Triple Planar Heterojunction of SnO$_2$/WO$_3$/BiVO$_4$ with Enhanced Photoelectrochemical Performance under Front Illumination

Swetha S. M. Bhat, Sol A Lee, Jun Min Suh, Seung-Pyo Hong and Ho Won Jang *

Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 08826, Republic of Korea; smjbhat@gmail.com (S.S.M.B.); leesola21@snu.ac.kr (S.A.L.); junminsuh@snu.ac.kr (J.M.S.); hong0133@snu.ac.kr (S.-P.H.)
* Correspondence: hwjang@snu.ac.kr

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Abstract: The performance of a BiVO$_4$ photoanode is limited by poor charge transport, especially under front side illumination. Heterojunction of different metal oxides with staggered band configuration is a promising route, as it facilitates charge separation/transport and thereby improves photoactivity. We report a ternary planar heterojunction photoanode with enhanced photoactivity under front side illumination. SnO$_2$/WO$_3$/BiVO$_4$ films were fabricated through electron beam deposition and subsequent wet chemical method. Remarkably high external quantum efficiency of ~80% during back side and ~90% upon front side illumination at a wavelength of 400 nm has been witnessed for SnO$_2$/WO$_3$/BiVO$_4$ at 1.23 V vs. reversible hydrogen electrode (RHE). The intimate contact between the heterojunction films enabled efficient charge separation at the interface and promoted electron transport. This work provides a new paradigm for designing triple planar heterojunction to improve photoactivity, particularly under front illumination, which would be beneficial for the development of tandem devices.

Keywords: heterojunction photoanode; photoelectrochemical; SnO$_2$/WO$_3$/BiVO$_4$; charge transfer

1. Introduction

Since we are heavily dependent on fossil fuels, harvesting clean energy in an efficient way is a pressing problem for mankind. Photoelectrochemical water splitting offers the capabilities to harness sunlight and convert it in the form of chemical storage through chemical bonds in the form of hydrogen [1–4].

Among various metal oxides such as Fe$_2$O$_3$, TiO$_2$, WO$_3$, and BiVO$_4$, BiVO$_4$ have attracted immense attention due to their promising photoelectrochemical performance, photostability, and non-toxicity [5–9]. BiVO$_4$ has been recognized as a promising photocatalyst, as it possesses a relatively small band gap. However, BiVO$_4$ suffers from low efficiency due to poor electron transport and slow water oxidation kinetics [10–12]. Therefore, various strategies have been adopted to overcome the limitations of BiVO$_4$. Doping with Mo and W, and surface modifications with co-catalysts are the most common strategies adopted to improve the water oxidation efficiencies [13–16]. The main disadvantage of BiVO$_4$ is the short electron diffusion length, ranging from 10–70 nm, which is lesser than the light absorption depth (~250 nm) [11,17,18]. The hole diffusion length of BiVO$_4$ is around 100 nm; therefore, it is of less concern. Due to short electron diffusion length, BiVO$_4$ exhibits high photocurrent density under backside illumination. Photogenerated electrons at the surface need to travel across a BiVO$_4$ film during front side illumination to reach the current collector, which usually results in bulk recombination. The tandem cells have been fabricated using BiVO$_4$ with
a superior photocurrent under back illumination [19]. Performance under backside illumination is limited due to the absorption of UV photons and blue light from the transparent conducting surface. Most of the reports on BiVO$_4$ focused on improving performance under back side illumination [20,21]. Therefore, it is necessary to fabricate BiVO$_4$ photoanode which delivers superior PEC performance during front side illumination. This would help in designing the future energy materials for the industrial scale applications.

Recently, there have been few reports of BiVO$_4$ with heterojunction showing enhanced water oxidation performance under front illumination [22,23]. A thin film of BiVO$_4$ was found to exhibit superior performance during front illumination [24]. BiVO$_4$/WO$_3$ type II heterojunctions have been intensively constructed in order to improve the light absorption capacity [25]. SnO$_2$ thin films were found to be a hole blocking layer for BiVO$_4$ [26]. Nanorods of SnO$_2$ have also been used to improve the performance of BiVO$_4$, especially under front illumination [27–29]. Double heterojunction of BiVO$_4$ with SnO$_2$ and WO$_3$ has been fabricated to achieve an unassisted water splitting reaction [30]. However, studies on heterojunction photoanodes tuning the front illumination are rarely found in the literature.

