Surface functionalized atomic layer deposition of bismuth vanadate for single-phase scheelitel

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Monoclinic bismuth vanadate is one of the most promising oxide photoanodes for solar – assisted water splitting. To date, the atomic layer deposition of bismuth vanadates has relied on the catalytic codeposition of BiPh3 with VTIP to produce vanadium-rich compounds that undergo spinodal decomposition to multiphase mixtures upon crystallization. A surface functionalization (SF) step of ROH/VTIP/H2O was developed to inhibit V2O5 deposition for adjustable Bi : V stoichiometry. Ethanol, 2-propanol, and methanol were each found to inhibit V2O5 deposition, in order of increasing effect. Applying this SF step with ternary Bi – V – O depositions (ROH/VTIP/H2O/BiPh3/H2O) enabled composition tuning. The use of methanol enabled 45.9 : 54.1 Bi : V atomic ratio as-deposited, and was crystallizable to phase-pure scheelite, depending on the thickness. The resulting films were applied towards photo-assisted water splitting with a hole-scavenging sulfite where films up to 60 nm thick were free from apparent charge transport limitations. The optoelectronic properties were markedly improved by a novel photoelectrochemical activation step.

Introduction and background

Solar photoelectrochemistry (PEC) is an attractive source for sustainable fuels such as hydrogen.3 Bismuth vanadate was first demonstrated as a photocatalyst for water oxidation in 1998, with the monoclinic-scheelite phase (m-BiVO4) showing the highest efficiency.2, 3 The m-BiVO4 phase has a band gap of 2.4 eV,3, 4 a conduction band edge near 0 V vs. the reversible hydrogen electrode (RHE)5 and a valence band edge near 2.4 V vs. RHE. Thus electrons in the conduction band have appropriate potential to support the hydrogen evolution reaction (0 V vs. RHE) at the counter electrode with a small applied bias and holes in the valence band have ample potential to support the oxygen evolution reaction (1.23 V vs. RHE) at the semiconductor-electrolyte interface. Electrons and holes generated by photoabsorption are thus able to support photoassisted water splitting with a low onset potential (ca. 0.25 V vs. RHE) for the photoanode. The performance of BiVO4 photoanodes has progressed quickly with many recent advances.4–9

For solar-fuel applications, bismuth vanadate requires an optical thickness of ~700 nm for efficient light harvesting near the band edge (discussed in ESI†) that is much larger than the sum of the depletion width and the limiting carrier diffusion length.5, 9, 10 Thus, many recent devices with record photocurrents used BiVO4 thin films supported upon transparent, conductive scaffolds. Such “host-guest” or extremely thin absorber approaches have been largely successful at decoupling optical absorption from carrier transport.11–13 Thus far, all BiVO4 host-guest reports have utilized non-uniform depositions or used cathodic depositions that limited the use of hole blocking layers at the host-guest interface.7, 8, 14, 15 In contrast, atomic layer deposition (ALD) enables controlled growth onto arbitrary 3D porous scaffolds independent of substrate electronic properties, bringing distinct advantages to the development of efficient host-guest nanostructures. Such structures have been developed for optoelectronics including α-Fe2O3,16–18 Cu2O,39–42 and other photoelectrodes.40–42

Thus far, all reports of ALD bismuth vanadates had >65 at% V, leading to spinodal decomposition into Bi2O3 with an additional V2O5 phase.43 With conventional ALD, the amount of material deposited per cycle is fixed due to a self-limiting reaction of each precursor at surface saturation. The deposition rate is a constant for each precursor/oxidant combination under steady state.44 While this is a significant benefit for conformal thin-film growth, the quantized nature of deposition limits stoichiometry tuning. Surface-functionalized atomic layer deposition (SF-ALD) enables further stoichiometry tuning by modifying the amount of material deposited per cycle. SF-ALD can thus reduce the amount of material deposited by partially blocking deposition sites. For example, alcohols can undergo a condensation reaction with surface hydroxyl groups to inhibit the deposition of the subsequent metal precursor.45–46 The subsequent oxidant pulse removes the remaining ligands from the metal as well as the SF-species. Since the SF step is self-limiting, the overall deposition remains conformal and self-
limiting, but with more granular control over the amount deposited. Although SF-ALD was developed to modify the extent of doping, it is also conceptually suitable for tuning the stoichiometry of multi-metal compounds.

Here, SF-ALD with alkyl alcohols (ROH) enables the most Bi-rich depositions of bismuth vanadate to date, including nearly stoichiometric BiVO$_4$. Crystallization of the amorphous films led to the phase-pure photoactive form of m-BiVO$_4$ depending on film thickness. In addition, a PEC activation treatment was found to significantly improve PEC efficiency.

