e-ISSN: 2682-8588

Available online at
http://journal.uitm.edu.my/ojs/index.php/MJCET

Malaysian Journal of Chemical Engineering & Technology 7(2) 2024, 205–223

Malaysian Journal of Chemical Engineering and Technology

An overview of catalyst development for enhanced green hydrogen production

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ARTICLE INFO

Article history:
Received 31 March 2024
Revised 20 October 2024
Accepted 28 October 2024
Online first
Published 31 October 2024

Keywords:
Electrocatalyst
Photocatalyst
Hydrogen production
Sustainable energy
Green hydrogen

DOI:
10.24191/mjcet.v7i2.1294

ABSTRACT

The persistent release of greenhouse gases, primarily due to the heavy reliance on fossil fuels in transportation and energy-intensive industries, necessitates urgent research into sustainable alternatives. These sectors, regarded as the foundation of civilisation, make significant contributions to environmental degradation. In response, hydrogen (H_2) emerges as a promising energy source capable of meeting global energy needs while reducing harmful emissions. This article provides a comprehensive overview of cutting-edge H_2 production technologies, focusing on a critical issue within this landscape: the use of precious metals in catalysts. While precious metals such as platinum have excellent catalytic activity, their scarcity and high cost make widespread implementation difficult. A careful review of catalyst support materials to improve overall performance and stability is also provided. It explores the wider field of catalysts for producing green H_2, including needs, recent findings, theoretical effectiveness, and developing approaches to lessen reliance on precious metals. The article concludes with perspectives on the future, promoting a better understanding of the complex interplay between catalyst design, sustainability, and green H_2 production.

1. INTRODUCTION

The urgent need to tackle climate change has accelerated the worldwide transition to sustainable energy into high gear (Ahmad et al., 2020; Nikolaidis & Poullikkas, 2017). Sustainable sources that split water into hydrogen and oxygen are currently generating interest in green hydrogen (Shiva Kumar & Himabindu, 2019; Zainol et al., 2017). This versatile energy carrier has the potential to significantly reduce carbon emissions in a variety of industries, including transportation, manufacturing, and power generation.

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https://doi.org/10.24191/mjcet.v7i2.1294

Currently, numerous methods for producing green hydrogen are gaining interest. These include solar-powered water splitting, electrolysis, photovoltaic electrolysis, and wind electrolysis. The development of high-performance catalysts essentially determines the efficiency and economic viability of these approaches (Mohd Shah et al., 2021; Rosman et al., 2022). These catalysts accelerate the chemical reactions involved in water splitting, increasing both the speed and efficiency of the process (Wang et al., 2021).

Although the science behind these catalysts is complex, their significance is well understood. This overview seeks to bridge this gap by offering a clear and simple overview of catalyst development for enhanced green hydrogen production, thereby developing an essential understanding of this key component of green hydrogen technology. This overview will be a valuable reference for everyone looking to grasp the critical role of catalysts in promoting green hydrogen technologies for a cleaner, more sustainable energy future.

2. PHOTOELECTROCHEMICAL (PEC)

2.1 Solar-driven water splitting

The need to develop sustainable and clean energy solutions has driven research into cutting-edge technologies. Among these technologies, photoelectrochemical (PEC) water splitting is particularly noteworthy as a viable approach to harnessing solar energy to generate H_2. This process entails the utilisation of specialized semiconductors, referred to as photoelectrodes, which, upon exposure to sunlight, enable the direct separation of water molecules into H_2 and O_2. PEC water splitting is a green energy solution that tackles the environmental issues (Harris-Lee et al., 2023). This section investigates the PEC cell, its mechanism, and its effectiveness.

PEC water splitting is an environmentally friendly and renewable method that uses photoelectrodes made of semiconductors to produce excited electron-hole pairs when exposed to sunlight, leading to the separation of water molecules (Kumar et al., 2022). There are two different types of photoelectrodes: the photoanode, a *n*-type semiconductor, and the photocathode, a *p*-type semiconductor. In a PEC with a photoanode, H_2 is generated at the cathode while oxygen (O_2) is evolved at the photoanode (Li & Wu, 2015). The semiconductor materials utilised in PEC are similar to those used in photovoltaic solar power generation. However, they are immersed in a water-based electrolyte, which allows solar energy to irradiate the catalyst for the water splitting reaction. Direct PEC involves submerging a photoelectrode in an aqueous solution (Chang et al., 2013). Fig. 1 shows the schematic process of O_2 and H_2 generation in a PEC cell.

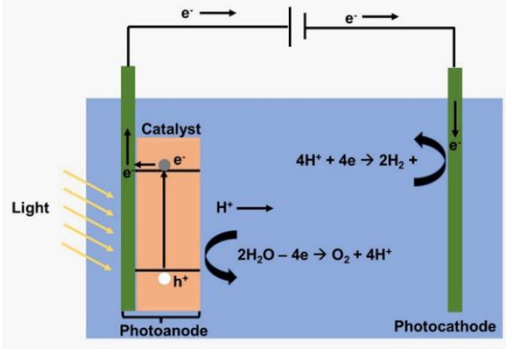

Fig. 1. Schematic diagram for PEC water splitting

Source: Chang et al. (2013)

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The process achieves a high level of efficiency, exceeding 30 %, and generates useful by-products such as hydrocarbons and O_2 (Ghosh & Hajra, 2021). The theoretical maximum of STH conversion efficiency of PEC for water splitting is 47.3 %. The solar-assisted water splitting system is aimed to achieve a net primary energy balance only when the STH value exceeds 3–5%. Furthermore, for economic viability, the STH must meet a 10% barrier (Zhang et al., 2020). Despite being considered a viable approach for H_2 generation due to the fact that it utilises sunlight and does not emit CO_2 (Yu et al., 2020), the potential of PEC water splitting is hindered by its restricted efficiency caused by charge carrier recombination, high overpotential, and slow kinetic reaction (Kumar et al., 2022).

