Artificial Photosynthesis: Beyond Mimicking Nature

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Emission of carbon dioxide by the burning of fossil fuels is the predominant driving force of global warming and related climate changes with potentially catastrophic consequences. The evidence for this statement has been summarized in detailed reports of the Intergovernmental Panel on Climate Change (IPCC, see http://www.ipcc.ch/). The IPCC proposes to limit the temperature rise to a maximal level of 2 °C, in order to avoid the most severe consequences of global warming. Reaching the 2 °C goal will require a drastic reduction in CO₂ emissions and thus a global transition towards CO₂-neutral energy systems. The recent IPPC reports emphasize the necessity of reducing the net CO₂ emission on a global scale to the zero level within the second half of the 21st century. This requirement is not only well accepted among climate scientists, but is also largely accepted in the political arena, as manifested by the Paris agreement, which was signed in December 2015 by nearly all countries organized within the United Nations framework. The Paris agreement declares a limitation on the rise of the globally averaged air temperature to ideally 1.5 °C and minimally 2 °C (Article 2), and specifies (Article 4): “In order to achieve the long-term temperature goal set out in Article 2, Parties aim to reach global peaking of greenhouse gas emissions as soon as possible, recognizing that peaking will take longer for developing country Parties, and to undertake rapid reductions thereafter in accordance with best available science, so as to achieve a balance between anthropogenic emissions by sources and removals by sinks of greenhouse gases in the second half of this century, on the basis of equity, and in the context of sustainable development and efforts to eradicate poverty.” It is remarkable and quite extraordinary in an international treaty that the role of “best available science” is emphasized. Moreover, the Paris agreement leaves no doubts that the well-developed economies should reach a CO₂-neutral energy system earlier than in the second half of this century. This implies that already in 2050, the burning of fossil fuels should no longer be the rule but the exception in the technologically well-developed parts of the world. Such an earlier deadline for complete mitigation of fossil-fuel usage clearly applies to the countries represented by the contributors to this special issue of ChemSusChem on artificial photosynthesis (AP). The Paris agreement may have stimulated their research efforts in addition to the fascinating, but formidable scientific challenges associated with research on artificial photosynthesis.

Non-Fossil Fuels

Massive use of renewable electricity from wind and solar power will be a key element of a global, CO₂-neutral energy system; energy storage in the form of batteries also will play an increasingly important role. However, the renewable production of electricity and its direct storage cannot facilitate a complete substitution of fossil fuels. The storage density of batteries is far below that of fuels with respect to both weight and volume. Consequently, parts of the transportation sector cannot operate well with electricity only, specifically air transport and large overseas vessels. Even more striking is the unsolved storage problem. Conventional storage involving, for example, pump stations for water reservoirs powering electrical generators, cannot meet the demand on a global scale. Large-scale battery-based storage systems that compensate for the diurnal rhythm of solar energy already represent a major scientific, technological and economic challenge—even more
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so as the availability of the current raw materials for large-scale applications may become increasingly problematic. However, storage capacity for meeting diurnal fluctuations is not even the main problem. Large-scale storage for clearly more extended periods ranging from several weeks to about one year is required to deal with the fluctuating wind energy supply, the annual rhythm of solar energy, and, last but not least, comfortable reserves for unforeseen developments relating to, among other factors, (inter)national security issues.

A future free of fossil fuels does not need to be a fuel-free future. Alternative options for CO₂-neutral production of fossil fuels are listed in Figure 1. The sequence in this (incomplete) list is determined by the relatedness of the respective route to oxygenic photosynthesis in its native environment, with power-to-X in position 9 being the least related technological route.

Mimicking Biological Photosynthesis?

