Electrochemical water oxidation reaction (WOR) to hydrogen peroxide (H$_2$O$_2$) via a 2e$^-$ pathway provides a sustainable H$_2$O$_2$ synthetic route, but is challenged by the traditional 4e$^-$ counterpart of oxygen evolution. Here we report a CO$_2$/carbonate mediation approach to steering the WOR pathway from 4e$^-$ to 2e$^-$. Using fluorine-doped tin oxide electrode in carbonate solutions, we achieved high H$_2$O$_2$ selectivity of up to 87%, and delivered unprecedented H$_2$O$_2$ partial currents of up to 1.3 A cm$^{-2}$, which represents orders of magnitude improvement compared to literature. Molecular dynamics simulations, coupled with electron paramagnetic resonance and isotope labeling experiments, suggested that carbonate mediates the WOR pathway to H$_2$O$_2$ through the formation of carbonate radical and percarbonate intermediates. The high selectivity, industrial-relevant activity, and good durability open up practical opportunities for delocalized H$_2$O$_2$ production.
Electrochemical water (H₂O) oxidation to hydrogen peroxide (H₂O₂) via a 2e⁻– pathway (2e⁻-WOR) represents a green and sustainable route to produce H₂O₂ compared to traditional anthraquinone process, but is currently challenged by low selectivity and activity due to strong competition from the typical 4e⁻– oxygen evolution reaction pathway (OER or 4e⁻-WOR)1-6. Traditional approaches to promoting 2e⁻-WOR to H₂O₂ have been mostly focused on exploring catalysts with relatively weak binding strength with intermediate O species compared to that in the 4e⁻– counterpart7-11. These catalysts (typically made of inert metal oxides7-10 as well as other materials12-18) require large overpotentials to activate the water oxidation step, but their 2e⁻– WOR current densities are usually limited at ~10 to 200 mA cm⁻², as the extra overpotentials to drive larger currents would start to push the water oxidation reaction all the way down to O₂ with significantly decreased H₂O₂ selectivity19-21,15,16. As a result, the state-of-the-art 2e⁻– WOR performances are still far below the requirements in practical applications22.

Reaction redox mediators as “electron shuttles” have been playing important roles in facilitating desired reaction pathways (especially for intermediate products) in electrocatalysis16,19, electroorganic synthesis20-22 and bioelectrocatalysis23,24 and could become a solution to the H₂O₂ activity-selectivity dilemma. While exploring such kind of reaction mediators for selective 2e⁻– WOR is challenging, our nature may have an answer for us. H₂O₂ commonly exists in biosystems as one type of reactive oxygen species (ROS)24 which are essential in signal transduction25,26. However, researchers have found out that high concentrations of CO₂ could cause ROS burst (rapid release of ROS from cells), leading to destructions of redox-sensitive proteins and cell structures (Supplementary Note 1)27,28.

Inspired by this phenomenon and previous studies in electro-generated chemiluminescence29,30 and peroxyxenate synthesis31, here we hypothesize that CO₂ (or carbonate as its ionic form in water) may serve as an effective mediator to promote the H₂O₂ pathway in electrochemical water oxidation (Fig.1a)32-34. Using fluoride doped tin oxide (FTO) as a model catalyst electrode, we demonstrated high H₂O₂ selectivity up to 87%, delivered high H₂O₂ partial current densities up to 1.3 A cm⁻², and achieved a long-term stable and continuous H₂O₂ generation for 250 hours with over 80% H₂O₂ selectivity at 150 mA cm⁻² current density in carbonate solutions. The electrochemical performance of our work represents orders of magnitude improvement compared to previous works. We studied the mechanism of the carbonate mediation effects using molecular dynamics simulations, coupled with electron paramagnetic resonance and isotope labeling experiments. Simulation and experimental results suggested that carbonate mediates the WOR pathway through carbonate radical and percarbonate intermediates.

