



Article

Synergistic Promotion of Selective Oxidation of Glycerol to C3 Products by Mo-Doped BiVO₄-Coupled FeOOH Co-Catalysts Through Photoelectrocatalysis Process

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Abstract

The Mo:BiVO₄/FeOOH photoelectrode was synthesized through the deposition of FeOOH onto the surface of the Mo:BiVO₄ photoelectrode. The composite photoelectrode demonstrated a photocurrent of 1.8 mA·cm⁻², which is three times greater than that observed for pure BiVO₄. Furthermore, the glycerol conversion rate was recorded at 79 μmol·cm⁻²·h⁻¹, approximately double that of pure BiVO₄, while the selectivity for glyceraldehyde reached 49%, also about twice that of pure BiVO₄. The incorporation of Mo has been shown to enhance the stability of the BiVO₄. Additionally, Mo doping improves the efficiency of electron-hole transport and increases the carrier concentration within the BiVO₄. This enhancement leads to a greater number of holes participating in the formation of iron oxyhydroxide (FeOOH), thereby stabilizing the FeOOH co-catalyst within the glycerol conversion system. The FeOOH co-catalyst facilitates the adsorption and oxidation of the primary hydroxyl group of glycerol, resulting in the cleavage of the C–H bond to generate a carbon radical (C). The interaction between the carbon radical and the hydroxyl group produces an intermediate, which subsequently dehydrates to form glyceraldehyde (GLAD).

Keywords: BiVO₄; FeOOH; glycerol; photoelectrochemical; water splitting



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1. Introduction

In recent years, the substantial utilization of biomass-derived diesel has led to a significant increase in the production of glycerol, and the conversion of glycerol into high-value products represents a critical strategy for addressing this surplus [1–6]. Notable conversion products include glyceraldehyde (GLAD), 1,3-dihydroxyacetone (DHA), glycerol acid (GLA), and formic acid (FA), among others [7–9]. These high-value products have applications across various sectors, including biology, pharmaceuticals, cosmetics, and food industries, underscoring the importance of glycerol conversion for value addition [10,11]. Photoelectrocatalysis (PEC) offers a promising approach due to its energy-efficient and environmentally friendly photocatalytic processes, coupled with controllable electrocatalytic reactions. The synergistic interaction of light and electricity enhances the efficiency of

glycerol conversion, garnering considerable interest from researchers in recent years [12,13]. Significant progress has been made in recent years in photoelectrochemical (PEC) systems for glycerol electrooxidation. Researchers have developed various highly efficient photoelectrode materials, such as BiVO₄-based, Si nanowire, WO₃, and Bi₂O₃-based photoelectrodes, enhancing performance through heterostructure construction and defect engineering. Additionally, multi-field driving and synergistic catalytic strategies, such as photoelectric-bioelectric coupling systems, have been employed to effectively improve catalytic efficiency. Furthermore, the selectivity of target products has been significantly improved through catalyst surface engineering and other methods. However, the system still faces challenges such as photogenerated carrier recombination, catalyst poisoning, and low system integration efficiency. Future research should focus on the development of non-precious metal catalysts, all-solid-state device design, and large-scale validation to drive the technology toward practical applications. Therefore, selecting and modifying appropriate photoelectrocatalysts is crucial for achieving efficient glycerol conversion and high product selectivity [14].

It has been demonstrated that doping modification of BiVO₄ can help to improve the glycerol conversion performance. For instance, Tateno et al. prepared Ta-doped BiVO₄ photoelectrode (Ta:BiVO₄), which could achieve 96% selectivity of DHA [15]. Liu et al. demonstrated that fluorination of BiVO₄ surface changes the coordination environment around Bi for the photoelectrochemical oxidation of glycerol, with a formic acid selectivity of 79% at the anode [16]. Cristian et al. found that doping modification of BiVO₄ with Mo, Pt, and Zr improved the stability of the photoelectrode and the glycerol conversion rate, but had no effect on the selectivity of the glycerol conversion product [17]. In addition, the co-catalyst modification of the BiVO₄ surface is also an important way to increase the surface active sites for glycerol oxidation. For example, the NiOOH/BiVO₄ photoelectrode prepared achieved a conversion rate of 76 $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ and 68% DHA selectivity [18]. Gao et al. synthesized FeOOH/BiVO₄ photoelectrodes and established that the formation of Bi-O-Fe bonds enhances the adsorption of primary hydroxyl groups from glycerol. These bonds also serve as hole trapping centers, facilitating the cleavage of C-H bonds, which in turn promotes the generation of GLAD with over 60% selectivity [19]. Yang et al. developed a ternary BiVO₄ photoanode that incorporated a dual co-catalyst layer of MnO_x and FeOOH. Their findings indicated that MnO_x exhibited a superior adsorption capacity for the secondary hydroxyl group of glycerol, and the presence of FeOOH on the photoanode's surface lead to the formation of additional intermediate active surface states and hydroxyl radicals, which effectively oxidized glycerol to produce DHA [20]. Wu et al. demonstrated that the combined effects of tungsten (W) doping and nickel oxide hydroxide (NiO_x(OH)_y) loading significantly enhanced the conversion of glycerol to formic acid using BiVO₄ photoelectrodes [21].

In this paper, the surface of the Mo:BiVO₄ photoelectrode was photodeposited with FeOOH co-catalyst, aiming to establish a synergistic interaction between the doping strategy and surface modification. A gradient in loading concentration was achieved based on varying loading times, allowing for the identification of an optimal loading duration. The research evaluates the optical and photovoltaic characteristics, as well as the glycerol conversion efficiency of the Mo:BiVO₄/FeOOH photoelectrode, to elucidate the synergistic effects of Mo doping and FeOOH loading on these properties. Additionally, glycerol conversion product tests, scavenger tests, and electron spin resonance (ESR) analyses were conducted to elucidate the glycerol conversion mechanism and potential conversion pathways associated with the Mo:BiVO₄/FeOOH photoelectrode. The findings of this study serve as a valuable reference for future researchers exploring photocatalytic glycerol conversion utilizing BiVO₄ photoelectrodes.

2. Materials and Methods

2.1. Preparation of BiVO₄/Mo:BiVO₄ Photoanodes

BiVO₄ photoanodes were prepared according to previously documented methods. During the synthesis, 1.46 g of Bi(NO₃)₃·5H₂O was dissolved in 75 mL of 4.98 g KI solution and the pH was adjusted to 1.7 by adding nitric acid solution and the mixture was stirred for 30 min. The solution was then mixed with a 30 mL ethanol solution containing 0.747 g of 1,4-Benzoquinone and stirred for 30 min to obtain an electrodeposition solution. Cathodic deposition was carried out at a constant potential of −0.1 V vs. Ag/AgCl and at room temperature for 300 s to prepare BiOI electrodes. Dimethyl sulfoxide (DMSO) solutions with different molar percentages of VO(acac)₂ and Na₂MoO₄·2H₂O were prepared at a total concentration of 0.2 M in the ratios of 100:0, 99:1, 98:2, 97:3, 95:5, and 90:10, respectively, and 0.15 mL of the solution was pipetted onto the obtained BiOI/FTO electrodes and dripped uniformly and gently dried. Then, the electrode was annealed at 450 °C for 2 h at a heating rate of 2 °C/min to convert BiOI to BiVO₄. After naturally cooling to room temperature, the electrode was taken out and soaked in 1 M NaOH solution for 15 min to remove the excess V₂O₅ and possibly MoO₃. Finally, the electrode was rinsed several times with deionized water and anhydrous ethanol, respectively, and dried at room temperature, and the preparations were obtained as BiVO₄, Mo:BiVO₄ (1%), Mo:BiVO₄ (3%), Mo:BiVO₄ (5%), Mo:BiVO₄ (10%).

2.2. Preparation of Mo:BiVO₄/FeOOH Photoelectrodes

One mol (1 mol) of ferrous nitrate heptahydrate (FeSO₄·7H₂O) was weighed and dissolved in 100 mL of deionized water to form a photodeposition solution, and electrically assisted photodeposition (EAPD) was carried out on the Mo:BiVO₄ photoelectrode. Before depositing FeOOH, the solution was purged with nitrogen for 1 h to remove oxygen to prevent Fe²⁺ from oxidizing to Fe³⁺ prematurely and to ensure that FeOOH was uniformly deposited on the Mo:BiVO₄ photoelectrode. A three-electrode system was used, with Mo:BiVO₄ as the working electrode, a platinum sheet as the counter electrode, and Ag/AgCl as the reference electrode, and a 300 W Xe lamp was used to irradiate the Mo:BiVO₄ photoelectrode so that the light intensity on the surface of the Mo:BiVO₄ photoelectrode was 100 mW/cm^{−2}. During the illumination process, the holes generated in the valence band of the BiVO₄ photoelectrode oxidized Fe²⁺ to Fe³⁺ and deposited it on the surface of the Mo:BiVO₄ photoelectrode in the form of FeOOH. The reaction process is FeOOH (Fe²⁺ (aq) + h⁺ + 3OH[−] → FeOOH (s) + H₂O). To promote photodeposition, an external bias voltage of 0.25 V, which is the open-circuit potential of the Mo:BiVO₄ photoelectrode in dark solution, was applied using an Ag/AgCl (4 M KCl) reference electrode. The Mo:BiVO₄/FeOOH (10 min), Mo:BiVO₄/FeOOH (15 min), Mo:BiVO₄/FeOOH (20 min), Mo:BiVO₄/FeOOH (25 min) photovoltaic electrodes were formed by deposition for different times (i.e., 10 min, 15 min, 20 min, 25 min).

