Enhancing interfacial charge transfer in a WO3/BiVO4 photoanode heterojunction through gallium and tungsten co-doping and a sulfur modified Bi2O3 interfacial layer†

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Photoanodes containing a WO3/BiVO4 heterojunction have demonstrated promising photoelectrochemical water splitting performance, but the ability to effectively passivate the WO3/BiVO4 interface has limited charge transport and collection. Here, the WO3/BiVO4 interface is passivated with a sulfur-modified Bi2O3 interfacial layer with a staggered band edge alignment to facilitate charge transfer and lifetime. Additionally, BiVO4 was co-doped with Ga3+ at Bi3+ sites and W6+ at V5+ sites (i.e., (Ga,W):BiVO4) to improve the light absorption and photogenerated charge carrier concentration. The optimized WO3/S:Bi2O3/(Ga,W):BiVO4 photoanode exhibited a photocurrent density of 4.0 ± 0.2 mA cm−2 compared to WO3/(Ga,W):BiVO4 with 2.8 ± 0.12 mA cm−2 at 1.23 V RHE in K2HPO4 under simulated AM 1.5G illumination. Time-resolved photoluminescence spectroscopic analysis of the WO3/S:Bi2O3/(Ga,W):BiVO4 electrode validated the enhanced interfacial charge transfer kinetics. In operando femtosecond and nano-second transient absorption spectroscopy confirmed the presence of long-lived photogenerated charge carriers and revealed lower recombination initially due to rapid charge separation of WO3/S:Bi2O3/(Ga,W):BiVO4. The distribution and role of sulfur was further investigated using EDAX, XPS and TOF-SIMS depth profiling. Finally, a Co-Pi co-catalyst layer was added to achieve a photocurrent of 5.1 ± 0.25 mA cm−2 and corresponding H2 generation rate of 67.3 μmol h−1 cm−2 for the WO3/S:Bi2O3/(Ga,W):BiVO4/Co-Pi photoanode.

1. Introduction

Hydrogen generation by solar assisted photocatalytic water splitting is an attractive route to store solar energy in the form of chemical fuels.1–3 For such an application, efficient photon harvesting semiconducting oxides have been studied extensively due to their superior electrochemical stability, low cost and natural abundance.4 Monoclinic n-type bismuth vanadate (BiVO4) is a promising semiconductor material for the oxygen evolution reaction (OER).4 It possesses a bandgap of ~2.4 eV, conduction band (CB) edge close to 0 volt vs. the reversible hydrogen electrode (V RHE) and deep valence band (VB) position (~2.4 VRHE) that generates a substantial thermodynamic driving force for oxygen evolution.5,6 The effective defect-tolerant nature5 with moderate charge transport properties facilitates BiVO4 to achieve a theoretical photocurrent density (PCD) of up to ~7.5 mA cm−2 at 1.23 VRHE under simulated AM 1.5G illumination (100 mW cm−2). However, OER properties of BiVO4 suffer from low charge transfer rates due to excessive surface recombination on the ps–ns time scale.7,8 In parallel, the desirable water oxidation occurs at a slower time scale, typically over the ms–s range, due its four-electron reaction mechanism.6,7,9 Fast charge separation and transport of photo-generated electron–hole pairs are essential for efficient water oxidation.6,9 Several strategies have been employed to enhance the charge separation and transfer such as composition tuning or doping,5,10 and formation of homo- and hetero-junctions,6,7,9,11,12 passivation layer11 and co-catalyst.14 Tungsten (W) and molybdenum (Mo) have been extensively studied as donor-type dopants in BiVO4 to increase the charge carrier density,
mobility and minimize recombination pathways at solid/solid and solid/electrolyte interfaces.\textsuperscript{15,17} Along with composition tuning, formation of heterojunctions, particularly, type-II heterojunction formation between \( \text{WO}_3 \) (bandgap: 2.7 eV, VB: 0.4 eV & CB: 3.1 eV) and \( \text{BiVO}_4 \) (VB: 0.02 eV & CB: 2.4 eV) is efficient due to appropriate band alignment, which promotes spatial charge separation and relatively better charge transfer by providing a substantial thermodynamic driving force and interfacial electric field.\textsuperscript{6,18} However, the \( \text{WO}_3/\text{BiVO}_4 \) heterojunction suffers from slow charge transfer (sub \( \mu \)s) from \( \text{BiVO}_4 \) to \( \text{WO}_3 \) due to poor charge transport properties of \( \text{BiVO}_4 \) and the presence of recombination centers at the heterojunction interface.\textsuperscript{8,17} For such issues, adding an interfacial layer between the \( \text{WO}_3/\text{BiVO}_4 \) heterojunction is a promising approach to reduce the interfacial charge recombination and promote charge transfer.

In the present study, a multifaceted approach was implemented for addressing the interfacial charge recombination in the \( \text{WO}_3/\text{BiVO}_4 \) heterojunction where (i) \( \text{BiVO}_4 \) was co-doped and (ii) an interfacial layer was implemented to improve the effective charge separation and transfer. Initially, \( \text{BiVO}_4 \) was co-doped with Ga\textsuperscript{3+} and W\textsuperscript{6+} at the Bi\textsuperscript{3+} and V\textsuperscript{5+} sites, respectively, to enhance the light absorption, concentration of photogenerated charge carriers, and improve bulk charge separation. A uniquely prepared sulfur (S) modified \( \text{Bi}_2\text{O}_3 \) \([\text{S:Bi}_2\text{O}_3]\) layer was implemented so that S diffused to the adjacent underlayer (\( \text{WO}_3 \)) and overlayer \([\text{(Ga,W):BiVO}_4]\) which helped in increasing the number of additional reactive sites for charge transport. Energy-dispersive X-ray analysis (EDAX), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling were used to determine the qualitative and uniform distribution of sulfur in all layers. The PCD increased from 2.8 ± 0.12 to 4.0 ± 0.2 mA cm\textsuperscript{-2} for \( \text{WO}_3/(\text{Ga,W}):\text{BiVO}_4 \) and \( \text{WO}_3/\text{S:Bi}_2\text{O}_3/(\text{Ga,W}):\text{BiVO}_4 \), respectively. Additionally, the photocurrent increased to 5.1 ± 0.25 mA cm\textsuperscript{-2} after adding cobalt phosphate (Co-Pi) to yield a hydrogen generation rate of 67.3 \( \mu \)mol h\textsuperscript{-1} cm\textsuperscript{-2} for \( \text{WO}_3/\text{S:Bi}_2\text{O}_3/(\text{Ga,W}):\text{BiVO}_4 \) Co-Pi photoanode at 1.23 \( V_\text{RHE} \) in K\textsubscript{3}HPO\textsubscript{4} (KPi) under simulated AM 1.5G illumination. Time-resolved photoluminescence (TRPL) and in \textit{operando} femto- and nano-second transient absorption spectroscopy (fs- and ns-TA) results are consistent with more holes being rapidly directed to the reactive surface initially and fast electron transfer occurring from \( \text{Ga,W}):\text{BiVO}_4 \) to \( \text{S:Bi}_2\text{O}_3 \) in the ps–ns and from \( \text{S:Bi}_2\text{O}_3 \) to \( \text{WO}_3 \) in the ns–\( \mu \)s time scale. From the detailed analysis, we show that the insertion of a \( \text{S:Bi}_2\text{O}_3 \) interfacial layer resulted in the best charge separation and transfer kinetics, as well as reduced interfacial recombination sites for all architectures tested. The achieved results are among the highest reported photocurrent densities and hydrogen production rates in the literature.

