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Review article

Advances of nanostructured metal oxide as photoanode in photoelectrochemical (PEC) water splitting application

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ABSTRACT

Water splitting via photoelectrochemical (PEC) cells offers a promising route to generate hydrogen fuel using solar energy. Nanostructured metal oxides have emerged as leading candidates as photoelectrodes in photocatalytic H_2 production due to their photo-electrochemical stability, large surface area, earth abundance, and suitable band gap energies. This review reports the recent advancements of nanostructured metal oxide as photoanodes in photoelectrochemical (PEC) water-splitting applications. This review focuses on recent advancements in metal oxide photoanodes, their synthesis methods, modification strategies, and performance in PEC water splitting. Critical materials such as TiO_2, Fe_2O_3, WO_3, and $BiVO_4$ are discussed in detail, highlighting their strengths, limitations, and future research directions to enhance efficiency and stability. This review will give clear insight into the trends and the critical factors for efficient metal oxide photoelectrode to improve the photocatalytic effectiveness in generating hydrogen fuel as an alternative energy source in the future. Finally, this study emphasises the potential of incorporating machine learning methods into experimental workflows to accelerate the optimisation of electrocatalysis performance, representing a significant advancement in developing efficient and sustainable hydrogen production technologies.

1. Introduction

Photoelectrochemical (PEC) water splitting is a transformative technology that harnesses solar energy to produce hydrogen, a clean and renewable energy source. This process involves the use of semiconductor materials as photoelectrodes, which absorb sunlight and facilitate the chemical reactions necessary for water splitting. Among the various materials explored for this purpose, nanostructured metal oxides have emerged as a focal point due to their unique properties and potential for enhancing PEC performance.

The interest in metal oxides as photoanodes for PEC water splitting has significantly increased over the past few decades. This surge can be attributed to their favourable characteristics, including stability, low cost, and the ability to be synthesized in various nanostructured forms. Notable examples of metal oxides utilized in PEC applications include titanium dioxide (TiO_2), iron oxide (Fe_2O_3), tungsten oxide (WO_3), and bismuth vanadate ($BiVO_4$) [1,2]. These materials not only exhibit good photocatalytic activity but also possess the ability to withstand the harsh conditions present in electrochemical environments, making them suitable candidates for

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practical applications.

Despite the promising advancements, challenges remain in optimizing the efficiency and stability of metal oxide photoanodes [3]. Issues such as poor electrical conductivity, limited light absorption, and susceptibility to photo-corrosion hinder the widespread adoption of PEC technology. Researchers are actively exploring various strategies to mitigate these limitations, including elemental doping [4], the formation of heterojunctions, and the integration of co-catalysts [5]. These approaches aim to enhance the intrinsic properties of metal oxides, thereby increasing their efficacy as photoanodes in PEC water splitting applications.

Recent advances in the synthesis of nanostructured metal oxides have further propelled their use in PEC water splitting [6]. Techniques such as sol-gel processes, hydrothermal synthesis, and electrochemical deposition have enabled the fabrication of metal oxides with tailored morphologies and enhanced surface areas. Recent studies have focused on developing diverse nanostructures of metal oxides for PEC water splitting using solution-based processes. Some notable examples include TiO_2 nanoparticles and SnO_2 nanowires uniformly assembled onto P-doped g-C_3N_4 nanosheets, CdSSe layer-sensitized TiO_2 nanowire arrays as efficient photoelectrodes, Au nanoparticles and WO_3 as plasmonic photocatalysts for visible-light-induced photocatalytic activity, and Zn-doped α-Fe_2O_3 as an efficient material for UV-driven photocatalysis and electrical conductivity [7].

These structural modifications are crucial as they improve light absorption, charge separation, and overall efficiency of the photoanodes. For example, enhanced charge separation efficiency and photocurrent density of 2.2 $mAcm^{-2}$ at 0.6 V vs Ag/AgCl was achieved in the heterojunction photoanode of $BiVO_4/SnO_2$ nanorod array as it increases the volumes of the depletion regions in both $BiVO_4/SnO_2$ heterojunction [8].

In this review, we will delve into the latest developments in the field of nanostructured metal oxides. We will examine the performance metrics and the underlying mechanisms that contribute to the efficiency of these materials in PEC systems. Additionally, we will discuss the current challenges and future directions for research, emphasizing the need for innovative solutions to enhance the practical viability of PEC water splitting as a sustainable energy technology. Through this comprehensive review, we aim to provide insights into the potential of nanostructured metal oxides in addressing the global energy crisis while contributing to environmental sustainability.

2. Fundamental concept

2.1. Photoanode

Photoanodes play a crucial role in photoelectrochemical (PEC) water splitting, a promising method for converting solar energy into hydrogen fuel. Understanding their basic functions and principles is essential for enhancing the efficiency of this process.

Photoanodes in PEC are typically made from semiconductor materials that can absorb sunlight. The absorption of light generates electron-hole pairs to produce ion radicals, which are essential for the water-splitting reaction. The semiconductor must have a suitable bandgap to absorb solar radiation efficiently.

The energy excites electrons from the valence band to the conduction band upon light absorption, creating electron-hole pairs. This process is fundamental for initiating the electrochemical reactions necessary for water splitting. After generation, the electrons and holes must be effectively separated and transported to their respective sites—electrons to the cathode and holes to the anode. The efficiency of this charge separation is critical, as the recombination of these carriers can significantly reduce the overall efficiency of the PEC system.

At the photoanode, the holes participate in the oxidation of water, leading to the generation of oxygen gas. This reaction requires that the photoanode's potential be sufficiently high (greater than 1.23 V) to drive the water oxidation reaction. The photoanode must also exhibit stability under operational conditions, particularly in the presence of corrosive electrolytes. Material selection and surface modifications are often employed to enhance the durability of photoanodes.

$$2H_2O \rightarrow 2H_2 + O_2$$

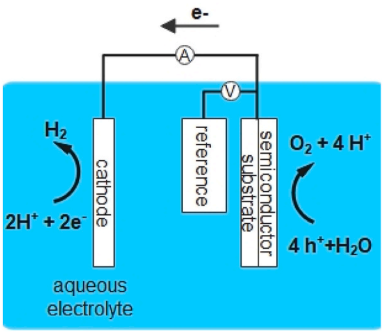


Fig. 1. Schematic diagram of a photoelectrochemical water splitting cell.

2.2. Water splitting process

Photocatalysts are employed in two primary ways to split water: photoelectrochemical cells and particulate photocatalytic systems. In photoelectrochemical cells, photocatalysts create electrodes immersed in an aqueous electrolyte. These electrodes can transport electrons to the electrode through an external circuit or directly absorb photons without any dye sensitization or activation. On the other hand, in particulate photocatalytic systems, photocatalysts are suspended in a solution, acting as micro photoelectrodes and conducting the redox reaction of water molecules. Although this system has some drawbacks, mainly related to charging and H_2 and O_2 gas separation, it has gained significant attention due to its simplicity, scalability, and cost-effectiveness.

In particulate photocatalytic systems, as shown in Fig. 1, when a photocatalyst absorbs light, an electron is excited from the valence band to the conduction band. These excited electrons then reduce water molecules into hydrogen gas on the active sites of the photocatalyst. Simultaneously, the positive holes left in the valence band oxidize water molecules into oxygen gas.

The overall water-splitting process involves three main steps.

1. Semiconductive materials absorb light photons, creating electron-hole pairs in the conduction and valence bands.
2. Charge separation and migration occur through the photogenerated carriers. The photocatalyst's crystallinity, size, shape, and crystal structures are crucial parameters in this step. Dislocations and structural defects should be minimized as they can act as recombination or trapping centres for photogenerated carriers.
3. Water decomposition reactions take place on the surface of the photocatalyst. Important parameters include the number of active surface areas and the surface-active sites for the cocatalyst. Cocatalysts (e.g., Pt and RuO_2) are attached to the photocatalyst surface to enhance the separation of photogenerated electron-hole pairs. Smaller particle sizes lead to better photocatalytic behaviour due to increased active sites.

Metal oxides typically use the 2p orbital of oxygen to oxidize water molecules, so they usually do not require a cocatalyst for water oxidation [9].

It takes 1.23 V to dissociate 1 mol of water into hydrogen and oxygen completely. However, due to water's very low ionization constant ($Kw = 1.0 \times 10^{-14}$), the process of splitting water is thermodynamically unfavourable at standard temperature and pressure, with a Gibbs free energy change (ΔG°) of 237 kJ/mol, or 2.46 eV per molecule. This Gibbs free energy is calculated at standard temperature and pressure using the thermodynamic parameters (ΔH, ΔT, and ΔS) essential for the water-splitting reaction [10]:

$$\Delta G = \Delta H - T\Delta S = 285.83\ \text{kJ} - 48.7\ \text{kJ} = 237.13\ \text{kJ}$$

With the calculated Gibbs free energy, the standard cell potential (E°) of the reaction can be determined using the Nernst Equation:

$$E^\circ = -\Delta G^\circ / zF$$

In this equation, z represents the number of electrons transferred during the reaction (two in this case), and F is the Faraday constant (96,485C/mol). Applying the Nernst equation, the standard potential for water electrolysis is 1.229 V at 25 °C. This cell potential reflects the difference in electrical potentials between the two half-cell reactions: the cathodic reduction (hydrogen evolution reaction, HER) and the anodic oxidation (oxygen evolution reaction, OER). The Nernst equations for the half-cell reactions involved in water splitting are detailed below:

Anode (oxidation): $4OH^- + 4h^+ \rightarrow O_2 + 2H_2O$ $E = 1.23$ V versus NHE

Cathode (reduction): $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E = 0.00$ V versus NHE.

