

Article

Cooperative Catalytic Behavior of SnO_2 and NiWO_4 over BiVO_4 Photoanodes for Enhanced Photoelectrochemical Water Splitting Performance

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Received: 3 September 2019; Accepted: 19 October 2019; Published: 23 October 2019



Abstract: n-BiVO_4 is a favorable photoelectrode candidate for a photoelectrochemical (PEC) water splitting reaction owing to its suitable energy level edge locations for an oxygen evolution reaction. On the other hand, the sluggish water oxidation kinetics of BiVO_4 photoanodes when used individually make it necessary to use a hole blocking layer as well as water oxidation catalysts to overcome the high kinetic barrier for the PEC water oxidation reaction. Here, we describe a very simple synthetic strategy to fabricate nanocomposite photoanodes that synergistically address both of these critical limitations. In particular, we examine the effect of a SnO_2 buffer layer over BiVO_4 films and further modify the photoanode surface with a crystalline nickel tungstate (NiWO_4) nanoparticle film to boost PEC water oxidation. When NiWO_4 is incorporated over $\text{BiVO}_4/\text{SnO}_2$ films, the PEC performance of the resultant triple-layer $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ films for the oxygen evolution reaction (OER) is further improved. The enhanced performance for the PEC OER is credited to the synergetic effect of the individual layers and the introduction of a SnO_2 buffer layer over the BiVO_4 film. The optimized $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ electrode demonstrated both enriched visible light absorption and achieves charge separation and transfer efficiencies of 23% and 30%, respectively. The photoanodic current density for the OER on optimized $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanode shows a maximum photocurrent of 0.93 mA/cm^2 at 1.23 V vs. RHE in a phosphate buffer solution (pH~7.5) under an AM1.5G solar simulator, which is an incredible five-fold and two-fold enhancement compared to its parent BiVO_4 photoanode and $\text{BiVO}_4/\text{SnO}_2$ photoanodes, respectively. Further, the incorporation of the NiWO_4 co-catalyst over the $\text{BiVO}_4/\text{SnO}_2$ film increases the interfacial electron transfer rate across the composite/solution interface.

Keywords: photoelectrocatalysis; bismuth vanadate; nickel tungstate; water splitting

1. Introduction

Solar-assisted electrolysis is recognized as a promising process for the commercial production of hydrogen from water. The US Department of Energy has estimated the hydrogen threshold cost at $<4/\text{Kg}$ for future solar hydrogen production [1]. Numerous sustainable hydrogen production technologies are commercially available, and these can be categorized into three main types: thermal processes, electrolytic processes, and photolytic processes. Among the available photoelectrochemicals (PECs), water splitting is the most favorable technology for the sustainable manufacturing of clean and renewable fuels. However, the sluggish kinetics of the OER still presents a challenge [2,3]. Recently,

Pinaud et al. assessed the feasibility of centralized facilities in a techno-economical way; the hydrogen production costs of a PEC system are in a range of \$1.60–\$10.40 per kg H₂ [4]. Moreover, it is evidenced that an industrial-scale PEC splitting system can be cost-efficient with fossil-based fuels. Besides, to compete commercially, highly effective and robust solar-assisted electrolysis reactors will need to be fabricated very cheaply [5]. Ideal photoelectrodes for PEC systems involve a small band gap to arrest visible-light photons, high conversion efficiency, and a good durability in aqueous environments [6].

During the past few decades, n-type semiconductors such as TiO₂ [7,8], Fe₂O₃ [9,10], WO₃ [11,12], and BiVO₄ [13–19] have been surveyed as photoanode materials for the development of PEC water oxidation technology because their valence band positions are more positive than the potential for the O₂/H₂O couple. Among these n-type materials, BiVO₄ is recognized to be a favorable photoanode for the OER in PEC water splitting systems [20] owing to its suitable energy level positions, light absorption, cost-effectiveness, and easy accessibility in large quantities. The maximal theoretical photoanodic current for BiVO₄ films that is practicable with its narrow band gap of ~2.4 eV, is ~7.5 mA.cm^{−2} at 1.23 V_{RHE} [21,22]. In particular, BiVO₄ films tends to possess relatively good stability, as they can reach a theoretical solar to hydrogen efficiency of 9.2% [23]. In this regard, the sluggish water oxidation kinetics, high exciton recombination rate, and also the lower conductivity of BiVO₄ are the major hurdles that must be overcome to realize this photocurrent value [24].

To improve the photon absorption and carrier transport of BiVO₄ photoanodes, numerous modifications have been reported. During the past few decades, significant research work has been carried out to incorporate oxygen evolution catalysts over BiVO₄ photoanodes. For instance, a more efficient approach includes the incorporation of oxygen evolution catalysts such as cobalt phosphate (CoPi), CoO_x, and NiFeO_x onto BiVO₄ photoanodes, thereby reducing surface recombination at the interface [25–32]. Very recently, we demonstrated the incorporation of silver phosphate (AgPi) [33] and nickel hydroxyl phosphate (Ni-OH-Pi) [34] over BiVO₄ photoanodes, and investigated their use as electrode materials for energy applications. Nano-structuring is an alternative process for performance enhancement of BiVO₄ photoanodes and other semiconductor materials with relatively poor carrier dynamics [35,36].

Another remarkable tactic was the incorporation of a new kind of metal oxide layer, namely WO₃ and SnO₂, between BiVO₄ and a fluorine-doped tin oxide (FTO) conducting substrate, the widely used conducting parts for PEC cells [37–39]. In particular, the incorporation of a metal oxide at the interface between FTO and BiVO₄ results in: (i) band bending of the BiVO₄ that assists the flow of suitable charge carriers and (ii) the passivation of trapping states, resulting in the suppression of charge recombination. For instance, BiVO₄/SnO₂ electrodes displayed an improved PEC activity over a bare-BiVO₄ photoanode owing to the hole-mirroring nature of the SnO₂ layers [40]. Very recently, Byun et al. explored the influence of the thickness of the SnO₂ layer in BiVO₄ films on PEC water oxidation [41]. These reports demonstrate that the incorporation of a SnO₂ buffer layer is a crucial part of assembling photoanodes with improved performance based on BiVO₄ [38,39]. The incorporation of an added metal oxide (SnO₂ buffer layer) as well as an OER catalyst cooperatively boosts the catalytic efficiency of BiVO₄ photoanodes for PEC water oxidation. As stated earlier, coupling a semiconductor with an electrochemical OER co-catalyst is another way to promote the activity of photoanodes materials for water oxidation, because the co-catalyst can improve the charge transfer rate at the interface. In earlier reports, Sn-doping was found to be effective in promoting the electronic conductive nature of the photoanodes. In particular, the incorporation of Sn also dramatically reduces the resistivity of the electrodes [42–46]. In recent years, metal tungstates have been shown to be efficient co-catalysts that possess interesting properties [47–49] and have the potential to boost the performance of photoanode materials for PEC OER. In particular, NiWO₄ nanoparticles exhibit fascinating electrochemical behaviors, including electro-catalysis for OER [50]. Moreover, NiO_x based materials have been widely considered as extraordinary hole-conducting protection layers for catalysts because of its hole-transfer and electron-blocking nature due to the relatively higher CB edge positions [51–54].