Terrestrial plants, algae, and cyanobacteria are capable of photosynthesis. Driven by solar energy, they use water and atmospheric CO₂ as raw materials for the formation of carbohydrates. These carbohydrates ‘fuel’ biological cells regarding metabolic maintenance and growth (biomass formation). Atmospheric O₂ is formed as a byproduct. Consequently, this form of photosynthesis, which clearly is predominant on earth, is denoted as oxygenic photosynthesis. Without any overstatement: Life on earth is fueled in a highly sustainable way by oxygenic photosynthesis. Without any overstatement: Life on earth is fueled in a highly sustainable way by oxygenic photosynthesis. The “success” of oxygenic photosynthesis renders the biological process a paradigmatic demonstration of large-scale production of non-fossil fuels driven by solar energy. This has led to the idea of artificial photosynthesis as a biomimetic version of biological photosynthesis. Yet today, close synthetic mimics of the biological system are no longer conceived as a technologically attractive option. Why is that?

Biological photosynthesis has been evolutionarily optimized for billions of years and refined by breeding of agricultural plant species. In several regards, the performance characteristics of photosynthetic organisms are unmatched by recent technological systems. This applies especially to self-reproduction (and repair), reduction of dilute CO₂ in an O₂-rich atmosphere, and the ability to synthesize with high specificity a wide range of complex compounds. However, there are serious limitations regarding efficient, large-scale production of fuels:

a) Low energetic efficiency of photosynthetic organisms

In oxygenic photosynthesis, the annually averaged solar energy conversion efficiency is species dependent but generally low. For agricultural plants, the fraction of the incoming solar energy that is converted into chemical energy typically does not exceed 1%. In this case, the stored chemical energy...
is measured as the heating value of dried biomass; the efficiency is even lower at the level of a technically relevant fuel formed from biomass, such as ethanol (for genetically modified microalgae or cyanobacteria in specific photo-bioreactors, higher values may be obtainable, but measured values for the annual biomass production driven solely by sunlight have, to our knowledge, not been reported to date). The efficiency of solar energy conversion matters. The Department of Energy (DOE) of the United States (USA) mentioned in its 2005 report on Basic Research Needs for Solar Energy Utilization[25] “At a typical latitude for the United States, a net 10% efficient solar energy “farm” covering 1.6% of the U.S. land area would meet the country’s entire domestic energy needs; indeed, just 0.16% of the land on Earth would supply 20 TW of power globally” (with an estimated global energy demand of about 30 TW by 2050). These figures suggest that the availability of land for installation of solar energy farms is unlikely to become a limiting factor. However, the situation is different when viewed from a more regional perspective, for example, by considering Germany, an industrialized country with a comparatively high population density and only moderate exposure to solar energy. In Germany, about 10% of the land area could supply all primary energy currently needed (in Germany) if solar energy were converted with an efficiency of 10% towards a useful energy carrier (electricity and technically relevant fuels). However, for employment of photosynthetic organisms with an energy efficiency below 1%, the complete German land area would be insufficient.

There are several reasons for the typically low efficiency of photosynthetic organisms, including the energetic costs for maintenance and repair of the biological system. Another reason is the issue of light saturation characteristics, which is a basic design aspect of the photosynthetic apparatus that should be avoided rather than mimicked in artificial systems. By means of an extended system of 100–300 “antenna pigments” that drive charge separation in a single “reaction center”, photosynthetic organisms are evolutionarily optimized for harvesting solar energy efficiently at low levels of solar irradiation[3]. Light saturation is often already reached at 10–20% of the maximal solar power (1000 W m⁻²) because the high capacity for light absorption and fast primary reaction steps are not matched by the capacity of subsequent redox chemistry. Especially critical is the complex chemistry of CO₂ reduction and carbohydrate formation, which is mostly rate-limiting at high light intensities. Consequently, bright sunlight, which without saturation would contribute strongly to the annual biomass production, is largely dissipated in the form of heat. In clear contrast, photovoltaic cells can also operate close to their maximal efficiency (15–20% in typical commercial silicon solar cells) at the highest light intensities. Any synthetic systems of technological relevance need to be designed such that there is no major performance mismatch between the initial light-driven charge separation processes and subsequent catalytic steps, at low and high light intensities.