PEC reactors can be designed in various ways. Fig. 2 depicts the basic PEC setup. It consists of a transparent vessel containing an electrolyte, which is fitted with a window to allow the light to reach the photoelectrode. Other PEC reactors have various shapes and configurations and could be grouped into single-chamber vessels with gas separation and photocells with fixed-area photoelectrodes (Minggu et al., 2010). Each configuration offers distinct advantages and challenges. For the large-scale application, PEC reactors were assembled on a flat surface to ensure maximum exposure to light. The structure and complexity of the reactor depend on the bias of the photoelectrode. The route to converting solar energy into H_2 holds promise for achieving great efficiency at low temperatures by utilising affordable semiconductor materials in the form of thin films or particles.

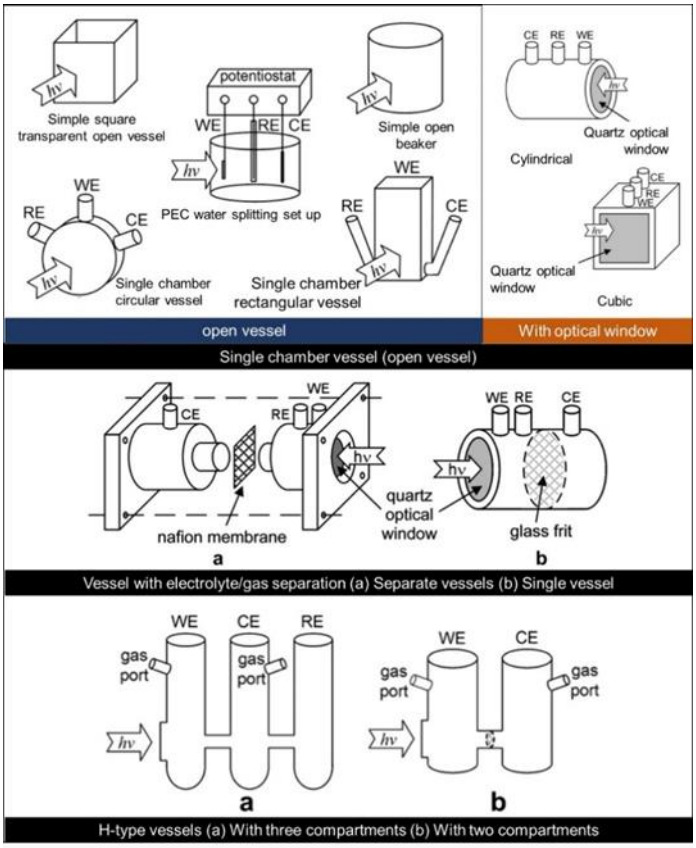

Fig. 2.Various photocell types

Source: Minggu et al. (2010)

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However, the success of the market depends on continuous enhancements in efficiency, durability, and cost-effectiveness. Current endeavours aim to improve the efficiency of sunlight absorption, promote surface catalysis, increase material durability, and develop advanced protective coatings. The primary goal is to decrease the costs of H_2 production by selecting and processing materials optimally.

2.2 Photoelectrode

The efficiency of green H_2 production is determined by the band structure of the photoelectrode, which requires a band gap higher than 1.23 eV. The band alignment must straddle the redox potential of water, with the conduction band being more negative than the reduction potential of water and the valence band being more positive than the oxidation potential of water (Mohd Shah et al., 2021; Thakur et al., 2020). Semiconductor materials such as ZnO, TiO_2, Fe_2O_3, MoS_2, Cu_2O, g-C_3N_4, $BiVO_4$, SnO_2, CdS are commonly used to convert absorbed photons into H_2 fuel because of the photogenerated charges that have high kinetic energy, due to their photoactive behavior (Mamiyev & Balayeva, 2022; Ta et al., 2016; Thakur et al., 2020; Zhang et al., 2023). Photoelectrodes can be classified based on their achieved solar-to-H_2 (STH) value, which measures the ability to convert solar into the production of H_2. An STH value exceeding 10 % indicates a highly efficient photoelectrode, while below 1 % suggests a poor photoelectrode (Thakur et al., 2020). In addition to environmental and industrial criteria, designing a high efficiency photoelectrode requires particular parameters such as low cost, clean, renewable, stable, abundant and environmentally friendly. However, their rapid electron-hole pair recombination rate and low solar energy utilisation are the main drawbacks of photoelectrode (Mamiyev & Balayeva, 2022).

Stability of photoelectrodes in the aqueous solution at the band edge straddling the redox potential of water is an important challenge in the design of stable photoelectrodes (Thakur et al., 2020). Thus, understanding and controlling the kinetic mechanisms that influence photovoltage is critical in the design of efficient semiconductor photoelectrodes (Walter et al., 2010). Several efforts have been undertaken to develop an efficient photoelectrode, as illustrated in Fig. 3., including morphology-engineered nanostructures, nanocomposites and nanomaterials, as well as multilayered heterostructures (Dai et al., 2020; Samuel et al., 2020). Furthermore, the synthesis process also plays an important role in controlling the composition and morphology of the photoelectrode and catalyst, as modifications to the morphology and composition may possess a major impact on the photoelectrode and catalyst's performance (Kang et al., 2015).

