

Recent advances in BiVO₄ semiconductor materials for hydrogen production using photoelectrochemical water splitting

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ABSTRACT

Numerous efforts have been made to find, produce and utilize renewable energy to replace fossil fuels that have seriously degraded the environment. Photoelectrochemical (PEC) water splitting has been considered a promising route for the production of hydrogen (H₂) applying for free solar energy. PEC systems to produce H₂ have the great advantages of simple process steps and very low environmental burdens. However, many challenges must be overcome for commercial applications, particularly for fabricating the necessary materials for PEC water splitting. Among many candidate semiconductor materials for photoelectrode utilization, BiVO₄ is a very promising semiconductor because it is an **inexpensive n-type photocatalyst with a moderate bandgap of 2.37 eV** for PEC water oxidation. BiVO₄ as a photoanode can theoretically **absorb almost 10% of the solar energy** with an appropriate valence band (VB) position to drive water oxidation with an identified maximum photocurrent of 7.5 mA/cm². Many bismuth vanadate (BiVO₄)-based semiconductors that have been developed for PEC water splitting to produce H₂ have been troubled by the easy recombination of the photoinduced electrons and holes. None of the numerous nanocomposites and nanostructures that have been developed are perfect materials capable of satisfying all the criteria necessary for practical photocatalysis with sufficient solar energy conversion efficiency. Most semiconductor materials with highly efficient PEC water splitting have used ultraviolet (UV) as a light source. However, UV has only a small fraction (2–3%) of the solar spectrum and is therefore not considered a sustainable energy source to provide sufficient PEC-based hydrogen production for industrial utilization. This review examines very recent progress of 11 Strategy for improving the photocurrent density and especially hydrogen production of BiVO₄ semiconductors using PEC techniques, and also highlights the challenges faced in the design of visible light-active water splitting photocatalysts.

1. Introduction

The total anthropogenic energy consumption keeps increasing, particularly in modern societies. The great increases in population, economic advances and new technology development are responsible for the continuously increasing request for energy across the world. Thermal power using fossil fuels, such as coal, petroleum oil, and natural gas, and nuclear power are the main sources of energy utilized worldwide with a relatively small fraction of renewable energy utilization of hydroelectric, wind, geothermal and solar power. All of these renewable energy resources have their own disadvantages and advantages, which require different energy sources or their mixed utilization [1]. However, solar energy via sunlight utilization is one of the most promising future energy resources that can provide sustainable solutions for the shortage of fossil fuels and fulfill the rising global energy demand [2,3]. Energy production for modern societies should be

stable, sustainable, and always available. . However, many of the currently viable renewable energy forms cannot be generated at all times.

To overcome this issue of stability and availability in different environments, many techniques have been investigated for developing electrochemical storage methods and chemical energy storage methods using specific molecules [4,5]. Hydrogen gas has been widely used for chemical energy storage [6]. Producing hydrogen using water electrolysis via water splitting is considered a promising option for providing renewable hydrogen energy [6,7]. Water splitting using the photoelectrochemical (PEC) reaction can be achieved using any available energy source that can dissociate water molecules into oxygen and hydrogen molecules [3,8,9]. PEC water splitting is a preferred way of directly producing solar fuel, such as hydrogen, from water using photocatalysis techniques [10–12]. This review summarizes the basics of PEC water splitting principles and the essential characteristics of bismuth vanadate (BiVO₄) semiconductor materials for

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photoelectrocatalytic hydrogen production.

2. Basics of PEC water splitting

PEC hydrogen production has received a lot of attention which coincides with the increasing demand for renewable carbon energy production [13–15]. The water splitting process lies in the redox reaction with the participation of generated charge carriers through solar radiation at the catalyst surface (or active sites). Materials used for photocatalysts or photoelectrode preparations are semiconductors in nature. Therefore, they have a defined band gap which is a result of the separation of the conduction band (CB) and the valence band (VB). Moreover, band edges also play an important role in the selection of the semiconductor material. The CB edge should have a more negative potential than the reduction of the hydrogen. Also, the VB edge should have a more positive potential than the oxidation potential of oxygen for water splitting. When light of a particular wavelength is incident on the catalyst, an electron-hole pair is generated only if the absorbed photon energy is more than the band gap of the material. The electron then migrates to the CB leaving a hole in the VB.

In PEC water splitting, hydrogen and oxygen gases are generated from water dissociation on the surface of PEC materials with enough solar energy absorption and proper use of electrolysis. Thus hydrogen energy production from water using PEC techniques does not produce greenhouse gases, such as carbon dioxide (CO_2), nitrogen oxide (N_2O) and methane (CH_4) which have been greatly involved in conventional energy production using fossil fuels.

The photochemical materials (semiconductors) utilized for PEC water splitting techniques are similar to the materials used in photovoltaic cells to produce solar electricity. The only difference in PEC water splitting for hydrogen production from the photovoltaic cell for electricity generation is the use of immersed semiconductor materials as the photoanode and photocathode. In the water-based electrolyte, when the semiconductor materials absorb solar light, photoinduced electrons at the photoanode are transferred to the photocathode, where hydrogen evolution occurs by combining hydrogen ions transferred from the electrolyte or produced from water dissociation [15,16]. After absorbing more energy than the band gap of the semiconductor, the photons create free electron and hole pairs. In jumping from the VB to the CB, the electrons leave holes on the VB and then migrate to the semiconductor-electrolyte interface where they react with hydrogen generated on the surface of the semiconductor from water reduction with half reaction and electron acceptors (electron scavengers) are oxidize water [17]. Fig. 1 shows a schematic of an apparatus configuration for PEC water splitting [18]. One of the basic requirements for practical PEC water splitting is to obtain high solar-to-hydrogen (STH) efficiency. Many efforts applying various approaches have been made to improve STH efficiency. Many researchers have investigated the mechanistic aspects of PEC water splitting with the goal of enhancing PEC techniques [19–25]. However, despite the numerous studies on PEC performance improvement, large-scale production of hydrogen for industrial applications remains technologically difficult and relatively unadvanced [19].

In n-type semiconductors, the hydrogen is produced on the counter electrode and oxygen is produced on the working electrode. H_2 and O_2 gas evolutions should be spatially separated to increase the safety of PEC production systems. Thus it is also important to reduce the costs for the evolved gas separation [26].

By 2020, it is expected that renewable PEC water splitting with suitable hydrogen generation technologies will have been advanced with a projected hydrogen production cost of \$4.00/gge at the plant gate, which is cheaper than the hydrogen production cost from petroleum oil using pyrolysis or cracking or catalytic process [27,28]. Therefore, PEC water splitting can be an attractive and viable option for solar hydrogen production. To increase the feasibility of practical production of hydrogen gas through PEC water splitting techniques for

commercial purposes, an ideal PEC cell development should be fulfilled with high STH efficiency, long-term and sustainable stability and low capital costs [29].

PEC water splitting for hydrogen generation is based on solar energy and water, both of which are renewable sources. Energy for stationary and transportation applications can be retrieved from hydrogen with low carbon foot print and climate impact. Yokohama first reported in 1972 the feasibility of hydrogen generation via PEC splitting of water. Most studies have focused on searching for ideal semiconductors that can be used as efficient photoelectrodes. However, the long-cherished goal of 10% conversion efficiency has so far remained unachieved. Working at this efficiency, photocurrent generation at the rate of $10\text{--}15\text{ mA cm}^{-2}$ implies economical hydrogen production cost that would be commercially viable and cost competitive against the existing costs of conventional fuels. Semiconductor material durability in contact with PEC cell electrolyte is also important, with a target stability of at least 2000 working hours.

