

Mechanism of Bicarbonate-Enhanced Solar Oxidation of Water to Hydrogen Peroxide over BiVO₄

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ABSTRACT: Proper coupling of electrode and electrolyte chemistries can enhance both activity and selectivity in photoelectrocatalysts, but the mechanisms for efficient interface engineering are not well understood. This study examines hydrogen peroxide production via solar-driven water oxidation on a BiVO₄ photoanode in the presence of bicarbonate ions. Using *ab initio* calculations, we show that adsorbed HCO₃ species act as reaction centers, promoting selective H₂O₂ production. Hybrid functional first-principles molecular dynamics simulations reveal that surface hole polarons accelerate H₂O₂ formation by stabilizing the transient HCO₄ intermediate. In this process, surface-bound HCO₃ serves as a hole



Supporting Information

acceptor, facilitating reaction kinetics. Our findings offer mechanistic insights into the activation of electrolytic species by photogenerated charge carriers, enhancing selectivity for the thermodynamically less favorable product (H_2O_2) .

KEYWORDS: photoelectrochemistry, hydrogen peroxide, selectivity, electrolyte ions, molecular dynamics

INTRODUCTION

Reaction selectivity is a major challenge in chemistry^{1–4} especially when one needs to produce thermodynamically less stable products with high selectivity. In electrochemistry, this is exemplified by the formation of hydrogen peroxide (H_2O_2) through the two-electron water oxidation reaction (2e-WOR), which competes with the more favorable four-electron oxygen evolution (4e-WOR). Other industrially relevant processes include the oxygen reduction reaction (ORR), producing either water (2e-ORR) or H_2O_2 (4e-ORR), and the reduction of CO_2 (CO_2RR) and nitrate (NO_3RR) competing with the more facile hydrogen evolution (HER).

One strategy to enhance selectivity toward a less stable product is to create reaction conditions favoring kinetic over thermodynamic control.^{5–7} In electrocatalysis, it was recently demonstrated on the example of a single cobalt atom embedded into the nitrogen-doped graphene (Co–N–C) that the selectivity of H₂O₂ formation via the ORR can be as high as 90%.^{8,9} This experimental fact was at odds with DFT thermodynamic modeling showing that the breaking of the O– OH bond is more favorable than the breaking of *-O by ~0.5 eV, thus suggesting a more preferential formation of water.⁹ This contradiction was later resolved through *ab initio* molecular dynamics (AIMD) simulations of activation barriers, which revealed the kinetic origin of H₂O₂ selectivity.¹⁰

A potentially even more powerful strategy could be a rational coupling between the electrode and electrolyte chemistries. In this case, one can hope to realize the synergistic potential of such an interfacial pairing to further improve activity and selectivity. For example, it was found that some metal-oxide semiconductors in contact with certain electrolytes can substantially enhance the selectivity of H_2O_2 formation via 2e-WOR under light illumination.^{11–17} The combination of

the BiVO₄ photoanode and bicarbonate electrolyte turned out to be one of the best performing systems, enabling a Faradaic efficiency of about 98% for the photoelectrosynthesis of H_2O_2 .^{18,19}

Yet, the underlying mechanistic origin of such reactivity enhancement remains unclear. This impedes our efforts to rationally design highly selective photoelectrochemical systems. The superior selectivity of some photoanodes like $BiVO_4$ in certain electrolytes was hypothesized to be caused by adsorbed anions acting as hole polaron scavengers. It was assumed that the holes activate surface-bound ions through their oxidation. This results in the formation of highly reactive transient intermediates, crucial for improving product selectivity. In the case of bicarbonate-containing electrolytes, the following reaction mechanism, composed of electrochemical and chemical steps, was proposed:

$$HCO_{3}^{-} + H_{2}O \rightleftharpoons HCO_{4}^{-} + 2(H^{+} + e^{-}); E^{\circ}$$
$$= +1.8V \text{ vs RHE}$$
(1)

$$HCO_{4} + H_{2}O \rightleftharpoons H_{2}O_{2} + HCO_{3}$$
(2)