**Figure 1.** Alternative (or complementary) routes to sustainable production of non-fossil fuels from highly abundant molecules (water, CO₂ or N₂) and energetically driven by solar energy (1–8). Further routes towards solar fuels, such as such as thermochemochemical fuel production, are not considered. The power-to-X approach (9) can be employed in a largely sustainable way once grid electricity is provided predominantly by renewable sources. The employment of (1) and (2) is well established; further upscaling of their employment for sustainable replacement of fossil fuels is mostly conceived as problematic. Power-to-X is running in numerous pilot plants; this technology is commercially available for production of hydrogen and methane, the latter of which typically uses flue gas as a carbon source. Routes 3–8 form a rapidly developing research field often denoted as “solar fuels”. Artificial photosynthesis (4–8) aims at integrated devices that facilitate the efficient local coupling of solar energy conversion and fuel production.

b) Extreme complexity of biological photosynthesis and reliance on self-repair

In oxygenic photosynthesis, hundreds of distinct polypeptides and numerous cofactors are needed for light-driven formation of carbohydrates from water and atmospheric CO₂[26]. Even iso-
Artificial Photosynthesis

As outlined above, close synthetic mimicry of biological systems in artificial photosynthesis will not lead to solutions of technological relevance. The situation may be comparable to the development of the first airplanes. Studies of bird flight have not only motivated the development of airplanes, but also provided (scientific) insight into the detailed aerodynamic characteristics of the bird wing. Otto Lilienthal was the first person to achieve repeatedly (well-documented) flights with unpowered airplanes. In a paradigm of knowledge-based technology development, he published his monograph “Der Vogelflug als Grundlage der Fliegekunst” (translatable as “Bird flight as the basis of aviation art”, 1889[7]). Birds and airplanes, both indeed can fly—or rather glide—based on identical physical principles discovered in the 18th century by Bernoulli and Venturi, when analyzing fluid dynamics. However, the use of biological wing material (feathers), as well as all attempts to mimic the flapping of a bird’s wings, blatantly failed (often dramatically). Use of completely different wing materials and combinations with technologies that had been previously developed in a different context (e.g., combustion engines) were required to construct airplanes of practical importance. By analogy, the development of artificial photosynthesis may also require the use of currently unforeseen material combinations and new technological solutions, but are likely to benefit from solutions in other scientific and technological areas (e.g., fuel cell and battery technologies, nanostructures, microfluidics). At the present stage, the multitude of approaches and research directions represents a strength in research on artificial photosynthesis. However, the pace of progressing towards technological relevance is accelerated so that artificial photosynthesis will contribute to the CO₂-neutral energy systems of the future.

1. Molecular Catalysts for Water Oxidation and Hydrogen Evolution Reactions

Molecular catalysis for artificial photosynthesis remains a hot research topic, which is reflected in this Special Issue, in which a range of molecular catalysts based on transition metal complexes and hybrid systems are reported for the oxygen evolution reaction (OER) and hydrogen hydrogen evolution reaction (HER).