Despite numerous efforts, to overcome these hurdles, practical or commercial usage has not been achieved. Thus, better understanding of the fundamental mechanisms involved in the PEC processes are necessary to construct efficient photoelectrodes materials for improving PEC water splitting performance. PEC hydrogen production must be efficient for improving sustainability. The solar photon energy absorbed by the semiconductor is not last in PEC reactions until the efficiency of PEC water splitting get maximized under the sun light (visible light) irradiation, which occupies a large proportion (44–47%) of the solar spectrum [30]. The energy harvested from the light absorption is not completely utilized due to the several types of recombination of electrons and holes, which results in energy lost in the form of internal energy. After solar photons are absorbed on photochemical materials, the photoinduced electrons and holes are relaxed to the band edges of the semiconductor to form excitons with some energy lost in the form of heat. The charge carrier recombination of photoinduced electrons and holes is a major mechanism of energy loss in PEC. In order to improve hydrogen production efficiency, photochemical materials, which can maximize solar light (photon) absorption and minimize their charge carrier recombination, should be developed [18,29,31,32]. This review paper analyzes hydrogen production pathways with PEC process from BiVO_4 semiconductors.

3. Development of BiVO_4 photoanodes

Among hundreds of semiconductors known for their photocatalytic activity, no single material satisfies all the requirements of PEC water splitting. Hence materials development remains the key issue for improving PEC performance. More recently, BiVO_4 has received great attention as a photoanode material for PEC water splitting because some developed BiVO_4 photoanodes satisfy many of the necessary requirements listed above [33–35]. BiVO_4 is an n-type semiconductor photocatalyst with a direct band gap of 2.4 eV. BiVO_4 absorbs ample visible light and is also used as stable, neutral, nontoxic and relatively cheap electrolyte [36–38]. Compared to other common oxygen evolution photocatalysts like WO_3 and Fe_2O_3 , BiVO_4 has a relatively high CB edge (0.02 V vs. RHE) and, consequently, need less bias potential to enhance the photoelectrons upper the water reduction potential (0.0 V vs. RHE). But it has its own shortcomings of poor electron conductivity and sluggish water oxidation kinetics. The monoclinic scheelite form of BiVO_4 has shown optimistic promise as an effective photoanode material [39,40] because of its remarkable theoretical efficiency of 9.1% of half-cell STH conversion [29,33]. To use BiVO_4 for making an efficient photoanode of PEC cell, these undesirable properties of poor electron conductivity and sluggish water oxidation have to be improved by a variety of modifications, such as construction of heterostructures, nanostructures, and doping with other functional materials like another semiconductor, charge mediator, or cocatalyst.

Various improvement strategies have been attempted to overcome

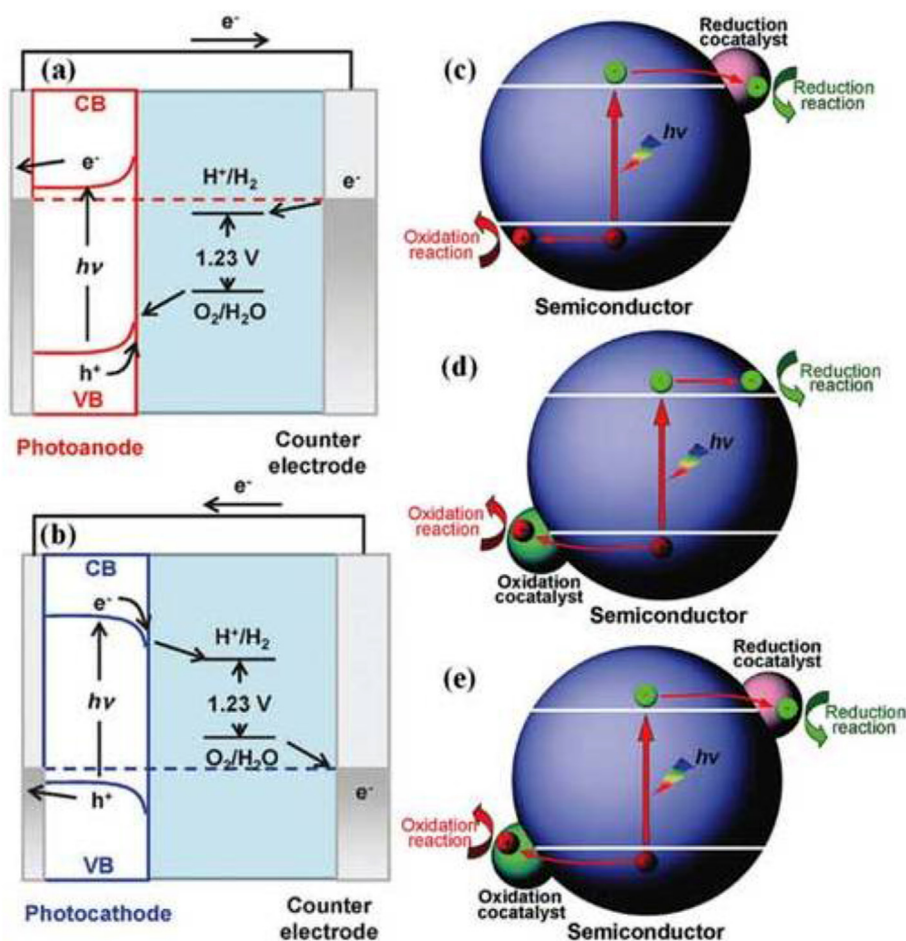


Fig. 1. a,b) illustration of PEC water splitting using a photoanode and a photocathode. c–e) Mechanism of semiconductors with cocatalysts of different shapes. Copyright @ Royal Society of Chemistry).

the drawbacks of BiVO_4 as a photoanode and to efficiently enhance its PEC properties by combining heterostructure catalysts (e.g., $\text{WO}_3/\text{BiVO}_4$ and $\text{SnO}_2/\text{BiVO}_4$) [41–44] and depositing catalyst layers on the BiVO_4 surface with cobalt phosphate, CoOx , or metal oxyhydroxides [45–48]. Doping BiVO_4 with transient metals (such as W and Mo) is also a good way to increase PEC water splitting by improving electron transport [49]. Doping with addition of a small amount of impurities into the BiVO_4 crystal lattice can effectively modify the optical and electronic properties of pure semiconductors [50]. Metal doping into BiVO_4 can also greatly minimize the recombination by enhancing the mobility of photoinduced charge carriers, which increases the available concentration of photocharge carriers and improves the PEC water splitting performance [51,52]. Table 1 summarizes the hydrogen production features for BiVO_4 photoanodes with the various modification techniques that have been reported to improve hydrogen production using PEC water splitting.

4. Strategy for improving PEC performance of BiVO_4

4.1. Doping

Because bismuth vanadate is suffering for transfer electron, so doping of BiVO_4 can be good strategy to improve its electron transfer and hence photocurrent and PEC performance. Patil et al. reported that 2% Ag doping in pure BVO increased its photocurrent density 3-fold as compared to undoped BVO [53]. Fang et al. showed that the photocurrent density of a Ag ion- BiVO_4 structure was 4.7-fold higher than that of the pure BVO [54].

Martin Rohloff et al. [55] reported that the PEC water splitting performance of the Mo-doped BiVO_4 film photoanodes is greatly improved compared to their pure BVO. The photocurrent densities for MO-BVO reached to 1.9 mA cm^{-2} at 1.23 V vs. RHE under solar light illumination (100 mW cm^{-2}).

Diane K. Zhong et al. [56] reported that the photocurrent densities after W doping were increased to 0.7 mA cm^{-2} at 1.23 V vs. RHE under 1 sun light illumination (100 mW cm^{-2}).

