Carbon Neutrality

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Recent advances in efficient and scalable solar hydrogen production through water splitting

Yihao Zheng[1,2], Ming Ma[2*] and Huaiyu Shao[1*]

Abstract

Solar hydrogen production through water splitting is the most important and promising approach to obtaining green hydrogen energy. Although this technology developed rapidly in the last two decades, it is still a long way from true commercialization. In particular, the efficiency and scalability of solar hydrogen production have attracted extensive attention in the field of basic research. Currently, the three most studied routes for solar hydrogen production include photocatalytic (PC), photoelectrochemical (PEC), and photovoltaic-electrochemical (PV-EC) water splitting. In this review, we briefly introduce the motivation of developing green hydrogen energy, and then summarize the influential breakthroughs on efficiency and scalability for solar hydrogen production, especially those cases that are instructive to practical applications. Finally, we analyze the challenges facing the industrialization of hydrogen production from solar water splitting and provide insights for accelerating the transition from basic research to practical applications. Overall, this review can provide a meaningful reference for addressing the issues of efficiency improvement and scale expansion of solar hydrogen production, thereby promoting the innovation and growth of renewable hydrogen energy industry.

Keywords Solar hydrogen production, Water splitting, Photocatalytic, Photoelectrochemical, Photovoltaic-electrochemical, Industrialization

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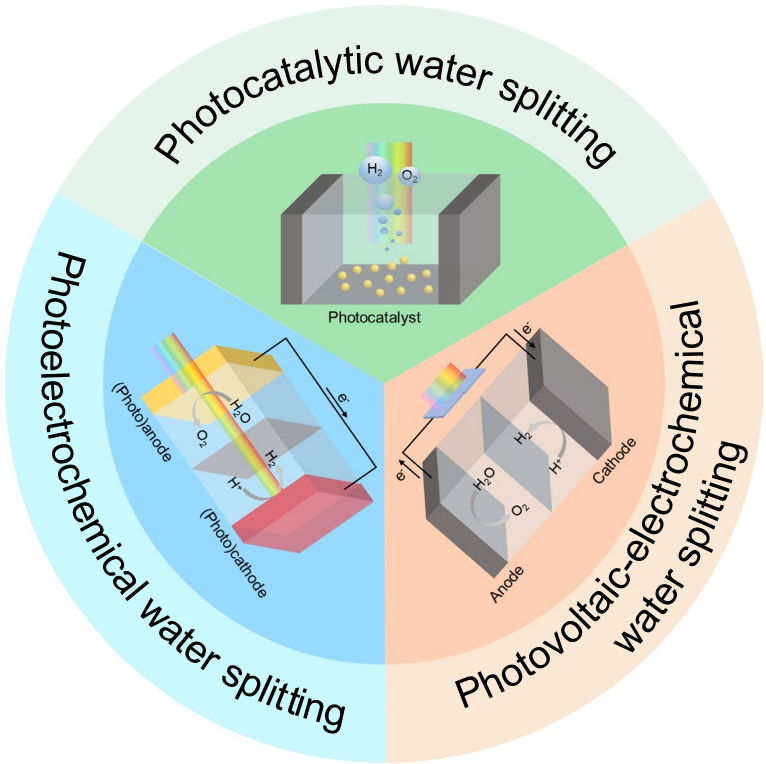
Graphical Abstract



1 Introduction

Carbon emissions from the burning of fossil fuels are the main cause of global warming, the consequences of which have begun to emerge in recent years [1–3]. Therefore, it is urgent to develop low-carbon, efficient, sustainable and clean energy, which is beneficial to mitigate climate change and achieve carbon neutrality [4]. Hydrogen energy is a promising clean energy due to its zero-carbon emission during consumption. Hydrogen fuel cell technology is even considered as one of the ultimate solutions to the energy crisis in the future [5]. The current industrial hydrogen production is mainly from fossil fuels and industrial by-products. In particular, as raw materials, coal and natural gas account for 80% of hydrogen production, simultaneously generating a large amount of carbon emissions in the production process [6]. In order to realize hydrogen production with zero carbon emission, the approach of producing green hydrogen from solar water splitting has been endowed with great expectations. In addition, the conversion of solar energy into chemical energy, such as hydrogen, methanol or ammonia, etc., can solve the storage problem of intermittent solar energy, supporting wider applications such as electric vehicles, power grid peak shaving, etc. [7].

The research on solar hydrogen production from water splitting has aroused great interest worldwide in multiple fields such as materials, chemistry, physics, energy, and power engineering, etc. Among them, three typical technologies could be divided, as photocatalytic (PC) water splitting, photoelectrochemical (PEC) water splitting, and photovoltaic electrochemical (PV-EC) water splitting (Fig. 1) [8]. The first two technologies are still in the research stage of rapid development. While the third technology has been used in industrialization pilot projects. Related to these technologies, there have been all kinds of review articles introducing or discussing some specific topics, such as particulate photocatalysts [9], photoanode/photocathode [10, 11], specific types of hydrogen production [12, 13], and specific principles and strategies [14–16], but lacking the inventory and analysis of efficient and scalable laboratory cases that are instructive for practical applications. Of course, the scope of our discussion is limited to the field of basic research.

Therefore, in this review, from the perspective of high efficiency and scalability, we will focus on some

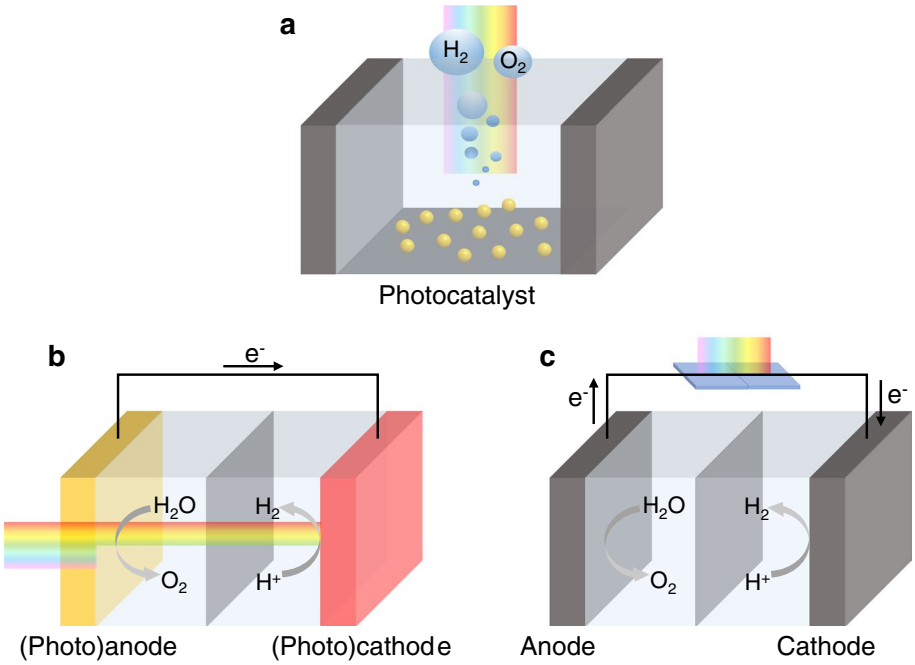


Fig. 1 Three most studied routes for solar hydrogen production. Schematic of (**a**) photocatalytic (PC), (**b**) photoelectrochemical (PEC), and (**c**) photovoltaic-electrochemical (PV-EC) water splitting

representative works that have guiding significance for practical applications with the above three technologies. Especially for some influential works, the research motivations and foundations are introduced in detail to highlight the continuity of the work, which will give us some inspiration on how to conduct in-depth research in the field. Finally, challenges and perspectives towards future industrialization for solar hydrogen production are presented.

