Solar-Driven Hydrogen Production: Recent Advances, Challenges, and Future Perspectives

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ABSTRACT: Solar H2 production is considered as a potentially promising way to utilize solar energy and tackle climate change stemming from the combustion of fossil fuels. Photocatalytic, photoelectrochemical, photovoltaic−electrochemical, solar thermochemical, photothermal catalytic, and photobiological technologies are the most intensively studied routes for solar H2 production. In this Focus Review, we provide a comprehensive review of these technologies. After a brief introduction of the principles and mechanisms of these technologies, the recent achievements in solar H2 production are summarized, with a particular focus on the high solar-to-H2 (STH) conversion efficiency achieved by each route. We then comparatively analyze and evaluate these technologies based on the metrics of STH efficiency, durability, economic viability, and environmental sustainability, aiming to assess the commercial feasibility of these solar technologies compared with current industrial H2 production processes. Finally, the challenges and prospects of future research on solar H2 production technologies are presented.

Global warming, which is primarily caused by CO2 emission from the burning of fossil fuels (coal, oil, and natural gas), is expected to have potentially devastating consequences for planet Earth.1 The reduction of CO2 emission and the search for clean and sustainable alternatives to fossil fuels are thus becoming extremely urgent, especially under the recent very ambitious international climate policies toward the phase-down of the use of coal. Hydrogen (H2), a versatile energy carrier, is considered as one of the most promising sources of clean energy to tackle many energy challenges and has recently received unprecedented attention worldwide, due to its extremely high gravimetric energy density (i.e., a low heating value of ∼120 MJ kg−1), near-zero greenhouse gas emissions property, and capability to be used for existing industrial infrastructure or power plants powered by fossil fuels.1,2 Many countries launched projects and policies to foster the deployment and use of H2 technologies across a variety of sectors. For example, Japan established “Basic Hydrogen Strategy” in 2017 and renewed the existing “Strategic Roadmap for Hydrogen and Fuel Cells” in 2019 to develop a wide range of H2 applications including fuel cell vehicles, residential fuel cells, large power generation turbines, and steelmaking, moving forward to the realization of a hydrogen-based society.1,4 The European Commission published “A hydrogen strategy for a climate-neutral Europe” in 2020, aiming to accelerate widespread H2 use and achieve a carbon-neutral European Union.5 However, currently, more than 90% of the world’s H2 is produced from fossil fuels through steam methane reforming, methane partial oxidation, and coal gasification processes, leading to the emissions of around 830 million tons of CO2 per year, which accounts for over 2% of global annual CO2 emissions.6,7 Accordingly, the potential contribution of H2 fuels that are produced from conventional fossil-fuel-based routes to mitigating global warming is negligible or even negative. It is thus highly essential to develop efficient pathways for H2 production with low or net-zero carbon emissions.

The carbon emissions of H2 production through current routes can be divided into two parts. The first part comes from the reactions: all the carbon in methane or coal is eventually converted into CO2 when reacting with water or oxygen to produce H2. The second part is mainly associated with the combustion of methane or coal to provide high temperatures and energy needed for the reactions. To achieve low-carbon H2 production, the carbon footprint of these two parts should be considered together. One solution is to replace methane and...
coal with zero-carbon feedstocks such as water to produce H₂. Another solution is to develop innovative systems that are able to use renewable energy as an energy input to drive the reactions for producing H₂ in eco-friendly manners. Solar energy, the most abundant and renewable energy, is the most promising energy source for sustainable H₂ production in terms of its abundance and the potential for energy production. 6–14 In the past 5 decades, various solar-driven H₂ production technologies have been greatly developed, and the number of annual research papers on solar-driven H₂ production has grown rapidly since 2005, as shown in Figure 1. Tremendous progress has been made in accelerating the application and deployment of solar H₂ production by addressing the issues of performance, durability, and system costs. 12,15–19

The current solar-driven H₂ production technologies can be generally classified into photocatalytic (PC) water splitting, photoelectrochemical (PEC) water splitting, photovoltaic—electrochemical (PV-EC) water splitting, solar thermochemical (STC) water splitting, photothermal catalytic (PTC) H₂ production from fossil fuels (mainly CH₄), and photobiological (PB) H₂ production (as shown in Figure 2). 10,12,16,20,21

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Figure 1. Number of publications searched by the words (Solar® or Photo® or Sunlight® or Light®) and (Hydrogen or H₂) and (Production® or Generation® or Evolution®) in their titles. Inset is the contribution ratios of published records from different countries/regions. The data were collected from Web of Science Core Collection on November 11, 2021.

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Therefore, in this Focus Review, we will comprehensively review technologies toward solar-driven H₂ production. First, we briefly introduce the above six routes to H₂ production utilizing solar energy. Recent progress in solar-driven H₂ production is then summarized, highlighting the state-of-the-art systems for each route. Subsequently, a comprehensive evaluation and comparison of these six routes will be presented on the basis of solar energy conversion efficiency, durability, cost, and environmental impacts. Finally, according to the statistical analysis, we attempt to estimate and elucidate the challenges and perspectives on future research directions of solar H₂ production. We anticipate that this Focus Review could contribute to the development of a low-carbon society through the application of solar H₂ production in the future.

### Approaches to Solar H₂ Production

#### PC Water Splitting

PC water splitting is a process that utilizes only light and a particulate semiconductor to split water into H₂ and O₂ under mild conditions (eq 1). Many reviews have provided a thorough overview of the fundamentals of PC water splitting. 13,14,24,25

\[
\text{H}_2\text{O} + \nu \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2, \quad \Delta G^0_{\text{f}(298 \text{ K})} = +273 \text{ kJ mol}^{-1}
\]

(1)

As shown in Figure 2a, briefly, when a semiconductor absorbs photons with energy exceeding the bandgap, electrons and holes are generated and then diffuse to the semiconductor surface to respectively drive reduction and oxidation reactions, i.e., the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) (Figure 2a, left). Because of thermodynamic constraints, a semiconductor photocatalyst that has the ability to trigger water splitting reaction must have a conduction band minimum (CBM) with potential energy less than that of the HER (H⁺/H₂, 0 V versus normal hydrogen electrode (NHE) at pH 0) and a valence band maximum (VBM) with potential energy higher than that of the OER (O₂/H₂O, +1.23 V versus NHE at pH 0). In addition, to ensure the durability of the photocatalyst in the reaction, the reductive and oxidative decomposition of the semiconductor should be less than and higher than the H⁺/H₂ and O₂/H₂O potentials, respectively. These requirements immensely restrict the selection of suitable semiconductors that are active for PC water splitting. To overcome these constraints, inspired by natural photosynthesis, the Z-scheme system was developed, in which two types of semiconductor photocatalysts are combined so that H₂ and O₂ are produced separately on their respective semiconductors (Figure 2a, right). In this case, although semiconductors cannot produce H₂ and O₂ simultaneously, as long as they are able to produce either H₂ or O₂ from water, they can be employed in this system, especially with the assistance of redox mediators. Therefore, Z-scheme systems undoubtedly expand the choice of semiconducting materials. In terms of kinetics, co-catalysts are generally indispensable components in photocatalysts which can act as catalytically active sites to facilitate the HER and OER, thus lowering the kinetic overpotentials of water splitting.

#### PEC Water Splitting

A typical PEC cell consists of either an n-type semiconductor-based photoanode for OER or a p-type semiconductor-based photocathode for HER and the counter electrode for the other half-reaction. 15,26–28 Analogous to the Z-scheme, it is not necessary for the CBM and VBM of the photoanode and photocathode to simultaneously straddle the O₂/H₂O and H⁺/H₂ potentials, as long as the CBM/VBM of photocathode/photoanode is less than/higher than the water reduction/oxidation potential, since an external bias is generally applied to promote the redox reactions. Taking a photoanode-based PEC cell as an example (Figure 2b, left), upon light irradiation, electrons and holes are generated in the photoanode. Electrons are transferred to the counter electrode through the...
external circuit to drive the HER, while the holes migrate to the photoanode surface where they drive the OER. Coupling a photoanode and a photocathode into a PEC system to construct a tandem cell has a potential of reducing the applied bias or even eliminating it to achieve spontaneous PEC water splitting (Figure 2b, right).

**PV-EC Water Splitting.** By definition, the PV-EC system is made up of two separate parts: the PV cell and the electrolyzer (Figure 2c). The PV cell is utilized to absorb solar energy for generating electricity that can be directly transferred to the EC cell to split water into H$_2$ and O$_2$ separately at the cathode and anode. The PV cell is commonly wired to the cathode and anode but is completely out of the water electrolyte, thus preventing corrosion caused by water. Both PV cells and water electrolysis are technically mature and have already been commercialized, which is the main advantage of PV-EC water splitting compared with PC and PEC water splitting. The efficiencies for commercial PV cells and electrolyzers are >18% and in the range of 60–83%, respectively, and thus a high solar-to-H$_2$ efficiency larger than 10% is easily accessible.$^{10,28,30}$

**STC Water Splitting Cycles.** STC water splitting cycles technology transforms concentrated solar energy into thermal energy to split water into H$_2$ and O$_2$ at high temperatures through a series of successive chemical reactions.$^{17}$ In general, STC cycles include two main categories: two-step processes and multi-step processes.$^{17,22,31}$ Two-step cycles enable easier operation processes for scale implementation but need high temperatures (1300–1800 °C) to become thermodynamically favorable. By contrast, multi-step cycles achieve better performances at relatively low temperatures (<1000 °C) but at the expense of increased system complexity.$^{17}$ Figure 2d shows the typical chemical reaction process of two-step cycles based on metal oxides. In the first step, exothermic reduction of the metal oxide allows the formation of activated (reduced) metal oxide and O$_2$ at high temperatures (eq 2). The activated metal oxide easily strips O atoms from water in the second water-splitting step at relatively low temperatures, accompanied by the production of H$_2$ (eq 3). This overall cycling process leads to the release of only H$_2$ and O$_2$ (eq 4), with solar energy and water being the process inputs. The metal oxide can be repeatedly recycled in the cycling system. In addition, because H$_2$ and O$_2$ are produced in different steps, the generated H$_2$ is readily collected with high purity, thus removing the demand for high-temperature gas separation.

