



Review

Recent advances in bismuth vanadate-based photocatalysts for photoelectrochemical water splitting

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ABSTRACT

Photoelectrochemical (PEC) technology is considered to be a promising approach for solar-driven hydrogen production with zero emissions. Bismuth vanadate (BiVO₄) is a kind of photocatalytic material with strong photoactivity in the visible light region and appropriate band gap for PEC water splitting. However, the solar-to-hydrogen efficiency (STH) of BiVO₄ is far away from the 10% target needed for practical application due to its poor charge separation ability. Therefore, this review attempts to summarize the strategies for improving the photocurrent density and especially hydrogen production of BiVO₄ materials through PEC techniques in the last three years, such as doping nonmetal and metal elements, depositing noble metals, constructing heterojunctions, coupling with carbon and metal-organic framework (MOF) materials to further enhance the PEC performance of BiVO₄ photoanode. This review aims to serve as a general guideline to fabricate highly efficient BiVO₄-based materials for PEC water splitting.

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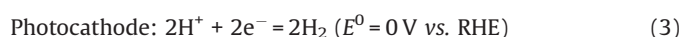
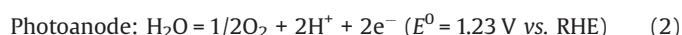
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1. Introduction

In view of fossil energy consumption that has been resulting in current global energy shortage and the accompanying environmental crisis, direct conversion of naturally abundant solar energy into chemical energy in a sustainable manner is one of the most promising solutions to solve the energy crisis and environmental pollution in the future [1]. Since the pioneering work of photoelectrochemical (PEC) water splitting into oxygen and hydrogen using TiO₂ as the photoanode in 1972 [2], PEC hydrogen production technology, a process to convert and store solar energy in chemical bonds, has attracted great attention [3]. This may be due to external bias potential, which can help minimize electron-hole recombination rate and increase the generated electrons and holes that take part in the water splitting process.

A typical PEC cell is composed of two conductively connected electrodes immersed in an electrolyte with at least one electrode

containing semiconductors (*i.e.*, a photoelectrode) for light harvesting, where the photoanode is made of an n-type semiconductor and the photocathode is made of a dark metal electrode [4]. Generally, PEC water splitting involves four basic steps (Fig. 1): Firstly, absorbs light to generate a pair of hole-electrons in a photoactive photoelectrode under visible sunlight illumination. Secondly, the holes on the surface of the photoanode cause water oxidation (OER) [5]. Thirdly, the electrons generated by the photoanode transfer from the photoanode to the photocathode surface through external wires. Finally, the electrons on the surface of the photocathode reduce H⁺ to form hydrogen (HER) [6]. The mechanism of the whole reaction is shown in the following equations (Eqs. 1–3):



From a thermodynamic point of view, a suitable semiconductor photoelectrode for PEC water splitting must fulfill the following several demands: (1) The minimum value of conduction band (CB)

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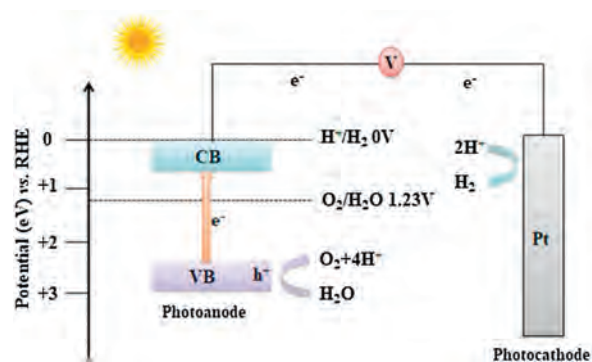


Fig. 1. The basic mechanism of PEC water splitting.

edge should be more negative than the reduction potential of hydrogen [7]; (2) the maximum value of valence band (VB) edge should exceed the potential of oxidizing H_2O to O_2 ; (3) the photoelectrode should absorb photon energy equal to or greater than 1.23 eV to undergo a water splitting reaction [8]. Therefore, the band gap energy (E_g) of the semiconductor photoelectrode should be in the range of 1.5–3.1 eV [9]. To date, no single material completely fulfills all the thermodynamic requirements of PEC water splitting [10]. Hence materials development remains the key issue for improving PEC performance.

As an important semiconductor photocatalyst, bismuth vanadate (BiVO_4) has been widely examined because of its plentiful abundance, low cost, excellent (photo)-electrochemical stability in aqueous solutions and nontoxic. The BiVO_4 exists in three crystal structures: Scheelite structure with tetragonal phase and monoclinic phase and zircon structure with tetragonal phase. Among the three crystal structures, scheelite structure with monoclinic phase has higher thermodynamic stability and higher catalytic activity than other structures, and is most commonly used in photo-electrocatalysis. For the scheelite structure, BiVO_4 with tetragonal and monoclinic phases are dissimilar as the local environments of V and Bi ions are notably distorted in the latter. Hence, the V—O bonds in tetragonal scheelite BiVO_4 are all of equal length (1.72 Å), while two different V—O bond lengths (1.77 Å and 1.69 Å) are present in monoclinic scheelite BiVO_4 . In particular, the Bi^{3+} lone electron on the Bi 6s orbital causes the partial deformation of the Bi—O ionic bond to enhance the distortion of the BiO_8 dodecahedron. The distortion of the VO_4 octahedron causes the center positions of the positive and negative charges to be separated. As a result, an internal electric field is generated, which is very conducive to the separation of photogenerated electron-hole pairs, so monoclinic BiVO_4 has higher photocatalytic performance than the other two structures. More recently, monoclinic BiVO_4 has received great attention as a photoanode material for PEC water splitting because BiVO_4 photoanode satisfy the necessary requirements listed above [11]. This interest originates from an appropriate bandgap structure ($E_g \approx 2.4$ eV) of BiVO_4 that not only favors good light absorption but also provides a relatively negative CB edge (~ 0.02 V vs. RHE) to undergo water oxidation reaction driven by visible light. However, it has its own shortcomings of poor electron conductivity and sluggish water oxidation kinetics [12]. The poor electron transport performance of BiVO_4 may be due to the disconnection of VO_4 tetrahedron units in the crystal structure of the material, indicating that that the photoexcited electrons in the V 3d conduction band have to hop between the VO_4 tetrahedra [5]. In contrast, a theoretical study on the hole transport in BiVO_4 revealed a relatively weak hole localization in this material [6], again signifying that the charge transport in BiVO_4 is primarily

limited by electron mobility. For example, the photocurrent densities achieved for unmodified BiVO_4 photoanodes (1.0 mA/cm^2 and 0.81 mA/cm^2) are still far below its theoretical maximum photocurrent of 7.5 mA/cm^2 under standard AM 1.5 solar light irradiation [13]. In addition, Subramanyam *et al.* reported that the solar-to-hydrogen conversion (STH) for pure BiVO_4 photoanode is 0.82% at 0.61 V vs. RHE, much lower than that the theoretical STH value of 9.2% [14].

Therefore, it is of great significance to overcome shortcomings of BiVO_4 for promoting its broad application in PEC water splitting. To this end, we summarize recent three years' reports (2017–2020) in the area of BiVO_4 -based materials for the PEC water splitting applications. A distinct emphasis of the review is that it aims to provide a better understanding of the fundamental design, fabrication, mechanisms and performance of BiVO_4 for PEC water splitting applications. Various strategies such as doping with noble metal, metal and nonmetal element, constructing a heterojunction, as well as combining with carbon and MOF materials will be discussed to enhance PEC performance of water splitting of BiVO_4 . Finally, further challenges to explore highly efficient BiVO_4 material systems are also presented.

2. Methods to enhance the PEC performance of BiVO_4 for water splitting

The main drawback of BiVO_4 photoanode is their limited light absorption, poor charge separation and lower surface charge transfer efficiencies. To overcome those drawbacks, enormous efforts have been focused on how to optimize BiVO_4 photoelectrode, such as doping of metal/nonmetal atoms, depositing noble metals, constructing heterojunctions, coupling with carbon and metal-organic framework (MOF) materials.