Results and discussion

Verification of the CO₂/carbonate mediation effects. To support the CO₂/carbonate mediator strategy, an oxidation catalyst electrode which meets the following criteria is a prerequisite: first, it should be an inert catalyst for the 4e⁻– oxygen evolution reaction (OER); second, it has a high electrical conductivity to deliver high currents; third, it should remain stable under high oxidation potentials in water. After an initial screening process, FTO (Supplementary Fig. 1) was selected as the catalytic electrode compare to other materials (Supplementary Fig. 2). While FTO has also been used in some previous studies of photoelectrochemical or electrochemical water oxidation reaction, in most cases it was used as the substrate for studying other catalytic materials7,8. Additionally, the H₂O₂ selectivity and activity on FTO reported before are rather low8, and the surface reaction mechanism of 2e⁻–-WOR is still unclear yet. We evaluated the electrochemical WOR performance using a standard three-electrode setup in an H-type cell. Sodium phosphate buffer (0.65 M Na₂HPO₄ and 0.35 M NaH₂PO₄, pH ~7) was chosen as the aqueous electrolyte, due to its high stability under oxidative potentials35 and strong buffering capability36, for investigating the possible impacts of CO₂ on WOR pathways (Fig. 1b and Supplementary Fig. 3). In Ar-saturated 1.0 M sodium phosphate buffer, only trace amount of H₂O₂ was detected within a wide range of applied water oxidation potentials, with H₂O₂ Faradaic efficiencies (FEs) less than 1% (Fig. 1b). This result suggests that FTO presents an intrinsic selectivity towards the 4e⁻–-WOR pathway. Surprisingly, when the solution was saturated with CO₂, a significant jump of H₂O₂ selectivity was achieved under the same reaction conditions (Fig. 1b), supporting our hypothesis that CO₂ can play a role in steering the WOR reaction pathway towards H₂O₂.

As CO₂ exists in different types of species in aqueous solutions37, including dissolved CO₂, carbonate, and bicarbonate, we therefore designed control experiments to better identify the key factors that are at play in promoting H₂O₂ generation. We first used 1.0 M NaHCO₃ as the electrolyte, while bicarbonate is the dominant species, to evaluate FTO’s 2e⁻– WOR performance. As shown in Fig. 1c–e and Supplementary Fig. 4, the peak H₂O₂ FE was ~ 34%, corresponding to a H₂O₂ partial current density of only 5.6 mA cm⁻². We further switched the electrolyte to carbonate dominated 1.0 M Na₂CO₃ solution and performed the same test, and observed a drastic change. The H₂O₂ FE jumped up to a maximal of 56% at 3.2 V versus reversible hydrogen electrode (vs. RHE) with a significantly improved H₂O₂ partial current density of over 50 mA cm⁻² (Fig. 1e), representing over one order of magnitude increase compared to that in either CO₂ saturated electrolyte or bicarbonate electrolyte. To explore if this promotion effect on 2e⁻– WOR pathway is an intrinsic catalytic property of the FTO catalyst, or specifically exists in the CO₂/bicarbonate/carbonate systems, we also tested the H₂O₂ selectivity in other commonly used electrolytes containing different anion species, including sodium sulfate, sodium nitrate, sodium hydroxide, sodium perchloride, as well as the sodium phosphate buffer we showed earlier (Fig. 2a–d and Supplementary Fig. 5). To further confirm the carbonate promotion effects, we then tested the electrochemical water oxidation performance in Na₂CO₃ + NaOH electrolyte (Supplementary Fig. 6a). In alkaline electrolytes, OH⁻ absorption plays a key role in oxygen evolution reaction38. With the increase of NaOH concentration, OH⁻ absorption will decrease the coverage ratio of carbonate on FTO surface, and thus leading to decreased H₂O₂ selectivity and increased OER, which further demonstrates that high pH is not the reason for high H₂O₂ selectivity when compared to bicarbonate solutions. As a result, none of them presented any preferences for 2e⁻– WOR pathway, with negligible H₂O₂ selectivity of less than 2%, which indicates the participation of CO₂-related species in the electrochemical H₂O-to-H₂O₂ conversion process on the FTO surface.