Reduction (endothermic): $\text{MO}_x \rightarrow \text{MO}_{x-1} + \frac{1}{2}\text{O}_2$  

(2)
Oxidation (exothermic): \[ \text{MO}_{x-1} + \text{H}_2\text{O} \rightarrow \text{MO}_x + \text{H}_2 \] (3)

Net water splitting: \[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \] (4)

**PTC H₂ Production from Fossil Fuels.** The PTC reaction is primarily based on plasmonic metal nanostructures and/or semiconductors catalysts.²⁸⁻³² As shown in Figure 2e, upon light irradiation, energetic or hot carriers are generated from the excitation of localized surface plasmon resonance (LSPR) on metal nanostructures or from the excitation of semiconductor supports. These energetic carriers would either recombine to induce local heating through relaxation or interact with reactants adsorbed on the surface of catalysts through transferring their energy into surface-absorbed reactants. The induced local heating can heat catalysts to a certain temperature, and the interaction between energetic carriers and reactants at the metal/reactant interface is beneficial for activation of chemical bonds, both of which can synergistically accelerate surface catalytic chemical reactions, with an activity higher than that of purely thermocatalytic reactions. In addition, considering that the energy exchange between metal nanostructures and reactant molecules preferentially takes place when the orbitals (electronic states) of reactants and/or intermediates match well with those of plasmonic nanometals, only specific chemical bonds of reactants and/or intermediates can be excited, potentially leading to distinctive product selectivity that cannot be realized in thermocatalytic processes.³⁵ Thanks to the simultaneous utilization of both the thermal and light characteristics of sunlight, photothermal catalysis is very attractive for chemical transformations, including steam reforming of methane (SRM, eq 5), dry reforming of methane (DRM, eq 6), and water–gas shift reactions (WGS, eq 7) for H₂ production.

SRM: \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}, \]
\[ \Delta G_{(298 \text{K})}^0 = +142 \text{ kJ mol}^{-1} \] (5)

WGS: \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2, \]
\[ \Delta G_{(298 \text{K})}^0 = -28 \text{ kJ mol}^{-1} \] (6)

DRM: \[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}, \]
\[ \Delta G_{(298 \text{K})}^0 = +171 \text{ kJ mol}^{-1} \] (7)

**PB H₂ Production from Water and Biomass.** PB H₂ production is an environment-friendly technology that uses microorganisms to transform solar energy into H₂ from water and biomass such as glycogen and starch (Figure 2f).¹⁹⁻²¹,³⁷,³⁸ It simply includes two categories: (1) biophotolysis and (2) photofermentation. Biophotolysis uses a green-algae-based photosynthesis system for directly splitting water into H₂ and O₂. In this process, photosystem II (PSII) absorbs photons to oxidize water into O₂ and protons (eq 8) as well as to reduce the plastocyanine pool, and then the electrons are transferred to photosystem I (PSI), resulting in highly reduced ferredoxin (Fd) driven by light (eq 9). The reduced Fd acts as an electron carrier for the generation of H₂ from protons, catalyzed by hydrogenases (eq 10).

\[ 2\text{H}_2\text{O} + 4\hbar \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-, \]
\[ \text{PSII}, \quad E_0^{\prime} = +0.82 \text{ V} \] (8)

\[ \text{plastoquinol (PSII)} \rightarrow \text{Fd (PSI)} \] (9)

\[ 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 + \frac{1}{2}\text{O}_2, \]
\[ \text{hydrogenase}, \quad E_0^{\prime} = -0.41 \text{ V} \] (10)

In addition to the above direct route, biohydrogen can be produced via an indirect route, starting with the production of carbohydrates and O₂ from water and CO₂ by photosynthesis, followed by the fermentation of carbohydrates to produce CO₂ and H₂. Direct biophotocatalysis has more advantages since the process is more facile and no organic carbon substrate is needed for the growth media, with water as the hydrogen source and no greenhouse gases emission. The photofermentation process utilizes sunlight as the energy input for converting organic substrates into H₂ by photosynthetic bacteria or purple non-sulphur bacteria, which is compelling for removing environmental pollutants and industrial organic wastes, along with the generation of renewable H₂ (eq 11).³⁵,³⁷

\[ \text{C}_6\text{H}_4\text{O}_2 + 10\text{H}_2\text{O} + h\nu \rightarrow 12\text{H}_2 + 6\text{CO}_2 \] (11)

**PERFORMANCE METRICS FOR DIFFERENT SOLAR H₂ PRODUCTION APPROACHES**

As solar H₂ production can be realized by the different approaches described above, several metrics have been utilized to characterize their performance for H₂ production, including production rate, solar-to-H₂ (STH) conversion efficiency, and apparent quantum efficiency (AQE).³⁹ Considering that H₂ production is considerably dependent on experimental setups and reaction conditions (e.g., temperature, light intensity, and catalyst amount), STH, determined by the irradiation of simulated AM 1.5G sunlight at near room temperature, is the most standard and reliable metric that can be used to reasonably compare and assess the performance from different research works under proper measurements. Theoretically, STH efficiency is applicable to the processes using only water as the H₂ source, while for the PTC process, where H₂ is produced from fossil fuels/biomass and/or water under high temperatures with the formation of other valuable fuels such as CO, solar-to-fuel (STF) conversion efficiency is more appropriate to evaluate the efficiency of solar energy conversion.³⁸,³⁹ It is noted that both STH and STF efficiencies are only available in thermodynamically uphill reactions, i.e., with the Gibbs free energy of reactions (\(\Delta G > 0\)) in overall. In general, PC water splitting, AQE is an important parameter to evaluate and compare the performance of photocatalysts under monochromatic light irradiation. Similar to AQE, incident (or absorbed) photon-to-current efficiency (IPCE or APCE) is used to determine the contribution of a certain wavelength of light to photocurrent in a PEC water splitting system.⁴⁰ What’s more, applied-bias photon-to-current efficiency (ABPCE) is also an important criterion to describe the activity of PEC system.⁴⁰ The definition of these efficiencies can be found in other reviews.³⁵,⁴⁰⁻⁴² In addition to activity, durability is another key metric in assessing the performance for solar H₂ production. Long-term stability is an essential prerequisite for large-scale practical implementation of solar H₂ production.
H₂ Production from Overall PC Water Splitting. Since the pioneering work on electrochemical photolysis of water into hydrogen and oxygen on a TiO₂ photoanode was reported by Fujishima and Honda in 1972, extensive research efforts have been made worldwide to develop efficient particulate photocatalysts for PC water splitting in the past 5 decades. These photocatalysts include oxides (Inₓ₋₀.₅NiₓTaO₅, NaN₂Ta₅O₁₄, SrTiO₃:Al), oxynitrides (GaN:ZnO, TaON, Ta₃N₅), oxysulfides (Y₂Ti₂O₅S₂), and metal-free semiconductors such as carbon nitride (C₃N₄). Numerous effective strategies such as doping, solid solutions, and co-catalyst loading have been explored to modify photocatalysts to increase visible light absorption, improve photogenerated charge separation, and thus promote H₂ and O₂ evolution rates. The historical progress in PC water splitting, including the development of photocatalysts and the exploration of strategies to enhance PC performances, has been comprehensively summarized in several excellent reviews. Here, we mainly focus on the representative PC materials and systems with outstanding performance reported in the past few years.

Domen’s group recently found that Al-doped SrTiO₃ (SrTiO₃:Al) is an excellent UV-light-responsive photocatalyst for PC water splitting. Using Rh/Cr₂O₃ and CoOOH-loaded SrTiO₃:Al as a photocatalyst, they showed an external quantum efficiency of approximately 96% at 350–360 nm for overall water splitting and an STH efficiency of 0.65% under simulated sunlight illumination, with the evolution of H₂ and O₂ in a 2:1 stoichiometric ratio. The key to achieving such a high AQE lies in the selective photodeposition of Rh/Cr₂O₃ and CoOOH co-catalysts for H₂ and O₂ production reactions on the facets of SrTiO₃:Al, leading to anisotropic charge transport with minimal charge recombination and thus an AQE of almost unity. In contrast, the random dispersion of Rh/Cr₂O₃ and CoOOH on SrTiO₃:Al using an impregnation method resulted in an AQE of only about 50% at 365 nm. Meanwhile, the impregnation method can enable mass production of modified photocatalysts with higher stability (over 1600 h) compared with photo-deposition. In spite of the high AQE in the UV region, the intrinsic property of SrTiO₃:Al that only absorbs UV light limits its maximum STH efficiency to no more than 2%. It is essential to develop visible-light-responsive photocatalysts because visible light accounts for ∼50% of solar energy. C₃N₄, as a metal-free polymeric semiconductor, absorbs light with wavelengths up to 460 nm with appropriate band structure for overall PC water splitting. Wang et al. reported that C₃N₄ coupled with LaOCl can photocatalytically split pure water into H₂ and O₂ in a stoichiometric ratio of 2:1 with an AQE of 0.35% at 400 nm (Figure 3a–c). In addition, C₃N₄ modified with carbon dots was reported to show a stepwise two-step pathway for PC water splitting; i.e., H₂O is first transformed into H₂ and H₂O₂ over C₃N₄, and then the formed H₂O₂ decomposes into H₂O and O₂ over carbon dots, thus generating a remarkable STH efficiency of 2.0% with high durability of over 200 days (Figure 3d–f). Pt nanoparticles (NPs) and Ru complex co-modified Cds was able to catalyze water into H₂ and O₂ under visible light (460 ± 50 nm) irradiation, although the molar ratio of H₂ to O₂ (∼20:1) was much lower than the stoichiometric value of 2 due to the occurrence of photocorrosion. With much narrow bandgaps, Ta₅N₃ (2.1 eV) and Y₂Ti₂O₅S₂ (1.9 eV) loading as appropriate co-catalysts were demonstrated to be active for overall PC water splitting with stoichiometric amounts of H₂ and O₂ in a wide range of wavelengths up to 600 nm and thus represent promising photocatalysts for future solar H₂ production, despite their current low STH values (<0.02%).

