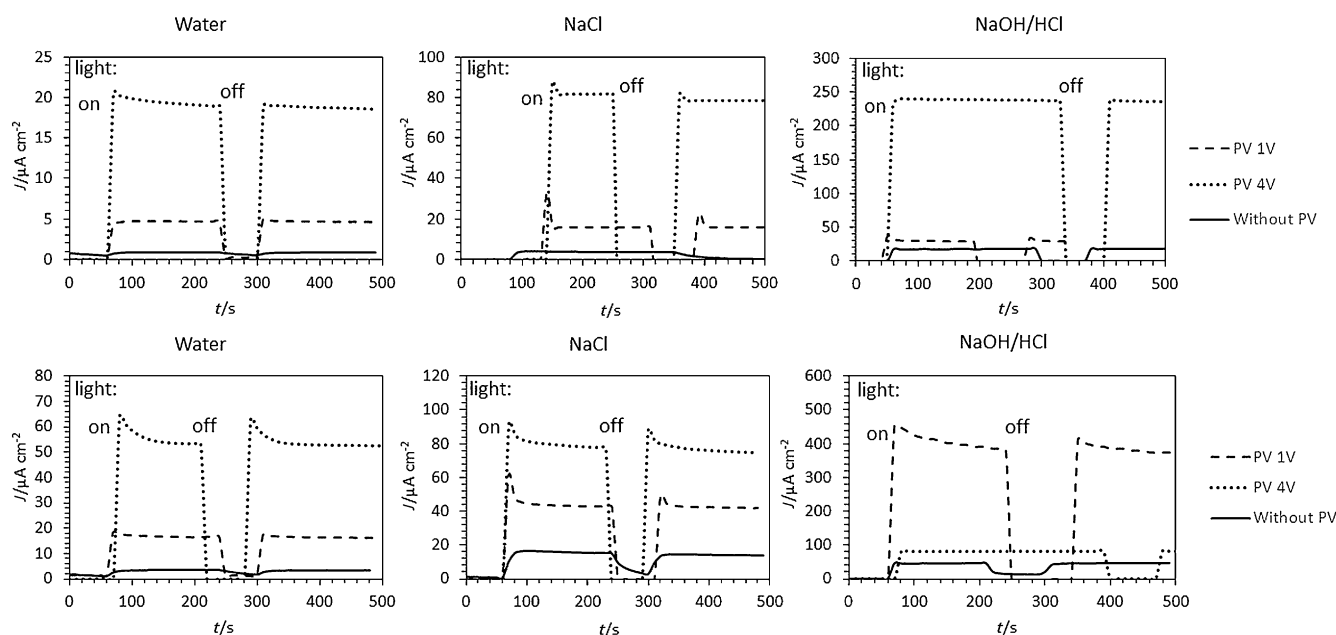


Figure 8. Upper figures: photocurrent measurements of PEC A for different electrolytes and combinations with photovoltaic cells, in the dark and during irradiation (100 mW cm^{-2} sun simulator). Lower figures: photocurrent measurements of PEC B for different electrolytes and combinations with photovoltaic cells, in the dark and during irradiation (100 mW cm^{-2} sun simulator).

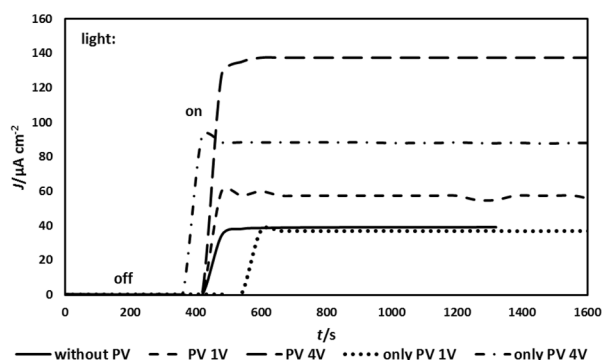


Figure 9. Photocurrent measurements of PEC A with 1 M NaOH at the anode side and 1 M HCl at the cathode side, in the dark and during irradiation (100 mW cm^{-2} sun simulator) for different setups.

