

# Semi-artificial Photosynthesis for Green Hydrogen Production- Overview, Challenges and Possibilities

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**Abstract:** Humanity is looking for green energy production and storage techniques to meet the rising energy demand in a sustainable way. Especially the carbon dioxide emissions of currently used fuels is not acceptable. An alternative to the fossil fuel-based economy can be a “Hydrogen Economy”, based on environmentally friendly produced hydrogen. This can be realized by using solar energy to split water and produce hydrogen using certain catalysts. Photosystem II and I are nature’s catalysts for this reaction and have a high charge separation efficiency. This advantage can be used when these photo-enzymes are implemented into tailored setups as building blocks. Even though the proof-of-concept was shown, these “semi-artificial” photosynthesis cells still pose many challenges before industrial use is possible.

**Keywords:** green hydrogen, semi-artificial photosynthesis, Z-scheme, photosystem

## 1 Introduction

Global energy consumption is rising and sustainable and environmentally friendly ways to produce and store this energy are needed. A promising mode of energy storage is the use of hydrogen (H<sub>2</sub>) because of the potential of decoupling energy storage from carbon dioxide production [1]. After combustion with the oxygen available in the air, only water is produced. The so-called “Hydrogen Economy” is possible but still needs to overcome many challenges, including introducing sustainable H<sub>2</sub> production, storage technologies and infrastructure [2]. Currently, H<sub>2</sub> is mainly produced using fossil fuels and is therefore not a sustainable alternative to gas, oil or coal. Only about 4 % of the H<sub>2</sub> are obtained by electrolysis of water, which can be environmentally friendly if renewable energy sources are used to power this process [3].

An alternative to applying an external current is to use photocatalytic materials. The sun radiation can be used to excite electrons in suitable catalysts to provide energy for water splitting and hydrogen production. Both educts are easily available. Nature also uses this principle in oxygenic photosynthesis and produces Oxygen (O<sub>2</sub>) and glucose. Especially the efficiency of the first step, the light-induced charge separation, is very high and is of great academic interest [4], [5]. This charge separation happens in the photo-enzymes and was also used as inspiration for artificial systems. Additionally, researchers isolated the photo-enzymes and implemented them as parts for photoelectrochemical cells, paving the way for so-called “semi-artificial” photosynthesis [6]. The advantage of these systems is the literally green reaction center which is produced environmentally friendly in a carbon fixating process, namely by growth of plants or microalgae. Working, H<sub>2</sub>-producing cells have been realized, but still need a lot of work to be ready for industrial application.

We want to provide a short overview about semi-artificial photosynthesis for H<sub>2</sub> production and present some of the challenges to tackle and possible solutions for advancing the technology readiness towards industrial application.

## 2 Hydrogen: raw material and energy storage

The element hydrogen has only one proton and is the lightest of all chemical elements. During combustion, H<sub>2</sub> reacts with O<sub>2</sub> to water which also gave this element the Latin name “hydrogenium”. The high gravimetric energy density of about 120 kJ/g [1] combined with the fact that no carbon is involved in the combustion reaction, make H<sub>2</sub> a promising candidate for decoupling energy storage from carbon dioxide (CO<sub>2</sub>) production.

H<sub>2</sub> is promising for use in mobility, where H<sub>2</sub> is combusted in fuel cells and provides electrical energy for the vehicle. Especially heavy transport can benefit, where vehicles drive long distances and have short breaks. H<sub>2</sub> is also interesting as fuel for ships or aero planes [7]. In stationary applications, H<sub>2</sub> may be used as storage for excess electrical energy which can be used when consumption exceeds energy production. Green energy production through solar cells or wind turbines is happening according to environmental conditions and need such a buffer energy storage.

Another longer established use of hydrogen is as raw material for chemical synthesis. Exemplary processes are the Haber-Bosch-Process, where H<sub>2</sub> and N<sub>2</sub> form ammoniac, and the direct reduction of steel, which enables carbon neutral steel production.

### 2.1 Hydrogen production

In 2019, about 70 Mio.t were produced as main product and another 48 Mio.t were produced as byproduct [3]. This amount will rise strongly if direct reduction of steel and H<sub>2</sub> in mobility applications get more frequent.

