Innovation Challenge 5:

Converting Sunlight into Solar Fuels and Chemicals Roadmap 2020–2050

February 2021

Table of Contents

List of Figures

List of Highlights

Executive Summary

This **Innovation Challenge "Converting Sunlight into Solar Fuels and Chemicals" Roadmap 2020–2050** highlights the scientific and technical challenges and opportunities for international cooperation to accelerate the development and deployment of new solar conversion technologies worldwide.

In November 2015 in Paris, 195 countries pledged to limit global temperature rise below 2°C by 2100. At the same time, 22 countries acknowledged that research and innovation activities were essential in reaching that goal. These countries took the commitment to double their own funding in clean energy technology by 2020. The European Commission on behalf of the European Union joined soon after. They also recognised that research cooperation was a key enabler and initiated seven Innovation Challenges in 2016 and an eighth in 2018 with the explicit aims of promoting research collaboration and accelerating technology development between the members of Mission Innovation.

Inspired by natural photosynthesis, Innovation Challenge "Converting Sunlight into Solar Fuels and Chemicals" responds to the opportunity of converting sunlight directly into chemically stored energy. Solar fuels can be an important enabler for decarbonisation and a clean energy transition, in addition to furthering sustainable development worldwide and being a game changer for industrial applications. Mission Innovation members recognise that directly harnessing the sun´s energy to generate solar fuels, chemicals, and products could significantly help mitigate climate change, create a circular carbon economy, enhance energy security, and provide opportunities for economic development across the globe.

Researchers and industrial players around the world were brought together through three workshops: in Europe under the framework of SUNRISE (October 2019), in Japan during the 3rd International Solar Fuels Conference (November 2019), and at a web-based virtual workshop with the United States and other North American and South American participants (November 2020). Workshop participants contributed based on their knowledge and existing national roadmaps in a draft document framework.

This roadmap identifies major research and innovation needs for a number of solar fuels technology pathways. It also considers how these emerging technologies could be integrated into existing industrial infrastructures and processes, including upstream and downstream of solar fuel conversion to address the entire solar value chain. While there have been considerable advances in solar fuels, research and development is needed to address critical challenges including cost, performance, durability, and integration and to create a solar fuels industry. Scientific publications in this area increased by ten-fold in the past ten years. Prototypes are being tested around the world.

The Innovation Challenge 5 (IC5) is focused on addressing these challenges where scientific advances are needed to make solar fuels competitive with other technologies. Individual approaches for the direct conversion of sunlight to chemical energy were grouped into the following topical areas:

- Catalyst development for water splitting, CO_2 reduction, and other key reactions
- Improved solar light harvesting, charge separation, and coupling to catalysts
- Photoelectrochemical and photocatalytic devices
- Photobiological and biohybrid approaches
- Thermochemical pathways using concentrated sunlight
- Design, engineering, and demonstration of devices and systems at scale.

This roadmap presents major challenges and specific research goals, key enabling research and some high-level milestones for these technical approaches. Addressing these needs can be accelerated through international cooperation. In addition, there are significant synergies as well as some common development challenges for these approaches. Another key challenge is design, engineering, and demonstration of devices and systems within the context of existing infrastructures. There are also potential synergies within Mission innovation on other Innovation Challenges, particularly renewable and clean hydrogen (Innovation Challenge 8) and carbon capture (Innovation Challenge 3).

This roadmap completes this first phase of Mission innovation Challenge "Converting Sunlight into Solar Fuels and Chemicals" and serves as a starting point for the discussion of opportunities and challenges in a more global context and for the next stage of this Innovation Challenge under the framework of Mission Innovation 2.0.

Contribution to the IC 5 Roadmap[1]:

We thank the contribution of the members of Mission Innovation Challenge "Converting Sunlight into Solar Fuels and Chemicals" and of the participants from the respective workshops held in Europe (October 2019, with project SUNRISE), Japan (November 2019) the USA (November 2020). The editing team was led by Dr. Thomas Schleker, European Commission, and Dr. Philippe Schild, European Commission, and comprises Dr. Peter Vach, Federal Ministry for Economic Affairs and Energy, Germany; Prof. Dr. Leif Hammarström, University of Uppsala, Sweden; Prof. Dr. James Durrant, Imperial College London, UK; Dr. Sacha Corby, Imperial College London, UK; Dr. Oytun Babacan, Imperial College London, UK; Dr. Alessandra Sanson, National Research Council of Italy (CNR), Italy; Dr. William Tumas, National Renewable Energy Laboratory, USA; Prof. Dr. Antonio Otavio Patrocinio, Federal University of Uberlandia, Brazil; Prof. Dr. Hongxian Han Chinese Academy of Sciences, China; Prof. Dr. Can Li, Chinese Academy of Sciences China. The leaders of the three roadmapping workshops also made contributions to this document: Dr. Carina Faber, UCLouvain Belgium; Prof. Akihiro Kudo, Tokyo University of Science Japan; Prof Ryu Abe, University of Kyoto Japan; Prof Osamu Ishitani, Tokyo Institute of Technology Japan, Prof, Prof. Dr. Harry Atwater, JCAP USA, Prof. Dr. Jillian Dempsey, University of North Carolina USA; Dr. Frances Houle, Lawrence Berkeley National Laboratory USA; Prof. Dr. Jerry Meyer, University of North Carolina USA, Prof. Dr. Ellen Stechel, Arizona State University USA along with a number of workshop participants. Illustrations for the figure were provided in courtesy by Dr. Sacha Corby, Dr. Alessandra Sanson, Prof. Dr. Harry Atwater and Dr. Thomas Schleker.

[1] [1] This document only reflects views of the authors and contributors, and not necessarily the views of their respective institutions

1. The Role of Mission Innovation Challenge 5 in the Global Context

As codified in the Innovation Challenge 5 (IC5) of Mission Innovation (http://mission-innovation.net) converting sunlight directly into chemical energy for fuels, chemicals and energy storage represents a grand challenge and opportunity. By directly harnessing the sun, the most ubiquitous source of energy, to generate solar fuels would significantly help mitigate climate change, create a circular carbon economy, enhance energy security, and provide opportunities for economic development across the globe. This report provides a preliminary roadmap to address key challenges and capture major opportunities for solar fuels with a focus on research and innovation needs.

1.1. Climate Change and the Paris Agreement

The International Panel on Climate Change (IPCC) comprises over 1,300 scientific experts to analyse the extent of climate change. The IPCC reported that the last 40 years have produced as much as half of the cumulative anthropogenic carbon dioxide (CO_2) emitted since 1750: a direct result of increased population and global energy consumption [1]. As population and energy consumption are predicted to continue to increase over this century, so, too, are emissions and global temperature set to rise further. Figure 1.1 shows the climbing global CO_2 emissions produced each year since 1990 alongside future projections [2]. Without energy policies in place, the IPCC predicts emissions to soar towards 100–200 Gt of annual CO_2 by 2100, accompanied by temperature increases of up to 4.5°C over preindustrial levels. This temperature increase would induce such dramatic changes to our planet that it is not possible to predict the full impact. Even if temperatures are limited to a 2°C increase, the IPCC Special Report states that all marine coral will be wiped out (affecting ~0.5 billion people who depend on it) [3]; multiple regions of the oceans will become dead zones that cannot support aquatic life; habitable environments for many species of insects and vertebrate will shrink; and food security and water resources will be of increasing concern, thrusting millions into extreme poverty [4]. The loss of plant and animal life as a result of human-induced climate change has already been so severe that it is widely considered we are entering into a new mass-extinction event, greater than its five predecessors, including that which eradicated the dinosaurs [5].

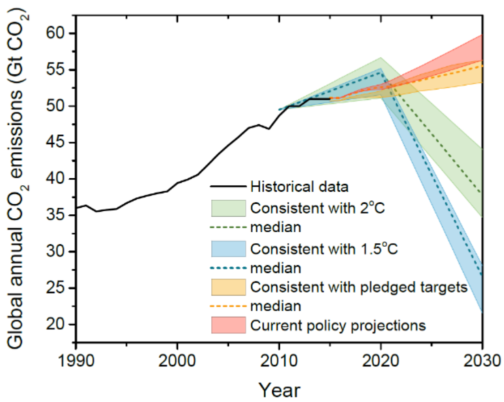


Figure 1.1. *Annual CO_2 emissions in gigatonnes (1 billion tonnes) and the current projections for future emissions. The current projections remain higher than those pledged (median given to account for different pledges) and significantly greater than the target emissions required to limit global warming to 2°C (Cancun Agreement) and 1.5°C (Paris Agreement). Taken from Sacha Corby Ph.D. Thesis, 2020 [6] and adapted from Climate Analytics and New Climate Institute, 2019 [2].'*

In 2015, a monumental step was achieved when the Paris Agreement was reached, with 195 nation states (including the European Union) signing a pledge to keep the global average temperature this century under a 2°C increase over preindustrial levels [7]. The secondary aim of the agreement is to limit the temperature increase below 1.5°C, which the IPCC Special Report has outlined as essential to mitigate the worst of the damage. However, while the agreement is promising, the annual CO_2 projections based on currently pledged targets leave us far short of the 2.5°C, let alone the 1.5°C aspiration. If warming is to be limited to 1.5°C, net CO_2 emissions must drop to zero by 2050. As such, we cannot rely on the finite fossil fuels remaining until a solution is found. An entire shift in energy production and consumption is required, and quickly.

Mission Innovation is a global initiative launched at COP21 in 2015 to help achieve the ambitious goals of the Paris Agreement. Mission Innovation is comprised of 24 countries and the European Commission (on behalf of the European Union) working to reinvigorate and accelerate global clean energy innovation with the objective to make clean energy widely affordable [8].

> *"In support of economic growth, energy access and security, and an urgent and lasting global response to climate change, our mission is to accelerate the pace of clean energy innovation to achieve performance breakthroughs and cost reductions to provide widely affordable and reliable clean energy solutions that will revolutionize energy systems throughout the world over the next two decades and beyond."*
>
> – Enabling Framework for Mission Innovation

The Clean Energy Ministerial, a global forum to promote policies and programs that advance clean energy technology, is working towards the transition to a global clean energy economy and supports the development of solar fuels [14]. Mission Innovation, including IC5, will transition into Mission Innovation 2.0 (MI 2.0) to be launched at the Sixth Innovation Ministerial Minister. This document represents the first step towards development of a detailed long-term roadmap for solar fuels research and development, also in the context of MI 2.0.

1.2. Solar Fuels as an Important Enabler for a Clean Energy Transition

The renewable energy resource with the largest potential to help meet the challenge for a decarbonised energy system is solar energy, providing thousands times more energy to the Earth per year than our global annual energy consumption. We have witnessed incredible progress converting solar energy to electricity using photovoltaics (PV). The cost of PV modules has dropped dramatically since their first manufacture in the 1970s, plummeting from ∼100 $/W down to between 0.20–0.40 $/W in 2018 [[10]–[12], thereby making the current cost of solar electricity below that derived from fossil fuels and enabling widespread installation (global installations are approaching a terawatt), even in remote off-grid locations. Major advances in solar thermal technologies and applications include small-scale systems, usually used to heat water for residential purposes, and large-scale concentrated solar power (CSP) plants that employ a large number of mirrors to concentrate sunlight onto a receiver to either generate steam directly or indirectly through a storable heat transfer fluid to generate electricity. Thermal energy can be stored and used to produce electricity on demand. Alternatives to steam-based processes being pursued for CSP include supercritical CO_2 Brayton cycles that can operate at higher temperatures and have a smaller footprint than steam, as well as concepts incorporating thermophotovoltaics.

Solar fuels involve the direct production of energy-rich chemicals and fuels from sunlight, air (e.g., CO_2 and nitrogen), and water. Solar fuels generation embodies a number of anthropogenic and biologically assisted processes to convert solar energy directly to fuels, chemical products, and materials. Like solar electricity, solar fuels can be generated using the light energy directly from sunlight, often termed *artificial photosynthesis* or the use of heat from sunlight to drive high-temperature thermal processes.

