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# Near-Complete Suppression of Oxygen Evolution for Photoelectrochemical H<sub>2</sub>O Oxidative H<sub>2</sub>O<sub>2</sub> Synthesis

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KEYWORDS: Water oxidation, Hydrogen peroxide, Fermi level pinning, BiVO<sub>4</sub> photoanode

**ABSTRACT:** Solar energy-assisted water oxidative hydrogen peroxide  $(H_2O_2)$  production on an anode combined with  $H_2$ production on a cathode increases the value of solar water splitting, but the challenge of the dominant oxidative product,  $O_2$ , needs to be overcome. Here, we report a SnO<sub>2-x</sub> overlayer coated BiVO<sub>4</sub> photoanode, which demonstrates a great ability to near-completely suppress  $O_2$  evolution for photoelectrochemical (PEC)  $H_2O$  oxidative  $H_2O_2$  evolution. Based on the surface hole accumulation measured by surface photovoltage, downward quasi-hole Fermi energy at the photoanode/electrolyte interface and thermodynamic Gibbs free energy between 2-electron and 4-electron competitive reactions, we are able to consider the photoinduced holes of  $BiVO_4$  that migrate to the  $SnO_{3-x}$  overlayer kinetically favour  $H_2O_2$  evolution with great selectivity by reduced band bending. The formation of  $H_2O_2$  may be mediated by the formation of hydroxyl radicals (OH•), from 1-electron water oxidation reactions, as evidenced by spin-trapping electron paramagnetic resonance (EPR) studies conducted herein. In addition to the H<sub>2</sub>O oxidative H<sub>2</sub>O, evolution from PEC water splitting, the  $SnO_{2-x}/BiVO_4$  photoanode can also inhibit  $H_2O_2$  decomposition into  $O_2$  under either electrocatalysis or photocatalysis conditions for continuous H<sub>2</sub>O<sub>2</sub> accumulation. Overall, the  $SnO_{2,x}/BiVO_4$  photoanode achieves a Faraday efficiency (FE) of over 86% for  $H_2O_2$  generation in a wide potential region (0.6~2.1 V vs. reversible hydrogen electrode (RHE)) and an  $H_2O_2$ evolution rate averaging 0.825  $\mu$ mol/min/cm<sup>-2</sup> at 1.23 V vs. RHE under AM 1.5 illumination, corresponding to a solar to H<sub>2</sub>O<sub>2</sub> efficiency of  $\sim$ 5.6%; this performance surpasses almost all previous solar energy-assisted H<sub>2</sub>O<sub>2</sub> evolution performances. Because of the simultaneous production of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> by solar water splitting in the PEC cells, our results highlight a potentially greener and more cost-effective approach for "solar-to-fuel" conversion.

#### INTRODUCTION

As an important chemical in industrial chemistry, the market size for hydrogen peroxide  $(H_2O_2)$  has reached 3.5 billion USD in 2015 with a compound annual growth rate of more than 5% from 2016 to 2024. <sup>1</sup> Because traditional anthraquinone oxidative  $H_2O_2$  production requires large plants and suffers from inconvenient transportation, <sup>2</sup> photocatalytic or electrochemical (EC)  $H_2O_2$  production has attracted considerable attention, partially due to onsite production and low cost. Currently, photocatalytic or EC  $O_2$  reductive  $H_2O_2$  production through the two-electron pathway has been widely studied. <sup>3-8</sup> However, the reduction reaction needs to continuously supply a feedstock of  $O_2$  gas, which sacrifices  $H_2$  production due to water reduction. <sup>9</sup> Catalysing water oxidation for  $H_2O_2$  production is, therefore, an alternative strategy since  $H_2$  production by water reduction does not need to be sacrificed to generate dual-energy carriers through the redox coupling of water. <sup>10, 11</sup> Unfortunately, the production of  $H_2O_2$  via an oxidative water process is a formidable challenge, which requires the two-electron transfer from the photoanodes.  $H_2O_2$  evolution is thermodynamically less favourable than  $O_2$  evolution, as shown in the following equations: <sup>12</sup>

 $_{2}H_{2}O + _{4}e^{-}/h^{+} \rightarrow O_{2} + _{2}H_{2} (E^{o} = +1.23 V vs. RHE)$  (1)

 $_{2}H_{2}O + 2e^{-}/h^{+} \rightarrow H_{2}O_{2} + H_{2} (E^{\circ} = +1.77 \text{ V vs. RHE})$  (2)

Therefore, there is no significant concern for  $H_2O_2$  evolution by EC water oxidation.