H<sub>2</sub> is mainly produced in a non-sustainable way using natural gas or coal as educts for steam reforming or partial oxidation [8]. Only a small part of about 4 % are obtained by electrolysis of water [3]. Commercially available electrolysis includes alkaline electrolysis or proton exchange membrane (PEM) electrolysis cells and are reviewed by Carmo et al. with the advantages and disadvantages described below [9]. Alkaline electrolysis is a well-established technique which has good long-term stability and low relative costs, but low current density and eventually lower hydrogen purity by gas cross-over. Additionally, the alkaline electrolyte is corrosive. PEM electrolysis has the advantages of high current density and efficiency, compact design and high hydrogen gas purity. The disadvantages are high component costs and corrosive, acidic environment in the cells.

Electrolysis in general is normally costly and the economic feasibility strongly depends on the electrical energy price. If the electrical energy is obtained through sustainable, so-called green methods, then the hydrogen is also called green. The cost of green hydrogen is between 2.5-5.5 EUR/kg, which is higher than for conventionally produced hydrogen [10]. Photocatalytic techniques like artificial photosynthesis and semi-artificial photosynthesis are still in the research phase. H<sub>2</sub> production by fermentation can be used to promote circular economy by using wastewater as substrate for hydrogen producing microorganisms [11].

An overview of the above-mentioned hydrogen production methods is listed in Table 1.

Table 1 Hydrogen production methods

Method	Description
Steam reforming	Methane or coal and steam are used in an endothermic reaction to produce hydrogen and carbon monoxide. This step needs a heat source. Carbon monoxide and water then react exothermic and yield carbon dioxide and hydrogen. Currently one of the main hydrogen production methods.
Partial reduction	Methane is partially combusted with pure oxygen gas and produces carbon monoxide and hydrogen. This reaction is exothermic and does not need an additional heat source. The carbon monoxide is then converted to hydrogen with water. Currently one of the main hydrogen production methods.
Electrolysis	Water is split by applying potential. Electrolysis is a sustainable production method if electrical energy is produced by green methods. Prominent, commercial electrolysis techniques include alkaline electrolysis and proton-exchange membrane (PEM) electrolysis.
Photocatalytic water splitting (PWS)	Mostly inorganic catalysts split water by using sun radiation as energy source. Different photocatalytic systems are known: Single-component photocatalysts, Type-II heterojunction photocatalysts and Z-scheme systems. Semi-artificial photosynthesis is similar to photocatalytic water splitting and uses naturally occurring photocatalytic parts or organelles in microalgae or plants as catalysts in combination with a Z-scheme. Combined with hydrogenases or gold nanoparticles, hydrogen is formed. The technology readiness level is still very low.
Fermentation	Living microorganisms produce hydrogen in the presence (photofermentation [12]) or absence of light (dark fermentation [13]). Wastewater can be used as substrate, which promotes circular economy. The generation capacity is low.

## 2.2 Photocatalytic water splitting

Photocatalytic water splitting (PWS) is a green hydrogen production technique since it splits water into H<sub>2</sub> and O<sub>2</sub> powered by sunlight in the presence of a catalyst [14]. The catalyst converts a part of the sun's radiation energy into electrical energy. The wavelengths which can be used for this process depend on the catalyst. PWS has the advantage to work with easily available educts, water and sunlight. Suitable materials include semi-conductors or certain enzymes. Theoretically, the energy needed for PWS is 1.23 eV per electron. In practice, the required energy is about 1.6 to 1.8 eV due to overpotentials [15].

The first approach for PWS was done by single-component systems which need to have a fitting band gap and suitable band edge potentials for H<sub>2</sub> and O<sub>2</sub> production. A challenge of single-component catalysts is the fast recombination of the photogenerated electron-hole pairs and the proximity of oxidation and the reduction site, which can lead to reactions between H<sub>2</sub> and O<sub>2</sub>. A well-researched and long-known single-component system is Titanium dioxide (TiO<sub>2</sub>). The influence of crystal structure, particle dimensionality and size of TiO<sub>2</sub> on stability and photocatalytic properties were intensively researched [16], [17].