In this work, we focus on the different thickness of double heterojunction photoanode and their influence on the performance under front illumination. We have studied SnO$_2$/WO$_3$/BiVO$_4$ triple planar double heterojunction with different thicknesses and observed the change in the behavior of front illumination performance. This study would be beneficial for the construction of efficient tandem devices.

2. Experimental Section

2.1. Synthesis

Triple planar double heterojunction SnO$_2$/WO$_3$/BiVO$_4$ photoanode has been fabricated through the combination of electron beam (e-beam) deposition and metal organic decomposition (MOD) technique. A SnO$_2$ layer, followed by the deposition of a WO$_3$ layer, has been deposited on FTO (Fluorine doped Tin Oxide) by e-beam deposition with varying thicknesses, particularly 50 nm and 100 nm at the rate of 0.3–0.4 Å/s. After depositing SnO$_2$ on FTO, the samples were annealed at 450 °C for 1 h. WO$_3$ has been subsequently deposited on SnO$_2$; the samples were annealed at 500 °C for 1 h.

BiVO$_4$ has been coated on SnO$_2$/WO$_3$ according to the previous report, with slight modifications [29]. The typical procedure is as follows: A drop casting solution was prepared from (0.243 g) Bi(NO$_3$)$_3$·5H$_2$O and (0.123 g) VO(C$_5$H$_7$O$_2$)$_2$, which were dissolved in acetic acid and acetylacetone. The dark green solution was stirred for 1 h to get a transparent solution. Two drops of the 5 µL were drop casted on the SnO$_2$/WO$_3$ and followed by heating in air at 350 °C on a hot plate for two minutes. The fabricated heterojunction photoanode was annealed in the furnace at 500 °C for 3 h in air.

2.2. Materials Characterization

The phase of SnO$_2$/WO$_3$/BiVO$_4$ was confirmed by a Bruker D8 advance diffractometer, equipped with a Cu Kα source. The morphology of the SnO$_2$/WO$_3$/BiVO$_4$ photoanodes was characterized using a field-emission SEM (SU-70, Hitachi), with an acceleration voltage of 5 kV and working distance of 8 mm by field emission SEM (SU-Hitachi).

2.3. Photoelectrochemical Characterization

Photoelectrochemical performances of SnO$_2$/WO$_3$/BiVO$_4$ photoanodes were measured with a typical three electrode configuration, using an Ivium potentiostat with Pt plate as a counter electrode and Ag/AgCl as a reference electrode. A 0.5 M Na$_2$SO$_3$ with potassium phosphate buffer solution was used as the electrolyte for all the measurements. The light intensity of a solar simulator with an AM 1.5 G filter was calibrated to 1 sun (100 mW/cm$^2$), using a reference cell. Linear sweep voltammetry (LSV)
measurements were carried out by sweeping in the anodic direction with a scan rate of 20 mV/S. The incident photon to current conversion efficiency (IPCE) values were measured at 1.23 V vs. Reversible hydrogen electrode (RHE) using light source with monochromator. Electron impedance spectroscopic (EIS) measurement was conducted at 1.23 V vs. RHE with a frequency range of 10 mHz–1000 Hz in aqueous 0.5 M Na$_2$SO$_3$ with phosphate buffer.

3. Results and Discussion

SnO$_2$/WO$_3$/BiVO$_4$ photoanode was fabricated through the combination of e-beam deposition and MOD method. First, SnO$_2$ was deposited on FTO with 50 and 100 nm thickness. The obtained samples were annealed at 450 $^\circ$C for 1 h. WO$_3$ was deposited on SnO$_2$/FTO using the same technique, followed by annealing at 500 $^\circ$C for 1 h. BiVO$_4$ was coated on SnO$_2$/WO$_3$ using the well-known MOD technique. X-ray diffraction patterns shown in Figure 1a confirm the formation of pure phases of SnO$_2$, WO$_3$, and BiVO$_4$. SEM images in Figure 1b–g reveal the morphology of triple planar heterojunction photoanode. As is clearly evident from the SEM images, the triple layers are intact with each other. There was no obvious change in the morphology of SnO$_2$/WO$_3$/BiVO$_4$ after inserting the WO$_3$ layer.