Leading to an overall reaction of the following:

$$2H_2O(l) + 4e^- + 4h^+ \rightarrow O_2(g) + 2H_2(g)\quad E = 1.23\ \text{V}$$

2.3. Standard measurements

A variety of evaluation metrics are employed to gauge the performance of photoelectrode materials in photoelectrochemical (PEC) cells. Key parameters for evaluation include incident photon-to-electron conversion efficiency (IPCE), absorbed photon-to-current efficiency (APCE), applied bias photon-to-current efficiency (ABPE), and solar-to-hydrogen efficiency (STH). Typically, ABPE, STH, and IPCE are assessed using a three-electrode PEC configuration that applies a bias [11].The connection between the applied bias and the Reversible Hydrogen Electrode (RHE) can be described using the Nernst equation, as shown in Equation (1). This equation incorporates three important electrochemical parameters within the PEC system:

$$E_{RHE} = E_{REF} + 0.059\, pH \tag{1}$$

Here, E_{ref} is the potential associated with the selected reference electrode (RE), such as Ag/AgCl. E^0_{ref} indicates E_{ref} in relation to the Standard Hydrogen Electrode (SHE) at 25 °C, while pH represents the electrolyte's pH level. The efficiency of the photoelectrode's conversion is generally evaluated by applying an external bias between the active and counter electrodes. The ABPE for water-splitting photoelectrodes is determined using the following formula, Equation (2):

$$ABPE = \frac{J_{ph} \times (1.23 - V_{app})}{P_{light}} \tag{2}$$

in this equation, V_{app} denotes the voltage applied concerning the reversible hydrogen electrode (RHE), while J_{Ph} refers to the externally measured photocurrent density under the applied voltage V_{app}. P_{light} indicates the power density of incident light. The incident photon-to-current efficiency (IPCE) serves as a performance metric for photoelectrode materials in PEC cells, quantifying how effectively the PEC cell converts incoming light into electrical energy at specific wavelengths. Comprehensive research is often required to understand the mechanisms behind current generation in PEC cells, which involves charge transfer and diffusion processes. According to Equation (3), IPCE is associated with three fundamental efficiencies:

$$IPCE\,(\lambda) = LHE \times n_{cs} \times n_{ct} \tag{3}$$

in this context, LHE represents light harvesting efficiency, calculated as ($10X10^{-A}$), where A denotes absorption at particular wavelengths. This efficiency pertains to charge separation within the photoelectrode. The term n_{ct} refers to charge transport efficiency at the semiconductor-electrolyte interface. Equation (4) provides a method to calculate IPCE:

$$IPCE\,(\lambda) = \frac{1240 \times J_{ph}}{\lambda \times P_{light}} \times 100\% \tag{4}$$

in this equation, J_{ph} signifies the photocurrent density (mA cm^{-2}) at a specific wavelength λ, while P_{light} denotes light energy density (mW cm^{-2}) at that wavelength. The overall solar-to-hydrogen (STH) efficiency of a PEC cell can be assessed under solar illumination that simulates AM 1.5 G conditions through a non-uniform process. The conversion efficiency for STH is calculated using Equation (5):

$$n_{sth} = \frac{r_{H2} \times \Delta G}{P_{light} \times S} \times 100\% \tag{5}$$

in this context, r_{H2} represents the hydrogen production rate measured by a mass spectrometer (mmol/s), "S" denotes the area of the illuminated electrode, and " ΔG ″ indicates the change in Gibbs free energy per mole of H_2 produced (237 kJ/mol) [9,12]. Four essential steps influence the overall effectiveness of PEC water splitting: (i) light absorption and charge carrier generation, (ii) charge separation, (iii) charge transport, and (iv) charge carrier extraction and electrochemical product formation. Therefore, Equation (6) can represent solar-to-hydrogen efficiency (η_{STH}).

$$n_{STH} = n_A \times n_{cs} \times n_{CT} \times n_{CR} \tag{6}$$

in this equation, each η represents efficiencies for light absorption (η_A), charge separation (η_{CS}), charge transport (η_{CT}), and charge collection/reaction efficiency (η_{CR}) [13].

3. Metal oxide photoanode

For efficient water splitting, semiconductors should have a bandgap greater than 3 eV, such as TiO_2 and ZnO. However, semiconductors with such a bandgap only absorb UV light, which comprises 2–5% of the solar spectrum. Therefore, tuning the bandgap for visible light absorption of near IR light is advisable. Fig. 2 shows the band structure of some semiconductors. A complex three-component semiconductor material based on metal oxides can vary the band structure to obtain the optimal photoelectrode material for high-efficiency water splitting.

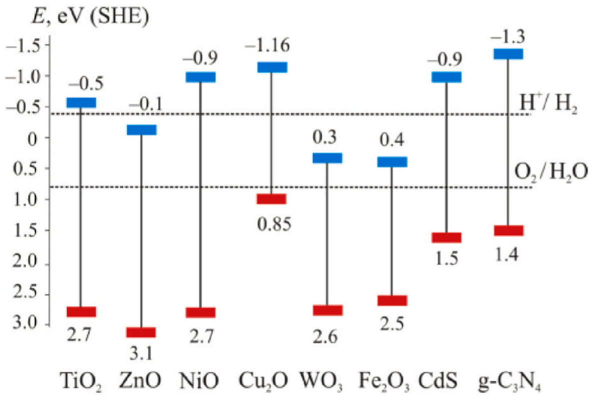


Fig. 2. Band structure of some semiconductors. Reproduced from Ref. [14].

The evaluation of various semiconductor materials as photoanodes for water splitting—specifically TiO_2, ZnO, Fe_2O_3, WO_3, and $BiVO_4$—reveals advantages and disadvantages that impact their efficiency and practical applications. Table 1 shows the comparative analysis based on the research findings.

$BiVO_4$ is currently recognized as the leading material for photoelectrochemical (PEC) water oxidation among metal oxide light absorbers. Fig. 3 illustrates the top reported performances (photocurrent density (J_{ph}) at 1.23 VRHE) of stable metal oxide photoelectrodes, including TiO_2, WO_3, Fe_2O_3, and $BiVO_4$. Notably, $BiVO_4$ and $BiVO_4/WO_3$ have shown significant advancements compared to the other materials, particularly between 2014 and 2015, when $BiVO_4$ emerged as the premier choice for metal oxide-based photoanodes. By 2018, $BiVO_4$ nearly achieved its theoretical performance limit of 7.5 mA cm^{-2} at an energy bandgap (E_g) of 2.4 eV, similar to the earlier accomplishments of TiO_2 and WO_3 [17].

In summary, TiO_2 and ZnO are stable and widely used, but their limited light absorption and charge recombination issues hinder their efficiency. Fe_2O_3 and $BiVO_4$ offer advantages in visible light absorption but face challenges related to charge mobility and stability. WO_3 presents a balance between stability and efficiency but is limited by its absorption spectrum. Each material has unique properties that can be optimized through heterojunctions and composite structures to enhance their performance in photoelectrochemical water splitting.

The synthesis of metal oxide photoanodes is critical for applications in solar energy conversion and photocatalysis. Various methods have been developed, each offering unique advantages and challenges. For example, the solvothermal and hydrothermal method is widely employed for synthesizing metal oxide photoanodes, such as Fe_2O_3. This technique involves the growth of crystals in a high-temperature and high-pressure aqueous environment. The resulting materials often exhibit improved crystallinity and enhanced photoelectrochemical performance due to optimized preparation conditions [18].

The sol-gel method is another prevalent technique for producing metal oxide nanoparticles. This process involves the transition of a solution (sol) into a solid (gel) phase, allowing for the uniform distribution of metal oxide precursors. The sol-gel method is known for its simplicity and ability to produce homogeneous materials with controlled morphology and composition. It is frequently used for synthesizing titanium dioxide (TiO_2) and zinc oxide (ZnO) as photoanode [19].

Electrochemical methods involve the application of electrical current to induce the formation of metal oxides. This method allows for precise control over the morphology and composition of the nanostructures [20].

Chemical vapor deposition, CVD is a method that allows for the deposition of thin films of metal oxides on substrates through chemical reactions in the vapor phase. This technique is particularly useful for creating high-purity and high-quality films with precise thickness control. CVD is commonly used for materials like tin oxide (SnO_2) and zinc oxide (ZnO) in photoanode applications [21].

Lastly, microwave-assisted synthesis is a newer approach that utilizes microwave energy to accelerate the chemical reactions involved in the formation of metal oxides. This method can lead to shorter synthesis times and improved material properties due to the uniform heating provided by microwave radiation. It is being explored for various metal oxide systems, including those used in photoanodes [22].

The selection of a method frequently relies on the specific attributes sought in the photoanode, including its crystallinity, morphology, and efficiency. Current research is actively enhancing these techniques to improve the performance of metal oxide photoanodes in energy conversion applications.

3.1. TiO_2

Titanium dioxide, TiO_2, is one of the extensively investigated metal oxide materials for PEC water splitting. It has good stability and is non-toxic. The band gap is appropriate for visible light absorption. However, its wide bandgap (~3. 2 eV for anatase) restricts the extent to which it can cover the solar spectrum.

TiO_2 photoanodes can be prepared using sol-gel, hydrothermal methods, and electrodeposition techniques. Some strategies to modify TiO_2 include forming nanotubes, nanorods, or mesoporous structures and increasing surface area and charge transport characteristics.

Among the various materials, titanium dioxide (TiO_2) has been extensively investigated for the application of photoanode in

Table 1
Advantages and disadvantages of metal oxide photoanode.

