SASTA OLIPHANT SCIENCE AWARDS

SOUTH AUSTRALIAN SCIENCE TEACHERS ASSOCIATION

Prize Winner

Science Writing

Year 9-10

Benita Wu

Seymour College

Artificial Photosynthesis through Photoelectrochemical Water Splitting: A Pathway to Renewable Hydrogen

By: Benita Wu

Energy Innovations

Abstract

As the world faces rising energy demands and climate challenges, scientists are looking for clean, renewable alternatives to fossil fuels. One promising solution is hydrogen, a carbon-free energy carrier. This article explores photoelectrochemical (PEC) water splitting, a process that mimics natural photosynthesis to produce hydrogen from sunlight and water. It explains how PEC cells work, the role of semiconductors and catalysts, and how innovations like perovskites and tandem cells are improving efficiency. By outlining the science and development of PEC technology, this piece highlights its potential to help power a sustainable, hydrogen-based energy future.

1. Introduction

The world is at a turning point. Fossil fuels, once the engines of technological progress, are now the leading cause of pollution and climate change (United Nations, 2025). As the global population grows, so does the demand for energy. Yet, how can we meet this demand without harming our planet?

One promising answer lies in hydrogen – an energy-rich and carbon-free gas (Kumar, 2022). But hydrogen gas doesn't exist freely in nature; it must be produced (CSIRO, 2025). Among various production methods, photoelectrochemical (PEC) water splitting stands out. Using only sunlight and water, PEC systems can generate hydrogen cleanly and sustainably, much like natural photosynthesis (Kumar, 2022). This article examines how PEC works, its importance, and where the technology is heading.

2. The Principle of PEC Water Splitting

PEC systems are composed of a semiconductor-based photoanode and a metal cathode, typically immersed in water-based electrolyte (Wu, 2021). In semiconductors, electrons occupy a lower energy valence band (VB) (Jiang, 2017). When excited by sunlight, they jump to a higher energy conduction band (CB), leaving behind holes in the valence band (Asthana, 2020). This energy gap is known as the bandgap (E_g) (Tseng, 2011). The excited electrons travel through an external circuit to the cathode, where they reduce hydrogen ions (H^+) into hydrogen gas (see Fig. 1) (Asthana, 2020). The remaining holes migrate to the photoanode surface and participate in the oxidation of water to produce oxygen gas (Asthana, 2022).

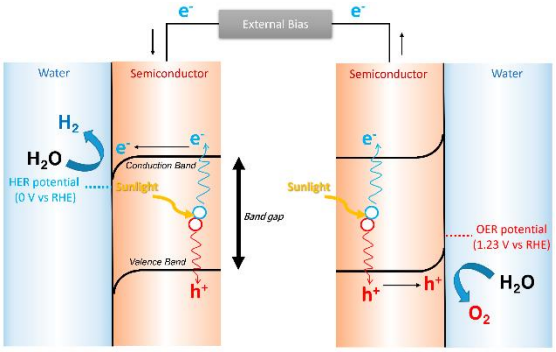

Figure 1: A diagram of a PEC water splitting system showing sunlight-driven charge separation for hydrogen and oxygen evolution (Son, 2023).

This process involves two key electrochemical reactions – the hydrogen evolution reaction (HER) at the cathode where hydrogen ions (H^+) gain electrons to form hydrogen gas (H_2), and the oxygen evolution reaction (OER) at the photoanode where water molecules lose electrons to form oxygen gas (O_2) (Plevová, 2021).

These can be summarized as follows (see Fig. 2):

Light absorption excites electrons:

$$2h\nu \rightarrow 2e^- + 2h^+$$

At the photoanode (oxidation) – Oxygen Evolution Reaction (OER):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

At the cathode (reduction) – Hydrogen Evolution Reaction (HER):

$$2H^+ + 2e^- \rightarrow H_2(g)$$

Overall reaction:

$$H_2O + 2h\nu \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

Figure 2: Stepwise chemical reactions involved in PEC water splitting, including excitation, oxidation (OER), reduction (HER), and the overall net reaction (Sreekantan, 2020).

