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2023 roadmap on photocatalytic water splitting

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


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Abstract

As a consequence of the issues resulting from global climate change many nations are starting to transition to being low or net zero carbon economies. To achieve this objective practical alternative fuels are urgently required and hydrogen gas is deemed one of the most desirable substitute fuels to traditional hydrocarbons. A significant challenge, however, is obtaining hydrogen from sources with low or zero carbon footprint i.e. so called 'green' hydrogen. Consequently, there are a number of strands of research into processes that are practical techniques for the production of this 'green' hydrogen. Over the past five decades there has been a significant body of research into photocatalytic (PC)/photoelectrocatalytic processes for hydrogen production through water splitting or water reduction. There have, however been significant issues faced in terms of the practical capability of this promising technology to produce hydrogen at scale. This road map article explores a range of issues related to both PC and photoelectrocatalytic hydrogen generation ranging from basic processes, materials science through to reactor engineering and applications for biomass reforming.

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1. Introduction

The awareness of the need for clean and secure sustainable energy resources has significantly increased over the past decade [1]. While there have been important global commitments made by governments to put in place measure to limit the global temperature rise to 1.5° from the 1990 benchmark value, there are substantial challenges in how this is going to be achieved [2]. In the UK the Westminster government and each of the devolved assemblies have committed to achieving Net Zero Carbon by between 2045 and 2050 [3]. Hydrogen gas has been proposed a potential low/zero carbon fuel, however as most hydrogen that is currently available, so called ‘grey hydrogen’ is a by-product of the oil and gas industry and has a considerable carbon footprint [4]. As the significance of hydrogen gas as a potential sustainable fuel has increased, particularly over the past decade, the so called ‘spectrum’ of hydrogen from different sources has been the subject of much discussion [5]. This includes from ‘grey’ hydrogen which as already detailed is a by-product of the oil and gas industry, ‘blue’ hydrogen, which is also produced from natural gas with the carbon footprint being off-set, ‘green’ hydrogen which is generated from carbon free sources such as electrolysis of water using renewable energy sources and ‘gold’ hydrogen which is naturally occurring hydrogen [6–8]. ‘Green’ and ‘gold’ hydrogen are currently the only truly sustainable and low/zero carbon sources of this fuel product.

As described above, one particular route that has been considered in detail for the generation of ‘green’ hydrogen, is via electrolysis of water, powered by renewable energy such as wind or photovoltaic (PV) power. This road map article considers an alternative route to ‘green’ hydrogen using photocatalytic (PC) or photoelectrocatalytic techniques for either splitting or reduction of water. While the use of photo(electro)catalytic methods for generation of hydrogen has been the subject of extensive research over the past four decades, it has still to be demonstrated as a practical process to produce significant quantities of this gas [9–12]. This article looks at the current challenges and opportunities that are being faced by the research community in this area. The first section by of the paper discusses photoelectrochemical (PEC) methods for hydrogen generation considering different photoelectrode materials and looking at the main challenges and opportunities for this process for hydrogen generation moving forward. The section by Kisch looks at the key considerations that need to be considered when measuring efficiencies of water splitting processes. This is an important and often overlooked consideration and is critical when trying to compare work carried out by different laboratories. The roadmap then goes on to consider different material for water splitting reactions including metal oxides and visible light active (VLA) materials and also emerging materials that are showing promise for this process. These chapters provide a good overview of the current state of the art in these key areas on photoactive materials for the hydrogen generation from water. The section by Skillen *et al* considers the emerging area where photocatalysis has been applied to the reforming of biomass wastes generating both hydrogen and potential higher value platform chemicals. This is an interesting approach as it may also have a positive impact on the sustainability of the anaerobic digestion sector through valorization of digestate waste. The final section of this roadmap article by Escobedo and de Lasa, provides an interesting discussion of issues around reactor engineering for PC generation of hydrogen. Again, this is often a frequently overlooked topic and having a practical reactor where the most effective materials can be deployed that is capable of producing cubic meter quantities of hydrogen will be critical if this technology is going to be realized as a practical source of ‘green’ hydrogen.

In conclusion this article provides a clear overview of the current state of the art of photo(electro)catalytic water splitting together with the challenges and opportunities that are faced in realizing this as a practical and sustainable process for hydrogen generation.

2. PEC methods for hydrogen generation

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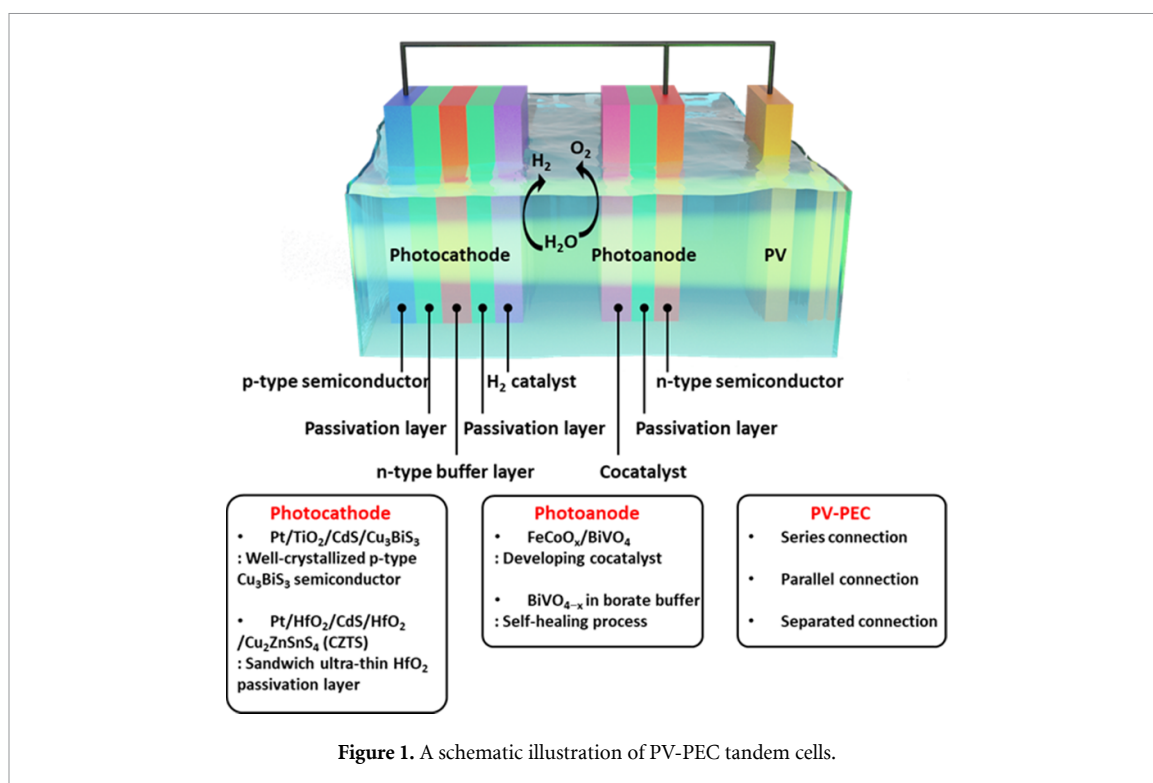
Status

A clean fuel of hydrogen (H₂) is a new emerging energy carrier that has been attracting intense attention as a carbon-free solution for mitigating the global warming. The PEC method is a promising approach that produces green H₂ by utilizing only sunlight and water. Compared to PC solar-to-hydrogen conversion method, it offers potential of higher conversion efficiency together with cost-effective operation and maintenance.

Early studies on PEC water splitting had been mainly focused on the development of photoanodes for which various n-type oxide semiconductors like TiO₂, WO₃, BiVO₄, and α -Fe₂O₃ were employed to attain highly efficient and stable generation of O₂ through engineering the properties of photoanodes [13, 14]. Tested strategies include loading metal (oxide) catalysts onto the photoanodes, doping the photoanodes with foreign elements, sensitizing the photoanodes by organic molecules, and morphological control of the photoanodes. On the other hand, a new strategy for H₂ production in PEC systems employs photocathode which serves as both a light-absorber and a water reduction site. Copper-based p-type oxide semiconductors, oxy(nitrides), perovskites and III–V semiconductors have been widely employed as photocathode materials [14–16]. One key issue in photocathodic systems is that the durability of the cathode materials in an aqueous electrolyte solution is low since copper-based p-type semiconductors are very vulnerable under light irradiation with an applied potential due to their PEC corrosion. Another is that most photoanode/photocathode materials possess their optimized electrolyte condition (pH, ions, etc), which makes it more difficult to combine both photoanode and photocathode in a single cell. Moreover, despite the intensive research efforts, both photoanode- and photocathode-based PEC systems require external bias to drive the water splitting reaction for most cases, which limits the practical applications. To settle down the latter issue, which is required to make the PEC systems commercialized, research on the development of the systems enabling bias-free PEC H₂ generation has recently been conducted [17]. Accordingly, a bias-free PEC system has been emerging and it is usually demonstrated by employing multiple light-absorbing electrodes such as utilizing both photoanode and photocathode (tandem cell) [18]. Various photoanode and photocathode configuration have been studied to maximize solar to hydrogen (STH) efficiency. Tandem cell using BiVO₄ and CuO as photoanode and photocathode, respectively, achieved 3.0% STH efficiency [18]. Recently, an alternative device architecture in PEC hydrogen generation using PV-combined PEC system has emerged [19]. The structure of this PV-PEC system is to make direct contact between photo-electrodes and PV modules. Since PV modules can supply the required potential to drive water splitting reaction, the PV-PEC system can operate by sunlight alone without external energy input. Therefore, STH efficiency achieved using the PV-PEC system could achieve relatively high efficiency, reaching 8.1% and 19% STH efficiencies using BiVO₄/WO₃–InGaP/GaAs and GaInP/GaInAs/GaAs, respectively [20, 21]. However, the system has more complexity of design, which induces unfeasibly high system cost. More concern on the PEC system for practical application is to construct large-scale prototype systems for H₂ production. Unlike the PC system, the PEC system is more challenging to scale up due to its complexity in cell architecture and device operability, which requires intensive development of the PEC system in terms of devices.

Current and future challenges

The fore-mentioned current PEC STH efficiency have motivated the needs of improving under-developed PEC system. The ultimate goal of PEC system for practical commercialization of hydrogen production is to achieve 10% STH efficiency with 10 years of operation durability [21]. The development of highly efficient and robust photoelectrode materials harvesting the full solar spectrum is under active investigation to achieve high STH efficiency of PEC system. The candidate materials should have: (a) a small bandgap to harvest wide range of solar spectrum; (b) band edges that are capable of oxidizing and reducing water; (c) high stability during chemical reactions in electrolytes; (d) low cost of raw materials; (e) better configuration (photoanode||photocathode or photoelectrodes||PV cell) to maximize solar light absorption in the overall system. To date, a wide range of materials including metal oxides, (oxy)nitrides, chalcogenides,



III–Vs and Si have been employed for photoelectrodes. In addition, various modification strategies including doping, morphology control, heterojunction, surface passivation and co-catalyst loading have demonstrated to improve the PEC activity. However, no PEC system has successfully demonstrated the low-cost production of hydrogen at a large scale. The relatively less costly materials such as metal oxides suffer from low efficiency due to limited options of narrow bandgap materials, while high-cost materials such as III–Vs suffer from intrinsically low stability.

With the selection of materials, large-scale manufacturing in terms of catalyst synthesis, electrode fabrication and reactor design need to be widely investigated to meet the commercialization target of PEC H₂ generation. The current PEC system is still lacking reliable information for an up-scaled system. Therefore, there are urgent needs for (a) up-scaled synthesis of catalyst; (b) fabrication technique for photoelectrode on a large scale; (c) up-scaled reactor engineering and design of cell architectures to maximize light utilization and absorption by photoelectrode with effective fuel production.

