# Strategies to improve light utilisation in solar fuels synthesis

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**Abstract**

The synthesis of fuels using sunlight offers a promising sustainable solution for chemical energy storage, but inefficient utilisation of the solar spectrum limits its commercial viability. Apart from fundamental improvements to (photo)catalyst materials, solar fuel production systems can also be designed to improve solar energy utilisation by integrating complementary technologies that more efficiently utilise the solar spectrum. Here we review recent progress on emerging complementary approaches to better modify, enhance, or distribute solar energy for sunlight-to-fuel conversion, including advanced light management, integrated thermal approaches, and solar concentrators. These strategies can improve the efficiency and production rate of existing photo(electro)chemical systems and, therefore, the overall economics of solar fuel production. More broadly, the approaches highlight the necessary collaboration between materials science and engineering to help drive the adoption of a sustainable energy economy in the near future using existing technologies.

Solar-driven photo(electro)chemical systems utilise solar energy to split water ($H_2O$) and convert carbon dioxide ($CO_2$) to produce hydrogen gas ($H_2$) and carbon-based fuels in a process usually referred to as 'artificial photosynthesis'. Many artificial photosynthetic technologies exist in various stages of development, and these can be broken down into the following three main categories: photocatalysis, photoelectrochemistry, and photovoltaic-driven electrolysis (PV-electrolysis) (**Figure 1a-c**).[1] However, techno-economic analyses have shown that none of current laboratory-scale technologies meet the criteria for practical sustainable fuel production due to insufficient solar-to-chemical conversion efficiency ($\eta_{chem}$), the absence of catalysts that are highly active and selective, and unsatisfactory scalability and stability.[2]

In general, PV-electrochemical systems benefit from commercially available components and already display high $\eta_{chem}$. Nonetheless, PV-electrochemical and photoelectrochemical devices still face technical challenges due to high materials and manufacturing costs, mass transport limitations, and substantial resistive losses that must be addressed before such systems can be efficiently scaled up.[3] In contrast, photocatalytic systems are relatively simple, requiring far less auxiliary hardware, and are therefore expected to generate solar fuels more cost-effectively on a large scale, even though the $\eta_{chem}$ of such systems are currently limited to 1-2%.[4,5] Economic viability of solar fuels from artificial photosynthesis may be achieved by reducing the fabrication and operation costs, improving $\eta_{chem}$ without substantial increases to costs, or employing low-cost materials and auxilliary systems at sufficient scale (or with high enough production rates) to meet fuel production cost-thresholds despite relatively low efficiency.

This review presents a range of complementary solar technologies, including light management, photon wavelength manipulation, solar concentration, and thermal-related approaches to maximise solar energy utilisation for the synthesis of chemical fuels. We discuss the benefits of such approaches in terms of increasing $\eta_{chem}$ and production rates, which can further enhance the best existing solar

fuel technologies to achieve economic viability. Implementing these complementary approaches will require collaboration of a multidisciplinary research community and accelerate the realisation of practical devices.

**Light management**

According to thermodynamic analysis based on a thermo-chemical equilibrium between the Sun and a semiconductor, $\eta_{chem}$ reaches an entropy-limited ideal maximum of 67% under 1 sun irradiation (100 mW $cm^{-2}$), assuming all the photogenerated electron-hole pairs without recombination can be used to produce storable chemical energy in artificial photosynthesis (**Table 1**).[6] However, thermalisation of super-bandgap photons ($E > E_g$; $E_g$: bandgap) and the inability to absorb sub-bandgap photons ($E < E_g$) amount to considerable combined losses.[7] Owing to the mismatch between photon energy and a given semiconductor bandgap across the entire solar spectrum, a maximum achievable efficiency exists and is known as the Shockley–Queisser limit.[8] Thus, the theoretical maximum $\eta_{chem}$ of a photo(electro)chemical system based on single light absorber decreases to ~30% (under 1 sun irradiation) when considering thermalisation losses in addition to entropy increase (**Table 1**).

**Figure 2** shows representative experimental systems with their solar-to-hydrogen conversion efficiency ($\eta_{H_2}$), all of which are much lower than the theoretical maximum values based on the thermo-chemical equilibrium analysis. One of the most significant challenges in realising efficient solar fuel production is utilisation of the full solar spectrum. The infrared (IR) region, which accounts for approximately 50% of total solar irradiance, cannot usually contribute directly to artificial photosynthesis because its photon energies are smaller than the semiconductors' bandgaps and contain less energy than needed for typical processes (*e.g.* water splitting; 1.23 eV at 1 atm and 25 °C). Accordingly, reports of visible-light-driven artificial photosynthesis using single light absorber

photocatalytic without sacrificial reagents remain scarce due to stringent thermodynamic and kinetic requirements.[9]

Instead, Z-scheme (tandem) systems using two light-absorbers that combine smaller bandgap semiconductors are constructed and provide a higher maximal efficiency due to less restrictive or complementary light absorption.[10] For example, the front/top photoelectrode in a photoelectrochemical tandem cell is transparent with a wider bandgap ($E_{g1}$) to absorb short-wavelength light, allowing the penetration of long-wavelength light for utilisation by the back/bottom photoelectrode which has a narrower bandgap ($E_{g2}$) (**Figure 1b**), thereby avoiding competition between the two light absorbers and minimising thermalisation.[11,12] Tandem cells with good light management represent an effective way to reduce thermalisation losses, and a theoretical tandem cell consisting of infinitely many light absorbers with different bandgaps estimates a maximum $\eta_{chem}$ of 86% or 67% for 45900 suns and 1 sun intensities, respectively.[6,11]