PV cells in Figure 9 and prove that the overall performance of these setups is improved when the proposed concept for the efficient use of polychromatic light is applied. In numbers, this translates to an increase of the steady-state photocurrent of about 50% almost independent of the used PV cell.

As indicated by the experiments with the NaCl solution, ohmic losses reduce the efficiency of the whole setup. Hence, reducing the distance between the electrodes should increase the efficiency further. This could be verified by the use of reactor B, in which the distances between the two electrodes are reduced from 4 to 1.5 cm. Figure 8 shows the photocatalytic activities of reactor B. Compared with reactor A, reactor B only differs in size. Both the total irradiation surface and the distance between two electrodes changes depending on the size of the reactor. Construction, working principle and manufacturing are the same as for reactor A. For ease of comparison, the same measurements were carried as described for reactor A. With water as electrolyte, no photocatalytic activity could be observed when the PV was removed. For the 1 V PV about $20 \mu\text{A cm}^{-2}$ and for the 4 V PV approximately $60 \mu\text{A cm}^{-2}$ were measured. Similar to reactor A, the photocatalytic activity increases further when the electrolyte is exchanged with a 3.5% NaCl solution. Even without PV a photocurrent density of about $15 \mu\text{A cm}^{-2}$ was observed. Depending on the used PV, the photocurrent density increased to about $40 \mu\text{A cm}^{-2}$ for the 1 V PV and approximately $80 \mu\text{A cm}^{-2}$ for the 4 V PV. When applying a chemical bias by using a NaOH solution and an HCl solution at the anode side and the cathode side, respectively, the photocatalytic activity increased to $100 \mu\text{A cm}^{-2}$ when the 4 V PV was used. In contrast, the 1 V PV produced a photocurrent of $400 \mu\text{A cm}^{-2}$ (STH 0.49%). The surprisingly low activity of the 4 V PV cell is attributed to the technical characteristics of the cell. The actual cell potential was measured to be 4.8 V, which is far outside the technical specifications of the PV cell. Experiments without a PV produce photocurrents of only about $50 \mu\text{A cm}^{-2}$. With this, the photonic efficiency could be increased by a factor of 8 for the 1 V PV and a factor of 2 for the 4 V PV. The decrease in activity that can be observed for the experiments with PEC B is attributed to gas that accumulates at the photoanode and that increases the overpotential.

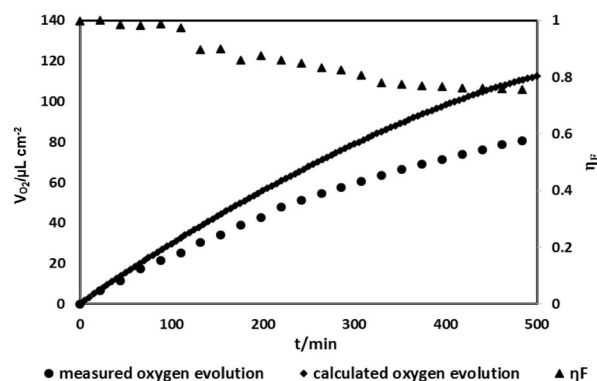


Figure 10. Measured photocatalytic oxygen evolution of PEC A with 3.5% NaCl solution at the anode side and cathode side during irradiation (100 mW cm^{-2} sun simulator). Faraday efficiency (η_F) is shown on right axis, calculated with respect to measured photocurrent density.

When NaCl is used as an electrolyte, chlorine evolution may compete with oxygen evolution. This is most likely when the 4 V PV cell is used. Hence, the produced oxygen was determined. The results are shown in Figure 10. At the cathode side, only hydrogen with a Faraday efficiency of 100% could be detected as reaction product. Whereas only oxygen could be detected at the anode side, interpretation of the faradaic efficiency suggests that chlorine formation indeed competes with oxygen production. During none of the experiments chlorine was detected in the gas phase. Most probably Cl_2 dissolves in water upon formation, leading to disproportionation into Cl^- and ClO^- . Indeed, the presence of ClO^- was colorimetrically proven by using 3,3',5,5'-tetramethylbenzidine.^[25] The concentrations found were in the range of 0.1 to $0.5 \mu\text{mol L}^{-1}$. The increase of the faradaic efficiency with time is attributed to an increasing overpotential.