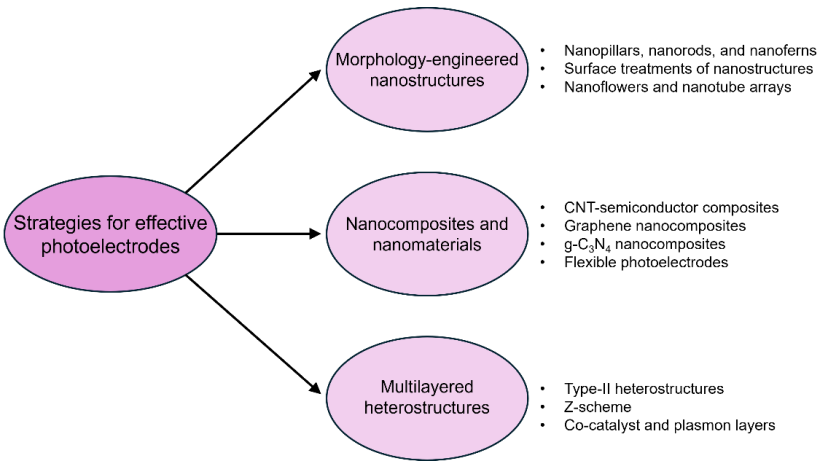

Fig. 3. Strategies for designing high efficiency photoelectrodes

Source: Authors' own illustration

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The theoretical maximum photocurrent is 38.48 mA cm^{-2} (Zhang et al., 2020), where the highest photocurrent was achieved using nickel foils-GaIn eutectic-layered double hydroxides is 15.10 mA cm^{-2} at 1.23 V vs RHE with 4.33 % STH value (Yu et al., 2020). Despite advances in photoelectrode development, to achieve and sustain 10 % efficiency for STH energy conversion is still challenging (Samuel et al., 2020).

2.2.1 Transition metal based

The transition metal based photoelectrodes have emerged as promising candidates for overall water splitting due to their unique properties and potential advantages like abundance, tunable properties, high efficiency and stability (Li et al., 2021). Recently, Kiptarus et al. introduced Co into ZnS/rGO through a hydrothermal method for 16 hours at 200 °C. SEM analysis (Fig. 4) revealed a mixed morphology of cuboidal and spheroidal ZnS covering the rGO surface, with some agglomeration observed. Interestingly, increasing the Co dopant concentration from 0 to 6 amt.% decreased the size of agglomeration and the existence of graphene helps to reduce electron-hole pair recombination. As a result, the highest H_2 production rate of 7648.9 µmol/h was achieved with a 4% Co doping concentration in the ZnS/rGO as shown in Fig. 4 (Kiptarus et al., 2024). Dong et al. (2019) combined ZnO/MoS_2/graphene heterostructure utilising chemical and liquid-phase exfoliation methods. The success of this ternary structure was observed by the SEM image, where ZnO was consistently distributed on the interlayers of MoS_2 and graphene. This structure results from the van der Waals effect. Thus, a high efficiency of H_2 production (5.4 mmol/g/h) was attained as shown in Fig. 5 (Dong et al., 2019).

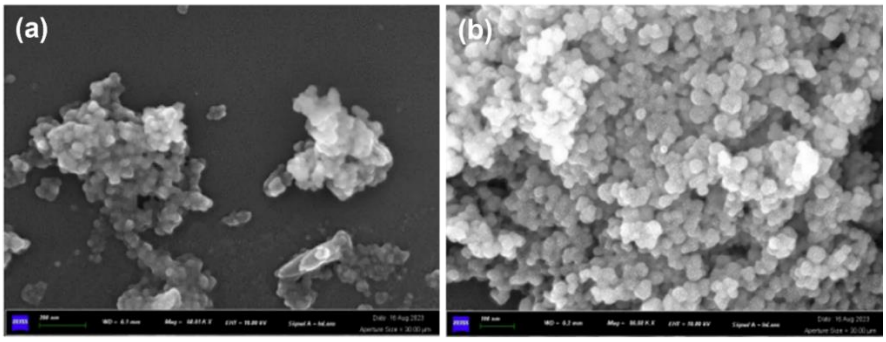

Fig. 4. SEM images of 4% Co-doped ZnS/rGO at (a) 40.00 kx and (b) 80.00 kx magnifications

Source: Kiptarus et al. (2024)

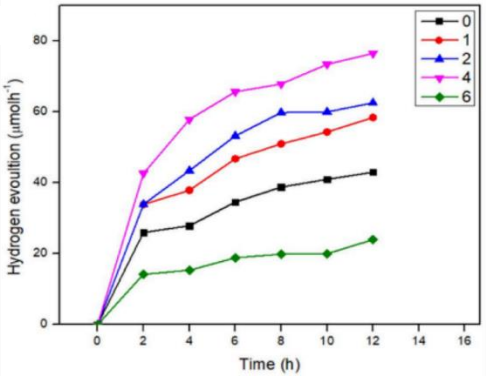

Fig. 5. H_2 production at various Co-doping concentrations on ZnS/rGO

Source: Kiptarus et al. (2024)

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2.2.2 Metal-free based

Ensuring long-term stability and durability is essential for the practical application of metal-free photoelectrodes. The common types of metal-free photoelectrodes include carbon-based materials, semiconductor-based materials and hybrid materials (Chen et al., 2024). For instance, Zhang et al. (2023) developed dual-layer carbon nitride (DCN) photoanodes with a porous microtubular top layer to increase the interfacial area with the electrolyte and a thin bottom layer for enhanced substrate adhesion. DCN was synthesised using a combination of spin-coating and chemical vapor deposition. A precursor solution was spin-coated onto a fluorine-doped tin oxide (FTO) glass substrate and subsequently heated in a sealed crucible with melamine. The resulting DCN photoanodes exhibited exceptional photocurrent densities of up to 910 μA/cm at 1.23 V vs. RHE, demonstrating superior solar-to-chemical energy conversion efficiency. Compared to traditional g-C_3N_4 electrodes, the DCN structure exhibited enhanced charge mobility and reduced charge recombination, leading to a longer charge carrier lifetime and improved overall performance. Zhu et al. formed double perovskite cobaltite catalyst, $Ba_{1-x}Gd_{1-y}La_{x+y}Co_2O_{6-\delta}$ known as BGLC, using the sol-gel citrate method. The resulting BGLC587 film with x = 0.5 and y = 0.2 was deposited onto FTO coated glass via pulsed laser deposition at 100 °C in an oxygen-rich atmosphere (Zhu et al., 2021). STEM images indicated that BGLC587 exhibits high crystallinity, which is important to its catalytic performance in the PEC system. The photocurrent density of BGLC582 is 10 mA/cm^2 at 1.23 V vs RHE, with no significant degradation over 71 hours. These findings emphasize the potential of metal-free photoelectrodes for sustainable energy applications.