A key challenge is the search for a low-cost transparent front/top photoelectrode with both high transmittance of longer wavelengths and sufficient absorbance of shorter wavelengths. $BiVO_4$ ($E_g$: 2.4 eV) shows high transmittance of wavelengths >500 nm and it has been widely used as a relatively inexpensive and stable photoanode in bias-free photoelectrochemical tandem cells.[13,14] A recent efficiency milestone demonstrated an $\eta_{H_2}$ of 19% for unbiased water splitting using $Ga_{0.41}In_{0.59}P$ ($E_{g1}$ = 1.78 eV) as the top photocathode coupled to a $Ga_{0.89}In_{0.11}As$ ($E_{g2}$ = 1.26 eV) bottom photoanode under 1 sun irradiation.[15] In a tandem configuration, the optimal $E_{g1}$ and $E_{g2}$ have been estimated as 1.9 and 1.0 eV, respectively, attaining an ideal maximum $\eta_{chem}$ of ~42% under 1 sun.[11] Accounting for realistic losses in a photo(electro)chemical system, including electrode polarisation, overpotential requirement for catalysis (0.6–0.8 eV), and solution resistance, results in an optimal $E_{g1}$ and $E_{g2}$ of ~1.6 and ~1.0 eV, respectively, with a maximum $\eta_{H_2}$ of ~27%.[12,16]

Spectral beam splitting is used extensively to address the spectral mismatch problem of photonic devices. Sunlight can be split into several bands using strategies such as dichroic mirrors, holographic concentrators, and rugate filters.[17] Spectral beam splitting in an integrated PV-driven photoelectrochemical system, where PV cells provide an extra bias for the photoelectrochemical device, allows wavelength bands to be directed to the most efficient converter. For example, directing ultraviolet (UV) and short visible wavelengths to a photoelectrochemical device while the long visible wavelengths and near-infrared (NIR) are directed to a solar cell maximises solar energy utilisation (**Figure 3a**).[18] As an example, a beam splitter was integrated into a PV-photoelectrochemical system consisting of a photoelectrochemical element with a Mo-doped $BiVO_4$ ($BiVO_4$:Mo) photoanode modified with a water-oxidising Fe(Ni)OOH catalyst and a $H_2$-evolving Pt cathode connected to a single-junction perovskite PV cell, producing a $\eta_{H_2}$ of ~6% for water splitting.[19] The beam splitter separated solar irradiation (1 sun) into two light beams, directing wavelengths >515 nm to the solar cell and wavelengths <515 nm to the $BiVO_4$:Mo photoanode.

Another feature of the beam splitter is the possibility of filtering the spectrum to avoid heating of PV devices, which can increase the durability and efficiency of solar cells,[17,20] instead redirecting the heat to enhance catalysis processes. However, beam splitters always introduce energy losses (~1–3%),[21] which must be offset by the resulting decrease in thermalisation losses. Careful design of such devices is necessary as the elastic energy stored in thick, multi-layer coatings can cause internal stresses which reduce the durability and lead to cracking or delamination.[21] Ultimately, the increased cost of fabricating quality splitters with tight optical tolerances and high durability must be justified by the gain in efficiency.

One, two, or three-dimensional periodic dielectric structures or gratings,[22] and isotropically scattering (or Lambertian) surfaces[23] are commonly used in the PV community to increase the absorption and solar-to-electricity conversion efficiency ($\eta_{elec}$) of solar cells via light trapping. Light

trapping schemes are generally based on geometric structures or features that elongate the optical path length through random scattering from a roughened front surface and reflective back surface.[24] Solar cell transmission losses can be reduced by guiding light multiple times into its absorbing region, increasing the optical path length of the light, and thereby the probability of light absorption, while keeping its physical thickness unaltered.[24]

Based on these advantages, light-trapping is also a promising strategy for improving efficiency of photoelectrochemical and photocatalytic systems, as shown in **Figure 3b**. In particular, the front photoelectrode in tandem devices is expected to effectively harvest super-bandgap photons while being transparent enough to feed the back absorber with sub-bandgap photons. As an example of a light-trapping strategy, a distributed Bragg reflector designed to reflect <500 nm and transmit >500 nm light was installed between a $BiVO_4/WO_3$ photoanode and a dye sensitised solar cell to increase the light utilisation of the PV-photoelectrochemical tandem device resulting in a 24% improvement to photocurrent and a $\eta_{H_2}$ of 7.1%.[25] Through such a photon recycling strategy, the trade-off between light absorption and transmittance for the front photoelectrode can be lessened. Additionally, fabricating thin-film photoelectrode and solar cell assemblies with an active layer thickness in the range of hundreds of nanometers has the advantage of reduced material usage, shorter carrier collection lengths, and lower series resistance.[24]

**Solar spectrum adaptation**

Efficiencies exceeding the Shockley–Queisser limit can be reached by converting the solar spectrum to wavelengths that match the absorption edge of the light absorber; an approach that has received the most attention in solar cells and is comparatively underdeveloped in solar fuel production devices. By doing so, energy from sub-bandgap photons and excess energy from super-bandgap photons can contribute to the quantum efficiency (QE; the ratio of charge carriers used for current

generation/chemical reaction to incident photons) of the device, sidestepping the Shockley–Queisser assumption that this energy would otherwise be lost.

The thermalisation of charge carriers caused by the absorption of super-bandgap photons is one of the major loss mechanisms leading to low efficiency, particularly in the case of narrow-bandgap semiconductors. Downconversion (quantum cutting) (**Figure 4a**) splits one high-energy photon into two lower-energy photons that can each excite an electron-hole pair.[7] For example, singlet exciton fission is a downconversion process in organic semiconductors, spontaneously converting one spin-singlet electron-hole pair into two spin-triplet excitons.[26,27] This process can reduce energy loss related to the thermalisation of hot charge carriers, predicting an upper $\eta_{elec}$ limit of ~40% for PV systems (single light absorber, $E_g$: ~1.0 eV) under 1 sun.[28,29] By cutting one high-energy photon into two low-energy photons that can both be absorbed by the semiconductor, the current generated from photons with $E \geq 2E_g$ can be doubled.