2 Recent advances in solar hydrogen production

2.1 PC water splitting

Photocatalysts dispersed in water are particularly suitable for low-cost and large-scale hydrogen production processes [17]. Over past decades, various efficient photocatalysts have been reported for PC water splitting, including oxides, (oxy)sulfides, (oxy)nitrides, oxyhalides, carbonitrides, and chalcopyrites, etc. [18]. For improving the catalytic properties of these materials, numerous strategies have been developed, such as bandgap engineering, crystal facet engineering, and cocatalyst loading. With the effort for improving solar catalytic efficiency, many world-class scholars are working hard to promote the industrialization process of large-scale PC hydrogen production. This section mainly focuses on their representative works in recent years.

2.1.1 Design of highly efficient photocatalysts

Domen's group has been working in the field of PC hydrogen production for more than 40 years and made great contributions to pushing forward its industrialization. Especially in recent years, Domen et al. has greatly improved the efficiency of $SrTiO_3$-based photocatalysts, accelerating the development of large-scale PC hydrogen production. $SrTiO_3$ is a good photocatalyst with a bandgap energy of 3.2 eV and an ever-improving quantum efficiency [19]. In 2016, Domen et al. found that a small amount of Al doped into $SrTiO_3$ from an alumina crucible is the main reason for enhancing the PC water splitting activity of $SrTiO_3$, thereby achieving an apparent quantum efficiency of 30% at 360 nm [20]. In order to obtain high solar-to-hydrogen (STH) conversion efficiency, narrow-bandgap photocatalysts with high quantum efficiency for overall water-splitting must be developed. As we all know, the strategy of spatial charge separation between different crystal facets has inspired extensive attention in the development of highly efficient photocatalysts. Such phenomenon could also be found on high symmetry $SrTiO_3$ exposed with anisotropic facets [21]. On this basis, Domen et al. reported the selective photodeposition of Rh/Cr_2O_3 and CoOOH cocatalysts on different crystal facets of $SrTiO_3$:Al (aluminum-doped strontium titanate), which can suppress charge recombination and enable efficient generation of separated hydrogen and oxygen via anisotropic charge transport

(Fig. 2a). Meanwhile, a combination of multiple strategies was adopted such as flux treatment to enhance crystallinity, Al doping strategy to reduce lattice defects, and supporting CrO_x shell on Rh catalyst to suppress oxygen reduction side reaction. An external quantum efficiency of 96% under 350–360 nm UV light was finally achieved for overall water splitting (Fig. 2b) [22]. This inspiring work demonstrated that a perfect photocatalyst with nearly 100% quantum efficiency was achievable through accurate material design and provided a direct reference for the fabrication of visible-light-driven photocatalysts.

Very recently, some impressive breakthroughs in efficiency improvement have been reported from other groups. Liu et al. proposed a reproducible and economical pre-encapsulation technique for stabilizing highly dispersed and highly loaded (1.5 wt%) Cu single atoms (CuSA-TiO_2) on the surface of TiO_2 [24]. During the photocatalytic HER process, the reversible change of Cu^{2+} and Cu^{+} greatly facilitated the separation and transfer of photogenerated electrons and holes, enabling CuSA-TiO_2 to achieve higher photocatalytic activity than conventional Pt/TiO_2. The resulting CuSA-TiO_2 showed a high hydrogen evolution rate of 101.7 mmol g^{-1} h^{-1} and an apparent quantum efficiency of 56% at 365 nm, which exceeded all previously reported TiO_2-based photocatalysts. It is worth mentioning that the sample still has good performance equivalent to that of the freshly prepared sample after storage for 380 days. This work provides an efficient, low-cost, high-stability, and easy-to-prepare TiO_2-based single atom catalyst for solar hydrogen production. Yang et al. found that the lifetime of charge carriers could be extended by introducing a suitable donor-acceptor structure (β-ketene-cyano) into covalent organic framework nanosheets [25]. By combining this organic nanosheet with a Pt cocatalyst, a record-breaking apparent quantum efficiency of 82.6% at 450 nm was achieved, surpassing all previously reported polymeric

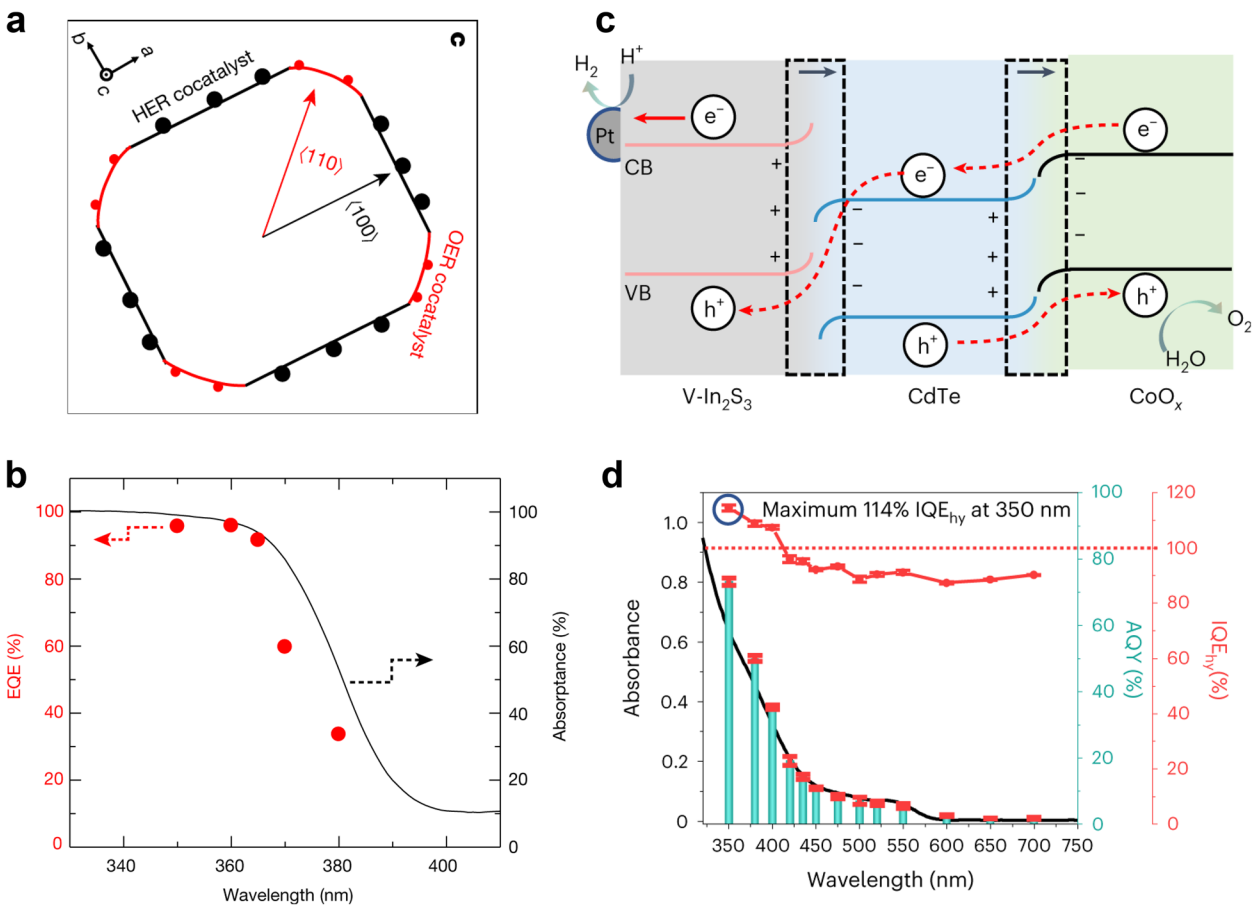


Fig. 2 Highly efficient photocatalysts. **a** Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) cocatalysts supported on different facets of the $SrTiO_3$:Al particle. **b** UV-vis diffuse reflectance spectrum of bare $SrTiO_3$:Al (black line) and wavelength-dependent external quantum efficiency (EQE) for water splitting on Rh/Cr_2O_3/CoOOH-loaded $SrTiO_3$:Al (red dots). Reproduced with permission [22]. Copyright 2020, Springer Nature. **c** Schematic of the photogenerated carrier transfer and H_2 and O_2 evolution process. **d** The absorption spectrum, AQY, and IQE_{hy} of CdTe/V-In_2S_3 photocatalysts. Reproduced with permission [23]. Copyright 2023, Springer Nature

