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ABSTRACT

Water oxidation is an important chemical reaction that yields electrons for downstream reduction reactions such as hydrogen generation or CO_2 and/or N_2 reduction. When producing O_2 , the reaction involves 4 electrons and 4 protons and tends to be kinetically unfavored. A competing pathway leading to the formation of H_2O_2 would only involve 2 electrons and 2 protons and may serve as a favorable alternative to O_2 formation while meeting the needs for electron production by water oxidation. Although H_2O_2 as a product of water oxidation has been observed experimentally, the bifurcating point that determines whether O_2 or H_2O_2 is the favored product has not been identified by experiments previously. Here, we report a detailed experimental study aimed at correcting this deficiency. We propose that the ease or difficulty of protonation or deprotonation of $-\text{OOH}$ intermediates is a key to the selectivity between H_2O_2 and O_2 . That is, we hypothesize that the (de)protonation of $\text{M}-\text{OOH}$, where M represents an active metal center, is the bifurcating point of the water oxidation catalytic cycle. Ready deprotonation of this intermediate leads to the eventual formation and release of O_2 , whereas the protonation of this intermediate enables the formation of H_2O_2 . The dependence of product selectivity on pH as observed by quantitative H_2O_2 detection supports this hypothesis. Additional experimental evidence based on isotope effects is also obtained. The results will likely find broad implications in catalyst design for high-performance water oxidation reactions.

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I. INTRODUCTION

As the first step of natural photosynthesis, water oxidation is a critical chemical process that yields electrons and protons for downstream chemical transformations such as the synthesis of hydrogen, hydrocarbons, and ammonia.^{1–7} Due to the multi-proton and multi-electron nature of this reaction, however, water oxidation is kinetically hindered, presenting one of the most important challenges in modern efforts focused on large scale solar energy storage and utilization.^{8–12} Decades of intense research have generated important insights into the detailed mechanisms of this reaction, especially on processes involving homogeneous catalysts.^{9,13–15} Increasingly, the knowledge has been successfully transferred to heterogeneous catalysts, which are believed to be more amendable to large scale

implementations.^{16,17} For instance, it is generally agreed upon that water oxidation starts from the formation of $\text{M}=\text{O}$ or $\text{M}-\text{O}^\bullet$ (where M represents an active metal site and $\text{O}^\bullet$ is a radical) that gradually leads to the intermediates of $\text{M}-\text{OOH}$ species.^{18–20} While alternative pathways involving dual metal sites have been proposed, where $\text{M}-\text{O}-\text{O}-\text{M}$ intermediates are generated, the protonation of this species would lead to the formation of $\text{M}-\text{OOH}$ as well.²¹ In other words, the $\text{M}-\text{OOH}$ species has been regarded as a critical one in water oxidation, whose deprotonation is pivotal to the release of O_2 as the product.²² This understanding is illustrated in Fig. 1 (right branch) and is supported by a large body of literatures. For example, the performance of NiOOH was found to be pH-dependent by *in situ* Surface Enhanced Raman Spectroscopy (SERS) studies, highlighting the importance of the deprotonation of $-\text{OOH}$.²³ Moreover, it was

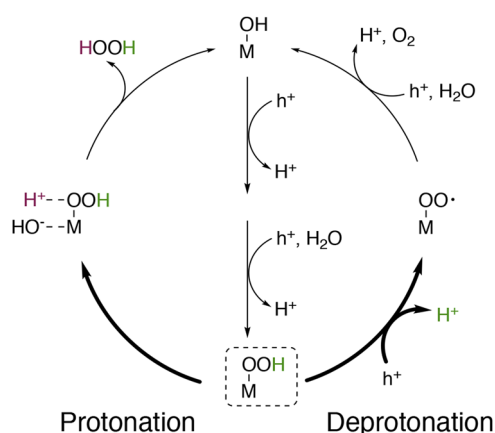


FIG. 1. Simplified schematic representations of possible water oxidation mechanisms. Right branch: conventional water oxidation mechanism with the deprotonation of the $\text{M}-\text{OOH}$ intermediate. Left branch: proposed water oxidation mechanism with the protonation of the $\text{M}-\text{OOH}$ intermediate at the proximal oxygen site.