Another process, down-shifting (**Figure 4b**), transforms one absorbed high-energy photon into one lower-energy photon with a wavelength change known as the Stokes shift.[7] Down-shifting is useful for improving the $\eta_{elec}$ of PV by shifting short-wavelength sunlight to the longer-wavelength region where the semiconductor exhibits higher QE due to less surface recombination.[30] Lanthanide ions, quantum dots, singlet fission materials and organolanthanide complexes have been explored as wavelength-shifting materials.[7,27]

Sub-bandgap photons are transmitted through semiconductors, resulting in limited utilisation of photons. Upconversion is a process that absorbs low energy photons and 'combines' their energies, re-emitting a photon with $E \geq E_g$. This technique offers a means of mitigating transmission losses and increasing the $\eta_{elec}$ of PV (single light absorber, $E_g$: 1.76 eV) to a limit of ~43% under 1 sun.[28] This anti-Stokes emission can be achieved through two main pathways: lanthanide-doped upconversion nanoparticles and triplet-triplet annihilation systems.[31] The lanthanide ions possess multiple long-

lived and ladder-like electronic states, allowing even two- to six-photon upconversion processes to realise large anti-Stokes shifts from NIR excitation to visible and UV emission. In triplet−triplet annihilation-based upconversion, the photon energy absorbed by a sensitiser is transferred to an acceptor, and two excited acceptors undergo triplet−triplet annihilation, producing upconverted singlet fluorescence.

The $\eta_{chem}$ of standalone photoelectrochemical tandem cells is very sensitive to the shape and current densities at the intersection point of current density–voltage (J-V) curves of the two individual photoelectrodes.[12] The J-V curve of a photoelectrode can be readily tuned by manipulating the sunlight and enhancing the intensity of absorbable portion, leading to an increased operating current density ($J_{op}$) and $\eta_{chem}$, as shown in **Figure 4c.** Estimates have demonstrated that the limiting $\eta_{elec}$ (and $\eta_{chem}$ assuming that electrical energy can be transformed into chemical energy without loss) of these semiconductors under 1 sun irradiation can be improved by a factor of ~1.8–2.8 when combining ideal photon up- and down-conversion, reaching 45% when the bandgap is 0.9–1.4 eV (**Table 1**).[28]

Moreover, product selectivity of a standalone photoelectrochemical tandem cell for water splitting and $CO_2$ conversion is sensitive to the shared electrode potential (operating potential $V_{op}$),[32] where photoelectrodes generate both photocathodic and photoanodic currents. By using solar spectrum adaptation to adjust the $V_{op}$, control over the selectivity of desired products may be possible (**Figure 4c**).

As an example of combined up- and down-conversion, a luminescent back reflector (LBR) consisting of an organic fluorophore pair *meso*-tetraphenyltetrabenzoporphine palladium (PdTPBP) and perylene, has been applied to increase the fraction of light usable by a $BiVO_4$:Mo photoelectrode connected to a Pt cathode for overall water-splitting with external bias.[33] $BiVO_4$:Mo absorbs light most efficiently at a wavelength of ~470 nm, therefore the LBR was designed to absorb light in the

wavelength ranges of 350-450 nm and 600-650 nm, and emit light at 470 nm. Specifically, the PdTPBP absorbed 600–650 nm light and re-emitted it at 470 nm by Dexter energy transfer and triplet-triplet annihilation, whereas perylene facilitated conversion from 350–450 nm to 470 nm through down-shifting. The LBR enhanced the photocurrent density over an applied potential range of 0.3–1.23 V (versus reversible hydrogen electrode (RHE)), experimentally demonstrating a modest increase from 4.48 to 5.25 mA $cm^{-2}$ at 1.23 $V_{RHE}$.

Wide-bandgap photocatalysts that are only active under UV light would greatly profit from highly efficient hybrid upconversion systems. Despite their large bandgaps, most research still focuses on oxide materials because they are cheap, stable, and easy to prepare.[4,9] By incorporating upconversion materials to absorb lower-energy photons and emit higher-energy photons in the absorbable range of a wide-bandgap photocatalyst ($E_g$ > 3.0 eV) as shown in **Figure 4d and e**, the limiting $\eta_{elec}$ (and $\eta_{chem}$ assuming that no loss in electrical-to-chemical energy conversion) under 1 sun irradiation may be improved from ~2 to 40%.[34] An example is given by a hybrid electrode composed of hematite ($\alpha$-$Fe_2O_3$, $E_g$ = 2.1 eV) films and upconversion rare-earth nanocrystals ($NaYF_4$:Yb,Er),[35] in which the nanocrystals absorb IR radiation (980 nm) and emit at 550 and 670 nm. Hence, photon energy from incident light in the IR range was rendered usable by hematite that absorbs only UV and a part of visible radiation, resulting in water splitting driven by a 980 nm laser with a QE = $1.24 \times 10^{-4}$ % at 1.43 $V_{RHE}$.

The main drawback of using lanthanide-doped upconverters is their low upconversion efficiency — generally well below 5% due to their narrow light absorption range.[31,36] Triplet-triplet annihilation systems suffer from a relatively small anti-Stokes shift and low stability, requiring specific operating conditions (*e.g.* anoxic, non-aqueous) for efficient conversion.[31,37] The oxygen sensitivity can be diminished if the converter's triplet-state energies are below oxygen's singlet-state energy ($^1\Delta_g O_2$ = 0.98 eV), and under certain conditions, the presence of oxygen can enhance upconversion.[38]

Alternatively, additional engineering (*e.g.* enclosed in microcapsules) may facilitate operation in ambient, oxygen-rich aqueous phase environments.[39] To increase the efficiency of photon upconversion, hybrid upconversion nanosystems combining organic dyes and inorganic nanoparticles, especially in the form of dye-sensitised lanthanide-doped upconversion nanoparticles, nanoparticle-sensitised molecular triplet-triplet annihilation systems, and metal–organic-framework nanoparticles, have been developed and offer exciting opportunities for applications with photonic devices.[31] Down-conversion has been reported with quantum efficiencies above 100%,[40] and exhibits the potential to improve $\eta_{elec}$ of PV with a single light absorber to ~40% (**Table 1**), yet challenges remain in the integration into the devices and the stability in ambient conditions.