2.1. Doping metals or nonmetals

Doping of BiVO_4 is considered as a process of introducing additional elements and impurities into the BiVO_4 framework to distinctly tune the optical, electronic, luminescent and other physical properties of BiVO_4 . There are two main types of elemental doping that will be discussed in this section, namely nonmetal doping and metal doping. In the field of photocatalysis, band gap engineering of BiVO_4 via the incorporation of anions, cations or the incorporation of both plays a predominant role to enhance the spectral responsive region and redox band potentials for targeted photocatalytic applications. Hitherto, numerous studies on the doping of metallic elements such as Fe, Co, Ni, Ga, Zn and Mn and some non-metallic elements including F, N and B elements into BiVO_4 have been extensively reported.

Recently, it was reported that the 7% In^{3+} -doped BiVO_4 photoanode shows optimal PEC water oxidation activity (Figs. 2a and b) [15]. At 1.23 V vs. RHE, the 7% In^{3+} -doped BiVO_4 photoanode exhibits a photocurrent density of 1.56 mA/cm^2 in 0.1 mol/L Na_2SO_4 , which is over 200% greater than that of the undoped BiVO_4 photoanode. This change in water oxidation activity is attributed to the In^{3+} -doping that passivated the surface states of BiVO_4 and thus inhibited the surface charge recombination. Similarly, Yang's group synthesized Mo doped BiVO_4 photoanode on the fluorine-doped tin oxide substrate by electrodeposition method, the optimized Mo doped BiVO_4 (3AMo:BV, a substitute for ammonia-based precursor) shows ~ 1.5 times higher activity in water oxidation kinetics efficiencies than that of undoped BiVO_4 at 1.23 V vs. RHE under AM 1.5 G illumination [16]. The high oxidation kinetics efficiencies of the Mo doped BiVO_4 photoanode can be ascribed to the crystal deformation caused by larger tetrahedral ionic VO_4 and higher photovoltage generated by the interface of photoanode and electrolyte.

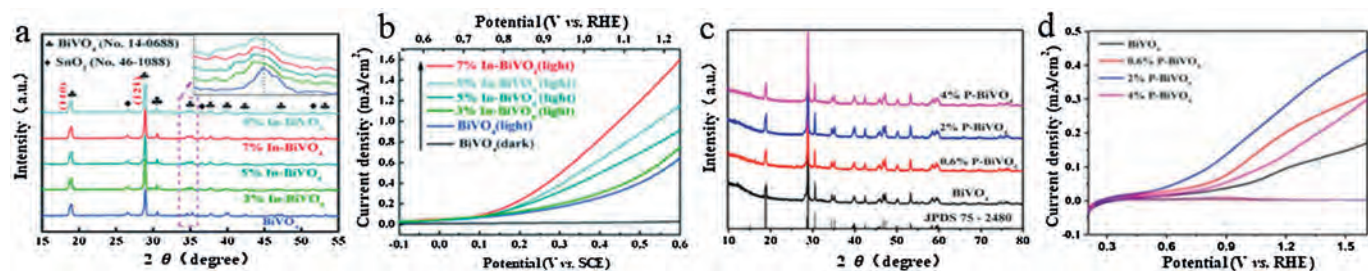


Fig. 2. (a) XRD patterns of undoped BiVO₄ and In³⁺-doped BiVO₄ films (inset: the diffraction peak at 35.25°). (b) LSV scans for undoped BiVO₄ and In³⁺-doped BiVO₄ films. (c) XRD patterns of BiVO₄, 0.6% P-BiVO₄, 2% P-BiVO₄ and 4% P-BiVO₄. (d) Photocurrent-potential curves of pristine BiVO₄, 0.6% P-BiVO₄, 2% P-BiVO₄ and 4% P-BiVO₄ in 0.5 mol/L Na₂SO₄ electrolyte with the AM 1.5 G simulated solar light at 100 mW/cm² (dashed lines represent dark currents). (c, d) Reproduced with permission [20]. Copyright 2018, Elsevier.

Meanwhile, Shi *et al.* also reported that 2% W-BiVO₄ showed a remarkable photocurrent increase with respect to the pristine BiVO₄ at 1.23 V vs. RHE under back side illumination. The improvement was attributed to the W doping that does have an effect on charge transfer at the semiconductor/electrolyte interface [17]. Chakthranont *et al.* fabricated a core-shell black-Si/W-doped BiVO₄ photoanode structure for unassisted water splitting, which achieved an average STH of 0.45% over the course of 1 h at pH 7 [18]. Moreover, it is the first time to reported that Li doped nano-porous BiVO₄ photoanode showed an increase (>20 times) in the PEC water splitting compared to pristine BiVO₄ photoanode [19]. The enhancement in PEC performance of Li: BiVO₄ is related to the formation of inter-band with band gap reduction due to interstitial Li doping in BiVO₄ through density functional theory calculations.

Apart from the metal doping, non-metallic elements doping has also been broadly employed to modify the optical and electronic properties of BiVO₄ by efficiently increasing the light absorption, reducing the band gap, accelerating the charge mobility, and prolonging the lifetime of charge carriers, all of which are necessary for pronounced PEC water splitting activity. Xia *et al.* synthesized P doped BiVO₄ by a dip-coating route and subsequent thermal treatment process (Figs. 2c and d) [20]. The incident photon-to-current conversion efficiency (IPCE) value for 2% P-BiVO₄ photoelectrode is boosted to 37.24% (at 360 nm), which is higher than that of pristine BiVO₄ (13.17%). From the X-ray photoelectron spectra, the P-BiVO₄ possessed abundant oxygen vacancies, which can account for enhancing PEC water splitting performance of P-BiVO₄. Apart from that, Irani *et al.* obtained N-modified BiVO₄ photoanode through chemical and physical methods [21]. Due to the nitrogen bonded with two vanadium atoms in the lattice, a new empty state ~0.1 eV below the conduction band minimum (CBM) was introduced. This state may act as an electron trap center, where photogenerated charge carriers are trapped and PEC water splitting performance is consequently increased. Anke *et al.* reported the preparation of fluorine-containing bismuth vanadate (F: BiVO₄) powder using a new, clean, and simple solid-vapor reaction [22]. Notably, F-incorporation significantly improves the performance of BiVO₄ photoanodes for PEC water oxidation. Namely, an increase of charge carrier density as well as a substantial suppression of charge-carrier recombination in the F:BiVO₄ result in higher PEC performance.

In addition to the above-mentioned metal and non-metallic elements doping, metal and non-metallic elements co-doping are also proved to enhance light absorption and charge separation, and thereby to improve the PEC water splitting performance of BiVO₄. Rohloff's group has reported that F and Mo co-doping can significantly improve the PEC water oxidation properties of BiVO₄ [23]. They also found that Mo doping mainly improves light-

harvesting, charge transport, and charge separation efficiencies, while F modification was demonstrated to primarily affect the charge transfer efficiency at the semiconductor-electrolyte interface. Besides that, Guan *et al.* demonstrated that the decorate BiVO₄ with Ag and N-doped carbon exhibits a maximum IPCE value of 30% at 1.23 V vs. RHE, which is ~7.5 times to that of the bare BiVO₄. This was attributed to the excellent light trapping capability, enhanced charge transport process as well as efficient photoexcited electron-hole separation of BiVO₄-C/N-Ag. It is interesting to note that the BiVO₄-C/N-Ag also showed outstanding photoelectric durability in comparison to the bare BiVO₄ [24].

2.2. Deposition of noble metals

Noble metal deposited on BiVO₄ is also effective in enhancing the photocatalytic properties of BiVO₄ materials. Significantly, the plasmonic noble metals such as Au, Ag and Pd act as charge sinks in the BiVO₄ to prevent the recombination of charge carriers, which evidently facilitate the redox reactions that enhance PEC performance. Furthermore, noble metal can improve the visible light harvesting of the BiVO₄ photocatalytic systems.

Among various plasmonic nanoparticles, Au nanoparticles deposited on various materials are the most investigated ones in the field of PEC water splitting. For example, BiVO₄ with Ag and N-doped carbon (BiVO₄-C/N-Ag) was successfully developed via in-situ dip/redox capture for the first time by Guan *et al.* [24]. The resulting composite was found to exhibit the following features, i.e., the maximum photocurrent (2.42 mA/cm² at 1.23 V vs. RHE) and IPCE value (30%) were obtained, which is 4.32 times and 7.5 times higher than bare BiVO₄ (Fig. 3a). The enhanced PEC activity can be due to the excellent light trapping capability and efficient photoexcited electron-hole separation (Fig. 3b). Besides, the outstanding photoelectric durability for BiVO₄-C/N-Ag was achieved in comparison to the bare BiVO₄.

