# Tuning the Conduction Band for Interfacial Electron Transfer: Dye-Sensitized $Sn_xTi_{1-x}O_2$ Photoanodes for Water Splitting

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show that incorporation of Ti d-character in the conduction band plays a crucial role in promoting ultrafast electron injection. **KEYWORDS:** conduction band tuning, interfacial electron transfer, ultrafast spectroscopy, water splitting, dye-sensitized,

# INTRODUCTION

aqueous electrolyte

Rising energy demands and concerns regarding climate change have fostered recent efforts for developing clean, renewable energy resources using solar technologies based on semiconductor materials.1 These technologies rely on efficient charge separation of electrons and holes and strive to use materials that are earth-abundant and inexpensive, such as metal oxides. Water splitting dye-sensitized photoelectrochemical cells (WS-DSPECs) offer an attractive technology for producing clean energy carriers (H<sub>2</sub>) from water and solar energy. WS-DSPECs accomplish overall water splitting by driving water oxidation at a photoanode, a reaction that evolves oxygen and generates protons that can be reduced at the cathode to form H<sub>2</sub>. The photoanode typically involves molecular sensitizers and water oxidation catalysts (WOCs) coadsorbed on a nanoparticulate, mesoporous metal oxide film.<sup>2,3</sup> Under illumination, the sensitizer is photoexcited and injects an electron into the conduction band of the metal oxide. The electron then travels to the cathode to form  $H_2$  by proton reduction. To regenerate the oxidized sensitizer, a WOC transfers electrons to the oxidized dyes and subsequently oxidizes water to generate oxygen and protons as mentioned above.<sup>3</sup> Herein, we focus on the primary interfacial electron transfer (IET) dynamics triggered by photoexcitation of a ruthenium(II) polypyridyl dye sensitizer, as modulated by the variable composition of a  $Sn_rTi_{1-r}O_2$ (where  $0 \le x \le 1$ ) semiconductor substrate.

acceptor states in the conduction band. Periodic DFT calculations

Understanding the efficiency limiting factors of photoanode materials used in WS-DSPECs remains an outstanding challenge, despite significant advances in developing these systems.<sup>4-6</sup> While there has been a plethora of work focused on developing improved, tunable dye sensitizers<sup>7</sup> and WOCs,<sup>8-10</sup> there has been significantly less work focused on the development of tunable metal oxide substrates. In addition to supporting both the dye and the catalyst, the metal oxide acts as the "acceptor" in these systems and plays an essential role in tuning IET behavior and by extension the overall performance of a WS-DSPEC. In addition, the ability to tune the semiconductor conduction band to more positive potentials enables the use of strongly oxidizing organic dye sensitizers such as porphyrins<sup>7,11</sup> and perylenes,<sup>12-14</sup> while maintaining high injection yields.

Core-shell structures (e.g., SnO<sub>2</sub>-core/TiO<sub>2</sub>-shell)<sup>4,5</sup> have been shown to be effective at mediating IET by slowing down recombination rates. However, these structures often reduce the electron injection rates and injection yields,<sup>15</sup> which ultimately limit the efficacy of the device. To date, almost all

Received: January 28, 2021 Accepted: April 27, 2021 Published: May 5, 2021





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reports of WS-DSPECs have utilized either anatase TiO<sub>2</sub> (a-TiO<sub>2</sub>) or rutile SnO<sub>2</sub>.<sup>16</sup> with the exception of one recent report utilizing rutile TiO<sub>2</sub> (r-TiO<sub>2</sub>).<sup>17</sup> Both a-TiO<sub>2</sub> and SnO<sub>2</sub> exhibit radically different electron transport behavior due to their different electronic structures.<sup>18,19</sup> This is in part due to the potential of the conduction band minimum ( $E_{CBM}$ ) in SnO<sub>2</sub> being positioned 0.6 V more positive than that of a-TiO<sub>2</sub>, which results in a greater driving force for forward IET. In addition to the relative energetics, the conduction band of a-TiO<sub>2</sub> is primarily of Ti 3d character,<sup>20,21</sup> while in SnO<sub>2</sub>, it is primarily of 5s–5p character, which have drastically different density of states (DOS).<sup>22</sup> Therefore, using a ternary metal oxide such as Sn<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> (where  $0 \le x \le 1$ ) that offers the ability to tune the  $E_{CBM}$  as a function of composition is one strategy that can be used to control IET in WS-DSPECs.

