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Roadmap

The 2022 solar fuels roadmap

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Abstract

Renewable fuel generation is essential for a low carbon footprint economy. Thus, over the last five decades, a significant effort has been dedicated towards increasing the performance of solar fuels generating devices. Specifically, the solar to hydrogen efficiency of photoelectrochemical cells has progressed steadily towards its fundamental limit, and the faradaic efficiency towards valuable products in CO_2 reduction systems has increased dramatically. However, there are still numerous scientific and engineering challenges that must be overcame in order to turn solar fuels into a viable technology. At the electrode and device level, the conversion efficiency, stability and products selectivity must be increased significantly. Meanwhile, these performance metrics must be maintained when scaling up devices and systems while maintaining an acceptable cost and carbon footprint. This roadmap surveys different aspects of this endeavor: system benchmarking, device scaling, various approaches for photoelectrodes design, materials discovery, and catalysis. Each of the sections in the roadmap focuses on a single topic, discussing the state of the art, the key challenges and advancements required to meet them. The roadmap can be used as a guide for researchers and funding agencies highlighting the most pressing needs of the field.

Keywords: solar fuels, catalysis, CO_2 reduction, water splitting

(Some figures may appear in colour only in the online journal)

Contents

1. Introduction 4
2. Comparison of state of the art electrocatalysts for water splitting, CO_2 reduction, and N_2 reduction 7
3. Efficiency and stability benchmarking. What is required to bring a solar fuels system to market? 9
4. Comparing artificial and natural photosynthesis—bio concepts and hybrid systems 11
5. Design and scale-up of solar fuels systems using current technologies—neutral pH, vapor-fed devices 13
6. Particle-based systems: lessons learned and guidelines for large area systems 16
7. Device design considerations for scale-up: managing photons, electrons, and ions 18
8. Membranes for solar fuels 21
9. Photoelectrodes based on conventional semiconductors (silicon, III–V) 24
10. Nanostructures for light management in solar fuels and photoelectrochemistry 27
11. Accelerating discovery of photoactive materials 29
12. From materials discovery to functional photoelectrodes 32
13. Molecular photoreduction and photocatalysts on photofunctional solid materials 34
14. Photocathode design: fundamental challenges and paths forward for CO_2 reduction 36
15. Oxygen evolution reaction: catalysts, mechanisms, and durability 38
16. Remaining challenges for the hydrogen evolution reaction (HER): catalysts and mechanism 40
17. CO_2RR catalysis: surface reactivity and products selectivity 42

Acknowledgments 44

References 46

1. Introduction

Gideon Segev[1], *Roel van de Krol*[2] *and Frances Houle*[3]

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Status

The concept of using artificial systems that emulate natural photosynthesis to generate fuels from CO_2 and H_2O with sunlight as the sole source of energy dates from the 1970s, and has stimulated active research worldwide to make the idea a reality, and pave the way to a solar fuels industry [1]. As renewable energy sources have developed in the intervening 50 years, the uses for chemicals synthesized using sunlight have expanded beyond the initial focus on fuels. It now encompasses green sources of feedstocks such as syngas for other processes, specialty chemicals, and storage of intermittent renewable electricity from photovoltaic and wind sources in chemical form. This complements conventional energy storage technologies such as batteries and pumped-storage hydroelectricity.

Two basic architectures have emerged—fully integrated photoelectrochemical systems, and electrochemical systems coupled to an external photovoltaic element. Both have enjoyed continuous improvements in stability, efficiency, and selectivity thanks to intensive research programs on light absorbers and catalysts—especially in the last decade. Now that reported efficiencies for lab-scale photoelectrochemical devices regularly exceed 10%, which has long been considered a minimum threshold for any practical application, engineering will play an increasingly important role in the field. This is not only because it is important to show practical demonstrations to governments and the public, but also because the design of a system must be set before the performance requirements for the absorber and catalyst materials can be specified. For the more challenging reactions, such as photoelectrochemical CO_2 reduction, many fundamental questions on reaction mechanisms, selectivity, and stability remain. This is in contrast to the progress made in dark electrocatalysis of CO_2 reduction, and can be attributed to the lack of integrated catalyst-photocathode candidates for this reaction. Answering these questions increasingly requires close integration of theoretical and experimental efforts and the use of *operando* methods. This highlights the interdisciplinary nature of the field, where advances in a variety of scientific and engineering disciplines are required to make progress (figure 1).

Technoeconomic analysis and lifecycle assessment (TEA/LCA) studies have been invaluable for guiding performance targets [2–7], even though the uncertainties inherent to any early stage technology mean that there is still significant spread in the projected efficiency and cost targets for solar fuel generators. This also explains the differences in performance targets that the reader may notice in the different sections of this Roadmap; formulating a consistent set of agreed-upon targets is still a work in progress in the field of solar fuels. However, there seems to be broad agreement that the lifetime of a solar fuel module should exceed ten years in the field, manufacturing processes should be scalable and ultra-low cost (<300 \$ m^{-2} [3]), and the efficiency of selective generation of a specific product should exceed 10% solar-to chemical energy. For lower-value products such as hydrogen, an efficiency close to the theoretical limit (which is about 22% for H_2 generation [8]) is probably needed for economic viability.

Current and future challenges

Efficiency, selectivity, lifetime and scalability are the predominant scientific challenges facing the field (figure 2). In most cases, the efficiencies are not only well below the theoretical limit, but also fall short of the performance targets from TEA/LCA studies. This is particularly true when multicarbon products are targeted. Moreover, lifetimes are measured in hours, not months or years as required for a sustainable technology. The reality is that the CO_2 reduction products are usually mixtures because perfect selectivity and single-pass CO_2 consumption efficiency have not been realized. Thus, downstream separation and purification costs, both in terms of energy and capital, must be evaluated [7].

To make improvements, there is a tendency to propose increasingly complex architectures at both micro and macro length scales, e.g. multi-layer structures (tandem devices), hybrid solid state/molecular/bio-inspired assemblies, membrane/electrode assemblies, nano-structured catalysts, etc, which pose counterbalancing manufacturing and materials lifetime challenges. The materials complexity and the nature of the solar resource pose challenges not faced by electrochemical systems. In practice, photoelectrochemical systems must deal with the natural intermittency of solar radiation diurnally and seasonally, as well as the variability of direct and diffuse illumination as a function of geography. A fluctuating supply may, however, also be leveraged to re-distribute ionic species in dark periods and thereby reduce pH gradients and enable recovery or even self-repair mechanisms. The combination of low stability and slow and insufficiently sensitive product detection methods makes product selectivity optimization slow and tedious. This challenge is further amplified in CO_2 reduction photocathodes where the products of surface corrosion can be easily mistaken for favorable photoelectrochemical reactions (section 14) and in mechanistic studies where unstable intermediates are mostly examined in synchrotrons which have limited availability (section 12).

The main engineering challenges in the field are scale-up and performance and stability benchmarking. Scaling-up fully integrated photoelectrochemical systems is especially challenging due to the fact that one needs to manage photons, electrons and ions. In contrast, photovoltaic systems and electrolyzers each only have to manage two out of these three species, which greatly simplifies the architectures of these devices. Assessment of solar fuels system improvements requires that

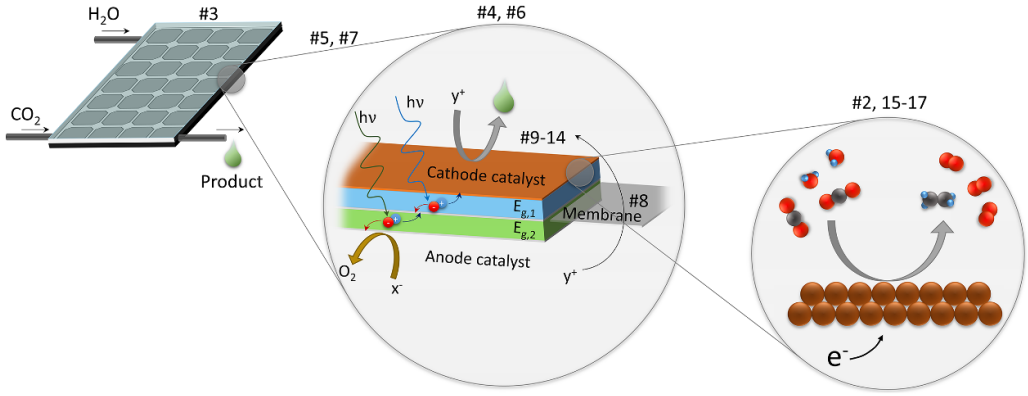

Figure 1. Conceptual drawing of a solar fuel generator (left), showing the functional layers of the device (middle) and the atomic-scale electrochemical processes that occur at the catalytically active surfaces. The numbers indicate the section addressing every component or challenge.

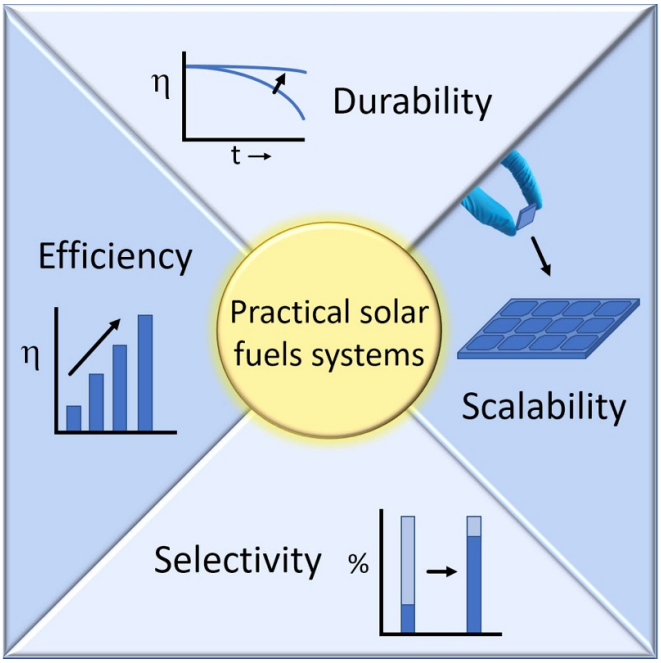

Figure 2. The main performance metrics and challenges for advancing solar fuel systems.

benchmarking protocols and standards be in place to establish efficiency in all laboratories: currently these are in development by various groups such as the U.S. DOE HydroGEN Energy Materials Network project. Successful benchmarking requires a portfolio of design architectures for solar fuel devices that offer potential for scale-up and high efficiency. As mentioned above, without such designs it is difficult to formulate specific materials requirements.

Advances in science and technology to meet challenges

Improvements in efficiency can be achieved if the rates of semiconductor excitations and charge transport are matched with those of the electrocatalytic reactions, and if the photovoltages achievable with semiconductors are 1.6 V (for water splitting) or well above 2 V (for CO_2 and N_2 reduction) under operation. Efficiency is also governed by system designs, and an improved understanding of how fluctuating sunlight and feedstocks affect mass transport and concentration gradients will serve to optimize system performance. In addition, it can provide insights on how to incorporate self repair mechanisms such as those found in natural systems. Efficiency also requires effective product separation and collection over large surface areas. Strategies to achieve these by minimizing feedstock/product purification units and piping are critical, and can involve reactor designs that avoid mixing of gaseous and liquid products, for example. Bubble formation at liquid electrolyte-electrode interfaces (section 16) reduces efficiency by blocking catalytic sites and increasing solution resistance, as well as scattering incident light in front illumination configurations. They can also affect durability by inducing mechanical damage when they detach, and alter local current density distributions which can adversely affect system lifetimes. Designs that eliminate active liquid-solid interfaces or inhibit bubble nucleation and growth while preserving other benefits of the liquid-solid interface will be valuable. Several demonstrations of vapor-fed devices have shown this is feasible ([9], section 3).

Although the integration of photovoltaic and electrocatalytic functionalities into a photoelectrochemical cell presents a fundamental challenge, synergistic effects might provide opportunities to increase both system efficiency and product selectivity. Strategies to improve the selectivity of multi-electron transfer reactions include hybrid solid state/biomimetic and molecular approaches (sections 4 and 13), plasmonics (section 10), electrolyte engineering, use of semiconductor surfaces for CO_2 reduction (section 14) and cascade catalysis, all of which use local atomic and molecular structure and the electron energy landscape to promote specific reaction pathways. Overcoming the limitations of catalytic scaling relations, which lock in product selectivities, by

novel materials designs are an important opportunity. Several strategies are proposed in this Roadmap, and implementation of these strategies in practical devices will further advance the field. New instrumentation for rapid detection of a broad range of liquid and gas phase products can significantly accelerate the optimization of light coupled systems that in most cases cannot be studied with fast detection instrumentation such as differential electrochemical mass spectrometry.

Improvements in stability require a detailed mechanistic understanding of all degradation processes leading to loss of efficiency or device failure. Further development of *operando* analysis tools and theory will be invaluable to pinpoint where losses originate from. Systems designs that control the chemical environment surrounding all the active elements and ensure their long-term stability while preserving efficiency are essential. Environments that promote stability without introducing unwanted mass transport limitations will be a key advance. An example of recent progress toward this dual goal of efficiency and stability is given for FeNi oxygen evolution reaction catalysts, where Fe^{3+} in solution stabilizes performance (section 15), and for electrolyte engineering to push the limits of ion diffusion (section 16).

Concluding remarks

This roadmap highlights our views of the most pressing scientific and engineering challenges that must be met before a wide scale solar fuels technology can be implemented. Section 2 discusses the state-of-the-art catalysis in the field; sections 3–8 address system level concepts; various aspects of photoelectrodes for solar fuels are surveyed in sections 9–14; and catalysis related challenges are analyzed in sections 15–17. The numbers in figure 1 indicate the sections addressing every system component and challenge. Although many aspects of this field are still at an early stage of development, it is never too early to conduct a macro scale assessment of the manufacturing and operation costs, and the carbon footprint of different designs and concepts. Such an analysis should rule out concepts that are incompatible with the end goal and provide guidelines for economically and environmentally viable technologies.

2. Comparison of state of the art electrocatalysts for water splitting, CO_2 reduction, and N_2 reduction

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Status

The production of sustainable fuels and chemicals through Power-to-X processes has been subject to intense research efforts in the last decade and is presently also gaining increased political awareness. Independently of whether these fuels and chemicals are produced by coupling photovoltaics (or wind turbines) to an electrolyzer unit or by an integrated photoelectrochemical device, good catalysts are needed to lower the overpotential and thus the energy required to make the reactions run and ultimately make the production economically viable [10].

Much of the attention has centred on water electrolysis (hydrogen evolution reaction (HER, section 16) [11–13] and oxygen evolution reaction (OER, section 15) [14–17]), CO_2 reduction (CO_2R, section 17) [18–21] to fuels and chemicals, and recently N_2 reduction (N_2R) to ammonia [22, 23]. These processes involve different number of proton-electron transfers and have different complexities in terms of activity, selectivity, and stability.

The direct impact that the increased complexity imposes to the catalytic activity is perhaps best viewed by comparing the turnover frequency (TOF). TOF is the scientifically relevant metric when comparing the intrinsic activity as it measures the number of product molecules produced per time per active site. Figure 3 shows a compilation of state-of-the-art TOF values for HER, OER, CO_2R (to both CO and ethylene), and N_2R as a function of applied overpotential relative to the thermodynamic potential required for the respective reactions. It is immediately apparent that TOF values for HER are orders of magnitude higher at a given overpotential as compared to OER, CO_2R, and N_2R. This is a direct consequence of scaling relations between reaction intermediates [10]. HER is a two-electron reaction with only one catalytic intermediate, H^*, where * denotes a surface site. Consequently, the rate of the overall HER reaction is largely determined by a single optimizable quantity namely the hydrogen adsorption free energy, ΔG_H. When plotting the intrinsic HER activity against ΔG_H a volcano relationship emerges [10], with Pt located at the top with negligible overpotentials for large TOFs, see figure 3, exemplifying an ideal catalyst in terms of activity. OER, CO_2R, and N_2R involve multiple intermediates of which the binding energies scale linearly and thus cannot be optimized independently; this poses a fundamental barrier to optimizing the catalytic activity [10].

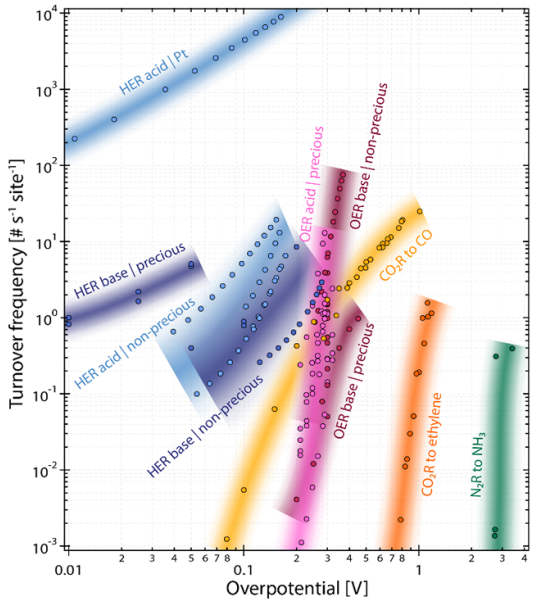

Figure 3. Turnover frequency (TOF) of state-of-the-art catalysts for HER [11–13], OER [14–16], CO_2R to CO [18, 19], CO_2R to ethylene [20, 21] and N_2R [24] (and references within) plotted against the overpotential relative to the thermodynamically required potential for the respective reactions. Shadings are a guide to the eye. Note the N_2R data is for lithium-mediated reactions and the lithium plating potential thus sets a minimum required overpotential.

Current and future challenges

Circumventing scaling relations between reaction intermediates poses a monumental scientific challenge that must be conquered to bring down the overpotential for especially OER, CO_2R, and N_2R.

Moreover, for CO_2R, the similar standard reduction potentials for many products makes selectivity to a desired product challenging, as it requires controlling the kinetics of competing reaction pathways. Similarly, while the thermodynamically required potential for N_2R is close to that of HER, the large kinetic barrier associated with splitting the N_2 triple bond requires a much larger overpotential than HER [10]. Consequently, HER is always favoured over N_2R and to date direct N_2R in aqueous electrolytes remains to be successfully shown [23]. Only by controlling the proton availability in, e.g. non-aqueous electrolyte as is done in the Li-mediated approaches, the faradaic efficiency towards N_2R becomes reasonable.

Electrocatalysts also have a complex microenvironment, i.e. the confined space in close proximity to catalyst, which can have significant extrinsic influence on steering reactivity. Polar and charged reaction intermediates on heterogeneous catalysts can be stabilized or destabilized by the solvent, electrolyte ions, and polymer coatings through non-covalent interactions (e.g. dipole-dipole, ion-dipole, and ion-ion), similar to how the secondary coordination sphere of a molecular catalyst interacts with reaction intermediates. Field effects from the electrochemical double layer are a key contributor to the high intrinsic activity of Au for CO_2R to CO, see figure 3, by stabilizing the transition state for CO_2 adsorption [25].

Apart from catalytic activity, stability is an equally important metric and achieving long-term stability for especially non-precious catalysts in acidic environments may pose a challenge. The stability number (S-number = ratio of evolved product molecules to the amount of dissolved catalyst) of electrocatalysts has been proposed as a stability metric to allow a reasonable comparison of diverse materials [26]. In alkaline environments and cathodic conditions, catalyst dissolution may be less significant in influencing the surface stability. However, the adsorbents induced thermodynamic minima state change of the catalyst surface during the catalysis may cause the surface segregation of the alloy catalysts and it may in long-term affect the stability [27].

Advances in science and technology to meet challenges

A multitude of different catalysts have over the years been synthesized and tested for HER, OER, CO_2R, and N_2R, but to our knowledge, there are virtually no examples of effectively circumventing the scaling relations and thereby significantly lowering the overpotential speaking to the grand challenge of accomplishing that. That being said, several ideas of selectively stabilizing certain intermediates over others have been proposed with the common theme of creating multi-functional and three-dimensional active sites [28]. Precise engineering of the individual active site motif will further enable steering the selectivity to the desired product for, e.g. CO_2R. While controlling the microenvironment provides avenues to circumvent scaling relations, the chemical complexity and dynamics of the electrocatalyst/liquid interface present significant challenges for interface modelling and *in situ* characterization. These challenges must be overcome to co-design catalysts and microenvironments and accurately predict reactivity.

Furthermore, as the field of catalyst discovery continues to grow, the need for rigorous experimentation including product detection increases. Erroneous claims on catalytic activity have especially plagued the fields of OER and N_2R, which dilutes properly conducted literature and worse potentially leads the field down a wrong path wasting time and resources. Much of this can be avoided if published protocols were followed [22, 29]. Further, the need to ensure comparability of activity and stability calls for the community to agree on proper benchmarking protocols and metrics.

While scientific breakthroughs are needed in obtaining improved catalysts, equally important is enabling more efficient ways to translate new scientific insights into industrial devices. Conditions under small-scale benchtop experimentation may not translate into, e.g. a membrane electrode assembly (MEA), section 8. For example, a catalyst in an MEA is likely to be interacting directly with a polymer electrolyte microenvironment whose charged functional groups likely contribute different non-covalent interactions than that of typical solvents and ions used for benchtop experiments. In addition, the chemical potentials of key reaction species may be significantly different in MEAs as they typically operate at much higher reaction rates, providing a different microenvironment than that of benchtop experiments that may lead to emergent phenomena. Difficulties in translating benchtop catalytic activities to prototype devices are well-known in the fuel cell community [30] and will also pose challenges for emerging technologies based on CO_2R and N_2R. Thus, to facilitate technology breakthroughs that can form the basis for industrial devices, integration of research at prototype level is needed, see figure 4.