2. Experimental

2.1 Thin film fabrication

The \( \text{BiVO}_4 \) based thin films were fabricated on a 1 \( \times \) 1 cm\textsuperscript{2} fluorine-doped tin oxide (FTO) glass substrate (Aldrich Chemistry: 2.3 mm thick, \( \sim 7 \Omega \) sq\textsuperscript{-1} surface resistivity) using ultrasonic spray coating (Sono-Tek Corporation, USA). A precursor solution of \( \text{BiVO}_4 \) was prepared by dissolving 3 mM \( \text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O} \) (Alfa-Aesar, CAS#10035060) and 3 mM \( \text{NH}_4\text{VO}_3 \) (Sigma-Aldrich, CAS#7803556) in 2 M H\textsubscript{2}O (Sigma-Aldrich, CAS#7803556). The precursor solution was sprayed at a flow rate of 0.1 ml min\textsuperscript{-1} for 4 cycles over a FTO substrate held at 70 °C, and then annealed for 10 min at 500 °C in a furnace (Thermo Scientific Thermolyne, model: F48028). The annealed film was sprayed for an additional 4 cycles to obtain the optimized film thickness and then annealed at 500 °C for 2 h. Ga doping was performed by dissolving 3 mM \( \text{Ga(NO}_3)_3 \cdot 2\text{H}_2\text{O} \) (Sigma-Aldrich, CAS#69365726) in the \( \text{BiVO}_4 \) precursor solution to get various \( \text{Bi}_1-x\text{Ga}_x\text{VO}_4 \) compositions where \( x = 0.01-0.06 \) and \( x = 0.04 \) were found to be optimal (Fig. S1a†). W doping was carried out non-stoichiometrically\textsuperscript{15} by mixing 3 mM (\( \text{NH}_4 \))\textsubscript{10}\( \text{H}_2(\text{W}_2\text{O}_7)_6 \) (Sigma-Aldrich, CAS#11140775) in the \( \text{BiVO}_4 \) precursor solution to acquire \( \text{Bi}_{0.96}\text{Ga}_{0.04}\text{Vo}_{0.992-} \text{W}_{0.018} \) \( \text{O}_3 \) (termed \( \text{W:BiVO}_4 \)).

\( \text{WO}_3 \) films were fabricated by dissolving 3 mM (\( \text{NH}_4 \))\textsubscript{10}\( \text{H}_2(\text{W}_2\text{O}_7)_6 \) (Sigma-Aldrich, CAS#10031513) in 2 M H\textsubscript{2}O (Sigma-Aldrich, CAS#7803556). The precursor solution was sprayed for 4 cycles over the FTO substrate (kept at 40 °C) at a flow rate of 0.1 ml min\textsuperscript{-1} using an ultrasonic spray coating tool. The film was annealed at 500 °C for 2 h in air to obtain a thin adherent \( \text{WO}_3 \) film. (Ga,W):\( \text{BiVO}_4 \) was then sprayed over the \( \text{WO}_3 \) film to form \( \text{WO}_3/(\text{Ga,W}):\text{BiVO}_4 \).

The precursor solution of \( \text{Bi}_2\text{O}_3 \) was prepared by dissolving 1 mM \( \text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O} \) (Alfa-Aesar, CAS#10035060) in 10 ml acetic acid (Sigma-Aldrich, CAS#64197). The \( \text{WO}_3/\text{Bi}_2\text{O}_3 \) film was fabricated by ultrasonically spraying the \( \text{Bi}_2\text{O}_3 \) precursor solution on the \( \text{WO}_3 \) film (kept at 70 °C) for 3 cycles. The \( \text{WO}_3/\text{Bi}_2\text{O}_3 \) bilayer was then annealed at 500 °C for 2 h in air. (Ga,W):\( \text{BiVO}_4 \) was subsequently sprayed (as discussed) to form \( \text{WO}_3/(\text{Bi}_2\text{O}_3/\text{Ga,}W):\text{BiVO}_4 \).

Fig. 1 and S1b† show a schematic of the \( \text{WO}_3/\text{S:Bi}_2\text{O}_3/(\text{Ga,}W):\text{BiVO}_4 \)/Co-Pi film fabrication process. The sprayed \( \text{Bi}_2\text{O}_3 \) film was immersed in 35 ml methanol (Sigma-Aldrich, CAS#67561) and 0.4 mM dibenzyl disulfide (Alfa Aser, CAS#150607) for 20 min and then annealed in sulfur vapor using a tube furnace (Thermo Scientific Thermolyne, model: HTF55322C). Sulfur vapor was generated by heating 2.5 g of sulfur powder (Alfa Aser, CAS#7704349) at 120 °C in the tube furnace’s upstream section. Argon (purity: 99.99%) was used as a carrier gas for the sulfur vapor downstream where the thin film was placed in the hot zone of the tube furnace at 445 °C in air for 1 h to incorporate S into \( \text{Bi}_2\text{O}_3 \) and \( \text{Bi}_2\text{O}_3 \) in the final step, the sulfur-rich film with the \( \text{WO}_3 \) layer was used as a substrate to spray (Ga,W):\( \text{BiVO}_4 \) precursor solution and annealed in air at 500 °C for 2 h to obtain the \( \text{WO}_3/\text{S:Bi}_2\text{O}_3/(\text{Ga,}W):\text{BiVO}_4 \) film.

