H$_2$O$_2$ formation mechanisms on the (112) and (310) facets of SnO$_2$ via water oxidation reaction with the participation of Bicarbonate: DFT and experimental Investigations

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1. Introduction

Hydrogen peroxide (H$_2$O$_2$) is an important chemical with many uses, such as medical sterilization, chemical product synthesis, environmental pollution treatment, and the electronics industry.[1–3] Among the methods for H$_2$O$_2$ synthesis, the electrocatalytic processes has been widely favored by researchers due to its environmental friendliness, high safety, and in-situ synthesis.[4–8] Compared with the H$_2$O$_2$ production by reducing oxygen at the cathode,[49–53] the generation of H$_2$O$_2$ via two-electron water oxidation reaction (2e$^{-}$ WOR) at the anode has encouraging advantages and attractive prospects.[9–12] This procedure allows the production of value-added H$_2$O$_2$ at the anode and simultaneously evolution of H$_2$ at the cathode. Typically, the anode materials currently used for the generation of H$_2$O$_2$ are metal oxides, including MnO$_x$,[13] WO$_x$,[14,15] SnO$_2$,[14] TiO$_2$,[14–16], ZnO,[17,18] BiVO$_4$,[19–24] CaSnO$_3$,[25,26] Mn$_3$Bi$_2$WO$_6$,[27] and TiO$_2$.[28] This is primarily because metal oxides exhibit distinctive stability under the oxidation potential in the aqueous solution. It is worth noting that H$_2$O$_2$ preparation based on these oxides through electrochemical or photoelectrochemical processes almost requires bicarbonate (HCO$_3^-$) salt as the electrolyte.[14–27] This suggests that HCO$_3^-$ species play an important role in the production of H$_2$O$_2$.

Experimentally, Fuku and coauthors studied H$_2$O$_2$ generation on metal oxides via the 2e$^{-}$ WOR and proposed a mechanism where H$_2$O$_2$ is a product of the hydrolysis of percarbonates species (HCO$_4^-$ and C$_2$O$_7^{2-}$) which are formed by the oxidation of HCO$_3^-$ at high applied voltages on the electrodes.[15,28] In their work, the KHCO$_3$ electrolyte can significantly facilitate oxidative H$_2$O$_2$ production compared with other electrolytes including LiSO$_4$, NaClO$_4$, H$_3$BO$_3$ + KOH, K$_2$CO$_3$, and a phosphate buffer. Subsequently, the experimental result that HCO$_3^-$ electrolyte can promote the generation of H$_2$O$_2$ via the 2e$^{-}$ WOR on metal oxides was confirmed by a number of other studies.[27,29] Very recently, Zheng’s group investigated the role of bicarbonate-based electrolyte species (HCO$_3^-$ and CO$_3^{2-}$) for 2e$^{-}$ WOR using a combination of electrochemical and spectroscopic methods with BiVO$_4$ as an anode.[30] The findings of these authors show that HCO$_3^-$/HCO$_3^-$ serves
as a redox catalyst for H$_2$O$_2$ production in KHCO$_3$ electrolytes. Theoretically, Nørskov and coauthors show that the selectivity trends of an electrocatalyst between the 2e$^-$ WOR and 4e$^-$ WOR can be evaluated based on the free energy of adsorbed OH$^+$ group.\cite{14,31} Using density functional theory (DFT) calculations, the authors proposed that the ZnO (10 T 0) surface and BiVO$_4$ doping with optimal concentrations of gadolinium are effective catalysts for 2e$^-$ WOR; these predictions were confirmed experimentally.\cite{17,20} Khushalani et al. studied the co-adsorption of H$_2$O$_2$ and HCO$_3$ species and their calculations show that the adsorption behavior of HCO$_3$ species have different effects on the stability of H$_2$O$_2$ molecules on the (−1 2 1) and (0 4 0) planes of BiVO$_4$.\cite{19} Despite these efforts, the role of HCO$_3$, and especially the mechanism of adsorption and peroxidization of the HCO$_3$ species on the catalyst surface and its influence mechanism on the generation of H$_2$O$_2$, needs to be further explored.