In this work, we demonstrate triple-layer $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoelectrodes with superior PEC performance and light absorbance. The photoanodes were prepared through a simple electrodeposition process. Firstly, a SnO_2 nanoparticle film was loaded onto a FTO substrate. Afterwards, a BiVO_4 mid layer and a NiWO_4 top layer were electrodeposited. We found that the obtained $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ nanocomposite demonstrated considerably enhanced performance for PEC OER. Further, the superior PEC performance of the triple-layer nanocomposite was ascribed to its high specific surface area and the enhanced electron–hole separation rate due to the $\text{NiWO}_4/\text{BiVO}_4$ heterojunction. There have been a few reports concerning the incorporation of hole-blocking SnO_2 [41], but we believe that this is the first work to demonstrate the material properties of triple-layered $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ films.

2. Results and Discussion

2.1. Fabrication of Triple-Layer Photoanodes

As schematically shown in Figure 1, compact but porous SnO_2 buffer layers comprising of SnO_2 nanoparticles were loaded onto FTO substrates by means of an electrodeposition process. Subsequently, BiVO_4 and NiWO_4 photoanodes were loaded over these SnO_2/FTO layers through an electrodeposition process and the fabricated photoanodes were annealed to obtain $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes. Figure 1 illustrates the various phases of the synthesis process used to obtain the triple-layer $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes. For comparison, pure BiVO_4 photoanodes were also fabricated by means of an electrodeposition process on bare FTO substrates.

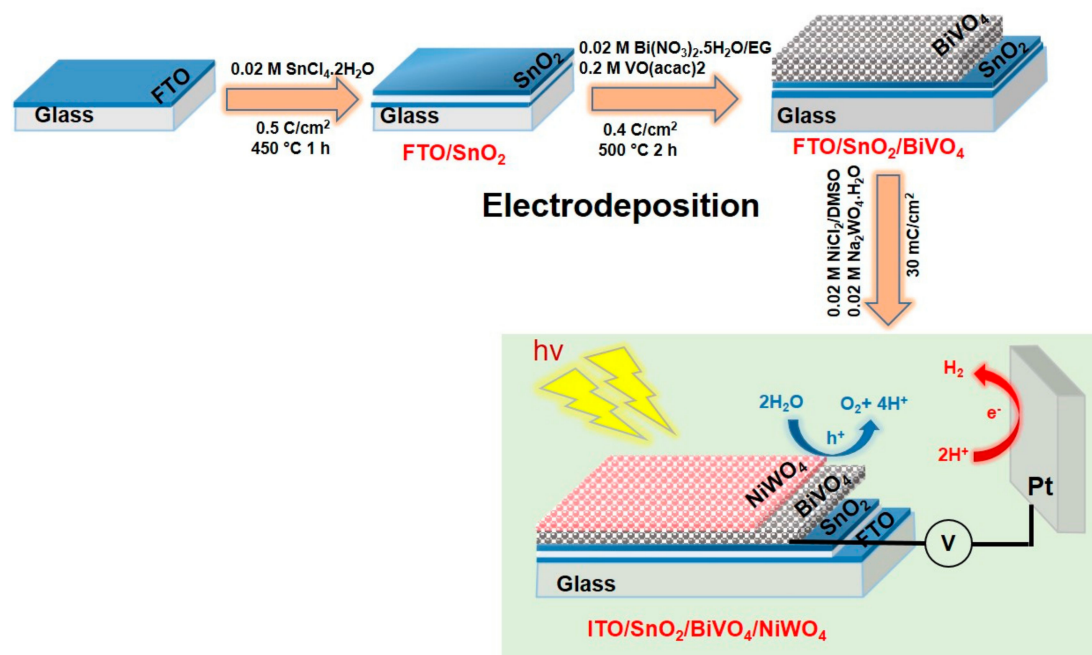


Figure 1. Fabrication of Triple-layer photoanodes. Schematic representation of $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ triple-layer photoanode film on an fluorine-doped tin oxide (FTO) substrate deposited via a method that involves electrodeposition processes.

2.2. Material Characterization of $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ Photoanodes

The phase compositions of the fabricated photoanodes were explored by X-ray diffraction (XRD). Figure 2 shows the XRD patterns for the bare FTO substrates (curve (i)) and after the incorporation of SnO_2 onto FTO substrates (SnO_2/FTO) by electrodeposition (curve (ii)). There were no considerable variations in the diffraction patterns of SnO_2 over FTO, demonstrating that there was no creation of new kinds of phases in the as-synthesized photoanodes. Moreover, BiVO_4 was also deposited over FTO substrates (curve (iii)) and SnO_2/FTO (curve (iv)) using the same technique, which was subsequently

subjected to an annealing process at 300 °C for 1 h. Further, a NiWO_4 layer was electrodeposited over the $\text{BiVO}_4/\text{SnO}_2$ photoanodes using the same electrodeposition technique. For the as-synthesized BiVO_4 (curves (iii) and (iv)), obtained sharp peaks credited to the BiVO_4 film, well matched with the JCPDS # 00-014-0688, were evidenced. After the incorporation of NiWO_4 , Figure 2 curve (iv) displayed peaks corresponding to the NiWO_4 layer, matching the standard JCPDS pattern (00-015-0755) of pure NiWO_4 . The XRD patterns displayed in Figure 2 provide evidence of the generation of pure phases of SnO_2 , BiVO_4 , and NiWO_4 . Hence, we can conclude that the $\text{NiWO}_4/\text{BiVO}_4$ composite was successfully prepared by means of electrodeposition.