This mechanism was hypothesized based on prior nuclear magnetic resonance (13 C NMR) measurements 20,21 in the context of H₂O₂ activation by bicarbonate ions in aqueous solutions (*aka* bicarbonate activated peroxide), which is the

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reverse reaction in eq 2. It was suggested that the $HCO_4^$ intermediate adopts the peroxymonocarbonate structure $(HOOCO_2^-)$, while other electrolyte anions can form analogous peroxy species such as peroxymonosulfate $(HOOSO_3^-)$ and peroxynitrite $(ONOO^-)$. In a recent investigation, the formation of carbonate radical and percarbonate intermediate in bicarbonate electrolytes was also suggested based on the combination of electron paramagnetic resonance and isotope labeling experiments.¹⁴

In this study, we investigate the formation of H₂O₂ via 2e-WOR involving bicarbonate species adsorbed on the $BiVO_4(010)$ surface as a model photoelectrochemical interface. We especially focus on interfacial reaction dynamics, examining how photo-generated holes activate bicarbonate ions to enhance H₂O₂ selectivity. To this end, we employ density functional theory (DFT) calculations within the computational hydrogen electrode (CHE) approach to evaluate reaction thermodynamics, and ab initio molecular dynamics (AIMD) simulations combined with the thermodynamic integration method to estimate kinetic activation barriers. Prior theoretical investigations have demonstrated that hybrid functionals are necessary for a reasonable description of localized polaronic states in the bulk and at the metal-oxide/water interfaces, including BiVO₄.²²⁻²⁶ Therefore, to properly account for the localization properties of excess hole polarons, we perform calculations using the hybrid PBE0 functional.

COMPUTATIONAL DETAILS

The BiVO₄(010)/water interface was modeled using an orthorhombic supercell (10.372 × 10.20 × 32.416 Å³), consisting of a six-layer semiconductor slab and a vacuum region of 16 Å. The β angle of the C2/c monoclinic structure was approximated to 90° similar to prior computational studies.^{22,23}

Static spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP).^{27,28} The projector augmented wave (PAW) potentials (Bi_d, V_sv, O, C, H) were employed²⁹ and exchange-correlation interactions were described using the hybrid PBE0 functional.^{30,31} A plane-wave cutoff energy of 450 eV was used. The Brillouin zone was sampled at the Γ point. Gaussian smearing was employed with a smearing width of 0.05 eV. The truncation criterion for electronic steps was chosen to be 10^{-4} eV. All atoms were relaxed until all atomic forces were less than 0.05 eV/Å and the precision was set to the accurate setting.

Spin-polarized *ab initio* molecular dynamics (AIMD) simulations were conducted using the CP2K package to account for explicit water interactions.³² 56 water molecules were inserted into the vacuum gap to achieve a total water density of about 1 g/cm³. The hybrid PBE0 functional was employed with the input parameters reproduced from a previous study on the BiVO₄(010)/water system.²² The temperature was set to 350 K and controlled by a CSVR thermostat.³³ A 1 fs time step was used in AIMD simulations, with the hydrogen mass set to 3 atomic mass units. The system was initially pre-equilibrated using the PBE functional in a two-stage process: (1) using the CSVR time constant of 10 fs for 3 ps (strong thermostatting, faster equilibration) and (2) the CSVR time constant of 100 fs for 7 ps (weak thermostatting, slower equilibration). This water structure was subsequently

equilibrated for an additional 3 ps using the hybrid PBE0 functional in the presence of hole polarons in the slab.