Another strategy was the combination between two pigments. Two system architectures containing two photocatalysts are described by Ng et al. [14]: (1) the type-II heterojunction photocatalysts and (2) the Z-scheme System. The first system directly connects two semi-conductors to each other, while the second system uses an electron mediator in between. The O<sub>2</sub> and H<sub>2</sub> evolution sites are spatially separated and when well-designed, both systems can increase charge carrier lifetime. The Z-scheme was originally found in nature in photosynthesis of green plants and the idea of mimicking the Z-scheme in artificial systems was first proposed by Bard in 1979 [18].

### 2.3 Semi-artificial photosynthesis

Kothe et al. define the semi-artificial approach for hydrogen production as “integration and combination of isolated photosynthetic proteins in photoelectrochemical cells” [6]. This method occupies a niche where the highly efficient biological photo-enzymes are combined with a designed electron transfer system. The biological photo-enzymes, namely Photosystem I (PSI) and Photosystem II (PSII), are membrane-integrated redox-enzymes which are involved in the oxygenic photosynthesis reaction, a process existing for over 3.2 billion years [19]. Both enzymes are embedded in the thylakoid membranes, which contain freely diffusing plastoquinone and plastocyanin as electron carriers.

The photosynthesis reaction and the photo enzymes have been intensively studied [20]–[24]. PSII harvests light with 680 nm wavelength and uses the photoexcited electrons to split water into O<sub>2</sub>, H<sup>+</sup> and e<sup>-</sup> at the Mn-containing reaction center at a theoretical rate of up to 125 mol<sub>O<sub>2</sub></sub>/mol<sub>PSII</sub>·s<sup>-1</sup> [25]. The electrons are carried to cytochrome b<sub>6</sub>f (Cyt b<sub>6</sub>f, location of ATP synthesis) and then further to PSI, which can be excited by light with 700 nm wavelength. These electrons are further used for NADPH synthesis. These steps are part of the Z-scheme and is pictured in Figure 1.

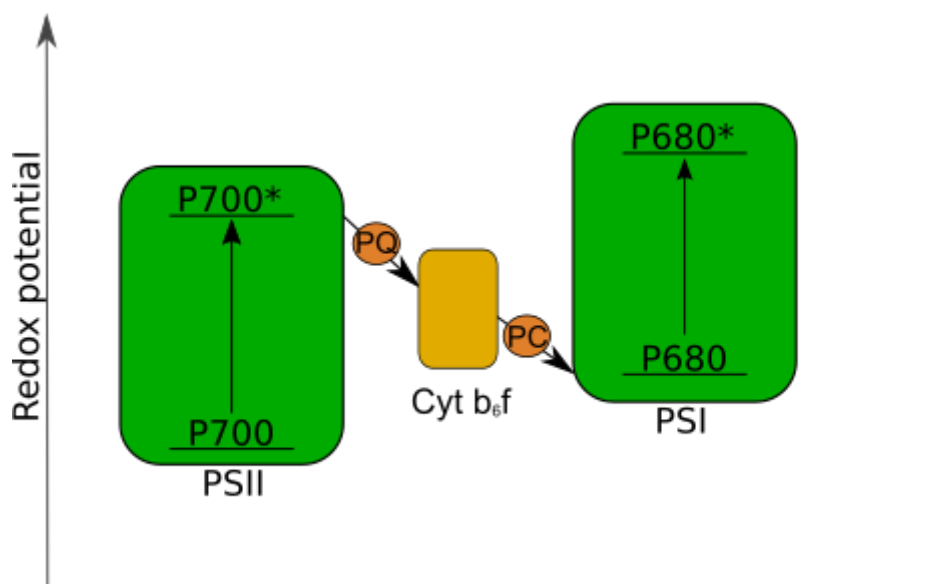


Figure 1 Z-Scheme of photosynthesis. Electrons are excited in PSII and are transported toward cytochrome  $b_6/f$ , the location of ATP synthesis, by plastoquinone. After this, electrons are transported by plastocyanin to PSI, where they are excited again to reach a redox potential needed for NADPH synthesis.