Similarly, the plasmonic effects of octahedral Au nanoparticles (NPs) on BiVO₄ for PEC water splitting was reported by Lee's group [25]. The investigations indicate that the octahedral Au NPs/BiVO₄ achieved an improved photocurrent of 2.4 mA/cm² at the 1.23 V vs. RHE and IPCE values approaching 50% in the wavelength of 450 nm (Figs. 3c and d). The great enhancement is attributed to the effective absorption, charge generation and separation via localized surface plasmon resonance, direct electron transfer (DET) and plasmonic resonant energy transfer (PRET). Moreover, they suggested that PRET is the critical effect in enhancing the plasmonic water splitting efficiency of the octahedral Au NPs/BiVO₄ over DET. Later, Ghobadi *et al.* synthesized Au capped BiVO₄ (Au-BiVO₄) photoanode by using oblique angle physical vapor deposition [26]. Owing to the hot electron injection of plasmonic Au, the maximum photocurrent density of 1800 μA/cm² at 1.23 V vs. RHE was obtained (1.6 times than pure BiVO₄).

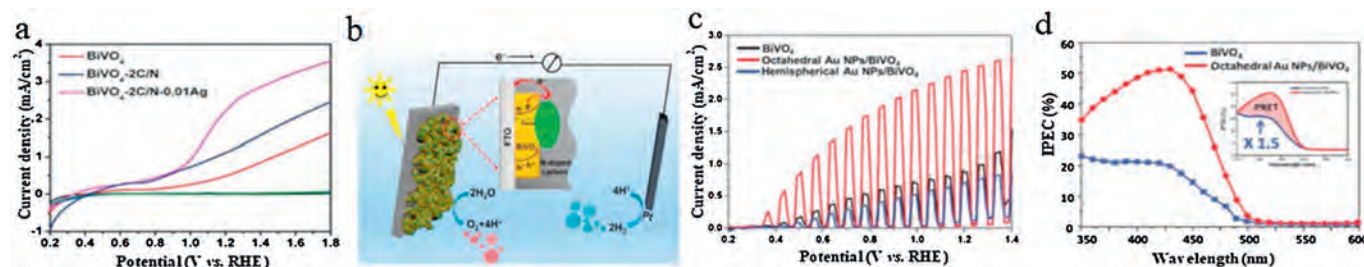


Fig. 3. (a) The linear-sweep-voltammetry (LSV) under 100 mW/cm² illumination (scan rate: 50 mV/s). (b) Schematic mechanism of BiVO₄-C/N-Ag photoanode for PEC water oxidation. (a, b) Reproduced with permission [24]. Copyright 2019, Elsevier. (c) Linear sweep voltammograms for BiVO₄ film, hemispherical Au NP/BiVO₄, and octahedral Au NP/BiVO₄ photoelectrodes measured in 0.5 mol/L phosphate buffer with 1 mol/L Na₂SO₃ at a scan rate of 10 mV/s under 1.5 G solar light under the chopped light condition. (d) IPCE spectra of bare BiVO₄ and octahedral Au NP/BiVO₄ photoelectrodes at 1.23 V vs. RHE. (c,d) Reproduced with permission [25]. Copyright 2017, Wiley VCH.

Also, Yang's group has found that the introduction of Pd nanoparticles (NPs) and nanorods (NRs) can effectively enhance PEC water splitting performance of BiVO₄ [27]. The photoinduced electron-hole pair recombination might be depressed due to the hot electron injection upon SPR excitation of Pd NPs and NRs act as a sensitizer in both visible and NIR regions and thus it was possible for the charge carriers to endure effective PEC water splitting. The same conclusions were also observed in other literature [28–31]. The above studies demonstrated that through rational design of noble metal/BiVO₄ nanostructures, both light absorption ability and charge separation efficiency can be enhanced, and the PEC activities of BiVO₄ are consequently improved.

2.3. Constructing heterojunctions

Constructing a heterojunction structure is an effective way to improve the PEC water decomposition ability of the BiVO₄ [32]. Depending on their band structures of the coupled semiconductors, a built-in electric field was introduced in the interfaces, and thus a prolonged carrier lifetime and an enhancing interfacial charge transfer can be obtained from such heterostructures. Moreover, introducing second semiconductor often provides additional benefits, such as promoted light harvesting, advantageous surface states, and structural properties [33]. At present, BiVO₄-based heterojunction are the most widely studied photocatalysts in the field of PEC water splitting. Generally, the BiVO₄-based heterojunction for PEC water splitting can be categorized into two different types depending on the charge carrier separation mechanism: 1) Conventional type-II and p-n junction; 2) direct Z-scheme. In this section, the basic principles and applications of these three heterojunctions for PEC water splitting are discussed.

2.3.1. Conventional type-II heterojunction

The type II heterojunction is the most typical heterojunction system created to enhance the PEC performance of BiVO₄ [33]. In type II systems, the CB position of semiconductor A is more negative than that of semiconductor B, and the VB position of semiconductor B is more positive than that of semiconductor A. Under light irradiation, the electrons in the CB of semiconductor A migrate to the CB of semiconductor B, while the holes in the VB of semiconductor B migrate to the VB of semiconductor A. Therefore, the photo-generated carriers effectively separate in the space.

Recently, Chae *et al.* has proved that WO₃/BiVO₄ heterojunction showed promising PEC water splitting activity than the pure WO₃ and BiVO₄, respectively [34]. The type-II heterojunction can be produced between WO₃ and BiVO₄. When the WO₃/BiVO₄ heterojunction is radiated by visible light, the generated excited-electrons transfer from BiVO₄ CB to WO₃ CB, and the holes transfer from WO₃ VB to BiVO₄ VB, which can accelerate the separation of electron-hole pairs and also enhance the fascinating optical properties. Similarly, Zhou *et al.* prepared hierarchical WO₃/

BiVO₄ nano-porous sphere arrays (Fig. 4a), and it revealed a high photocurrent of 5.5 mA/cm² at 1.23 V vs. RHE under one sun illumination (Fig. 4b) [35]. Meanwhile, W-doping, and oxygen vacancy creation can be directly incorporated into the as-obtained WO₃/BiVO₄ type-II nanojunction, which can further increase charge separation and transfer efficiencies.

Other examples of type II BiVO₄-based heterostructures are as follows. Zhang *et al.* reported that a three-dimensional FTO/TiO₂/BiVO₄ core-shell was fabricated for PEC hydrogen production by combining atomic layer deposition and electro-deposition routes [36]. It was found that the optimized FTO/TiO₂/BiVO₄ exhibited a significantly improved PEC performance of 4.11 mA/cm² in the presence of holes scavenger (Fig. 4c). The significantly enhanced PEC performance is attributed to the 3D continuous conductive FTO ordered inverse opals improving the charge transport and collection efficiency as well as the excellent contact between the TiO₂ and BiVO₄ with a large interface area facilitating the type II charge transfer process (Fig. 4d). In this respect, very recently, Liu *et al.* reported that optimized TiO₂/BiVO₄/Co-Pi photoanode yielding a photocurrent density of ~4.96 mA/cm² (0.63 V vs. Ag/AgCl), leading to a photo-to-energy conversion efficiency that was 9.0 times better than TiO₂ inverse opals and 2.3 times better than the TiO₂/BiVO₄ photoanode [37]. Likewise, CdS quantum dots sensitized olive-shaped mesoporous BiVO₄ was successfully synthesized by Zhou and co-workers [38]. Apparently, an improved photo-electrical conversion efficiency of ~1.29% is achieved for this photoelectrode material, which is ascribed to the formation of CdS/BiVO₄ type II heterostructure that can effectively promote the charge transfer behavior.

Similarly, Gao *et al.* synthesized NiMoO₄/BiVO₄ photoanode for PEC water splitting via hydrothermal method, and cobalt phosphate (CoPi) as an oxygen evolution reaction (OER) co-catalyst was deposited on the above electrode [39]. They achieved an improved photocurrent density of 5.3 mA/cm² at 1.23 V vs. RHE. This enhanced photocurrent density was originated from the development of a type II heterojunction at the NiMoO₄/BiVO₄ interface. Other than this, Palaniselvam *et al.* reported the loading of NiCoO₂ nanoparticles on BiVO₄ thin film for PEC oxygen evolution reaction [40]. The resulting BiVO₄/NiCoO₂ composite electrode manifested a high charge separation efficiency than pure BiVO₄ owing to type II charge transfer mechanism between BiVO₄ and NiCoO₂.