![Figure 1](image-url).

**Figure 1.** (a) XRD patterns of SnO$_2$/WO$_3$/BiVO$_4$. Scanning electron microscopic (SEM) top images of (b) SnO$_2$ 50 nm/WO$_3$ 100 nm/BiVO$_4$, (c) SnO$_2$ 50 nm/WO$_3$ 50 nm/BiVO$_4$, (d) SnO$_2$ 100 nm/WO$_3$ 50 nm/BiVO$_4$. SEM cross-section images of (e) SnO$_2$ 50 nm/WO$_3$ 100 nm/BiVO$_4$ on FTO substrate (f) SnO$_2$ 50 nm/WO$_3$ 50 nm/BiVO$_4$ (g) SnO$_2$ 100 nm/WO$_3$ 50 nm/BiVO$_4$.

Photoelectrochemical properties of triple planar heterojunction were evaluated in three electrode configurations, using aqueous Na$_2$SO$_3$ with buffer solution as electrolyte (pH 7). Figure 2a presents...
LSV diagrams of SnO$_2$/WO$_3$/BiVO$_4$ photoanode under one sun illumination. The photocurrent obtained from front and back illumination behavior was compared for different thicknesses of SnO$_2$. We have noticed that the photocurrent obtained from front and back illumination varies with the thickness of SnO$_2$ and WO$_3$. Among various thicknesses of SnO$_2$ and WO$_3$ in SnO$_2$/WO$_3$/BiVO$_4$, SnO$_2$ 50 nm/WO$_3$ 50 nm/BiVO$_4$ triple planar heterojunction exhibits superior performance compared to SnO$_2$ 100 nm/WO$_3$ 50 nm/BiVO$_4$, and SnO$_2$ 50 nm/WO$_3$ 100 nm/BiVO$_4$. SnO$_2$ 50 nm/WO$_3$ 50 nm/BiVO$_4$ shows photocurrent density of ~2.01 mA/cm$^2$ at 1.23 V under front side illumination, while the photocurrent during back illumination is 1.80 mA/cm$^2$. As the thickness of WO$_3$ increases to 100 nm, photocurrent density decreases. However, SnO$_2$ 50 nm/WO$_3$ 100 nm/BiVO$_4$ shows a high photocurrent under front illumination compared to its back illumination. It is interesting to note that the behavior of the front and back illumination is unaffected by increasing the thickness of WO$_3$. Figure 2b presents the LSV of SnO$_2$ 50 nm/BiVO$_4$ under directional illumination. SnO$_2$/BiVO$_4$ photoanode shows ~1.2 mA/cm$^2$ at 1.23 V during backside illumination, while it shows a photocurrent density of ~0.5 mA/cm$^2$ under front side illumination. Photoelectrochemical properties of heterojunction SnO$_2$ 50 nm/WO$_3$ 50 nm are shown in Figure 2c.

Figure 2. (a) LSV of SnO$_2$/WO$_3$/BiVO$_4$ under front (F) and back (B) illumination; (b) Photocurrent density under back and front illumination for SnO$_2$/BiVO$_4$ in comparison with SnO$_2$/WO$_3$/BiVO$_4$; (c) LSV of SnO$_2$/WO$_3$ photoanode measured using a three-electrode configuration set up in aqueous phosphate buffer (pH 7.0) with 0.5 M Na$_2$SO$_3$.