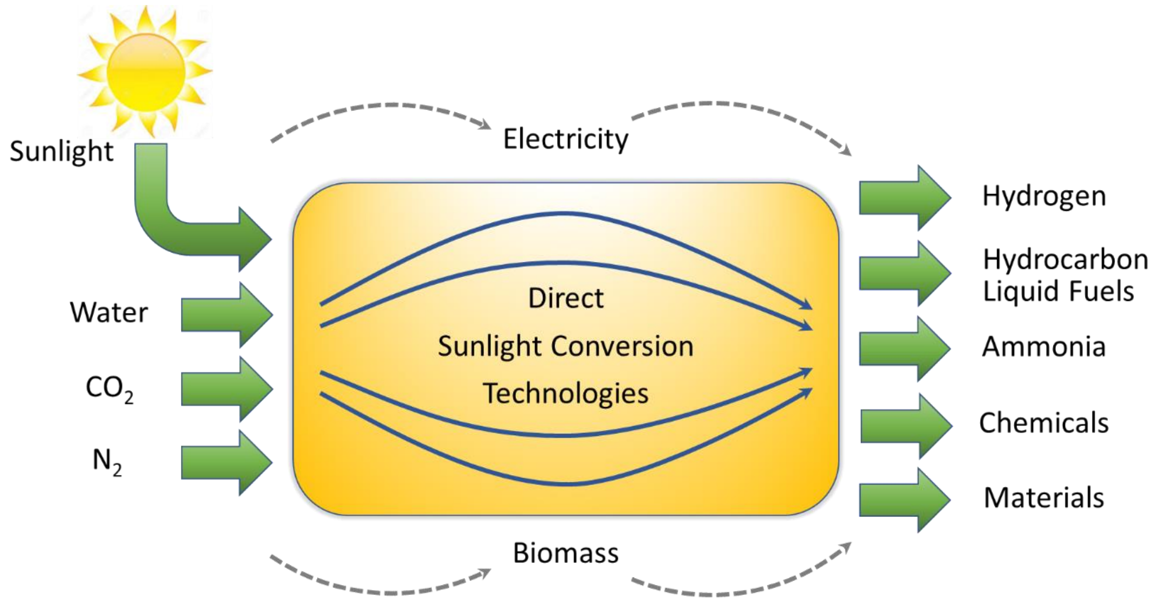


Figure 1.2. *Overview of the conversion of abundant water, CO_2, and N_2 into useful fuels and chemicals using sunlight. The focus of this roadmap is the direct conversion technologies (yellow box), which have the potential to, in a single process, perform the necessary conversion steps to obtain these desirable products.*

Solar fuels offer the potential for economically and environmentally beneficial routes to plentiful, sustainable, transportable, and storable energy that would be complementary to products derived from biomass (bottom of figure) or electrochemical processing using renewable electricity (top of figure). Solar fuels take inspiration from natural photosynthesis but could also circumvent certain limitations of biological systems to provide efficient, robust, and sustainable pathways for fuel generation (e.g., harvesting more of the solar spectrum to increase the overall efficiency or directing pathways to specific molecules or fuels). Generating ammonia (and/or other nitrogen-containing chemicals) from sunlight and atmospheric nitrogen (N_2) would lead to sustainable routes to fertilizers as well as other fuels and commodities. As a technology, solar fuels generation is much less mature than PV and CSP for electricity generation; however, advances in solar fuels can build on scientific and technological advances in these areas.

Solar fuels can play an important role in the clean energy transition by enabling broader deployment of solar energy. Electricity generation from PV is intermittent and variable due to geographical location, changes in weather and seasons, and for solar, the diurnal cycle (e.g., night and daytime). These factors have less effect on solar thermal conversion systems and other low-carbon renewable energy technologies such as wind. Large-scale deployment of low-carbon renewable energy, therefore, requires grid integration, demand response, and energy storage to avoid mismatches of supply and demand. The mismatch in periods of renewable energy generation and consumption poses a great challenge for achieving the high renewable energy fraction needed to meet global CO_2 reduction commitments. Storing chemical energy using solar fuels offers a complementary approach to electrical energy storage through batteries to enable full deployment of renewable energy with low emissions and a carbon footprint, even offering the potential for seasonal storage of sustainable energy. Energy-dense fuels such as hydrocarbons, which could be produced from sunlight, water, and carbon dioxide, can also significantly impact the transportation sector, particularly heavy-duty transportation and aviation. Furthermore, chemicals generated by solar fuels processes can be compatible with existing industrial and commercial infrastructure and provide important feedstocks to chemical and materials industries. Solar-driven processes for CO_2 conversion could also be integrated with carbon capture concepts, including direct air capture.

1.3. Solar Fuels Can Address Global Challenges and Opportunities

The United Nations Sustainable Development Goals (SDGs) are set with the aim of achieving a sustainable future for all world citizens [15]. The importance of affordable and clean energy is acknowledged in SDG7. MI's Converting Sunlight Challenge can greatly contribute to achieving this goal by increasing global access to renewable energy. Solar fuels may generate new opportunities in Africa within the development of new regional value chains. The 17 SDGs are interconnected, and solar energy, in particular, interlinks to the other SDGs focused on Climate Action (SDG13), No Poverty (SDG1), and Sustainable Cities and Communities (SDG11) as well as others. There is also potentially strong synergy between the IC5 and other global development targets, such as responsible production and consumption (SDG12), and innovation, industry, and infrastructure (SDG9).

As described below, large-scale development of solar fuels technologies and creation of a solar fuels industry requires advances in performance (e.g., efficiency, selectivity), cost, durability, and integration. The IC5 is focused on addressing these challenges [13] where scientific advances are needed to make solar fuels competitive with other technologies, including fuels/chemical generation from electrolysis using renewable electricity or products derived from fossil fuels using processes decarbonised by carbon capture and sequestration. Six topical areas have been identified for this preliminary roadmap. The first five topics involve the direct conversion of sunlight to chemical energy (solar fuels conversion, see Chapter 3) with the research goals needed to bring these technologies to market. The final topic is discussed in Chapter 4 within the context of energy and industrial infrastructures.

- Catalyst development for water splitting, CO_2 reduction, and other key reactions
- Improved solar light harvesting, charge separation, and coupling to catalysts
- Cyanobacteria and microalgae that excrete fuels or chemicals into a surrounding medium
- Photoelectrochemical, photocatalytic, and hybrid bio/inorganic devices
- Thermochemical pathways using concentrated sunlight
- Design, engineering, and demonstration of devices and systems.

In this first IC5 roadmap, important connections to creating a global circular economy, including a circular carbon economy centered around capture and utilization of CO_2, is presented along with critical needs for developing an eventual solar fuels industry and its supply chains. Value chains for solar fuel production can have significant impact and, if well established, benefits relative to other aspects of our energy transformation on material, water, and land usage. Therefore, it is critical that circular economy concepts be embedded early into any Converting Sunlight innovation pathway, accounting for scale in each case and required resources and materials. There is also a need for cooperation across industrial sectors in the areas of precompetitive research and development, standardization, performance analysis, durability testing of devices, materials and systems, and life-cycle analyses to quantify the potential benefits of different approaches.

2. A Vision for Solar Fuels and Solar Chemicals – The Value Chain for Converting Sunlight

The value chain for the production of solar fuels comprises three functional parts: (i) the upstream feedstock interface, (ii) the central solar energy utilisation and chemical conversion processes, and (iii) the downstream chemical conversion/separation platforms and interfaces with existing chemical and fuels infrastructures. It is difficult to define a distinct boundary between the conversion and distribution aspects of the value chain *a priori*, as this boundary will be highly specific to the nature of the conversion process and final products obtained. Solar fuels conversion processes are at the heart of this roadmap. Nevertheless, supply chains as well as economic, environmental, and societal factors need to be considered across the entire value chain if emerging technologies are to be successfully implemented. A schematic of the sunlight-to-fuels value chain is provided in Figure 2.1. Before considering each of the functional parts in detail, it is important to note that the specifics of any value chain will be regionally dependent, with strengths and weaknesses in different aspects, but offers the prospect of growth in emerging economies, especially in sun-rich regions of the world. Furthermore, new approaches to financial derisking are required, which should be facilitated by methodologies and guidelines developed within the Mission Innovation framework.

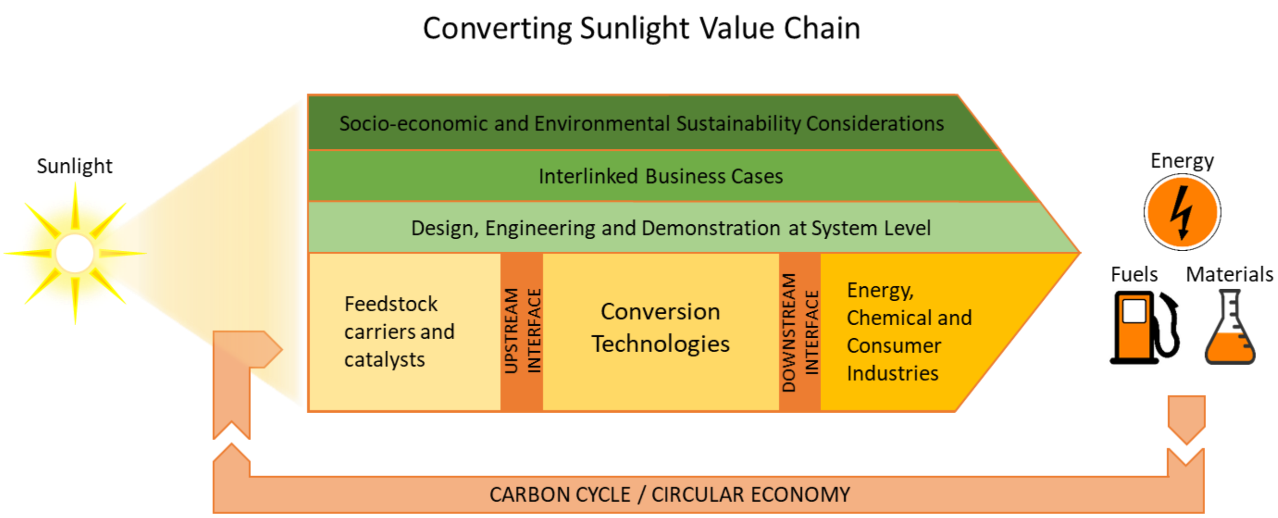


Figure 2.1. *The Converting Sunlight Value Chain. Primary processes and interfaces are given in orange, with ongoing support activities shown in green. It should be noted that several elements of this value chain are currently covered primarily by research and development programs.*

2.1. Feedstocks and Materials

The direct conversion of sunlight into solar fuels ideally has a number of requirements for feedstocks and materials, several of which are described below.

2.1.1. Sunlight

Solar radiation is the essential energy source behind generating solar fuels. It can be used to provide energy in the form of light (photons), heat, or indirectly through electricity (e.g., using PV). Detailed solar resource maps exist for much of the globe. An efficient conversion process for solar fuels might require a certain solar irradiance, which may differ for given subsets of technologies. A location best suited for the particular technological value chain is therefore an integral part of the broader solar fuels value chain, as site-specific factors like temperature, cloud cover, humidity, wind, rain, inclination of terrain, latitude, environmental factors, and pollution are important. Moreover, a given subset of solar conversion technologies may have different degrees of sensitivity to these factors such as local temperature, cloud coverage, humidity, terrain, etc. For example, some location-technology combinations may require the employment of solar concentrators that require direct normal irradiance solar radiation.

2.1.2. Water (H_2O)

H_2O is a critical component in any solar fuels conversion. H_2O is split by solar energy into oxygen (O_2), electrons, and protons—or directly into essentially oxygen and hydrogen (H_2) by solar thermal systems. The protons and electrons can combine to form H_2 (H_2, a solar fuel itself—see Highlight 1 on solar H_2 production), or they can be used to chemically convert feedstocks such as CO_2 into energy-dense fuels and products. While H_2O availability may not currently be as limiting as other feedstock issues in the value chain, most current conversion technologies require purified water sources, adding cost and complexity to the systems. Developing concepts that could employ brackish water, seawater, or contaminated water could be very important [17]. Coupling solar fuels processes with solar-driven H_2O purification creates potential new opportunities.

2.1.3. Carbon Dioxide (CO_2)

Carbon-based fuels and products are central to our global economy, and CO_2 is the largest contributing greenhouse gas towards climate change, trapping heat within the Earth's atmosphere, resulting in global warming and climate risks. Capturing CO_2 (from industrial processes and/or directly from air or seawater) and providing it as a feedstock is critical for solar fuels processes that convert CO_2 to fuels and products. Creating a circular economy in carbon requires processes to not only capture but recycle CO_2. Anthropogenic CO_2 feedstock capture and purification (if needed) for solar fuels align closely with some of the key elements in Innovation Challenge 3, which focuses on CO_2 capture, utilisation, and storage. Green plants and algae convert CO_2 as part of their photosynthesis processes, e.g., to generate essential sugars and liquids that act as both a food source for growth and building blocks for the formation of more complex carbohydrates.

