Influence of Sr leaching on the catalytic activity of reconstructed SrTiO$_3$ photoelectrodes

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Perovskite photoelectrodes are being extensively studied in search for photocatalytic materials for hydrogen production through water splitting. The solar-to-hydrogen efficiency for these materials is critically dependent on the electrochemical state of their surface. Here, we develop an embedded quantum-mechanical approach using the self-consistent continuum solvation (SCCS) model to predict the relation between electrochemical stability, band alignment, and photocatalytic activity taking into account the long-range polarization of the semiconductor electrode under electrical bias. Using this comprehensive model, we calculate the charge-voltage response of various reconstructions of a solvated SrTiO$_3$ surface, revealing that interfacial charge trapping exerts primary control on the electrical response, electronic structure, and surface stability of the photoelectrode. Our results provide a detailed molecular-level interpretation of the enhanced photocatalytic activity of SrTiO$_3$ upon voltage-induced restructuring of the semiconductor–solution interface.

I. INTRODUCTION

Hydrogen is a sustainable energy carrier whose photocatalytic reaction with oxygen produces electricity and heat without emitting carbon dioxide. A highly attractive approach for the massive production of hydrogen fuels consists of splitting water molecules by photocatalytic means; however, engineering photoactive electrode materials that can efficiently promote this reaction remains an outstanding question at both the experimental and theoretical levels. Strontium titanate (SrTiO$_3$) is a photocatalytic material that has shown promising solar-to-hydrogen conversion performance [1-4]; under ultraviolet light, this wide-bandgap semiconductor exhibits a high quantum efficiency in converting incident photons into charge carriers [3, 4].

To date, considerable efforts have been dedicated to understanding the microscopic mechanisms that underlie its water-splitting performance [3-6]. A central aspect of these studies has been to elucidate the interface structure of SrTiO$_3$ under electrochemical conditions. Through surface-sensitive characterization and electronic-structure calculation, it has been shown that SrTiO$_3$ can undergo a TiO$_2$-rich surface reconstruction when exposed to an electrolytic environment under applied voltage [7, 9]. This result has been further confirmed by the detailed comparison of the computationally predicted structures with accurate x-ray reflectivity data [10].

Beyond their descriptive power, density-functional theory simulations are now frequently applied to address many of the questions that surround the performance of water-splitting catalysts. These calculations have been used to evaluate the band edge positions against redox potentials in electrolytic media [11, 12], elucidate catalytic reaction pathways [13-16], and narrow down the choice of candidate photocatalysts [17, 18]. Furthermore, it is now possible to achieve a microscopic understanding of the electrical conditions that exist in the subsurface depletion region of photoelectrodes through first-principles Mott–Schottky analysis, which enables one to capture the driving forces that drag or push the photogenerated charge carriers to the interface [19, 20].

Using these newly available computational models, we undertake here a detailed analysis of various reconstructions of SrTiO$_3$ electrodes to predict and understand their photoelectrochemical properties. By capturing the effects of band bending and band alignment, we examine the influence of surface termination on the electronic structure and electrochemical stability of SrTiO$_3$ under voltage to shed light into the its photocatalytic performance as a function of preparation and operation conditions.

First, we outline the computational methods in Sec. II with a presentation of the surface models and description of voltage-dependent surface simulations. We then report computational predictions of voltage-induced charge accumulation, band bending, and charge pinning as a function the surface termination in Sec. III. Finally, we discuss the consequences of these predictions in understanding the electrochemical stability and photocatalytic activity of the reconstructed SrTiO$_3$ electrodes.

II. COMPUTATIONAL METHOD

A. First-principles simulations and bulk structure

Self-consistent-field calculations are performed at the semilocal Perdew–Burke–Ernzerhof level [21] with the on-site Hubbard $U$ parameterization of the self-interaction correction to the effective potential using the PW code of the QUANTUM-ESPRESSO distribution [22]. Ionic cores are represented by ultrasoft pseudopotentials with kinetic-energy cutoffs of 70 and 700 Ry for