semiconductors for photocatalytic HER. This work provides an effective solution to enhance the photocatalytic activity of polymeric semiconductors. Li et al. reported a CdTe/V-In_2S_3 heterojunction photocatalyst, in which CdTe quantum dots were anchored on surface of V-In_2S_3 via an electrostatic self-assembly method and Pt and CoO_x dual-cocatalysts were loaded as the H_2- and O_2-evolving sites (Fig. 2c) [23]. Under the synergistic effect of robust interfacial built-in electric field and cascade energy band structure, the charge separation kinetics and multi-exciton generation effect of CdTe-4.2/V-In_2S_3-3 hybrid were effectively promoted and utilized, resulting in an internal quantum efficiency of up to 114% and an apparent quantum yield of 73.25% at 350 nm (Fig. 2d). Nevertheless, the STH efficiency of this work was only 1.31% under the simulated solar light, which was at the same low level as most reported STH efficiencies of PC water splitting. Jiang et al. constructed reductive high index facet (002) and oxidative low index facet (110) co-exposed CdS by a one-step hydrothermal method [26]. They found that optimizing the ratio of high and low index facets could tune the *d*-band center, and subsequently affect chemisorption and conversion of intermediates (*-OH and *-O) on reduction and oxidation sites. Finally, an improved STH efficiency of 2.20% was achieved. Mi et al. recently reported a new record-setting STH efficiency from PC water splitting [27], using a highly integrated InGaN/GaN nanowire arrays on commercial silicon wafers through molecular beam epitaxy growth technology. The InGaN/GaN nanowire was decorated by Rh/Cr_2O_3/Co_3O_4 cocatalyst by in situ photodeposition. It was found that the infrared thermal effect generated by high-intensity concentrated solar light could not only promote the forward water splitting reaction but also inhibit the reverse hydrogen-oxygen recombination during the PC overall water splitting (Fig. 3a-c). This strategy enabled the as-prepared photocatalysts to exhibit an STH efficiency of up to 9.2% under concentrated simulated solar light (Fig. 3d), which is much higher than that of previously reported unassisted PC water splitting systems and close to the requirement of industrial applications (10% for STH efficiency [28]).

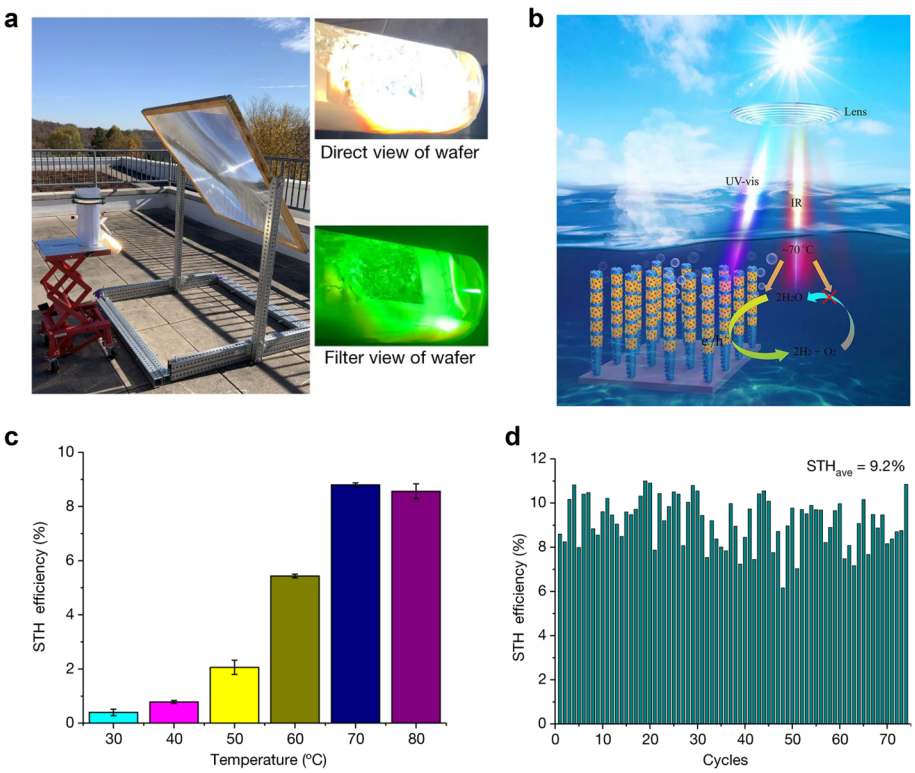


Fig. 3 Photocatalytic overall water-splitting (OWS) system with ultra-high STH efficiency. **a** Photograph of a photocatalytic OWS system outdoors. **b** Schematic of the synergetic effect in the photocatalytic OWS system. **c** The variation of the STH efficiency of photocatalyst with temperature. **d** The stability test of the photocatalyst in the self-heated photocatalytic OWS system. Reproduced with permission [27]. Copyright 2023, Springer Nature

2.1.2 Hydrogen farm project for scalable hydrogen production

Li's group has been committed to the basic research and industrialization of "green hydrogen energy" and "liquid sunshine methanol" for many years, which is very hopeful to become the main path to help achieve the goal of carbon neutrality. In the field of PC hydrogen production, Li et al. has explored a "Hydrogen Farm Project" (HFP) approach for scalable solar hydrogen production. The achievement was widely regarded as a stark example of the transformation of scientific research into practical applications. Based on their more than 20 years of research in the field of PC water splitting, Li et al. revealed and proved the significance of charge separation. Li et al. successively studied the spatial separation of photogenerated electrons and holes between the {010} and {110} crystal facets of $BiVO_4$ [29], and conducted the rational assembly of dual-cocatalysts on different crystal facets to construct efficient photocatalysts [30]. Subsequently, they investigated the direct imaging of the separation of highly anisotropic photogenerated charges on different facets of a single $BiVO_4$ particle, revealing the influence of built-in electric field on charge transfer [31]. These works provided an opportunity to optimize the photocatalysts based on the principle of charges separation between different crystal facets.