Our research group also prepared the MFe₂O₄ (M = Ni, Co)/BiVO₄ composite photoelectrodes via electrophoretic deposition process, ensuing heating treatment and electrophoretic deposition technology [41]. It was observed that MFe₂O₄ (M = Ni, Co)/BiVO₄ showed higher photocurrent response values (at 1.23 V vs. RHE) and superior PEC hydrogen evolution performance than pure BiVO₄ electrode under visible light illumination. The improved PEC activity of water splitting was attributed to electrons in the CB of MFe₂O₄ (M = Ni, Co) that transferred to CB of BiVO₄ and the holes in

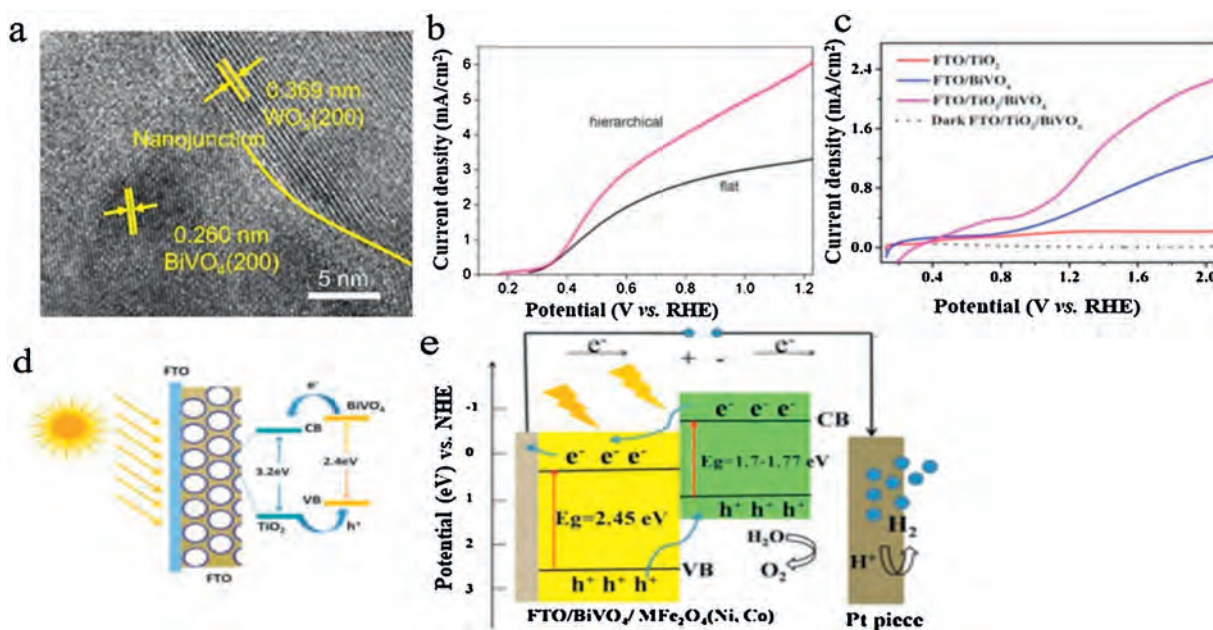


Fig. 4. (a) HRTEM image of nanoparticle from hierarchical BiVO_4 nanostructured film. (b) Photoelectrochemical activities for sulfite oxidation of nanoporous $\text{WO}_3/\text{BiVO}_4$ electrodes with hierarchical structure and flat structure, measured in a 0.5 mol/L phosphate buffer (pH 7) containing 0.5 mol/L Na_2SO_3 under AM 1.5 G, 100 mW/cm^2 illumination with a scan rate of 20 mV/s. (a, b) Reproduced with permission [35]. Copyright 2017, American Chemical Society. (c) Linear sweep curve of the FTO/ TiO_2 / BiVO_4 /Co-Pi and FTO/ TiO_2 / BiVO_4 /Co-Pi composite inverse opals measured in 0.5 mol/L Na_2SO_4 solution. (d) The charge transfer mechanism of the FTO/ TiO_2 / BiVO_4 composite inverse opals. (e) Reproduced with permission [36]. Copyright 2017, American Chemical Society. (e) The possible PEC hydrogen generation mechanism of MFe_2O_4 ($\text{M} = \text{Ni}, \text{Co}$)/ BiVO_4 electrodes at 1.23 V vs. RHE in 0.5 mol/L Na_2SO_4 under visible light. Reproduced with permission [41]. Copyright 2017, Elsevier.

VB of BiVO_4 that transferred to the VB of MFe_2O_4 ($\text{M} = \text{Ni}, \text{Co}$) (Fig. 4e). Balamurugan *et al.* reported that the core-shell $\text{BiVO}_4/\text{FeVO}_4$ inverse opal (IO) films presented higher activity for PEC hydrogen production than unmodified BiVO_4 , probably resulting from a favorable charge transfer/transport phenomenon under type II band alignment [42].

These outcomes demonstrate that type II heterojunction engineering can effectively promote charge separation, increasing the conductivity and thereby enhance the photocurrent density and PEC water splitting properties.

2.3.2. P-N junction

As for the p-n junction, when p- and n-type semiconductor contacted, the p-n junction with a space charge area forms at the interface under the diffusion of electrons and holes, causing the internal electric field build up [33]. Under light irradiation, the electrons in the CB of p-type semiconductor transferred to the CB of n-type semiconductor due to the internal electric field, while the holes finally gathered in the VB of the p-type semiconductor. The fast separation of electron-hole at the p-n heterojunction interface greatly reduces their recombination probability, and prolongs the life of photogenerated charges, thus improving the photocatalytic efficiency.

In the early study, Khoomortezaei *et al.* developed a triple heterojunction $\text{WO}_3/\text{BiVO}_4/\text{BiFeO}_3$ porous photoanode via a sol-gel method. It was found that formation of a p-n junction at $\text{BiVO}_4/\text{BiFeO}_3$ can enormously enhance the charge separation and PEC water splitting performance [43]. Recently, a p-n heterojunction of $\text{Cu}_2\text{O}/\text{BiVO}_4$ was prepared for PEC water oxidation by a two-step electrodeposition method on an FTO substrate followed by annealing treatment [44], with a high photocurrent density of 1.72 mA/cm^2 at 1.23 V vs. RHE obtained (4.5 times higher than that of pristine BiVO_4 thin films). In addition, the cathodic shift of the onset potential of $\text{Cu}_2\text{O}/\text{BiVO}_4$ was about 420 mV, which is the largest shift amongst all BiVO_4 based p-n hetero-junction photoanodes ever reported. The authors demonstrated that the

enhancement of carrier density and negative shift of flat band potential are attributed to the p-n junction at the interface of semiconductors and an inner electronic field from n-type BiVO_4 to p-type Cu_2O . Pan *et al.* fabricated Ag-embedded $\text{MoS}_2/\text{BiVO}_4$ p-n heterojunction ternary composite ($\text{BiVO}_4\text{-Ag-MoS}_2$) electrode [45]. Owing to the formation of a p-n heterojunction between MoS_2 and BiVO_4 to boost its poor electron-hole separation and transport properties by the built-in electrical potential, the photocurrent density of $\text{BiVO}_4\text{-Ag-MoS}_2$ (2.72 mA/cm^2 at 0.6 V vs. RHE) can be enhanced 2.44 times compared with pure BiVO_4 electrode (0.79 mA/cm^2).

Apart from the hybridization of metal oxide or sulfide semiconductor photocatalysts with BiVO_4 , some p-type VIII (Fe, Co, Ni) hydroxides such as FeOOH , NiOOH and CoOOH are deemed to be cost-effective and good cocatalysts for the modification of n-type BiVO_4 for enhanced PEC activity. For instance, Kim *et al.* modified BiVO_4 with $\text{FeOOH}/\text{NiOOH}$ as an efficient cocatalyst for the PEC water oxidation [46]. The presence of $\text{FeOOH}/\text{NiOOH}$ reduces interface recombination at the BiVO_4/OEC junction. The resulting $\text{BiVO}_4/\text{FeOOH}/\text{NiOOH}$ photoanode achieves a photocurrent density of 2.8 mA/cm^2 at 0.6 V vs. RHE. In another study, Zhang *et al.* demonstrated that the n-type BiVO_4 photoanodes modified by ultrathin p-type CoOOH structure (~ 2 nm) could significantly improve the PEC activities [47].