Experimental

Materials

Triphenyl bismuth (BiPh$_3$, 99%) and vanadium(v) triisopropoxy oxide (VTIP, 98+%) were used as received from STREM. Deionized (DI) water was prepared using a Siemens Labostar model; where specified, deionized ultra-filtered (DIUF) water (Fisher) was used in place of DI water. Methanol (ACS Grade, Fisher), 2-propanol (70% lab grade, BDH), ethanol (95%, Fisher), H$_2$BO$_3$ (ACS Grade, VWR Life Science), HNO$_3$ (Fisher, Optima grade), Na$_2$SO$_3$ (ACS Grade, Macron), and KOH (ACS Grade, Fisher) were used as received. TEC-15 fluorine-doped tin oxide coated glass (FTO) was purchased from Hartford Glass. The FTO substrates were cleaned extensively before use with 2-propanol and DI water before sonication in 2-propanol, followed by additional rinses with water and 2-propanol, followed by sonication in 2-propanol. Polished n-doped silicon wafers with (100) orientation were purchased from University Wafers, USA. The cleaned FTO substrates and silicon wafers were calcined using a Barnstead Thermolyne muffle furnace at 450 °C for 1 h immediately prior to use. High-temperature grade Kapton tape was purchased from McMaster-Carr, USA. Ultra-high purity nitrogen (99.9999%) and oxygen (99.5%) were used as received from Praxair.

Atomic layer deposition of bismuth vanadate films

Samples were masked using Kapton tape to define the deposition region. Samples for composition analysis were masked on the front to provide clean electrical contacts for PEC measurements. The BiPh$_3$ and VTIP were each loaded into separate stainless steel vessels at 180 °C for 5 h. The resulting solution was diluted to 50 mL using DI water. A Finnigan ELEMENT XR double-focusing magnetic sector field-inductively coupled plasma-mass spectrometer (SF-ICP-MS) was used for analyzing V (51, LR), Bi (209, LR), and internal standard Rh (103 LR). A Micromist U-series nebulizer (GE, Australia) was operated at 0.2 mL min$^{-1}$ with a quartz torch and an injector (Thermo Fisher Scientific, USA) for sample introduction. The gas flow was set to 1.08 mL min$^{-1}$. The forwarding power was 1250 W. Composition analysis was based on a five-point calibration curve for both V and Bi. The calibration range was from 10 to 600 ppb. The $R^2$ values for the initial calibration curves were greater than 0.999.

Film treatments

The ALD films were heated to induce crystallization. Samples were heated at 5 °C min$^{-1}$ to 200 °C, followed by 10 °C min$^{-1}$ to 450 °C, held constant at 450 °C for 1 h, and allowed to cool in the furnace.
Diffraction

X-ray diffraction experiments were conducted using a SAXSLab Ganesha at the South Carolina SAXS Collaborative. A Xenics GeniX 3D microfocus source was used with a Cu target to generate a monochromatic beam with a 0.154 nm wavelength. The instrument was calibrated using silicon powder (NIST 640e). Scattering data were processed from the scattering vector \( q = \frac{4\pi}{\lambda} \sin \theta \) where \( \lambda \) is the X-ray wavelength and \( 2\theta \) is the total scattering angle. A Pilatus 300 K detector (Dectris) was used to collect the two-dimensional (2D) scattering patterns. Samples were measured at an incident angle of 8° relative to the film plane. SAXSGUI software was used to radially integrate the 2D patterns to reduced 1D profiles. The conversion of the resulting intensity versus \( q \) data was converted to \( 2\theta \) using the above formula.

Photoelectrochemical and electrochemical measurements

Linear sweep voltammograms were measured using a three-electrode potentiostat (BioLogic SP-150) with a Ag/AgCl/KCl (saturated) reference electrode (Pine Instruments) and a platinum wire counter electrode (Pine Instruments). Samples on FTO substrates were clamped with a titanium sheet to provide an ohmic contact. The electrodes were placed into a cell made of polyether ether ketone (PEEK) with a fused-silica window. Simulated sunlight was generated using a 75 W xenon lamp (OBB, Horiba) that passed through a water infrared filter (OBB, Horiba), a KG-3 filter (317–710 nm pass, Edmund Optics), and a BG-40 filter with an antireflective coating (335–610 nm pass, Thorlabs). This combination of filters removed much of the UV light where the Xe lamp has the most spectral mismatch from the AM 1.5 spectrum. The transmitted light was collimated using a fused-silica lens (Thorlabs) and passed through an engineered diffuser with a top–hot profile to provide a homogeneous intensity profile with a slight 10° divergence. The transmitted light was corrected for brightness in the 335–610 nm spectral range to generate a photocurrent identical to AM 1.5 sunlight. The illumination intensity was measured using a calibrated UV-enhanced silicon photodiode (Thorlabs) equipped with a neutral reflective filter (optical density 1.0, Thorlabs) to maintain a linear and calibrated photodiode response. This calibration practice provides accurate solar simulation in terms of both spectral distribution and brightness with a minimal correction factor.47

