

Reviving Inert Oxides for Electrochemical Water Splitting by Subsurface Engineering

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Cite This: https://dx.doi.org/10.1021/acs.chemmater.0c00763



ABSTRACT: Recently, it was theoretically predicted and experimentally validated that subsurface alloying of $SrRuO_3$ (SRO) beneath the $SrTiO_3$ (STO) capping layer can significantly promote the otherwise inert STO surface toward oxygen evolution [Akbashev et al. *Energy Environ. Sci.* **2018**, *11*, 1762–1769]. Herein, we provide a generalized framework behind the concept of subsurface alloying with different transition-metal dopants, host metal oxides, and doping levels. Based on density functional theory (DFT) calculations and detailed electronic-structure analysis, we first identify the electronic structure origin of the activation and stabilization phenomena and propose a tuning mechanism that enables the identification of candidate subsurface dopants in STO, with the highest activity for both oxygen and hydrogen evolution reactions. We then show that the proposed mechanism is applicable to subsurface alloys



formed with other host materials such as $SrZrO_3$, TiO_2 , and ZrO_2 . Finally, we propose a materials design scheme using partial subsurface alloying for more precise tuning of surface reactivity and activity. By generalizing the concept of subsurface alloying of metal oxides, our work explains why the SRO subsurface alloyed STO has among the highest OER enhancements and importantly provides a new route in tailoring the activity and stability of earth-abundant electrocatalysts for water splitting.

INTRODUCTION

Achieving a sustainable energy future remains one of the grand challenges of the 21st century. Electrochemical water splitting to its constituents hydrogen and oxygen, where the hydrogen gas can be used as a fuel directly or be converted to other useful chemicals such as ammonia, has long been thought of as a possible route to achieve sustainability.² Despite considerable progress in electrochemical water splitting, there is a need for earth-abundant alternatives to the traditional IrO2 and RuO2 catalysts used for the oxygen evolution reaction (OER) and Pt for the hydrogen evolution reaction (HER).^{3,4} In addition to the cost, it is now well-known that there are significant stability issues with some of the traditional OER electrocatalytic materials including RuO₂ especially in acidic media.^{5,6} Further, several other metal oxides, including perovskite oxides, have also been shown to undergo structural transformations in most cases resulting in deactivation.⁷⁻⁹ This therefore poses severe challenges in the design of electrocatalysts for fuel cells and water electrolyzers.^{2,10–13}

Over the years, approaches such as core–shell nanoparticles, especially the ones consisting of metals, have been shown to exhibit improved stability, as well as enhanced catalytic activity.^{14–18} The extension of similar ideas to oxides has proven far more difficult owing to the challenges in the synthesis of oxide core–shell nanoparticles,^{19–21} although a couple of oxide-based core–shell nanocatalysts have shown water-splitting capabilities.^{22,23} However, recently it was shown

that for Ir-based catalysts such as the perovskite SrIrO₃ and pyrochlore Y₂Ir₂O₇, the reported exceptionally high OER activity was the result of an OER active protective IrO_x overlayer formed due to large surface reconstructions.^{9,24} This observation of a natural protective capping oxide layer led to the concept of an artificially protective capping oxide layer and consequently resulted in the design of epitaxial ultrathin heterostructured perovskite oxide structures. Specifically, the SrTiO₃–SrRuO₃ (STO/SRO/STO) heterostructure was shown to have good OER activity and much improved stability, both computationally and experimentally, in our previous work.¹

Herein, the concept of subsurface alloying is first extended from the STO/SRO/STO heterostructure system to other 3*d*, 4*d*, and 5*d* transition metals, by preferential subsurface doping of the B-site metal of STO, thereby excluding the effects of strain. STO is chosen as the host material, owing to its stability, earth-abundance, and relatively low electrochemical activity for water splitting in the dark. It should be noted that while it is a

Received: February 21, 2020 Revised: May 15, 2020 Published: May 20, 2020



semiconductor, Nb doping in the bulk of STO has been shown to improve its electronic conductivity without perturbing the crystal structure,²⁵ making it an ideal host material for the heterostructures. Further, while we have only considered B-site doped subsurface alloys in this paper, it is worth noting that using a perovskite as a host material provides an additional tuning option by preferentially doping the A-site metal as well. Based on density functional theory (DFT) calculations and detailed electronic structure analysis, we formulate a tuning mechanism that enables the identification of candidate subsurface dopants in STO, with the highest activity for both OER and HER. We also show that the proposed mechanism is applicable to subsurface alloys formed with other host materials including SrZrO₃, TiO₂, and ZrO₂, hence, establishing the generality of the concept and providing a new route in tailoring the activity and stability of earth-abundant electrocatalysts for water splitting.