Recently, Fuku and Sayama demonstrated that BiVO<sub>4</sub>based photoanodes can selectively catalyse  $H_2O$  to  $H_2O_2$  in the presence of HCO<sub>3</sub><sup>-</sup>. <sup>13</sup> Norskov and Zheng's groups have subsequently exhibited the EC oxidation of water to  $H_2O_2$ in a HCO<sub>3</sub>-containing electrolyte using various kinds of photoanode materials, such as BiVO<sub>4</sub>, SnO<sub>2</sub>, and WO<sub>3</sub>; these authors demonstrated that the free energy of absorbed OH is a key factor in thermodynamically favourable H<sub>2</sub>O<sub>2</sub> evolution. <sup>14, 15</sup> Despite the numerous efforts regarding this advanced water oxidation process, the EC approach resulted in an unsatisfactory Faraday efficiency (FE) ( $\leq 80\%$ ) and required a high operation potential with a narrow potential window between 2.7 and 3.2 V (vs. reversible hydrogen electrode (RHE)). 16-20 In addition to the thermodynamic issue regarding the competitive oxidation reaction between oxygen evolution and H<sub>2</sub>O<sub>2</sub> production, the decomposition of highly reactive  $H_2O_2$  readily occurs at the photoanodes (Eq 3)<sup>2</sup>

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 $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- E^\circ = +0.68 \text{ V vs. RHE}$  (3)

Therefore, competitive  $O_2$  evolution may occur in two ways: 4-electron transfer or stepped 2-electron transfer via a  $H_2O_2$  intermediate, which highlights a key counterbalance between suppressing  $H_2O_2$  decomposition and boosting 2electron water oxidation.

Here, we report a photoelectrochemical (PEC) approach for highly selective water oxidative  $H_2O_2$  production using a surface-modified BiVO<sub>4</sub> photoanode. An electrodeposited SnO<sub>2</sub> overlayer with oxygen vacancies on the BiVO<sub>4</sub> photoanode significantly modulates the surface hole oxidation reaction kinetics. This process turns the complete reaction of  $H_2O_2$  and  $O_2$  evolution at the photoanodes into  $H_2O_2$  evolution and OH radical (OH·) generation during the water oxidation process, accompanied by the suppression of  $H_2O_2$  decomposition in the hole re-oxidation process. As a result, the  $O_2$  evolution is almost completely suppressed by substituting OH·, achieving an average FE for  $H_2O_2$  evolution of 86% at a widely applied bias ranging from 0.6 to 2.1 V (vs. RHE).

#### **RESULTS AND DISCUSSION**

The BiVO<sub>4</sub> electrodes were prepared by electrodeposition based on a previous report. <sup>21</sup> The SnO<sub>2</sub> overlayer with controllable oxygen vacancies was electrochemically deposited on the porous BiVO<sub>4</sub> electrodes in a mildly acidic plating solution using SnCl<sub>2</sub> as a precursor, followed by annealing at 450 °C under air or argon (Ar) conditions (see the experimental section in detail). The oxygen vacancies were determined by electron paramagnetic resonance (EPR) spectra, as shown in Figure 1a. The strong EPR signal with g=2.25 for SnO<sub>2</sub> annealed at 450 °C in Ar can be assigned to ionized oxygen vacancies ( $V_0$ ). <sup>22</sup> The X-ray photoelectron spectroscopy (XPS) Sn 3d spectra of SnO<sub>2</sub> annealed at 450 °C in Ar shows an ~0.4 eV blueshift compared to the sample annealed at 450 °C in air (Figure S1), which is ascribed to fewer O neighbours around Sn on average. <sup>23</sup> The X-ray diffraction (XRD) pattern of SnO<sub>2</sub> annealed at 450 °C in Ar also displays relatively weaker



**Figure 1** (a) EPR spectra of electrodeposited  $SnO_2$  annealed at 450 °C in Ar and air, (b) top-view and (c) cross-sectional SEM image, (d) and (e) HR-TEM image with the corresponding electron diffraction spot and (f) HAADF-STEM-EDX elemental mapping of the  $SnO_{2-x}/BiVO_4$  photoanode.

