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MORALITY BEFORE KNOWLEDGE

A review of photoelectrochemical water oxidation using hematite photoanode

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ABSTRACT
Background: The sun, as an abundant and renewable energy source, provides a sustainable alternative to fossil fuels, which contribute significantly to CO_2 emissions and global warming. With CO_2 emissions surpassing 35 billion tons in 2023, the need for clean energy solutions has become increasingly urgent. Solar energy utilization includes photoelectrochemical (PEC) water splitting, where hematite is widely recognized as an efficient photoanode material due to its availability, stability, and favorable band gap for visible light absorption. However, hematite faces challenges such as poor conductivity, surface recombination, and slow oxygen evolution reaction (OER) kinetics, which limit its performance. **Methods:** This review examines various strategies to enhance hematite photoanode performance for PEC water splitting. The study explores three key approaches: (1) using three-dimensional conductive substrates with high surface area to facilitate heterojunction formation, (2) doping with tetravalent metal ions (e.g., Ti^{4+}) to improve conductivity and charge carrier density, and (3) integrating Bi_2WO_6 with hematite to enhance charge separation and photoelectrochemical efficiency. The hydrothermal method was applied for hematite fabrication due to its feasibility, cost-effectiveness, and scalability. **Findings:** The analysis highlights the effectiveness of each strategy in overcoming hematite's inherent limitations. The use of 3D conductive substrates improves electron transport and surface reaction sites, while Ti^{4+} doping enhances charge carrier density and conductivity. **Conclusion:** Hematite remains a promising photoanode material for PEC water splitting, but its limitations must be addressed to maximize efficiency. The combination of 3D conductive substrates, metal ion doping, and Bi_2WO_6 integration has shown potential in improving hematite's photoelectrochemical performance. **Novelty/Originality of this article:** This review provides a comprehensive analysis of hematite performance enhancement strategies, focusing on the synergistic effects of 3D conductive substrates, Ti^{4+} doping, and Bi_2WO_6 integration.

KEYWORDS: hematite photoanode; 3D electrodes; PEC water splitting.

1. Introduction

The issue of energy is becoming more significant as the world's population steadily increases. The probable rise in energy usage is linked to the continuous expansion of the world's population. A number of studies have been carried out in the energy sector to identify sustainable energy sources capable of supporting the expected population growth in the coming decades (Tahir et al., 2009). The consumption of fossil fuels to fulfil human requirements results in the emission of CO_2 gas into the atmosphere. In line with United Nations Framework Convention on climate change (UNFCCC), several nations have implemented specific measures to decrease greenhouse gas (GHG) emissions. Carbon dioxide emissions represent the primary source of global greenhouse gas emissions and are on increasing levels globally, even in the midst of international agreements intended for managing climate change (Crippa et al., 2023). Solar energy represents the most important

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renewable energy source present on our planet. The Earth's surface absorbs 1.2×10^{14} kJ of solar energy every second, a volume sufficient to fulfil all human energy needs (Zhang et al., 2021). One way to utilizes abundant solar energy to produce H_2 gas is the water splitting process, potentially acting as a sustainable energy source.

The water splitting process utilizing the photoelectrochemical (PEC) method offers significant advantages includes a hydrogen (HER) and oxygen evolution reactions (OER) appearing in the photocathode and the photoanode, respectively, designed efficiency, scalability, security, and cost-effectiveness (Mushtaq et al., 2024). The PEC system for water separation requires a photoanode with excellent surface properties and durable stability. Various photoanode materials, including metal oxides, organic conductors and semiconductors, polymers, and perovskites, have been extensively examined due to their significant optoelectronic properties. Examples of metal oxide nanostructures encompass TiO_2, WO_3, $BiVO_4$, ZnO, CeO_2, $NaNbO_3$ and Fe_2O_3, among others (Kumar et al., 2020; Koyale & Delekar, 2024).

Hematite (α-Fe_2O_3) has been widely used as a photoanode for the oxygen evolution reaction (OER) because of its significant abundance and its band gap energy, which is suitable for visible light absorption 2.0-2.2 eV (Tahir et al., 2009). The earth's surface primarily absorbs visible light from the solar spectrum, making this range crucial for the effective PEC reaction (Kay et al., 2006). Nevertheless, hematite suffers a significant limitation due to its low photon absorption particularly near the band edge, which leads to insufficient PEC performance (Rahman & Joo, 2013). Enhancing the thickness of the photoelectrode layer can lead to improved light absorption (Amano et al., 2020).