The energy input required to split water comes from two components: the Gibbs free energy (237.2 kJ/mol), which is the minimum energy required to drive the reaction, and additional heat energy (48.6 kJ/mol) to overcome practical losses (Sreekantan, 2020). This totals to approximately 285.8 kJ/mol, equivalent to the energy released when hydrogen combusts with oxygen to form water (Kumar, 2022).

PEC water splitting performs this reaction in reverse (see Eq. 1):

$$H_2O\ (1) + 237.2\ kJ\ mol^{-1} + 48.5\ kJ\ mol^{-1} \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

Equation 1: Overall reaction for PEC water splitting (Kumar, 2022).

The Gibbs free energy corresponds to a theoretical voltage of 1.23 V per electron, and considering inefficiencies and overpotentials in HER and OER, the total energy required becomes 1.4~1.9 V (Sreekantan, 2020).

The total voltage needed in practical PEC systems can be expressed in a formula (see Eq. 2):

$$V = 1.23V + \eta_{HER} + \eta_{OER} + iR$$

$1.23V$ is the minimum theoretical voltage to split water
η_{HER} is the overpotential required for HER
η_{OER} is the overpotential required for OER
iR is voltage loss due to electrical resistance in the system

Equation 2: General formula for calculating the total voltage required in practical PEC systems (Sreekantan, 2020).

3. The Role of Semiconductors

Semiconductors play the critical role in PEC water splitting of absorbing sunlight and generating the voltage needed to drive the chemical reactions that split water into hydrogen and oxygen (Sreekantan, 2020).

Photovoltage (V_{ph}) is the voltage a semiconductor generates when it absorbs sunlight and excites electrons (DiMase Architects, 2025). To split water, this photovoltage must exceed 1.23 V (Kumar, 2022). Usually, a semiconductor's photovoltage produced is about 0.4 V less than bandgap energy losses (Yang, 2022). Therefore, semiconductors must have a bandgap of larger than 1.6 V to generate more than 1.23 V (Kumar, 2022).

Band bending occurs at the interface between the semiconductor and the electrolyte, creating an internal electric field that drives the electrons and holes in opposite directions (Kumar, 2022). This happens as the energy levels in the semiconductor shift to align with the redox potential of the electrolyte – the energy level at which electrons are transferred in oxidation or reduction reactions (Kumar, 2022).

Therefore, proper band alignment is crucial. The valence band of the photoanode must be more positive than the water oxidation potential to drive OER ($E_{VB} > E^0{}_{ox}$), and the conduction band of the photocathode must be more negative than the hydrogen ion

reduction potential to enable HER ($E_{CB} < E^0{}_{red}$) (Kumar, 2022). Without these internal charge dynamics, the electrons and holes would quickly recombine, and no useful hydrogen would be produced (Kumar, 2022).

4. What Makes PEC Efficient?

While the semiconductor is responsible for generating energy from sunlight, the efficiency of the overall system determines whether PEC water splitting is truly viable. Achieving high efficiency means ensuring that light energy is effectively converted into chemical energy and minimal energy is lost on the way (Solubility of Things, 2025). The two factors that are especially important in this process are catalysis and charge separation.

Catalysis is an essential aspect of artificial photosynthesis, accelerating the chemical reactions that produce hydrogen and oxygen through catalysts, materials that speed up reactions without being consumed (Wang, 2023). These catalysts drive HER at the cathode and OER at the photoanode, working together at the electrode-electrolyte interface where they provide active sites for oxidation and reduction (Kumar, 2022). This makes it easier for the excited electrons and holes to react with water molecules and ions, increasing efficiency (Kumar, 2022). Catalysts also reduce the energy activation required in both HER and OER, allowing these reactions to occur more readily and at lower energy thresholds (Libretexts, 2013).