PEC measurements were performed in 1 M potassium borate with or without 0.2 M sodium sulfite \((Na_2SO_3)\) as hole scavenger at pH 9.35. It has been well established that potassium phosphate buffers dissolve BiVO \(_4\) at working pH values; \(^5,46,49\) however, BiVO \(_4\) photoanodes are stable in alkaline borate buffers. The potassium borate solution was prepared by adjusting the pH of 1 M \(H_2BO_3\) in DIUF water to 9.35 ± 0.02 with KOH as confirmed by a calibrated Thermo Scientific OrionStar A211 pH meter. The sulfite acted as a hole scavenger to provide quantitative charge injection from the semiconductor to the electrolyte for the measurement of film performance without catalysts. The samples were scanned from −0.600 to 0.650 V vs. Ag/AgCl reference electrode at 10 mV s \(^{-1}\). Multiple scans were completed at each condition to confirm reproducibility and the second scan results were reported. Film stability was measured by chronoamperometry (CA) at 0.6 V vs. RHE under simulated AM 1.5 illumination to measure the photocurrent stability of SF ALD 30 nm-4k film over 17 h. The film was freshly calcined prior to the stability measurement.

Quantum efficiencies were calculated based on CA measurements made with monochromatic light while using the same potassium borate buffer described above. Illumination was generated using a 150 W xenon lamp (OBB, Horiba) that passed through an 180° monochromator with a 5 mm slit width and 1200 grates per mm diffraction grating (OBB, Horiba). Transmitted light was collimated using a fused-silica lens (Thorlabs) and passed through an engineered diffuser with a top-hot profile to provide a homogenous intensity profile with a slight 10° divergence. CA measurements were recorded at −0.153 V vs. Ag/AgCl reference unless otherwise noted. All electrochemical potentials \( E \) were reported versus \( \text{RHE} \) the reversible hydrogen electrode (RHE) using the formula \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{ref}}(\text{Ag/AgCl}) + 0.059 V \times \frac{V}{\text{pH}} \) where \( E_{\text{ref}} = 0.197 V \) in this case.

For both CA and LSV measurements, representative samples of a given set were plotted with the mean (indicated as ‘x’) and bars for the error of the mean.

Prior to LSV and CA measurements, films were exposed to an external bias of 0.6 V vs. RHE (−0.153 V vs. Ag/AgCl) under AM 1.5 illumination for 1 hour. To compare different aspects of film activation (Fig. 8), freshly calcined samples were measured for UV-vis absorbance and CA data (Control). Following this, these same samples were either allowed to soak in potassium borate solution for 1 h (Soak), applied 0.6 V vs. RHE for 1 h in dark (EC-Only), exposed to AM 1.5 solar simulator for 1 h (Photo-Only), or treated with the standard PEC activation treatment (PEC) before measuring LSV and CA once more (except in the case of Soak, where only CA was measured). Additionally, another set of freshly calcined samples were soaked in electrolyte for 1 h followed by LSV and CA (LSV-Only, Fig. S4†) to observe the effects of LSV measurement, which is a combination of photo- and electrochemical treatments. It is important to note that for this series of measurements, samples all came from the same 4000-cycle SF-ALD film; additionally, for each test condition samples were selected from a variety of locations within the film to avoid local thickness or crystal quality variance within the film.

Optoelectronic properties

The optical response of thin films was measured using a Shimadzu UV-2450. A sandwich configuration of FTO-water-fused quartz was used to minimize light scattering differences between the blank measurement of bare FTO and samples coated onto FTO. Identical measurements on FTO were used to establish the baseline for the measurement of the optical properties of the deposited films alone.

X-ray photoelectron spectroscopy

A Kratos Axis UltraDLD instrument equipped with a monochromated copper K\( z \) X-ray source (wavelength of 0.154056 nm \(^{-1}\), operating at 10 kV and 15 mA). A hybrid lens mode was
employed during analysis, with an analysis area of approximately 700 μm × 300 μm. The XPS spectra for all samples were taken at a photoemission angle of 0°, relative to the surface normal. A Kratos charge neutralizer system was used on all samples with a filament current of between 1.8–2.1 A and a charge balance of 3.6 V.

Morphology

A Zeiss Ultra Plus scanning electron microscope (SEM) was operated at 5 kV using an in-lens secondary electron detector to observe the film surface and cross-sectional acquisition. ALD growth rates were calculated based upon cross-sectional SEM imaging of films in the 50–100 nm thickness range.