In 2020, inspired by the natural photosynthesis, and learning from the practice of large-scale crop planting on farms, Li et al. took the lead in proposing and verifying the HFP strategy of solar hydrogen production based on particulate photocatalysts (Fig. 4a and b) [32]. By using the Z-scheme structure to spatially separate the water oxidation reaction from the proton reduction reaction, this strategy could avoid the reverse reaction of hydrogen and oxygen, and further achieve the safe production of them. Based on $BiVO_4$ crystals for HFP, the solar conversion performance was optimized by precisely regulating the exposure ratio of different facets (for oxidation and reduction reactions) of $BiVO_4$, with Fe^{3+}/Fe^{2+} pair used as shuttle ions for energy storage (Fig. 4c). In this HFP system, the PC water oxidation quantum efficiency was as high as 71%, and the STH conversion efficiency exceeded 1.8%, which is the highest value based on particulate photocatalysts reported internationally at that time. As a demonstration of large-scale HFP, a photocatalyst panel of 1 m^2 for solar energy storage was successfully implemented (Fig. 4d). This work has broken the technical bottleneck of large-scale PC hydrogen production and provided an effective approach to safe and efficient industrial application. In addition, Li et al. further enhanced the PC water oxidation ability of particulate $BiVO_4$ photocatalyst by in situ facet-selective

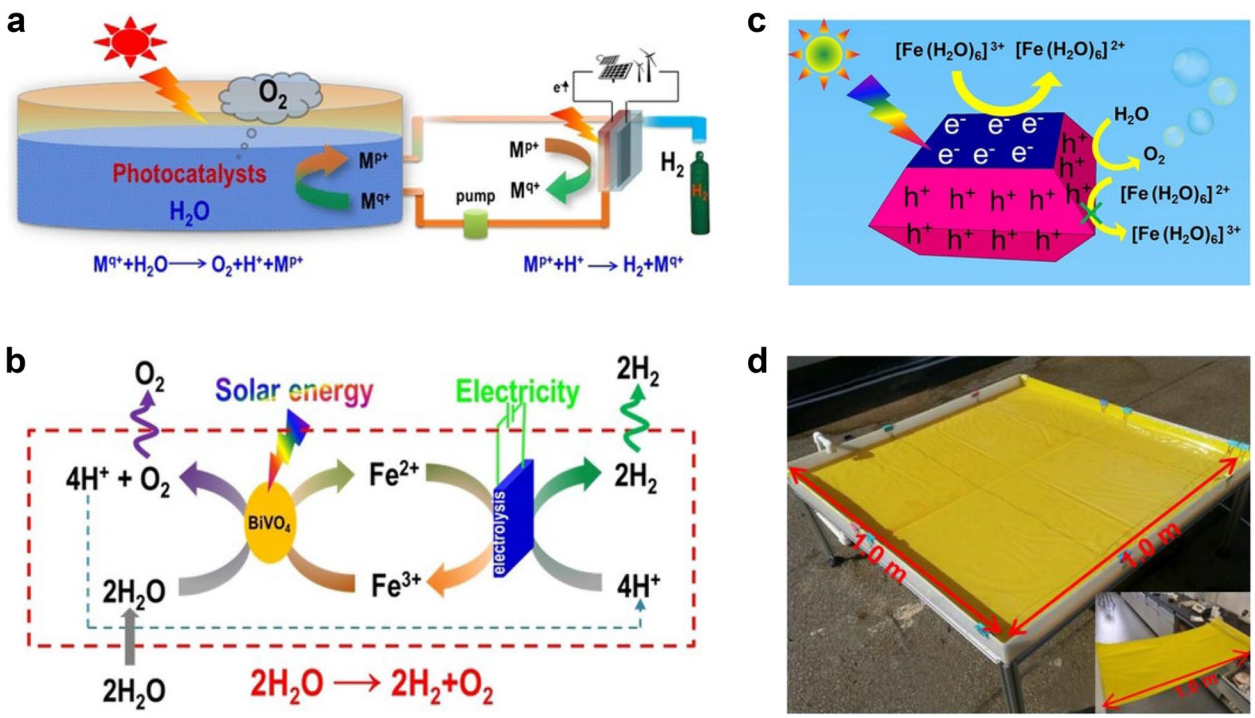


Fig. 4 Hydrogen farm project. **a**, **b** Schematic of the hydrogen farm project for scalable solar hydrogen production. **c** Surface reaction process of $BiVO_4$ in Fe^{3+} solution. **d** Photograph of a photocatalyst panel for large-scale solar energy storage (1.0 m × 1.0 m). Reproduced with permission [32]. Copyright 2020, Wiley

photodeposition of dual-cocatalysts (Ir, $FeCoO_x$) in a later report [33].

2.1.3 Large-scale experiment for PC hydrogen production

In the large-scale hydrogen production, Domen et al. designed a PC water-splitting panel with a light receiving area of 1 m^2 [34]. Using particulate $RhCrO_x$/$SrTiO_3$:Al as photocatalyst, the flat panel reactor achieved an STH efficiency of 0.4% under natural sunlight. With the special design, this panel reactor can maintain the intrinsic activity of photocatalysts when its size is scaled up, which also can sustain a high gas evolution rate at a 10% STH value. Therefore, photocatalysts with higher STH efficiency to be developed in the future can be directly installed in such reactors without worrying about mass transfer limitations. This work marked the first step from the laboratory to practical application of solar hydrogen production through PC water splitting. Subsequently, Domen et al. scaled up the 1 m^2 panel reactor system to 100 m^2 panel reactor arrays in last work, with the modified $SrTiO_3$:Al photocatalyst (Fig. 5) [35]. This "big" breakthrough was considered to have directly raised the threshold for using the word "large-scale" in this field. In addition, the system was very safe and durable, capable of stable operation for several months. However, the maximum STH efficiency of this system was 0.76%, which was still much lower than that of the PV-assisted and PEC water-splitting systems. Overall, this study demonstrated the feasibility of large-scale PC water splitting for hydrogen production, which held a "big" promise for industrial application.

In a recent report, Takanabe and Domen et al. pointed out that large-scale outdoor tests need to consider the impact of volume change of liquid water on the photocatalyst sheets caused by the temperature difference between day and night, as well as the elution, dissolution and removal of the photocatalyst caused by the flowing liquid water [36]. Therefore, they adopted water vapor feeding, a milder method, to replace liquid water feeding to reduce external corrosion for photocatalyst sheets. For capturing enough water vapor and forming a liquid water reaction environment, the TiO_x or TaO_x nanolayers of less than 3 nm were uniformly coated on surface of the CoOOH/Rh loaded $SrTiO_3$:Al photocatalyst. Excitingly, this work achieved an apparent quantum yield of 54 ± 4% comparable to liquid water reactions. In addition, long-term operation (over 100 h) at high pressure (0.3 MPa) and seawater as a water vapor source have also been proven feasible. This vapor-feeding strategy provided a new idea for the design of durable, corrosion-free, large-scale, and high-pressure PC reactors, and to a certain extent, further removed the barriers for industrial application of PC hydrogen production.