First semi-artificial electrodes consisted of planar metal electrode with adsorbed photo-enzymes. The orientation of the photo-enzymes was randomly distributed and only correctly orientated photo-enzymes contributed a measurable current [26]. A better controlled orientation of PSII can be achieved by a negative surface charge, which can interact with the positive dipole of PSII [27]. Another strategy is to provide other electron carriers, either freely diffusing or immobilized [28].

To increase the photocurrent and therefore the hydrogen production capacity, the loading density of photo-enzymes on the electrode was increased [29]. Planar Au electrodes were substituted with transparent Indium-doped tin oxide (ITO) electrodes and porosity was increased. One system described in literature has ITO electrodes with micro- and macro-porosity in combination with a redox polymer and reached loadings of  $336 \text{ pmol}_{\text{PSII}}\text{cm}^{-2}$  and a photocurrent of  $381 \text{ } \mu\text{A cm}^{-2}$  [30]. Table 2 gives a selection over the performance of semi-artificial  $\text{H}_2$ -producing systems with an anode containing isolated PSII.

Table 2 Performance of  $\text{H}_2$ -producing cells, anode containing isolated PSII [19], IO=inverse opa, DPP=diketopyrrolopyrrole

Anode	Cathode	Input	Output	Ref
IO-mesoITO PSII	IO-mesoITO [Ni FeSe ] $\text{H}_2$ ase	Applied bias 0.8-0.9 V, 660 nm; $450 \text{ } \mu\text{W cm}^{-2}$	$\text{H}_2$ : $0.96 \text{ } \mu\text{molcm}^{-2}$ $\text{O}_2$ : $0.52 \text{ } \mu\text{molcm}^{-2}$	[31]
Electrode PSII	ITO Si Pt	[ $\text{Fe}(\text{CN})_6$ ] $^{2-}$ in anodic compartment receives electrons from PSII. No applied bias. AM1.5G	$\text{H}_2$ : $30 \text{ } \mu\text{molh}^{-1}$ $\text{O}_2$ : $15 \text{ } \mu\text{mol}^{-1}$	[32]

IO-mesoITO PSII	p-Si IO-mesoTiO <sub>2</sub>  [NiFeSe]-H <sub>2</sub> ase	Applied bias: 0.4 V AM1,5G ( $\lambda > 420\text{nm}$ )	H <sub>2</sub> : 0.70 $\mu\text{molcm}^{-2}$	[33]
IO-mesoTiO <sub>2</sub>  DPP dye Os redox polymer PSII	IO-mesoITO [NiFeSe]-H <sub>2</sub> ase	Applied bias: 0.3 V, AM1,5G ( $\lambda > 420\text{nm}$ )	H <sub>2</sub> : 0.06 $\mu\text{molcm}^{-2}$	[34]

Related systems use immobilized thylakoid membranes [35], [36] or whole cells [29] of isolated photo-enzymes.

### 2.3.1 Challenges

The TRL of semi-artificial photosynthesis is still low (3-4, functionality is demonstrated and experimental setup in the lab was built) and there are a lot of challenges that need to be addressed before commercial use will be possible. Two of these challenges are listed and discussed below.

#### Limited lifetime

The first challenge is the limited lifetime of available systems. In general, isolated photocatalytic enzymes are short-lived. In literature, the lifetime of the proposed systems ranges from some minutes to weeks. Systems using whole thylakoid membranes show slightly increased lifetime and whole microorganisms are even better in this aspect [19].

One reason is the production of reactive oxygen species (ROS) through the enzymes. This happens, when photoexcited electrons react with oxygen and lead to the destruction of the enzymes. In their natural environment, the thylakoid membranes, there are several mechanisms to avoid ROS production. An excess of electron acceptors, like quinones and carotenoids, is available near the enzyme inside the thylakoid membrane. Therefore, electrons preferentially react with the provided electron acceptors. Additionally, the enzymes are replaced after a certain time in living organisms. This can explain the observed increase in lifetime from isolated enzyme to embedded enzyme to living cell.