In a work by Wang *et al.*, they employed a facile electrodeposition and thermal treatment method to develop a novel $\text{BiVO}_4/\text{FeOOH}/\text{NiOOH}$ ($\text{BiVO}/\text{FeOOH}/\text{NiOOH}$) dual photoanodes [48]. The successful development of the ternary hybrid photoanodes was demonstrated by the XRD, XPS and TEM. It was found that the $\text{BiVO}/\text{FeOOH}/\text{NiOOH}$ photoanodes exhibit a remarkable and highly stable photocurrent density of 5.87 mA/cm^2 at 1.23 V vs. RHE under AM 1.5 G illumination. Similar to most of the previous reports, the formation of p-n junction photoanodes led to the rapid migration of photo-generated charge carriers to suppress the recombination rate. Most importantly, the as-obtained $\text{BiVO}/\text{FeOOH}/\text{NiOOH}$ delivers a STH as high as 6.5% for unbiased water splitting.

In our previous work, the novel $\text{FeF}_2/\text{BiVO}_4$ photoanode was successfully synthesized via electric deposition method for PEC generated hydrogen during water splitting process [49]. The $\text{FeF}_2/\text{BiVO}_4$ photoanode features greatly enhanced the performance for hydrogen evolution rate around $635 \mu\text{mol}$ within 3 h, three times more than pure BiVO_4 (Fig. 5a). This is because of the formation of p-n heterojunctions between FeF_2 and BiVO_4 which can effectively prohibit carriers from recombining and enhance the efficiency of electrons and holes separation (Fig. 5b). Subsequently, our group synthesized F-incorporated FeOOH (F:FeOOH) cocatalyst modified BiVO_4 photoanode by a one-step hydrothermal deposition method for PEC water oxidation [50]. The resulting composite photoanode shows an impressive photocurrent density and a notable initial potential that is negatively shifted by 150 mV relative to the pure BiVO_4 electrode (Fig. 5c). We also found that a p-n junction is formed between F:FeOOH and BiVO_4 , which is a promising property to spatially separate the charges to retard the recombination of charge carriers (Fig. 5d).

All the above studies elucidate that the construction of p-n heterojunction is one of the most promising strategies to enhance the PEC water splitting activity of BiVO_4 by combining the effects of the built-in electric field and the band alignment between two semiconductors.

2.3.3. Z-scheme heterojunction

The Z-scheme heterojunction has both a high charge separation efficiency and a remarkably high redox ability by retaining a highly negative CB edge and a highly positive VB edge [51–53]. Briefly, for the semiconductor-semiconductor Z-scheme heterojunction, the photogenerated electrons from the less negative CB edge of semiconductor 2 will interact with the less positive VB edge of semiconductor 1, leaving behind the electrons and holes in the CB of semiconductor 1 and the VB of semiconductor 2, respectively [54]. Therefore, the Z-scheme heterojunction evidently has more advantages for achieving more efficient photocatalytic reduction compared with the conventional type-II heterojunction.

Recently, a Z-scheme $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ heterojunction was prepared for PEC water splitting by Safaei's group [55]. It was found that PEC performance of $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ heterojunction is 4 times than that of bare BiVO_4 at 1.23 V vs. RHE under visible light irradiation. There are three possible reasons for high PEC properties of $\text{g-C}_3\text{N}_4/\text{BiVO}_4$: 1) V^{4+} was formed in the presence of hydrogen in the interplanar of $\text{g-C}_3\text{N}_4$, thus improving the mobility of charge carriers. 2) The oxygen vacancy generated by V^{4+} as the central role of catalytic sites and chemisorption substances, ultimately achieving higher photocurrent response. 3) Experimental observations and Density Functional Theory simulations justified that the $\text{g-C}_3\text{N}_4$ and BiVO_4 formed a Z-scheme heterojunction, where the electrons of CB of BiVO_4 recombined with the holes of VB of $\text{g-C}_3\text{N}_4$, resulting in the consequence that the photogenerated electrons directly reduce water from CB of $\text{g-C}_3\text{N}_4$ while holes oxidize water at VB of BiVO_4 .

Additionally, Nasir *et al.* synthesized a direct Z-scheme Se/BiVO_4 heterojunction by aerosol-assisted chemical vapor deposition method for PEC water splitting [56]. An enhanced PEC activity is observed in case of Se/BiVO_4 heterojunction, as compared to Se and BiVO_4 , due to the Se makes a direct Z-scheme (band alignments) with BiVO_4 where the photoexcited electron of BiVO_4 recombines with the VB of Se , giving electron-hole separation at Se and BiVO_4 , respectively. Radzi *et al.* constructed $\text{TiO}_2/\text{BiVO}_4$ photoelectrode using simple spin coating procedure for PEC water splitting [57]. As a result, a highest photocurrent ($35 \mu\text{A}/\text{cm}^2$, at 1.23 V vs. RHE) was obtained for $\text{TiO}_2/\text{BiVO}_4$ photoelectrode, which is more than ~ 3 times compared with bare TiO_2 and BiVO_4 . This enhanced performance was due to the Z-scheme charge transfer between TiO_2 and BiVO_4 , and thus efficiently improves the separation of the electron-hole pairs.

On the contrary, for the semiconductor-conductor-semiconductor Z-scheme heterojunction, a conductor as an intermediate is employed to bridge two semiconductors for the relative ease of electron transportation from semiconductor 2 to semiconductor 1. For example, an unconventional Z-scheme $\text{BiVO}_4\text{-W-WO}_3$ photoanode is fabricated by Wang and co-workers for PEC water splitting [58], and they found that the resulting $\text{BiVO}_4\text{-W-WO}_3$ photoanode showed a highest photocurrent density of $5 \text{ mA}/\text{cm}^2$ in 0.1 mol/L Na_2SO_4 electrolyte under visible light illumination, as well as possessed highest IPCE values ($> 60\%$ at wavelengths less than 460 nm) (Figs. 6a–c). Meanwhile, the PEC stability of BiVO_4 was improved by restricting the electrolyte corrosion with coating WO_3 layers (Fig. 6c). Interestingly, the remarkably enhanced PEC performance of $\text{BiVO}_4\text{-W-WO}_3$ photoanode is attributed to the metal W acts as the recombination site of photogenerated electrons and holes, which are obtained from the CB of WO_3 and the VB of BiVO_4 , respectively (Fig. 6d). Another group of researchers has also fabricated PEC cell with a Ru-loaded ($\text{CuGa}_{0.5}\text{ZnS}_2$) photocathode and a CoO_x -modified BiVO_4 photoanode in order to enhance the PEC water splitting efficiency [59], and they found that the CoO_x played an important role in the Z-scheme system (Ru-loaded ($\text{CuGa}_{0.5}\text{ZnS}_2\text{-BiVO}_4$)) to promote water oxidation on BiVO_4 , resulting in the enhancement of the electron injection from BiVO_4 to Ru-loaded ($\text{CuGa}_{0.5}\text{ZnS}_2$) through CoO_x .

The above results indicate that Z-scheme BiVO_4 -based constructions can not only favor the photogenerated charge separations in space but also promote the redox reactions during PEC water splitting processes. However, only few studies have focused on developing the BiVO_4 -based Z-scheme system in the photoanode or photocathode composite. Therefore, the development and design of Z-scheme BiVO_4 -based PEC water splitting systems with high stability, cyclability, high efficiency, and wide spectral response under sunlight irradiation has very critical significance in both theory and practice.