diffraction peaks compared to SnO<sub>2</sub> annealed at 450 °C in 1 air (Figure S<sub>2</sub>), and no diffraction peaks can be assigned to 2 SnO, indicating that neither Ar nor air annealing affects 3 the crystal structure of SnO<sub>2</sub>. Herein, the SnO<sub>2</sub> overlayer 4 obtained by this means on the BiVO<sub>4</sub> photoanode can be 5 labeled as SnO<sub>2-x</sub>/BiVO<sub>4</sub> and SnO<sub>2</sub>/BiVO<sub>4</sub>. The scanning 6 electron microscopy (SEM) image of a typical SnO<sub>2-</sub> 7  $_{x}$ /BiVO<sub>4</sub> electrode is shown in Figure 1b, which displays a similar porous morphology to the pure BiVO<sub>4</sub> electrode 8 9 (Figure S<sub>3</sub>) because of the very thin  $SnO_2$  (<6 nm) layer on the BiVO<sub>4</sub> surface. The total thickness of the  $SnO_{2-x}/BiVO_4$ 10 electrode is approximately 800 nm, as shown in Figure 1c, 11 elemental mapping shows the homogeneous and 12 distribution of Sn in the entire electrode (Figure S4). 13 Additionally, the XRD patterns and Raman shifts of the 14  $SnO_{2-x}/BiVO_4$  or  $SnO_2/BiVO_4$  photoanodes do not show an 15 obvious effect on the BiVO<sub>4</sub> crystals by the SnO<sub>2</sub> coating 16 (Figure S<sub>5</sub>). Note that an overly negative potential for 17 electrodepositing SnO<sub>2</sub> can reduce Bi<sup>3+</sup> to Bi<sup>o</sup>, <sup>24</sup> although it 18 seems to form a thick SnO<sub>2</sub> overlayer (Figure S6). The 19 thickness of the SnO<sub>2-x</sub> overlayer is determined by high-20 resolution transmission electron microscopy (HR-TEM), 21 which demonstrates a 6 nm thick SnO<sub>2</sub> layer that 22 conformally covers the BiVO<sub>4</sub> particles (Figure 1d). The fast 23 Fourier transform (FFT) pattern exhibits a highly 24 crystalline nature with characteristic crystallographic 25 orientations of (100), (110), and (010) for monoclinal BiVO<sub>4</sub>, 26 which is simultaneously accompanied by crystallographic 27 orientations of (110) for tetragonal SnO<sub>2</sub>. A HR-TEM image 28 taken from the SnO<sub>2-x</sub>/BiVO<sub>4</sub> interface region reveals a less 29 than 2 nm channel in addition to the lattice spacings of 30 0.467 and 0.475 nm corresponding to the (110) and (011) 31 planes of monoclinic BiVO<sub>4</sub>, respectively, and the lattice 32 spacing of 0.23 nm is consistent with the d value of the (1-33 1-1) plane of SnO<sub>2</sub> (Figure 1e). The Bi 4f and V 2p XPS 34 spectra peaks of BiVO<sub>4</sub> are shifted to higher binding 35 energies after coating with  $SnO_2$  or  $SnO_{2-x}$ , which might be 36 caused by the interactions of Sn<sup>4+</sup> with Bi and V atoms in 37 the interfacial region (Figure S7).<sup>25</sup> The high-angle annular dark-field scanning transmission electron microscopy 38 (HAADF-STEM) image with elemental maps in Figure 1f 39 solidly demonstrates the surface coverage of SnO<sub>2</sub> with a 40 maximum thickness of 6 nm. The HAADF-STEM-EDS 41 elemental mapping for cross-view demonstrated the 42 conformal coating of  $SnO_{2-x}$  on BiVO<sub>4</sub> surface (Figure S8). 43 As the O is XPS spectra of annealed pure BiVO<sub>4</sub> at 450 °C 44 in either Ar or air overlap, excluding the possible  $V_{0}$ 45 induced by this process (Figure S9). The optical absorption 46 spectra show no significant change in the band gap of 47  $BiVO_4$  with either  $SnO_2$  or  $SnO_{2-x}$  coverages (Figure S10). 48 PEC H<sub>2</sub>O<sub>2</sub> generation was performed in 1 M NaHCO<sub>3</sub> 49 50

solution with a pH of 8.3 under AM 1.5 illumination (100 mW/cm<sup>2</sup>). As shown in Figure 2a, the dark currents of BiVO<sub>4</sub>, SnO<sub>2-x</sub>/BiVO<sub>4</sub>, and SnO<sub>2</sub>/BiVO<sub>4</sub> photoanodes demonstrate that either SnO<sub>2</sub> or SnO<sub>2-x</sub> coverages are responsible for suppressing the surface reaction kinetics of BiVO<sub>4</sub>. Although it is consistent with the activity trends in EC oxidative H<sub>2</sub>O to H<sub>2</sub>O<sub>2</sub> predicted by Nørskov and Zheng et al., <sup>14</sup> the SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanode exhibits an enhanced