4.2. Doping with modified surface of BiVO_4 using

Among surface modification deposition of catalysts layers on the BiVO_4 surface, cobalt phosphate(Co-Pi) showed the noteworthy advantages of being easily confederate with the BiVO_4 surface. Co-Pi modification is a simple and effective method to fabricate an earth-abundant water-oxidation electrocatalyst for improving PEC water oxidation [57]. After modified surface of BiVO_4 semiconductor with Co-Pi for W-doped BiVO_4 and Mo-doped BiVO_4 , photocurrent densities are increased to 1.25 and 4.6 mA cm^{-2} at 1.23 V vs. RHE under illumination 1 sun light, respectively [55,56].

4.3. Nanostructure

Recently, 2D material such as graphene oxide (GO) and reduced GO have been utilized as photocatalysts for PEC water splitting and hydrogen production because GO has excellent electric conductivity and a high surface area that increases the charge carrier [58–61]. Fang et al. [62] reported that the photocurrent density of $\text{BiVO}_4\text{-rGO}$

Table 1
A summary of hydrogen production of BiVO₄ photoanodes with various modifications.

Photo-catalyst	Light source (Power type)	Electrolyte	Photocurrent density(1.23 V vs. Ag/AgCl)	Evolved Hydrogen gases ($\mu\text{mol cm}^{-2} \text{ h}^{-1}$)	After	Year of publication/Reference
Mo-doped BiVO ₄	AM 1.5G simulated sunlight, 1000 W m ⁻² (1 Sun).	seawater	15 mA cm ⁻²	7 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$		2011/[42]
RhO ₂ /Mo-BiVO ₄	AM1.5G solar light	seawater	19 mA cm ⁻²	9 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$		2011/[42]
WO ₃ -NRs/BiVO ₄ + Co-Pi	AM1.5G solar light	potassium phosphate (pH = 7)	6 mA cm ⁻²	102 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$		2016/[53]
WO ₃ /(W, Mo)-BiVO ₄ /FeOOH/NiOOH	AM 1.5 G, 100mWcm ⁻² illumination	0.5M K ₂ SO ₄ in phosphate buffer (pH 7)	3 mA cm ⁻²	75 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$		2014/[54]
Bi ₂ S ₃ /BiVO ₄	1000 W m ⁻² (1 Sun).	Na ₂ S/Na ₂ SO ₃	3.3 mA cm ⁻²	417 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$		2018/[55]
BiVO ₄ +MDH	AM1.5G illumination	0.5M phosphate buffer	2.1 mA cm ⁻²	21 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$		2017/[56]
CDs/BiVO ₄ QDs	300 W Xe-lamp	0.5M phosphate buffer	600 mA cm ⁻²	0.92 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$		2016/[57]
Nb-TiO ₂ /W- BiVO ₄ Co-Pi photoanode	AM1.5G illumination	0.5M phosphate buffer	4.5 mA cm ⁻²	80 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$		2018/[58]
HDP (BiVO ₄ Fe ₂ O ₃)	1 sun illumination	1.0M KCl at pH 9.2	8 mA cm ⁻²	121 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$		2016/[59]
3-Fe ₂ O ₃ /BiVO ₄	AM1.5G illumination	phosphate buffer solution	1.65 mA cm ⁻²	27.34 $\mu\text{mol h}^{-1} \text{ cm}^{-2}$		2017/[60]

nanocomposite was around 3-fold higher than that of pure BiVO₄ under 300 W Xe-lamp in 0.25 M Na₂SO₄ aqueous solution, which they attributed to the transfer property of the photogenerated carriers (electron-hole pairs) after adding rGO to BiVO₄.

4.4. Heterojunction

Several reports have demonstrated that different semiconductors can be junctioned with BiVO₄. Successful heterojunction formation of BiVO₄ has been reported with WO₃ [63–65], SnO₂ [66,67], Fe₂O₃ [68,69], CuWO₄ [70], and CdS [71,72].

Kim et al. [69] reported hetero-type dual photoanodes (HDP) of BiVO₄ and α -Fe₂O₃. Fig. 2 shows that the photocurrent was greatly improved after (HDP) BiVO₄/ α -Fe₂O₃ became stable. The photocurrent reached 7 mAcm⁻² at 1.23 V vs. RHE under 1 sun irradiation and the H₂ evolution for BiVO₄/ α -Fe₂O₃ was around 80 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$.

Xia et al. [68] reported that the Fe₂O₃/BiVO₄ photoanode with 3 spin-coated layers showed a photocurrent density of 1.63 mA cm⁻² at 1.23 V vs. RHE, which was around 2.2 times higher than that of the pristine BiVO₄ photoanode in a 0.1 M KH₂PO₄ (pH 7) electrolyte under simulated AM1.5G solar light. The H₂ evolution rates for Fe₂O₃/BiVO₄ were approximately 28 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$, which is much higher than that of the BiVO₄ photoanode.

Pilli et al. [70] prepared BiVO₄/CuWO₄ heterojunction electrodes with using spray deposition method and the photocurrent density was twice that of pure BVO at 1.0 V vs. Ag/AgCl in 1.0 M Na₂SO₄ electrolyte at pH 7. Grimes et al. [73] reported that BiVO₄/WO₃ greatly improved the Incident Photon to Current Efficiency (IPCE) from 9.3% to 31% compared to that of pure BVO, which they ascribe to the increased electron transfer from BiVO₄ to WO₃. This strategy can overcome the poor charge transport issues observed for BiVO₄. Savioet al. [74] reported that BiVO₄ coupling with ZnO (BiVO₄/ZnO nanorod photoanodes) had a high photocurrent density (2 mA/cm² at 1.23V vs. RHE) under visible light irradiation. Kimura et al. [75] also reported that the identified photocurrent of BiVO₄ after coupling with TiO₂ (BiVO₄/TiO₂) was increased around 4 times as compared to that of pure BiVO₄ under 100 mW cm⁻² illumination, which they attributed to the structural modifications of BiVO₄ that increased the electron transfer across the junction. Mahadik et al. [76] prepared Bi₂S₃/BiVO₄ photoanodes with PEC transformation using ion exchange reactions of Na₂S/Na₂SO₃ contained in the aqueous electrolyte solution. Fig. 3 shows that ABV3 (deposited films 0.1 M of Bi(NO₃)₃·5H₂O on the FTO by drop casting method) greatly increased the photocurrent density (3.3 mA cm⁻²) with a hydrogen generation rate of ~417 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$ under simulated sunlight at 0.67 V vs. RHE compared to ABV1 (deposited 0.025M of Bi(NO₃)₃·5H₂O on the FTO) and ABV2 (deposited 0.05 M of Bi(NO₃)₃·5H₂O on the FTO).

4.5. Heterojunction with modified surface

Kim et al. [77] reported that CaFe₂O₄/BiVO₄ heterojunction modification with cobalt phosphate (Co-Pi) doubled the photocurrent as compared to that of pure BiVO₄ under simulated 1 sun (100 mW cm⁻²) irradiation, which they attributed to the reduced charge recombination on the electrode surface and the increased stability of CaFe₂O₄/BiVO₄ heterojunction structures.