2.3. PEC Testing

To evaluate electrochemical properties, a three-electrode setup connected to a Autolab PGSTAT302N (Metrohm, Herisau, Switzerland) electrochemical workstation was used. Photocurrent (I-t), electrochemical impedance (EIS), and linear scanning voltammetry (LSV) were evaluated, all in the 0.1 M Gly presence under different conditions performed on a single photoanode. For the purpose of simulating solar exposure, a 300 W xenon lamp (sunlight) was used next to an AM 1.5 G filter (100 mW/cm^{−2}). It is worth noting that all

potential values quoted in this study have been adjusted to reversible hydrogen electrode (RHE) potentials, expressed in volts as specified in Equation (1):

$$E_{RHE} = E_{Ag/Ag/Cl} + 0.059pH + 0.1976 \quad (1)$$

The incident photon-to-current conversion efficiency (IPCE) was determined using a PLS-MC300 monochromator (Perfect Light, Beijing, China) in conjunction with a PLX-SXE300 xenon lamp (Perfect Light). The equations used to calculate IPCE are summarized below:

$$IPCE = \frac{1240/\lambda \times (J_{light} - J_{dark})}{P} \times 100\% \quad (2)$$

In the Equation, λ denotes the wavelength, J_{light} denotes the density under irradiation, J_{dark} denotes the density under dark conditions, and P denotes the incident light power density.

When evaluating carrier transport efficiency and interface injection efficiency, the photocurrent generated by the photoanode in the electrolyte consists of three main components:

$$J_e = J_{abs} \times \eta_{sep} \times \eta_{inj} \quad (3)$$

The measured photocurrent density J_e is compared with the theoretical photocurrent density of the photovoltaic cation material, J_{abs} , which is calculated by Equation (4). In this equation, η_{sep} and η_{inj} describe the efficiency of carrier migration from the semiconductor bulk phase to the catalyst surface and the efficiency of injection from the catalyst surface to the electrolyte, respectively.

$$J_{abs} = \int_{\lambda}^{\lambda_e} \frac{\lambda}{1240} \times N_{ph}(\lambda) \times LHE(\lambda) d\lambda \quad (4)$$

$$LHE = 1 - 10^{-A(\lambda)} \quad (5)$$

The incident wavelength (λ in nm) and the absorption termination wavelength (λ_e) of the UV-visible absorption spectrum of a photoanode indicate the light absorption range. The photon flux ($N_{ph}(\lambda)$ in $\text{mW} \cdot \text{cm}^{-2}$) describes the optical power density per unit wavelength, while the absorbance $A(\lambda)$ characterizes the intensity of absorption in the UV-Vis spectrum.

In the case of using an electron or hole trapping agent (adding Na_2SO_3 to the electrolyte), the surface charge transfer efficiency reaches 100%, in which case the optical current density can be expressed according to Equation (6):

$$J_{\text{Na}_2\text{SO}_3} = J_{abs} \times \eta_{sep} \quad (6)$$

The bulk-phase charge transfer efficiency and surface charge separation efficiency of the carriers are obtained from Equations (7) and (8), respectively:

$$\eta_{sep} = \frac{J_{\text{Na}_2\text{SO}_3}}{J_{abs}} \quad (7)$$

$$\eta_{inj} = \frac{J_e}{J_{\text{Na}_2\text{SO}_3}} \quad (8)$$

The carrier concentration (N) can be calculated using the MottSchottky equation:

$$\frac{1}{C_{cs}^2} = \frac{2}{\epsilon_r \epsilon_0 N A^2} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (9)$$

where N is the carrier density; C_{sc} is the space charge capacitance; ϵ_r is the relative permittivity of the semiconductor at room temperature; ϵ_0 is the vacuum permittivity of the material; A is the surface contact area between the specimen and the electrolyte; E is the applied voltage; E_{fb} is the flat band voltage; k is the Boltzmann constant (1.38×10^{-23} J/K); T is the thermodynamic constant (K); e is the charge constant (1.62×10^{-19} C); kT/e at room temperature is about 25 mV and usually considered negligible.

Glycerol oxidation was evaluated according to standard reaction conditions by immersing the photoelectrode anode in an H-type quartz electrolyzer containing a 0.1 M aqueous Na_2SO_4 solution and an additional 0.1 M GLY. The solution was stirred continuously at a rate of 500 revolutions per minute. Subsequently, the oxidation process was executed under AM 1.5 G irradiation ($100 \text{ mW}/\text{cm}^2$) for a duration of 2 h. The consistent potential was set to 1.23 V vs. RHE while maintaining the ambient temperature (~ 298 K). The selectivity of A can be evaluated using the forthcoming Equation:

$$\text{Selectivity(A)} = \frac{n_A}{n_{\text{GLAD}} + n_{\text{DHA}} + n_{\text{GLA}} + n_{\text{FA}} + n_{\text{Others}}} \times 100\% \quad (10)$$

Calculate the production (or conversion) rate of A according to the following equation:

$$\text{Formation rate(A)} = \frac{n_A}{t \times \text{Area}} \times 100\% \quad (11)$$

Here, t denotes the reaction time in hours, while area denotes the surface area of the photoanode in square meters.

3. Results

3.1. Synthesis and Morphology Analysis

A scanning electron microscope was employed to analyze the morphology of the photoelectrodes. The morphological characteristics of the BiVO_4 photoelectrode are depicted in Figure 1a,b, while those of the Mo-doped BiVO_4 photoelectrode (Mo: BiVO_4) are illustrated in Figure 1c,d. It is evident that there is no significant alteration in the morphology of the Mo: BiVO_4 photoelectrode when compared to that of the BiVO_4 photoelectrode [17,22–24]. Upon the deposition of FeOOH onto the BiVO_4 and Mo: BiVO_4 photoelectrodes, flocculent precipitates are observed on the surface of the photoelectrodes, as shown in Figure 1e–h. The presence of flocculated FeOOH co-catalysts on the surface of the BiVO_4 photoelectrode occurs at low loadings, which does not significantly impede the light absorption capabilities of the BiVO_4 photoelectrode itself. Furthermore, the FeOOH co-catalysts can establish multiple interfaces with the surface of the BiVO_4 photoelectrode, potentially influencing the photoelectric performance of the photoelectrode [25–28].

Figure 2a presents a high-resolution transmission electron microscopy (TEM) image of the Mo: $\text{BiVO}_4/\text{FeOOH}$ photoelectrode, revealing an internal lattice spacing of 0.474 nm. This measurement aligns closely with the crystal spacing of the monoclinic scheelite-type BiVO_4 as indicated by the standard card (PDF#14-0688), implying that the incorporation of molybdenum does not alter the lattice spacing of the BiVO_4 photoelectrode [29–31]. Additionally, a layer of FeOOH, approximately 5–10 nm in thickness, is observed to be tightly enveloping the Mo: BiVO_4 photoelectrode; however, no distinct lattice spacing for FeOOH is detected, indicating that this layer is amorphous in nature. As illustrated in Figure 2b, the TEM morphology of the Mo: $\text{BiVO}_4/\text{FeOOH}$ photoelectrode exhibits a worm-like structure. Energy-dispersive spectroscopy (EDS) analysis confirms the uniform presence of the elements bismuth (Bi), vanadium (V), iron (Fe), molybdenum (Mo), and oxygen (O) on the surface of the photoelectrode.

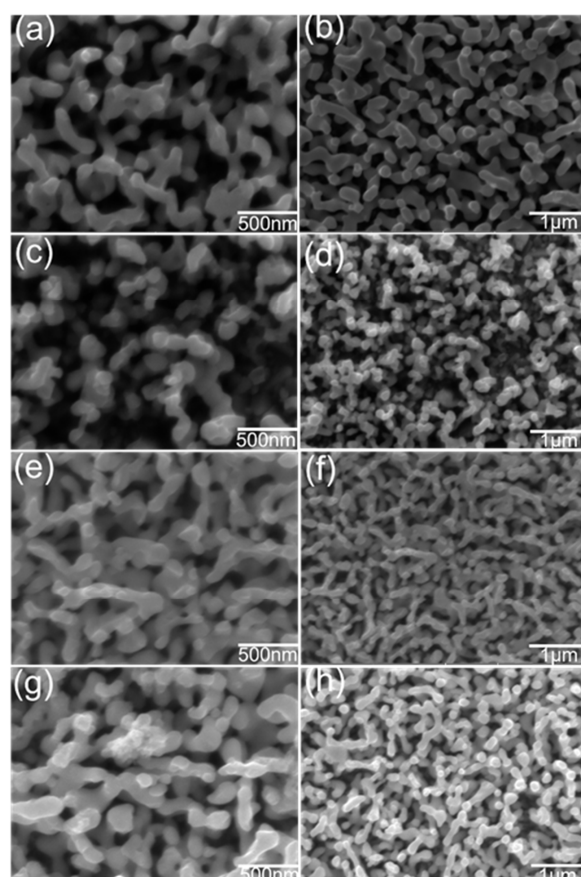


Figure 1. SEM images of (a,b) BiVO_4 ; (c,d) Mo:BiVO_4 ; (e,f) $\text{BiVO}_4/\text{FeOOH}$; (g,h) $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes.