Advances in science and technology to meet challenges

Developing tandem PEC devices to use optimal light-harvesting and bias-free operation is the most promising strategy, which requires optimization of each photoelectrode part as a prerequisite. The biggest problem still unresolved in the PEC production of hydrogen is to improve both photoanode and photocathode working stability. Studying the role of each phase comprising multi-junction is pivotal to maximizing and stabilizing the performance of tandem cells of which multi-layer structure facilitates efficient interfacial charge transfer and separation in both photoanode and photocathode (figure 1). For the photoanode parts, BiVO₄-based heterojunction materials have achieved many technological advances. FeCoO_x (cocatalyst)/BiVO₄ heterojunction photoanode shows a high photocurrent density of 4.82 mA cm⁻² at 1.23 V and photo-stability for 10 h by suppressing the surface charge recombination [22]. In addition, oxygen-deficient BiVO_{4-x} photoanode in borate buffer exhibits 4.60 mA cm⁻² at 1.23 V and photo-stability over 100 h by the self-healing process, which allows stabilizing passivation layer and inhibiting photo-corrosion [23].

On the other hand, advanced photocathode systems have been developed as a form of Pt/n-type buffer/p-type semiconductor multiple layers in decades [24–26]. Here, the p-type semiconductor is used only for light absorption, and the excited electrons migrate through the p–n junction to the hydrogen generating site, Pt. However, due to several reasons encompassing photo-corrosion of n-type buffer and p-type semiconductor, the PEC working stability is as low as the maximum of one day. Recently, as a breakthrough, a study on the Pt/TiO₂ (passivation layer)/CdS (n-type buffer)/Cu₃BiS₃ device which used well-crystallized p-type Cu₃BiS₃ (E_g ≈ 1.4–1.7 eV), reported a substantial improvement of 60 h durability [25]. The employed heterojunction of CdS/Cu₃BiS₃ layer promoted the separation and transport of photoexcited

charge carriers by reducing surface recombination of the carriers. As another approach, Pt/HfO₂ (passivation layer)/CdS/HfO₂ (passivation layer)/Cu₂ZnSnS₄ device, which had a sandwich ultra-thin HfO₂ passivation layer to protect the CdS buffer layer, also presented high working stability for 60 h [26]. As small changes in the kind and thickness of the thin passivation layers significantly influence the stability of the buffer layer and transport of charge carriers, the continuous exploration of the passivation layer remains necessary.

Last but not least, to drive low-cost operation with high performance on the field scale, we should enlarge the viewpoint into whole-cell architecture. Figure 1 shows the schematic illustration of PV-PEC tandem cell devices, promising for self-powered overall water splitting (OWS). A type of series-connected PV-PEC is used as a conventional model, however, more innovative systems like various types of parallel-connected and separated-connected cells must be pursued to overcome the limitations of the PEC methods to practical applications.

Concluding remarks

The sustainable production of green hydrogen by the PEC methods is a promising way to relieve the global warming and energy crisis. The operational stability of hydrogen production—the biggest obstacle—has been improved by designing both photoanode and photocathode architectures consisting of various multiple layers. Because the extent of the separation and transport of photoexcited charge carriers depends on the adjustment of the interfaces between each layer, engineering multi-junction like cocatalyst and ultra-thin passivation layers is a crucial strategy. Developing a photoanode is necessary for bias-free tandem devices for water splitting, and cocatalyst/BiVO₄ heterostructured photoanodes have achieved high photocurrent and photo-stability. In addition, the photocathode systems comprising p-type semiconductor, n-type buffer layer, passivation layer, and H₂ generation catalyst demonstrated the effectiveness of enhancing the low intrinsic photo-activity and photo-stability, increasing the operational efficiency. Despite this progress, the current status of the PEC methods still has many obstacles in extending it from laboratory-scale to industrial-scale. In terms of realizing commercialization, PV-PEC tandem cell systems developed for low-cost solar water splitting may be a more promising candidate for future green hydrogen production.

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3. Comparing efficiencies of PC water splitting

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Status

Semiconductor photocatalyzed splitting of water into hydrogen and oxygen is the most promising way of solar energy utilization. Different from PVs it produces easy storable hydrogen gas in a single-step process, whereas the PVs-based two-step method requires the combination with electrolysis. While up to 30% STH energy conversion efficiencies (equation (1)) were reported for the latter, values of the former are below 1% [27]. In equation (1) $r(\text{H}_2)$ and $\Delta G(\text{H}_2\text{O})$ represent the H_2 formation rate and the reaction Gibbs energy of water splitting (237 kJ mol^{-1}). I_{sun} (W m^{-2}) and S (m^{-2}) correspond to the incident solar light intensity (number of photons arriving at the reactor surface within the unit of time) and irradiated area, respectively. In laboratory experiments solar light is generally simulated by applying an Air Mass 1.5G filter. Using ultraviolet (UV) light of 350–360 nm, an extremely high external quantum efficiency EQE (equation (2)) of 96% was reported:

$$\text{STH} = [r(\text{H}_2) \Delta G(\text{H}_2\text{O})] / I_{\text{sun}} \times S. \quad (1)$$

Analogous to equation (1), I_0 corresponds to the number of incident photons (polychromatic) emitted by the artificial light source [27]:

$$\text{EQE}(\text{H}_2) = [r(\text{H}_2) / I_0] \times 2. \quad (2)$$

In homogeneous photochemistry, the quantum yield (QY) is the correct parameter to be used for comparing the efficiency of photoreactions (equation (3)). Therein $r(P)$ and $I_a(\lambda)$ correspond to the rate of product formation and the numbers of photons of monochromatic light of

$$\phi_P(\lambda) = r(P) / I_a(\lambda) \quad (3)$$

wavelength λ absorbed by the dissolved reactant per unit of volume and time.

Both STH and EQE values published in the literature are not quantitatively comparable since the number of photons absorbed by the heterogeneous photocatalyst suspension is usually not known due to varying amounts of reflection and scattering. This applies also for the ‘PC space-time yield’ recommended very recently on basis of a critical summary of all reported figures of merit [28]. However, comparable values can be obtained employing a ‘black-body photoreactor’ as reported for the degradation of dichloroacetic acid. Total light absorption is obtained by placing the light source through a wave guide *in the centre* of the irradiation flask. Under sufficient catalyst powder concentration all the incoming light is absorbed. Therefore, I_0 becomes equal to I_a and the as obtained QYs (monochromatic) or efficiencies (polychromatic) are now comparable [29, 30]:

$$\text{OQE} = \left[r(\text{H}_2)_{\text{opt}} / I_0(\lambda_1 \dots \lambda_2) \right] \times 2. \quad (4)$$

Within one research group, employing a standard photoreactor, a rough comparison of PC activities is reliable when the catalyst concentration corresponds to the optimal value $m(\text{SC})_{\text{opt}}$ inducing an optimal reaction rate (figure 2, equation (4)) [31].

Obviously, comparable quantum efficiencies are the basis for the development of highly efficient solar light active semiconductor photocatalysts [32–35].

Current and future challenges

A current challenge in this interdisciplinary research area is the use of a nomenclature understandable both for chemists and physicists. Misunderstanding is already manifested even in publication titles. Although the expression ‘water splitting’ correctly signals the reader that water was cleaved into H_2 and O_2 (or rarely H_2O_2), in many cases only hydrogen or oxygen have been produced in the presence of a reducing and oxidation agent, respectively, often called *sacrificial agent*. However, these reactions are commonly titled as ‘hydrogen generation’ or ‘oxygen generation’. We therefore again propose to name them more precisely as ‘reduction of water’ or ‘oxidation of water’ signalling immediately the correct over-all reaction [36]. It is

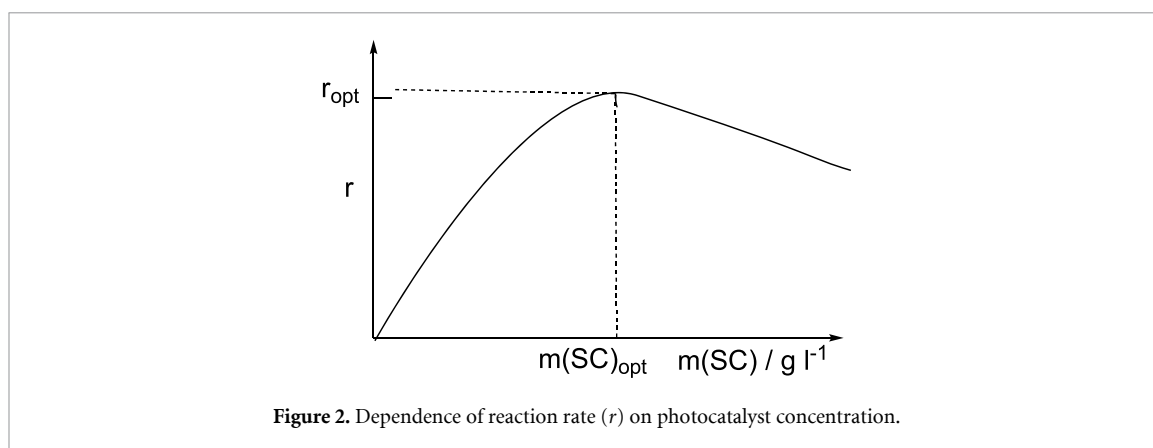


Figure 2. Dependence of reaction rate (r) on photocatalyst concentration.

noted that in such systems H_2 may originate even not from water but from the reducing agent [37, 38]. Furthermore, the usually as proof taken D_2 formation in presence of D_2O is a necessary but not sufficient criterium. It must be complemented by measuring the decrease of water concentration [37].

It is further recalled that the generally accepted definition of a QY according to equation (3) does not assume any reaction mechanism. This definition is not obeyed in equation (2), wherein the factor of 2 considers the fact that in water splitting *two photons* are necessary to generate *two electrons* for the formation of *one* H_2 molecule. But this assumption is unjustified in the case of the reduction of water when the reducing agent exhibits a *photoredox amplification effect* (Corresponding to the *current amplification effect* in photoelectrochemistry) [36]. Typical reducing agents are amines or alcohols. In the latter case the electron–hole pair formed by absorption of one photon generates by hole oxidation of EtOH an intermediate $MeC^{\cdot}H(OH)$ radical and a proton. The strongly reducing hydroxyethyl radical subsequently injects an electron into the conduction band (CB) resulting in generation of *two* CB electrons through absorption of only *one* quantum of light. Therefore, it is not correct using a factor of 2 in equation (2). Accordingly, only reductants of photoredox amplification properties enable a *one-photon/two-electron* reduction, as observed for the photoreduction of N_2 by ethanol [39].

Obviously, the greatest challenge in water splitting by visible light is to improve the EQE values. Since the latter depend on processes localized in the semiconductor solid *and* at the solid–liquid phase, EQE can be factorized into the product of the two corresponding efficiencies according to equation (5). Therein η_r and η_p corresponds to the efficiency of formation of reactive electron–hole pairs and

$$EQE = \eta_r \times \eta_p \quad (5)$$

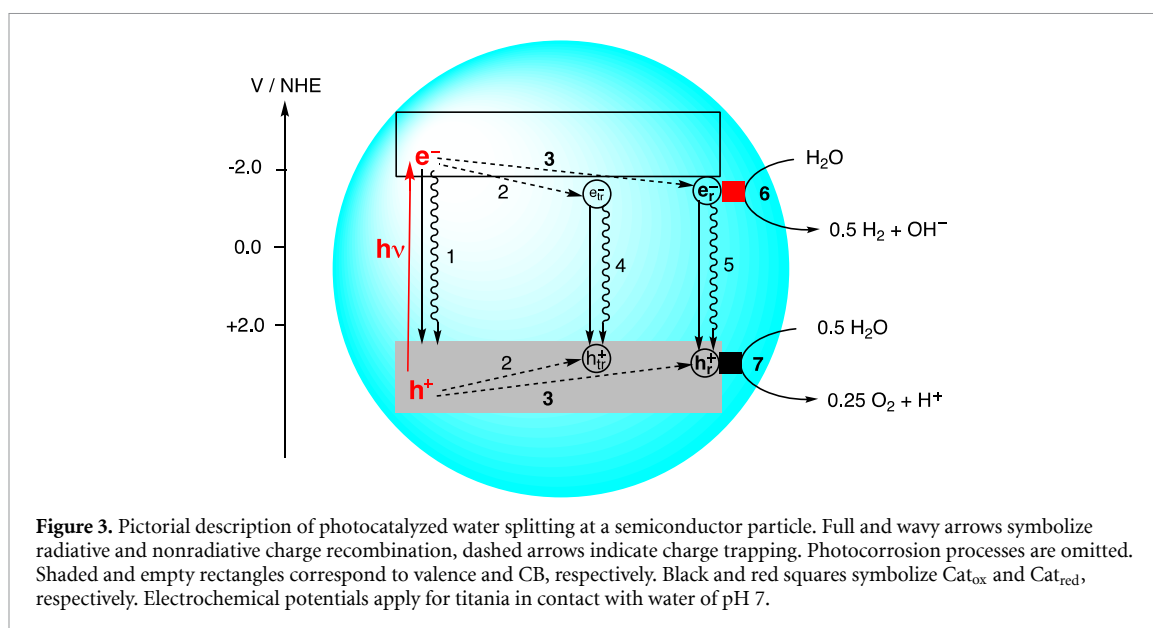
to the interfacial hydrogen (HER) and oxygen (OER) evolving reactions (equations (6) and (7), respectively, wherein the reduction and oxidation catalyst are omitted. See figure 3) [40]:



Advances in science and technology to meet challenges

As mentioned above, the ‘black body’ photoreactor enables the measurement of light absorbed by the semiconductor suspension. When operated at optimal photocatalyst concentration with a standard LED, the resulting quantum efficiencies, and QYs of various photocatalysts can be quantitatively compared. It may be useful defining a standard reaction of known QY to test this experimental set-up (via the International Standard Organization) [29, 30]. Although work on general photoreactors was growing exponentially in the last 30 years, no internationally accepted apparatus is known for semiconductor photocatalysis [28, 33, 41].