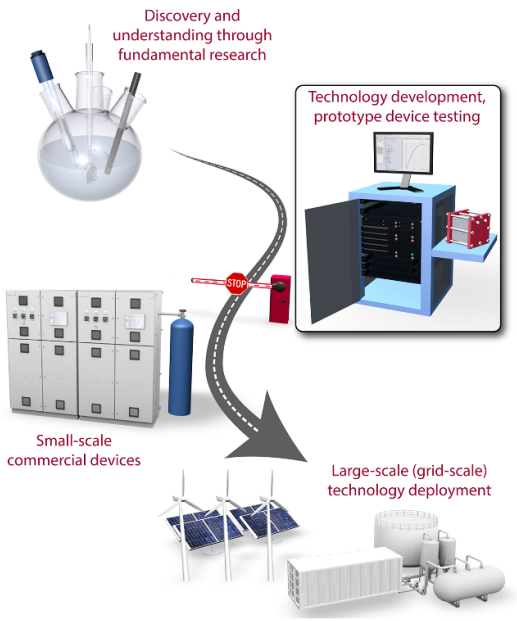

Figure 4. Roadmap for taking fundamental catalysis research to large-sale industrial deployment. Integration of research at the prototype level is needed to facilitate technology breakthroughs that can form the basis for industrial devices for solar fuels and chemicals.

Concluding remarks

Improved catalysts for converting sustainable energy into fuels and chemicals are essential if we are to phase-out the use of fossil resources in our society. While many areas can be directly powered by renewable electricity, high energy density chemical fuels will likely still be necessary for applications such as shipping and aviation. In addition, a sustainable production of various feedstock chemicals will allow for a greater penetration of renewable energy in the chemical industry. Significant research efforts have been placed on developing better catalysts for water electrolysis, CO_2 reduction and lately N_2 reduction, but there are still several challenges to conquer to make these processes economically viable. Specifically, improvements on both activity, selectivity, stability, and upscaling of many of these catalysts are still required to produce the fuels and chemicals we ultimately need for a sustainable future.

3. Efficiency and stability benchmarking. What is required to bring a solar fuels system to market?

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Status

Transforming solar energy into energy stored in the form of chemical bonds as a long-term sustainable solution for energy storage has drawn much attention in the past decades due to environmental concerns. Utilizing photon generated carriers for catalyzing both the reduction reaction, e.g. hydrogen evolution reaction (HER), CO_2 reduction (CO_2R) or N_2 reduction and the oxidation reaction, e.g. oxygen evolution reaction (OER), completes the full cycle of fuel production. A spectrum of system configurations ranging from stand-alone photovoltaic system coupled with commercially available electrolysers (PV-EC) to fully integrated photoelectrochemical (PEC) or photocatalytic (PC) systems has been developed to generate low levelized cost hydrogen. One key figure of merit that differentiates the three systems is the operating current density, where PV-EC system operates at >1 A cm^{-2} in water electrolysis, PEC system typically operates at 10–100 mA cm^{-2} to match solar flux potentially with low sunlight concentrations, and PC system has unique advantage to operate at <1 mA cm^{-2} [4, 31]. Other system configurations, such as wired photoelectrodes, redox couple assisted water-splitting cells and others, have unique attributes for specific materials or operating conditions. Generally, the component benchmarking includes catalytic properties defined with overpotential at 10 mA cm^{-2}, membrane performance defined with pH operation window and ion conductivity. The device benchmarking requires determining a spectral correction factor and translating performance measured under a simulated light source to the AM1.5 reference spectrum without additional bias to present direct conversion of solar to fuels [32]. While it may be helpful to benchmark components that require a bias for diagnostic purposes in the laboratory, it is not a practice used for complete solar fuels devices due to the confusion, even among experts, of identifying a system bias vs. an electrode bias. Stability benchmarking protocols are much less established; constant illumination using a simulated light source is commonly used where instead diurnal cycles or natural sunlight with intermittency—representing realistic operation—should also be considered. While PEC H_2 or CO_2R in general is still at low technical readiness level, the adoption of standardization through benchmarking protocols can help lower the barrier of entry for new researchers and serve as a basis for comparing results across institutions to accelerate the development of this early stage technology. Figure 5 presents the summary of historical demonstrations of solar driven water splitting devices with three key merits: solar-to-hydrogen (STH) conversion efficiency, areal normalized lifetime H_2 production (g m^{-2}), and rate of H_2 production (μg h^{-1}) [31, 33–35]. The best few demonstrations with higher numbers for the merits utilize III–V based light absorber with concentrator in PV-EC (STH 31%, ~10 000 g m^{-2} under 42 suns [36]), or PEC-B (catalyst at backside of the light absorber, ~200 000 μg h^{-1} under 117 suns [35]) configuration. Even though there are exciting progress with PEC and PV-PEC (couple low voltage PEC device with PV to meet the potential requirement) especially in STH conversion efficiency, they are currently limited by stability and overall generation rate. In contrast, for the PC configuration, while meter-scale demonstration or 1000 h operation has been demonstrated, the STH conversion efficiency is limited to <1%. More endeavours need to be focused on to improve the different approaches toward the target. To bring the solar-driven water-splitting system to market, the throughput of the system needs to approach small size PEM systems with a typical H_2 production rate of ~1 kg h^{-1}. To achieve <\$1 kg^{-1} of H_2 in the long term, system level STH conversion efficiency of about 15% is needed for a concentrator system between 100–150× where an \$800 m^{-2} absorber has at least a two year lifetime [37]. New system design or breakthrough of technology to significantly reduce the cost would be necessary to bridge the gap between current demonstrated devices and target for the real market.

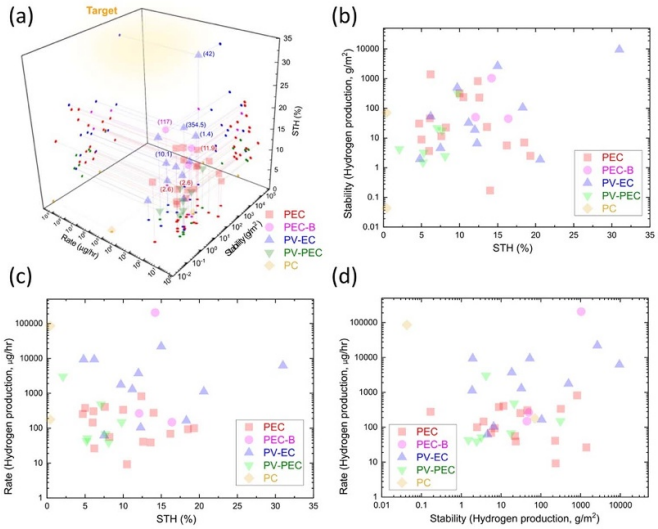

Figure 5. Review of the historical demonstration of solar driven water splitting devices. (a) Correlation of the STH, stability (lifetime hydrogen production, g m^{-2}), and rate (rate of hydrogen production, μg h^{-1}). The numbers in bracket indicate the irradiance multiply concentration factor. (b) Correlation of the STH and stability. (c) Correlation of the STH and rate. (d) Correlation of the stability and rate. Photoelectrochemical (PEC) device in red; photoelectrochemical device with catalyst at backside of the light absorber (PEC-B) in pink; photovoltaic wired with electrolyser (PV-EC) in blue; photovoltaic wired with photoelectrochemical device (PV-PEC) in green; photocatalytic device (PC) in yellow [31, 33–35].

Current and future challenges

Different device configurations (PV-EC, PEC, PC and others) face very different challenges in materials, components and device developments. As no reasonably efficient material is intrinsically stable in the PEC configuration, the most significant challenge is discovering a barrier layer to protect the absorber that possesses appropriate properties [38]. The barrier layer has to be conductive, transparent, catalytic, and stable under operating conditions. There have been some successes using this approach on smaller scale, but a technique for depositing large-area films without pinholes has remained elusive. While still having the similar operating current density (10–100 mA cm^{-2}) at the catalytic sites as PEC configuration, the most direct and effective routes to long-lived device performance is to decouple the absorber from the catalyst site. This relaxes the barrier requirements as the functions can be split over two physically separated interfaces and there are many options for stable, transparent, insulating films and non-transparent, catalytic layers. Several demonstrations have showed good durability by decoupling the light absorber from catalytic sites. In the PC system, low absorption in PC materials as well as low quantum yield for water-splitting reactions resulted relatively low STH conversion efficiency. Selective catalysis in the presence of redox couples sets significant materials challenges. Device level PC operation and optimization as well as membrane separator consideration remain under explored.

Integration of materials and components is another technological consideration. Deposition techniques that require high temperatures could degrade absorbers or lead to compromised adhesion from mismatched thermal expansion coefficients. Protective layers, such as MoS_2, exhibit native catalytic activity, while others require application of cocatalysts. Efficient charge transfer and in particular long stability among the interfaces of the light absorber, protective layer and co-catalysts remain a challenge. Epoxy, which can be prone to failure itself, is often used to mount absorbers and protect electrical contacts from electrolyte. Although there are numerous commercially available epoxy formulations with variable adhesion characteristics and chemical compatibilities, none have been tested for long durations under the harsh conditions of photoelectrolysis. In the PC system, multi-dimensional optimization that includes particle dimensions, redox couple properties (concentration, optical transparency, energetics), co-catalyst loading and energetics with light absorbers, etc, remains a significant challenge for producing efficient and long lasting devices. As devices transition from bench scale to pilot scale (discussed in depth in section 7), efficiency and stability benchmarking will also have to expand to cover larger absorber areas, a greater number of components, and to environments that are less artificially controlled (i.e. outside). Development of long-term stability protocols, corrosion analysis at materials, component, and device level as well as establishment of standard protocols for dynamic operations (e.g. diurnal cycles and under intermittency nature of the sunlight) are important and should remain a priority in the near future.

Advances in science and technology to meet challenges

Research and development of new light absorbers with a set of unique materials properties for efficient and stable water splitting are important for the field. While leveraging the rapid progress of semiconductor materials development in the photovoltaic field can improve the performance of PEC systems, demonstration of a combination of intrinsically stable light absorbers with high optoelectronic qualities for un-assisted PEC water splitting would be a game changer. Membrane materials can play a critical role in various PEC designs, in particular, vapor fed and wire embedded PEC devices have unique requirements for the optical, electronic and ionic transport properties of the membranes. Cationic and anionic conducting membranes from the low temperature electrolysis community can be leveraged with additional consideration in optical transparency, dynamic operating conditions as well as ion transport other than proton and hydroxides in near neutral pH operations. Electrocatalysts development in PEC has revealed a collection of highly efficient OER and HER catalysts with low overpotentials at an operating current density of $\sim$10 mA cm^{-2} in various electrolytes. One of the missing pieces is earth-abundant OER catalyst operating in acidic environments, such as in 1.0 M H_2SO_4 or in direct contact with Nafion [39]. Various PEC systems configurations ranging from particle based PC cells, fully integrated catalyst-coated semiconductor devices, to PV wired electrochemical cells all have the opportunity to showcase a practical PEC system operating under real-world conditions. This demonstration effort is very important for the field as other renewable hydrogen generation methods are rapidly developing and scaling in the coming decades.

Concluding remarks

Solar-driven hydrogen generation is still in low technology readiness level relative to low temperature or high temperature electrolysis, however, the unique aspects of producing the important energy carrier directly from sunlight and independent of electricity grid are appealing and can be an important part of more resilient long-term energy storage system. To bring the solar hydrogen to market, it is very important to demonstrate a stable system with a H_2 generation rate of 1 kg h^{-1} in the coming years. Along the technological pathway to economical H_2 production, where high STH efficiency (>15%) from absorbers with long durability (ten year) and low cost (<\$1000 m^{-2}) are needed, there may be opportunities for H_2 to gain a foothold in markets willing to pay a premium for fuel (e.g. military) or niche applications such as biomethanation that can accept low-pressure, wet H_2 and reduce costly balance of system components.

4. Comparing artificial and natural photosynthesis—bio concepts and hybrid systems

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Status

Fair comparisons in solar energy conversion between artificial and natural photosynthesis can be difficult to draw since the two emerged under vastly different circumstances. Fortunately, Blankenship *et al* addressed this a decade ago [40], concluding that artificial photosynthesis (coupled to photovoltaics) is overall more energy efficient under AM1.5 light conditions, whilst biological photosynthesis is adaptable to a wider range of conditions, offers sustainability advantages and produces more complex products. Ultimately, both approaches were envisioned necessary for adapting to different future situations and research in both spheres have been highly active. Complementing these efforts, the past decade has also seen a surge in the development of biohybrids, where desirable artificial (e.g. molecular, colloidal or bulk materials) and biological (e.g. enzymes or whole cells) components are combined with the aim to arrive at 'best-of-both-worlds' scenarios for solar energy conversion.

On one end of the biohybrids spectrum are biomimetics, where motifs associated with the active sites of enzymes such as hydrogenases and CO_2 reductases are used as blueprints for catalyst design (figure 6) [41]. Several first-row transition metal catalysts have been developed and tethered to various scaffolds for (photo)electrocatalysis. There are also the protein-based biohybrids, where purified enzymes and proteins (typically the most efficient parts of a biological pathway) are employed as the electrocatalysts or light-harvesters in an artificial device [42]. Notable achievements include the 're-wiring' of biological photosynthesis where photosystem II was coupled to hydrogenase or formate dehydrogenase, which omitted bottlenecks within photosynthesis to streamline complete water splitting or perform new modes of CO_2 reduction [43]. Living biohybrids have been developed where microorganisms are employed as self-repairing/recycling catalysts that can perform complex transformations, typically via a series of enzymes orchestrating the exchange of many electrons and bonds. Here, electron transport chains could be hijacked *in vivo* to interface with electrodes for the production of electricity (e.g. photo-microbial fuel cells) and/or chemicals [44]. Some configurations have already reached solar-to-biomass conversion efficiencies of >10% [45]. The advancement of such biohybrids is crucial for arriving at technologies that can blend efficiency, sustainability with versatility.

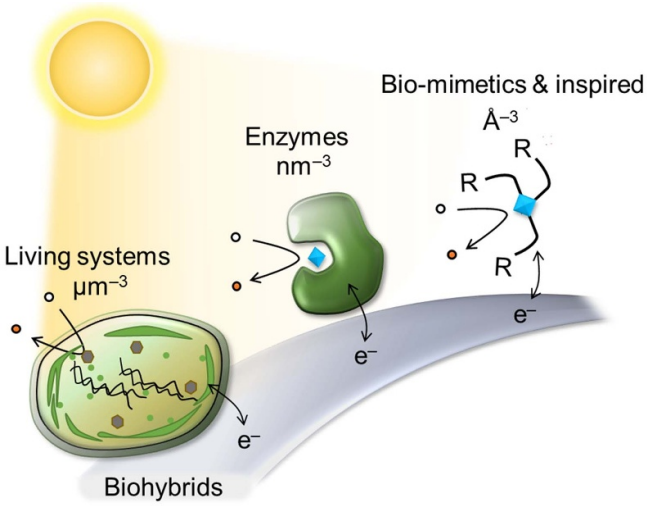

Figure 6. The spectrum of biohybrids for solar energy conversion.

Current and future challenges

Artificial and natural photosynthesis have complementary strengths and weaknesses, and it is the grand mission of biohybrid research to synergize their strengths [42]. Artificial photosynthesis benefits from the matured, efficient and broad-spectrum absorbing light-harvesting materials already available. Its main limitation lies in the lack of catalysts that simultaneously exhibit energy efficiency (low overpotential), selectivity, durability, and scalability. Moreover, presently top molecular catalysts are limited to simple transformations [41].

On the biological side, certain proteins and enzymes, aided by a combination of natural evolution, bio-engineering and even directed evolution [46], can be extremely scalable, efficient and selective in the catalysis of energetically and kinetically demanding multi-electron reactions in ambient conditions. Their main limitation is their fragility outside of native *in vivo* environments. Living microorganisms on the other hand are widely abundant, self-renewing and possess a multitude of refined enzymatic pathways to confer high synthetic versatility. In some cases, extraordinary mechanisms have evolved to compensate for unfavorable reaction conditions, e.g. photosynthetic microorganisms possess potent carbon concentrating mechanisms to sequester atmospheric CO_2. However, it can be difficult to channel substrate/product fluxes along a chosen pathway and mitigate down-regulation pathways. Furthermore, some intrinsic limitations (including limited solar spectrum utilization) in natural systems still need to be overcome [40].

Altogether, there are several challenges facing biohybrids. For protein-based systems, the fragility of the enzymes must be resolved for ambient and industrially relevant conditions (e.g. extreme pH and temperatures on the surface of electrode during high currents). In living biohybrids, strategies are needed to match the incoming and outgoing fluxes at the complex cell-material boundary. Additionally, in systems where cells exchange electrons with the electrode, there are additional considerations where electron carriers need to bypass

membrane barriers and charge recombination pathways to reach the target. As such, careful selection of mediators and understanding of the redox chemistries at the bio-material interface is crucial for rational design of both sides of the bio-electrode interface. Importantly, fair comparisons between biohybrids for solar energy conversion can be confusing due to the different combinations of half-cells, conditions and inputs/outputs possible—standardized approaches for output determination by the community are needed.

Advances in science and technology to meet challenges

Studies of artificially matured apo-[FeFe]-hydrogenases have demonstrated that the tuning of the 3D environment around the catalytic site is important for overall catalytic performance [47]. To advance biomimetics, the immobilization of efficient catalysts onto appropriate material scaffolds, perhaps in combination with polymer matrices, will bestow greater control over the local environment of the active sites and could impart favorable asymmetry properties, selectivity and protection.

In the case of protein-based biohybrids, redox-active polymers have recently been demonstrated to be a highly effective medium for facilitating reversible catalysis by [FeFe]-hydrogenases with minimum energy loss and also in protection against oxygen de-activation at the bio-electrode interface [48]. When assisted by computational modelling, the precise redox polymer conditions required for semi-infinite electrochemical protection and mediation was predicted, then experimentally validated to result in high and stable electrocatalytic currents from [FeFe]-hydrogenases. This strategy will be effective for other oxygen-sensitive reduction (bio)catalysts, though other modes of deactivation pathways (e.g. high temperature and pH) can still exist. More aggressive bio-engineering efforts, perhaps with the help of directed evolution, is needed to further increase the robustness of proteins. Further advancements would also involve the building of more complex reaction pathways via the use of protein cascades. Here, efforts to understand and match the kinetic parameters of each enzyme to minimize bottlenecks will be important. Where photosynthetic machineries are employed, strategies to incorporate artificial light harvesters to enhance solar spectrum utilization will also be important.

In living biohybrids, a better understanding of biosynthetic pathways and their regulation are required to enable microorganisms to sustain output in desired pathways, which could be aided by CRISPR technology, whilst still upkeeping physiological viability. Moreover, the engineering of reactors or bio-electrodes to accommodate higher cell densities whilst maximizing access to substrates, mediators and light will be crucial for reaching required titres and industrial competitiveness.

Although the energy conversion efficiency will not be the ultimate singular factor that determines applicability, it is an important consideration that helps the community to benchmark and build upon each other's work. A didactic review is in place that shows how to make these calculations more accurately in the future [49].

Concluding remarks

Biohybrid approaches for solar energy conversion is still a nascent field and if the challenges can be overcome, they could be amongst the most sustainable means of energy conversion. This is because unlike bioenergy, it does not depend on farmland or air-polluting combustion practices; and unlike photovoltaics-electrolysis, it does not have to depend on mined low-abundance materials and can produce more complex molecules. The road to the maturation of these approaches will require enormous cooperative efforts across disciplines, making this one of the most exciting and dynamic research spaces to be in for the next decades to come.

5. Design and scale-up of solar fuels systems using current technologies—neutral pH, vapor-fed devices

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Status

Fujishima and Honda's 1972 communication of light-mediated water oxidation over rutile TiO_2 concludes with quaint understatement, noting that with future improvements of semiconductor electrodes, 'electrochemical photolysis of water may occur more effectively [50].' That simple understanding, and the promise it carried, seeded the field of electrochemical solar-fuels research as we know it today. Currently, the domain of solar-fuels remains dominated by aqueous-immersion devices, where catalytic/photocatalytic electrodes separated by a membrane or electrolyte are submerged in protic media and chemistry is facilitated by an electrode/bulk-solution interface [51]. While less work has been committed to resolving the challenges of operating light-driven systems using reactants delivered in the vapor phase, this now represents an intensifying effort in the photoelectrochemical (PEC) device community (figure 7) [52]. Vapor-fed systems carry the potential for operating at high current densities [53], while mitigating light scattering induced by solvent-suspended particulates, and near-infrared absorption interference from water's vibrational modes. Furthermore, the use of vapor feeds—particularly under neutral-pH conditions (albeit with the use of membrane ionomers often containing acidic or alkaline groups)—could slow corrosive processes via reduced exposure of redox-active system components to the caustic electrolytes often used in electrolyzers. Finally, implementing vapor feed in membrane-electrode-assembly configurations provides a promising method of optimizing substrate delivery while minimizing ion transport distances. These possibilities speak to the potential for vapor-fed devices in extending the operational lifetimes and scale of solar-fuels systems—chief bottlenecks in the advancement of PEC systems—from those of benchtop curiosities to those of real-world deployments. Although aqueous electrocatalyst immersion makes particular sense for anodic water oxidation (see section 15), where the reactant concentration is high (55.4 M), such considerations do not generally apply to the favored set of candidate transformations for solar-fuels devices. Notably, the low water solubility of CO_2 and N_2 make photoelectrochemical systems converting these substrates highly susceptible to mass-transport limitations, and may therefore preclude their future applicability in solar-concentrated systems. Vapor-phase systems offer one possible route around such mass-transport roadblocks, enabling direct chemical reactivity between electrodes and gaseous reactants without having to pre-dilute them in liquid media. However, adoption of vapor-fed technologies will require an improved understanding of performance degradation mechanisms and the phenomena influencing product distributions in CO_2 and N_2 reduction in these devices (see section 17). Furthermore, expanding the array of economical electrocatalysts and solar absorbers available for practical solar-fuels synthesis will also be critical.