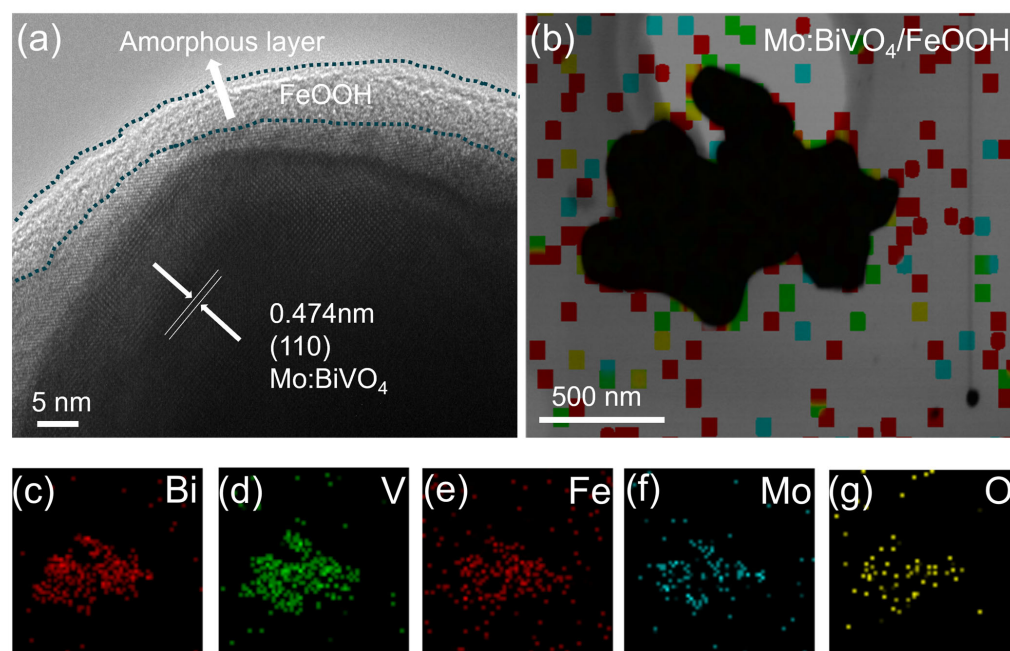


Figure 2. (a) High-resolution TEM image of $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode; (b) TEM image of $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode; (c–g) EDS energy spectra of elemental Bi, V, Fe, Mo, and O of $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode, respectively.

3.2. Structure and Composition Analysis

The X-ray diffraction (XRD) patterns of the BiVO_4 , Mo:BiVO_4 , $\text{BiVO}_4/\text{FeOOH}$, and $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes were examined, as illustrated in Figure 3. The XRD patterns of the BiVO_4 photoelectrode exhibited prominent diffraction peaks at 18.7° , 19.0° , 28.6° , 28.8° , 29.0° , and 30.5° , which are associated with the (110), (011), (-130), (-121), (121), and (040) crystal planes, respectively, in accordance with the monoclinic scheelite-type BiVO_4 standard (JCPDS 14-0688) [32,33]. Additionally, peaks at 26.6° , 33.8° , 37.8° , 51.7° , 61.7° , and 65.7° in the XRD pattern of the BiVO_4 photoelectrode correspond to the SnO_2 standard (JCPDS 46-1088) derived from the fluorine-doped tin oxide (FTO) glass substrate [34–36]. The XRD patterns of the Mo:BiVO_4 photoelectrode and the BiVO_4 photoelectrode modified with the FeOOH co-catalyst exhibited minimal changes following Mo doping ($\text{BiVO}_4/\text{FeOOH}$). This lack of significant alteration can be attributed to the low concentration of Mo doping, the limited loading of FeOOH , and the amorphous nature of FeOOH , which collectively result in negligible differences in the XRD patterns when compared to those of the BiVO_4 photoelectrode. Similarly, the XRD patterns of the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode did not show substantial variations relative to those of the BiVO_4 photoelectrode.

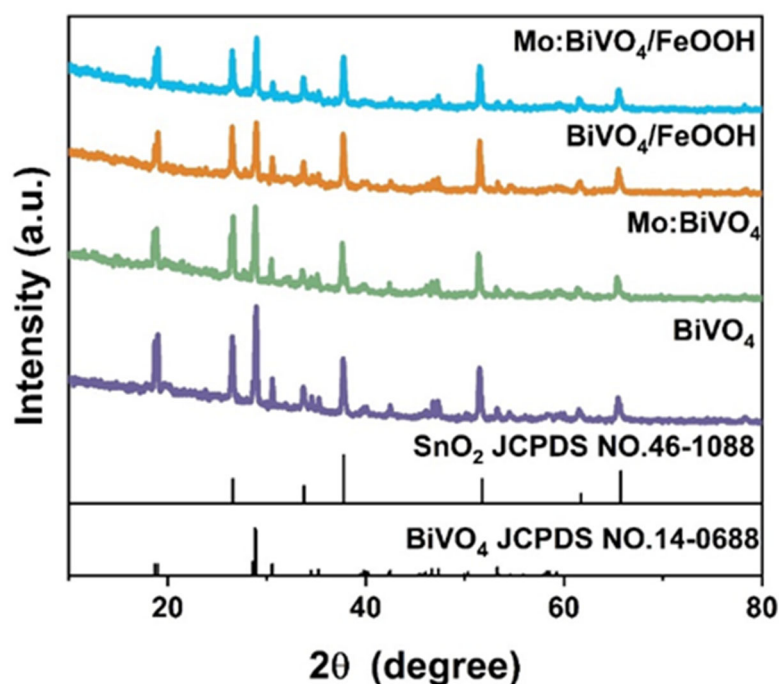


Figure 3. XRD plots of BiVO_4 , Mo:BiVO_4 , $\text{BiVO}_4/\text{FeOOH}$, $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes.

The X-ray photoelectron spectroscopy (XPS) analysis of BiVO_4 , Mo:BiVO_4 , $\text{BiVO}_4/\text{FeOOH}$, and $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes is presented in Figure 4. In Figure 4a, the XPS energy spectrum for the Bi 4f region reveals double peaks at binding energies of 158.8 eV and 164.1 eV, which correspond to the Bi 4f_{7/2} and Bi 4f_{5/2} orbitals of Bi^{3+} in the BiVO_4 photoelectrode, respectively [37–40]. The observed shift of the Bi 4f peak in the Mo:BiVO_4 photoelectrode towards higher binding energies, relative to that in the BiVO_4 photoelectrode, may be attributed to the partial substitution of vanadium (V) by the more electronegative molybdenum (Mo) in the Mo:BiVO_4 photoelectrode. This substitution likely facilitates the transfer of electrons from Bi^{3+} to Mo^{6+} . The XPS spectra for the $\text{BiVO}_4/\text{FeOOH}$ photoelectrode indicate a shift of the Bi 4f peak towards lower binding energy compared to the Bi 4f peak in the BiVO_4 photoelectrode, suggesting an electron transfer from FeOOH to Bi^{3+} . The combined effects of Mo and Fe result in the Bi peak

position in the Mo:BiVO₄/FeOOH photoelectrode being situated between the Bi 4f peaks of the Mo:BiVO₄ and BiVO₄/FeOOH photoelectrodes.

