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Sustainable Development Approach Of Green Hydrogen From Photocatalytic Process

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ABSTRACT: Green hydrogen is a promising technology for sustainable energy production, with photocatalytic water splitting offering several advantages over wind/solar-powered water electrolysis. The focus of this review paper is on high-performance photocatalysts, which are key to improving the efficiency of photocatalytic hydrogen production. First, the general principles of photocatalytic hydrogen production and the factors affecting photocatalytic performance are summarized. Then, the conventional semiconductor photocatalysts including methods to improve their catalytic activities are comprehensively reviewed, which is followed by a detailed discussion of representative nano-photocatalysts. The performance of photocatalysts is affected by various factors, such as optical absorption, separation and transport efficiency of photocarriers, and redox capacity. The entire process of photocatalytic hydrogen production can be optimized through methods such as element doping, cocatalyst location, morphology adjustment, and heterojunction construction. Finally, photocatalysts of different dimensions, along with the challenges and future research directions, are summarized based on comparisons of numerous studies. This review provides a quick start guide for investigating the application of high-performance photocatalysts in green hydrogen production from photocatalytic hydrolysis, and offers insight into the latest advancements in photochemical conversion efficiency. It also provides a valuable reference for selecting nanomaterials and optimizing photocatalytic hydrogen production.

KEYWORDS- green hydrogen, photocatalyst, sustainable, development, photocarriers

I.INTRODUCTION

Energy security concerns require novel greener and more sustainable processes, and Paris Agreement goals have put in motion several measures aligned with the 2050 roadmap strategies and net zero emission goals. Renewable energies are a promising alternative to existing infrastructures, with solar energy one of the most appealing due to its use of the overabundant natural source of energy. Photocatalysis as a simple heterogeneous surface catalytic reaction is well placed to enter the realm of scaling up processes for wide scale implementation. Inspired by natural photosynthesis, artificial water splitting's beauty lies in its simplicity, requiring only light, a catalyst, and water. The bottlenecks to producing a high volume of hydrogen are several: Reactors with efficient photonic/mass/heat profiles, multifunctional efficient solar-driven catalysts, and proliferation of pilot devices. Three case studies, developed in Japan, Spain, and France are showcased to emphasize efforts on a pilot and large-scale examples. In order for solar-assisted photocatalytic H₂ to mature as a solution, the aforementioned bottlenecks must be overcome for the field to advance its technology readiness level, assess the capital expenditure, and enter the market. We recently automated laboratory scale reactor, and two pilot devices: A panel photocatalytic array and a compound parabolic collector (CPC). The reasoning is to highlight the international efforts toward improving laboratory photocatalytic systems and the transition into pilot and large-scale processes. The first step toward large-plants, however, is the development and refinement of effective PC devices capable of promising performance on the pilot scale.[1,2,3]

Considerations of the complexities of benchmarking and effective engineering challenges in developing lab-scale PC materials was addressed in our recent work designing and constructing a compact automated stainless steel reactor, of 40 cm³ of volume.^[41] H₂ photoproduction and quantum yields exhibited onefold- to twofold increases when compared to literature equivalent materials. This result emphasizes that reactor geometry and configuration setup play a key role in the performance of PC materials and reveals insights into ideal (minimal losses) heat/mass/photonic profiles.

An unprecedented 100 m² arrayed panel system led by Professor Domen, comprising 1600 units has been recently launched at Kakioka Research Facility at the University of Tokyo.^[44] This system design has achieved 0.76%



solar-to-hydrogen (STH) conversion, similar to ideal lab scale efficiency, $\approx 1\%$ STH. The configuration attractiveness relies in being simple, cheaper, and more amenable to scale-up compared with solar cells and/or electrolysis systems. Each panel plate was sprayed with a modified aluminum-doped strontium titanate photocatalyst layer, one of the most efficient photocatalysts to date.^[45] The highlight of this panel array is its H_2 recovery after several months of continuous operationality, starting with a moist gas product mixture, and H_2 capture with a polyimide membrane.