Rao et al. [78] reported that BiVO₄/WO₃ heterojunction modified with Co-Pi catalyst increased the photocurrent to 5.1 mA cm⁻² (at 1.23 V vs. RHE) under 1 sun illumination. Nanoparticulate BiVO₄/ZnO with cobalt phosphate (Co-Pi) on the surface showed a 12-fold increase in the photocurrent to 3 mA/cm² compared to BiVO₄ and IPCE to 47% at 1.23V vs. RHE, which was attributed to the improved electron transfer from BiVO₄ to ZnO and hole transfer to Co-Pi for water oxidation, leading to enhanced PEC performance [74]. Cheng et al. [79] reported that a BiVO₄/TiO₂ heterojunction modified with Co-Pi cocatalyst exhibited a photocurrent density double that of pure BVO under

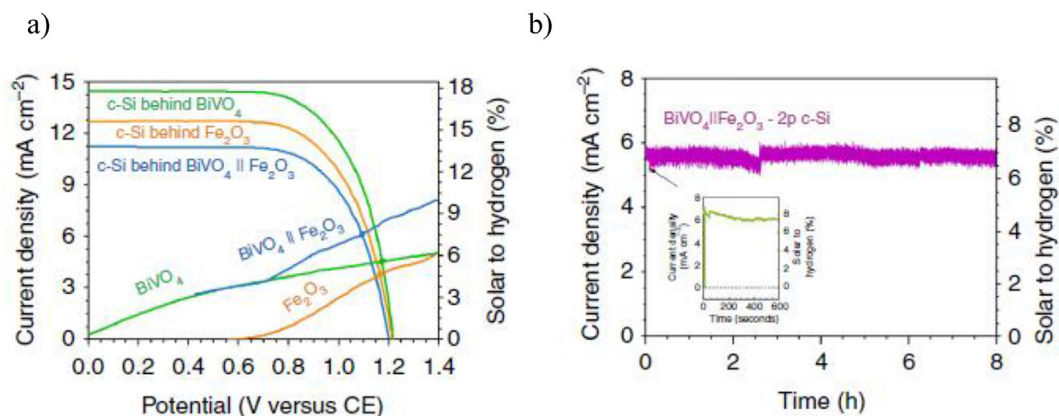


Fig. 2. (a) Linear scan voltammetry of BiVO_4 , Fe_2O_3 and $\text{BiVO}_4||\text{Fe}_2\text{O}_3$ electrodes. (b) Stability of HDP ($\text{BiVO}_4||\text{Fe}_2\text{O}_3$) electrodes in 0.0V vs. CE. Copyright @ NATURE COMMUNICATIONS | <https://doi.org/10.1038/ncomms13380>.

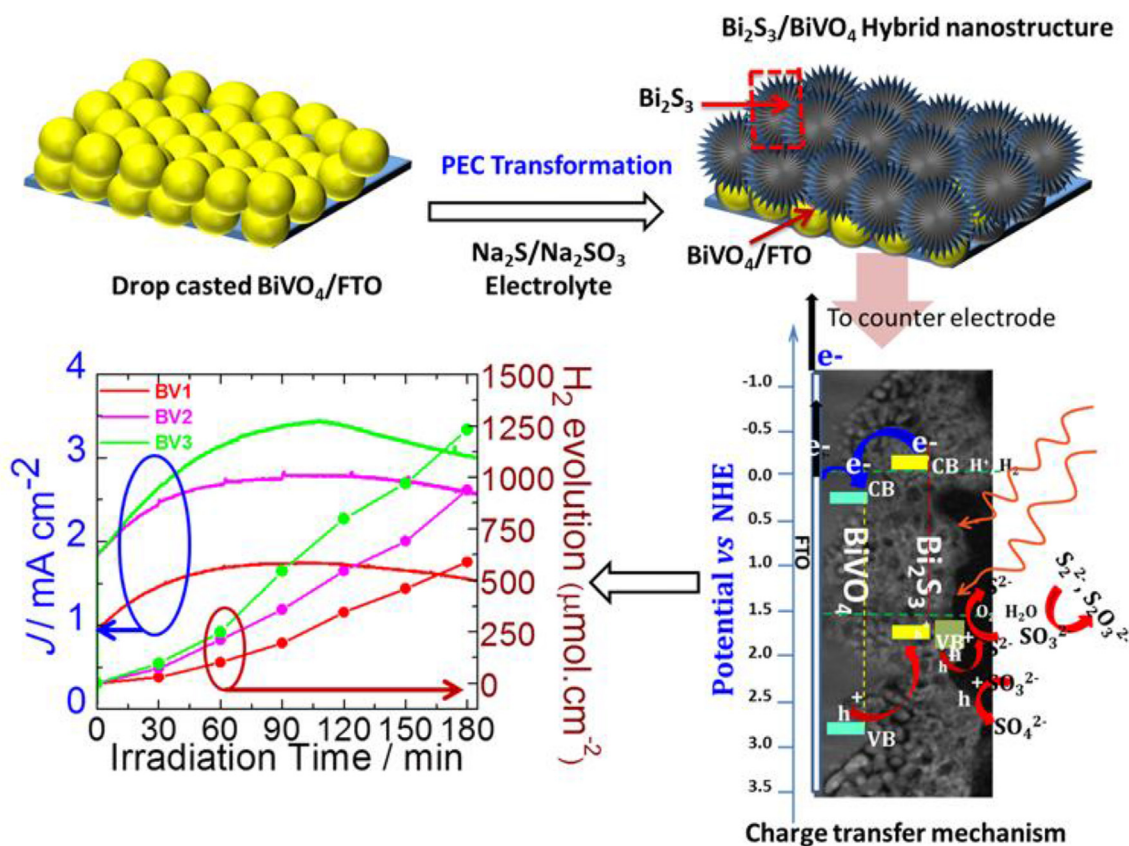


Fig. 3. (a–d) Mechanism of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterostructure photoanodes. Photocurrent density and hydrogen production versus time for BV1, BV2, and BV3 photoanodes under irradiation of AM1.5G illumination at 0.67 V vs. RHE in 0.1 M $\text{Na}_2\text{S}/0.025$ M Na_2SO_3 electrolyte. Copyright @ ACS Sustainable Chem. Eng. 2018, 6, 12489–12501.

AM 1.5 simulated sunlight at 100 mW cm^{-2} in 0.5 M Na_2SO_4 electrolyte with KPi buffered at pH 7, which they attributed to the improved hole injection efficiency.

4.6. Heterojunction with doping and nanostructured

Fig. 3, from Hou et al. [80], shows a schematic for the energy band structure of the $\text{Mo:BiVO}_4/\text{RGO}/\text{Fe}_2\text{O}_3$ – NA heterojunction. As a semiconductor photocatalyst is less conductive than conductors, the combination of a semiconductor with conductive materials that can more easily transfer photogenerated carriers could improve its conductivity. Because conductive materials having conjugated carbon

networks can raise the conductivity, carbon materials like graphene, fullerene, carbon nanotube (CNT) and their derivatives have been frequently used as an electron mediator and even as a photocatalyst itself [81,82]. In particular, BiVO_4 is known for poor electron conductivity so CNT and graphene derivatives were reported as effective conductive charge mediators. As shown in Fig. 4, RGO is the electron mediator between poorly conducting BiVO_4 and Fe_2O_3 to connect them electronically into a working heterojunction. In the $\text{BiVO}_4/\text{Fe}_2\text{O}_3$ heterostructure, the photocurrent density was increased around 9 times and the transient photocurrent decay was reduced, indicating reduced recombination of photogenerated charge carriers. Although the obtained absolute photocurrent was rather low due to unoptimized syntheses of