**Solar concentrators**

PV-electrochemical and photoelectrochemical systems suffer from scale-up issues due to their complex fabrication processes and area-related costs including the price of reactors, module and encapsulation, installation, and cabling. Concentrating solar power offers a way to improve the production rate and efficiency of these systems, achieving concentrated fuel production on a smaller active material footprint, thereby reducing the overall system cost. Practical solar concentrators focus light onto devices with small areas following the basic optical principles of Snell's law for reflection by specular surfaces using parabolic mirrors, Fresnel lenses, dish–collectors, or heliostat power towers.[41]

In PV systems, the use of concentrated sunlight benefits $\eta_{elec}$ due to the increase of both current (linearly) and voltage (approximately logarithmically) up to a saturation point, where resistance losses prevent further increases in efficiency.[42,43] The same is not true for $\eta_{chem}$ in photo(electro)chemical devices where efficiency is only dependent on the linear increase in current provided by concentrated irradiation. High-efficiency concentrated photovoltaic (CPV) devices operating under concentrated

sunlight have been directly coupled with electrolysis cells: for example, a PV-electrochemical water splitting system with an $\eta_{elec}$ of 39% reported a record $\eta_{H_2}$ of >30% using two electrolysers under 42 suns irradiation.[44] Recent efforts have demonstrated a six-junction III-V solar cell with $\eta_{elec}$ of 47.1% under 143x solar concentration.[45] Coupled with optimised electrolyser systems, such CPV devices have the potential to further increase $\eta_{H_2}$ above the current record of 31.2%. Even so, working at such elevated current densities for PV introduces complexities such as excessive operating temperatures and overpotentials, which can exacerbate degradation of the light-absorbing materials.[46] Since the required operating temperature of PV is lower than that of electrolysis, controlled heat exchange between the two components is a promising way to improve device lifetime.[47] As a consequence, a thermally integrated PV-electrochemical $H_2$-generation device, where controlled flow of electrolyte was used to facilitate heat exchange, was stable for over 100 h in a water decomposition system and achieved $\eta_{H_2}$ of ~18% under 207 suns irradiation, while maintaining a working temperature below 30 °C.[48]

In addition to $\eta_{chem}$, production rate is another key metric in solar fuel production. A recent techno-economic analysis on photocatalytic reforming of waste organics to $H_2$ suggested that a four-fold increase in $H_2$ production rate would lower the cost of hydrogen production by 76% and quadruple the energy returned on energy invested.[49] In a pair of experimental demonstrations, the apparent rate constant ($k_{app}$) for photocatalytic production of $H_2$ over Au/$TiO_2$ was found to be proportional to light intensity ($I$) through the relationship $k_{app} = k \cdot I^{0.65}$ at 25 °C and increase with temperature according to an Arrhenius relationship, seeing a six-fold increase in rate over a temperature increase of 50 °C at 1.5 mW $cm^{-2}$ UV-A irradiance (320–400 nm).[50,51] Increased light intensity and temperature for photocatalytic solar fuels processes, achieved through use of solar concentrators, shows the possibility of achieving economic feasibility at higher production rates through reactor design.[50,52]

Some drawbacks of adopting solar concentrators are that only direct sunlight can be concentrated on the receiver effectively (thus losing energy from diffuse sunlight), and that both optical and resistive losses are more significant under concentration.[43] To obtain the optimal concentration at the receiver for solar fuel production, the daily and seasonal motion of the Sun must be considered. Hence, tracking-integrated concentrating systems, where the module is physically adjusted to optimise the collector's acceptance angle, are anticipated to be employed for solar fuel production systems (**Figure 5a**). The integration of a tracking system allows the elimination of cosine losses which affect fixed-angle systems and may offset the efficiency loss incurred by failing to capture diffuse sunlight with a solar concentrator. The fraction of diffuse sunlight in Air Mass 1.5 Global spectrum (AM1.5G) is 10%, but on cloudy or hazy days, or at higher air mass, this fraction can increase substantially and proportionally diminish the efficacy of the solar collector.[43] Overall, tracking-integrated solar concentration is believed to reduce system and maintenance costs, and their compact geometry would allow them to be opened up to the growing residential market.[53]

Apart from the increased light intensity, solar concentrators also focus thermal energy which can be readily harvested. Using a variety of mirror designs, sunlight can be focused onto a relatively small absorber area, generating high temperatures typically ranging from 200 °C to 1500 °C.[54] This concentrated solar energy (5000 suns and beyond) has been proposed as useful for increasing or controlling heat to perform other solar fuel generation processes, such as solar thermolysis, solar thermochemical cycles, solar reforming, solar cracking, and solar gasification (**Figure 1d**).[55] For example, $\eta_{chem}$ of 0.8% and 0.7% for $CO_2$ and $H_2O$ splitting to produce CO and $H_2$, respectively, were achieved using porous monolithic $CeO_2$ in a state-of-the-art solar-cavity receiver reactor following the two-step thermochemical reactions:[54]

$\frac{1}{\delta}CeO_2 \rightarrow \frac{1}{\delta}CeO_{2-\delta} + \frac{1}{2}O_2(g)$ at 1500 °C (endothermic)

$H_2O(g) + \frac{1}{\delta}CeO_{2-\delta} \rightarrow \frac{1}{\delta}CeO_2 + H_2(g)$ at 800 °C (exothermic)

$$CO_2(g) + \frac{1}{\delta} CeO_{2-\delta} \rightarrow \frac{1}{\delta} CeO_2 + CO(g) \qquad \text{at 800 °C (exothermic)}$$

This system demonstrated stable fuel generation over 500 cycles. Such two-step thermochemical reactions based on metal oxide redox cycles are capable of producing $H_2$ at more technically feasible reduction temperatures (1200 to 1500 °C) compared to direct thermolysis (>2700 °C).[56] Additionally, since only the first step is endothermic, the second step can be carried out at night or on-demand.[41]