In order to obtain higher STH efficiency, two kinds of photocatalysts that produce H₂ and O₂ separately can be integrated together to form a Z-scheme system. Wang and Domen et al. designed a Z-scheme system in which H₂ evolution photocatalyst Ru/Cr₂O₃ loaded SrTiO₃:La,Rh and O₂ evolution photocatalyst BiVO₄:Mo were embedded on a conductive Au layer. By annealing the photocatalyst sheet at 300 °C for 20 min to enhance the electric contact of each component and to facilitate the charge transfer, and further by modifying the Ru co-
Table 1. Performance of Representative PC Water Splitting Systems

| Photocatalyst          | Co-Catalyst | Absorption Edge, nm | Efficiency, % | Durability, h (Lifetime, %) | Ref. |
|------------------------|-------------|---------------------|---------------|-----------------------------|------|
| Al-doped SrTiO3 (SrTiO3:Al) | Rh/CrO3, CoOOH (photodeposition) | 390 | AQE = 96 at 350–360 nm, STH = 0.65 | 12.5 (94) | 45 |
| Al-doped SrTiO3 (SrTiO3:Al) | Rh/CrO3, CoOOH (impregnation) | 390 | STH = 0.51 | 1600 (~80) | 46 |
| C2N4/LaOCl             | Pt, CoO2    | 430 | AQE = 0.35 at 400 nm | 20 (~100) | 47 |
| C2N4                  | carbon dots | 450 | AQE = 16 at 420 nm, STH = 2.0 | 4800 (~98) | 48 |
| Ta2N4/KTaO3            | Ru/CrO3     | 600 | AQE = 0.024 at 500 nm, STH = 0.014 | 15 (~86) | 50 |
| Y2Ti2O5S3              | Ru/CrO3, IrO2 | 650 | AQE = 0.05 at 600 nm, STH = 0.007 | 20 (~81) | 51 |
| SrTiO3La/Rh/C/BiVO4:Mo | Ru/CrO3     | 520 | AQE = 26 at 419 nm, STH = 1.2 | – | 53 |
| aza-CMP/C2N            | Pt, Co(OH)2 | 610 | AQE = 4.3 at 600 nm, STH = 0.73 | 32 (~88) | 54 |
| B-doped, N-deficient C2N | Pt, Co(OH)2 | 500 | AQE = 11.76 at 420 nm, STH = 1.16 | 24 (~90) | 55 |

catalyst with Cr2O3 to suppress the reverse reactions of H2 oxidation and O2 reduction, a high AQE of 33% at 419 nm and an STH efficiency of 1.1% were obtained. To replace the expensive Au layer and improve water splitting activity at ambient pressure, the authors further used a conductive carbon film for electron transfer and achieved an STH of 1.0% at 58°C and 91 kPa in pure water (pH 6.8) (Figure 3g,h).53 Xu et al. developed a van der Waals heterostructures-based metal-free Z-scheme by coupling C2N (H2-evolving photocatalyst), aza-CMP (O2-evolving photocatalyst), and reduced graphene oxides (electron mediator) and obtained an STH efficiency of 0.73%.54 In addition, Shen et al. constructed a B-doped, N-deficient, C2N4-based Z-scheme for efficient overall PC water splitting.55 By tuning the levels of B dopants and N defects to promote charge separation, an optimal STH efficiency can amount to 1.16%.

Table 1 shows the performances of the representative PC water splitting systems. Although the AQE is up to nearly ~100% in the UV regions (350 nm < λ < 360 nm), the AQE at wavelengths longer than 420 nm is unanimously low (<30%). The resulting maximum STH efficiencies are in the range of 1–2%, and the initial activities generally decay with long-term continuous light, both of which remain still far away from the desired performance (10% STH efficiency with a lifetime of 10 years). Therefore, more efforts and research are needed to further improve both the STH efficiency and the durability of PC water splitting systems by the design and development of efficient photocatalysts, especially for visible-light-responsive photocatalysts.

H2 Production from PEC Water Splitting. Photoanodes. Until now, BiVO4 has been demonstrated to be the best metal-oxides-based photoanode.27 Choi showed that a nanoporous BiVO4 photoanode loaded with FeOOH/CoOOH co-catalysts allowed a photocurrent density of ~4.5 mA cm−2 at 1.23 V versus the reversible hydrogen electrode (VREHE) and an ABPC of ~1.72% at 0.6 VREHE.28 Wang et al. constructed a dual BiVO4 photoanode with enriched oxygen vacancies by an electrodeposition method with a subsequent thermal treatment process.29 After deposition of FeOOH/CoOOH co-catalysts, a high and stable photocurrent density of ~5.9 mA cm−2 at 1.23 VREHE and an ABPC of 2.2% at 0.7 VREHE were obtained under simulated sunlight irradiation. Because of the narrow bandgap (2.1 eV), hematite (Fe2O3) is also a promising material for photoanodes, with a theoretical STH efficiency of up to 15%.27 A benchmark photocurrent density of ~4.5 mA cm−2 at 1.23 VREHE was achieved by Kim et al. through a series of modifications including Ti doping, H2 treatment, and NiFeO2 co-catalyst loading.30 Ta2N5, with a bandgap similar to that of Fe2O3, is also an excellent candidate for photoanode material. Li et al. discovered that a Ta2N5 photoanode integrated with Ni(OH)/ferrhydrite and a TiO2 blocking layer showed a record photocurrent of up to 12.1 mA cm−2 at 1.23 VREHE, close to its theoretical limit of 12.9 mA cm−2.31 PV-grade semiconductors made up of Si, In, Ge, As, P, etc. can also be employed for photoanodes with remarkable performance, although protection layers are generally required to prevent corrosion.32 For instance, Lewis et al. introduced an interfacial CoO2 layer (2 nm) between a protective NiO2 layer and SiO2/n-Si, delivering a record photocurrent of 27.7 mA cm−2 at 1.23 VREHE over more than 1700 h of continuous illumination.33

Photocathodes. The choice of semiconductor materials for photocathodes is relatively limited compared with the choice for photoanodes because of the need for p-type semiconductors. Cu2O, with a bandgap of 2.0 eV, is the most widely reported metal-oxide-based photocathode, albeit with modest performances and relatively poor long-term stability. Luo et al. designed a Cu2O/Ga2O3 photocathode modified with a TiO2 protection layer and a NiMo co-catalyst that allowed a photocurrent of ~10 mA cm−2 at 0 VREHE, representing the best oxide-based photocathode for water splitting.34 PV-grade semiconductor materials like Si and III–V semiconductors (GaNP, InP, etc.) as photocathodes exhibited the best performances in PEC water splitting, with photocurrents ranging from 10 to 35 mA cm−2.35 Ji et al. reported that epitaxial SrTiO3/P-Si(001) heterojunction photocathodes loaded with Ti/Pt nanostructured catalysts exhibited a stable photocurrent of 35 mA cm−2 at 0 VREHE over 35 h, thanks to the efficient transfer of photoexcited electrons resulting from the conduction band alignment and lattice match between Si and the productive SrTiO3 layer.6 In addition to oxides-based photocathodes, Tang et al. recently found that an n-type C2N4 can be transformed into a photocathode via the introduction of N-defects and C-OH terminal groups as the electron trap states, showing a negative photocurrent of ~10 μA cm−2 at 0 VREHE.62 In spite of the low performance, their work demonstrates that the metal-free g-C2N4 can be used as not only a photoanode but also a photocathode through reasonable modification.

Unassisted PEC Water Splitting. The single light-absorber-based photoanodes or photocathodes discussed above for PEC water splitting inevitably require external electric energy. In contrast, unassisted PEC water splitting, powered only by solar energy, is more attractive for practical applications and generally includes two systems: (1) a photoelectrode–photovoltaic (PEC-PV) tandem cell and (2) a photoanode–photocathode (PEC) tandem cell. Obviously, two light absorbers are coupled in series to construct the tandem cells, wherein the front absorbers with a large bandgap absorb high-energy photons of incident light while the low-energy photons transmitted from...
the front absorbers are absorbed by the rear absorbers with a narrow bandgap. Sunlight can be used maximally in tandem cells, thus theoretically giving a high STH efficiency. In this case, balancing the sunlight absorption and efficiency of these two absorbers is of importance to optimize the tandem configuration. Currently, the obtained highest STH efficiency values (AM 1.5G) for PEC-PV and PEC tandem cells are 19.3% and 13.1%, respectively, using III−V semiconductors (GaAs, GaInP, etc.) as the light absorbers.63,64 Despite the impressive efficiency, the cost, stability, and scalability of this classic semiconductors restrict their large-scale application. Alternatively, metal oxide semiconductors, being more stable, potentially cheaper, and easily fabricated light absorbers, are also excellent candidates in unassisted PEC water splitting.

In terms of PEC-PV tandem cells, because of the large overpotentials required for overcoming the sluggish kinetics of OER, a photoanode−PV system is the most favorable configuration. BiVO4, which exhibits the best performance in metal-oxides-based photoanodes, is thus widely used. Pihosh et al. demonstrated that the core−shell WO3/BiVO4 loaded with a CoPi nanostructured photoanode, coupled with a double-junction GaAs/InGaAsP PV cell, afforded a photocurrent of 6.56 mA cm−2 under 1 sun illumination, corresponding to an STH efficiency of 8.1% and representing the highest efficiency among the oxides-based PEC-PV tandem cells.65 However, the
costly III–V semiconductors, GaAs/InGaAsP, were still used for the PV cell. To reduce the cost of tandem cells, low-cost PV cells like perovskite solar cells (PSCs) and dye-sensitized solar cells (DSSCs) were chosen to integrate with oxide-based photocathodes. Park et al. introduced a hybrid optical layer (conductive distributed Bragg reflectors (cDBRs), ITO/TiO2/SiO2 layers) between a BiVO4/WO3 photoanode and a DSSC (dye/TiO2) to promote photon recycling and thus efficiently exploit the incident sunlight (Figure 4a–c). A record STH efficiency of 7.1% was obtained, with a high stability over 10 h. Wang et al. constructed unbiased water splitting cells by combining the dual BiVO4 photoanodes and a single-sealed PSC, generating an STH efficiency of 6.5% without an obvious decrease in 10 h of consecutive illumination (Figure 4d–f). Two kinds of photocathodes, Mo:BiVO4 and Ti:Fe2O3, and a Si solar cell were connected in sequence, and the incident sunlight was thus utilized efficiently, delivering an STH efficiency of 7.7% (Figure 4g–i). In addition to BiVO4, a BaSnO3 photocathode with well-tuned oxygen vacancies was coupled with a PSC to construct a tandem device, exhibiting an outstanding STH efficiency of 7.9% for 100 h. Fe2O3 has a narrow bandgap but shows a relatively high performance, although Fe2O3 and WO3 are also widely studied. Meanwhile, for the photocathode, both metal oxides and PV-grade non-oxides can be employed. Grätzel et al. designed an efficient unassisted PEC tandem cell, in which the front Mo:BiVO4 photocathode was connected with the rear RuO2/TiO2/Ga2O3/Cu2O photocathode. By balancing the light transmittance and PEC performance of the BiVO4 photoanode, a peak photocurrent of ∼2.5 mA cm−2 was obtained, corresponding to an STH efficiency of ∼3%. Domen et al. developed a Pt and CdS-modified CuIn2−xGaxSe2 (CIGS) photocathode for efficient PEC H2 production by tuning the band offsets at the CdS/CIGS interface. A stand-alone tandem PEC cell constructed by combining this photocathode with a BiVO4-based photoanode showed a 3.7% STH efficiency. Mi et al. designed double-band GaN:Mg/InGaN:Mg nanosheet structures grown on Si substrate that gave rise to a ∼3.3% of STH efficiency under concentrated simulated sunlight irradiation, thanks to the existence of a built-in electric field that leads to the precise control of charge carrier flow in the nanostructures. Very recently, Li et al. designed an efficient unassisted PEC tandem cell, consisting of a Co4O4/BiVO4-based photocathode with charge-transfer mediators (pGO and SnO2) and a Pt/organic semiconductor (PBDB-T:ITIC:PC71BM (PIP))-based photocathode with charge-transfer mediators (CuOx and TiO2) (Figure 4j–l). A high STH efficiency of 4.3% was generated thanks to the efficient charge separation and complementary light absorption.