Coupling of water splitting with another photochemical reaction could be demonstrated by utilizing the synthesis of ascaridole through photooxygenation starting from α -terpinene and oxygen.^[21] Oxygen was provided directly from the water oxidation cell of PEC A, exemplifying the use of the side product oxygen, which is often not considered for further usage. Delivery of oxygen was realized by connecting the anode compartment with a glass photoreactor through PTFE tubing. Hence, the overpressure generated by the evolved oxygen caused the oxygen to flow directly into the photoreactor. The results show that full conversion of α -terpinene into ascaridole could be achieved with a selectivity of 60%. Under the investigated conditions, $1.24 \cdot 10^{-9} \text{ mol s}^{-1}$ of oxygen were generated on average. Ensuring equimolar reaction conditions results in a residence time of the liquid of about 900 min. Assuming an irradiated area of 12.5 cm^2 and a 36.8% overlap of the irradiated area with the area covered by reaction solution, a utilizable photon flux of $3.22 \cdot 10^{-7} \text{ mol s}^{-1}$ drives the reaction.^[21] Considering the high quantum yield of $^1\text{O}_2$ generation of rose bengal (80%),^[24] which is significantly higher than the quantum yield of $^3\text{O}_2$ evolution, along with the fact that four photons are required to generate one dioxygen molecule, it becomes clear

that the water oxidation reaction limits the overall process under similar irradiation.

To enable an unbiased evaluation of improvements accessible through optimization of the materials, a comparison of the utilized TiO_2 -anode to reported data is required. Therefore comparative measurements with an aqueous potassium phosphate buffer solution (ca. pH 7) were conducted. This allows comparisons with the prominent BiVO_4 -electrodes. McDonald and Choi observed a peak photocurrent of about $150 \mu\text{A cm}^{-2}$ and a steady-state photocurrent of approximately $10 \mu\text{A cm}^{-2}$ with a solar simulator as the light source (100 mW cm^{-2} ; 0.5 V vs. RHE). Through integrating a BiVO_4 -anode into a tandem cell,^[20,22] this performance was improved to about $1400 \mu\text{A cm}^{-2}$ peak and approximately $50 \mu\text{A cm}^{-2}$ steady-state photocurrent density (100 mW cm^{-2} ; 0.45 V vs. RHE). Through gradient-doping of the BiVO_4 , this performance can be further improved to about $4000 \mu\text{A cm}^{-2}$ for the peak and the steady-state performance (100 mW cm^{-2} ; 1.2 V PV). Figure 11 illustrates

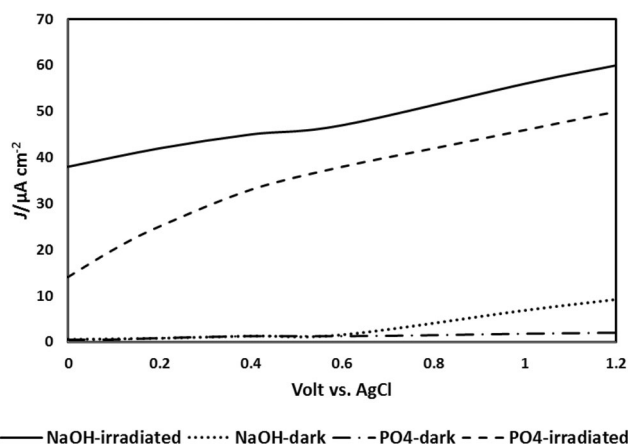


Figure 11. Photocurrent–voltage curves for PEC A when applying an external bias versus AgCl, during irradiation and in the dark, for 1 M NaOH and PO_4 -buffer as electrolyte at both electrodes.