Another pilot device for solar H_2 generation and removal of wastewater pollutants was tested at Plataforma Solar de Almeria.^[46] This setup consists of a CPC, which is a reactor type enabling highly efficient solar photon collection. Two materials were tested, Pt/(TiO₂-N) and Pt/(CdS-ZnS), with the former outperforming the latter in combination with two sacrificial electron donors: formic acid and glycerol. This system evidences other proof-of-concept of H_2 production, though this time using municipal wastewaters, enabling simultaneous waste water depollution and energy vector generation.

Though several photocatalytic WS prototypes are available, their efficiency is still low ($< 1\%$). From a photochemical process perspective, reactor design and process optimization are needed to make this technology viable and feasible on a relevant scale. Furthermore, from a materials science perspective, higher-performing photocatalysts with better stability and H_2 production efficiency (5–10% STH) are needed for economic viability.

Public and private partnerships are proliferating internationally to tackle these bottlenecks; The Green Deal (European Union) in particular is investing a significant amount into finding tangible renewable solutions. By maturing solar-assisted photocatalytic H_2 technologies on a pilot scale, like in the three case studies, the proof-of-concept stage can be bypassed and thus enable the new chapter of TRL acceleration. The innovation of advanced H_2 pilot devices in the next half-decade will be key to unlocking new engineering advances for large-scale that may foster both the commercialization of H_2 from solar-fueled photocatalysis across the global market and the circular economy (while decarbonizing with clean energy).

For solar scale up reactor design and dimensional technological transfer analysis, we propose a (non-exhaustive) list of parameters extracted from the selected case studies to implement in higher TRL projects, essentially in four axes: operational, photonic, mass, and heat transfer profiles. We suggest such considerations with the intention that WS PC pilot devices proliferate and unlock further technological barriers.[4,5,6]

Operational considerations include quantification of H_2 (data acquisition) within an integrated on-line analytical equipment (gas chromatography) to reduce operational costs in human resources—which is essential for scaling up to TRL ≥ 3 (pilot prototypes). Reactor components should have resistance to pH, corrosion, and exposed environmental conditions. Furthermore, components must be easy to handle and accessible (with a modular assembly design providing an optimal solution to this point), and finally low-cost (low CAPEX and OPEX). Photonic considerations for catalyst activation focus on efficient photon capture and distribution, with suitable geometry to maximize collected light, suitable light absorbing materials, and maximizing use of the solar spectrum. Mass transfer considerations facilitate adsorption–desorption interactions, for example the reactor must guarantee minimal pressure from the gas flow, ensure suspended particle homogeneity in the contained volume, and avoid creation of pronounce vortexes of sufficient agitation to disrupt processes. Heat transfer considerations include the use of recirculating chillers directly in the path of the light source or inside the reactor (but not in contact with the particle dissolution) to guarantee a constant temperature, ideally of 20 °C, to avoid thermal catalysis contributions.

Ultimately, for large-scale setups, the inclusion of wastewater and or organic pollutants as for substrate source and electron or proton donors or so-called sacrificial agents, respectively, should not be negligible while planning of building the plant. Contrarily, optimal processes envisage the simultaneous reuse of one of source (wastewater)—resulting in the production of decontaminated (of organic pollutants) water and concomitant generation of energy solar carriers.[7,8,9]



II.DISCUSSION

Photocatalytic hydrogen production from water and renewable feedstocks is gaining tremendous attention as a potential standalone process for efficient energy production. In this Review, the crucial effect of the cocatalyst and the sacrificial agent are critically discussed and the recent progress on the development of novel photocatalysts is presented with particular attention to organic and hybrid organic/ inorganic materials.