2.1.4. Nitrogen (N_2)

A potential alternative to the generation of hydrocarbon-based fuels from sunlight is to generate ammonia (and other N_2-containing chemicals) as a high-energy-density carrier through the reduction of N_2. This approach benefits from the abundance of N_2 in our atmosphere and could also produce ammonia (NH_3) for use as fertilizer, an H_2 carrier, or a fuel, in addition to other N_2-based chemicals, materials, and fuels. N_2 is the most ubiquitous component in air (~78%); however, purification, pressurization, and separations processes may still be needed for solar fuels technologies. Although biological systems use nitrogenases to "fix" N_2 into chemicals, and commercial, large-scale Haber-Bosch processes use H_2 to reduce N_2 to ammonia, direct anthropogenic reduction of N_2 (solar or electrochemically driven) remains a grand challenge where fundamental research and breakthroughs are needed.

2.1.5. Oxidation Feedstocks or Substrates

A potential opportunity exists to drive additional organic chemical transformations using oxidation and/or reduction chemistry on substrates other than H2O and CO_2. For example, oxidation of biomass or wastes could lead to new product streams, including fuels. For example, solar-driven fuels production can also be performed by solar thermochemical reforming, in which plastic waste (e.g., polymers such as polyethylene terephthalate or polyurethane, among others) or biomass residues such as glycerol and lignocellulose are gasified (oxidised), resulting in the production of syngas and its downstream product synthesis pathways. Although these processes are outside the “must have” requirements for solar fuels, it is important to consider these additional options on a case by case basis as the field progresses.

2.1.6. Light Absorbers and Catalysts (for Light-Driven Solar Fuels Production)

Independent of the conversion technology applied, systems to harvest solar radiation and convert it to chemical or heat are required to drive the conversion process. Solar harvesting in anthropogenic systems requires photo-absorbing materials or, for CSP systems, large-scale collector systems (heliostats), which can be capital-intensive and represent a significant cost of the entire system. A number of functional materials (e.g., catalysts, electrode materials, photoelectrodes, or for thermally driven processes, regenerable stoichiometric reagents) affect desired chemical conversion(s). Functional materials, catalysts, and light absorbers are important cost drivers. In addition to cost, performance, and durability, these materials must be considered within the framework of a sustainable value chain (e.g., availability, waste minimisation, recyclability, and circularity). Of course, processing and manufacturing costs must also be considered. A wide range of other components may also be involved in solar fuels generation systems, including ionomers or membranes (for mass and ion separation), supports or substrates for catalysts and metals/metal oxides, protective coatings and interfacial materials, and electrolytes for solution-based processes.

Increasing the efficiency of solar fuels will require more efficient use of a larger portion of the solar spectrum. In current PV and many solar fuels conversion technologies, a large amount of solar radiation is lost to heat. Biological systems such as algae already have solar harvesting architectures; however, most of these only use certain parts of the solar spectrum.

2.2. The Conversion of Solar Energy to Fuels and Chemicals

Solar fuels generation constitutes a complex set of physical, chemical, and interfacial processes including sunlight harvesting, energy conversion and transport, ion and mass transport, and multistep oxidation and reduction reactions. Many of the chemical processes are driven by charge separation and catalysis (for light-driven processes) or stoichiometric, regenerable metals/metal oxides for thermally driven processes. For the former, there is often a correlation with analogous electrochemical or electrocatalytic processes. Figures of merit for the conversion processes from feedstocks, water, and sunlight include overall energy efficiency of conversion (i.e., solar energy is divided by chemical energy in the products); energy density of products; product yields and selectivity (i.e., how much and how preferential certain products are formed); durability, reliability, and lifetime of the solar conversion system types; and net present cost of products as well as capital costs. The conversion efficiency of a technology is an important precondition for effective and cost-competitive value chains of solar fuels and chemicals. Efficiency will depend on finding optimal interfaces with the upstream feedstock value chain and optimal reaction pathways with good kinetics, and on creating intermediate products of increased value for downstream product pathways.

2.3. Products and Downstream Processes

Potential solar fuels products could include gases such as hydrogen (H_2), syngas (H_2/CO mix), and methane (CH_4), as well as one-carbon or short-chain hydrocarbons containing heteroatoms (e.g., oxygen or nitrogen) such as ethanol, methanol, dimethyl ether or longer-chain, more complex liquid hydrocarbons. These compounds could serve as fuels and chemical products themselves or serve as intermediates that could be converted further to other desired products. Effectively interfacing with existing energy and consumer goods markets and creating viable supply chains may require downstream processing of products or intermediates generated from solar fuels processes. For example, syngas (a mixture of H_2 and carbon monoxide gases) might be upgraded into longer-chain hydrocarbons (e.g., kerosene) through, for example, Fischer-Tropsch-like chemistry; and methanol could be converted to olefins using commercial catalytic chemistries. Similarly, H_2 (the focus of Innovation Challenge 8) could be used as a fuel itself but could also be an important feedstock for the chemical, steel, cement, and fertilizer industries. Methane could be fed into the existing gas grid infrastructure, whereas more complex molecules such as methanol and ethanol can either be considered as platform chemicals or also used directly. The direct reduction of nitrogen is also a potential route to the production of ammonia for fertilizer, as an energy, or H_2 carrier.

The conversion aspects of the value chain may extend to production of more complex chemicals or energy carriers, as well as molecules of lower complexity that could be directly deployed to the existing chemical industry. Existing sectorial needs (e.g., heating and cooling or transport), regional value and supply chains, trade relationships, and logistics will all be important factors in determining where the interface between solar fuels conversion and downstream value chain lies in the end. Solar fuels can also provide energy storage and provision to regional energy systems at times when limited energy generation is available or for seasonal shifts to avoid overbuilding for winter production. There are significant opportunities for process integration and process intensification where a number of unit operations would be required that could lead to lower capital and operating costs and/or higher performance.

A number of processes ancillary to the solar-driven chemical conversions processes may be needed for effective solar fuels generation. For example, a number of materials and components may be necessary for the balance of plant (balance of system) including ancillary systems for storing, purification, separation, compression, delivering reactants, and collecting products as well as enabling thermal/heat management and mass transport.

3. At the Core of the Roadmap for Converting Sunlight – Solar Fuels Conversion Technologies

A number of conversion technologies are currently being developed to obtain a range of solar fuels and chemicals.

Figure 3.1 illustrates some of these technologies, which are at various stages of development or technology readiness level (TRL), with some closer to applicability than others. This section discusses the major challenges that must be overcome and introduces research goals and future milestones that should enable the development and eventual deployment of these technology options.

Efficiency is one of a number of important figures of merit for solar fuels conversion. For example, the conversion performance of photoelectrochemical water splitting devices to produce H_2 and O_2 can be quantified by the solar-to-hydrogen (STH) efficiency (η_{STH}), measured under standard irradiation conditions (AM 1.5 G, 100 mW·cm^{-2}). η_{STH} is defined as the amount of chemical energy (H_2) produced from the incident solar energy. For the commercially established approach of PV cells coupled with electrolysis (PV+e) (Section 3.1), η_{STH} is typically around 15% [20]. For direct photoelectrochemical water splitting (Section 3.2) employing sandwiched electrodes, STH efficiencies of up to 19% in full sunlight has been reported for small bench-scale prototypes. For thermochemical technologies, thermal energy to fuel efficiencies is used instead. In practice, the average energy output over the year is important, and different technologies respond differently to varying conditions such as solar irradiation, temperature, etc. While a higher η_{STH} would lower the cost of a solar fuel (e.g., H_2 fuel) produced, other factors including device cost, balance-of-systems costs, system lifetime, replacement and maintenance, and material requirements will all contribute to the deliverable product price. A viable device needs to simultaneously meet several important criteria including *efficiency/selectivity, durability, and scalability*, where scalability depends on costs and energy input for materials, processes, and deployment as well as on availability of elements, toxicity, and other environmental factors.

The success of each conversion technology also requires reference to competitive alternatives that provide benchmarks for research and technology development. For example, H_2 generated by nonrenewable methods, with steam methane reforming (SMR) accounting for ~95% of today's H_2 production, is priced at <€2/kg H_2. Solar fuels conversion processes must approach this value to become competitively viable, accommodating a price on carbon or accruing a value for decarbonisation. "Blue" H_2 from SMR with CO_2 capture and sequestration could be established as another benchmark for low-carbon H_2 production (Section 3.2). CO_2 and N_2 reduction are more scientifically and technically challenging for low-temperature, nonbiological approaches, with typically lower efficiencies and selectivities, yet offer the potential to yield higher-value products. One attribute of solar thermochemical technologies is that they can split H2O or CO_2 with equal ease and can process them separately or together, similar to high-temperature electrolysis. Approaches with photosynthetic micro-organisms take advantage of engineered metabolic pathways to convert CO_2 to multicarbon fuels with comparatively high efficiency.

A number of challenges and research goals common to all or most of the solar fuels conversion technologies are considered here:

Major challenges: Avoiding energy losses and degradation reactions. Costs and simultaneously reaching high efficiency, selectivity, durability, and scalability.

Research goals: New materials and components for light-harvesting (or collection), charge separation, catalysis, or high-temperature redox cycles with improved performance. Demonstration of direct CO_2 capture, CO_2 activation, and selective conversion to liquid carbon fuels. Low-temperature systems that can operate with sea water and nonpurified water.

Key enabling research: *Ab initio* computational, bioinformatic, artificial intelligence methods and high-throughput screening methods for redox materials, catalyst, and organism discovery and development. Development of *in situ* and *operando* methods to understand transport, reactions, and other processes at surfaces, interfaces, and in the bulk. Multiscale modelling and design of devices, reactors, and systems. Degradation studies. Technoeconomic and life cycle analysis.

Milestones:

- A large-scale, integrated research and development program leading to demonstration of scalable, direct-solar H_2 production that is cost-competitive with steam reforming, carbon capture, and sequestration carbon capture and storage (five years).
- Demonstration of efficient and selective CO_2 reduction to a liquid product in bench-scale prototypes with overall solar-to-fuel efficiencies competitive with biomass conversion.
- Demonstration of solar fuels production from just sunlight and air or sunlight, air, and seawater with direct air capture of CO_2 (water coming from humidity or sea water).