The efficiency of PEC could be increased by optimizing the morphology, particle size, and thickness of hematite. Synthesizing dendritic hematite has improved the reduction of the space between the hole and the interface (Kay et al., 2006). Modifying hematite with controlled thickness to raise the donor density can be obtained by atmospheric pressure chemical vapor deposition (Cesar et al., 2009). Furthermore, enhancing the performance of Hematite (α-Fe_2O_3) can be achieved through various methods, including surface nanostructuring using nanowires or nanotubes, doping with four-valent metals such as Si^{4+}, Mn^{4+}, Sn^{4+}, and Ti^{4+}, incorporating an oxygen evolution catalyst, and building a heterojunction structure with a semiconductor material.

Developing a hematite photoanode has the potential to enhance PEC activity through the utilization of a substrate area with high surface conductivity. The conductive substrate applied to hematite often utilizes indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) electrodes, as their small surface area can exhibit inadequate solar-to-chemical energy conversion efficiency. The classification of these materials falls under the category of two-dimensional (2D) conductive substrates. To address this limitation of conductive substrate characteristics, three-dimensional (3D) structures featuring microporous designs can be utilized, including sintered titanium and carbon microfibers, which is then called Ti microfiber felt. Previous studies on Ti microfibers indicate a notable increase in porosity, reaching 66.7%, and classify them as macroporous. The level of porosity observed is adequate for facilitating mass transport. The specific surface area measured shows an enhancement, reaching 444 cm^2g^{-1} compared to the 2D Ti substrates, which had a surface area of 45 cm^2g^{-1}. This approach enhances the surface area, allowing for a greater number of active site groups within the materials and broader semiconductor-electrolyte interfaces (Amano et al., 2020). Through surface modification, novel heterojunction electrodes can be synthesized to obtain higher catalytic sites for reduction and oxidation process in water-splitting reactions at low overpotential. Based on previous research, modified semiconductor catalysts assembled in heterojunction structures exhibit excellent catalytic activity, surface-bound reactions, and charge-bearing (Monny et al., 2021).

2. Methods

This review investigates different approaches to improve the hematite photoanode performance for PEC water splitting. This examination makes a study using three key

courses: (1) using three-dimensional conductive substrates with high surface area to facilitate heterojunction formation, (2) doping with tetravalent metal ions (e.g., Ti^{4+}) to improve conductivity and charge carrier density, and (3) integrating Bi_2WO_6 with hematite to enhance charge separation and photoelectrochemical efficiency. The hydrothermal method was utilized in the hematite fabrication because of its feasibility, cost-effectiveness, and scalability.

3. Results and Discussions

3.1 Photoelectrochemistry

Hydrogen has become the ultimate candidate for replacing fossil fuels as an environmentally friendly energy source, yet many researches is required to find the most effective method. One of the most effective methods to generate hydrogen is using water-splitting PEC reactions consisting of HER and OER. A restriction of OER is the sluggish reaction kinetics at the photoanode, requiring a catalyst to enhance HER and OER activity, such as a platinum-based catalyst with an appropriate active site (Zhang et al., 2020b). The PEC reaction incorporates three interconnected physicochemical processes, including the separation of electrons, the absorption of photons, and their existing holes, and the electrocatalytic activity at the surface (Verma & Pala, 2022). In a water-splitting reaction, hydrogen is generated at the photocathode, while oxygen is generated at the photoanode. The effectiveness of separation and charge transfer, driven by photons, in the PEC active material is crucial for successful water splitting.

In PEC water splitting, At the photocathode, hydrogen is generated, while oxygen is produced at the photoanode. The efficiency of the separation and charge transfer (produced by photons) in the photoelectrochemical active material is the key to the success of water splitting (Cheng et al., 2024).

Photoelectrochemistry is the arrangement of connections between semiconductors and redox electrolytes, which is the conceptual and scientific basis for current and future research (Mayer, 2017). A scheme of the typical PEC reaction mechanism of the water splitting under sun irradiation is presented in Figure 1.

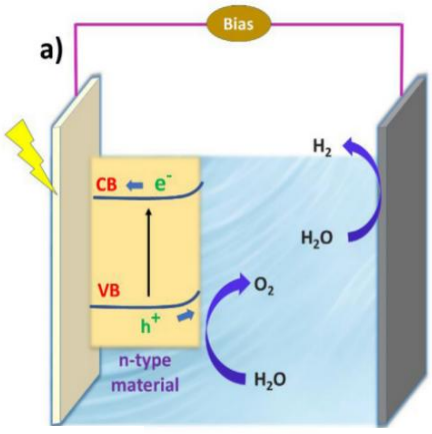

Fig. 1. Illustrative representation of a PEC water-splitting system using n-type semiconductor as the photoanode, reprinted by permission (Koyale & Delekar, 2024)