Table 2 shows the performances of the representative PEC-PV tandem cells and PEC tandem cells. Clearly, the STH efficiencies of PEC-PV tandem cells are generally superior to those of PEC tandem cells, mainly because of the mismatch of light absorption and onset potentials of both photocathode and photodetector. The high-performance PEC tandem cells are necessarily composed of PV-grade photocathodes that require complicated multi-layers to guarantee satisfactory stability and efficient charge separation. The utilization of noble metals for (photo)anode/cathode in both of these tandem devices unavoidably limits their practical application, and low-cost alternatives need to be developed. In addition, the activity degradation is observed in most PEC systems after a long time of continuous irradiation, and it is important to further improve the long-term stability of tandem cells.

| Table 2. Performance of Representative Tandem Cells for Unassisted PEC Water Splitting |
|------------------|------------------|------------------|------------------|------------------|
| (photo)anode | (photo)cathode | PV electrolyte | STH, % (durability, h) |
|------------------|------------------|------------------|------------------|------------------|
| RuO2 | Rh/TiO2/AlInP/GaInP/GaInAs/GaAs | 0.5 M KH2PO4/KH2PO4 phosphate buffer (pH 7) | 19.3 (20 (83)) |
| WO3/BiVO4/with CoPi | Pt | GaAs/InGaAsP | potassium phosphate buffer solution (pH 7.0) | 8.1 (1 (100)) |
| FeOOH/NaOOH/BiVO4 | Pt | DSC | 0.1 M KH2PO4/KH2PO4 phosphate buffer (pH 6.9) | 7.1 (10 (100)) |
| FeOOH/NaOOH/BiVO4 | Pt | PSC | 1.0 M KBr (pH 9.5) | 6.5 (10 (100)) |
| Mo:BiVO4/Ti:Fe2O3 | Pt | Si | 1.0 M KCl (pH 9.2) | 7.7 (8 (100)) |
| FeOOH/NaOOH/BaSnO3 | Pt | PSC | 1.0 M KBr | 7.9 (100 (83)) |
| Co/Pt/SnO2/Fe2O3 | Pt | PSC | 1.0 M NaOH (pH 13.6) | 3.4 |
| IrO2 | Cu2O/AZO/TiO2/RuO2 | PSC | 0.5 M Na2S2O4 + 0.1 M KBr (pH 5.0) | 2.5 (6 (83)) |
| IrO2/n-GaAs | Pt/Ti/Pt/Au/p-GaAs | 0.5 M H3PO4 (pH 0.55) | 13.1 |
| NiFeO2/Bi:Mo:BiVO4 | RuO2/TiO2/Ga2O3/Cu2O | 0.2 M KBr (pH 9.0) | 3.0 (100 (83)) |
| NiFeO2/Bi:BiVO4 | Pt/CdS/Culn2−xGaxSe2 | 0.5 M K2BO3 + KOH (pH 9.5) | 3.7 (100 (83)) |
| Co3O4/pGO/BiVO4/SnO2 | Pt/TiO2/PI/Pt/CuO | 0.2 M potassium phosphate buffer (pH 7.0) | 4.3 (6 (83)) |

**PEC-Tandem Cells**

| (photo)anode | (photo)cathode | PV electrolyte | STH, % (durability, h) |
|------------------|------------------|------------------|------------------|------------------|
| IrO2/n-GaAs | Pt/Ti/Pt/Au/p-GaAs | 0.5 M H3PO4 (pH 0.55) | 13.1 |
| NiFeO2/Bi:Mo:BiVO4 | RuO2/TiO2/Ga2O3/Cu2O | 0.2 M KBr (pH 9.0) | 3.0 (100 (83)) |
| NiFeO2/Bi:BiVO4 | Pt/CdS/Culn2−xGaxSe2 | 0.5 M K2BO3 + KOH (pH 9.5) | 3.7 (100 (83)) |
| Co3O4/pGO/BiVO4/SnO2 | Pt/TiO2/PI/Pt/CuO | 0.2 M potassium phosphate buffer (pH 7.0) | 4.3 (6 (83)) |
**Figure 5.** (a) Schematic energy diagram and (b) current density versus time curve under simulated AM 1.5G illumination of PV-EC tandem cells consisting of a perovskite/Si solar cell and a TiC-Pt/NiFe LDH-based EC cell. Reprinted with permission from ref 80. Copyright 2019 Elsevier B.V. (c) Scheme and (d) current density versus time curve under simulated AM 1.5G illumination of PV-EC tandem cells consisting of a perovskite/Si solar cell and a NiMo/NiFe-based EC cell. Reprinted with permission from ref 81. Copyright 2021 Wiley. (e) Scheme and (f) STH efficiency versus time of a PV-EC system consisting of a three-junction solar cell and a two-series-connected PEM electrolyzer. Reprinted with permission from ref 83. Copyright 2016 Nature Publishing Group.

**H₂ Production from PV-EC Overall Water Splitting.** The overall performance of a PV-EC system is dependent on the performance of the independent PV and EC systems. For the PV system, at present, the commercially available solar cells include monocrystalline Si, multi-crystalline Si, Cu(In,Ga)(Se,S)₂ (CIGS), and CdTe modules, with record efficiencies of 22.4%, 18.5%, 17.5%, and 18.6%, respectively.30 Among these PV cells, Si-based modules with relatively low cost, high reliability, and stability (<10% loss in efficiency after 25 years) account for more than 90% of the total market share.30 Although there is still room for a few absolute percentages of efficiency improvement in commercial PV cells, the efficiencies of these single-junction solar cells are constrained by the Shockley–Queisser (S-Q) limit (33.7% for a semiconductor with a bandgap of 1.34 eV).30 Multi-junction solar cells have the potential to break the S-Q limit. A record efficiency of 38.8% was achieved by constructing a GaInAs/GaInP/GaAs/AlGaInAs/AlGaInP five-junction tandem configuration, but it was accompanied by substantial manufacturing costs.30 Recently, PSCs have received considerable attention and have been extensively investigated, with a record efficiency exceeding 25%, yet they commonly suffer from degradation caused by UV light or reactions with water, which is the biggest obstacle to commercial implementation.30

For EC systems, an alkaline electrolyzer is a currently mature technology and has been commercially used worldwide, with an efficiency of 59–70%.29,71 Alkaline electrolyzers require only inexpensive catalysts (Ni catalysts) as for HER and OER and exhibit high durability and high H₂ purity (99.9%), but they have some disadvantages, such as low current density, low operating pressure, and slow loading response when supplied by intermittent and fluctuating power.79 A polymer electrolyte membrane (PEM) electrolyzer is also a commercially available technology with an efficiency ranging from 65% to 83%.29,75 It can overcome the drawbacks plaguing the alkaline electrolyzer but is more expensive because of the utilization of a high-cost membrane and noble metals such as Pt, Ir, and Ru. In comparison with alkaline electrolyzers, PEM systems are more appropriate for connecting with PV systems owing to their flexibility. Further research efforts are required to develop active, stable, and low-cost catalysts for both HER and OER with low overpotentials for alkaline and PEM electrolysis, which is central to maximize the STH efficiency of PV-EC. There are numerous reports on noble-metal-free electrocatalysts for HER and OER with comparable or better activities compared to those of noble-metal catalysts.74–76 McCrory et al. developed a benchmarking protocol to evaluate and compare the performances of existing electrocatalysts by combining many measurements, ensuring the reliability of results.77

With regard to PV-EC systems, Ye et al. demonstrated an average STH efficiency of 16.9% by a crystalline Si solar-cell-driven water electrolysis device, in which Co- and Fe-doped WO₃,77 was used as the oxygen evolution anode with a rather low overpotential of 226 mV.80 Guided by DFT calculations, Hsu et al. developed a selective OER catalyst, Co₂[Fe(CN)₆], in seawater.79 Using NiMoS as cathode to construct an EC cell, this device, powered by a commercial InGaP/GaAs/Ge three-junction solar cell, gave an STH efficiency of 17.9% with excellent stability over 100 h. Luo et al. reported a low-cost perovskite/Si tandem solar cell to power an alkaline EC cell, which consisted of the TiC-supported Pt nanoclusters for HER with performance comparable to that of Pt/C and the benchmark OER catalyst NiFe-LDH, with the STH efficiency reaching 18.7% (Figure 5a,b).80 Wang et al. replaced the Pt cathode with a NiMo-based catalyst and obtained a remarkable STH efficiency of ~20% by combining with a NiFe OER electrode, with the assistance of a high-performance perovskite/Si tandem cell (Figure 5c,d).81 The above efficiencies were all obtained under 1 sun illumination. Concentrated sunlight illumination can lead to substantially improved efficiencies of PV cells, thus improving the overall efficiencies of PV-EC systems. Bonke et al. utilized concentrated sunlight (~100 sun) by a GaInP/GaAs/Ge multi-junction solar cell to split water...
with an electrolyzer based on Ni foam, exhibiting an STH efficiency of 22.4%.82 Jia et al. coupled one InGaP/GaAs/GaInNAsSb triple-junction solar cell with a two-series-connected PEM electrolyzer to construct a highly efficient PV-EC system (Figure 5e,f).83 By adjusting the intensity of incident solar power to optimize the efficiency of system, a record average \(\sim 30\%\) STH efficiency was achieved over a 48-h test. These recent research reports demonstrate that there is much room for efficiency improvements through further optimizing each subsystem, especially electrolyzers. Table 3 shows the performance of representative PV-EC cells for water splitting. Almost all PV-EC systems have STH efficiencies of greater than 15%, with some exceeding 20%, and no obvious decreases in performance for most of systems are observed after long-term continuous operation, demonstrating the capability of PV-EC systems to exhibit high STH efficiency and high durability for solar H₂ production.