 $Sn_rTi_{1-r}O_2$  solid solutions have been studied as photoanode materials in conventional dye-sensitized solar cells (DSSCs),<sup>23–25</sup> batteries,<sup>26,27</sup> and for photocatalysis.<sup>28,29</sup> In addition, there have been several experimental<sup>30,31</sup> and theoretical<sup>32</sup> studies on the properties of  $Sn_xTi_{1-x}O_2$  solid solutions. Notably in the context of DSSCs, Zhang et al. suggested that Ti<sup>4+</sup> atoms incorporated into SnO<sub>2</sub> act as trap states that inhibit electron transport within the material, but increase the recombination lifetime.<sup>25</sup> This sentiment was also expressed in recent work by James et al., which suggested that  $Sn_xTi_{1-x}O_2$  formed at the interface of  $SnO_2$ -TiO<sub>2</sub> core-shell particles acts as a thermodynamic sink for photoinjected electrons, though they were not able to study transport through the material.<sup>33</sup> However, it remains unclear how  $Sn_xTi_{1-x}O_2$  can be used to tune photoinduced electron injection dynamics by alteration of the electronic properties of the metal oxide in DSSCs and WS-DSPECs. In addition to the implications in solar energy conversion, understanding how IET can be mediated at the molecule-semiconductor interface is an outstanding question in donor-acceptor interactions that has the potential to apply broadly to other multinary materials.<sup>3</sup>

This work investigates how IET dynamics can be modulated using  $Sn_rTi_{1-r}O_2$  sensitized with a prototypical dye-sensitizer, ruthenium(II) bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'bipyridine) bromide or RuP, in aqueous electrolyte (0.1 M HClO<sub>4</sub>, pH 1) using a combination of femtosecond transient absorption spectroscopy (fs-TAS), linear absorption spectroscopy, and density functional theory (DFT) calculations.<sup>35</sup> In metal oxides sensitized with a ruthenium polypyridyl complex such as RuP, IET is typically modeled as a two-state process where ultrafast injection occurs from the singlet metal-toligand charge transfer (<sup>1</sup>MLCT) excited state, followed by a slower injection process from the triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT) excited state.<sup>18,36</sup> Injection from the <sup>1</sup>MLCT state is competitive with intersystem crossing ( $\tau_{\rm ISC}$  < 30 fs), $^{37-39}$  and its detection is limited by the instrument response function (IRF) in the fs-TAS experiments discussed herein. Figure 1 shows a schematic representation of IET and photophysical processes in RuP depicting IET from both the <sup>1</sup>MLCT and <sup>3</sup>MLCT states, intersystem crossing (ISC), and vibrational relaxation (VR) in the <sup>3</sup>MLCT manifold.

## RESULTS AND DISCUSSION

Four compositions of  $Sn_xTi_{1-x}O_2$  (x = 0.25, 0.5, 0.75, and 1, denoted herein as Sn25, Sn50, Sn75, and SnO<sub>2</sub>, respectively) were synthesized using the procedure described by Trotochaud



Figure 1. Energetic scheme showing RuP potentials relative to the conduction band (CB) relevant for interfacial electron transfer and photophysical processes.

and Boettcher,<sup>40</sup> and Sn<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> pastes for doctor-blading were made by a following standard procedure.<sup>41</sup> Synthesis of  $TiO_2$  (x = 0) resulted in anatase-polymorph, opaque films that were unsuitable for fs-TAS, so a commercial a-TiO<sub>2</sub> paste was utilized (Solaronix). A r-TiO<sub>2</sub> sample was also synthesized for characterization and comparison based on a literature procedure,<sup>17</sup> but could not be used for fs-TAS measurements due to the probe wavelength being above the 3.0 eV (413 nm) bandgap of r-TiO2.<sup>42</sup> A SnO2 paste with commercial nanoparticles (Alfa Aesar, 22-43 nm) was also prepared and used as a reference material. The band schemes of  $Sn_xTi_{1-x}O_2$ were studied using near-infrared (NIR) spectroelectrochemistry to determine  $E_{\text{CBM}}$  (see Figures  $(51-2)^{43,44}$  and Tauc analysis to determine the band gap,  $E_g$  (see Figure S4), and valence band maximum,  $E_{\rm VBM}$  (see Experimental Section for details).

Figure 2a shows the experimentally determined band schemes of  $Sn_xTi_{1-x}O_2$  used in this work, illustrating the monotonic tunability of  $E_{\rm CBM}$  as a function of composition. Sample morphology and composition were characterized by powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS), respectively. PXRD showed that mixed compositions of  $Sn_xTi_{1-x}O_2$  adopted the rutile polymorph with the peak positions shifting linearly between r-TiO<sub>2</sub> and rutile  $SnO_2$  (see Figure 2b), corresponding to a change in lattice constants and unit cell volume. The fact that PXRD peaks shift rather than split is indicative that solid solutions were formed, consistent with the literature.<sup>40</sup> In addition, the PXRD peak shifts deviate from Vegard's Law by less than 1%,<sup>745,46</sup> providing evidence that solid solutions of the target composition were formed. This was confirmed by XPS measurements showing that the relative Sn:Ti ratios were within error of the target composition (see Figure S6). PXRD measurements were also used to characterize the crystallite sizes of  $Sn_xTi_{1-x}O_2$  using the Scherrer equation.<sup>47</sup> Mixed compositions (Sn25, Sn50, and Sn75) yielded ~5 nm crystallites, while synthesized SnO2 crystallites were slightly larger at ~7 nm (see Table S5). Transmission electron microscopy of Sn50 showed ~5 nm particles (see Figure S7), suggesting that the synthesized particles were nearly singlecrystalline nanoparticles. These smaller particles yielded thinner film thicknesses of  $\sim 1 \ \mu m$  (see Table S6), compared to typical 4–6  $\mu$ m films achieved using larger particles (e.g., ~15–20 nm commercial a-TiO<sub>2</sub> used in this work). The