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the reciprocal-space expansion of the wave functions and of the charge density, respectively. For the bulk structure of SrTiO$_3$, the Brillouin zone is sampled with a 6 × 6 × 6 Monkhorst–Pack grid [23]. The effective Hubbard interaction is computed from linear-response theory [24, 25], yielding a $U$ parameter of 5.48 eV for the Ti sites. Through variable-cell relaxation, the lattice constant is predicted to be 3.97 Å in good agreement with experiment (3.91 Å). The bandgap of the optimized structures is calculated to be 2.4 eV, which is lower than the experimental bandgap of 3.2 eV [26] but significantly improved compared to the band gap of 1.6 eV obtained without self-interaction correction. The calculated bandgap is also concordant with previous computational studies using an on-site $U$ correction for the Ti atoms of the SrTiO$_3$ structure [27, 29]. We note that an overestimated bandgap of 4.8 eV is predicted when the on-site Hubbard correction is applied to the oxygen 2p orbitals. Therefore, the Hubbard correction is only applied to Ti in all the calculations reported in Sec. III.

B. Surface structure of slab models

We consider four types of SrTiO$_3$(001) surface structures to investigate their influence on interfacial properties. These surfaces include (i) the single-TiO$_2$ terminated slab (1 ML), (ii-iii) the stoichiometric double-TiO$_2$ terminated slabs in the (1×1) and (2×1) surface unit cells (2 ML (1×1) and 2 ML (2×1)), and (iv) the non-stoichiometric triple-TiO$_2$ terminated slab (3 ML) that is deficient in oxygen.

The 1 ML interface is obtained by cleaving SrTiO$_3$ between its SrO and TiO$_2$ layers along the [001] direction. The double-TiO$_2$ structural motif on SrTiO$_3$ has been previously observed by high-resolution electron microscopy and confirmed to be a low-energy configuration through theoretical calculations [7, 9], while the 3 ML reconstructed surface has been recently observed experimentally by Plaza and coworkers under positive bias in alkaline solution, leading to significantly improved photocatalytic activities [10].

The corresponding slab structures are shown in Fig. 1 (the slabs are constructed symmetrically with a periodic separation of 15 Å along the transverse axis). Prior to geometry optimization in the continuum dielectric environment, the terminal oxygen atoms of the outermost layer are completely protonated, and the Brillouin zone is sampled using a 6 × 6 × 1 grid of wave vectors. To retain the bulk characteristics of SrTiO$_3$, the middle 2 layers are fixed and other atoms are fully relaxed until interatomic forces are brought down to 0.01 eV Å$^{-1}$. Five layers of bulk SrTiO$_3$ are found to be sufficient to converge the Fermi level within a few meVs.

Figure 1. (a) Perovskite cubic structure of SrTiO$_3$. (b) Single-TiO$_2$ termination (1 ML), (c) double-TiO$_2$-terminated (1×1) reconstruction (2 ML (1×1)), (d) triple-TiO$_2$ termination (3 ML) and (e) double-TiO$_2$-terminated (2×1) reconstruction (2 ML (2×1)). The colored regions represent the continuum electrolyte, showing the dielectric transition.

C. Solvation effects

To describe the solvation environment, the structure is immersed in an implicit polarizable solvent parameterized by the self-consistent continuum solvation (SCCS) model [19]. In this model, the shape of the dielectric cavity is defined self-consistently from the electron density of the solvated surface that is directly computed at the quantum-mechanical level. The SCCS model has been shown to efficiently capture the essential features of liquid–solid interface through its logarithmically smooth definition of the solvation shell: $\epsilon(\rho) = \exp[(\zeta - \sin(2\pi \zeta)/2\pi)\ln\rho_s]$, which involves the smooth switching function $\zeta(r) = (\ln\rho_{\max} - \ln\rho) / (\ln\rho_{\max} - \ln\rho_{\min})$ that defines the gradual dielectric transition. $\rho_{\max}$ and $\rho_{\min}$ denote the thresholds of the electron density that define the frontiers of solute ($\epsilon = 1$) and solvent ($\epsilon = \epsilon_\infty$), respectively. Non-electrostatic cavitation contributions including surface tension, external pressure, dispersion and repulsion interactions are also incorporated into the model. These contributions are explicitly expressed as $F_{\text{tens}} = \gamma S$ and $F_{\text{disp+rep}} = \alpha S + \beta V$, where $\gamma$ stands for the surface tension of the solvent, $\alpha$ and $\beta$ are parameterized against experimental solvation energies, and $V$ and $S$ are the quantum volume and quantum surface area that are defined as $V = \int \Theta \rho \, d\mathbf{r}$ and $S = -\int \frac{d\rho}{\rho} |\nabla \rho| \, d\mathbf{r}$ using the additional switching function $\Theta(\rho) = (\epsilon_\infty - \epsilon(\rho)) / (\epsilon_\infty - 1)$. This parameterization of the continuum permittivity en-
sures the convergence of surface simulations by eliminating the sharp variations in the electron density that typically occur at solid–solution interfaces. Specifically, we utilize the parameterization: $\epsilon_{\text{rms}} = 78.3$ is the dielectric constant of water. $\rho_{\text{min}} = 10^{-4}$ a.u., $\rho_{\text{max}} = 5 \times 10^{-3}$ a.u., $\gamma = 72.0$ dyn/cm, $\alpha = -22$ dyn/cm, and $\beta = -0.35$ GPa. The validity of this parameterization has been benchmarked for a range of molecules, charged ions, and electrodes \cite{30, 31}, thereby providing a transferable computational method to simulate quantum systems in aqueous environments.