In a Minireview, Zhang and co-workers have summarized their efforts on the design and synthesis of Mn₄Ca clusters by mimicking the oxygen-evolving complex (OEC) in photosystem II. New strategies are suggested for constructing more stable and efficient catalytic materials for the water splitting reaction based on the artificial Mn₄Ca cluster, providing a direction for developing future Mn-based molecular catalysts. In a Review article, Liao and Siegbahn discuss the recent progress in applications of DFT to elucidate the O₂—O bond formation mechanisms of molecular water oxidation catalysts (WOCs). This Review covers molecular WOCs composed of various transition metal complexes, in particular, manganese, iron, cobalt, nickel, copper, ruthenium, and iridium complexes.
In terms of molecular catalysts for hydrogen generation, Blakemore and co-workers report on hydrogen evolution catalyzed by [RhCp*] complexes bearing substituted bipyridine ligands. The use of different metal–ligand cooperativity was found to give rise to effective catalysis, including formation of 19-Cp*H en route to H2 production. Synthetic and electrochemical studies support the assignment of a new mechanism of catalysis involving bpy-centered reduction. Cao and co-workers report graphene-supported molecular cobalt corroles as active and stable catalysts for the hydrogen evolution reaction in water over the wide pH range of 0–14. The introduction of a pyrenyl group to the corrole macrocycle and the use of a triphenylphosphine axial ligand on Co improved the catalytic efficiency significantly. Alberto, Probst, and co-workers investigate structure–activity and stability relationships for cobalt polypyridyl-based HER catalysts in water, also by using py5-type ligands. The acyclic, methylene bridged bisbipyridyl framework emerged as a superior polypyridyl ligand framework, both in terms of catalytic rate and catalyst stability. The developed design strategy, coupled with their synthetic scheme, allows for future rational design of new polypyridyl scaffolds to further corroborate the elaborated trends. Sarthor, Bonchio, and co-workers introduce a novel iron(III) molecular electrocatalyst for the hydrogen evolution reaction that undergoes pH-controlled interconversion between the mononuclear and dinuclear structures. The FeL/Fe2L2 manifold enables investigation of possible synergistic effects of proximal metal centers in HER electrocatalysis.

Regarding light-driven hydrogen generation systems, Hanan and co-workers report a three-component system with a heteroleptic bisamide Ru photosensitizer and a cobaloxime-based catalyst, giving rise to a large improvement in photocatalytic stability, rate of activity, and efficiency in photocatalytic H2 production compared to [Ru(bpy)3]2+. The bisamide ruthenium poly(pyridyl) complex was found to be highly efficient under blue-light and green-light irradiation whereas [Ru(bpy)3]2+ was significantly less effective. In their Full Paper, Schmuttenmaer, Crabtree, Brudvig, and co-workers report a new photoanode containing a molecular [IrCp*] WOC and a porphyrin photosensitizer. Departing from the traditional use of phosphate as the anchoring group, saltrane and tetrahydroxypropyl hydroxamic acid anchors were used to bind the molecules to a SnO2 electrode. The photosensitizer/catalyst ratio varied to optimize the electrodes for best performance. Photocatalytic water oxidation was confirmed over 20 hours in real time by using a Clark-type electrode, though the photocurrent density was not high. Shafaat and co-workers report light-driven hydrogen evolution by an enzymatic system in which a ruthenium chromophore covalently attaches at four different positions of nickel-substituted rubredoxin. The photo-induced activity of the hybrid enzyme is significantly greater than that of a two-component system, but the activity is dependent on the effective distance between the ruthenium center and the nickel center, indicating that intramolecular electron transfer plays an important role.

2. Solid-State Materials for Water Oxidation and Hydrogen Evolution Reactions

The catalytic center of photosynthetic water oxidation contains a protein-bound Mn4Ca–oxo cluster (see the Minireview by Zhang and co-workers). There are remarkable similarities regarding structure and function between the biological catalyst and some synthetic manganese oxides, so it may be appropriate to denote these materials as biomimetic oxides. Three contributions address new synthetic routes and the catalytic activity of manganese oxides. Kurz, Messinger, and co-workers present a method for in situ synthesis of manganese oxides on carbon materials and discover that only specific graphitic carbon substrates are stable at the potential required for electrocatalytic water oxidation. Sun and co-workers describe electrocatalytic water oxidation by nano-architected turbostratic δ-MnO2 on carbon nanotubes and report that manganese oxides, as a structural and functional model of the OEC in photosystem II, can reach a comparable level of performance to most Ni- and Co-based catalysts. Risch and co-workers address the mechanism of electrocatalytic water oxidation by means of an outstandingly thorough electrochemical characterization of LiMn2O4 electrodes and discuss similarities with the biological paradigm. Mei and co-workers report a significant improvement in the quantum yield of the well-established photocatalyst SrTiO3 by controlled incorporation of magnesium. In photocatalytic overall water splitting, the Mg:SiTiO3 composite has an efficiency up to 20 times higher than the parent oxide.