**Figure 2.** (a) Experimentally determined  $\text{Sn}_x \text{Ti}_{1-x} O_2$  band schemes in 0.1 M HClO<sub>4</sub> as determined by NIR spectroelectrochemistry<sup>43</sup> (conduction band minimum,  $E_{\text{CBM}}$ ) and UV–vis measurements (band gap,  $E_{g'}$  and valence band maximum,  $E_{\text{VBM}}$ ). Relevant potentials of **RuP** are noted for reference.<sup>48</sup> Anatase TiO<sub>2</sub> (a-TiO<sub>2</sub>) is plotted for  $\chi_{\text{Sn}} = 0$ . (b) Powder X-ray diffractograms of  $\text{Sn}_x \text{Ti}_{1-x} O_2$  illustrating that solid solutions form the rutile polymorph with peak shifts consistent with Vegard's Law. Rutile TiO<sub>2</sub> (r-TiO<sub>2</sub>) is plotted for reference.

volumetric dye loadings determined by UV-vis measurements (see the Experimental Section for details) for these smaller particles exhibited almost no difference within our experimental uncertainty compared to commercial a-TiO<sub>2</sub> (( $\sim$ 1.0-1.5)  $\times$  10<sup>-8</sup> mol cm<sup>-2</sup>  $\mu$ m<sup>-1</sup>; see Table S6). However, SnO<sub>2</sub> films prepared with larger (22-43 nm) commercial particles exhibited an appreciably smaller loading of  $(0.5 \pm 0.2) \times 10^{-8}$ mol cm<sup>-2</sup>  $\mu$ m<sup>-1</sup>. This observation suggests that the loading density (molecules per unit of metal oxide surface area) for the smaller particles is not as high as the commercial a-TiO<sub>2</sub> films used in the work and is likely more similar to the SnO<sub>2</sub> films prepared with larger commercial particles. However, it is unclear if this is an effect based solely on differences in surface area or is related to the polymorph. While this effectively lower surface density likely plays a role in overall injection efficiency, the electron injection dynamics that are the focus of this work are not expected to be significantly affected. Further details regarding sample characterization, including additional representative measurements and tabulated fit parameters, are provided in the Supporting Information (SI).

The IET dynamics were investigated using fs-TAS by monitoring the bleach in the signal at 402 nm, corresponding to the  $\mathbf{RuP}^{2+}$  ground—excited-state isosbestic point (see Figure S13) upon photoexcitation at 515 nm with a pump fluence of 200  $\mu$ J cm<sup>-2</sup>. Probing at 402 nm allows for the unambiguous assignment of the bleach at that wavelength to an oxidation state change in  $\mathbf{RuP}$  (e.g.,  $\mathbf{RuP}^{2+} \rightarrow \mathbf{RuP}^{3+}$ ). In the case of  $\mathbf{RuP}$ -sensitized  $\mathrm{Sn}_x\mathrm{Ti}_{1-x}\mathrm{O}_2$ , we assign this bleach and corresponding oxidation state change to electron injection (i.e., dye loses an electron to the metal oxide). This is a strategy commonly applied to study recombination in suprananosecond TAS.<sup>49</sup> Based on fs-TAS measurements of **RuP**sensitized ZrO<sub>2</sub> shown in Figure S13, which probes the



Figure 3. (a) Representative ultrafast transient absorption spectroscopy measurements for RuP-sensitized rutile  $Sn_xTi_{1-x}O_2$  and anatase TiO<sub>2</sub> (a-TiO<sub>2</sub>) in 0.1 M HClO<sub>4</sub>. Circles represent the measured data and solid lines represent the fits. Traces are normalized and offset for clarity. Dashed lines represent where  $\Delta OD = 0$  for each trace to illustrate sub-0.1 ps injection amplitudes. Samples were photoexcited at 515 nm (200  $\mu$ J cm<sup>-2</sup>) and probed at 402 nm, corresponding to the RuP<sup>2+</sup> ground-excited-state isosbestic point. Data were fit to the injection model described in eq 1. (b) Relative <sup>1</sup>MLCT (purple) and <sup>3</sup>MLCT (red) injection amplitudes. (c) Mean lifetime of <sup>3</sup>MLCT injection. Injection amplitude errors bars correspond to the standard deviation from at least three measurements. Error bars for  $\langle \tau_3 \rangle$  are numerically propagated based on the standard deviations of  $\tau_3$  and  $\beta$  for at least three measurements.

photophysics of an adsorbed dye in the absence of electron injection and allows us to measure where the isosbestic point occurs, this strategy also holds and is applicable for ultrafast measurements outside of the temporal range of the coherent artifact (>0.1 ps). Representative fs-TAS traces and fits for **RuP**-sensitized  $Sn_xTi_{1-x}O_2$  in 0.1 M HClO<sub>4</sub> are shown in Figure 3a. It is worth noting that the  $SnO_2$  measurement plotted represents the synthesized, small nanoparticles. However, the  $SnO_2$  samples prepared with the aforementioned commercial, larger nanoparticles exhibited identical injection dynamics within our experimental error (see Figure S14 and Table S1), suggesting that particle size does not play a major role in modulating IET for particles larger than ~5 nm in diameter.