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photocurrent density compared to the BiVO<sub>4</sub> and SnO<sub>2</sub>/BiVO<sub>4</sub> photoanodes, along with an obvious cathodic shift of the onset potential. The results clearly indicate that the SnO<sub>2-x</sub> overlayer can efficiently improve the PEC performance of the BiVO<sub>4</sub> photoanode. However, the SnO<sub>2</sub> overlayer plays a negative role with respect to the photocurrent density. A more in-depth discussion and analysis regarding PEC performance and dark current are provided in Figure S11. Because the band edge potentials of SnO<sub>2</sub> straddle that of BiVO<sub>4</sub>, the decreased photocurrent density of  $SnO_2/BiVO_4$  photoanode indicates that the Type I band edge configuration somewhat affects the number of surface-reaching holes, even though the thickness of SnO<sub>2</sub> is only 6 nm. <sup>26</sup> Compared with SnO<sub>2</sub>, the valance band (VB) edge of  $SnO_{2-x}$  is shifted up by ~0.5 eV, as determined by VB-XPS (Figure S12), presumably ascribing to the presence of V<sub>o</sub>. As evidenced by first-principles calculations, a new band state appears and up-shifts the VB edge for SnO<sub>2-x</sub>, which is consistent with the results of the valence band XPS spectra (Figure S13). The upward VB edge will reduce the energy barrier of the hole migration from  $BiVO_4$  to SnO<sub>2-x</sub> to improve the water oxidation photocurrent. The possible hole migration can be further demonstrated by the transient-state surface photovoltage (TS-SPV) responses, in which the photoanodes exposed to the air atmosphere give rise to upward band bending that leads to the surface migration of photoinduced holes due to the surface absorbed water. <sup>27</sup> As shown in Figure 2b, the surface migration behaviour of the photoinduced hole enables positive SPV signals for all photoanodes. Clearly, the  $SnO_{2-x}/BiVO_4$  photoanode has the highest signal intensity, indicating that the photoinduced holes that reach the photoanode surface are dramatically promoted by the  $SnO_{2-x}$  overlayer. Moreover, both the  $SnO_2/BiVO_4$ and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes favour long-lived holes at the surface, as the delay times of the photovoltage signals are significantly prolonged as a result of the reduction of surface recombination. <sup>28</sup> The PEC water oxidative H<sub>2</sub>O<sub>2</sub> evolution was quantified by the N,N-diethyl-1,4phenylene-diamine (DPD) method, which was determined by calibrating the standards of the H<sub>2</sub>O<sub>2</sub> solution (Figure S14). The real-time FE for  $H_2O_2$  production is displayed in Figure 2c. In the PEC reaction region, the real-time FE for all photoanodes can be maintained at a steady level, and either the SnO<sub>2</sub> or SnO<sub>2-x</sub> overlayers significantly increase the real-time FE of the BiVO<sub>4</sub> photoanode from an average of 23% to an average of 61% and 86% in the applied bias ranging from 0.6 to 2.1 V (vs. RHE). The enhanced realtime FE by either the  $SnO_2$  or  $SnO_{2-x}$  overlayers is suddenly dropped from 88% to 66% and from 81% to 39%, respectively, when the applied bias is larger than 2.1 V (vs. RHE) where the EC reaction occurs. The phenomenon is in good agreement with their dark current behaviours in which the  $SnO_2/BiVO_4$  and  $SnO_{2-x}/BiVO_4$  photoanodes show a larger overpotential and a lower current density. In most cases, beyond EC water splitting, not only one but several EC products (e.g., H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, or OH·) are generally thermodynamically favoured. 29-31 From an EC viewpoint, the applied bias is associated with the Fermi level at the