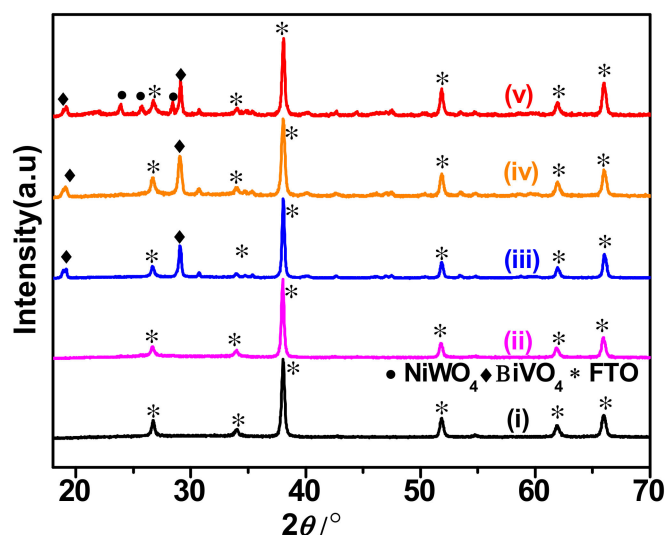


Figure 2. Normalized X-ray diffraction patterns for (i) FTO electrodes, (ii) SnO_2 loaded FTO, (iii) two-step electrodeposited BiVO_4/FTO photoanodes, (iv) $\text{BiVO}_4/\text{SnO}_2$ loaded over FTO, and (v) $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ loaded over FTO.

The structures of the films during the different photoelectrode fabrication steps were inspected using Field Emission Scanning electron microscope (FE-SEM). Figure 3a–f display typical SEM images of SnO_2 nanoparticles, $\text{BiVO}_4/\text{SnO}_2$, and $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes deposited on FTO substrates. The optimized SnO_2 nanoparticle films on FTO fabricated by an electrodeposition process are shown in Figure 3a. As shown in Figure 3a,b, FTO substrates were obviously covered by a dense, pin-hole free buffer layer of SnO_2 crystal grains, in which the massive but irregular lumps of ~ 150 nm are comprised of small nanoparticles. Planview FE-SEM images of bare- BiVO_4 as well as BiVO_4 layers deposited on SnO_2 are shown in Figure 3c,d, and Figure S1. In BiVO_4 films with a buffer SnO_2 layer, a BiVO_4 particle size of 200 ± 20 nm was observed (Figure 3c,d) from the FESEM images and these particles were much smaller in comparison than those observed in the bare- BiVO_4 films (500 ± 20 nm), where the morphological nature of BiVO_4 was not considerably influenced by a SnO_2 layer underneath, and was similar to that of other samples. Figure 3e,f show microscope images of the deposited NiWO_4 layer (charge: 30 mC cm^{-2}) over the $\text{BiVO}_4/\text{SnO}_2$ films. In particular, the FE-SEM of $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ evidences that the NiWO_4 layer incorporation was mostly uniform as well as thin layer to see the substantial changes in the morphological nature of the bare- BiVO_4 films. The cross sectional FESEM shows a well-connected SnO_2 layer of approximately 310 nm thick with an increase in film thickness to 520 nm after deposition of the BiVO_4 layer and the results are shown in Figure S2. Changes in the elemental distributions of the fabricated photoanodes were studied by energy dispersive X-ray analysis (EDAX). These investigations evidenced the existence of Sn, Bi, V, Ni, W, and O in the fabricated photoanodes, as shown in the Figure S3.