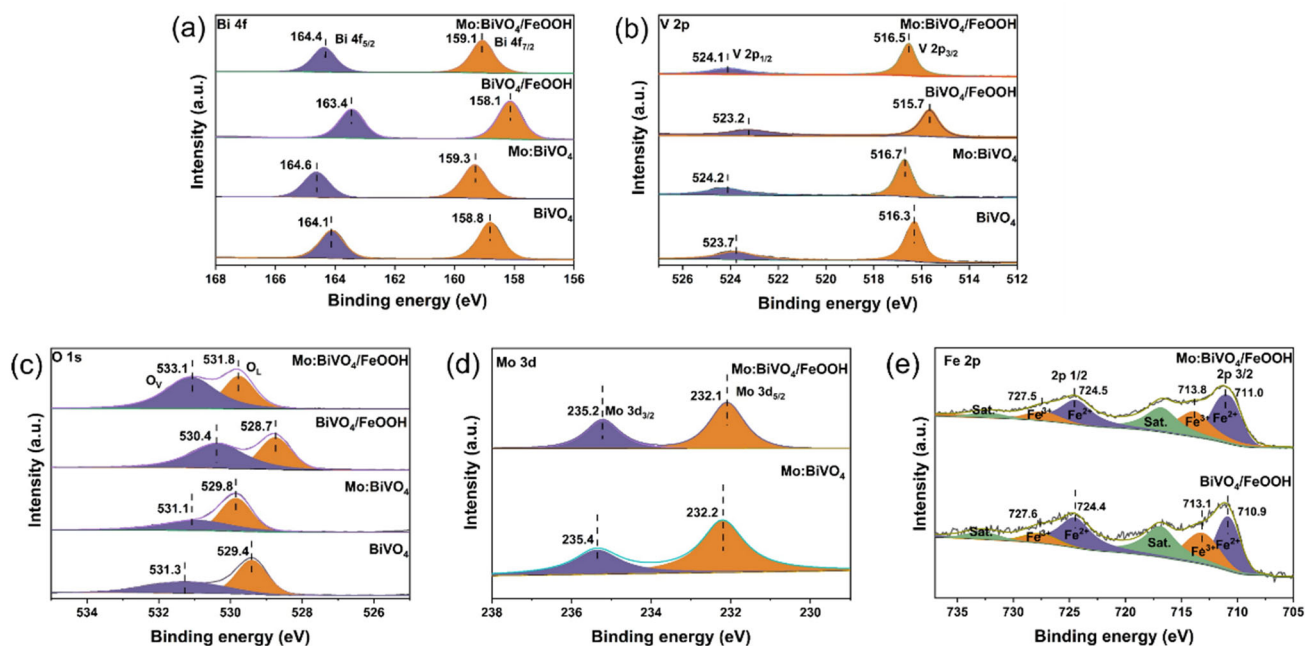


Figure 4. XPS profiles of BiVO₄, Mo:BiVO₄, BiVO₄/FeOOH, and Mo:BiVO₄/FeOOH photoelectrodes for (a) Bi 4f, (b) V 2p, (c) O 1s, (d) Mo 3d, (e) Fe 2p.

Figure 4b illustrates the XPS energy spectrum for the V 2p region in the BiVO₄ photoelectrode. The double peaks observed at binding energies of 516.3 eV and 523.7 eV correspond to the V 2p_{3/2} and V 2p_{1/2} orbitals of V⁵⁺, respectively [41–43]. In the Mo:BiVO₄ photoelectrode, the V 2p peak is shifted towards higher binding energy compared to that in the BiVO₄ photoelectrode, which can be explained by the greater electronegativity of Mo relative to V, resulting in a more significant electron transfer from V⁵⁺ to Mo⁶⁺. Conversely, the V 2p peak in the BiVO₄/FeOOH photoelectrode is shifted towards lower binding energy compared to the peak in the BiVO₄ photoelectrode, indicating an electron transfer from FeOOH to V⁵⁺. The synergistic interaction between Mo and FeOOH leads to a shift of the V 2p peak in the Mo:BiVO₄/FeOOH photoelectrode towards higher binding energy compared to the V 2p peak in the BiVO₄ photoelectrode, with the V 2p peak positioned between those of the Mo:BiVO₄ and BiVO₄/FeOOH photoelectrodes. Consequently, it can be inferred that there exists a strong interaction between the FeOOH and the BiVO₄ and Mo:BiVO₄ photoelectrodes, potentially resulting in the formation of Bi-O-Fe, V-O-Fe, and Mo-O-Fe chemical bonds.

Figure 4c presents the O 1s X-ray photoelectron spectroscopy (XPS) energy spectra, illustrating lattice oxygen (O_L) and oxygen vacancies (O_V) arranged from right to left. A comparative analysis of the XPS energy spectra for the four photoelectrodes reveals that the incorporation of FeOOH results in an increased density of oxygen vacancies on the surface of the BiVO₄ photoelectrode. This moderate enhancement in oxygen vacancies is beneficial as it mitigates electron-hole recombination and facilitates charge transport. In Figure 4d, the observed double peaks at binding energies of 232.2 eV and 235.4 eV correspond to the 3 d_{5/2} and 3 d_{3/2} orbitals of Mo⁶⁺ within the Mo:BiVO₄ photoelectrode. It is noteworthy that the Mo 3d peak in the Mo:BiVO₄/NiOOH photoelectrode exhibits a shift towards lower binding energy, which can be attributed to the FeOOH loading that enhances electron transfer to Mo⁶⁺. The electronegativity of Mo contributes to its affinity for additional electrons, resulting in a decrease in the binding energy of the Mo 3d peak. Figure 4e

displays peaks at binding energies of 710.9 eV and 713.1 eV, which correspond to Fe^{2+} and Fe^{3+} in the $\text{BiVO}_4/\text{FeOOH}$ photoelectrode. In the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode, the peaks for Fe^{2+} and Fe^{3+} are observed at higher binding energies compared to those in the $\text{BiVO}_4/\text{FeOOH}$ photoelectrode, indicating that the presence of Mo influences the electron distribution and enhances the transfer of electrons from FeOOH to the Mo:BiVO_4 photoelectrode.

3.3. PEC Performance Testing and Analysis

The results of the photoelectric tests conducted on Mo:BiVO_4 photoelectrodes, which were doped with varying molar percentages of Mo in a glycerol solution, are presented in Figure S1a. All tests were performed under neutral conditions at a voltage of 1.23 V (reversible hydrogen electrode, RHE). The findings indicate that the optimal Mo doping concentration is 3%. However, excessive Mo doping may alter the crystalline structure of BiVO_4 , thereby negatively impacting the light absorption capabilities of the photoelectrode. Figure S1b illustrates the photocurrent test results for Mo:BiVO_4 photoelectrodes that were loaded with FeOOH co-catalysts for varying durations. The analysis reveals that the optimal loading time for FeOOH co-catalysts is 20 min; prolonged loading may result in excessive FeOOH accumulation on the photoelectrode surface, which can hinder the inherent absorbance of the BiVO_4 photoelectrodes and, consequently, their photoelectric properties. A comparative analysis of the photoelectric properties of four types of photoelectrodes— BiVO_4 , Mo:BiVO_4 , $\text{BiVO}_4/\text{FeOOH}$, and $\text{Mo:BiVO}_4/\text{FeOOH}$ —is depicted in Figure 5a. The results indicate that the photocurrent of the Mo:BiVO_4 photoelectrode ($1.2 \text{ mA}\cdot\text{cm}^{-2}$) is double that of the BiVO_4 photoelectrode ($0.6 \text{ mA}\cdot\text{cm}^{-2}$). Furthermore, the photocurrent of the $\text{BiVO}_4/\text{FeOOH}$ photoelectrode ($1.1 \text{ mA}\cdot\text{cm}^{-2}$) represents an approximate 0.8-fold increase compared to that of the BiVO_4 photoelectrode. Notably, the photocurrent of the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode ($1.9 \text{ mA}\cdot\text{cm}^{-2}$) demonstrates an approximate twofold enhancement relative to the BiVO_4 photoelectrode. These findings suggest that the photoelectric performance of the BiVO_4 photoelectrode is significantly improved through the synergistic effects of Mo and FeOOH .

As illustrated in Figure 5b, the photoelectric performance of the photoelectrodes under illuminated conditions is markedly superior to their electrocatalytic performance under intermittent light exposure. The linear sweep voltammetry (LSV) curves indicate that the presence of glycerol enhances the photoelectric performance of the four photoelectrodes. This enhancement can be attributed to the preferential oxidation of glycerol over water when glycerol is present, as the kinetics of glycerol oxidation for the photoelectrodes is more rapid than that of water oxidation, particularly in a Na_2SO_4 electrolyte solution [33,39,44,45]. The incident photon-to-current efficiency (IPCE) results presented in Figure 5c demonstrate that the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode exhibits superior photoelectric conversion performance, achieving an IPCE value of 66.5% at 420 nm, in contrast to the 34.6% IPCE value of the pure BiVO_4 photoelectrode. This suggests that the combined effects of Mo doping and FeOOH loading significantly enhance the photoelectric conversion efficiency of the BiVO_4 photoelectrode [46–48]. Figure 5d depicts the bulk-phase charge separation efficiency of the four photoelectrodes, while Figure 5e illustrates their surface charge separation efficiency. It is evident that Mo doping substantially enhances the bulk-phase charge separation efficiency of the BiVO_4 photoelectrodes, although the improvement in surface charge separation efficiency is comparatively modest. Conversely, the incorporation of FeOOH onto the BiVO_4 photoelectrodes results in a slight increase in bulk-phase charge separation efficiency, accompanied by a more significant enhancement in surface charge separation efficiency. This phenomenon may be attributed to the introduction of oxygen vacancies by the FeOOH co-catalysts, which facilitate the separation of electrons and holes,

thereby enhancing the surface charge separation efficiency of the BiVO_4 photoelectrodes. The synergistic effects of Mo doping and FeOOH loading markedly improve both the bulk-phase and surface charge separation efficiencies of the BiVO_4 photoelectrodes, ultimately enhancing the carrier separation efficiency. Electrochemical impedance spectroscopy (EIS) tests were conducted on the four photoelectrodes under illuminated conditions to evaluate the charge transfer kinetics at the interface between the photoelectrode and the electrolyte, which was shown in Figure 5f. Notably, the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode exhibited the smallest diameter in the Nyquist plots, indicating the lowest resistance and the most rapid charge transfer kinetics relative to the other photoelectrodes [32,39,49]. These findings substantiate the conclusion that Mo doping and FeOOH loading significantly contribute to the enhancement of charge transfer at the interface between the BiVO_4 photoelectrode and the electrolyte.