**H₂ Production from STC Water Splitting Cycles.** In the past decades, more than 100 thermochemical cycles for water splitting have been reported.17,20,22,31 In the light of technical feasibility and ease of process implementation, two- and three-step cycles with a small number of reactions or steps are more suitable for STC water splitting for H₂ generation.17 These two cycles basically necessitate operating temperatures in the range of 800−1800 °C that are technically accessible, thanks to the impressive advances in concentrated solar power technologies such as solar energy collectors and concentrators.31

Redox materials such as volatile oxides (ZnO/Zn, SnO₂/SnO), ferrite-based oxides (Fe₃O₄/FeO), and fluorite-based oxides (CeO₂/CeO₂₋ₓ) are potentially good candidates for two-
thermodynamic analysis. For the endothermic reduction of SnO2 into SnO(g) and O2 at 500 °C and 0.1 bar. Then, the water hydrolysis reaction generated 112 mL of H2 within 28 min at 575 °C with an FeO conversion of 54%. Due to the rapid fuel consumption of H2, it is necessary to alleviate Zn recombination results in energy losses which represents the major challenge of this cycle. Similar to the ZnO/Zn cycle, a SnO2/SnO cycle includes the solar endothermic decomposition of SnO2 into SnO(g) and O2 at >1600 °C and the subsequent production of H2 and SnO2(s) through SnO(s) hydrolysis at 500–600 °C with a yield of H2 up to 90%. Based on the 86% absorption efficiency of a solar collector at 1600 °C, the overall exergy efficiency of this cycle amounted to ~29.8%, analogous to that of the ZnO/Zn cycle at 2000 °C. Compared with volatile oxides, a FeO/FeO redox cycle can potentially circumvent the issue of recombination of Zn or SnO with O2, relying on the continuous release of O2 by introducing inert gas as flushing gas. The FeO/FeO redox cycle proceeds through two steps: (1) FeO(s) + 2H2O(g) → FeO(1s) + H2(g) and (2) FeO(1s) + 1/2 O2(g) → FeO(s) + H2(g). Charvin et al. reported a laboratory-scale two-step iron oxide-based cycle for solar H2 production along with a detailed thermodynamic analysis. For the endothermic reduction reaction, nearly 100% yield of FeO was obtained within 2 min by a solar furnace at 1700 °C and 0.1 bar. Then, the water hydrolysis reaction generated 112 mL of H2 within 28 min at 575 °C, with an FeO conversion of 54%. Due to the rapid fuel generation kinetics and better selectivity, non-stoichiometric ceria oxides (CeO2/Ce2O3) have emerged as promising redox materials for STC cycles since 2006, following two-step redox reactions: (1) 2CeO2(s) → Ce2O3(s) + 1/2 O2(g); (2) Ce2O3(s) + H2O(g) → 2CeO2(s) + H2(g). Chueh et al. demonstrated stable and rapid thermochemical water splitting cycles driven by a high-flux solar simulator with ceria (Figure 6a–c). The reduction of ceria was conducted at ~1600 °C and the ensuing H2O dissociation occurred at 900 °C, with an average H2 production rate of 310 mL min⁻¹. The corresponding STH efficiency was calculated to be 0.7%, which was lower than the theoretical value (16–19%). Transition metals (such as Y, Nb, Zr)-doped ceria exhibited lower reduction temperatures and higher theoretical STH efficiency compared with pure ceria, based on the thermodynamic analysis. By optimizing the reactor and system integration as well as developing suitable dopants to improve efficiency, ceria-based metal oxides would be excellent candidates for STC redox cycles. In addition to metal oxides, SO2/SO3 can also be used for a two-step cycle, which is denoted as a hybrid sulfur (HyS) cycle. This HyS cycle involves a thermal splitting process (H2SO4 → H2O + SO3 → SO2 + 1/2 O2 + H2O), and a subsequent electrolysis process (2H2O + SO3 → H2SO4 + H2), and thus requires thermal and electrical energy that can be supplied by concentrated solar thermal energy and PV cells, respectively. The merits of this cycle are the relatively low temperatures (850–950 °C) required for the thermal splitting process and the reduced requirement for high-cost electricity compared with metal-oxide-based STC cycles and PV-EC systems. Therefore, the HyS cycle is considered as a promising STC cycle for large-scale H2 production in the near future.

In contrast with two-step cycles, multi-step cycles generally require the highest operating temperatures lower than 1000 °C. The sulfur–iodine (S–I) cycle is the most well-known three-step process, including H2SO4 thermal splitting (H2SO4 → SO2 +
H₂O + 1/2O₂ → H₂ + O₂ at ~850 °C, HI formation (I₂ + SO₂ + 2H₂O → 2HI + H₂SO₄) at ~120 °C, and H₂ production (2HI → H₂ + I₂) at ~360 °C. The efficiency of this cycle at 827 °C can reach as high as 42%. This process was even demonstrated in Japan as a pilot plant but involved corrosive halide mixtures. To solve the corrosive issues, Xu et al. reported a multistep Mn-based cycle for thermochemical water splitting without using any toxic or corrosive chemicals and with a maximum operating temperature of 850 °C, providing a potential way for low-temperature solar-driven water splitting cycles.

Compared with other approaches to solar-driven H₂ production, the STC splitting cycle is a process associated with chemical reactions rather than catalytic reactions. The STH efficiency is primarily dominated by the solar receiver configuration, and a high STH efficiency can be theoretically achievable by minimizing heat losses via reasonable device configuration, although the examples of experimentally reported STH efficiency are quite few, and the maximum efficiency is lower than 1%. Figure 6d showcases the energy distribution in a STC system over a ceria oxide cycle at the design point. Around 43.3% of the total energy collected from the receiver is used to run an endothermic reduction reaction, and the sum of losses from collection and receiver is up to 35.2%. Therefore, reducing the thermal energy losses is a useful strategy to promote the overall solar energy conversion efficiency of STC systems.

**PTC H₂ Production from Fossil Fuels.** The majority of the world’s H₂ comes from the SRM process, a highly endothermic reaction, and the subsequent WGS reaction processes. The carbon footprint is associated with reactant methane and reactor heating required to drive reactions. The former part can be solved using carbon capture and storage (CCS) technology. On the other hand, utilizing solar energy to drive the reactions can possibly circumvent the second part. To study the effect of light on the SRM reaction, Ye and co-workers developed TiO₂-supported Rh NPs as a prototype catalyst and found that visible-light illumination substantially promoted CH₄ conversion at an elevated temperature (200 °C).17 SrTiO₃-supported Rh NPs exhibited exceptional activity with no coke formation, respectively. Under focused light irradiation from a 500 W Xe lamp (35.4 W cm⁻²), Co/Co-Al₂O₃ exhibited a high STH efficiency of 27.1%. In addition to metal nanostructures, light-responsive supports also have great potential to promote CH₄ activation and conversion. Ye et al. reported a polar TaN that can harvest visible light to enhance the DRM reaction. Compared to dark conditions, the CH₄ conversion of TaN-supported Pt NPs was increased by 2.7 times with 0.42 W cm⁻² visible-light irradiation at 500 °C. The polarity of TaN was responsible for the performance enhancement by facilitating separation of electrons and holes. Shoji et al. found that UV-light-illuminated, SrTiO₃-supported Rh NPs exhibited exceptional activity with no additional heat input, which cannot be achieved by thermal processes. The authors think that photogenerated electrons and holes participate in the CO₂ reduction on Rh and CH₄ oxidation on SrTiO₃, respectively, and the lattice oxygen atoms of SrTiO₃ serve as mediators to promote the DRM reaction.

With regard to H₂ production from the WGS reaction (CO can be produced from methane reforming and coal gasification), an elevated temperature (200–250 °C) is essential for WGS to achieve a high reaction rate, despite its exothermic nature. To eliminate external heating, Ye et al. reported the solar-driven WGS reaction over a CuOₓ/Al₂O₃ catalyst with a CO conversion of ~95% and a H₂ production rate of 122 μmol g⁻¹ s⁻¹, which was even superior to those obtained with a Pt/Al₂O₃ catalyst (Figure 7d–f). The excellent activity resulted from the combination of photocatalysis over CuOₓ and photothermal catalysis over Cu. They further presented the highly dispersed CeO₂ on CuₓMnₓO₄ catalysts for light-driven WGS reaction. Owing to the charge carriers generated from CeO₂ and the transportation ability of lattice O atoms in CeO₂, a CO conversion of nearly 97% was attained in 0.5 h under 8-sun irradiation. In order to realize a 1-sun-driven WGS reaction, Li et al. designed a photothermal device in which a selective light absorber was coated on a double-layer quartz tube that contained a vacuum layer to prevent heat conduction. The selective light absorber can absorb light with wavelength from 0.4 to 2 μm, with almost no absorption in wavelength of 3–20 μm, to minimize heat dissipation. Consequently, after CuZnAl catalyst with high surface area was loaded on the inside of a photothermal device, the temperature of the catalyst reached as high as 297 °C under 1-sun illumination, generating 192 mmol g⁻¹ h⁻¹ of H₂ production rate, while only ~70 °C was achieved by directly illuminating the CuZnAl catalyst. The authors also scaled up the photothermal device and thereby obtained a total H₂ output of 6.6 m³ in 1 day under concentrated outdoor
sunlight irradiation (4.2 m² irradiation area), which makes this integrated system highly promising for practical implementation.