Constrained AIMD simulations using both slow growth (SG) and thermodynamic integration (TI) approaches with suitable collective variables (CV) were performed to estimate activation barriers of the water oxidation reaction.^{34,35} In this approach, the total energies are obtained by collecting and integrating the free energy gradients to reconstruct the free energy profiles. The CV for the first (electrochemical) step was taken as the distance between the terminal O atom in HCO_3 and an O atom of attacking H2O. After the formation of HCO₄, the CV was changed to the distance between the terminal O atom in HCO_{4}^{-} and an O atom of attacking $H_{2}O$ to simulate H₂O₂ formation (chemical step). In AIMD-SG simulations, both CVs were decreased at a velocity of 0.0005 Å/fs. Such a sampling rate enables a continuous propagation of polaronic states and reasonable equilibration of the solution environment during the interfacial reaction. AIMD-TI simulations were performed using the blue moon ensemble approach^{36,37} by creating several windows along the reaction pathway. Forces were averaged over a time period of 2 ps in each window. This approach allows one to perform sufficient averaging of the forces in each window and to evaluate the associated statistical errors. The uncertainties in each window were estimated employing the block averaging technique.³⁸ The simulation cell used to model the reactivity of the $BiVO_4(010)$ /water interface is shown in Figure 1. The exemplary input files for AIMD simulations are provided in the Supporting Information.

We considered four types of simulation cells for modeling water oxidation on the $BiVO_4$ surface: (1) pristine $BiVO_4$ slab with no polarons and HCO_{3} , (2) BiVO₄ with adsorbed HCO_{3} but without polarons, (3) $BiVO_4$ with two hole polarons but without HCO_3^- , and (4) BiVO₄ with two hole polarons and adsorbed HCO_3^- . Systems (1) and (2) correspond to dark reaction conditions, while systems (3) and (4) correspond to illuminated conditions for the photoelectrochemical production of H_2O_2 . The number of hole polarons was chosen as two to balance out the two electrons transferred during the proposed electrochemical reaction steps for H₂O₂ synthesis. To simulate hole polarons in systems (3) and (4), electrons were removed from the simulation cell for charge compensation. Two electrons were removed from system (3), and one electron was removed from system (4). In system (2), the negative charge on HCO_3^- was neutralized by placing an H⁺ ion on the opposite side of the BiVO₄ slab in static calculations, and by fixing a water-solvated Li⁺ ion near the opposite surface in AIMD calculations. In static calculations, comparable reaction energies were found by substituting H⁺ with Li⁺ attached to four H₂O molecules near the opposite surface. The polarons were localized using the bond distortion method, which was shown to be more efficient than the electron attractor method.³⁹ All of our simulations were spin-polarized to ensure that electrons in the spin-up and spin-down states could be distinguished.

RESULTS AND DISCUSSION

Electrochemical water oxidation can proceed through two competing reaction pathways involving either two or four coupled electron-proton steps. Specifically, the 2e-WOR proceeds as follows:



Figure 1. Simulation cell used to model the BiVO₄(010)/solution interface in the AIMD simulations. Adsorbed HCO₃⁻ and H₂O species participating in the HCO₃⁻-mediated mechanism of photoelectro-chemical H₂O₂ formation (see eqs 1 and 2) are labeled. The isosurface levels of spin density for the hole polarons of opposite spin states are also shown with isovalues of 0.005 e/Å³ (in yellow) and -0.005 e/Å³ (in cyan).



Figure 2. Schematic showing H_2O_2 formation via 2e-WOR mediated by HCO_3^- from solution adsorbed at the BiVO₄(010) surface involving two electrochemical steps and one chemical step according to eqs 1 and 2.

 $* + H_2O \rightarrow *OH + (H^+ + e^-)$ (3)

$$^{*}OH + H_{2}O \rightarrow H_{2}O_{2} + (H^{+} + e^{-})$$
 (4)

whereas the complete 4e-WOR occurs via the following steps:

$$* + H_2O \rightarrow *OH + (H^+ + e^-)$$
(5)

$$^{*}OH \rightarrow ^{*}O + (H^{+} + e^{-})$$
(6)

Table 1. Theoretical Overpotentials $(\eta_{\rm H_2O_2})$ Calculated within the CHE Approach for H₂O₂ Formation at the Pristine BiVO₄(010) Surface (*HCO₃-absent), at the Surface with HCO₃⁻ Adsorbed Next to the Reaction Site (*HCO₃-adjacent), and at the Surface-Bound HCO₃⁻ Ion (*HCO₃-mediated, See Figure 2)



Figure 3. (a) Free energy diagrams for competing 2- and 4-electron water oxidation reactions without (left) and with (right) $HCO_3^$ adsorbed on the BiVO₄(010) surface in the presence of two hole polarons. $\Delta \eta$ serves as a selectivity metric indicating the thermodynamic preference of H_2O_2 formation over O_2 evolution. The theoretical overpotential (η) for the HCO_3^- -mediated process is sizably lower than the one in the absence of HCO_3^- . (b) and (c) The isosurface levels of spin density for the hole polarons of opposite spin states at the BiVO₄(010) surface without and with adsorbed HCO_3^- , respectively. The yellow isosurface corresponds to an isovalue of 0.06 $e/Å^3$ and the cyan isosurface corresponds to $-0.06 e/Å^3$.