Based on the above-described efficiencies and figure 3, the origin of photoactivity changes can be discussed in more detail, but in many cases, conclusions drawn are too straightforward. As a first approximation it is often assumed that η_r and η_p are independent of each other. However, recently it was shown that the different work functions of crystal facets may induce face-selective deposition of Cat_{red} and Cat_{ox} [42]. This is the case for aluminium-doped strontium titanate loaded with 0.1–0.05 wt% of Rh/Cr_2O_3 and $CoO(OH)$. It enables water splitting with the unprecedented high EQE value of 96% upon irradiation at 350–360 nm. Most likely, the different facet work functions at the two redox catalyst surface centres enable a



very efficient charge separation (figure 3, step 3) and almost completely slow down recombination processes (figure 3, steps 1, 2, 4, 5). Another basic question is whether reactive and emitting surface states are identical or not. This is the case only if both luminescence and hydrogen evolution are inhibited by the same quencher. Thus, the observation that a decrease of photoluminescence correlates with an increase of hydrogen evolution, is a necessary but not sufficient criterium [43].

Concluding remarks

Whereas solar water splitting by the two-step PVs-electrolysis process is already technically applied, the simpler one-step process of semiconductor photocatalysis is still in the state of basic research. In the former light absorption and water splitting proceed in two reactors, while in the latter only one reactor is required for both reaction steps. It can be viewed as a type of short-circuited photo-electrochemical cell. Using UV light and an astonishing easily obtainable photocatalyst powder, an EQE of almost 100% was recently reported. Visible light-based efficiencies are in range of one per cent. Present research is focussed therefore on improvement of the latter by increasing light absorption and catalytic activity of the redox catalysts for the two interfacial reaction steps. A prerequisite for progress of the field is an internationally accepted standard photoreactor for obtaining quantitatively comparable efficiencies.

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4. Metal oxides for PC hydrogen generation

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Status

The need for solar hydrogen generation has risen in recent years. One of the most promising techniques in the conservation of solar energy is PC water splitting into hydrogen [44], which is cost-effective and environmentally benign [45, 46]. The factors such as bandgap energy, Fermi energy level, charge-carrier recombination rate, crystal structure, movement of free carriers, surface charge, and other surface properties play an important role in the PC process. The transition metal oxides (TMOs) are considered the most efficient water-splitting catalytic materials [47] as they fulfil a few of these properties. They are single-phase photocatalysts and have large bandgap energy, and can only absorb light in the short wavelength range [48]. The incorporation of binary or ternary structured nanocomposite photocatalyst materials and co-catalysts loaded on the surface of semiconductors should be given special consideration. As these photocatalysts would not only enhance the chemical kinetics of water reduction and oxidation, but they may also prevent photoexcited charge carriers from recombining [49, 50]. Moreover, combining old and modern materials is thought to be advantageous in the creation of efficient energy-generation technologies. Further research is needed to better apprehend the kinetics and thermodynamics of interfacial interactions on the surface properties of photocatalysts. To develop efficient ways for improving PC performances, a thorough knowledge of the mechanisms of PC processes and intrinsic charge-transfer dynamic forces at the atomic and nanoscale levels is required. It is also essential to increase the efficiency of H₂ generation when exposed to solar light (>10%) and to produce extremely stable PC materials that can operate for a longer time. Figure 4 depicts the band structure of several types of metal oxide semiconductors in relation to the redox potentials of water splitting.

Current and future challenges

PC performance is poor in pure metal-oxides, owing to their wide bandgap energy and rapid recombination of photogenerated charge carriers. As a result, design of metal oxides leading to effective charge separation remains a significant challenge. A few strategies, such as the construction of nanostructures [51] through the introduction of dopants [52], control of crystal facets [53], design of junctions, and alteration of interfaces, are some tactics used to extend the light absorption towards higher wavelength [54]. Although these methods could not extend the light absorption edge of the materials in some cases, they could still enhance the PC H₂ production due to better surface contact and uniform dispersion, simplifying efficient electron transfer with minimization of electron-hole pairs recombination rate. The metal oxides with a low bandgap, such as BiVO₄, WO₃, Fe₂O₃, Cu₂O, CuO, etc, are among the most promising materials for conducting water splitting [55–57].

The present perspective for effective water splitting depends on a novel PC material design. The heterojunction's architecture has directly impacted activity, which may lead to significant improvements. In addition to previous advancements in water splitting, designing and identifying commercially feasible heterogeneous catalysts based on earth-abundant elements remains essential for chemists. Most photocatalysts for water reduction and oxidation still have several common issues. The first and foremost criterion is the stability of the catalyst, with lifetimes varying from seconds to hours. Secondly, the optimum condition for water reduction is to promote hydrogen generation should be quicker than deactivation pathways. Thirdly, water tolerance is also a significant problem for several H₂-generating catalysts that have been an important concern for many reports. Thus, to meet 33% of the projected energy from solar energy for human society by the year 2050, about 10 000 solar plants with a solar energy renovation productivity of 10% would be required [58]. The necessary area, 250 000 km², equates to 1% of the earth's desert surface; 570 tons of H₂ gas would be generated daily [58]. This H₂ might be used as a 'recyclable' reactant in fuel cells and a raw material for synthesizing essential compounds like methanol and other molecules.

Advances in science and technology to meet challenges

To use semiconductors as PC water splitting, they must come across specific necessities, including suitable valence and CB positions to assure water reduction/oxidation potential, appropriate bandgap energy,

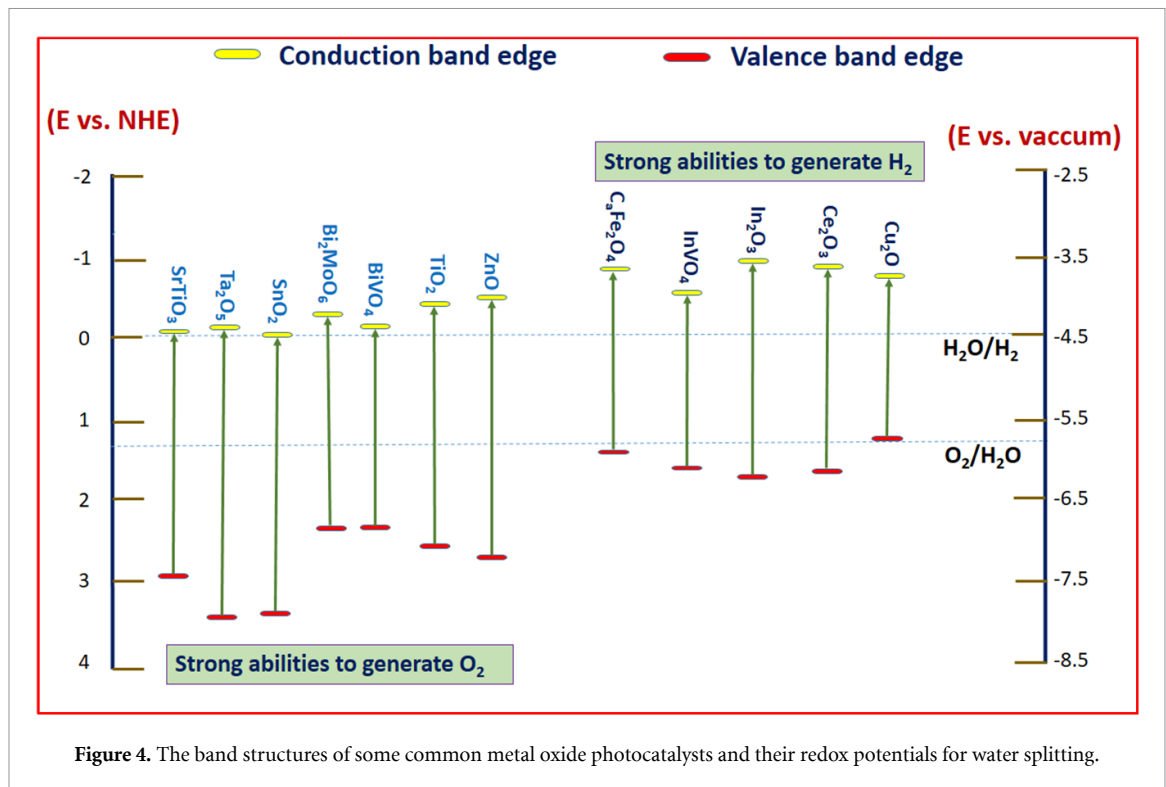


Figure 4. The band structures of some common metal oxide photocatalysts and their redox potentials for water splitting.

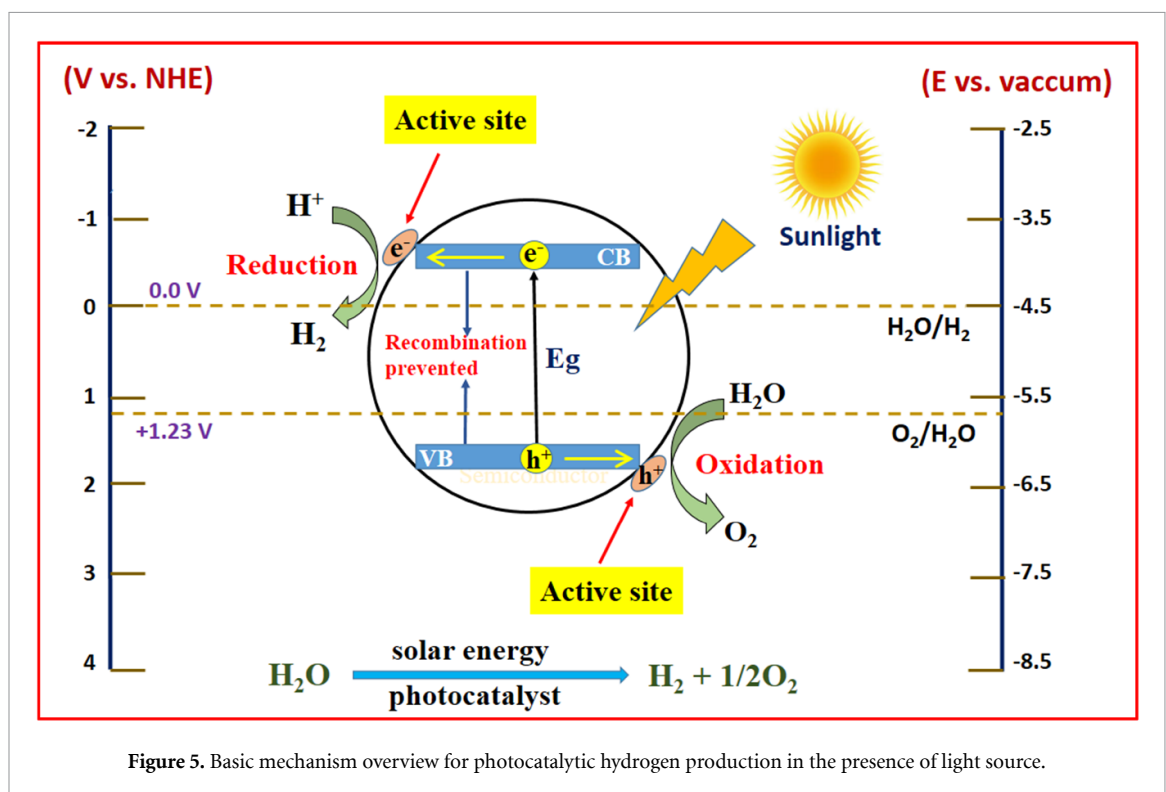


Figure 5. Basic mechanism overview for photocatalytic hydrogen production in the presence of light source.

chemical steadiness under light and dark conditions, high visible light absorption and commercial viability [59]. Furthermore, in heterogeneous photocatalysis, significant efforts have been made to analyse photocatalysts that respond to light to generate active sites and to understand more insite into the reaction mechanisms in water-splitting processes. Solar energy conversion efficiency rises when one can accomplish total water splitting under high wavelength illumination. This is because the number of accessible photons in the solar spectrum increased as wavelength increased. However, there are still difficulties in promoting electron transport between two semiconductors and suppressing backward processes involving shuttle redox mediators. Furthermore, a novel reactor for photochemical hydrogen synthesis may be presented.