The success of PEC cells, considering the photovoltaic energy conversion mode, was continued with efficient light-induced photoelectrodes (Holmes-Gentle et al., 2018). It should be highlighted that semiconductors show cathode and anode signals as its constituents, while their thermodynamic stability is an issue that needs to be further investigated (Tu et al., 2018). Therefore, the problem of developing and optimizing

photoactive materials and investigations to reduce photo corrosion and charge transfer has been considered since the beginning (Toe et al., 2019). In photoelectrochemical cells, the photoelectrode material could serve as a photon absorber and light harvester as well as an electrocatalyst simultaneously, or two different materials can be utilized to serve its purpose individually (Shaner et al., 2015). Photocurrent in photoelectrochemical cells is commonly related to the semiconductors' ability to absorb photons and harvest light, meanwhile the electrochemical process instantaneously uses flowing electrons (Abbas et al., 2019). Semiconductors are essential to convert superior light to electricity, whilst local charge transfer at the thin film interface is the bottleneck (Gong et al., 2019). Therefore, researchers have focused in improving the photon absorption capability by optimizing the photoelectrode's surface, interface, mass, and natural surface area. In contrast, the geometric area of the photoelectrode is not substantial (Zhao et al., 2020).

Table 1 Developments in Oxide Metal-Based PEC Water Splitting

Material	Synthesis Methods	Performance	Results	Ref.
SnO_2/ $BiVO_4$/ rGO	Chemical vapor deposition (CVD), metal organic decompositio n (MOD), spin coated rGO.	Photocurrent density of 2.05 mA cm^{-2} (3.73 times of the $BiVO_4$, 0.55 mA cm^{-2}, IPCE of 2.47 times that of $BiVO_4$ at 400 nm.	SnO_2 and $BiVO_4$ combine to form n-n heterojunctions, and rGO is decorated on these heterojunctions are increasing visible light absorption, charge separation efficiency, and electron transfer at the electrode/electrolyte interface.	(Bai et al., 2021)
Sn-doped Fe_2O_3/ Cobalt oxide layer	Two-step solvothermal synthetic	Photocurrent density of is improved from 0.83 to 1.40 mA cm^{-2} after the deposition of the CoOx surface layer.	The CoOx layer raises the charge carrier density, increases the concentration of oxygen vacancies, and introduces Co^{2+}/Co^{3+} redox couples. Both the efficiencies of surface and bulk charge separation are enhanced. Both the oxygen evolution reaction and the surface charge transfer process are accelerated.	(Huang et al., 2024)
$NiWO_4$/ $BiVO_4$/ SnO_2	Electrode-position	Photocurrent of 0.93 mA/cm^2	Both enhanced absorption of visible light and attains 23% and 30% charge separation and transfer efficiencies.	(Shaddad et al., 2019)
$BiVO_4$/ WO_3	Automated spray pyrolysis technique	Hydrogen production (155.7 µmol m^{-2} s^{-1}), on-off current density gap (0.66 mA cm^{-2}).	The complementary effects of WO3 and $BiVO_4$, clarifying how each contributes to improving light absorption and lowering electron-hole recombination, and establishing an ideal 80:20 ratio	(Merino-Garcia et al., 2024)
N-TiO_2/ NiFeOOH nanorod	Hydrothermal electroless deposition	Photocurrent density of 3.61 mA cm^{-2},	In comparison to the N-TiO_2 and original TiO_2 photoanodes, the photocurrent density is 1.2 and 2.4 times higher. The improvement in PEC efficiency and performance is ascribed to the combined action of NiFeOOH modification for the promotion of oxygen evolution reaction kinetics and substitutional N doping for defect modulation	(Fu et al., 2023)

The band gap of a photoconductor conforms to the solar spectrum range which could be utilized effectively for the process of water splitting. A reduction in the band gap value enhances the spectral response of the photoconductor. If the band gap is large, merely a tiny amount of the required light intensity could be absorbed, so the band gap must be tiny enough to absorb most of the solar spectrum. A band gap between 1.6 and 2.2 eV is considered effective for PEC water splitting., with a broadband absorption of the solar spectrum in this range, generating a high photo carrier mobility (Ali et al., 2021). The following research has been conducted to advance metal oxide as a photoanode for the PEC water splitting system, as shown in Table 1.

3.2 Ti Modification on Hematite Photoanode

Hematite (iron or ferric oxide or α-Fe_2O_3) is a type of iron oxide. This substance is among three highest abundance and naturally occurring iron oxides besides FeO (Iron (II) oxide) and Fe_3O_4 (Iron (III) oxide). The physical properties of Fe_2O_3 are summarized in the following Table 2.