Historically, noble metals like platinum (Pt), ruthenium (Ru), and rhodium (Rh) have been used as catalysts because of their high catalytic activity (Kwon, 2024). However, their high cost and scarcity limit large-scale use (Kwon, 2024). More recently, transition metals such as molybdenum (Mo), cobalt (Co), nickel (Ni) and iron (Fe) have been recognized as effective and affordable alternatives (Kumar, 2022). Research is now exploring a wide variety of compounds including alloys, sulfides, nitrides, and carbides to further improve performance and reduce cost (Jun, 2023).

Because improving PEC efficiency is a major focus of current research, scientists use a performance metric called solar-to-hydrogen (STH) efficiency (Hamdani, 2021). This metric measures how effectively the system converts sunlight into hydrogen fuel, and is calculated using the formula (Eq. 3):

$$\eta_{STH} = \frac{1.23 \times J_{ph} \times \eta_F}{P_{light}}$$

J_{ph} is photocurrent density
η_F is Faradaic efficiency
P_{light} is incident light power

Equation 3: The formula for calculating solar-to-hydrogen (STH) efficiency of a PEC system (Hamdani, 2021).

Recent advances in semiconductor materials and catalysts have steadily increased STH efficiency in laboratory settings (see Fig. 3). Understanding how PEC technology evolved from early lab experiments to today's developments reveals just how far the field has come.

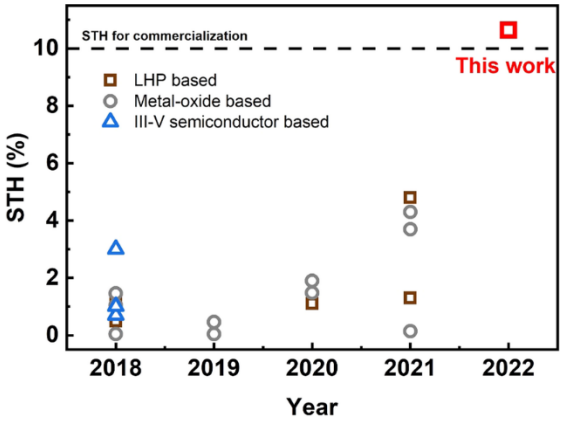

Figure 3: Solar-to-Hydrogen (STH) efficiency trends for various PEC systems from 2018-2022. The dashed line indicates the STH threshold (~10%) considered viable for commercialization (Rhee, 2024).

5. *The Evolution of PEC Technology: From Lab Curiosity to Cutting-Edge Innovation*

The concept of PEC water splitting was first demonstrated in 1968 by Boddy, who used a titanium dioxide (TiO_2) semiconductor to drive the reaction under ultraviolet light (Vilanova, 2024). This early result showed that light could be used to power chemical reactions and was a breakthrough at the time (Vilanova, 2024). A few years later, in 1972, Fujishima and Honda significantly boosted interest in the field by demonstrating a functional PEC cell with a TiO_2 photoanode (Kumar, 2022). Since then, researchers have spent decades developing new materials and device configurations to improve the efficiency, stability, and scalability of PEC systems (Vilanova, 2024).

One major challenge has been overcoming energy losses and limited absorption in single-semiconductor systems (Kumar, 2022). To address this, scientists have proposed tandem PEC cells, which are systems that combine two or more semiconductors, each designed to absorb a different part of the solar spectrum (See Fig. 4) (Bin, 2023). For example, one layer might absorb high-energy ultraviolet and visible light, while another captures lower-energy infrared light (Bin, 2023). This broader absorption increases the overall STH efficiency compared to traditional single-layer PEC cells.