Since in carbonate solution the FTO catalyst exhibited the best H₂O₂ generation performance, we thus tested the dependence of H₂O₂ selectivity over Na₂CO₃ concentration to further reveal the promotion effects of carbonate on 2e⁻– WOR. As shown in Fig. 2e, the H₂O₂ FE under 100 mA cm⁻² current presented a monotonic enhancement from 5% to 56% with increased Na₂CO₃ concentration from 0.1 M to 2.0 M, respectively, indicating the critical role of carbonate ions in promoting H₂O₂ selectivity. Possible promotion effects from sodium ions were excluded as the H₂O₂ FEs were similar under different Na⁺ concentrations (Fig. 2f). We also examined the O₂ FEs from the 4e⁻–-WOR pathway using gas chromatography quantification, which added
together with H$_2$O$_2$ are close to 100%, suggesting no significant side reactions in this electrochemical system (Fig. 2e, see Methods). In addition, FTO electrodes with different thicknesses, fluorine doping levels, or surface resistivity exhibited quite similar H$_2$O$_2$ selectivity (Supplementary Fig. 6b), further confirming that the dominant factor on WOR pathway is from carbonate concentrations. Other types of common conducting metal oxides, including alumina-doped zinc oxide and indium tin oxide, were also evaluated in carbonate electrolyte but showed poor stability under the WOR conditions (Supplementary Fig. 2). Titanium mesh, which is an OER inert metal catalyst, also exhibited good 2e$^-$-WOR performance in 1.0 M Na$_2$CO$_3$ with a maximum H$_2$O$_2$ FE of ~47% at 2.36 V (Supplementary Fig. 2e, f). However, it presented poor stability due to possible surface passivation under high oxidation potentials (Supplementary Fig. 2g). These above experimental results strongly support our hypothesis that CO$_2$/carbonate may directly participate in and promote the H$_2$O$_2$ generation process as a promising 2e$^-$-WOR mediator.

## Electrochemical H$_2$O$_2$ generation at industrial-relevant current densities

To further amplify the carbonate mediation effect for improved H$_2$O$_2$ generation performance, we evaluated the electrochemical 2e$^-$-WOR performance of FTO electrode in high concentration carbonate solutions. Figure 3a, b and Supplementary Fig. 7 show the I-V curves and corresponding H$_2$O$_2$ FE$^*$ under different potentials. In 2.0 M Na$_2$CO$_3$ solution, we achieved high H$_2$O$_2$ FEs of ~60 to 70%, while delivering large current densities of up to 800 mA cm$^{-2}$. This impressive H$_2$O$_2$ performance can be even further improved by using 5.0 M of K$_2$CO$_3$. The reason why we chose to use K$_2$CO$_3$ is due to its higher solubility in water (112.3 g in 100 g water at 25°C) than that of Na$_2$CO$_3$ (29.4 g in 100 g water at 25°C) $^{39}$. The FTO catalyst achieved a 10 mA cm$^{-2}$ onset current density at 2.75 V vs. RHE in 5.0 M K$_2$CO$_3$, which is 50 mV lower than that in 2.0 M Na$_2$CO$_3$. With the overpotentials gradually increased, the H$_2$O$_2$ FE quickly ramped up to a plateau of over 80% under a wide range of current densities of up to 1 A cm$^{-2}$ (Fig. 3b). We achieved a maximal H$_2$O$_2$ FE of 87% at 600 mA cm$^{-2}$, representing a 522 mA cm$^{-2}$ H$_2$O$_2$ partial current density (Fig. 3b). More impressively, at 3.7 V, the catalyst reached a current density of 1 A cm$^{-2}$ while still maintaining a high H$_2$O$_2$ selectivity of 78%, achieving an industrial-relevant H$_2$O$_2$ partial current density of 780 mA cm$^{-2}$. The H$_2$O$_2$ generation rate can be further boosted to a maximal partial current of 1.3 A cm$^{-2}$ (73% FE at 1.8 A cm$^{-2}$ overall current) using an extended-range power supply. This corresponds to an unprecedented H$_2$O$_2$ production rate of 24.3 mmol cm$^{-2}$ h$^{-1}$ and is orders of magnitude higher compared to previous reports (Fig. 3c, d). Please be noted here that this power supply was not equipped with a three-electrode system therefore the anode potential could not be accurately measured (see Methods). Such high electrochemical H$_2$O$_2$ generation rates benefit from the sufficient mass diffusions in aqueous solutions where no triple-phase boundary is needed, which shows an advantage compared to the cathodic H$_2$O$_2$ generation from 2e$^-$-ORR (oxygen reduction reaction) where O$_2$ gas diffusions typically limit its reaction rates to hundreds of millamps per square centimeter (Supplementary Note 2$^{3,40}$. Finally, long-stability is usually a big challenge for 2e$^-$-WOR due to the high oxidation potentials that could damage the electrode $^{2,3,11,16,17,41,42}$ (Supplementary Table 1). Besides, in traditional batch reactors, as the products continuous to accumulate during the long-term stability test (Supplementary Fig. 8a), the electrolyte environment will be changed and thus the electrocatalytic performance continuously decayed. Our FTO catalyst electrode, coupling with a flow reactor (Supplementary Fig. 8b), presented excellent durability under water oxidation conditions, maintaining a stable potential and high H$_2$O$_2$ FEs of over 80% to deliver a 150 mA cm$^{-2}$ current for 250 hours (Fig. 3e and Supplementary Table 1).