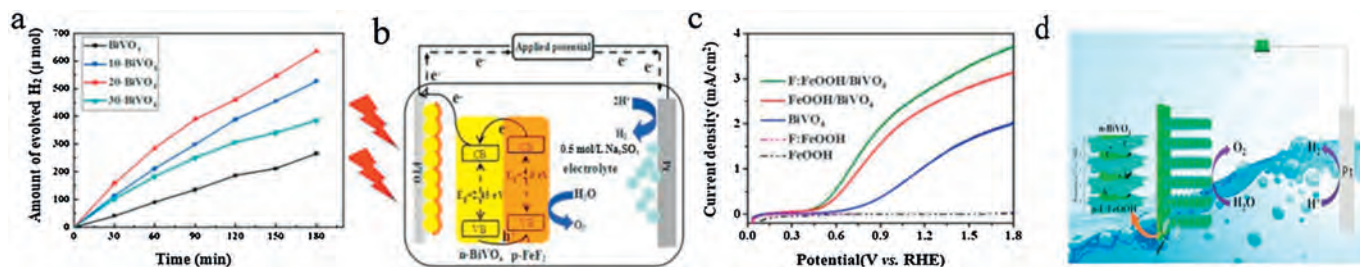


Fig. 5. (a) Time course of produced H_2 at 1.23 V vs. RHE in 0.5 mol/L Na_2SO_4 solution. (b) The possible PEC hydrogen generation mechanism of $\text{FeF}_2\text{-BiVO}_4$ electrode at 1.23 V vs. RHE in 0.5 mol/L Na_2SO_4 solution under visible light irradiation. (a, b) Reproduced with permission [49]. Copyright 2018, Elsevier. (c) LSV curves measured in 0.5 mol/L Na_2SO_4 with light. (d) The possible PEC hydrogen generation mechanism of $\text{F:FeOOH}/\text{BiVO}_4$ electrode at 1.23 V vs. RHE in 0.5 mol/L Na_2SO_4 solution under visible light irradiation. (c, d) Reproduced with permission [50]. Copyright 2020, Elsevier.

2.4. Coupling carbon materials

Carbon materials, such as graphitic carbon nitrides ($g\text{-C}_3\text{N}_4$), carbon nanotube (CNT), carbon quantum dots (CQDs), graphene (G) and reduced graphene oxide (rGO), can be coupled with BiVO_4 , thus the PEC activity of BiVO_4 can be significantly improved. This enhancement can be ascribed to the fact that these carbon materials can act as a photoelectron reservoir, which stores the photogenerated electrons from BiVO_4 to substrates, or perform as a photosensitizer, which improves the light absorption of photocatalyst as an organic dye.

As a famous 2D mono/multilayered material, $g\text{-C}_3\text{N}_4$ are also extensively applied as visible-light-driven catalyst for PEC water splitting due to its narrow bandgap of ~ 2.70 eV with suitable CB/VB levels (*ca.* $-1.10/1.60$ eV). Some studies have proven that combining $g\text{-C}_3\text{N}_4$ with BiVO_4 can strengthen the PEC performance of BiVO_4 . For example, an unprecedented heterojunctions of BiVO_4 quantum dots (QDs)/ $g\text{-C}_3\text{N}_4$ nanosheets (NSs) were synthesized by an *in-situ* growth strategy by Ye *et al.* [60]. It was found that the BiVO_4 QDs/ $g\text{-C}_3\text{N}_4$ NSs exhibited enhancement in visible-light-driven PEC performance. This was mainly due to the highly dispersed BiVO_4 nanocrystals, as well as the strong coupling and band alignment between BiVO_4 QDs and $g\text{-C}_3\text{N}_4$ NSs. In another report, Samsudin *et al.* fabricated the micro-flower $g\text{-C}_3\text{N}_4/\text{BiVO}_4$ photocatalysts for PEC water splitting using lake water without sacrificial reagents [61]. Fascinatingly, the 0.8 wt% $g\text{-C}_3\text{N}_4/\text{BiVO}_4$ evinced 21.4 mmol/h of hydrogen generated in comparison to other samples with an AQE of 4.27% at 420 nm. According to the experimental results and density functional theory (DFT) analysis of $g\text{-C}_3\text{N}_4/\text{BiVO}_4$ photocatalysts, the enhanced PEC property was attributed to better crystallinity, optical properties and efficient electron-hole separation corresponded to the synergistic effect of the band offset and built-in electric field.

In addition to $g\text{-C}_3\text{N}_4$, CNT and CQD are another carbon material with superior electronic properties and excellent conductivity. So far, there have been several reports to unite the advantages of BiVO_4 with the CNT or CQD to form the composite for promising catalytic applications. For example, Jessl *et al.* designed a honeycomb shaped 3D CNT/ BiVO_4 as a photoelectrode for solar water splitting [62]. Based on the experimental results, two main conclusions were drawn: 1) The as-obtained honeycomb structure allows for an efficient transport of electrons through the electrode and enhanced light-electrode interaction; 2) the developed CNT electrodes can survive harsh BiVO_4 synthesis conditions and subsequently be used as photoelectrodes for solar water splitting. In order to enhance the PEC water splitting efficiency, the $\text{NiOOH}/\text{FeOOH}/\text{CQD}/\text{BiVO}_4$ (NFCB) photoanodes were prepared successfully by Ye and co-workers [63]. The LSV curves of the NFCB photoanodes showed a remarkable photocurrent density of $5.99 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE under AM 1.5 G in KH_2PO_4 aqueous

solution without a hole scavenger (pH 7), which is about 4.4 times higher than the pristine BiVO_4 photoanode ($1.35 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE) (Fig. 7a). Meanwhile, this novel NFCB photoanode could operate stably for 10 h with a Faraday efficiency of $\sim 95\%$, demonstrating the great potential of using CQDs for solar water splitting. Not only that, they also discovered that the CQDs in NFCB system can not only broaden the light response range and increase the separation of electrons and holes, but also maintain the hole transfer ability from BiVO_4 to the OEC layer (Fig. 7b).

In addition to the above-mentioned carbon materials, G and rGO are also coupled with BiVO_4 to reinforce the PEC performance of BiVO_4 due to its excellent electric conductivity and a high surface area that increases the charge carrier. Pan and co-workers fabricated $\text{Zn-BiVO}_4/\text{graphene quantum dots (GQDs)}/\text{Co-Pi}$ film through a modified electrodeposition process [64]. As a result, the $\text{Zn-BiVO}_4/(\text{GQDs})/\text{Co-Pi}$ electrodes exhibited a photocurrent of $3.01 \text{ mA}/\text{cm}^2$ and an IPCE of 57% (at 0.6 V vs. RHE), which is 8.6 times of the pristine BiVO_4 . This finding vividly implies that the introduction of GQDs extends the light absorption and facilitates the charge transfer.

Most recently, Chen *et al.* prepared $\text{BiVO}_4/\text{rGO}/\text{NiFe}$ -layered double hydroxide (LDH) photoanode for PEC water splitting through spin-coating rGO nanosheets on BiVO_4 [65]. As compared to pristine BiVO_4 , BiVO_4/rGO , and $\text{BiVO}_4/\text{NiFe-LDH}$ counterparts, the $\text{BiVO}_4/\text{rGO}/\text{NiFe-LDH}$ photoanode showed a significantly higher photocurrent density ($3.26 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE) under AM 1.5 G illumination and excellent stability. It was demonstrated that rGO sheets act as an efficient electron shuttling mediator for suppressing the electron-hole recombination on the surfaces of BiVO_4 by quickly extracting the photogenerated holes from BiVO_4 and promoting the formation of NiFe-LDH at a mild potential. Additionally, upon the drop-casting method, Bi-rGO/ BiVO_4 photoanode was successfully achieved [14]. The Bi-rGO/ BiVO_4 photoanode benefited a low charge transfer resistance. As a result, improved charge transfer and separation efficiency were attained in the Bi-rGO/ BiVO_4 photoanode as supported by an increased photocurrent ($6.05 \text{ mA}/\text{cm}^2$ at 1.23 V) by 1.7 times compared to Bi- BiVO_4 ($3.56 \text{ mA}/\text{cm}^2$ at 1.23 V). Moreover, a better STH (2.34% at 0.61 V) was displayed for the Bi-rGO/ BiVO_4 photoanode (Fig. 7c). This enhancement in PEC activity is due to the combined action of Bi NPs in improving the charge carrier density and rGO in increasing the charge carrier mobility (Fig. 7d).