A variety of process technologies have been proposed so far including thermal chemical, chemical, biological, electrolytic, photoelectrolytic, and photocatalytic processes. These processes make use of carbon feedstocks (fossil fuels, biomass, wastes) or water as H-source.² Currently, the vast majority of H₂ is produced from natural gas through the steam reforming of methane (SRM), a process which is followed by the water-gas shift reaction (WGS) making use of the produced CO in the first step to maximize H₂ production.³ However, this approach cannot be considered sustainable owing to the limited availability of fossil fuels and the production of CO₂, a major GHG that contributes to the global warming. Most of the methods mentioned above require high pressures and temperatures, the application of an external bias or the use of non-renewable H₂ source. Amongst them, photoassisted processes making use of solar irradiation and H₂O or potentially renewable feedstocks present obvious advantages and have gained significant attention over the last years. Recent studies have shown that H₂ production using solar light driven approaches are potentially competitive compared to conventional methodologies based on non-renewable resources.⁴

Since the pioneering work of Honda and Fujishima in 1972 which demonstrated photoassisted electrochemical water splitting (WS) into H₂ and O₂,⁵ various approaches and photocatalysts have been applied for solar light driven catalytic H₂ production. Among these methods, photocatalytic H₂ production from water, operating under ambient conditions (pressure, temperature), is the most attractive and challenging. This approach correspond to a stand-alone process that harvests and stores solar energy into chemical energy. As an alternative process to pure WS, photoreforming makes use of oxygenated organic substrates and solar energy. In this case, when bio-available oxygenates are used as sacrificial agents, the method is considered to be close to a carbon-neutral process since the produced CO₂ can be converted again into biomass through plant photosynthesis. The entire sustainability strongly depends on the origin of the organic substrate, i.e. non sustainable first generation biomasses or attractive second/next generation biomasses.⁶

The importance of photocatalysis in H₂ production has been expressed by the fast growth of literature reports including reviews. The WS reaction has been reviewed extensively⁸ while the photoreforming process is less documented.^{7, 9} The present Review is a comprehensive, systematic, and up-to-date review, outlining the effect of the sacrificial agent and the cocatalyst used, presenting the advantages on the field in terms of novel photoactive materials and discussing the rationalization of the key parameters controlling activity. A brief introduction on the elementary steps of photocatalytic reactions will be given. The photoreforming process using oxygenates, carbohydrates and wastes, will be reviewed since pure WS or the use of sacrificial agents simple for charge consumption are more straightforward processes. The effect of using different organic substances on H₂ production will be critically discussed. Considering that recent developments in novel synthesis strategies allowed discriminating the effect of key materials properties on activity, herein the crucial effect of the cocatalyst will be critically analyzed. Finally, the recent progress related with the photocatalyst development will be discussed with particular attention to novel organic and hybrid organic/ inorganic photocatalysts.

A chain of events must take place in order to guarantee the occurrence of a photocatalytic reaction in the presence of a semiconductor (SC). These are summarized for both pure WS and photoreforming process under anaerobic conditions. The first and most crucial step is light absorption and the formation of charge carriers (electron and hole pairs, e⁻/h⁺). Preferentially e⁻ and h⁺ formation should take place under solar light irradiation making use of the visible region of light. When a SC is exposed to light irradiation of energy higher than its band gap energy (E_g), e⁻ from the valence band (VB) are excited to the conduction band (CB) leaving behind h⁺. The photogenerated e⁻ and h⁺ can follow several paths. Bulk and surface recombination can occur releasing heat, hindering activity. Once separated and transferred on the surface of the catalyst, these e⁻/h⁺ pairs are able to perform reduction and oxidation reactions.[10,11,12]

The realization of a specific reaction is strictly related to the actual band structure of a SC. The CB and VB edge potentials define the reduction and oxidation ability of e⁻ and h⁺, respectively. In the case of H₂ photoproduction, the bottom of the CB must be more negative than the H⁺/H₂ redox couple (0 V vs. NHE, pH 0). In the WS process, in order for the oxidation half reaction to occur the top of the VB should be more positive than the oxidation potential of