The good selectivity, activity, and stability of our carbonate mediated 2e$^-$-WOR makes it possible for this anode reaction to be coupled with 2e$^-$-ORR cathodic reaction to double the efficiency of
electrons in producing \( \text{H}_2\text{O}_2 \) from both electrodes (Supplementary Fig. 9a). On the anode side, \( \text{H}_2\text{O} \) can be oxidized to \( \text{H}_2\text{O}_2 \) via carbonate mediation by our high-performance \( 2e^- \) -WOR catalyst. On the cathode side, we used oxidized carbon black (demonstrated in our previous study\(^{40,43} \)) as the selective \( 2e^- \) -ORR catalyst to reduce \( \text{O}_2 \) to \( \text{H}_2\text{O}_2 \) (Supplementary Fig. 9b, c)\(^{40,43} \). Based on the previous definition of \( \text{H}_2\text{O}_2 \) FE on one side of the electrode, the maximal overall \( \text{H}_2\text{O}_2 \) FE in this two-electrode system is 200%. As shown in Supplementary Fig. 9d, our system delivered a 100-mA cell current (1 cm\(^2 \) FTO electrode) at 2.5 V cell voltage with a high overall \( \text{H}_2\text{O}_2 \) FE of 140%, suggesting a significant improvement compared to either \( 2e^- \) -WOR or \( 2e^- \) -ORR system. Furthermore, to fully use generated \( \text{H}_2\text{O}_2 \) and \( \text{Na}_2\text{CO}_3 \) mediator, we designed a process (Supplementary Fig. 9a) for a continuous generation of an adduct product between \( \text{Na}_2\text{CO}_3 \) and \( \text{H}_2\text{O}_2 \) (\( \text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2 \), Supplementary Fig. 9e–g)\(^{11,44} \).