III. RESULTS AND DISCUSSION

To derive the charge–voltage characteristics of the SrTiO$_3$–water interfaces, we employ the procedure initially proposed by Campbell and coworkers \cite{32} to convert a finite slab into a semi-infinite surface capturing the bending of the electronic bands in the subsurface layers. This procedure is depicted schematically in Fig. 2. Two planar countercharges are placed 3 Å away from both ends of SrTiO$_3$ surface to represent the Helmholtz contribution to the polarization of the interface, then the electrode is partitioned into an explicit interface finite region and an implicit semi-infinite bulk region by introducing a cutoff plane located a the inflection point of the average electrostatic potential difference $\bar{\varphi}$, represented by the upper dashed curve in Fig. 2(c). To describe the bending of the bands in the semiconductor, the electric field right below the surface is calculated and a Mott–Schottky extrapolation is performed to determine the position of Fermi energy deep inside the semiconductor according to the following equation:

$$\epsilon_F = \bar{\varphi}_0 - e\Phi_{\text{FB}} \quad (1)$$

where the $\bar{\varphi}_0$ stands for the asymptotic electrostatic potential that semi-infinitely extends in the bulk of the semiconductor and $\Phi_{\text{FB}}$ is the flatband potential corresponding to the opposite Fermi energy of the neutral surface (Fig. 2(a)). Finally, the Fermi levels of the bulk semiconductor and of the interface are equilibrated by changing the distribution of charge between the explicit and implicit region while ensuring charge balance with the Helmholtz plane of counterions, leading to the equilibrated profile that is schematically depicted in Fig. 2(d).

The capacitive responses of the electrode are obtained by varying the amount of charge added to the electrode (the opposite of the Helmholtz charge) \cite{33, 34}, and the resulting charge–voltage characteristics are reported in Fig. 3. The excess charge density that accumulates at the surface is also computed by subtraction of the neutral-slab electron density to that of the charged slab (Fig. 3). These simulations show that among the four terminations, 1 ML behaves similarly to an ideal semiconductor, with a limited amount of electronic charge trapped into surface states. In contrast, other surface terminations exhibit a much strong accumulation of the surface charge. Nevertheless, the mechanisms that lead to charge trapping are different in each case; for the 2 ML (1×1) surface, the excess charge is seen to mainly accumulate around the hydroxyl groups, whereas in the case of more substantially reconstructed 3 ML surface, the oxygen-deficient Ti sites located in the sublayer traps a sizable amount of charge, yielding a linear (ohmic) response due to the pinning of the Fermi level by mid-gap states. A similar trend is shown by the 2 ML (2×1) stoichiometric termination. By closely examining the structure of the surface, it is seen that despite the protonation of the outermost oxygen layer, the oxygen atoms that are located in the sublayer remain unsaturated, which leads to the formation of surface states associated with the resulting dangling bonds.