**Figure 2.** (a) J–V curves of BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes in 1 M NaHCO<sub>3</sub> electrolyte (pH = 8.3) under AM 1.5 illumination; (b) the TS-SPV responses of the BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes. The wavelength and intensity of the excitation pulse are 355 nm and 50  $\mu$ J, respectively; (c) calculated real-time FE of the H2O2 evolution at various applied biases of the BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes; (d) A simplified comparison depicting the fundamental differences in interfacial charge transfer energetics between EC and PEC WOR; (e) the actual quantities of the O<sub>2</sub> evolution amounts of the BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes at 1.23 V vs. RHE in 1 M NaHCO<sub>3</sub> electrolyte (pH = 8.3) under AM 1.5 illumination and corresponding overall FE values of both O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> evolution (navy, green and dark yellow columns are the FE values of H<sub>2</sub>O<sub>2</sub> evolution of the BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes, respectively); and (f) Mott-Schottky plots measured in under dark and 218

electrode/reactant interface; either an increase or decrease will cause a change in the potential drop across the EC double layer, thereby varying the activation energies and rate constants for all possible interfacial charge transfer processes. This process is hypothesized to be an essential reason for the applied bias depending on the EC product selectivity.<sup>32</sup> In contrast to the EC reaction, the quasi-Fermi level formed at the electrode/reactant interface in the PEC reaction is pinned; therefore, the activation energies and rate constants for the interfacial charge transfers are less affected <sup>33-35</sup>. Different mechanisms are responsible for the dramatic FE changes in water oxidative H<sub>2</sub>O<sub>2</sub> generation across the EC and PEC regions (Figure 2d).

Since the accumulation amount of  $H_2O_2$  was measured by the DPD method, the estimated amount that solely corresponds to the  $H_2O_2$  yield might not be accurate due to another possibility of the decomposition of  $H_2O_2$  by Eq 3. To explore the underlying mechanism, these photoanodes were continuously illuminated for 600 s at 1.23 V vs. RHE in a 1 M NaHCO<sub>3</sub> electrolyte, and the time courses of the PEC reaction are shown in Figure S15. The corresponding incident photon-to-electron conversion efficiency (IPCE) at 1.23 V vs RHE show that all photoanodes exhibit a maximum value of 65% at 460 nm (Figure S16), which is consistent with characteristic IPCE curve of BiVO<sub>4</sub> for PEC water splitting <sup>36, 37</sup>. Clearly, the SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes display better stability than the  $BiVO_4$  photoanode during the  $H_2O_2$ evolution process, ascribing to the passivation effect of the overlayers that suppresses the photo-corrosion of BiVO<sub>4</sub>. <sup>38,</sup> <sup>39</sup> Importantly, the  $O_2$  evolution over the SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanode is almost undetectable, whereas the BiVO<sub>4</sub> and SnO<sub>2</sub>/BiVO<sub>4</sub> photoanodes show total O<sub>2</sub> amounts of 2.628 and 0.773 µmol, respectively, during a H<sub>2</sub>O<sub>2</sub> evolution process of 600 s. The calculated overall real-time FE for  $H_2O_2$  and  $O_2$  evolution is exhibited in Figure 2e. Considering the total H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> amounts, the overall real-time FE of the BiVO4 photoanode is near 100%, corresponding to competitive H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> evolution processes. However, for SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes, the overall real-time FE is less than 100%, suggesting products other than H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> are generated by PEC water oxidation. In particular, the  $SnO_{2-x}/BiVO_4$ photoanode is not capable of O<sub>2</sub> evolution, which is an important indication of the near-complete suppression of  $O_2$  evolution that occurs by neither water oxidation nor H<sub>2</sub>O<sub>2</sub> decomposition.

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**Figure 3.** (a) Free energy diagram of water oxidation plotted at U=1.77 V vs. RHE on BiVO<sub>4</sub> (111), SnO<sub>2</sub> (110) and SnO<sub>2-x</sub> (110). (b) Disk-ring currents recorded at 1600 rpm in a 1 M NaHCO<sub>3</sub> electrolyte. EPR responses of OH-generation by BiVO<sub>4</sub>, SnO<sub>2</sub> and SnO<sub>2-x</sub> under visible light illumination in 1 M NaHCO<sub>3</sub> (c) and 1 M phosphate buffer (d) solutions, respectively without applied bias.