Mechanism studies. To gain a molecular level understanding of the reaction mechanism in our \( \text{CO}_2 \)/carbonate mediated \( 2e^- \) -WOR, we employed molecular dynamics simulations, coupled with experimental studies, to reveal the most possible reaction pathway. Reaction intermediates that could exist in electrolyte under the applied high oxidation potentials (~3 V vs. RHE)\(^{45} \), including \( \text{CO}_3^{2-} \), \( \text{OH}^- \), and percarbonates (\( \text{HCO}_3^- \) or \( \text{C}_2\text{O}_4^{2-} \)), were taken into consideration\(^{34,46} \). We first proposed several possible reaction pathways as summarized in Supplementary Fig. 10. After an initial screening based on theoretical studies and experimental observations, we proposed that the carbonate-mediated water oxidation to \( \text{H}_2\text{O}_2 \) could proceed via the following four reaction intermediate steps with most favorable thermodynamics\(^{28,47,48} \): \( \text{CO}_2^{2-} \rightarrow \text{CO}_3^{2-} + e^- \), \( \Delta G = -0.72 \text{ eV at } U = 3.0 \text{ V vs. RHE} \). Second, the generated \( \text{CO}_3^{2-} \) coupled with a \( \text{H}_2\text{O} \) molecule is further oxidized to \( \text{HCO}_3^- \) (\( \text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{HCO}_2^- + \text{H}^+ + e^- \), \( \Delta G = -0.27 \text{ eV at } U = 3.0 \text{ V vs. RHE} \)). Subsequently, \( \text{HCO}_3^- \) is hydrolyzed to generate \( \text{H}_2\text{O}_2 \) and converted back to \( \text{HCO}_2^- \) or \( \text{CO}_2 \) (\( \text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{HCO}_2^- + \text{H}_2\text{O} \) or \( \text{HCO}_2^- + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{OH}^- \), \( \Delta G = -0.31/0.42 \text{ eV without applied potential} \)). As shown in Supplementary Fig. 12, the first and second elementary reactions are electrochemical steps. Under an electrode potential of 3.0 V, both reactions are exothermic. The third fundamental reaction is a non-electrochemical step, and the calculation results show that the former is more likely to occur than the latter. During this reaction step, \( \text{H}^+ \) in \( \text{H}_2\text{O} \) combines with the \( -\text{O}^-\text{OH} \) group in \( \text{HCO}_3^- \) molecule to generate \( \text{H}_2\text{O}_2 \), and the remaining \( \text{OH}^- \) group from \( \text{H}_2\text{O} \) can combine with remaining \( \text{CO}_2 \) from \( \text{HCO}_3^- \) to form \( \text{HCO}_2^- \). We note here that this hydrolysis step involves O

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Fig. 2 Impacts of anion species and anion/cation concentrations on \( 2e^- \) -WOR. a–d \( j-V \) curves and \( \text{H}_2\text{O}_2 \) FEs of FTO catalyst using 1.0 M \( \text{Na}_2\text{SO}_4 \), 1.0 M \( \text{NaNO}_3 \), 1.0 M \( \text{NaOH} \), and 1.0 M \( \text{NaClO}_4 \), respectively. The \( \text{H}_2\text{O}_2 \) FEs in these electrolytes were lower than 2%, indicating there is no promotion effects for \( \text{H}_2\text{O}_2 \) formation using these anion species. e Dependence of \( \text{H}_2\text{O}_2 \) and \( \text{O}_2 \) selectivity on \( \text{Na}_2\text{CO}_3 \) concentration at 100 mA cm\(^{-2} \). The \( \text{H}_2\text{O}_2 \) FE was increased with increased \( \text{Na}_2\text{CO}_3 \) concentration, while the FE of side product \( \text{O}_2 \) was correspondingly decreased, indicating that \( \text{Na}_2\text{CO}_3 \) could be directly involved in the \( 2e^- \) -WOR process. f \( \text{H}_2\text{O}_2 \) FE in 1.0 M \( \text{Na}_2\text{CO}_3 \) with different concentrations of \( \text{NaClO}_4 \).
5.0 M K$_2$CO$_3$ solution. Its H$_2$O$_2$ selectivity and potential remained stable for a 250-hour continuous operation.

K$_2$CO$_3$ was chosen due to its higher solubility than Na$_2$CO$_3$. The maximal current density in our standard three-electrode cell was cut at 1 A cm$^{-2}$.

We used 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap to detect its resonance (EPR). Due to the short lifetime of carbonate radical, isotope experiments were therefore designed: First, to isotope labeling experiment to support the possible formation of carbonate and water via the percarbonate intermediate pathway, especially for those suffering from 4e$^-$ reaction pathways.