Table 2. Overview of the physical characteristics of hematite

Chemical Formula	Fe_2O_3
Density	5.24 g cm $^{-3}$
The boiling point	3414 °C
The melting point	1565 °C
Number oxidation	+3
Aroma	Odorless
Appearance	Solids brownish
Covalent bond unit	5
Bond donor hydrogen	3
Solubility	Insoluble in water and soluble in acidic solutions.

(Mushtaq et al., 2024)

Hematite (α-Fe_2O_3) is a photoanode material that, compared against other popular metal oxide photoanodes such as ZnO and WO_3, has a more suitable band gap energy (~2.1 eV) for the application of highly visible light in PEC water splitting, but also stable in alkaline and neutral solutions. On the other hand, hematite also has poor conductivity, slow kinetics of OER, and surface defects that can cause double recombination of photoelectrons and electron holes. Therefore, modifications are needed on the hematite surface, such as adding catalysts to hematite-based photoanodes to accelerate the transfer of surface holes, which can improve photoelectrochemical performance (Zhang et al., 2020b).

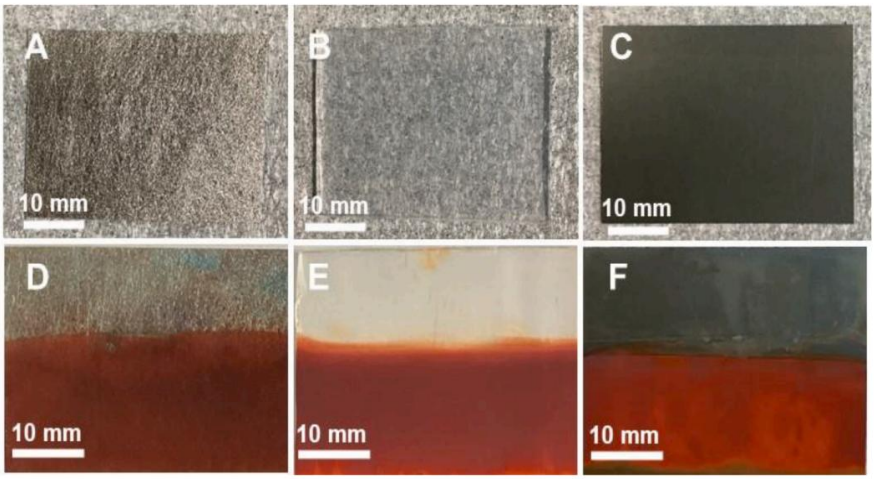

Fig. 2. Photographic images of Ti felt, FTO glass, and Ti sheet before (A to C, respectively) and after (D to F, respectively) modification with Ti-Fe_2O_3, reprinted by permission (Apriandanu et al., 2023a)

The use of Ti as a doping on α-Fe_2O_3 as the photoanode was reported to solve these problems. The synthesis of Ti-doped Fe_2O_3 films can be performed on some substrate types, including Ti felt and sheets as well as FTO surface. A hydrothermal method using a solution of titanium (IV) chloride in ethanol as the source of Ti^{4+}, followed with subsequently heating in air at and argon at was applied. (Apriandanu et al., 2023b). Figure 2 presents the photographic images depicting the substrate modifications utilizing Ti-doped Fe_2O_3 for photoanodes. The change of color from gray to red indicates that Fe_2O_3 films were successfully deposited.

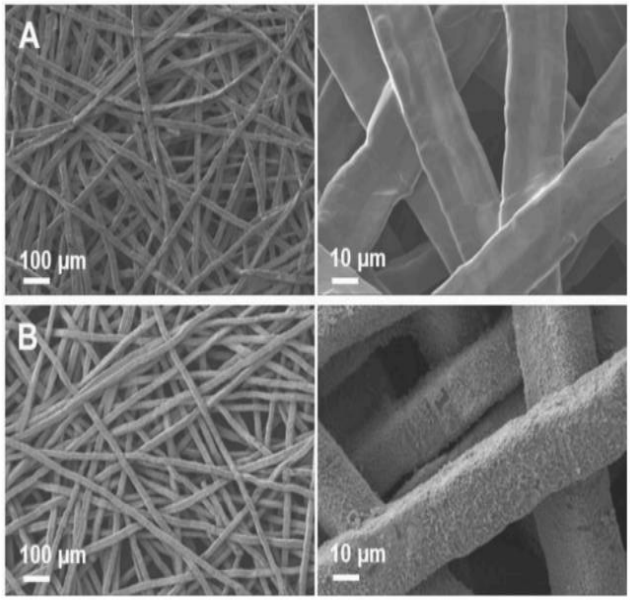

Fig. 3. SEM images of Ti felt (A) prior to and (B) subsequent to modification with Ti-Fe_2O_3 in two-different magnifications, reprinted by permission (Apriandanu et al., 2023a)