Comprising a solar hydrogen chemical plant, H₂ and O₂ gas separator, and the construction of the water-splitting reactor could be projected as the prospects for achieving practical application. It is particularly critical to explore the nature of the flaws in photocatalysts that might allow unwanted electron–hole recombination because existing reaction systems utilize less than 10% of incoming photons for PC OWS. As a result, more advanced strategies are needed to overcome the constraints associated with water-splitting technology in order to meet the worldwide need for clean and sustainable hydrogen generation. Figure 5 depicts the most recent successful PC mechanism for OWS.

Concluding remarks

Solar water splitting is a potential strategy for producing clean, sustainable fuels, with extraordinary speculative efficiency for renovating solar energy to a portable chemical energy form. Metal oxides offer numerous interesting qualities among the various water-splitting photocatalyst materials, including a lower bandgap (1.9–2.2 eV) that increases solar spectrum absorption and stability in an aqueous background under typical working circumstances, affordability, and abundance. With the significant rise in the use of surface engineering defects of TMOs, particularly oxygen vacancies, a fundamental knowledge of the many micro-effects is essential for future advances in material design and synthesis in photochemical water splitting. This is done by rationally engineering highly stable and active photocatalysts to improve reaction kinetics while lowering the required energy input. TMO-based materials (e.g. spinel oxides, rocksalt oxides, perovskites, rutile oxides) have gained considerable interest as ideal catalysts, particularly for photochemical hydrogen production reactions.

Acknowledgments

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Conflict of interest

There are no conflicts of interest to declare.

5. VLA materials for PC hydrogen generation

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Status

PC OWS to produce hydrogen is one of the most promising routes to realizing a ‘carbon-neutral’ society. The prerequisite for its commercialization is to reach a minimum STH efficiency of 10%. However, under UV light irradiation ($\lambda < 400$ nm), the maximum STH is less than 2% even though the quantum efficiency (QE) of photocatalysis reaches 100% (figure 6) [58, 60]. One example is the photocatalyst SrTiO₃:Al, which shows almost unity QE at 350–360 nm with the cocatalysts of Rh/Cr₂O₃ and CoOOH, but the STH is only 0.65% [42]. In contrast, extending absorption into the visible light region up to 700 nm would theoretically raise the STH to 25%. Thus, development of VLA materials for OWS is apparently necessary.

In the past decades, hundreds of new VLA materials have been developed, but most of them either need the addition of external scavengers or suffer from serious self-oxidation. Conjugated polymeric photocatalysts are boomed as promising alternatives to inorganic materials. However, their excitons have high binding energy (>100 meV) that limits the generation of free carriers [61, 62]. Hence most of polymeric photocatalysts exhibit moderate activity and are commonly used in the half-reaction of hydrogen generation. Very few of VLA materials can realize one-step OWS, which is to realize simultaneous and stoichiometric hydrogen and oxygen evolution over a single photocatalyst. This is attributed to the strict requirements on bandgap and band positions: the minimum bandgaps of photocatalysts should be ca. 1.8 eV in the consideration of overpotentials, and the CB and valance band (VB) should straddle the positions for hydrogen and oxygen generation [63]. A series of d⁰ (Ta⁵⁺, Nb⁵⁺, etc) and d¹⁰ (Ge⁴⁺, Ga³⁺, etc) metal (oxy)nitrides are capable for one-step OWS driven by visible light [64–66]. These oxynitrides have bandgaps in the range of ca. 1.8–2.5 eV (figure 6(b)), corresponding to the theoretical maximum STH of 8%–32%. Two-step OWS is achieved by using two photocatalysts that are only active for the respective half reaction of hydrogen or oxygen evolution. This mitigates the thermodynamic limitation and broadens the candidates of VLA materials. A scalable two-step OWS system based on La- and Rh-codoped SrTiO₃ and Mo-doped BiVO₄ powders embedded into a gold layer obtained a 1.1% STH [67]. However, the highest STH in the lab-scale is still around 1%. The huge energy loss can be mainly attributed to the undesirable light absorption ranges, significantly recombination of the photogenerated charges, competitive surface backward reactions, instability due to photocorrosion and self-oxidation of VLA materials. There is still a long way to obtain commercial hydrogen from OWS.

Current and future challenges

To achieve a high STH for hydrogen generation, the VLA materials should have such performance including light absorption matching solar spectrum, efficient separation of photogenerated charges and rapid surface water reduction and oxidation reactions. However, visible light photons provide low potentials to drive the transfer and surface reactions of electron–hole pairs, and inherent defects or vacancies as the recombination centres signify the invalid consumption of photons. Thus, the significant recombination is the main challenge limiting the STH for hydrogen generation. The (oxy)nitrides based on d⁰- and d¹⁰- type metal cations are typical VLA materials that can achieve one-step OWS. The introduction of N atom narrows bandgaps of oxides by shifting the VB maximum upwards due to the more positive level of N_{2p} than that of O_{2p} states. The nitrogen-incorporated metal oxides are generally synthesized through thermal (873–1273 K) treatment of the precursors under ammonia flow [68]. However, the reductive ammonia treatment tends to reduce the metallic cations and produce defects of low-valent metal cations. In addition, the charge imbalance between O²⁻ and N³⁻ also induces anion vacancies in the (oxy)nitrides [69]. Both the metallic defects and anion vacancies act as recombination centres to suppress charge separation, which is one main reason for the limited STH (<1%) of metal (oxy)nitrides. Another challenge needing to be solved is the backward reactions of oxygen reduction and hydrogen oxidation, which is a serious problem to decrease the STH. Noble metal nanoparticles (NPs) like Pt, Ru, Ir and Ni are common cocatalysts to promote HER, but they also accelerate oxygen reduction reaction (ORR), and the backward reactions are thermodynamically predominant over the forward reactions [60]. Thus, novel cocatalyst design is required to suppress the backward reaction but without affecting the forward reactions over the semiconductors. The third challenge is to develop highly stable VLA materials for OWS. The oxidation of N³⁻ to form N₂ and photocorrosion of

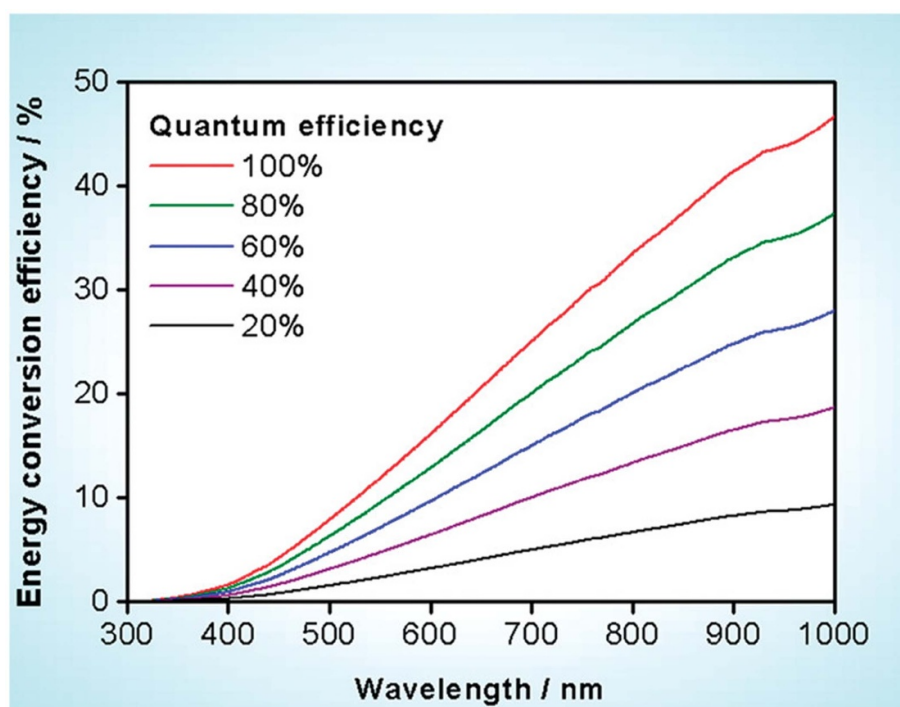


Figure 6. Energy conversion efficiency over photocatalysts under different wavelength with various quantum efficiency. Reprinted with permission from [58]. Copyright (2010) American Chemical Society.

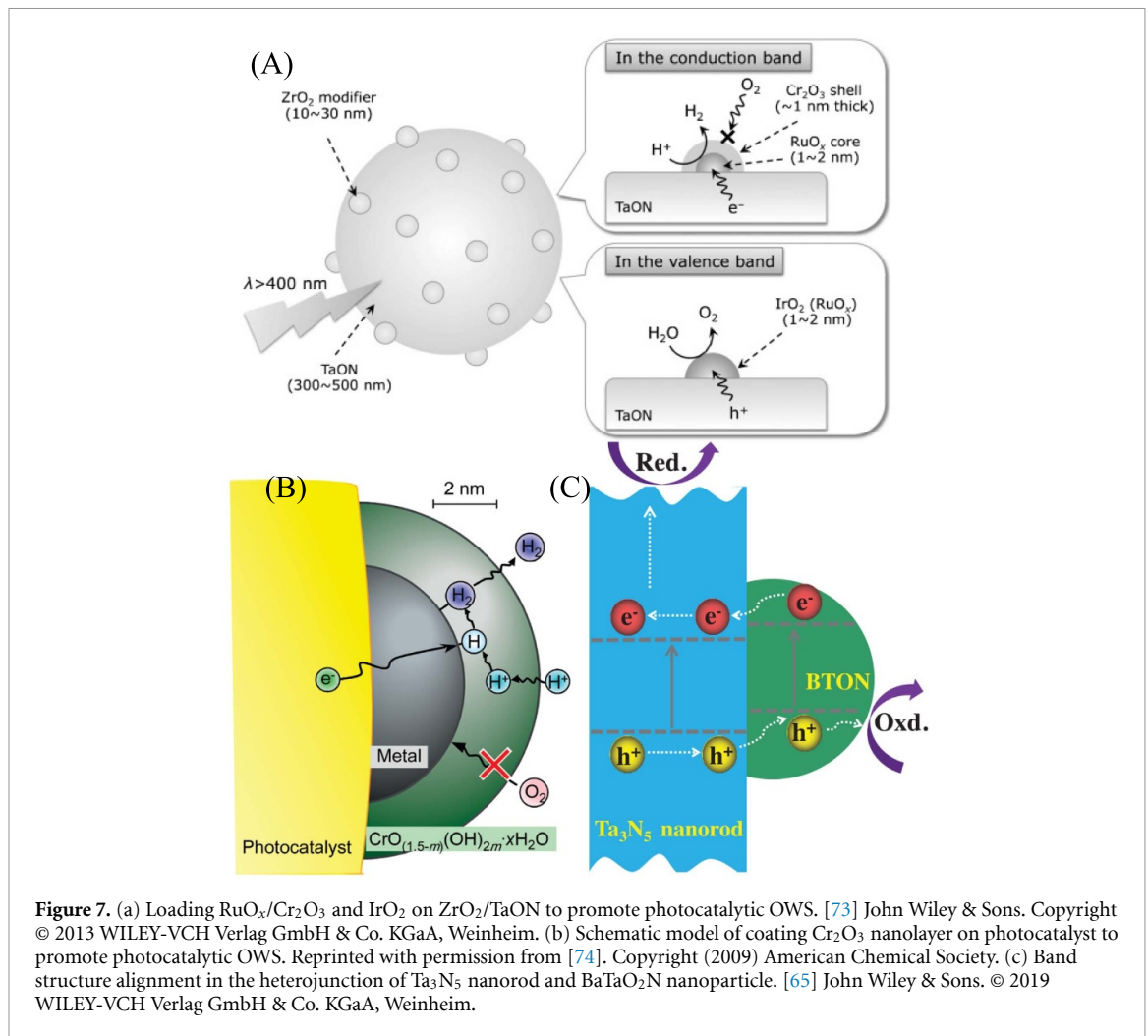
metal (oxy)nitrides was previously observed [70]. Due to the slow migration of holes and the natural lack of active sites for oxygen evolution, photogenerated holes tend to be accumulated in the defects and to induce self-oxidation, resulting a notably decreased activity upon prolonged irradiation.