METHOD AND MODELS

All calculations were performed using the Quantum ESPRESSO²⁶ Package in combination with the Atomic Simulation Environment $(ASE)^{27}$ utilizing spin-polarized density functional theory (DFT). The exchange and correlation terms were described with the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.²⁸ The Kohn–Sham wave functions were expanded in a plane-wave basis with a kinetic energy cutoff of 500 eV. Ultrasoft pseudopotentials were used to approximate the core electrons.²⁹ The obtained lattice constant for the bulk SrTiO₃(STO) in the cubic perovskite structure was 3.970 Å, which is less than 2% larger than the value determined by X-ray diffraction.³⁰

For all of the heterostructures, the TiO_2 -terminated (001) surface is chosen to estimate the inherent electrocatalytic activity of the material, since it is the most stable surface for undoped STO.³¹ As shown in Figure 1, the STO/SMO/STO heterostructures were



Figure 1. (a) Side view and (b) top view of the computational model used for STO/SMO/STO perovskite heterostructures. Cyan, gray, green, and red balls represent guest metal M (3*d*, 4*d*, 5*d* transition metals), Ti, Sr, and O atoms, respectively.

modeled with a four-layer (2×2) STO (001) slab with the subsurface layer substituted by different guest oxides (SMO), where the guest metal M corresponds to 3*d*, 4*d*, or 5*d* transition metals (TM) dopants. The bottom two STO layers of the slab were fixed to the bulk STO position, while all adsorbates, the guest SMO layer, and the topmost STO layer were fully relaxed. The Brillouin zone was sampled with a $(4 \times 4 \times 1)$ Monkhorst–Pack *k*-point grid.³² A vacuum spacing of at least 14 Å was added to all supercell models to avoid the interaction between periodic images. All geometries were considered optimized when the maximum force on each atom was less

than 0.01 eV/Å. A grid-based decomposition scheme of the electron density was used to perform the Bader charge analysis.^{33,34}

The surface reactivity was evaluated by computing the adsorption free energy of OER and HER relevant reaction intermediates using the same formalism and corrections as described in ref 35. The OER and HER performance of STO/SMO/STO (M= 3d, 4d, 5d TM) heterostructures was examined by calculating the corresponding theoretical overpotential (η_{OER} and η_{HER}), i.e., the minimum applied potential required to make each electrochemical step exergonic.³⁶ For the OER, a four-step mechanism that proceeds through OH*, O*, and OOH* was assumed on the surface Ti site at a coverage of θ = 0.25 monolayer (ML) relative to the surface Ti atoms.³⁷ We note that while the lattice oxygen mechanism could be another possible pathway for oxygen evolution, it is unlikely to be dominant, since the formation of lattice oxygen vacancies is not favored for the STO/ SRO/STO heterostructures under OER conditions, as discussed previously.¹ The mechanism used to evaluate the HER overpotential involves a single intermediate H*, where η_{HER} is given by $|\Delta G_{\text{H}}|^{.38,39}$ The optimal value of $|\Delta G_{\rm H}|$ for HER activity is 0.0 eV, where hydrogen is bound neither too strongly nor too weakly.³⁹ In this study, H* is modeled adsorbed either on the on-top Ti site or on the surface O site at a coverage of θ = 0.25 ML relative to the surface Ti atoms. In addition, for H* on the surface O site, the high coverage limit of θ = 2 ML relative to the surface Ti atoms (all eight surface O atoms are protonated) was also considered to assist the screening of HER catalyst candidates. The adsorption energies of surface species are all referenced to H₂O and H₂. Finally, we note that higher levels of theory (e.g., GGA+U or HSE), other reaction mechanisms, or a different surface termination of the host oxide might be more appropriate in certain cases, for example, under different reaction conditions. However, they are beyond the scope of this study, which focuses primarily on the fundamental understanding of general trends in surface reactivity.

RESULTS AND DISCUSSION

Surface Reactivity. Our analysis begins with the surface reactivity of STO/SMO/STO heterostructures as a function of the guest metal in the subsurface of the host oxide. Figure 2 presents the trends of the adsorption free energies of the 4*d* TMs subsurface doped STO/SMO/STO heterostructures, for O adsorbed on the surface Ti site ($\Delta G_{\rm O}$) and H adsorbed on the surface Ti site ($\Delta G_{\rm H@Ti}$) as well as the O site ($\Delta G_{\rm H@O}$). Elements on the *x* axis are sorted in ascending order of their



Figure 2. DFT calculated free energy of (a) O adsorbed on the surface Ti site, (b) H adsorbed on the surface Ti site, and (c) H adsorbed on the surface O site on the 4*d*-TM subsurface doped STO/SMO/STO (001) surface at a coverage of θ = 0.25 ML relative to the surface Ti atoms.

group numbers. Note that Tc is omitted due to its low abundance as a naturally occurring element and due to the challenges of describing it accurately by DFT. Although the following discussion and analysis in this section focus on the 4d TMs as guest metals, the general trends observed hold for 3d and 5d TMs as well (see Figure S1 in the SI).