For man-made systems we should learn from nature by providing suitable electron acceptors. We can use the naturally occurring electron acceptors or artificial electron acceptors and we have the choice between freely diffusing electron acceptors (e.g. 2,6-dichloro-1,4-benzoquinone [26]) and immobilized electron acceptors (e.g. redox polymers [37]). A recently published review discusses the challenges concerning lifetime of isolated PSI and can be an inspiration also for PSII containing systems [38].

#### Low hydrogen yield

Semi-artificial photosynthesis systems still have a low hydrogen yield. One reason is the limited quantum efficiency of the isolated PSII from cyanobacteria in visible light. Cyanobacteria are used for production of photo enzymes due to the fast growth in a controlled environment. In the living microorganism, light-harvesting antenna, the Phycobilisomes, are used to transfer energy to PSII and increase quantum efficiency. These Phycobilisomes can also be used for in a semi-artificial setup as shown by Hartmann et al. [39]. Artificial light-harvesting antennas may be another option for improved quantum efficiency.

Another reason is the limited active electrode area, where the enzymes are immobilized. This can be addressed by switching from a 2-dimensional setup to a more 3-dimensional setup. This is partly done by introducing porosity to the electrodes, but a bigger change of the system may lead to better results. A promising alternative to porous electrodes is the use of suspended particles. Suspended particle reactors are already implemented for some inorganic catalysts, but the targeted solar-to-hydrogen efficiency is about 10% to be economically viable was still not reached in 2021 [40]. For membrane-integrated enzymes like PSII and PSI, a suitable particle may be a liposome, which mimics the natural environment of these enzymes. Pannwitz et al. described a roadmap towards solar fuel synthesis using liposomes and discussed challenges like structural integrity or osmotic pressure of the liposomes which need to be solved before these mini-reactors can be used [41]. PSII containing liposomes are already used to answer different research questions about PSII and the light harvesting complex [42], [43].

### 2.3.2 Future/Possibilities

Semi-artificial photosynthesis can be used for hydrogen production as shown above. Sunlight energy is converted into usable energy through redox reactions. This energy may also be used to power different enzymes, not only hydrogenases. Nevertheless, the challenges towards commercialization for all systems using semi-artificial photosynthesis are similar and with more in-depth knowledge of photosynthesis in nature, new strategies to tackle the above-mentioned challenges will emerge.

The strategy of using liposomes as mini-reactors has a special appeal. The photo-enzymes are in their natural environment, a lipid bilayer. To enhance structural integrity of the liposome, stabilizing lipids, like archaeal tetraether lipids, can be used or added to conventional lipid mixtures. Lipid-soluble electron carriers can be incorporated into the lipid layer or water-soluble electron carriers can be encapsulated inside the liposome. The lipid-soluble electron carriers have the advantage of not influencing the osmotic pressure between inside and outside of the liposome. Additionally, this approach would be especially sustainable, if wastewater is used as substrate for the raw material providing microorganisms. This idea is something we will try to realize in the near future.

## References

- [1] K. T. Møller, T. R. Jensen, E. Akiba, and H. Li, "Hydrogen - A sustainable energy carrier," *Prog. Nat. Sci. Mater. Int.*, vol. 27, no. 1, pp. 34–40, Feb. 2017, doi: 10.1016/j.pnsc.2016.12.014.
- [2] Y. Dou, L. Sun, J. Ren, and L. Dong, "Chapter 10 - Opportunities and Future Challenges in Hydrogen Economy for Sustainable Development," in *Hydrogen Economy*, A. Scipioni, A. Manzardo, and J. Ren, Eds. Academic Press, 2017, pp. 277–305. doi: 10.1016/B978-0-12-811132-1.00010-9.
- [3] C. Hebling *et al.*, "Eine Wasserstoff-Roadmap für Deutschland," p. 51.
- [4] T. Cardona, A. Sedoud, N. Cox, and A. W. Rutherford, "Charge separation in Photosystem II: A comparative and evolutionary overview," *Biochim. Biophys. Acta BBA - Bioenerg.*, vol. 1817, no. 1, pp. 26–43, Jan. 2012, doi: 10.1016/j.bbabi.2011.07.012.
- [5] H.-G. Duan, V. I. Prokhorenko, E. Wientjes, R. Croce, M. Thorwart, and R. J. D. Miller, "Primary Charge Separation in the Photosystem II Reaction Center Revealed by a Global Analysis of the Two-dimensional Electronic Spectra," *Sci. Rep.*, vol. 7, no. 1, p. 12347, Sep. 2017, doi: 10.1038/s41598-017-12564-4.