Results and discussion

Effect of alcohol on surface functionalization

The ALD growth of bismuth vanadates (BVO) has not yet enabled phase pure scheelite due to limited stoichiometry control. We briefly note that bismuth vanadates are a class of compounds with various Bi : V ratios. The prior report of ALD BVO utilized triphenyl bismuth (BiPh3), vanadium triisopropoxy oxide (VTIP), and water. To the best of our knowledge, this remains the only prior reported ALD of BVO. Here, the film stoichiometry was >65 at% V-rich and required a post-treatment etch of V2O5 to achieve phase-pure m-BiVO4 stoichiometry.45 The ALD growth of bismuth vanadates (BVO) has not yet been controlled to achieve phase-pure m-BiVO4 since the Bi-V stoichiometry by reducing the amount of VTIP oxide (VTIP) and water. To the best of our knowledge, this remains the only prior reported ALD of BVO. Here, the film stoichiometry was >65 at% V-rich and required a post-treatment etch of V2O5 to achieve phase-pure m-BiVO4 films.45 Increasing the pulse ratio to favor Bi had limited benefits since the Bi-deposition is catalytically dependent on V-OH species.45 SF-ALD provides a novel and time-efficient alternative to improve the Bi : V stoichiometry by reducing the amount of VTIP deposited in each cycle. Starting from a prior ALD protocol for V2O5,45,50 a pulse of different alcohols were used to inhibit the subsequent VTIP deposition with a [ROH-VTIP-W] deposition cycle. The specific alcohols investigated included ethanol, 2-propanol, and methanol (EtOH, iPrOH, and MeOH, respectively). Starting from a V2O5 growth-per cycle (GPC) of 0.22 Å per cycle, the alcohols were found to have increasing inhibition effect in order of EtOH, iPrOH, and MeOH (Fig. 1 and Table 1). The alcohol pulse length was found to saturate growth inhibition well within 25 ms (Fig. S1†). MeOH had the largest effect on VTIP deposition with the lowest GPC. This deviates from prior reported SF-ALD trends with these alcohols applied towards other materials.44,45 Many aspects determine the efficacy of a particular SF-species, including the density and type of remaining active sites, side reactions between precursor and inhibitor, and inhibitor displacement by precursor.45

The SF-ALD of BVO was examined with the same series of alcohols examined above. The SF-ALD deposition sequence was [ROH-VTIP-W-BiPh3-W]x. The use of EtOH, iPrOH, and MeOH for SF-ALD were found to result in increasingly Bi-rich deposition (Fig. 2 and Table 2), following a consistent trend with GPC for SF-ALD of V2O5. The samples prepared using MeOH had stoichiometries closest to the 1 : 1 BiVO4 compound, with 45.9 at% Bi and 54.1 at% V determined by mass-spectrometry (MS). For the remainder of this paper we thus focus exclusively on ternary BVO produced by SF-ALD with MeOH (MeOH-BVO). Cross-sectional and top-view SEM confirmed conformal composition on both Si and FTO substrates (Fig. 4a–d). Measurements from the flat Si substrate were used to determine the growth rate of 7.5 nm for every 1000 cycles of SF-ALD. This corresponds to a GPC of 0.075 Å per cycle that is remarkably quite similar to 0.07 Å per cycle from conventional ALD.45 The combination of a similar GPC with enhanced Bi content suggests that the SF step not only inhibits VTIP deposition, but also that the resulting surface, after hydrolysis, enhances the following BiPh3 deposition. Such mechanismic changes could be attributed to a combination of steric effects with the spatial distribution of active V-OH surface sites for BiPh3 catalytic deposition.

The crystallization of MeOH-BVO films was examined by grazing incidence wide-angle X-ray scattering (GI-WAXS) and SEM after high temperature calcination. The as-deposited films were amorphous, similar to the prior reported bismuth vanadate films by conventional ALD (Fig. 3).45 After heating to 450 °C for 1 h, the MeOH-BVO films exhibited strong reflections consistent with nearly phase-pure m-BiVO4. In contrast, the

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Deposition cycle</th>
<th>Growth rate (Å per cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD-V2O5</td>
<td>[VTIP-W]x</td>
<td>0.22</td>
</tr>
<tr>
<td>EtOH-V2O5</td>
<td>[EtOH-VTIP-W]x</td>
<td>0.14</td>
</tr>
<tr>
<td>iPrOH-V2O5</td>
<td>[iPrOH-VTIP-W]x</td>
<td>0.08</td>
</tr>
<tr>
<td>MeOH-V2O5</td>
<td>[MeOH-VTIP-W]x</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 1 Growth rates of V2O5 with different alcohols used for surface functionalization

![Fig. 1](Image1.png) (SF)-ALD growth rates of V2O5 using different alcohols for surface functionalization with deposition cycles of [ROH-VTIP-W]x.

![Fig. 2](Image2.png) Compositions for (SF)-ALD of BiV2O5 prepared with different alcohols for surface functionalization using deposition cycles of [ROH-VTIP-BiPh3-W]x.