First, we observe that the surface reactivity on the STO capping layer of heterostructures can be effectively tuned by the guest metal dopant present in the subsurface, even though the guest metal has no direct contact with the adsorbates. Interestingly, we find that the adsorption free energies of the O and H adsorbed on the Ti surface sites show similar trends exhibiting a "checkmark"-like shape, with its minimum for the Nb dopant. A dramatic modification of the adsorption strength is found when the dopant is substituted from Zr to Nb. Doping with metals further to the right in the periodic table, i.e., increasing group number, results in a gradual weakening in the interaction between the adsorbate and the surface Ti atom. It is worth noting that other OER relevant intermediates, such as OH and OOH, present the same behavior when adsorbed on the surface Ti atom site (see Figure S2 in the SI). On the other hand, the adsorption free energy trend of H adsorbed on the surface O atom site shows a nearly opposite trend with a "reversed checkmark" shape, where the weakest adsorption (maximum) is found at the Nb doping as well.

Hence, there are strong nonmonotonic correlations between the surface reactivity and the group number of the subsurface guest metal. Adsorption energies on surface Ti and O sites show opposite trends with the variation of the subsurface guest metal. The above key findings are reported for the first time and are unique and interestingly different from the ones found in near-surface metal alloys both with respect to the tuning capability and trends in the adsorption energies (see Figure S3 in the SI) suggesting a new tuning mechanism beyond the description of the appealing *d*-band model for transition-metal systems.^{40–42}

Electronic Structure. To gain a fundamental understanding of how the surface reactivity of the STO/SMO/ STO heterostructures is affected by the guest metal, we performed a systematic electronic structure analysis of the 4*d* TM-doped heterostructures.

We first conducted a Bader charge analysis to resolve the valence electron charge redistribution induced by the subsurface dopant for clean STO/SMO/STO heterostructure surfaces in comparison to undoped STO. Figure 3a shows the calculated Bader charges of surface Ti (blue triangles), surface O (blue circles), and subsurface guest metal (red diamonds) of different STO/SMO/STO (M = 4d TMs) heterostructures. Although subsurface metal doping (except Zr) into STO increases the number of valence electrons of the system, we find that this results in only a negligible change in the charge of both surface Ti and O atoms. Instead, the excess electrons are essentially localized near the guest metal atoms in the subsurface layer, as evidenced by Figure 3b. Figure 3b shows a representative differential electron density namely of the subsurface Ru doped STO ($\Delta \rho = \rho_{\text{STO/SRuO/STO}} - \rho_{\text{STO}}$). The differential electron density clearly indicates that the excess electrons from Ru doping are centered around the guest Ru atoms with negligible charge transfer to the surface Ti or O atoms. The observed localization of the excess electrons around the guest metal in STO/SMO/STO heterostructure systems is again uniquely different from the near-surface metal alloys. In the latter system, there is significant charge



Figure 3. (a) Calculated net charge (units of electrons) of each subsurface guest metal atom in the SMO layer ($\rho_{\rm GM}$), surface Ti atom ($\rho_{\rm Ti}$), and surface O atom ($\rho_{\rm O}$) in the capping STO layer, of the STO/SMO/STO (001) surface systems with different guest metals from the 4*d* TMs series. (b) Calculated differential electron density of the subsurface Ru doped STO system ($\Delta \rho = \rho_{\rm STO/SRuO/STO} - \rho_{\rm STO}$). Electron depletion and accumulation are illustrated by blue and orange regions, respectively. Isosurfaces are set to 0.005 e/Å².

redistribution between guest and host metals, which effectively shifts the *d*-band center of the surface host metal consequently leading to the alteration of the surface reactivity (see Figure S4 in the SI).^{42,43} Hence, we conclude that such a simple surface reactivity tuning mechanism based only on the charge redistribution between guest and host metal cannot explain the surface reactivity trend found for STO/SMO/STO heterostructure systems as described in the previous section, calling for further investigation.