structures. Three [IrCp*] complexes with hydroxy- or amino-functionalized N-heterocyclic carbene (NHC) ligands are reported by Martin-Matute, Thapper, and co-workers as molecular catalysts for water oxidation. Hydroxy groups on the NHC ligands are proposed to structurally stabilize high-valent Ir species, increasing their activity up to 15 times over that of an [IrCp*] complex without heteroatom functionalization. In light of clues and doubts on the nature of the active species for water oxidation, Macchioni and co-workers have benchmarked WOCs based on molecular iridium complexes. The activity of archetypal iridium WOCs has been evaluated under exactly the same experimental conditions (pH 7, 25 °C), exploiting NaIO4 as an electron acceptor. [Ir(OH)3]2 was found to be the most active catalyst, reaching a record TOF value. Comparative kinetic analysis suggests that the active species has to be molecular in nature. In addition to molecular Ir and Co complex-based WOCs, two Cu complex-based molecular WOCs were investigated by Wang and co-workers. They found that one Cu catalyst exhibited a significantly smaller overpotential than the other under identical test conditions. Possible mechanisms for O2 evolution reactions catalyzed by both Cu complexes are discussed based on experimental evidence. Their comparative results indicate that fine-tuning the structures of tetradentate N4 ligands can bring about a significant change in the performance of Cu complexes for electrochemical water oxidation.
The use of metal phosphides in HER and OER catalysis represents a comparably recent development, which is reviewed by Chen and co-workers with a focus on the use of metal phosphides as cocatalysts in photocatalytic and photoelectrocatalytic systems. (We note that for direct coupling of a photoactive material, which promotes light-harvesting and charge separation, with a catalytic material, the latter is often denoted as a “cocatalyst.” In purely electrocatalytic systems, the same materials may be denoted simply as “catalysts.”) Kwong, Messinger, and co-workers address the important role of deviations from crystalline order as a promoter of efficient catalysis. They investigate how cationic vacancy defects support efficient and stable electrocatalytic hydrogen formation in iron phosphides. Downes and Marinescu review the progress in employment of specific metal–organic framework (MOF) materials for catalysis of OER, HER, ORR (oxygen reduction reaction), and CO2 reduction. They highlight the recent progress in this area, including the opportunities resulting from development of conductive MOFs.

3. Catalysis of CO2 Reduction

Contributions from CO2 reduction-related research papers include photochemical reduction using molecular catalysts, electrochemical CO2 reduction using a CuOx-coated glassy carbon electrode or a gas-diffusion layer-type electrode, and CO2 hydrogenation as an alternative to photo- and electrochemical CO2 reduction. In addition, there are also Reviews on CO2 reduction in this Special Issue.

In their Communication, Rao, Bonin, and Robert report visible-light photocatalytic CO2 reduction by using a tetraphenyl Fe porphyrin bearing trimethylammonio substituents at the para positions of the four phenyl rings as a catalyst, purpurin as a photosensitizer and sacrificial electron donor in a CO2-saturated acetonitrile/water (1:9 v/v) solution. CO is produced with 95% selectivity with a turnover number up to 120 after 94 h irradiation (λ > 420 nm) with triethylamine.

Electrochemical CO2 reduction with a Cu electrode is well known to produce higher-value products, such as ethylene and other hydrocarbons, but with relatively low efficiency and selectivity over CO. Strasser and co-workers demonstrate the tuning of the hydrocarbon selectivity during catalytic CO2 reduction by adjusting the particle density of CuOx nanoparticles (defined as catalyst mass per cm2 geometric electrode surface area) on a glassy carbon electrode. They observed a shift in faradaic efficiency toward ethylene over methane at higher density. Ampelli, Canivet, and co-workers carried out CO2 reduction by using a gas-diffusion layer-type catalytic electrode composed of a substituted imidazolate-based metal–organic framework (MOF) and Pt-doped carbon nanotubes (Pt/CNTs) on the MOF-free side. The selectivity to > C1 carbon-containing products, such as ethanol, acetone, and isopropanol, was enhanced compared to that by using Pt-based electrocatalysts, owing to the higher CO2 concentration at the active surface of the electrode.