While this two-step process offers easier product separation compared to direct thermolysis, the final products still need to be separated from unreacted $H_2O$ or $CO_2$ and from the purge gas used to dilute oxygen in the reduction step. Additionally, heating immense amounts of sweep gas (*e.g.* $N_2$) incurs an energy penalty.[57] Alternative methods, including vacuum pumping and chemical scavenging, have been investigated to reduce the partial pressure of oxygen and increase the efficiency.[58,59] The use of concentrated solar heat is a green alternative for upgrading the calorific value of the fuel by adding solar energy in an amount equal to the enthalpy of the reaction.[55] Two-step solar thermochemical cycles (**Figure 5b**) under concentrated irradiation using $MO_{ox}/MO_{red}$ (M=Zn, Ce, Fe) were reported to have a maximum $\eta_{chem}$ of 20–40% for $H_2$ or CO production, though this was dramatically affected by the operating conditions including heat recovery effectiveness, temperatures, pressures, and solar irradiation concentration.[60,61]

Such technologies provide an opportunity to use the waste heat in thermochemical processes. A spectral splitting concentrator, consisting of upper and lower mirrors, has been proposed and designed to achieve cascading utilisation of the full solar spectrum.[62] The upper mirror allows the visible light to be concentrated on photovoltaics, whereas the lower mirror enables the IR fraction to be focused on a solar thermochemical reactor. Accordingly, a higher solar conversion efficiency ($\eta$) has been estimated for such a hybrid system (19.0%) when compared to individual CPV (CdTe) (13.1%) and thermochemical methanol decomposition systems (13.5%). Recently, thermodynamic evaluation of a proposed concentrated photochemical-PV-thermochemical system that utilises the full solar

spectrum estimated a $\eta$ of ~67%, with output products of photo-isomers, electricity, and syngas ($H_2$ + CO).[63] The thermalisation loss was diminished by recycling photons with $E > E_g$ for a photochemical process (molecular isomerisation reaction) and employing the sub-bandgap photons to provide heat for thermochemical methanol decomposition to produce syngas.

Solar thermophotovoltaics (STPV) provide another strategy with the potential to exceed the Shockley–Queisser limit for PV by heating an intermediate absorber composed of a refractory metal (*e.g.* W) with concentrated solar radiation and emitting narrowband radiation to PV cells.[64,65] The essential advantage of such a system is the ability to choose an emitter material with a selective emission spectrum for illuminating the solar cell only with photons of $E = E_g$. Additionally, any photons not absorbed by the PV will be reflected back to the emitter. Thus, in theory, the thermalisation losses in a STPV system can be largely avoided, predicting a similar limiting $\eta_{elec}$ (85%) to an infinite tandem PV under 46200 suns (**Table 1**) when the intermediate absorber/emitter is operated at 2544 K.[66] Although STPV-driven water electrolysis was expected to attain a $\eta_{H_2}$ of 27% when efficiency of the thermal convertor was 80%,[67] experimental $\eta$ of STPV remains modest (< 30%),[68] mainly due to insufficient temperature control and inefficient energy transmission.[43,65]

**Thermal and related approaches**

Even under 1 sun irradiation, photo(electro)chemical systems are generally heated by absorbed sunlight via thermalisation, thermal heating, and radiative heat transfer by non-converted photons, leading to an increased working temperature of 60–80 °C.[69] While excessive heating will reduce the device lifetime and absorber efficiency,[70] careful manipulation of thermal energy to drive complementary approaches may improve overall solar energy conversion efficiency. Solar thermal technologies can take full advantage of solar IR radiation and are able to complement photo(electro)chemical processes, as depicted in **Figure 5c, d, e**.

**Thermally accelerated photocatalysis.** High temperature is normally avoided in photovoltaic applications due to its detrimental effect on the open-circuit voltage, particularly for CPV devices where a cooling system is necessary to maintain optimal PV performance and minimise degradation.[44] However, the efficiency loss caused by increased temperatures is much smaller in photoelectrochemical and photocatalytic systems due to cooling by the electrolyte solution and can also be offset by improved reaction kinetics and electrolyte ion mobility, especially in a convective flow system.[70]

Recently, an integrated photoelectrochemical device for hydrogen generation via water splitting over buried III–V-based photovoltaic components reached a $\eta_{H_2}$ of 17.1% under an irradiance of up to 474 suns owing to thermal integration, mass transport optimisation, and close electronic integration between the photo-absorber and electrocatalyst.[71] These results highlight that, compared to solar cell devices where waste heat is highly undesirable, photoelectrochemical systems can take advantage of thermal energy to enhance their performance. Such improvements are highly temperature dependent, therefore necessitating careful device design to optimise the volume, flow rate, and depth of the electrolyte layer above the photoelectrochemical devices for maximal efficiency.[48,70]

The thermal effects in the IR region increase photocatalytic activity owing to enhanced reaction kinetics on the semiconductor.[72] According to the Arrhenius law, it can be estimated that catalytic rates roughly double for every 10 °C increase in temperature.[73] Such thermal effects have been most successfully exploited using a photocatalyst sheet consisting of $Cr_2O_3$/Ru-loaded $SrTiO_3$:La,Rh and $BiVO_4$:Mo powder embedded into a gold layer, with record $\eta_{H_2}$ of 1.1% for a pure water-splitting reaction measured under 1 sun irradiation at elevated temperature (318 K), compared to ~0.3% at room temperature.[5]

Another theoretical strategy for improving $\eta_{chem}$ by utilising solar heating is through solar thermal electrochemical photo (STEP) processes. The mechanistic basis of this technique is decreasing the energy requirement for a chemical reaction, such as water or $CO_2$ splitting, by tuning the electrochemical potential and kinetics with temperature.[74] For example, the electrolysis voltage for water decreases with temperature from 1.229 V at 25 °C to 0.809 V at 600 °C and a $H_2O$ partial pressure of 500 bar.[75] The increased efficiency is derived from $\eta_{chem} = \eta_{elec} \times \eta_{electrolysis} \times A_{STEP}$ where $A_{STEP}$ is the ratio of electrolysis voltage at ambient temperature over high temperature, and is realised when the reactor is fully heated by solar IR that would otherwise go unused.[76] Although the electrochemical basis for STEP processes has been experimentally validated by electrolysis of water and $CO_2$ in molten salt solutions at 500 – 750 °C using low-potential electrolysis systems,[77,78] true experimental verification using solar heating and direct calculation of $\eta_{chem}$ remains elusive. The theoretical solar conversion efficiency limit for water and $CO_2$ splitting has been reported as >50% and 54.7%, respectively.[74,76]