To allow for an in-depth analysis in order to understand the observed trends, we plot the projected density of states (PDOS) of STO/SMO/STO heterostructures where the subsurface is doped with different 4d TMs (Figure 4). Surface Ti 3d, surface O 2p, and guest dopant metal 4d states are plotted with blue, red, and filled green curves, receptively. The Fermi levels and centers of occupied 2p states for surface O atoms are marked with black and red dashed lines, respectively. We identify a more significant change in the guest metal 4dstates than in the surface Ti 3d or surface O 2p states, which is similar to the findings from the Bader charge analysis above. The positions of the metal dopant PDOS vary throughout the 4d TMs series and can be present in one or multiple locations relative to the undoped STO, namely, (i) in the valence band of STO, (ii) both in the valence band and conduction band of STO, or (iii) in the band gap of STO forming surface states or resonances, which we discuss more closely next. First we note that the Fermi level of the undoped STO is at -4.05 eV relative to the vacuum level. Substituting subsurface Ti with Zr only causes the Fermi level to shift slightly (<0.1 eV) relative to the undoped STO system. However, in the case of Nb doping, the upper part of the introduced Nb 4d states appears around the conduction band of STO and therefore sets the Fermi level of the STO/SNbO/STO heterostructure system there, leading to a considerable rise of the Fermi level as compared to the undoped STO. From Nb to Ag (early to late transition metal in the 4*d* TM block), the corresponding upper part of the 4d state shifts toward lower energy positions. Meanwhile, the Fermi level of the heterostructures is substantially shifted down in energy with the upper part of the projected guest metal 4d states. Notably, however, the 2pband centers of the surface O atoms remain at almost the same position as that of the undoped STO (see Figure 4b). The overall trend of the Fermi level of the 4d TM doped STO/ SMO/STO heterostructures exhibits a "reversed checkmark"



Figure 4. (a) DFT calculated projected density of states (PDOS) of undoped STO surface and STO/SMO/STO surfaces with different guest metals from the 4*d* TM series. The 2*p* states of lattice O in the first surface layer, surface Ti 3*d*, and guest metal 4*d* states are plotted as red and blue solid lines and green filled lines, respectively. All the energies are referenced to the vacuum level. The Fermi level for each system is indicated as a vertical black dashed line. The center of the lattice O 2*p* band is indicated as red dashed lines. (The PDOS of O_{ads} can be found in Figure S5 in the SI.) (b) The trend of the Fermi energy level (blue diamonds) and the surface lattice O 2*p* center (red circles) with respect to the subsurface guest metal. (c) The trend of the OER descriptor $\Delta G_O - \Delta G_{OH}$ with respect to the subsurface guest metal.



Figure 5. Schematic density of states (DOS) illustrating the influence of the subsurface doped SMO layer on the interaction between adsorbates and the top STO layer for (a, b) electron-accepting adsorption and (c, d) electron-donating adsorption.

shape, which resembles the features of the surface reactivity trends identified in Figure 2. Similarly, the maximum Fermi level is also found for the Nb guest metal dopant. Taken together, all of the above findings suggest that there potentially exists a strong correlation between the surface reactivity and the Fermi level of the STO/SMO/STO heterostructures, which we explicitly discuss in the next section.

Tuning Mechanism for Surface Reactivity. On the basis of the above electronic structure analysis, we propose the following tuning mechanism for the surface reactivities of STO/SMO/STO heterostructures as illustrated by the schematics in Figure 5. In the case of undoped STO, the highest occupied state (HOS) and the lowest unoccupied state (LUS) are the valence band maximum (VBM) and conduction band minimum (CBM), respectively. For the adsorption process where the adsorbate accepts electrons (electron-accepting adsorption), e.g., O or H adsorbed on the surface Ti sites, electrons are transferred from the HOS of the catalyst

surface to the adsorbate. Subsurface doping introduces new states of the guest metal in the vicinity of the STO band gap. The HOS of the doped system becomes the new Fermi level pinned by the guest metal and is shifted from the VBM of STO to the upper part of the guest metal states. Such an upshift in the HOS substantially increases the energy of the electrons gained during adsorption, resulting in a stronger adsorption energy, as shown in Figure 5(a,b). In contrast, for the adsorption processes where the adsorbate donates electrons (electron-donating adsorption), e.g., H adsorbed on the surface O sites, electrons are transferred from the adsorbate to the LUS of the catalyst surface. Figure 5(c,d) shows that the higher the LUS is, the more energy is required for the charge transfer, and therefore the adsorption energy is weaker. Taken together, the introduction of guest metal states by subsurface doping provides new origins for charge transfer to adsorbates during electron-accepting adsorption and new destinations for charge transfer from adsorbates during electron-donating



Figure 6. Calculated differential electron densities of STO and the STO/SRO/STO heterostructures for (a, b) O adsorbed on the Ti surface site and (c, d) H adsorbed on the O surface site, $\Delta \rho = \rho_{A-sur} - \rho_{sur} - \rho_A$, where A is the corresponding adsorbate (O or H). Electron depletion and accumulation are illustrated by blue and orange regions, respectively. Isosurfaces are set to 0.005 e/Å².

adsorption. This potentially results in the surface reactivities being effectively modified by the subsurface doping.