Metal Oxide Photoanode	Advantages	Disadvantages
TiO_2	chemically stable and resistant to photo-corrosion abundant and inexpensive	its bandgap restricts its activity to UV light the recombination of electron-hole pairs occurs quickly [15]
	suitable bandgap (~3.2 eV) that allows it to absorb UV light effectively	fast charge recombination [16]
ZnO	bandgap of about 3.3 eV, allowing it to absorb UV light effectively high electron mobility	photo corrosion its bandgap restricts its activity to UV light
Fe_2O_3	absorb visible light due to its lower bandgap (~2.1 eV) abundant and inexpensive	low charge carrier mobility The kinetics of water oxidation are slower
WO_3	chemical stability and photocatalytic activity efficient charge separation	its bandgap restricts its activity to UV light complex synthesis
$BiVO_4$	bandgap of about 2.4 eV, allowing it to utilize visible light effectively high photocatalytic efficiency	rapid charge recombination stability issues

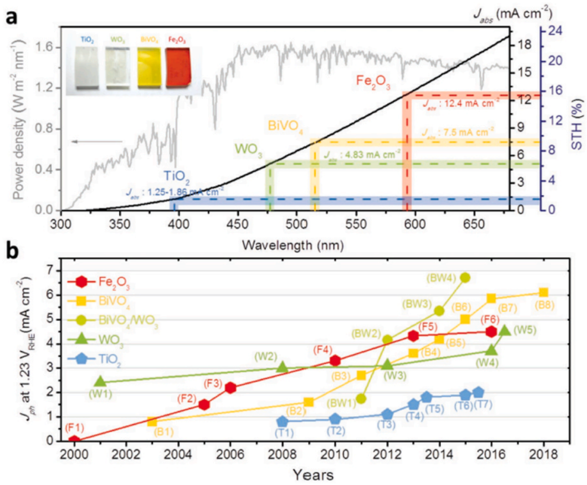


Fig. 3. Progress in the performance of metal oxide semiconductor photoanodes. a) Theoretical absorption photocurrent density (J_{abs}) and solar-to-hydrogen efficiency under 1 Sun irradiation. b) Reported photocurrent density of metal oxide photoanodes under simulated 1 Sun from PEC water oxidation. Reproduced from Ref. [17].

hydrogen generation through photoelectrochemical water splitting. Numerous studies have been devoted to improving the efficiency of TiO_2-based photocatalysts by deposition of noble metals, surface alteration, and employing nanotube or nanorod structures. Despite the benefits associated with TiO_2, including low cost, availability, and stability, it has drawbacks, such as a wide bandgap, high electron-hole recombination time, and large overpotential for HER. These challenges have been addressed through experimental and theoretical research to enhance the performance of TiO_2 photocatalysts for water splitting.

There are some reports of potential applications, such as the high efficiency of photoelectrochemical hydrogen generation on the sensitized TiO_2 nanorod arrays. Black TiO_2 nanomaterials have also been identified as potential photocatalysts to produce hydrogen using solar light. Hence, TiO_2 can be considered a promising photoanode for hydrogen production; further developments are being made to improve its efficiency and market prospects [23–25].

A study was conducted on photoelectrocatalytic hydrogen production utilizing a TiO_2/W$_{O3}$ bilayer photocatalyst under electric bias and a straightforward cathode electrode. This setup achieved a Faradaic efficiency of 58 % for hydrogen generation. Fig. 4 (a) depicts the reactor's schematic, while Fig. 4 (b) illustrates the band levels for the nanoparticulate TiO_2 and WO_3. The observed increase

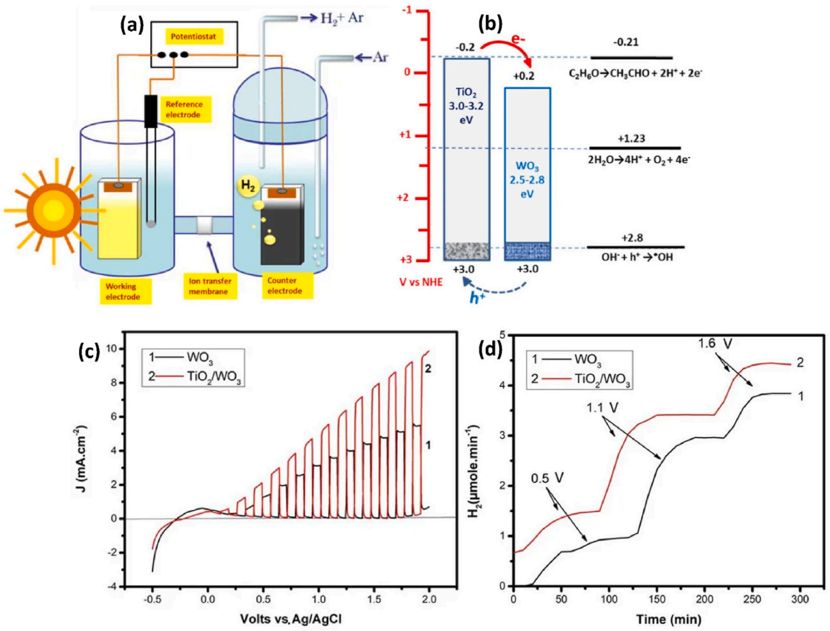


Fig. 4. Schematic representation of the reactor (a), band levels (b), current density-voltage curves (c), and photoelectrocatalytic hydrogen production rate (d). Reproduced from Ref. [26].

in current was primarily due to the passivation of surface recombination sites on WO_3, which helped limit charge recombination processes. Furthermore, the upper titania layer likely enhanced photon absorption through light backscattering, thereby improving light absorption by WO_3, as shown in Fig. 4(c) and (d). High charge densities were recorded, attributed to the enhanced performance of the photoanode from the combined photocatalyst and the use of ethanol as a fuel [26].

Pd/TiO_2 exhibited the highest hydrogen generation rate at 979.7 μmol h^{-1}, indicating a significant improvement in efficiency, likely due to the catalytic properties of palladium. Table 2 and Fig. 5 highlights the importance of selecting appropriate materials and structures in optimizing photoanodes for efficient hydrogen production through photoelectrochemical processes.

3.2. WO_3

Tungsten trioxide (WO_3) is another promising photoanode material with a bandgap of approximately 2.6–2.8 eV. This bandgap enables better visible light absorption than TiO_2. WO_3 is also chemically stable in acidic solutions, which is favourable for PEC applications.

WO_3 can be prepared by sputtering, chemical vapor deposition (CVD), and the hydrothermal method. To improve its photoactivity, the morphology of WO_3 can be adjusted to nanosheets, nanowires, or mesoporous structures.

Tungsten trioxide (WO_3) is one of the materials investigated for use as a photoanode in PEC water splitting to produce hydrogen. WO_3 has several advantages: high stability, good electrical conductivity, and appropriate bandgap for water oxidation. Some critical studies on WO_3 as a photoanode for hydrogen production include: Some critical studies on WO_3 as a photoanode for hydrogen production include:

A TiO_2/WO_3 bilayer photocatalyst was used for photo-electrocatalytic hydrogen production; the photoanode was prepared by coating TiO_2 on WO_3 [26]. Core-shell $WO_3/BiVO_4$ nanorods were synthesized and applied as a photoanode to reach the maximum photocurrent density of 6.72 mA cm^{-2} under one sun illumination at 1.23 V vs RHE, which is equivalent to roughly 90 % efficiency in water-splitting [32]. A nanostructured semi-transparent WO_3 photoanode was used in a PEC device to generate photocurrent densities over 6 mA cm^{-2} at 1.23 V vs RHE under simulated solar light [33].

These works show that WO_3 is a promising photoanode material for hydrogen generation and that continuous research is being conducted to improve its efficiency for real-world applications. However, issues like photo corrosion and stability in various electrolyte solutions still need to be solved [34].

3.3. ZnO

ZnO as a photocatalyst has been reported in several papers. Mainly, Zinc Oxide has been reportedly used in water treatment [35–37], biomedical devices [38], optoelectronics [39], and energy harvesting [40], highlighting their versatility and potential for diverse technological applications.

Furthermore, ZnO has been widely investigated as a photoanode material for hydrogen generation via PEC water splitting. ZnO has been reported to be a vital material in photocatalysis, and hence, it has received much attention in this area. Some of the previous research has been directed towards the improvement of the PEC performance of ZnO-based photoanodes, for example, doping with chromium (Cr) to the ZnO thin films to modify the electronic properties of ZnO for better PEC performance [41]. The photocurrent density and the stability of the photoelectrodes have been found to rise from 44 μA/cm^2 for 2 % Cr incorporated ZnO to 866 μA/cm^2 for 15 % Cr incorporated ZnO, as shown in Fig. 6 [41].

ZnO nanostructured photoelectrodes can also generate hydrogen, suggesting their possible use in green hydrogen generation. Studies have been carried out on other ZnO-based photoanodes, including CeO_2-decorated Ce-doped ZnO nanowire arrays for efficient hydrogen production as shown in Fig. 7 (a) and (b) [42].

Furthermore, ZnO and ZnO/Ag films have been investigated for hydrogen generation through a photocatalytic process using solar light [43]. ZnO/Ag/5 yields the maximum H_2, 30 μmol, after 3 h of reaction, which is tenfold higher than the ZnO undoped film as observed in Fig. 7 (c) and (d). These investigations show the possibility of using ZnO as a photoanode for hydrogen generation and further developments toward improving its efficiency for real-world applications.

Table 3 demonstrates that modifying the morphology and doping ZnO with metals like Au and Ce can significantly enhance its photocatalytic hydrogen production performance compared to bare ZnO. From illustration trend in Fig. 8, the ZnO nanofibers as a photocatalyst demonstrate exceptional and stable hydrogen production capabilities. ZnO nanofibers are composed of densely packed particles that create cylindrical fibers characterized by high crystallinity and purity. This strong one-dimensional nanostructure effectively prevents the clumping of nanoparticles while enhancing charge transfer between particles. Additionally, the mesoporous

Table 2

Hydrogen generation rate of TiO_2-based photoanodes for water splitting.

