Extending the Absorption Limit of BiVO₄ Photoanodes with Hydrogen Sulfide Treatment

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Bismuth vanadate is a promising photoanode material for photoelectrochemical water splitting due to its relative stability, low cost, and nontoxic properties. However, its performance is limited by the large bandgap (E₉) of 2.4 eV, and the record photocurrent is already within 90% of its theoretical limit. Further photocurrent enhancement could only be obtained by increasing its optical absorption, for example, by reducing E₉. Herein, sulfur-incorporated bismuth vanadate (S-BiVO₄) thin films are synthesized via spray pyrolysis combined with post-treatment in hydrogen sulfide environment. Under optimal H₂S treatment conditions, sulfur can be incorporated successfully into the BiVO₄ lattice, without the formation of any secondary phases. The use of reactive H₂S, instead of solid sulfur powders, allows us to decrease the required annealing temperature and increase the kinetics for sulfur incorporation into BiVO₄. The E₉ of the resulting S-BiVO₄ films is decreased by >200 meV (vs. pristine BiVO₄), which theoretically corresponds to a 20% increase in the theoretical photocurrent limit. Finally, the stability limitation of S-BiVO₄ is overcome by introducing pulsed-laser-deposited NiOₓ protection layers. The modified S-BiVO₄/NiOₓ film exhibits higher photocurrent density with no reduction of photocurrent during the 9 h stability test with AM1.5 illumination.

1. Introduction

The generation of hydrogen via photoelectrochemical (PEC) water splitting is among the promising approaches to fulfill the energy transition toward renewables.[1–2] The process uses semiconductors with suitable band-edge positions as photoelectrodes.[3] These semiconductors should also ideally be low cost, nontoxic, and stable when immersed in aqueous solutions. Mechanistically, when the semiconductor is illuminated with light, the photogenerated charge carriers, that is, electrons and holes, participate in the reduction and oxidation half reactions at the cathode and anode, respectively.[4] Water oxidation with its four-proton-coupled electron transfer pathway is kinetically the more difficult of the half reactions; more focus has therefore been placed on the fabrication of highly efficient photoanode materials. To this end, due to the high defect tolerance,[5] BiVO₄ has emerged as an interesting and exciting photoanode material. BiVO₄ photoanodes with photocurrents reaching ≈90% of the theoretical maximum have been reported, and PEC water-splitting devices based on BiVO₄ already demonstrate solar-to-hydrogen (STH) efficiencies as high as ≈8%.[6,7] The current performance is therefore limited by its relatively wide bandgap of 2.4–2.5 eV.[8]

To increase the photocurrent further, the optical absorption of BiVO₄ needs to be extended. The valence band maximum (VBM) of BiVO₄ is mainly composed of O 2p orbitals and the conduction band minimum (CBM) consists of mainly V 3d orbitals.[9,10] Therefore, the bandgap of BiVO₄ can be modified in two ways: 1) an upward shift of the VBM by an appropriate anion substitution or 2) a downward shift of the CBM by suitable cation substitution. As the CBM is already positioned close to the water reduction potential, the more appropriate approach is to shift the VBM. Efforts on tuning the valence band position of BiVO₄ by nitrogen incorporation have been reported, but only minimal band gap reduction was demonstrated.[8,11] On the other hand, sulfur incorporation results in a bandgap reduction of ≈0.3 eV as well as enhanced charge carrier dynamics.[12] Similar effects have also been reported in other sulfur-incorporated metal oxides (e.g., TiO₂, WO₃, Fe₂O₃, CsTaWO₄).[13–17] However, in the case of sulfur-incorporated BiVO₄, PEC measurements oxidized the sample and sulfur atoms leached out from the BiVO₄ films.
As a result, the improved optoelectronic properties with sulfur incorporation could not be translated into higher PEC performance.

To overcome the stability limitation, a protection layer is required that inhibits the direct exposure of the film to the electrolyte.[18,19] This approach has indeed been reported for various metal sulfides.[20,21] Among the many materials used as protection layers, NiO, is promising to be used on photoanodes due to its p-type characteristic, optical transparency due to the wide bandgap > 3 eV, and high stability.[18,22,23] It has also relatively good catalytic activity for water oxidation, which means that it can serve well as both a protection layer[22] and a cocatalyst. Here, we deposit a thin NiO layer using pulsed laser deposition (PLD) on sulfur-incorporated BiVO₄ films to address the instability issue. As a result, a stable AM1.5 photocurrent of ∼1.7 mA cm⁻² is demonstrated for 9 h at an applied potential of 1.23 V versus reversible hydrogen electrode (RHE). In addition, in contrast to previous reports,[12] we utilize postdeposition annealing in hydrogen sulfide (H₂S) atmosphere in this study to incorporate sulfur into BiVO₄ films. This is advantageous versus treatment using, for example, sulfur powder, because the higher reactivity of H₂S allows for incorporation at lower temperature with faster kinetics. The optoelectronic properties of these S-BiVO₄ films and their tunability will also be discussed.