The Fe_2O_3 was characterized using X-ray Fluorescence (XRF) to measure its loading X-ray diffraction (XRD) at 2θ 20–70° utilizing Cu Kα radiation at 45 kV and 200 mA to analyze the sample structure, alongside Spectroscopy Electron Microscopy (SEM) linked to an Energy-Dispersive X-ray Spectrometer (EDS) for examining the photoanode's morphology and elemental composition. In addition, UV–visible–Near-Infrared (NIR) and Raman spectra generated with a confocal Raman microscope at a laser wavelength of 532 nm were applied to study the optical properties besides an analysis of the nitrogen adsorption and desorption isotherms to measure the surface area (Apriandanu et al., 2023b). The typical characterization using SEM presented in Fig. 3 demonstrates the alteration in surface morphology following the deposition of Fe3O4 onto the Ti felt substrate. Various studies have been carried out to improve the function of hematite photoanodes, which are summarized in Table 3 below.

Table 3. Method Advancements in the Photoanode Hematite

Method	Modification	Performance	Results	Ref.
Hydro-thermal	Fluorine-doped tin oxide-coated glass was used as the surface for growing arrays of α-Fe_2O_3/WO_3 nanorods	The photocurrent density reaches about 1 mA/cm^2.	The photocurrent density is 2.9 times as that of pure WO_3 films and 50 times as that of the pristine Fe_2O_3 NRs under the same conditions.	(Li et al., 2016)
	In-situ Co and ex-situ Sn are co-doped into	Photocurrent density to	Sn doping primarily increases the density of carriers, whereas Co doping primarily	(Wang et al., 2017)

	α-Fe_2O_3 nanorods	0.93 mA/cm^2 (Sn mono doping), and 1.25 mA/cm2 (additional Co dopant).	enhances the oxygen evolution reaction's surface kinetics on Fe_2O_3 nanorods. Co and Sn work together to form Fe_2O_3 nanorods, which have a high incident photon-to-current conversion efficiency of 23% at 350 nm.	
Sol-gel	Ti-induced enhancement α-Fe_2O_3	Photocurrent increase (up to 1.3 mA cm^{-2}) and a 100-fold decrease in the charge transfer resistance.	Hematite-pseudobrookite heterojunctions exhibit a favorable cascade of charge transfers, whereas titania-pseudobrookite heterojunctions demonstrate a detrimental "hole mirror" mechanism that hinders water photooxidation.	(Monllor-Satoca et al., 2015)
	Porous electrodes encapsulation with a SiO_2 confinement scaffold before high temperature treatment	Photocurrent from 1.57 mA cm^{-2} (in the control case) to 2.34 mA cm^{-2}	This makes it possible to achieve the highest water oxidation photocurrent ever recorded for a solution-processed hematite photoanode in 1 M NaOH electrolytes. This increase is ascribed to the enhanced quantum efficiency, particularly with photons of longer wavelengths, that results from a smaller particle size, which our encapsulation strategy provides.	(Brillet et al., 2010)
Electrode position	Pt doping in α-Fe_2O_3 nanorod arrays	Solar-to-hydrogen conversion efficiency (~5%)	The maximum photocurrent was obtained on the 4% Pt-doped and 15 μm long nanorod arrays.	(Mao et al., 2011)
Atomic layer de-position	Fabrication of p-LaFeO3/n-Fe_2O_3 heterojunction on hematite nanorods	The photocurrent density is promoted from 0.37 to 0.58 mA/cm^2, and 1.12 (further modified by CoO_x)	The incident photon-to-current conversion efficiency is further promoted to 25.13% at 400 nm	(Peng et al., 2017)
	Fe_2O_3/ZnO/ TiO2 photoanode	Photocurrent density (to 4.25 mA cm^{-2})	The presence of surface holes and their swift involvement in water splitting reduces electron-hole recombination. The approximately 4.8-fold enhancement in the lifetime of photogenerated charge carriers compared to the pristine Fe_2O_3 sample further illustrates the impact of surface passivation on Fe_2O_3.	(Kim et al., 2019)

Chemical vapor de-position (CVD)	fabrication of the homogeneous silicon wire array	The saturated photocurrent is improved from 18.2 to 35.6 mA cm^{-2}	The findings suggest that the precise control over the performances of the different SiWA photocathodes, achieved through adjustments in wire diameter and length, can be attributed to a complex interplay of factors including overall optical absorption, carrier recombination, surface catalyst activity, and the flux profiles of the photogenerated carriers.	(Li et al., 2020)
	Nanostructured Fe_2O_3 thin films were grown from Ar/O_2 plasmas	Maximum photocurrent density close to 1 mA cm^{-2}	The significant contribution of engineering Fe_2O_3-based nanomaterials leads to a reduction in carrier diffusion length and facilitates the optimal diffusion of tin from FTO into thinner layers. The characteristics present a favorable avenue for capturing radiant energy to initiate water photoelectrolysis, thereby generating clean hydrogen in a carbon-neutral manner.	(Warwick et al., 2015)