In the photo-oxidative water process, the H<sub>2</sub>O<sub>2</sub> evolution reaction can compete with the O<sub>2</sub> evolution reaction if photogenerated holes in the VB edge of the photoanode are deeper than the overpotential required by  $H_2O_2$ evolution. 40, 41 Because of the same VB edge originating from BiVO<sub>4</sub>, the activity trends between the  $H_2O_2$  and  $O_2$ evolution processes can be considered the different surface thermodynamic processes as well as the hole quasi-Fermi level for BiVO<sub>4</sub>, SnO<sub>2</sub>, and SnO<sub>2-x</sub> to drive the water oxidation kinetics. The signatures of the quasi-Fermi level changes are displayed in Figure 2f. Notably, the Fermi level of BiVO<sub>4</sub> is pinned as observed at an unchanged flat-band potential under dark and illumination conditions. Significantly, the flat-band potential shifts anodically upon the SnO<sub>2-x</sub> coverage, and the positive shift does not contribute to the cathodic shift of the photocurrent onset potential in any case because it represents less upward band bending. 42, 43 Thus, we conjecture that the cathodic shift of the photocurrent for the SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanode may be the cause of the changing water oxidation reaction from  $O_2$  evolution to  $H_2O_2$  evolution. The mechanism diagram is shown in Figure S17. Figure 3a shows the calculated free energy diagram for the 2-electron and 4electron oxidation processes of water on the BiVO<sub>4</sub>, SnO<sub>2</sub>, and SnO<sub>2-x</sub> surfaces from the thermodynamic models in Figure S18. At a theoretical potential of 1.77 V vs. RHE for  $H_2O_2$  evolution, it can be seen that the free energy for absorbed OH<sup>\*</sup> ( $\Delta G_{OH^*}$ ) is the key bifurcating point to

determine the  $O_2$  or  $H_2O_2$  evolution. For the BiVO<sub>4</sub> photoanode, the reaction step from absorbed  $OH^*$  to  $H_2O_2$ evolution is downhill in the free energy, suggesting much more favourable thermodynamics for  $H_2O_2$  evolution. Remarkably, the  $\Delta G_{OH^*}$  of the SnO<sub>2</sub> and SnO<sub>2-x</sub> surfaces leads to an uphill reaction for H<sub>2</sub>O<sub>2</sub> evolution. However, compared with the  $O_2$  evolution, the  $H_2O_2$  evolution on the SnO2 surface is still favourable because of its smaller free energy barrier. In contrast, SnO<sub>2-x</sub> exhibits thermodynamically unfavourable H<sub>2</sub>O<sub>2</sub> evolution as a result of a much higher free energy barrier for  $H_2O_2$ formation. The results are consistent with their EC performances but inconsistent with their PEC activity trends for  $H_2O_2$  generation, as shown in Figure 2a. Therefore, the reduced band bending in  $SnO_{2-x}/BiVO_4$  that is associated with the hole quasi-Fermi level seems to be responsible for PEC H<sub>2</sub>O<sub>2</sub> generation with high selectivity. In addition to the water oxidative H<sub>2</sub>O<sub>2</sub> evolution, the  $H_2O_2$  decomposition performances on the BiVO<sub>4</sub>, SnO<sub>2</sub> and SnO<sub>2-x</sub> surfaces were monitored in real time using the ring-disk electrode technique. As shown in Figure S19, the reaction on the disk electrode is  $H_2O_2$  evolution by BiVO<sub>4</sub>, while the reaction on the ring electrode is H<sub>2</sub>O<sub>2</sub> decomposition by BiVO<sub>4</sub>, SnO<sub>2</sub> and SnO<sub>2-x</sub>. To avoid otherside reactions, the applied bias for the ring electrode is established at 0.7 V vs. RHE, at which the only possible EC reaction is  $H_2O_2$  decomposition. Figure 3b shows the linear



**Figure 4.** (a)  $\text{SnO}_{2-x}$  overlayer associated with the surface states that are energetically shifted away from the intrabandgap region, which overcomes the O<sub>2</sub> evolution reaction. (b) Plots of the theoretical charge number obtained from the J-t curves collected at 1.23 V vs. RHE and the actual quantities of H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> generated by  $\text{SnO}_{2-x}/\text{BiVO}_4$ photoanode under AM 1.5 illumination. (c) A summary of PEC H<sub>2</sub>O<sub>2</sub> production with various parameters under AM 1.5 illumination. The open-circuit voltage is converted applied bias vs RHE based on pH value of electrolyte.

sweep voltammetry (LSV) curves of different electrodes recorded at a scan rate of 10 mV s<sup>-1</sup> in a 1 M NaHCO<sub>3</sub> electrolyte solution at room temperature at 1600 rpm. Under the same disk current generated by water oxidative  $H_2O_2$  evolution, the ring currents that arise from oxidative  $H_2O_2$  decomposition can reflect the equilibrium of the reaction of  $H_2O_2$  evolution and decomposition. <sup>44, 45</sup> Remarkably, the ring current of SnO<sub>2-x</sub> approaches zero in the whole applied bias, indicating negligible  $H_2O_2$ decomposition on the SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanode.