the characteristics of the TiO_2 -anode used in this work. With a steady-state photocurrent density of about $15 \mu\text{A cm}^{-2}$ (0 V vs. Ag/AgCl) the performance of the anode is similar to that of the BiVO_4 -electrodes reported by McDonald and Choi.^[23] The performance of the $\text{Cu}_2\text{O/BiVO}_4$ -cell is roughly 3.5 times higher than for the TiO_2 system (ca. $35 \mu\text{A cm}^{-2}$).^[22] An even larger improvement by a factor of 90 was found in comparison to the gradient-doped BiVO_4 system (ca. $45 \mu\text{A cm}^{-2}$ for TiO_2). These values clearly indicate that for the proposed system further significant improvements of the performance of the overall system can be achieved through suitable material engineering.

It is clearly worth comparing the overall performance of the photoelectrochemical cells proposed herein with reported systems. For ease of comparison, operation with a PO_4 -buffer solution and a NaOH solution were considered. The results are represented in Figure 12. Steady-state photocurrents of 130 – $140 \mu\text{A cm}^{-2}$ can be reached without external bias only by utilizing the reflected light with a 4 V PV cell (STH 0.17%). Photocurrents for the 1 V PV cell were found to be in the range of

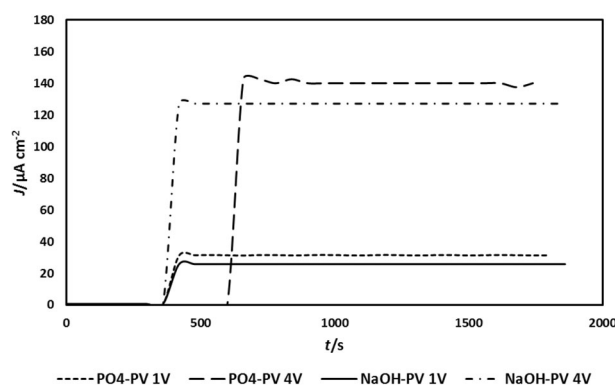


Figure 12. Photocurrent measurements of PEC A without external bias, with different electrolytes and photovoltaic cell combinations, during irradiation and in the dark.

$30 \mu\text{A cm}^{-2}$. With this, the system with the 1 V cell shows about 60% of the performance of the $\text{CuO}_2/\text{BiVO}_4$ discussed above, whereas in combination with the 4 V PV cell it outperforms the reported system by a factor of more than four. As noted above, the higher performance of the gradient-doped BiVO_4 system (factor 30) results from the superior performance of the photoelectrode, which arises from the sophisticated manufacturing process. Despite this, the benefits of the proposed TiO_2 route are threefold: Firstly, manufacturing of the TiO_2 electrodes is very simple and, with this, inexpensive. Secondly, the electrodes can be easily manufactured with large sizes and at large scale, enabling an easy transfer to technical scale, and, thirdly, TiO_2 is very stable, ensuring extended electrode lifetime.

Conclusions

In this work, a promising method to increase the overall efficiency of photocatalytic water splitting by optimizing the process on the system level has been reported. By utilizing one of the simplest photoanodes and commercially available photovoltaic cells, improved overall efficiency of photocatalytic water splitting with polychromatic light by more than an order of magnitude was achieved. Furthermore, the proposed reactor concept fulfills all requirements for an optimal photo(electro)chemical water splitting device, as pointed out by Ampelli et al.^[18] Improving the overall efficiency of TiO_2 -based photocatalytic water splitting is also very attractive from an economic point of view. TiO_2 can be synthesized easily in various modifications and morphologies with low to moderate effort and thus is available at low costs. A further benefit is the high stability of TiO_2 . Such a stable and low-cost catalyst significantly reduces the operational costs. All in all, the economic aspects will dominate the choice of the catalyst as well as the reactor concept, which will lead to the situation that, rather than using the most active catalyst in commercial systems, the most economic catalyst system will be employed.