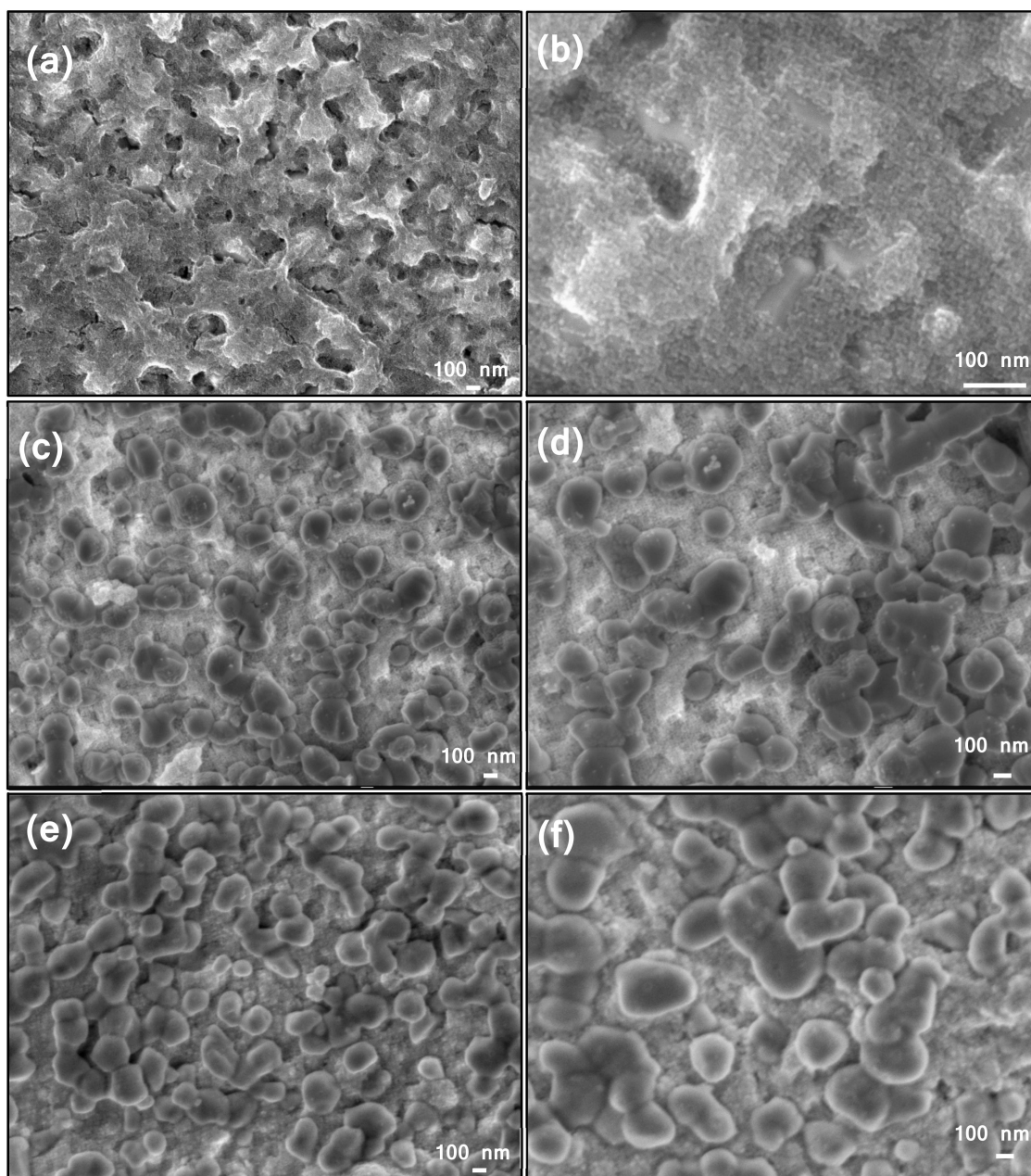


Figure 3. Structural characteristics of photoanodes. Field emission Scanning electron microscope images at (a) low-magnification and (b) high-magnification of SnO_2 nanoparticles fabricated using an electrodeposition process on FTO substrates. (c,d) FE-SEM images of the $\text{BiVO}_4/\text{SnO}_2$ films prepared via an electrochemical deposition process, exhibiting a uniform and tightly packed BiVO_4 layer over a SnO_2 buffer layer on FTO substrates. (e,f) FE-SEM images of NiWO_4 nanoparticles over $\text{BiVO}_4/\text{SnO}_2$ photoanodes at dissimilar magnifications fabricated by an electrodeposition process.

Diffuse reflectance ultraviolet-visible (DRS UV-Vis) was employed to determine the optical bandgap and absorption properties of SnO_2 , BiVO_4 , $\text{BiVO}_4/\text{SnO}_2$, and $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ layers deposited over FTO substrates; the obtained spectra are shown in Figure 4a. The spectrum of the $\text{BiVO}_4/\text{SnO}_2$ film deposited on a FTO substrate exhibits a different absorption profile than that of the FTO/ BiVO_4 film, thus resulted in the blue-shifted absorption edge, i.e., on the way to a larger band gap, as the SnO_2 film was loaded on the FTO substrate. The spectrum of the bare- BiVO_4 film shows absorption at wavelengths up to ~ 520 nm, corresponding to a band-gap of 2.4 eV. Because the bandgap of SnO_2 is 3.6 eV, the absorption of SnO_2 was not observed in this spectrum. Additionally, the incorporation of

NiWO₄ over BiVO₄/SnO₂ films resulted in considerably greater light absorption compared to other electrodes in the wavelength ranging from 300–500 nm (Figure 4a). The triple layer NiWO₄/BiVO₄/SnO₂ films revealed optimal light absorption, demonstrating that the Figure 4b presents the plotting of $(\alpha h\nu)^{1/2}$ versus the photon energy of BiVO₄, BiVO₄/SnO₂, and NiWO₄/BiVO₄/SnO₂, with band-gaps of 2.35, 2.40, and 2.25 eV, correspondingly. Lastly, the observed changes in the band gap of BiVO₄/SnO₂ are in agreement with the XRD measurements, since the tetragonal phase is recognized to have a larger band-gap [55].

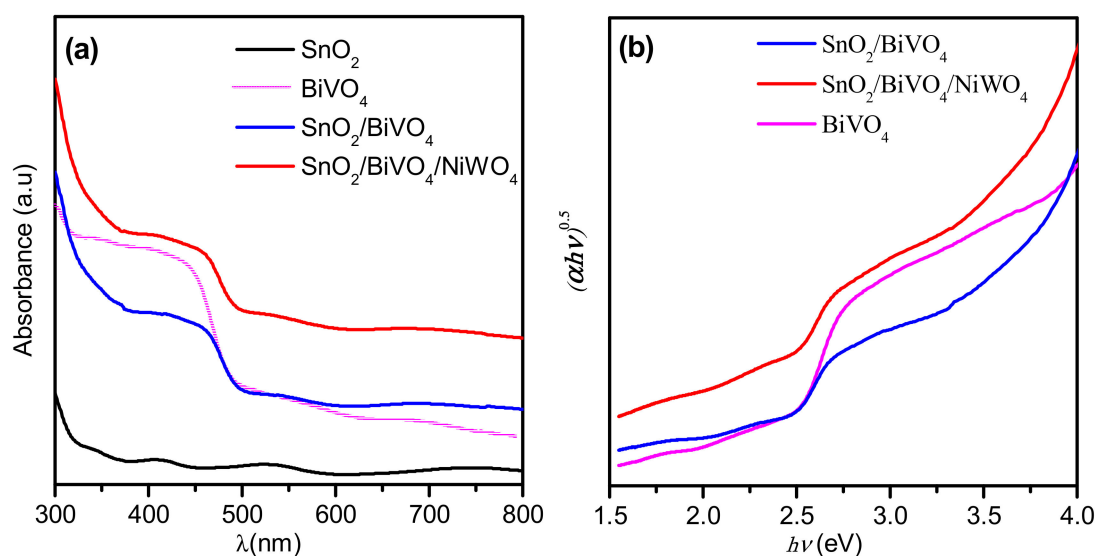


Figure 4. Optical properties of the photoanodes (a) UV-Vis absorption spectra of SnO₂, BiVO₄, BiVO₄/SnO₂, and NiWO₄/BiVO₄/SnO₂ electrodes deposited on FTO substrates. (b) The corresponding Tauc plots of NiWO₄/BiVO₄/SnO₂ electrodes with respect to BiVO₄ and BiVO₄/SnO₂ films.