3.3 Conductive Ti microfiber felt substrate

The conductive substrate with a macroporous structure and a high surface area is essential in their use as semiconductor electrodes as these properties can enhance PEC activity in water-splitting reactions. The structure of conductive substrates can be two-dimensional (2D) substrate, such as FTO, ITO, graphene, Mxene, CoP nanosheet and Ti sheets, and three-dimensional substrates, including carbon and titanium microfiber felt (Homura et al., 2017; Zhao et al., 2022).

The 3D-conductive substrate of Ti felt (mass density of 14.1 mg/cm^2 with 66.74% macroporous and high porosity straight) has a notably greater specific surface area (444 cm^2/g) compared to the 2D Ti sheet, which has a specific area of 45 cm^2/g. Ti felt with 0.2 mm-thickness has mass density of 4.50 g/cm^3, which is 19 times greater than that of Ti sheets has a specific surface area of 23.1 cm^2/g. Consequently, the surface area of titanium fiber felt is measured as 6.26 cm^2. This calculation shows that Ti felt has six times higher surface area compared to Ti sheets. This property allows the semiconductor substrate to simultaneously have a large interface and a thin layer surface during the substrate loading. The large surface area can provide an enhancement in light absorption and shorter carrier transport distance, results in an increase of the PEC reactions (Amano et al., 2020; Apriandanu et al., 2023a).

Amano et al. (2020) documented the application of sintered Ti felt as a substrate for the deposition of thin films of Cu_2O. The resulting microfibers demonstrate an increased surface area with a 3D-macroporous structure when compared to the flat substrates. The large surface area enables the Cu_2O crystal film to maintain sufficient photoabsorption while achieving a thickness within the photogenerated carriers' diffusion length. The movement of photo-excited electrons and holes to the interfaces can be executed accordingly. Alongside Ti felt, carbon felt serves as a conductive substrate for the fabrication of various semiconductor oxide, including WO_3, $BiVO_4$, and TiO_2 (Amano et al., 2019).

3.4 Doping of tetravalent metal Ti^{4+}

Elemental doping is an easy and efficient process to increase electrical conductivity, especially PEC activity. Research has proven several dopants to increase the PEC activity of Fe_2O_3, such as Si^{4+}, Ti^{4+}, Sn^{4+}, Ni^{2+}, Pt^{4+}, and Mn^{4+}. Specifically, high-valent metal ion doping (M^{4+}) can increase higher electrical conductivity of Fe_2O_3 compared to Fe^{3+}, which then causes an increase in photocurrent density (Amano et al., 2018; Apriandanu et al., 2023b).

A number process of synthesis for hematite photoanodes have been reported, namely magnetron sputtering, sol-gel and hydrothermal reactions as well as atmospheric pressure chemical vapor deposition. Hematite photoanodes with nanostructure, after doping, are excellent candidates to overcome the drawbacks of α-Fe_2O_3. Since hematite is an n-type semiconductor which naturally contains many O_2 vacancies, the introduction of the tetravalent dopants into the hematite lattice forms a covalent bond between dopant and O_2, ultimately increasing charge transport and charge carrier density. Moreover, although most dopants slightly improve PEC performance, dopants such as Si^{4+}, Sn^{4+}, and Ti^{4+} have significantly improved photocurrent and photoresponse (Subramanian et al., 2018).

Ti^{4+} doping has been widely used and effectively applied to dope hematite, frequently combined with co-catalysts or as a variety of surface combinations (Mazzaro et al., 2019; Eqi et.al., 2023). Besides, the effects of Ti doping on the structure, morphology, light absorption as well as electrical and PEC properties of α-Fe_2O_3 films were also studied. Characterizations carried out by SEM indicate a reduction in particle size at around 2% in Ti-doped α-Fe_2O_3, in opposite, larger particle size is produced when increasing the concentration of Ti. Meanwhile, the XPS spectrum indicated that the combination of Ti is affirmed in the form of Ti^{4+} as the dominant species without any impurities from the substrate (Chae et al., 2019).

Application of the 2% Ti-doped Fe_2O_3 film as the photoanode in the PEC system, at a bias potential of 1.8 V (relative to RHE) and under conditions of standard solar illumination, showing high density of photocurrent around 1 mA cm^2. This current density is two times greater compared to that of the undoped α-Fe_2O_3 (0.51 mA cm^2). This improvement is due to higher efficiency of charge separation and characteristic transport of α-Fe_2O_3 after doping of Ti, as confirmed by electrochemical impedance spectroscopy analysis (Chae et al., 2019).