2.2.3 Platinum (Pt) based

Despite the development of numerous high-performance Pt-based photoelectrodes, enhancing their performance and durability remains a critical research area in green technology. Choi et al. successfully controlled the size of Pt deposited on FTO/Cu_2O/Al:ZnO/TiO_2 using redox photoelectrodeposition. HRTEM revealed a uniform distribution of Pt on TiO_2 protective layer. This led to a current density of -6.2 mA/cm, with only a 5% decrease in photocurrent density after 50 hours of reaction (Choi et al., 2022). Sharifi et al. successfully synthesised Pt-doped Cr-doped TiO_2 nanotubes via an electro-anodization technique. Cr was incorporated into the TiO_2 structure during the synthesis process without affecting its morphology. This study demonstrated that Cr doping enhances the electronic properties of TiO_2 by reducing its bandgap energy. Subsequently, Pt was deposited onto the TiO_2 surface using photodeposition with a high-pressure Hg lamp. The deposition time was optimised to achieve complete surface coverage with Pt, as excessive exposure led to Pt agglomeration. The resulting Pt-TiO_2 electrodes exhibited significantly higher photocurrent densities (0.92 mA/cm²) and hydrogen production rates (1.08 ml/h) (Sharifi et al., 2021). An atomic layer deposition method was used by Li et al. (2015) to synthesise TiO_2/Pt/Si-nanowire and to evaluate their PEC performance as photocathode. As can be seen from 6a and 6b, the sandwich structure of TiO_2/Pt/Si-nanowire was observed, where Pt nanoparticles are imbedded between Si-nanowires and the surface of TiO_2 passivation layer. According to a thorough evaluation of the photocatalytic properties (6c), this material exhibits higher current density at 100 mW/cm^2 illumination which is around ~-27 mA/cm^2. Also, the onset potential of TiO_2/Pt/Si-nanowires shifted by 0.65 V compared to bare Si. It shows that when Pt were embedded within a protective TiO_2 layer, demonstrating that the catalytic effect of the Pt could still transmitted through the TiO_2 layer (Li et al., 2015).

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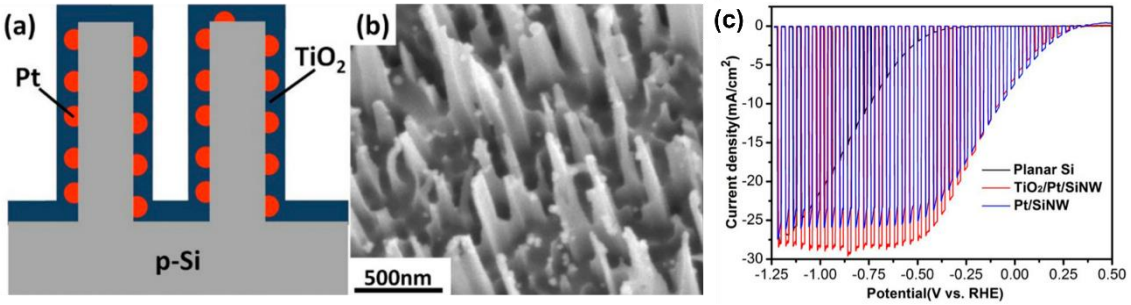

Fig. 6. (a) The illustration of TiO2/Pt/Si-nanowire, (b) SEM image of TiO2/Pt/Si-nanowire, and (c) Comparison of the photocurrent density between TiO2/Pt/Si-nanowire, Pt/Si-nanowire and Planar Si

Source: Li et al. (2015)

3. ELECTROCHEMICAL WATER SPLITTING

3.1 Water electrolyser

A water electrolyser is a device that converts electrical energy to chemical energy to split water into H_2 and O_2. Two reactions occur simultaneously in water electrolysis which is OER and HER at anode and cathode, respectively. There are three forms of low temperature water electrolysis: alkaline water electrolysis (AWE), proton exchange membrane water electrolysis (PEMWE), and anion exchange membrane water electrolysis (AEMWE). Typically, water electrolyser consists of an anode catalyst, a separator (membrane or separator), and a cathode catalyst. Among the current WE technologies, AWE stands out with a reported lifetime of 100,000 hours, making it a mature technology. PEMWE has a lifetime of 10,000 hours and is commercially available for small-scale applications. On the other hand, AEMWE had the shortest lifetime of 2,000 hours and the technology status remaining in research and development stage. In terms of cost, AWE is currently more economical than PEMWE. However, cost estimations for AEMWE are not readily available (Xu et al., 2022). It requires a power grid to operate water electrolyser that causes less sustainable way to produce H_2. Theoretically, water splitting processes occur at 1.23 V and thermoneutral voltage is 1.48 V which includes the internal heat accumulated, this is applicable for single cell only. The voltage increases proportionally to stack cells. Moreover, to achieve green manufacturing and zero carbon emission, water electrolyser needed to be incorporated with renewable energy sources such as PV and wind. Water electrolysis has several advantages, including high purity and production rate of H_2, a quick response to reaction, and compatibility with renewable energy, making it excellent for producing green H_2 (Haider et al., 2021).