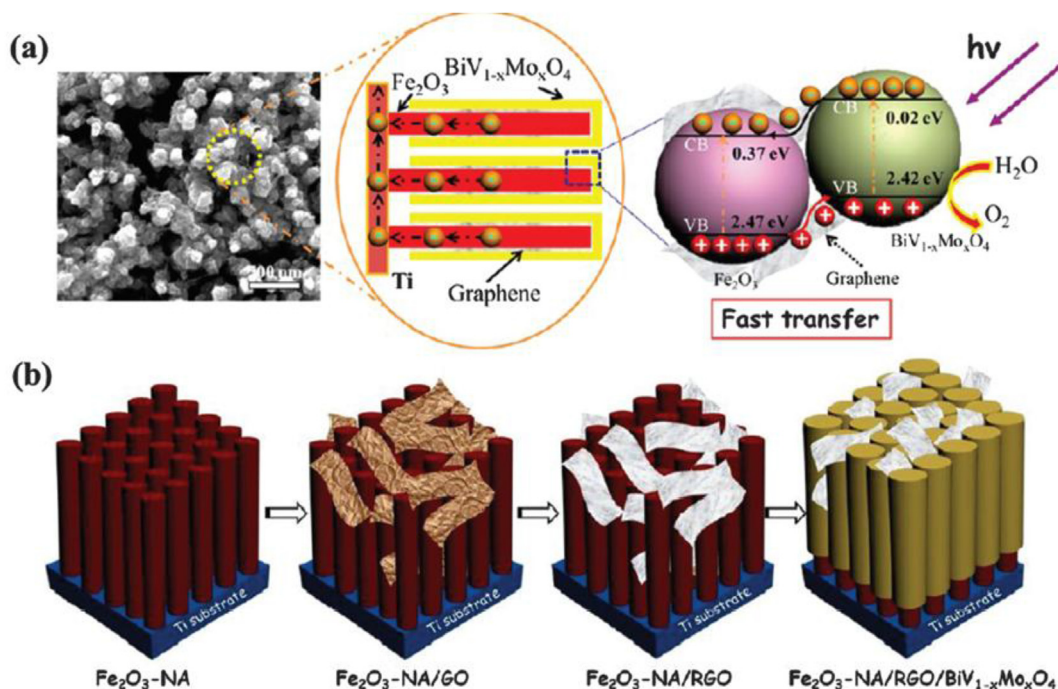


Fig. 4. (a) SEM and mechanism of the Mo:BiVO₄/RGO/Fe₂O₃-NA heterojunction and (b) synthetic route to the heterojunction. Hou et al., *Nano Lett.* 12, 6464 (2012). © 2012, American Chemical Society.

the materials, the report revealed that carbon-based materials can be an effective electron transfer mediator [34,83].

4.7. Heterojunction with a nanostructured and modified surface

Fig. 5 displays a schematic energy diagram of the WO₃-nanorods (NRs)/BiVO₄ with modified surface (Co-Pi) photoanode and

mechanism of the photovoltaic (PV)-assisted photocatalytic water-splitting process. As monoclinic BiVO₄ has a band gap of 2.37 eV, most of the solar light over a wavelength of 524 nm is absorbed by the BiVO₄ layer. Although the BiVO₄ layer is extremely thin at approximately 30 nm, it absorbs very efficiently due to the bandgap of BiVO₄ and the increased light trapping in the nanostructure with high aspect ratio [84,85].

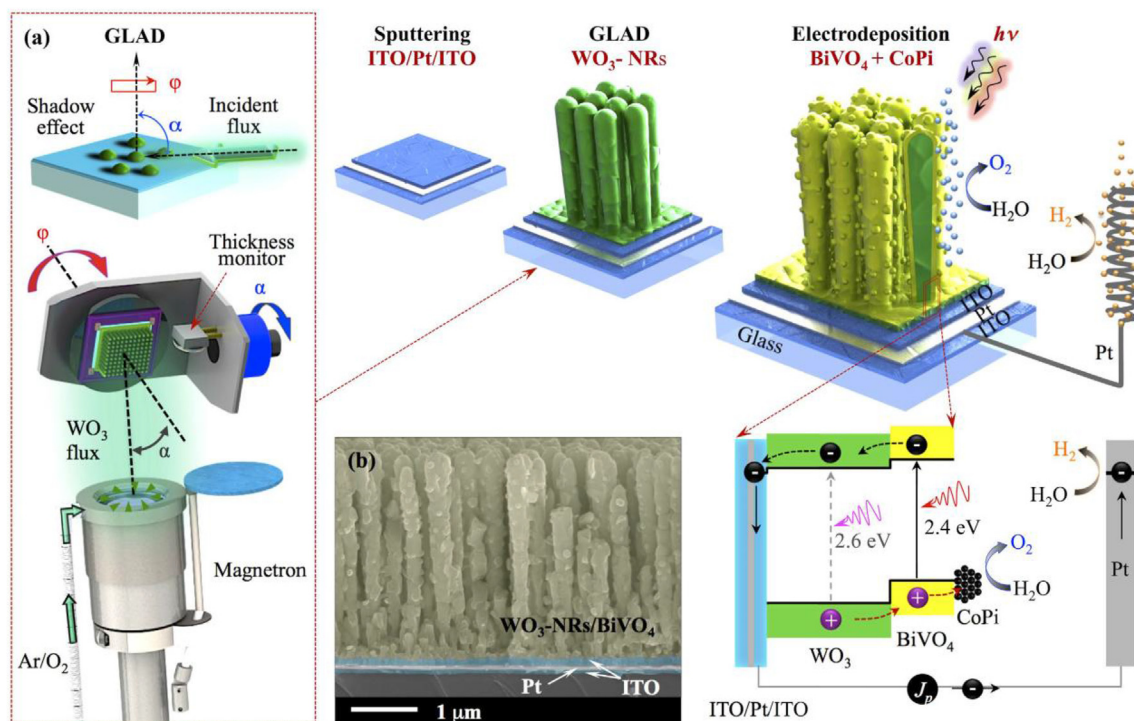


Fig. 5. Scheme of a WO₃-NRs/BiVO₄ photoanode prepared by glancing angle deposition (GLAD) of WO₃-NRs by electrodeposition (apply potential) of BiVO₄ with CoPi. The inset (a) illustrates GLAD. (b) Cross-sectional SEM image of the PEC cell based on ITO/Pt/ITO/WO₃-NRs/BiVO₄ + CoPi photoanode. Copyright © 2016 the Japan Society of Applied Physics.

Their result confirmed that the nanostructured layer recombination due to light trapping in the BiVO₄ and WO₃-NRs contributes to the electron transfer. The electron-hole pairs generated in the BiVO₄ layer are separated at the WO₃/BiVO₄ heterojunction interface. Finally, the cocatalyst Co-Pi clusters on the BiVO₄ surface transferred the holes remaining in the BiVO₄ layer to participate in the oxygen evolution reactor.

4.8. Heterojunction BiVO₄ photoanodes with Doping

Some of the limiting factors for BiVO₄ are poor electron transport ability and low PEC efficiency. Metal doping of BiVO₄ (Mo-BiVO₄ or W-BiVO₄) can improve its photocurrent because of the extra free electrons. Density functional theory (DFT) calculation of bulk BiVO₄ identified that Mo atoms prefer to replace the V atoms. However the surface Mo atoms is more easily substituted by the Bi atoms at the outermost layer [78,86]. These results indicated that Bi doping or the substitution of V⁵⁺ sites by Mo⁶⁺ atoms in bulk BiVO₄ strengthen the n-type characteristics of BiVO₄, which increases the electric conductivity and consequently improves the PEC performance by providing additional free electrons in BiVO₄ [49]. He et al. [87] reported that a MoO₃ heterojunction with 5% Mo doping BiVO₄ consisting of dispersed nano-MoO₃ on the surface of BiVO₄ greatly improved PEC water splitting. Fig. 6 shows that the photocurrent of the MoO₃/5% Mo BiVO₄ is around 8 times higher than that of pure BiVO₄, which improved the PEC performance due to increased surface charge transfer.

Shi et al. [88] reported that the photocurrent density of a

heterojunction of WO₃ with co-doping W-Mo-BiVO₄ increased to 3.9 mA cm⁻² (at 1.23 V vs. RHE), which is double that of W-Mo-BiVO₄.