O₂/H₂O (1.23 V vs. NHE, pH 0). Therefore, the theoretical minimal E_g for WS is 1.23 V. In practice this value rises to 2.0–2.4 eV, owing to kinetic overpotentials and energy losses during the process. In terms of thermodynamics, the WS reaction is an uphill reaction as evidenced by the large positive charge in Gibbs free energy ($\Delta G^0=+237.2 \text{ kJ mol}^{-1}$). This is attributed to the endothermic oxidation half reaction, which is however essential for the overall process providing protons and e⁻ for the reduction half reaction. The highly demanding oxygen evolution reaction is the bottleneck of the pure WS reaction since there are few narrow E_g materials that can catalyze both half reactions. Notably, working at neutral pH or pH>0 is thermodynamically more challenging due to the lower proton availability.

III.RESULTS

Green Hydrogen emerges as a promising energy solution in the quest for achieving Net Zero goals. The application of particulate semiconductors in photocatalytic water splitting introduces a potentially scalable and economically viable technology for converting solar energy into hydrogen. Overcoming the challenge of efficiently transferring photoelectrons and photoholes for both reduction and oxidation on the same catalyst is a significant hurdle in photocatalysis. In this context, we introduce highly efficient crystalline elemental boron nanostructures as photocatalysts, employing a straightforward and scalable synthesis method yield green hydrogen production without the need for additional co-catalysts or sacrificial agents. The resulting photocatalyst demonstrates stability and high activity in H₂ production, achieving over 1 % solar-to-hydrogen energy conversion efficiency (>15,000 μmol. g⁻¹.h⁻¹) during continuous 12-h illumination. This efficiency is credited to broad optical absorption and the crystalline nature of boron nanostructures, paving the way for potential scale-up of reactors using crystalline boron photocatalysts.

Considering the prevalent use of fossil fuels, the increase in the amount of combustion emissions in the atmosphere, and the weather-dependent reliability of renewable sources (e.g., wind power plants), there is a need for emissionless fuel with a high energy density; the search for such nonfossil-based power sources is a top priority within the scientific community. In this context, hydrogen, whose production is powered by renewable energy without direct CO₂ emission (often referred to as green hydrogen), could become one of the alternative fuels of the future due to a high gravimetric energy density of 122 kJ g⁻¹. (1,2) This could be a viable alternative to traditional energy storage methods for electrochemical batteries. In order to reach carbon neutrality in energy systems, the global production capacity for green hydrogen must increase by several orders of magnitude in the next decade. (3) This is a massive challenge, scientifically, technically, as well as politically.[13,14,15]

Hydrogen today is produced by the reverse Sabatier reaction (using direct steam reforming and/or water gas shift reaction, etc.) by stripping the hydrogens from fossil methane gas. This is not sustainable and produces CO₂ in the process.

Conventional electrolysis of water splitting into oxygen and hydrogen gases is a clean and nonfossil method, but the use of massive noble metal electrodes makes it expensive.

Currently, the main process on the industrial scale is electrolytic hydrogen production by water splitting. Today, the electrical power for H₂ production by water electrolysis comes mainly from nonrenewable fossil fuels, even in developed countries. If we address the question of the source of electrical power, electrification today is mostly based on fossil fuels, and then electrolysis is also fossil fuel-related and -dependent.

Furthermore, the main cocatalysts used therein, such as platinum, are often costly or toxic. (4,5) For these and many other reasons, looking for other effective alternative components for an environmentally friendly and fully renewable technology is necessary.

Direct photocatalysis has the advantage of directly utilizing solar energy, making it more ecologically valuable in remote places and small-scale applications. Today's drawback is that the overall conversion efficiency from "light energy converted into stored chemical energy" of direct photocatalysis is still lower than the indirect conversion using high-efficiency photovoltaics and subsequent electrocatalysis. That is scientifically a grand challenge to make direct photocatalysis more efficient. Many papers, books, and reports have been published in the last 50 years on the topic of "artificial photosynthesis". (2,6–9)