Photoanode	Year	Rate of hydrogen generation (μmol h^{-1})	Reference
TiO_2/MoS_2/graphene	2012	165.3	[27]
4%-MoS_2/TiO_2	2015	150.7	[28]
10 % V-doped TiO2/RGO	2016	120	[29]
Pd/TiO_2	2017	979.7	[30]
Cu/TiO_2@Ti_3- C_2T_x	2018	860	[31]

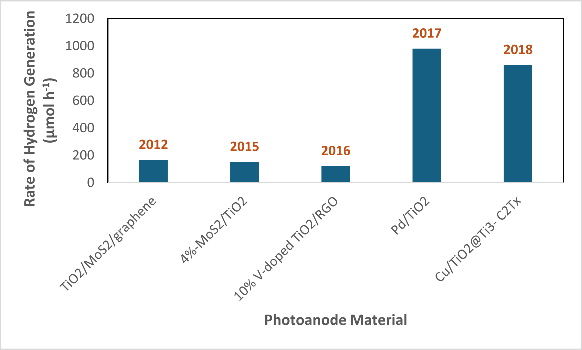


Fig. 5. Hydrogen generation rate of TiO_2 photoanodes.

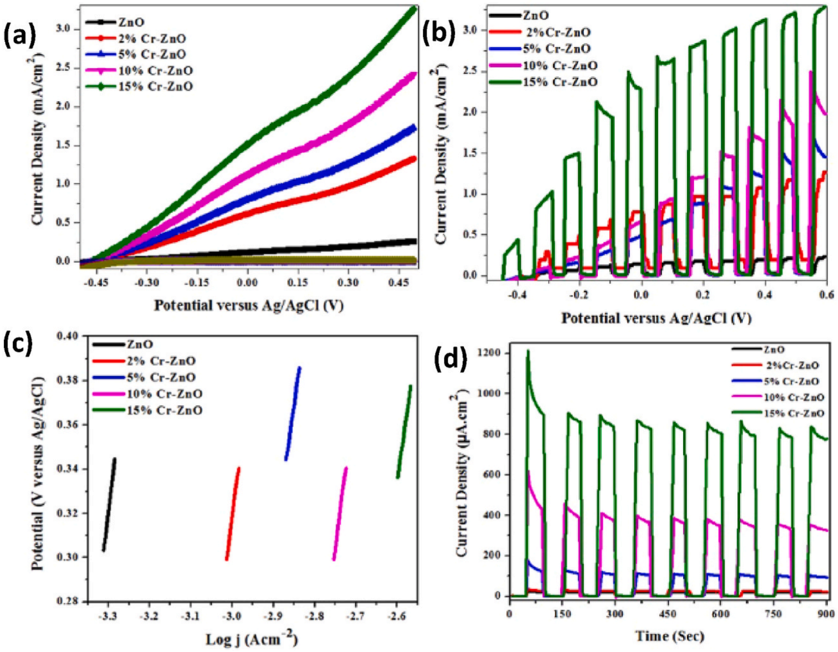


Fig. 6. (a) Photocurrent potential curves, (b) current density, (c) Tafel plots, and (d) the chronoamperometric measurements for as-fabricated plain and Cr-incorporated ZnO photoelectrodes. Reproduced from Ref. [41].

structure formed by the connections between ZnO particles aids in the adsorption of reactants and the desorption of products [44].

3.4. $BiVO_4$

Bismuth vanadate ($BiVO_4$) has recently been identified as one of the most efficient photoanode materials. Its bandgap is about 2.4 eV, suitable for visible light absorption. $BiVO_4$ has acceptable stability and appropriate conduction and valence band energies for water splitting.

$BiVO_4$ can be prepared using solution combustion synthesis, electrodeposition, and spray pyrolysis. These methods enable one to control the crystallinity and morphology of the $BiVO_4$ films, which are essential for high PEC performance.

Bismuth vanadate ($BiVO_4$) has been widely studied as a photoanode as shown in Fig. 10 for photocatalytic hydrogen generation through PEC water splitting [47,48]. Recent research has been directed towards improving the PEC performance of $BiVO_4$-based photoanodes. For example, a study showed the application of a $WO_3/BiVO_4$ core-shell nanostructured photoanode as shown in Fig. 9 that exhibited near-ideal water splitting performance, suggesting $BiVO_4$'s capability to deliver high PEC water splitting performance, with a photocurrent density of 6 mA cm^{-2}, corresponding to the STH efficiency of 8.1 % [32].

Furthermore, studies have been carried out on the doping of $BiVO_4$ to improve its PEC performance, such as using Bi nanoparticles to enhance the performance of $BiVO_4$ as a photoanode for efficient hydrogen production [50]. Moreover, evidence has been given for the enhancement of $BiVO_4$ photoanodes on porous Ti transport layers for the commercial application of the solar cell, which is vital for

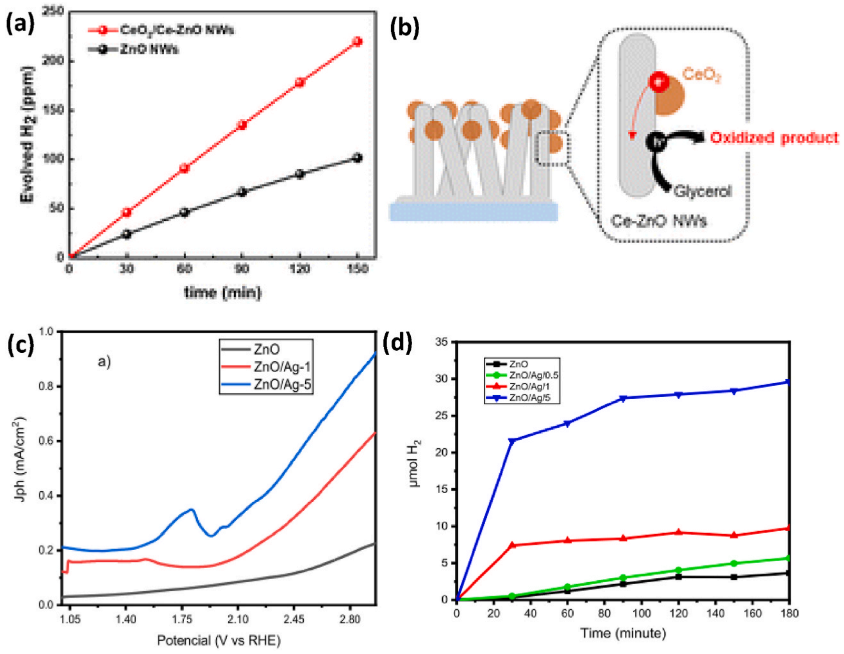


Fig. 7. Rate of evolved hydrogen produced (a), Schematic diagram of CeO2/Ce-doped ZnO photoelectrode (b), Current density (c), and Hydrogen photocatalytic tests using the ZnO and ZnO–Ag materials (d). Reproduced from Refs. [42,43].

Table 3

Hydrogen generation rate of ZnO-based photoanodes for water splitting.

Photoanode	Year	Hydrogen Production Rate (μmolh^{-1} g^{-1})	Reference
Au/ZnO NWs	2018	853	[45]
ZnO NPs	2018	709	[45]
Commercial ZnO	2018	559	[45]
ZnO Nanofiber	2020	1031.8	[44]
Ce/ZnO	2021	43	[46]
ZnO	2021	1.2	[46]

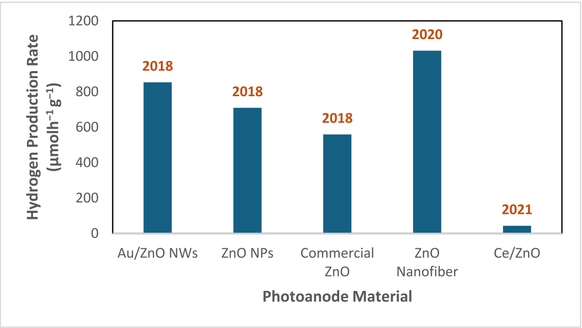


Fig. 8. Hydrogen generation rate of ZnO photoanodes.

its scalability [51]. These works demonstrate the continued development of $BiVO_4$-based photoanodes for hydrogen production via PEC water splitting.

Based on Table 4, the advancements in hydrogen generation rates from $BiVO_4$-based photoanodes illustrate the potential for significant improvements in photocatalytic water splitting technologies. The introduction of materials such as gold and cadmium sulfide not only enhances the production rates but also paves the way for more efficient solar energy utilization in hydrogen production. The dramatic increase observed with CdS/Au on $BiVO_4$ underscores the importance of material design and structural engineering in developing next generation photocatalysts for sustainable energy solutions.

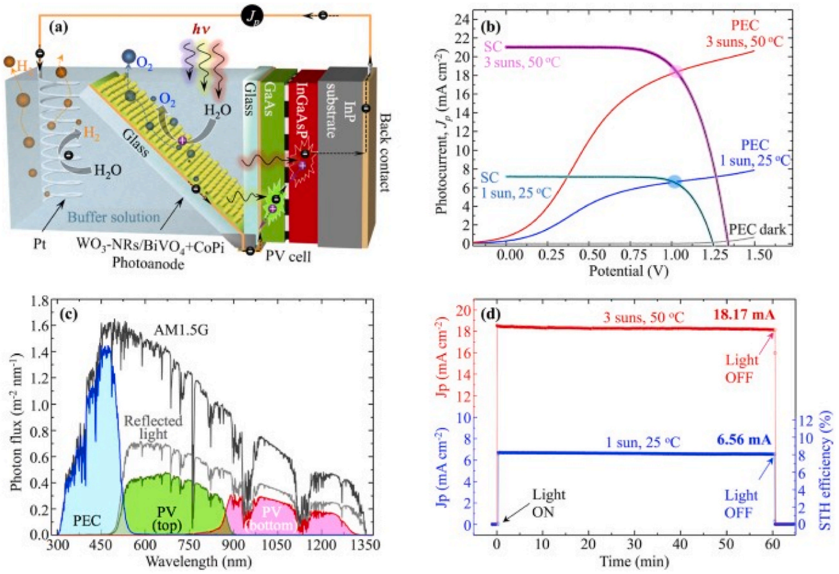


Fig. 9. (a) Schematic illustration of the PEC-PV tandem (b) I-V characteristics of the PV cell and the photoanode measured (c) the reflectance spectra of the photoanode (d) Jp-t profiles measured for the PEC-PV tandem. Reproduced from Ref. [32].