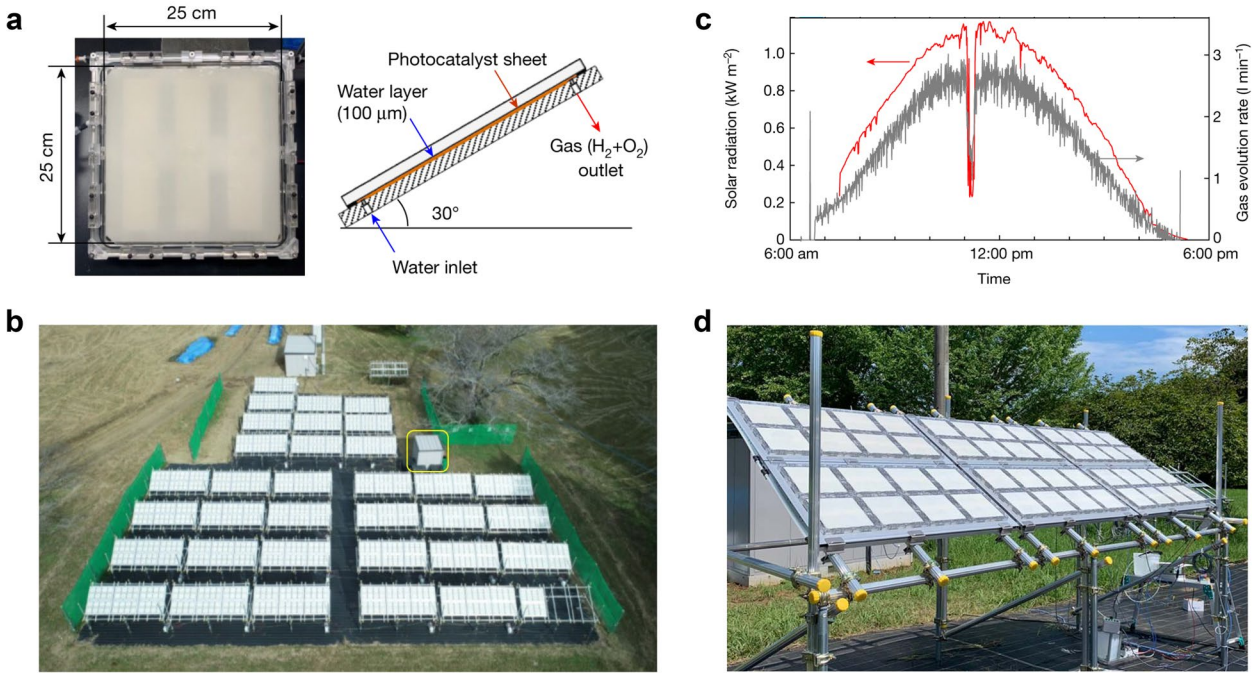


Fig. 5 Large-scale hydrogen production. **a** Photograph of a panel reactor unit (25 cm × 25 cm), and its structure viewed from the side. **b** A top view of the solar hydrogen production system of 100 m^2. **c** The variations of solar radiation intensity (red) and the gas evolution rate (grey) in the panel reactor. **d** Photograph of a 3 m^2 module composed of 48 panel reactor units. Reproduced with permission [35]. Copyright 2021, Springer Nature

2.1.4 Device fabrication for PC hydrogen production

In terms of device fabrication, printable solar water-splitting devices have the advantages of low cost, good processability, and easy scalability. Domen et al. reported a study on hybrid Z-type photocatalysts based on gold substrates [37]. In addition to the study of specific materials, they also demonstrated a printed version of the materials. Using screen printing, a photocatalyst sheet could be fabricated with the printing ink containing hydrogen evolution photocatalyst, oxygen evolution photocatalyst, and Au nanoparticles (Fig. 6a-c). However, the STH efficiency of the printed semiconductor sheet was only 0.1% due to the presence of a large amount of Au nanoparticles that caused reverse reactions and affected the light absorption of the catalyst. To address this issue, Domen et al. reported a scalable and highly efficient PC semiconductor sheet fabricated by screen printing utilizing transparent indium tin oxide (ITO) nanoparticles as the electron-conducting medium (Fig. 6d and e) [38], which could avoid reverse reactions and eliminate light blocking caused by Au nanoparticles, with greatly improved STH efficiency (0.4%). This printable, cost-effective device greatly increased the industrial possibility of PC water-splitting hydrogen production.

Hyeon et al. designed a floatable PC platform composed of porous elastomer-hydrogel nanocomposites, which can achieve long-term stability and large-scale hydrogen production in seawater (Fig. 7a) [39]. In the floatable platform, a high evolution rate of 163 mmol h^{-1} m^{-2} for hydrogen could be realized using Pt/TiO_2 cryoaerogel. When single-atom Cu/TiO_2 was used as the photocatalyst, 1 m^2 of the nanocomposites could produce 79.2 mL of hydrogen per day under natural sunlight (Fig. 7b and c). Large-scale hydrogen production of 100 m^2 is also simulated by calculation (Fig. 7d), which provides a feasible case for the industrial production of hydrogen.

2.2 PEC water splitting

PEC water-splitting cells are generally divided into two categories, including single photoelectrode-based PEC cells and unassisted PEC cells. The former usually requires an external bias, while the latter does not. Further, the unassisted PEC cells include PEC (photoanode-photocathode) tandem cell and PEC-PV

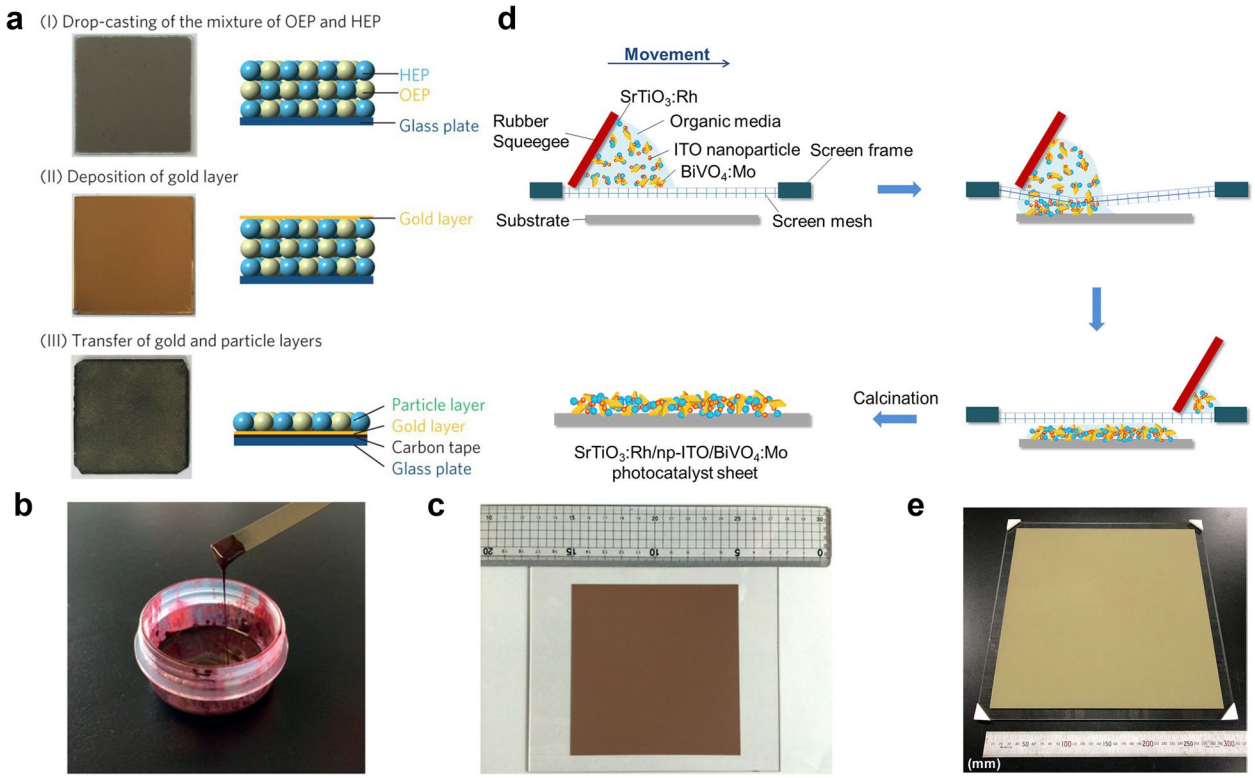


Fig. 6 Printable photocatalytic water-splitting sheets. **a** Schematic diagram of the photocatalyst sheet prepared by the particle transfer method. **b** Photograph of the ink used to screen print the photocatalyst sheet. **c** Photograph of a printed 10 cm×10 cm photocatalyst sheet. Reproduced with permission [37]. Copyright 2016, Springer Nature. **d** Schematic illustration of the preparation of photocatalyst sheets by screen printing. **e** Photograph of a printed 30 cm × 30 cm photocatalyst sheet. Reproduced with permission [38]. Copyright 2018, Elsevier B.V.

