The Potential of Overlayers on Tin-based Perovskites for Water Splitting

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ABSTRACT: Photoelectrochemical water splitting is a promising method of clean hydrogen production for green energy uses. Here, we report on a tin-based oxide perovskite combined with an overlayer that shows enhanced bifunctional hydrogen and oxygen evolution. In our first-principles study of tin-based perovskites, based upon density functional theory, we investigate how the formation of a surface affects the electronic properties of these materials. We show that the best candidate, SrSnO3, possesses hydrogen and oxygen overpotentials of 0.75 and 0.72 eV, respectively, which are reduced to 0.35 and 0.54 eV with the inclusion of a ZrO2 overlayer. Furthermore, this overlayer promotes charge extraction, stabilizes the reaction pathways, and improves the band gap such that it straddles the overpotentials between pH 0 and pH 12. This result indicates that SrSnO3 with a ZrO2 overlayer has significant potential as a highly efficient bifunctional water splitter for producing hydrogen and oxygen gas on the same surface.

As society moves toward greener energy sources, water splitting has gained increasing attention as a method for producing clean hydrogen.¹⁻⁴ Current hydrogen production involves significant use of fossil fuels, negating the positive effects of producing a green fuel.⁵⁻⁷ Water splitting offers a chance to easily and cleanly produce hydrogen gas, if the efficiency can be increased to make it economically viable. In this process, a semiconductor surface is used to split water into hydrogen and oxygen gas via an incident photon.⁸ The hydrogen gas can then be stored and burned at a later stage to release energy, releasing water as its only byproduct.

For a material to be an effective water-splitting catalyst, it must have a sufficiently large band gap that straddles both the evolution reaction levels and their overpotentials.⁹ However, a material’s capabilities can be improved through the introduction of an overlayer to its surface.¹⁰,¹¹ This improvement has been attributed to an improved electron extraction and to a reduction of both the overpotential and the work function of the catalyst due to its inclusion. While a range of overlayer materials has been considered, most of these materials are applied to hematite,¹²,¹³ with very few studies considering other catalysts such as perovskites.¹⁴

With oxide perovskites having shown great promise in many areas,¹⁵⁻¹⁹ including water splitting,²⁰⁻²² their bulk properties have been extensively explored.²³ They can be easily fabricated²⁴ and are relatively stable in water,²⁵ making them suitable for water-splitting applications. The effectiveness of a material as a photocatalyst is determined by its surface properties, which often differ from the bulk material.¹¹,²⁶⁻²⁸

Thus, a thorough investigation of the surface is necessary to understand photocatalysts.²⁹

In this study, we investigate the surface properties of a set of tin-based perovskites, CaSnO₃, SrSnO₃, BaSnO₃, and SnTiO₃, as candidates for bifunctional photocatalysts of hydrogen and oxygen evolution reactions (HER and OER). By considering the effects of forming surfaces, with focus on their band alignments with respect to the water-splitting reaction levels, we can identify which are suitable for the process. We further this study by exploring the effects of overlayers and how they can be used to optimize both band alignment and overpotentials.

The OER is given by the following four stages:

\[
\begin{align*}
\text{H}_2\text{O} + * & \rightarrow \text{HO}^* + \text{H}^+ + e^- \quad (R1) \\
\text{HO}^* & \rightarrow \text{O}^* + \text{H}^+ + e^- \quad (R2) \\
\text{O}^* + \text{H}_2\text{O} & \rightarrow \text{HOO}^* + \text{H}^+ + e^- \quad (R3) \\
\text{HOO}^* & \rightarrow * + \text{O}_2 + \text{H}^+ + e^- \quad (R4)
\end{align*}
\]

where * denotes a surface site (e.g., O* denotes an oxygen atom adsorbed to the surface). These also allow for calculation...
of the hydrogen- and oxygen-associated overpotentials (further
details in Supporting Information).

In general, the (001) surface termination offers two potential
surfaces, AO and BO2. However, various oxide perovskites
have been shown experimentally to favor the BO2 surface.30−32
Also, the electronic states associated with the A cation
generally lie far away from the Fermi level.33 As such, their
states will be of less importance to the surface electronics.
Hence, we focus on the results of the BO2 surfaces, as they are
of higher interest and importance (see Supporting Information
for a comparative study of the two potential surface ter-
minations). An example perovskite structure is presented
in Figure 1a, and the corresponding BO2 surface is presented in
Figure 1b.