suggested that on water oxidation catalysts such as LaNiO_3 , LaCoO_3 , and LaMnO_3 , the deprotonation of $\text{M}-\text{OOH}$ is rate determining.²⁴

Careful examinations of the reaction mechanisms as shown in Fig. 1 reveal that in addition to deprotonation, $\text{M}-\text{OOH}$ may undergo protonation as well, the product of which would be HOOH or H_2O_2 . As such, we would expect the $\text{M}-\text{OOH}$ species to be a bifurcating point, where both O_2 and H_2O_2 could be produced. Indeed, such a possibility has been tested by computational studies and proven reasonable.²⁵ Complementary research on oxygen reduction reactions (ORR) has shown that protonation of $\text{M}-\text{OOH}$ may lead to the formation of H_2O_2 .^{26,27} Experimental evidence supporting the reaction pathway on heterogeneous water oxidation catalysts as shown in Fig. 1, however, has been missing. Our work as reported here corrects this important deficiency. We show that water oxidation may lead to the formation of O_2 or H_2O_2 or both, the selectivity depending on the substrates used and the pH of the solution. The results provide mechanistic insights into recent observations of H_2O_2 when WO_3 or BiVO_4 was used as the substrates for water oxidation.²⁸ Given that the formation of H_2O_2 is a 2-electron reaction, the reaction pathway of water oxidation that produces H_2O_2 may be kinetically favored over the 4-electron pathway of O_2 formation. As such, our results may find important applications in the design of water oxidation catalysts for practical applications, especially when electrons, but not O_2 or H_2O_2 , are the most coveted products.

II. RESULTS AND DISCUSSIONS

A. Material choices and preparation

BiVO_4 and WO_3 were chosen as the material platforms for this body of work for the following reasons. First, both materials feature relatively positive valence band maximums

(VBMs), meaning that holes supplied by them are of high oxidizing power, enough to meet the thermodynamic needs for $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2$ transformation ($E^0 = 1.76$ V vs. RHE).²⁹ Second, H_2O_2 formation on these materials has been previously observed.²⁸ These prior results serve as an important foundation for the current study that minimizes the risks of our efforts. Third, both BiVO_4 and WO_3 feature relatively low point of zero charges (PZCs, 2.5–3.5 and 0.5–1.5, respectively).^{30–37} The acidity of their surfaces makes it possible to readily protonate $\text{M}-\text{OOH}$ intermediates to promote H_2O_2 formation. As an important control experiment, we also studied TiO_2 and Fe_2O_3 whose PZC are much higher (4.7–6.1 and 8.4–9.5, respectively) and indeed observed much less H_2O_2 production.^{35,36,38–42} The details of these experiments and their implications will be discussed later in this manuscript.

BiVO_4 films were prepared following a previously reported method.⁴³ The structure of BiVO_4 was confirmed by X-ray diffraction (XRD) (Fig. S1). WO_3 films on fluorine-doped tin oxide (FTO) were prepared using a doctor blade method adapted from literature reports.^{44–46} The XRD pattern confirmed the monoclinic phase of WO_3 (Fig. S2). For water oxidation reactions, a two-chamber electrochemical cell separated by a Nafion membrane was used (Fig. S3). For the studies of BiVO_4 , 3 types of buffer solutions, namely, 0.5M KHCO_3 , 0.5M potassium phosphate buffer (K–Pi), and 0.5M potassium borate buffer (K–Bi), were employed. We see from the current density-potential (J - V) plots as shown in Fig. S4 that water oxidation on BiVO_4 exhibits little dependence on the anions. As such, the system provides a desired platform to study how water oxidation reactions depend on pH in terms of product selectivity. Similarly, we have tested 0.5M K_2SO_4 and 0.5M K–Pi for WO_3 and observed similar independence on anions. Next, we focus our discussions on the dependence of product selectivity on pH.