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Based on these results, the function of the  $SnO_{2-x}$ overlayer can be considered to suppress  $O_2$  evolution from both the water oxidation and  $H_2O_2$  decomposition processes. The lower than real-time 100% FE of  $H_2O_2$ evolution, therefore, implies another completive reaction other than the  $O_2$  evolution reaction. To unmask the underlying reaction, EPR detection was used to record hydroxyl radical (OH·) generation as a result of 1-electron transfer during the water oxidation process:

 $H_2O \rightarrow OH + H^+ + e^- E^\circ = +2.73 \text{ V vs. RHE}$  (4)

As shown in Figure 3c, four characteristic peaks of DMPO- OH appear in the  $HCO_3$ -containing electrolyte in the presence of  $SnO_2/BiVO_4$  and  $SnO_{2-x}/BiVO_4$  photoanodes under visible light irradiation. The signal intensities of OH by the  $SnO_{2-x}/BiVO_4$  photoanode are stronger than those of the  $SnO_2/BiVO_4$  photoanode, whereas the OH signal in the spectrum of the  $BiVO_4$  photoanode is negligible. The results disclose the favoured

1-electron transfer by  $SnO_2$  and  $SnO_{2-x}$  overlayers. Furthermore, Figure 3d shows the EPR spectra of the BiVO<sub>4</sub>, SnO<sub>2</sub>/BiVO<sub>4</sub>, and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes in a 0.5 M phosphate buffer solution, which is a general electrolyte for O2 evolution. Note that without light illumination, no signals associated with OH can be detected (Figure S20); moreover, H2O2 would not be excited to OH in the absence of ultraviolet (UV) light. The trends of OH generation in the phosphate buffer solution are similar to that in  $HCO_3^-$  containing the electrolyte, suggesting essentially a complete reaction of 1-electron transfer during the water oxidation process. The photocatalytic H2O2 degradation over the BiVO4, SnO<sub>2</sub>/BiVO<sub>4</sub>, and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanodes was investigated under AM 1.5 illumination, which is direct evidence of H<sub>2</sub>O<sub>2</sub> accumulation during PEC water oxidation (Figure S21). The H<sub>2</sub>O<sub>2</sub> concentration is gradually and rapidly decreased on the illuminated BiVO<sub>4</sub> photoanode, which becomes undetectable for 60 min. In sharp contrast, the  $H_2O_2$  can be preserved by 79% and 81% in illuminated SnO<sub>2</sub>/BiVO<sub>4</sub> and SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanode solutions, respectively, which is slightly lower than the photocatalysis of H<sub>2</sub>O<sub>2</sub> (87%) during 60 min of illumination. The above results demonstrate that the SnO<sub>2</sub>- $_{\rm x}$  overlayer is responsible for the thermodynamic suppression of O<sub>2</sub> evolution upon the PEC water oxidation and H<sub>2</sub>O<sub>2</sub> oxidation processes.