2.3. Photo-Electrochemical Behavior of Photoanodes

Three-electrode J-V analysis were performed for PEC measurements under stimulated conditions in the presence of 0.1 M PBS. The electrochemical conditions during the deposition of NiWO₄ were adjusted by varying the total charge engaged for Ni electrodeposition (30 mC·cm⁻²) as well as the immersion time in the tungstate solution to obtain triple-layer NiWO₄/BiVO₄/SnO₂ photoanodes over FTO substrates. The distinctive J-V measurements under illumination condition presented in Figure 5a confirm that the optimized triple-layered NiWO₄/BiVO₄/SnO₂ photoanodes exhibited superior photocurrents compared to BiVO₄/SnO₂, bare-BiVO₄, and bare-SnO₂. At a potential of 1.23 V_{RHE}, the photoanodic current densities of the bare-BiVO₄, BiVO₄/SnO₂, and NiWO₄/BiVO₄/SnO₂ photoanode films were 0.18, 0.56, and 0.93 mA·cm⁻², correspondingly. Further, the photocurrent density of the triple-layered NiWO₄/BiVO₄/SnO₂ films increased considerably with applied potential, reaching nearly 0.93 mA·cm⁻² at 1.23 V_{RHE}, which is a five-fold enhancement of the photocurrent density of the bare-BiVO₄ photoanode (0.18 mA·cm⁻²). This significant photocurrent improvement is complemented by a substantial cathodic shift in the photocurrent onset potential of ~200 mV. Further, the J-V curve of the BiVO₄/SnO₂ photoanode shown in Figure 5a exhibits a three-fold enhancement in photocurrent density in comparison with bare-BiVO₄. An appreciable photocurrent measurements was acquired in the lower potential area (0.6 V_{RHE}) with all samples, as displayed in Figure 5b. Further, Figure 5c displays the J-V plots of the NiWO₄/BiVO₄/SnO₂, BiVO₄/SnO₂, and bare-BiVO₄ electrodes under chopped illumination. This investigation has elucidated that the construction of the BiVO₄/SnO₂ heterojunction is a major factor causing the enhancement of the activity toward PEC water oxidation. As predicted by earlier reports in the literature [39], the incorporation of a SnO₂ buffer layer between FTO and BiVO₄ resulted in enhanced PEC behaviors. This is credited to the downward band bending within the BiVO₄ and hole-mirroring effect of SnO₂.

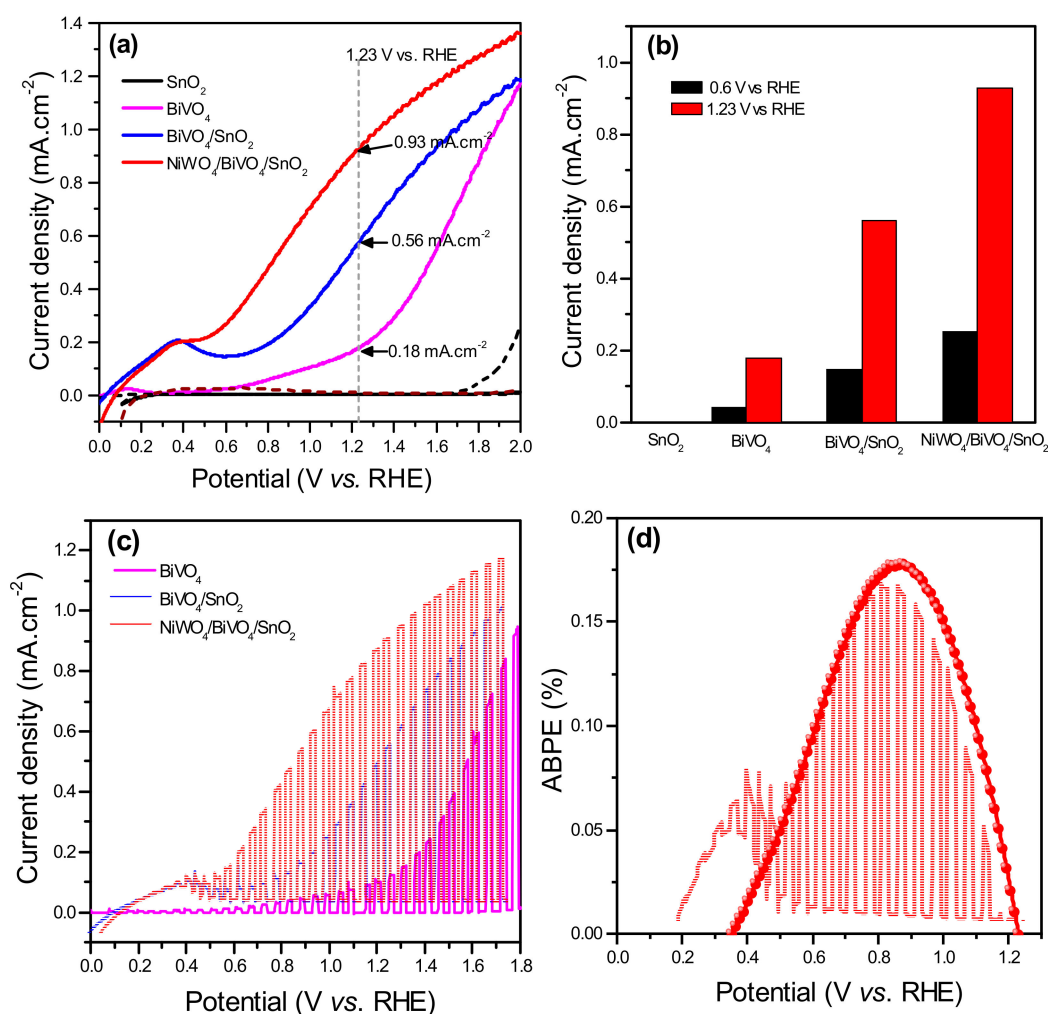


Figure 5. Photoelectrochemical properties of photoanodes. (a) Photocurrent-potential characteristics for bare-BiVO₄, BiVO₄/SnO₂, and NiWO₄/BiVO₄/SnO₂ photoanodes evaluated in PBS solution (0.1 M, pH 7.5) at AM 1.5G condition (sweep rate = 10 mV/s). (b) Changes in photocurrent for all photoelectrodes at 0.6 V_{RHE} and 1.23 V_{RHE}. (c) Photocurrent-potential characteristics under chopped illumination conditions of the bare-BiVO₄, BiVO₄/SnO₂, and NiWO₄/BiVO₄/SnO₂ photoanodes (d) and its corresponding applied bias photon-to-current efficiency of NiWO₄/BiVO₄/SnO₂ photoanodes.

The plots of calculated applied bias photon to current efficiency (ABPE) with respect to applied bias are displayed in Figure 5d. While the optimum photoconversion efficiencies were only 0.01% at 0.8 V_{RHE} and 0.03% at 0.8 V_{RHE} for bare-SnO₂ and bare-BiVO₄ electrodes, correspondingly, a much higher optimal conversion efficiency of 0.08% at 0.8 V_{RHE} was attained for the BiVO₄/SnO₂ photoanode. In addition, the optimum conversion efficiency of BiVO₄/SnO₂ photoanode was further enhanced to 0.21% at 0.8 V_{RHE} by electrodeposition of NiWO₄ on the BiVO₄ surface. From these PEC investigations, it is obvious that the combination of a SnO₂ buffer layer and NiWO₄ nanoparticles synergistically improved the PEC performance enough to meet the requirements for superior efficiency as well as electrochemical stability.