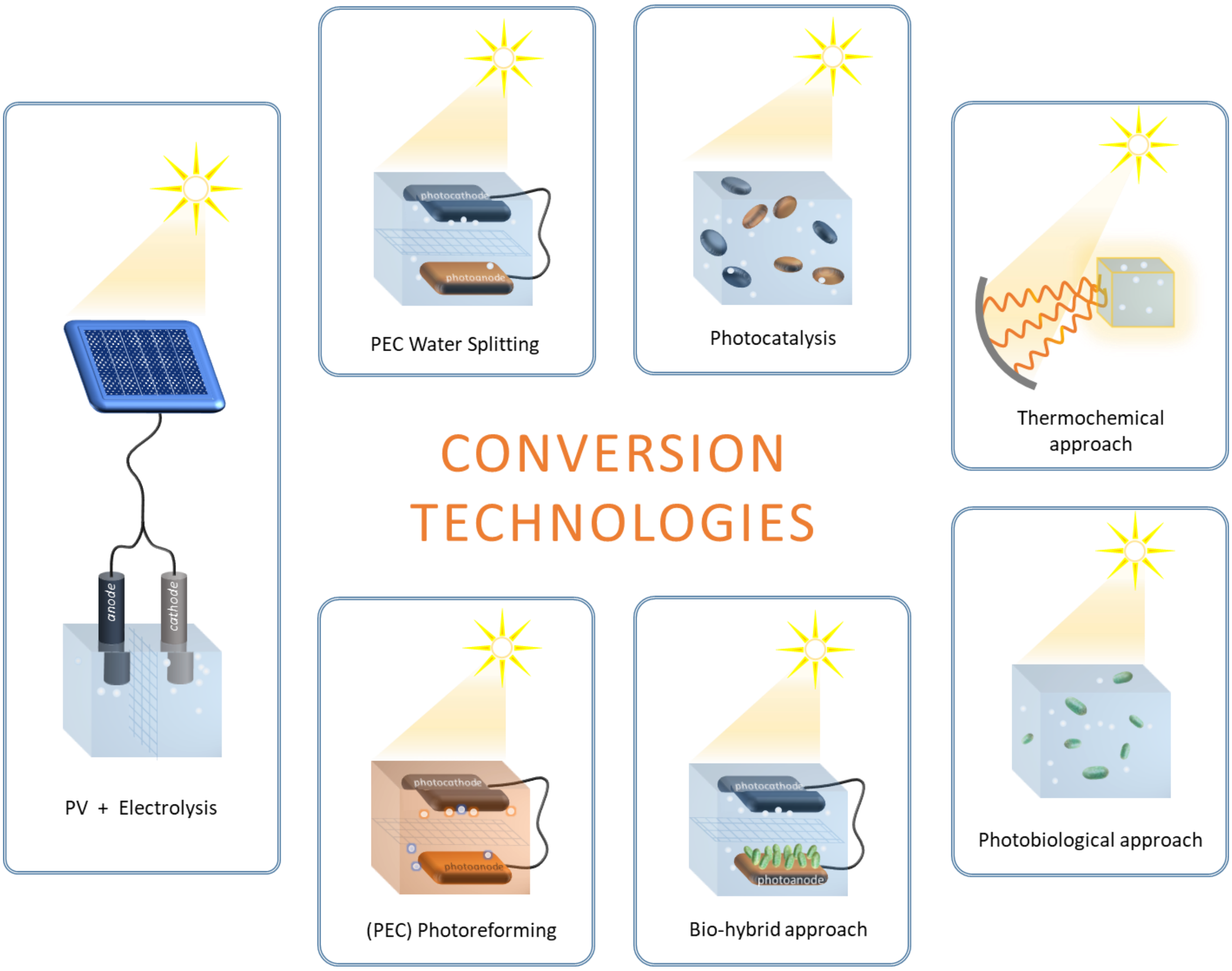


Figure 3.1. *An illustration of the major sunlight conversion technologies currently in development. Clockwise from left: PV+e is the most mature sunlight conversion technology, coupling PV cells to dark electrolysers. PV+e is almost exclusively used for H_2 generation with oxygen as a byproduct evolved at the anode. A membrane separates the evolved gases. Photoelectrochemical (PEC) water splitting is an integrated approach in which light absorption and catalysis occur in the same device. Photocatalysis (PC) typically utilises suspended particles or sheets and can be considered similar to a nonwired PEC module (an external bias is not needed). The solar thermochemical approach typically uses a two-step redox active metal oxide cycle, in which a field of thousands of tracking mirrors (heliostats) reflect and focus solar radiation to a central tower and into a metal oxide receiver, which contains the suitably designed active material that undergoes high-temperature reduction accompanied by oxygen evolution. In a second step at lower temperature, H_2O or CO_2, or a combination of both, is introduced, which serves as the oxidant to reoxidize the metal oxide back to its initial state for another cycle. The photobiological conversion route uses photosynthetic micro-organisms to generate and excrete fuels into the surrounding media for collection. The biohybrid approach combines biological and inorganic materials, and the tasks of light capture and catalytic fuel production are distributed between them. Finally, photoreforming replaces the evolution of oxygen as a byproduct with the synthesis of a higher-value commodity by substituting water oxidation for an alternative substrate. Photoreforming is shown here in a photoelectrochemical device but can be implemented into a number of the aforementioned conversion technologies.*

3.1. Reference Technology: PV Electrolysis and Synthesis Technologies as Benchmarks

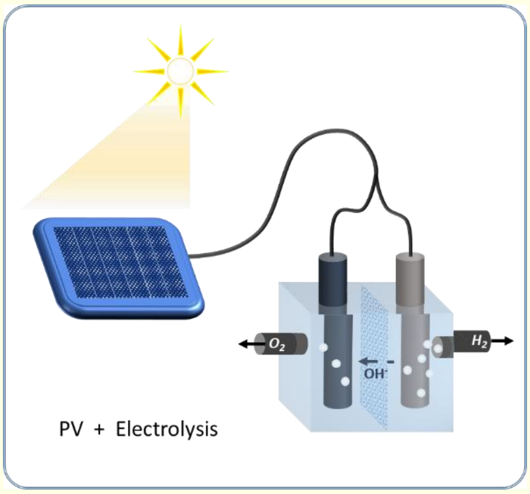
Currently, the sunlight conversion technology with the highest TRL is water electrolysis powered by photovoltaics (PV+e). This higher TRL for this process relative to direct solar fuels stems largely from the maturity of PV technology and electrolysers in comparison to the less mature approaches for direct solar fuels detailed below. The role of PV+e in generating renewable or “green” hydrogen is considered in more detail in Innovation Challenge 8, which also addresses H_2 storage and usage. We consider this technology an important benchmark for other pathways in terms of cost and performance. There are also synergies between PV+e and solar fuels approaches in the form of enabling technologies, multisectoral knowledge and skills, and catalyst design and application. Because both the fields of PV technology and electrolysis technology continue to develop with large-scale research and deployment efforts, this benchmark represents a moving target against which to gauge progress in solar fuels technology. Achievement of an electrolyser energy efficiency of 80% at 1 A/cm^2 represents a defining objective for PV+e. Building on expected progress in PV technologies, for example, would allow for energy-efficient H_2 production.

Solar fuels would be complementary to PV+e approaches. Given that PV+e is at a more mature stage of development, green hydrogen production by PV+e at scale could have a nearer-term impact than nascent direct solar fuels synthesis. It could also open new process streams and markets for CO_2 reduction to fuels, chemicals and materials, and ammonia synthesis using H_2. For example, PV+e can currently be part of an indirect solar fuels pathway by providing green hydrogen to react with CO_2 to make the forming gas (H_2 and CO), which the industrial-scale Fischer-Tropsch or direct CO_2 hydrogenation reactions convert to liquid fuels and chemicals. Significant progress is being made in catalysts and scale-up for the electrochemical reduction of CO_2 to a range of products with potential for cost reductions from economies of scale that could leverage advances in water electrolysers. Direct solar fuels synthesis can benefit from the supply chains, processes, and markets that would be established by PV+e generation of H_2 and other products. Many industrial companies have announced plans for large-scale production of green hydrogen by PV-e in recent years.

Direct electrocatalytic reduction of molecular nitrogen to ammonia is presently at a very early stage of development (TRL 1), and is thus an important area for future research. However, availability of green hydrogen produced by PV+e is likely to open pathways and markets for green ammonia, as H_2

generation is responsible for significant energy and cost contributions in ammonia synthesized by the Haber Bosch process. As direct reduction of molecular nitrogen and protons to ammonia moves out of research to yield scalable processes, these processes will be able to enter an existing market for green ammonia.

Highlight 1. PV Electrolysis (PV+e) for H_2 Production



The most mature of the conversion technologies to produce H_2 is that of water electrolysis, carried out by industry at scale for almost 100 years [21], and as such can be considered as a benchmark for emerging alternative technologies. Here, we consider electrolysis using PV+e, which is one of the least expensive alternative approaches of H_2 production [23]. This benchmark largely stems from the commercial success of silicon-based solar cells, whose cost has recently decreased dramatically and now provides utility-scale electricity at a levelized cost of energy as low as 5–6 eurocent/kWh. However, although the TRL for this benchmark is high, shortcomings in the electrolysers may inhibit sufficiently large-scale deployments (terawatts). These shortcomings may include the poor performance of alkaline electrolysers under intermittent use and the use of expensive (but potentially recyclable) precious metals in proton-exchange membrane (PEM) electrolysers. Maintaining long lifetimes is also an important issue, especially in a dynamic operation mode with rapid fluctuating power input (battery integration may mitigate such fluctuations). Membrane development is a key research goal—including mechanically stable and highly conducting anion exchange membranes to allow the alkaline electrolyte regime to be utilized in PEM electrolysers. Current costs are high, mounting up to 1,000€/kW for the electrolyser device (this is expected to decrease substantially with deployment and learning curves), resulting in typically 6€/kg H_2, depending on the scale and localisation of the plant and its operating capacity factor. When such electrolysers are coupled to PV devices, the STH efficiency tends to be around 15% at full sun.

PV+e operation at MW scale has already been achieved. Research and discovery of new catalyst materials based on Earth-abundant elements will advance the development of both electrolysers and photoelectrochemical systems (see below), specifically reducing the cost requirement for the scarce iridium catalyst (for the oxygen evolution reaction) and expensive platinum catalyst (for H_2 evolution reaction), for the PEM water electrolyser, or improving the efficiency and stability of electrocatalysts working at high current density for the alkaline water electrolyser. Advances in this field depend on technological breakthroughs in materials science (noble-metal free catalysts and membranes operating at different pH and impurity content, automated manufacturing technologies, system integration, and upscaling). Moreover, electrolyser systems are compact, necessitating no light management and thus enabling the stacking of different units. They also allow for easy collection of H_2 that can be readily pressurised (10–30 bar).

3.2. The Case for Direct Solar-Driven Production of Net-Zero Carbon Hydrogen from Water Splitting

Although there are a range of solar fuels processes and products, as discussed below, H_2, the world's smallest molecule (comprised of just two electrons and two protons), represents an excellent near-term solar fuels opportunity. We define ***"golden" hydrogen*** as H_2 that is produced from direct sunlight-driven water splitting processes (to produce H_2 and oxygen). H_2 can be used as a fuel itself to generate heat or power (e.g., in a fuel cell or a combustion engine), as an energy carrier, as an energy storage medium, and as a key component in reactions for a wide range of chemical processes to make fuels (e.g., with CO_2 and/or N_2), and products and materials (e.g., direct reduction of iron to make steel). A number of hydrogen roadmaps have been developed spanning production, infrastructure and utilization. Complementary methods to produce decarbonised H_2 include SMR (reacting methane and water to produce H_2 and CO_2 or H_2 and solid carbon) coupled to CO_2 capture and sequestration—so-called "***blue" hydrogen***—as well as "***green" hydrogen***, which is produced from water splitting using renewable (low to no greenhouse gas emissions) electricity (Section 3.1). As described in Innovation Challenge 8, there are "green" and "blue" hydrogen approaches that already correspond to higher TRLs, and large-scale demonstrations are being conducted across the globe in parallel to research agendas.

Over the last decade, a considerable knowledge base and literature have been establlished for direct solar H_2, or "**golden**" hydrogen, such as photoelectrochemical or solar thermochemical approaches to splitting water. Solar H2 production is therefore much more mature than other solar fuels processes such as CO_2 or N_2 reduction. The STH efficiency for photoelectrochemical production of H_2 now approaches 20%—a realm that technoeconomic analyses reveal could be cost-competitive with other technologies for H_2 production. A wide range of processes, functional materials, and even systems have been developed and demonstrated at small scale in a number of prototypes and architectures. For example, systems that integrate photoabsorbers, catalysts, electrolytes, and membranes into devices have been developed for photoelectrochemical water splitting. Important aspects of durability and integration are also being addressed. There are even some larger-scale demonstrations of solar hydrogen generation. Analogously, solar thermochemical processes for H_2 production have also been developed and demonstrated.

Given the higher level of maturity and already high overall energy efficiencies, there is a unique opportunity to rapidly develop direct solar-driven hydrogen (and related products) into a solar fuel technology platform through focused collaborative research, development, and demonstration. Building on decades of fundamental and applied research in solar hydrogen production as well as related fields of PV, electrochemistry, catalysis, materials science, and degradation science, key challenges in durability (at the materials, component, and system levels) and integration (of components, subsystems, and balance-of-plant considerations) can be addressed in a large-scale integrated research and development effort to create a viable, sustainable technology base. We are at the stage where a detailed technology development and demonstration roadmap (with timeline, e.g., five years) should develop direct sunlight-driven hydrogen production that would not only provide a complementary approach to decarbonised H_2 but would also provide an excellent foundation for initiating a solar fuels industry. The international community is poised to develop and execute such a roadmap.

3.3. Catalyst Development for Water Splitting, CO_2 Reduction, and Other Key Reactions

Many of the proposed sunlight conversion approaches rely on the splitting of water to obtain protons for H_2, ammonia, or hydrocarbon generation from CO_2. Water splitting necessitates the evolution of oxygen as a byproduct, but this oxidation step is chemically challenging, and current catalysts are relatively expensive, unstable, or inefficient. Likewise, the best-known proton reduction catalysts for H_2 fuel production are precious metals like platinum, the scarcity of which raises cost. In parallel, current CO_2 reduction catalysts that make liquid fuels or other multicarbon compounds show limited activity or selectivity (particularly over H_2 evolution). Therefore, the development of improved efficiency catalysts (preferably comprising Earth-abundant materials) is important for many of the conversion technologies discussed below. Most studies have focused on inorganic, heterogeneous catalysts, although there have recently been promising advances in the performance and stability of molecular catalysts. Molecular catalysts are particularly promising where product specificity is important, such as for CO_2 reduction to form liquid fuels.