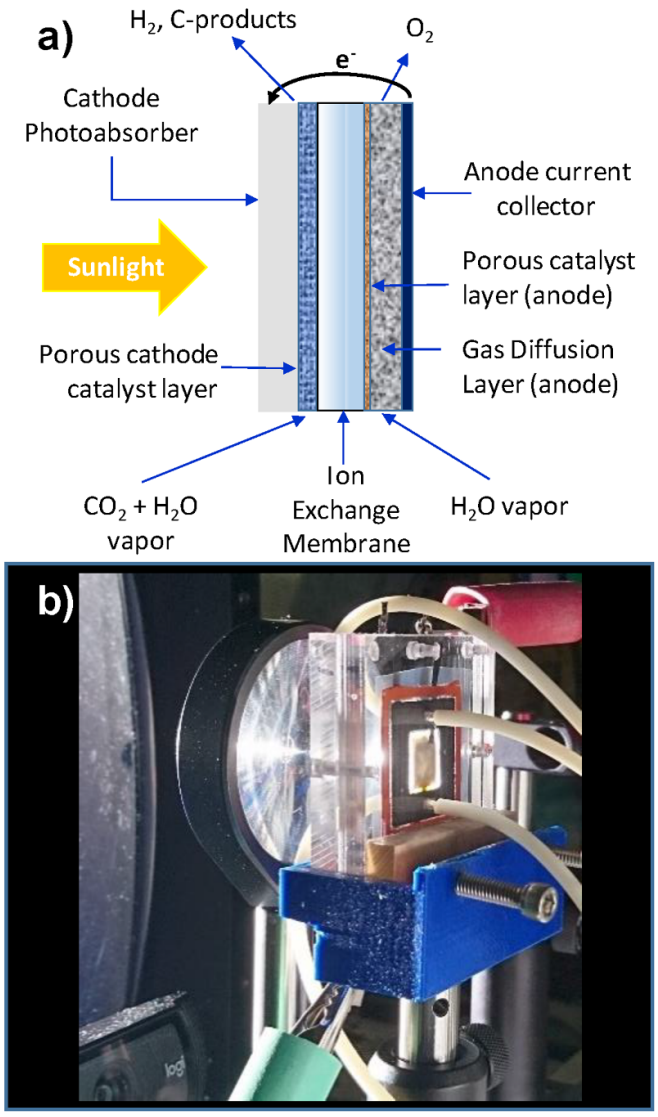

Figure 7. (a) A potential configuration for a future solar fuels device integrating light-absorbing and electrochemical subunits into a single platform. (b) A vapor-fed, integrated solar fuels prototype for CO_2 conversion to syngas ($H_2 + CO$), under solar concentration (5 suns). Light absorption occurs on the cathode side of the device at a centrally-located PV. The cathode operates in a vapor-fed configuration using a humidified CO_2 feed and carbon-supported gas-diffusion electrodes.

Current and future challenges

Despite significant progress made over the past half century, the field of solar fuels faces steep barriers towards real-world

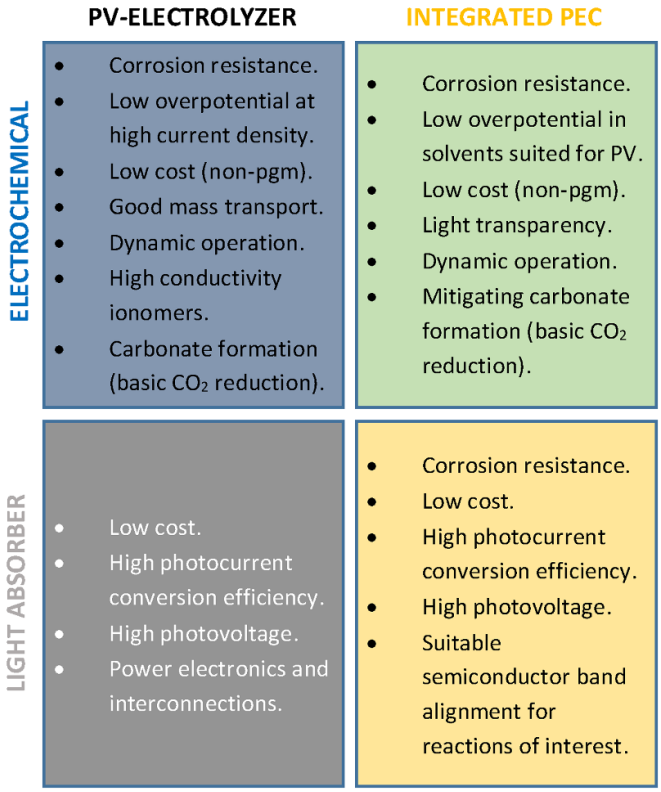

Figure 8. The various challenges facing solar fuels systems may be broadly partitioned among two device categories (integrated PEC devices vs discrete, PV-electrolyzer systems), with each architecture having a unique set of problems involving either the electrochemical or solar converting subunits of these devices.

implementation (figure 8; see sections 3 and 16). Key measures for the economic prospects of solar fuels systems include the requirements that such systems exhibit operational lifetimes of at least 10–30 years, while enabling reductions in the market-levelized cost of hydrogen and CO_2-derived fuels [3, 54]. Furthermore, the United States Department of Energy (DOE) has set an ultimate benchmark of 25% solar-to-hydrogen (STH) efficiency at a cost of \$2.10 kg^{-1} H_2, under concentrated illumination [55]; the 2021 launch of DOE's 'Hydrogen Energy EarthShot' initiative targets a price point of \$1 kg^{-1} H_2, sourced from a broad suite of renewables, within a decade [56]. While STH efficiency exceeding 30% under solar concentration has been reported, this required the use of platinum-group metal (pgm) catalysts under conditions of full aqueous immersion [36]. Past work suggests that electrochemical CO_2 reduction must reach energy conversion efficiencies of 60%, at renewable electricity costs below \$0.04 kW^{-1} h^{-1}, for broad deployment [54]. Realizing these targets will require the demonstration of devices using earth-abundant catalyst materials, and possibly alternatives to the expensive, III–V photovoltaics commonly used in lab-scale prototypes (see sections 3, 7 and 14). In the case of CO_2 electrolysis, enhancing CO_2 utilization by reducing carbonate formation, will be essential. Finally, enhanced device reliability under the intermittencies of diurnal illumination, rather than steady-state insolation, must be achieved.

Integrated PEC structures, where electrocatalytic and light-absorbing structures are collapsed into a single unit, have proven to be the more challenging of the solar-fuels device types, as they combine the complications of conventional PV-electrolyzer systems with the added constraint that the photoabsorber be chemically robust to degradative processes, such as solution-mediated photocorrosion. The requirement of chemical co-compatibility between PV materials and electrocatalyst operating conditions generally limits the options for device operation, often mandating techniques such as PV surface passivation when used in aqueous immersion PEC devices.

The problem of mitigating corrosion of electroactive components exposed to solution may find its resolution through the use of vapor feeds, where the effective concentration of water is substantially reduced relative to aqueous immersion. Recent work on vapor-fed PEC devices suggests that this may indeed be the case, with gas-fed systems displaying significant improvements in device lifetime upon transitioning from aqueous to vapor-fed cathodes [57].

Advances in science and technology to meet challenges

Addressing the challenges of vapor-fed solar fuels devices will require significant advancements in the domains of accelerated degradation testing, based on fundamental understanding of corrosion and operating stressors, and optimization of mass transport in these systems. Demonstrating a minimum viable product that can be readily scaled will also be key.

The severe disconnect between the timescales of device lifetime required for the economic deployment of solar-fuels devices, and the comparatively short timeframes available for their benchmarking, will make the development of accelerated-degradation test protocols crucial as these technologies mature. Insights into how this may be achieved may likely be adapted from extant work on dark electrolyzers, devices enjoying much higher degrees of technology readiness than their light-driven counterparts [58]. However, development and meaningful application of accelerated-degradation protocols will also require understanding the underlying stressors contributing to temporal performance losses. For example, drops in device current, increases in operating voltage or gradual efficiency losses over time, may conceivably find root in any number of causes, spanning electrocatalyst poisoning and delamination, to the flooding of electrode gas transport layers.

Substrate delivery in the vapor phase will also require the continued optimization of electrode microstructures and materials capable of reducing mass-transport-limited

currents, including both reactant gases and ions through solid-state ionomers (section 8). In particular, realizing optimized CO_2 electrolyzers will mandate devices that can saturate CO_2 at triple-phase boundaries—the confluence of ionomer, electrode and substrate junctions—while avoiding any potential flooding of the electrode structure (which impedes gas transport and, in CO_2/N_2 conversion, often exacerbates interfering H_2 evolution) [59]. In the context of atmospheric CO_2 removal, devices capable of either directly reacting CO_2 at atmospheric pressure or pre-concentrating it through the use of novel electrode microstructures, remains an area where significant breakthroughs may be realized. Neutral-pH feeds would also facilitate improved CO_2 utilization by reducing its conversion to carbonates relative to alkaline electrolysis. Finally, work optimizing mass transport in dark electrolyzers has demonstrated vapor-phase water oxidation occurring at 100 mA cm^{-2}, with low overpotentials [53]. Such advancements open the possibility of exploiting concentrated solar fluxes in driving vapor-fed, electrochemical hydrogen evolution and CO_2/N_2 reduction.

Concluding remarks

Neutral-pH, vapor-fed, solar fuels devices carry the potential to fulfill the promise of Fujishima and Honda. The intervening half-century since their initial discovery of PEC water-splitting has already delivered significant improvements in device efficiency, stability and solar utilization.

Yet, despite notable advancements by the field of solar-fuels, real-world devices will demand a continuation of breakthroughs. Economic viability of solar fuels technologies remains constrained, in part, by relatively short device lifetimes. These issues are especially pronounced for cases where non-pgm catalysts and solid-state polymeric conductors are employed, power intermittency is an issue or PV components are exposed to electrolyte. For solar-fuels devices where substrates other than protons are targeted for reduction, exerting control over the varied product distributions that can result from CO_2 and N_2 conversion to yield pure, or easily-separated fuel streams, will also be desirable. Such devices will minimize efficiency losses and the attendant costs of downstream separation processes.

6. Particle-based systems: lessons learned and guidelines for large area systems

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Status

The overall water splitting reaction driven by sunlight is studied as a means to produce renewable solar hydrogen on a large scale [60, 61]. Hydrogen produced in this way can be used not only as a fuel but also as a feedstock for various industrial chemical processes such as ammonia synthesis and carbon dioxide fixation. To put such technology to practical use, solar hydrogen production systems need to split water into hydrogen and oxygen efficiently and continuously, and be scalable over large areas. Particulate photocatalysts can theoretically fulfil these requirements, and thus have attracted significant attention in the past 40 years [62, 63].

In 1980, overall water splitting was first reported using particulate oxide semiconductors modified with nanoparticulate catalyst components [62]. The former is the photocatalyst generating photoexcited charge carriers, and the latter is the cocatalyst promoting surface redox reactions and charge separation from the photocatalyst. Since then, materials and structures of cocatalyst/photocatalyst composites effective in promoting the reaction have been investigated. Photocatalyst materials studied for overall water splitting in the early stages of development were mainly wide-bandgap oxides that only absorb ultraviolet light. In the 21st century, various types of photocatalysts were investigated to drive the reaction under visible light. These are typically based on narrow-bandgap non-oxides such as (oxy)nitrides and oxysulphides or wide-bandgap oxides doped with transition metals that induce mid-gap states. Often, two separate photocatalysts (one for hydrogen evolution and the other for oxygen evolution) are combined using electron mediators to construct two-step excitation (also known as Z-scheme) systems. Today, the solar-to-hydrogen energy conversion efficiency (STH) of photocatalytic water splitting achieved by particle-based systems reaches 1% at ambient pressure [64]. This value is one order of magnitude lower than those of electrolyzers and photoelectrochemical cells powered by photovoltaics. Nevertheless, recent improvements in the apparent quantum yield (AQY) (greater than 90% at 365 nm) [65], durability (maintaining 80% of the activity over 1300 h of constant illumination at ambient condition) [66], and visible-light response (utilizing light with wavelengths of up to 640 nm) [67] suggest that efficient sunlight-driven photocatalytic water splitting can be realized in the future.

Figure 9. An example of field test of solar hydrogen production by photocatalytic water splitting. Reprinted from [69] with permission. Copyright Agency for Natural Resources and Energy.

Current and future challenges

To make solar hydrogen production via photocatalytic water splitting economically feasible, photocatalysts are expected to split water at a STH of 5%–10% or higher [60]. To achieve this, photocatalytic systems must split water with an AQY of 30%–60% up to 600 nm [62]. Since no particle-based system has achieved high AQY and long-wavelength response simultaneously, the development of long-wavelength-responsive photocatalysts remains a critical challenge.

Attention should also be paid to the reactor, because solar hydrogen is not ready for use if hydrogen and oxygen are just evolved from the photocatalyst suspension. It is necessary to build systems that can receive sunlight adequately and equipment that can process the product oxyhydrogen gas efficiently and safely [63]. These should be scalable to the kilometer scale to produce a meaningful amount of solar hydrogen. Importantly, even assuming a system life of ten years and a system STH of 10%, the system cost should not exceed 100 USD m^{-2} to allow a reasonably low price for the products hydrogen and oxygen (3.5 and 0.1 USD kg^{-1}, respectively) [60].

The authors have been studying panel reactors and gas-separation membrane equipment to visualize critical challenges associated with scaling up particle-based systems beyond laboratory scale (figure 9) [68, 69]. A modified $SrTiO_3$ photocatalyst was immobilized on substrates, and the resulting photocatalyst sheets were wetted with water at a depth of 100 μm in panel reactors. Under natural sunlight irradiation, the product mixture of hydrogen and oxygen gas was collected smoothly. Notably, the activity of the photocatalyst was maintained without forced convection of water despite the large size of the reactor. Moreover, hydrogen was recovered from the mixed gas product (H_2:O_2 = 2:1) over several months without any accident. In fact, by suitably designing the reaction system, it was possible to avoid the explosion causing any damage

even under intentional ignition of oxyhydrogen gas in the system. Nevertheless, further improvements in the construction and operation costs and the energy efficiency are essential for real-world applications.

Advances in science and technology to meet challenges

The efficiency, lifetime, cost, and scalability requirements for the particle-based systems are very stringent. In fact, these are common to all solar fuel production systems, considering the cost competition with existing fuel technologies. Some visible-light-driven photocatalysts can drive overall water splitting under long-wavelength light irradiation. The target STH value of 5%–10% can be achieved if the AQY of such photocatalysts can be upgraded to similar levels to the efficient wide-bandgap oxide photocatalysts (figure 10). Recent progress in material preparation provides hints for the performance improvement of photocatalysts. In the study on the highly-efficient $SrTiO_3$ photocatalyst [65], decreased majority carrier and defect concentrations [70], reduced particle sizes, exposed non-equivalent crystal facets, and facet-selectively co-loaded cocatalysts played important roles in minimizing charge recombination during overall water splitting. For the development of $Y_2Ti_2O_5S_2$ [67] and Ta_3N_5 [71] that were active in visible-light-driven water splitting, single-crystalline particles with low trap densities were a key innovation. Sunlight-driven water splitting with sufficient STH may be realized if single-crystalline fine particles of visible-light-driven photocatalysts exposing different crystal facets are modified site-selectively with cocatalysts, so that charge separation can be promoted. Furthermore, photocatalysis is a phenomenon that occurs in a non-equilibrium state under photoexcitation, and particulate photocatalysts inherently have inhomogeneity in properties within and among particles. Therefore, the development of particle-based systems may be accelerated by advances in science and technology that can track the processes occurring under photoexcitation with high spatial and temporal resolutions [72]. An improved understanding and control of charge separation in particle-based systems is very important in this regard [60, 61, 65, 72, 73]. Additionally, the future of photocatalysts strongly depends on the availability of visible light active semiconductors that are stable under water splitting conditions [74].

Design of photocatalytic reactors and hydrogen recovery processes are also critical issues. To be outside the explosion limit, the product mixture of hydrogen and oxygen gas must be converted by membrane separators into >95% pure hydrogen in the filtered gas and <4% hydrogen in the residue gas [63]. The individual components of the panel reactor and the gas separation equipment and their integrated whole system should be improved considering the production and operation costs and energy. Because complete processes for solar fuel production using particle-based systems have not been established, various possible options need to be examined from a chemical engineering perspective.

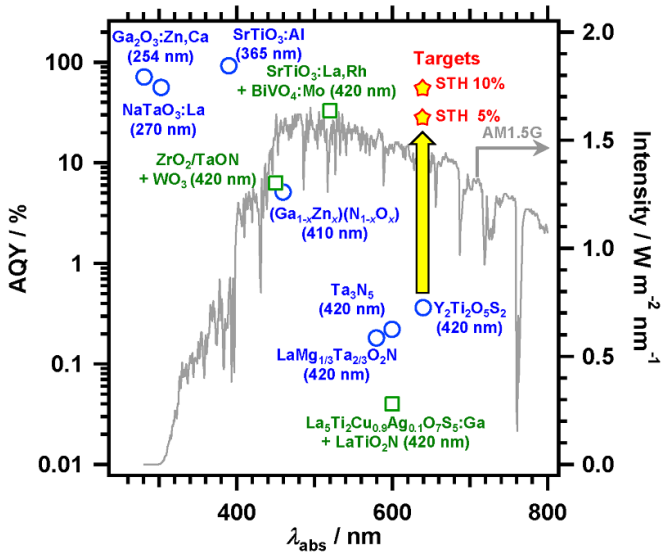

Figure 10. Relationship between the absorption edge wavelength (λ_{abs}) and the apparent quantum yield (AQY) for overall water splitting of some photocatalysts. Circles and squares represent one-step and two-step excitation systems, respectively. The wavelengths at which the AQY values were measured are shown in parentheses. The power spectrum of the reference sunlight (air mass 1.5 G) is also plotted on the right axis for comparison.

Concluding remarks

Large-scale solar hydrogen production will have a big impact on the energy industry. Particle-based systems are considered promising due to their low cost and scalability, and due to the option of immobilizing thin photocatalyst layers on substrates, as in panel reactors, and recovering hydrogen by membrane separation. However, many technological innovations on the individual components and the entire integrated system are still required for practical application. In particular, little technological development has been made on reactors and gas separators that are specialized in hydrogen production by photocatalytic sunlight-driven water splitting. It is very important to demonstrate a working prototype of the entire system and provide an outlook in the near future, because the entire process cannot be established if any of the essential technologies are missing. Such attempts will stimulate research in various fields with the aim of establishing large-scale, cost-effective, and energy-efficient renewable solar hydrogen production systems.

7. Device design considerations for scale-up: managing photons, electrons, and ions

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Status

With relatively high efficiency of >15% reported using integrated solar fuel devices, research efforts have been extended to include demonstrations beyond the typical laboratory scale. Indeed, several projects have targeted the demonstration of large-scale solar fuel devices. Scalable device designs are needed to minimize performance losses associated with scale-up, since the photoabsorbers and catalysts properties often do not limit the large-scale device performance. About 20 designs based on different integration levels have been proposed and demonstrated [75], but the most scalable ones are not clear. Here, we limit the discussion to devices using photoelectrochemical approaches, since photocatalytic and particle-based systems have been discussed in section 6.

There are at least three scaling methodologies for photoelectrochemical fuel generating devices (figure 11). The first, perhaps the most common one, is scaling by dimension or size of the device's photoactive area. Panel-type devices using tandem absorbers could be employed to ensure optimal sunlight utilization. A WO_3-based device with a photoactive area of ~130 cm^2 has been reported with an efficiency of ~2% [76]. Significant ohmic losses due to larger substrates and bubbles as well as concentration overpotentials due to unoptimized fluid dynamics have been identified as the main limitations. Multiphysics simulations using theoretical models have been conducted to quantify these losses [77, 78], which are found to be more important in devices operated in near-neutral pH electrolytes. These simulations are extremely useful in identifying the optimal design and operational conditions to be demonstrated at a larger scale. However, the established models often employ simplified boundary conditions, which need to be validated against experimental observations. Once a functional unit size (i.e. module) is identified, scaling can happen (or continue) by number. In this case, fluidic and electrical connections and the identification of sharing strategies for balance of system components become the challenge. A large modular device with a photoactive area of 6400 cm^2 has been demonstrated (100 units of 64 cm^2) [79], but its efficiency is limited to <4%. Scaling by flux or (irradiation) concentration is the third scaling approach. At high concentrations, heat management becomes extremely important; an integrated design allows for better heat transfer from the photoelectrode to the electrolyte. Efficient mass-transport is also essential at high concentrations with current densities approaching 1 A cm^{-2},

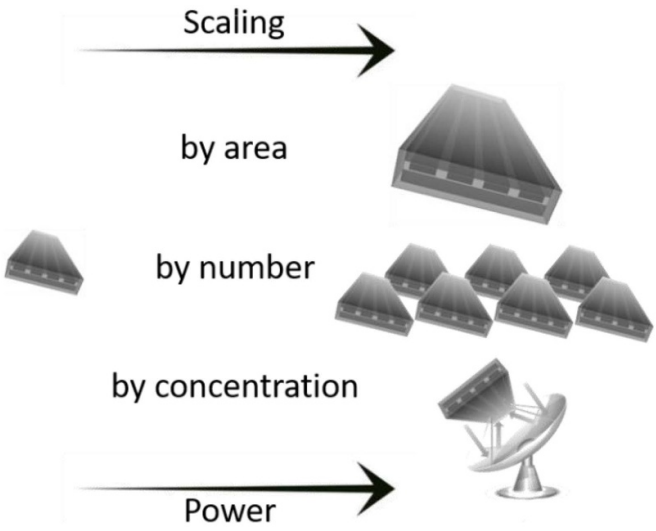

Figure 11. Possible scaling strategies of a photoelectrochemical device: (i) scaling by size, which includes the increase in the photoabsorber area, (ii) scaling by number, which includes the multiplication and connection of sizable units, and (iii) scaling by concentration, which includes the increase in irradiation concentration. All approaches (which can also be combined) will increase the input and output power of the system.

which can, for example, be achieved by decoupling the photoactive area from the electrochemical area via employing catalysts deposited on a gas diffusion layer. This approach is also used in solar-driven CO_2 reduction devices [80]. All scaling approaches work towards increasing the power of the device. The highest demonstrated output power of a photoelectrochemical water splitting device is ~27 W (under 474 suns concentration) at an efficiency of ~15% (figure 12) [35]. Even a higher output power of ~760 W has been reported by a 100 m^2 demonstration facility (1600 units of 625 cm^2) [68], but the facility utilized photocatalyst sheets instead of a photoelectrochemical approach, which is discussed in section 6.