Photocurrent-potential analysis was also carried out with the H₂O₂, where the charge collection efficiency can be assumed to be at its maximum. In particular, this investigation will assist us in estimating the efficiency of the NiWO₄ incorporation and subsequently assessing the charge separation (η_{CS}) as well as charge-transfer efficiencies (η_{CT}). Hence, photocurrent-potential data were acquired with and without H₂O₂ to examine the limitations of the PEC behavior of the bare-BiVO₄ and NiWO₄/BiVO₄/SnO₂ photoanodes (Figure 6a). Photocurrent-potential curves of NiWO₄/BiVO₄/SnO₂ photoanodes in the presence of H₂O₂ showed a substantial, but predicted, increase in the onset potential (~0.16 V

vs. RHE) as well as the photocurrent density ($3.1 \text{ mA} \cdot \text{cm}^{-2}$). Remarkably, these enhancements match well with the PEC performance of the triple-layered $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes (Figure 5a). These PEC comparative studies evidenced that the introduction of nanosized NiWO_4 particles is necessary to meet the requirements for superior PEC performances as well as stability.

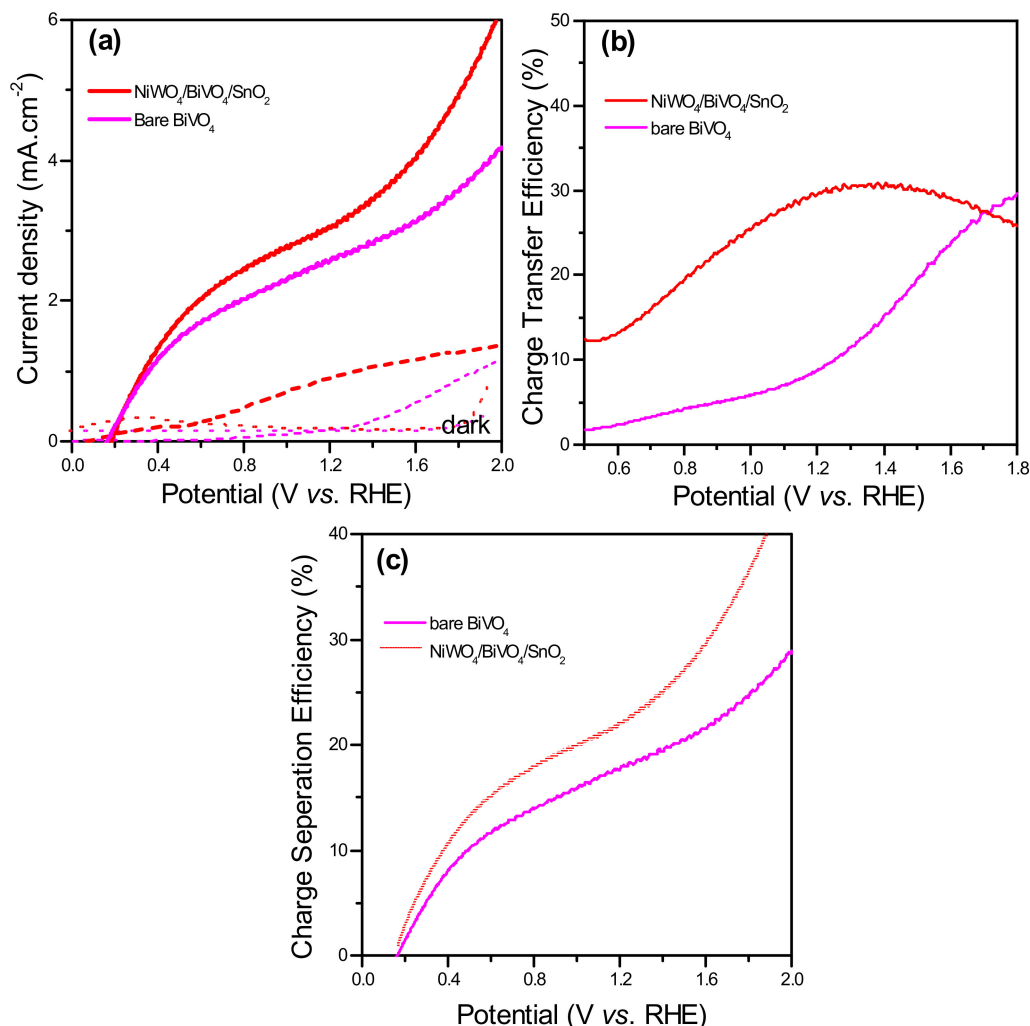


Figure 6. Photoelectrochemical (PEC) in presence of a hole scavenger (a) Comparison of the photocurrent-potential plots of the triple layered $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ films using a PBS solution (0.1 M pH 7.5) with respect to bare BiVO_4 in the presence and absence of 0.5 M H_2O_2 hole scavenger, respectively. (Solid line: with H_2O_2 ; dashed line: without H_2O_2). Calculated (b) charge-transfer efficiency (η_{CT}) and (c) charge separation efficiency (η_{CS}) versus the applied bias for the bare- BiVO_4 (red) and $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ (magenta) films.

The triple-layered $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes were further analyzed by examining their η_{CT} and η_{CS} efficiencies at different applied biases, and the results are displayed in Figure 6b,c. The bare- BiVO_4 films yielded η_{CT} values $<10\%$ (Figure 6b), even at an applied bias as high as $1.23 V_{RHE}$, where the strong electric field hampers surface recombination. After incorporation of NiWO_4 over $\text{BiVO}_4/\text{SnO}_2$, the η_{CT} of the $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ triple-layered photoanode was increased to $\sim 30\%$ at $1.23 V_{RHE}$, signifying improved charge-transfer kinetics and representing a nearly three-fold enrichment with respect to the bare- BiVO_4 . Besides, the SnO_2 buffer layer also improves the charge-transfer behavior of BiVO_4 by restricting the probable recombination that can happen at the interface between the $\text{BiVO}_4/\text{SnO}_2$ films. This behavior is consistent with the literature [41,56,57]. When the NiWO_4 layer was added between $\text{BiVO}_4/\text{SnO}_2$, the charge separation can be further enriched,

as seen from Figure 5a, where the photocurrent increased after the insertion of a NiWO_4 layer. As further evidence of this fact, the η_{CS} of the triple-layered $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ samples was assessed to be 23% at 1.23 V_{RHE} , which indicates a considerable enrichment relative to the bare- BiVO_4 photoanodes (18.2% at 1.23 V_{RHE}). The incorporation of NiWO_4 produces an energetically promising interface with BiVO_4 as well as water, as evidenced by the enriched separation efficiency. In any case, additional investigation is required to better understand this issue.