Figure 1. Structures of an orthorhombic perovskite (a) bulk unit cell and (b) BO2-termination. (c) Comparison of the HER/OER with the bulk
and surface band gaps for CaSnO3, SrSnO3, BaSnO3, and SnTiO3. The blue (green) dashed line indicates the HER (OER). The black bars denote
the bulk band gap, with the red-hashed region highlighting their surface reduction. Band gaps are obtained using HSE06, with energies being
normalized to the vacuum energy. Hole affinities are obtained using PBE.

The formation of a surface introduces surface states that
dramatically alter the electronic structure, leading to a large
decrease in the band gap of these materials. This is shown in
Figure 1c, where the black bars indicate the band gap for each
of the four bulk structures, while the red-shaded regions show
the reduction of the gap due to the creation of a surface. In
particular, we note that the formation of these surfaces
significantly reduces the band gap via a lowering of the
unoccupied states, which are mainly attributed to the Sn 5s
states34,35 (Supporting Information). This reduction can be
significant enough to reduce the band gap below the 1.23 eV
required to split water, as is the case with BaSnO3, which has a
band gap reduced from of 1.99 eV in bulk to 1.12 eV (see
Table S1 for further numerical details of the band gap
reductions).

Figure 2. (a) Top-down view of an orthorhombic perovskite surface, denoting the three potential adsorption sites. The DOS for (b) CaSnO3 and
(c) SrSnO3 systems, respectively. Black, blue, and red lines indicate the DOS for the clean, hydrogen-adsorbed, and oxygen-adsorbed surface
systems. Shaded regions indicate filled states (method used to align each DOS is outlined in Supporting Information).
In order for water splitting to be viable at the surface, the band gap of the material should closely straddle the evolution potentials. As such, the alignment of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with respect to the OER and HER, respectively, need to be considered. The alignments of the surface systems are shown in Figure 1c, with further numerical details found in Table S1. We show that the BaSnO₃ and SnTiO₃ surface systems do not straddle the reaction levels, with the LUMO of BaSnO₃ lying below the HER and the HOMO of SnTiO₃ above the OER. Hence, they are not ideal water splitters, and, instead, we will focus on CaSnO₃ and SrSnO₃.

To better consider how the perovskite surfaces might behave in practical situations, we consider hydrogen atoms, oxygen atoms, HO groups, and HOO groups (separately) adsorbed to the surface, as these are the intermediates formed at the surfaces during the water-splitting process. Three potential adsorption sites were identified (see Figure 2a). The HO and HOO groups energetically favor adsorption on the B-site (as also seen by Man et al.³⁶), whereas the O adsorption is more favorable on the O-site. The most energetically favorable sites at each step are used for the reaction pathways. As hydrogen adsorption is preferred on the O-site, we consider this site for the HER. See Table S4 for numerical values of adsorption energies.

Figure 2b,c shows the density of states (DOS) for the CaSnO₃ and SrSnO₃ clean-surface systems (with Figure 3a depicting an example clean-surface structure), and with hydrogen and oxygen adsorptions, with adsorptions introducing states into the band gap (Table S5). While the addition of these states should not prevent CaSnO₃ and SrSnO₃ from being a viable water splitter, the possibility for different excitation and recombination routes could reduce efficiency.

The free-energy reaction pathways allow for the water-splitting capabilities of a material to be thoroughly explored.
Figure 3c depicts the free energy changes associated with each step of the OER (Reactions R1–R4) for both the SrSnO3 surface and for the ideal water splitter. For SrSnO3, the Gibbs free energy changes of the steps are 1.74, 1.43, 1.95, and −0.20 eV, respectively. The HOO adsorption is found to be the rate-limiting step, which is the case for oxides where oxygen binds strongly to the surface.36 Hydrogen (0.75 eV) and oxygen (0.72 eV) overpotentials for SrSnO3 are presented for a range of pH values (Figure 3d). The hydrogen overpotential extends beyond the surface LUMO for all pH, while the oxygen overpotential lies above the HOMO between pH 5 and pH 14.