Figure 2. Band bending at the SrTiO$_3$–electrolyte interface accounted for by biasing the original electrostatic potential along transverse $z$ coordinate of the neutral slab (panel a) with explicit charge in the electrode ($\Phi_{\text{FB}}$) denotes the opposite of the Fermi energy ($\epsilon_F$) (per electron) with respect to asymptotic electrostatic reference. This is achieved by placing Helmholtz layers of countercharges at the interfaces while maintaining charge neutrality (panel b). A cutoff plane located at the inflection point of the difference between the charged- and neutral-slab potentials (shown by the upper dashed curve) defines the onset of the Mott–Schottky extrapolation of the potential inside the electrode (panel c). Finally, the Fermi levels of the bulk and interface are matched by varying the explicit charge on the electrode (panel d).
Figure 3. (a) Charge versus voltage characteristics of different SrTiO$_3$ interfaces. (b) Excess charge accumulating at the electrified interface, showing the spatial distribution of the charge-trapping centers.

the fact that the bandgaps of bulk SrTiO$_3$ and of the terminal TiO$_2$ are comparable. In contrast, the presence of sublayer oxygen vacancies in 3 ML causes strong changes in the energy gap due to the appearance of mid-gap states in the oxygen-deficient triple layers. Additionally, this surface termination strongly modifies the Fermi energy in comparison with the other interfaces; the shift in the flatband potential is calculated to be of $-0.88$ V (versus the standard hydrogen potential) in fair agreement with experimental Mott–Schottky measurements ($-1.0$ V).

Having determined the electrical characteristics of the proposed surface terminations, we now turn our attention to comparing their stability in electrolytic media in an effort to describe the voltage-induced reconstruction of the surface and its effects on photocatalytic durability and activity. Such surface-energy calculations are highly sensitive to the slab thickness and to the sampling of the Brillouin zone, potentially impacting the calculated surface energies. These sources of error can be eliminated by employing the methods proposed by Singh-Miller and Marzari [35]. In this approach, the surface free energy $\gamma_0$ of a stoichiometric, symmetric slab is obtained as the limit

$$\gamma_0 = \lim_{N \to \infty} \frac{1}{2A_s} (E_{\text{slab}}(N) - NE_{\text{bulk}}),$$

where $N$ is the number of slab layers, $E_{\text{slab}}$ and $E_{\text{bulk}}$ are the slab and bulk total energy, respectively, and $A_s$ stands for the surface area. In the limit of large $N$, Eq. 2 can be recast as

$$E_{\text{slab}}(N) = 2\gamma_0 + NE_{\text{bulk}},$$

reflecting the fact that the total energy of the slab should vary linearly as a function the slab thickness with a slope corresponding to the bulk energy $E_{\text{bulk}}$ of the material and an intercept corresponding to its surface energy $\gamma_0$.

We then consider the non-stoichiometry of the termination by taking into account the chemical potentials of the leaching and adsorbing elements in expressing the grand-canonical free energy $\gamma$ of the surface

$$\gamma = \gamma_0 - \mu_{\text{TiO}_2}\Gamma_{\text{TiO}_2} - \mu_{\text{OH}^-}\Gamma_{\text{OH}^-},$$

in terms of the chemical potentials $\mu_{\text{TiO}_2} = F(\text{TiO}_2)$ and $\mu_{\text{OH}^-} = F(\text{H}_2\text{O}) - \frac{1}{2}F(\text{H}_2\text{O}) + e\Phi_{\text{FB}} + k_B T \ln(10) p\text{H}$, with the $\Gamma$’s and $F$’s being the surface densities and the calculated reference state energies of the surface species, respectively.

Once the energy of the neutral interface is calculated, one obtains the free energy $\gamma^*$ of the charged interface from Lippmann’s equation

$$\gamma^* = \gamma - \int_{\Phi_{\text{FB}}}^{\Phi} \sigma(\phi) d\phi,$$

where $\Phi$ is the applied potential and $\sigma$ is the voltage-dependent surface charge density derived from the charge–voltage responses, leading in particular to significant changes in the surface stability of the more metallic (ohmic) interfaces at high voltage. The resulting surface stability analysis is reported in Fig. 5 for the 1 ML, 2 ML (1×1), 2 ML (2×1) and 3 ML terminations, with a pH of 14 corresponding to an alkaline environment. These results clearly indicate that under positive bias, the 3 ML becomes the most stable interface structure compared to the other termination and provides a direct first-principles confirmation that the 3 ML surface reconstruction is thermodynamically favorable under oxidizing conditions.