A co-catalyst Co-Pi was photo-electrodeposited by dissolving 0.1 M \( \text{K}_2\text{HPO}_4 \) (Sigma-Aldrich, CAS#7758114) and 0.5 mM \( \text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) (Sigma-Aldrich, CAS#10026229) in DI water at
0.71 V\text{Ag/AgCl} for 30 s under simulated AM 1.5G illumination to obtain WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$/Co-Pi.

### 2.2 Material characterization

The morphology and elemental spatial distribution of the prepared samples were characterized using field emission scanning electron microscope (FE-SEM, JEOL 7000F) equipped with EDAX at 25 kV. To investigate the chemical migration that occurs during the sample synthesis process, time of flight secondary ion mass spectrometry (TOF-SIMS) depth profiling was performed on films at various stages of the annealing process utilizing an ION-TOF TOF-SIMS V spectrometer. The analysis was completed using a 3-lens 30 kV BiMn primary ion gun (30 keV) Bi$^+$ analysis beam at 1 pA pulsed beam current, where a 50 $\times$ 50 $\mu$m area was analyzed while the dose density was kept below 1 $\times$ 10$^{12}$ ions cm$^{-2}$ to remain under the static SIMS limit. Sputter depth profiling was accomplished with a 3 kV cesium ion beam (20 nA sputter current) with a raster of 100 $\times$ 100 microns.

UV-visible spectroscopy was carried out using an Agilent Technologies (Model: Cary 6000i) optical spectrophotometer. XPS spectra were acquired with a 180° double-focusing hemispherical analyzer with a 128-channel detector using non-monochromatic Al Kz radiation as the X-ray source (1486 eV) (Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectrometer System; VG 220i-XL). This X-ray source beam (diameter: ~0.4 mm) was chosen to minimize the superposition of photoelectron and Auger lines of essential elements. The energy resolution was 0.73 eV with a sufficiently small broadening of natural core level lines and a reasonable signal-to-noise ratio. The binding energy scale was calibrated using C 1s peak at 285 eV, giving an accuracy of 0.1 eV. For depth profiling, a Thermo K-Alpha spectrometer was used with a flood gun for charge compensation and sputtering was carried out with a raster 2 mm in diameter using Ar sputtering at 3 keV. An X-ray beam with a 35 $\mu$m diameter was used every 60 s up to 200 cycles of etching. S 2s peaks were used for S concentration due to the high interference between S 2p and Bi 4f peaks. However, due to the very low relative sensitivity factor of S 2s, the signal-to-noise ratio is relatively low at the given S doping level as compared to that of the other elements, making the error range relatively larger. TRPL measurements were carried out using a setup similar to that described by Kuciauskas et al.$^{18}$ A PicoQuant 405 nm diode laser generated short pulses (pulse width: ~130 ps) with a repetition rate of 1 MHz, beam spot size of 50 $\mu$m and 11 $\mu$W power. A fibre-coupled avalanche photodiode with a time resolution of 40 ps was used as the detector. The photon counting rate was maintained at approximately 1% of the repetition rate. Lifetime values were calculated by fitting the decay section of each curve with a biexponential function.

Femto- and nano-second transient absorption spectroscopy (fs- and ns-TAS) was conducted with a Helios Fire spectrometer (Ultrafast Systems), employing a Pharos amplified laser (Light Conversion) as the excitation source. The Pharos was operated at 4 kHz and 4 W power, along with a small portion directed to a sapphire crystal to generate a supercontinuum probe (900–1600 nm). The pump wavelength was tuned to 430 nm with an Orpheus optical parametric amplifier and attenuated with neutral density filters to approximately 150 nJ before being directed to the sample with a spot size of ~0.5 mm. The probe was overlapped with the pump at the sample position and was detected with an InGaAs photodiode array, and photoinduced transmission changes were established by modulating the pump at 2 kHz and subtracting “pump off” from “pump on” probe spectra. The data were adjusted for chirp and background scatter using Surface Explorer. The ns–ms TA was performed with the same excitation beam but with an electronically controlled attenuating beam. Figure 1 provides a schematic illustration of the WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$/Co-Pi film fabrication process.
delayed supercontinuum probe (Ultrafast System, EOS) to achieve longer delay times. The in operando TA measurements were conducted at open circuit potential by placing the sample in a quartz cell in KPi electrolyte. The applied potential was controlled using a Pine WaveNow (Pine Research) Potentiostat/Galvanostat.

2.3 Photoelectrochemical measurements

Photoanodes were constructed from the prepared thin films by attaching a copper wire to the FTO, and silver paint was used to establish electrical contact. Epoxy (Loctite 9460) was applied to secure the connection and cover the copper wire, silver paint, and FTO edges. The PEC performance of the photoanodes was evaluated in a standard three-electrode configuration using Pt wire (Premion 99.997%) and Ag/AgCl (3 M NaCl filling solution) as the counter and reference electrodes, respectively. A solar simulator (Sun 3000, model#11000A, ABET Technologies, USA) was used as the light source. Simulated AM 1.5G illumination was established using a GaInP (bandgap: 1.8 eV) photovoltaic primary reference cell. Potentiostat/galvanostat (BioLogic SP-300) was used for photoelectrochemical (PEC) measurements in 0.1 M KPi solution in water (pH = 8.0). The electrolyte was degassed with N2 gas for about 20 min before every measurement. Incident photon-to-current efficiency (IPCE) measurements were conducted using a 300 W Xe lamp (Newport, 66883), monochromator (Acton SpectraPro-150), mono-Si cell (Hamasu) and potentiostat (VersaSTAT 4, Ametek, Princeton Applied Research) with a lock-in amplifier (SR530 Stanford Research System). A 495 nm longpass filter (Newport) was added after the monochromator for wavelengths >550 nm to filter second-order diffractions. Electrochemical impedance spectroscopy (EIS) measurements were performed at a frequency range of 100 kHz to 100 mHz under simulated AM 1.5G illumination.