The efficient charge transfer in the fabricated samples was examined further by photoelectrochemical impedance spectroscopic (PEIS) assessment, as presented in Figure 7. The PEIS Nyquist measurements of the fabricated electrodes investigated under the irradiation conditions at 1 V_{RHE} and their resultant equivalent circuit are presented in Figure 7. Obviously, the radius of the arc of the Nyquist plots of the $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ triple-layered films is comparatively lesser with respect to those of the bare BiVO_4 and $\text{BiVO}_4/\text{SnO}_2$ films, indicating quick interfacial charge-transfer and also the effective separation of induced charge carriers. In particular, the observed constant capacitance and reduction in RCT strongly suggest that NiWO_4 assists as an energetic electrocatalytic material and thereby improves the charge-transfer kinetics and it effectively decreases surface recombination.

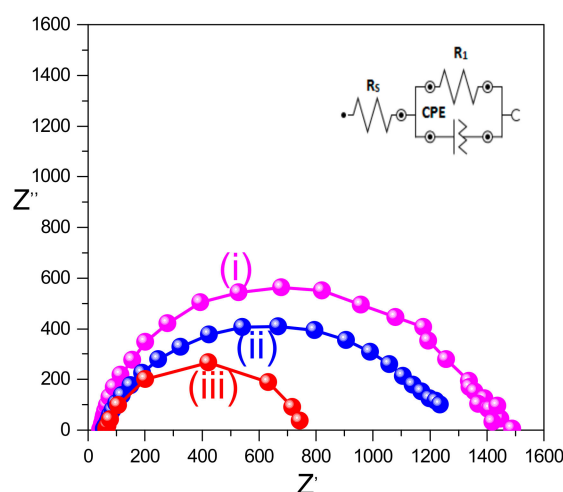


Figure 7. Impedance spectra investigation. Photoelectrochemical impedance spectroscopic (PEIS) of the (i) bare- BiVO_4 (ii) $\text{BiVO}_4/\text{SnO}_2$, and (iii) $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes. The PEIS analysis was performed at applied bias of 1.0 V_{RHE} in the frequency ranging from 100,000 Hz to 0.05 Hz and the figure inset represents the corresponding circuit for the electrodes.

The long-term stability of bare- BiVO_4 , $\text{BiVO}_4/\text{SnO}_2$, and $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes were relatively assessed in phosphate buffer solution over 3 h at 1.23 V vs RHE under constant illumination conditions and the results were shown in Figure 8. The photocurrent density of bare- BiVO_4 declined from 0.21 mA/cm^2 to 0.14 mA/cm^2 after constant illumination for 2.5 h, because the bare- BiVO_4 hurt from not only a continuous photocorrosion by means of illumination but also the chemical corrosion from H_2O_2 affected by oxygen reduction on BiVO_4 surface [34]. A similar behavior was ever observed in earlier reported studies [30,33,34]. The triple-layer films showed a considerable photocurrent density of $\sim 0.93 \text{ mA}\cdot\text{cm}^{-2}$, superior to other photoanodes, and there was certainly no apparent decay in the photocurrent, demonstrating their considerable long-term stability. After an early transient decrease of the photocurrent of triple-layered photoanodes over the course of the reaction, the photocurrent steadily improved, reaching $\sim 78\%$ of its original value in 2 h. When coating a NiWO_4 layer on $\text{BiVO}_4/\text{SnO}_2$ photoanodes, the photostability was greatly enhanced. This may have demonstrated that the photocurrent of triple layer was prone to be stable after a sharp decline in the initial 60 s. On the other hand, considerable photocurrent deterioration was noticed for the $\text{BiVO}_4/\text{SnO}_2$ film within 15 min, partially credited to the chemical nature and PEC uncertainty. The observed

photocurrent decay is credited to the photoanodic corrosion behavior of BiVO_4 , which in turn is attributed to the interfacial hole accumulation as a consequence of the sluggish transfer kinetics of interfacial holes in BiVO_4 during water oxidation. The XRD patterns of $\text{SnO}_2/\text{BiVO}_4/\text{NiWO}_4$ were acquired at 3 h to investigate the mass loss of fabricated photoanodes during the J–t measurement. The XRD pattern of $\text{SnO}_2/\text{BiVO}_4/\text{NiWO}_4$ obtained at 3 h exhibited no obvious changes in comparison with that of $\text{SnO}_2/\text{BiVO}_4/\text{NiWO}_4$ acquired before 3 h (Figure S4). Further, XPS was used to examine the surface composition of $\text{SnO}_2/\text{BiVO}_4/\text{NiWO}_4$ photoelectrodes before and after the 3 h of irradiation (Figure S5). Supplementary Figure S5 displays two main peaks with binding energies at 861.8 eV and 856.1 eV, matching well with the $\text{Ni } 2p_{1/2}$ and $\text{Ni } 2p_{3/2}$ spin-orbit peaks of the NiWO_4 phase, correspondingly [58]. Further, the W 4d peaks were considered instead of the high intensity W 4f peaks. This is because the binding energy of W 4f lies close to V 3p, and is also not very far from the Sn 4d and Bi 5d peaks. Therefore, W 4d were chosen in order to unambiguously confirm the NiWO_4 phase [59,60]. Moreover, for $\text{SnO}_2/\text{BiVO}_4/\text{NiWO}_4$ photoelectrodes, no significant change can be found from XPS spectra of the Ni, and W elements of the NiWO_4 photocatalyst before and after the irradiation. Thus the XPS investigations provide crucial information for the compositions and oxidation states of the NiWO_4 in fabricated $\text{SnO}_2/\text{BiVO}_4/\text{NiWO}_4$ photoelectrodes. The above investigation evidenced that conformal deposition of SnO_2 and incorporation of NiWO_4 cocatalyst could efficiently enhance the PEC performances and the stability of $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ triple layer photoanode.