Current and future challenges

Different photoelectrochemical reactions (hydrogen, CO, ethylene, ethanol, ammonia, etc) pose different challenges for scaling, owing to their variation in dominating physical phenomena, phase of reactant, production rates or product purity. One common challenge is related to the observation that there is no unique condition that describes the device operation, even when intended during design. The coupled transport of charge (electrons, holes, ions), mass (reactants, products) and energy (radiation, heat) leads to multiple orders of magnitude variations in the variable fields (e.g. ion concentration and current) of the reactor and individual components. These variations typically increase with larger physical dimension, i.e. scaling by size. Consequently, when optimizing a photoabsorber or co-catalyst for a certain pH condition, this condition might not be relevant for a large part of the scaled device. Understanding

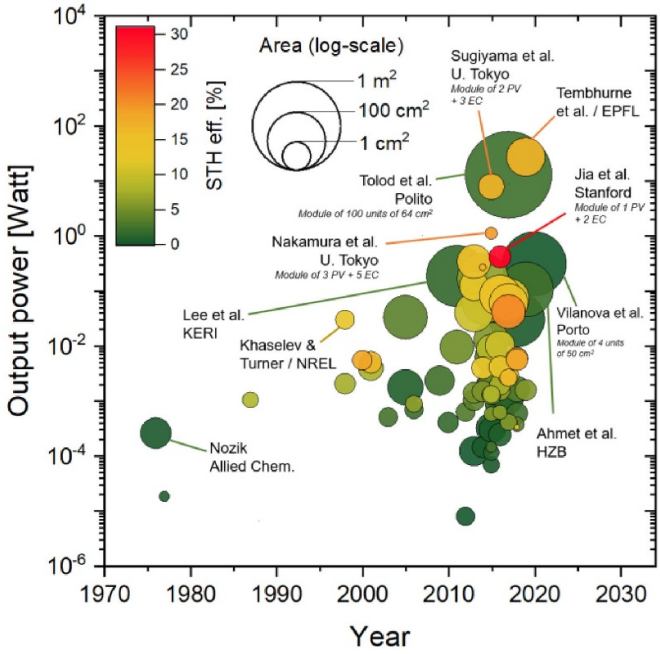

Figure 12. A comparison of photoelectrochemical water splitting devices (i.e. H_2 production) reported in the literature, taken from the combined lists of [35, 81]. The reported solar-to-hydrogen (STH) efficiency, device active (i.e. light absorber) area and the corresponding output power of the devices are shown. Five modular devices where multiple units are combined (i.e. scaling by number) are also identified.

the source of the heterogeneities and developing approaches to deal with them are needed. The same applies to external operating conditions. While lab-scale devices are investigated and demonstrated under controlled indoor conditions (AM1.5 spectrum, 1000 W m^{-2}) at their intended design point, one-sun large-scale operation will result in changes in spectrum and intensity of sunlight, dependent on location, atmospheric conditions, daytime, season, etc. Robust materials, (scaled) device and system designs, and/or controlling approaches are needed to ensure reliable and optimized operation.

Significant efficiency reductions are observed when devices are scaled by size [81]. Effects that are irrelevant at small scales (e.g. electrolyte ohmic losses) start to dominate the performance [79]. Similarly, scaling by concentration (i.e. increased current density) can lead to dominating mass transport effects and—in the case of CO_2 reduction—might significantly affect the operating conditions of the catalysts (i.e. selectivity and activity).

Scaling is currently also limited by the lifetime of materials, components and devices [31]. Understanding, quantification and mitigation of degradation is required (see section 3 on efficiency and stability benchmarking). Additional scale-up challenges exist in terms of the auxiliary components (e.g. pumps, separators), which might not exist in a fitting scale yet. They consume energy and will reduce the overall performance. Understanding how the device performance relates to the system performance has yet to be determined.

Advances in science and technology to meet challenges

Advances in the fabrication processes that allow reproducible and homogeneous deposition of photoelectrodes (absorbers, catalysts, buffer and protection layers) on large areas are needed. Current screen printing or dip/slurry coating methods are easily transferred to large areas—already done in industrial battery production—but the homogeneity and reproducibility are less guaranteed. On the other hand, more reproducible processes (atomic layer deposition, physical vapor deposition, molecular-beam epitaxy, etc) are challenging to scale to larger areas.

With scaling to larger device area or power, the development of transparent conducting substrates with metallic conductivity becomes important to minimize substrate ohmic losses. Similarly, electrolytes with superior conductivity are desired to minimize the electrolyte ohmic losses. This can be achieved using highly concentrated acid or base, but near-neutral pH electrolytes with similar conductivity are still elusive. Alternatively, a device design that minimizes the ionic transport pathway (e.g. perforated, Louvered design) [75] is needed. For a typical liquid electrolyte (conductivity 100–200 mS cm^{-1}) and a current density of $\sim$10 mA cm^{-2}, the ionic transport length-scale needs to be kept <1–2 cm for an acceptable level of ohmic losses (<50 mV) [78].

Advances in method development and understanding are also crucial. Extensive performance characterization requires a locally resolved assessment of operating conditions, efficiencies or production rates. This allows to identify if the photoelectrode and/or the complete device is fully or partially utilized. Simple current–voltage or efficiency measurements are not sufficient, and advanced experimental techniques that can provide locally resolved information on multiple scales need to be developed (e.g. in-operando nano-tomography, three-dimensional scanning electrochemical microscopy, segmented test cells).

Heat transfer is often neglected given the (perceived) isothermal R.T. operation of many devices, but this becomes more important at larger scale. The actual operating temperature in a device and its various components needs to be characterized, and heat management strategies are needed to control and maintain the desired temperature. Gas-bubble management is also needed in large-scale devices as longer transport pathway and/or higher bubble density are present. Product collection and mass-transport are important, and any further bubble-related losses (e.g. optical, activity) should also be minimized. Advanced modelling and validation experiments are needed to reveal key parameters to control bubble nucleation, growth and transport.

The development of transient multi-scale and multi-physics models is required to predict experimentally inaccessible information. These models need to be optimized for computational expense while providing sufficient physical detail. Robustness and versatility is a particular concern for such coupled and highly nonlinear problems to ultimately develop a digital twin of the component, device or system.

Finally, the operation of PEC devices requires the design of complete systems with matching auxiliary devices as well as the ability to adapt to rapid changes in the irradiation conditions and robustly operate at broad environmental conditions. Given the specific flow conditions and stream compositions, new auxiliary devices need to be developed that match the plant requirements [82]. Model predictive control may also be applied to ensure optimal performance while satisfying a set of constraints given by e.g. degradation mitigation strategies.

Concluding remarks

Scaling of photoelectrochemical processes is needed to ensure technology development and transfer from the laboratory to the market in the transition towards a sustainable energy economy and chemical industry. Scaling strategies include increasing the device power (density) by increasing the size of the photoactive component, increasing the irradiation concentration, and/or connecting and multiplying multiple units into a larger system. Successful scaling requires full understanding and control over the multi-physical and multi-phase transport aspects of a device and its integration into a full system including the auxiliary components. Specific transport aspects (e.g. bubbles, heat transfer) need considerable attention especially in large scale systems. Identifying the practical operating conditions of a device and its components is challenging, given the fluctuating solar irradiation or the heterogeneities in the component's or device's concentration, current or potential fields. Furthermore, the dominating (transport) losses might change when scaling a device, requiring re-focusing attention and optimization approaches.

8. Membranes for solar fuels

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Status

A membrane separates the cathode from the anode in a (photo)electrochemical solar fuels device. It functions as a transport medium for ions while limiting the transport of reactants and products, whose crossover can compromise device efficiency and safety. In a conventional electrochemical cell, liquid electrolyte is present between the electrodes and the membrane. In a membrane electrode assembly (MEA) configuration, the membrane is in direct contact with the electrodes, and is hydrated by a liquid electrolyte or by water vapor (section 5) through a gas diffusion electrode (GDE). A GDE also allows for a gaseous CO_2 or N_2 feed and, therefore, improved reactant mass transfer and larger current densities.

Solar fuels devices have, so far, largely employed commercial polymer electrolyte membranes optimized for other applications. However, the properties of these materials are, in many cases, inappropriate for water splitting and/or carbon dioxide reduction (CO_2R) at rates commensurate with the terrestrial solar photon flux, i.e. 1 sun of air mass 1.5 global (AM1.5 g) irradiance. For example, Nafion, a perfluorinated sulfonic acid polymer membrane used in state-of-the-art fuel cells and low-temperature electrolyzers, exhibits relatively high permeability to H_2 and O_2, which negligibly impacts performance at high current densities, but can result in an explosive mixture of gases (e.g. when operating at solar current densities ($\sim$20 mA cm^{-2}) for a typical membrane thickness (50 μm), at room temperature and at H_2 pressures as low as 1 atm) [83, 84]. Moreover, the temperature-dependent ionic conductivity of Nafion is orders of magnitude higher than necessary for small ohmic resistive voltage losses under 1 sun operation [84]. This example underscores how knowledge of incident light intensity (e.g. time of day, optical concentration) and photoabsorber efficiency are required to identify desired membrane properties for solar fuels devices.

Desirable membrane properties inextricably depend on other device components (e.g. electrocatalyst(s), electrolyte(s), photoabsorber(s)) and whether they are integrated or separated, because variations in component sizes can be used to match species fluxes through membranes and other components. Many electrocatalysts for CO_2R exhibit poor product selectivity (section 17), meaning that the membrane must limit transport of a multiplicity of products with differing physicochemical properties and concentrations while maintaining sufficient ionic conductivity [85, 86]. Notably, imidazolium-functionalized polymers have been investigated as anion-exchange membranes due to their relative stability in alkaline electrolytes, and at least one such material has been commercialized for application in artificial photosynthesis [87].

Current and future challenges

The principal function of membranes is to selectively control solute transport, which can be quantified in terms of, for example, solute permeability, solubility, diffusivity, mobility, and conductivity. For example, membranes in water splitting devices should readily permit transport of H^+/OH^- ions, but not H_2 and O_2 products.

Polymer electrolyte membranes with charged groups covalently bound to the polymer chains are attractive because they are generally highly hydrated, providing pathways for ion transport. However, optimization of membrane properties is a complex tradeoff (figure 13) because, in general, ions, soluble gases, and neutral liquids all transport via the same hydrated interstitial spaces among polymer chains. Transport is driven by gradients in electrochemical potential, and transport rates are determined by properties such as solute size and shape [85]. Control over transport during CO_2R is particularly complex, because the membrane should (a) limit transport of reaction products, including uncharged CO, alcohols (e.g. methanol, ethanol), other hydrocarbons (e.g. ethylene), and charged species (e.g. formate, acetate) [86], (b) promote transport of H^+/OH^- to provide mass balance with protonic species consumed or generated by redox reactions, and (c) mitigate transport of reactants, such as CO_2(aq) and dissolved inorganic carbon ions that are commonly present at mildly alkaline pH (e.g. bicarbonate, carbonate). Ionic current carried by species other than H^+/OH^- represents losses due to increased voltage demands from changes in local pH, unstable pH from loss of buffering capacity, loss of reactant CO_2 when dissolved inorganic carbon species crossover, and energy required to periodically refresh the electrolytes (to minimize scale formation, for example) [88].

Thermal, mechanical, and chemical stability are other critical parameters. Solar intensity fluctuations mean that membranes may be subject to elevated and varying temperatures, variable species concentrations or pressures that can stress membranes, and even ultraviolet light, which generates high-energy electronic states that are prone to side reactions known to degrade polymers. Water splitting devices are often operated under extreme electrolyte pH conditions, where many polymeric materials are kinetically unstable. CO_2R devices typically employ milder electrolytes. Mixed electrolytes, such as seawater, have been proposed, further complicating membrane optimization and likely requiring pretreatment to remove biological, organic, and inorganic components.

Advances in science and technology to meet challenges

Alternative membrane materials with, for example, new chemistries and morphologies are needed to selectively block small neutral solutes, such as gases and small alcohols, but

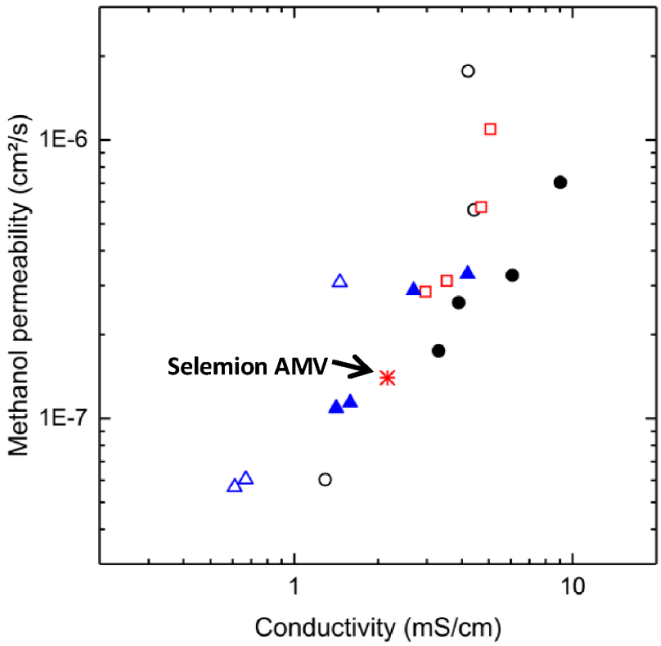

Figure 13. Experimental tradeoff between electrolyte ionic conductivity and CO_2 reduction product (methanol) permeability for a series of poly(vinyl imidazolium) membranes. For reference, a commercial anion exchange membrane, Selemion AMV, is indicated. Reproduced from [85] with permission from the Royal Society of Chemistry.

permit passage of ions, which are often larger due to solvent coordination. Non-polymeric electrolytes, which are typically used at elevated temperatures (e.g. solid oxide electrolytes), warrant consideration because they prevent virtually all reactant/product crossover, breaking the tradeoff exhibited by many polymeric membranes (figure 13) while providing sufficient ionic conduction for negligible resistive voltage losses under 1 sun operation. GDE–MEA designs provide opportunities for direct separation of solid products by coupling non-protonic ion transport to the vapor-fed catholyte, e.g. through direct formation of acetate salts from gaseous or aqueous reactants [89]. In MEA devices, close proximity of the membrane to electrocatalyst microenvironments also provides opportunities for membrane-gated control over the availability of reactants, electrolyte, water, and even photons, to (photo)catalytic sites.

Depending upon the kinetic stability and activity of various device components, a single electrolyte composition is not necessarily ideal. A bipolar membrane, which consists of a cation exchange material in direct contact with an anion exchange material, can overcome these stability and activity limitations by enabling the use of anolytes and catholytes of differing pH. For charge and mass balance, these membranes drive heterolytic water dissociation or formation, which is catalyzed by protic functional groups and the presence of electric fields, either at a planar membrane interface or interfaces between membranes and ionomers in catalyst layers [90]. Means to precisely alter the local microenvironment near these protic groups to tune their catalytic performance are warranted.

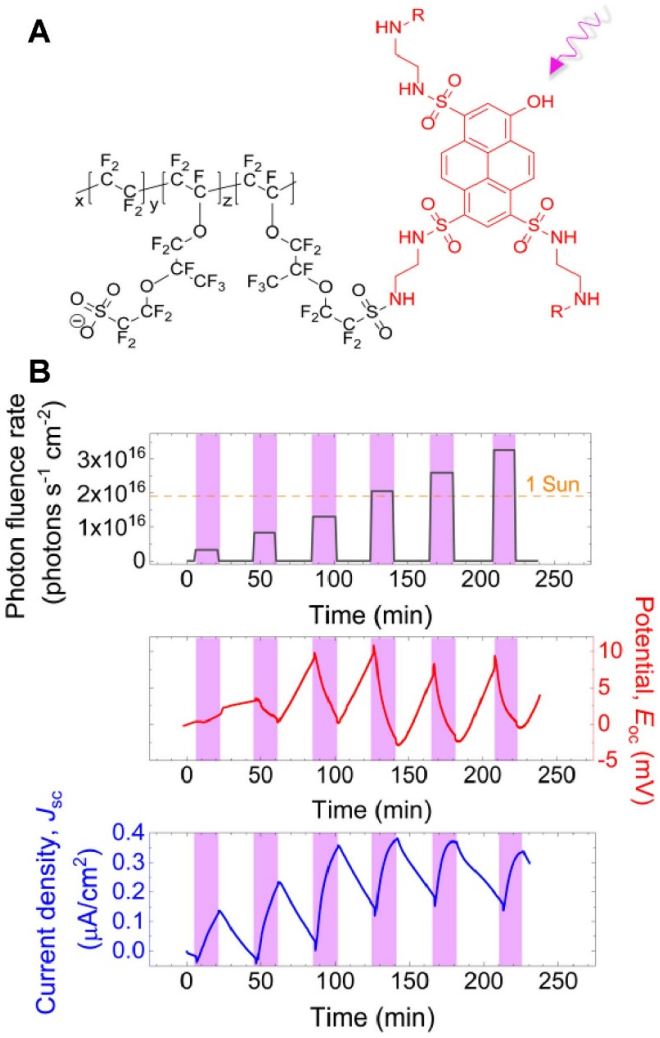

Figure 14. Photoelectrochemical data and analyses of representative protonic solar cells. (A) Chemical structure of pyrene-based photoacid dyes covalently bound to fixed-charge groups in a perfluorosulfonic acid cation exchange membrane that was interfaced with a Sustainion XA-9 anion exchange ionomer layer (not shown) to form a bipolar membrane protonic solar cell. (B) Photon fluence rate incident on the anion exchange layer side of a protonic solar cell MEA (top), transient open-circuit potential (E_{oc}, middle) and short circuit photocurrent density (J_{sc}, bottom) as a function of time, illuminated for 15 min (purple intervals) and then kept in the dark for 25 min (white intervals) for each fluence, and with the condition of 1 sun equivalent excitation indicated. Reprinted from [93] with permission from Elsevier.

Because of the use of sunlight in solar fuels devices, composite photoabsorber–membranes have been used [91, 92], including direct light-driven proton pumps where photoacids alter the electrochemical potential of H^+/OH^- [93] to provide an additional driving force for solar fuels reactions (figure 14). Light can also be used to modify membrane properties to control ion transport, mitigate product crossover, or change local pH to enhance kinetic stability and electrocatalytic activity. Polymer morphology and physicochemical properties can be adapted to alter solute transport and membrane stability using, for example, dye molecules that undergo photoinduced

isomerization processes or light-driven ligand rearrangement. Local pH can be modified using photoinduced changes in pK_a of photoacids, photobases, or polymer units that undergo dynamic shuffling of covalent bonds [94], to further control species transport and materials stability.

Concluding remarks

A polymeric or solid-state membrane is a critical component of solar fuels devices. While multi-disciplinary, collaborative experimental and theoretical/numerical work has provided valuable insight into membrane function at equilibrated, or nearly equilibrated, conditions [86, 88], a significant collaborative effort is needed to design membrane materials and understand their function under the highly dynamic conditions of varied light intensity and temperature. Successful next-generation membranes will likely require the development of polymers that exhibit new transport mechanisms and break empirical tradeoffs between the desirable transport of electrolyte ions and the undesirable transport of CO_2R reactants and products. When used in integrated design structures, membranes should be designed and developed in concert with electrocatalyst(s), electrolyte(s), photoabsorber(s), and other device components, because their performance and limitations are co-dependent. GDE–MEA configurations provide further opportunities for deep integration of materials function. Intentional introduction of photoabsorbers into membranes is a design concept that is still in its infancy and may provide unforeseen benefits to traditional uses of membranes in the dark.

9. Photoelectrodes based on conventional semiconductors (silicon, III–V)

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Status

Since the 1970s (e.g. [95]), researchers have investigated direct synthesis of fuels from sunlight by employing silicon (Si) and/or III–V semiconductor photoelectrodes in either single-junction or multijunction configurations. Photo-absorbers that target high solar-to-fuel (STF) efficiency in a range beyond 15% require tandem designs and suitable performance. For direct water splitting, two-junction configurations with optimized bandgap combinations of ca. $E_{gap}^{Si} = 1.1$ eV and $E_{gap}^{III–V} = 1.7$ eV can provide sufficient photovoltage whilst efficiently utilizing the solar spectrum, such that the only losses in performance are carrier thermalization and radiative recombination. These structures enable efficient absorption of sunlight by leveraging advances in (a) scalable, high-quality, and low impurity-level crystal growth by, for example, metal-organic chemical vapor deposition (MOCVD), (b) solid-solid junctions, and (c) interfacial chemistry designed for facile carrier separation while avoiding non-radiative recombination. Photoelectrochemical cells (PEC's) incorporating Si and/or III–V photo-absorbers are one of several distinct solar fuels approaches, which include PEC's that use metal oxide photoelectrodes to both generate energetic charge carriers and catalyze fuel evolution or water oxidation reactions, and wired systems that physically decouple electrochemical fuel synthesis from sources of wind- or solar-derived electricity. Unlike most metal oxide photoelectrodes, which are often stable but tend to be inefficient, Si and most III–V semiconductors corrode in aqueous electrolytes under wide-ranging potential and pH conditions [96]. Moreover, Si and III–V photoabsorbers must be connected in some fashion with active and selective electrocatalysts to achieve highly efficient fuel synthesis. Therefore, advances in corrosion protection, charge separation, and catalytic functionalization have been essential for PEC's incorporating Si and III–V semiconductors. These multiple functionalities can be achieved by layered structures such as the one sketched in figure 15. Atomic layer deposition [97, 98] has emerged as a key layer-coating method for both planar and complex surface topologies to suppress corrosion and provide additional functionality to these devices. Polymeric encapsulants with exposed catalysts [99] have also been studied recently as an integration scheme for the stable operation of multijunction semiconductor photocathodes. Moreover, the reactive transformation of surface layers on devices during catalyst deposition [100] can be leveraged to enhance PEC efficiency while achieving improved stability.