In this work, using DFT calculations and electrochemical measurements, we investigate the H$_2$O$_2$ generation mechanisms from the aspect of kinetics on the (1 1 2) and (3 1 0) surfaces of SnO$_2$. SnO$_2$ has been demonstrated to be a potential candidate for H$_2$O$_2$ production via the 2e$^-$ WOR.\cite{14} SnO$_2$ is the main component of the coating of the conductive glass which has been widely used in the field of catalysis.\cite{29} The H$_2$O$_2$ formation pathways and energy barriers with and without the participation of HCO$_3$ species are scrutinized-H$_2$O$_2$ production in bicerarbonate and non-bicerarbonate electrolytes for SnO$_2$ films are detected after a period of chronopotentiometry tests. Specifically, the peroxidation of HCO$_3$ and the hydrolyzation of HCO$_3$ species are investigated on the (1 1 2) and (3 1 0) facets of SnO$_2$. Moreover, the catalytic activities of the (1 1 2) and (3 1 0) crystal planes of SnO$_2$ for H$_2$O$_2$ generation are compared. Our work has deepened the understanding of the role of HCO$_3$ in H$_2$O$_2$ production and provided some suggestions for the design and synthesis of catalysts for 2e$^-$ WOR.

![Fig. 1](image.png)

**Fig. 1.** (a) MEP plots for the pathway of *H$_2$O $\rightarrow$ *OH $+$ *H $\rightarrow$ *O $+$ 2*H on the (3 1 0) and (1 1 2) facets of SnO$_2$ in the absence of HCO$_3$ species. The side view of the intermediates and transition states along the paths on the (3 1 0) (b) and (1 1 2) surfaces (c). The corresponding top views are shown in Figure S5. Sn and O are depicted as green and magenta spheres respectively. The adsorbed O and H atoms are blue and white respectively.

2. Computational and experimental methods

2.1. Computational details

The Vienna ab initio simulation package (VASP)\cite{32–34} using a plane wave basis set with a cut-off energy of 420 eV are used for all calculations.\cite{35,36} The electronic-correlation energies are calculated using the generalized gradient approximation functional of the Perdew–Burke–Ernzerhof form.\cite{37,38} (2 $\times$ 3 $\times$ 1) and (3 $\times$ 2 $\times$ 1) Monkhorst-Pack grids for the (2 $\times$ 2) surface unit cells of the SnO$_2$ (1 1 2) and (3 1 0) surfaces were used for Brillouin-zone integration, respectively.\cite{39} Slab structures included three layers where the bottom layer was fixed and the top layers were free to relax until all force components dropped below 0.01 eV/Å. Periodic slabs along the z-direction were separated by a vacuum region of 15 Å. The climbing-image nudged elastic band (CI-NEB) method is used to locate the transition states (TSs).

The adsorption energies of H$_2$O and HCO$_3$ species are calculated as follows:

$$E_{ads} = E_{SnO2/(H2O,OHCO3)} - (E_{SnO2} + (E_{H2O} + E_{OHCO3}))$$

where $E_{SnO2/(H2O,OHCO3)}$ is the total energy of the SnO$_2$-H$_2$O or SnO$_2$-HCO$_3$ system, $E_{SnO2}$ is the energy of the substrate, and $E_{H2O}$ and $E_{OHCO3}$ is the energy of an isolated water molecule and an isolated bicarbonate, respectively. The reaction pathways for 4e$^-$ WOR and 2e$^-$ WOR are as follows.\cite{31,41,42}

4e$^-$ WOR:

$$\text{H}_2\text{O} + * \rightarrow *\text{OH}_2$$

$$*\text{OH}_2 \rightarrow *\text{OH} + \text{H}^+ + e^-$$

$$*\text{OH} \rightarrow *\text{O} + \text{H}^+ + e^-$$

$$\text{H}_2\text{O} + *\text{O} \rightarrow *\text{OOH} + \text{H}^+ + e^-$$

2e$^-$ WOR:
\[ *\text{OOH} \rightarrow *\text{OO} + *\text{H} + e^- \] (6)

WOR:
\[ \text{H}_2\text{O} + * \rightarrow *\text{OH} \] (7)
\[ *\text{OH} \rightarrow *\text{OH} + \text{H}^+ + e^- \] (8)
\[ *\text{OH} + \text{H}_2\text{O} \rightarrow *\text{H}_2\text{O}_2 + \text{H}^+ + e^- \] (9)