Major challenges: Development of new processes and engineering solutions to decrease the losses in terms of conversion efficiency during scale-up. Identification of catalysts for the ambient reduction of N_2 to ammonia. Selectivity for CO_2 reduction products. Durability and stability of catalyst.

Research goals: Improved stability, energy conversion efficiency, and product selectivity relative to the state-of-the-art. Decreasing the catalyst costs and enhancing system scalability by using Earth-abundant materials or dramatically decreasing the noble metal content. Catalysts also need to be optimised for specific applications and devices; for example, catalysts need to be stable in different pH ranges, and some may need to be optically transparent to ensure efficient light harvesting in integrated solar fuels devices. Final catalysts need to fit into a circular economy approach, and nontoxic materials are preferable.

Key enabling research: Catalyst identification with *ab initio* modelling and high-throughput screening, machine learning, new *in situ* diagnostic tools on the molecular level, up-scalable synthetic strategies to produce catalysts with the desired properties, dynamic life cycle cost analyses. Reaction mechanisms and *in situ* characterization. Long-term performance testing of components and devices. Integration with catalyst supports, membranes, photoabsorbers, and other components.

Milestones: A comprehensive database of potentially effective, well-characterized catalysts that serve as benchmarks. Identification of sets of CO_2 reduction and water oxidation catalysts for different specific applications. Optimized CO_2 reduction catalysts ready for application in pilot plants. Water oxidation catalyst from Earth-abundant elements that is stable in acidic environments.

3.4. Improved Solar Light Harvesting, Charge Separation, and Coupling to Catalysts

Another challenge common to many different solar conversion approaches is the efficient harvesting of light, i.e., materials and/or molecules with good photon absorption and subsequent charge carrier generation. This is distinctly different from approaches where solar photons are used solely as a heat source (see Section 3.6.). Many light-harvesting systems experience efficiency losses due to charge recombination and energy dissipation to heat. The overall efficiency can be optimized by improved device architecture and optoelectronic properties and by utilizing the heat generated to improve catalytic reactions. Light-harvesting efficiencies are closely coupled to material properties and processing. Continued research and development into light absorbers is essential. For example, metal oxides often prove the most stable light absorbers for driving water oxidation (as they are resistant to further oxidation) but typically exhibit poor visible light absorption and conversion efficiencies. A broad range of light-absorber materials is currently being investigated for sunlight conversion, including not only metal oxides but also other inorganic semiconductors (silicon, chalcogenides, nitrides, etc.) and a diverse range of other light absorber materials including tandem concepts, quantum dots, polymers, and dye molecules. A common challenge for all these light-harvesting systems is to reduce internal energy losses and to increase stability under operating conditions. The surfaces of some light-absorber materials can directly catalyse sunlight conversion reactions, while most require the addition of catalysts to function efficiently.

Major challenges: Current materials are limited by one or more of the following: poor solar harvesting, poor charge separation efficiency, poor stability, poor processability/scalability, or high cost. The understanding of materials and device function is often limited by the difficulty of undertaking operando measurements. Modelling and simulation are powerful tools to aid design but are currently limited in scope.

Research goals: The development of low-cost, efficient, stable, and scalable light-absorber materials, functionalised by co-catalysts as needed, to drive efficient photoelectrochemical or photocatalytic sunlight conversion**.**

Key enabling research: High-throughput materials discovery and characterization (theory and experiment). Bandgap engineering and doping, control of molecular and materials structure at the nanoscale, junction formation (buried solid-state junctions, semiconductor/catalyst junctions), surface passivation, materials development (e.g., metal oxides, carbon nitrides), transient and operando spectroscopies, and modelling and simulation. Coupling of photoabsorbers to catalysts. Durability and degradation science. Protection schemes. Accelerated testing and *in situ* characterization.

Milestones: Comprehensive databases of known light absorbers and their properties (theory and experiment) that are available to the international community (linked to the catalyst database in Section 3.2). Technoeconomic assessment of the relative costs of the components on the overall cost of the different integrated devices. Light absorbers with bandgap energies optimized for solar fuels production with stability in acidic and alkaline media. Integration of light absorbers into new device architectures.

3.5. Photoelectrochemical and Photocatalytic Devices

The sunlight conversion approaches with TRLs closest to the benchmark PV+e are those that couple light absorption and conversion catalysis in one material or device. Photocatalytic (PC) systems typically consist of solutions or suspensions of molecules, polymers, or nanoparticles that evolve the products into the surrounding media. Charge recombination loss is a challenge, and several approaches are used to minimize these. Achieving high efficiencies with PC systems is challenging due to the material constraints imposed, including high aqueous stability at a range of pH values, adequate light absorption, and suitable redox energies for catalysis. Photoelectrochemical (PEC) routes build on photoactive anodes and/or cathodes that are in electrical contact, typically as separate units (Highlight 2) or back-to-back in a monolithic device. However, any external energy input detracts from the total conversion efficiency, whereas the more complicated structure of tandem devices may also present limitations in module design. Finally, PEC systems can be coupled with the biochemical approaches considered in Section 3.4 to aid catalytic conversion.

Product separation can be an issue in all three conversion technologies above, with costly proton permeable membranes often required for PEC and PC systems. Although membranes allow short cathode-anode diffusion distances, they may also partially block incident light. This illustrates the main challenge in making solar fuels devices scalable: it requires efficient management of photons, electrons, and ions. The design of the device or module also determines the level of performance required for the individual components (i.e., light absorbers, catalysts, electrolytes, and membranes). The modelling and simulation of new designs is, therefore, an important prerequisite for defining performance targets for the materials that need to be developed. This task can be challenging, as each single element interplays with, and affects, the others in defining the final performances, which necessitates development of simplified and robust models. Two major approaches can be differentiated. The first is scalable devices/systems, which need to become more efficient and economical with plant size (e.g., PEC or PC systems). The second is mass-producible devices, which get cheaper with the increasing number of produced devices (e.g., roof-top systems, containerized solutions).

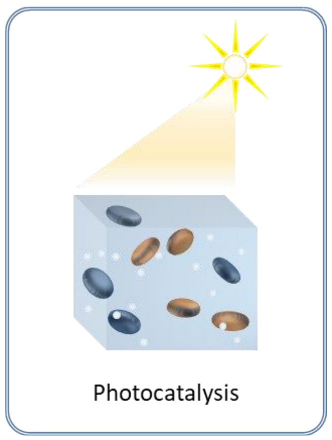
Major challenges: Device integration; reliability for systems at scale and lifetime prediction; and cost-reduction of components, processes, and systems. Control of reactants, intermediates, and products. Direct air capture of CO_2.

Research goals: Scalable and/or mass-producible systems. Cost-competitive H_2 production. Efficient and selective CO_2 reduction.

Key enabling research: Device/system design and fabrication. Multiscale imaging and modelling. Degradation mechanisms. Rapid prototyping and testing. Technoeconomic/life cycle analyses.

Milestones: Demonstration of stable PC/PEC device for solar-driven water splitting with a solar-to-hydrogen efficiency > 10 %, projected to be cost-effective at scale compared to PV+e. Large-scale (1,000 m^2) demonstration of solar H_2 production (Section 3.2). Demonstration of efficient, durable prototypes for selective CO_2 reduction to a solar fuel.

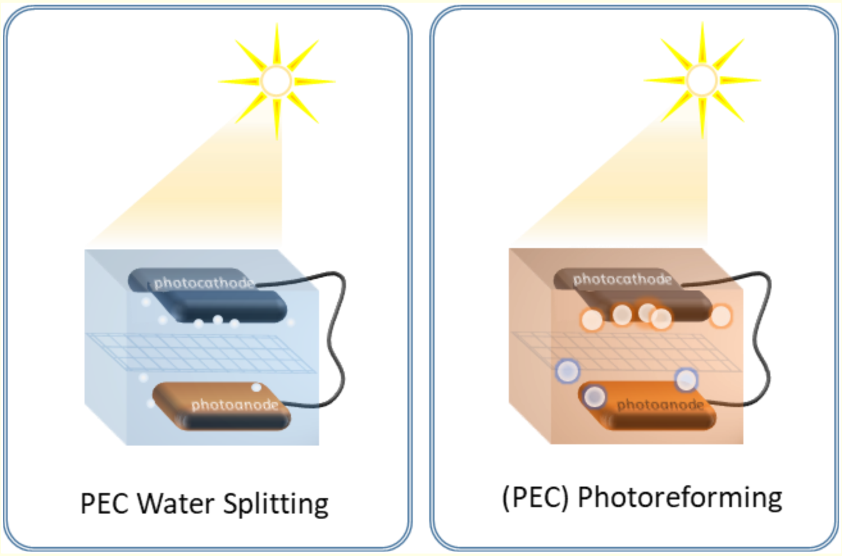
Highlight 2. Direct Photocatalysis for Generation of Solar Fuels



Technoeconomic analyses have indicated that suspended photocatalyst systems in transparent "baggies" have the potential to be competitive in terms of cost to produce H_2 fuels. Another approach, now demonstrated at the 100-m^2 scale in Japan, employs photocatalyst sheets deposited directly on glass or plastic substrates. Water splitting is directly achieved under solar irradiation, though solar-to-hydrogen conversion efficiencies (η_{STH}) are usually low, in the range of 1% [20]. System architectures are considered, in which one particle or a mixture of particles performs both the oxidation and reductive reactions required, thereby generating O_2 and H_2 together, as well as other architectures in which two particle types are separated by a membrane, such that gases are separated. Extremely low system costs, without requiring wiring or complex housing, are potential advantages of this technology, although product separation and the associated safety issues may be a concern.

	TRL	Research Goals	Major Challenges	Key Enabling Technologies	Milestones
PC	H_2: 3–4 C-fuels: 2–3	Scalable systems with improved conversion efficiencies, durability, and selectivities Cost-effective technologies for product separation.	Prevention of aggregation, precipitation, and photcorrosion. Separation of oxidation and reduction products. CO_2 product selectivity. Direct air capture of CO_2.	Materials capable of enhanced light harvesting of the solar spectrum. Device modelling. Technoeconomic analyses.	Demonstration of STH 10% conversion efficiency. Demonstration of selective CO_2 conversion prototypes.

Highlight 3. Photoelectrochemical (PEC) Routes to Hydrogen and Carbon Fuels



An alternative approach to PV+e hydrogen generation from water is to combine light harvesting and catalysis within a signal device. PEC water splitting has been argued to potentially offer a cheaper, higher-efficiency alternative to electrolysis using PV+e. Several device architectures have been examined for PEC, employing various combinations of component electrodes. The most common approach couples two semiconductors together, each absorbing a proportion of the solar spectrum, with protons shuttling internally across a membrane between the electrodes (as in the electrolysers in PV+e) and current passing externally. The integration of light absorption and catalysis in one device places greater restrictions on potential materials (e.g., good aqueous stability). However, PEC offers significant benefits for decentralisation, which could minimise fuel transportation costs and use of interconnecting electronics. Best performing lab-scale devices have shown η_{STH} around 20% with estimate costs for H_2 fuel following compression at 10 €/kg [23]. Photocurrent densities generated in PEC water splitting are significantly lower than current densities employed by existing electrolyser technologies, but this low current density offers the advantage that cheaper, nontoxic, Earth-abundant materials can be employed as catalysts, which would be inadequate in higher-turnover electrolyser systems. With continued development of efficient photoelectrodes and co-catalysts and research in module design, PEC devices may be able to provide decentralised, local production of H_2, even at a small scale suitable for individual households.

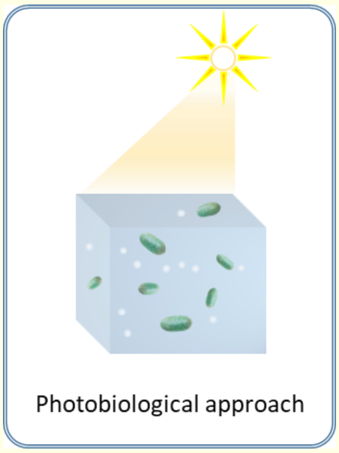
Beyond H_2, PEC approaches are also considered for the generation of hydrocarbon-based fuels. In such instances, the protons generated from the oxidation of water at the anode would be used in CO_2 reduction at the cathode. This coupled set of reactions requires either a CO_2-saturated electrolyte or the use of gas diffusion electrodes as well as new catalyst materials.