LSV of SnO$_2$/WO$_3$/BiVO$_4$ photoanode has been carried out in the absence of a hole scavenger, which is shown in Supplementary Material Figure S1a. SnO$_2$/WO$_3$/BiVO$_4$ shows a reasonably good photocurrent of 1.5 mA/cm$^2$ under front illumination at 1.23 V vs. RHE. The typical transient photo response was shown in Supplementary Material Figure S1b under chopped illumination. The instantaneous photocurrent under illumination corresponds to the immediate hole arrival at
the surface. It is interesting to note that the transient photocurrent spikes are suppressed in the LSV and also in the stability measurement under chopped illumination. Usually, spikes in the transient photocurrent measurements indicate surface recombination, due to the presence of the surface states or slow water oxidation kinetics. SnO$_2$/WO$_3$/BiVO$_4$ photoanode shows negligible spikes and a steady photocurrent, which demonstrates that the holes accumulated at the surface readily react with the water and hence improve photocurrent density without producing transient spikes [31].

Further, charge transfer properties have been investigated by Nyquist plots. Figure 3 depicts the Nyquist plots of SnO$_2$/WO$_3$/BiVO$_4$ photoanodes. EIS were measured at 1.23 V vs. RHE under 1 Sun illumination. Nyquist plots were fitted with the equivalent circuit, using Zview software; they are presented in Figure 3 and Supplementary Material S2. Parameters extracted from the Nyquist plots are listed in Supplementary Material Table S1. In the equivalent circuit, $R_s$ represents solution resistance, and $R_{ct}$ can be ascribed to charge transfer resistance at the electrode/electrolyte interface. Generally, a smaller semicircle represents the higher ability of charge transfer property of the photoanode. It is clearly evident from Figure 3 and Table S1 that the charge transfer resistance for SnO$_2$ 50 nm/WO$_3$ 50 nm/BiVO$_4$ is lesser than that of SnO$_2$ 50 nm/BiVO$_4$ and other thicknesses of SnO$_2$/WO$_3$/BiVO$_4$ photoanodes. It demonstrates that, as the SnO$_2$/WO$_3$ layer is introduced beneath the BiVO$_4$ layer, the charge transfer resistance dramatically decreases compared to the pristine BiVO$_4$. This trend is in line with pce performance. As the thickness of WO$_3$ and SnO$_2$ increases from 50 nm, the electrical resistance increases. It indicates that the SnO$_2$ 50 nm/WO$_3$ 50 nm/BiVO$_4$ has high charge separation efficiency and high water oxidation kinetics.

![Figure 3.](image)

Figure 3. (a) Electron impedance spectra (EIS) of SnO$_2$/WO$_3$/BiVO$_4$; (b) Zoomed region of EIS spectra of (a) for SnO$_2$/WO$_3$/BiVO$_4$ photoanode, measured using a three-electrode configuration set up in an aqueous phosphate buffer (pH 7.0) with 0.5 M Na$_2$SO$_3$ at 1.23 V vs. Reversible hydrogen electrode (RHE).

The stability of SnO$_2$ 50 nm/WO$_3$ 50 nm/BiVO$_4$ has been measured in the three electrode configuration and presented in Figure 4a. It shows considerably good stability for 5 h, with negligible decrease in the photocurrent. Post mortem analysis was carried out to investigate any change in the morphology of SnO$_2$/WO$_3$/BiVO$_4$ photoelectrode (Figure S3) after photostability measurement. As is evident from the SEM images of SnO$_2$/WO$_3$/BiVO$_4$ (Figure S3), no serious damage to the morphology of the photoelectrode was found after photostability measurement. This result aligns with the previous reports that the photoelectrode used for the sulfite oxidation shows considerable photostability, although there could be slight dissolution of V$^{5+}$ from BiVO$_4$ [32,33]. In the present case, photostability has been studied for sulfite oxidation, as sulfite ions quickly consume the holes available on the surface of BiVO$_4$, it does not allow holes to accumulate and trigger the photoanodic corrosion of BiVO$_4$ very easily. It is also reported that the high quality BiVO$_4$ can show the photostability of 500 h without undergoing any major compositional and morphological changes [32]. In addition, the WO$_3$/BiVO$_4$ system also exhibits considerable photostability [34]. Therefore, it is quite obvious
that there is no significant change in the morphology of SnO$_2$/WO$_3$/BiVO$_4$ photoelectrode after 5 h of photostability measurement.