The reaction pathways for the peroxidation of HCO$_3$ species and the hydrolyzation of HCO$_4$ groups are as follows.\cite{2,3,43}.

\begin{align*}
*\text{HCO}_3 + *\text{H}_2\text{O} & \rightarrow *\text{HCO}_3 + *\text{OH} + \text{H}^+ + e^- \quad (10) \\
*\text{HCO}_3 + *\text{OH} & \rightarrow *\text{HCO}_3 + *\text{OH} + \text{H}^+ + e^- \quad (11) \\
*\text{HCO}_3 + *\text{O} & \rightarrow *\text{HCO}_4 \quad (12) \\
*\text{HCO}_4 + *\text{H}_2\text{O} & \rightarrow *\text{H}_2\text{CO}_4 + *\text{OH} \quad (13) \\
*\text{HCO}_4 + *\text{OH} & \rightarrow *\text{HCO}_3 + *\text{H}_2\text{O}_2 \quad (14)
\end{align*}

where * represents an active surface site and the group with the * represents a group adsorbed on an active surface site.

2.2. Material synthesis, characterization, and testing

All chemicals were obtained from commercial sources and used without further purification. The SnO$_2$ nanosheets were synthesized according to the literature.\cite{44} Briefly, 0.2 g of urea (J.T.Baker, 99.0–100.5%) was dissolved into a mixed solution of 35 mL deionized water and 15 mL ethanol. 10 mM SnCl$_2$ (Adamas, 99%+) was then added into the above solution. Next, 1 mL of 6 M NaOH was slowly added into the solution. Then, 17 mL of the solution was transferred into a Teflon-lined autoclave. The autoclave was kept at 180 °C for 18 h and naturally cooled to room temperature. The product was centrifuged and washed three times with a rotation speed of 10,000 rpm and a time of 10 min. The washed sediments were dispersed into the deionized water again and the gray sediments were removed after 5 min to obtain an upper layer of a yellow–brown suspension. The suspension was centrifuged and washed three times (10,000 rpm, 10 min). Finally, the product was dried in an oven at 60 °C for 12 h.

X-ray diffraction (XRD) measurements with Cu Kα X-rays (SHIMADU) were used to determine the phases of the synthesized nanosheets. X-ray photoelectron spectroscopy (XPS, Escalab) was conducted to detect the electron binding energies of Sn and O elements of the SnO$_2$ nanosheets. The morphology of the SnO$_2$ nanosheets was measured using a scanning electron microscope (SEM, FEI Inspect F50 (FSEM)). For electrochemical testing, the SnO$_2$ nanosheets were spin-coated on fluoride-doped tin oxide (FTO) conductive glass which had been ultrasonically cleaned in deionized water and ethanol for 30 min. SnO$_2$ nanosheets were dispersed in isopropanol and ultrasonically treated for 30 min. The speed of spin coating was 500 rpm for 5 s and then 2500 rpm for 20 s. The obtained film was annealed in a box furnace at 350 °C for 2 h to remove residue and for better attachment.

An H-type three-electrode quartz cell was used to conduct the electrochemical measurements with an Ag/AgCl (in saturated KCl) as the reference electrode and a Pt wire as the counter electrode. The SnO$_2$ film was applied as the working electrode with a reaction area of 4 cm$^2$. The anode and cathode were separated using a Nafion ion exchange membrane.
membrane; the volume of electrolyte was 30 mL. A CHI 760E workstation was applied to calculate the potentials versus reversible H2 electrode (RHE) as follows:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + E_{\text{Ag/AgCl}}^0 (0.197 \text{ V}). \]

The standard test strips and the KMnO4 reaction method combined with a UV–vis spectrophotometer were used to measure H2O2 concentrations. The amount of H2O2 was calculated by the consumption of MnO4\(^-\) whose absorption wavelength is selected as 525 nm.

3. Results and discussions

We first calculated the reaction pathways and energy barriers for 4e\(^-\) WOR and 2e\(^-\) WOR on the (1 1 2) and (3 1 0) surfaces of SnO\(_2\) in the absence of HCO\(_3\)\(^-\). The geometric and structural descriptions of the optimized bulk SnO\(_2\), SnO\(_2\) (1 1 2), and SnO\(_2\) (3 1 0) facets are shown in Figure S1. The minimum energy paths (MEP) and the intermediates and transition states along the paths on the (3 1 0) (b) and (1 1 2) surfaces (c). The corresponding top views are shown in Figure S7. Sn and O are depicted as green and magenta spheres, respectively. The adsorbed C, O, and H atoms in HCO\(_2\) group are grey, yellow and white, respectively. The adsorbed O and H atoms in H\(_2\)O molecule are blue and white respectively.