The results reveal that optimizations on the system level comprise huge potential. By considering photons and their characteristics not just as a constraint, it is possible to improve the overall process. This is especially important if large-scale

processes are considered, but it is not necessarily limited to this scale. In fact, small-scale, on-site energy harvesting and storage in regions without well-developed infrastructure would also benefit from such optimizations. For such applications a “care-free” operation with low to no maintenance is highly beneficial. Reduced performance, which tends to accompany increased demand for irradiated electrode area, is typically not critical because space is usually available in such regions. In contrast, high investment costs and extensive training requirements are problematic. The proposed reactor concept ensures low investment and operational costs as well as compatibility with light-concentrating devices, along with scalability and wide access to required components. Furthermore, the concept can be realized in such a manner that the whole system is mobile. Compared with tandem solar cells, the reactor concept proposed herein might be less efficient on a fundamental level, but it can offer a technical solution. With respect to ongoing research, the concept also breaks ground for the development of catalysts especially optimized to the requirements noted above.

In an attempt to raise the level of optimization even further, it could be shown that light that does not contribute to water splitting can be used to initiate synthetic photochemical reactions. This ensures that optimization is not stopped at the level of water splitting, but is extended to the process level. By following this approach, it was possible to directly utilize oxygen as a reactant for subsequent synthetic steps. Although the proof-of-concept was demonstrated with a benchmark reaction, the general concept can be used to improve the overall energy and photon balance when commercially relevant products are synthesized.

Experimental Section

Experiments for photocatalytic water splitting reactions were performed with a sun simulator (100 mW cm^{-2}) equipped with an AM 1.5 filter, from LOT-QuantumDesign company (LS0306). The current and voltage measurements were performed with a bench-type multimeter from UNI-T (Model UT803). A potentiostat from Bank Elektronik-Intelligent Controls company, with a three electrode system, was used for the measurements with an applied external bias.

The photoanode was prepared from a commercially available titanium plate with purity degree of 1. This titanium plate was bought as a large sheet of thickness 0.5 mm and cut to the desired size. In all experiments, an oxidized titanium sheet as a photoanode and a platinum wire as a cathode were used. For preparation, these titanium sheets were washed several times with acetone and with deionized water. After drying at RT, the surface was oxidized in a calcination oven at 800°C for 12 h and cooled slowly to RT. For electrical contact, the oxide layer was removed where the cables were contacted.

Deionized water was used as electrolyte and all solutions were prepared with deionized water. For the preparation of solutions, NaOH (Sigma–Aldrich, ACS reagent), NaCl (Sigma–Aldrich, ACS reagent) and 37% HCl (Fluka, for trace analysis) were used. The phosphate buffer solution was prepared with 0.5 M Na_2SO_4 (Sigma–Aldrich, ACS reagent), 0.09 M KH_2PO_4 (Sigma–Aldrich, ACS reagent)

and 0.01 M K_2HPO_4 (Sigma–Aldrich, ReagentPlus, 99%). The solution was buffered to pH 7 with 1 M NaOH.

Synthesis of ascaridole

α -Terpinene (Sigma–Aldrich, >95%; 2.5 mL) was dissolved in methanol (100 mL total volume; 0.14 mol L^{-1}). To this solution, rose bengal (Sigma–Aldrich, dye content >85%; 0.5 g, $0.0049 \text{ mol L}^{-1}$) was added as a photosensitizer. Reaction progress was determined by GC-analysis with a Agilent Technologies 7890A apparatus equipped with a HP-5 column (30 m, $0.25 \mu\text{m}$, $d=0.32 \text{ mm}$, $3 \text{ mL min}^{-1} \text{ N}_2$; FID detector; injector temperature 175°C , split injection mode, $1 \mu\text{L}$; 35°C maintained for 1 min, then ramped to 240°C at 20 K min^{-1}). As internal standard *n*-dodecane (3 mL, 0.14 mol L^{-1}) was added. As a reactor PEC A was used in combination with a residence time module LTF-V (1.256 mL internal volume, 1 mm channel diameter, Little Things Factor, Germany) made of borosilicate glass as photoreactor. The photoreactor was placed in front of the side window, as illustrated in Figure 3. The upper outlet of the photoanode compartment (Figure 6, top of the larger compartments of PEC A) was connected to the inlet of the photoreactor through a PTFE capillary. The generated oxygen was flowed to the photoreactor driven by the pressure generated by the evolving oxygen. Oxygen was contacted with the reaction solution via a T-mixer, which was installed just before the inlet of the photoreactor. The reaction solution was fed into the photoreactor by using two syringe pumps (neMESYS Low Pressure Syringe Pump, CETONI GmbH, Germany). The flow rate was set to produce an equimolar ratio of oxygen and α -terpinene.