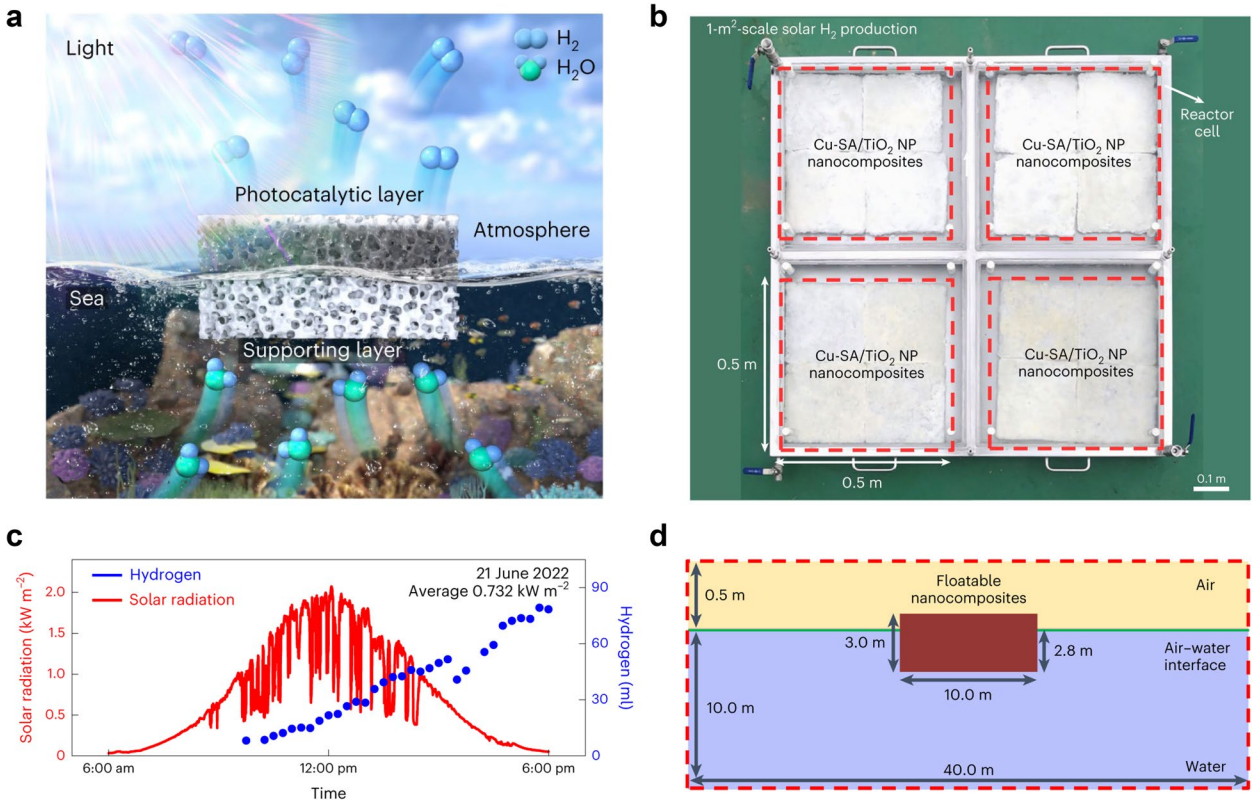


Fig. 7 Floatable photocatalytic nanocomposites. **a** Schematic of the practical application of nanocomposites in a real environment. **b** Photograph of 1-m^2-scale arrayed nanocomposites. **c** The variations of solar radiation intensity (red) and production rate of H_2 by the 1-m^2-scale nanocomposites (blue). **d** Schematic of the 100-m^2-scale simulation domain. Reproduced with permission [39]. Copyright 2023, Springer Nature

(photoelectrode-photovoltaic) tandem cell. Unassisted PEC cells usually have high STH efficiency [40], but the device configuration is more complex. In addition, the stability and cost of PEC cells still cannot meet the requirements of industrialization at the current stage.

This paragraph mainly introduces a few PEC (photoanode-photocathode) tandem cells with high STH efficiency over 3%. In PEC tandem cells, metal oxide-based photoelectrodes have been extensively studied. $BiVO_4$ has been proven to be one of the most promising photoanodes, while metal oxides (e.g., Cu_2O) and photovoltaic semiconductor materials are usually used as photocathodes [40]. Grätzel and Luo et al. developed a Cu_2O/Ga_2O_3-buried p-n junction photocathode with a large visible-light-absorption range and an external quantum yield close to 80% [41]. With the assistance of TiO_2 protective layer and RuO_x HER cocatalyst, the above photocathode was connected in series with $BiVO_4$ photoanode to form a tandem PEC cell (Fig. 8a), achieving a STH efficiency of 3% in weak alkaline electrolyte with a pH of 9.0 for stable operation over 100 h (Fig. 8b). Gong et al. developed a $BiVO_4$ photoanode with abundant surface oxygen vacancies that can facilitate charge separation at the $BiVO_4$ electrode/electrolyte interface. With FeOOH/NiOOH OER catalyst loading, the $BiVO_4$ photoanode was connected with Pt-deposited TiO_2/Si photocathode to construct a PEC tandem cell, realizing a STH efficiency of 3.5% for stable operation of 10 h [42]. Domen et al. developed $CuIn_{1-x}Ga_xSe_2$ photocathode with specific composition (x = 0.5) for remarkable HER performance [43]. The $CuIn_{0.5}Ga_{0.5}Se_2$ was modified with CdS and Pt and then connected in series with $NiFeO_x$-Bi/$BiVO_4$ photoanode to form a PEC tandem cell, achieving a STH efficiency of 3.7%. Inspired by the Z mechanism of natural photosynthesis, Li et al. reported a very high STH efficiency of 4.3% in a PEC tandem cell by rationally designing photoanode and photocathode with complementary light absorption and efficient charge transfer mediators (Fig. 8c and d) [44]. For the front light absorber, the photoanode was formed by $BiVO_4$ with Co_4O_4 as OER cocatalyst and pGO/SnO_x as the charge transfer mediator. For the back light absorber, the photocathode was constructed by using the organic polymer semiconductor PBDB-T:ITIC:$PC_{71}BM$ (PIP) with Pt as HER cocatalyst and CuO_x/TiO_x as the charge transfer mediator. Although the STH efficiency of the PEC