![Fig. 3. (a) MEP plots for the pathway of \( ^*\text{H}_2\text{O} \rightarrow ^*\text{OH} + ^*\text{H} \rightarrow ^*\text{O} + 2^*\text{H} \) on the (3 1 0) and (1 1 2) facets of SnO\(_2\) in the presence of HCO\(_3\)\(^-\). The side view of the intermediates and transition states along the paths on the (3 1 0) (b) and (1 1 2) surfaces (c). The corresponding top views are shown in Figure S7. Sn and O are depicted as green and magenta spheres, respectively. The adsorbed C, O, and H atoms in HCO\(_2\) group are grey, yellow and white, respectively. The adsorbed O and H atoms in H\(_2\)O molecule are blue and white respectively.](image-url)

For comparison, we calculate the 2e\(^-\) WOR to generate \(^*\text{H}_2\text{O}_2\) in the absence of HCO\(_3\)\(^-\). Not unexpectedly, the H2O2 molecule does not stably adsorb on the (1 1 2) and (3 1 0) surfaces and instead decomposes spontaneously; H\(_2\)O2 is extremely unstable on these surfaces and it is difficult to generate H\(_2\)O\(_2\) through the 2e\(^-\) WOR on SnO\(_2\) in an actual electrocatalytic process. SnO\(_2\) nanosheets have been synthesized and
coated on FTO conductive glass to conduct electrochemical measurements. The XRD spectrum of the SnO$_2$ nanosheets matches the main characteristic peaks of SnO$_2$ (PDF#41–1445), indicating that the phase of the prepared SnO$_2$ nanosheets is adequately pure (Figure S2). XPS spectra of Sn 3d and O 1 s collected from the SnO$_2$ nanosheets are shown in Figure S3. The binding energies of Sn 3d$^{5/2}$ and Sn 3d$^{3/2}$ locate at 486.7 and 495.2 eV respectively, confirming the presence of Sn$^{4+}$ ions.

Typical morphologies of SnO$_2$ nanosheets synthesized by the hydrothermal method are shown in Figure S4. We selected several non-bicarbonate solutions (Na$_2$SO$_4$, K$_2$HPO$_4$, and KH$_2$PO$_4$) to test the performances of SnO$_2$ films for electrocatalytic H$_2$O$_2$ production. As shown in Fig. 5d, after 15 min of the chronoamperometry test, the H$_2$O$_2$ concentrations in the electrolytes are negligibly small.

From the above discussion, H$_2$O$_2$ generation through the 2e$^-$WOR on the (1 1 2) and (3 1 0) surfaces are kinetically unfavorable compared with the O$_2$ evolution via the 4e$^-$WOR without the participation of HCO$_3$. These calculation and test results are consistent with the experimental observations of various metal oxides for H$_2$O$_2$ production tested in non-bicarbonate solutions in previous work. [15,29] In order to explore the role of bicarbonate, the HCO$_3$ group is introduced onto the (1 1 2) and (3 1 0) surfaces of SnO$_2$. Similarly, the 4e$^-$WOR and 2e$^-$WOR on the (1 1 2) and (3 1 0) in the presence of *HCO$_3$ are calculated. The pathways and energy barriers for the dehydrogenation of H$_2$O are calculated and the MEP plots and the involved intermediates and transition structures on the (1 1 2) and (3 1 0) surfaces are shown in Fig. 3. The HCO$_3$ species is adsorbed on the top-site of a Sn atom with the O end and the H$_2$O molecule adsorbed on the adjacent Sn atom (Fig. 3b and c). Various adsorption sites for HCO$_3$ on the (1 1 2) and (3 1 0) surfaces have been considered, the most stable of which are used as the subsequent reactants (see Figure S1 and Table S1). As in the absence of *HCO$_3$, the process of removing the first H atom from *H$_2$O occurs without an energy barrier on the (1 1 2) surface. As shown in Fig. 3a, different from the (1 1 2) surface, the *H$_2$O dehydrogenation requires an energy barrier of 0.85 eV on the (3 1 0) surface. Similar to the situation with no bound *HCO$_3$, the processes of splitting *H$_2$O into *H and *OH on the (1 1 2) and (3 1 0) surfaces with the co-adsorption of the HCO$_3$ group are exothermic. The energies of the final states of this process are 1.54 and 0.57 eV lower than the initial states for the (1 1 2) and (3 1 0) facets, respectively. The dehydrogenation of *OH changes from exothermic to endothermic on the (1 1 2) surface with high energy barrier of 2.68 eV, indicating that, in the presence of *HCO$_3$, the breaking of *OH on the (1 1 2) surface becomes relatively difficult. On the (3 1 0) surface, the energy barrier for the *OH dehydrogenation decreases from 1.79 to 0.79 eV after introducing *HCO$_3$ although this process is still endothermic by 0.38 eV. As shown in Fig. 4, the structures for the co-adsorption of *HCO$_3$ and *OOH are derived from the products after H$_2$O dehydrogenation in the last step. For the dehydrogenation of *OOH, the energy barrier lowers from 1.24 to 0.42 eV on the (1 1 2) surface. In contrast, the energy barrier for *OOH dehydrogenation to *OO and *H on the (3 1 0) surface increases from 0.08 to 0.51 eV, changing the process from