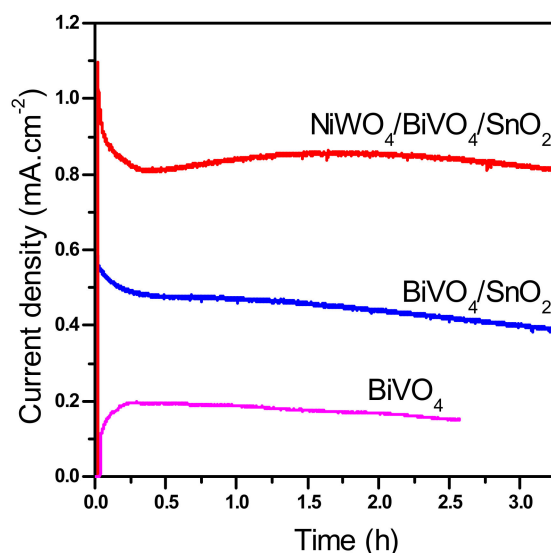


Figure 8. Long-term stability investigation. J–t curves for long-standing photostability of triple-layered $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ photoanodes (red), $\text{BiVO}_4/\text{SnO}_2$ photoanode (blue), and bare BiVO_4 (magenta) evaluated in phosphate buffer (0.1 M, pH 7.5) at $1.23 V_{\text{RHE}}$ under illumination conditions for all samples.

3. Experimental

3.1. Chemicals

Bismuth(III) nitrate [$\geq 98.0\%$], vanadyl acetylacetonate [$\geq 97.0\%$], stannous chloride ($\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.9\%$), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$) and sodium tungstate (NaWO_4 , $\geq 99.9\%$) were acquired from Aldrich.

3.2. Preparation of Photoanodes

3.2.1. Electrodeposition of SnO_2 onto FTO Substrates

In this work, electrodeposited SnO_2 nanoparticles were loaded over FTO substrates (Hartford glass $15 \Omega \cdot \text{cm}^{-2}$) by using a solution of 0.02 M $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ in EG subjected to purging under an argon

for 15 min. Afterwards, the electrochemical deposition process was performed in an undivided electrochemical cell via an Autolab PGSTAT302 potentiostat. In particular, a classical 3-electrode setup was employed, which comprised of an FTO working electrode, a Ag/AgCl (3 M KCl) reference electrode, and a Pt counter electrode. Sn was electrodeposited from the 0.02 SnCl₄·2H₂O solution by continuously applying a bias at $-2.0 V_{Ag/AgCl}$, the solution was stirred, and the electrodeposition process was iterated. This cycle was repeated for a different number of times (2 to 8 times) to pass a total charge between 200 and 800 mC·cm⁻² and control the film thickness. The resulting film was annealed in an oven at 450 °C for 1 h in air atmosphere (rate = 2 °C/min) to convert Sn into SnO₂. The optimized charge density was found to be 500 mC·cm⁻² in order to obtain a SnO₂/FTO substrate.

3.2.2. Electrodeposition of BiVO₄ onto SnO₂/FTO Substrates

Electrodeposition of BiVO₄ photoanodes over SnO₂/FTO substrates was conducted by following a previously reported process [11]. For comparison, BiVO₄/FTO electrodes were fabricated by following similar procedures.

3.2.3. Preparation of NiWO₄ on BiVO₄/SnO₂ Photoanodes

After electrodeposition of the SnO₂ and BiVO₄ films over the BiVO₄ photoanodes, NiWO₄ films were incorporated using an electrodeposition process. Initially, metallic Ni was deposited from a 20 mM NiCl₂ solution dispersed in DMSO. In particular, cathodic deposition was performed potentiostatically at $-2.0 V_{Ag/AgCl}$, and the most optimized procedure was achieved by changing the electrodeposition charge from 10 to 50 mC·cm⁻². In this regard, the best optimal charge density was assessed to be 30 mC·cm⁻². Subsequently, for the electrochemical deposition of the greatly dispersed metallic Ni particles over the BiVO₄ film, the fabricated electrode was dipped in a 20 mM Na₂WO₄·H₂O solution at 25 °C without stirring. The optimized immersion time was assessed to be 20 min to obtain triple-layered NiWO₄/BiVO₄/SnO₂ photoanodes over FTO substrates.

3.3. Materials Characterization

The morphological nature and chemical composition of the fabricated electrodes were investigated via field effect SEM (FE-SEM; JEOL JSM-7000F). DR UV-Vis spectra were measured in a Shimadzu UV-3600 spectrophotometer. XRD analysis was carried out in a Rigaku XtaLAB Mini II benchtop system. XPS measurements were carried out using an X-ray Photoelectron Spectrometer (JEOL JPS-9030, Japan) with AlK α radiation source (1486.7 eV). PEC analysis of the fabricated electrodes were performed through an electrochemical workstation (PGSTAT30) in the dark as well as under AM 1.5G simulated solar illumination. Moreover, 0.5 M H₂O₂ (30%) was used to estimate the charge collection properties of the fabricated photoanodes.

The ABPE is given by:

$$ABPE (\%) = \frac{J_{PEC} (mA/cm^2) * (1.23 - V_{bias}) V}{Pin (mW/cm^2)} \times 100$$

where J_{PEC} is the photocurrent density, V_{bias} is the applied bias, and Pin is the incident illumination power density (AM 1.5G).

4. Conclusions

In summary, we demonstrated a simple electrochemical deposition approach for developing a triple-layered NiWO₄/BiVO₄/SnO₂ electrode for PEC water oxidation reaction. The electrodeposition approach produced a highly uniform NiWO₄ layer that exhibited considerable resistance to chemical dissolution in a phosphate buffer solution. The optimized NiWO₄/BiVO₄/SnO₂ photoanodes exhibited a photocurrent density of $\sim 0.93 \text{ mA}\cdot\text{cm}^{-2}$ at 1.23 V_{RHE} and a nearly five-fold improvement in comparison with bare-BiVO₄. The charge-transfer and charge separation data, together with the PEC

measurements, demonstrated that the NiWO_4 layer boosts the photoanodic current by increasing the photon absorption nature and efficient charge separation of the BiVO_4 electrodes.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/11/879/s1>, SEM and EDAX analysis of the fabricated electrodes of SnO_2 , $\text{BiVO}_4/\text{SnO}_2$, $\text{NiWO}_4/\text{BiVO}_4/\text{SnO}_2$ electrodeposited over FTO substrates.

Author Contributions: M.N.S. and P.A. performed the experiments and wrote the manuscript. A.M.A.M. provided suggestions and assistance in experimental design. M.H. assisted in experimental work and manuscript editing.

Funding: This research was funded by King Saud University, the Vice Deanship of Scientific Research Chairs.

Acknowledgments: The authors are grateful to the Deanship of Scientific Research, King Saud University for funding through Vice Deanship of Scientific Research Chairs. The authors also thank the Deanship of Scientific Research and RSSU at King Saud University for their technical support.

Conflicts of Interest: The authors declare no conflict of interest.

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