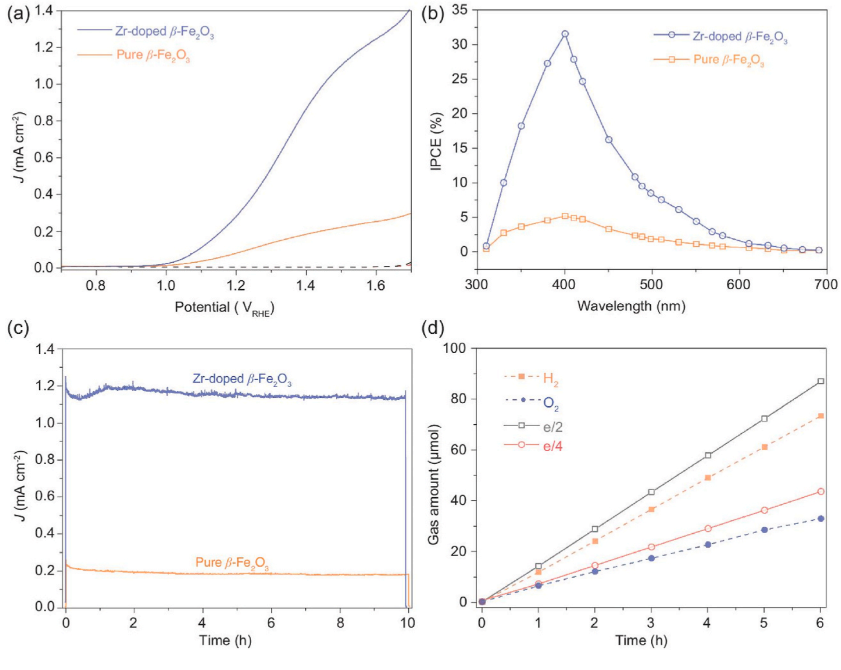


Fig. 10. (a) Photocurrent density, (b) IPCE, (c) photochemical stability at 1.6 V vs RHE, and (d) Faradaic efficiencies of the particle-assembled β-Fe_2O_3 films with Zr doping. Reproduced from Ref. [49].

Table 4
Hydrogen generation rate of $BiVO_4$-based photoanodes for water splitting.

Photoanode	Year	Hydrogen Production Rate (μmolh−1 g−1)	Reference
Pt-$BiVO_4$	2020	1.66	[52]
CdS/Au on $BiVO_4$	2024	2366	[53]
CdS/$BiVO_4$	2024	305	[53]

3.5. Fe_2O_3

Iron oxide (Fe_2O_3), is inexpensive and readily available. Its bandgap is about 2.1 eV, well-suited for visible light absorption. However, the charge's low electrical conductivity and rapid recombination rate hamper its PEC efficiency [54].

Some methods of synthesizing Fe_2O_3 include chemical vapor deposition, electrodeposition, and hydrothermal processes. Fe_2O_3 can be prepared in various forms, such as thin films, nanorods, or mesoporous structures, which can enhance the material's PEC properties.

Beta-phase iron oxide (β-Fe_2O_3) has been investigated as a PEC photoanode for hydrogen generation through water-splitting. It has a relatively low bandgap of 1.9 eV for β-Fe_2O_3, making it a very suitable material for application in solar water splitting. However, the applicability of β-Fe_2O_3 in water splitting for hydrogen production has been difficult due to the stability issues. Recent studies have also been directed towards the enhancement of the stability of the β-Fe_2O_3 photoanodes, for instance, through element doping to hinder phase transformation to α-Fe_2O_3 and strengthening of metal-oxygen bonding to reduce surface oxide reconstruction [55,49].

Adding Zr to the β-Fe_2O_3 photoanode resulted in a fivefold increase in the photocurrent generated by solar water splitting compared to the pure β-Fe_2O_3 photoanode as shown in Fig. 10. Moreover, Zr-doped β-Fe_2O_3 demonstrated exceptional stability during the solar water splitting process. The results suggest that enhancing the thermal stability of the metastable β-Fe_2O_3 film makes it a highly promising photoanode for solar water splitting [49].

Also, a recently published work described the stability of β-Fe_2O_3 photoanodes in highly corrosive environments like seawater over a long period, thus suggesting practical applicability [55]. Other researchers have also examined the possibility of using alpha-phase iron oxide (α-Fe_2O_3) for hydrogen production as a photoanode [56–58]. These studies show that continuous attempts have been made to improve the efficiency and stability of iron oxide-based photoanodes for hydrogen generation.

Based on Table 5 and Fig. 11, the resulting CoOOH-rGO/Fe_2O_3 demonstrates a significantly improved photocurrent density of 2.56 mA cm−2 at 1.23 V. It has been observed that rGO functions as a conductive network, facilitating electron transfer from Fe_2O_3 to the substrate. Meanwhile, CoOOH effectively passivates the surface states of Fe_2O_3, enhancing charge separation and providing catalytic active sites for water oxidation. The spatial charge separation and transfer induced by CoOOH and rGO contribute to the enhanced photoelectrochemical (PEC) performance in water oxidation [59]. This thoughtful design and straightforward fabrication approach show considerable promise for application in other highly efficient PEC systems.

4. Key factors for efficient photoanodes

Improving the performance of a photoanode for hydrogen production via photoelectrochemical water splitting is a challenging task that involves several aspects. Many approaches have been proposed to enhance the photoanodic performance, including light trapping, charge separation, and catalytic activity. Fig. 12 summarises some fundamental strategies researchers have explored in the quest to improve the efficiency of the photoanode.

4.1. Bandgap and band Alignment

Ideally, the material's bandgap should be between 1.7 and 2.2 eV to absorb visible light well. It is crucial to align the conduction and valence bands of the material with the water redox potentials. Optimisation of the bandgap of photoanode materials to allow for the absorption of a broader range of light wavelengths. Selecting or doping the photoanode material so that the bandgap is suitable for the absorption of solar radiation, particularly in the visible region [63–66].

Doping with metal ions like V, Cr, Mn [67], Fe [68], Ni, Cu [69,70], and Pt [68] can shift the absorption band towards the visible-light region, promoting photocatalytic activities under visible light or UV irradiation. To be more precise, at 1.23 V versus RHE, the photocurrent density of the 2 mol% Fe-doped WO_3 was 0.88 mA cm^{-2}, which is almost 30 % more than that of the undoped WO_3 (0.69 mA cm^{-2} at 1.23 V vs RHE). The absorption spectra and the Mott–Schottky plots supported the theory that the lowered band gap and the doping-enhanced charge carrier density caused this augmentation.

Doping with non-metal ions like C [71], N, and S can shift the valence-band edge upward, improving photocatalytic activities in the visible-light region. The most significant effect is achieved when oxygen atoms are substituted by carbon or nitrogen atoms, which narrows the semiconductor bandgap due to the upward displacement of the valence-band edge [14].

4.2. Surface catalysts

The OER kinetics at the photoanode surface are usually boosted with co-catalysts such as IrO_2 or RuO_2. Integration of secondary promoters to increase the oxygen evolution reaction (OER) rate and general catalytic performance. Introducing highly efficient co-

Table 5
Hydrogen generation rate of Fe_2O_3-based photoanodes for water splitting.

Photoanode	Year	Photocurrent density (mA/cm2) at 1.23 V vs. RHE	Reference
(Sn, Zr) α-Fe_2O_3	2015	1.64	[60]
CoOOH-rGO/Fe_2O_3	2021	2.56	[59]
Fe_2O_3/MoO_3	2023	1.09	[61]
Co-MOF/Ti:Fe_2O_3	2024	1.8	[62]

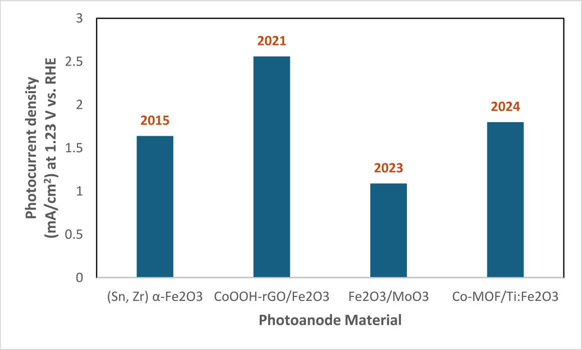


Fig. 11. Hydrogen generation rate of Fe_2O_3 photoanodes.

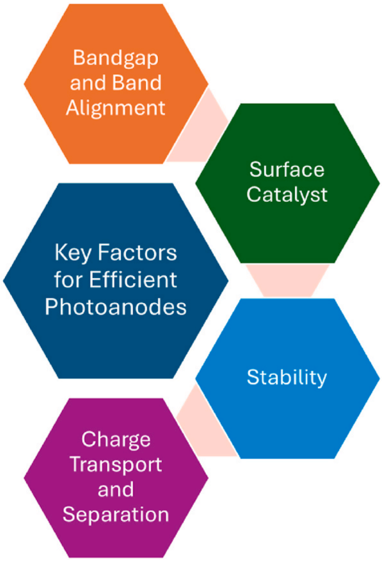


Fig. 12. Critical factors for efficient photoanodes.

catalysts on the surface of the photoanode increases the OER kinetics and, thus, the catalytic efficiency of the whole system, as observed in Fig. 13 [72,73]. The co-catalysts are noble metals, metal oxides, and other catalytic materials.