The fitting function used to describe the fs-TAS data based on the two-state injection model discussed previously is shown below in eq 1 where  $\Delta A$  is the change in absorbance at 402 nm, A is the amplitude,  $\tau$  is the lifetime,  $\beta$  is the stretching parameter ( $0 < \beta \le 1$ ),  $\otimes$  represents a convolution, and  $G_{\rm IRF}$  is a Gaussian IRF with a 200 fs full width at half-maximum. Subscripts 1 and 3 correspond to processes from the <sup>1</sup>MLCT and <sup>3</sup>MLCT states, respectively. This function has been previously utilized to analyze electron injection dynamics of a-TiO<sub>2</sub> and SnO<sub>2</sub> sensitized with an analogous ruthenium polypyridyl complex using optical-pump terahertz probe spectroscopy.<sup>18</sup>

$$\Delta A = \left\{ A_1 \left[ \exp\left(\frac{t}{\tau_1}\right) - 1 \right] + A_3 \left[ \exp\left(\left(\frac{t}{\tau_3}\right)^{\beta}\right) - 1 \right] \right\} \otimes G_{\text{IRF}}$$
<sup>(1)</sup>

Because injection from the <sup>1</sup>MLCT is IRF-limited (i.e., appears as an drop in signal at time zero), the lifetime was fixed at 25 fs based on literature results for **RuP** on a-TiO<sub>2</sub>.<sup>50</sup> For injection from the <sup>3</sup>MLCT state, a stretched exponential function was used to account for the heterogeneity in IET dynamics expected for dye-sensitized mesoporous films, as previously reported.<sup>18</sup> The use of a stretched exponential (i.e., distribution of injection lifetimes) in lieu of multiple exponentials for <sup>3</sup>MLCT injection is beneficial, because it is a minimally parametrized model and does not assume distinct, separate kinetic pathways that can be challenging to assign. The expectation value of the heterogeneous distribution of lifetimes coming from the <sup>3</sup>MLCT,  $\langle \tau_3 \rangle$ , is determined using eq 2 as shown below.<sup>51</sup>

$$\langle \tau_3 \rangle = \frac{\tau_3}{\beta} \Gamma \left( \frac{1}{\beta} \right) \tag{2}$$

Figure 3b-c shows a summary of the fitting results for **RuP**sensitized  $Sn_xTi_{1-x}O_2$ , comparing the relative amplitudes of injection from the <sup>1</sup>MLCT (purple) and <sup>3</sup>MLCT (red) excited states, respectively, and  $\langle \tau_3 \rangle$ , corresponding to the injection lifetime for the <sup>3</sup>MLCT excited state. It is worth noting that the error bars reported in Figure 3b represent the standard deviation of independent measurements of different samples. The error bars in Figure 3c are numerically propagated based on the standard deviations of  $\tau_3$  and  $\beta$  for at least three independent measurements. In addition, these results were collected on two functionally identical spectrometers at two different locations and times, indicating a high level of reproducibility. www.acsaem.org

There are two possible causes of the differences in IET shown in Figure 3: (1) changes to the electron donor (**RuP**) upon adsorption to  $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$  and (2) changes in the DOS of the acceptor ( $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ ). The contribution from changes to the donor was investigated by analysis of the linear UV-vis absorption spectra of **RuP** adsorbed on  $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ . The contribution from the acceptor was investigated using DFT calculations of the DOS of  $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ , supported by X-ray absorption spectroscopy (XAS) measurements at the Ti K-edge.

The ground-state absorption spectrum of ruthenium(II) tris(bipyridine), of which **RuP** is an analogue, exhibits "excess" absorption in the red tail of the MLCT absorption band which is not well described by a series of <sup>1</sup>MLCT vibronic transitions. This "excess" absorption has been reported to correspond to a direct <sup>3</sup>MLCT excitation in contrast to shorter wavelengths, which excite vibronic transitions into the <sup>1</sup>MLCT manifold.<sup>52</sup> Photoexcitation at 515 nm, although relevant to solar energy conversion, lies on the red tail of the MLCT absorption band and therefore has the potential to produce an excited state with mixed multiplicity. In order to investigate this possibility, the linear UV–vis absorption spectra were fit to a series of Gaussians as described for **RuP** in solution by Cheshire et al.<sup>39</sup>