B. Dependence of product selectivity on pH

Central to our hypothesis as shown in Fig. 1 is the ease or difficulty of $\text{M}-\text{OOH}$ (de)protonation. Preferred protonation would lead to the formation of H_2O_2 , and deprotonation would lead to the formation of O_2 . A natural prediction by this hypothesis is the dependence of the products on the pH of the solution. Lower pH means abundance of protons and, hence, would favor protonation and more H_2O_2 production. Conversely, lower yield of H_2O_2 would be expected at higher pH. To test this prediction, we employed two complementary techniques, namely, iodometry and colorimetric analysis, to quantitatively measure H_2O_2 as a water oxidation product on BiVO_4 and WO_3 .^{47,48} More details of these techniques are provided in Sec. 1 of the [supplementary material](#). Quantitatively comparable results of H_2O_2 yield were obtained by these methods. Important to our discussions, O_2 detection by a Clark-type oxygen sensor was also carried out. The combined yield of O_2 and H_2O_2 accounts for a total Faradaic efficiency at or close to 100%.

As shown in Fig. 2, a clear dependence of H_2O_2 yield on pH was observed for all 3 electrolyte systems. For instance, at

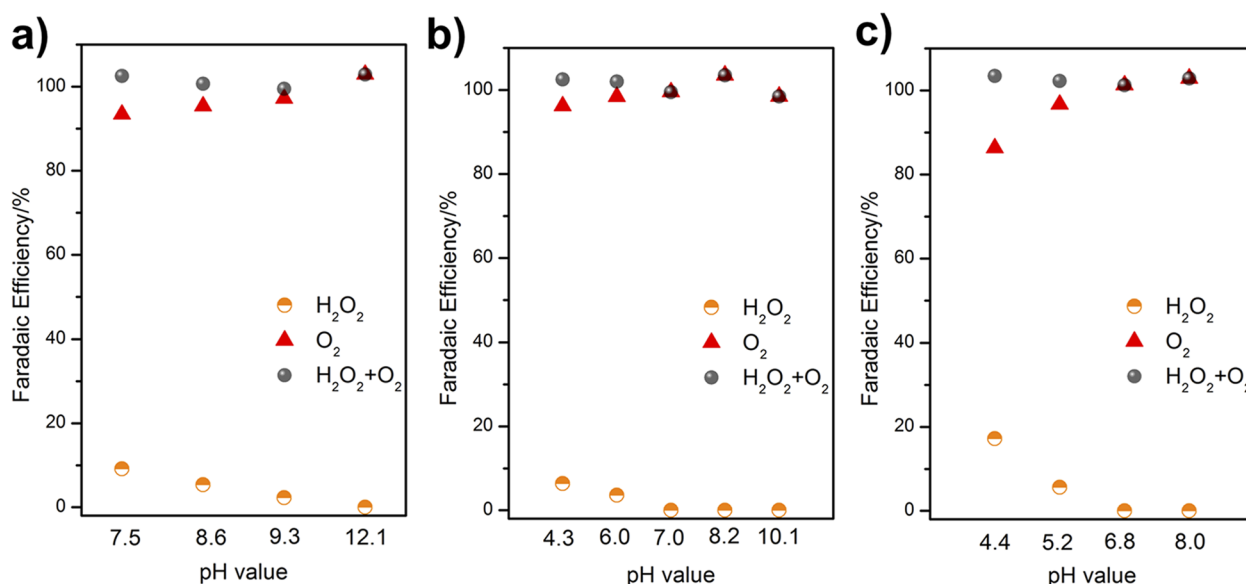


FIG. 2. Faradaic efficiencies of H_2O_2 and O_2 in (a) 0.5M KHCO_3 , (b) 0.5M K-Pi, and (c) 0.5M K-Bi for BiVO_4 at fixed potentials (1.5, 1.8, and 1.7 V vs. RHE for 0.5M KHCO_3 , 0.5M K-Pi, and 0.5M K-Bi, respectively).

pH 8.6 in KHCO_3 , we measured a H_2O_2 yield of 5.4% of the total products; this value increased to 9.1% at pH 7.5. Similarly, a H_2O_2 yield of 3.6% was measured at pH 6 in K-Pi buffer, which increased to 6.4% at pH 4.3. The highest yield of H_2O_2 (17.2%) was measured in borate buffer at pH 4.4. Note that the highest pH (~ 7) at which H_2O_2 was detected was similar for K-Pi and K-Bi buffer, but was higher (pH 9.3) for KHCO_3 . This phenomenon can be explained by the lower pK_a of the HCO_3^- ion in comparison with phosphate or borate, meaning that HCO_3^- is a less efficient proton acceptor. As such, the pH range of $-\text{OOH}$ protonation for bicarbonate buffer is shifted to the higher region, as shown in Fig. 2.