As an alternative to photo- and electrochemical CO2 reduction using H2 that can be generated by artificial photosynthetic methods, Ertém and co-workers used [IrCp*] complexes with proton-responsive azole-type ligands for selective CO2 hydrogenation to formate. Spectroscopic and computational investigations revealed that the deprotonation of the ligand and a second coordination sphere effect led to high catalytic activity with a turnover frequency of 2000 h−1 and a turnover number of 8200 in 24 h at 50 °C.

Recent developments in metal-based electrocatalysts for CO2 reduction to liquid hydrocarbons are reviewed by Lu, Amal and co-workers. They address the limitations of the current understanding of the reaction mechanisms, and suggest design guidelines and research strategies based on their findings regarding high-performance catalysts. In the aforementioned Minireview by Downes and Marinescu on electrocatalytic MOFs for energy applications, several CO2 reduction studies using copper MOFs, metalloporphyrin based MOFs, and tricarbonyl rhenium bipyridine based MOFs are also summarized. The incorporation of redox-active complexes in the MOF structure can facilitate not only efficient charge transfer, but also an increase in the stability of the catalytic systems. As a complementary technique to laser flash photolysis, Grills, Polyansky,
and Fujita highlight thermodynamic and kinetic investigations of CO₂ binding to reduced metal centers for obtaining knowledge of CO₂ reduction catalysis by using pulse radiolysis in their Minireview on applications of pulse radiolysis for investigations on artificial photosynthesis including water oxidation and reduction. The pulse radiolysis technique, which utilizes short, high-energy electron pulses from an accelerator, is found to be a powerful method for preparing catalytic intermediates and investigating the reaction mechanisms. Recent developments of photoelectrochemical technology using silicon materials for solar-to-chemical conversion, including applications in photoelectrochemical CO₂ reduction, are discussed in the Minireview by Jingying Shi and co-workers. They conclude that silicon is an ideal material for the cost-effective production of solar chemicals. Molecular photocatalysts and photoelectrocatalysts have also undergone some impressive recent advancements, as exemplified by Feng Wang in a Minireview on cobalt complexes for CO₂ reduction.

4. Solid-State Materials for Photoelectrochemistry

Photoelectrochemical systems involve the direct coupling of a photoactive semiconductor material, which facilitates light-harvesting and initial charge separation, with a cocatalyst promoting the desired electrochemical reaction. Four contributions address optimization of the interface between photoactive semiconductor and catalyst materials. Galan-Mascarós and co-workers employ density functional theory (DFT) to estimate the energy-level alignment for thermodynamically favored hole transfer from photoactive semiconductor to cocatalyst. They address specifically hematite/cobalt hexacyanoferrate photoanodes and point out that predictions of plausible semiconductor/catalyst combinations may generally accelerate the development of improved photoelectrocatalytic systems. Brunschwig, Lewis, and co-workers investigate Pt nanoparticles (Pt NPs) on p-Si and p⁺-Si electrodes by using a combination of scanning probe methods. Their single-particle imaging approach addresses the heterogeneity of the nanoparticle–semiconductor connection and reveals that only a minor fraction of the “electro-less” deposited Pt particles support high current densities. Ong, Chen, Peng, and co-workers investigate the optimized ZnIn₂S₄/MoS₂ heterojunctions for noble-metal-free photocatalytic hydrogen evolution. Their results illustrate the potential of hierarchical nanoarchitectures for a multitude of energy storage and solar energy conversion applications. In the aforementioned Minireview by Shi and co-workers, the recent developments of crystalline and thin-film silicon-based photoelectrodes—including amorphous, microcrystalline and nanocrystalline silicon—for photoelectrochemical HER and CO₂ reduction are discussed, as well as photoelectrochemical regeneration of discharged species in redox-flow batteries.