Figure 4. (a) Representative spectrum of dry RuP-sensitized  $Sn_{0.5}Ti_{0.5}O_2$  (Sn50) fit to a series of Gaussian functions. (b) Relative injection amplitudes from the <sup>1</sup>MLCT state determined from ultrafast transient absorption spectroscopy (purple squares) and the corresponding fraction of <sup>1</sup>MLCT excitation at 515 nm (black circles). Error bars correspond to the standard deviation of at least three independent measurements.

representative spectra and fitting parameters are included in the SI. These fits showed that the relative fraction of <sup>1</sup>MLCT to <sup>3</sup>MLCT excited at 515 nm changed as a function of composition in  $Sn_xTi_{1-x}O_{2}$ , which is shown in Figure 4b in relation to the relative injection amplitudes originating from the <sup>1</sup>MLCT excited states shown in Figure 3b. It is also important to note that the peak energies of the <sup>1</sup>MLCT vibronic transitions did not appreciably shift, suggesting that overall dye energetics remain largely unchanged. It is unlikely that the surface composition of the metal oxide would have a large effect on spin-orbit coupling in RuP due to the relatively large distance of the dye from the surface and poor electronic coupling of the phosphonate anchoring group.<sup>7</sup> Even if this were the case, one would expect the opposite trend where <sup>3</sup>MLCT excitation would be enhanced with increased Sn content, due to the larger atomic weight of Sn compared to Ti. It remains unclear, however, why the composition of the metal

oxide modulates the strength of direct <sup>3</sup>MLCT excitation in **RuP**, a phenomenon that warrants further study.

The mixed multiplicity describes the relative differences in injection from the <sup>1</sup>MLCT and <sup>3</sup>MLCT excited states within experimental errors; however, mixed multiplicity cannot adequately describe the lack of ultrafast <sup>1</sup>MLCT injection observed in SnO<sub>2</sub> and does not explain differences in the <sup>3</sup>MLCT injection lifetimes,  $\langle \tau_3 \rangle$ . Therefore, it is necessary to explore changes in the conduction band DOS. We used periodic DFT calculations with the Heyd-Scuseria-Ernzerhof (HSE06) functional to determine the total DOS and atom-specific partial DOS.<sup>53,54</sup> Figure 5a shows the calculated DOS



**Figure 5.** (a) Conduction band density of states (DOS) for  $Sn_xTi_{1-x}O_2$  calculated using periodic DFT. Partial DOS for Sn, Ti, and O are shown in orange, blue, and green solid lines, respectively. The total DOS is shown as a dashed black line. Excited-state potentials of **RuP** are included for reference.<sup>48</sup> (b) Normalized X-ray absorption spectroscopy (XAS) measurements of  $Sn_xTi_{1-x}O_2$  at the Ti K-edge, offset for clarity. Peak positions are labeled relative to rutile TiO<sub>2</sub> (r-TiO<sub>2</sub>) for reference. (c) Pre-edge region of XAS measurement showing slight peak shifts relative to r-TiO<sub>2</sub>.

of  $\text{Sn}_x \text{Ti}_{1-x} O_2$  with **RuP** excited-state potentials plotted for reference. The total DOS for each material was normalized (both valence and conduction bands) and shifted to match the experimentally determined values for  $E_{\text{CBM}}$ . Details regarding the computational methodology and method of correcting  $E_{\text{CBM}}$  can be found in the Experimental Section.

Although it is challenging to quantify the actual DOS available as an acceptor for electron injection, it is clear that the Ti density is dominant in  $a-TiO_2$  and all mixed composition samples. The same can be observed with r-TiO<sub>2</sub>, which is included in the SI for completeness (see Figure S11). The fact that SnO<sub>2</sub> exhibits low ultrafast <sup>1</sup>MLCT

injection, while having a large fraction of <sup>1</sup>MLCT character in the initially photoexcited state, suggests that the much larger conduction band DOS afforded by Ti 3d orbitals is critical to obtain appreciable ultrafast injection from the <sup>1</sup>MLCT state. As the Sn composition of the metal oxide increases,  $E_{CBM}$  is lowered along with the Ti partial DOS, correlating with increased <sup>1</sup>MLCT injection, which we suggest corresponds to preferential injection into Ti states in the conduction band for mixed composition samples.

This result was further explored using XAS measurements at the Ti K-edge (see Figure 5b-c). Figure 5b shows near-edge XAS measurements of  $Sn_xTi_{1-x}O_2$  with transitions labeled relative to r-TiO<sub>2</sub>. Notably, there are three pre-edge transitions  $(A_1, A_3, and B)$  which have been assigned to  $1s \rightarrow 3d$ transitions, where the final state is a hybridized 3d-4p state.<sup>31</sup> Furthermore, A<sub>1</sub> and A<sub>3</sub> have been reported to be transitions to t<sub>2g</sub>-like and eg-like band states, respectively.<sup>55</sup> An additional peak  $(A_2)$  was observable in a-TiO<sub>2</sub>, which has been assigned to penta-coordinated Ti atoms (i.e., exposed surface sites), though this was not observed in rutile polymorph samples.<sup>31</sup> Although not labeled in Figure 5b-c, the A<sub>2</sub> peak was included in the fit of  $a-TiO_2$  that is detailed in the SI. The on-edge peak (C) corresponds to a 1s  $\rightarrow$  4p transition,<sup>55</sup> while the post-edge peaks are continuum resonances corresponding to L = 1projections of d-like  $(D_1 \text{ and } D_2)$  and p-like (E) Ti orbitals.<sup>31,57</sup> Because the post-edge features are also influenced by interference effects pertaining to the near-edge structure, these features were not included in the fitting. Interestingly, the position of  $A_1$  does not appear to shift, while the position of  $A_3$ appears to shift slightly to lower energy by  $\sim 0.3$  eV (see Table S18). Likewise, the position of  $D_1$  and  $D_2$  appear to shift downward in energy by ~1 eV with increasing Sn content. These results suggest that the Ti 3d density in the conduction band is shifted down in energy, consistent with the calculations of the partial DOS, shown in Figure 5a.