An important concern we had to address in carrying out this group of experiments was the accuracy of H_2O_2 detection because the disproportionation of H_2O_2 is known to depend on pH. That is, higher yield of H_2O_2 at lower pH could very well be a result of less decomposition of H_2O_2 . To rule out such a possibility, we conducted the following experiments. The same amount of H_2O_2 was added to electrolytes with different pHs. After 1 h of decomposition, the remaining H_2O_2 was measured, from which the rates of H_2O_2 disproportionation were derived. It was found that the difference of the detected H_2O_2 amount in our experiments was much greater than what one would expect from the natural disproportionation. As such, we are confident that the results as shown in Fig. 2 are reliable. It is, nevertheless, cautioned that the data should be treated quasi-quantitatively in nature because we could not completely rule out the influence of disproportionation in a quantitative fashion. To offer an example of the above analysis, let us examine the data as shown in Fig. 3(a). If H_2O_2 produced in 0.5M KHCO_3 at different pHs were the same and that the difference in the detected amount was purely due

to disproportionation, we would expect the yield of H_2O_2 at pH 8.6 to be 98.3% of that at pH 7.5. In reality, the detected H_2O_2 at pH 8.6 was 67.4% of that at pH 7.5, strongly supporting that less H_2O_2 was produced at pH 8.6 than at 7.5. The full dataset of such comparison is presented in Fig. 3 to support our understanding.

H_2O_2 production was studied on WO_3 , and similar results were obtained (as shown in Fig. S5). For this group of experiments, we chose 0.5M K_2SO_4 and 0.5M K-Pi with pH 1.7 and 4.3, respectively, as the electrolytes because WO_3 would be dissolved at higher pH. As expected, a higher H_2O_2 yield (47.9%) was measured at lower pH (1.7) in 0.5M K_2SO_4 electrolyte (by comparison, 8.0% H_2O_2 was detected at pH 4.3); similarly, the yield was 29.9% at pH 1.7 in 0.5M K-Pi electrolyte, which was lower (9.9%) at higher pH (4.3). An alternative we considered for this set of experiments was possible oxidation of the anions, which would lead to the formation of proxy disulphate/diphosphate instead of H_2O_2 and O_2 . Ionic chromatography (IC) was employed to detect proxy disulphate and diphosphate in the electrolyte after photoelectrolysis. No measurable such products were detected. Finally, possible H_2O_2 formation by water oxidation was examined for two popularly studied photoelectrode materials, TiO_2 and Fe_2O_3 . Of them, only a low yield ($\sim 3.7\%$ in 0.5M KHCO_3 at pH 8.6) was detected on TiO_2 . No H_2O_2 was detected on Fe_2O_3 in all electrolytes (0.5M KHCO_3 , 0.5M K-Pi, and 0.5M K-Bi).

C. Kinetic isotope effects

To further understand the effects of protonation and deprotonation on the product selectivity, we next conducted H/D kinetic isotope effect (KIE) experiments. In the first set