Prevalently, molecular-based H₂-evolving systems are multicomponent. Arguably, the development of the photosensitizer is a considerable research challenge as it plays the important role of capturing initial solar irradiation and consequent photoexcited electron transfer through the system to a photochemically unreactive substrate. In the



view of light harvesters, inorganic semiconductors (transition-metal oxides or hydroxides and their derivatives); (10,11) organic polymeric semiconductors; (12) graphitic materials; (13) metal–organic frameworks with photoresponsive metal ions surrounded with organic ligands; (14) organic dyes; (15) and organometallic complexes are several established divisions. (16,17) The value of the photosensitizer increases with the abundance of the material, good photostability and stability in neutral aqueous media, efficient working, and competitive cost. (17,18)

Biological photocatalytic processes like natural photosynthesis evolved over billions of years, resulting in the Calvin cycle combined with effective photosensitizer/photon converter photosystems (PS1 and PS2). For efficient photocatalysis, the active molecule should harvest as many photons in the visible region as possible. (19) This property is tunable in organic molecules via highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) band gap engineering to fit the electrochemical window for a given process. Systems like TiO₂ (3.2 eV band gap, UV-light irradiation) are much more challenging to modify to achieve a band gap alteration. (20) Eosin Y is frequently used as a photosensitizer, although its fast photodegradation causes problems. (15,21)

Alloxazines have attracted our attention as a part of the flavin family. Flavins are present in most biological systems, which take on diverse roles, from photosynthesis (22) to soil detoxification. (23) One outstanding example is vitamin B2, riboflavin, (24,25) which contains the isoalloxazine tautomeric core. The change in visible light absorption has been achieved by fusing aromatic molecules to the pteridine moiety or substituting the nitrogen atoms (see Figure 1). (26,27) While isoalloxazines are more frequent, the alloxazine isomer has superior photostability and a more straightforward synthesis. A previous study (28) showed the variability of optical, electrochemical, and morphological properties of alloxazine derivatives. This property was applied by Golczak et al. (29) in a fluorescence microscopy study of human red blood cells. Presently, flavins are used for the photocatalysis of various oxidative reactions—the preparation of sulfoxides (30) or some cycloeliminations. (31)

Our experiments demonstrate the use of a novel flavin derivative acting as a photosensitizer compared to Eosin Y for water splitting and HER. The system works with the highest efficiency when the concentration of the FP is 0.5 mM. The optimal cocatalyst K₂PtCl₄ ratio was determined to be 1:6. This system was capable of continuous hydrogen production without a significant decline over 18 h, indicating sufficient photostability and reproducibility by repeated measurements. Moreover, we have proved that the system can work even under low irradiation in comparison to, e.g., the use of the solar simulator or xenon lamp.

These pilot experiments can serve as a springboard for future, more comprehensive work, which includes several other applications, such as the reduction of CO₂ to methane or alcohols. Furthermore, to increase the attractiveness and competitiveness of photocatalytic processes, the reliance on sacrificial reagents will have to be eliminated to simplify the overall material balance and stop the use of potentially harmful chemicals.[16,17,18]

IV.CONCLUSION

Experimental Section

Commercially available chemicals were used as received. ¹H- and ¹³C NMR spectra were recorded in CDCl₃ using a Bruker AVANCE III 500 MHz spectrometer (Bruker, BioSpin GmbH, Germany) with working frequencies of 500 and 126 MHz, respectively, at 30 °C. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃; δ7.25 ppm). Coupling constants (J) are given in Hz with coupling expressed as d—doublet, dd—doublet of doublet, t—triplet, ddd—doublet of doublet of doublets, p—pentet, and m—multiplet. Melting points were determined using the Kofler apparatus with a microscope Nagma PHMK 05 (Nagma, Dresden, Germany).[19,20]

REFERENCES

1. Deign, Jason (29 June 2020). "So, What Exactly Is Green Hydrogen?". Greentechmedia. Archived from the original on 23 March 2022. Retrieved 11 February 2022.
2. ^ "The role of hydrogen and ammonia in meeting the net zero challenge" (PDF). The Royal Society. June 2021.
3. ^ "What is Green Hydrogen? Benefits, role, state, and challenges". 8 October 2023.
4. ^ ° IPCC (2022). Shukla, P.R.; Skea, J.; Slade, R.; Al Khourdajie, A.; et al. (eds.). *Climate Change 2022: Mitigation of Climate Change* (PDF). Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, UK and New York, NY, USA: Cambridge University Press (In Press). pp. 91–92. doi:10.1017/9781009157926. ISBN 978-1-009-15792-6.