3.1.1 Photovoltaic-electrolyser (PV-E)

There are several advantages of incorporating PV along with electrolyser which are sustainable and environmentally friendly, low cost and successive developments. However, PV has limited efficiency and is dependent on the solar radiation and temperature (Alhaj Omar, 2023). PV-E is classified as direct and indirect coupling, where distinction between them is that direct coupling does not require any extra equipment such as DC/DC converter and maximum power point tracker (MPPT) (Gu et al., 2023). Fig. 7 illustrates the schematic diagram of PV-E. Thus, implementation of MPPT can fully utilise the PV panel to maximize the power absorption. However, this contributed to a high-cost system. A simple PV-E made up of a PV generator, electrolyser, DC/DC convertor and MPPT (Gu et al., 2023). PV power is dependent on

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the weather prediction; high electrical generation occurs on sunny days, while low electrical generation occurs on cloudy days, making PV power unreliable and decreasing the efficiency of water electrolysis (Kojima et al., 2023). The direct coupling efficiency can be up to 99 %. To do so, the efficiency of the electrolyser needed to be improved by its gas diffusion layer, catalysts, and membrane. Not only that, but the PV panel needs to be enhanced to increase overall efficiency (Martinez Lopez et al., 2023). In contrast, an indirect coupling PV-E often incorporates battery storage to manage the excess energy and provide on-demand power for WE when necessary (Tam et al., 2024). Kim et al. conducted a study of PV-E systems in the Korean Peninsula, utilising a PEMWE. Their findings indicated that a PV system capable of generating 58.5 GW of power would be sufficient to meet the hourly energy demand of 4,200 MW. However, further economic analysis is necessary to fully assess the feasibility and cost-effectiveness of the PV-E system in the region (Kim et al., 2021).

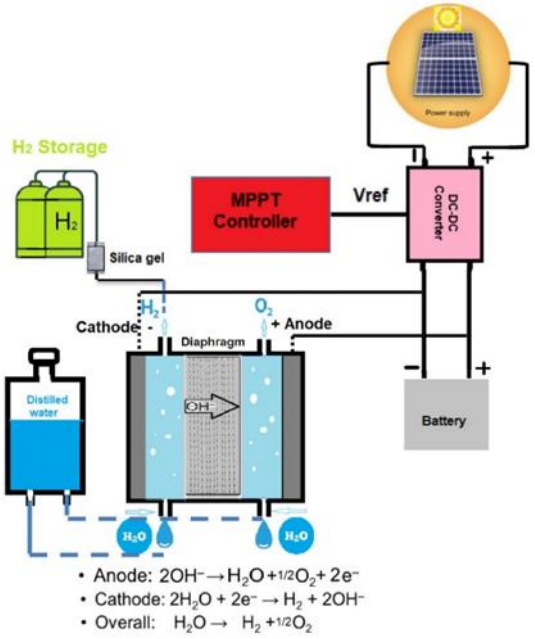

Fig. 7. Schematic diagram of PV-E

Source: Benghanem et al. (2023)

3.1.2 Wind electrolysis

Wind energy is an alternative renewable source that can be used in green H_2 production device (Brauns & Turek, 2020). However, wind electrolysis is more complicated than PV-E. Wind-water electrolysers can be implemented both onshore and offshore. Installing an offshore wind farm and electrolyser necessitates a high voltage alternating current (HVAC) system, resulting in expensive infrastructure. This problem can be solved by using an offshore wind farm and an onshore electrolyser. This system is flexible and excess electricity produced can be sold into the power grid (Calado & Castro, 2021). A general wind electrolysis system consists of a wind turbine generator, AC/DC convertor and water electrolyser (Benghanem et al., 2023).

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3.2 Electrocatalyst

Considering several technologies of H_2 production, electrochemical water splitting is considered the most promising technology to efficiently produce green H_2. To achieve high H_2 production efficiency, an excellent catalyst is required to reduce the energy barrier for water splitting (Broicher et al., 2019). Ideally, the electrocatalyst should have a high surface area, high catalytic activity, excellent electrical conductivity, and long-term stability. In electrochemical water splitting, there are two half-reactions involved: H_2 evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode of an electrochemical device as summarised in Table 1 (Li et al., 2020). Fig. 8 illustrates the mechanism reactions of HER and OER in alkaline and acidic environments.

Table 1. Detailed reaction mechanism for HER/OER in alkaline/acidic conditions

Step	Alkaline media	Acidic media
	HER	
Volmer	$H_2O + e- \rightarrow H^* + OH-$	$H_3O+ + e- \rightarrow H^* + H_2O$
Heyrovsky	$2H^* + \rightarrow H_2$	$2H^* + \rightarrow H_2$
Tafel	$H^* + H+ + e+ \rightarrow H_2 + OH-$	$H^* + H+ + e+ \rightarrow H_2$
	OER	
(1)	$OH- \rightarrow *OH + e-$	$H_2O \rightarrow *OH + H+ + e-$
(2)	$*OH + OH- \rightarrow *O + H_2O + e-$	$*OH \rightarrow *O + H+ + e-$
(3)	$*O + OH- \rightarrow *OOH + e-$	$*O + H_2O \rightarrow *OOH + H+ + e-$
(4)	$*OOH + OH- \rightarrow O_2 + H_2O + e-$	$*OOH \rightarrow O_2 + H+ + e-$

Source: Li et al. (2020)

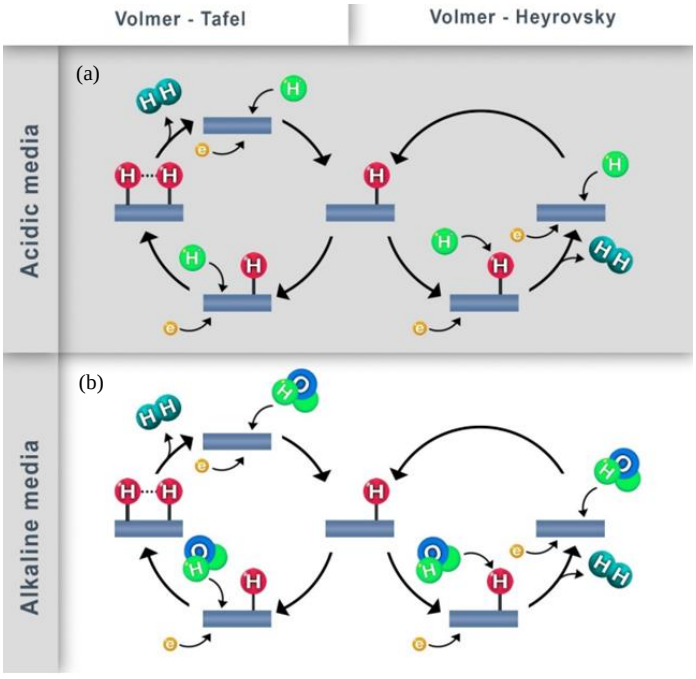

Fig. 8. Mechanism of (a) HER and (b) OER in alkaline/acidic media

Source: Farajzadeh & Rahsepar (2023)