In addition to H₂ production, H₂ storage and transportation are greatly challenging, thanks to H₂’s low volumetric energy density and safety issues. Using liquid chemicals to transport H₂ with in situ generation provides a prospective method for tackling these issues. Methanol and ammonia, which can be industrially produced from hydrogenation of CO and N₂, are two of the most extensively studied organic liquids, benefiting from their relatively high gravimetric hydrogen content, and ammonia is even a zero-carbon-emission carrier. H₂ production from methanol steam reforming (CH₃OH + H₂O → H₂ + CO) or ammonia decomposition (2NH₃ → 3H₂ + N₂) generally requires high temperatures (>200 °C), consuming massive energy. To this end, Ye and co-workers presented an efficient ZnCu alloy catalyst for solar-driven steam reforming of methanol without any heat input. The introduction of Zn in Cu NPs promotes water activation, and hot carriers generated from the excitation of Cu LSPR facilitate methanol activation. Under around 8-sun irradiation, 328 mmol g⁻¹ of H₂ was produced along with 1.2% solar energy conversion efficiency. Halas et al. reported the manipulation of plasmonic RuCu alloy NPs for efficient light-driven NH₃ decomposition. Under white light (9.6 W cm⁻²) illumination without external heating, a surface temperature of ~475 °C was detected over RuCu photocatalysts, and a high H₂ production rate of 1200 μmol g⁻¹ s⁻¹ was achieved, which was ~20 and ~177 times higher than those of Cu and Ru NPs, whereas RuCu NPs displayed only ~100 μmol g⁻¹ s⁻¹ of H₂ under a thermocatalytic process at the same temperature. The authors revealed that photoinduced hot carriers could reduce the activation energy effectively by exciting the adsorbed molecules, either electronically or vibrationally, thus resulting in a high H₂ production rate.

Table 4 shows the performance of representative PTC H₂ production from methane reforming. It is clear that only using solar energy as the energy input can realize appreciable or considerable H₂ production with both high STF efficiency and durability, representing sustainable and effective routes to produce H₂ by utilizing renewable energy. Meanwhile, further efforts are still desirable to develop more efficient and coke-resistant catalysts and catalytic systems under much lower operating temperatures.

**PB H₂ Production from Water and Biomass.** For H₂ production from direct biophotolysis, because O₂ produced from the photosynthesis process can poison active sites of hydrogenases, H₂ production is difficult to maintain for a long time and gradually decreases with the increase of O₂. To overcome the limitation of hydrogenases’ sensitivity to O₂, one strategy of temporally separating photosynthetic growth and H₂ evolution was introduced. The activity of PSII with O₂ production was inhibited by sulfur deprivation, resulting in an anaerobic condition. Thus, sustained H₂ generation was achieved under light irradiation using the degradation of starch as one of the electron sources. Torzillo et al. presented a D1 protein mutant strain modified by double substitution for direct biophotolysis H₂ generation under sulfur deprivation, exhibiting a maximum apparent light-to-H₂ conversion efficiency of 3.2%. Mamedov et al. found that simply adjusting the ratio of PSI to PSII could bring out the decreased PSII activity and reduced plastoquinone pool, thus enabling continuous photogeneration of H₂ over 42 days.

![Figure 8](https://doi.org/10.1021/acsenergylett.1c02591)
impressive advances over sulfur deprivation strategy, this method entails extensive and time-consuming centrifugations and generally shows low energy conversion, making it practically unfeasible. Instead, consuming O$_2$ by in situ generation of O$_2$ scavengers is a potential way to create anaerobic conditions for continuous H$_2$ generation. For this purpose, Fan et al. constructed a chemoenzymatic cascade (CEC) system, containing glucose, glucose oxidase (GOx), catalase (CAT), and magnesium hydroxide Mg(OH)$_2$ (Figure 8).107 In this system, the generated O$_2$ was consumed by the reaction with glucose using GOx/CAT as an O$_2$ scavenger, thus causing long-term sustainability of an applicable anaerobic environment, and meanwhile Mg(OH)$_2$ was responsible for maintaining near-neutral pH and microalgae aggregation. The resulting PB system exhibited a durable H$_2$ generation over nearly 1 month with a mean rate of 0.44 μmol h$^{-1}$ mg(Chl)$^{-1}$. Kosourov et al. found that, by changing continuous illumination into a series of strong light pulses interrupted with low illumination or darkness, sustained H$_2$ generation was also realized for up to 3 days, with the best H$_2$ generation rate reaching 25 μmol h$^{-1}$ mg(Chl)$^{-1}$.108 In addition, in order to eliminate the competing reaction of CO$_2$, the study by Kanygin et al. and Appel et al. and Kanygin et al. reported the fusion of hydrogenase to PSI in vivo for photosynthetic H$_2$ production separately.109,110 With the assistance of an O$_2$ scavenger to incessantly remove O$_2$ in the medium, Appel et al. achieved a H$_2$ production rate of 0.63 μmol h$^{-1}$ mg(Chl)$^{-1}$ over several hours. The study by Kanygin et al. did not require the O$_2$ scavenger, because the abundance of PSI-hydrogenase chimera was 7 times lower than that of wild-type PSI, which indicated a reduced PSI/PSII ratio and thus led to decreased O$_2$ evolution. As a result, a continuous long-lasting H$_2$ production rate amounted to 14 μmol h$^{-1}$ mg(Chl)$^{-1}$ for 5 days, with the light-to-H$_2$ conversion efficiency reaching 1.75% under the optimized conditions.

Compared with direct biophotolysis, photofermentation has great advantages in a wide range of available substrates, including high H$_2$ yield and high conversion efficiency of organic substrates. 59,21,37 The theoretical H$_2$ yield in a photofermentative process can amount to 8–12 mol of H$_2$ per mole of glucose.111 In this regard, tremendous efforts, such as the regulation of related genes of bacteria and the optimization of operating conditions, have been made to improve the H$_2$ yield and productivity. Kim et al. used a two-step conversion process, i.e., anaerobic conversion of biomass to organic acids and H$_2$ under dark and following photofermentation of organic acids to H$_2$, achieving a total H$_2$ yield of 8.3 mol/mol starch–glucose equivalent algal biomass.112 Abo-Hashesh et al. designed a continuous photobioreactor to carry out photofermentative H$_2$ generation from glucose, which enabled a high and almost stoichiometric H$_2$ yield from glucose, with the rate of 9.0 mol H$_2$/mol glucose and 75% glucose conversion.113 Despite the high H$_2$ yield that is close to the theoretical value, harsh reaction conditions are essential. The development of photofermentation that can be used for practical applications is desirable. One tricky task is realizing high performance at high operating temperatures, since the temperatures of the reaction systems vary with the seasons and tend to be high in summer under practical process, and the resulting high temperatures commonly weaken the performances of photofermentation and hamper cell growth. Controlling the culture temperature is one solution but brings about maintenance cost. Exploring high-temperature-tolerant mutant strains is a more promising method. To this end, Guo et al. found that Rhodobacter capsulatus (MX01) mutants were able to transform HCl-treated cornstalk into H$_2$ with higher activity than that of the wild-type strain at higher operating temperatures (33–37 °C) and light intensity (7–10 suns).114 The total H$_2$ generation rate reached 3.6 mol H$_2$/g cornstalk, with a 10.6% light-to-H$_2$ conversion efficiency. The high-temperature- and light-intensity-tolerant MX01 is a potential mutant that is available for eco-friendly practical implementation of PB H$_2$ production from agricultural waste.

In addition, coupling enzymes or microorganisms with particulate photocatalysts or photoelectrodes to construct hybrid PB-PEC or PB-PC systems offers an alternative way for solar H$_2$ production.114 Enzymes and microorganisms are generally employed as light absorbers or catalysts in such hybrid systems to enhance water reduction reactions by working synergistically with semiconductors. In terms of hybrid PB-PC systems, [NiFeSe]-hydrogenase, as a kinetically active enzyme toward H$_2$ evolution, has been widely integrated with particulate semiconductors such as CdS, C$_3$N$_4$, and dyes/TiO$_2$ for solar H$_2$ production.114–117 These semiconductors function as light absorbers to generate electrons, and then [NiFeSe]-hydrogenase can accept photogenerated electrons to reduce protons to H$_2$, acting like a co-catalyst in PC systems. However, sacrificial agents such as triethanolamine are required to bypass the kinetically difficult water oxidation reaction, making these systems less sustainable for solar H$_2$ production. To realize simultaneous H$_2$ and O$_2$ evolution from pure water, the rational design of hybrid PB-PEC systems is an efficient strategy by constructing a photocathode with hydrogenases or a photoanode with PSII.114,118–122 For instance, Reisner and co-workers demonstrated unassisted water splitting into H$_2$ and O$_2$ by coupling a BiVO$_4$ photoanode with a [NiFeSe]-hydrogenase-loaded TiO$_2$/Si photocathode.121 They further combined the [NiFeSe]-hydrogenases with a triple-cation mixed-halide perovskite-based photoanode and obtained an STH efficiency of 1.1% without an external voltage by designing a tandem cell with a BiVO$_4$ photoanode.122 Reisner et al. also integrated sufficient amounts of PSII and [NiFeSe]-hydrogenases on hierarchically structured indium–tin oxide (ITO) electrodes, respectively, and wired them to construct a bias-assisted PEC cell, in which photogenerated electrons from PSII can be transferred to hydrogenase with the evolution of O$_2$ and H$_2$ being spatially separated.123 At an applied bias of 0.8 eV, the STH efficiency amounted to 5.4% under low-intensity red-light illumination. Despite some examples of hybrid PB-PC and PB-PEC systems for solar H$_2$ production with impressive performances, they are still primarily in the early stages of proof-of-concept, and some critical issues such as instability of separated enzymes and their O$_2$-sensitivity remain to be resolved.