![Figure 4](image_url)

**Figure 4.** (a) Stability measurement for SnO$_2$/WO$_3$/BiVO$_4$; (b) Incident photon to current conversion efficiency (IPCE) of SnO$_2$/WO$_3$/BiVO$_4$ photoanode measured using a three-electrode configuration set up in an aqueous phosphate buffer (pH 7.0) with 0.5 M Na$_2$SO$_3$ at 1.23 V vs. RHE.

IPCE of SnO$_2$/WO$_3$/BiVO$_4$ photoanode is shown in Figure 4b. Remarkably high external quantum efficiency of ~80% during back side and ~90% upon front side illumination has been witnessed for SnO$_2$/WO$_3$/BiVO$_4$ at 1.23 V vs. RHE. The photocurrent obtained by integrating the IPCE spectra (1.5 mA/cm$^2$) is found to be in consistent with that of LSV photocurrent density. This is the highest IPCE value obtained for SnO$_2$/WO$_3$/BiVO$_4$ photoanode to date.

Previous report demonstrated that the photoelectrochemical property of WO$_3$/SnO$_2$/BiVO$_4$ is inferior to that of SnO$_2$/WO$_3$/BiVO$_4$ [30]. Therefore, we have restricted our study only to the SnO$_2$/WO$_3$/BiVO$_4$ system. It is known from the literature that introducing SnO$_2$ under the BiVO$_4$ layer enhances pec performance [26–28]. The SnO$_2$ layer enhances the charge transfer properties of BiVO$_4$ by suppressing the possible recombination that can occur at the interface of SnO$_2$/BiVO$_4$. When the WO$_3$ layer is introduced between SnO$_2$/BiVO$_4$, the charge separation can be further enhanced, as seen from Figure 2a, where the photocurrent increased after the insertion of WO$_3$ layer. It is evident from the published results that the heterojunction of nanostructured WO$_3$/BiVO$_4$ performs better than either of the individual materials due to the formation of type II heterojunction [35,36]. Since the band positions of both materials are suitable to construct type II heterojunction, significant separation of the photogenerated electron hole pairs can be achieved to enhance pec performance. The photogenerated electrons are transferred from BiVO$_4$ to WO$_3$, which has excellent electron transport property compared to BiVO$_4$. While WO$_3$ improves the electron transport properties, BiVO$_4$ enhances the overall optical property of WO$_3$ in heterojunction of SnO$_2$/WO$_3$/BiVO$_4$. It is also proved in the literature that the lifetime of the photogenerated holes increases in the heterojunction compared to the individual material [37]. However, the photoelectrochemical enhancement in WO$_3$/BiVO$_4$ is limited by the efficient transfer of the electrons from WO$_3$ to BiVO$_4$. From this point of view, the double heterojunctions of SnO$_2$/WO$_3$/BiVO$_4$ would certainly enhance pec performance, as can be seen from the LSV curves of SnO$_2$/WO$_3$/BiVO$_4$. The schematic diagram depicting the mechanism of water splitting is demonstrated in Figure 5.
Figure 5. Schematic diagram for SnO$_2$/WO$_3$/BiVO$_4$, depicting the mechanism of water splitting.

Band alignments of double heterojunction SnO$_2$/BiVO$_4$ also improves separation efficiency due to the lower laying valence band position [27,38,39]. Charge carrier transport has been depicted in Figure 5 for SnO$_2$/WO$_3$/BiVO$_4$, which has been constructed according to the previous report [30]. The band positions have been adopted from the recent works on SnO$_2$/WO$_3$/BiVO$_4$ which were determined by ultraviolet photoelectron spectroscopy and optical band gap [30,40,41]. The described band position and electron transfer in type II heterojunction, as shown in Figure 5, match well with the reported literature [36,42]. All the three layers form staggered band alignment and thereby achieve type II heterojunction, facilitating the efficient charge transport across the interface. The improved pce performance of this double heterojunction proves that there is an intimate contact between the two layers.