**Table 2** Composition of (SF)-ALD BVO films with different alcohols used for surface functionalization

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Deposition cycle</th>
<th>at% Bi</th>
<th>at% V</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD-BVO</td>
<td>[VTIP-W-BiPh₃-W]₁ₓ</td>
<td>33.2%</td>
<td>66.8%</td>
</tr>
<tr>
<td>EtOH-BVO</td>
<td>[EtOH-VTIP-W-BiPh₃-W]₁ₓ</td>
<td>34.6%</td>
<td>65.4%</td>
</tr>
<tr>
<td>tPrOH-BVO</td>
<td>[tPrOH-VTIP-W-BiPh₃-W]₁ₓ</td>
<td>40.2%</td>
<td>59.8%</td>
</tr>
<tr>
<td>MeOH-BVO</td>
<td>[MeOH-VTIP-W-BiPh₃-W]₁ₓ</td>
<td>45.9%</td>
<td>54.1%</td>
</tr>
</tbody>
</table>

**Fig. 3** GI-WAXS of MeOH-BVO films, both as-made and calcined. For comparison, a calcined film from ALD-BVO is presented. All samples had \( x = 4000 \) deposition cycles. Graphs were offset vertically for clarity and fit data correspond to PDF#14-0688, 83-1812, and 89-0611, respectively. The calcination step was to 450 \( ^\circ \)C at 10 \( ^\circ \)C min\(^{-1}\) with a 60 min hold.

**Fig. 4** SEM of bismuth vanadates prepared by MeOH-BVO on Si (a, c, e) and FTO substrates (b, d, f). As-made films are shown in cross-section (top row, a, b) and top view (middle row, c, d). Crystallized films heated to 450 \( ^\circ \)C are shown in top view (bottom row, e, f). The deposition cycle was \([\text{MeOH-VTIP-W-BiPh}_3-W]_x\) where \( x \) was either 3000 (b, e, f) or 6000 (a, c, d).

ALD-BVO sample exhibited a pattern consistent with a mixture of m-BiVO₄, tetragonal bismuth vanadate (t-BiVO₄), and orthorhombic vanadium oxide (o-V₂O₅), consistent with the significant excess of vanadium detected by MS. The MS data also indicated a 4.1 at% V excess for the MeOH-BVO samples. This slight excess of vanadium did not result in an observable \( V_2O_5 \) phase for films \( \leq 30 \) nm (Fig. S2\(^{\dagger}\)). Additional GI-WAXS data for MeOH-BVO films on FTO substrates matched that of films on Si, albeit with additional substrate peaks (Fig. S3\(^{\dagger}\)). Film calcination also resulted in minor morphology changes from crystallite formation. Films calcined on FTO substrates remained fairly uniform whereas films on Si substrates underwent dewetting (Fig. 4e and f). MeOH-BVO samples enabled the crystallization of phase-pure and nearly stoichiometric m-BiVO₄.

**PEC performance vs. thickness**

The calcined MeOH-BVO films were applied towards solar-assisted PEC water splitting with thickness ranging from 7.5 to 75 nm. With a GPC of 0.075 Å per cycle, this corresponds to samples made using 1000–10 000 SF-ALD cycles. Here, the thickest samples examined were commensurate to the reported electron diffusion length of ca. 70–75 nm in BiVO₄.\(^{5,8,31,33}\) The PEC performance is a product of several terms, including the light harvesting efficiency (LHE), the charge separation efficiency, and the charge injection efficiency [eqn (1)], where \( J_{\text{PEC}} \) is the measured photocurrent density, \( J_{\text{abs}} \) is the photon absorption rate expressed as current density (determined from LHE), \( \phi_{\text{sep}} \) is the carrier separation efficiency, and \( \phi_{\text{inj}} \) is the charge injection efficiency.\(^{5,31–35}\)

\[
J_{\text{PEC}} = J_{\text{abs}} \times \phi_{\text{sep}} \times \phi_{\text{inj}}
\]