	TRL	Research Goals	Major Challenges	Key Enabling Technologies	Milestones
PEC	H_2: 3–4 C-fuels: 1–3	Scalable systems with improved conversion efficiencies, durability, and selectivities.	Device integration Stable catalysis Product separation Transfer to mass production CO_2 product selectivity.	Device and system modelling, production, and engineering. Technoeconomic analyses.	Pilot plant for H_2 of 1,000 m^2 (solar area). Energy efficiency for CO_2-to-CO better than RWGS. Prototype for 50% selective CO_2 reduction to liquid fuel with (η = 5%).

3.6. Photobiological and Biohybrid Approaches

Solar fuels and chemicals can also be generated using photosynthetic organisms such as cyanobacteria and microalgae, in which H_2, alcohols, and organic acids are commonly secreted metabolic products. Genetic engineering of existing strains have been shown to enhance their photosynthetic efficiency, tailor their metabolism towards the generation of specifically targeted products, and improve electron transport at biohybrid materials interfaces. The metabolic machinery has a powerful capacity for

Highlight 4. Photobiological and Biohybrid Approaches to Solar Fuels



Photosynthetic micro-organisms such as specific strains of cyanobacteria or algae are capable of converting sunlight into fuels like H_2, alcohols, and hydrocarbons in a variety of media. Generally, these organisms show high stability in their native state, and cultures can be readily replaced. Furthermore, advances in metabolic engineering allow bacteria to be tailored to specific reactions or products. Biohybrid approaches are also being considered in which, for example, bacteria are coupled to photoelectrodes to provide a steady supply of electrons, thereby aiding reduction chemistry. Alternatively, the required enzymes may be isolated and charged by (photo)electrochemical means, although the stability of this approach is not known. However, such biological-material interfaces, while offering the potential for higher conversion efficiencies to multiple products, are currently at a lower TRL than the suspended biological systems.

	TRL	Research Goals	Major Challenges	Key Enabling Technologies	Milestones
Bio	H_2: 3–4 NH_3: 1-2 C-fuels: 1–6	Commercially viable photosynthetic and carbon conversion efficiencies. Operation in nonpure electrolyte media (e.g., sea water). Cost reductions by large-scale manufacturing process development. Avoid negative environmental impacts	Culture and strain stability. Achieving scalability and cost effectiveness. Social acceptance of modified micro-organisms.	Genetic engineering and understanding of metabolic pathways. Development of cost-effective device manufacturing. Novel biological material interfaces for biohybrid devices.	Achieve commercially viable efficiencies at lab scale. Demonstration of complete photobioreactor systems, on stepwise increasing scale from 1,000 to 10,000 m^2. Demonstration on industrial scale.

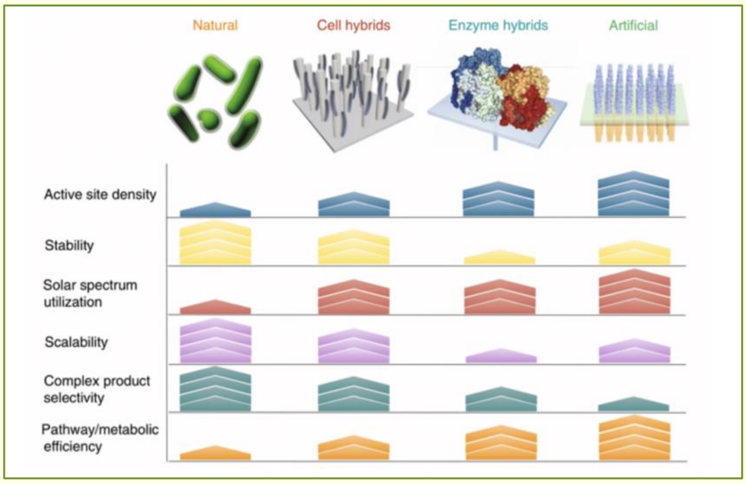


Figure 3.2. *Different degrees of biological input into potential solar-to-fuel conversion systems, with the advantages and disadvantages of each. Taken from Energy-X Roadmap, from Reisner, Nature Nanotechnology, 13, 890, (2018).*

converting CO_2 directly to complex multi-carbon fuels and interesting chemicals that are excreted, thereby bypassing biomass generation. Thus, this process is independent of harvesting of cellular biomass, and the fuels and chemicals are used instead as continuous cultures in a photobioreactor system. Production of chemicals has already been demonstrated, while cost-competitive fuel formation remains to be proven.

Major challenges: Stable product quantity and quality without excessive post-harvest processing. Operation under harsh environments (e.g., arid climate, saline water, high temperature). Micro-organisms and culturing systems may not be sufficiently robust and stable for industrial scale processes. Societal acceptance of genetic engineering approaches.

Research goals: Genetically optimized organisms with significantly increased photosynthetic efficiency and product yields. Improved and highly automated processes and plant designs, along with lower photobioreactor costs. Ability to operate with marine saltwater. Avoid negative environmental impacts starting from design phase, ideally in a closed system with highly efficient nutrient recycling, the inputs being primarily CO_2 and sunlight, and the main output being selected fuels or chemicals. Prevent consumption of products in active systems, and eliminate or significantly reduce microbial contamination. Large-scale and effective system integration, including energy-efficient product recovery.

Key enabling research: New tools for genetic engineering, improved understanding of relevant organisms and their metabolic pathways, artificial intelligence and robotics for plant construction, operation, and maintenance. Rapid, cost-effective, and scalable manufacturing of novel photobioreactor and downstream processing equipment designs.

Milestones: Improved micro-organisms with photosynthetic and conversion efficiencies at lab scale that would be required for commercial feasibility. Demonstration of complete photobioreactor systems, including recovery and upgrading of the selected fuel, on stepwise increasing scale from 1.000 to 10.000 m^3. Demonstration of most promising approaches on industrial scale.

3.7. Thermochemical Pathways Using Concentrated Sunlight

Solar fuels can also be generated by converting thermal energy into chemical energy using concentrated solar radiation. CSP technologies are already used in favourable climates for electricity generation. Similarly, solar-driven thermochemical water- or CO_2- splitting cycles can produce H_2 or carbon monoxide with very low greenhouse gas emissions. In such pathways, solar energy is used to drive highly endothermic reactions, exploiting the cyclic reduction and reoxidation of redox active metal oxides or the hybrid sulfur cycle, which uses sulfuric acid in a cyclic manner. Unlike other sunlight mediated approaches, however, cyclic thermochemical reactions are reversible and strongly related to the thermodynamic conditions of the functional material (redox active metal oxides or sulfuric acid) chosen, therefore affecting the conversion efficiency and providing complete selectivity (no undesirable side reactions) of the systems.

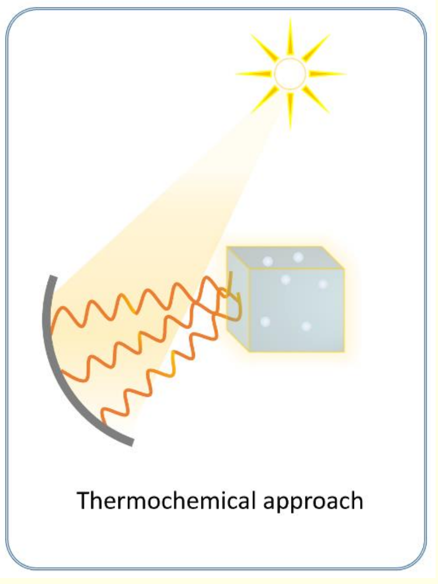
Major challenges: Materials design to achieve optimal balance between reduction and reoxidation thermodynamics, efficient and cost-effective reactor design for the high temperatures and controlled environments, separations, and high-effectiveness heat recuperation.

Research goals: Achieving efficiency targets and cost reductions by: improved materials, reactor designs, heat recuperation, oxygen pumping or separations, H_2 separations from steam without condensing, producing pressurized hydrogen, heat integration, and integration with downstream chemical processes for producing hydrocarbon fuels and chemicals; pathway to $2/kg at scale.

Key enabling research: Advances in concentrating solar technologies to produce electricity and to store thermal energy. Cost reductions in heliostats and high-temperature receivers. Heliostat design allowing for high light/heat concentration to limit re-radiation, while maintaining low cost and high-optical efficiency. High-throughput materials discovery for the redox active materials.

Milestones: 20% efficiency of thermal energy to fuel conversion (H_2 and CO) at 5–10-kW_{th} thermal input and 1,000 cycles (near term). Demonstrations at 100 kW_{th} followed by 1 MW_{th} in the mid term. Demonstration of complete system on industrial scale followed by large-scale commercial deployment in the long term (1-GW_{th} cumulative deployment).

Highlight 5. Thermochemical Routes to Fuels and Chemicals



Other appealing alternatives for solar fuels conversion are thermochemical routes, which require an input of heat instead of photonic absorption and charge separation as in PEC, PC, and photobiological systems. The heat input can be delivered using renewable resources (e.g., by concentrating solar technologies), as already used in high-insolation regions to produce electricity. Because heat is directly converted to chemical energy without an intermediate electricity production step, the theoretical efficiency of such processes is higher than in electrolysis. Despite this theoretical high efficiency, large optical and re-radiation losses result in practical efficiency decreases. A large amount of redox material must be heated to very high temperatures in the reduction step. Challenges remain in recovering that heat while cooling down for the re-oxidation step and then using that heat to again raise the temperature of the material. Efficient heat recovery would reduce the amount of heat needed from the sun and increase the overall fuel production efficiency. One strategy that some are pursuing is to reduce the temperature difference between the oxidation and reduction steps, while others seek to optimize the thermodynamics and tackle the solid-solid heat recuperation challenge. In addition to thermal management, the reduction step needs to operate in a controlled environment of low-oxygen partial pressure (pO_2). Various pumping strategies or sweep gas strategies serve to lower the pO_2. In the re-oxidation step, the amount of excess H_2O controls the oxidizing power. Excess H_2O then requires separation of the H_2 product stream. The resulting low-partial pressure of H_2 must be recovered and delivered at the required pressure for storage or downstream processing.

	TRL	Research Goals	Major Challenges	Key Enabling Technologies	Milestones
Thermo-chemical	C-fuels: 3–4	Performance increases and cost reductions through improved materials, reactors, heat integration, and system design.	Heat management Gas management Separations Material and reactor design.	Advances in concentrating solar technologies to produce electricity and to store thermal energy. Cost reductions in heliostats and high-temperature receivers. High-throughput materials.	20%-efficiency thermal to fuel (H_2 and CO) HHV at 5–10 kW_{th} and 1,000 cycles Demonstrations at 100 kW_{th} followed by 1 MW_{th} in the mid-term. Demonstration of complete system on industrial scale.

Summary of Key Technological Challenges and Milestones

	TRL	Research Goals	Major Challenges	Key Enabling Technologies	Milestones
PEC	H_2: 3–4 C-fuels: 1–3	Scalable systems with improved conversion efficiencies, durability, and selectivities.	Device integration Stable catalysis Product separation CO_2 product selectivity.	Device and system modelling, production, and engineering. Technoeconomic analyses.	Pilot plant for H_2 of 1,000 m^2 (solar area). Energy efficiency for CO_2-to-CO better than RWGS. Prototype for 50% selective CO_2 reduction to liquid fuel with (η = 5%).
PC	H_2: 3–4 C-fuels: 2–3	Scalable systems with improved conversion efficiencies, durability, and selectivities. Technologies for product separation.	Prevention of aggregation and precipitation. Separation of products. CO_2 product selectivity.	Materials capable of enhanced light harvesting of the solar spectrum. Device modelling. Technoeconomic analyses.	Demonstration of STH 5% conversion efficiency. Demonstration of selective CO_2 conversion prototypes.
Bio-(hybrid)	H_2: 3–4 NH_3: 1–2 C-fuels: 1–6	Commercially viable photo-synthetic and conversion efficiencies. Operation in nonpure electrolyte media, e.g seawater Cost reductions by process innovation. Avoid environmental impacts.	Culture and strain stability. Achieving scalability and cost effectiveness. Social acceptance of modified microorganisms.	Genetic engineering and understanding of metabolic pathways. Development of cost-effective device manufacturing. Novel biological material interfaces for biohybrid devices.	Achieve commercially viable efficiencies at lab scale. Demonstration of complete photobioreactor systems, including recovery and upgrading of selected fuel on stepwise, increasing scale from 1,000 to 10,000 m^2. Demonstration of the most promising approaches on industrial scale.
Thermo-chemical	C-fuels: 3–4	Performance increases and cost reductions through improved materials, reactors, heat integration, and system design.	Heat management Gas management Separations Material and reactor design.	Advances in concentrating solar technologies to produce electricity and store thermal energy. Cost reductions in heliostats and high-temperature receivers. High-throughput materials discovery for the redox active materials.	20% efficiency thermal to fuel (H_2 and CO) HHV at 5–10 kW_{th} and 1,000 cycles Demonstrations at 100 kW_{th} followed by 1 MW_{th} in the mid term. Demonstration of complete system on industrial scale

4. The Roadmap for System Integration

Solar fuels conversion pathways are illustrated in Figure 4.1 with sunlight, CO_2, water, and air as feedstocks. The development and large-scale implementation of solar fuels technologies does not only depend on a number of figures of merit for conversion (efficiency, selectivity, durability) but also requires effective integration with upstream feedstocks and downstream processes, along with interfaces with existing industries and distribution infrastructure.