![Fig. 4. (a) MEP plots for the pathway of *OOH $\rightarrow$ *OO + *H on the (310) and (112) facets of SnO$_2$ in the presence of HCO$_3$ species. The side view of the intermediates and transition states along the paths on the (310) (b) and (112) surfaces (c). The corresponding top views are shown in Figure S8. Sn and O are depicted as green and magenta spheres respectively. The adsorbed C, O, and H atoms in HCO$_3$ group are grey, yellow and white, respectively. The adsorbed O and H atoms are blue and white respectively.](image-url)
exothermic to endothermic. Typically, the co-adsorption of $^4\text{HCO}_3^-$ makes the cleavage of $^*\text{OH}$ on the (3 1 0) surface easier, while it makes this reaction more difficult on the (1 1 2) surface. The rate-determining steps for 4e WOR on the (1 1 2) and (3 1 0) surfaces are changed to be the dehydrogenations of $^*\text{OH}$ and $^*\text{H}_2\text{O}_2$, respectively. By calculating the adsorption energies, it is found that the existence of $^4\text{HCO}_3^-$ increases the adsorption energy of $\text{H}_2\text{O}$ on the (1 1 2) surface from $-0.83$ to $-1.12$ eV, while decreases the adsorption energy of $\text{H}_2\text{O}$ on the (3 1 0) surface from $-2.53$ to $-1.14$ eV. Taking into account the differences in the energy barriers and reaction characteristics for the dehydrogenations of $^*\text{H}_2\text{O}$, $^*\text{OH}$, and $^*\text{OOH}$ on the (1 1 2) and (3 1 0) surfaces with and without $^4\text{HCO}_3^-$, it can be speculated that $^4\text{HCO}_3^-$ affects the water oxidation kinetics by changing the adsorptions of $\text{H}_2\text{O}$ and intermediates. For 2e WOR in the presence of $^4\text{HCO}_3^-$, stable structures of $\text{H}_2\text{O}_2$ and suitable pathways are not found in this work. Therefore, it could be concluded that the co-adsorption of $^4\text{HCO}_3^-$ has no obvious promotion effect on the $\text{H}_2\text{O}_2$ generation via 2e WOR although $^4\text{HCO}_3^-$ would affect the oxidation kinetics of $\text{H}_2\text{O}$ on $\text{SnO}_2$. However, decent production rates and Faradic efficiencies of $\text{H}_2\text{O}_2$ have been observed for $\text{SnO}_2$ and $\text{SnO}_2$-based anodes tested in bicarbonate aqueous solution in previous work.\textsuperscript{14,29} In this work, the $\text{H}_2\text{O}_2$ production of $\text{SnO}_2$ film in bicarbonate and non-bicarbonate solutions are measured. As expected, overwhelming $\text{H}_2\text{O}_2$ concentration is detected in $\text{KHCO}_3$ after 15 min reaction at 3.08 V vs RHE compared to those tested in non-bicarbonate solutions (Fig. 5d). In addition, as the concentration of $\text{HCO}_3^-$ in the electrolyte increases, the generation of $\text{H}_2\text{O}_2$ increases linearly (Fig. 5c). A comparison of the $\text{H}_2\text{O}_2$ production rate between our work and other reports of $\text{SnO}_2$ is provided in Table S1. The linear sweep voltammetry (LSV) plots for $\text{SnO}_2$ films tested in $\text{KHCO}_3$ solution with various concentrations are tested and shown in Fig. 5a. Note that the current density gradually increases as the concentration of $\text{HCO}_3^-$ in the solution increases. These results demonstrate that $\text{HCO}_3^-$ plays a key role in the formation of $\text{H}_2\text{O}_2$. Combined with the calculation results, $\text{HCO}_3^-$ is likely to directly participate in the formation of $\text{H}_2\text{O}_2$ on the $\text{SnO}_2$ surface. Considering the current proposed mechanism that $\text{H}_2\text{O}_2$ is generated by the hydrolysis of $\text{HCO}_3^-$ which is derived from the electrochemical oxidation of $\text{HCO}_3^{-}$,\textsuperscript{15,28,30} the conjecture that $\text{HCO}_3^-$ acts as a catalytic medium in the generation of $\text{H}_2\text{O}_2$ is understandable. In fact, $\text{HCO}_3^-$ has been detected in $\text{KHCO}_3$ aqueous solution after a period of electrochemical measurements in a recent work.\textsuperscript{47} In addition, oxidation peaks are observed in the LSV curves of the $\text{SnO}_2$ films tested in $\text{KHCO}_3$ electrolyte with various concentrations, which indicates the oxidation of $\text{HCO}_3^-$ to $\text{HCO}_4^-$ (Fig. 5a).\textsuperscript{30} In contrast, there are no similar oxidation peaks in the LSV plots tested in the non-bicarbonate solutions (Fig. 5b).