The H2 and O2 gases generated in the PEC process were collected in a three-electrode setup by tracking the electrolyte volume from a filled tube.19 The faradaic efficiency (ηH2) was calculated using,

\[
\eta_{H2} = \frac{P_{H2}V}{\frac{RT}{6.023 \times 10^{23}}} \times (\text{mole 96485} \text{C}) \times (\text{mol H2 per 2 mole})
\]

where \( P_{H2}, V, R, T \) are the pressure from H2 evolution (hPa), volume (L), gas constant (0.08206 L atm K\(^{-1}\) mol\(^{-1}\)) and T temperature (K), respectively. PH2 was calculated by subtracting the water vapor pressure (PH2O vapor) and pressure from the suspended solution (P suspended) from atmospheric pressure (P atm) measured using a barometer.

\[
PH2 = Patm - PH2O vapor - P suspended
\]

where, \( P_{suspended} \) is calculated by measuring the height \( h_1 \) of the suspended solution above the solution level in the setup:

\[
P_{suspended} = h_1 \times \frac{\text{Hg density}}{\text{solution density}} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = h_1 \times 0.0736 \text{ (torr per mm)}
\]

The faradaic efficiency measurement was validated using Pt electrodes as an anode and cathode for electrolysis and obtained \( \eta_{H2} = 0.98 \pm 0.02 \). The measurements were conducted at 1.23 V RHE in KPi electrolyte under simulated AM 1.5G illumination.

3. Results and discussion

3.1 Photoelectrochemical and optical measurements

Looking first at films, Fig. 2a and Table S1a† compare the PEC performance of intrinsic BiVO4 (i-BiVO4), Ga:BiVO4, W:BiVO4 and (Ga,W):BiVO4 under chopped light up to 2.4 VRHE. Ga:BiVO4 exhibited a photocurrent density of 0.4 ± 0.02 mA cm\(^{-2}\), which is almost twice that of i-BiVO4 (0.25 ± 0.01 mA cm\(^{-2}\)); this improvement is attributed to the increased Fermi-level splitting and therefore decreasing carrier recombination via incorporation of Ga\(^{3+}\) at Bi\(^{4+}\) sites.20 Similarly, W:BiVO4 exhibited enhanced PCD (1.02 ± 0.04 mA cm\(^{-2}\)) of over four times that of i-BiVO4, which is attributed to the improved carrier concentration of W\(^{6+}\) donors at V\(^{5+}\) sites.21 Finally, (Ga,W):BiVO4 demonstrated superior (~7 times) PEC performance (1.68 ± 0.1 mA cm\(^{-2}\)) compared to i-BiVO4, likely due to the combined effects of Ga and W doping.

Next, the PEC performance of heterojunctions was evaluated (Fig. 2b, S2a and Table S1b†). Based on Fig. 2a, (Ga,W):BiVO4 was selected to form a type-II heterojunction with WO3. By doing so, the WO3/(Ga,W):BiVO4 photoanode exhibited a photocurrent density of 2.8 ± 0.12 mA cm\(^{-2}\), which nearly doubled compared to (Ga,W):BiVO4, likely due to the improved light absorption at λ ~ 450 nm, charge transfer kinetics and reduced recombination sites.22,23 However, the WO3/BiVO4 interface is also known to have a high defect density, which can lead to significant recombination and slow charge transport.8,17 Therefore, a thin layer of bismuth oxide (Bi2O3) was inserted at the WO3/BiVO4 interface. While Bi2O3 has appropriate band alignment to promote charge transfer (validated in Fig. S2b†), the PEC measurement was not significantly enhanced relative to WO3/(Ga,W):BiVO4 (only 1.2 times higher), likely due to the higher levels of recombination in this layer.24 Therefore, sulfur (S) was incorporated into Bi2O3 such that, along with passivating the Bi2O3 bulk, S also diffused into the adjacent WO3 and (Ga,W):BiVO4 layers (Fig. 2b and S2c†). Sulfur is expected to enhance water oxidation by generating oxygen vacancies and forming new reaction sites that help charge migration/separation and reduce carrier recombination.25,26 The optimized WO3/S:Bi2O3/(Ga,W):BiVO4 photoanode demonstrated an excellent photocurrent density of 4.0 ± 0.2 mA cm\(^{-2}\) at 1.23 V RHE which was ~1.2 and ~1.5 times higher than that of the WO3/Bi2O3/(Ga,W):BiVO4 and WO3/(Ga,W):BiVO4 photoanodes, respectively.

A surface catalyst (Co-Pi) deposited WO3/S:Bi2O3/(Ga,W):BiVO4/Co-Pi photoanode exhibited a remarkably high
photocurrent density of 5.1 ± 0.25 mA cm⁻² at 1.23 V_RHE in KPi. The Co-Pi layer facilitates hole collection at the photoanode/electrolyte interface to participate in the water oxidation reaction.⁵ The photocurrent measurement with the hole scavenger and the Mott–Schottky analysis at different frequencies are discussed in the ESI (Sections 3 and 4).†

The spectral response was investigated to understand the impact of doping, co-doping and heterojunction formation. From Fig. S5a† it was observed that doping BiVO₄ with Ga enhanced total light absorption and extended the onset from ~520 to ~535 nm. A similar trend was observed for the co-doped (Ga,W):BiVO₄ sample, likely due to the redshift in light absorption caused by Ga doping.²⁹ There was no substantial change in absorption observed for W doping.³⁰ Moreover, the light interaction improved by forming a heterojunction with WO₃ (i.e., WO₃/(Ga,W):BiVO₄) where WO₃ (λ ≤ 450 nm) absorbs high energy photons along with modified BiVO₄ (300–530 nm), which absorb a wide range of photons. S:Bi₂O₃ (λ ≥ 430) further improved the light absorption of WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ compared to that of WO₃/Bi₂O₃/(Ga,W):BiVO₄ due to the formation of interband on S modification which causes the redshift in the light absorption.²⁴,²⁵ The respective absorption efficiencies (ϕ_abs) were calculated by integrating the absorption spectra from 300 to 550 nm for all samples, as indicated in Fig. 3a and 85a†: inset. The measured bandgaps were 2.71 and 2.8 eV (Fig. S5b†) for WO₃ and Bi₂O₃, respectively. There was a slight (~0.04 eV) reduction in the optical bandgap of Ga:BiVO₄ (2.39 eV) and (Ga,W):BiVO₄ (2.38 eV) compared to that of i-BiVO₄ (2.42 eV), which was expected due to the redshift in the absorption edge upon Ga doping. Bulk charge separation and surface charge transfer efficiencies are discussed in the ESI (Section 5, Fig. S5c–f†).