Cocatalysts work as hole reservoirs that accept the photogenerated holes from the photoanode and promote their transportation to the electrolyte to oxidize water. This minimises the recombination of charge at the surface of the photoanode, thereby increasing photocurrent [74,75]. The cocatalysts, including CoOx and NiFe-LDH, exhibit high intrinsic catalytic activity for the OER process. When these cocatalysts are loaded on the surface of the photoanode, the OER kinetics improve greatly [76,77]. Cocatalysts can also

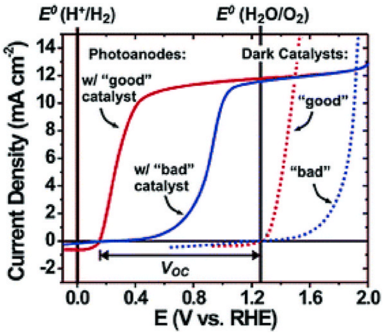


Fig. 13. The qualitative effect of a surface co-catalyst on photoanode water oxidation performance. Reproduced from Ref. [72].

change the work function and band structure in the photoanode/electrolyte interface. This may result in enhanced charge separation and reduced onset potentials for water oxidation [74,78]. Cocatalysts with large surface areas, like nanoparticles, enhance the charge transfer and catalytic activity at the photoanode surface. The size and the shape of the cocatalyst nanostructures can be adjusted for the best performance [77]. For instance, cocatalysts such as NiCoP can shield the photoanode from photocorrosion and improve long-term performance under working conditions [78].

The type of cocatalyst and its deposition technique (for example, spin coating, electrodeposition) may be optimized depending on the type of photoanode material and required characteristics of the cell. Cocatalysts' functions are reversible, and depending on the applied bias, they can act as either hole reservoirs or catalytic centres according to the systematic investigations [74]. More research is being conducted to enhance the interaction between photoanodes and cocatalysts, which will enhance the efficiency and stability of the PEC water-splitting devices.

4.3. Charge transport and separation

It is essential to ensure that the photogenerated electron-hole pairs are well separated and transported. This can be supported by Nanostructuring the photoanode to minimise recombination. Introducing a barrier shielding the electrode from corrosion enhances the charge transfer process. Designing photoanodes with tandem or multijunction configurations to absorb light more efficiently or designing tandem or multijunction photoelectrodes to absorb the solar spectrum selectively, thus enhancing light absorption and photoconversion efficiency [79].

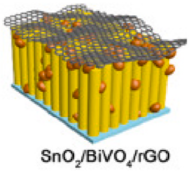
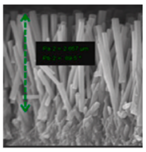
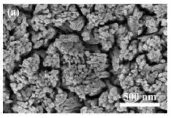
Furthermore, optimizing the concentration of the electrolyte material enhances the ionic conductivity and minimises charge recombination. Optimisation of the electrolyte composition enhances the ionic conductivity, reduces charge recombination, and enhances the system's performance [80].

The advantages of building MOs/2D materials heterostructures are described in a review article, and the state-of-the-art of MOs/2D materials heterostructures as photoelectrodes for various applications is presented. The review is stated based on photoelectrodes that refer to the heterostructure of MOs and an emerging group of carbides/nitrides/carbo-nitrides (MXenes), boron carbon nitride (BCNs), transition metal dichalcogenides (TMDs), metal-organic frameworks (MOFs), and bismuth oxyhalides (BiOX) [81,82].

A review article also highlights the recent developments in PEC water splitting, emphasizing the function of cocatalysts in the process. The article lays importance on the synthesis of efficient cathodic and anodic photoelectrodes of Fe_2O_3 and Si with the help of cocatalysts [77].

The third review article concerns the properties, synthesis, and new advances in post-transition metal oxide semiconductors for water splitting. The article also describes how gallium nitride nanowall networks and alloys of gallium with indium, for example,

Table 6
Performance of metal oxide heterojunction-based photoanodes for water splitting. Figures reproduced from Refs. [84–86].

Material	Synthesis method	Photocurrent density	Morphology	Reference
$SnO_2/BiVO_4/$ rGO	Chemical Vapor deposition, metal-organic decomposition, and spin coated RGO	2.05 mA/cm^2 at 1.23V vs RHE.	Nanorods 	[84]
Fe/ZnO NRs	Chemical bath deposition	OER: 6 mA/cm^2 HER: 1.3 mA/cm^2 STH: 4.7 %	Nanorods 	[85]
Sn-doped Fe_2O_3	Solvothermal synthetic	1.40 mA/cm^2 at 1.23V vs RHE.	Nanowire 	[86]
N-CFO/$BiVO_4$	in situ synthesis route	4.83 mA/cm^2 at 1.23 V vs RHE.	Thin film	[87]
$WO_3/BiVO_4$	Sol-gel and thermal decomposition.	0.64 mA/cm^2 at 1.23 V Vs RHE	Thin film	[88]
Nb–Zr: Fe_2O_3/ FTO	facile two-step synthesis	2.05 mA/cm^2 at 1.23V vs RHE.	–	[89]
rGO/ZnO/CdO	electrochemical deposition and thermal decomposition	1.15 mA/cm^2 at 1.23 V vs RHE.	–	[90]

indium gallium nitride, may improve photocurrent density and photon capture [83].

Therefore, although metal oxides have been explored for PEC water splitting, they could be more efficient due to their unfavourable band position, low charge mobility, and poor stability. To overcome these challenges, heterostructure MOs with other materials and cocatalysts have been suggested. This is because post-transition metal oxide semiconductors like gallium nitride and indium gallium nitride can improve the efficiency of PEC water splitting.

The performance improvement can be credited to creating n-n heterojunctions between SnO_2 and $BiVO_4$ and adding rGO to these heterojunctions. This combination enhances the absorption of visible light, improves the efficiency of charge separation, and speeds up electron transfer at the interface between the electrode and electrolyte [84]. Table 6 summarises metal oxide heterojunction-based photoanodes for water splitting highlighting their synthesis methods, photocurrent densities, and morphologies.

The illustration in Fig. 14 indicates a range of photocurrent densities among different materials, with N-CFO/$BiVO_4$ exhibiting the highest performance at 4.83 mA/cm^2, while WO_3/$BiVO_4$ shows the lowest at 0.64 mA/cm^2. The synthesis methods vary significantly, including chemical vapor deposition, solvothermal synthesis, and electrochemical deposition, which may influence the resulting morphology and performance characteristics of each photoanode.

Overall, these results reflect ongoing advancements in the development of metal oxide heterojunctions for efficient solar water splitting applications, with various strategies being employed to enhance photocurrent output and stability in photoelectrochemical systems.

4.4. Stability

Photoanodes should resist degradation under long-term illumination and in the electrolyte environment. Therefore, corrosion-resistant material or protective coatings may be required. Stability of photoanodes in extreme operating conditions. We are working on photoanodes with improved stability when exposed to extreme operating conditions for a long time, which may lead to the deterioration of the material [91].

The cobalt-oxide phosphate co-catalyst photo deposits at locations with high photo hole concentrations, protecting ZnO from photo corrosion. Moreover, combining Al_2O_3 and TiO_2 layers significantly reduces Cu_2O photo corrosion [92].

5. Perspectives and challenges

Recent advances in photoelectrochemical water splitting for hydrogen production present promising material, structure, and catalyst progress. Nevertheless, several key issues remain unsolved in the field, including the materials' stability, integration of the systems into a single unit, and overall efficiency. Such problems can only be solved through interdisciplinary approaches, underscoring the importance of developing practical solutions that can be scaled up from the laboratory. Although achieving sustainable and efficient photoelectrochemical water splitting is still a work in progress, researchers must adopt a more critical and realistic perspective in this promising but challenging discipline (see Fig. 15).

5.1. Significant remaining challenges and future perspectives

- Increasing solar to hydrogen conversion efficiencies above 10 % [93].
- Improving the durability of the component over thousands of operating hours [94].
- Designing low-cost fabrication techniques that can be used to manufacture large quantities of the product [95].
- Designing practical solar fuel generation systems and processes

Further work on the photoanode material, interfaces, and devices based on nanostructured metal oxide materials will help to advance the PEC water-splitting technology to be efficient, stable, and economical.

Future research directions in the field of metal oxide photoelectrodes for water splitting are poised for significant advancements,

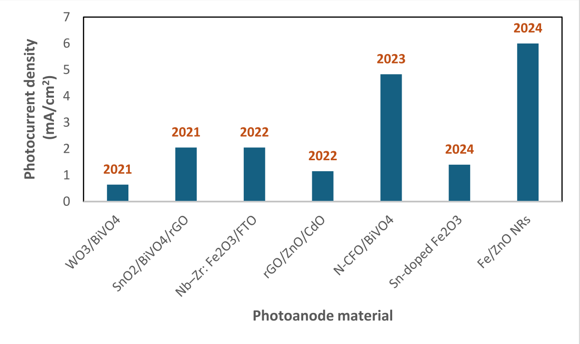


Fig. 14. Photocurrent density of metal oxide heterojunction-based photoanodes at 1.23V vs RHE.

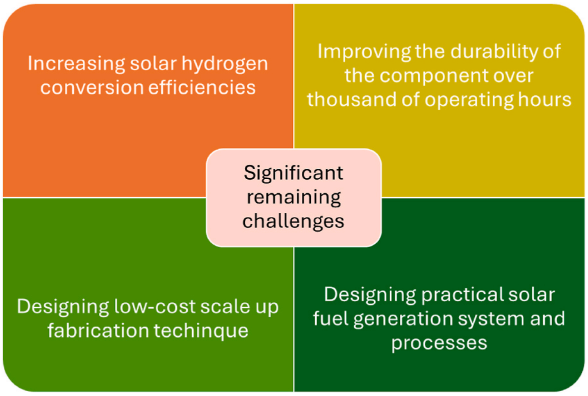


Fig. 15. The significant remaining challenges.

driven by emerging trends, potential breakthroughs, and the integration of novel technologies such as machine learning. This exploration highlights unexplored areas and aims to inspire further research.