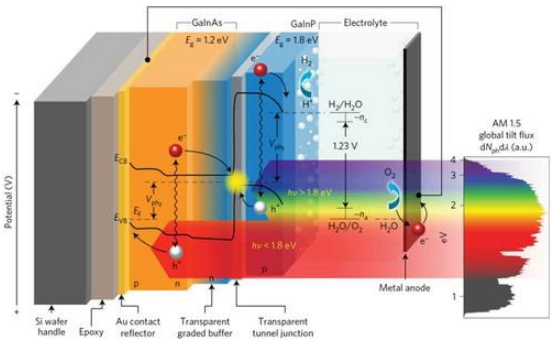

Figure 4: A cross-sectional diagram of a tandem PEC cell driving water splitting under solar illumination (Chen, 2018).

Another approach is Licht's model, which separates the solar spectrum into high-frequency sunlight which drives the chemical reaction, and low-frequency (infrared) light which heats the electrolyte (Tseng, 2011). This thermal assistance lowers the required voltage, significantly improving overall efficiency (Tseng, 2011).

Researchers have also explored perovskite photoanodes, a new class of semiconductors known for their excellent light absorption and tunable electronic properties (Perovskite-info, 2025). An example is the work of a team at UNIST, who developed a PEC cell using formamidinium lead triiodide perovskites (Perovskite-info, 2025). These materials can be engineered to absorb specific wavelengths of light, making them promising candidates for highly efficient PEC systems (Perovskite-info, 2025).

Despite these advances, scaling up PEC systems for real-world use remains a challenge. Many experimental setups still experience instability, high costs, or low efficiency outside of laboratory conditions (Kumar, 2022). However, PEC technology's ability to produce hydrogen directly from sunlight and water without external power sources keeps it at the forefront of green energy research (Kumar, 2022).

6. *Real-World Applications and the Road Ahead*

As PEC systems move out of the lab and into the real world, researchers are exploring different designs to make them more scalable and practical (U.S. Department of Energy, 2025). The two most common system types are panel-based PEC systems and slurry-based PEC systems, each with unique advantages and challenges (U.S. Department of Energy, 2025).

Panel-based PEC systems are the most widely studied. These modular systems resemble solar panels and are used for hydrogen production, able to be integrated into existing solar infrastructure such as rooftop arrays or solar farms (See Fig. 5) (U.S. Department of Energy, 2025). Their compact design and solid-state components make them easier to scale, operate, and maintain than more experimental systems (U.S. Department of Energy, 2025).

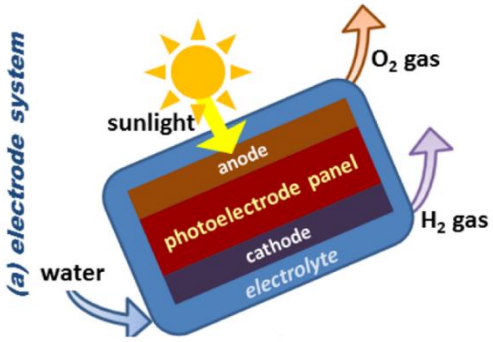

Figure 5: A diagram of a panel-based PEC system generating O_2 gas and H_2 gas under sunlight (U.S. Department of Energy, 2025).

In contrast, slurry-based PEC systems use light-absorbing particles, usually titanium dioxide (TiO_2) or bismuth vanadate ($BiVO_4$) nanoparticles, suspended in a liquid solution (Xing, 2013). These particles act as photocatalysts that trigger the water-splitting reaction (Xing, 2013). Slurry systems have a simple design and offer a large reactive surface, making them especially useful for small-scale use (See Fig. 6) (U.S. Department of Energy, 2025). However, they come with drawbacks including lower efficiency compared to panel systems and greater difficulty in collecting the generated hydrogen gas separately (Fernandez-Ibanez, 2021).