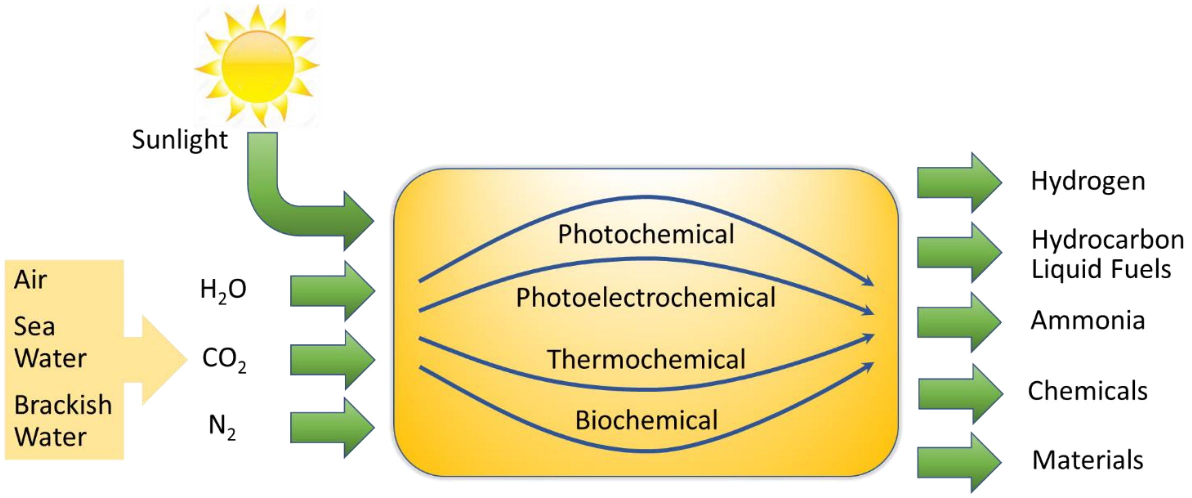


Figure 4.1. *An overview of of the direct solar fuels conversion technologies*

In addition to the scientific and technical challenges presented in this roadmap, it is also important to address environmental, societal, economic, political, and legislative factors related to system integration. Within the international context of Mission Innovation, it is critical to eventually connect the solar fuels value chain at the systems level with upstream and downstream processes, looking into possible interconections between different value chains and considering their socioeconomic and environmental sustainability throughout. Interlinking value chains requires connecting supply chains and integrating with a range of renewable energy sources. There are a number of common challenges and research goals that can be stated, independent of the final product obtained from direct sunlight conversion:

Major challenges: Identify boundaries, synergies, effects, and interactions at the system level with the current industrial processes.

Research goals: Identification and analysis at the system level of the main components of solar fuels value chains. Analysis of scenarios for solar fuels deployment.

4.1. The Upstream Interface with Industrial Feedstock Streams

Direct carbon capture from atmospheric CO_2 ("direct air capture" or "DAC") will allow for decentralized systems for converting sunlight, which do not depend on using CO_2 feedstock from industrial sources. Although DAC is an attractive prospect for solar fuels production in the long term, TRL and poor energy and cost efficiency are current bottlenecks, particularly for large-scale carbon capture from diluted sources such as air and seawater. Therefore, the use of industrial CO_2 waste streams available primarily at point sources of emissions such as biomass fermentation, electric power generation, and industrial process plants can be an important avenue to start solar fuels development in industrial settings, depending upon stream purity. Solar-driven CO_2 sequestration, even that originated from fossil fuel utilization, can reduce emissions at short term and be a pathway towards large-scale implementation of DAC technologies. Furthermore, this approach offers mutual synergies with related technological challenges, particularly carbon capture and storage (CCS) and carbon capture and utilization (CCU); see also Mission Innovation Challenge 3.

Solar-driven CCU, employing PV+electrolysis and either solar-driven DAC or CO_2 waste streams to synthesis products such as alcohols, are already being demonstrated at scale (TRL 4–6) but require further cost reductions for large-scale commercial viability.

Major challenges: Scale-up and integration: transfer from laboratory scale to a commercial setting is often challenging, as different industries, locations, and business cases can be difficult to address. Moreover, interdependence with other industries raises investment risk. CO_2 waste stream characteristics may differ between emitting industries, necessitating source-specific solutions such as purification steps and/or pressurisation. Water quality and purification.

Research goals: Determine and analyse efficient interfaces of solar fuels with industrial CO_2 waste streams in terms of general factors (e.g., economics, rural development, sustainability), and technological challenges (e.g., gas composition and continuity, impurities, connecting infrastructure, logistics). Identify potential benefits of decentralised conversion driven by sunlight and optimum geographical requirements.

Key enabling research: Advances in CO_2 capture and separation from waste streams, scalable DAC systems, and solar conversion technologies.

Milestones:

- Continuous use of CO_2 waste streams from industry in solar fuels production. Robust solar fuels production technologies accept a large variety of CO_2 waste streams.
- Demonstrate a 500-kW_p solar fuels facility that converts a waste stream of CO_2 to a reduced product by 2030.
- Large-scale ($MtCO_2$/year) demonstration of a DAC system integrated with solar fuels production by 2035.

4.2. The Downstream Interface with Existing and Future Fuels and Chemical Industries and Infrastructures

An effective interface to downstream energy and consumer good markets and to chemical industry is essential to provide economic value to the converting sunlight core value chain. It is the task of both this value chain and existing industries to best position this interface in terms of technical efficiency, economic sustainability, and practicality. Small molecule products, like carbon monoxide and H_2, can be directly deployed to downstream value chains and upgraded to more complex molecules (e.g., alcohols, aldehydes, alkenes, ethers) for logistics or profit reasons. Also, decentralized production schemes will generally require an energy carrier that is easy to transport and store and should align with existing infrastructure where possible. Obvious candidates for chemicals produced at these interfaces are methane (gas grid) and ethanol (existing infrastructure for bioethanol use, e.g., transportation and food industries) and ethene as a chemical feedstock. Further opportunities may arise for monetising oxidation products, such as markets for oxygen or alternative oxidation substrates to water (e.g., glycerol oxidation). Suitable product selection may also aid product separation, which may be undertaken locally or centrally. Direct conversion may offer greater potential to address the intermittent and decentralised nature of sunlight compared to PV + electrolysis + catalysis (such as Fischer-Tropsch or direct CO_2 hydrogenation reactions). The downstream interface value chain will have an important role in connecting solar fuels production to platform chemicals, and as such, establish a link to the production of more sophisticated chemicals and products. Synergies with existing infrastructure for the conversion, storage, and transportation of fossil-fuel-based chemicals should be exploited but will require upgrading as well as, in some cases, the establishment of specific infrastructure for solar energy carrier delivery and product distribution. Technoeconomic analysis can be used to identify regional-specific products that maximize return on investment on initial solar fuels facility deployments.

Major challenges: Establishment of the most efficient interfaces to downstream technologies and markets. Infrastructure development and deployment. Addressing, and where possible exploiting, the decentralised and intermittent nature of sunlight conversion.

Research goals: Definition of the most efficient, sustainable, and effective interfaces to downstream technologies, energy markets, and product value and supply chains.

Key enabling research: Efficient C-chain elongation and conversion technologies, allowing for the use of existing fuels and chemicals infrastructure.

Milestones:

- Link solar energy carriers to energy markets and platform chemical markets in terms of the number of compounds available and proven feed-in.
- Demonstrate solar-driven jet fuel production from CO_2 and H_2O with 5% conversion efficiency by 2035.
- Use technoeconomic and life cycle analysis to identify existing Fischer-Tropsch facilities that would be most advantageous for co-locating a 5-MW_p (75 bbls/day) solar fuels syngas plant.

4.3. Design, Engineering, and Demonstration at System Level

Industrial-scale demonstration of sunlight conversion needs to address the technology-specific challenges at the design and engineering level as well as establish functional interfaces with upstream and downstream value chains where necessary. Interacting with local stakeholders, creating sufficient visibility for further upscale, and integrating with clusters and networks of expertise are important factors that should not be undervalued. To be successful, models for financing the demonstration projects, as well as business models for commercial operation, have to be established at this stage. The entire balance of plant for a solar fuels systems (e.g., reagent/product handling, gas handling) must also be considered in terms of cost, performance, scalability, and reliability.

Direct PC sunlight conversion has been demonstrated at the 100-m^2 scale (ARPChem in Japan) but currently remains at a lower TRL (and performance) than benchmark PV+e pathways.

Major challenges: Determine all important and relevant variables at the system level. Determine the regional and/or value-chain-specific-requirements. Balance-of-plant costs and performance.

Research goals: Develop guidelines, standards, and protocols for effective and sustainable demonstration and commercialisation of durable sunlight conversion technologies.

Key enabling research: Process management and planning, life cycle analysis.

Milestones:

- Established guidelines, standards, and protocols for effective demonstration and commercialisation of durable sunlight conversion technologies.
- Demonstration of direct solar-driven water splitting, delivering H_2 at lower comparable cost than benchmark PV+e by 2030.

- Demonstration of direct solar-driven CO_2 reduction cost-competitive with SMR coupled to CCS by 2035.
- Demonstration at pilot scale production of direct green methanol (or other C-1 product) from CO_2 with efficiencies comparable to hydrogenation system, using H_2 from PV+e.

4.4. Integration of Solar Fuels Technology with Other Technologies

For upstream (e.g., CCU), central (e.g., fuel conversion), and downstream (e.g., Fischer-Tropsch-like chemistries or other conversions through methanol or ethanol) parts of the integrated converting-sunlight value chain, interfaces with other value chains and their respective technological developments can be established. Their integration at local nodes of the respective process can be beneficial or even required in terms of economies of scale or technical feasibility. One example is the co-processing of syngas from biomass and solar hydrogen to synthetic fuels.

Major challenges: Different scales of processes and incompatibility issues (in time, flow rate, chemical composition etc.)

Research goals: Define, analyse, and establish interfaces with other clean energy and circular economy technologies.

Key enabling research: Chemical engineering, process design and management, life cycle analysis.

Milestones:

- Proven compatibility of sunlight conversion technologies with other technologies in the areas of clean energy and the circular economy. Demonstrated integration of sunlight conversion technologies with other value chains.
- Technoeconomical analysis of solar-driven H_2 production from biofuel and cellulose/paper industries employing sideproducts (e.g., glycerol or lignocellulose) to improve the energy balance and ensure a circular economy.

5. Solar Fuels within a Green Circular Economy

The current environmental and climate situation not only pushes towards the development of a decarbonised energy system but also requires a deep analysis of current industrial production to promote the diffusion of renewables into these sectors as well. Global warming and economic growth are only part of the challenge facing the global community, along with depleting natural resources and surmounting waste.

The production of fuels, chemicals, and materials from the solar-energy-mediated splitting of water and captured CO_2 can play a fundamental role for a transition towards the Green Circular Economy concept and, therefore, the reduction of human impact on the environment. In this respect, alternative technologies (and related materials) seeking to penetrate the market will have to out-compete more established technologies, not only in terms of costs but also in consideration of their environmental impact and efficient use of natural resources. A holistic approach towards sustainability must therefore consider the energy sector, but also the chemical industry (as the producer of most hydrocarbon-based products), along with the major emitting industries (fossil-based power generation, plants for cement, steel and iron, ammonia for fertilizers, etc.), and final waste and recycling management.

More than 20 different C1–C3 species can be directly obtained by the technologies presented in the previous chapters, and many materials (such as polymers) can be further derived from them. These compounds can replace the fossil-fuel derived ones in existing infrastructure, helping the transition towards a zero-carbon emission cycle.