2. Results and Discussion

A series of sulfur-incorporated bismuth vanadate thin films were first synthesized by spray pyrolysis using a reported procedure,[24] followed by post-deposition annealing in H₂S. Figure 1a shows the X-ray diffractograms (XRD) of BiVO₄ films that were annealed under 5% H₂S/Ar flow for 20 min at different temperatures from 100 to 300 °C. All films show a pure BiVO₄ monoclinic phase, matching well with JCPDS Card No. 14-0688, but the film annealed at 300 °C also shows the presence of a Bi₂S₃ phase. Postdeposition annealing treatments at different concentrations of H₂S and for longer durations were also performed, and the phases identified are summarized in Table S1, Supporting Information. We limit our discussions in the manuscript to films annealed in 5% H₂S/Ar in which no Bi₂S₃ phase segregation is observed. It can be deduced from Table S1, Supporting Information, that sulfur incorporation via H₂S treatment is highly sensitive to the reaction temperature.

Raman spectra of the films annealed in 5% H₂S/Ar for 20 mins were also recorded, which are shown in Figure 1b. For films annealed at 250 °C or lower, vibrational bands at wavenumbers 126, 212, 327, 369, 637, 707, and 827 cm⁻¹ are observed, which can be assigned to the vibrational modes of the monoclinic BiVO₄ phase.[26] However, prominent additional peaks at wavenumbers 187, 237, and 260 cm⁻¹ can be observed for the film annealed at 300 °C. These peaks can be attributed to the Bi₂S₃ phase.[27] This observation agrees very well with the XRD results.

The optical properties of the films were investigated by UV–vis absorption spectroscopy measurements. A redshift of the absorption onset is observed for the H₂S-treated samples (Figure S1, Supporting Information). A similar absorption trend is reported in literature for S-incorporated BiVO₄ powder by the hydrothermal method.[28] Tauc plots were derived from the absorption spectra to evaluate the bandgap (Figure S2, Supporting Information). The derived bandgaps of all the films are depicted in Figure 2, clearly indicating that the H₂S treatment decreases the bandgap of BiVO₄ films. A bandgap shift of larger than 200 meV, for the indirect bandgap, is obtained at temperatures higher than 200 °C. Such a bandgap shift corresponds to ~20% increase in the theoretical AM1.5 photocurrent density limit. This bandgap reduction is confirmed to originate from an upward shift of the VBM upon sulfur incorporation. Figure 2b shows the VB spectra of pristine and H₂S-treated BiVO₄ measured with hard X-ray photoelectron spectroscopy (HAXPES), using a photon energy of 6 keV (see Experimental Section). Indeed, the VBM of the H₂S-treated film is shifted closer to the Fermi level by ~200 meV as compared with the pristine BiVO₄, which agrees very well with the bandgap shift.

To determine the concentration of sulfur in the films, bulk-sensitive X-ray fluorescence (XRF) and surface-sensitive X-ray photoelectron spectroscopy (XPS) measurements were carried out. Figure 3 depicts the sulfur-to-vanadium (S/V) atomic ratio of the various films, determined from the XRF and XPS data. Both measurements show increasing S/V atomic ratio with increasing H₂S annealing temperature. However, the values

![Figure 1](https://example.com/figure1.png)

**Figure 1.** a) XRD and b) Raman spectra of a pristine BiVO₄ film and BiVO₄ films that undergo postdeposition annealing in 5% H₂S/Ar for 20 min at different temperatures. The star (*) symbols identify peaks and wavenumbers corresponding to Bi₂S₃, indicating phase segregation.
obtained from XPS are consistently higher than those obtained from XRF. For example, XRF data indicate that the film annealed at 250 °C has an S/V atomic ratio of 0.2, but XPS quantification indicates a much higher value of 1.5. This suggests that a sulfur gradient exists from the surface to the bulk of the films.