New approaches for improved performance of the photoactive semiconductors are of obvious importance. Xie, Zhang, Xie, and co-workers have investigated the beneficial influence of fluorine doping on the performance characteristics of hematite nanocrystals. They detect remarkably improved visible light absorption, as well as enhanced OER catalysis. Kudo, Kato, Miyasaka, and co-workers describe a complete photoelectrochemical system for H₂ formation from water, which comprises a Pt-loaded SiC photocathode, a CoOₓ-loaded BiVO₄ photoanode, and a perovskite solar cell. They used a combination of photoactive materials that absorb a major fraction of the visible light. The solar-to-hydrogen (STH) efficiency is 0.55%, without any external bias voltage and at 100% faradaic efficiency. Zhang and co-workers have investigated the use of carbon quantum dots (CQDs) for photocatalytic applications. They report that controlled nitrogen doping represents a useful strategy for optimizing the performance of CQD–semiconductor hybrid photocatalysts.

Photoelectrochemistry and related photocatalytic systems are not restricted to the formation of molecular hydrogen or products obtainable by the reduction of CO₂. Yuan, Wang, and co-workers report the performance of graphitic carbon nitrides regarding benzyl alcohol oxidation by photocatalytic nanoparticles in solution. Their results confirm, among other observations, that a high crystallinity accelerates the separation and transfer of photogenerated charge carriers in the nanoparticles. Mao and Cong report the light-induced radical addition by atom-transfer to unactivated terminal alkenes. This photocatalytic process is facilitated by titanium dioxide as a photoactive material and a hypervalent iodine(III) reagent as co-initiator.

5. Alternative Device Components and Process Schemes in Artificial Photosynthesis

The upconversion of photon energies may facilitate the use of low-energy photons of the solar spectrum for driving reactions that otherwise can be driven only by high-energy photons. The use of nonlinear optics for upconversion of photon energies is still at a very early stage of research and development, at least regarding employment in artificial photosynthesis. Zeng, Li, and co-workers converted red excitation into green emission photons. They achieved an upconversion quantum yield of 0.29 ± 0.02% upon excitation with a 640 nm laser of only 120 mW/cm². Bipolar membranes (BPMs) could facilitate the efficient operation of anodic and cathodic reactions at different pH values, provided their H⁺/OH⁻ conductivity is high enough. McDonald, Freund, and Hammond investigated conductive BPMs that they obtained through layer-by-layer deposition. Seo, Woodbury, and co-workers investigated an especially sophisticated biological hybrid system. They report enhanced photocurrent generation for the photosynthetic reaction of the reaction center (RC) in a photoelectrochemical cell. The enhancement of light-induced current results from in vitro coupling of the reaction center protein with an additional light-harvesting antenna comprising DNA and dye molecules.

In their Review, Fukuzumi, Lee, and Nam discuss fuel production from seawater and fuel cells operated with seawater.
Aside from examples of light-driven water electrolysis, unusual systems are also discussed, such as reversible metal hydrolysis or H₂ formation from deep-sea H₂S. In their Essay, Centi, Perathoner, and co-workers discuss general opportunities for creating various chemical compounds energetically driven by renewable energy, with a focus on compounds that are more complex than H₂ or the primary products of electrochemical CO₂ reduction.

By summarizing the above investigations that depart from the usual realm of research on artificial photosynthesis, we close this Editorial. We hope that the articles in this Special Issue of ChemSusChem provide a useful overview on the broad range of topical subjects investigated by an increasing number of researchers around the world, who jointly aim at progress along the route towards artificial photosynthesis.

Keywords: artificial photosynthesis · CO₂ conversion · electrocatalysis · photocatalysis · solar fuels