The quantification of the absorbed photons undergoing photoactivity corresponding to the wavelength was determined from the IPCE. The measurements for all heterojunction based photoanodes were conducted at 1.23 V_RHE (Fig. 3b). The WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ photoanode showed a maximum IPCE value of 63 ± 3%, followed by WO₃/Bi₂O₃/(Ga,W):BiVO₄ (52 ± 2%) and WO₃/(Ga,W):BiVO₄ (42 ± 1.6%), respectively at 460 nm. The WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ photoanode with Co-Pi exhibited the highest IPCE (72 ± 3.2%). The IPCE was integrated over the AM1.5G reference spectrum, and the resulting photocurrent...
densities for each sample (Fig. 3b) agreed with those measured under simulated AM 1.5G illumination at 1.23 V_{RHE} (Fig. 2b). A small variation (~5%) in the photocurrent measured by LSV and integrated current from IPCE is a general phenomenon due to measuring uncertainty.

3.2 Surface morphology, crystal structure and elemental analysis of thin films

To better understand the PEC performance trends, the physicochemical characterization of intrinsic and doped samples was carried out to evaluate the morphology, elemental mapping, crystal structure and oxidation state. The SEM images in Fig. S6a–c† show that i-BiVO₄, WO₃ and Bi₂O₃ have a planar structure with uniform nanoporous morphology. Fig. 4a shows that after co-doping the i-BiVO₄ film with Ga and W, the overall porosity increased substantially without changing the grain size (50–200 nm). The inset image illustrates the uniform growth of nano-sized grains, leading to better light absorption and more electrochemical active surface area by increasing the contact area between the film surface and electrolyte. The cross-sectional image (Fig. 4b) of WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ showed the uniformly connected nanoporous grains. The layer thicknesses are 200–300, 200–300 and 500–750 nm for the WO₃, S:Bi₂O₃ and (Ga,W):BiVO₄ layers, respectively. It was observed that the clear separation of all three layers is difficult as layers amalgamated due to the porous nature of all films. The FTO coating thickness on the glass substrate was ~50 nm (Fig. S6d†). The composition and elemental distribution of the as-deposited WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ were mapped based on the integrated intensities of peak signals of Bi, V, O, W, Ga and S as a function of beam position using FESEM-EDAX mode. Fig. 4c–h show the uniform distribution of elements Bi, V, O, W, Ga, and S. Consequently, the element spectra in Fig. 4i demonstrates the uniform presence of S along with other elements. In the Fig. 4i inset, Bi and S peaks were deconvoluted to determine the distinct measure of S due to the near overlap of the two peaks. S and Bi peaks were observed at 2.36 and 2.45 keV, respectively. Additionally, the quantification of S was determined to be 2.77 at% from EDAX analysis (Fig. 4i: inset).

The crystal structure was determined using X-ray diffraction (XRD) analysis for intrinsic, doped BiVO₄, Bi₂O₃, WO₃ and heterojunction samples without any impurity, complex phases and S peaks (discussed in the ESI, Fig. S7a and b†). The oxidation state of Bi, V, W, Ga and O in the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ sample was determined using surface XPS (discussed in ESI, Fig. S8a–f†). However, subsequently employed XPS depth profiling could not identify S in any layers due to the low concentration of S and detection limit of XPS (Fig. S8g†). In order to determine the oxidation state of sulfur, two distinct

![Fig. 4](image-url) (a) Surface morphology. (b) Cross-sectional, (c–h) plan view elemental mapping and (i) elemental spectra (inset: deconvolution of Bi and S peaks and at%) of the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ sample.
samples were prepared (Fig. S8†): intermediate S treated WO₃/ Bi₂O₃ and WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ with a high S content (total S treatment to the WO₃/Bi₂O₃ layer was 4 h, 4 times higher than that of the actual sample). From the S 2s spectrum in Fig. 5a, the oxidation state of S was attributed to –2 in the form of Bi₂S₃ (224.8 eV) and Bi₂O₃ (230.6 and 233.8 eV) peaks for the S treated WO₃/Bi₂O₃ sample.²⁷ Similarly, the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ sample with high S content validated –2 states (Bi₂S₃ (223.4 eV) and Bi₂O₃ (233.3 eV)). However, it is possible that peaks at 233.8 eV and 233.3 eV could also have sulfates or highly oxidized sulfur species (SO₄).²⁷ Additionally, depth profiling was performed, as shown in Fig. 5b, for WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ sample with high S content to determine the atomic concentration of Bi 4f, V 2p, O 1s, W 4f, Ga 2p and S 2s with depth. It was observed that the S distribution was uniform throughout the film depth except that it was slightly higher at the film surface. The atomic concentration of S was approximately 12 at% uniformly distributed in the sample with high S content. It may be estimated that sulfur could be approximately 3 at% uniformly distributed in the actual sample considering S diffusion rates as sulfur treatment was 4 times in the high S content sample. The atomic concentration of Bi 4f, V 2p, O 1s, W 4f, Ga 2p and S 2s as a function of the etch level for the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ film with high S content. Negative polarity TOF-SIMS depth profiles of the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ sample in three distinct (Fig. S5a†) environments: (c) control (no annealing), (d) short annealing (5 min at 500 °C) and (e) complete annealing (2 h at 500 °C) for Bi³⁺, VO⁻, WO⁵⁻, GaO⁻ and S⁻ species.

Fig. 5 (a) S 2s XPS spectra of S treated WO₃/Bi₂O₃ and high S concentrated WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ films. (b) XPS depth profiling spectra for the atomic concentration (%) of Bi 4f, V 2p, O 1s, W 4f, Ga 2p and S 2s as a function of the etch level for the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ film with high S content. Negative polarity TOF-SIMS depth profiles of the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄ sample in three distinct (Fig. S5a†) environments: (c) control (no annealing), (d) short annealing (5 min at 500 °C) and (e) complete annealing (2 h at 500 °C) for Bi³⁺, VO⁻, WO⁵⁻, GaO⁻ and S⁻ species.
W 4f and Ga 2p was distributed as per the filmstack structure. V 2p and Ga 2p were noticed to have minor diffusion in the adjacent layers, which was possible due to the porous nature of the film.