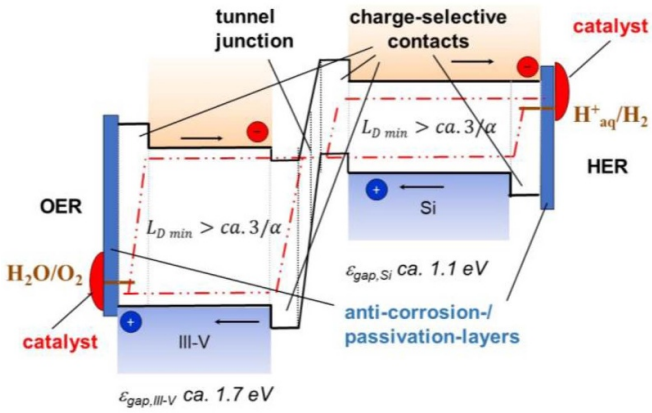

Figure 15. An idealized electronic band diagram and the charge carrier trajectories in a Si/III–V tandem structure plus surrounding functional layers, catalysts, Fermi-levels, and redox potentials for water splitting.

Current and future challenges

State of the art PEC demonstrations have focused almost exclusively on water splitting because of present-day limitations on electrocatalyst selectivity in producing value-added chemicals other than hydrogen whilst achieving low separation cost. Multijunction PEC devices fabricated using either silicon or III–V semiconductors have achieved solar-to-hydrogen conversion efficiencies exceeding 10%, and continuous operation for 10's–100's of hours [8, 101]. Progress was made recently in the low-defect heteroepitaxy of III–V-on-Si by MOCVD. In this case, 2 μm III–V layers deposited on Si are sufficient to produce a tandem absorber that meets the requirements of efficient PEC. Compared to III–V multijunction PEC devices, relatively little work has been reported on Si/III–V tandem structures, which may provide a cost-competitive approach to photoelectrode-based fuels production.

Among the photoelectrode measurements reported, most have been performed under continuous 1 sun simulated insolation. Although testing under moderate (<50 suns) concentration and on-sun testing have been reported in some studies, reports of diurnal solar cycles that reveal real-world relevant durability have been less common. The stability of both the semiconductor photoabsorbers and catalysts on the photoelectrodes remains a significant challenge for their future commercial adoption. Moreover, mechanisms underlying PEC device failures are poorly understood. These may include a combination of (photo)corrosion of the semiconductor electrodes, catalyst poisoning, catalyst debonding (akin to stress-corrosion cracking) under redox conditions that cause local

expansion of catalyst layers or nanoparticle, erosion of surfaces due to cavitation around bubbles, and coating deterioration due to porosity and redox cycling. Indeed, little consensus exists among researchers as to the most appropriate methods for stability testing or of standards to be used in reporting such data. High-rate oxygen evolution on anodic photoelectrodes tends to generate acidic pH locally. It occurs at the positive potentials that cause oxidative corrosion of most semiconductors and metals, and the highly anodic potential may cause electrochromism of the coating leading to the undesirable optical absorption. Some device architectures reduce the risk of attack of the semiconductor photoabsorbers by using a dark anode wired to a multijunction photocathode. If configured so that both hydrogen and oxygen are evolved in a compact electrochemical cell attached to the unilluminated side of the photoelectrode, losses due to bubbles that nucleate on the electrode surfaces, scattering light and transiently occluding reactive sites on surface catalyst layers can also be avoided. Therefore, photoelectrode designs and operational principles of PEC's incorporating Si/III–V semiconductors in planar or wire architectures also require substantial development and testing.

Advances in science and technology to meet challenges

Important advances are required in functional components to meet these challenges including: (a) multijunction photoabsorbers that permit efficient light capture and conversion, (b) multifunctional interfacial electronic passivation for preventing non-radiative recombination and chemical passivation for corrosion protection, (c) stable catalyst binding to protective coatings, and (d) electronic state alignment of all functional components. Besides, both experimental and theoretical understanding of the corrosion mechanisms, light-driven electrochemical reactions, and the interfacial charge carrier dynamics are needed. For example, advanced characterization, including operando methods, can reveal the mechanisms underlying PEC device failures specific to exposed surfaces and local corrosion environments. Understanding the corrosion mechanisms will inform new designs that are tolerant to corrosion defects [102]. These corrosion defects can be further mitigated and repaired by developing inspection and deposition technology. Consistent effort by the research community will help establish best practices for stability testing and eventually a consensus for reporting such results [103].

Co-designing Si/III–V photoelectrodes and their catalysts and functional layers (e.g. protective coatings) for efficiency, stability, and cost-effective manufacturing is required to meet practical production and scale-up challenges. An opportunity to address such challenges is to develop cost-effective manufacturing processes for III–V/Si tandem absorbers. A combination of GaAsP as the top cell and Si as a bottom cell protected by functional coatings appears to be a particularly attractive solution. Figure 16 represents the depiction of the III–V-semiconductor compounds, Si, and Ge with their nature of bandgaps and lattice constants. These sketches show some of

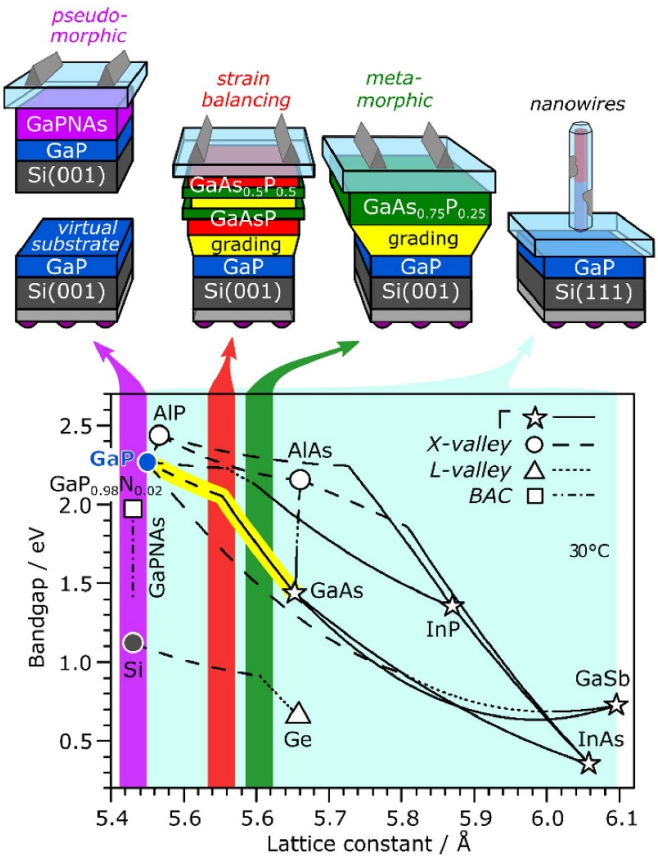

Figure 16. Integration of III–V materials with silicon substrates: variations of epitaxially grown III–V-on-Si device structures for advanced photoelectrodes.

the possible variants of epitaxially grown photoelectrochemical III–V-on-Si device structures for the highest STFs conversion efficiency together with sketches of functional layers (e.g. protection and passivation) and catalyst structures. Via the variation of stoichiometries of the III–V compounds, pseudomorphic, strain-balanced, metamorphic and nanowire-based top cell approaches can be realized, identified by pink, red, green, and light blue colors, respectively. In addition, co-designing III–V multijunctions and electrochemical membrane electrode assemblies can take advantage of thermal energy resulting from high solar concentration to increase electrocatalytic reaction rates to match with the high currents per catalyst surface area [35]. A great potential for full spectrum and efficient photovoltaics has been ascribed to III-nitride-based absorber layers already for a long time [104]. Hitherto, they are still lacking of competitive PV performance due to low minority charge carrier life times and, thus, greatly reduced diffusion lengths. Nevertheless, they can also be considered as functional overlayers of photoelectrodes such as passivation layers and catalyst support [105].

For cost-effective manufacturing of III–V/Si tandem photoabsorbers at an industrially relevant scale, MOCVD is well-established. Major advances in *in situ* growth control and *ex situ* characterization, as well as molecular level theory and kinetic growth simulations increasingly elucidate

critical processes such as surface evolution, nucleation, interfacial reactions, and vapor phase chemistry and transport. Building on recent experience, new reactors and processes should allow high-quality layer structures to be deposited in a few minutes, for the absorber films at growth rates in the range of 100 μm h^{-1} with substrate diameters or lengths of 100–150 mm.

Concluding remarks

Multi-disciplinary efforts are needed to advance the efficiency, stability, and scalability of solar-driven chemical production. These include engineering of semiconductor morphology and multijunction architectures, protection layers, contact arrangement (e.g. charge selective contacts), and reactor-engineering considerations such as product transport, separation, and compression. Co-design is essential for future solar fuel demonstrations. Section 7 by Abdi and Haussener showcases such co-design by which solar concentration makes relatively expensive but highly efficient photovoltaic components economical, and additionally, can leverage co-generated heat to promote faster electrochemical kinetics. In general, co-design refers to the co-optimization of various aspects of materials design and processing, including semiconductor manufacturing, enhanced light capture, and specific charge separation and electrolyte transport schemes. Such co-optimization can ensure matching of the chemical reaction rate and the light absorption flux in a solar fuel generator. In parallel, fundamental investigations of the mechanisms limiting endurance of photoelectrochemical cells are required to achieve stable operation of such co-designed devices.

10. Nanostructures for light management in solar fuels and photoelectrochemistry

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Status

Photo(electro)chemical devices enable the transformation of light to energy stored in chemical bonds, to be utilized on demand. Sunlight is the world's most abundant primary energy source and is also thus an abundant resource for synthesis of solar fuels. The overall process for generation of solar fuels includes light absorption, excited carrier generation, charge separation, carrier transport and recombination, interfacial electron transfer, catalytic reaction, ion transport, product collection and separation. Many of these steps are correlated with one another, and the cooperative interplay between the steps must be considered to realize efficient device operation. For example, a thick light absorber favors full absorption, but can result in poor charge separation and transport efficiency if the carrier diffusion length is considerably smaller than the absorber thickness. As another example, a high surface area catalyst can lead to a high catalytic current density but can also significantly shadow the incoming light, reducing photocarrier generation.

Anti-reflection coatings with index matching material are commonly used to reduce device reflection losses and improve the band alignment between the absorber and front contact or catalyst. Nanophotonic design principles have yielded a diverse array of approaches to nanostructuring for light harvesting in solar fuels. Figure 17 illustrates different light management strategies to enhance absorption or reduce the shadow loss from catalysts, from structuring of the semiconductor light absorber, and tailoring interfaces in dielectric media to the design of metallic catalysts.

Micro- and nano-scale semiconductor wire arrays can exhibit enhanced absorption at certain wavelengths due to light coupling into resonant waveguide modes [106]. Nanocone arrays of semiconductor light absorbers can be used for broadband enhancement of absorption by introducing a continuous radius change that enables excitation of a continuum of resonant waveguide modes across the visible solar spectrum [107]. Such nanocone arrays can either be fabricated via etching or formation of conical templates that conformally shape a deposited semiconductor layer [108].

By synthesizing dielectric rather than semiconductor nanocone arrays, the high index and low loss of the dielectric material allows incident light to be resonantly transmitted via waveguide modes of the lossless dielectric cone array, into

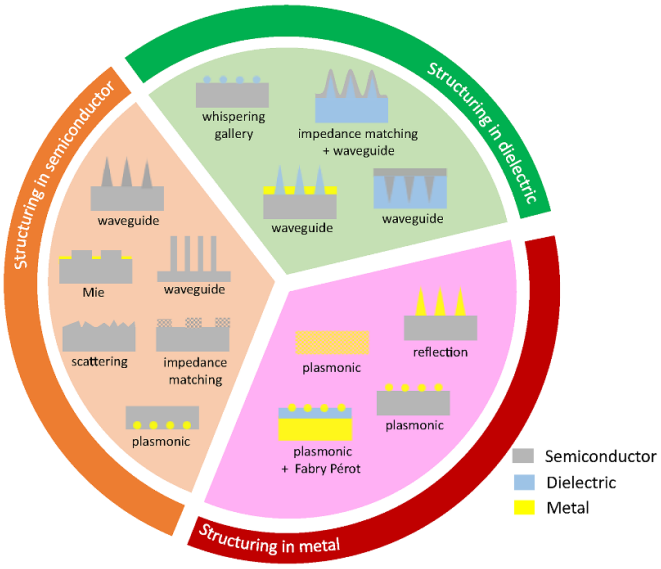

Figure 17. Summary of optical management strategies utilizing structuring in semiconductor, dielectric, and metal for photo(electro)chemical applications.

the device active absorber layer. Catalysts can then be deposited in the surrounding space between the dielectric nanocones [109]. The dielectric nanocone serves multiple functions such as a mould for the deposited thin film semiconductor, to boost absorption by introducing an impedance matching condition and waveguide mode [110].

Other light management schemes include control of reflection and scattering, excitation of Mie resonances in semiconductors and dielectrics, impedance matching to free space, coupling to whispering gallery modes, and plasmonic structures with various geometries—all these are tools to enable light management for solar fuels. Specifically, the strongly localized electric fields near plasmonic nanoparticle catalysts can facilitate absorption in semiconductors. Shifting the plasmonic resonance away from the visible to shorter ultraviolet wavelengths can result in an effectively transparent metal catalyst with limited reflection loss [8]. Moreover, plasmonic materials can themselves harvest light and generate non-equilibrium 'hot' carriers for fuel generation [111]. Other new approaches to light management include nanoporous structures and generation of a strong coupling condition between absorbers and optical modes of a Fabry–Pérot nanocavity [112].

The idea of nanostructuring in materials for light management in solar fuels is general and is not limited to a specific chemical reaction. However, appropriate catalytic materials need to be utilized according to the reactions and desired products to allow efficient conversion. Taking CO_2 reduction for example, Au, Ag, Cu, Pd are usually chosen as catalysts. Moreover, due to the relatively larger overpotential for CO_2 reduction, optical designs allowing more catalytic surface area and higher catalytic current are desirable.

Current and future challenges

Nanostructuring of materials to introduce new optical modes is an interesting approach for energy harvesting applications, including photovoltaics and solar fuels. However, scalability of nanofabrication is a prominent concern. Standard nanofabrication methods including epitaxial growth, pattern definition by electron beam lithography and dry etching, are costly and limited in area scalability. In the field of solar energy, there are widely agreed-upon targets for success, for example, a levelized cost of electricity of <\$0.02 kWh^{-1} for photovoltaics, and cost of <\$2 kg^{-1} H_2 for solar hydrogen production [3]. Therefore, scalable, cost-effective, energy-efficient fabrication technologies are needed for future applications of photonic nanostructures in solar fuels.

In addition, parasitic absorption in materials can lead to efficiency losses in real-world structures. There are many aspects of material microstructure and morphology to be considered, including defect density, crystallinity, and doping concentration. These among other factors can influence the optical and electrical properties, resulting in variability and degradation of device efficiency relative to design targets.

Nanostructuring of the catalytic interfaces can increase the catalytic active site density until mass and charge transport limitations are encountered. The high curvature of nanostructured morphologies leads to strong localized electric fields that can influence the cation concentration in the electrolyte, yielding higher catalytic current density, introducing a local pH enhancement and possibly tailoring the reaction kinetics [113]. A full understanding of these interrelated factors affecting device performance remains challenging.

For example, nanostructured plasmonic materials are distinctly suited to hot carrier generation. The tunable geometry and composition of plasmonic materials and interfaces opens the intriguing possibility to access chemical reaction pathways for solar fuels that are not available in conventional solar fuels generators based on transport of thermalized carriers. Bimetallic nanostructures ranging from antenna-reactors to core–shell structures or alloys further expands the design space for controlling of photocatalysis. However, the excited states lifetimes of hot carriers are extremely short, so careful design is important to facilitate charge transfer before thermalization or recombination.

Thus to date, challenges associated with charge transfer of hot carriers have resulted in incident photon-to-electron conversion efficiency for such systems typically <1%. Fundamental studies and innovative design strategies are needed to enable efficient interfacial electron transfer and extreme light confinement at catalyst/light absorber interfaces, to enable highly efficient hot carrier photoelectrochemical devices.

Advances in science and technology to meet challenges

For the past several decades, extensive effort has been devoted to development of economical nanostructure manufacturing methods, including nanoimprint lithography, metal assisted chemical etching, and thin film transfer methods that can be adapted to the fabrication of photo(electro)chemical devices. Availability of repeatable and vacuum-free processes are important to address the cost of scalable fabrication.

Thanks to advances in optical simulation methods, quantitative determination of the role parasitic absorption of specific materials within complex solar fuels devices is now possible, which is not easily accessed experimentally. However, electromagnetic simulations reveal that the performance of a solar fuels device is sensitive to both its material properties and its geometrical configuration. Imperfections and nonidealities resulting from structure fabrication and defects can lead to discrepancies between optical simulations and experimental measurements.

In order to design photo(electro)chemical device with the highest possible fidelity, optical parameters such material refractive index should be first experimentally characterized. The measured refractive index information can then be directly imported into electromagnetic simulations that are predictive of realistic device performance. The actual geometrical parameters including shape, dimensions and surface roughness can also be determined from experiments and incorporated into simulations to more accurately predict the optical response in comparison with measured spectra.

In a more advanced approach, optimization algorithms can be applied to realize an inverse design process, where parameters can be optimized base on a desired figure of merit. Machine learning and artificial intelligence could allow training with minimum data sets for optimization of performance in complex and nontrivial optical designs in the future.

In addition, photonic approaches that employ the full solar spectrum, extending into the infrared, enables the introduction of a solar heating source to drive photocatalytic reactions. As photo(electro)chemical devices involve many interacting processes, multi-physics simulation tools can help the community achieving better understanding of system operation, from light harvesting to fuel production. Characterization of non-equilibrium processes with short time constants requires advanced optical techniques like pump-probe transient absorption and emission spectroscopies, to fully reveal underlying photoelectrochemical processes [114].

Concluding remarks

In summary, sophisticated optical designs can now be developed for solar fuels generator that maximize light harvesting in absorber materials, without optical losses from catalysts and other optically inactive materials, allowing for efficient carrier transport and device operation. Innovation in the area of scalable nanostructure fabrication techniques is needed to enable practical application of nanostructures in scalable solar fuels generators. Lastly, a promising future direction for solar fuels devices is to embrace inverse design, machine learning, and artificial intelligence methods to enable improved structure design or even global optimization for superior photonic performance.

11. Accelerating discovery of photoactive materials

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Status

Herein we discuss the materials discovery challenges and opportunities that are particular to the aforementioned approaches to photoelectrode and hybrid photoelectrode development: solid state photoelectrodes (section 12), nanostructures thereof (section 10), molecular (photo)catalysts (section 13), and their integration to photoelectrodes. Commensurate with their utilization in early solar photochemistry devices and parallel development for photocatalytic degradation of organics, solid-state photoelectrode materials have been a common target of accelerated materials discovery efforts, and the critical role of molecular specificity for controlling specificity defines a primary opportunity for continued advancement of solar fuels systems. New materials and molecular catalysts will be needed to establish an efficient, durable, and scalable solar fuels technology, providing an opportunity for well-conceived and executed strategies for accelerated discovery to transform the field.

Methods to accelerate discovery and development of solid-state solar fuels materials build on advancements in high throughput and combinatorial materials science [115]. High throughput computation for solar fuels materials discovery has similarly leveraged first principles-based screening techniques in broader efforts such as the Materials Genome Initiative. As a result of the combined solar energy conversion and catalysis requirements for a solar fuels photoelectrode, materials discovery efforts have leveraged and expanded techniques developed for photovoltaics and electrocatalysis research. Consequently, accelerated screening of solar fuels materials has resulted in foundational advancements in the integration of materials physics and chemistry, as well as theory and experiment, to accelerate screening. Despite the efforts for discovery of molecular and material catalysts for solar fuel generation, high throughput experiments and computation to screen hybrid photoelectrode systems is an underexplored research area that critically needs advancement of techniques to accelerate discovery efforts.

Current and future challenges

Commencing with pioneering high throughput experimentation [116], accelerated photoelectrode discovery efforts have been prolific with respect to discovery of new candidate photoelectrode materials for development into solar fuels systems (figure 18) [117], although for the most part such discoveries have yet to lead to commensurate success in advancing the efficiency, durability, and scalability of solar fuels generators, which has been identified as a grand challenge for the field [118]. While solar absorber discovery for photovoltaics includes consideration of environmental stability, the requisite interactions with the environment are relatively limited, i.e. light in and electricity out. For photoelectrodes, the environmental interactions include chemical transformations that occur at an interface with electrolyte, whose support of the chemical transformations poses limitations far beyond those that exist in the solid-state junctions between the photoabsorber and current collectors in photovoltaics. The most central consequence of this environmental interaction is the propensity for the solar absorber materials to corrode, and the thermodynamics of corrosion vary substantially with composition and phase [119]. In metal oxide photoanodes, the breadth of elements from which solar fuels materials can be made has greatly expanded in recent years (figure 18), creating opportunities for designing chemistries with enhanced stability and/or functional passivation layers. Since the durability requirements must be simultaneously met with the solar energy conversion requirements, desirable chemistries for durability and visible light absorption may only be applicable if they can lead to photoelectrodes with the

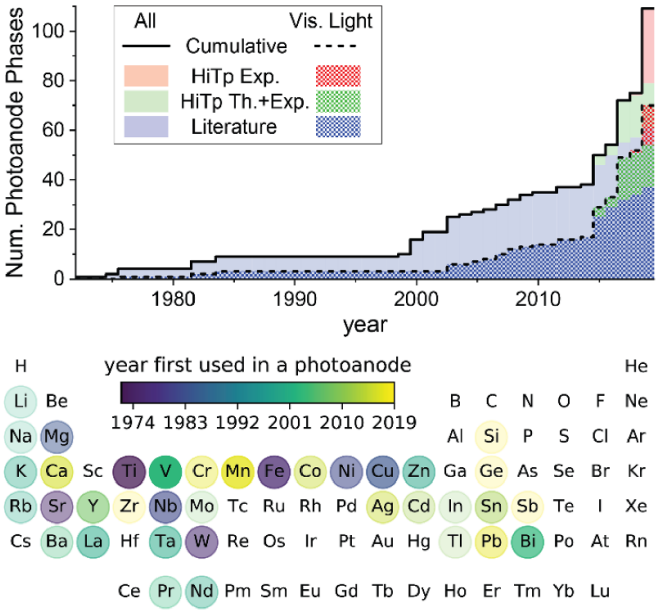

Figure 18. The evolution of solar fuels photoanode materials discovery. (top) The number of metal oxide phases demonstrated to be a photoanode, along with the subset demonstrated using visible light, are shown with breakdown by literature discovery (primarily by traditional methods), by high throughput experimental validation of theory predictions, and by combinatorial screening around theory predictions. (bottom) The map of the first time a metal element was demonstrated in a metal oxide photoanode demonstrates the rapidly expanding chemistry applicable for solar fuels photoelectrode development. Reproduced from [117] with permission.

requisite charge separation and charge carrier properties. The potential benefits of nanostructuring are not easily realized in any given material since the etch and/or selective growth processes are customized for specific semiconductors. High throughput efforts can best contribute by providing the information necessary to design specific nanostructures for targeted synthesis.