Unlike the previous report on SnO$_2$/WO$_3$/BiVO$_4$ heterojunction, this work sheds light on photocurrent behavior under directional illumination [30]. It can clearly be seen that the performance under front and back illumination has improved after the fabrication of SnO$_2$/WO$_3$/BiVO$_4$ double heterojunction. It is known that the directional dependent photoelectrochemical properties are governed by the electron transport efficiency of the materials, along with the morphology of the nanostructure [22]. In the present study, all three layers are planar and hence the directional photoelectrochemical property could be decided by both the electron transport property and the thickness of the heterojunction. The photoelectrochemical performance under front side illumination can easily be realized if the thickness is less than 100 nm, which is very close to the hole diffusion length. In the case of SnO$_2$/WO$_3$/BiVO$_4$, introducing SnO$_2$ is advantageous, as it forms cascade alignment of the band positions. The electron-hole transport also improves as the SnO$_2$ layer acts as a hole mirror. The middle layer WO$_3$ in SnO$_2$/WO$_3$/BiVO$_4$ helps effectively in charge transport, which results in improved photoactivity of BiVO$_4$. It is observed from SnO$_2$/BiVO$_4$ heterojunction that the performance under back illumination enhances, while in SnO$_2$/WO$_3$/BiVO$_4$ front illumination the photocurrent is increased compared to that of back illumination. This change in the performance under directional illumination could be due to the insertion of the WO$_3$ layer. In the case of SnO$_2$/BiVO$_4$ heterojunction, majority carrier transportation was limited and hence the photogenerated electron at the interface can easily reach the contact without undergoing recombination under back illumination. However, when the WO$_3$ layer is introduced between SnO$_2$/BiVO$_4$ heterojunction, photocurrent density behavior
changes. WO$_3$ improves charge separation efficiency, as demonstrated by previous reports [43]. Adding SnO$_2$/WO$_3$ beneath the BiVO$_4$ effectively reduces carrier recombination. Performance under front illumination is enhanced in SnO$_2$/WO$_3$/BiVO$_4$, as the hole blocking layer prevents recombination. Therefore, photogenerated holes at the surface are effectively extracted to electrolyte for water oxidation while it facilitates electron diffusion to the back contact without being vulnerable to recombination. Therefore, the front illumination photocurrent has been enhanced in SnO$_2$/WO$_3$/BiVO$_4$.

4. Conclusions

SnO$_2$/WO$_3$/BiVO$_4$ planar heterojunction has been fabricated through a combination of the e-beam deposition method and the MOD technique. Photocurrent behavior under back and front illumination was studied for different layers of SnO$_2$/WO$_3$/BiVO$_4$ planar heterojunction. When a WO$_3$ layer was introduced between SnO$_2$/BiVO$_4$, photocurrent density under front illumination increased compared to that under back illumination. This indicates that poor charge carrier transport property of BiVO$_4$ can be successively suppressed by triple planar double heterojunction. By inserting WO$_3$ in SnO$_2$/BiVO$_4$, the charge transport property was improved considerably. Remarkably high IPCE of ~80% during back side and ~90% upon front side illumination was witnessed for SnO$_2$/WO$_3$/BiVO$_4$ at 1.23 V vs. RHE. This study gives insights to tuning photocurrent density under directional illumination by constructing triple planar double heterojunction.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/8/10/1765/s1, Figure S1: (a) LSV of SnO$_2$/WO$_3$/BiVO$_4$ measured using a three-electrode configuration in aqueous phosphate buffer (pH 7.0) with 0.5 M Na$_2$SO$_4$ in the absence of a hole scavenger. (b) LSV of SnO$_2$/WO$_3$/BiVO$_4$ in an aqueous phosphate buffer (pH 7.0) with 0.5 M Na$_2$SO$_4$ under chopped illumination. (c) Stability measurements of SnO$_2$/WO$_3$/BiVO$_4$ under chopped illumination in an aqueous phosphate buffer (pH 7.0) with 0.5 M Na$_2$SO$_4$, Figure S2: Equivalent circuit model of Nyquist plot for SnO$_2$/WO$_3$/BiVO$_4$ photoanode, Figure S3: SEM images of SnO$_2$/WO$_3$/BiVO$_4$ (a) before and (b) after photostability measurement, Table S1: Nyquist plot fitted results for SnO$_2$/WO$_3$/BiVO$_4$ photoanode.

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