 $^{*}O + H_{2}O \rightarrow ^{*}OOH + (H^{+} + e^{-})$ (7)

$$^{*}OOH \rightarrow * + O_{2} + (H^{+} + e^{-})$$
 (8)

These two reaction pathways have been previously investigated for a variety of electrode materials, including BiVO₄ by means of DFT-based computational hydrogen electrode (CHE) calculations.^{18,40–43} Within this approach, the difference between theoretical overpotentials estimated for different reaction pathways can serve as a measure of reaction selectivity. In this work, we focus on understanding the mechanistic role of bicarbonate (HCO₃⁻) species from the electrolyte in promoting selectivity of H₂O₂ production at the photocatalytic BiVO₄(010) surface.

Before examining the role of adsorbed bicarbonate species in photoelectrochemical H_2O_2 formation, we first discuss the localization properties of hole polarons at the $BiVO_4(010)/$ water interface. Previously, several studies have investigated the formation of electron and hole polarons in bulk and at the



Figure 4. Free energy profiles from AIMD slow-growth (SG) and thermodynamic integration (TI) simulations of the electrochemical step of H_2O_2 formation (eq 1) with and without hole polarons. The error bars for AIMD-TI are estimated by using the block averaging approach. Distance d_1 stands for the collective variable constrained during AIMD simulations. The bottom panels show the atomic structures of key reaction intermediates along the profile for the system with hole polarons. The triangle on the no-polaron profile (dashed line) corresponds to the location where the C–O bond of the bicarbonate ion breaks to yield CO_2 and H_2O_2 . The triangle on the polaron profile (straight line) corresponds to the location where the HCO_4^- intermediate is formed. Dynamic trajectories from AIMD simulations associated with this electrochemical step can be found as Movies in the Supporting Information.

surfaces of BiVO₄ using both GGA+U and hybrid functionals.^{22–24} Two geometries for hole polarons in bulk were proposed: one h⁺(BiO₈) with the hole residing within a BiO₈ dodecahedron and the other h⁺(O) with the hole localized on an oxygen atom, with the relative stability of the two depending upon the fraction of exact exchange interactions (α) used with the HSE hybrid functionals.²⁴ In a recent AIMD-based study using the PBE0 hybrid functional, most of the hole polaron configurations at 300 K were found to be in the h⁺(BiO₈) structure, and about 20% were closer to the h⁺(O) structure.²² Another AIMD investigation of the BiVO₄(010)/water interface at 300 K showed that the hole polaron structure on the solvated surface is different from the bulk; namely, the charge is mostly shared among two oxygen atoms neighboring an interfacial V atom.²³

In our static DFT calculations performed at 0 K, the hole polarons are localized on two oxygen atoms, each from a surface VO₄ unit. The O–O distance is reduced to 2.49 Å compared to 2.71 Å without the polarons, which is consistent with previous studies.²³ When HCO₃⁻ is added to the surface, one of the polarons moves to the BiO₆ unit centered on the Bi adsorption site, with two oxygen atoms shared with surfacebound HCO₃⁻. The Bi–O bond lengths are 2.25 and 2.35 Å, which are shorter than the bond lengths of 2.54 and 2.28 Å found for the pristine (no polarons, no bicarbonate ion) BiVO₄(010) surface. In AIMD simulations, we observe that one hole polaron remains mostly localized on the surface VO₄ unit neighboring adsorbed HCO₃⁻. Meanwhile, the second hole



Figure 5. Free energy profile from AIMD slow-growth (SG) and thermodynamic integration (TI) simulations of the chemical step of H_2O_2 formation (eq 2). The error bars for AIMD-TI are estimated using the block averaging approach. Distance d_2 stands for the collective variable constrained during AIMD simulations. The bottom panels show the atomic structures of key reaction intermediates along the profile. Dynamic trajectory from AIMD simulations associated with this chemical step can be found as a Movie in Supporting Information.