4.9. Heterojunction with a Doping and modified surface

Fig. 7 shows that the highest photocurrent density reached 5.3 mA cm⁻² at 1.23 V vs. RHE for WO₃/(W, Mo)-BiVO₄/FeOOH/NiOOH, in comparison with other planar photoanodes of thin films. These improved results indicate that the helical structure greatly enhances the properties for improved PEC water splitting, such as enhancing light harvesting due to strong light-scattering. The helical structures also provide other advantages such as an appropriate radius and an increased surface area for enhancing charge separation, and improved single crystallizing for increasing charge separation. In addition, WO₃/(W, Mo)-BiVO₄/FeOOH/NiOOH can facilitate the diffusion of W from WO₃ into BiVO₄, leading to a gradient doping of W, which is beneficial for improving the charge separation [88].

Zeng et al. [89] deposited cobalt-phosphate (Co-Pi) on the surface of WO₃/Mo-BiVO₄ to produce an increased photocurrent density of 5.38 mA cm⁻². This catalyst deposition led to stoichiometric gas evolution of H₂ and O₂ of around 94.7 mmol cm⁻²h⁻¹ and 46.5 mmol cm⁻²h⁻¹, respectively. Shi et al. [88] reported that a cocatalyst Co-Pi and FeOOH/NiOOH on the surface of a heterojunction of WO₃/W-Mo-doped BiVO₄ photoanode significantly improved the photocurrent density to 4.2 mA cm⁻² and 5.35 mA cm⁻² respectively.

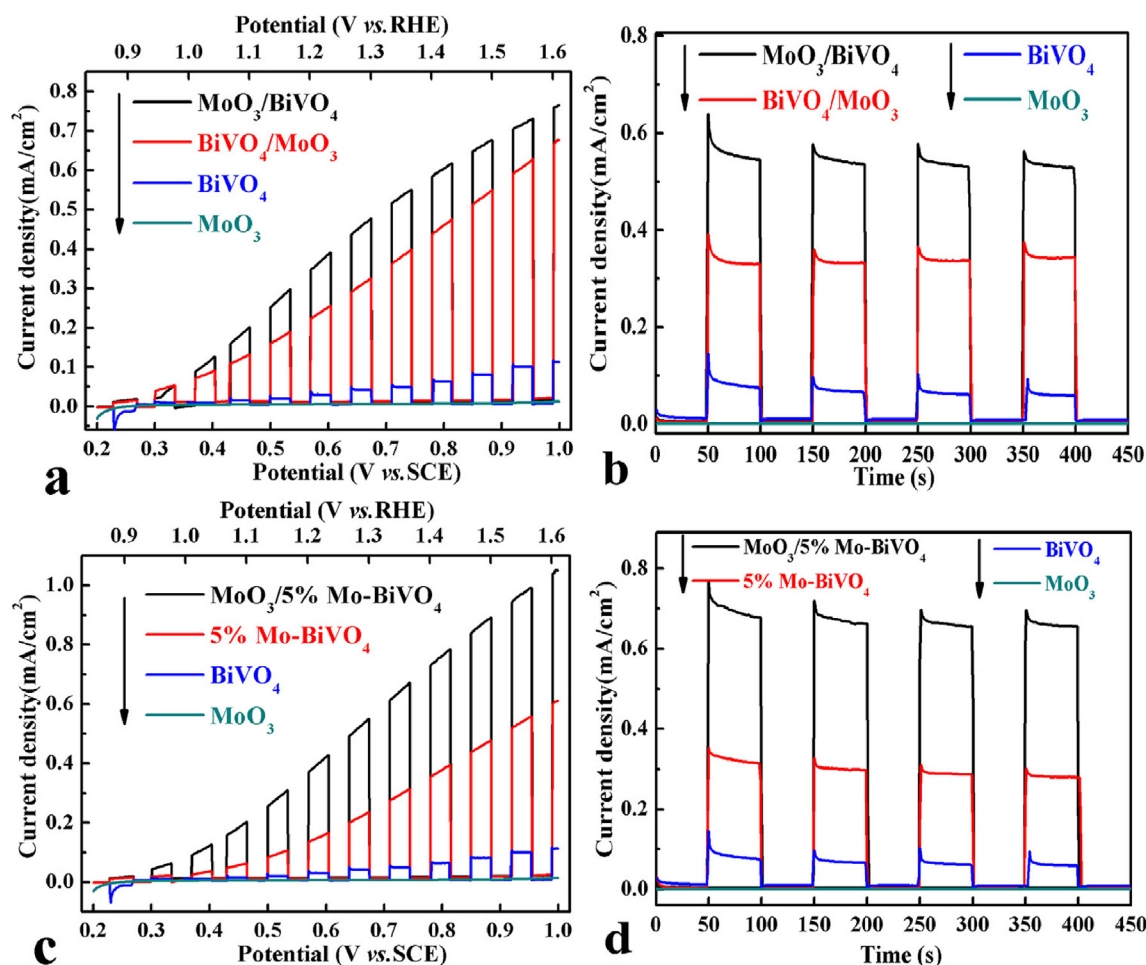


Fig. 6. (a) and (c) Chopped Linear scan voltammetry (LSV) of MoO₃, BiVO₄, heterojunction of BiVO₄/MoO₃ and heterojunction of MoO₃/BiVO₄ films. (b) and (d) The photocurrent density versus time film at 0.8 V vs. SCE in 0.2 M Na₂SO₄ (pH 7) under illumination with 1 sun simulated solar light. Copyright © Electrochimica Acta 257 (2017) 181–191.