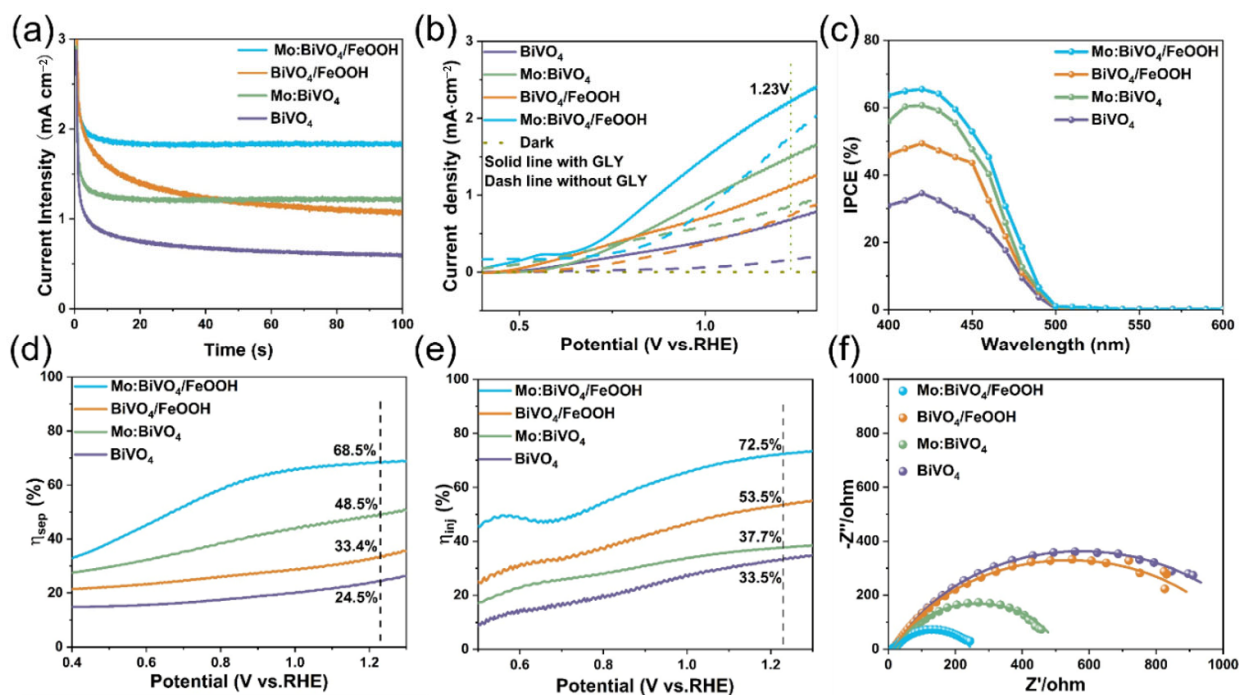


Figure 5. (a) Current-time (i-t) plot of photoelectrode, (b) Linear scanning voltammetric curve (LSV) plot of photoelectrode, (c) Incident photon-electron conversion efficiency (IPCE) curve of photoelectrode, (d) Volume-phase separation efficiency of photoelectrode, (e) Surface-separation efficiency of photoelectrode, (f) Impedance (EIS) of photoelectrode.

3.4. Optical Performance Testing and Analysis

To elucidate the optical characteristics of BiVO_4 , Mo:BiVO_4 , $\text{BiVO}_4/\text{FeOOH}$, and $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes, an initial investigation into the charge complexation of these four materials was conducted utilizing steady-state photoluminescence (PL) spectroscopy. As illustrated in Figure 6a, the intensity of the PL peaks follows the order: $\text{Mo:BiVO}_4/\text{FeOOH} < \text{Mo:BiVO}_4 < \text{BiVO}_4/\text{FeOOH} < \text{BiVO}_4$, from lowest to highest. This trend confirms that the synergistic effects of molybdenum doping and iron oxyhydroxide loading enhance the ability of the $\text{Mo:BiVO}_4/\text{FeOOH}$ photovoltaic electrode to effectively separate photogenerated charge carriers. Figure 6b,c present the UV-visible diffuse reflectance spectra and bandgap diagrams for the four photoelectrodes, demonstrating robust light absorption within the 300 nm to 500 nm range for all samples. The monoclinic scheelite phase BiVO_4 photoelectrode exhibits an absorption edge at 510 nm and a bandgap of 2.46 eV. The Mo:BiVO_4 photoelectrode shows a modest enhancement in light absorption intensity between 300 nm and 500 nm, accompanied by a slight red shift

of the absorption edge to 516 nm and a reduction in the bandgap to 2.43 eV. Following modification with FeOOH, the BiVO₄/FeOOH photoelectrode displays an absorption edge at 513 nm and a bandgap of 2.45 eV. In summary, the optical absorption characteristics and bandgap of the BiVO₄ photoelectrode are more significantly influenced by molybdenum doping than by iron oxyhydroxide doping. The combined effects of Mo-doping and loading FeOOH result in a visible absorption edge for the Mo:BiVO₄/FeOOH photoelectrode at 523 nm, with a bandgap of 2.41 eV, thereby enhancing its optical performance to a certain degree. An analysis of the Mott-Schottky curves for the four photoelectrodes, as depicted in Figure 6d, reveals positive slopes, indicating that all four materials function as n-type semiconductors. The flat-band potentials for BiVO₄, Mo:BiVO₄, BiVO₄/FeOOH, and Mo:BiVO₄/FeOOH are measured at 0.37, 0.25, 0.14, and 0.02 eV, respectively, relative to the standard hydrogen electrode (NHE). The slope order of the Mott-Schottky curves is BiVO₄ > BiVO₄/FeOOH > Mo:BiVO₄ > Mo:BiVO₄/FeOOH, suggesting a progressive increase in carrier concentrations among the four photoelectrodes, with calculated carrier concentrations following the sequence: BiVO₄ > BiVO₄/FeOOH > Mo:BiVO₄ > Mo:BiVO₄/FeOOH. Based on the calculations derived from Equation (9), the carrier densities for the four electrodes have been determined to be 2.8×10^{20} , 4.4×10^{20} , 4.8×10^{20} , and 1.0×10^{21} . A comparative analysis of these specific values indicates a sequential increase in the carrier concentrations of the photovoltaic electrodes. In the context of n-type semiconductors, it is generally observed that the conduction band (CB) position is situated approximately 0.2 eV below the flat band potential. Consequently, the conduction band values for the four photoelectric materials were established as 0.17, 0.05, −0.06, and −0.18 eV for BiVO₄, Mo:BiVO₄, BiVO₄/FeOOH, and Mo:BiVO₄/FeOOH, respectively, referenced to the Normal Hydrogen Electrode (NHE) [50–52]. Utilizing these conduction band values, the corresponding valence band (VB) values were calculated to be 2.63, 2.48, 2.39, and 2.23 eV (NHE), respectively.