In order to understand the nature of the sulfur diffusion process in the actual film from the Bi2O3 interfacial layer to the WO3 and (Ga,W):BiVO4 adjacent layers, TOF-SIMS depth profiling was employed for the WO3/S:Bi2O3/(Ga,W):BiVO4 sample under three distinct annealing conditions after (Ga,W):BiVO4 precursor deposition on the sulfur treated WO3/Bi2O3 film. The prepared samples, as shown in Fig. S9a, were the control (without annealing), short annealed (5 min) and completely annealed (final sample) samples. Secondary ion signals were selected which were of high intensity and represented major components of the various layers in the filmstack. These species were Bi+, VO−, BiO−, GaO−, and S− which represent Bi, V, W, Ga and S elements, respectively. The layer interface was not measured due to high surface roughness and it was also observed that the clear distinction of each layer was difficult to achieve (Fig. 4b and 5b) due to their porous nature. However, a rough estimation is shown in Fig. S9b–d. The control sample showed that sulfur was contained to the Bi2O3 layer only, as observed by the pronounced peak of sulfur in the Bi2O3 layer in Fig. 5c. On the contrary, Fig. 5d showed that even on short annealing of 5 min at 300 °C, significant migration of sulfur occurred as the sulfur distribution migrated significantly into the (Ga,W):BiVO4 and WO3 layers, also noted from the significant broadening of the sulfur trace. Subsequently, in Fig. 5e, a completely annealed sample (2 h time at 500 °C) showed that the sulfur distribution was uniform throughout the film thickness, which was also corroborated by EDAX analysis (Fig. 4c–i) and XPS depth profiling (Fig. 5b). However, the sulfur content was higher on the (Ga,W):BiVO4 surface, possibly due to the small deposition of sulfur during migration from the Bi2O3 layer and a similar behavior was observed in the XPS depth profiling (Fig. 5b). It was assumed that sulfur was passivated in all grain boundaries and surfaces/interfaces/defects throughout all layers, rather than being a bulk alloy element. Along with sulfur, a less extreme amount of diffusion observed for the Bi, V, W and Ga components in the film thickness (Fig. 5c–e) may be due to the highly porous nature of the film (Fig. 4a) and a similar behavior was observed in the XPS depth profiling. The distribution of the substrate elements (F−, Sn− and Si+) is shown in Fig. S9b–d.

### 3.3 Electrochemical impedance analysis

Fig. 6a shows the impedance patterns of photoanodes with the WO3 heterojunction and Bi2O3 interface layer without and with sulfur modification. The WO3/(Ga,W):BiVO4 photoanode shows lower impedance than WO3/Bi2O3/(Ga,W):BiVO4 in the low-frequency region. Interestingly, the WO3/S:Bi2O3/(Ga,W):BiVO4 photoanode demonstrated even lower real impedance at a lower frequency than WO3/Bi2O3/(Ga,W):BiVO4. Resistance and capacitance in the bulk and at the surface were evaluated as a function of voltage using the Randles circuit (Fig. S10a & b), which consists of resistance related to connections ($R_{\text{series}}$), bulk resistance ($R_{\text{bulk}}$), surface resistance ($R_{\text{surface}}$), bulk capacitance ($C_{\text{bulk}}$) and surface capacitance ($C_{\text{surface}}$) connected to a Helmholtz layer at the photoanode and electrolyte interface. Fig. 6b shows that $R_{\text{bulk}}$ and $R_{\text{surface}}$ tend to drop gradually until ~1 V$_{\text{TH}}$ after which, the photocurrent was mainly controlled by photogenerated holes reaching the surface.$^{28}$ $R_{\text{bulk}}$ followed the order of WO3/S:Bi2O3/(Ga,W):BiVO4 < WO3/Bi2O3/(Ga,W):BiVO4 < WO3/(Ga,W):BiVO4. The evaluated capacitance of photoanodes shown in Fig. 6c illustrated that $C_{\text{bulk}}$ decreases with increasing potential and exhibits less recombination in the bulk and facilitated charge transfer. The $C_{\text{surface}}$ gradually increased with potential, and followed the trend of WO3/S:Bi2O3/(Ga,W):BiVO4 > WO3/Bi2O3/(Ga,W):BiVO4 > WO3/(Ga,W):BiVO4. The interfacial layer with S enhanced the charge transfer rate, facilitated the charge accumulation and transport by reducing the density of surface trapped holes in the bulk and the surface.

The total resistance ($R_{\text{tot}}$), which represents the combination of charge transport (bulk) and interfacial charge transport (surface), was evaluated using $R_{\text{tot}} = \left(\frac{dI}{dV}\right)^{-1}$ in Fig. 6d. A valley was observed at ~1 V$_{\text{TH}}$ for all photoanodes (fitting curve is shown in Fig. S10c). A cathodic shift of 164.3 and 33.5 mV in the valley implied higher charge extraction and a decrease in the $R_{\text{tot}}$ of 39.2 and 12 Ω cm$^{-2}$ for WO3/S:Bi2O3/(Ga,W):BiVO4 and WO3/Bi2O3/(Ga,W):BiVO4, respectively, compared to that of WO3/(Ga,W):BiVO4. The PL lifetime ($\tau$) of each sample was determined from the $\frac{dI}{dV}$ and impedance measurements ($R_{\text{tot}} = R_{\text{bulk}} + R_{\text{surface}}$), as shown in Fig. 6d. This excellent agreement substantiates the photocurrent obtained from the experiment.

### 3.4 Time-resolved study of charge dynamics

The photogenerated charge carrier dynamics and kinetics were explored by TRPL measurements of the WO3/(Ga,W):BiVO4 and WO3/S:Bi2O3/(Ga,W):BiVO4 samples. Fig. 7a shows the PL intensity decay after exciting the thick (Ga,W):BiVO4 layer and likely produces excited states in this layer using a laser source centered at 405 nm. The PL decay ($I(t)$) was fit with a second-order exponential function $I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$, where $A_1$ and $A_2$ are amplitudes of components with lifetimes $\tau_1$ and $\tau_2$, respectively.$^{28}$ The average PL lifetime ($\langle \tau \rangle$) of each sample was calculated using $\langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$ (all calculated parameters are presented in Table S2). The average carrier lifetimes of WO3/(Ga,W):BiVO4 and WO3/S:Bi2O3/(Ga,W):BiVO4 were 0.477 ± 0.05 and 0.418 ± 0.04 ns, respectively. Interestingly, the two dominant benefits which are expected from S:Bi2O3 incorporation (i.e., reduced recombination and fast charge transport) have competing effects on the carrier lifetime, where reduced recombination increases the lifetime while fast charge...
transport reduces it. This may be the reason that the lifetime was not found to vary significantly between the two samples. The charge transfer rate constant ($k_{ct}$) can also be calculated using $k_{ct} = \frac{1}{\tau_{m}}$. The obtained $k_{ct}$ for WO$_3$/[Ga,W]:BiVO$_4$ and WO$_3$/S:Bi$_2$O$_3$/[Ga,W]:BiVO$_4$ were 2.095 ± 0.2 ns$^{-1}$ and 2.393 ± 0.22 ns$^{-1}$, respectively, suggesting that the enhanced charge transfer may be slightly more dominant.