The following are the benefits of Ti doping on Fe_2O_3 from various studies that have successfully increased the efficiency of Fe_2O_3 photoanodes in water-splitting reactions, observing the passivation of crystal grain interfaces called grain boundaries and reduced crystallinity in magnetron sputter polycrystalline hematite samples. Thus, the PEC performance is significantly better in comparison to Si-doped films, that show limited improvement because the decrease in crystallite size (Lee et al., 2014). Ti doping results in increased hole mobility and surface layer activation. Optimization of the photoanode improves its efficiency, achieving 1.2 mA cm^{-2} photocurrent with an applied external bias of +0.8 V. These results pave the way for large-scale research on Ti-doped nanostructured hematite as a photodetector for industrial use (Mazzaro et al., 2019).

3.5 Heterojunction structure Fe_2O_3/Bi_2WO_6

Hydrogen as a storage of energy can be generated by the enhancement of its electrodes. Heterostructure of an electrode can be formed by generally two semiconductors used for morphological variability, physicochemical and structural variability, and understanding photoelectrochemical properties (Su et al., 2011). Most metal oxides have expansive energy of band gap, more than 3 eV. A UV light source is essential for the induction of metal oxides and their heterostructures to participate in the water-splitting reaction, where the range of both reaction rates is limited to visible solar irradiation (Sadhasivam et al., 2023).

Despite their high band energies, metal oxide semiconductors have several advantages, namely diverse morphologies and nanostructures, hierarchical architectures, and specific facets. Accordingly, it is essential to transform their surfaces to allow photons to be observed to obtain efficient photocatalysts that could successfully reduce the kinetic limits

on photocarrier formation and separation (Song et al., 2022). In general, surface modification enables co-catalyst loading and more catalytic sites for water oxidation and reduction reactions, which can be used to develop new electrodes with heterostructure-type and low overpotential for water-splitting reaction.

Semiconductor catalysts with layer structure offer extraordinary surface-bound reactions, resulting in high catalytic activity and charge density. In addition, good binding stability in heterostructure assembly was reported (Monny et al., 2021). Semiconductors from metal oxide semiconductors can be made heterostructure by integrating to materials with narrower energy bands. Combination of metal oxide with molecules having visible light-activated photocatalytic properties, can promote water-splitting performance over a wide pH range with high stability.

In comparison with the heterostructure photoanodes, single semiconductors show high density of photocurrent as its good charge separation and imperfect photoresponse caused by the diverse morphological structures. Therefore, effective water oxidation with heterojunction structures is an advanced concept for water splitting. It is interesting to note that Bi_2WO_6, semiconductor containing oxide structure exhibits an optical bandgap of approximately 2.91 eV, it is abundant compound on earth, photostable, non-toxic, and has excellent water-splitting activity (Dong et al., 2017). Recent report showed that Bi_2WO_6-based heterostructure molecules generated high photocurrent density of 4.91 mA/cm^2. In addition, improvement performance of PEC was observed in terms of triadic passivation of semiconductors with more catalytic sites as oxidation reactions on the photoanode surface require catalytic sites to facilitate recombination with reduced charge transfer. Figure 4 shows the characterization results of the reported using FESEM.