- [6] T. Kothe, W. Schuhmann, M. Rögner, and N. Plumeré, 9 *Semi-artificial photosynthetic Z-scheme for hydrogen production from water*. De Gruyter, 2015, pp. 189–210. Accessed: Aug. 27, 2021. [Online]. Available: <https://www.degruyter.com/document/doi/10.1515/9783110336733.189/html>
- [7] H. T. Arat and M. G. Sürer, “State of art of hydrogen usage as a fuel on aviation,” *Eur. Mech. Sci.*, vol. 2, no. 1, pp. 20–30, Dec. 2017, doi: 10.26701/ems.364286.
- [8] C. Acar and I. Dincer, “3.1 Hydrogen Production,” in *Comprehensive Energy Systems*, Elsevier, 2018, pp. 1–40. doi: 10.1016/B978-0-12-809597-3.00304-7.
- [9] M. Carmo, D. L. Fritz, J. Mergel, and D. Stolten, “A comprehensive review on PEM water electrolysis,” *Int. J. Hydrog. Energy*, vol. 38, no. 12, pp. 4901–4934, Apr. 2013, doi: 10.1016/j.ijhydene.2013.01.151.
- [10] “Fragen und Antworten: Eine Wasserstoffstrategie,” *European Commission - European Commission*. [https://ec.europa.eu/commission/presscorner/detail/de/qanda\\_20\\_1257](https://ec.europa.eu/commission/presscorner/detail/de/qanda_20_1257) (accessed Sep. 06, 2021).
- [11] J. Baeyens *et al.*, “Reviewing the potential of bio-hydrogen production by fermentation,” *Renew. Sustain. Energy Rev.*, vol. 131, p. 110023, Oct. 2020, doi: 10.1016/j.rser.2020.110023.
- [12] C. N. C. Hitam and A. A. Jalil, “A review on biohydrogen production through photo-fermentation of lignocellulosic biomass,” *Biomass Convers. Biorefinery*, Nov. 2020, doi: 10.1007/s13399-020-01140-y.
- [13] S. Rittmann and C. Herwig, “A comprehensive and quantitative review of dark fermentative biohydrogen production,” *Microb. Cell Factories*, vol. 11, no. 1, p. 115, Aug. 2012, doi: 10.1186/1475-2859-11-115.
- [14] B. Ng, L. K. Putri, X. Y. Kong, Y. W. Teh, P. Pasbakhsh, and S. Chai, “Z-Scheme Photocatalytic Systems for Solar Water Splitting,” *Adv. Sci.*, vol. 7, no. 7, p. 1903171, Apr. 2020, doi: 10.1002/advs.201903171.
- [15] J. S. Jang, H. G. Kim, and J. S. Lee, “Heterojunction semiconductors: A strategy to develop efficient photocatalytic materials for visible light water splitting,” *Catal. Today*, vol. 185, no. 1, pp. 270–277, May 2012, doi: 10.1016/j.cattod.2011.07.008.
- [16] H. Eidsvåg, S. Bentouba, P. Vajeeston, S. Yohi, and D. Velauthapillai, “TiO<sub>2</sub> as a Photocatalyst for Water Splitting—An Experimental and Theoretical Review,” *Molecules*, vol. 26, no. 6, p. 1687, Mar. 2021, doi: 10.3390/molecules26061687.
- [17] B. Fu, Z. Wu, S. Cao, K. Guo, and L. Piao, “Effect of aspect ratios of rutile TiO<sub>2</sub> nanorods on overall photocatalytic water splitting performance,” *Nanoscale*, vol. 12, no. 8, pp. 4895–4902, 2020, doi: 10.1039/C9NR10870J.
- [18] A. J. Bard, “Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors,” *J. Photochem.*, vol. 10, no. 1, pp. 59–75, Jan. 1979, doi: 10.1016/0047-2670(79)80037-4.
- [19] J. Z. Zhang and E. Reisner, “Advancing photosystem II photoelectrochemistry for semi-artificial photosynthesis,” *Nat. Rev. Chem.*, vol. 4, no. 1, pp. 6–21, Jan. 2020, doi: 10.1038/s41570-019-0149-4.
- [20] E. El-Mohsnawy *et al.*, “Structure and Function of Intact Photosystem I Monomers from the Cyanobacterium *Thermosynechococcus elongatus*,” *Biochemistry*, vol. 49, no. 23, pp. 4740–4751, Jun. 2010, doi: 10.1021/bi901807p.
- [21] J. Gao, H. Wang, Q. Yuan, and Y. Feng, “Structure and Function of the Photosystem Supercomplexes,” *Front. Plant Sci.*, vol. 9, p. 357, 2018, doi: 10.3389/fpls.2018.00357.
- [22] J. Z. Zhang *et al.*, “Photoelectrochemistry of Photosystem II in Vitro vs in Vivo,” *J. Am. Chem. Soc.*, vol. 140, no. 1, pp. 6–9, Jan. 2018, doi: 10.1021/jacs.7b08563.
- [23] H. Kuhl *et al.*, “Towards Structural Determination of the Water-splitting Enzyme,” *J. Biol. Chem.*, vol. 275, no. 27, pp. 20652–20659, Jul. 2000, doi: 10.1074/jbc.M001321200.
- [24] D. J. Vinyard, G. M. Ananyev, and G. Charles Dismukes, “Photosystem II: The Reaction Center of Oxygenic Photosynthesis,” *Annu. Rev. Biochem.*, vol. 82, no. 1, pp. 577–606, Jun. 2013, doi: 10.1146/annurev-biochem-070511-100425.
- [25] G. Ananyev and G. Charles Dismukes, “How fast can Photosystem II split water? Kinetic performance at high and low frequencies,” *Photosynth. Res.*, vol. 84, no. 1–3, pp. 355–365, Jun. 2005, doi: 10.1007/s11120-004-7081-1.