Figure 6. Atomic structure of the HCO_4^- intermediate on the $BiVO_4(010)$ surface. The corresponding interatomic distances and angles are given in Table 2.

polaron tends to fluctuate between the subsurface Bi sites. This can be observed in the Supporting Information Movie for the first electrochemical step.

We next investigated the reactivity of the BiVO₄(010) surface in the presence of bicarbonate species using *ab initio* thermodynamics. Figure 2 illustrates the examined bicarbonate-mediated mechanism for H_2O_2 formation occurring at surface-bound HCO₃ species (eqs 1 and 2). Table 1 compares the DFT-calculated overpotentials for different reaction mechanisms. The *HCO₃-mediated mechanism is found to be more thermodynamically favorable than competing pathways. This result aligns with previous DFT simulations¹⁸ showing a preference for H_2O_2 formation over O_2 evolution in the absence of bicarbonate (Figure 3). However, overpotentials for all three mechanisms, with and without hole polarons, are similar. This contradicts experimental observations of greatly enhanced H_2O_2 selectivity with BiVO₄ in bicarbonate electrolytes under illumination compared to dark

Table 2. Structural Parameters (Bond Distances in Å, Angles in Degrees) of the HCO_4^- Intermediate Formed at the BiVO₄/ water Interface (See Figure 6) Calculated by Averaging over 3 Ps of Unconstrained AIMD Trajectory

								2	2
Bi-O1	Bi-O2	Bi-C	C-01	C-02	C-O3	04-03	O4-H	O1-C-O2	C-O3-O4
2.85	2.79	3.10	1.25	1.24	1.40	1.45	1.01	129.2	111.5

conditions.^{18,19} Thus, computational thermodynamic results cannot explain the beneficial role of holes in the reaction.

To better understand the dynamic coupling between photogenerated hole polarons in $BiVO_4$ and electrolytic $HCO_3^$ toward H_2O_2 formation, we next carry out hybrid functional AIMD simulations. First, we confirm that our AIMD calculations of the pristine $BiVO_4$ surface with hole polarons in water (no bicarbonate species) fully agree with the results of prior theoretical studies.^{23,24} For example, we also observe that the hole is mostly shared between two oxygen atoms neighboring an interfacial V ion. We find, however, that HCO_3^- prefers to attach to the surface Bi site in the presence of hole polarons. In this case, the polaron density largely shifts to the O atoms of the surface Bi site.

To evaluate the kinetics of the *HCO₃⁻-mediated mechanism, we employ accelerated AIMD simulations using slow growth (SG) and thermodynamic integration (TI) approaches. In doing so, we simulate the electrochemical (eq 1) and chemical (eq 2) steps of H_2O_2 formation separately. For the electrochemical step, we introduce two excess hole polarons to the BiVO₄ surface, oxidizing adsorbed HCO₃⁻, as per eq 1. The chemical step does not require extra holes (eq 2).

We conduct at least two independent AIMD-SG simulations starting from different initial pre-equilibrated configurations and observing no significant differences in the free-energy profiles. For the no-polaron case, we find a steadily increasing energy profile during the electrochemical step (Figure 4). When the CV value approaches a certain critical value, the C– O bond of the adsorbed bicarbonate ion breaks to produce CO₂ and H₂O₂ species (see the Movie in Supporting Information). In contrast, upon the introduction of excess hole polarons to the system, we observe the formation of transient HCO_4^- with an activation barrier of 0.14 eV. The Movie in Supporting Information demonstrates the dynamic evolution of the atomic structure and hole density distribution during the considered water attack. It can be observed that the hole density fluctuates inside the BiVO₄ slab when moving along the A \rightarrow B trajectory. This is consistent with prior modeling results revealing the highly mobile nature of the hole polaron at the BiVO₄/water interface at room temperature.²² Upon approaching the transition state B, the hole density moves across the interface toward the adsorbed HCO_3 to oxidize it. Eventually, the hole density disappears when HCO_{4}^{-} is formed, thus completing the electrochemical step. To further probe the stability of HCO_{4}^{-} at the interface, we remove the CV constraint and observe that HCO_{4}^{-} remains stable for at least 3 ps of unconstrained AIMD equilibration (see the Movie in Supporting Information).