Advances in science and technology to meet challenges

To meet the above challenges and increase STH, great advances have been made in the development of novel VLA materials with less defects and vacancies, design of delicate cocatalysts and fabrication of advanced heterostructures. To enhance the separation of electron–hole pairs, one approach is to synthesize crystals with less defects and vacancies. The metallic cation doping is an effective strategy to obtain metal (oxy)nitrides with decreased metallic defects and nitrogen vacancies, because the positively charged cations can compensate the charge imbalance induced by N. Incorporation of Mg atoms into Ta_3N_5 or $\text{BaTaO}_{2+x}\text{N}_{1-y}$ shows the capability to suppress the formation of nitrogen vacancies and restrain the formation of Ta^{4+} species [71, 72]. Thus, the charge separation is promoted, accordingly enhancing PC activity of OWS and suppressing photocorrosion.

Development of cocatalysts shows great potential to inhibit backward reactions and enhance STH. Both HER and OER cocatalysts deposited photocatalysts, such as $\text{RuO}_x/\text{Cr}_2\text{O}_3$ and IrO_2 loaded ZrO_2/TaON (figure 7(a)), shows the capability to accelerate OWS reactions and suppress self-oxidation [73]. A bimetallic cocatalyst of $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$, a nanolayer of Cr_2O_3 over Rh NPs has the capability to suppress backward reactions (figure 7(b)) [74]. This is attributed to that the Cr_2O_3 nanolayer in the cocatalyst can block O_2 diffusion to Rh but not limit the permeation of the generated H_2 . Design of more delicate nanolayer of cocatalysts is promising to deal with the problem of backward reaction.

Fabrication of heterostructure is an attractive way to develop novel VLA materials with enhanced performance. A heterostructure consisting of carbon nanodots and graphitic C_3N_4 shows very stable activity with the STH reaching 2%. The unique OWS mechanism involves a two-electron pathway via formation and decomposition of H_2O_2 [75]. In a type II heterojunction, electrons and holes can be separated by the potentials at the interface and delocalized to the respective hetero-components. For the heterojunction $\text{Ta}_3\text{N}_5/\text{BaTaO}_2\text{N}$ (figure 7(c)), the rate of hydrogen evolution is 16-time higher than that over BaTaO_2N [65]. In Z-scheme or S-scheme heterostructures for two-step OWS, electron transfer can either be facilitated by a solid-state electron mediator or spontaneously occur across the two components. A Z-scheme system with a high STH efficiency of 1.16% is developed by using both boron-doped C_3N_4 nanosheets, whose band positions are modulated by boron dopants and nitrogen defects [76]. Because in the two-step OWS, the



numbers of photons for one cycle of OWS is double of that in one-step OWS, and the backward reaction pathways are increased, the design of heterostructures need more considerations.

Concluding remarks

Although VLA materials has been rapidly expended, the STH in the lab-scale trials is still much lower than the requirement of 10%. More efforts should be addressed to understand elementary steps in OWS and the mechanism on relationship between the structure and performance of the photocatalysts. This need to advance operando and *in-situ* characterization as well as the theoretical simulation. Moreover, the long-term stability of these materials should also be addressed before applications, and the suppression of photocorrosion over photocatalysts should be paid more attention. Recently, a 100 m² array of panel reactors to produce hydrogen from OWS over SrTiO₃:Al runs over several months [27]. The results bring confidence to OWS that can be safely operated in a large-scale by combining with some additional functions like gas collection and separation. We believe that with the continuous advances in the novel VLA materials, we can industrialize OWS and enter a hydrogen energy society in near future.

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6. Emerging materials for PC hydrogen generation

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Status

Hydrogen energy is considered as an ideal new energy in view of its merits of high value-added and zero emission of greenhouse gas (GHG), thus developing high-efficient hydrogen generation measures has increasingly attracted extensive attention in material chemistry and energy fields. PC H₂O-to-H₂ conversion is identified as a promising strategy to achieve the conversion of solar energy-to-chemical energy with high-value due to the advantages of simple operation, eco-friendliness, and low cost, etc [77]. For instance, Domen *et al* recently achieved the solar-induced hydrogen production from water on a 100 m² scale [27]. During the past decades, a large number of traditional semiconductor materials have been served as PC materials for H₂O-to-H₂ conversion process, such as TiO₂, transition metal sulphides (TMSs), zinc compounds, copper compounds, bismuth compounds and silver compounds, etc [78]. However, the traditional semiconductor photocatalysts generally possess the defects of poor light-harvesting or weak body-to-surface photo-carriers' migration.

Aiming at the drawbacks of traditional PC materials, some emerging PC materials have been developed for highly efficient hydrogen generation, such as carbon nitride (C₃N₄) and black phosphorus (BP), etc. For instance, in 2009, Wang *et al* investigated the semiconductor characteristics of polymeric C₃N₄ as a metal-free photocatalyst with visible light harvesting capacity for hydrogen generation [79]. In 2017, Yang *et al* firstly reported the visible-light-driven H₂O-to-H₂ conversion on the BP nanosheets by using Na₂S + Na₂SO₃ as the sacrificial reagent [80]. Beyond that, some emerging non-semiconductor materials have also been extensively employed to construct high-efficient photocatalysts or improve the performance of traditional semiconductor photocatalysts for enhanced hydrogen generation photoactivity under broadband light irradiation, such as graphene, MXene, metal-organic-frameworks (MOFs), and covalent-organic-frameworks (COFs), etc. For example, Iwashina *et al* used graphene oxide (GO) as solid-state electron mediator to construct Z-schematic water splitting photocatalyst with metal sulphide [81], Zuo *et al* used Ti₃C₂T_X MXene to support the ultrathin ZnIn₂S₄ nanosheets for high solar-to-hydrogen conversion efficiency [82], Zhu *et al* reviewed the MOFs based catalysts for highly efficient HER [83], and Wang *et al* activated the carbonyl oxygen sites in β -ketoenamine-linked COFs via cyano conjugation for enhanced stable PC hydrogen generation due to the efficiently improve photoinduced charge separation and effectively decrease the energy barrier [84].

In recent years, increasing attention has been drawn to the cadmium sulphide (CdS) as an important TMS PC material for hydrogen generation under visible-light. Based on the characters of narrow bandgap (~ 2.5 eV) and low work function, it is widely used to prepare high-efficient photocatalysts or serve as co-catalyst to improve the performance of other semiconductor-based photocatalysts due to its merits of excellent visible-light harvesting ($\lambda \geq \sim 580$ nm), high-density photo-carriers generation and appropriate band structure for water splitting [85].

Current and future challenges

The current challenge of CdS based PC materials for practical application is the weak structural stability for the easy photo-corrosion under long-term irradiation, which seriously restricts its PC performance for hydrogen generation. Moreover, the toxicity of the released metal ions for TMS based nanomaterials in application also requires special attention. Therefore, extensive efforts have been devoted to suppress the photo-corrosion of CdS for acquiring excellent structural stability and enhanced HER photoactivity. For instance, Domen *et al* introduced a thin TiO₂ coating layer on the surface of heterostructured CdS-(ZnSe)_{0.5}(CuGa_{2.5}Se_{4.25})_{0.5} to inhibit the photocorrosion of CdS and suppress the backward reaction of water formation from hydrogen and oxygen [87]. Li *et al* chosen CdS NPs as cocatalyst to construct a core-shell CdS@h-BN heterostructure on reduced GO nanosheets via a structural reconstruction strategy, and 11-fold greater HER rate of bare CdS NPs was achieved under simulated sunlight irradiation [88]. However, the majority of improvements possess the obvious defects of complicated technology and high cost, which is hard to meet the standards of practical application. Therefore, more simple and effective strategies need to be developed.

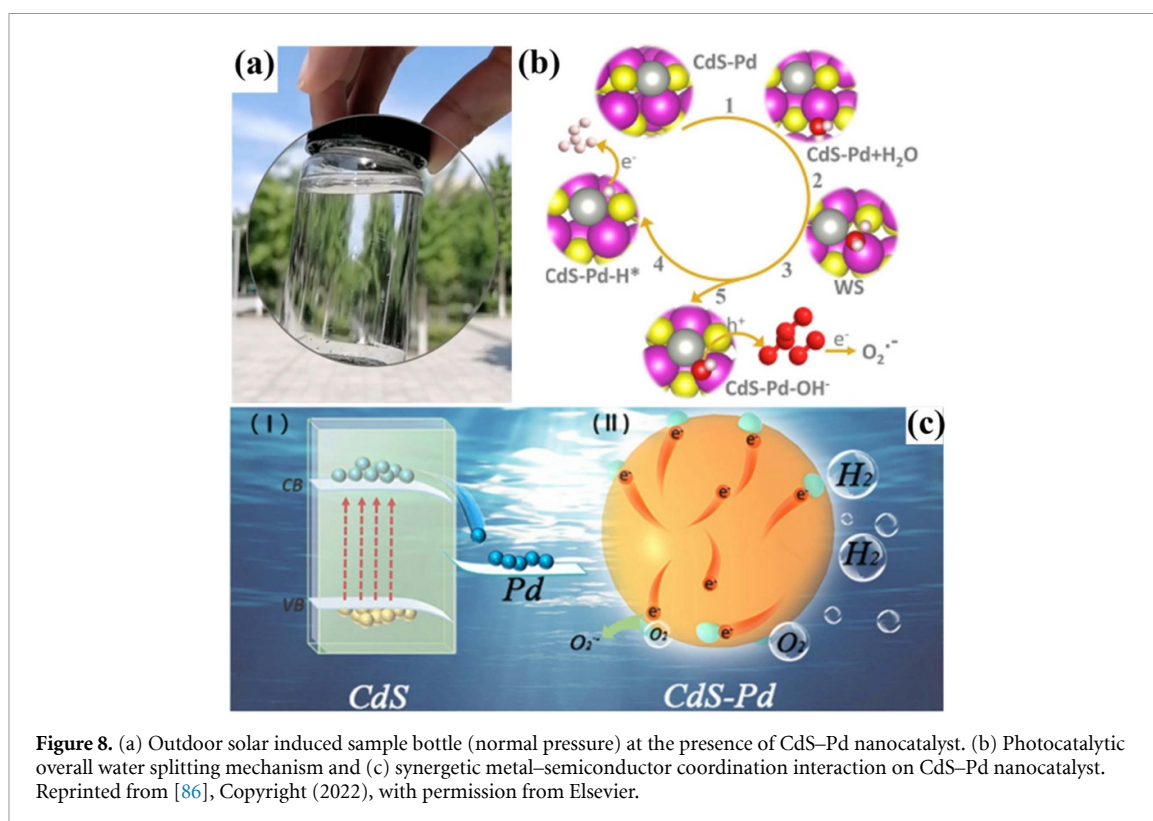


Figure 8. (a) Outdoor solar induced sample bottle (normal pressure) at the presence of CdS–Pd nanocatalyst. (b) Photocatalytic overall water splitting mechanism and (c) synergetic metal–semiconductor coordination interaction on CdS–Pd nanocatalyst. Reprinted from [86], Copyright (2022), with permission from Elsevier.