Upon establishing the bandgap reduction and the presence of sulfur in the films, we now proceed to more detailed discussions of the impact of H2S annealing on the properties of BiVO4. From this point onward, we will evaluate and compare the pristine film and the one that underwent postdeposition annealing treatment in 5% H2S/Ar at 250 °C for 20 min; for brevity, these two films will be referred to as “BiVO4” and “S-BiVO4,” respectively.

The chemical nature of BiVO4 and S-BiVO4 films was determined by XPS. As expected, we do not observe any peak in the S 2s core-level spectrum of the BiVO4 film, while the S-BiVO4 film shows a clear presence of a peak (see Figure 4a). The peak for S-BiVO4 can be deconvoluted into two components: one at a binding energy of 225.4 eV (≈83%), which corresponds to S2−, and another component at 227.6 eV (≈17%), which can be attributed to the loosely bound sulfur at the surface.[29] The fact that the majority of sulfur is in the S2− oxidation state further supports that the incorporation of sulfur occurs via the substitution of O2− in the BiVO4 lattice.

Figure 4b shows the Bi 4f core-level spectra, which consist of peaks with a spin–orbit splitting of 5.3 eV. The peaks are located at the binding energies of 164.3 and 159 eV (labeled as Bi–O) and correspond to Bi 4f5/2 and Bi 4f7/2, respectively.[30] However, the S-BiVO4 film shows additional components at 163.6 and 158.3 eV (labeled as Bi–S). We attribute these peaks to the presence of Bi–S bonding,[31] although peaks at this binding energy range have also been attributed to reduced Bi.[32–35] The ratio of Bi–O-to-Bi–S peak in the S-BiVO4 film is 1:0.9. Besides this, small peaks can be observed at the binding energies of 162.1 and 160.9 eV. These peaks correspond to S 2p1/2 and 2p3/2 and the position is again in agreement with sulfur being in the S2− oxidation state.[36]

Figure 4c shows the V 2p core-level spectrum of BiVO4 film shows two peaks due to the spin–orbit splitting (see Figure 4c). The peaks located at the binding energies of 516.6 eV and 524.0 eV correspond to V 2p3/2 and 2p1/2, respectively. These peaks can be fitted each with a single component, showing that V is present in a single oxidation state, that is, +5.[36] However, the V 2p spectrum of S-BiVO4 film can be deconvoluted into two components. Like pristine BiVO4, the peak located at 516.6 eV binding energy can be assigned to +5 oxidation state and the one at 515.4 eV corresponds to +4 oxidation state.[32–33] The ratio of V5+ to V4+ components in the film is 1:0.4. We speculate that this reduction to V4+ is related
to the conversion of H₂S to S on the surface of BiVO₄, as it has indeed been reported that vanadium-based mixed oxide (including BiVO₄) acts as a good catalyst for this conversion. In short, a redox reaction takes place between metal oxide and H₂S, resulting into the reduction of metal ions (vanadium, in our case) and the oxidation of H₂S to S. Figure 4c also shows the O 1s spectrum, being composed of two peaks. The peak at 529.7 eV binding energy corresponds to lattice oxygen (labeled as O-latt.) while the peak at 531.4 eV corresponds to the adsorbates like OH, CO, etc. (labeled as O-ads.). In the case of S-BiVO₄ film, the O-ads. peak becomes more pronounced, which may be related to the reduction of V and Bi atoms (see above). Overall, it can be concluded that H₂S treatment of the BiVO₄ film results in partial reduction of the metal ions along with S incorporation.

We now turn our attention to the effect of H₂S treatment on the photovoltaic (Δ ) and charge carrier dynamics of BiVO₄. Time-resolved microwave conductivity (TRMC) measurements were performed, and the peak of photovoltaic change (Δ ), which is related to the charge carrier mobility, is plotted as a function of the excitation wavelength to generate the photoconductivity action spectra (PCAS) as shown in Figure 5a. For comparison, the values were normalized to the maximum value, which in this case is the value for pristine BiVO₄ at 470 nm. While the Δ of S-BiVO₄ is significantly lower than that of BiVO₄, the PCAS onset for S-BiVO₄ is extended to 700 nm versus 520 nm for BiVO₄. These onset values match well with the absorption onset, suggesting that sulfur incorporation by H₂S treatment has indeed extended the absorption limit as well as the threshold for generating mobile carriers in BiVO₄ film. Figure 5b shows the normalized photoconductivity (Δ/Δ) of BiVO₄ and S-BiVO₄ film as a function of time. The two curves show the same decay profile, indicating that the lifetime of charge carriers is unaffected by the H₂S treatment.