Next, we model the second (chemical) step of H_2O_2 formation according to eq 2. Figure 5 shows the free-energy profile and key reaction intermediates. The activation barrier for this step is only 0.06 eV from AIMD-SG. The Movies in Supporting Information show the dynamic evolution of the atomic structures during this chemical step. Interestingly, in

one set of constrained AIMD simulations, we also observe that the HCO_4^- intermediate can follow a different chemical reaction pathway with identical reaction kinetics. Namely, HCO_4^- undergoes a spontaneous protonation rather than a water attack to yield H_2O_2 and CO_2 products. In this case, however, CO_2 leaves the surface, requiring the adsorption of a new HCO_3^- ion before the HCO_3^- -mediated mechanism can proceed.

To provide better statistical sampling and estimate the uncertainties associated with activation barriers, we also carry out AIMD-TI simulations, splitting the reaction pathway into several windows (see Figures 4 and 5). As seen from the figures, AIMD-TI profiles are expectedly lower than those obtained in AIMD-SG. Overall, our AIMD simulations identify the electrochemical step $(HCO_4^-$ formation) as the ratedetermining step in 2e-WOR with bicarbonate species. The kinetics of this step are found to be strongly influenced by hole polaron dynamics at the $BiVO_4(010)$ surface. In addition, we provide some structural information for the identified HCO₄ transient intermediate (see Figure 6 and Table 2) as obtained by averaging over the 3 ps unconstrained AIMD trajectory. Movies for all the described interfacial processes generated based on our AIMD simulations are provided in Supporting Information.

It is important to point out here that our present investigation cannot rule out other possible mechanisms through which bicarbonate species can enhance H_2O_2 formation via 2e-WOR (see, e.g., the discussion in ref. 19). Nevertheless, our estimates of activation barriers associated with the bicarbonate-mediated mechanism involving the formation of the HCO₄ intermediates lend strong support to this reaction pathway.

Recent experimental investigations have focused on enhancing catalytic properties through the rational coupling of electrode and electrolyte chemistries. However, the mechanistic basis for the improved product selectivity in photoelectrochemical systems remains largely unclear. In this study, we used DFT thermodynamics and molecular dynamics free-energy simulations to explore how photo-generated holes activate bicarbonate species for H_2O_2 production at the BiVO₄(010) surface. Our work identifies the formation of the short-lived HCO_{4} intermediate in the peroxymonocarbonate structure as the rate-limiting step in H₂O₂ production. These intermediates are stabilized by hole polarons, which oxidize adsorbed bicarbonate ions, thereby significantly improving the H₂O₂ generation under light illumination. This work paves the way for predictive modeling of various photoelectrode/electrolyte interfaces to enhance selectivity for thermodynamically less favorable products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.5c00478.

CP2K input files for AIMD slow-growth simulations for the first (electrochemical) step of H_2O_2 formation(ZIP)

Movie of AIMD slow-growth simulations for the first (electrochemical) step of H_2O_2 formation with two hole polarons. Movie of AIMD slow-growth simulations for the first (electrochemical) step of H_2O_2 formation with no hole polarons. Movie of AIMD slow-growth simulations for the second (chemical) step leading to HCO_3^- and H_2O_2 . Movie of AIMD slow-growth simulations for the second (chemical) step leading to CO_2^- and $H_2O_2^-$. Movie of unconstrained AIMD simulations of HCO_4^- equilibration with polarons. Movie of unconstrained AIMD simulations of HCO_4^- equilibrations of HCO_4^- equilibrations of HCO_4^- equilibrations of HCO_4^-

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Notes

The authors declare no competing financial interest.

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