Previously, Man et al. described a 3.2 eV difference between the HO* and HOO* steps for oxides;36 we find a clear agreement for SrSnO3, which has a value of 3.38 eV. As such, we use this relation to identify the overpotentials for CaSnO3 (Supporting Information). Both the hydrogen (1.77 eV) and the oxygen (1.20 eV) overpotentials are larger than those for SrSnO3. Furthermore, the hydrogen overpotential of CaSnO3 occurs at the same level as its LUMO, while, in SrSnO3, it sits at the surface band edge—well below the bulk LUMO of SrSnO3. As SrSnO3 is shown to have a better alignment between its band gap and overpotentials, we now focus on this material.

A set of lattice-matched oxide overlayers were added to the surface of SrSnO3 using our in-house interface generator code, ARTEMIS.37,38 These overlayers (ZrO2, TiO2, Ta2O5, RuO2, and SnO2) were considered, as each displays either strong stability in water, low overpotentials, or desirable band alignments with respect to SrSnO3.13,36,39 Of these, ZrO2 was found to be the most favorable addition, with a surface formation energy of 0.03 eV/Å2. The other considered oxides reduced the band gap below that of the clean surface, with the exception of Ta2O5, which was found to be unstable. The

Figure 4. Properties of the SrSnO3/ZrO2 surface. (a) Structure and (b) layer-decomposed DOS (calculated using PBE) for a SrSnO3 slab with a ZrO2 overlayer. The red dashed line denotes the band edge curvature of the HOMO from the center of the slab to the surface. The black dash-dotted line denotes the HOMO. The density of unoccupied states is scaled by a factor of 10. (c) Free-energy diagram of OER performed on a SrSnO3/ZrO2 surface. (d) HER and OER overpotentials for a SrSnO3/ZrO2 surface, given at 0 V vs the standard hydrogen electrode, and pH 0. Band gap in (d) is obtained using HSE06.
relaxed structure of the perovskite surface with a thin overlayer of ZrO₂ is shown in Figure 4a.

Figure 4b displays the layer-projected density of states (LPDOS) of the SrSnO₃ surface with a ZrO₂ overlayer. Compared with Figure 3b, the inclusion of the overlayer is seen to suppress the band gap reduction seen for the perovskite surface, removing s-states and significantly reducing contributions from p- and d-states at the surface (Supporting Information). The unoccupied states of the coated surface also show far less reconstruction with respect to the clean SrSnO₃ surface. In addition, we see only minor variation in the LPDOS for the unoccupied states across the entire SrSnO₃ slab. The suppression of these surface states removes alternative decay paths that would otherwise hinder the efficiency of water splitting. Further, a curvature arises in the valence band edge of the SrSnO₃ surface with a ZrO₂ overlayer. In addition, we see only minor variation in the LPDOS of the SrSnO₃|ZrO₂ system with a ZrO₂ overlayer.

The Gibbs free energy changes for the SrSnO₃|ZrO₂ are found to be 0.58, 1.47, 1.77, and 1.10 eV, respectively (Figure 4c). Here, the formation of the HOO* reactant is still the rate-limiting step, indicating that the oxygen is still strongly bonded with the surface. Comparison between Figures 3d and 4d shows a reduction in the overpotentials, from 0.75 and 0.72 eV to 0.35 and 0.54 eV for hydrogen and oxygen, respectively. These are now straddled by the HOMO and LUMO of the SrSnO₃|ZrO₂ system for pH values between 0 and 12. With the improvement of the electronic properties, alongside the improvements to the reactivity with the various water-splitting adsorbates, SrSnO₃ with an overlayer of ZrO₂ offers great promise as a catalyst for the water-splitting process.