TA was employed for an in-depth understanding of the charge dynamics behavior across the WO$_3$/[Ga,W]:BiVO$_4$ interface without and with the S:Bi$_2$O$_3$ interfacial layer by placing the sample in air and electrolyte (operando). First, fs-TA data were collected for the sample in air, pumped at 430 nm and probed in the range from 900–1400 nm for WO$_3$/[Ga,W]:BiVO$_4$ and WO$_3$/S:Bi$_2$O$_3$/[Ga,W]:BiVO$_4$ samples. It is believed that this infrared probing range tracks the free and trapped photo-generated carriers, while the excitation first strikes the thick (Ga,W):BiVO$_4$ layer and likely predominately produces excited states in this layer. The intensity decay curve plotted in Fig. 7b demonstrates faster initial decay on the ps time scale for the WO$_3$/[Ga,W]:BiVO$_4$ sample compared to that of WO$_3$/S:Bi$_2$O$_3$/[Ga,W]:BiVO$_4$. This fast decay likely corresponds to the geminate electron–hole recombination, which is ameliorated with the additional Bi$_2$O$_3$ layer, facilitating electron movement away from BiVO$_4$ and suppressing initial recombination. The recorded decay ($\Delta A$) signal was fitted using the exponential decay model $\Delta A = \sum A_i \exp\left(-\frac{t}{\tau_i}\right)$ where $A_i$ and $\tau_i$ are the amplitude and the lifetime of an exponential decay component, respectively. The calculated fitting parameters are summarized in Table S3,† and the values are commensurate with those found in the literature. The fs-TA is best fitted with 3 exponentials in the ns regime without an extended component in the microsecond regime due to absence of electrolyte that stabilizes separated charges. Time constants $\tau_1$, $\tau_2$ and $\tau_3$ can be inferred as loss of excited states due to hole trapping and the depletion of the trapped holes due to electron–hole recombination with free and thermalized electrons. It is inferred from $\tau_1$ that the initial fast processes leading to carrier loss are reduced in the WO$_3$/S:Bi$_2$O$_3$/[Ga,W]:BiVO$_4$ sample, as all decay time constants are slower than those of the WO$_3$/[Ga,W]:BiVO$_4$ sample. The subsequent remaining carriers are left to undergo slower interfacial recombination on a ns timescale without electrolyte. We note that unlike TRPL, which only measures radiative
electron–hole recombination and thus separation leads to reduced lifetime, the absorptive TA signal represents carrier population and as such, a persistent signal also indicates carrier motion to avoid recombination.

Next, the ns-TA measurement was conducted with samples submerged in the electrolyte to evaluate hole transfer kinetics at the semiconductor/electrolyte interface. The measurement was conducted at open circuit potential, pumped at 430 nm and probed in the range of 900–1400 nm in KPi electrolyte. It was predicted that at open circuit potential, a partially occupied electron trap state can exhibit optical transition behavior to a localized trap state. The band bending at the photoanode/electrolyte interface can prolong the photogenerated hole lifetime (μs) and accumulation. This was confirmed by measuring the open circuit potential (~0.5 and ~0.55 V_RHE) in the dark and flat-band potential (0.092 and 0.041 V_RHE [ESI Section 4]) exhibited significant band bending for WO_3/(Ga,W):BiVO_4 and WO_3/S:Bi_2O_3/(Ga,W):BiVO_4 photoanodes. From the fs-TA data described above, it is known that a larger number of holes survived the initial electron–hole recombination due to rapid charge separation/transport and subsequent transport to the reactive film surface for the water oxidation reaction. Subsequently, from the normalized ns-TA data tracking secondary decays in Fig. 7c, it was observed that WO_3/S:Bi_2O_3/(Ga,W):BiVO_4 exhibited slightly faster ns decay than WO_3/(Ga,W):BiVO_4 but otherwise had nearly identical kinetics. The recorded decay signal was fitted using the exponential decay model. The calculated fitting parameters are summarized in Table S4.† The ns-TA best fit with 4 exponentials due to the presence of long-lived carriers. The electron extraction (K_TA) rate was higher for the WO_3/S:Bi_2O_3/(Ga,W):BiVO_4 photoanode that denoted the enhanced electron mobility after placing the S:Bi_2O_3 layer and impact of S diffusion to adjacent layers.

Correspondingly, the recombination between trapped holes and free electrons (τ_2) on the >30 ns timescale was similar in WO_3/S:Bi_2O_3/(Ga,W):BiVO_4 (36 ns) compared to that in WO_3/(Ga,W):BiVO_4 (43 ns). The recombination of the trapped hole with thermalized electrons (τ_3) occurred in the μs range (1.1 to 1.3 μs) and it was expected that it would not significantly impact the overall water splitting process. By the time the μs timescale is reached, the leftover carriers surviving recombination have been swept far away from the internal interface, where composition is distinct between the samples, to the
semiconductor/electrolyte interface where composition and thus the kinetics become similar. This study provides evidence that the number of long-lived photogenerated charge carriers is improved after adding the S:Bi$_2$O$_3$ interfacial layer. In addition, we conclude that WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$ decays faster in the $<10$ ns regime compared with WO$_3$/(Ga,W):BiVO$_4$, suggesting an improved electron transfer rate and accumulation of holes at the (Ga,W):BiVO$_4$ surface for water oxidation kinetics.

The primary electron and hole separation and transfer pathways occurring among three oxides were shown in the band diagram (Fig. 7d). The CB edge was determined using the flat-band potential considering the negligible difference between the flat-band and bottom of the CB edge.$^{22}$ It was assumed that the small amount of S would not significantly change the VB and CB position of Bi$_2$O$_3$, WO$_3$ and (Ga,W):BiVO$_4$ layers. Being the main absorber, BiVO$_4$ will absorb low energy photons ($\lambda \leq 530$), while WO$_3$ ($\lambda \leq 450$) and S:Bi$_2$O$_3$ ($\lambda \leq 430$) will absorb high energy photons. Due to the stepped alignment and the appropriate VB and CB configurations, electrons can readily transport from the CBs of BiVO$_4$ into WO$_3$ via the S:Bi$_2$O$_3$ interfacial layer and into the current collector.$^{24}$ Simultaneously, photogenerated holes at WO$_3$ will transport to and be collected at (Ga,W):BiVO$_4$ through the S:Bi$_2$O$_3$ interfacial layer.