Photocatalysts and hybrid photoelectrodes with molecular catalysts anchored on heterogeneous materials are especially promising for selective photoreduction of CO_2 to specific carbon products, with durability being a primary challenge. Advancements in integration strategies considering the local microenvironment of catalyst-semiconductor interfaces is critical to enhance the durability of hybrid photoelectrodes during multi-electron/proton catalytic reactions. Another key challenge for the development of hybrid photoelectrode systems is that despite their high selectivity for specific carbon products (e.g. CO), only a few molecular catalysts could convert CO_2 to liquid solar fuels (e.g. methanol) which presents an opportunity for theory guided accelerated discovery of new candidate molecular catalysts. Furthermore, computational screening of hybrid photoelectrode systems requires accurate and efficient theoretical approaches to model the complex semiconductor—catalyst interfaces with consideration of the local microenvironments including interactions with and variation of the electric field, solvent, ions, cocatalysts, etc.

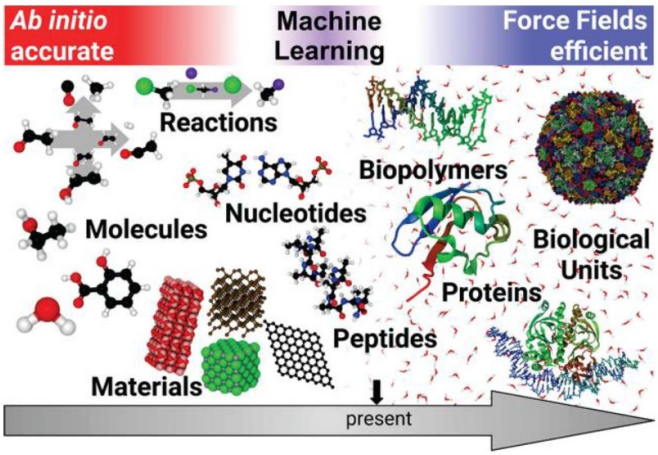

Figure 19. Development of machine learning based methods affording *ab initio* level accuracy with enhanced computational efficiency will greatly facilitate modeling computationally demanding systems such as hybrid photoelectrodes featuring complex semiconductor—catalyst interfaces with consideration of the local microenvironments including solvent, ions, cocatalysts, etc. Reproduced from [122] with permission.

Advances in science and technology to meet challenges

The comprehensive evaluation of all possible photoelectrode materials with all possible coatings is untenable, and ultimately optimized coatings are only required when surface recombination and/or catalysis have been identified as performance-limiting, which is not the case in nascent photoelectrode materials. While high throughput synthesis methods of photoelectrode materials have been demonstrated with a material quality sufficient for materials discovery campaigns, existing high throughput workflows are insufficient to answer the subsequent critical question regarding intrinsic performance limitations. Given the importance of controlling defect concentrations and grain boundaries in such studies, a moderate throughput synthesis of high semiconductor quality photoelectrodes could be transformative, although planning e.g. epitaxial syntheses are far from automated and generally-applicable, motivating some community brainstorming at how theory and experiment can be integrated to tackle this challenge. Following identification of hero candidates with respect to electronic properties, high throughput coating integration and photoelectrochemical screening can then be deployed to identify the transformative photoelectrodes.

The interface discovery efforts to complement down-selection by bulk properties can benefit from computational prediction of kinetic (through the development of a self-passivation layer) or thermodynamic corrosion protection, with evaluation of whether the resulting multi-layered semiconductor-to-liquid transition inhibits charge separation. Emerging methods such as real-time corrosion measurements can accelerate our understanding of the evolution of photoelectrodes under operation [120], and electronic structure theory should greatly facilitate understanding the heterojunctions as well as recombination centers that are introduced so that next generation materials can be designed to avoid the pitfalls of under-performing materials to date.

The most promising opportunities for accelerating the development of optimized nanostructured photoelectrodes is the combination of detailed characterization of the semiconductor material and parameterized models of the impact of nanostructuring in photoelectrode performances. Example properties of interest for characterization include whether majority and minority carrier transport are governed by polaronic or band-like transport, anisotropies in carrier transport, facet-dependent surface dipoles, and the relevant chemistry and structure of intentional or self-forming surface coatings. This information can guide design of nanostructures, for example epitaxial nanowires with specific dimensions, providing sufficiently specific instructions for nanostructure synthesis so that the synthesis can proceed using traditional methods.

Computational high throughput screening and machine learning methods could provide a venue to accelerate the discovery of the molecular catalysts especially for the reduction of CO_2 to liquid solar fuels (Figure 19). Transition-metal based catalysts are prime targets for CO_2 reduction and in recent years machine learning models have been developed to predict the chemical properties of transition-metal complexes despite the challenges such as availability of robust data sets and transferability issues [121]. The advances in the ML

models with increased benchmark data from experimental and theoretical studies is expected to accelerate the discovery of transition-metal based catalysts for the reduction of CO_2 to valuable products beyond CO and formate. In addition, (a) the progress in ML force fields [122] to provide *ab initio* level accuracy with enhanced computational efficiency, (b) application of ML techniques to improve the accuracy and accelerate quantum chemical calculations (e.g. density functional theory) [123], and (c) their application to molecule and material systems could enable efficient detailed computational modeling of hybrid photoelectrode systems taking into account the effect of the solvent, ions etc at the semiconductor—catalyst interface. Such advancements together with multiscale modeling approaches will enable high throughput screening of hybrid photoelectrodes for different semiconductor, catalyst, linker, solvent etc combinations. As computational workflows accelerate their generation of candidate (photo)catalysts, a commensurate advancement in experimental validation of predictions will be needed, which can be further accelerated when coupled with artificial intelligence guidance, e.g. active learning. A robotic platform for conducting such experiment was recently demonstrated for molecular hydrogen evolution photocatalysts [124], highlighting that this futuristic opportunity is rapidly becoming a central strategy in accelerated discovery efforts.

Concluding remarks

Collectively, accelerated photoelectrode materials discovery and development should proceed under recognition of several cross-cutting challenges: (a) computational methods have to-date facilitated the study of individual materials properties, providing opportunity to develop methods that simultaneously consider multiple requisite properties; (b) accelerated discovery efforts have focused on finding any candidate materials, and as limiting factors of those materials are elucidated, the new generation of materials discovery efforts needs to explicitly design materials that avoid the same pitfalls; (c) the discovery and reporting of individual component materials lacks the context of the materials integration that is necessary for a solar fuels generator, creating on opportunity to accelerate the characterization of interfaces and microenvironments for improved solar conversion efficiency and durability; (d) establishing absorption and transport properties of light harvesting materials will enable principled design of high performance photoelectrodes, demonstrating how accelerated characterization of intrinsic properties can complement study of interfaces and device-level properties; (e) automation of computational experimental workflows will help address these challenges and be strengthened with data science-based integration of theory and experiment.

12. From materials discovery to functional photoelectrodes

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Status

Semiconductor photoelectrodes serve as the engines of solar fuels devices and must simultaneously fulfil several important requirements in order to drive the efficient conversion of light to chemicals. In addition to capturing solar energy, promoting charge carrier separation and transport, and permitting efficient interfacial carrier injection, these materials must be stable (or stabilized) under resting and operating conditions. Many potentially promising photoelectrode materials have been identified in the last decade, aided by advances in computational materials predictions and high throughput synthesis and screening approaches [117], as described in section 11. However, photoelectrodes that can significantly outperform previously developed materials have not yet emerged from these efforts. Understanding the underlying reasons is necessary to improve the effectiveness of our future photoelectrode development.

Developing high-performance photoelectrodes depends not only on discovering new bulk compositions but also on optimally controlling semiconductor defects, dopants, and interfaces. In order to rationally control the latter aspects, an atomic-level understanding of their influences on charge transport and recombination, as well as interfacial energetics, must be achieved. Fortunately, significant knowledge has been accumulated in the last decade on these matters, increasingly aided by surface, *in situ*, and *operando* techniques, as well as the tight integration of experiment and computation. These advancements, which contributed significantly to the understanding and continuous improvement of existing photoelectrode materials (figure 20) [31], will help to accelerate the optimization of any promising photoelectrodes developed in the future.

Another notable advancement made in the last decade is the assembly of multi-layer photoelectrodes where photon-absorbing layers are coupled with buffer, protection, and catalyst layers with optimal interfaces [38]. These multilayer structures may effectively relax some of the critical requirements for photoelectrodes. For example, protection layers that can supress photocorrosion have made it possible to reconsider the use of efficient and inexpensive photoelectrodes that are not photostable. The progress on buffer, protection, and catalyst layers has therefore become an important part of photoelectrode development that directly affects the evaluation of future materials. Based on these considerations, this piece of the roadmap aims to discuss the current challenges of and future strategies for developing efficient and stable (i.e. functional) photoelectrodes.

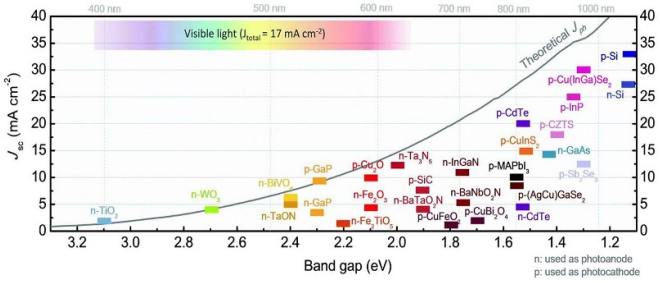

Figure 20. The state-of-the-art photocurrent density (Jsc) of photoelectrodes for PEC water splitting under standard conditions of 1.0 sun at 1.23 V_{RHE} for photoanodes and 0.0 V_{RHE} for photocathodes. Adapted from [31] with permission from the Royal Society of Chemistry, copyright 2019.

Current and future challenges

While general requirements for photoelectrodes are well-established, screening and down-selecting new photoelectrode materials is not straightforward. The major difficulty in rapidly evaluating photoelectrodes is that many photoelectrochemically important features such as the photocurrent onset potential and electron–hole recombination rate are affected considerably by factors that are not intrinsic to the materials (e.g. purity, crystallinity, defects and disorder, grain structure). Therefore, when a new semiconductor is prepared as a low-quality polycrystalline photoelectrode, the properties and limitations that are truly intrinsic to the material may not be accurately evaluated, leading to incorrect assessments. In order to effectively prioritize materials for future studies, preparing photoelectrodes with sufficient quality is crucial to determining the nature of the limitations and whether or not they can be resolved.

To elaborate, many photoanodes developed in the past decade based only on the metric of their bandgap did not become successful because their photovoltage gain was insufficient (e.g. <0.6 V) [125]. Various factors affect the photocurrent onset potential, and some of them, such as surface and bulk recombination, doping density, and surface termination, may be optimized. However, if the onset is fundamentally limited by poorly aligned band edge energetic positions, it is significantly more challenging to make meaningful improvements to the material as a photoelectrode [126].

Some materials with promising bandgaps and band positions still did not lead to successful photoelectrode developments because they suffer from extremely short carrier diffusion lengths, fast photocarrier recombination times, and low electron–hole separation yields [127]. Considering that most of these materials possess partially occupied *d*-bands, one straightforward future direction is the prioritization of photoelectrodes on the basis of their electronic structure, emphasizing materials that do not contain partially occupied

d-bands. Another important consideration is that certain semiconductors exhibit a strong electronic tolerance to structural defects, which can greatly accelerate their development towards high performance photoelectrodes. Several properties have been identified to promote such tolerance [128]. For example, a large dielectric constant yields strong electronic screening, which reduces trap state capture cross-sections, decreases ionized impurity scattering, and lowers exciton binding energies, all of which are favorable for increasing carrier extraction efficiencies. This improved understanding of defect tolerance offers another new guideline for future photoelectrode development.

Even for those materials that can support high efficiency light capture and charge separation, (photo)chemical stability under both reaction and resting conditions remains a critical challenge. Application of advanced corrosion mitigation strategies, such as integration of conformal protection layers and electrolyte engineering [129], can greatly extend operational lifetimes. Self-passivating materials featuring dense and non-soluble corrosion products are of particular interest as their chemical tolerance to interfacial imperfections may significantly increase their chance to reach long-term durability targets [102].

Advances in science and technology to meet challenges

The advances made in computational materials predictions in the past decade may aid in discovering new photoelectrodes using the aforementioned guidelines. High throughput synthesis and screening may also help to expedite materials discovery, but it is important to recognize that these methods typically yield polycrystalline materials with limited control over purity, disorder and defects, which affect the screening results considerably. The materials deserving more focused future studies should be prioritized based on the accurate assessment of limitations and strategies to address them (figure 21).

Studies on bulk single crystals and epitaxial films will be highly beneficial in understanding orientation-dependent optical and electronic properties, as well as surface-dependent photoelectrochemical characteristics. By offering surfaces that can be modeled relatively easily, these studies will also enable more tightly integrated experimental and computational investigations to elucidate the impacts of interfaces on photoelectrochemical function [130]. The results obtained from these studies can then be used to produce device-level, inexpensive polycrystalline photoelectrodes whose surfaces and interfaces are rationally tailored to maximize the photoelectrochemical properties.

Currently, a large gap is the lack of physically reasonable accelerated testing protocols and standardized tests that can be applied to truly predict the operational stability of photoelectrodes. Underpinning accelerated testing strategies is the need to understand (photo) corrosion mechanisms occurring over a broad range of time scales. While photo electrode degradation is ubiquitous, detailed studies of (photo) corrosion processes are much less common. Thus, photo electrode development efforts would greatly benefit from a concerted international effort devoted to improved understanding of instability, with the aim of establishing meaningful accelerated stability testing protocols.

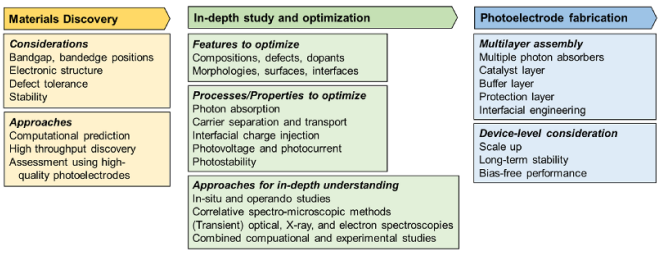

Figure 21. A scheme summarizing efforts required for functional photoelectrode development.

Major advances in *in situ* and *operando* characterization, as well as correlative spectro-microscopic methods, offer an increasingly powerful toolset for understanding the complex and often interrelated processes that govern efficiency loss and degradation in photoelectrodes and their assemblies. The ability to apply (transient) optical, x-ray, and electron spectroscopies, as well as advanced scanning probe methods, to working photoelectrochemical interfaces has been and will continue to be crucial for developing functional photoelectrodes. New advances in these and related methods will be essential, and especially exciting opportunities emerge as next generation synchrotrons come online during the next decade.

Concluding remarks

Decades of research in both photoelectrochemical and photovoltaic energy conversion provide a difficult lesson: the path from the initial discovery of a new material to a functional light absorber capable of reaching high energy conversion efficiencies can be long and tortuous. Along this pathway, the critical role of defects, impurities, and interfaces on the optoelectronic and photoelectrochemical properties of the semiconductor must be understood and precisely controlled. Fortunately, considerable accumulated knowledge regarding semiconductor physics, materials synthesis, and interface science can be leveraged to accelerate these development efforts. With the advent of predictive computational materials discovery and high throughput synthesis and screening, an emerging challenge for the researcher is to rationally select photoelectrode materials with a probable pathway towards efficient and stable photoelectrochemical energy conversion. In this regard, assessment of the semiconductor band gap is insufficient. Key selection criteria must be expanded to critically include band energetics, electronic structure, defect tolerance, and surface chemistry before precious time and resources are invested in development and optimization of functional photoelectrode materials.

13. Molecular photoreduction and photocatalysts on photofunctional solid materials

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Status

Research on artificial photosynthesis garnered significant attention during two different periods: one period started during the oil crisis in the 1970s as a countermeasure against the shortage of energy and carbon resources, whereas the other period is presently as a countermeasure against the global warming problem. During both periods, metal complexes were used as one of 'central players,' particularly for photocatalytic CO_2 reduction, mainly owing to their high CO_2 reduction selectivity against proton reduction. Visible-light-driven CO_2 reduction to useful and high-energy carbon materials might provide a solution for the above-described serious problems for human beings.

Lehn *et al* firstly reported selective and efficient photocatalysts for CO_2 reduction using *fac*-Re(bpy)$(CO)_3$X (X = Cl, Br; bpy = 2,2′-bipyridine) as a 'photocatalyst' and triethanolamine as a reductant [131]: the only product was CO with relatively high quantum yield (Φ_{CO}) of 14% but a low turnover number. This is also the first study to prove that the carbon source of the product is CO_2 by using isotope-laveled $^{13}CO_2$, which is an essential experiment in the field of photocatalytic CO_2 reduction. Mechanistic studies clarified that *fac*-Re(bpy)$(CO)_3$X changed its structure in the initial stage of the photocatalytic reaction to two different complexes as a redox photosensitiser that initiates photochemical one-electron transfer and as a catalyst that accepts the electron from the redox photosensitizer, stores multiple electrons, and activates CO_2, both of which are necessary for constructing efficient photocatalytic systems for CO_2 reduction [132, 133].

Based on these findings, various molecular photocatalytic systems consisting of both the photosensitiser and the catalyst have been developed [134, 135]. As the photosensitszers, mainly Ru(II) trisdiimine complexes have been used, and Ir(III)- and Os(II)-complex photosensitizers have been recently reported. Re(I), Ru(II), and Mn(I) diimine carbonyl complexes were used as efficient catalysts. In addition, the development of the molecular photocatalysts without using rare and/or precious metals, such as Cu(I)-complex and organic photosensitisers and Mn(I), Ni(II)-, Co(I)-, and Fe(II)-complex catalysts has become an active topic [136]. To develop practical systems for photocatalytic CO_2 reduction, numerous functions should be added to the system, as described in the following section. Reduction products are CO and/or HCOOH in most of the reported photocatalytic systems consisting of the molecular photosensitizer and catalyst.

The product distribution strongly depends on the catalyst used in the photocatalytic system and reaction conditions such as solvent and pH [135]. For example, the systems using the Re(I) complexes as the catalyst selectively give CO as the only product almost without HCOOH and H_2 formation even in an aqueous solution. In the case of $[Ru(bpy)_2(CO)_2]^{2+}$which was firstly reported by Koji Tanaka' s group as the catalyst, HCOOH is the main product in basic solvent while, in an acidic solution, CO and H_2 form as main products.

Current and future challenges

Highly efficient, durable, and selective photocatalytic systems consisting of transition metal complexes and a relatively strong reductant, such as aliphatic tertiary amine, have been reported for CO_2 reduction by using transition metal complexes both as the photosensitizer and the catalyst ($\Phi \leqslant 83\%$, TON > 3000) [135]. For developing artificial photosynthesis as a practical CO_2 utilization system, however, there should be numerous additional functions that must be added. Figure 22 shows the necessary functions.

(a) Light harvesting: The photon flux of solar light is very low, and the visible-light absorption ability of molecules is not very high. To minimize the number of the photocatalyst molecules that usually require complicated structures and of which synthesis requires high costs, simple and low-cost light-harvesting systems are required for practical use.
(b) Visible light should be used because the content of high-energy ultraviolet light is 5%–6% in solar light. From this view point, modeling of the Z-scheme in natural photosynthesis should be one of the ideal solutions. The Z-scheme induces both strong reduction and oxidation powers via the step-by-step absorption of two low-energy photons, which causes the transfer of one electron from the oxidation site to the reduction site.
(c) Capture of CO_2 from exhaust fumes from large sources such as thermal power plants and iron manufactures, which contain several %–20% of CO_2. CO_2 capture from air (∼400 ppm CO_2) and usage of captured CO_2 is a desirable challenge.
(d) The use of water as the reductant, which can be used in substantial quantities and is low-cost. Because the oxidation power of the frequently used photosensitisers in their excited state is relatively low, expensive and quantitatively restricted sacrificial reductants have to be used in the reported photocatalytic systems consisting of only metal complexes.
(e) Efficient and durable catalysis with high selectivity for CO_2 reduction even in an aqueous solution because water should be used as the reductant as previously described.

Advances in science and technology to meet challenges

Recently, hybrid systems consisting of the CO_2 reduction photocatalyst and materials with other functions have been reported.

Inagaki *et al* reported that periodic mesoporous organosilica (PMO), which acts as a light-harvesting material in which numerous organic groups are embedded in the silica

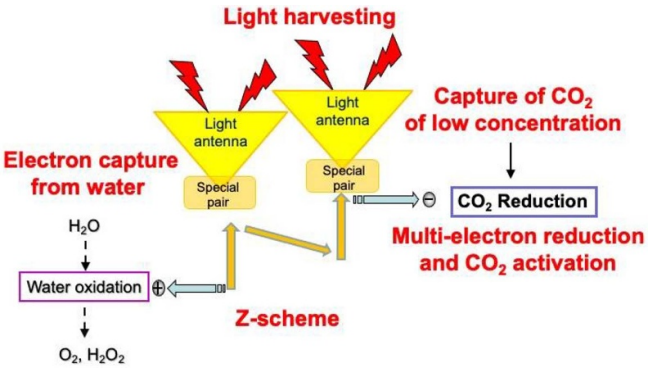

Figure 22. Required functions for CO_2-reduction photocatalytic systems.

framework as visible-light absorbers was hybridised with the supramolecular photocatalyst constructed with Ru(II) photosensitizer and Re(I) catalyst units that are connected to each other with a bridging ligand for accelerating electron transfer between the photosensitiser and catalyst units; the supramolecular photocatalyst was grafted onto the PMO mesochannels with acridone embedded in the walls (figure 23(a)): photons absorbed by several tens of the acridone groups are accumulated into one photosensitiser of the supramolecular photocatalyst and then efficient CO_2 reduction was induced [137].