In this study, the overlayers are considered to cover the entire surface and to be very thin (4 Å). This overlayer is used to stabilize the surface’s interactions and to suppress the surface band gap reduction (with the potential added benefit of increasing band edge curvature). For the real system to replicate these behaviors, it should be limited to a few nanometers to prevent the properties of the surface coating from dominating those of the perovskite. By being thin, it should appear as transparent to the incident light, thus still absorbing in the perovskite. Notably, such thin layers of ZrO₂ have already been experimentally realized.59,47

We present a first-principles study of four oxide perovskites for photocatalysis. Though bulk band gap values of all candidates appear suitable for water splitting, investigation of the surface properties reveals that both the LUMO of BaSnO₃ and the HOMO of SnTiO₃ are poorly aligned to the reaction pathways. Meanwhile, CaSnO₃ and SrSnO₃ maintain their overpotentials from 0.75 and 0.72 eV down to 0.35 and 0.54 eV, respectively. Also, the band gap of this system straddles both overpotentials for pH values between 0 and 12. This study demonstrates the importance of overlayers in water splitting and presents SrSnO₃|ZrO₂ as a potential ideal candidate offering high efficiencies through means of lowering overpotentials and maintaining a suitable band gap, enabling simultaneous hydrogen and oxygen evolution. We believe this system, if fabricated, would be a leading candidate for bifunctional water splitting.

COMPUTATIONAL METHODS

In this work, first-principles techniques based on density functional theory (DFT) were used to determine structural and energetic properties of selected tin-based perovskites CaSnO₃, SrSnO₃, BaSnO₃, and SnTiO₃. These calculations were performed using VASP.48,49 The valence electrons for each atomic species are considered as follows: Ca 3s²3p⁶4s², Sr 4s²4p⁶5s², Ba 5s²5p⁶6s², Ti 3p⁶3d⁴⁴², Sn 5s²5p², and O 2s²2p⁴. The projector augmented wave method was used to describe the interaction between core and valence electrons, and a plane-wave basis set was used with an energy cutoff of 700 eV. All calculations were completed using the Perdew-Burke-Ernzerhof (PBE)50 functional. This includes structural relaxation, density of states, and local potential calculations. However, to accurately assess materials for their potential as water splitters, HSE0651 was used to accurately calculate the band gaps. All forces are relaxed to less than 0.01 eV/Å per atom, and electronic self-consistency is accurate to within 10⁻⁷ eV. As the primitive cells of CaSnO₃ and SrSnO₃ are orthorhombic, they contain four perovskite units (AOBO₂), whereas the BaSnO₃ and SnTiO₃ primitive cells, being cubic, contain a single perovskite unit. All considerations of k-point grids are performed using a single cubic perovskite unit as the reference, with 9 × 9 × 9 Monkhorst-Pack grid52 equivalents being used.

It has been noted that perovskite structures prefer to terminate on (001) surfaces.53–55 Thus, to generate our surface systems, supercells equivalent to a 2 × 2 (a × b) extension of an orthorhombic unit cell were formed, with a 14 Å vacuum gap introduced along the [001] Miller direction. Our surfaces were structurally relaxed, and electronic properties were studied, using appropriate k-point grids. Electronic structure calculations were performed using slabs four formula units thick, and clean-surface/adsorbate calculations were performed with slabs three formula units thick. All slabs had an additional BO₂ layer to ensure both surfaces terminated with BO₂. This unit cell geometry leads to surface adsorptions with an effective concentration of 7.7 × 10¹³ cm⁻².

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.0c00964.

Bulk material band structures and density of states; comparison of the electronic and energetic properties of multiple surface terminations; surface structures densities of states; calculation methods for the HER and OER steps; free-energy diagrams for the HER and OER at different applied biases; adsorption energies, adsorption defect state locations, energy corrections for the reaction pathways (PDF)

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https://dx.doi.org/10.1021/acs.jpcl.0c00964
J. Phys. Chem. Lett. 2020, 11, 4124–4130
The authors acknowledge financial support from the Engineering and Physical Sciences Research Council (EPSRC) of the United Kingdom, via the EPSRC Centre for Doctoral Training in Metamaterials (Grant No. EP/L015331/1). Via our membership of the UK’s HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202, EP/R029431), this work used the ARCHER UK National Supercomputing Service (http://www.archer.ac.uk). The authors also acknowledge the use of the Univ. of Exeter High-Performance Computing facility in carrying out this work. Finally, the authors thank F. Huw Davies, S. Graham Davies, and E. L. Martin for their useful discussions.

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