To support the proposed reaction mechanism, we first tested the formation of carbonate radical by electron paramagnetic resonance (EPR). Due to the short lifetime of carbonate radical, we used 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap and an in-situ trapping method (see Methods) to detect its generation under electrolysis (Supplementary Fig. 16a). Compared to the direct mixture of DMPO and before/post-electrolysis carbonate solution, the solution obtained from the in-situ trapping method under electrolysis exhibit a clear four-line 1:2:2:1 splitting pattern characteristic of the DMPO$^-$–OH adduct (Fig. 4c and Supplementary Fig. 16a), indicating that carbonate radical was formed at the surface of FTO electrode under oxidation potentials. Furthermore, we performed an $^{18}$O isotope labeling experiment to support the possible formation of HCO$_3^-$ intermediates. As we mentioned earlier, the hydrolysis process of HCO$_3^-$, if existing in the electrolyte, will lead to oxygen exchange between carbonate and water (Supplementary Fig. 16b). Therefore, if we use $^{18}$O-isotope-labeled water as the electrolyte, we would expect an increased abundance of $^{18}$O (δ$^{18}$O) in Na$_2$CO$_3$ after electrolysis compared to that of natural exchange without electrolysis (Methods). Two sets of $^{18}$O isotope experiments were therefore designed: First, to figure out the natural exchange rate as the background, we tested δ$^{18}$O as a function of time in Na$_2$CO$_3$ after it was dissolved in $^{18}$O labeled water; Next, we did the same tests of δ$^{18}$O at the same time points under WOR electrolysis. As clearly shown in Fig. 4d, the abundance of $^{18}$O isotope in Na$_2$CO$_3$ under electrolysis condition continues to increase over time, and is several orders of magnitude higher than that without electrolysis, suggesting the violent interaction and chemical bond reconfiguration between carbonate and water via the percarbonate intermediate pathway, instead of a direct water oxidation pathway (Supplementary Fig. 17).

In conclusion, we demonstrated a CO$_2$/carbonate mediated electrochemical water oxidation for high-performance H$_2$O$_2$ generation, where carbonate ions help to steer the 4e$^-$ reaction pathway to 2e$^-$ via intermediates such as carbonate radicals and percarbonate, and FTO electrode provides a highly conductive, stable, and 4e$^-$-OER inert surface. As a result, we achieved a high H$_2$O$_2$ selectivity of up to 87%, industrial-relevant H$_2$O$_2$ generation partial current of up to 1.3 A cm$^{-2}$, as well as excellent stability, suggesting a promising route for the renewable and onsite -OER competition such as chlorine evolution, hydrocarbon oxidation, nitrogen oxidation, etc. Future works can be focused on exploring other catalytic materials enabling this mediation reaction, improving the onset potentials, and further extending the durability.

**Methods**

**Materials:** FTO was purchased from MSE Supplies (2.2 mm 7-8 Ohm/Sq FTO TEC 7 Coated Glass Substrates, used in all experiments if there is no other noting) and Sigma (SKU: 735159 and 735256). AZO and ITO were purchased from Sigma. Titanium mesh was purchased from Kunshan GuangJiaYuan new materials Co.
The oxidized carbon was prepared according to a previous report. Hydrophobic carbon fiber paper (CFP, PTFE loading 60%) was purchased from Fuel Cell store. Chemicals were purchased from Sigma and VWR International Company.

**Electrocatalytic oxidation of H$_2$O$_2$**. The electrochemical measurements were run at 25 °C in a customized gas-tight H-type glass cell separated by Naion 117 membrane (Fuel Cell Store). A BioLogic VMP3 workstation was employed to record the electrochemical response. In a typical three-electrode system, a platinum foil (Beaumont Chemical, 99.99%) and a saturated calomel electrode (SCE, CH Instruments) were used as the counter and reference electrode, respectively. The FTO electrodes were used as the working electrodes, and stainless-steel alligator clip was used to connect the FTO glass electrode. The alligator clip was not visible in the image.

**Electrolysis setup.** The alligator clip was used to connect the FTO glass electrode. The alligator clip was not visible in the image.