Hybrids of metal complexes with semiconductor materials have been actively investigated. For instance, Son, Pac, and Kang reported that both photosensitisers and catalysts are connected on TiO_2 can photocatalyse efficient CO_2 reduction and H_2 evolution in which TiO_2 works as an 'electrical wire' between the photosensitiser and catalyst [138].

The Z-scheme systems were constructed as hybrids consisting of the supramolecular photocatalyst and semiconductor with high photooxidation power, in which both the photosensitiser unit of the supramolecular photocatalyst and semiconductor absorb photons and can produce both CO_2-reduction photocatalysis and high oxidation power. In photoelectrochemical systems, visible-light-driven photocatalytic CO_2 reduction was achieved by using water as a reductant: a combination of a Ru(II)-Re(I) supramolecular photocatalyst, which is adsorbed on a $CuGaO_2$ (p-type) electrode, photocathode and a TaON (n-type) photoanode with CoO_x co-catalyst for water oxidation (figure 23(b)) [139].

Direct photocatalytic reduction of low concentrations of CO_2 is possible in molecular photocatalytic systems in which the catalyst unit can accept CO_2 by insertion into a meta–oxygen bond [132] or metal-organic frameworks with selective affinity for CO_2 [140].

Thus, one or two of the necessary function(s) can be added to the molecular photocatalysts for CO_2 reduction. However, we must mention that all of the functions shown in figure 22 must be combined in one system. In addition,

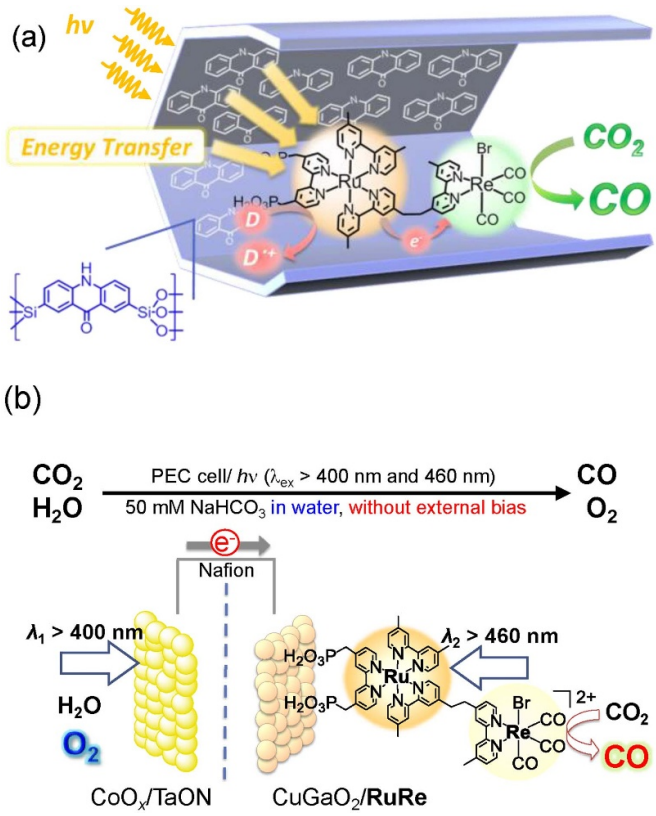

Figure 23. Photocatalytic hybrid systems of the Ru(II)-Re(I) supramolecular photocatalyst for CO_2 reduction with (a) periodic mesoporous organosilica as light harvester and (b) semiconductor photoelectrodes for water oxidation.

we need new chemical engineering for constructing the artificial photosynthesis for CO_2 reduction as a practical solar-energy-conversion plant.

Concluding remarks

In this section, we focus on the molecular photocatalysts for CO_2 reduction. Other molecular photocatalysts for H_2 evolution, water oxidation, and N_2 fixation have also been actively investigated. Although the target reactions of these systems are different, all of them should have the same or similar additional photofunctions as the CO_2 reduction systems, as shown in figure 22, for practical usage. As described in the previous part, the development of the new chemical engineering is also required for the application of all the artificial photosynthesis. The plants should efficiently absorb solar light, introduce CO_2 into the photocatalytic system, and separate the reduction product(s) of CO_2 and the oxidation product(s) of water, and so on. Both chemists and chemical engineers should discuss this issue and work together for the future of humankind.

14. Photocathode design: fundamental challenges and paths forward for CO_2 reduction

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Status

The prospect of performing solar to chemical energy conversion using the using non-equilibrium electrons and holes produced by illumination of semiconducting materials has been of interest since the pioneering work of Fujishima and Honda on water splitting by TiO_2. A large number of photoelectrochemical (PEC) configurations are possible, ranging from wide band gap semiconductors capable of driving water splitting and CO_2 reduction without additional energy input to combinations of photocathodes and photoanodes in different illumination configurations [141]. Considered here are photocathodes in which illumination produces a non-equilibrium population of electrons, which can be used to drive the hydrogen evolution reaction (HER) and CO_2 reduction (CO_2R). However, in contrast to water splitting, there are very few reported photocathodes which drive CO_2R reactions without any co-catalysts [142].

The simplest reduction reaction relevant to solar energy conversion is two-electron conversion of protons to $H_2(g)$, $2H^+ + 2e^- \rightarrow H_2(g)$ ($E^0 = 0.0$ vs SHE). From an energetic point of view, the requirement to drive this reaction (HER) to the right is well-established: the electrochemical potential of the electrons (or equivalently, their (quasi-)Fermi level) must be more negative than the corresponding E^0 at the location where the reaction is possible. Thus, if a direct contact between the semiconductor and electrolyte is envisioned, the conduction band of the semiconductor must be more negative than the target redox reaction. This situation, depicted in figure 24, is realized by a number of semiconductors such for typical CO_2R conditions at pH 7.

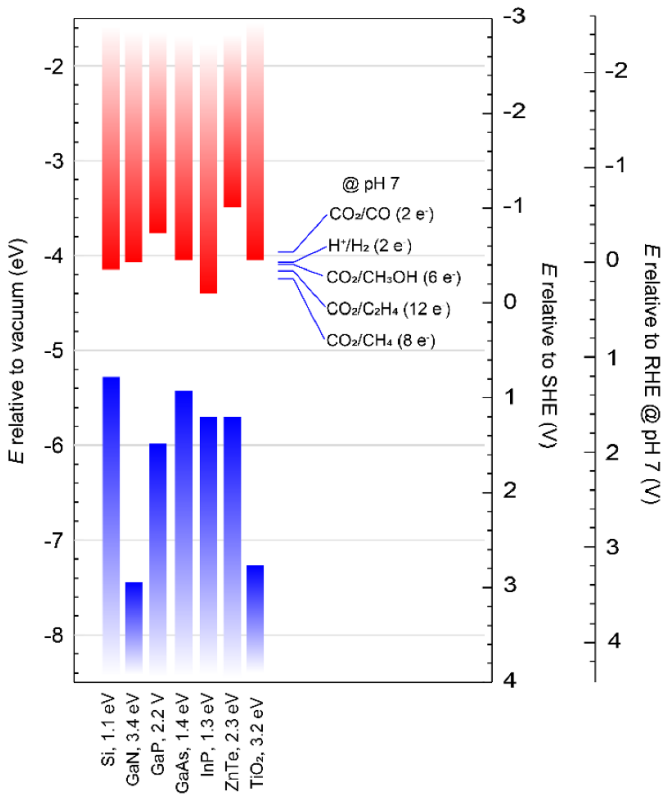

Figure 24. Schematic band alignment for selected group IV, III–V, II–VI, and oxide semiconductors with the valence band shaded in blue and the conduction band in red. The equilibrium potentials for CO_2 reduction reactions and for the hydrogen evolution reactions are also shown for pH 7, a typical experimental condition.

Current and future challenges

However, this picture is necessarily incomplete, especially for the more challenging multielectron reactions associated with CO_2 reduction. It should be emphasized that the formal band alignments shown in figure 24 represent the equilibrium potential for a hypothetical concerted reaction, i.e. eight electrons and eight protons reacting to make methane. Clearly this is an oversimplification: extensive work over the last ten years has shown that electrochemical CO_2 reduction on metal surfaces occurs via a sequence of proton-coupled electron transfer steps [143]; referring to figure 24, each of these would be expected to have its own equilibrium potential. Moreover, the reaction intermediates are adsorbed on the metal surface; in the case of semiconductors, one would expect these to modify the surface density of states as well.

Moreover, while it was reported in the 1970s that GaAs photocathodes could produce multi-electron products such as methanol, evidence emerged that corrosion of the surface may have been responsible [144]. In fact, there are very few reports of CO_2R which can be interpreted simply with the alignment scheme in figure 24 [145]; many studies employ electron transport layers such as TiO_2 in concert with known CO_2 co-catalysts [146]. In these cases, the photocathode is basically functioning in series with the potentiostat to reduce the amount of required negative bias.

Still, there are intriguing reports of CO_2R to multi-electron products from the semiconductor photocatalysis (PC) literature (there is no applied bias on a photocatalyst as opposed to a photocathode). While most PC studies employ a sacrificial hole scavenger, it appears clear that it is possible to raise the electrochemical potential of the electrons in the particles to a sufficiently negative value to drive the multi-electron processes shown in figure 24. It is also clear that the product distributions reported are very different than known electrocatalysts: e.g. formation of methanol as a major product and also carboxylic acids up to C6 [147, 148]. Thus, to the extent to

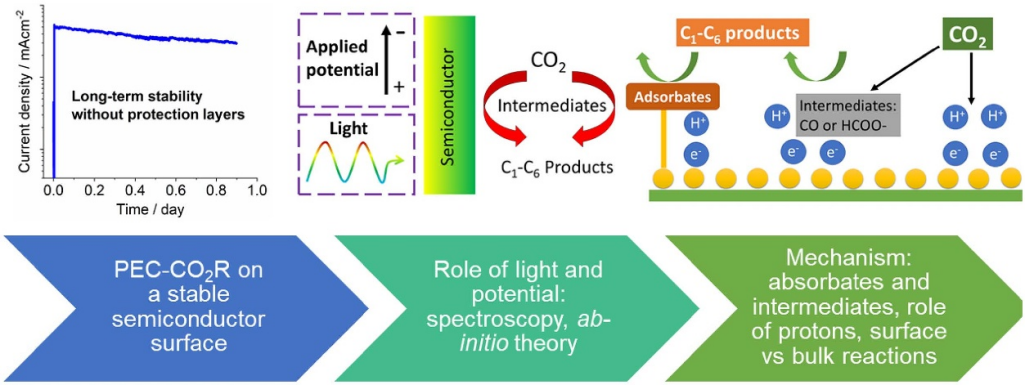

Figure 25. A roadmap for deeper fundamental understanding of the CO_2R reaction mechanism on semiconductor photocathodes.

which the environments at the surface of illuminated photocatalysts and photoelectrocatalysts are similar, these findings suggest that PEC CO2R under the right conditions may lead to improved selectivity to C2+ products compared to currently known electrocatalysts.

Advances in science and technology to meet challenges

The challenge thus becomes elucidation of the nature of the semiconductor-electrolyte interface under the conditions of non-equilibrium carrier populations and in the presence of the intermediates, mostly likely adsorbed on the surface, of the multi-electron pathways associated with CO_2R products such as methanol (6 electrons), ethanol (12 electrons), etc. Such an effort can be informed by the substantial recent progress on understanding CO_2R on metal electrodes [149], keeping in mind the difference in the electrochemical activity of the electrons. In the case of metals, they can be assumed to be in infinite supply at a well-defined Fermi level and potential drop across the double layer but in a semiconductor the situation is more complex [150]. While the quasi-Fermi level position can be assessed, as in photovoltaics, by drift-diffusion simulations incorporating known recombination pathways, there may be an interplay between the active sites for catalysis and surface recombination. There have been efforts to consider these effects for water oxidation on photoanodes (four electron process); this approach could be adapted for the more complicated CO_2R pathways [151].

A specific advantage of photocathodes is that time-resolved spectroscopic probes can yield detailed information about electrons including lifetimes and occupation of surface states as discussed in section 12. Recently, these types of studies have elucidated the detailed, multi-hole mechanism of water oxidation on metal oxide photoanodes [152]. However, a major practical challenge is the lack of a stable corrosion-resistant semiconductor on which similar studies for CO_2R photocathodes could be performed.

We propose a possible roadmap towards deeper fundamental understanding of CO_2R photocathodes built upon 3 main pillars (figure 25). First would be the development of a corrosion resistant CO_2R semiconductor photocathode which could be used as a model system. Using such a stable photocathode, the influence of light and applied potential should be investigated on the selectivity of the CO_2R products. This would elucidate the roles of CO_2R intermediates, protons and surface reactions on the semiconductor surface which would complement and extend the already existing understanding of CO_2R on metallic electrocatalysts.

Concluding remarks

It remains an open question as to whether semiconductor photocathodes can drive photoelectrochemical CO_2 reduction 'directly,' that is using electrons formed by illumination and residing in either the conduction band or surface states close to it, without the assistance of electron transport (aka 'protection') layers and metal co-catalysts. Still, the substantial body of work on oxide photoanodes which drive water oxidation and the smaller, but nevertheless significant, number of reports on photocatalytic CO_2R to multi-electron products suggest that it is possible. A full understanding of the process must consider the much lower concentration of electrons as compared to metals and will require a comprehensive treatment of the interplay between reaction intermediates and surface recombination. It can be expected, based on the PC literature, that quite different reaction mechanisms and products might be possible. Optimistically, such a system might be capable of improved product selectivity compared to metal electrocatalysts, which provides motivation for undertaking such an effort.

15. Oxygen evolution reaction: catalysts, mechanisms, and durability

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Status

The oxygen-evolution reaction (OER) is the critical (photo)anode reaction for (photo)electrochemical production of solar fuels including H_2 from water and hydrocarbons from CO_2. Efficient catalysts are required with stability of at least a decade. Under acidic conditions, the only stable catalysts are iridium-containing oxides, and these are used in proton-exchange-membrane (PEM) electrolyzers that operate above 2 A cm^{-2}, offer direct electrochemical compression, and output high-purity H_2. The major challenge facing PEM electrolysis is minimizing Ir utilization due to its scarcity and thus high and volatile price [153]. Under basic conditions, by far the most-active catalysts are earth-abundant Ni-Fe-based (oxy)hydroxides which can be prepared directly and also form naturally on the surfaces of Ni and steel anodes in traditional alkaline electrolyzers that have been commercialized for over a century. They also form from all highly-active oxides/phosphide/sulfides used for the OER. These catalysts are potentially relevant to new alkaline-membrane electrolyzers that, in principle, offer the advantages of the PEM systems but use abundant, low-cost catalyst and cell components [154].

Because the electrochemical reduction of CO_2 occurs most-effectively under alkaline conditions (where hydrogen-evolution kinetics are suppressed), anion-conducting membranes are often used to separate the catholyte from the anolyte with OER thus also taking place under alkaline conditions. Unfortunately, much of the CO_2 feed crosses from the catholyte to the anolyte as HCO_3^- and CO_3^{2-}, reducing the utilization of CO_2. The crossover can be largely eliminated using bipolar membranes, which also provide an alkaline environment for OER [155].

OER in alkaline conditions is the focus of this section. The principle challenges include understanding how the activity and stability of the catalyst are related to composition, structure, and dynamics, particularly at the active site [156]. Metrics for activity are the overpotential at a given current density (defined per unit of superficial or microscopic area), the turnover frequency based on the concentration of hypothesized active-sites, and the Tafel slope (the inverse of which is a measure of how rapidly the current increases with voltage). Typical values for the 'overpotential' range from 150–300 mV at the low current density of 10 mA cm^{-2}, depending on catalyst mass loading and surface area, and for the Tafel slope, 30–40 mV decade^{-1} (see, e.g. figure 3 in section 2).

Current and future challenges

While significant progress has been made in understanding the relationships between the structure/morphology of $Fe_xNi_{(1-x)}O_yH_z$ and related materials, defining the identity, oxidation state, local structure, and dynamics of the active site(s) as well as the role of sites at the edge of (oxy)hydroxide platelets vs their surface, are topics of ongoing research. The relationships between structure/morphology and the loss/recovery of catalyst activity over time is also important.

Insights into the structure of $Fe_xNi_{(1-x)}O_yH_z$ and related materials under OER conditions have been obtained by combining information from *in situ* characterization using wide-angle x-ray scattering (WAXS), x-ray absorption spectroscopy (XAS), and Raman and Mössbauer spectroscopy. As-prepared Fe–Ni layered double hydroxides, nominally $Fe_xNi_{(1-x)}(OH)_{(2+x)}$, undergo oxidation to nominally $Fe_xNi_{(1-x)}OOH$ at a potential below the onset of the OER [157]. XANES shows that the *average* oxidation state of Ni increases from +2 to between +3 and +3.8, whereas the *average* oxidation state of Fe remains close to 3+ with only small edge shifts observed in samples with high electrochemical accessibility [156]. EXAFS data show that the Fe–O distance in $Fe_xNi_{(1-x)}OOH$ resembles that for NiOOH and is 8% shorter than in FeOOH indicating some oxidation of Fe^{3+} [157]. XAS measurements alone, however, have not yielded a definitive structure under OER conditions. The substitution of Fe for Ni in NiOOH occurs for $x < \sim 0.2$, but at higher values of x, FeOOH nucleates as a separate phase [157]. Since the intrinsic OER activity of both NiOOH and FeOOH is considerably lower than that of $Fe_xNi_{(1-x)}OOH$ [156], the activity is maximized for $x \sim 0.15$–0.20.

Attempts to address the precise nature of the active site have been made using density-functional theory calculations. These require assumptions regarding the structure of $Fe_xNi_{(1-x)}OOH$ and its surface termination at different potentials, and often ignore explicit water and ions in the electrolyte or absorbed on the surface. Most theoretical studies conclude that the active sites are either Fe^{3+} or Fe^{4+} cations affected by Ni^{3+} cations in the host lattice. However, it is important to note that in these structures the cations are all electronically coupled and assignment of formal oxidation states may be misleading. Fe^{4+} is found by *in situ* Mössbauer under OER potentials, and this oxidation state largely remains after removal of the bias [158]. Evidence for minority highly-active 'edge' or 'defect' Fe sites have been found [156]; consistent with the Mössbauer study that suggest the majority of Fe^{4+} (likely sitting in internal sites in the (oxy)hydroxide sheet) do not exhibit fast OER kinetics (which would lead to fast discharge to Fe^{3+}).

Advances in science and technology to meet challenges

Recent WAXS and XAS experiments coupled with calculations provide new data on the structures and dynamics

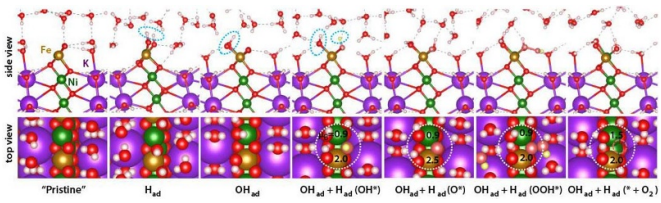

Figure 26. Water oxidation on the 'γ-phase' of Ni–Fe oxyhydroxides. A reasonable reaction mechanism involves under-coordinated Fe edge sites and the oxidation of a bridging hydroxo. The reaction center is highlighted by the white dashed circle. The numbers indicate the calculated magnetic moment of the metal cations. The ability of Fe cations to access oxidation states of 4+ and above are found to stabilize the key rate-limiting O^* intermediates at the Fe–O–Ni reaction center. The inclusion of explicit water, realistic chemical and electronic structures, and cations, makes the model a better representation of the real catalyst than most. Adapted from [158].

of Ni–Fe and Co–Fe oxyhydroxides under OER conditions [159]. The experiments show that oxidative phase transitions from the resting state lead to ~8% contractions in both the in-plane lattice constant and inter-layer distances induced by oxidation of the cations and the dynamics of the intercalated ions. Modeling, including explicit water and ions via *ab-initio* molecular dynamics, suggests OER on the active-phase structures proceeds by a Mars van Krevelen mechanism starting with the oxidation of bridging Fe–(OH)–Ni (figure 26). A key result from the computations is that Fe is easier to oxidize to higher oxidations above +4 compared to Ni, which stabilizes O^* intermediates at the Fe–O–Ni reaction center compared with that at Ni–O–Ni. This consequently lowers the barrier for OH^* oxidation to O^*, the potential limiting step.

Stability is also critical. The ratio of the O_2-production rate to the metal-dissolution rate is defined as the activity-stability factor [160]. While incorporation of Fe into Ni or Co (oxy)hydroxide significantly increased activity, Fe-doped catalysts lost activity with time. The loss was essentially eliminated if 0.1 ppm of Fe^{3+} was added to the KOH electrolyte. Experiments in which the electrode contained ^{56}Fe and the electrolyte contained ^{57}Fe demonstrated that Fe^{3+} cations *dynamically exchange* between the electrolyte and the catalyst surface; stable performance requires the rate of Fe deposition be equivalent to the rate of dissolution (figures 27(A) and (B)).

To better unravel mechanistic details of OER, new characterization methods are needed to follow precise local structures and dynamics [162]. A new approach is correlative *operando* microscopy. A recent study combined *operando* scanning-pipette electrochemical experiments, electrochemical atomic-force microscopy, and x-ray absorption microscopy to study well-defined single-crystal β-$Co(OH)_2$ microplatelets and resolve localized OER activity at the reactive edge facets that correlated with Co^{3+} concentration (figure 27(C)) [161]. These powerful techniques are poised to shed light on the more-complicated, and more-active, Fe-containing mixed-metal systems.