- [26] M. Kato, T. Cardona, A. W. Rutherford, and E. Reisner, "Photoelectrochemical Water Oxidation with Photosystem II Integrated in a Mesoporous Indium–Tin Oxide Electrode," *J. Am. Chem. Soc.*, vol. 134, no. 20, pp. 8332–8335, May 2012, doi: 10.1021/ja301488d.
- [27] M. Kato, T. Cardona, A. W. Rutherford, and E. Reisner, "Covalent Immobilization of Oriented Photosystem II on a Nanostructured Electrode for Solar Water Oxidation," *J. Am. Chem. Soc.*, vol. 135, no. 29, pp. 10610–10613, Jul. 2013, doi: 10.1021/ja404699h.
- [28] A. Badura, T. Kothe, W. Schuhmann, and M. Rögner, "Wiring photosynthetic enzymes to electrodes," *Energy Environ. Sci.*, vol. 4, no. 9, pp. 3263–3274, Aug. 2011, doi: 10.1039/C1EE01285A.
- [29] X. Fang, S. Kalathil, and E. Reisner, "Semi-biological approaches to solar-to-chemical conversion," *Chem. Soc. Rev.*, vol. 49, no. 14, pp. 4926–4952, 2020, doi: 10.1039/C9CS00496C.
- [30] K. P. Sokol *et al.*, "Rational wiring of photosystem II to hierarchical indium tin oxide electrodes using redox polymers," *Energy Environ. Sci.*, vol. 9, no. 12, pp. 3698–3709, 2016, doi: 10.1039/C6EE01363E.
- [31] D. Mersch *et al.*, "Wiring of Photosystem II to Hydrogenase for Photoelectrochemical Water Splitting," *J. Am. Chem. Soc.*, vol. 137, no. 26, pp. 8541–8549, Jul. 2015, doi: 10.1021/jacs.5b03737.
- [32] W. Wang *et al.*, "Spatially Separated Photosystem II and a Silicon Photoelectrochemical Cell for Overall Water Splitting: A Natural–Artificial Photosynthetic Hybrid," *Angew. Chem.*, vol. 128, no. 32, pp. 9375–9379, Aug. 2016, doi: 10.1002/ange.201604091.
- [33] D. H. Nam *et al.*, "Solar Water Splitting with a Hydrogenase Integrated in Photoelectrochemical Tandem Cells," *Angew. Chem. Int. Ed.*, vol. 57, no. 33, pp. 10595–10599, Aug. 2018, doi: 10.1002/anie.201805027.
- [34] K. P. Sokol *et al.*, "Photoreduction of CO<sub>2</sub> with a Formate Dehydrogenase Driven by Photosystem II Using a Semi-artificial Z-Scheme Architecture," *J. Am. Chem. Soc.*, vol. 140, no. 48, pp. 16418–16422, Dec. 2018, doi: 10.1021/jacs.8b10247.