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Presently, state-of-the-art HER and OER electrocatalysts are PGM-based due to their excellent H_2 binding energy, near-zero overpotential, and small Tafel slope (Yan et al., 2022). Despite that, the large scalability of PGM-based electrocatalysts is hindered by their expensive cost due to their inadequate reserve in nature (Wu et al., 2023). Researchers have made significant efforts to develop electrocatalysts with excellent catalytic performance and cost efficiency comparable to PGM-based electrocatalysts. Classes of electrocatalysts have been reported in the expansion of noble metal-free electrocatalysts and recent achievements have been summarised in Table 2. Amongst various approaches towards discovery of outstanding electrocatalyst, to overcome this key issue, strategies like introducing transition metal based-, noble metal based- and metal-free electrocatalyst have been extensively research due to their huge potential for scalability besides excellent catalytic performance.

Table 2: Summary of types of electrocatalysts in water splitting

Class of Electrocatalysts	OER/HER	Overpotential (mV/cm^2@ mA)	Tafel Slope (mV/dec)	Electrolyte	Ref.
		PGM-based			
Pt	HER	~ 0@10	30	0.5 M H_2SO_4	(Tai et al., 2021)
RuO_2	OER	411@10	97	1M KOH	(Wenelska et al., 2023)
		Transition metal-based			
$ZnCo_2S_4$/NF	OER HER	278@10 185@10	64.3 110.4	1M KOH	(Song et al., 2019)
		MOF-derived			
CoMoP	OER HER	273@10 89@10	54.9 69.7	1M KOH	(X. Wang et al., 2022)
		Carbon-based			
NRPC/NiMn	OER HER	370@10 136@10	64 78	1M KOH	(Periyasamy et al., 2023)
		Graphene and Carbon nanotube (CNT)			
FexMo1-xS$_2$/CNT@CC	OER HER	273@100 116@10	24.5 44.7	1M KOH	(Z. W. Chen et al., 2023)
CoFeP/rGO	OER HER HER	275@10 101@10 76@10	79 169 104	1M KOH 1M KOH 0.5 M H_2SO_4	(Cai et al., 2022)
		g-C3N4 hybrid			
g-C_3N_4/C_2	OER HER	303@10 173@10	114 55	0.5 M KOH 0.5 M H_2SO_4	(Sowmya & Vijaikanth, 2023)

Source: Authors' own illustration

3.2.1 Transition metal based

As of late, more studies on electrocatalysts have been reported as water splitting technologies develop rapidly, especially on transition metals-based electrocatalysts. Given their abundance and promising catalytic activity, transition metals like Ni, Co, Fe, Mn, Mo and also Cu have been studied extensively for their performance (Liu et al., 2021). Starting from pure transition metal electrocatalysts, likewise, in extreme conditions such as alkaline or acidic, poor stability of single metal has hindered its practical application so varied improvements have been done to enhance both the stability and catalytic activity of that transition metal based electrocatalyst. Rapid advancements in materials for electrocatalysts have brought much more extensive reports of TM-based electrocatalysts. Generally, graphene, MOFs, CNT,

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TiO_2, carbon cloth or nickel foam (NF) are used as catalyst support to provide structural stability. A recent study by Zhang et al. utilised NF as a substrate for Fe-doped Ni_3S_2 array growth using the conventional solvothermal method (Zhang et al., 2024). Amongst other transition metals, to improve the intrinsic activity, the synergistic effect from the Fe-Ni bimetallic is crucial to form the key active intermediates (FeOOH-NiOOH). Fig. 9a shows the schematic illustration of the synthesis of Fe_x-Ni_3S_2/NF electrodes using the solvothermal approach at 140 °C for 12 h to produce the Fe-Ni-MOF precursors and then second solvothermal sulfurization treatment at 140 °C for 4 h. Scanning electron microscopy (SEM) images as in Fig. 9b display the irregular growth and vertical distribution of MOF precursors growing on NF for the sample $Fe_{2.3\%}$-Ni_3S_2/NF while Fig. 9c shows the same sample after undergoing second solvothermal sulfurization treatment. Excellent OER performance can be analysed through the electrochemical testing in Fig. 9d showing the LSV curves and comparison of the overpotential value at 10 and 100 mA/cm^2. Results showed that the optimised $Fe_{2.3\%}$-Ni_3S_2/NF performed the best with an overpotential of 233 mV at 10 mA/cm^2 with a corresponding value of 66 mV /dec for the Tafel slope. The latest work by Marquez et al. tested the growth of a wide range of transition metals (Fe, Co, Cu and Mn) incorporation with NiOOH deposited on NF substrate (Marquez et al., 2024). Similar to the previous report by Zhang et al. electrochemical performances for both samples Ni_3S_2/NF and NiOOH/NF show improvement with lower overpotential value at 10 mA/cm^2 with the addition of Fe when compared to the sample without Fe element.

Other than Ni and Fe, recent work by Alotaibi et al. introduced a manganese-cobalt oxyhydroxide (MnCo_OOH) electrocatalyst that has low overpotential compared to CoOOH with approximately four times higher current density at 75 mA/cm^2 catalyst highlighting the advantages of the additional Mn (Alotaibi et al., 2024). Tuning of electrochemical and structural properties of nickel oxide and hydroxides is possibly done by introducing transition metals (Armstrong et al., 1988)**.** In this work, green synthesis was employed using alkanna root extract and by that, they were able to avoid unnecessary toxic chemical usage for synthesis. A comparison of both MnCo-OOH and Co-OOH seemed to demonstrate the advantage of bimetallic oxyhydroxide compared to single metal oxyhydroxide, especially in terms of MnCo-OOH has higher electronic properties and lower charge transfer resistance due to its higher intrinsic OER properties. The main challenge of water splitting technology is that the performance of transition metal-based electrocatalysts is unable to fully perform as good as noble metal-based electrocatalysts, especially in alkaline environments. Along the discovery process for advanced electrocatalyst water splitting technologies, despite various attempts on the strategies reported, the full potential of transition metal has yet to reach its end. As overall water splitting technologies considered aspects from both OER and HER sides, existing studies are more towards OER exploration as it is considered a sluggish reaction. Until now, extensive studies have reported strategies from transition metal oxide-, transition metal sulphide-, metal-organic framework (MOF)-, and also single-atom catalysts (SACs).