**Comparison of Solar H$_2$ Production Approaches**

The above section briefly summarized the most recent advances in producing solar H$_2$ through PC, PEC, PV-EC, STC, PTC, and PB approaches, and we can witness significant and striking progress in performance improvement of H$_2$ production. There is an urgent need to compare the performance criteria and scrutinize intrinsic similarities and differences among these six processes, which would provide a constructive guideline for the future implementation of reliable solar H$_2$ production. Therefore, in this section, we select four critical criteria, that is, efficiency, durability, cost, and environmental impact, to comparatively assess the performance of different processes for solar H$_2$ production.
Efficiency. Many studies and reviews have reported the theoretical maximum STH efficiencies of solar H₂ production technologies. For PC water splitting, the minimum photon energy necessary for driving water splitting is 1.23 eV theoretically over single-semiconductor photocatalysts. Taking into account the necessary overpotentials (0.4−0.6 eV) for HER and OER as well as energy loss (<0.4 eV) during water splitting, the optimal band gap is around ~2.0 eV, which gives rise to a theoretical STH efficiency of ~18%, meeting the threshold of 10% STH for practical application. The maximum STH efficiency of PEC systems ranges from ~11% to 30% based on system configurations such as single-absorber (11.2%) or two-absorber (22.8%) photoelectrodes and photoanode/photo-cathode configuration (29.7%). The PV-EC system can reach a theoretical efficiency of ~28% when utilizing a two-junction PV cell with ~40% efficiency and an alkaline electrolyzer with efficiency of ~70%, and even a ~37% STH efficiency when utilizing three-junction III−V material-based PV cells with ~43% efficiency and an efficient PEM electrolyzer with 87% efficiency. The theoretical STH efficiency for STC is determined by the metal oxides and chemicals used for the redox cycles. On the basis of the thermodynamic analysis, the maximum efficiency on extensively studied ZnO/Zn cycles and CeO₂/Ce₂O₃ cycles is theoretically assessed to be ~29% and ~22.4%, respectively. With regard to PTC systems, STF commonly replace STH for representing solar energy conversion efficiency, and there is usually no uniform theoretical maximum efficiency. PB H₂ production systems have a maximum STH of ~12% according to the photosynthetic glucose generation from water and CO₂ over two photosystem with a theoretical limit of ~12%. The trend of efficiency shows that the highest solar-to-H₂ efficiency, amounting to ~32%, is obtained for photovoltaic–electrochemical systems, followed by photoelectrochemical systems (~19%), then photocatalytic and photobiological systems (1−3%), and finally solar thermochemical systems (<1%).

According to the summary of the above section, we compare the experimental solar energy conversion efficiency based on STH or STF over different approaches, as shown in Figure 9a. Generally, the trend of efficiency is very obvious, in that the highest STH efficiency, amounting to ~32%, is obtained for PV–EC systems, followed by PEC systems with ~19% STH, then PC and PB systems (1−3%), and finally STC systems (<1%). The STH efficiencies of most PV–EC systems easily exceed 10%, while the PEC systems that show STH efficiency higher than 10% are generally composed of PV-grade material photoanodes, with the efficiency of the remaining PEC systems lower than 8%. The maximum STH efficiencies of PC systems are still in the range of 1−3%, being far from the threshold of 10% STH for commercial implementation. As for PTC systems, since STF efficiencies are unexceptionally achieved under concentrated light irradiation using CH₄ and/or H₂O as H₂ source, the highest STF efficiency reaches ~27%. It is also clear that the efficiencies of PE-VC systems are close to the theoretical limit. However, there is much room for improvement in the efficiency of all other systems, considering the huge gaps between experimental and theoretical values.

Durability. As shown in Figure 9a, although the experimentally reported test time is not necessarily indicative of system lifetime, the trend is very obvious. PV–EC systems generally exhibit the best durability as long as stable inorganic PV cells are used. For instance, Si-based PV cells provide high stability for more than 25 years with very limited efficiency reduction, and meanwhile commercially available electrolyzers show long-term stability with a lifetime of up to ~10 000 h (<90 000 h for alkaline electrolyzer and <20 000 h for PEM electrolyzer). Then, excellent durability can be obtained in PC and PEC systems in which stable metal oxides or C₃N₄ are used as catalysts, in spite of the slight degradation that probably ensues from co-catalysts’ deterioration and/or co-catalysts leaching into aqueous solution during long-term light irradiation (>1000 h). Other semiconductors such as (oxy)sulfides, (oxy)nitrides, Cu₂O, ZnO, and PV-grade materials are susceptible to decomposition or corrosion in water under light illumination when used as photocatalyst in PC systems or as photoelectrodes, especially as photocathode, in PEC systems. A protection strategy integrating an ultrathin layer is an effective way to attain stable liquid/solid interfaces, yet it increases the complexity of devices, and the persistence of the protected devices over a long period of time (>1000 h) is still a concern. Likewise, STC systems using stable metal oxides and PTC systems using coke-resistant oxide-supported nanometals as catalysts are able to deliver excellent stability (>500 h). Due to the high sensitivity to reaction conditions (e.g., atmosphere and temperatures), the long-term durability of PB systems is considerably challenging and can only be observed under strictly limited conditions. Therefore, it seems that only PV–EC systems have the potential to guarantee the long-lasting durability of more than 10 years for practical solar H₂ production, while other systems are confronted with many critical problems for meeting the expected lifetimes.

Cost. The cost of solar H₂ production is one of the most important factors for commercial implementation, and it is mostly associated with feedstocks, the main components of systems, and the balance of system (BoS) expenses, operating costs, and solar energy conversion efficiency. Because most of the solar H₂ production approaches presented in this Focus Review are in the research stages, and many key components of these systems are unavailable in the markets or are under research and development (R&D), only rough economic evaluations can usually be obtained. These evaluations, however, offer a clear perspective for the future application of solar H₂ production. As shown in Figure 9b, we summarize the levelized cost of H₂ (LCOH) of different technologies for H₂ production. Currently, commercial SRM or coal gasification (CG) is the most cost effective process for H₂ production, with a LCOH of US$1.03−2.16 kg⁻¹ for SRM and US$0.96−2.16 kg⁻¹ for CG without considering external
Factors such as ecosystem quality and resources depletion, and the price increases to US$1.93−2.26 kg⁻¹ and US$2.24−2.68 kg⁻¹ by integrating CCS technologies to reduce CO₂ emission.¹²⁹,¹³⁰

For a PC water splitting system, the LCOH values of US$1.60 kg⁻¹ and US$3.20 kg⁻¹ are estimated over single- and dual-bed particle suspension systems, respectively.¹²⁷ However, the quite low LCOH is established on the STH efficiency reaching 10% and 5% with the system lifetime of up to 5 years. The state-of-the-art STH efficiencies of PC water splitting systems are ∼1% and on a laboratory scale with limited test time, remaining far from the required conditions. Very recently, Domen’s group reported PC water splitting on a 100 m² scale with H₂ collection using a commercial polyimide membrane, delivering a maximum STH efficiency of 0.76%, which demonstrates the feasibility of safe and large-scale PC H₂ production from water along with gas collection and separation.⁶⁶ But the overall production and operation costs were not considered in this process, and more efforts are still required before potential application, such as improving photocatalyst stability and STH efficiency. Based on the currently reported STH efficiency of 0.7%, the calculated LCOH reaches US$18.32 kg⁻¹, with the biggest cost (accounting for 49%) associated with operating and maintaining systems.¹³¹

Modular PEC and PV-EC systems have received the most techno-economic analyses, since they both have exhibited high STH efficiency of more than 10%. LCOH values of US$5.78−23.27 kg⁻¹ and US$2.9−18.8 kg⁻¹ were reported for PV-EC and PEC systems, respectively.¹²⁷,¹³² With the increasing development of the PV market, the capital costs and energy consumption of PV cells have been reduced substantially, particularly for Si-based solar cells (US$∼0.3 W⁻¹ in 2018), thereby leading to a remarkable decline in the costs of PV-EC systems. A techno-economic analysis reported in 2020 shows that the LCOH for PV-EC systems with an STH efficiency of 10.9% (18% for Si panel and 61% for PEM electrolyzer) was US$6.22 kg⁻¹, lower than that of PEC systems (US$8.43 kg⁻¹) with a similar efficiency of 10%, indicating that PV-EC systems are more cost-competitive for practical solar H₂ production than PEC systems.²⁹

For STC systems, the estimated LCOH varies with the cycle system used. The reported most cost-effective cycle is the HyS cycle, with a LCOH of US$2.96−8.84 kg⁻¹, followed by the S-I cycle, with a LCOH of US$3.11−10.40 kg⁻¹, and a metal oxide/metal cycle, with a LCOH of US$5.46−15.44 kg⁻¹.²⁰ Calculated

Because most of these production approaches are in the research stage and many key components of systems are unavailable in the markets or are under research and development, only rough economic evaluations can usually be obtained.
H₂ costs of US$7.98 kg⁻¹ and US$8.8 kg⁻¹ were reported over the ZnO/Zn cycle and Fe₃O₄/FeO using SS and 64 MW solar tower plants, respectively, with the operation time over 40 years.¹³³

For the PTC systems, almost no report has been noted to analyze the techno-economic of PTC H₂ production, mainly because the PTC systems are a newly emerging technology and lack data availability. Yet we can refer to the solar SRM process, in which concentrated solar energy is used to supply process heat for driving the SRM and subsequent WGS reactions. The corresponding H₂ cost in this process was estimated to be US $2.55–3.64 kg⁻¹, lower than that of other methods for solar H₂ production.⁶⁰ Based on the observed photoinduced activity enhancement and coke resistance in PTC SRM or DRM processes, the LCOH of PTC H₂ production could be lower than or at least equal to that of reported solar SRM process.