- [35] L. M. Utschig, S. R. Soltau, K. L. Mulfort, J. Niklas, and O. G. Poluektov, "Z-scheme solar water splitting via self-assembly of photosystem I-catalyst hybrids in thylakoid membranes," *Chem. Sci.*, vol. 9, no. 45, pp. 8504–8512, Nov. 2018, doi: 10.1039/C8SC02841A.
- [36] S. I. Kim, Y. J. Kim, H. Hong, J. Yun, and W. Ryu, "Electrosprayed Thylakoid–Alginate Film on a Micro-Pillar Electrode for Scalable Photosynthetic Energy Harvesting," *ACS Appl. Mater. Interfaces*, vol. 12, no. 49, pp. 54683–54693, Dec. 2020, doi: 10.1021/acsami.0c15993.
- [37] A. Badura *et al.*, "Photo-Induced Electron Transfer Between Photosystem 2 via Cross-linked Redox Hydrogels," *Electroanalysis*, vol. 20, no. 10, pp. 1043–1047, May 2008, doi: 10.1002/elan.200804191.
- [38] F. Zhao, A. Ruff, M. Rögner, W. Schuhmann, and F. Conzuelo, "Extended Operational Lifetime of a Photosystem-Based Bioelectrode," *J. Am. Chem. Soc.*, vol. 141, no. 13, pp. 5102–5106, Apr. 2019, doi: 10.1021/jacs.8b13869.
- [39] V. Hartmann *et al.*, "Improved quantum efficiency in an engineered light harvesting/photosystem II super-complex for high current density biophotoanodes," *J. Mater. Chem. A*, vol. 8, no. 29, pp. 14463–14471, 2020, doi: 10.1039/D0TA03444D.
- [40] M. A. Nadeem, M. A. Khan, A. A. Ziani, and H. Idriss, "An Overview of the Photocatalytic Water Splitting over Suspended Particles," *Catalysts*, vol. 11, no. 1, Art. no. 1, Jan. 2021, doi: 10.3390/catal11010060.
- [41] A. Pannwitz *et al.*, "Roadmap towards solar fuel synthesis at the water interface of liposome membranes," *Chem. Soc. Rev.*, vol. 50, no. 8, pp. 4833–4855, 2021, doi: 10.1039/D0CS00737D.
- [42] F. Zhou, N. W. Qiu, Z. J. Gu, B. J. Zhang, and C. Hua, "Thermal stability studies of photosystem II complexes reconstituted into phosphatidylcholine liposomes," *Russ. J. Plant Physiol.*, vol. 61, no. 1, pp. 26–32, Jan. 2014, doi: 10.1134/S1021443714010191.
- [43] A. W. D. Larkum and J. M. Anderson, "The reconstitution of a Photosystem II protein complex, P-700-chlorophyll a-protein complex and light-harvesting chlorophyll ab-protein," *Biochim. Biophys. Acta BBA - Bioenerg.*, vol. 679, no. 3, pp. 410–421, Mar. 1982, doi: 10.1016/0005-2728(82)90162-1.