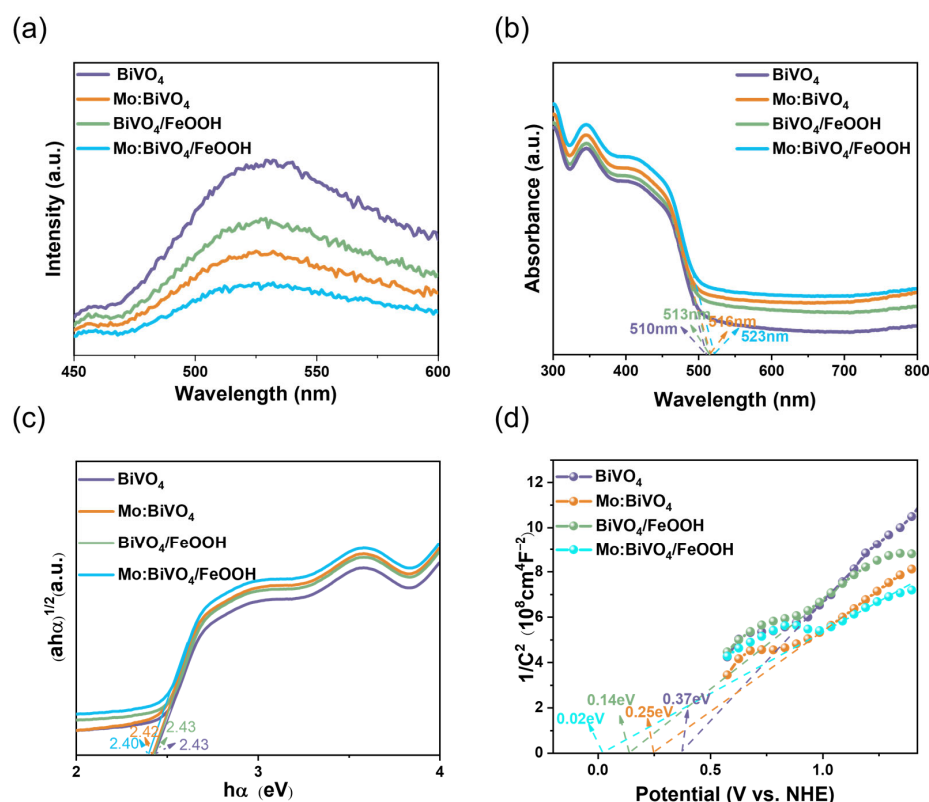


Figure 6. (a) Photoluminescence spectral (PL) plot, (b) ultraviolet (Uv-Vis) spectral plot, (c) bandgap plot, (d) Mott Schottky (M-S) plot for four photoelectrodes.

3.5. Glycerol Conversion Properties

To evaluate the glycerol conversion performance of BiVO_4 photoelectrodes doped with different concentrations of molybdenum, photocatalytic performance tests were conducted in an H-type quartz cell using a three-electrode configuration. The prepared photoanode was used as the working electrode, Pt foil as the cathode, and Ag/AgCl electrode as the reference electrode (Figure S2). A four-hour glycerol conversion test was performed. The results, depicted in Figure 7a, illustrate the conversion efficiency of glycerol per hour alongside the selectivity of glycerol products. It can be inferred that the different concentrations of molybdenum doping exert minimal influence on the selectivity of glycerol conversion products for the BiVO_4 photoelectrode. Notably, the highest glycerol conversion efficiency was observed at the optimal molybdenum doping concentration. Subsequently, to further investigate the glycerol conversion performance of Mo:BiVO_4 photoelectrodes with varying loading times of FeOOH, another glycerol conversion test was performed for four hours. The selectivity of each product and the average conversion efficiency per hour following the four-hour conversion period are presented in Figure 7b. The data indicate that FeOOH loading significantly impacts the selectivity of glycerol conversion products in Mo:BiVO_4 photoelectrodes, with a marked tendency towards the production of glyceraldehyde (GLAD). The optimal selectivity for glyceraldehyde in the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode reached 49% at an ideal FeOOH deposition time of 20 min. However, excessive loading times of FeOOH co-catalysts resulted in the formation of precipitated agglomerates on the surface, which adversely affected the light absorption properties of the BiVO_4 material. This, in turn, diminished the generation of photogenerated holes and their subsequent participation in the FeOOH-catalyzed conversion of glycerol to GLAD. Figure 7c presents the results of a four-hour glycerol conversion test involving four types of photoelectrodes. The selectivity of each product and the average conversion efficiency per hour were assessed, leading to the conclusion that molybdenum doping enhances the glycerol conversion and selectivity towards glyceraldehyde in the FeOOH-deposited BiVO_4 photoelectrode, achieving a selectivity of 49% and a glycerol conversion rate of $79 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$. Figure 7d illustrates the hourly glycerol conversion rate and GLAD yield after four hours of glycerol conversion, providing a clearer visualization of these rates. Figure 7e depicts the changes in glycerol conversion rate, glyceraldehyde production rate, and DHA production rate over the four-hour period for the four types of photoelectrodes. The data suggest that as the glycerol conversion rate increases, there is a substantial rise in glyceraldehyde production, while the changes in DHA production are relatively minor. Figure 7f illustrates the selectivity of glycerol conversion products following ten cycles of $\text{Mo:BiVO}_4/\text{FeOOH}$, with each cycle lasting four hours [53,54]. The findings demonstrate that the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode maintains a notable level of selective stability throughout the multiple glycerol conversion cycles, indicating its potential for prolonged effectiveness in glycerol conversion applications. Finally, as shown in Table S1, compared with previously reported photoanodes, the prepared $\text{Mo:BiVO}_4/\text{FeOOH}$ photoanode exhibits higher glycerol conversion rates and GLAD selectivity.

The analysis of scanning electron microscopy (SEM) images of the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode, both prior to and following ten cycles of glycerol conversion (refer to Figure S3a,b)), revealed minimal alterations in the morphology of the photoelectrode. Notably, a significant amount of flocs remained deposited on its surface. Furthermore, the XRD patterns of the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode, assessed before and after the glycerol conversion reaction (illustrated in Figure S4a), exhibited no discernible changes, indicating that the physical phase of the material remained stable throughout the reaction. The combined SEM and XRD analyzes suggest that the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes demonstrate commendable stability. In addition, the photocurrent responses of the

four photoelectrodes during prolonged glycerol conversion were evaluated (as shown in Figure S4b), confirming the stability of the Mo:BiVO₄/FeOOH photoelectrodes throughout the process. It was observed that the photocurrent of the pure BiVO₄ photoelectrodes exhibited a declining trend after four hours of glycerol conversion, likely attributable to photocorrosion leading to increased ionic solubility. Similarly, the BiVO₄/FeOOH photoelectrode displayed a marked decrease in photocurrent after four hours, which may be linked to the suboptimal electron-hole separation efficiency of the BiVO₄ photoelectrode, resulting in insufficient holes for the sustained generation of FeOOH on the surface. In contrast, the photocurrent of the Mo:BiVO₄ photoelectrode stabilized after four hours of glycerol conversion, suggesting that the surface doping of Mo enhances the stability of the BiVO₄ photoelectrode. The Mo:BiVO₄/FeOOH photoelectrode also exhibited robust stability after this duration, attributed to both the inherent stability of the Mo:BiVO₄ photoelectrode and the stability of the FeOOH co-catalyst.

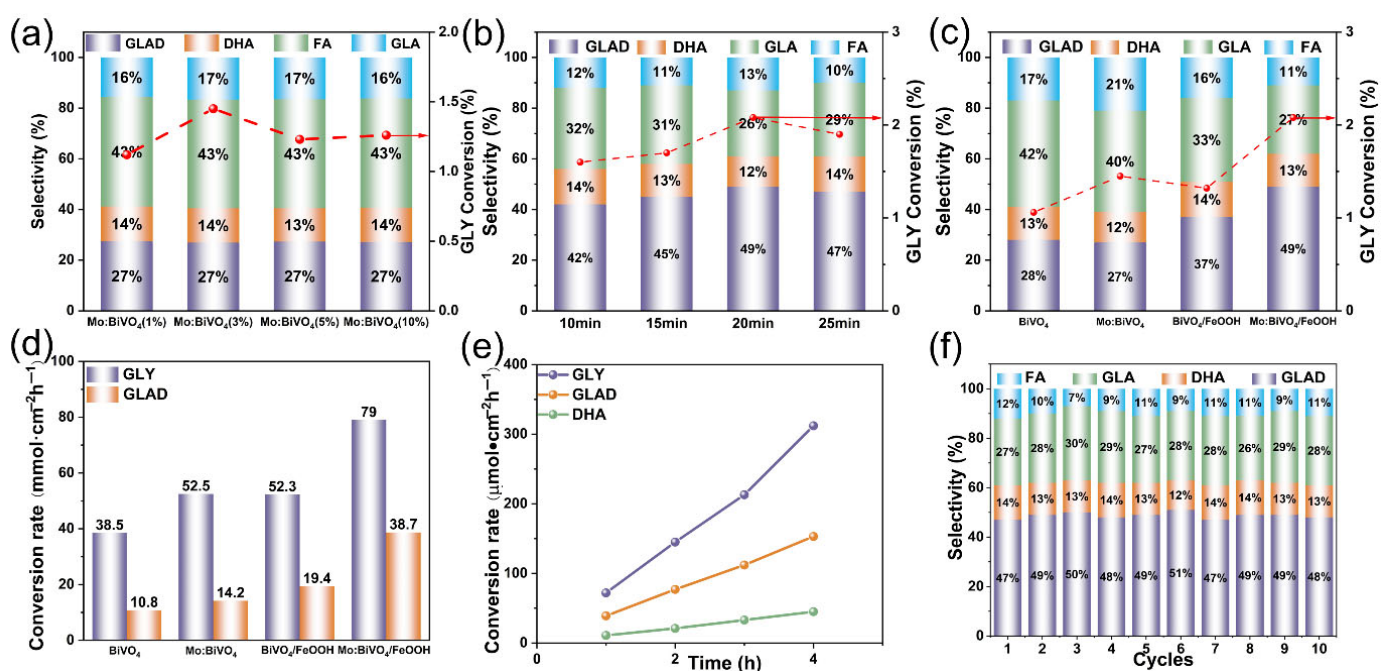


Figure 7. (a) The hourly conversion and selectivity of glycerol for photoelectrodes with varying concentrations of molybdenum doping, (b) The hourly conversion and selectivity of glycerol for photoelectrodes subjected to different loading durations of FeOOH, (c) The hourly conversion and selectivity of glycerol for BiVO₄, Mo:BiVO₄, BiVO₄/FeOOH, and Mo:BiVO₄/FeOOH photoelectrodes, (d) The hourly consumption rate of glycerol conversion and the yield of GLAD for the four photoelectrodes, (e) A graphical representation of the changes in the four-hour glycerol conversion consumption rate, glycerol yield, and DHA yield across the four photoelectrodes, and (f) A plot illustrating the glycerol selectivity of the Mo:BiVO₄/FeOOH photoelectrodes over ten cycles.