**Pyroelectric and thermoelectric effect.** Thermal fluctuations and/or transient waste heat in the operating environment have the potential to be harnessed by pyroelectric and thermoelectric materials to provide voltage to support photo(electro)chemical reactions (**Figure 1e**).[79] Pyroelectric materials rely on time-dependent temperature fluctuations that induce changes in polarisation of the material to provide voltage.[80] An estimation has shown that electricity can be generated on pyroelectric materials ($Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ single crystal) by natural temperature variations over 24 hours.[81] The coupling of pyroelectric effects with electrochemistry can be realised in either external or internal configurations.[80] In an externally positioned system, the pyroelectric materials are not in direct contact with the electrolyte and are instead simply used as a thermal energy harvester and source of charges to drive electrochemical reactions. An internal system, where finely dispersed pyroelectric

391 particulates, for example $Ba_{0.7}Sr_{0.3}TiO_3$,[82] are suspended in the reactant (*e.g.*, $H_2O$), can provide a
392 large pyroelectric surface area and total charge to stimulate $H_2$ production from water using thermal
393 fluctuations.

394 In contrast to pyroelectric materials that provide voltage from temperature fluctuations,
395 thermoelectric materials, such as $Bi_2Te_3$, PbTe, Bi-Sb, and Si-Ge alloys,[83] rely on a temperature
396 gradient to transport charges based on the Seebeck effect. For example, a dark Ni nanosheet capable
397 of reaching an average temperature of 92 °C within 2 min under simulated sunlight irradiation was
398 directly integrated on the hot end of thermoelectric generator for $H_2$ evolution from water.[84] The Ni
399 nanosheet not only provides sufficient temperature differences for thermoelectric generation but also
400 functions as a $H_2$ evolution catalyst, thereby improving water splitting overall.

401 Combining a photoelectrochemical module and a solar thermoelectric generator (**Figure 5e**)
402 would enable the utilisation of transmitted photons and waste heat, which can be directed to the
403 thermoelectric modules to generate electricity, leading to an increased $\eta_{chem}$. A conceptual design of
404 a thermoelectric-photoelectrochemical hybrid system was proposed to harness solar radiation and
405 waste heat, leading to efficient water splitting with $\eta_{H_2}$ ~20% over a 56 °C temperature gradient using
406 a Si photocathode wired to a Pt anode under 1 sun irradiation without an external applied voltage.[85]
407 Integrating thermoelectric module in a tandem photoelectrochemical device also provides another
408 means of adjusting the J-V curve intersection point for the two individual photoelectrodes. Very recently,
409 a thermoelectric generator was directly mounted on the bottom of a photoelectrochemical cell
410 consisting of a Si photocathode and a $BiVO_4$ photoanode.[86] An additional bias of 100 mV was
411 generated from thermoelectric device by making use of the temperature difference between the
412 aqueous electrolyte warmed by incident sunlight irradiation and cooler, unirradiated water. The
413 addition of the thermoelectric system in this particular combination improved the

photoelectrochemical water splitting by a factor of 1.6 under 1 sun because the current $J_{op}$ was increased by shifting $V_{op}$, as shown in **Figure 4c**.

Although the full solar spectrum can be exploited by combining thermoelectric modules and solar fuel production devices in the examples above, the efficiency enhancement of the hybrid system is still modest. This is mainly due to the limitations of present integrated designs, which cannot provide sufficient temperature gradients on the thermoelectric modules to deliver meaningful voltage. According to the exergy and energy analysis, the maximal $\eta_{elec}$ of solar-driven thermoelectric generator under 1 sun irradiation was expected to be only ~5% (**Table 1**),[87] and current thermoelectric technology is not yet cost-effective.[88] Future efforts should not only focus on the development of high-efficiency, low-cost thermoelectric modules, but also the utilisation of concentrated solar light to enhance the thermal effect and optimisation of the integrated design to maximise temperature gradients and heat transfer.[89,90] A simulation has estimated that the $\eta_{elec}$ enhancement for integrating thermoelectric device into a PV system is limited to 1.6% and 4.1% for p-type Si and copper indium gallium selenide solar cell, respectively, due to large exergy losses.[91] However, this exergy loss may be reduced by using a PV cell with higher efficiency, thereby increasing the $\eta_{chem}$ of thermoelectric and PV-electrolysis hybrid systems.

The efficiency and output power of pyroelectric energy harvesting are expected to be greater than thermoelectric methods due to their easier overall optimisation.[81] The high thermal conductivities typical of thermoelectric materials decrease the actual temperature gradient, making practical implementation difficult. On the other hand, pyroelectric effects are limited by heat capacity, a factor for which volumetric optimisation may easily compensate.

## Conclusions and Outlook

A key challenge limiting the application of photo(electro)catalysis for artificial photosynthesis

438 is inefficient utilisation of the solar spectrum, resulting in more than half of the energy being lost as
439 waste heat. While there are still substantial efficiency benefits to be gained from improving and
440 understanding (photo)catalyst materials at a fundamental level, this review highlights how existing
441 complementary technologies can be coupled with photo(electro)chemical systems to increase solar
442 conversion efficiency and production rates. Adoption of solar fuel technologies can be accelerated
443 through exploring such complementary approaches which will improve the efficiency and economic
444 feasibility of such fuel production.

445 Of the techniques reviewed here, the most readily and widely applicable to most systems is that
446 of light management and solar spectrum adaptation. Instead of constraining photocatalyst absorbance
447 to match the solar spectrum, efficient photocatalysts may be selected for performance under ideal
448 illumination conditions and the solar spectrum may be adapted to meet these specifications. In
449 particular, hybrid up-/down-conversion systems capable of transforming a wide spectrum into a
450 tailored band of wavelengths have been shown to substantially improve $\eta_{chem}$. These up-/down-
451 conversion systems have benefited from considerable research efforts in recent years, making it
452 possible to immediately deploy this technology in existing solar fuel devices. For example, a filter
453 containing up-/down-conversion systems may be installed in front of the photocatalyst or light
454 absorber, or in some cases, up-/down-conversion materials might be deposited directly on, or be
455 suspended in a slurry with, the photocatalyst or light absorber.