The roles of various carbon nanomaterials such as CNT, rGO, or $g\text{-C}_3\text{N}_4$ (GCN) in BiVO_4 photoanode were investigated for PEC water oxidation by Prakash *et al.* [66]. It was observed that PEC performance toward water splitting follows the order, $\text{BiVO}_4 < \text{BiVO}_4/\text{CNT} < \text{BiVO}_4/\text{rGO} < \text{BiVO}_4/\text{GCN}$. The enhanced PEC performance could be due to the nanojunction formation between BiVO_4 and CNT or rGO or GCN minimizing the chances of charge recombination. As for BiVO_4/GCN , the lower bulk and interfacial

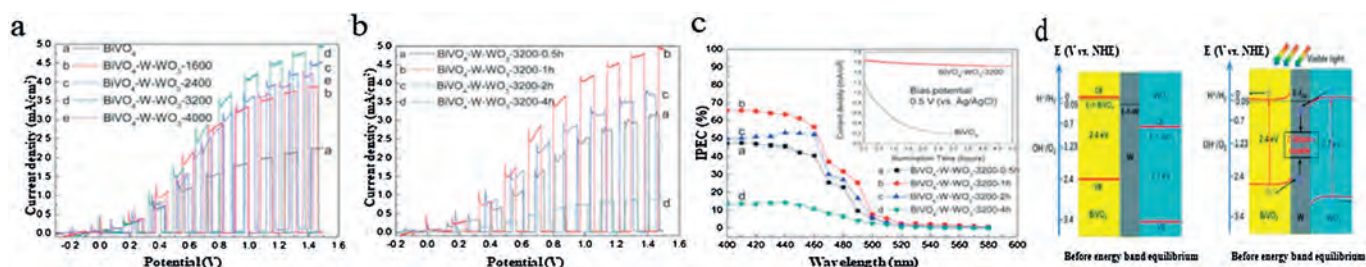


Fig. 6. (a) Photo-induced linear sweep voltammetry (LSV) curves of BiVO_4 and $\text{BiVO}_4\text{-W-WO}_3$ photoanodes with different deposition times. (b) LSV curves and (c) Incident photon-to-current conversion efficiency (IPCE) at bias potential of 1.5 V (vs. Ag/AgCl) of $\text{BiVO}_4\text{-W-WO}_3\text{-3200}$ photoanodes with different annealing times (0.5 h to 4 h) under 500 °C in oxygen atmosphere; Photoelectrochemical stabilities of BiVO_4 and $\text{BiVO}_4\text{-W-WO}_3\text{-3200}$ photoanodes are shown inset (c); Testing was conducted under a bias potential of 0.5 V (vs. Ag/AgCl). All tests were carried out in 0.1 mol/L Na_2SO_4 electrolyte. For LSV performance testing, $100 \text{ mW}/\text{cm}^2$ visible light ($\lambda > 420 \text{ nm}$) was employed. (d) Energy band structure of FTO- $\text{BiVO}_4\text{-W-WO}_3$ Z-scheme photoanode. Copied with permission [58]. Copyright 2018, Royal Society of Chemistry.

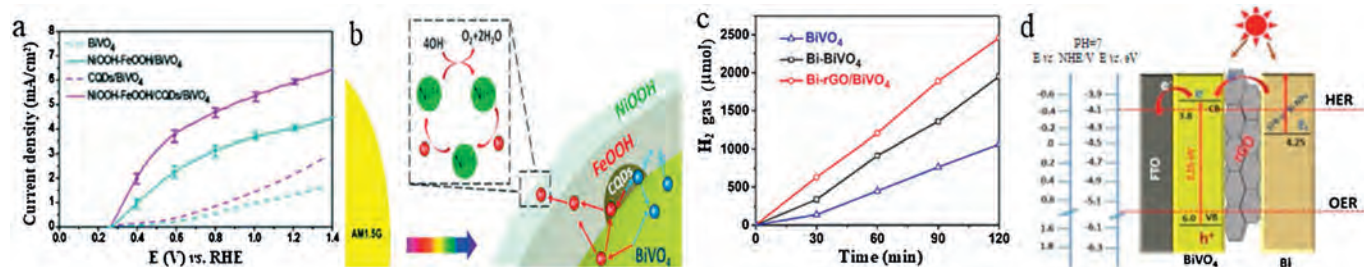


Fig. 7. (a) J - V curves recorded at a scan rate of 25 mV/s under AM 1.5 G irradiation in potassium phosphate solution with no hole scavenger (pH 7). (b) Illustration of the PEC water oxidation at the NFCB photoanode; (a, b) Copied with permission [63]. Copyright 2017, Royal Society of Chemistry. (c) H_2 evolution of Bi-rGO/BiVO₄ under light illumination under 2 h in comparison with pure BiVO₄ and Bi-BiVO₄. (d) Schematic diagrams of energy level alignment and charge transfer in Bi-rGO/BiVO₄ photoanode under solar light illumination. (c, d) Copied with permission [14]. Copyright 2020, Elsevier.

resistance, high charge donor, and efficient charge transfer led to the better performance in comparison to other photoanodes.

To sum up, it is anticipated that the formation of BiVO₄/carbon materials heterojunctions is a promising pathway for the development of BiVO₄-based photoanode with high quality to achieve large specific surface areas, prolonged lifetime of charge carriers, enhanced electron transport property, improved charge transfer and separation efficiency and reduced recombination rate of charge carriers for favorable PEC water splitting.

2.5. Coupling metal-organic framework (MOF) materials

Metal organic frameworks (MOFs) are a class of crystalline organic-inorganic compounds, which are covalently linked by the inorganic building block and also organic linkers. Similar to other semiconductors, MOF photocatalysts can photo-generate holes and electrons upon visible-light irradiation with redox activity, leading to the transfer of holes and electrons to the desired reactant molecules to initiate the light driven photo-redox processes. In view of band structures of MOFs, the outer orbitals of organic linkers construct the VB, whereas the empty outer orbitals of metal contribute to the CB of MOFs. Thus far, the incorporation of MOFs with BiVO₄ has widely attracted increasing attention due to a variety of structural and species diversities as well as tunable cavities, porosity and high surface areas of MOFs.

For instance, Liu *et al.* synthesized MIL-101(Fe)/Mo:BiVO₄ photoanode through hydrothermal method to overcome the poor electron-hole separation and utilization efficiency of BiVO₄ [67]. Notably, a remarkable stable photocurrent density of 4.01 mA/cm² was observed for optimized MIL-101(Fe)/Mo:BiVO₄ anode at 1.23 V vs. RHE in Na₂SO₄ aqueous, about 4 times higher than that of pristine BiVO₄ photoanode (Fig. 8a). Moreover, the MIL-101(Fe)/Mo:BiVO₄ photoanode possessed excellent stability for fast light off-on cycles. The greatly improved PEC performance of the photoanode is due to the ultrathin MIL-101(Fe) layer as an oxygen

evolution cocatalyst can effectively extend the visible-response region, accelerate the charge separation, and provide more accessible active sites for water oxidation (Fig. 8b).

Recently, our research group synthesized BiVO₄@Co-MIm film by a simple water bath deposition method for PEC water splitting [68]. Three noteworthy phenomena were observed for the BiVO₄@Co-MIm electrode: 1) A higher photocurrent of 3.16 mA/cm² at a potential of 1.23 V vs. RHE under simulated sunlight, which is 2.4 times that of BiVO₄ photoanode (Fig. 8c); 2) a higher charge injection efficiency and charge separation efficiency than that of BiVO₄ photoanode; 3) a stable H_2 producing Faradic efficiency of 91.8% can be gained. Additionally, the enhancement of PEC properties of BiVO₄@Co-MIm electrode due to Co-MIm could accept photogenerated holes transferred from BiVO₄ to catalyze water oxidation reaction and accelerate surface reaction kinetics (Fig. 8d). In our other work, CoNi-MOFs/BiVO₄ photoanode was successfully prepared for PEC water oxidation *via* a facile hydrothermal deposition method [69]. In particular, the CoNi-MOFs/BiVO₄ exhibited an excellent photocurrent density of 3.2 mA/cm² at 1.23 V vs. RHE, which is 3 times higher than that of pristine BiVO₄.

As a result, the ratio of evolved O₂ and H₂ on the surface of CoNi-MOFs/BiVO₄ photoanode is close to the theoretical value. In addition, the Faradaic efficiencies of the H₂ and O₂ evolution reaction were about 90%. Finally, it is worth mentioning that the CoNi-MOFs layer not only greatly increases the surface reaction sites but also remarkably enhances the charge separation of BiVO₄ photoanode.