3.6. Promotion of Glycerol Selective Adsorption by Photoelectrode

The adsorption and desorption characteristics of glycerol and glyceraldehyde on four distinct photoelectrodes were investigated utilizing an electrochemical quartz crystal microbalance (EQCM). The EQCM functions based on the principle of mass-frequency correlation, where the adsorption curves exhibit a notable negative frequency shift corresponding to an increase in the amount of adsorbed material. Figure 8a,b present the EQCM test results for the four photoelectrodes in solutions of 0.1 M Na₂SO₄ combined with 0.1 M glycerol and 0.1 M glyceraldehyde, respectively. Preliminary tests conducted with a solution containing solely 0.1 M Na₂SO₄ indicated that the frequency of the EQCM test curves for the photoelectrodes approached zero (as illustrated in Figure 8a,b). Analy-

sis of the EQCM curves for the four photoelectrodes in glycerol solution revealed that the EQCM frequencies for the Mo:BiVO₄ and BiVO₄/FeOOH photoelectrodes exhibited a more pronounced negative shift compared to the BiVO₄ photoelectrodes, with the Mo:BiVO₄/FeOOH photoelectrodes demonstrating the most significant negative shifts. This finding suggests a hierarchy in the adsorption capacity of the photoelectrodes for glycerol, ranked as follows: BiVO₄ < BiVO₄/FeOOH < Mo:BiVO₄ < Mo:BiVO₄/FeOOH. In the context of glyceraldehyde solution, as depicted in Figure 8b, the BiVO₄ and Mo:BiVO₄ photoelectrodes exhibited superior adsorption capacities for glyceraldehyde, followed by the BiVO₄/FeOOH photoelectrodes, while the Mo:BiVO₄/FeOOH photoelectrodes displayed the least adsorption capacity for glyceraldehyde. The EQCM tests indicated that the Mo:BiVO₄/FeOOH photoelectrode possessed the highest adsorption capacity for glycerol and the most effective desorption capacity for glyceraldehyde. This observation elucidates the enhanced glycerol conversion efficiency and selectivity for glyceraldehyde associated with the Mo:BiVO₄/FeOOH photoelectrode during photoelectrocatalytic glycerol conversion. Subsequently, the Mo:BiVO₄/FeOOH photoelectrodes underwent 100-s photocurrent tests in various solutions, including 0.1 M glycerol, 0.1 M glyceraldehyde, 0.1 M glyceric acid, 0.1 M formic acid, 0.1 M DHA, and 0.1 M Na₂SO₄, as illustrated in Figure 8c. The results indicated that the photoelectrode exhibited the highest photocurrent density in glycerol solution, with relatively high photocurrent densities in formic and glyceric acid solutions, while the lowest photocurrent density was observed in glyceraldehyde solution, which was comparable to that in Na₂SO₄ solution. The photocurrent density of the Mo:BiVO₄/FeOOH photoelectrode in glyceric acid solution was intermediate between those observed in glyceraldehyde and 1,3-dihydroxyacetone solutions. These findings imply that glyceraldehyde, as an oxidation product, can be rapidly desorbed from the surface of the Mo:BiVO₄/FeOOH photoelectrode catalyst, thereby inhibiting its continuous involvement in the conversion reaction. The results indicate that the addition of the hole scavenger Na₂SO₃ significantly affects the glycerol conversion rate and glyceraldehyde production rate, leading to a marked decrease in production rate, which suggests that holes are the source of all oxidizing species in the glycerol oxidation process. After introducing the hydroxyl scavenger TBA, both the glycerol conversion rate and glyceraldehyde production rate showed a noticeable decrease, indicating that hydroxyl radicals are the primary oxidizing species in glycerol oxidation. Even in the absence of hydroxyl radicals, glyceraldehyde continues to be produced, which may be because some holes directly oxidize glycerol to produce glyceraldehyde.

The intensities of hydroxyl radicals generated by four distinct photoelectrodes were evaluated under both dark and illuminated conditions (refer to Figure 9a). The findings revealed that the hydroxyl radical signal intensities for the BiVO₄ and Mo:BiVO₄ photoelectrodes were markedly lower compared to those of the BiVO₄/FeOOH and Mo:BiVO₄/FeOOH configurations. In the absence of light, the hydroxyl radical signal intensity approached zero; conversely, under illumination, there was a notable increase in hydroxyl radical signal intensity, with the Mo:BiVO₄/FeOOH photoelectrode exhibiting the highest signal. These results underscore the significant role of hydroxyl groups in the reaction mechanism during the glycerol conversion process facilitated by the modified Mo:BiVO₄/FeOOH photoelectrode. Subsequent tests were conducted to assess the carbon radical and hydroxyl signals from the Mo:BiVO₄/FeOOH photoelectrodes following one hour of glycerol conversion (see Figure 9b). The analysis indicated the presence of both carbon radical and hydroxyl signals when 0.1 M glycerol was combined with 0.1 M Na₂SO₄ in the solution. In contrast, carbon radical signals were observed in a solution containing only 0.1 M glycerol, while hydroxyl signals were detected solely in a 0.1 M Na₂SO₄ solution. Notably, carbon radicals were identified in the 0.1 M glycerol solution,

whereas hydroxyl radicals were exclusively found in the 0.1 M Na_2SO_4 solution. The detection of hydroxyl radicals in the Na_2SO_4 solution occurred without the presence of carbon radicals. These findings suggest that the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode facilitates the generation of both carbon radicals and hydroxyl radicals during glycerol conversion, with hydroxyl radicals originating from water oxidation and carbon radicals resulting from glycerol oxidation.

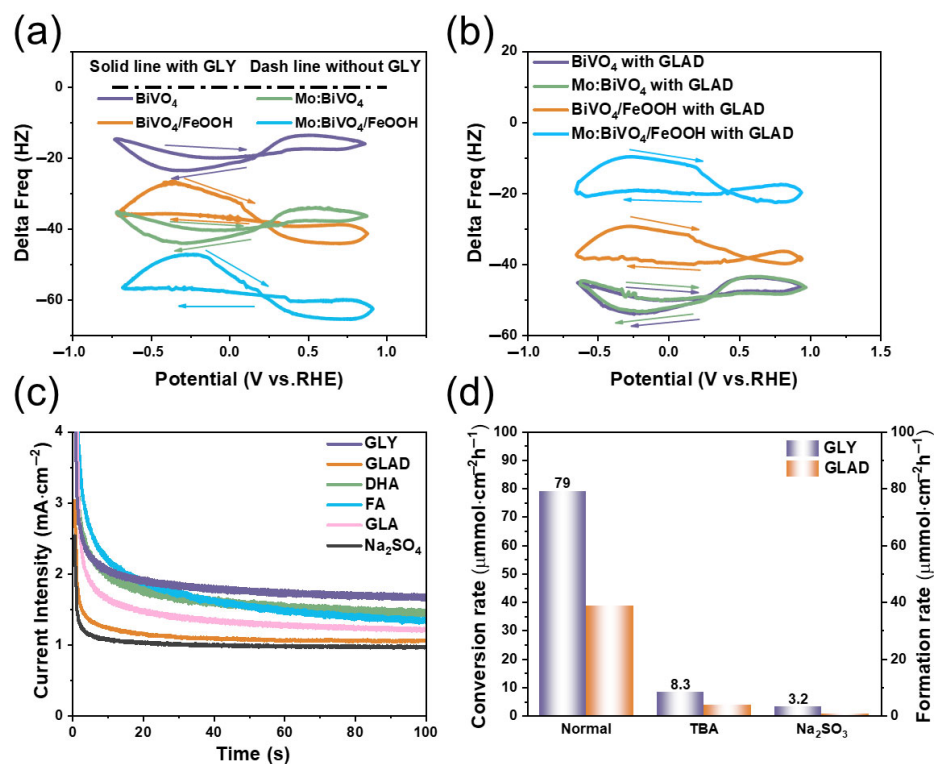


Figure 8. The EQCM test curves of the four photoelectrodes in 0.1 M Na_2SO_4 plus 0.1 M glycerol solution (a) and 0.1 M Na_2SO_4 plus 0.1 M glyceraldehyde solution (b), (c) photocurrent curves of $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes in glycerol, glyceraldehyde, sodium sulfate, glyceric acid, and formic acid solutions, and (d) experimental results of the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes scavengers.