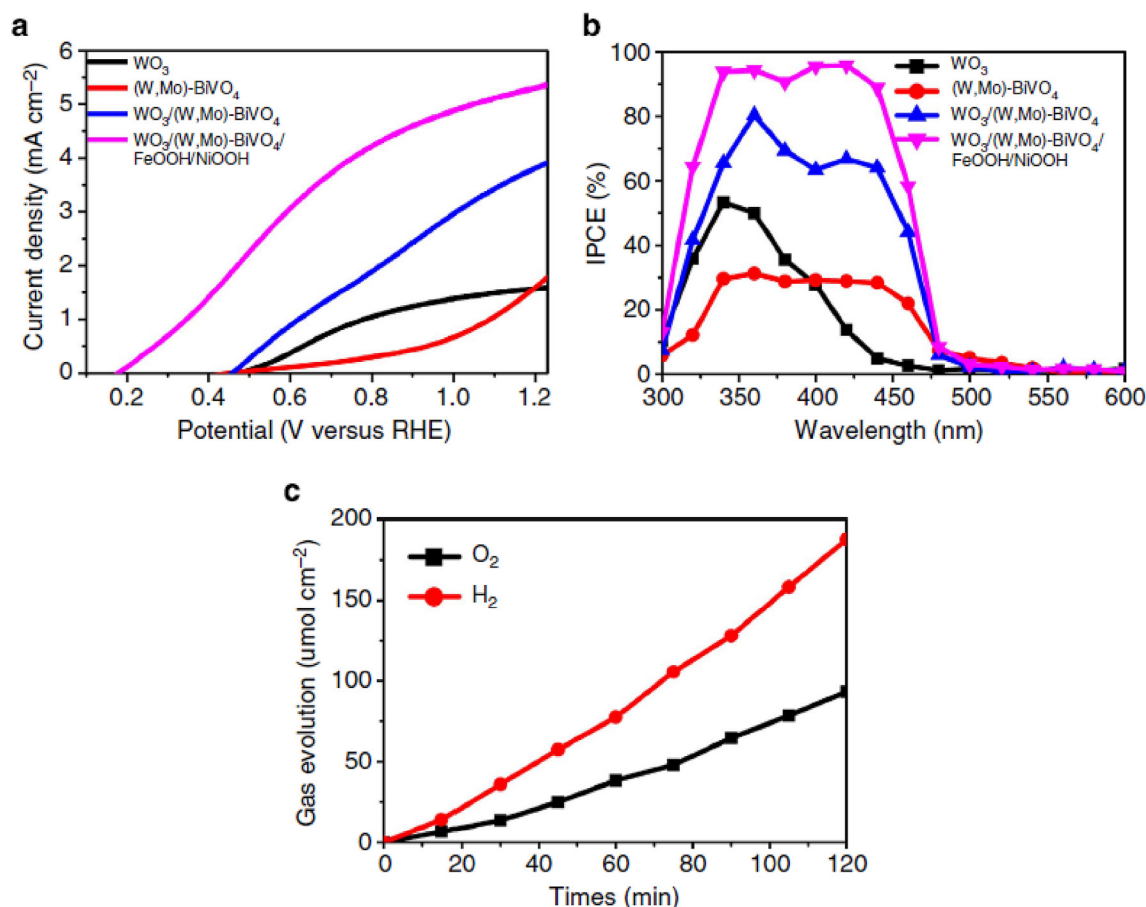


Fig. 7. PEC performances. (a) LSV and (b) IPCE curves of a heterojunction with doping ($\text{WO}_3/(\text{W}, \text{Mo})\text{-BiVO}_4$) and modified surface with $\text{FeOOH}/\text{NiOOH}$ in 0.5M K_2SO_4 in phosphate buffer (pH 7) under AM 1.5 G, 100mWcm^{-2} illumination. (c) $\text{H}_2(\text{O}_2)$ evolution versus time, H_2 measured every 20 min 1.2 V vs. RHE. Copyright © NATURE COMMUNICATIONS | <https://doi.org/10.1038/ncomms5775>.

4.10. Change in structure (surfactant)

Tayyebi et al. [90] reported that monoclinic bismuth vanadate $\text{Bi}_{1-x}\text{VO}_4$ (s-m) with surface defect states improved PEC water splitting performance. BiVO_4 (s-t) exhibited poor mobility of charge carriers, while $\text{Bi}_{1-x}\text{VO}_4$ (s-m) exhibited great enhancement by transforming the tetrahedron structure BiVO_4 (s-t) into monoclinic phase. The $\text{Bi}_{1-x}\text{VO}_4$ (s-m) structure formed new surface defect states with a more porous structure. In addition, $\text{Bi}_{1-x}\text{VO}_4$ (s-m) demonstrated an enhanced and stable photocurrent density of 1.2 mA/cm^2 at 1.0 V vs. Ag/AgCl under Xe lamp in 0.1 M Na_2SO_4 aqueous solution.

Kim et al. [91] reported that a change in the structural properties of BiVO_4 improved the photocurrent density and hydrogen production of the photocatalyst without changes in the position of the Fermi energy level, light absorption, or charge carrier. They altered the structure of BiVO_4 with electrodeposition of Bi metal on the surface by changing the potential and temperature. After Bi electrodeposition, the morphology, particle size, and porosity of BiVO_4 were changed and the photocurrent density was increased around 2.5 times compared to that without optimized BiVO_4 . Monfort et al. [11] reported in Fig. 8 that surfactant template carbon paste named Elcocarb C/SP (Solaronix) can increase the hydrogen production of BiVO_4 with greatly increased surface area of the semiconductors. They identified a maximum hydrogen production rate of 0.15 umol/h under an electric bias of 1.4 V vs. Ag/AgCl plus 0.37 V chemical biases.

4.11. Effect of electrolyte

Several different electrolytes with different pHs such as Na_2SO_4

[92], Na_2SO_3 [93,94], K_2SO_4 [95,96], KHCO_3 [95,97], and NaHCO_3 [98] have been investigated for the PEC performance on the BiVO_4 . More recently, the effects of the electrolyte and its pH on the PEC performance and photocatalytic activities of BiVO_4 have been investigated [99,100]. They found that increasing the pH of the electrolyte solution from 2.5 to 9.5 efficiently increased the band bending and electron-hole separation. In the basic (pH = 9.5) media, therefore, the BiVO_4 anodes showed increased photocurrent and PEC performance. Choi et al. [101] reported that the use of the electrolyte saturated with V^{5+} can be an effective method to enhance the long-term stability of photoelectrodes of BiVO_4 . Fig. 9a and c shows the long term photo-stability of $\text{BiVO}_4/\text{FeOOH}/\text{NiOOH}$ photoanode in a solution containing $\text{KB} + \text{V}_2\text{O}_5$ (pH 9.3) and in 0.5 M KB solution (pH 9.3) with 0.7 M Na_2SO_3 as an electrolyte, respectively. Choi et al. also reported the gas evolution of H_2 and O_2 around 225 umol and 125 umol as shown in Fig. 9a respectively.

With the study goal of overcoming the high recombination issue of photoinduced charge carrier of BiVO_4 , Kim et al. [83] demonstrated three kinds of heterostructuring techniques that are commonly employed by combining with other semiconductors (heterojunction), charge mediators, and oxygen evolution cocatalysts. Fig. 10 shows a scheme of heterojunction configuration and performance evolution of $\text{Co-Pi}/\text{W}:\text{BiVO}_4/\text{WO}_3$ to demonstrate the general effects of heterostructure for their heterostructure effects to improve PEC performance. Doping can increase the carrier density and mobility to improve the charge transport properties of BiVO_4 . BiVO_4 and WO_3 form a heterojunction so that electrons can trickle down from the CB of BiVO_4 to that of WO_3 by through the CB energy level offset effects resulting improving the charge carrier separation [102,103].

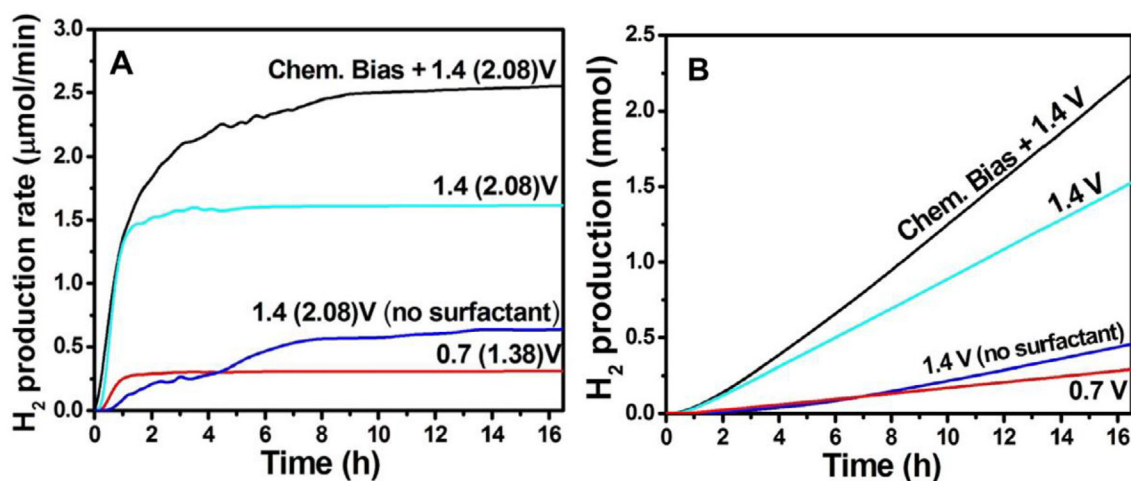


Fig. 8. Hydrogen evolution rate (A) and cumulative hydrogen evolution (B) of BiVO₄ photoanode prepared without surfactant templates. Copyright @ Chemical Engineering Journal 286 (2016) 91–97.