Photoelectrochemical cells

The two photoelectrochemical cells used are shown in Figure 13. Design was carried out with Creo Parametric design 2.0 and manufactured by selective laser sintering (SLS) technology from polypropylene (PP). Polypropylene was used because of its chemical resistance. The individual parts of the PEC were clamped together by threaded rods, which were pushed into small holes at the edges of the compartments. Nuts were screwed on to the loose ends of the threaded rods to realize sufficient pressure on the membrane, which was used as sealing. For PEC B, the anode and cathode compartment could be directly screwed together because a thread was directly designed onto the openings of these parts. All compartments exhibit two holes in the side panel of the compartment and one hole in the top panel of the compartment. The two holes in the side panel can be used to continuously pump electrolyte into the compartments as well as for circulating the electrolyte. The hole in the top panel enables continuous withdrawal of the gasses.

The photovoltaic cells PV 1 V (monocrystalline YH-45X60) und PV 4 V (monocrystalline YH-39X35) have an open cell voltage of 1 V (200 mA) and 4 V (35 mA), respectively. Photovoltaic cell 1 V has a total area of 27 cm^2 and 4 V cell 14 cm^2 .

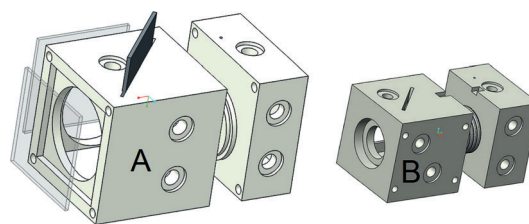


Figure 13. Three-dimensional models of both photoelectrochemical cells (left: cell A, right: cell B).

Determination of oxygen and hydrogen during operation was realized by connecting the outlets of PEC A to an online Agilent Technologies 7890A GC, equipped with a J&W column (19095P-QO4: 30 m, 530 μm , 40 μm) for FID and J&W column (19091J-413: 30 m, 320 μm , 40 μm) for TCD. Injector temperature 150 $^{\circ}\text{C}$, splitless injection mode; 50 $^{\circ}\text{C}$ maintained for 9.7 min, then ramped to 150 $^{\circ}\text{C}$ at 20 Kmin^{-1} . To enable continuous measurements, the compartments were continuously flushed with N_2 . The N_2 flow rate was controlled with a mass flow controller (Bronkhorst EL-Flow Select). A valve in front of the GC inlet enabled switching between the anode and the cathode compartment. The 4 V PV was used for the experiments.

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Keywords: energy conversion • energy transfer • hydrogen • photochemistry • titanium

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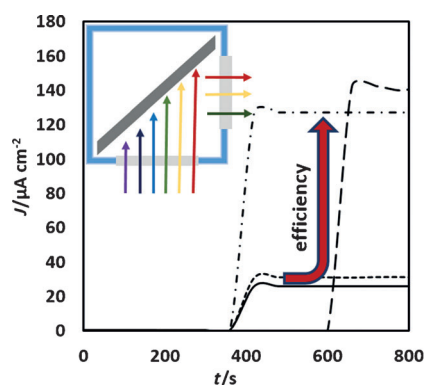
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FULL PAPER

■ Photocatalysis

Ü. Taştan, D. Ziegenbalg*

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Getting the Most out of Solar
Irradiation: Efficient Use of
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Splitting

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