Injection from the  ${}^{3}MLCT$  state was the slowest for a-TiO<sub>2</sub>, likely due to the higher  $E_{\text{CBM}}$  and low Ti DOS available as an acceptor isoenergetic with or below the <sup>3</sup>MLCT excited-state potential. In contrast, Sn25 and Sn50 exhibited the fastest <sup>3</sup>MLCT injection dynamics, owing to the greater driving force for injection and higher Ti DOS available as an acceptor. This is reasonable because a larger density of acceptor states is expected to increase the rate of electron transfer in the Marcus-Gerischer picture.<sup>36</sup> While Sn75 also has a higher Ti DOS according to periodic DFT calculations, the slower relative <sup>3</sup>MLCT injection rates were more comparable to SnO<sub>2</sub>, which is in contrast to the high <sup>1</sup>MLCT injection amplitude observed in Sn75. Although the reason for this dichotomy is not entirely clear, it is plausible that injection from the <sup>1</sup>MLCT state is largely mediated by discrete surface states, while injection from the <sup>3</sup>MLCT is mediated by the band structure of the metal oxide.

# CONCLUSION

We have shown that mixed metal oxides such as  $Sn_xTi_{1-x}O_2$  can offer a viable strategy for tuning ultrafast IET in photoelectrochemical cells based on inexpensive, earth-abundant materials for applications in solar energy conversion. The reported results on ultrafast injection, along with previous insights into trapping and recombination dynamics in  $Sn_xTi_{1-x}O_2^{-25}$  suggest that these semiconductor materials are particularly suited for WS-DSPECs and other photoelectro-

chemical devices. Because altering the composition alters  $E_{\text{CBM}}$  (and consequently the Fermi level in the material),  $\text{Sn}_x \text{Ti}_{1-x} \text{O}_2$  can be used to optimize the IET behavior in addition to other parameters critical to device performance, such as the opencircuit photovoltage of the cell. The resulting tunability in  $E_{\text{CBM}}$  also enables the use of other classes of dye-sensitizers, such as porphyrins<sup>7,11</sup> and perylenes,<sup>12–14</sup> which cannot efficiently inject into a-TiO<sub>2</sub> or exhibit poor injection yields, while balancing improved IET from the Ti-character in the conduction band DOS and photovoltage.

# EXPERIMENTAL SECTION

Sample Preparation. Nanoparticulate  $Sn_xTi_{1-x}O_2$  solid solutions were synthesized as previously described by Trotochaud and Boettcher.<sup>40</sup> In this work, four composition of  $Sn_xTi_{1-x}O_2$  were prepared: Sn<sub>0.25</sub>Ti<sub>0.75</sub>O<sub>2</sub> (Sn25), Sn<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>2</sub> (Sn50), Sn<sub>0.75</sub>Ti<sub>0.25</sub>O<sub>2</sub> (Sn75), and SnO<sub>2</sub>. The resulting nanoparticles were fabricated into a paste as previously described.<sup>41</sup> Pastes were also prepared with larger particle size SnO<sub>2</sub> (Alfa Aesar, 22-43 nm). Anatase TiO<sub>2</sub> and ZrO<sub>2</sub> films were prepared using commercially available pastes (Solaronix Ti-Nanoxide T/SP and Solaronix Zr-Nanoxide ZT/SP, respectively). Samples for fs-TAS were prepared by doctor blading the paste onto a glass microscope slide  $(2.54 \text{ cm} \times 2.54 \text{ cm})$  followed by annealing. After doctor blading, samples were dried on a hot plate at 80 °C for 10 min before annealing in a box oven. Samples were annealed at 370 °C for 10 min followed by 470 °C for 30 min using a 3 °C min<sup>-1</sup> temperature ramp rate. The samples were then sensitized in a 100  $\mu$ M solution of **RuP** in ethanol for 22 h.<sup>58,59</sup> **RuP** was synthesized based on a previously reported literature procedure.<sup>60</sup> After sensitization, the samples were then sealed using a second glass microscope slide with a 60  $\mu$ m Surlyn spacer (Solaronix) and were vacuum backfilled with 0.1 M HClO<sub>4</sub> (pH 1) through a hole drilled in the second piece of glass as previously described.5