5.2. *Advanced material engineering*

i. **Heterostructuring and Doping:** The use of heterostructures and doping strategies has shown promise in enhancing the efficiency of photoelectrodes [82,96]. Recent research has shown that the combination of various metal oxides can enhance charge separation and lower recombination rates, both of which are essential for boosting photocatalytic performance [13,97]. To find effective photoelectrodes for solar water splitting, recent research has focused on various multinary transition metal oxides, especially ternary transition metal oxides, as potential photoelectrode materials [97]. Future research can explore novel combinations of metal oxides and the optimisation of dopant types and concentrations.
ii. **3D Ordered Macroporous Structures:** The development of three-dimensional ordered macroporous (3DOM) metal oxide structures can significantly enhance light absorption and charge transport efficiency. These structures facilitate multiple light scattering and slow photon effects, which can be leveraged to improve the overall performance of photoelectrochemical (PEC) cells [98]. Investigating the scalability and reproducibility of these structures will be crucial for practical applications.
iii. **Perovskite Oxides:** Perovskite-based metal oxides are emerging as low-cost, abundant alternatives for photocathodes and photoanodes. Their tunable band gaps and high absorption coefficients make them suitable candidates for PEC applications. Research should focus on the stability and long-term performance of these materials under operational conditions [99,100].
iv. **Integration of Machine Learning:** Machine learning (ML) presents a transformative opportunity for accelerating the discovery and optimisation of metal oxide photoelectrodes. By employing ML algorithms, researchers can analyze large datasets from previous experiments to identify promising material compositions and processing conditions. This approach can lead to:

Predictive Modeling: Developing models that predict the performance of new metal oxide formulations based on their structural and electronic properties.

Optimisation of Synthesis Parameters: Using ML to optimize synthesis conditions, such as temperature and precursor concentrations, to achieve desired material characteristics.

Real-time Monitoring: Implementing ML for real-time monitoring of PEC systems, allowing for adaptive control of operational parameters to maximize efficiency.

5.3. *Unexplored areas*

i. **Photoelectrode Stability:** While many studies focus on enhancing efficiency, the long-term stability of metal oxide photoelectrodes under operational conditions remains underexplored. Research should aim to understand degradation mechanisms and develop protective coatings or composite materials that enhance durability.
ii. **Co-catalyst Integration**: The role of co-catalysts in improving the charge transfer processes at the photoelectrode/electrolyte interface is critical. Future studies should investigate the synergistic effects of various co-catalysts when combined with metal oxides, particularly in tandem systems that utilize multiple photoactive materials [13,100].
iii. **Environmental Impact Assessment:** As the field progresses, it will be essential to assess the environmental impact of synthesizing and deploying metal oxide photoelectrodes. Research should focus on sustainable synthesis methods and the lifecycle analysis of materials used in PEC systems.

The future of metal oxide photoelectrodes in water splitting is bright, with numerous avenues for exploration. By focusing on advanced material engineering, integrating machine learning, and addressing underexplored areas, researchers can pave the way for breakthroughs that enhance the efficiency and sustainability of solar-to-hydrogen conversion technologies. Continued investment in this field, particularly in the last few years, has laid a solid foundation for transformative advancements in the coming years [94,97,98].

iv. **Utilizing External Fields to Enhance Metal Oxide Photoanode Performance:** The introduction of external fields, such as magnetic and thermal fields, can potentially improve the activity and stability of metal oxide photoanodes. Magnetic fields can influence the charge carrier dynamics and surface reactions, leading to enhanced PEC performance [101]. Thermal fields can increase the reaction kinetics and promote the formation of desired surface oxygen species, as demonstrated in the case of $BiVO_4$ photoanodes. Investigating the effects of these external fields on various metal oxide photoanodes and optimizing their application can result in significant improvements in PEC efficiency and selectivity.

$BiVO_4/BiFeO_3$ (as shown in Fig. 16) significantly reduces the charge recombination rate from 17 s^{-1} to 0.6 s^{-1} compared to plain $BiVO_4$. The ferroelectric $BiFeO_3$ serves both as a passivation layer and a catalyst, enhancing the properties of $BiVO_4$. It effectively suppresses charge recombination and enhances charge separation. The photoelectrochemical (PEC) performance of the $BiVO_4/BiFeO_3$ composite can be adjusted by altering the direction of self-polarization in $BiFeO_3$. Additionally, this composite demonstrates superior stability compared to both $BiVO_4$ and $BiVO_4$/Co-Pi. The mechanism behind the improved PEC performance is attributed to $BiFeO_3$'s role as a bifunctional film, acting as a buffer layer that significantly lowers charge recombination while also serving as an efficient catalyst for charge separation and transfer [102].

5.4. Machine learning in water splitting for optimisation

Fig. 17 shows that machine learning is being deployed to enhance the process of designing effective catalysts for water splitting, an essential process in the generation of green hydrogen. This integration aims to enhance efficiency and reduce the costs associated with catalyst development. Here are some critical applications.

5.4.1. Catalyst optimisation

Machine learning has emerged as a catalyst to shift a paradigm from a conventional trial-and-error approach to a data-based prediction as depicted in Fig. 18 [103]. Machine learning is used to predict a material's target properties based on its chemical composition, crystal structure, and basic material properties. For catalyst design, the target properties could be the binding energy of adsorbate during intermediate reaction or conductivity.

The integration of machine learning and catalyst optimisation is rapidly increasing and expanding its application area. Computational materials databases are steadily developed with efficient data structures that become workhorses for the application of machine learning [104].

Machine learning models based on the experimental data are employed to fine-tune the composition of electrocatalysts to reduce the overpotentials of the oxygen and hydrogen evolution reactions [105]. The most accurate predictions have been made in the case of the composition of the catalysts with the help of neural networks [106].

For instance, a notable study demonstrated the effectiveness of neural network-based models to optimize precursor ratios of hydroxide-based electrocatalysts. This approach led to significant improvements in electrocatalytic performance, achieving overpotentials of 266 mV for oxygen evolution and 272 mV for hydrogen evolution reactions in alkaline conditions. The optimized catalyst, identified as a molybdate-intercalated CoFe layered double hydroxide (LDH), exhibited stability over extended periods, making it suitable for industrial applications [106].

The application of ML in this field involves various algorithms, including Gaussian Process Regression, Gradient Boosting, and Neural Networks [107,108]. These methods facilitate the exploration of different catalyst compositions and correlate them with experimental performance metrics. The use of a small initial dataset has proven effective in rapidly converging on optimal catalyst compositions, thereby streamlining the traditionally labor-intensive process of catalyst discovery [109]. The uses of machine learning in water splitting are summarized in Fig. 19.

5.4.2. High-throughput screening

Machine learning is being used to screen many potential catalyst materials simultaneously. For example, generative models were used to design a new 2D photocatalyst for water splitting by drawing samples from the learned material space. The bandgaps and band edge positions of generated materials are predicted with the help of graph neural networks [110].

5.4.3. Accelerating research

The incorporation of machine learning in experimental procedures is enhancing the rate at which researchers improve the performance of electrocatalysts, which is usually a lengthy process [110]. There are several approaches to reduce the time and labour-consuming nature of experimental optimisations, and these are machine learning strategies.

5.4.4. Enabling industrial application

The conditions required for synthesizing machine learning-optimized catalysts are relatively low, making them suitable for large-scale production of green hydrogen [109]. However, there are still some issues to be solved, such as how to design and synthesise earth-abundant and low-cost catalysts with high-activity [111].

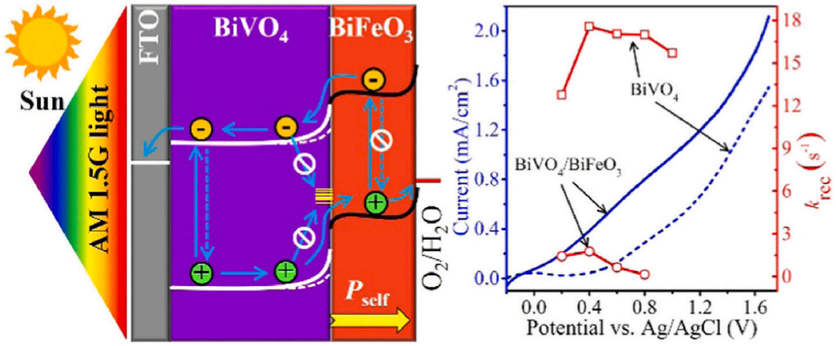


Fig. 16. Schematic illustration of the PEC water oxidation mechanism occurring at BVO/BFO (a), and photoelectrochemical measurements (b). Reproduced from Ref. [102].

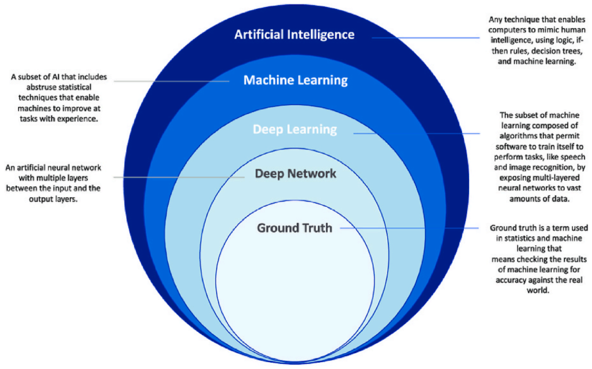


Fig. 17. Machine learning diagram.