456 Solar concentrators are components that can be relatively easily added to most solar fuels
457 systems to improve incident intensity, and they are anticipated to play an important part in the future
458 development of solar fuel technologies. In particular, PV-electrolysis and photoelectrochemical cells
459 would benefit from increased solar fuel production rate under concentrated light, leading to a reduced
460 embodied energy payback time, improving the sustainability and economic viability of such devices,
461 and allowing the use of more costly catalyst or PV components. Solar concentration can also be used

462 to gather heat which, with proper temperature management, may be used to improve reaction kinetics
463 or drive thermally activated processes.

464 While light management and solar concentration address the key issues of inefficient light
465 utilisation and increased production rate, integrated thermal approaches present a transformational
466 approach to solar fuels system design, presenting an opportunity to maximise solar energy conversion.
467 For example, thermally accelerated photocatalysis can be achieved by capturing solar heat to maintain
468 an optimal reaction temperature, further increasing the overall $\eta_{chem}$ due to improved reaction
469 kinetics. IR radiation not typically absorbed by photocatalysts could instead be captured by thermal,
470 thermoelectric, and pyroelectric devices to generate extra bias or perform thermochemical processes,
471 complementing the light-driven devices. Such thermal approaches may also offer integrated solutions
472 to challenges such as the intermittent nature of solar energy. Heat collected during daytime operation
473 may reduce thermocatalysts which can then continue to drive fuel conversion processes at night.
474 While the potential benefits of such systems are great, the cost of integrating thermal approaches
475 should be justified by overall the efficiency gain of the system.

476 As an example of a device that approaches maximal utilisation of solar energy, we propose a
477 design that combines photo(electro)chemical processes, solar concentration, thermoelectric power
478 generation, and a thermal management strategy (**Figure 6a**). The integration of these various
479 technologies would lead to more efficient solar fuel production than the sum of each system applied
480 individually**.** A parabolic solar concentrator provides high solar irradiation intensity and abundant
481 heat to the integrated photoelectrochemical-thermoelectric generator, the thermoelectric element
482 utilises the heat gradient within the device to provide extra electrical bias, and the heat management
483 scheme is implemented to maintain the optimum device operating temperature while reusing the
484 excess heat to provide hot water for households and industry.

Although the integration of complementary technologies may improve the economic viability of solar fuels processes, consideration of engineering design requirements to optimise implementation of this technology is still important. The economic barrier-to-entry for artificial photosynthesis is raised by the requirement for clean $H_2O$ and $CO_2$ streams. By considering the design requirements and available energy within the solar spectrum, engineering designs can implement strategic plant locations and complementary approaches to maximise energy efficiency. Light management strategies may direct IR irradiation not used by the photocatalytic process to drive desalination of seawater and purification of wastewater using solar vapour generators (**Figure 1f**). Locating such a solar fuel plant near the ocean and in close proximity to industrial sources of $CO_2$ will also reduce the energy and financial cost required for reagent transportation which would be otherwise significant considering the need for ~9,000 kg of water for every tonne of $H_2$ produced via water splitting (**Figure 6b**).[92] Plant location should also be dictated by access to abundant sunlight, ideally at equator latitudes, to maximise operating hours and shorten the energy and investment payback periods. Additionally, although the produced gaseous mixture of hydrogen and oxygen from water splitting may be separated by introducing molecular sieve membranes,[93] safely separating, transporting and storing the produced $H_2$ still needs to be carefully considered as $H_2$ has a broad flammability range (4–94% in $O_2$ at ambient temperature and pressure). Employing commercial electrolysers (*e.g.*, polymer electrolyte membrane electrolysers) in PV-electrolysis can eliminate the need for product purification and separation which can be challenging and costly.[94]

The intermittent nature of solar energy remains a challenge to its utilisation. In order to minimise the risk factor and provide uninterrupted and reliable fuel production, round-the-clock fuel production photocatalysts and systems are desirable.[95] For example, an integrated photoelectrochemical-electrolysis system that performs photoelectrochemical reactions under sunlight irradiation and utilises renewable electricity, such as generated by wind or hydropower, to drive electrolysis at night

has also been proposed recently.[96]

Industrialisation of solar fuels is a critical and revolutionary step toward a sustainable energy system. While the materials and device architecture for artificial photosynthetic systems can still be improved in terms of light utilisation and energy conversion efficiency, such improvements are also possible through considered engineering design to integrate complementary technologies. Global adoption of solar-powered sustainable processes is dependent on multidisciplinary collaboration between scientists, engineers, and industry to establish the feasibility and design of such systems.

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**Competing interests**

The authors declare no competing interests.

**Table 1 | Theoretical limits of solar energy conversion efficiency.** The limiting efficiencies for these solar-driven processes are based on thermodynamic considerations, assuming no losses during the current-chemical conversion ($\eta_{chem} = \eta_{elec}$).

| | | $\eta$ (1 sun) (%) | $\eta$ (concentrated) (%) |
|---|---|---|---|
| PV-electrolysis<br>Photoelectrochemistry<br>Photocatalysis | Single light absorber[a]<br>(without thermalisation losses) | ~67 | ~86 |
| | Single light absorber[b]<br>(with thermalisation losses) | ~30 | ~40 |
| | Dual light absorbers[c]<br>(with thermalisation losses) | ~42 | –[k] |
| | Infinite tandem[d] | ~67 | ~86 |
| | Single light absorber<br>(with up-conversion)[e] | ~43 | –[k] |
| | Single light absorber<br>(with down-conversion)[f] | ~40 | –[k] |
| | Single light absorber<br>(with combined up- and down-conversion)[g] | ~45 | –[k] |
| Two-step solar thermochemical cycles[h] | | –[j] | ~20–40 |
| Thermoelectric generator[i] | | ~5 | –[k] |