3.2.2 Precious metal based

For HER activity, the most efficient electrocatalyst is based on Pt group. Despite its excellent performance in acidic conditions, a significant decrease was observed for its catalytic activity in alkaline conditions most likely due to the sluggish water association step that occurs in alkaline. As one of the plausible strategy towards greatly reducing the Pt loading, Zheng et al. had reported on the heterostructure approach of $LiCo_2O$ with Pt species in their work (Zheng et al., 2020). Both catalyst ($LiCo_2O$ and Pt) can act as an active centres and co-catalyst alternatively depending on HER on OER in the electrocatalyst system designed making them as multifunctional electrocatalysts for excellent overall water splitting. A wet chemical process was done to deposit the Pt species towards the exfoliated $LiCoO_2$ nanosheet and the schematic illustration is portrayed as in Fig. 10a. Meanwhile, Fig. 10b and Fig. 10c displays SEM image of $LiCoO_2$ and the exfoliated $LiCoO_2$ nanosheet, respectively. It can be observed that Pt nanoparticles anchored on $LiCoO_2$ nanosheet. Defect-rich $LiCoO_2$ can provide rich water adsorption/dissociation sites, functional support for Pt species deposition and confinement, and the ability to modify Pt's electronic structure to lower the energy barrier for hydrogen evolution. The electrochemical testing for HER activity

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shows enhanced performance with a smaller overpotential of 138 mV compared to Pt/C (149 mV) at 50 mA/cm^2 while for OER activity the onset potential reported is ~1.36 V, which is much lower than IrO_2 (1.52 V) or Pt/C (1.57 V). Iridium (Ir), a metal belonging to the platinum group, possess inherent qualities for electrocatalytic and anticorrosion applications because of its high conductivity, excellent catalytic activity and good corrosion resistance. By using galvanostatically electrodeposition, iridium-cobalt (Ir-Co) was successfully deposited on Cu foam to form an electrode to perform as an electrocatalyst in an alkaline solution (W. Wu et al., 2021). The electrochemical performance of different loading of Ir (0.8, 3.2, and 4.6 mg/cm^2) in Ir-Co were analysed and it is observed that Ir loading of 3.2 mg/cm^2 has the lowest overpotential value of 108 mV at 30 mA/cm^2. Enhanced performance of Ir-Co can be contributed by the incorporation of Co to significantly modulate the electronic structure of Ir. Reducing the loading of precious metal is indeed a noteworthy approach that can be considered as the general catalytic activity of the catalyst able to perform on par with the current state-of-art electrocatalyst for water splitting.

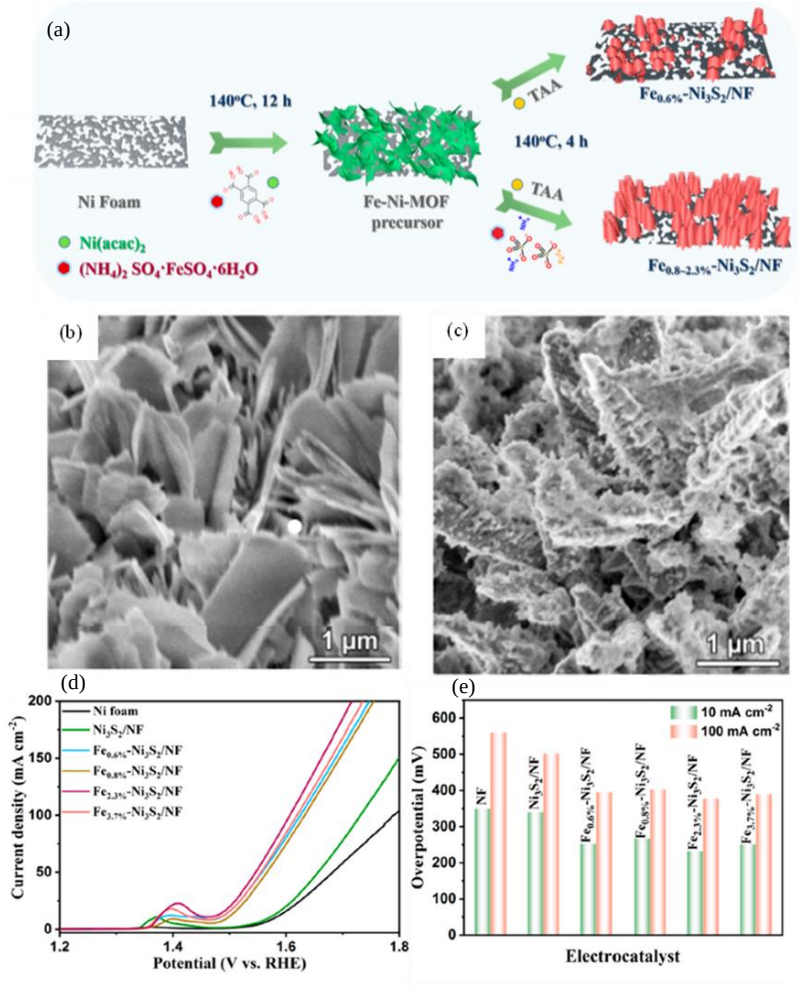

Fig. 9. (a) Illustration of Fe-Ni_3S_2/NF electrodes synthesis, SEM images of $Fe_{2.3\%}$-Ni_3S_2/NF for (b) Fe-Ni BTEC MOF precursors, (c) after second solvothermal sulfurization treatment process, the electrochemical performance of series electrodes (d) LSV curves and (e) overpotential comparison of bare NF, Ni_3S_2/NF and Fe_x%/Ni_3S_2/NF at 10 mA/cm^2 and 100 mA/cm^2