**Materials Characterization.** The composition and polymorphism of synthesized  $Sn_xTi_{1-x}O_2$  were characterized using X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (PXRD), respectively. PXRD measurements were collected using a Rigaku SmartLab X-ray Diffractometer and XPS measurements were collected using a PHI VersaProbe II Scanning XPS Microprobe. Crystallite sizes were calculated from the PXRD patterns using the Scherrer equation as shown below in eq 3, where  $\tau$  is the crystallite size, K is a dimensionless shape factor set to 0.9,<sup>40</sup>  $\lambda$  is the X-ray wavelength (Cu K<sub>av</sub> 1.540562 Å),  $\beta$  is the full width at half-maximum of the PXRD peak, and  $\theta$  is the Bragg angle.<sup>47</sup>

$$\tau = \frac{K\lambda}{\beta\cos\theta} \tag{3}$$

Compositions were calculated from XPS measurements by calculating relative sensitivity factors (RSF) relative to the oxide (O<sup>2-</sup>) and hydroxide (<sup>-</sup>OH) O 1s peaks (signal from the water peak was not included) for the pure oxides, TiO2 and SnO2, assuming a 1:2 empirical formula. Both commercial and synthesized samples of TiO<sub>2</sub> and SnO<sub>2</sub> were used in this analysis and provided nominally identical RSF values. Transmission electron micrographs were collected using a FEI Tecnai Osiris 200 kV TEM. Dye loadings and spectra of RuP on Sn<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> were measured on dry films in a transmission geometry using a Shimadzu UV-2600 spectrophotometer immediately following sensitization. Scattering backgrounds were corrected by subtracting the absorption spectrum of the same bare film collected prior to dye deposition. Volumetric dye loadings were determined as previously described using a modified version of Beer's Law<sup>7,61</sup> based on the absorbance at 454 nm, where RuP has a molar absorptivity of ~13,400 M<sup>-1</sup> cm<sup>-1,61</sup> and film thicknesses determined by mechanical profilometry. Mechanical profilometry measurements were made using a KLA Tencor Alphastep 200 profilometer. XAS measurements at the Ti K-edge were collected on bare Sn<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> films in an emission geometry at 6-BM of the National Synchrotron Light Source II at Brookhaven National Laboratory. A Si(111) monochromator

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was used. Nitrogen gas was used in the incident beam ionization chamber and the X-ray emission from the sample was detected using a four-element Si drift detector (Vortex ME4).

**Band Scheme Determination.** The band schemes of  $Sn_xTi_{1-x}O_2$  were determined using a combination of NIR spectroelectrochemistry (NIR-SEC)<sup>43,44</sup> and UV–vis Tauc measurements.<sup>62,63</sup> In short, NIR-SEC yielded the conduction band edge ( $E_{CBM}$ ), while the UV–vis Tauc measurements yielded the bandgap, thereby allowing the valence band edge ( $E_{VBM}$ ) to be determined.

NIR-SEC was performed using a Shimadzu UV-2600 spectrophotometer and Bio-Logic SP-50 potentiostat. Samples were prepared by doctor blading  $Sn_xTi_{1-x}O_2$  on a fluorine-doped tin oxide (FTO) glass slide (TEC 15, Hartford Glass) that fits in a standard 1 cm path length cuvette, followed by the aforementioned annealing and sensitization procedures. Measurements were performed in 0.1 M HClO<sub>4</sub> using the resulting **RuP**-sensitized  $Sn_xTi_{1-x}O_2$  films on FTO as the working electrode, a platinum mesh as the counter electrode, and a low profile Ag/AgCl (saturated NaCl) reference electrode (Pine Research, #RRPEAGCL), which was subsequently converted to V vs NHE.<sup>64</sup> Each sample had spectra collected at approximately ten different potentials around the expected  $E_{\rm CBM}$  for each material (see Figure S3). After a potential was applied, both the current response and change in absorption at 800 nm were monitored and allowed to equilibrate for approximately 10 min before the NIR spectrum was collected. Difference spectra were calculated with respect to the lowest energy potential (most positive).  $E_{CBM}$  was extracted by fitting the resulting data to eq 4 shown below, where  $\Delta A$  is the change in absorption at 800 nm as a function of potential,  $\Delta A_0$  is the total amplitude of the change in absorption, E is the applied potential, a is a dimensionless parameter that accounts for the shape of the conduction band edge,  $^{65}$  and  $k_{\rm B}T$  is the thermal energy, fixed at 25.9 meV, corresponding to room temperature. It should be noted that  $\Delta A$  and  $\Delta A_0$  are proportional to the number of electrons in the conduction band and the total conduction band DOS, respectively.43,44

$$\Delta A(E) = \Delta A_0 \exp\left[\frac{a(E_{\rm CBM} - E)}{k_{\rm B}T}\right]$$
(4)