To conclude the discussion, we examine the influence of the reconstructed surface structure of SrTiO$_3$ on the theoretical hydrogen evolution overpotential, as it has been reported that sublayer oxygen vacancies at an anatase TiO$_2$ surface can tune the adsorption strength of protons from the solution, resulting in potentially enhanced catalytic activities [36]. Motivated by these findings, we estimated the hydrogen evolution overpotentials by calculating the opposite absolute binding free energy of a
Figure 4. Local density of states of SrTiO$_3$ surface structures (a) 1 ML, (b) 2 ML (1×1), (c) 2 ML (2×1) and (d) 3 ML are plotted with labeled alternative SrO and TiO$_2$ layers within the bulk region. Fermi energies are aligned to 0 eV. The 2ML (2×1) and 3 ML termination show stronger variations in their electronic structures due to reconstruction-induced surface states.

Figure 5. Calculated surface energy showing a transition from the 1 ML to the 2 ML (2×1) to the 3 ML terminations when applying an increasingly positive bias to the SrTiO$_3$ electrode.

Figure 6. Proton adsorption sites on the reconstructed surfaces of (a) 1 ML, (b) 2 ML (1×1), (c) 3 ML and (d) 2 ML (2×1) with a focus on adsorption at the hydroxyl group (H$_h$), and at the bridge (H$_b$), valley (H$_v$) and top (H$_t$) oxygens.

The adsorption energy $\Delta F_H$ is expressed as

$$\Delta F_H = F_{H^*} - F_* - \frac{1}{2} F_{H_2},$$  \hspace{1cm} (6)$$

where $F_{H^*}$ is the energy of the proton adsorbed on the SrTiO$_3$ surface and $F_*$ is the total energy of the adsorption site. The adsorption free energy of H$^*$ is then calculated from:

$$\Delta G_H = \Delta F_H + \Delta ZPE_H - T \Delta S_H,$$  \hspace{1cm} (7)$$

where $\Delta ZPE_H$ is the change of zero-point vibrational en-
energy of hydrogen, and $\Delta S_H$ is the change in entropy upon the adsorption. We compute the $ZPE_{H^*}$ on all surfaces by finite difference. The zero-point energy of reference hydrogen is computed in the gas phase as $\frac{1}{2} ZPE_{H^*}(g)$. The entropy contributions are obtained from experimental data at 300 K [37]. Based on these calculations, we construct a volcano plot shown in Fig. 7, where the peak stands for the thermodynamic conditions most favorable to hydrogen evolution, according to the Sabatier principle [38, 39].

The volcano plot shows a wide range of overpotentials for different surface structures. While protons tend to adsorb more strongly at the interface of the stoichiometric 1 ML and 2 ML (1×1), adsorption on the more reconstructed 2 ML (2×1) and 3 ML interface exhibits moderate adsorption strength. In fact, both adsorption sites on 3 ML are estimated to have overpotentials of 0.60 and 0.72 V, respectively. We note that the hydroxyl sites from the 2 ML (2×1) surface show the lowest overpotential (0.23 V), while all other sites on this particular termination correspond to lower activities compared to 3 ML surface. Comparing these results to the previous surface reconstruction diagram (Fig. 5), the 3 ML surface termination is anticipated to dominate the voltage reconstruction and hydrogen evolution of the SrTiO$_3$, providing a quantitative interpretation of its unexpectedly high photocatalytic activity upon anodic preparation.

IV. CONCLUSION

In this work, we have investigated the surface structure of SrTiO$_3$ under electrochemical conditions. By applying embedded quantum-mechanical model based on the self-consistent continuum solvation approach, we determined the electrical response of the reconstructed interfaces of SrTiO$_3$ from first principles. We have shown that surface terminations strongly affect the electrification of SrTiO$_3$ photoelectrodes, leading to a predicted ohmic response for the oxygen-deficient, 3 ML SrTiO$_3$ termination as a result of Fermi level pinning by midgap states. Further examination of the local density of states has shown that the sublayer, under-coordinated titanium site acts as the main charge-trapping centers. We have then computed the surface free energies of all interface structures under applied potential in alkaline solutions. The stability calculations have suggested that the 3 ML is the most stable of the structures considered under positive bias. The catalytic activity the 3 ML termination has been estimated to be the strongest for the hydrogen evolution reaction based on vacuum calculations of hydrogen binding energies. Our calculations provide direct insights into the voltage-induced formation of triple-TiO$_2$ termination and into the beneficial influence of this reconstruction on the photocatalytic activity of SrTiO$_3$.

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