We note that the impact of sulfur incorporation in this study on Δ—which again is a measure of charge carrier mobility—is different compared with our previous study where S-BiVO₄ films were obtained via annealing in an S-rich environment (i.e., not H₂S). In that case, S-BiVO₄ films were shown to possess higher charge carrier mobility than BiVO₄ films.

Figure 4. a) S 2s, b) Bi 4f, and c) O 1s + V 2p core-level X-ray photoelectron spectra of BiVO₄ films and S-BiVO₄ films. The S-BiVO₄ films were synthesized by annealing the BiVO₄ film in 5% H₂S gas atmosphere at 250 °C for 20 min.

Figure 5. a) PCAS as a function of laser excitation wavelength taken at the absorbed photon intensity of ≈3 × 10¹³ cm⁻² and b) normalized photoconductivity measured as a function of time with a nanosecond pulsed laser of 420 nm wavelength and intensity of ≈4.0 × 10¹² cm⁻² for BiVO₄ and S-BiVO₄ films deposited on quartz substrates.
Nevertheless, the H₂S treatment in the current study is much more effective in extending the photocactivity onset; annealing in an S-rich environment only shifts the onset to \( \approx 580 \text{ nm} \), while annealing in H₂S results in an onset shift up to \( \approx 700 \text{ nm} \). We speculate that this variation of photocactivity onset is related to the way that sulfur atoms are configured inside the BiVO₄ lattice. Indeed, we have shown in our previous study through density functional theory (DFT) calculations that the configuration of sulfur incorporation (i.e., well-dispersed pairing, around Bi, around V, linear, or random) largely affects the electronic bandgap. At the same time, H₂S treatment seems to introduce higher degree of cation reduction in BiVO₄ (e.g., from V⁵⁺ to V⁴⁺) than annealing in an S-rich environment; this may be the reason behind the lower charge carrier mobility. Overall, this suggests that the intricacy of sulfur incorporation and its effect on the electronic structure of BiVO₄ is very much dependent on the postannealing environment and the sulfur source.

The PEC properties of the films were characterized by performing chopped linear scan voltammetry (LSV) in 0.1 M potassium phosphate buffer (KPi) at pH 7 under back-side AM1.5 illumination. A photocurrent density of \( \approx 1.1 \text{ mA cm}^{-2} \) at 1.23 V versus RHE was obtained for the S-BiVO₄ films (see red curve in Figure 6a). However, the photocurrent decreases in the subsequent LSV cycles (see Figure S3, Supporting Information), suggesting that the films are unstable during PEC measurements. Indeed, chronoamperometric measurements reveal that the photocurrent density decreases from 1.5 to \( \approx 0.4 \text{ mA cm}^{-2} \) within 20 min (see Figure 6b). We attribute this photocurrent decrease to the (photo)electrochemical oxidation of S-BiVO₄ film back to BiVO₄ and removal of sulfur from the films. This is supported by the observation that the color of the films turns back to yellow after PEC measurement, just like the films prior to H₂S treatment (see Figure S4a,b, Supporting Information). Indeed, no sulfur peak can be detected during the XPS measurement of the sample after PEC measurement (see Figure S5, Supporting Information), and the LSV curve shows similar photocurrents to that of non-H₂S-treated BiVO₄ films (see Figure S6, Supporting Information). Similar behavior has been reported earlier for S-incorporated BiVO₄ films and sulfide semiconductors.[12,21]

To prevent this unfavorable reoxidation and extend the stability of the S-BiVO₄ films, we deposited a 20 nm-thick hole-conducting NiOₓ protection layer using PLD (see Experimental Section for detailed procedures). The PLD process was done at lower oxygen partial pressure in order to prevent the oxidation of S-BiVO₄ during deposition. Following the activation of the film (see Figure S7, Supporting Information), as is typical for the nickel oxide-based catalyst,[39,40] the modified film (S-BiVO₄/NiOₓ) was subjected to the same chopped LSV measurements under AM1.5 illumination. A photocurrent density of \( \approx 1.7 \text{ mA cm}^{-2} \) was obtained at 1.23 V versus RHE (see Figure 6a), which is higher than that obtained with the bare S-BiVO₄ film.