UV–vis Tauc measurements were performed using a Shimadzu UV-2600 spectrophotometer with an ISR-2600Plus integrating sphere accessory. Transmittance and reflectance spectra for each sample were collected and converted to an absorption coefficient using eq 5 shown below, where  $\alpha$  is the absorption coefficient, *d* is the film thickness as measured by mechanical profilometry, *T* is the fractional transmittance, and *R* is the fractional reflectance.<sup>63</sup>

$$\alpha = \frac{-1}{d} \ln \left( \frac{T}{1-R} \right) \tag{5}$$

The absorption coefficient spectra were then used for a Tauc analysis<sup>62,63</sup> to determine the bandgaps assuming an indirect transition for Sn<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub>, which is reported to be the lowest energy transition,<sup>32</sup> and a-TiO<sub>2</sub>. Both the direct and indirect bandgaps were determined for SnO<sub>2</sub>.

**Ultrafast Transient Absorption.** Femtosecond UV–vis transient absorption spectroscopy (fs-TAS) measurements were collected using two functionally identical Ultrafast Systems Helios transient absorption spectrometers at two different locations (Brookhaven National Laboratory or Drexel University). Samples were photoexcited at 515 nm (200  $\mu$ J cm<sup>-2</sup>) from the output of an optical parametric amplifier (Light Conversion TOPAS or Coherent OPerA Solo) pumped by a chirped-pulse regeneratively amplified Ti:Al<sub>2</sub>O<sub>3</sub> laser system (Spectra Physics Spitfire Pro or Coherent Libra). In both cases, the white light continuum probe was generated in continuously translated CaF<sub>2</sub>.

**Periodic Density Functional Theory Calculations.** Periodic DFT calculations were performed using the Vienna Ab Initio Simulation Program (VASP) version 5.4.<sup>66–69</sup> Bulk optimizations were conducted using the Perdew–Burke–Ernzerhof (PBE) functional<sup>70</sup> and the projector-augmented wave (PAW) method.<sup>71,72</sup> PAW

potentials were selected such that Sn 4d and Ti 3s and 3p electrons were treated explicitly, using a plane wave cutoff energy of 500 eV. The convergence criterion for the electronic energy was  $10^{-6}$  eV while that for the optimization was 0.01 eV/Å. All calculations were performed with a 9  $\times$  9  $\times$  9  $\gamma$ -centered k-point grid and Gaussian smearing ( $\sigma = 0.1$  eV) to describe the partial occupancies. DOS calculations were performed on the optimized bulk structures using the Heyd-Scuseria-Ernzerhof (HSE06) functional<sup>53,54</sup> with the same parameters used for the PBE optimization. Coordinates for the bulk structures are provided in the SI (Table S20). Periodic DFT calculations were corrected for the experimental value determined for  $E_{\text{CBM}}$  by integrating the DOS at the conduction band edge and fitting the data to eq 4, analogous to how  $E_{\text{CBM}}$  values were determined in the NIR-SEC measurements. The integrated DOS around  $E_{CBM}$  the corresponding fits, and fit parameters can be found in the Supporting Information (Figure S12 and Table S4).

### ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.1c00305.

Spectroelectrochemistry measurements with fits, Tauc plots, XPS measurements and relative  $Sn_xTi_{1-x}O_2$  composition, powder X-ray diffractograms, steady-state UV–vis measurements with fits, transmission electron micrograph of  $Sn_{0.5}Ti_{0.5}O_2$ , calculated density of states with r-TiO<sub>2</sub>, fits to correct the calculated conduction band edges, pre-edge X-ray absorption spectra with fits, fs-TAS measurement of **RuP**-sensitized ZrO<sub>2</sub>, comparison of SnO<sub>2</sub> fs-TAS, fs-TAS fit parameters, tabulated fit parameters from all materials characterization data, DFT-optimized coordinates and lattice vectors of  $Sn_xTi_{1-x}O_2$  (PDF)

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#### Notes

The authors declare no competing financial interest. <sup>§</sup>Deceased: July 26, 2020

# ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE), Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Science (DE-FG02-07ER15909), and by a generous donation from the TomKat Charitable Trust. J.A.S. acknowledges support from the Onsager Graduate Research Fellowship in Chemistry. V.S.B. acknowledges high-performance computing time from the Yale Center for Research Computing and the National Energy Research Scientific Computing Center (NERSC). This research used resources of the Center for Functional Nanomaterials (CFN) and 6-BM of the National Synchrotron Light Source II, which are U.S. DOE Office of Science User Facilities operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. The authors would like to thank Matthew Sfeir (formerly CFN, Brookhaven National Laboratory, measurements made under user proposal #36447), Mircea Cotlet (CFN, Brookhaven National Laboratory, measurements made under user proposal #38744), Mohammad M. Taheri (Department of Chemical and Biological Engineering, Drexel University), and Jason B. Baxter (Department of Chemical and Biological Engineering, Drexel University) for their help in performing fs-TAS experiments. The authors thank Bruce Ravel for his assistance with the XAS measurements. PXRD and XPS measurements were carried out with the assistance of Min Li at the Yale West Campus Materials Characterization Core.

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