5. ^ Global Hydrogen Review 2022 – Analysis. International Energy Agency. p. 71. Retrieved 13 May 2023.
6. ^ Murtaugh, Dan (21 September 2022). "China Leading Race to Make Technology Vital for Green Hydrogen". Bloomberg.com. Retrieved 12 May 2023.
7. ^ Dutta, Suman (2018). "Hydrogen as Sustainable and Green Energy Resource". Kirk-Othmer Encyclopedia of Chemical Technology. pp. 1–23. doi:10.1002/0471238961.0825041802091212.a01.pub3. ISBN 9780471484943. S2CID 139161918.
8. ^ b c Squadrito, Gaetano; Maggio, Gaetano; Nicita, Agatino (1 November 2023). "The green hydrogen revolution". *Renewable Energy*. 216: 119041. doi:10.1016/j.renene.2023.119041. ISSN 0960-1481.
9. ^ Gupte, Eklavya (11 July 2023). "Several deals focused on carbon, hydrogen signed at climate finance forum". www.spglobal.com. Retrieved 8 September 2023.
10. ^ "The GH2 Green Hydrogen Standard". Green Hydrogen Organisation. Retrieved 8 September 2023.
11. ^ Sasidhar, Nallapaneni (November 2023). "Carbon Neutral Fuels and Chemicals from Standalone Biomass Refineries" (PDF). *Indian Journal of Environment Engineering*. 3 (2): 1–8. doi:10.54105/ijee.B1845.113223. ISSN 2582-9289. S2CID 265385618. Retrieved 29 December 2023.
12. ^ Velazquez Abad, Anthony; Dodds, Paul E. (1 March 2020). "Green hydrogen characterisation initiatives: Definitions, standards, guarantees of origin, and challenges". *Energy Policy*. 138: 111300. doi:10.1016/j.enpol.2020.111300. ISSN 0301-4215. S2CID 212782998.
13. ^ International Renewable Energy Agency (29 March 2022). "World Energy Transitions Outlook 1-5C Pathway 2022 edition". IRENA. p. 227. Retrieved 6 October 2023.
14. ^ Kjellberg-Motton, Brendan (7 February 2022). "Steel decarbonisation gathers speed | Argus Media". www.argusmedia.com. Retrieved 7 September 2023.
15. ^ Blank, Thomas; Molly, Patrick (January 2020). "Hydrogen's Decarbonization Impact for Industry" (PDF). Rocky Mountain Institute. pp. 2, 7, 8. Archived (PDF) from the original on 22 September 2020.
16. ^ Liptak, Bela (21 March 2022). "Batteries or fuel cells for energy storage?". *Control*. Endeavour Business Media.
17. ^ Plötz, Patrick (31 January 2022). "Hydrogen technology is unlikely to play a major role in sustainable road transport". *Nature Electronics*. 5 (1): 8–10. doi:10.1038/s41928-021-00706-6. ISSN 2520-1131. S2CID 246465284.
18. ^ Lipták, Béla (24 January 2022). "Hydrogen is key to sustainable green energy". *Control Global*.
19. ^ Weaver, John Fitzgerald (17 February 2022). "LA could soon be home to the nation's largest green hydrogen infrastructure system". *PV Magazine USA*. Retrieved 12 May 2023.
20. ^ Lin, Janice (June 2020). "Beyond Power: Opportunities and Challenges for Green Hydrogen" (PDF). California Air Resources Board. Green Hydrogen Coalition.



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