Recently, increasing efforts have been devoted to the exploitation of photocatalysts with single-atomic active sites due to the sufficient atomic exposure, high atomic utilization, unique electronic structure and unsaturated coordination environment, etc. For instance, Tiwari *et al* decorated Pd SASs on Co₂P NPs [89], and Wang *et al* loaded Ir SASs on NiO matrix [90]. Moreover, TiO₂, CdS, and C₃N₄-based catalysts were successively decorated by various metallic SASs. Notably, SASs decoration can effectively improve the HER performance and enhance the structural stability of conventional catalysts, even realizing the photocatalysis of OWS due to the synergetic host-guest interaction. To improve the PC performance of CdS PC material, the single-atomic Pt, Ru, Pd, Au etc were successively decorated on the surface of CdS-based catalysts, even the superior OWS photoactivity was achieved due to the synergetic metal–semiconductor coordination interaction.

In general, the single-atomic active sites are easily formed on the surface or in the body structure of traditional PC materials via a simple operation, but the existing challenge is how to ensure the stable existence of the single-atomic active sites in long-term activated state. After all, the single-atoms are difficult to be retained in long-term activated state due to the ultrahigh surface energy. Moreover, if the SASs improved PC materials prepared through simple operation can hold a highly efficient and stable PC OWS performance, it will possess both the theoretical and realistic significance for actual hydrogen energy production. Therefore, the great challenge is faced to seek the suitable methods to address abovementioned scientific problems.

Advances in science and technology to meet challenges

Recently, the study on the host-guest interaction have been studied extensively in heterogeneous catalysis field, and these researches indicated that the strong metal-support interaction (SMSI) can not only effectively promote the photo-carriers' migration but also obviously enhance the stability of the cocatalyst. For instance, Wang *et al* supported Au NPs on the surface of MnO to form the SMSI, which leads to the electron migration of the support onto the Au NPs to form thin overlayers [86]. If the SMSI is applied in the SASs based PC material, the stability problem of SASs is very likely to be addressed. In fact, the attempts have been carried out by some researchers. For instance, Han *et al* [91] covered Pt SASs on the surface of TiO₂ to build the SMSI. Also, Li *et al* [92] effectively stabilized the Pd SASs on the surface of hexagonal CdS NPs through the metal–semiconductor interaction (figure 8). Due to the synergetic effect of SMSI, the improved nanocatalyst (CdS–Pd) presented excellent durability and reproducibility under long-term irradiation. Moreover, the sample bottle containing a very little amount of CdS–Pd nanocatalyst gives a large number of bubbles under outdoor sunlight irradiation.

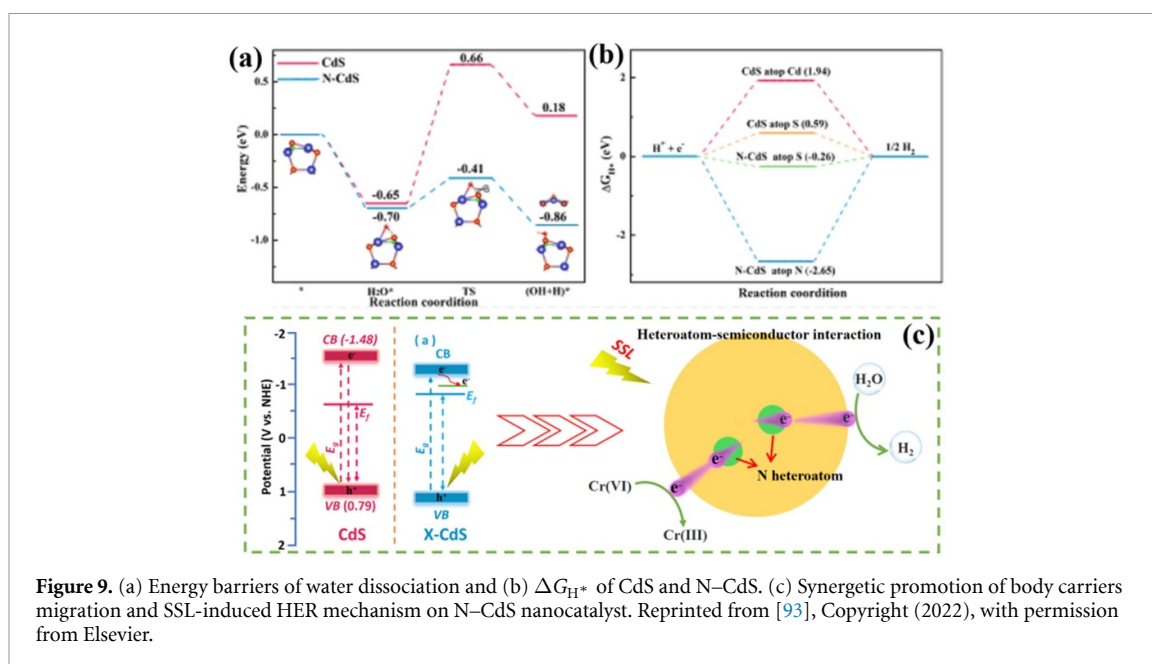


Figure 9. (a) Energy barriers of water dissociation and (b) ΔG_{H^*} of CdS and N-CdS. (c) Synergetic promotion of body carriers migration and SSL-induced HER mechanism on N-CdS nanocatalyst. Reprinted from [93], Copyright (2022), with permission from Elsevier.

Additionally, heteroatom doping is also a simple and effective strategy to promote the body carriers' migration of CdS PC material due to the synergetic electronic effect of heteroatom sites in body structure. Compared with metal doping, non-metallic atoms with high electronegativity can form strong coordination interaction with metal atoms in semiconductor, effectively modulating the band structure and improving the migration behaviour of carriers. Inspired by this, Li *et al* [93] doped N heteroatoms into the lattice of hexagonal CdS NPs to synthesize the nitrogen-doped CdS nanocatalyst (N-CdS) (figure 9). Due to the synergetic nonmetallic (N) heteroatom-semiconductor (CdS) coordination interaction, the energy barriers of water cracking and hydrogen generation on N-CdS nanocatalyst were dramatically decreased, and the body carriers' migration was significantly accelerated, thereby the highly improved HER activity can be achieved for high-efficient utilization of photo-carriers. Obviously, it suggests that the formation of synergetic nonmetallic (N) heteroatom-semiconductor (CdS) coordination interaction in body structure of CdS PC material can effectively boost the body carriers' migration and hamper their recombination, so the high HER photoactivity can also be achieved by this method.

Of course, the combination of metallic SASs surface decoration and nonmetallic heteroatom doping in body structure may also be an effective technology to improve the HER performance of CdS PC materials, but how to realize the combination may become the emerging challenge in the near future.

Concluding remarks

PC water splitting for hydrogen generation is a promising strategy to achieve the conversion of solar energy-to-chemical energy with high-value, and numerous emerging PC materials with excellent photoactivity for hydrogen generation have been developed. CdS semiconductor is indeed an outstanding material for synthesizing HER photocatalysts with high performance. The current challenge of CdS based PC materials for practical application is the weak structural stability for easy photo-corrosion under long-term irradiation, which seriously restricts its PC performance for hydrogen generation. Apparently, further improving the PC performance of CdS based photocatalyst through the simple and green strategy has theoretical and practical significance. Recently, heteroatom doping and metallic SASs surface decoration are identified as the very effective strategies to promote the body carriers' migration and body-to-surface carriers' migration due to the synergetic metal-support and heteroatom-semiconductor coordination interactions. In the future studies, the combined technology of heteroatom doping and metallic SASs surface decoration should be considered to synergistically promote the body-to-surface carriers' migration of CdS based photocatalyst for higher efficient HER photoactivity under broaden light irradiation, which may provide an insight for developing more emerging CdS based photocatalysts for achieving highly efficient hydrogen generation.

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7. PC reforming of biomass for hydrogen generation

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Status

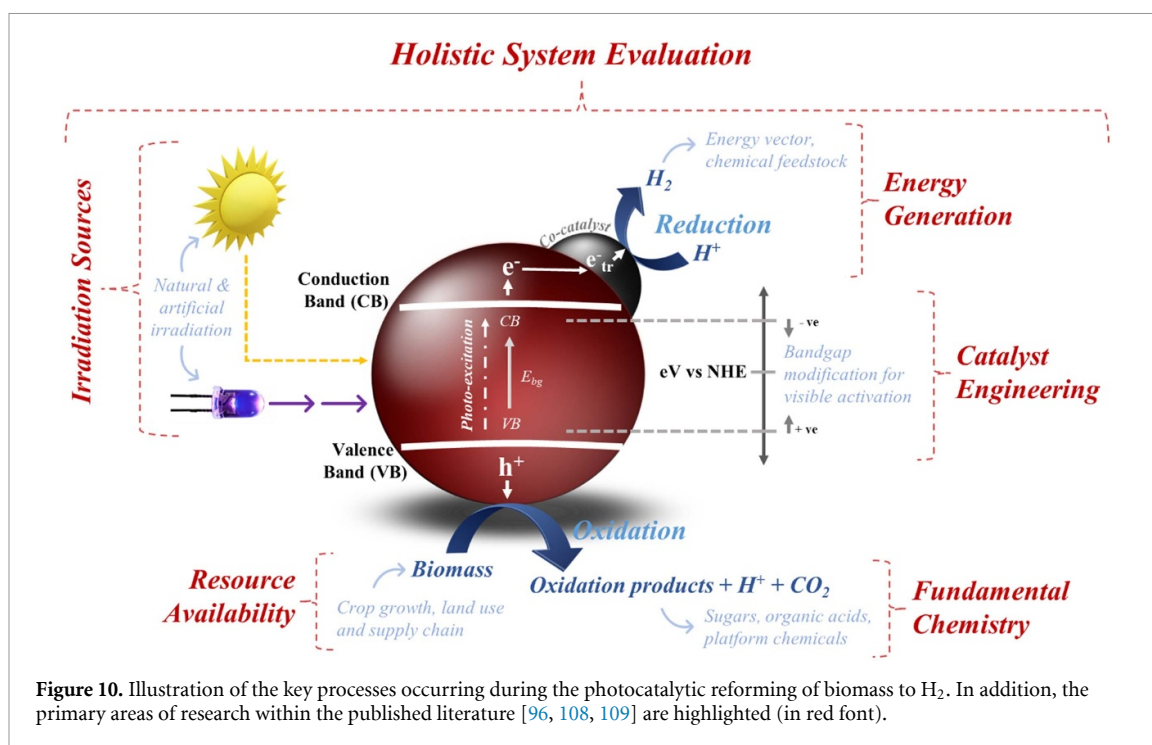
The current global energy transition towards achieving Net Zero Emission commitments has already demonstrated the importance of utilising a range of technologies to deliver sustainable energy. Moreover, hydrogen (H₂) has been identified as a vector that can support the decarbonisation of sectors which are challenging to electrify. As a route towards H₂ production, photocatalysis has been shown to have significant potential, often due to the water splitting capabilities under ambient operating conditions [27, 94, 95]. More recently, the potential to produce H₂ has been enhanced by utilising biomass as a feedstock for PC reforming to H₂ [12, 96–98]. As a sacrificial electron donor, biomass can overcome the limitations associated with water splitting such as unfavourable thermodynamics, electron–hole recombination and back reactions. On a more holistic level, however, it represents a method for valorising non-fossil fuel based feedstocks for sustainable H₂ production.