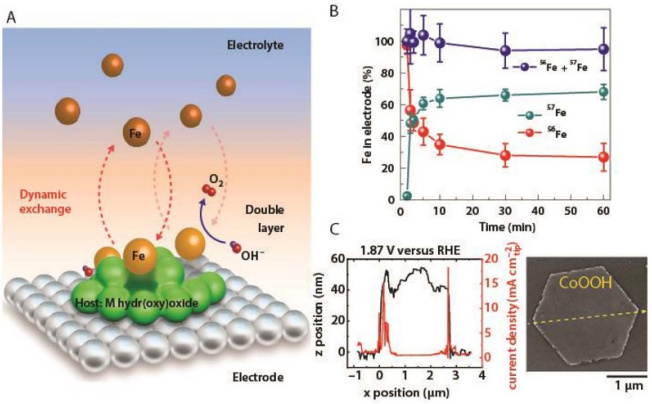

Figure 27. Water oxidation with dynamic catalysts. (A) Substantial experimental data points to the dynamic exchange of cations between soluble and surface-absorbed species during catalysis. This is particularly key for Fe cations which have non-negligible solubility in alkaline conditions. (B) An isotope labelling experiment unequivocally shows how Fe is simultaneously leached from the catalyst and absorbed from the solution during catalysis leading to stable steady-state water oxidation activity. Adapted from [160]. (C) Scanning-probe electrochemical experiments show water-oxidation active sites located at the edges of the well-defined nanosheet structures. Adapted from [161].

Concluding remarks

While the fundamental understanding of the OER in alkaline media has rapidly progressed, catalysts with higher performance have not clearly emerged. This is in part because the precise mechanisms and active structures are not fully known. It is also likely because of the general inability to systematically modulate the structure of the *naturally forming active surface species*. Continued work is needed, for example:

- Improve computational models that more-accurately represent the complex and dynamic experimental structures including the electrolyte and ionic double layer.
- Develop experimental model systems with well-defined surfaces and Fe-absorption sites.
- Understand dynamic active species and the thermodynamic (solubility, absorption energy) and kinetic factors governing their concentration and activity.
- Apply comprehensive *ex-situ* and *operando* correlative microscopies combined with judicious analysis of electrochemical and spectroscopic data.
- Test how the new chemical pictures of dynamic mixed-metal (oxy)hydroxide catalyst phase are able to drive optimization of traditional water electrolysis under industry-relevant conditions (concentrated hot alkaline electrolyte at currents near or above 1 A cm^{-2}).
- Extend understanding to alkaline-exchange-membrane electrolyzers without soluble supporting electrolyte, identifying how ionomer and catalyst interact and modulate activity and durability.

16. Remaining challenges for the hydrogen evolution reaction (HER): catalysts and mechanism

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Status

Considering only catalytic performance and stability, there is no better catalyst than Pt for the hydrogen evolution reaction (HER) [11]. However, this rare metal has a low abundance in the Earth's crust, is only mined as coproduct of other first-row transition metals and is valuable for many other applications: as just one example, it is used as both anode and cathode catalyst in proton-exchange membrane fuel cells. With ∼500 million tons of H_2 to be produced by 2050 according to the Net Zero by 2050 report from IAE, the search for other HER catalysts represents one of the greatest challenges of this future energetic transition. While Pt exhibits turnover frequencies (TOF) around 4.4×10^3 $H_2 \cdot site^{-1}$ s^{-1} at 100 mV overpotential in acid [11], other catalysts based on transition metal phosphide or sulphides, although they are also remarkably stable in acid, fail to display reversible behavior for electrochemical hydrogen evolution/oxidation reactions (HER/HOR), and this translates into significant overpotential requirement for HER catalysis and TOFs of only a few units per site per second at 100 mV overpotential (see figure 3, section 2) [10]. The binding energy of hydrogen (described as $H^{\cdot}$ or H^-) to the electrode surface has been identified as a descriptor for such activity, but fails to explain the order of magnitude difference in TOFs between Pt and other catalysts such as $Fe_{0.5}Co_{0.5}P$ or Ni_5P_4 [163], when mass transfer limitations and active site determinations are correctly taken into account [11], and this discrepancy may be related to the H_2 evolution step via the Heyrovsky or Tafel mechanisms (figure 28). Actually, only microbial hydrogenases [164], having [NiFe] or [FeFe] catalytic sites, can compete with Pt for both reversible behavior and a TOF as high as $(21 \pm 12) \times 10^3$ $H_2 \cdot site^{-1}$ s^{-1} at ca 100 mV overpotential [165]. Interestingly, the enzymes also operate at near-neutral pH where HER catalysis is most problematic due to the demands of H–OH cleavage prior to the Heyrovsky or Tafel step. Advances in neutral HER catalysis will be important to enable safer deployment of HER technologies, as well as H_2 generation from waste water sources [166].

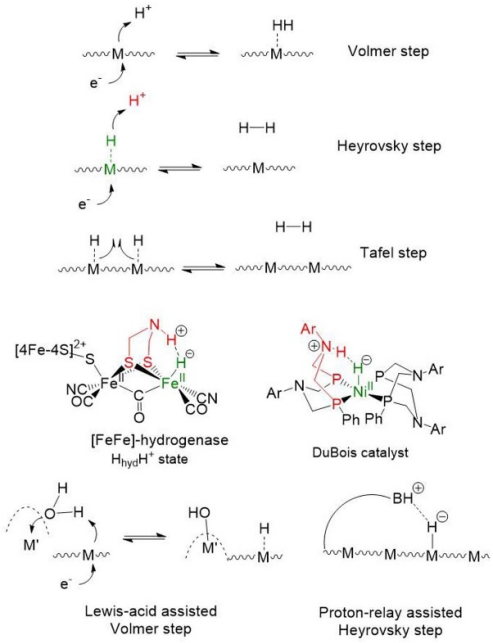

Figure 28. Key steps involved in the HER (top), involvement of proton relays at the active site of [FeFe]-hydrogenases and bioinspired DuBois' catalyst (middle) and possible implementation of such molecular mechanisms at inorganic surfaces (bottom).

Current and future challenges

The anticipated shortage of an increasing number of critical elements, especially metals, requires a shift towards molecularly-defined materials with lower metal loadings and enhanced performances, encompassing the design of single-atom catalysts (SACs) embedded in carbon matrices [167] or surface-anchored molecular catalysts [168, 169] (figures 29(a) and (b)). In that context, the design of more efficient HER catalysts requires a better identification of the determinants of, and relationships between, reversibility, overpotential requirement and catalytic bias towards HER/HOR catalysis. Such a knowledge can be informed by a deeper analysis of structure-function relationships observed for hydrogenases and related bioinspired molecular catalysts and will be very helpful to promote HER at the surface of inorganic materials in a bioinspired fashion (figure 28). While limited stability and low active site density make hydrogenases unlikely to be viable for HER technologies, key design features seem to be: H_2 formation from poised H^-/H^+ held on respective Lewis acid/Lewis base sites (figure 28), extensive delocalization to minimize charge build-up during catalysis, and significant tolerance towards common catalyst poisons, O_2, CO or sulfides.

In addition, engineering design principles should be implemented to allow the electrode material to operate efficiently, continuously and stably over its lifetime. At the heart of these engineering aspects lies the control over the density and nature of active sites. Variation in HER activity at edge vs basal sites on MoS_2 [10] or at amorphous molybdenum sulfide [170]

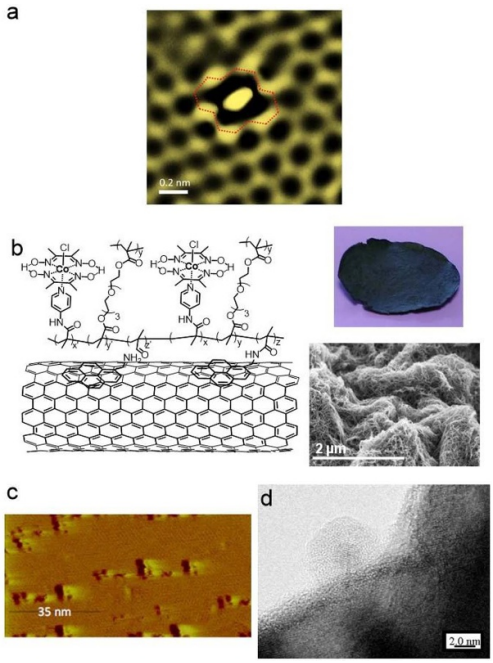

Figure 29. (a) TEM image of atomic Ni trapped in graphene defects as single-atom catalyst (SAC) for the HER, reproduced with permission from [169]; (b) structure (left) of carbon nanotubes coated with a polymeric matrix stabilizing cobaloxime catalysts forming a free standing buckypaper electrode (top right) images by SEM (bottom right); adapted from [174]; (c) STM for $Ni(OH)_2$/Pt(111) in the HER region [175]; (d) TEM images of Rh/Cr_2O_3 core–shell nanoparticle-modified GaN:ZnO [176].

illustrates such a challenge in optimization of electrode architecture. Thicker electrodes are commonly developed to compensate for a lower TOF, but then require optimization of the mass transport of reactants, intermediates and products throughout the device [171]. Electrolyte engineering is a tool to push the limits of ion diffusion. Local pH shift is often observed at high current density, causing additional potential loss especially under near-neutral pH conditions [166]. Another problem is H_2 bubble formation, which may cause additional resistance by insulating the active sites from electrolyte. Overcoming such issues requires control over wetting/aerophobicity and morphology of the (porous) electrode materials.

Finally, and perhaps of primary importance for industrial implementation, efforts should be pursued to provide catalysts with a greater stability, allowing HER to cope with intermittency of renewable energy sources and to tolerate the presence of contaminants, particularly O_2 which is produced at the anode during water splitting.

Advances in science and technology to meet challenges

Progress has been made by replicating features found at the active sites of hydrogenase enzymes in molecular catalysts through the installation of proton relay sites/frustrated Lewis pairs or redox active ligands to manage charge build-up at the vicinity of the active site [168]. Namely the role of pendant proton relays at the vicinity of the active site are exhibited in the Ni-based DuBois catalysts (figure 28) which provide an important proof of concept that bioinspired catalysts can catalyze HER and HOR reversibly and with high TOF [168]. Grafting such catalysts on carbon nanotubes generates porous electrode materials with remarkable activity for HER, including under very acidic conditions [172]. In parallel, synthetic methods recently emerged to enable high control and almost molecularly defined design of active centers in SACs for HER [167, 169]. Still, the integration of such alternative materials into practical devices requires rethinking the whole system of materials [173]. Polymeric matrices (figure 29(b)) have been developed to maximize molecular catalyst loading and provide a stabilizing environment to the catalyst leading to further enhancement in catalytic performance and/or to shield against O_2 [174]. Similar approaches have been implemented on metal electrode surfaces, for example with the introduction of $M(OH)_x$ (M = Fe, Ni or Co) islands on Pt (figure 29(c)) to facilitate O–H bond breaking, assisting the Volmer step (figure 28(bottom)) in the case of H_2O reduction [175]. A successful nanomembrane coating includes the core–shell Rh–Cr_2O_3 HER catalyst used in powder semiconductor photocatalytic systems (figure 29(d)), where access of O_2 to the Rh metal core is shielded by the Cr_2O_3 shell, preventing competitive reduction of O_2 [176]. The development of such membrane-coated catalysts [177] is thus a promising approach to achieving stable and tunable electrocatalysts.

Concluding remarks

There are still key challenges regarding HER catalysis, especially in the context of the production of solar fuels, where there is a demand for scalable catalyst materials—i.e. Earth-abundant, efficient and stable. While it has not yet been possible to reach the intrinsic turnover frequency of platinum using non-noble metals, hydrogenase enzymes can inspire design principles for boosting the kinetics of key reaction steps, e.g. via the introduction of proton relays. Similarly, Lewis-acid assistance has proved effective in enabling water, instead of protons, to act as HER substrate. These approaches can be implemented using surface chemistry or via the design of functional matrices and will be instrumental in reaching long-term stability and tolerance to O_2 and other contaminants, and in facilitating the shift towards operation under neutral conditions needed for safe and deployable technologies. Additional features such as transparency and efficient interfacing with light absorbers will also be key in the development of solar hydrogen systems.

17. CO_2RR catalysis: surface reactivity and products selectivity

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Status

Taking advantage of renewable energy sources to convert CO_2 to fuels and chemicals electrochemically has the potential to sustainably produce currently fossil-derived molecules artificially, using systems that mimic photosynthesis. The ultimate goal is solar fuels or 'electrofuels', and by developing the technology into an efficient and scalable one, a circular economy can be formed around CO_2-neutral production and subsequent use of fuels, figure 30. In addition, it presents an avenue for efficient utilization of intermittent, renewable energy along with the vast, pre-existing infrastructure for storing and transporting these molecules. Nonetheless, considerable progress must still be made to achieve industrially relevant targets for the technology to be considered for large-scale implementation, as featured in a recent technoeconomic and carbon emissions analysis [54].

At the heart of this development is the electrochemical CO_2 reduction reaction (CO_2RR), which takes place on the surface of an electrocatalyst. Thus, it is vital to gain a fundamental understanding of how different parameters influence the selectivity and efficiency of the CO_2RR. Over the past few years, considerable work has been done to gain mechanistic insight into various aspects of the electrocatalysis, such as the initial activation of CO_2, the importance of stabilizing key intermediates, and their relation to the observed overpotentials [178]. The effect of the molecular nature or catalyst morphology (particle size, shape, roughness, defect density and composition) on CO_2RR selectivity has also been examined [179, 180] in detail. More recently, attention has been given to (local) electrolyte effects and the role of mass transport [181] in relation to product selectivity. Finally, potential pulses leading to a change in the catalyst morphology, oxidation state and local pH have been featured as an additional avenue to tune the product selectivity [182]. Progress in understanding these fundamental aspects of the CO_2RR will be crucial in developing both solar-driven and electricity-driven systems.

Currently, the best Faradaic efficiencies (FEs) have been reported for the two-electron products carbon monoxide (CO) and formic acid (HCOOH) as well as 12-electron product ethylene (C_2H_4). Electrochemical engineering efforts are progressing these best candidates towards commercial relevancy through innovations in gas diffusion electrodes, ion-exchange membranes, flow-cell architectures and process optimization. In order to enhance this progress and expand the range of favorable CO_2RR products, further advancements must be made in understanding the electrocatalysis.

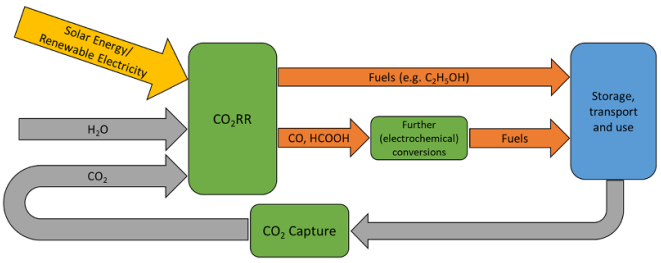

Figure 30. The role of the CO_2RR in a circular economy for production of fuels from solar energy and renewable electricity.

Current and future challenges

One of the core issues for the CO_2RR is the competing hydrogen evolution reaction (HER) that limits the FE of desired (carbon containing) products, hindering the overall energy efficiency, especially at low potentials, and requires additional steps downstream for the H_2 gas [54]. Under alkaline conditions often used for aqueous CO_2RR, the slow rate of water reduction helps to suppress the HER. However, alkaline conditions lead to the formation of carbonates that trap the CO_2 and cross the anion-exchange membrane used in those systems [183]. Strategies to overcome the challenges presented by the HER will be necessary as the technology progresses.

Since the pioneering work of Hori [184], Cu has been known as a promising catalyst for C–C bond formation, with computational calculations and experimental evidence showing that the mechanism proceeds through a CO-dimer [185]. Despite the remarkable ability of Cu to effectively catalyze the CO_2RR towards C_2 products, high overpotentials are required. There are also issues with selectivity, with a large product distribution often observed [186]. The C_2 products formed with the highest FE are ethylene and ethanol, but it remains a challenge to direct the reaction towards a single target molecule to avoid additional separation steps. Furthermore, the surface of Cu has been shown to restructure under CO_2RR conditions [187], limiting its durability and consequently commercial viability. For next generation catalyst design, Cu surfaces should be further tailored to facilitate C–C bond formation and improve their stability. Recently, it was shown that rather than targeting ideal surfaces with specifically oriented facets, selectivity tuning can be achieved through catalyst pretreatments, leading to specific surface defects [187], the nature of which and their correlation to a specific selectivity trend is still to be unveiled.

Efficient catalysis towards other valuable CO_2RR products is another significant research challenge. This includes C_1 molecules methanol and methane, with a huge demand for a low-carbon production pathway, together with C_2+ molecules of high value. Understanding the factors that govern the formation of these molecules, even as minor products, will aid the development of future catalysts. One such study outlines strategies for catalyst design for C_2+ products whilst giving attention to the critical role of the electrolyte for these reactions [186]. Further insight into selective catalysts for methane

[188] and methanol [189] is also needed. Finally, real world industrial applications of this technology will likely involve hybrid processes where the CO_2RR will be integrated within a catalytic system comprising steps to be carried out within a coupled thermal reactor.

Advances in science and technology to meet challenges

Further advancements in CO_2 electrolysis will be necessary to reach a level similar to that of the more mature H_2O electrolysis technology for 'green hydrogen' production. The selectivity, durability and rate of reaction of current state-of-the-art catalysts can be improved through the modification of surface morphology and composition to optimize the activity, figure 31. More detailed work on electrolyte effects will also be required to meet the ambitious goals for the technology. Another avenue to tune the selectivity towards C_2 products over Cu catalysts is to increase the CO surface coverage, with higher coverages favoring the C–C coupling [190]. This can be achieved by combining Cu with CO-making metals such as Ag, resulting in enhanced ethylene and ethanol production. Hybrid approaches, such as combinations of molecular and heterogeneous catalysts, may also be advantageous for future catalysts.

Further analysis of mass transport and pH effects on different catalysts will help to suppress the HER and thus improve the FE for desired products. For this purpose, pulsed electrochemistry approaches are also being considered [191], with the value of the anodic potential pulse drastically influencing the reaction selectivity through the associated changes in the morphology, adsorbate coverage and local pH [192]. As recent work has shown [193, 194], investigations into the CO_2RR in acidic conditions with different electrolytes and mass transport control could alleviate some of the aforementioned HER issues. To improve the selectivity towards a single C_2 product on Cu, similar strategies should be employed, with a focus on achieving good selectivity to one molecule. For effective CO_2RR to additional products of interest, other approaches may be considered, such as a tandem-electrolysis approach, where CO_2 is initially reduced to CO or COOH, then converted further to a higher value product.

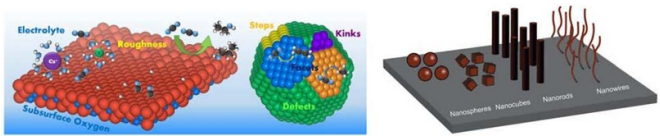

Figure 31. Illustration of catalyst surface effects on the CO_2RR activity and selectivity. Reproduced with permission from [178, 179].

Many experimental spectroscopic, microscopic and diffraction techniques that allow for detailed analysis of catalyst surface and bulk structures, chemical composition and reaction will require greater sensitivity and a more realistic operation environment. Detecting intermediates at very low coverage will enable more insights into reaction mechanisms as well as the effect of different surface structures. Finally, complimentary progress in theoretical methods is vital. Realistic models for electrolyte-electrolyte interfaces and mass transport effects, using explicit solvent and electrolyte ions, will progress the understanding of such effects at an atomic level. Machine learning approaches will become increasingly important for the evaluation of large microscopy or spectroscopy datasets experimentally generated under *operando* reaction conditions.

Concluding remarks

Gaining a fundamental understanding of the electrocatalysed CO_2RR will help to progress the technology towards commercialization, where it has the opportunity to play a significant role in the energy transition. Mechanistic understanding of the different reactions that occur on the catalyst surface will help to rationalize activity and selectivity, aiding both the optimization of current catalysts and design of next generation catalysts. Studying the effect of *in situ* conditions, including pH and mass transport effects, on the CO_2RR will enable further progress to be made with catalyst performance. The catalyst morphology and degradation mechanisms must be understood in order to enhance the durability to the level required for large-scale implementation. To enable this progress to be made, *in silico* theoretical and *operando* experimental techniques must be further developed and utilized in tandem.

Data availability statement

No new data were created or analysed in this study.

Acknowledgments

1. Introduction
Gideon Segev, Roel van de Krol and Frances Houle

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2. Comparison of state of the art electrocatalysts for water splitting, CO_2 reduction, and N_2 reduction
Jakob Kibsgaard, Christopher Hahn and Zhichuan J Xu

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3. Efficiency and stability benchmarking. What is required to bring a solar fuels system to market?
Wen-Hui (Sophia) Cheng, Todd G Deutsch and Chengxiang Xiang

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4. Comparing artificial and natural photosynthesis—bio concepts and hybrid systems
Jenny Z Zhang, Leif Hammarström and Daniel G Nocera

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5. Design and scale-up of solar fuels systems using current technologies—neutral pH, vapor-fed devices
Adam Z Weber and Peter Agbo

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6. Particle-based systems: lessons learned and guidelines for large area systems
Takashi Hisatomi, Frank E Osterloh and Kazunari Domen

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7. Device design considerations for scale-up: managing photons, electrons, and ions
Fatwa F Abdi and Sophia Haussener

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8. Membranes for solar fuels
Daniel J Miller and Shane Ardo

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9. Photoelectrodes based on conventional semiconductors (silicon, III–V)
Paul C McIntyre, Thomas Hannappel and Shu Hu

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10. Nanostructures for light management in solar fuels and photoelectrochemistry
Wen-Hui (Sophia) Cheng and Harry Atwater

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11. Accelerating discovery of photoactive materials
John M Gregoire and Mehmed Z Ertem

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12. From materials discovery to functional photoelectrodes
Ian D Sharp, Kyoung-Shin Choi and Jae Sung Lee

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13. Molecular photoreduction and photocatalysts on photofunctional solid materials
Osamu Ishitani

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14. Photocathode design: fundamental challenges and paths forward for CO_2 reduction
Joel W Ager and Rajiv Ramanujam Prabhakar

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15. Oxygen evolution reaction: catalysts, mechanisms, and durability
Alexis T Bell and Shannon W Boettcher

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16. Remaining challenges for the hydrogen evolution reaction (HER): catalysts and mechanism

Kylie Vincent, Kazuhiko Takanabe and Vincent Artero

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17. CO_2RR catalysis: surface reactivity and products selectivity

Ryan Napier, Beatriz Roldan Cuenya and Marc T M Koper

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