For PB systems, the estimated minimum LCOH is reported to be US$1.42–2.13 kg⁻¹ for biophotolysis, with STH efficiency reaching 10%; however, these low costs have not been realized due to the low energy efficiency and instability of the processes.¹³² At the current STH efficiency (~2.0%), the calculated LCOH of a direct biophotolysis system amounts to US$18.45 kg⁻¹, with nearly 75% of the LOCH composed of bioreactor costs that mainly originate from the costs of bioreactor materials and nutrients.¹³¹ In terms of photofermentation, the lowest LCOH reaches US$18.30 kg⁻¹ using a pond-type flow reactor at a 1.5% STH efficiency.¹³⁴ Integrating a dark fermentation process before photofermentation can potentially produce H₂ from low-cost feedstocks such as agricultural or animal residues with high yield, resulting in a higher LCOH. For example, the cost of H₂ production from a process that combines dark fermentation and photofermentation with barley straw as the raw source was found to be US $~65.85 kg⁻¹, due to the low H₂ yield and productivity.¹³⁵

Environmental Impacts. Although H₂ is considered a clean fuel with the potential for near-zero greenhouse gas emissions, the routes for H₂ production are associated with environmental impacts from processing and construction. The environmental impacts can be described by two main indicators: global warming potential (GWP) that ensues from the emissions of CO₂, N₂O, and CH₄ and can be normalized to CO₂ equivalent emissions (kg CO₂ equiv) for presenting all contributions, and acidification potential (AP) that ensues from the emissions of SOₓ and NOₓ and is presented as kg of SO₂ equivalent (kg SO₂ equiv).¹³⁶–¹³⁹ A lifecycle assessment (LCA) as a systematic analysis approach has been widely used to completely identify and assess the GWP and AP of the processes for H₂ production.¹³⁶–¹⁴¹ We summarize the LCA results of GWP and AP of different technologies for H₂ production from relevant researches,¹³⁶–¹⁴¹ as shown in Figure 9c. The conventional route of H₂ production from SRM has the largest emissions and thus is the most environmentally harmful approach, while the application of CCS technology can reduce emissions. It is clear that all processes of solar H₂ production show considerably low GWP and AP. PC, PEC, and PB approaches are demonstrated to be the most environmentally benign technologies, with the lowest GWP and AP. PTC H₂ production exhibits the highest environmental impacts in solar-powered methods because methane is still used as the H₂ source, but it is believed that the integration of CCS with PTC processes can further abate the impacts. The relatively high emissions of STC systems mainly originate from the synthesis and processing of chemicals utilized in the chemical cycle. In terms of PV-EC approaches, high GWP and AP are also observed compared to other approaches, which can be clarified by the high proportion of CO₂ and SO₂ emissions in the manufacturing process of Si-based PV panels. Considering that most solar H₂ technologies are still in very early stages of proof-of-concept, with key components and device constructs still in the R&D stage and without commercial market or technology demonstrations, the GWP and AP values of solar hydrogen technologies may vary significantly with the future development of performances, key constituent materials, and system-level designs in multiple technological approaches. However, on the basis of the analysis in Figure 9c, solar H₂ production technologies demonstrate great potential in tackling the environmental issues resulting from conventional processes.

Solar H₂ production technologies demonstrate great potential in tackling the environmental issues resulting from conventional processes.

Based on the above evaluation of efficiency, durability, cost, and environmental impacts, we can see a trend that the currently demonstrated approaches of solar H₂ production with high efficiency and durability generally show low cost but high environmental impact. The trade-off relationship between the cost of H₂ production and the environmental impact impedes the large-scale implementation of solar H₂ production. Breaking this trade-off thus becomes an urgent research topic for the future development of solar H₂ production for improving both activity and stability.

This Focus Review discusses the different approaches to solar H₂ production, including PC water splitting, PEC water splitting, PV-EC water splitting, STC water splitting cycle, PTC H₂ production, and PB H₂ production, and introduces the recent cutting-edge achievements in these different routes. The comparative assessment and evaluation of solar-based H₂ production routes are performed in terms of solar energy conversion efficiency, durability, economic viability, and environmental sustainability. Based on this, we summarize the key benefits and existing critical challenges of various routes of solar H₂ production, as shown in Table 5. In brief, PC and PB systems are much more environmentally sustainable, but they show quite low efficiency at present. PEC and PV-EC systems are highly efficient, but the cost of solar H₂ production from these two systems is high. STC and PTC systems potentially give rise to low-cost H₂ production with high efficiency, but the STC system suffers from the challenges associated with the efficient and robust reactor design and durability of reactant materials, and the PTC system leads to high CO₂ emission derived from fossil fuels. In addition, all routes confront a considerable challenge: intermittent operation caused by sunrise and sunset and the resulting adverse effects on the durability and reliability of systems. As a result, despite the recent substantial advances, none of these routes has been industrially implemented on a large scale. The low solar energy conversion efficiency, technical issues, and environmental impacts in concert result in a high cost of solar H₂ production, making them economically uncompetitive compared to industrially fossil-based H₂ production processes. Nonetheless, as the worldwide pressure to limit the emission of greenhouse gases increases, coupled with the improvements of efficiency and technology, the large-scale solar production of H₂ would be technically available and economically feasible with significant environmental benefits.
In the future, however, many challenges still remain to be resolved for these six solar H₂ production technologies, as discussed below.

**PTC and STC Technologies.** Currently, the utilization of fossil fuels to produce hydrogen in industry is still expected to be the most cost-effective route. PTC and STC technologies have the ability to reduce the CO₂ emission during H₂ production. In addition, relatively low H₂ costs for PTC steam methane reforming and H₂S STC cycles on the basis of present process designs reveal that these routes show high potentials for practical application. However, more research work on exploring efficient catalysts and optimizing reactors designs is required, along with the detailed investigations and studies to more accurately assess these technologies by considering the underlying factors that increase the costs.

**PV-EC and PEC Technologies.** Although many examples of H₂ production have been demonstrated by PV-EC water splitting in many parts of the world, the resulting high cost has been the major bottleneck to large-scale solar H₂ production. With increasing efforts devoted to reducing the capital investment and energy consumption of PV cells manufacturing, together with the improvement of PV and EC efficiencies, the cost of H₂ production from PV-EC water splitting is expected to decrease considerably. PEC systems have the advantages in cost, while their low efficiency and poor durability substantially limit their application for H₂ production. Therefore, the deployment of H₂ production by PV-EC water splitting would be possibly far ahead of PEC water splitting. To improve efficiency and thus obtain a viable and cost-competitive PEC device, future studies could be focused on the development of new photoelectrodes with small band gaps (<2.3 eV) and abundant elements, the rational design of novel tandem device configurations, such as introducing multiple photoelectrodes or PV modules to increase sunlight absorption, and the fundamental understanding of PEC systems on the basis of the effect of external field, the role of surface states, charge transfer at the photoelectrode/electrolyte interface, etc.

**PC and PB Technologies.** At present, the experimentally demonstrated low efficiency (<2%) and relatively poor stability make these two technologies practically infeasible for large-scale H₂ production. High efficiency is the most crucial factor to achieve practical applications for H₂ production. For the discovery of photocatalysts for PC water splitting, an absorption threshold longer than 600 nm and the corresponding AQE value larger than 60% are the main prerequisites for meeting the target of 10% STH efficiency. On the other hand, the narrowing of the band gap of the photocatalyst weakens reduction and oxidation driving forces, making the realization of the PC water splitting process more difficult. It is thus important to balance the trade-off between decreasing the band gap to increase light absorption and increasing the band gap to achieve strong driving forces for water splitting. Some oxysulfide- and (oxy)nitride-based semiconductors have been demonstrated to be active for PC water splitting under irradiation up to 600 nm, but these photocatalysts show rather low efficiencies and poor photosensitivity. In addition, the development of low-cost photocatalysts and co-catalysts that are composed of abundant and inexpensive elements is another central challenge. Inspired by natural photosynthesis, in which the splitting of water to O₂ and the reduction of CO₂ to carbohydrates are spatially separated and proceed under light and dark conditions, respectively, the decomposition of water splitting into two spatially separated steps, i.e., proton reduction and water oxidation reactions, is a potentially effective strategy to improve the solar conversion efficiency by suppressing the backward reactions and avoiding H₂/O₂ separation. For PB H₂ production, it is crucial to reduce or even eliminate the oxygen sensitivity of hydrogenases while maintaining high performance for notably improving the efficiency and sustainability of direct biological H₂ production. Some effective strategies, including the genetic and metabolic engineering of microorganisms to accelerate H₂ production by targeting and manipulating enzymatic, regulatory, and transport pathways, the improvement of biological process constructs, and the optimization of bioreactors, could be given more attention.

These approaches possibly offer avenues toward future commercial development of PB H₂ production.

Finally, it is worth noting that the future development and roadmap of solar H₂ production is also influenced by many other factors, such as the prices of fossil fuels, especially methane, the geographical location and environment of different countries/regions, political policies, H₂ demand in the market, the issues of H₂ storage and transportation, and the development of other competitive renewable energy (e.g., nuclear energy), and thus it possibly varies over time. However, there is no doubt that solar H₂ production will play a considerable role in making H₂ an important part of our clean, secure, and affordable energy future.

### Table 5. Key Benefits and Critical Challenges of Different Approaches of Solar H₂ Production

| approaches for solar H₂ production | key benefits | critical challenges |
|-----------------------------------|--------------|---------------------|
| **PC water splitting**            | • most ideal method for solar H₂ production | • low light conversion efficiency |
|                                   | • low complexity | • unsatisfactory stability |
|                                   | • clean and sustainable | • requirement for gas (H₂ and O₂) separation |
| **PEC water splitting**           | • highly efficient | • high cost |
|                                   | • low environmental impact | • high complexity |
|                                   | • long lifetime | • unsatisfactory stability |
| **PV-EC water splitting**         | • mature technology and commercially viable | • high cost |
|                                   | • easily scalable | • high complexity |
|                                   | • highly efficient | • relatively high environmental impact for manufacturing the PV cell |
|                                   | • long lifetime | • efficient and robust re-actor design |
| **STC water splitting cycle**     | • highly efficient | • requirement for an effective solar collector |
|                                   | • relatively low cost | • requirement for acid- and heat-resistant materials |
|                                   | • reliable and viable | • efficient and robust re-actor design |
| **PTC H₂ production from methane reforming** | • feasible technology (based on currently main H₂ production process from SRM) | • high operation and maintenance costs |
|                                   | • high conversion efficiency (>80%) | • high CO₂ emissions |
|                                   | • H₂ produced with high purity (>99.95%) | • mitigation of catalyst deactivation by light |
| **PB H₂ production**              | • uses low light intensities and a wide spectrum of light | • low light conversion efficiency |
|                                   | • uses water or abundant organic substrates derived from waste | • requirement for anaerobic photobioreactors |
|                                   | • clean and sustainable | • high costs |

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