The time scales for charge separation and transport from TRPL, fs- and ns-TA analysis indicate that more holes are directed to the reactive surface on the ps–ns range in (Ga,W):BiVO$_4$. Subsequently, photogenerated electrons will transfer from S:Bi$_2$O$_3$ to WO$_3$ on a ns–μs time scale. Recombination of photoexcited free electrons in (Ga,W):BiVO$_4$ is reduced by them being transferred into the CB of WO$_3$ via the S:Bi$_2$O$_3$ layer. Once in WO$_3$, the electrons have a longer lifetime.$^9$ In this process, S:Bi$_2$O$_3$ plays a key role in facilitating rapid charge transfer initially to WO$_3$ to improve the photoactivity of the WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$ photoanode. Furthermore, the backflow of charge carriers within the photoanode is reduced by the CB and VB energy barriers present among the WO$_3$, S:Bi$_2$O$_3$ and (Ga,W):BiVO$_4$ layers that suppress hole and electron backflow.$^{13-15}$

As observed from Fig. 8a, the photocurrent density of all photoanodes decreases initially due to dominant photocorrosion of (Ga,W):BiVO$_4$ from the loss of V$^{5+}$ ions in the form of V$_2$O$_5$. However, the photocurrent density further ameliorates when V$_2$O$_5$ dissolution gets saturated$^{36}$ as can be observed for the WO$_3$/(Ga,W):BiVO$_4$ photoanode, which could retain $\sim$60% of the initial photocurrent density. Further, the effect of the Bi$_2$O$_3$ and S:Bi$_2$O$_3$ interfacial layers becomes more pronounced in ameliorating the charge dynamics and photocatalytic performance of WO$_3$/Bi$_2$O$_3$/(Ga,W):BiVO$_4$ and WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$ photoanodes by retaining $\sim$80 and $\sim$85% of the initial photocurrent density. Consequently, adding a protective layer of Co-Pi demonstrates a self-healing nature and the WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$/Co-Pi photoanode performance improves by retaining 90% of the photocurrent density compared to $\sim$85% for the WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$ photoanode after 10 h.$^5$ The repeatability of the photoanodes after stability measurement demonstrated no significant change in the photocurrent onset and PCD at 1.23 $V_{RHE}$ (Fig. S11†). The amount of H$_2$ and O$_2$ gases generated was measured to verify the faradaic efficiency of each water splitting half-reaction. The measurement was performed for the WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$/Co-Pi photoanode at 1.23 $V_{RHE}$ under simulated AM 1.5G illumination in KPi electrolyte. Fig. 8b shows the H$_2$ and O$_2$ gas generation rate ($67.3$ and $33.6 \mu$mol h$^{-1}$ cm$^{-2}$, respectively) along with the theoretical production rate and the corresponding faradaic efficiency (secondary Y-axis in Fig. 8b) values (91.5 and 88%, respectively). The slightly lower values of faradaic efficiency are attributed to the inhibition of proton reduction, diffusion of H$_2$ gases, and potential back reactions at the counter electrode from dissolved O$_2$.$^{22,23}$

Several efforts have been made by our or other groups in the field for improving interfacial passivation, charge transfer and reducing recombination sites by additional (interfacial or under/over) layers in WO$_3$/BiVO$_4$ heterojunction photoanodes. The obtained photocurrent densities at 1.23 $V_{RHE}$ are plotted in Fig. 9a and Table S5.† Choi et al.$^{37}$ incorporated a mild W doped BiVO$_4$ interfacial layer in the WO$_3$/BiVO$_4$ heterojunction for unidirectional charge flow. Zhang et al.$^{38}$ designed a three-story

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**Fig. 8** (a) Photoelectrochemical stability measurements of photoanodes with the WO$_3$ heterojunction and Bi$_2$O$_3$ interface layer without and with sulfur modification. (b) Evolution of H$_2$ and O$_2$ gases from the WO$_3$/S:Bi$_2$O$_3$/(Ga,W):BiVO$_4$/Co–Pi photoanode. The measurements were conducted at 1.23 $V_{RHE}$ in KPi electrolyte under simulated AM 1.5G illumination.
device to improve the conductivity by placing reduced graphene oxide between WO₃ and BiVO₄ layers that acted as a multi-channel pathway. A Z-scheme device was designed by Wang et al. by incorporating a W-layer between BiVO₄ and WO₃ layers for accessing holes. Beak et al. used a porous SnO₂ underlayer in the WO₃/BiVO₄ heterojunction where WO₃/(WO₃ + SnO₂) layers formed a mixed composite for better contact and low resistance. Fig. 9b and Table S6† compare hydrogen production rates at 1.23 VRHE under simulated AM 1.5G illumination for BiVO₄ based heterojunction photoanodes along with the present results of our WO₃/S:Bi₂O₃/(Ga,W):BiVO₄/Co-Pi photoanode. Our results are among the highest reported photocurrent densities and hydrogen production rates.

4. Conclusion

The performance of photoanodes containing a WO₃/BiVO₄ heterojunction is limited, in part, by charge separation, transfer and recombination across the heterojunction interface. To mitigate these losses, a sulfur modified Bi₂O₃ interfacial layer was introduced between WO₃ and BiVO₄ layers. The BiVO₄ layer was optimized with co-doping at Bi³⁺ and V⁵⁺ sites with Ga³⁺ and W⁶⁺, respectively, to improve the light absorption and photogenerated charge carrier extraction. The S:Bi₂O₃ layer between WO₃ and (Ga,W):BiVO₄ and the Co-Pi co-catalyst led to achieving a photocurrent density of 5.1 ± 0.25 mA cm⁻² and a hydrogen generation rate of 67.3 μmol h⁻¹ cm⁻² for the WO₃/S:Bi₂O₃/(Ga,W):BiVO₄/Co-Pi photoanode. EDAX, XPS and TOF-SIMS depth profiling corroborated the uniform diffusion of S in all layers whereas EIS and TRPL confirmed the enhanced interfacial charge transfer kinetics. Subsequently, operando fs- and ns-TA analysis concluded that more long-lived photogenerated charge carriers remain after adding the S:Bi₂O₃ interfacial layer, providing more holes directed to the reactive surface due to effective charge separation/transfer, and improved the overall photoanode performance. The photocurrent density and hydrogen production rates are among the highest reported for interlayer enhanced WO₃/BiVO₄ heterojunction photoanodes.

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**Conflicts of interest**

The authors declare no conflicts of interest.

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**References**