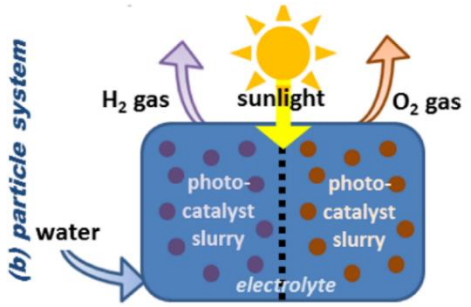

Figure 6: A diagram of a slurry-based PEC system generating O_2 gas and H_2 gas under sunlight (U.S. Department of Energy, 2025).

Recent innovations have also demonstrated the potential for PEC systems to purify wastewater while generating hydrogen (Dang, 2023). In these setups, negatively charged bacteria naturally move toward the positively charged photoanode, allowing the photocatalysts to break down organic pollutants while producing hydrogen gas at the cathode (Dang, 2023). These dual-function systems offer a sustainable solution to both water pollution and clean energy production.

7. Conclusion

Who would have thought that mimicking one of nature's oldest processes could help shape one of humanity's newest energy frontiers?

Photoelectrochemical water splitting combines the principle of photosynthesis with modern energy science. By using sunlight to produce clean hydrogen fuel from water, PEC systems offer a promising path toward a carbon-free future. Whilst challenges in efficiency, durability, and scale remain, slowing commercial deployment, ongoing research continues to deliver promising breakthroughs in semiconductors, catalysts and system design.

As the demand for scalable and sustainable hydrogen production intensifies, PEC technology remains a critical area of focus, heralding a greener, and more sustainable future.

Word Count: **1630** *(Excluding titles, labels, referencing and figures)*

Reference List

Asthana, N. (2020) “Polymerized hybrid nanocomposite implementations of energy conversion cells device,” in *Nanofabrication for Smart Nanosensor Applications*. Elsevier, pp. 349–397.

Chen, Q. (2018) “Tandem photoelectrochemical cells for solar water splitting,” *Advances in physics: X*, 3(1), p. 1487267. Available at: https://doi.org/10.1080/23746149.2018.1487267.

CSIRO (2025) *Green, blue, brown: the colours of hydrogen explained*, *CSIRO*. Available at: https://www.csiro.au/en/news/all/articles/2021/may/green-blue-brown-hydrogen-explained (Accessed: June 27, 2025).

Dang, Qizhendong (2023) “Bias-free driven ion assisted photoelectrochemical system for sustainable wastewater treatment,” *Nature communications*, 14(1), p. 8413. Available at: https://doi.org/10.1038/s41467-023-44155-5.

DiMase Architects (2025) *The Science Behind Solar Panels - guest blog*, *DiMase Architects Melbourne*. DiMase Architects. Available at: https://www.dimasearchitects.com.au/insights/the-science-behind-solar-panels (Accessed: June 27, 2025).

Fernandez-Ibanez, P. (2021) “New trends on photo electrocatalysis (PEC): nanomaterials, wastewater treatment and hydrogen generation,” *Current opinion in chemical engineering*, 34(100725), p. 100725. Available at: https://doi.org/10.1016/j.coche.2021.100725.

Hamdani, I.R. (2021) “Recent progress in material selection and device designs for photoelectrochemical water-splitting,” *Renewable and Sustainable Energy Reviews*, 138(110503), p. 110503. Available at: https://doi.org/10.1016/j.rser.2020.110503.

Jiang, C. (2017) “Photoelectrochemical devices for solar water splitting - materials and challenges,” *Chemical Society reviews*, 46(15), pp. 4645–4660. Available at: https://doi.org/10.1039/c6cs00306k.

Jun, S.E. (2023) “Single atom catalysts for photoelectrochemical water splitting,” *ChemCatChem*, 15(21). Available at: https://doi.org/10.1002/cctc.202300926.

Kumar, M. (2022) “Recent trends in photoelectrochemical water splitting: the role of cocatalysts,” *NPG Asia materials*, 14(1), pp. 1–21. Available at: https://doi.org/10.1038/s41427-022-00436-x.