The postulated adsorption mechanism appropriately explains the observed surface reactivity trends. The positions of the HOS and LUS of STO/SZrO/STO are nearly the same as for the undoped STO, resulting in a similar surface reactivity. STO/SNbO/STO has the highest HOS and LUS which gives rise to the strongest binding on the surface Ti sites and the weakest binding on the surface O sites, respectively. From group V to group XI TMs, the HOS and LUS of the STO/ SMO/STO heterostructures are equivalent to the Fermi level. Both the HOS and LUS are brought down in energy with the shift of the guest metal states toward the lower energy side, resulting in the weakening of adsorption on Ti sites and the enhancement of adsorption on O sites, respectively. Hence, the Fermi level is negatively correlated with the adsorption energy of intermediates adsorbing on the Ti surface sites, while a positive coefficient is found for the correlation between the Fermi level and the adsorption energy of H adsorbed on the O surface sites (Figure S6).

To further prove the proposed tuning mechanism, we compare the differential electron densities of the undoped STO and the STO/SRO/STO heterostructures (see Figure 6) for electron-accepting adsorption and electron-donating adsorption processes using (a) O adsorption on the Ti surface site and (b) H adsorption on the O surface site as a representative example, respectively. The differential electron density is obtained using the following formula, $\Delta \rho = \rho_{A-sur} - \rho_{A-sur}$ $\rho_{\rm sur} - \rho_{\rm A}$, where A is the adsorbate of interest. In both cases, we find that there is almost no charge contribution from the subsurface Ti to the charge involved in the adsorption processes on the undoped STO surface. However, Figure 6(a,b) clearly demonstrates the involvement of the subsurface Ru dopant in the O adsorption process on the Ti surface site and H adsorption on the O surface site. In the former case (Figure 6a), the adsorbed O atom gains electrons from the STO/SRO/STO heterostructure substrate with a significant contribution from the subsurface Ru, while in the latter (Figure 6b), the subsurface Ru atoms provide an alternative reservoir for electrons transferred from the adsorbed H which is adsorbed on the O surface site.

Application to Electrochemical Water Splitting. The introduced STO/SMO/STO heterostructures promise a novel route for the design of robust and efficient catalysts. To illustrate its efficacy, we exemplify by performing a detailed

DFT study of the catalytic performance of STO/SMO/STO heterostructures for the constituent half reactions of electrochemical water splitting: oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).

The free energies of adsorption of O^{*}, OH^{*}, and OOH^{*} were calculated to derive the theoretical overpotential η_{OER} to evaluate the OER activity using the same framework as described in ref 37. Consistent with previous studies, we found that there is a linear adsorbate scaling relation between the adsorption energy of OH^{*} and OOH^{*}, as shown in Figure S7 in the SI. On the basis of such a linear adsorbate scaling relation, a contour plot of the theoretical overpotential volcano (Figure 7) was constructed with $\Delta G_{\rm O} - \Delta G_{\rm OH}$ and $\Delta G_{\rm OH}$ as descriptors. The hottest (dark red) region of the contour plot corresponds to the lowest OER overpotential, where the best trade-off is made between the elementary steps R2 (OH^{*} \rightarrow O^{*}) and R3 (O^{*} \rightarrow OOH^{*}). On the undoped STO (marked with the black solid point on the right side of Figure 7), OER is limited by R2 with an overpotential of 1.41 V. As can be seen



Figure 7. Calculated theoretical overpotential (η_{OER}) volcano plot with $\Delta G_{O} - \Delta G_{OH}$ and ΔG_{OH} as descriptors, using the adsorbate scaling relationship between OH* and OOH* (see Figure S7 in the SI). The black solid point represents the undoped SrTiO₃, and the open circles represent STO/SMO/STO heterostructures with different guest metal dopants.