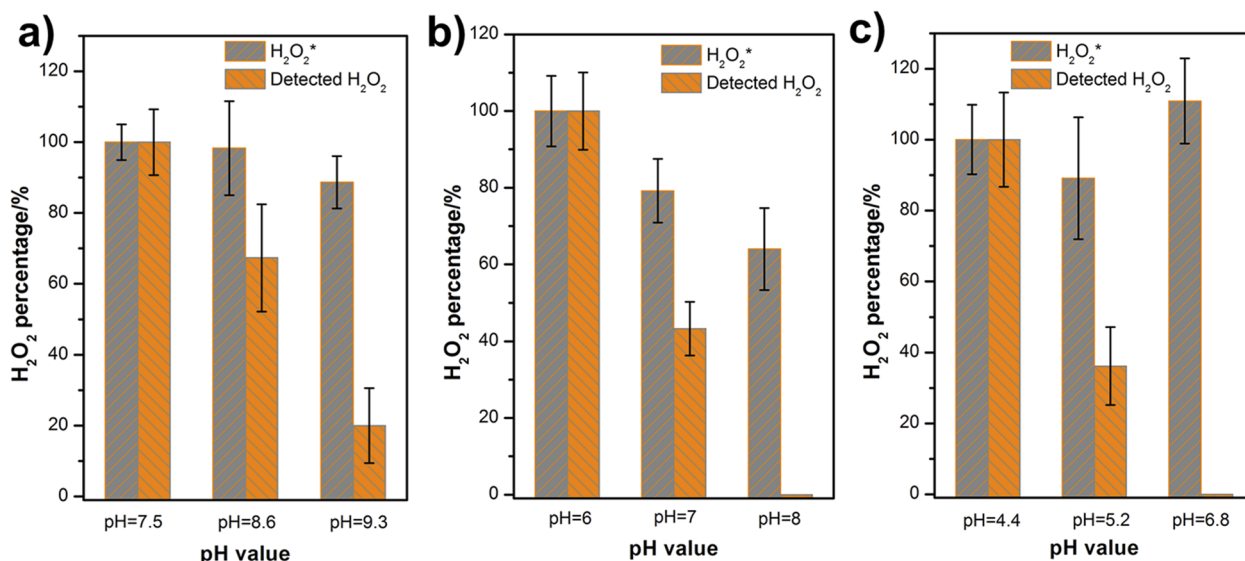


FIG. 3. pH-dependence of H_2O_2 generation on BiVO_4 (yellow bar) and decomposition (gray bar) in (a) 0.5M KHCO_3 , (b) 0.5M K-Pi, and (c) 0.5M K-Bi. The amount of H_2O_2 at different pHs was normalized to that at the lowest pH in each electrolyte.

of experiments, we measured the yield of H_2O_2 and D_2O_2 in H_2O and D_2O electrolytes by BiVO_4 (see the [supplementary material](#) for more details). As shown in Fig. 4(a), a higher yield of D_2O_2 (30.2%, 17.7%, and 14.4% in 0.5M K-Bi, 0.5M K-Pi, and 0.5M KHCO_3 , respectively) was obtained in the D_2O electrolyte than that of H_2O_2 (8.5%, 2.6%, and 8.3%, respectively) in the H_2O electrolyte. It is noted that no obvious difference was observed in the disproportionation rates of D_2O_2 and H_2O_2 at the pH/pD of our experiments, as shown in Fig. 4(b) (pH/pD 5.5 for 0.5M K-Bi, pH/pD 5.6 for 0.5M K-Pi, and pH/pD 8.5 for 0.5M KHCO_3). We understand the high yield

of D_2O_2 as a result of more difficult deprotonation and easier protonation of $-\text{OOD}$ than $-\text{OOH}$ since D_2O_2 features a higher pK_a (12.4) than H_2O_2 (11.8). The understanding is consistent with our proposed mechanism, as shown in Fig. 1. Next, we compared the kinetics of water oxidation by BiVO_4 in H_2O and D_2O electrolytes at high pH (pH/pD 8 for 0.5M K-Bi, pH/pD 8.2 for 0.5M K-Pi, and pH/pD 12.1 for 0.5M KHCO_3). The idea was to observe the system under conditions where the predominant reactions were O_2 evolution. As shown in Fig. S6, water oxidation in D_2O exhibits slower kinetics than that in H_2O , suggesting that proton transfer is involved in the rate