Libretexts (2013) *The Effect of a Catalyst on Rate of Reaction*, *Chemistry LibreTexts*. Libretexts. Available at: https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Catalysis/The_Effect_of_a_Catalyst_on_Rate_of_Reaction (Accessed: June 27, 2025).

Perovskite-info (2025) *Researchers develop a scalable all-perovskite photoelectrochemical system for solar hydrogen generation*, *Perovskite-info.com*. Available at: https://www.perovskite-info.com/researchers-develop-scalable-all-perovskite-photoelectrochemical-system-solar (Accessed: June 27, 2025).

Plevová, M. (2021) “Electrocatalysts for the oxygen evolution reaction in alkaline and neutral media. A comparative review,” *Journal of power sources*, 507(230072), p. 230072. Available at: https://doi.org/10.1016/j.jpowsour.2021.230072.

Rhee, R. (2024) *STH efficiency benchmarks for unbiased PEC system. LHP, lead halide*, *ResearchGate*. Available at: https://www.researchgate.net/figure/STH-efficiency-benchmarks-for-unbiased-PEC-system-LHP-lead-halide-perovskite-PEC_fig5_361488339 (Accessed: June 27, 2025).

Solubility of Things (2025) *Photosynthesis: Conversion of Light Energy to Chemical Energy*, *Solubilityofthings.com*. Available at: https://www.solubilityofthings.com/photosynthesis-conversion-light-energy-chemical-energy-0 (Accessed: June 27, 2025).

Son, M.-K. (2023) "Key strategies on Cu2O photocathodes toward practical photoelectrochemical water splitting," *Nanomaterials (Basel, Switzerland)*, 13(24), p. 3142. Available at: https://doi.org/10.3390/nano13243142.

Sreekantan, S. (2020) "New-generation titania-based catalysts for photocatalytic hydrogen generation," in *Nanostructured, Functional, and Flexible Materials for Energy Conversion and Storage Systems*. Elsevier, pp. 257–292.

Tseng, C.-J. (2011) "The reactor design for photoelectrochemical hydrogen production," *International journal of hydrogen energy*, 36(11), pp. 6510–6518. Available at: https://doi.org/10.1016/j.ijhydene.2011.03.025.

United Nations (2025) "Renewable energy – powering a safer future | United Nations." Available at: https://www.un.org/en/climatechange/raising-ambition/renewable-energy (Accessed: June 27, 2025).

US Department of Energy (2025) *Hydrogen Production: Photoelectrochemical Water Splitting*, *Energy.gov*. Available at: https://www.energy.gov/eere/fuelcells/hydrogen-production-photoelectrochemical-water-splitting (Accessed: June 27, 2025).

Vilanova, A. (2024) "The route for commercial photoelectrochemical water splitting: a review of large-area devices and key upscaling challenges," *Chemical Society reviews*, 53(5), pp. 2388–2434. Available at: https://doi.org/10.1039/d1cs01069g.

Wang, L. (2023) "Principles of photocatalysis," in *Interface Science and Technology*. Elsevier, pp. 1–52.

Wu, L. (2021) "Monolithic integrated multifunctional photoelectrochemical device for smart ultraviolet management," *Materials today energy*, 20(100676), p. 100676. Available at: https://doi.org/10.1016/j.mtener.2021.100676.

Xing, Z. (2013) "On the engineering part of solar hydrogen production from water splitting: Photoreactor design," *Chemical engineering science*, 104, pp. 125–146. Available at: https://doi.org/10.1016/j.ces.2013.08.039.

Yang, R.Q. (2022) "Narrow bandgap photovoltaic cells," *Solar energy materials and solar cells: an international journal devoted to photovoltaic, photothermal, and photochemical solar energy conversion*, 238(111636), p. 111636. Available at: https://doi.org/10.1016/j.solmat.2022.111636.