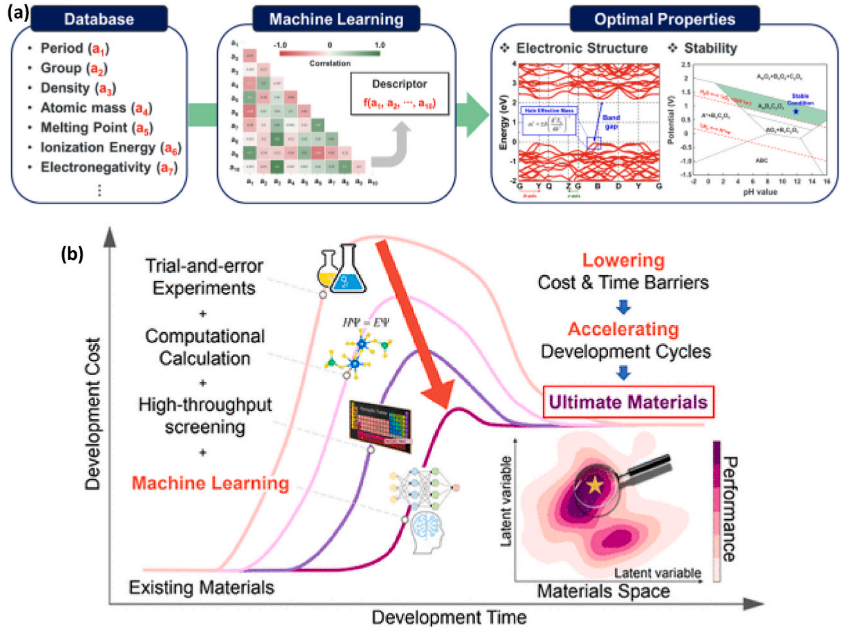


Fig. 18. (a) Workflow of optimisation using machine learning, and (b) Recent trends of materials development paradigm with machine learning [103,104].

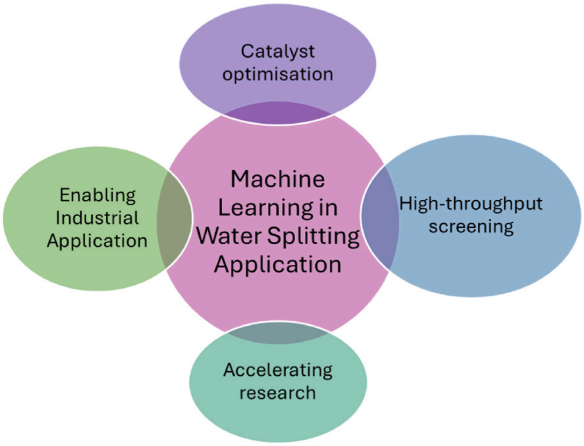


Fig. 19. Advantages of machine learning in water splitting.

A recent study by Lim et al. indicates that combining machine learning with lab automation is ideal for identifying efficient catalysts for hydrogen and oxygen evolution reactions [111]. The study focuses on transition metal layered double hydroxide (LDH) catalysts, notable for their unique lamellar structure and adjustable chemical compositions. By examining five metal components (Ni, Co, Fe, Mo, and W) in various ratios, the study effectively used machine learning to explore different compositions and correlate them

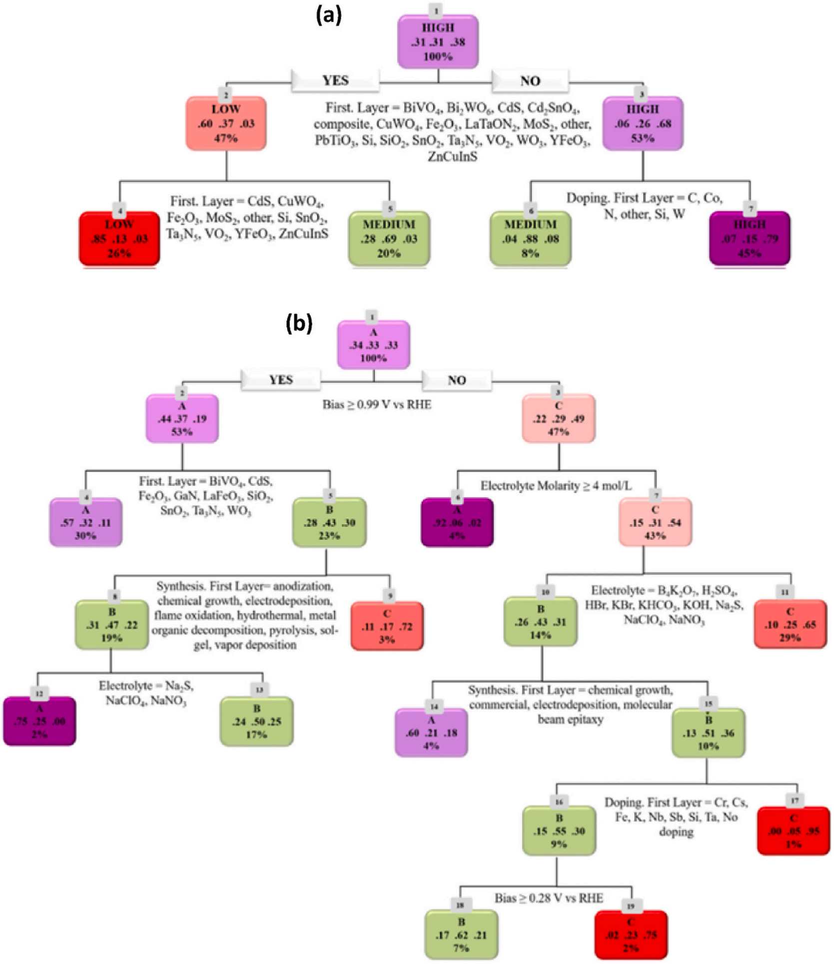


Fig. 20. The decision tree for (a) band gap and (b) current density classification [105].

with experimental electrochemical performance. This method followed a straightforward yet effective machine learning optimisation workflow, as shown in Fig. 18, employing a small initial dataset, Bayesian Optimization [112], and three machine learning algorithms: Gaussian Process Regression [113], Gradient Boosting [114], and Neural Networks [115].

Neural networks were the most effective in predicting optimal catalyst compositions. The leading catalyst was the molybdate-intercalated CoFe LDH, which exhibited 266 and 272 mV overpotentials for the oxygen and hydrogen evolution reactions, respectively, and maintained stability for over 50 h. It is believed that integrating molybdate disrupts the LDH's turbostratic structure, thereby increasing the number of active sites.

An automated synthesis system provided an effective platform for scaling up these materials without significantly changing their physical and chemical properties, highlighting the potential for industrial application. This sets a precedent for scaling up electrocatalytic materials in the field. This study emphasises the possibility of incorporating machine learning methods into experimental workflows. This approach accelerates the optimisation of electrocatalysis performance, representing a significant advancement in developing efficient and sustainable hydrogen production technologies.

Moreover, Oral analysed a comprehensive dataset comprising 10,560 data points from 584 experiments across 180 articles on photoelectrochemical water splitting using n-type semiconductors with machine learning techniques. et al. Initially, simple descriptive statistics were used for pre-analysis. Following this, association rule mining (ARM), random forest (RF), and decision tree (DT) techniques were employed to discern patterns and establish relationships between photocurrent density and 33 descriptors, including electrode materials, synthesis methods, and the properties of irradiation and electrolyte solution. ARM effectively identified critical factors for band gap and photocurrent density. As shown in Fig. 20, the DT model achieved high accuracy for band gap prediction, with training and testing accuracies of 78 % and 72 %, respectively, though it was less accurate for photocurrent density (training accuracy: 61 %; testing accuracy: 54 %). The predictive model for band gap developed using RF was also notably effective, with root mean square errors of validation and testing at 0.24 and 0.27, respectively [105].

6. Conclusion

In conclusion, the ongoing advancements in photoelectrochemical (PEC) water splitting for hydrogen production have made significant strides, particularly in the development and optimisation of nanostructured metal oxide photoanodes. Some of important materials, including TiO_2, WO_3, $BiVO_4$, and Fe_2O_3, have shown promise due to their appropriate bandgap energies, stability, and the potential for large-scale hydrogen generation using solar energy. However, several critical challenges remain to be addressed to fully harness the potential of PEC water splitting technology.

The efficiency of these systems is still hampered by issues such as rapid electron-hole recombination, limited charge transport, and the instability of materials under operational conditions. Furthermore, scalability and the high costs associated with material synthesis and device fabrication pose additional hurdles. Addressing these challenges requires a multi-faceted approach that includes the optimisation of material properties, the development of cost-effective manufacturing techniques, and the integration of advanced technologies such as machine learning to accelerate research and development.

Machine learning offers a promising avenue for optimizing the composition and structure of photoanodes, thereby enhancing their performance and stability. By leveraging large datasets and predictive algorithms, researchers can rapidly identify and fine-tune materials that meet the stringent requirements of PEC water splitting.

Ultimately, overcoming these challenges through interdisciplinary research and innovative technological solutions is essential for the practical application of PEC water splitting in hydrogen production. As the global energy landscape shifts towards renewable sources, efficient and sustainable hydrogen generation through PEC technology could play a pivotal role in achieving a carbon-neutral future. Continued research and collaboration across scientific disciplines will be crucial in advancing this promising field and realizing its full potential.

CRediT authorship contribution statement

Aini Ayunni Mohd Raub: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Raihana Bahru:** Writing – review & editing, Visualization, Validation, Supervision, Conceptualization. **Siti Nur Ashakirin Mohd Nashruddin:** Writing – review & editing, Conceptualization. **Jumril Yunas:** Writing – review & editing, Writing – original draft, Validation, Supervision, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Ethical approval

Not applicable.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:Jumril Yunas reports financial support was provided by National University of Malaysia. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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