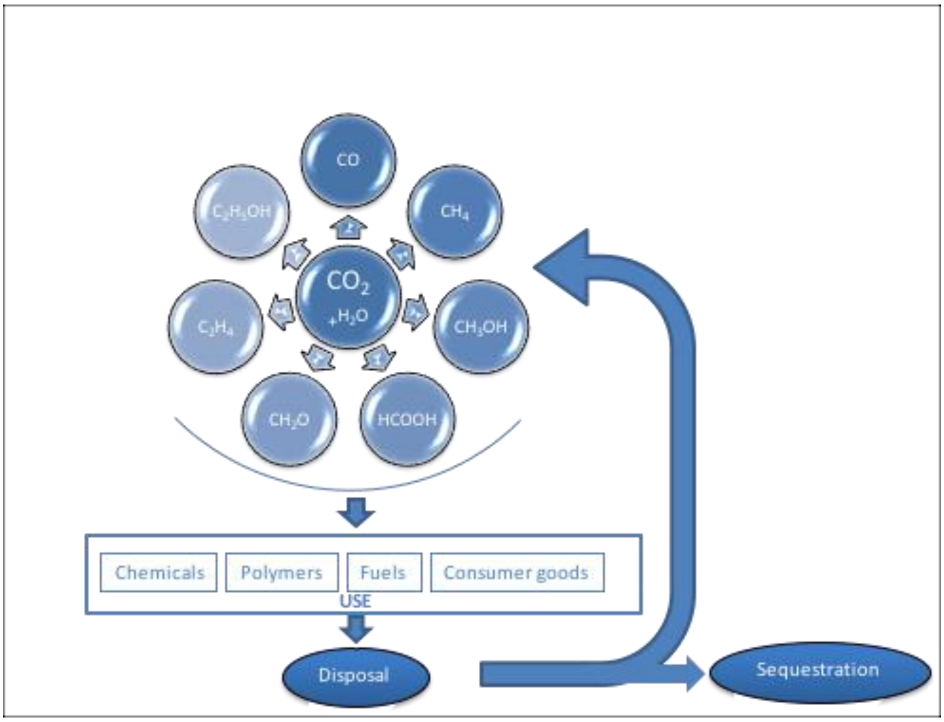


Figure 5.1. *Circular cycle of solar fuels and commodities*

Developing suitable solar technologies to convert CO_2 into fuels and products can also help create a circular carbon economy. Decarbonisation concepts could include solar-driven direct air capture and conversion of CO_2. Synergy with a wide range of industrial processes could also help decarbonise other aspects of our economy, leading to new and important value chains and promoting new business models. Solar fuels can also be used to create energy-dense fuels that can be used to store renewable energy.

This roadmap completes this first phase of Mission innovation Challenge “Converting Sunlight into Solar Fuels and Chemicals” and serves as a starting point for the development of a detailed research agenda and implementation plan in a global context. Accelerating the development of solar fuels could play a vital role in decarbonisation, energy system transformation, sustainable economic development, and the creation of a circular carbon economy.

6. Workshops, Key Documents and References

Workshops

Participants and leaders from three workshops contributed significantly to this roadmap:

- Europe, October 2019, held during a SUNRISE consortium & Mission Innovation meeting: https://sunriseaction.com/sunrise-consortium-mission-innovation-meeting/
- Japan, November 2019, held with participants from the 3rd International Solar Fuels Conference (ISF-3): http://photoenergy-conv.net/ICARP2019/
- United States, November 2020, a virtual workshop, hosted by the Liquid Sunlight Alliance (LiSA, https://www.liquidsunlightalliance.org) and the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE, https://solarhub.unc.edu), with participants from the US, Canada, Mexico, and countries in South America, Japan, and Europe: https://www.liquidsunlightalliance.org/ic5workshop

Key Documents

The following documents can be downloaded from the SUNERGY webpage: https://www.sunergy-initiative.eu/documents. SUNERGY is the European initiative that results from the merging of SUNRISE and ENERGY-X, and which aims at becoming a large European research and innovation initiative working towards the conversion and storage of renewable energy into fossil-free fuels and chemicals.

- Faber, Carina, et al. (2019): SUNRISE, Solar Energy for a circular economy – technological roadmap.
- Nørskov, Jens K. et al. (2019): ENERGY X – Research needs towards sustainable production of fuels and chemicals

Additional documents describing solar fuels include:

- Report on the Basic Energy Sciences Roundtable on Liquid Solar Fuels, available at: https://science.osti.gov/bes/Community-Resources/Reports
- Gabrielli, P., M. Gazzani, M. Mazzotti, The role of carbon capture and utilization, carbon capture and storage, and biomass to enable a net-zero-CO_2 emissions chemical industry. *Ind. Eng. Chem. Res.* 59 (2020) 7033–7045. https://pubs.acs.org/doi/10.1021/acs.iecr.9b06579.
- Nocera, D. G., Solar Fuels and Solar Chemicals Industry. *Accounts of Chemical Research* **2017,** *50* (3), 616–619.
- Spitler, M. T.; Modestino, M. A.; Deutsch, T. G.; Xiang, C. X.; Durrant, J. R.; Esposito, D. V.; Haussener, S.; Maldonado, S.; Sharp, I. D.; Parkinson, B. A.; Ginley, D. S.; Houle, F. A.; Hannappel, T.; Neale, N. R.; Nocera, D. G.; McIntyre, P. C., Practical challenges in the development of photoelectrochemical solar fuels production. *Sustainable Energy & Fuels* 2020,4, 985–995. https://doi.org/10.1039/C9SE00869A.
- Moss, O. Babacan, A. Kafizas, A. Hankin, “A Review of Inorganic Photoelectrode Developments and Reactor Scale-Up Challenges for Solar Hydrogen Production” *Advanced Energy Materials*, DOI: 10.1002/aenm.202003286.

Hydrogen roadmaps and related initiatives:

- Australia national hydrogen roadmap: https://www.csiro.au/en/Do-business/Futures/Reports/Energy-and-Resources/Hydrogen-Roadmap

- Chehade, Z.; Mansilla, C.; Lucchese, P.; Hilliard, S.; Proost, J., Review and analysis of demonstration projects on power-to-X pathways in the world. *International Journal of Hydrogen Energy* **2019,** *44* (51), 27637. https://doi.org/10.1016/j.ijhydene.2019.08.260
- China hydrogen roadmap: https://green-bri.org/hydrogen-chinas-progress-and-opportunities-for-a-green-belt-and-road-initiative/.
- EU strategy: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0301
- Fuel Cells and Hydrogen Joint Undertaking: https://www.fch.europa.eu/
- Germany hydrogen roadmap: https://www.bmbf.de/files/bmwi_Nationale%20Wasserstoffstrategie_Eng_s01.pdf
- H2@Scale: https://www.energy.gov/eere/fuelcells/h2scale
- IEA future of hydrogen (2019): https://www.iea.org/reports/the-future-of-hydrogen
- India:https://s3.amazonaws.com/documents.jdsupra.com/1515db26-0f76-42eb-be2a-d866785e4a42.pdf
- Japan hydrogen roadmap: https://www.meti.go.jp/english/press/2019/0312_002.html
- Mission Innovation IC8. Renewable and clean hydrogen: http://mission-innovation.net/our-work/innovation-challenges/renewable-and-clean-hydrogen/
- U.S. Hydrogen Roadmap Executive Summary (FCHEA): http://www.fchea.org/us-hydrogen-study.

Some technoeconomic analyses:

- Mayyas, A., M. Ruth, B. Pivovar, G. Bender, and K. Wipke. *Manufacturing cost analysis for proton exchange membrane water electrolyzers* (2019). NREL/TP-6A20-72740. https://www.nrel.gov/docs/fy19osti/72740.pdf.
- Pinaud, B. A.; Benck, J. D.; Seitz, L. C.; Forman, A. J.; Chen, Z.; Deutsch, T. G.; James, B. D.; Baum, K. N.; Baum, G. N.; Ardo, S.; Wang, H.; Miller, E.; Jaramillo, T. F., Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy & Environmental Science* 2013**,** *6* (7), 1983–2002. https://pubs.rsc.org/en/content/articlehtml/2013/ee/c3ee40831k.

References

[1] Edenhofer, O. *et al.* IPCC, 2014: Summary for Policymakers. In *Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the 5th Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge University Press, Cambridge, 2014).

[2] Climate Action Tracker. 2030 Emissions Gaps (2019). https://climateactiontracker.org/global/cat-emissions-gaps/.

[3] Buis, A. & NASA. A degree of concern: Why global temperatures matter (2019). https://climate.nasa.gov/news/2865/a-degree-of-concern-why-global-temperatures-matter/.

[4] Hoegh-Guldberg, O. *et al.* Impacts of 1.5 degrees: global warming on natural and human systems. In *Global Warming of 1.5 degrees: An IPCC Special Report on the impacts of global warming of 1.5 degrees Celsius above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty* 2018. https://www.ipcc.ch/sr15/chapter/chapter-3/.

[5] Ceballos, G. & Ehrlich, P. R. The misunderstood sixth mass extinction. *Science* 2018*,* 360, 1080.

[6] Corby, S. Transient optical studies of metal oxides for water oxidation. *PhD Thesis, Imperial College London* (2020).

[7] United Nations. The Paris Agreement. Tech. Rep., Paris (2015). https://unfccc.int/files/essential_background/convention/application/pdf/english_paris_agreeMent.pdf.

[8] Mission Innovation overview. http://mission-innovation.net/about-mi/overview/.

[9] Recent record for single silicon panel PV efficiency: https://www.pv-magazine.com/2020/01/20/longi-claims-22-38-efficiency-world-record-for-perc-mono-panel/.

[10] Woodhouse, M., Smith, B., Ramdas, A. & Margolis, R. Crystalline silicon photovoltaic module manufacturing costs and sustainable pricing: 1h 2018 benchmark and cost reduction roadMap (2019). URL http://nrel.gov/docs/fy19osti/72134.pdf.

[11] Kavlak, G.,McNerney, J. & Trancik, J. E. Evaluating the causes of cost reduction in photovoltaic modules. *Energy Policy* 2018**,** 123, 700–710, http://www.sciencedirect.com/science/article/pii/S0301421518305196.

[12] Historic crystalline silicon photovoltaics pricing. https://www.economist.com/graphic-detail/2012/12/28/pricing-sunshine.

[13] Mission Innovation IC5 Action Plan. http://mission-innovation.net/wp-content/uploads/2019/11/IC5-Cambridge-2019-Draft-1.pdf.

[14] Clean Energy Ministerial. http://www.cleanenergyministerial.org/about-clean-energy-ministerial.

[15] UN Sustainable Development Goals. https://www.un.org/sustainabledevelopment/sustainable-development-goals/.

[16] UN SDG 7, Energy. https://www.un.org/sustainabledevelopment/energy/.

[17] McCafferty, L., et al. Light-driven generation of chlorine and hydrogen from brine using highly selective Ru/Ti oxide redox catalysts. *Sustainable Energy & Fuels*, 2017**,** 1, 254–257. https://doi.org/10.1039/C6SE00057F.

[18] Miyamoto, F., Kazuhisa. Renewable biological systems for alternative sustainable energy production, Chapter 1 - Biological Energy Production. (1997). http://www.fao.org/3/W7241E/W7241E00.htm.

[19] Gust, D., Kramer, D., Moore, A., Moore, T., & Vermaas, W. Engineered and Artificial Photosynthesis: Human Ingenuity Enters the Game. *MRS Bulletin*, 2018**,** 33, 383–387. https://doi.org/10.1557/mrs2008.78.

[20] Jia, J., Seitz, L., Benck, J. et al. Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nat Commun* 2016, 7, 13237. https://www.nature.com/articles/ncomms13237.

[21] Wang, Q., et al. Printable photocatalyst sheets incorporating a transparent conductive mediator for Z-scheme water splitting. *Joule* 2018, 2, 2667–2680. https://doi.org/10.1016/j.joule.2018.08.003.

[22] Santos, D. M. F. et al. Hydrogen production by alkaline water electrolysis. *Química Nova*, 2013, 36, 1176–1193. http://dx.doi.org/10.1590/S0100-40422013000800017.

[23] Parkinson, B., et al. Levelized cost of CO2 mitigation from hydrogen production routes. *Energy & Environmental Science* 2019, 12, 19–40. https://doi.org/10.1039/C8EE02079E.

[24] Cheng, W.-H., et al. Monolithic photoelectrochemical device for direct water splitting with 19% efficiency. *ACS Energy Letters* 2018**,** 3, 1795–1800. https://doi.org/10.1021/acsenergylett.8b00920.

[25] Young, J., Steiner, M., Döscher, H. *et al.* Direct solar-to-hydrogen conversion via inverted metamorphic multi-junction semiconductor architectures. *Nat Energy* 2017, 2**,** 17028. https://www.nature.com/articles/nenergy201728.