The combination of oxygen evolution cocatalysts like cobalt phosphate (Co–Pi) with BiVO₄ improves the hole transfer at the electrolyte/photocatalyst interface, thereby increasing the surface charge separation. Thus, the observed photocurrents at 1.23 V vs. RHE under AM 1.5 G solar light were improved with successive modifications: bare BiVO₄ (0.2 mA/cm²) < doped BiVO₄ (0.7 mA/cm²) <

heterojunction with WO₃ (1.6 mA/cm²) < Co–Pi cocatalyst (3.7 mA/cm²). Loading of the cocatalyst also brings a cathodic shift of 0.3 V in the current onset potential.

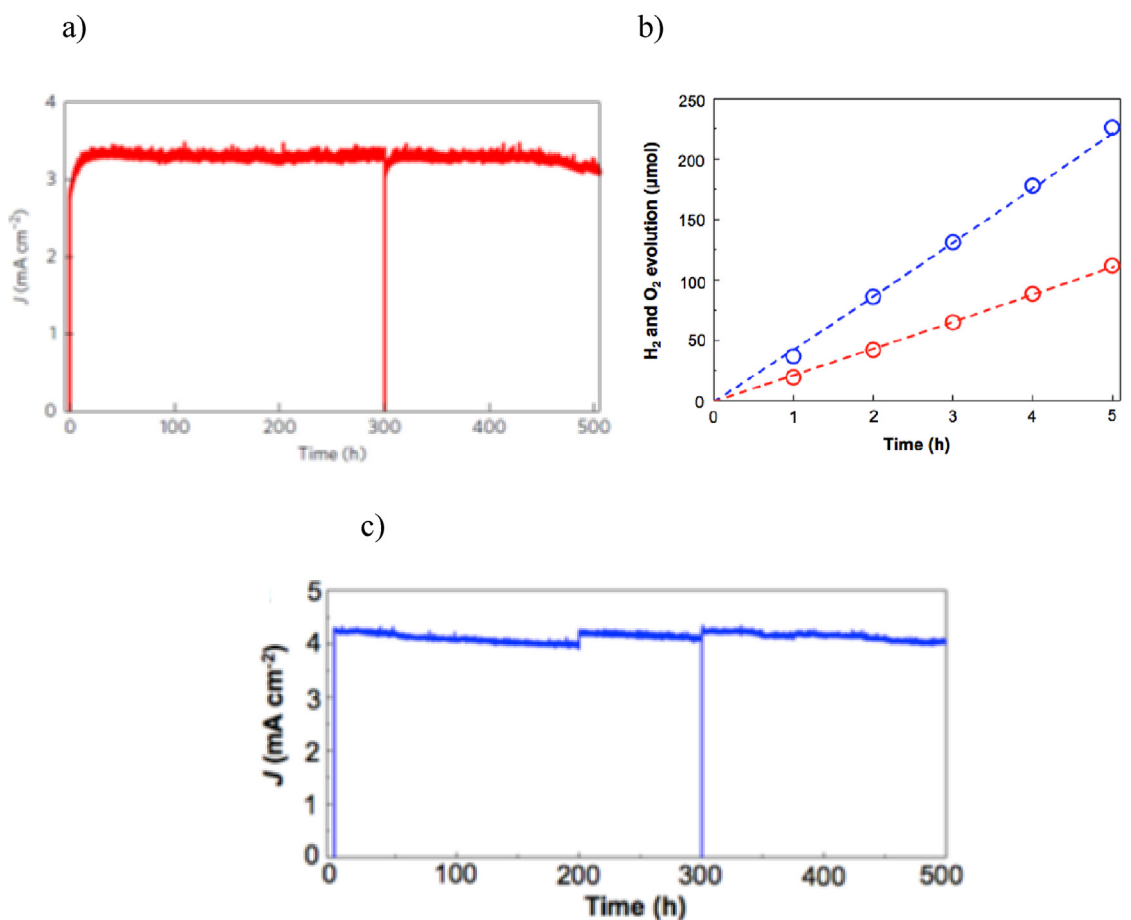


Fig. 9. (a) Photostability of the BiVO₄/FeOOH/NiOOH film in KB + V at 0.6 V vs. RHE. (b) Amount of H₂ (blue circles) and O₂ (red circles) gases produced by BiVO₄/FeOOH/NiOOH at 0.6 V vs. RHE in the KB + V solution. (c) photostability of BiVO₄/FeOOH/NiOOH for sulfite oxidation at 0.6 V vs. RHE in 0.5 M KB solution (pH 9.3) containing 0.7 M Na₂SO₃. Copyright @ Nature Energy | DOI: 10.1038/s41560-017-0057-0. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

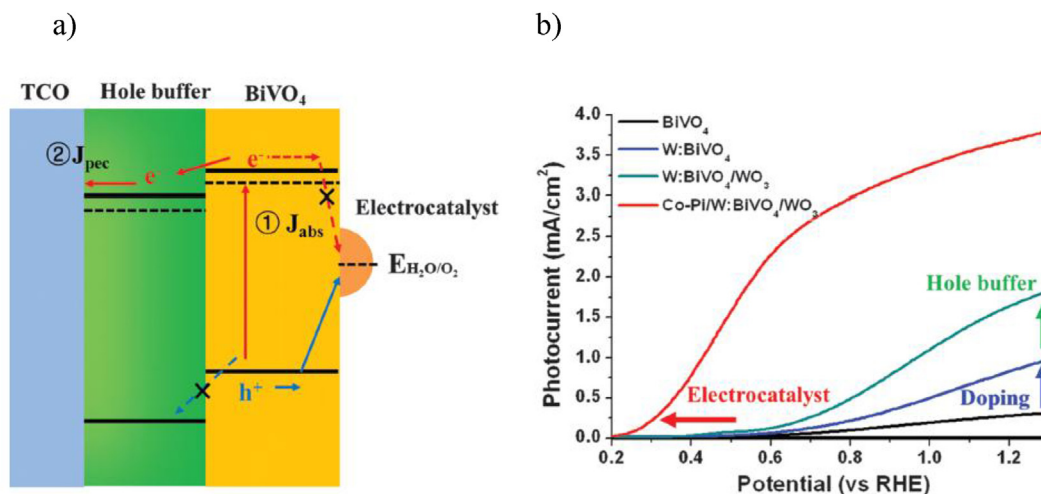


Fig. 10. (a) A scheme of heterojunction configuration with a cocatalyst (cocatalyst/BiVO₄/WO₃) and (b) *I*-*V* curve of Co-Pi/W:BiVO₄/WO₃ photoanode (light source - AM 1.5 G, 0.1 M KPI (pH 7), scan rate 20 mV/s, front illumination). Copyright © Energy Environ. Focus 2014, Vol. 3, No. 4.

5. Summary and future outlook

In the last decade, numerous efforts have been made to improve solar hydrogen production via PEC water splitting using solar irradiation. In this work, we reviewed recent reports using engineering techniques to fabricate efficient and enhanced photoactive BiVO₄ materials for solar renewable energy production of hydrogen gas.

However, we have found that there is still limited information for enhancing the stability of modified BiVO₄ structures, which increases the remaining challenges. PEC water splitting for hydrogen gas production using modified BiVO₄ nanostructure, metal doping, cocatalyst, structural modification, or heterojunction structure of BiVO₄ can be promising routes to produce hydrogen gas for commercial purposes. Renewable energy production, using PEC solar hydrogen production gas with less environmental impacts can solve the air pollution and global warming issues associated with conventional energy production via fossil fuel combustion.

For fabricating highly efficient and stable photoelectrodes with visible light response, future studies should focus on developing new photoactive materials and composites with computational aid work of modeling and mechanistic studies. The PEC water splitting systems should be improved for minimizing the recombination of photoinduced charge carriers of photoactive materials for enhancing the transport of electrons or holes between the electrodes – electrolyte interfaces with better understanding of the photocatalysis mechanism and more engineering optimization.

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