Figure 8. (a) Top view of computational models considered for HER calculations, from left to right: 1/4 ML H* on Ti sites, 1/4 ML H* on O sites, and 2 ML H* on O sites with respect to surface Ti atom. Hydrogen atoms are illustrated as white balls. (b–d) DFT calculated Gibbs free energies of H adsorption $\Delta G_{\rm H}$ on STO/SMO/STO heterostructures with different guest dopant metals from 3*d*, 4*d*, and 5*d* TMs, respectively. For each heterostructure, $\Delta G_{\rm H}$ of H@Ti(1/4 ML), H@O(1/4 ML), and H@O(2 ML) are plotted with blue diamonds, red circles, and red solid dots, respectively.

in Figure 7, the subsurface guest metal doping effectively alters the STO surface reactivity thereby shifting the activity of the STO/SMO/STO heterostructures toward the left side of the volcano. Among all of the screened guest transition-metal dopants, we find that the subsurface doping with Ru makes the STO/SRO/STO heterostructure the one with highest OER activity, with a significant reduction in the calculated theoretical overpotential η_{OER} from 1.41 V for undoped STO to 0.61 V. Such a pronounced activation of STO by using subsurface Ru doping has been demonstrated both experimentally and theoretically in our recent study.¹

Subsurface doped SrTiO₃ also has a great potential to catalyze HER. As shown in Figure 8a, there are two possible sites for H adsorption: on top of surface Ti or O atoms. With the size of the supercell in the present study, the lowest simulated H coverage is 1/4 ML for the Ti site or O site relative to the surface Ti atoms. In general, H atoms bind weakly to Ti sites such that even at low H coverage ($\theta_{\rm H} = 1/4$ ML) none of the surfaces of the screened STO/SMO/STO heterostructures can reach a stronger $\Delta G_{\rm H}$ than the optimal $\Delta G_{\rm H}$ = 0 for HER. In most cases (except Ta), H interacts with surface O atoms more strongly than surface Ti atoms. Figure 8(b-d) also shows H binding energies on O sites at both the low coverage limit of 1/4 ML (red open circles) and the high coverage limit of 2 ML (red solid points) for 3d, 4d, and 5d TMs. Guest dopant metals with the corresponding STO/ SMO/STO heterostructures that have negative $\Delta G_{\rm H}$ at low coverage limit and positive ΔG_{H} at high coverage limit are highlighted in red as potential HER catalysts, where the optimal $\Delta G_{\rm H} = 0$ can be reached at an intermediate H coverage. It is worth noting that undoped STO, which is known to be a photocatalytic water-splitting catalyst,^{44,45} itself is among those promising candidates for HER in the dark, with an overpotential of 180 mV at $\theta_{\rm H} = 1/4$ ML.

Stability Screening. In addition to the activity, stability is another crucial criterion for evaluating the performance of a catalyst material. Specifically, for the studied heterostructures, one of the most relevant properties to quantify the thermodynamic stability is the energy for the guest dopant metal oxide layer to segregate onto the surface (E_{seg}) , as defined below

$$E_{\rm seg} = (E_{\rm SMO/STO/STO} - E_{\rm STO/SMO/STO})/N_{\rm M}$$

where $E_{\rm STO/SMO/STO}$ is the calculated energy of the subsurfacedoped heterostructure, $E_{\rm SMO/STO/STO}$ is the calculated energy of the structure where guest dopant metal atoms are all segregated to the surface, and $N_{\rm M}$ is the number of guest dopant metal atoms in the supercell. The concept of $E_{\rm seg}$ has been widely used for near-surface metal alloy systems to evaluate their thermodynamic stability.^{46–48} Figure 9 summa-



Figure 9. Calculated segregation energy E_{seg} of STO/SMO/STO heterostructures with different guest dopant metals from 3d (red diamonds), 4d (green circles), and 5d (blue triangles) TMs. The right insets illustrate the corresponding heterostructures that thermodynamically favor the presence of the SMO layer in the subsurface (blue region) and as the topmost surface layer (pink region).

rizes the calculated E_{seg} for all the subsurface-doped heterostructures screened as part of this study. For most of the 4*d* and 5*d* TMs, the corresponding heterostructures fall in the light purple region with positive E_{seg} indicating the preference of the SMO layer to remain in the subsurface. In the case of V, Cr, Fe, Zr, and Ru, a negative E_{seg} (highlighted with light pink) suggests that SMO on the topmost layer is thermodynamically more favorable. However, these heterostructures should not be ruled out, as a subsurface SMO layer could still be kinetically stabilized. For example, STO/SRO/ STO has a negative E_{seg} of -0.10 eV per Ru atom, indicating a weak preference for Ru being in the surface layer. However, recent experimentally achieved STO/SRO/STO heterostructures when analyzed with low energy ion scattering (LEIS) have demonstrated that there is no surface segregation of Ru before and after OER was performed confirming the possibility of kinetic trapping.¹

Generalized Tuning Mechanism. In the previous sections, we presented the tuning mechanism of STO surface chemistry by subsurface doping and demonstrated its capability to design efficient and robust catalysts for electrochemical water splitting. In this section, we show that the same scheme can be generalized to other host oxides with a finite band gap, such as SrZrO₃ (SZO), TiO₂, and ZrO₂.