Here, the PEC performance was measured in the presence of a hole-scavenging sulfire electrolyte to pin the charge injection efficiency at 100% (\( \phi_{\text{inj}} = 1 \)). Thus, the measured photocurrents represent the voltage dependent product of light harvesting efficiency and charge separation efficiency. For this sample series, the photocurrent monotonically increased with sample thickness (Table 3 and Fig. 5), corresponding to the expected trend in light harvesting efficiency, as confirmed by UV-vis measurements (Fig. 6a). The highest photocurrent was measured with sample 75 nm-10k with 0.69 and 1.21 mA cm\(^{-2}\) at 0.60 and 1.23 V vs. RHE, respectively. For thicknesses from 15–60 nm the photocurrent performance monotonically increases with one exception, vide infra, and notably all exhibited performance that was independent of the illumination direction. In contrast, after 60 nm of thickness there is a statistically significant difference where backside illumination results in more photocurrent than front side illumination. Since m-BiVO₄ has a lower electron diffusion length (majority carrier) than hole diffusion length (minority carrier), one expects better performance when carriers are generated closer to the electron-accepting FTO contact. This observation shows the transition to transport limited performance occurs between 60 and 75 nm, similar to prior estimations.\(^{5,30}\) The thinnest 7.5 nm film produced negligible photocurrent, presumably due to poor crystallization (Fig. S2a\(^{\dagger}\)) or excessive recombination due to the...
FTO proximity. Such a “dead layer” effect has been noted before for PEC thin films, including Fe$_2$O$_3$ and BiVO$_4$. In contrast to prior reports, however, MeOH-BVO yields photoactive films when >15 nm whereas a different synthesis route required >50 nm. A notable curiosity was the similar photocurrent response from both 30 nm-4k and 45 nm-6k. This exception to the trend discussed above was confirmed with multiple sample measurements produced from multiple SF-ALD depositions. There is a change in the GI-WAXS patterns between these two samples where a second phase of o-V$_2$O$_5$ is apparent in >30 nm film (Fig. S2b†). This suggests a threshold thickness for accommodation of the excess 4.1 at% V as amorphous V$_2$O$_5$ or within the m-BiVO$_4$ lattice. At this transition, the second phase and the associated interfaces lowered the charge separation efficiency to a similar extent as the increase in the light harvesting efficiency, resulting in comparable performance. From these results, it is concluded that MeOH-BVO films <75 nm are viable thin films for host-guest applications.

Further PEC insights were gained by examining the wavelength dependent incident photon-to-current efficiency (IPCE, Fig. 6b) and the absorbed photon-to-current efficiency (APCE, Fig. 6c). As expected, IPCE increases with thickness, albeit with a decrease for film thicknesses >30 nm for IPCE and >60 nm for APCE. These results are consistent with the absorbance spectra (Fig. 6a) which show a decrease in absorbance with increasing film thickness.

**Table 3** A series of films with different thicknesses were prepared using the MeOH–BVO protocol. All samples were calcined after growth via the deposition cycle of [MeOH–VTIP–W–BiPh$_3$–W]$_x$ with varying values for $x$.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Film thickness$^a$ (nm)</th>
<th>$x$, number of deposition cycles (k cycles)</th>
<th>Photocurrent$^b$ at 0.6 V vs. RHE</th>
<th>Photocurrent$^b$ at 1.23 V vs. RHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5 nm-1k</td>
<td>7.5</td>
<td>1</td>
<td>0.098 ± 0.002</td>
<td>0.035 ± 0.005</td>
</tr>
<tr>
<td>15 nm-2k</td>
<td>15</td>
<td>2</td>
<td>0.08 ± 0.01</td>
<td>0.22 ± 0.01</td>
</tr>
<tr>
<td>22.5 nm-3k</td>
<td>22.5</td>
<td>3</td>
<td>0.14 ± 0.02</td>
<td>0.34 ± 0.05</td>
</tr>
<tr>
<td>30 nm-4k</td>
<td>30</td>
<td>4</td>
<td>0.35 ± 0.02</td>
<td>0.70 ± 0.02</td>
</tr>
<tr>
<td>45 nm-6k</td>
<td>45</td>
<td>6</td>
<td>0.30 ± 0.02</td>
<td>0.67 ± 0.03</td>
</tr>
<tr>
<td>60 nm-8k</td>
<td>60</td>
<td>8</td>
<td>0.42 ± 0.03</td>
<td>0.81 ± 0.03</td>
</tr>
<tr>
<td>75 nm-10k</td>
<td>75</td>
<td>10</td>
<td>0.69 ± 0.04</td>
<td>1.21 ± 0.04</td>
</tr>
</tbody>
</table>

$^a$ Film thickness calculated from the product of the growth-per-cycle with the number of cycles (GPC $x$).

$^b$ Mean back-side photocurrent (mA cm$^{-2}$).

Fig. 5 Photocurrent response for calcined MeOH–BVO films as a function of film thickness and applied potential. The electrolyte was 1.0 M potassium borate with a pH of 9.36 with 0.2 M Na$_2$SO$_3$ as hole scavenger. The dark current (dotted), photocurrent with backside illumination (dashed) and photocurrent with front side illumination (solid) are presented. The film thickness is specified in the legend followed by the corresponding number of MeOH–BVO deposition cycles $x$.

Fig. 6 The (a) absorbance, (b) incident photon-to-current efficiency and (c) absorbed photon-to-current efficiency are shown for calcined MeOH–BVO films of various thicknesses. The IPCE and APCE were measured at 0.6 V vs. RHE in 1.0 M potassium borate with 0.2 M Na$_2$SO$_3$ as hole scavenger. The film thickness is specified in the legend followed by the corresponding number of MeOH–BVO deposition cycles, $x$. 