[a] Assumptions: (1) Only radiative recombination takes place (no leak and accumulation of electrons and holes); (2) No thermalisation losses; (3) Rate of generation is at maximum; (4) No losses due to electrode polarisation and overpotential; (5) Device operating temperature is 300 K (concentrated sunlight: 45900 suns). Data were obtained from refs. 6, 11.
[b] No losses due to electrode polarisation and overvoltage. Device operating temperature is 300 K (concentrated sunlight: 45900). Data were obtained from refs. 11.
[c] No losses due to electrode polarisation and overvoltage. Device operating temperature is 300 K (concentrated sunlight: 45900 suns). The bandgaps of the light absorbers are 1.0 and 1.9 eV, respectively. Data were obtained from ref. 11.
[d] No losses due to electrode polarisation and overvoltage. Device operating temperature is 300 K (concentrated sunlight: 45900 suns). Data were obtained from refs. 6, 11.
[e] Bandgap is 1.76 eV. Device operating temperature is 300 K. Data were obtained from refs. 28.
[f] Bandgap is ~1.0 eV. Device operating temperature is 300 K. Data were obtained from refs. 28, 29.
[g] Bandgap is 0.9–1.4 eV. Device operating temperature is 300 K. Data were obtained from ref. 28.
[h] Two-step solar thermochemical cycles with $MO_{red}/MO_{ox}$ (M=Zn, Ce, Fe). For $CO_2 \rightarrow CO + \frac{1}{2}O_2$ and water splitting using $CeO/CeO_{2-\delta}$, the reduction and oxidation temperatures are 1805.4 and 1000 K, respectively. For $CO_2 \rightarrow CO + \frac{1}{2}O_2$ using Zn/ZnO and $FeO/Fe_3O_4$, the reduction and oxidation temperatures are 2000 and 298 K, respectively. Data were obtained from refs. 60, 61.
[i] Data were obtained from refs. 87, 97. The cold and hot side temperatures are ~293 and ~470 K, respectively.
[j] "–" indicates "Not applicable".
[k] "–" indicates "Lack of available data".

**Figure 1 | Solar energy conversion technologies. a-c**, Schematic representation of particulate photocatalysis (**a**), photoelectrochemistry (**b**), and photovoltaic-powered electrolysis (**c**) for solar-to-chemical conversion. **d-f**, Schematic illustrations of complementary conversion technologies that can take advantage of the IR component of the solar spectrum, including solar-powered thermocatalysis

(**d**), a solar-driven thermoelectric/pyroelectric generator (**e**) and a solar vapour generator (**f**). UV, Vis, IR represent ultraviolet, visible, and infrared light, respectively.

**Figure 2 | Solar-to-hydrogen conversion efficiencies ($\eta_{H_2}$) for selected water splitting systems.** The triangles, squares, and circles indicate particulate photocatalytic systems (PC), bias-free photoelectrochemical cells (PEC), and photovoltaic-powered electrochemical cells (PV-electrolysis), respectively under 1 sun irradiation. The absorption edge of the device was determined by the light receiver with smaller bandgap. The AM1.5G solar spectrum is based on the ASTM G173-03 reference spectrum, and the cumulative energy content as a function wavelength are shown in the grey and blue curves, respectively, for comparison. Data were obtained from ref. 4 ($SrTiO_3$:Al), ref. 5 ($BiVO_4$:Mo-$SrTiO_3$:La,Rh sheet), ref. 14 ($BiVO_4$:Mo-CIGS), ref. 13 ($BiVO_4$:Mo-$Cu_2O$), ref. 98 ($Ta_3N_5$-$CuInSe_2$), ref. 15 (GaInP-GaInAs), ref. 99 (Perovskite-NiFe), and ref. 100 (*multi* Si-Ni).

**Figure 3 | Light management for hybrid systems. a,** The utilisation of a beam splitter to separate incident sunlight and direct each band to the most efficient convertor. **b,** A photoelectrochemical system using a photoanode with a light-trapping layer on its back to recycle short-wavelength photons. The yellow, blue, and red arrows represent incident light, short-wavelength photons, and long-wavelength photons, respectively. UV, Vis, NIR, IR represent ultraviolet, visible, near-infrared and infrared light, respectively.

**Figure 4 | Photon wavelength manipulation using up- and down-conversion for photo(electro)chemical systems. a-b**, Schematic illustrations of photocatalysts combined with a downconverter (**a**) and downshifter (**b**). **c**, Illustration showing the expected effect of light adaptation on the performance of a bias-free photoelectrochemical system. $J_{op}$: operating current density. $V_{op}$:

operating potential. The current density–voltage (J-V) curves of photoanode and photocathode are represented in pink and blue, respectively. The dotted, dashed and solid curves represent ideal J-V behaviour, real J-V performance and predicted J-V performance with light adaption, respectively. **d-e**, Schematic illustrations of upconversion mechanisms for photocatalysts combined with Ln-doped upconverter (**d**) and triplet-triplet annihilation upconverter (**e**). $E_1$, $E_2$, and $E_3$ are excited states, and $S_1$, and $T_1$ are excited singlet states and triplet states, respectively. Ln represents lanthanide. UV, NIR represent ultraviolet and near-infrared light, respectively.

**Figure 5 | Solar concentrator and thermal related approaches. a**, Schematic illustration of a tracking-integrated concentrating system for a photoelectrochemical device. **b-e**, Illustration showing solar-powered two-step thermochemical fuel synthesis (**b**), thermally accelerated photocatalysis (**c**), thermally-assisted photoelectrochemical fuel synthesis (**d**) and solar fuel synthesis using thermoelectric-assisted photoelectrochemical processes (**e**). NIR represents near-infrared light.

**Figure 6 | Systems combining solar thermal approaches and photo(electro)chemical processes. a**, An integrated system consisting of a photoelectrochemical cell, a solar concentrator and a thermoelectric generator with thermal management. **b**, The utilisation of water vapour and waste $CO_2$ feedstocks provided by a solar vapour generator and a factory, respectively, for artificial photosynthetic systems.

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