We first show that the surface reactivity of SZO, TiO_2 , and ZrO_2 can be tailored in the same way as the one for STO, using the free energy of O adsorption ΔG_0 as an example. Figure 10 presents ΔG_0 for subsurface doped SrTiO₃, SrZrO₃,



Figure 10. DFT calculated free energy for O adsorption $\Delta G_{\rm O}$ on undoped and 4*d*-TMs subsurface doped SrTiO₃ (blue circles), rutile TiO₂ (blue diamonds), SrZrO₃ (green circles), and rutile ZrO₂ (green diamonds). The heat map in the background is constructed by assuming linear adsorbate correlations between $\Delta G_{\rm O}$, $\Delta G_{\rm OH}$, and $\Delta G_{\rm OOH}$. The hottest region marks the optimal $\Delta G_{\rm O}$ to give the lowest theoretical OER overpotential. The 2D contour plot as a function of $\Delta G_{\rm O}$ and $\Delta G_{\rm OH}$ is also provided in Figure S9 in the SI.

rutile TiO₂, and rutile ZrO₂ with different guest metals TM from the 4*d* TM series. For all subsurface doped oxides, the O adsorption free energies exhibit very similar trends displaying a "checkmark" shape, akin to subsurface doping in STO. We also show in Figure S8 that the electronic structure modification in the subsurface doped rutile TiO₂ system follows the same mechanism as the SrTiO₃ system, where the guest metal states

effectively tune the HOS levels of the oxide heterostructures. The similarity in trends of both the surface reactivity and, more fundamentally, the electronic structure demonstrates the generalization of our proposed tuning mechanism, which is independent of the host oxide and introduced guest metal.

As we have shown for STO (Figure 7), the tuning of surface reactivity by subsurface doping promises potential activation of the otherwise inert oxides. To better evidence the activation, we show the OER overpotential heat map as a single function of $\Delta G_{\rm O}$ by adding the linear correlation between $\Delta G_{\rm O}$ and ΔG_{OH} (Figure S9) superimposed on top of the assumptions that are used to construct Figure 7. The hotter (more dark red) the region is, the lower the OER overpotential is, hence, the higher the surface activity is toward oxygen evolution. The optimal ΔG_{Ω} (hottest region) of the map coincides with the middle of the "checkmark" curves. All four undoped oxides (STO, SZO, TiO₂, and ZrO_2) have very weak interaction with the O adsorbate and are located far above the optimal line, with OER overpotentials larger than 1.0 V. Doping with either Zr or Nb is able to activate the oxides for OER, due to too weak and too strong O adsorption, respectively. Starting from Mo doping, the interaction between O and the surface is gradually weakened. Subsurface doping with Mo gives the lowest OER overpotential for rutile TiO₂ and ZrO₂, while the corresponding dopant with the lowest overpotential is Ru for STO and SZO. Doping with late 4d TMs, such as Rh, Pd, and Ag, deviates from the optimal line again, resulting in lower OER activity. Although these different host oxides present similar surface reactivity trends, it should be noted that the choice of the best doping candidate is also affected by the starting point, namely the undoped oxide itself. In the above example, the ΔG_0 of undoped rutile TiO₂ and ZrO₂ is higher (weaker O adsorption) than those of undoped STO and SZO. Therefore, earlier intersections with the optimal line are found for TiO₂ and ZrO₂, which gives rise to the differences in the best subsurface doping candidates.

Partial Subsurface Doping. Previous studies of alloycore@shell metal nanoparticles demonstrated that the concentration of guest material in the subsurface can provide an additional degree of freedom for tuning the chemical properties of the outermost surface layer.^{48–52} In this section, we show that a similar catalyst design strategy can be applied to the subsurface doped metal oxide heterostructure systems. We studied a series of STO/SRu_xTi_{1-x}O/STO structures with



Figure 11. (a) Calculated theoretical OER overpotential as a function of $\Delta G_{\rm O} - \Delta G_{\rm OH}$ for a series of STO/STi_{1-x}Ru_xO/STO structures with different Ru concentrations in the subsurface layer (x = 0, 0.25, 0.50, 0.75 and 1.0). The green level in the open circle indicates the Ru concentration in the subsurface. (b) Calculated $\Delta G_{\rm O} - \Delta G_{\rm OH}$ on the topmost surface as a function of Ru concentration in the subsurface layer for STO and TiO₂ systems.