Apart from coupling MOFs with BiVO₄ directly, MOFs are also frequently used as precursor materials to synthesize high surface area effective cocatalysts to decorate the BiVO₄ photoanode. For example, Cardenas-Morcoso *et al.* coupled BiVO₄ with MOF-derived, highly porous cobalt oxide (CoO_x) *via* calcination in air [70]. After the introduction of CoO_x, the resulting BiVO₄-CoO_x revealed 4-times higher photocurrents compared to the bare

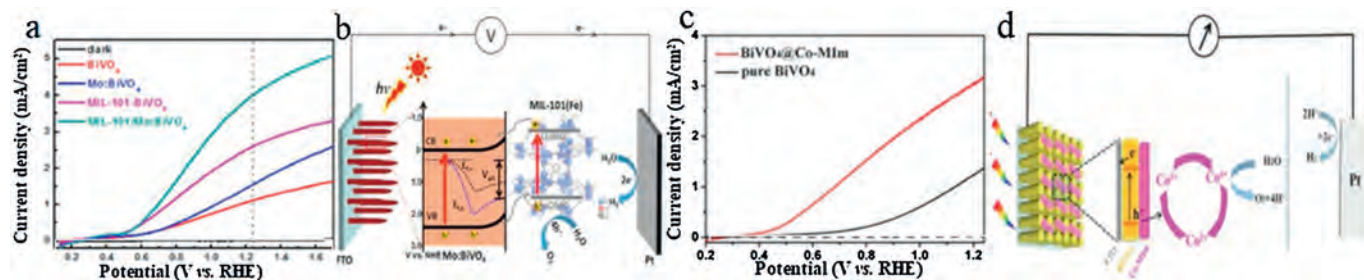


Fig. 8. (a) Photoelectrochemical performance tests of different photoanodes: LSV curves recorded under illumination and dark condition. (b) Schematic presentation of band level positions for Mo:BiVO₄ and MIL-101(Fe) showing the charge transfer path. (a, b) Reproduced with permission [67]. Copyright 2019, Elsevier. (c) LSV curves of BiVO₄ and BiVO₄@Co-MIm electrodes under illumination (the dotted line is LSV curve of BiVO₄@Co-MIm without illumination for comparison). (d) The proposed photogenerated charges transporting process and the process of water oxidation on the BiVO₄@Co-MIm anode. (c, d) Reproduced with permission [68]. Copyright 2019, Elsevier.

BiVO₄. Furthermore, The LSV and EIS analysis confirmed that the ZIF-67 MOF-converted CoO_x co-catalysts significantly accelerate the kinetics of water oxidation, due to a large amount of catalytically-active water oxidation sites were exposed. Similarly, Co₃O₄/BiVO₄ photoelectrode was obtained via annealed Co-MOF/BiVO₄ photoanode in air by Xu's group [71]. There was no doubt that the Co₃O₄/BiVO₄ photoanode exhibited the highest photocurrent density (2.35 mA/cm² at 1.23 V vs. RHE) and PEC hydrogen production rate (0.61 mmol/cm² in 5 h), which was about 3.2 times higher than that of bare BiVO₄. The significant enhancement of PEC performance over Co₃O₄/BiVO₄ could be attributed to suppression of charge recombination.

In short, numerous MOFs/BiVO₄ heterojunction systems have been developed for the past few years. As anticipated, a greater PEC water splitting activity over the bare BiVO₄ photoanode was achieved on the hybrid nanocomposites, signifying the advancements of heterojunction. Capitalizing on the current phase forward, it is expected that the development of more MOFs/BiVO₄ PEC systems for multifarious energy and environmental applications.

3. Conclusion and outlook

Over the past three years, numerous efforts have been made to improve solar hydrogen production via PEC water splitting under solar irradiation. In this work, we reviewed recent reports using engineering techniques to fabricate efficient and enhanced photoactive BiVO₄ materials for PEC water splitting. These engineering techniques include: doping nonmetal and metal elements, depositing of noble metals, constructing heterojunctions, as well as coupling with carbon and MOF materials. To this end, the enhancement of the PEC water splitting performance of BiVO₄-based nano-structures was large recognized by two main far-reaching criteria, such as harvesting visible light and hindering the recombination rate of photoinduced charge carriers. In spite of some promising results reported thus far, the studies in this field are still in preliminary stages and further developments are prominently required. Notably, the works still suffer from the relatively low efficiency and low stability of the BiVO₄-based nanocomposites, which are far from the requirements of industrial needs (Table 1).

Therefore, for exploring more highly efficient and stable BiVO₄-based photoelectrodes that can efficiently retard the charge recombination and capture the solar spectrum is of paramount importance in the field of PEC water splitting. Until now, most of the BiVO₄-based nanomaterials possess a type II heterojunction

system, which have been proven to be outstanding for harvesting visible light and hindering the recombination rate of photoinduced charge carriers. However, few studies have focused on the BiVO₄-based Z-scheme heterojunction for PEC water splitting. Therefore, exploring more active BiVO₄-based Z-scheme photocatalytic systems with additional properties such as earth abundance, low cost, nontoxicity, and scalability will be more attractive in the future. Besides, the mechanisms of Z-scheme BiVO₄-based photocatalysts remain largely unclear and must be extensively studied. Various characterization methods such as, radical-species trapping test, time-resolved photoluminescence emission decay spectra, X-ray photoelectron spectroscopy characterization can be an effective strategy for providing a full image of the PEC water splitting reaction for a direct Z-scheme.

Apart from that, BiVO₄ act as matrix material for the decoration of nanoparticles to form a hybrid system. However, it is challenging to control the particle size on the BiVO₄ substrate at the molecular level, resulting in severe aggregation. Consequently, the well-contacted heterojunction interface between BiVO₄ and the nanoparticles is difficult to accomplish. This markedly affects the intimate interfacial interaction between BiVO₄ and the other composite for effective charge transport and separation. To address this shortfall, surface functionalization of BiVO₄ to tune the surface charge with specific surface groups will be a positive point to strengthen the anchoring ability of BiVO₄.

Last but not least, some key issues that account for the high PEC activity, i.e., optical absorption, electronic band structure and interfacial charge transfer across the BiVO₄-based nanocomposites, should be exhaustively investigated to gain theoretical insights by means of first principles DFT calculations. A combination of experimental and theoretical results from fundamental studies and computer simulations should be preferred as it is the best approach to advance the current state of knowledge on PEC water splitting mechanisms of BiVO₄-based photoelectrodes.

In general, PEC water splitting is a promising route for the production of H₂ applying for free solar energy. Therefore, the development and design of BiVO₄-based systems for PEC water splitting with high stability, cyclability, nontoxicity, high efficiency, and wide spectral response under sunlight irradiation has very critical significance in both theory and practice.

Declaration of competing interest

All authors declared that they do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Table 1
Overview of BiVO₄-based photoanodes for PEC water splitting.

Photocatalyst	Photocurrent density (mA/cm ² , at 1.23 V vs. RHE)	Reaction rate (water splitting)	IPCE (%)	Light source	Ref.
In ³⁺ -BiVO ₄	1.56	–	–	300 W Xe lamp	[15]
P-BiVO ₄	0.28	44.5 mmol h ⁻¹ m ⁻² H ₂	37.24	Simulate dsunlight (AM1.5 G)	[20]
BiVO ₄ -C/N-Ag	2.42	–	30	300 W Xe lamp	[24]
Hierarchical WO ₃ /BiVO ₄	5.5	–	80–90	Simulated sunlight (AM1.5 G)	[35]
FTO/TiO ₂ /BiVO ₄	4.11	–	80	Simulated sunlight (AM1.5 G)	[36]
NiFe ₂ O ₄	0.35	85.6 μmol/h H ₂	5.0	300 W Xe lamp	[41]
CoFe ₂ O ₄ /BiVO ₄	0.65	158.6 μmol/h H ₂	6.7	300 W Xe lamp	[41]
U-CoOOH/BiVO ₄	4.9	96 μmol/h H ₂ and 47.5 μmol/h O ₂	76.2	Simulated sunlight (AM1.5 G)	[47]
FeF ₂ /BiVO ₄	2.49	211.6 μmol/h H ₂	28	LED lamp	[49]
F:FeOOH/BiVO ₄	2.7	–	50	300 W Xe lamp	[50]
FTO-BiVO ₄ -W-WO ₃	5	–	60	Simulated sunlight (AM1.5 G)	[58]
Bi-rGO/BiVO ₄	6.05	1233 μmol/h	41	250W quartz tungsten halogen lamp	[14]
NiOOH/FeOOH/CQD/BiVO ₄	5.99	33 μmol/h O ₂ and 66.4 μmol H ₂	–	Simulated sunlight (AM1.5 G)	[63]
BiVO ₄ /rGO/NiFe-LDH	3.26	25.4 μmol/h O ₂	40	Simulated sunlight (AM1.5 G)	[65]

“–” means it is not mentioned in reference.

Acknowledgments

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