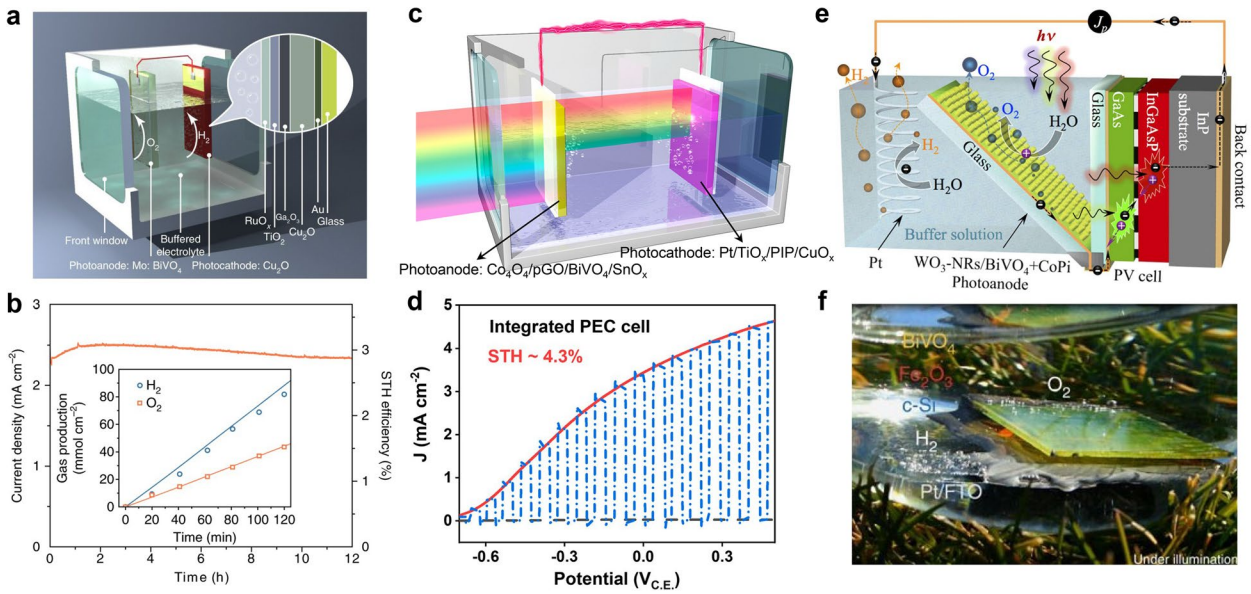


Fig. 8 PEC water splitting. **a** Schematic and (**b**) stability test of an all-oxide PEC tandem cell with the Mo: $BiVO_4$ photoanode and Cu_2O photocathode. Reproduced with permission [41]. Copyright 2018, Springer Nature. **c** Schematic of a PEC tandem cell with the Co_4O_4/pGO/$BiVO_4$/SnO_x photoanode (front) and Pt/TiO_x/PIP/CuO_x photocathode (behind), and (**d**) the current-potential curve of two-electrode configuration. Reproduced with permission [44]. Copyright 2021, American Chemical Society. **e** Schematic of a PEC-PV tandem cell. Reproduced with permission [45]. Copyright 2015, Springer Nature. **f** Photograph of an artificial leaf (monolithic PEC-PV tandem cell). Reproduced with permission [46]. Copyright 2016, Springer Nature

tandem cell is close to the requirement of 5% for the industrial pilot test, the feasibility of its large-scale application still needs to be verified urgently.

Photovoltaic materials, such as crystalline silicon [46], dye/TiO_2 [47], organic semiconductors [48], III-V semiconductors [49–51], Cu_2ZnSnS_4 [52, 53], and perovskite [54–56] are usually used as light absorbing layers to maximize the utilization of sunlight. The STH efficiencies of PEC-PV tandem cells can easily exceed that of photoanode-photocathode tandem cells, even reaching more than 10% [50, 51, 56]. The photovoltaic materials are partially/fully integrated into PEC cells, which can construct wired or wireless PEC-PV tandem cells. For the former, photovoltaic materials are often integrated or connected in series with the photoanode (Fig. 8e) [45], which can increase the photovoltage to meet the large overpotential of OER. In this configuration, the photogenerated electrons are transferred to the counter electrode via external wires. For the latter, the photovoltaic absorber layer is integrated together with other functional layers into a monolithic photoelectrode. This kind of unassisted wireless device can be directly immersed in electrolyte to drive solar water splitting, so it is vividly called "artificial leaf" (Fig. 8f) [46], in which the photogenerated electrons and holes transfer towards the catalyst surface of both sides for HER and OER separately. It is worth mentioning that the STH efficiency of the latest reported artificial leaf has exceeded 20% [57]. In order to achieve effective charge separation, PEC-PV tandem cells often require a multi-layer design, which has higher requirements on the manufacturing process, and their durability cannot be guaranteed. For large-area PEC-PV devices, the current research is less and enlarging the area will lead to a significant decrease in efficiency [52, 53]. In addition, the noble metal Pt has been generally used as the counter electrode in previous reports, with the cost issue to be considered.

2.3 PV-EC water splitting

The PV-EC water splitting system is coupled by a photovoltaic device and a water electrolyzer, which are two wired-connected independent devices different from PEC cells integrated with PV materials. The overall STH efficiency depends on both the photovoltaic and electrolyzer sections. Currently, the highest photovoltaic efficiency reaches 39.2% (under 1 sun irradiation) from a six-junction III-V semiconductor-based solar cell [58]. The state-of-the-art conversion efficiency of electrolyzer reaches 98% from a high-performance capillary-fed electrolysis cell [59]. Therefore, the theoretically assessed STH efficiency could reach about 38%. Harris and Jaramillo et al. demonstrated a PV-EC system with an average STH efficiency of 30% for 48 h of continuous operation (Fig. 9a and b), which is still the highest STH efficiency reported so far for solar hydrogen production from water splitting