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the same performance overlap observed in the $J$–$V$ data and discussed above. This is consistent with the expectation of improved LHE with thicker films. The APCE was calculated by normalizing the IPCE with the LHE, resulting in the wavelength dependent $\phi_{\text{sep}}$ for each sample. The monotonic trend of higher APCE with thicker films was attributed to lower recombination rates in thicker films (due to the distance from the FTO/BiVO$_4$ interface). This observation suggests the future development of hole-blocking layers to mitigate recombination at the FTO interface.

To confirm the validity of these measurements, the photocurrent at 0.6 V vs. RHE ($J_{\text{PEC}}$) was compared to the integrated product of IPCE with the AM 1.5 spectrum ($J_{\text{IPCE}}$, Table S1†). The photocurrents were matched within 15% for sample 75 nm-10k. However, it was apparent that thinner films exhibited a greater difference that was attributed to the varying intensity between the simulated AM 1.5 spectrum used for $J$–$V$ and the monochromator used IPCE measurements. Previous reports indicated a significant dependence of m-BiVO$_4$ quantum efficiencies with illumination intensity.$^{10,51}$

The PEC performance of SF-ALD BiVO$_4$ electrodes were compared to BiVO$_4$-V$_2$O$_5$ electrodes prepared by conventional ALD that were subsequently etched to yield a porous film of phase-pure scheelite.64 Please note that conventional ALD routes do not yet exist for phase pure BiVO$_4$ without subsequent etching. Comparing films of similar thickness, these two synthesis methods result in similar plateau photocurrents with the SF-ALD BiVO$_4$ exhibiting an improved onset potential 120 mV lower (Fig. S4†). The photocurrent stability of SF-ALD BiVO$_4$ films was examined under continuous illumination for 17 h (Fig. S5†). After the initial PEC activation ($t = 1$ h), the photocurrent decreased by 11% over this period.

The SF-ALD BiVO$_4$ films presented here are promising for application towards host–guest composites. Prior works have demonstrated mesoporous films with photocurrents over 3 mA cm$^{-2}$ at potentials as low as 0.6 V vs. RHE.$^{5,9}$ In the past year, photocurrents at the thermodynamic water splitting potential of 1.23 V vs. RHE of $\geq$5 mA cm$^{-2}$ have been reported with host–guest composites.$^{5,9}$ These prior works used cathodic electrodeposition to produce BiVO$_4$ films and thus are not ideally suited for elaboration with hole blocking materials at the FTO-BiVO$_4$ interface. In contrast, the SF-ALD route presented here is compatible with arbitrary substrates, independent of their electronic properties. We anticipate that future studies with the SF-ALD of BiVO$_4$ onto high surface area conductive substrates (such as nanostructured Sb : SnO$_2$)$^{29}$ will lead to improvements in overall performance.

**Effects of PEC activation treatment**

A pronounced effect of PEC measurement time was noted for the performance of the above-discussed films. In all cases, the photocurrent continuously increased with measurement time until a plateau. Improvements as large as 380% were found in some cases. We thus developed a PEC activation treatment to quickly stabilize film performance before the above measurements were performed. Recent reports with other fabrication routes have also indicated that various pretreatments improve PEC performance. Pretreatments have been reported using controlled reduction and/or oxidation of V cations,$^{9,60}$ ultraviolet light,$^{61}$ and open-circuit exposure to AM 1.5 illumination.$^{62}$ It was suggested that the elimination of surface oxygen by producing oxygen vacancies is the source of improved PEC performance.$^{9,60–64}$

A PEC activation treatment was developed to establish stable photocurrents before performance measurements (described in Experimental). The improved IPCE after PEC activation treatment was surprising since the films had uniformly reduced optical absorption (Fig. 7a). The extent of change in performance was found to vary with film thickness. For 30 nm films the IPCE and APCE increased by 2.6× and 3.1× with the PEC activation treatment. For 60 nm films the IPCE and APCE...
increased by 3.8× and 4.1× with the PEC activation treatment (Table 4 and Fig. 7). We note that GI-WAXS of calcined MeOH-BVO films presented above indicated a change from single-phase m-BiVO₄ for ≤30 nm thick films to a mixture of m-BiVO₄ and o-V2O₅ for ≥45 nm thick films (Fig. S2†). These thicker films with crystalline o-V2O₅ exhibited the most change during PEC activation treatment, suggesting a dependence on the nature of the slight V-excess with MeOH-BVO deposition.