While the first report on this topic was in 1980 [99], it is only within the last 8 years that an increase in interest has been observed. An expansive and growing range of studies has demonstrated the ability to generate H₂ from both biomass-derived model compounds (e.g. sugars [96]) and raw biomass feedstocks (e.g. energy crops and lignocellulosic waste materials [100–102]), utilising both UV and visible active photocatalysts under simulated and natural irradiation [103–105]. Figure 10 illustrates the fundamental processes occurring during PC biomass reforming while also highlighting active areas of research. Within this, two core themes are catalyst engineering towards visible and solar activation (which is a dominant theme across many PC applications) and the use of lignocellulosic biomass substrates. While the mechanism is still to be fully understood, photo-reforming is thought to occur via direct and indirect oxidation promoting bond cleavage in the biomass structure using valence band generated holes and/or radicals. This subsequently promotes proton reduction via electrons at the CB to form H₂. For cellulose, the mechanism has been proposed to occur through (photo)hydrolysis of cellulose by the initial attack of OH radicals (generated from the reaction of water with photogenerated holes) on the cellulose chains generating smaller cellulose units, sugars and further oxidation products such as formic acid. The formation of such compounds could also more efficiently hinder the recombination of photogenerated e⁻ and h⁺ on the catalyst [106]. With continued optimisation, PC reforming of biomass (and biomass-derived) substrates has the potential to generate H₂ at <\$1.5 USD Kg⁻¹ [107] whilst utilising renewable energy. In that respect, it therefore can become a route for ‘green’ or low-carbon H₂ generation which can support national and international energy strategies.

Current and future challenges

Several challenges exist within PC research that are often independent of the application or deployment sector. Generally, these challenges can be separated into two areas: fundamental chemistry and technology/engineering. The former includes the overall stability, activity, visible-light responsiveness, and efficiency of photo-materials along with the impact they have on reaction kinetics (e.g. H₂ formation rate) and mechanisms at the catalyst surface (e.g. selectivity towards bond cleavage). Subsequently this may also include the cost-effectiveness and commercial synthesis of novel materials. The technology and engineering challenges are centred on transitioning from the laboratory to larger scale application and include effective reactor design which incorporates enhanced light distribution and reduced mass transfer to enable effective pilot scale studies, particularly for the use of insoluble biomass substrates. In addition, there are challenges that underpin both areas which include the use of appropriate metrics to determine efficiency, increased standardisation, and improved industrial stakeholder engagement.

Specific challenges for the development of a biomass photo-reforming process are associated with improved understanding of the fundamental chemistry of the biomass-to-H₂ mechanism. Biomass is a broad term that covers a diverse range of potential feedstocks with H₂ production already demonstrated from biomass feedstocks including grass, wood, rick husk and bagasse [101, 102, 110], however the H₂ yield varies considerably between PC systems (catalyst-reactor-irradiation source). While determination of the H₂ yield



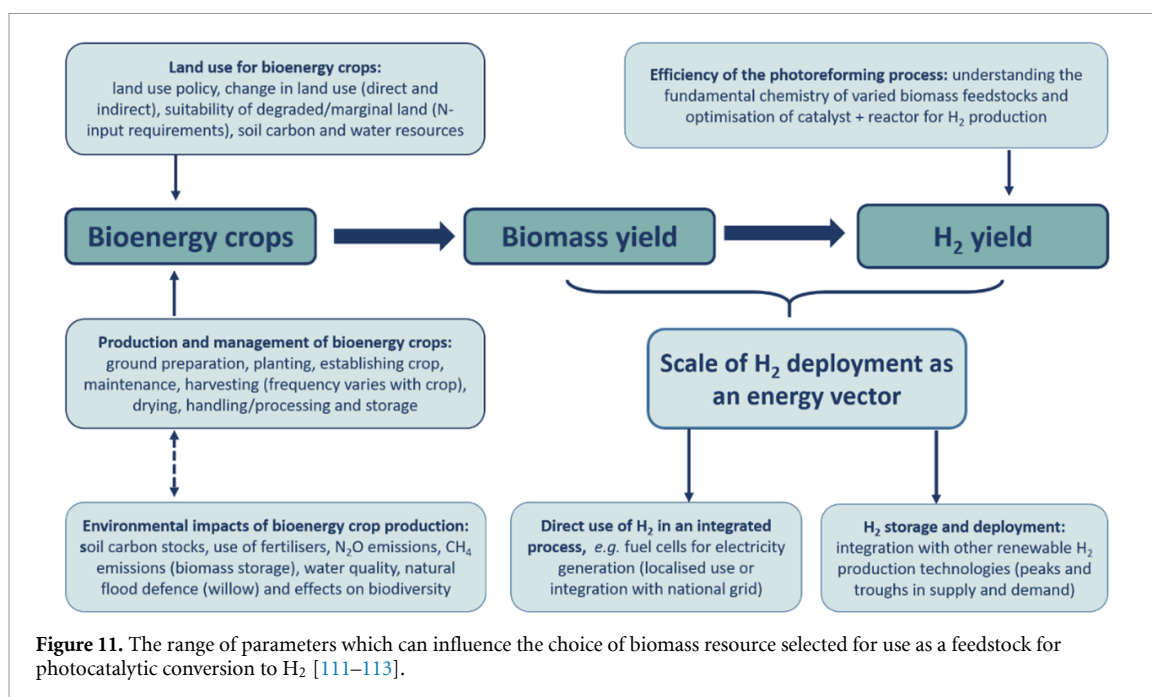
from photo-reforming of processed feedstocks (e.g. cellulose, hemicellulose and lignin) can aid development of the catalyst and reactor system, this must be coupled with comparison to raw biomass resources. The comparison of H₂ yields from processed constituents to raw biomass resources such as second-generation energy crops (i.e. short rotation coppice willow, poplar and miscanthus, currently grown commercially in the UK) as well as forestry and agricultural wastes is needed to determine and develop the overall process sustainability. Understanding the effect of varied biomass chemical compositions (i.e. lignin-to-cellulose ratio and feedstock purity) and physical properties (i.e. water content and particle size/form) on the yield of H₂ production could highlight viable resources for photo-reforming.

The potentially lower yields of H₂ generated from photo-reforming (in comparison to more established blue and green-H₂ routes), however, could influence the scale at which the technology is deployed and integrated within the bioenergy sector. Moreover, the scale of the application will also be determined by the availability of biomass feedstocks, H₂ yield and supply chain uncertainties. Therefore, an additional future challenge for development of a photo-reforming biomass-to-H₂ process would be an assessment of the efficiencies of an integrated system (i.e. environmental and economic efficiencies of the feedstock generation and the conversion process) in conjunction with the availability of renewable energy (e.g. wind and/or solar). This would be crucial to ensure a consistent and sustainable production of H₂ is achieved for deployment as an energy vector.

Advances in science and technology to meet challenges

Regarding advancing the science and technology to meet the challenges of PC biomass reforming, we can consider two streams. The first being the challenges associated with catalyst and reactor engineering to improve the overall process. The second, deploying the technology as an approach for low-carbon H₂ production. These two streams are interdependent and, therefore, must be actively researched in tandem to ensure continued advancement of the field.

As the primary drivers for the first stream are applicable to most PC applications (e.g. enhanced catalyst engineering to facilitate reactor design towards pilot scale deployment), focus here is given towards addressing the challenges for the second stream. In the development of a biomass conversion processes, key considerations for the use of bioenergy crops (or waste residues from forestry and agriculture) are land utilisation, resource management, supply chains, market dynamics and GHG emissions. The study by Whitaker *et al* has shown potential benefits in terms of GHG emissions from the repurposing of land for growing perennial bioenergy crops [111]. In conjunction with this, identifying areas of significant uncertainty (e.g. supply chains and processing of biomass [112]) can highlight benefits and risks in developing an efficient biomass-to-H₂ process from crop cultivation through to H₂ production and utilisation.



An overview of some of the key considerations and impacts of bioenergy crops as resources for PC H₂ production are outlined in figure 11. It is evident that with such diverse parameters influencing the yield of energy crops, there must be cohesion and alignment between the selection of biomass resources and PC technology. Moreover, there is justification that this should be a current research priority as it can influence both the design of catalysts and reactor systems (for enhancing light distribution and mass transfer with insoluble substrates) with a view towards being tailored to a specific resource and required scale of H₂ production. To date, however, there are no studies reported in the literature which have determined the impact of such parameters on the PC formation of H₂ from biomass.

In view of a more holistic evaluation of PC biomass-to-H₂ systems, advances must also be made in technology integration and whole systems analysis. Specifically, this should include Life Cycle Analysis and Techno-Economic Analysis to ascertain the feasibility of generating H₂ from PC biomass reforming. Within this, coupling PC technology with renewable energy such as wind and solar should be validated by using appropriate metrics such as Global Warming Potential (e.g. kg CO₂ eq) and levelized cost of H₂ production. In doing so this will encourage greater engagement with industry which can facilitate the technology readiness level of photocatalysis increasing towards pilot scale deployment.

Concluding remarks

While the non-selective nature of photocatalysis is often a beneficial characteristic for valorisation and remediation, for photo-reforming (to H₂ production), that does not necessarily translate to meaning a comparable H₂ yield would be obtained from biomass compared to bio-derived SEDs (i.e. organic acids and sugars). With incentives predicted to increase towards technologies that can produce low-carbon H₂, PC biomass reforming will continue to gain interest within the next decade. Unlike other photocatalysis applications, however, this topic could be substantially influenced by resource availability and management. Therefore, it is vital that while core research is conducted on catalyst and reactor engineering to enhance H₂ yields, simultaneously this must be coupled with research on understanding how parameters associated with energy crop growth can influence this process. In doing so, this will provide a platform for photocatalysis to be assessed as a technology that can be incorporated into a distributed energy system capable of achieving Net Zero Emission targets.

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8. Reactor engineering for PC hydrogen generation

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Status

Photocatalysis is an emerging technology for chemical processes. Fujishima and Honda introduced it as a concept, in the early 1970s. These researchers pioneered water splitting for hydrogen generation [114]. Following this work, in 1974, Carey *et al* proposed the use of photocatalysis for the degradation of organic pollutants in water [115]. These preliminary photoreactor designs were limited to the purification of polluted water, and involved suspended TiO₂, whether doped or not, under UV irradiation. Nowadays, these designs have evolved into more advanced photoreactors (e.g. Batch and Continuous Stirred Tanks) operated under different conditions [116]. For instance, some of these new designs allow solid–liquid or solid–gas phase enhanced interactions, using different types of light sources (e.g. UV or visible). These reactors manage large ranges of temperatures, pressures, compositions, and pHs. Despite of these advancements, there are still challenges for hydrogen production in PC reactors including their ability to provide (a) homogeneous and uniform irradiation throughout the reactor volume, (b) high mixing of the semiconductor slurry, interacting efficiently with photons [117], and (c) high photon absorption promoting e⁻/h⁺ pair formation. New designs should also include carefully selected (a) irradiation sources, (b) light source placement, and (c) photocatalyst state, either fixed or suspended [116]. Furthermore, and for widespread hydrogen production, it is felt that the following are needed: (a) environmentally friendly and cost-effective photocatalysts [118], (b) established protocols for photon efficiency utilization evaluations, (c) simple designs operated at room temperature and pressure, to facilitate their operation by low skilled technical personnel. It was with these objectives in mind, the Photo-Chemical Reactor Engineering Centre (CREC) water-II reactor (PCW-II) (refer to figure 12) was developed at CREC-UWO. The PCW-II is a laboratory scale reactor that involves a concentric cylindrical geometry with a lamp placed at the centre of the unit, providing radial and axial symmetrical irradiation. The PCW-II operates at room conditions with high slurry mixing, free of semiconductor-fluid mass transfer limitations [119]. The PCW-II was designed to be employed for the development of kinetic models and macroscopic radiation balances. This unique unit described for the first time by CREC-UWO researchers [116], provides a rigorous assessment of photocatalyst performance using both QYs and thermodynamic efficiency factors (PTEFs). It is anticipated that PC reactors such as the PCW-II, validated with QYs and PTEFs, will assist in the development of suitable designs for widespread hydrogen production, at various reactor scales for households, towns, and cities worldwide.

Current and future challenges

While PC reactor engineering is valuable, it is one of the least studied subjects in hydrogen production. Most of the published articles, focus on new semiconductor synthesis [11, 120] and their performance. There are limited studies addressing reactor designs with high fluid-semiconductor mass transfer and optimized photon absorption. It is our view that these matters, are essential for the implementation of promising reactor configurations [121].

Reactor configuration assessments

The engineering of PC reactors must be developed to make possible future commercial applications. Reactor enhancements could include (a) construction materials, (b) geometries allowing maximum radiation absorption, (c) light sources and light source positioning, (d) flow patterns and residence times [27]. For instance, one can consider the PC reactors most used for hydrogen production, which include either slurry or packed-bed units. If not properly designed, these photoreactors may display uneven radiation and mass transfer limitations, and other issues such as deficient photocatalyst recovery and poor *in-situ* regeneration.