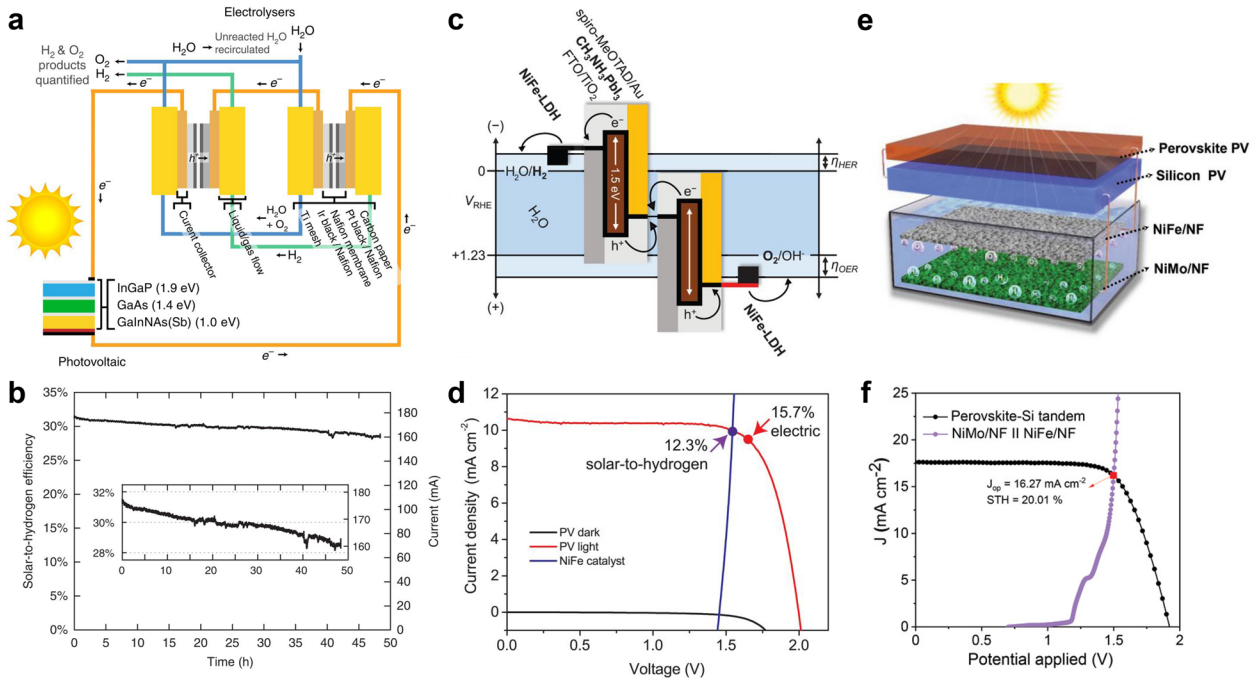


Fig. 9 PV-EC water splitting. **a** Schematic and (**b**) STH efficiency measured for 48 h of the PV-EC device, consisting of a triple-junction solar cell and two PEM electrolysers connected in series. Reproduced with permission [60]. Copyright 2016, Springer Nature. **c** Schematic energy diagram of the PV-EC device for water splitting, consisting of the perovskite tandem cell and NiFe LDH/Ni foam electrodes, and (**d**) *J-V* curves of the perovskite tandem cell and the NiFe LDH/Ni foam electrodes. Reproduced with permission [61]. Copyright 2014, American Association for the Advancement of Science. **e** Schematic of the PV-EC device consisting of perovskite/Si tandem cell and Ni-based electrodes. **f** Overlay of the *J-V* curve of perovskite/Si tandem cell and the LSV curve of NiMo/NiFe electrodes. Reproduced with permission [62]. Copyright 2021, Wiley

[60]. The developed system coupled two polymer electrolyte membrane electrolyzers using Pt black/Ir black catalysts in series with a highly efficient InGaP/GaAs/GaInNAsSb triple-junction solar cell, and the simulated solar concentration was adjusted to 42 suns to optimize the overall efficiency of the system. However, the high prices of III-V semiconductors and noble metal catalysts render this type of PV-EC system low cost-effectiveness at the current stage. Therefore, the development of low-cost alternatives becomes particularly important. Grätzel and Luo et al. achieved a STH efficiency of 12.3% by using the perovskite tandem cell to drive a water-splitting electrolyzer, in which two NiFe layered double hydroxide (LDH)/Ni foam electrodes serve as highly active bifunctional catalyst electrodes to generate hydrogen and oxygen (Fig. 9c and d) [61]. The use of earth-abundant bifunctional catalysts in PV-EC systems simplified the system configuration and reduced the cost of hydrogen production. But the instability of perovskite solar cell and durability of the system could not be ignored. Zhao and co-workers reported a 20% STH efficiency by a low-cost PV-EC system consisting of a perovskite/silicon tandem cell and a nickel-based catalytic water electrolyzer (Fig. 9e and f) [62]. The NiMo/Ni foam catalyst with an extremely low HER overpotential of 6 mV at 10 mA cm^{-2} was combined with NiFe/Ni foam OER catalyst to achieve alkaline water splitting, with the levelized cost of hydrogen estimated to be \$4.1 kg^{-1}. In a word, it is easy to achieve STH efficiencies over 15% for many reported PV-EC water splitting systems so far [63–68], which also indicates that PV-EC is the most commercially promising route at the current stage.

3 Challenges and perspectives

As a simple way to produce hydrogen, PC water splitting has the advantages of low cost and easy expansion and is the most ideal method for solar hydrogen production. However, some issues such as low STH efficiency, difficult separation of hydrogen and oxygen, and insufficient stability limit practical applications. Numerous researchers have tried to address these issues and achieved many good results. For example, Prof. Can Li has made remarkable achievements in hydrogen and oxygen separation through the rational design of particulate photocatalysts. Prof. Kazunari Domen has made many impressive attempts at the design of a large-scale panel reactor for PC water splitting. Prof. Zetian Mi proposed effective strategies to significantly improve PC STH efficiency. If

their work experience is fully combined, the performance indicators of PC hydrogen production may be comprehensively improved. Nevertheless, in terms of STH efficiency, there is still an urgent need to develop more efficient narrow-bandgap photocatalysts. With the development of this field, the advantages of PC hydrogen production will become more and more prominent. Perhaps safe, reliable, efficient, low-cost, large-scale PC hydrogen production will gradually replace PEC and PV-EC hydrogen production in the future.

PV-EC water splitting is the most mature pathway for solar hydrogen production with high efficiency, long lifetime, and good scalability. Since both photovoltaic devices and water electrolyzers have been commercialized, PV-EC technology has entered the stage of industrial application. For example, a "liquid sunlight" demonstration project led by Li et al. has been put into operation in Northwest China [69]. The core step of this project is to produce hydrogen through photovoltaic-powered water splitting. The successful operation of this project also indicates that it is feasible to produce green hydrogen on a large scale through the PV-EC route. In addition, the group led by Xie et al. has achieved stable and large-scale direct seawater electrolysis for hydrogen production [70]. This is considered promising in combination with offshore photovoltaic platforms to achieve large-scale production of green hydrogen. As we all know, improving efficiency is the most fundamental strategy for reducing the cost of hydrogen. With the efficiency improvements of photovoltaic and electrolysis devices, the input-to-output ratio of PV-EC hydrogen production projects will be greatly reduced, and affordable green hydrogen energy will be more easily obtained.

The STH efficiency of PEC is between that of PC and PV-EC, and its high cost and complexity, and poor durability are still big challenges. Future improvement directions mainly include material design and device optimization. Efficient and stable photoelectrodes with small band gaps and long charge carrier diffusion lengths need to be designed with earth-abundant elements. It is very important to rationally introduce efficient cocatalysts to promote both HER and OER with low overpotentials. For tandem cells with semiconductors as light-absorbing layers, it is necessary to optimize the layout of semiconductors, catalysts, and interlayers to reduce internal resistance and accelerate charge separation and transfer, as well as reduce cost. Finally, the simultaneous use of hydrogen to produce high value-added chemicals during the PEC hydrogen production process can increase the value of the output and enhance the economic feasibility of the technology [71].

Industrialized solar hydrogen production has a high demand for durability. However, the currently reported stability tests for solar hydrogen production usually range from several hours to 100 h, which is far below the expected service lifetime of commercial devices. In fact, only a few reported stability tests have reached the thousand-hour level [35, 72, 73]. Therefore, the accelerated stability test for solar hydrogen production system can be developed with reference to the accelerated aging test system in the field of solar cells [74]. For example, using simulated irradiation light or external bias as the acceleration condition, the degradation of the catalyst is accelerated by increasing the light intensity or external bias, and then the service lifetime of the system can be predicted by directly calculating the acceleration ratio. With regard to reaction area, the hydrogen production panels reported in past usually show a significant drop in STH efficiency after the size is enlarged. Therefore, it is necessary to further optimize the scale-up production process to reduce efficiency loss. In addition, the safety performance of the large-scale solar hydrogen production system also needs to be further verified, which is a key step in the scale-up production process and a prerequisite for commercialization. Finally, we hope to speed up the pilot test process of mature solar hydrogen production technology, build a complete green hydrogen energy industry system and standard including preparation, storage, and commercial use, and increase the proportion of hydrogen energy in the entire energy system.

Abbreviations

PC	Photocatalytic
PEC	Photoelectrochemical
PV-EC	Photovoltaic-electrochemical
STH	Solar-to-hydrogen
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
SA	Single atoms
OWS	Overall water-splitting
HFP	Hydrogen farm project
ITO	Indium tin oxide
LDH	Layered double hydroxide

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Authors' contributions

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Availability of data and materials
Not applicable.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
All authors agree to the publication of this manuscript.

Competing interests
The authors declare no competing financial interest.

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