To evaluate the efficacy of this multicomponent PEC activation treatment, multiple control experiments were run to isolate the effects of each component of the treatment. Measurements were performed on photo-only treated (Photo-Only), electrochemical-only treated (EC-Only), and electrolyte-only (Soak) treatments (Table 5, see Experimental for details). As seen in Fig. 8a and b, each aspect of the PEC activation treatment improves both the IPCE and APCE performance of the films to some degree. The largest effect was found for the complete treatment (Activated). All treatment conditions, except Soak, reduced the absorptance of the films (Fig. 8c). Thus the improvement with Soak may be attributed to surface changes such as the hydrolytic formation of hydroxyl groups and is not consistent with dissolution nor significant internal changes to oxidation states. In contrast, all other components of the PEC activation treatment (Photo-Only and EC-Only) resulted in a concomitant reduction of absorptance with the improved performance. Previous reports have indicated that the V oxidation state in BiVO₄ plays an important role with some hints of an optimal V⁴⁺/V⁵⁺ ratio.⁹,₆₀,₆₂ It was also demonstrated that AM 1.5 illumination under open circuit can markedly improve some films where it was suggested that removing surface states assisted to unpin the Fermi level.⁶²,⁶₅ Fermi level pinning from surface states has been identified in other photoanode materials, including Fe₂O₃ and TiO₂.⁶₆,₆₇ However, the changes in absorptance observed with Photo-Only, EC-Only, and Activated are consistent with additional redox changes.

X-ray photoelectron spectroscopy (XPS) was performed on 30 nm-4k samples promptly after calcination as well as after the PEC activation treatment (Fig. S6;† Calcined and PEC Activated).

Table 4 The effectiveness of sample activation pretreatment varied with film thickness. All samples were calcined after growth from the same MeOH-BVO deposition cycle: [MeOH-VTIP-W-BiPh₃-W]x, where x was either 4k or 8k corresponding respectively to the 30 and 60 nm films

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Treatment</th>
<th>Film thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 nm</td>
<td>None. Used directly following calcination</td>
<td>30 nm</td>
</tr>
<tr>
<td>30 nm-activated</td>
<td>1 h at 0.6 V vs. RHE with AM 1.5 illumination</td>
<td>30 nm</td>
</tr>
<tr>
<td>60 nm</td>
<td>None. Used directly following calcination</td>
<td>60 nm</td>
</tr>
<tr>
<td>60 nm-activated</td>
<td>1 h at 0.6 V vs. RHE with AM 1.5 illumination</td>
<td>60 nm</td>
</tr>
</tbody>
</table>

Table 5 The effect of each component of the PEC activation were investigated separately. All samples are calcined MeOH-BVO films prepared with [MeOH-VTIP-W-BiPh₃-W]₄₀₀₀ resulting in a thickness of 30 nm

<table>
<thead>
<tr>
<th>Sample names</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>None</td>
</tr>
<tr>
<td>Soak</td>
<td>Soaked in electrolyte for 1 h (open circuit, no illumination)</td>
</tr>
<tr>
<td>EC-Only</td>
<td>Applied 0.6 V vs. RHE for 1 h (no illumination)</td>
</tr>
<tr>
<td>Photo-Only</td>
<td>AM 1.5 illumination for 1 h (open circuit)</td>
</tr>
<tr>
<td>Activated</td>
<td>Applied 0.6 V vs. RHE during AM 1.5 illumination for 1 h</td>
</tr>
</tbody>
</table>
respectively). Changes to both the Bi and V oxidation states were detected at the sample surface as a result of the PEC activation treatment. Following calcination, films contained a minor component of reduced Bi\(^{3+}\) and V\(^{4+}\) in addition to the expected BiVO\(_4\) states. The PEC activation treatment was found to fully oxidize these reduced states to Bi\(^{3+}\) and V\(^{5+}\). This oxidation process is consistent with the observed oxidation current during CV cycling in the dark. The ALD of bismuth titanates with BiPh\(_3\) and water was previously reported to result in a mixture of Bi\(^{3+}\) and Bi\(^{4+}\). A recent study also identified switchable oxidation states of V\(^{4+/5+}\) during electrochemical cycling below 0.5 V vs. RHE. In contrast, a recently reported open-circuit illumination pretreatment identified the reduction of V from the +5 to the +4 state with a corresponding increase in performance. These results highlight the connection of synthetic route and defect chemistries that can enhance the performance of BiVO\(_4\) photoanodes.

Neither crystallographic nor surface morphology changes were observed for any of the treatments (Fig. S7 and S8†). While mechanistically intriguing, the detailed study of PEC activation is outside the scope of this SF-ALD study. The developed PEC activation treatment resulted in a marked improvement of MeOH-BVO film performance.

**Conclusions**

The uniform deposition of thin film m-BiVO\(_4\) onto arbitrary hosts is necessary for the development of next-generation host-guest architectures for solar water splitting. The capability to deposit BiVO\(_4\) by ALD enables the further development independent of substrate properties. Phase pure monoclinic-scheelite BiVO\(_4\) was obtained by MeOH SF-ALD and the resulting films were highly photoactive. Photoactivity was improved by applying a novel PEC activation treatment. Development of a layer-by-layer technique for PEC-functional BiVO\(_4\) with improved control over stoichiometry allows for the development of efficient multi-layer devices with advanced architectures.

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**Notes and references**