More importantly, the NiOₓ-coated film demonstrates superior stability. Chronoamperometric measurement was performed for 9 h—again, following the activation step—and the photocurrent density remains relatively stable at \( \approx 1.5 \text{ mA cm}^{-2} \) (see Figure 6c). Note that the minor current fluctuations observed after every \( \approx 100 \text{ min} \) are caused by the accumulation and release of oxygen bubbles from the surface of the film. No noticeable change is observed in the color of the film before and after PEC measurements (see Figure S4c,d, Supporting Information), indicating that the NiOₓ protection layer has prevented the reoxidation of the S-BiVO₄ film. Chopped LSV measurement after the chronoamperometric measurement also results in no degradation of photocurrent (see Figure S8, Supporting Information). Overall, these results demonstrate that NiOₓ can act as an effective protection layer for S-BiVO₄ photoanodes.

### 3. Conclusion

In summary, we have incorporated sulfur into BiVO₄ films by performing postdeposition annealing under the continuous flow of hydrogen sulfide. Under optimum annealing conditions (temperature, pressure, and time), the formation of a secondary phase (e.g., Bi₂S₃) can be avoided and sulfur can be largely

![Figure 6](image-url)

**Figure 6.** a) Chopped voltammogram of S-BiVO₄ and S-BiVO₄/NiOₓ recorded in 0.1 M potassium phosphate buffer (KPi) pH 7 under AM 1.5 back illumination with 2 s intervals. Photocurrent response \((i-t)\) curve of b) S-BiVO₄ and c) S-BiVO₄/NiOₓ films, derived from the chronoamperometric data of the films carried out at 1.23 V versus RHE in 0.1 M potassium phosphate buffer (KPi) at pH 7 with chopped AM1.5 back illumination with 10 s intervals.
introduced to substitute oxygen in the lattice of BiVO₄. The optical absorption onset of these sulfur-incorporated BiVO₄ (S-BiVO₄) films is red shifted to 700 nm, which is caused by the upward shift of the VBM, as shown by HAXPES data. TRMC analysis reveals that the photogenerated charge carriers are mobile across the entire absorption range. Stability during PEC conditions is, however, an issue, and we show that the deposition of a NiO₂ protection layer of ~20 nm thickness can overcome this limitation. Long-term chronoamperometric measurement (9 h) using a NiO₂-coated S-BiVO₄ film demonstrates no degradation in the photocurrent. Overall, this study presents a new approach to extend the absorption limit of BiVO₄ (i.e., via hydrogen sulfide treatment) and at the same time enhance the stability of the modified photoelectrode.

4. Experimental Section

Synthesis: BiVO₄ thin films were synthesized by the spray pyrolysis technique, following the recipe reported in literature. Deposition was carried out onto fluorine-doped tin oxide (FTO)-coated glass substrates (TEC7, Pilkington) and quartz substrates (Spectrosil 2000, Baumbauch & Co. LTD). These substrates were initially cleaned by 10 vol% Triton X-100 solution (Sigma-Aldrich), followed by ultrasonication using acetone, ethanol, and deionized water and dried using N₂ stream. The precursor solution was prepared by dissolving 1.2 mmol VO(C₂H₇O₂)₂ (99%, Alfa Aesar) and 1.2 mmol Bi(NO₃)₃·5H₂O (98%, Alfa Aesar) in 270 mL solvent consisting of acetic acid (98%, Sigma Aldrich) and ethanol (Sigma Aldrich) in a 1:8 ratio. Prior to BiVO₄ deposition, a thin interfacial layer of SnO₂ was deposited as a hole blocking layer by rf magnetron sputtering using a target of 99.99% SnO₂ (Ficiu, Romania) with Ar as the process gas. The SnO₂ deposition was performed with a repetition rate of 10 Hz and a laser fluence of 2 mJ/cm². During deposition, an oxygen back-pressure of 5 mbar was kept in the chamber and the base pressure in the chamber was ~10⁻¹² mbar. The as-deposited films were then annealed in air at 450 °C for 2 h to form the pristine BiVO₄ films.

For sulfur incorporation, the pristine BiVO₄ films were annealed in H₂S/Ar gas environment (various conc. of H₂S: 1–5%) using a tube furnace. The annealing temperature was varied from 100 to 300 °C, and the duration was between 20 and 60 min. A constant ramp rate of 10 °C per min was used.

The NiO₂ protection layers (20 nm thick) were deposited using PLD. In short, a Ni target (99.99%, Alfa Aesar) was ablated in a hot plate at 425 °C, and the as-deposited films were then annealed in air at 450 °C for 2 h to form the pristine BiVO₄ films.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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