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The  $SnO_{2-x}$  overlayer regulates the surface reaction kinetics of the BiVO<sub>4</sub> photoanode from the completive 2 reactions of the 2-electron and 4-electron transfers to 3 completive reactions of the 1-electron and 2-electron 4 transfers. The processes of water oxidation are 5 schematically illustrated in Figure 4a. It is well known that 6 the interfacial energetics at semiconductor photoanode is 7 associated with surface state, in general, intra-gap states. Especially for BiVO<sub>4</sub> photoanode, the surface state enables 8 significant regulation of hole transfer kinetic constant for 9 O<sub>2</sub> evolution.<sup>42, 43</sup> The passivating surface state is of the 10 essence, even in case of co-catalyst deposition.46 The 11 mechanism of such passivation typically is strong 12 interacted by the orbitals of the new surface component to 13 modulate surface states, resulting in formation of new 14 bonding and antibonding orbitals that are energetically 15 shifted out of the bandgap.<sup>47, 48</sup> Considering the interface 16 fusion (Figure 1e) and quasi-Fermi level change (Figure 2f), 17 the reducing band bending is hypothesized to be 18 independent of the thermodynamic process for H<sub>2</sub>O<sub>2</sub> 19 evolution. Since the PEC water splitting over the SnO<sub>2</sub>-20 <sub>x</sub>/BiVO<sub>4</sub> photoanode involves the H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> evolution 21 processes, the time courses of PEC water oxidative H<sub>2</sub>O<sub>2</sub> 22 production and water reductive H<sub>2</sub> production are 23 investigated. At an applied bias of 1.23 V vs. RHE, the 24 obtained H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> quantities as a function of the 25 theoretical electron number calculated on the basis of its 26 photocurrent density are shown in Figure 4b. It can be 27 clearly seen that the H, amounts are well-matched to their 28 theoretical value, while the measured H<sub>2</sub>O<sub>2</sub> amounts 29 deviate from the stoichiometric 2-electron transfer with an 30 average production rate of 0.825 µmol/min/cm<sup>-2</sup>. The 31 stable photocurrent density and constant FE produce a 32 solar to H<sub>2</sub>O<sub>2</sub> efficiency of ~5.6% at 1.23 V vs RHE under 33 AM 1.5 illumination. As mentioned above, the 34 photocurrent for water oxidation involves OH. generation, 35 which is mainly a side reaction to consume the 36 photogenerated holes during H<sub>2</sub>O<sub>2</sub> evolution. Nevertheless, 37 to our knowledge, our  $SnO_{2-x}/BiVO_4$  photoanode demonstrates superior PEC H<sub>2</sub>O<sub>2</sub> evolution relative to 38 other photoanodes for both PEC water oxidative H<sub>2</sub>O<sub>2</sub> 39 evolution and PEC O<sub>2</sub> reductive H<sub>2</sub>O<sub>2</sub> evolution (Table S1 40 and Figure 4c).<sup>12, 13, 19, 49, 50</sup> Furthermore, the SEM, XRD and 41 XPS results of these photoanodes after the long-term H<sub>2</sub>O<sub>2</sub> 42 evolution show no detectable change in morphology and 43 component (Figure S22), indicating a well structure 44 stability for PEC H<sub>2</sub>O<sub>2</sub> evolution. The HAADF-STEM-EDX 45 images of the SnO<sub>2-x</sub>/BiVO<sub>4</sub> photoanode taken after the 46 long-term H<sub>2</sub>O<sub>2</sub> evolution confirm the uniform SnO<sub>2-x</sub> 47 coverage (Figure S23). Most recently, Surendranath et al. 51 48 and Wang et al. 52 reported the highly selective H<sub>2</sub>O<sub>2</sub> 49 synthesis via a flow system using  $H_2$  and  $O_2$  as the reactants, 50 beyond which, the PEC H<sub>2</sub>O<sub>2</sub> synthesis by direct water 51 oxidation holds the key to advances required in low-cost 52 and eco-friendly applications. 53 54

#### **CONCLUSION**

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In this work, we reported that a SnO<sub>2</sub> overlayer with oxygen vacancies  $(SnO_{2-x})$  can tune the activity and

selectivity for PEC water oxidative H<sub>2</sub>O<sub>2</sub> generation using a BiVO<sub>4</sub> photoanode under simulated solar light. Our investigations on the charge exchange mechanism demonstrated the near-suppression of O<sub>2</sub> evolution during PEC water splitting, due to the photogenerated holes of  $BiVO_4$  migrating to the  $SnO_{2-x}$  overlayer; this process regulated the competitive 2-electron/4-electron transfer to a 2-electron/1-electron transfer by interface energetics and the concomitant suppression of H<sub>2</sub>O<sub>2</sub> decomposition. As a result, the FE for H<sub>2</sub>O<sub>2</sub> generation reached ca. 86% over a wide potential range from 0.6 to 2.1 V vs. RHE with an average  $H_2O_2$  evolution rate of 0.825 µmol/min/cm<sup>-2</sup> at 1.23 V vs. RHE. Because the thermodynamically less favourable H2O oxidative H<sub>2</sub>O<sub>2</sub> reaction, this study highlighted the significance of a surface state modulation on the photoanode/electrolyte interface, opening the possibility of highly selective H<sub>2</sub>O<sub>2</sub> synthesis from PEC water splitting by Fermi level pining effect.

#### ASSOCIATED CONTENT

Supporting Information. Detailed experimental sections; figures; tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interests.

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