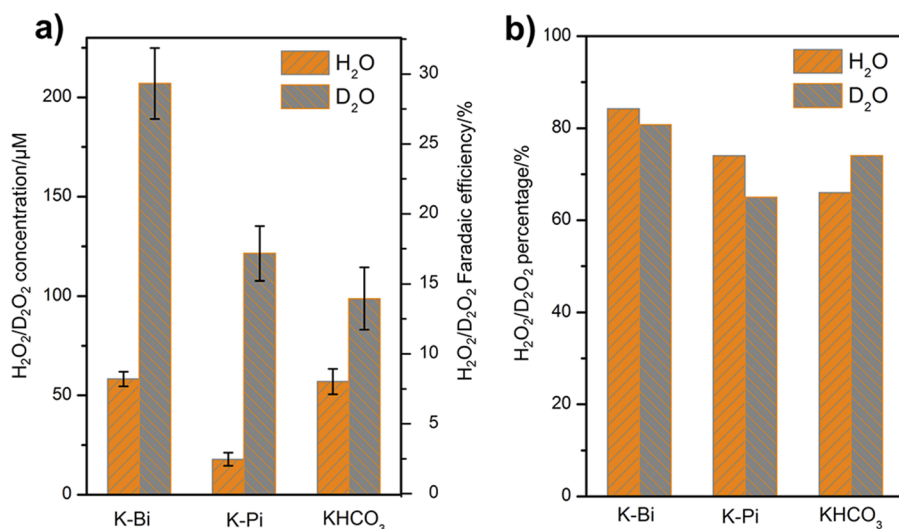


FIG. 4. $\text{H}_2\text{O}_2/\text{D}_2\text{O}_2$ generation on BiVO_4 (a) and decomposition (b) in H_2O (gray bar) and D_2O (yellow bar). In (a), the left y-axis and right y-axis represent concentration and corresponding Faradaic efficiency, respectively, for both H_2O_2 and D_2O_2 .

determining step (RDS) of water oxidation. As suggested by Durant *et al.*, the RDS of water oxidation on BiVO_4 involves 3 surface holes when the surface hole concentration is high.⁴⁹ We suggest that the deprotonation of $-\text{OOH}$ is the RDS of water oxidation on BiVO_4 .

D. Protonation and deprotonation of surface species on metal oxides

When immersed in H_2O , metal oxide surfaces are saturated by oxygen species. Whether the species are protonated depends on the pH of the solution as well as the intrinsic properties of the oxide substrate. The lowest pH at which the surface is neutral is often referred to as the point of zero charge (PZC).³⁷ Below this pH, the surface would be protonated to feature a positive charge; above this pH, the surface would be deprotonated and features a negative charge. The definition of PZC of a solid surface is consistent with the pK_a of a chemical species. Solid surfaces with lower PZCs are considered more acidic, which tend to protonate surface adsorbed species more strongly. With this background information in mind, we see that of the oxides studied for this work, WO_3 features the lowest PZC (0.5–1.5) and, hence, is the strongest in protonating surface $-\text{OOH}$ intermediates, leading to the highest yield of H_2O_2 .^{34–36} The next one is BiVO_4 , with a PZC between 2.5 and 3.5,^{30–33,37} followed by TiO_2 (PZC = 4.7–6.1).^{35,36,38,39} Fe_2O_3 , by comparison, features a PZC between 8.4 and 9.5 and produces no detectable H_2O_2 .^{40–42} This understanding adds a new dimension to considerations for catalyst design for H_2O oxidation. In addition to the Sabatier principle that considers the binding energies, the electronic structures may be adjusted to tune the PZC (or pK_a 's) to influence the key steps that would lead to different products when multiple possibilities exist. Note that tuning pK_a of adsorbed species for desired reaction selectivity is by no means a new concept. It has been widely explored for the design of homogeneous catalysts.^{50–52} Its implementations in heterogeneous design, however, are much rarer.

III. CONCLUSIONS

Water oxidation reactions were studied on various oxide surfaces. It was discovered that high yield of H_2O_2 could be obtained on BiVO_4 and WO_3 . The relative yield of H_2O appeared to depend on the pH, where higher yield was obtained at lower pH. We proposed that the initial steps of water oxidation are identical for O_2 and H_2O_2 formation and the key bifurcating point is at the $-\text{OOH}$ intermediate. Upon deprotonation, this species yields O_2 ; upon protonation, it yields H_2O_2 . The mechanism is further supported by the isotope experiments. Although H_2O_2 formation has been previously observed on both WO_3 and BiVO_4 , the mechanism as proposed here is new. Given the two-electron, two-proton nature of H_2O_2 formation, it might be a kinetically favored route for H_2O oxidation when electrons are the most important products, such as for H_2 generation or CO_2 reduction purposes. The understanding also has important implications for the design of heterogeneous catalysts.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for experimental details, other H_2O_2 formation mechanisms, and the supporting figures and tables.

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