Source: Marquez et al. (2024)

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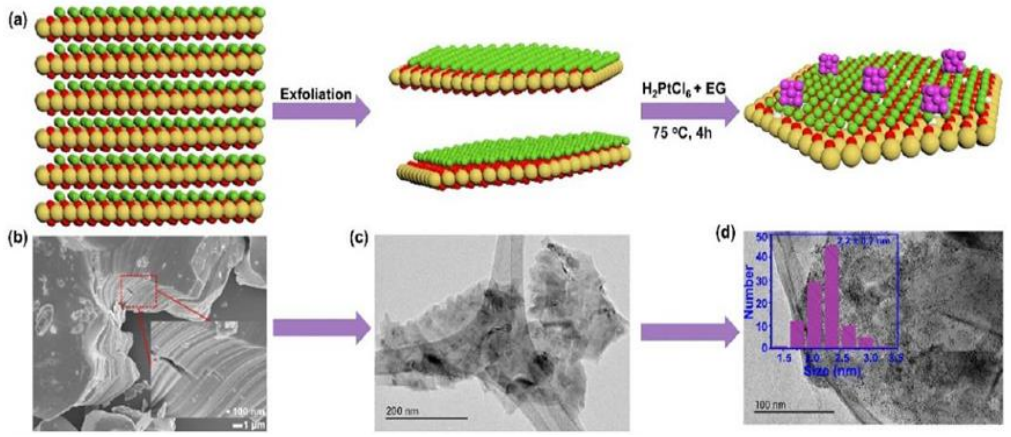

Fig. 10. (a) Schematic illustration of synthesis process for Pt/$LiCoO_2$, (b) SEM image of $LiCoO_2$, (c) SEM image of $LiCoO_2$ nanosheets that had been exfoliated, (d) SEM image of 30 % Pt/$LiCoO_2$ with the corresponding statistical analysis of the particle size of Pt nanoparticles confined on $LiCoO_2$ in the inset

Source: Zheng et al. (2020)

In conclusion, other strategies such as structural engineering of electrocatalysts are also implemented such as core-shell structure, nanosheets, nanotubes, single-atom-catalyst (SAC), etc. It is indeed a crucial approach for electrocatalyst optimisation by fully considering the structure and morphology of the potential materials as electrocatalyst. Electrocatalyst performance involves many factors including its morphology, composition, support, and material engineering.

4. SUMMARY AND FUTURE OUTLOOK

The rise in greenhouse gas emissions and our heavy reliance on fossil fuels highlight the need for cleaner alternatives. Green H_2, derived from the electrolysis of water using renewable energy sources, offers a viable path for reducing carbon emissions and moving toward environmentally sustainable energy practices. This review provides a comprehensive overview of green H_2 production technologies, which involves solar driven water splitting and electrochemical water splitting with a particular emphasis on development of catalysts. The clean and sustainable nature of PEC water splitting makes it an attractive option for harnessing solar energy to produce green H_2, contributing to a more environmentally friendly for future energy system. The primary objective in advancing PEC water splitting systems is to enhance their overall efficiency. To achieve this goal, the focus is on developing photoelectrodes that exhibit efficient light absorption across a broad spectrum of wavelengths to improve STH efficiency. By optimising the photoelectrode design, researchers aim to ensure that a maximum amount of sunlight is captured and efficiently converted into the energy required for the chemical reaction involved in water splitting. For example, one promising technique involves the combination of materials with complementary bandgaps, including wide-bandgap semiconductors (e.g., TiO_2, $BiVO_4$) and narrow-bandgap semiconductors (e.g., Cu_2O, Fe_2O_3). This method facilitates the absorption of a broader spectrum of solar photons, resulting in enhanced photocurrent production. Furthermore, the integration of plasmonic nanoparticles (e.g., Au, Ag) into the photoelectrode structure may improve light absorption via localised surface plasmon resonance (LSPR) phenomena. Moreover, optimising reaction conditions, including electrolyte composition and pH, can substantially affect the performance of photoelectrodes. Utilising electrolytes with elevated

https://doi.org/10.24191/mjcet.v7i2.1294

concentrations of redox couples can enhance charge transfer at the electrode-electrolyte interface, hence enhancing overall efficiency. On the other hand, the development of low-cost, high-performance catalysts for H_2 synthesis in industry is a critical challenge for electrochemical water splitting. While many alternative electrocatalysts have been investigated for electrocatalytic H_2 production, only a small number of them are as efficient as precious metal-based electrocatalysts. Their stability and longevity are also challenges. Therefore, research should be done on inexpensive, high catalytic activity electrocatalysts, and stability over a wide pH range. Investigation of the application of bimetallic and multimetallic catalysts, which, by maximising the binding energies of process intermediates, can also improve catalytic activity and stability. Hence, green H_2 holds considerable promise in facilitating the transition to a more sustainable energy system and mitigating the effects of global warming. The optimistic future prospects for green H_2 are required to fully realise the efficiency of green H_2 in addressing critical environmental and energy challenges.

ACKNOWLEDGEMENT

The authors would like to acknowledge the technical and the management support given by the Research and Instrumentation Management Center (CRIM), Universiti Kebangsaan Malaysia and Ministry of Higher Education, Malaysia.

FUNDING

This research was funded by the Ministry of Higher Education (MOHE) through the Fundamental Research Grant Scheme (FRGS) under grant number (FRGS/1/2024/STG05/UKM/02/11).

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

AUTHORS' CONTRIBUTIONS

All authors contributed to the design of the research including conception and design of study, drafting and reviewing the manuscript critically for important intellectual content. All authors have read and approved the final manuscript.

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