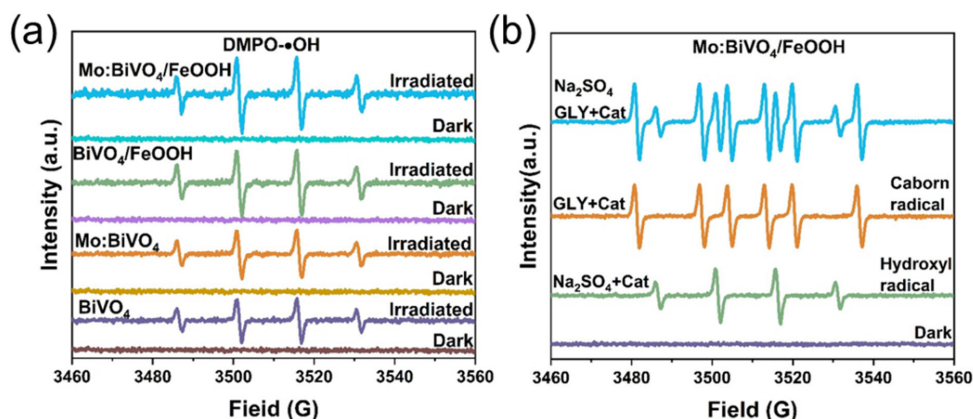


Figure 9. (a) Hydroxyl test curves of four photoelectrodes, (b) $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode carbon radical and hydroxyl radical intensity test curve.

4. Discussion

The photoelectrocatalytic conversion of glycerol utilizing the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode is illustrated in Figure 10. Initially, the incorporation of molybdenum (Mo) into

the BiVO_4 photoelectrode enhanced its stability, light absorption, and carrier concentration, which effectively mitigated the formation of electron-hole pairs, thereby improving both photoelectric conversion efficiency and glycerol conversion efficiency. The subsequent deposition of FeOOH resulted in the formation of chemical bonds with Mo:BiVO_4 , facilitating rapid electron-hole transfer and increasing the number of surface oxygen vacancies, which serve to capture electrons and diminish complexation. Furthermore, FeOOH functioned as a hole extraction layer, enhancing hole transfer efficiency and providing additional active sites for glycerol conversion, thereby promoting glycerol adsorption and the desorption of glyceraldehyde. The Mo doping also augmented the electron-hole transfer capacity, allowing for greater participation of holes in the cyclic conversion of $\text{FeOOH}/\text{Fe}(\text{OH})_2$, which is essential for maintaining the stable presence of FeOOH as a co-catalyst, thus contributing to the overall stability of the system. The $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode demonstrated efficient and highly selective glycerol conversion rates of up to $79 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, with a glyceraldehyde selectivity of 49% under neutral conditions. This remarkable performance can be attributed to the synergistic effects of Mo doping and FeOOH . Mo doping optimizes the charge separation efficiency of BiVO_4 , while FeOOH facilitates the glycerol conversion pathway through a hole-driven mechanism that involves the formation of FeOOH , which adsorbs the primary hydroxyl group of glycerol to generate carbon radicals. These radicals are subsequently oxidized and dehydrated by the hydroxyl group, leading to the final conversion to glyceraldehyde. This synergistic mechanism enables the photoelectrode to catalyze glycerol conversion in a sustained and efficient manner.

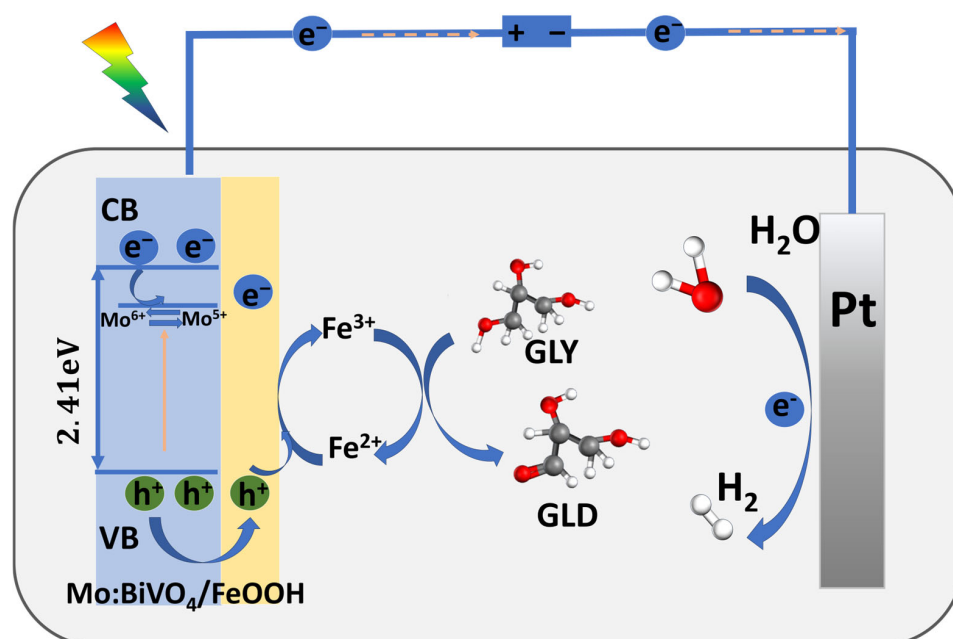


Figure 10. Schematic diagram of glycerol conversion using the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode.

5. Conclusions

Mo doping has been demonstrated to enhance the stability and light absorption characteristics of BiVO_4 photoanodes, effectively mitigating the challenge of electron-hole recombination. This enhancement results in an increase in both photoelectrochemical conversion efficiency and glycerol conversion efficiency, achieving a glycerol conversion rate of $52.5 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, which is approximately 1.37 times greater than that of pure BiVO_4 . The deposition of iron oxyhydroxide (FeOOH) on the surface of the Mo:BiVO_4 photoanode establishes chemical bonds that promote rapid electron-hole transfer. Furthermore, the incorporation of FeOOH leads to an increased density of oxygen vacancies on the BiVO_4

surface, which can effectively capture electrons and diminish electron-hole recombination. Additionally, FeOOH functions as a hole extraction layer, thereby enhancing hole transport efficiency and glycerol conversion efficiency, culminating in a glycerol conversion rate of $79 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, nearly double that of pure BiVO_4 . As for the $\text{Mo:BiVO}_4/\text{FeOOH}$, Mo doping facilitates improved electron-hole transport efficiency and carrier concentration within the BiVO_4 photoanode, enabling a greater number of holes to rapidly engage in the formation of FeOOH. The stability of the FeOOH co-catalyst within the glycerol conversion system significantly contributes to the overall performance of the $\text{Mo:BiVO}_4/\text{FeOOH}$ composite. Moreover, the FeOOH loading on Mo:BiVO_4 introduces additional active sites for glycerol conversion, thereby promoting glycerol adsorption and glyceraldehyde desorption, with a selectivity for glyceraldehyde of 49%, approximately twice that of pure BiVO_4 . It is posited that the glycerol conversion pathway on the $\text{Mo:BiVO}_4/\text{FeOOH}$ photoanode involves the facilitation of carbon free radicals by FeOOH, which subsequently interact with hydroxyl groups to form intermediates that undergo dehydration to yield glyceraldehyde.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs9080381/s1>, Figure S1: (a) i-t curves of the photocurrent test in glycerol solution for Mo:BiVO_4 photoelectrodes with different Mo doping concentrations (x% Mo:BiVO_4), (b) i-t curves of the photocurrent test in glycerol solution for $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrodes with different FeOOH loading times ($\text{Mo:BiVO}_4/\text{FeOOH}$ (x min)); Figure S2: PEC reaction apparatus: H-type electrolytic cell; Figure S3: SEM image of $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode before 10 h glycerol conversion reaction, (b) SEM image of $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode after 10 h glycerol conversion reaction; Figure S4: (a) XRD plots of $\text{Mo:BiVO}_4/\text{FeOOH}$ photoelectrode before and after 10 cycles of reaction, (b) Photocurrent diagram of photovoltaic electrodes converted by four hours of glycerol; Table S1: Summary of PEC glycerol selective oxidation over different photoanodes.

Author Contributions: J.W.: Resources, Methodology, Investigation, Data curation, Writing—original draft, Writing—review and editing, Validation. X.G.: Methodology, Data curation. H.G.: Resources, Investigation, Methodology. W.Z.: Project administration, Validation. Y.L.: Methodology, Formal analysis, Project administration, Funding acquisition, Writing—review and editing, Supervision. B.L.: Methodology, Project administration, Conceptualization, Supervision, Validation. All authors have read and agreed to the published version of the manuscript.

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