Based upon these results, it is necessary to investigate the pathways and energy barriers for the peroxidation of $^*\text{HCO}_3$ and the hydrolyzation of $^4\text{HCO}_4^-$ species on the surfaces of $\text{SnO}_2$. The peroxidation process in which $^4\text{HCO}_3^-$ interacts with the $^*\text{O}$ species derived from the $^*\text{H}_2\text{O}_2$ dehydrogenation to form $^*\text{HCO}_4^-$ on the (1 1 2) and (3 1 0) facets is
calculated; the MEP plots and the involved intermediates and transition states are shown in Fig. 6. The energy barrier for the *HCO$_3$ peroxidation is 1.78 and 3.60 eV on the (1 1 2) and (3 1 0) facets, respectively. The reaction is endothermic on both surfaces; the energies of the final states are 1.58 and 2.89 eV higher than those of the initial states on the (1 1 2) and (3 1 0) surfaces, respectively. This suggests, both thermodynamically and kinetically, that this reaction is not facile on these surfaces. Nevertheless, these calculation results are consistent with the experimental measurements. In the experimental tests, the measurable production of H$_2$O$_2$ only can be obtained at relatively high potentials (2.4–3.3 V vs RHE). The standard potential at which HCO$_3$ is oxidized to HCO$_4$ is 1.80 V vs RHE. This indicates that a high overpotential is needed for the peroxidation of HCO$_3$. In this work, the range of overpotentials to reach a current density of 5 mA/cm$^2$ is from 1.0 to 1.3 V for SnO$_2$ films tested in KHCO$_3$ with various concentrations. By comparison, our calculations show that the occurrence of this reaction is relatively easier on the (1 1 2) facet than that on the (3 1 0) facet, indicating that the (1 1 2) facet is kinetically favorable for HCO$_3$ peroxidation than the (3 1 0) facet. The adsorption energies of HCO$_3$ on the (1 1 2) and (3 1 0) planes are −1.96 and −3.04 eV, respectively. It is likely that the adsorption energy on the (3 1 0) facet is overly strong, which is not conducive to the peroxidation of HCO$_3$.