Kinetic rate equation analysis

The development of kinetic models requires experimental data describing the chemical species changes with irradiation time [117]. Furthermore, a good kinetic model should be based on applicable assumptions (i.e. a well-mixed condition). With the proposed approach, kinetics could be established under desirable conditions, including sunlight irradiation, and close to room temperature and pressure. It is expected that photoreactors with high photon absorption and with the special ability to lead to trustable kinetics, will provide a benchmark for self-sustainable hydrogen production [122, 123].

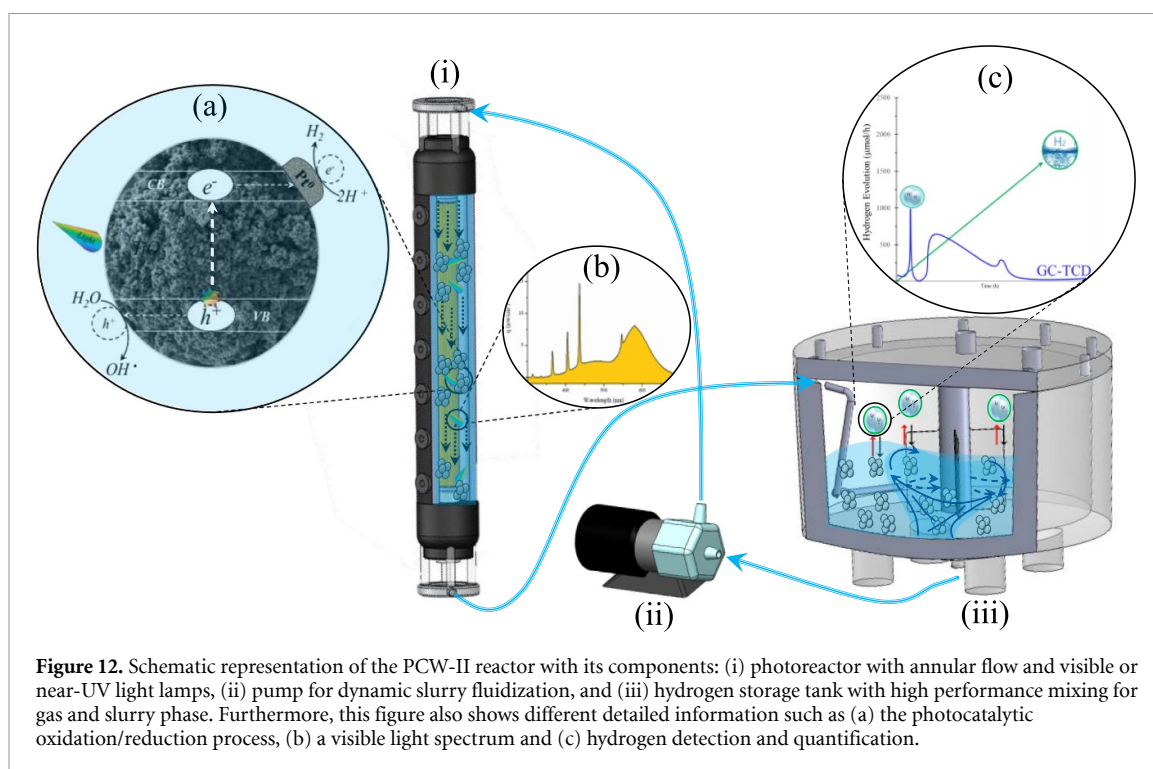


Figure 12. Schematic representation of the PCW-II reactor with its components: (i) photoreactor with annular flow and visible or near-UV light lamps, (ii) pump for dynamic slurry fluidization, and (iii) hydrogen storage tank with high performance mixing for gas and slurry phase. Furthermore, this figure also shows different detailed information such as (a) the photocatalytic oxidation/reduction process, (b) a visible light spectrum and (c) hydrogen detection and quantification.

To understand the significance of PC reaction rates for hydrogen production, it is important to emphasize the importance of kinetic evaluations and modelling. This can be done through the establishment of redox networks based on sound principles and the accounting of (a) light irradiation, (b) chemical species concentrations, (c) temperature and (d) pH [124]. It is also important to establish redox reaction networks and carbon balances to accurately quantify hydrogen and other formed organic scavenger intermediate species. Reaction networks could also assist in the calculation of the consumed OH^\cdot radicals, at every stage of the irradiation period. This allows the calculation of QYs and photo thermodynamic efficiency factors (PTEF) based on OH^\cdot radicals consumed and photons absorbed, as high as 1.45% for visible light [123]. These experimental studies could produce large datasets for computer simulations, which could also help in reducing the photoreactor design time, facilitating the scaling-up from pilot to industrial size units for hydrogen production.

Advances in science and technology to meet challenges

Developing photoreactors requires adequate and representative mathematical models (i.e. kinetics rate and radiation), as well as intensive computer simulations. These models should be validated with the data obtained from experiments such as, the detection and quantification of individual chemical species and their changes with irradiation time. Chemical species should be measured as individual entities, or as lumps using total-organic carbon. In addition, these data will require irradiation information at various reactor positions. Experimental data should be compared with CFD computations for parameter model optimization. Moreover, experimental data should be analysed using machine learning (ML). A combination of CFD and ML approaches would assist in (a) describing the chemical species produced via redox reactions, (b) establishing the spatial distribution of radiation, and (c) validating the postulated predictive models.

Advanced analytical instrumentation

Standard analytical testing requires high precision detectors for quantification of chemical species. Chemical species measurements can be made by using combined gas chromatography and mass spectrometry (GC-MS), high-pressure liquid chromatography (HPLC), Raman spectroscopy and other methods. These advanced analytical techniques are essential for both the proper identification and quantification of products (i.e. hydrogen and organic scavenger derived chemical species (see figure 13(a))) [125]. Furthermore, the determination of irradiation densities at various reactor locations, requires high precision scanning photometric detectors that provide rapid and precise spectra analysis. All these methods will help to build chemical reaction mechanisms and kinetic reaction rate models that include irradiation, intrinsic reaction and adsorption phenomena.

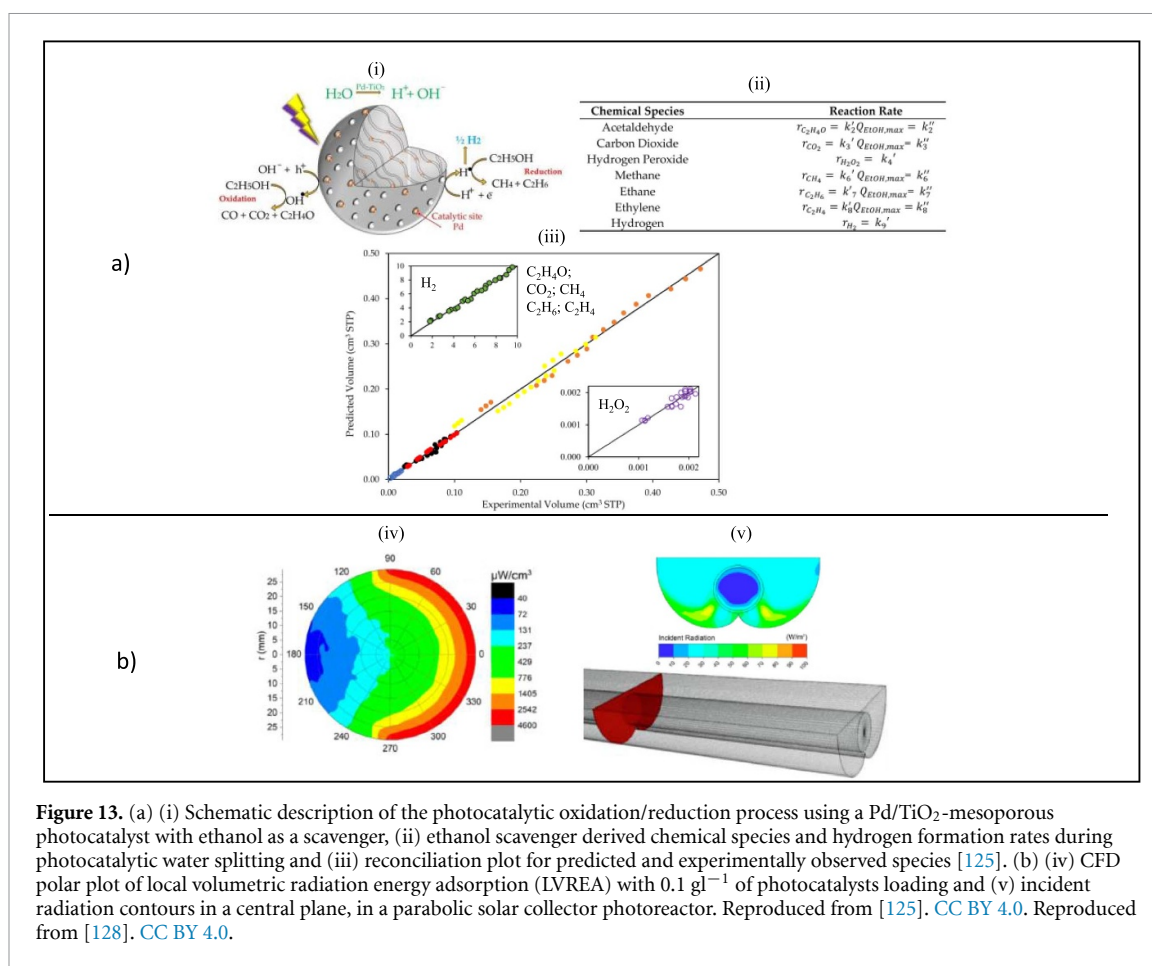


Figure 13. (a) (i) Schematic description of the photocatalytic oxidation/reduction process using a Pd/TiO₂-mesoporous photocatalyst with ethanol as a scavenger, (ii) ethanol scavenger derived chemical species and hydrogen formation rates during photocatalytic water splitting and (iii) reconciliation plot for predicted and experimentally observed species [125]. (b) (iv) CFD polar plot of local volumetric radiation energy adsorption (LVREA) with 0.1 gl⁻¹ of photocatalysts loading and (v) incident radiation contours in a central plane, in a parabolic solar collector photoreactor. Reproduced from [125]. CC BY 4.0. Reproduced from [128]. CC BY 4.0.

Computational fluid dynamics (CFD) and machine learning (ML)

For the evaluation of proposed photoreactor designs, combined CFD and ML techniques are advisable. Validated CFD models and trustable experimental data could complement each other, assisting in the simulation of photoreactors for hydrogen production, using optimized QYs and PTEFs. Once this laboratory phase is completed, reactor scale-up could be addressed via CFD with a reliable kinetic-radiation model [126–128]. CFD would provide flow patterns, radiation and chemical species distributions and reactor performance (see figure 13(b)). In this respect, by evaluating new designs with the proper instrumentation and data acquisition, large databases could become available, for ML applications [129, 130]. ML (i.e. artificial neural networks, nonlinear, random forest, and decision tree regression models) would allow the identification of major data patterns, and the acquisition of model parameters. ML would reduce the development time of the most promising designs, allowing effective scale-up of photoreactors for hydrogen production.

Concluding remarks

Photocatalysis for hydrogen production is a promising sustainable technology. There are, however, still significant issues, to make it viable and compatible for household, town, and city applications. For instance, the development of reaction models for the evaluation of possible photoreactor designs, using CFD and ML are still pending issues. To accomplish this, analytical instruments including GC-MS, HPLC, Raman spectroscopy should be adapted for the detection and quantification of organic scavenger derived chemical species. In addition, applicable reaction models are required for the establishment of reliable kinetics, consistent with postulated reaction mechanics [117, 125]. These kinetic models should be studied and developed to lead to PC reactor operations with high QYs and PTEFs. Thus, and to achieve this, accurate assessment of macroscopic energy balances and maximum photon absorption are also pressing issues. Furthermore, the use and incorporation of both CFD [131] and ML [129] models validated with large experimental datasets are essential for the optimization of model parameters. It is our belief that experimental data obtained in laboratory scale reactors such as the PCW-II, with high QYs and PTEFs, could be integrated very effectively with CFD and ML computer technologies to set the foundation for highly efficient scaled-up photoreactors for hydrogen production.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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