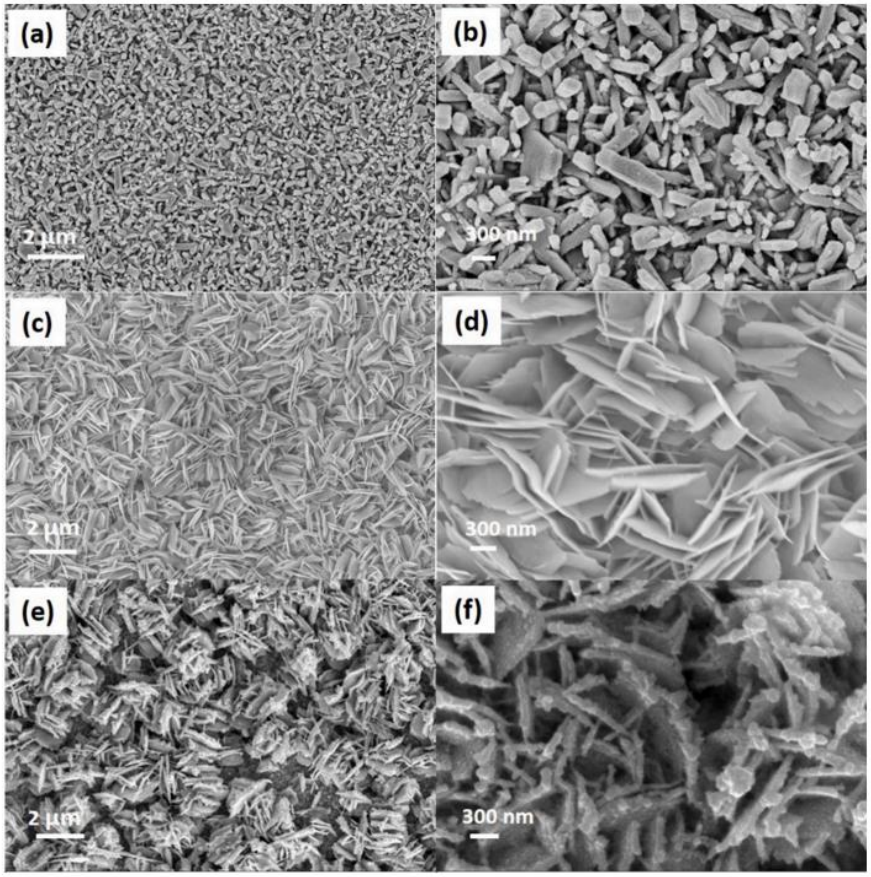

Fig. 4. FESEM images of the FTO substrate at various magnifications of WO_3 (a and b), Bi_2WO_6 crystal with ion exchange (c and d), and In_2S_3-modified WO_3/Bi_2WO_6 (e and f)., reprinted by permission
(Sadhasivam et al., 2023)

The self-assembly of vertical WO_3 sheets was synthesized using the hydrothermal method, followed by heating and depositing the layers of Bi_2WO_6 through ion exchange process. WO_3/Bi_2WO_6 photoelectrode showed better electrochemical performance than the intrinsic WO_3 with its good electron transport pathway and the intrinsic Bi_2WO_6 with its visible-light absorption. Due to its characteristics of lower electron affinity and resistivity, metal sulfide presents a suitable doping partner for the WO_3/Bi_2WO_6 heterojunction structure, effectively minimizing the recombination process (Zhang et al., 2020a).

4. Conclusions

With its abundance, stability, and appropriate band gap for visible light absorption, hematite (α-Fe_2O_3) photoanode is suitable in PEC water-splitting. However, hematite's sluggish kinetics of OER, low conductivity, and small surface reactions cause recombination process of electron-hole pairs generated by photons. Several methods can enhance the characteristics of hematite as a photoanode, including: To begin with, in the incorporation of metal ions as doping pairs, such as Ti^{4+}, to improve the conductivity and photocurrent density. Second, using three-dimensional conductive substrates, Ti microfiber felt to improve PEC activity employing its high surface area, macroporous structure, and better mass transfer capability. This allows for better loading of semiconductor materials, better light absorption, and shorter carrier transport distances. The last is combining hematite with other semiconductor materials, such as Bi_2WO_6, can improve charge separation and PEC performance by forming heterojunction structures. For example, heterojunctions between WO_3 and Bi_2WO_6 can reduce carrier recombination and improve carrier separation efficiency.

4.1 Challenges

Although these methods can improve photoanode performance, there are still some challenges in developing efficient and stable hematite. These include improving carrier transport properties. Although doping can improve conductivity, it is essential to achieve higher efficiency by minimizing charge recombination and maximizing carrier time in the reaction. Surface properties can be optimized by developing co-catalysts and surface passivation techniques, overcoming surface trapping and slow OER kinetics, and improving photocurrent density and PEC performance. Increasing the scalability and cost-effectiveness of developing large-scale synthesis methods for high-performance hematite photoanodes is essential to transforming a successful laboratory technology into a commercially viable one.

Exploring new materials, more advanced synthesis methods, and more innovative designs should be the focus of future research to address these issues. This could include research on new dopants and doping techniques to improve conductivity and charge carrier dynamics in hematite photoanodes. Development of efficient surface modification techniques and co-catalysts to improve OER kinetics and reduce surface recombination. Development of heterojunction structures with new materials to enhance charge separation and efficient light absorption. Development of large-scale and cost-effective synthesis methods for high-performance hematite photoanodes that can be easily integrated into PEC devices.

4.2 Future perspectives

By overcoming these challenges and for the future development of PEC, hematite-based photoanodes have significant potential to contribute to sustainable hydrogen production through efficient PEC water splitting. Thus, this review is expected to be an essential foundation for understanding the material on hematite-based PEC water splitting and heterojunction structures. In addition, this review can be used by researchers and students

because it covers several aspects of PEC studies and photoanode engineering to design adequate method preparation for hydrogen production.

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