The hydrolyzation of the HCO$_4$ group on the (3 1 0) and (1 1 2) surfaces of SnO$_2$ are calculated as shown in Fig. 7. The reaction that *HCO$_4$ hydrolyzes to produce *HCO$_3$ and *H$_2$O$_2$ is assumed to be divided into two steps (Equations 13 and 14). First, *HCO$_4$ and *H$_2$O interact to generate *H$_2$CO$_4$. Second, *H$_2$CO$_4$ and OH combine to form *HCO$_3$ and *H$_2$O$_2$. As displayed in Fig. 7a, the interaction of *HCO$_4$ and *H$_2$O to generate *H$_2$CO$_4$ needs to overcome an energy barrier of 0.67 eV on the (1 1 2), while no energy barrier is needed on the (3 1 0) surface. The energy barrier of the second hydrolysis process on the (1 1 2) surface is 0.97 eV. Compared to the (1 1 2) surface, this process needs to conquer a high energy barrier of 2.73 eV on the (3 1 0) surface. Therefore, in terms of the energy barriers through the pathways that *HCO$_3$ is oxidized and the subsequent hydrolysis process to generate *H$_2$O$_2$, the (1 1 2) surface is kinetically more favorable than the (3 1 0) facet. The peroxidation of HCO$_3$ is the rate-determining step in the pathway of H$_2$O$_2$ formation in which HCO$_3$ participates. It is interesting and worth mentioning that *H$_2$O$_2$ formed by the hydrolysis of HCO$_4$ can remain stable on the surface of SnO$_2$. In experiment, the consumption of H$_2$O$_2$ on ZrO$_2$ was found to be considerably slower in the presence of HCO$_3$. The mechanism for this phenomenon and the stabilizing effect of HCO$_3$ on *H$_2$O$_2$ need to be further studied.

4. Conclusions

The H$_2$O$_2$ formation mechanisms on the (1 1 2) and (3 1 0) facets of SnO$_2$ via water oxidation reaction with and without the bicarbonate are
investigated using DFT calculations and electrochemical measurements. In the absence of HCO$_3^-$ species, the H$_2$O$_2$ formation on SnO$_2$ through 2e$^-$ WOR is difficult, that is, the O$_2$ evolution reaction via 4e$^-$ WOR is predominant. The performance test of SnO$_2$ films confirms these calculations in that negligible H$_2$O$_2$ is generated in non-bicarbonate solutions after a period of chronoamperometry tests. In the presence of HCO$_3^-$ species, the co-adsorption of HCO$_3^-$ groups adjacent to the H$_2$O molecule could not significantly promote 2e$^-$ WOR on the (1 1 2) and (3 1 0) surfaces. Considering that more H$_2$O$_2$ production is detected in KHCO$_3$ aqueous solution compared to those in non-bicarbonate electrolytes, it is reasonable that HCO$_3^-$ directly participates in the generation process as a catalytic medium of H$_2$O$_2$. The oxidation peaks in the LSV tested in KHCO$_3$ solutions indicate the formation of HCO$_4^-$ during the electrochemical process. We therefore calculate the peroxidation of HCO$_3^-$ species and the subsequent hydrolysis of HCO$_4^-$ groups on the (1 1 2) and (3 1 0) surfaces of SnO$_2$. While the energy barriers in these reaction pathways are relatively high, stable H$_2$O$_2$ is formed through these routes on both the (1 1 2) and (3 1 0) facets. The (1 1 2) surface of SnO$_2$ is more kinetically favorable for H$_2$O$_2$ generation compared to the (3 1 0) facet. Our work has deepened the understanding of the H$_2$O$_2$ formation mechanism in the presence of bicarbonate and provides insights into the design of catalysts for H$_2$O$_2$ generation that a suitable catalyst should have an appropriate adsorption for HCO$_3^-$ and an effective catalytic ability for the peroxidation of HCO$_3^-$.

Author: Contributions

Wenlong Guo: Measurements, Characterization, DFT calculations, Writing.
Yinqiong Xie: Material synthesis.
Shi Tang: Material synthesis.
Bo Yu: Characterization.
Xi Liu: Measurements, DFT calculations, Writing.
Graeme Henkelman: DFT calculations.
We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “H$_2$O$_2$ Formation Mechanisms on the (1 1 2) and (3 1 0) Facets of SnO$_2$ via Water Oxidation Reaction with the Participation of Bicarbonate: DFT and Experimental Investigations”.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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