different Ru concentrations in the subsurface layer (x = 0, 0.25, 0.50, 0.75 and 1.0). With the increase of Ru concentration x[rising green fillings in circles in Figure 11(a)], we find both the OER descriptor $\Delta G_{\rm O}$ – $\Delta G_{\rm OH}$ and the theoretical overpotential η_{OER} are gradually reduced. This capability to fine-tune the catalytic performance of the surface by varying the subsurface alloying ratio can also be extended to other oxide systems. Corresponding results for the TiO₂ systems are shown in Figure 11(b). It is worth noting that the surface reactivities, such as $\Delta G_{\rm O}$ and $\Delta G_{\rm OH}$, show an armchair-shaped relationship with the subsurface %Ru (see Figure S10 in the SI), where more significant variations were seen around the two extreme ends (x: $0.0 \rightarrow 0.25$ and $0.75 \rightarrow 1.0$) than for the moderately alloyed systems (0.25 \rightarrow 0.75). The identified nearly linear relationship between the $\Delta G_{\rm O} - \Delta G_{\rm OH}$ values and the subsurface Ru concentration is most likely due to a correlation between $\Delta G_{\rm O}$ and $\Delta G_{\rm OH}$.

CONCLUSION

In conclusion, we present a new catalyst design strategy for metal oxides with a finite band gap using subsurface doping or heterostructuring and identify the underlying electronic structure origin of the chemical reactivity and stability phenomena. The host metal oxides are usually inert and protect the subsurface reactive materials against degradation under harsh reaction conditions. On the other hand, the subsurface guest oxide effectively modifies the surface reactivity of the capping host metal oxides by introducing new electronic states of the guest oxides in the vicinity of the host metal oxides' band gap. We demonstrate using the STO/SMO/STO systems that the new electronic states of the guest metal oxide set the Fermi level of the STO/SMO/STO heterostructures, substantially altering the energetics of reaction intermediates interacting with the topmost STO surface layer.

To reveal the potential of the proposed oxide heterostructures as efficient and robust catalysts, we predict using the DFT catalytic performance and stability of STO/SMO/STO for the two half-reactions of electrochemical water splitting: OER and HER. Furthermore, we show that our proposed surface reactivity tuning mechanism through subsurface doping can be generalized to a wide range of metal oxides with a finite band gap. Finally, we find that the dopant concentration in the subsurface provides another tuning parameter to tailor the surface reactivity and activity, leveraging the precision of the catalyst design. A recent experimental study involving varying amounts of Ir in STO was shown to have much improved catalytic activity for OER in acidic conditions, validating our design scheme.⁵³

The proposed metal oxide heterostructures set the stage for the rational design of core-shell oxide nanoparticles and their use for chemical reactions under harsh chemical environments. Importantly, such a heterostructure design also promises significantly lower loading of precious metals, e.g., Ir or Ru, improving the economic viability of technologies that rely on oxide catalysts involving massive loading of precious metals. The herein proposed materials can be potentially realized through several epitaxial growth methods, such as atomic layer deposition (ALD), pulsed laser deposition (PLD), and molecular beam epitaxy (MBE). The recent successful preparation of the computationally identified STO/SRO/ STO heterostructures using PLD as an efficient OER catalyst demonstrated the predictability power of our design scheme.¹ The proposed design principle opens up a new dimension for engineering active and robust oxide electrocatalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c00763.

Trends in adsorption free energy for STO/SMO/STO heterostructures with respect to group number: O (Figure S1), OH and OOH (Figure S2), with respect to Ru subsurface concentration (Figure S10), Comparison of adsorption free energy trends of O between STO/SMO/STO heterostructures and Ti/M/Ti (Figure S3), Differential electron densities of subsurface doping of Ru in Ti (Figure S4), Density of states (PDOS) for O adsorbed on STO/SMO/STO heterostructures (Figure S5), clean surface of TiO₂/MO₂/ TiO₂ heterostructures (Figure S8), Correlation between adsorption free energy and Fermi Level (Figure S6), OER adsorbate scaling relations (Figure S7), 2D contour plot of OER overpotential of 4d TM subsurface alloyed heterostructures (Figure S9), and information on number of valence electrons (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.V. acknowledges the Canadian Institute for Advanced Research (CIFAR) for support through the Bioinspired Solar Energy Program. A.S.R. would like to thank the Vagelos Institute for Energy Science and Technology (University of Pennsylvania) for support through a graduate fellowship. The authors acknowledge the use of the computer time allocation at the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 and the Extreme Science and Engineering Discovery Environment (XSEDE) supported through National Science Foundation Energy under Award Number CHE160084, and DMR180108.

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