**Electrolyte measurements.** The electrolyte in the anodic compartment was stirred at a rate of 1,600 r.p.m. during electrolysis. All the measured potentials were manually compensated unless stated otherwise. The overall resistance was determined by potentiostatic electrochemical impedance spectroscopy at frequencies ranging from 0.1 Hz to 200 kHz, and manually compensated as $E$ (IR corrected versus RHE, where $iR$ is the voltage drop from overall resistance) = $E$ (versus RHE) - $R$ (the overall resistance, including the electrolyte resistance and the intrinsic resistance of the electrode) x i (amps of average current). The impedance number was about 12 to 17 Ω. DC stabilized power supply (ITECH) was used for the ultra-high current density (over 1 A cm$^{-2}$) electrolys. The volume of the electrolyte solution was 25 mL, and the reaction time was determined by the electrolysis current to insured the total electrolysis coulomb was about 10 to 50 C. After electrolysis, the generated H$_2$O$_2$ was detected by using the standard potassium permanganate (0.1 N KMnO$_4$ solution, Sigma-Aldrich) titration process, according to the following equation:

\[ 2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O} \]

The typical quantification time is about 5-10 min, which was much longer than the lifetime of carbonate radical (the lifetime of radical is about several microseconds). In this work, sulfuric acid (2.0 N H$_2$SO$_4$, VWR International Company) was used as the H$^+$ source. The FE for H$_2$O$_2$ production is calculated using the following equation:

\[ \text{FE} = \frac{\text{generated H}_2\text{O}_2\text{ (mol) \times 2 \times 96485 (C mol}^{-1})}{\text{total amount of charge passed (C)}} \times 100 \quad \text{(maximum 100%)} \]

For the stability test, a continuous three-electrodes flow cell was employed to continuously produce H$_2$O$_2$ (Supplementary Fig. 8b). The electrolyte in the anodic compartment was stirred at a rate of 1600 r.p.m. during electrolysis. A peristaltic pump (Longer) was used to pump in K$_2$CO$_3$ electrolyte to the WOR side, and another peristaltic pump was used to pump out generated H$_2$O$_2$ in the WOR side. The electrolyte flow rate of the WOR side was 6 mL min$^{-1}$. The FE for H$_2$O$_2$ production is calculated using the following equation:

\[ \text{FE} = \frac{\text{generated H}_2\text{O}_2\text{ (mol l}^{-1}) \times 2 \times 96485 (\text{C mol}^{-1}) \times \text{flow rate (mL s}^{-1})}{j_{\text{ave}}(\text{mA})} \times 100 \quad \text{(maximum 100%)} \]

For the 2e$^-$ WOR/2e$^-$ ORR electrosynthetic cell test, 0.5 mg cm$^{-2}$ oxidized carbon catalyst was air-brushed onto 2 cm$^2$ Sigracet 35 BC gas diffusion layer (Fuel Cell Store) electrodes as 2e$^-$ ORR cathode. Then, a 1-cm$^2$ FTO electrode was used as anode. The two electrodes were therefore placed on opposite sides in the H cell. O$_2$-saturated 2.0 M Na$_2$CO$_3$ was used as electrolyte. The cathode was open to the atmosphere. The flow rate of 2.0 M Na$_2$CO$_3$ electrolyte was 3 ml min$^{-1}$ at both sides, as controlled by a peristaltic pump. A current of 100 mA was employed for H$_2$O$_2$ production. The FE of the electrosynthetic cell for H$_2$O$_2$ production is calculated using the following equations, respectively:

\[ \text{FE} = \frac{\text{generated H}_2\text{O}_2\text{ (mol l}^{-1}) \times 2 \times 96485 (\text{C mol}^{-1}) \times \text{flow rate (mL s}^{-1})}{j_{\text{ave}}(\text{mA})} \times 100 \quad \text{(maximum 200%)} \]
To obtain solid H₂O₂, the electrolyte after electrolysis (two-electrode configuration) was firstly concentrated by rotary evaporator, then about 100 ml of absolute isopropanol was added. The box of this size, CO₂, HCO₃⁻, HCO₂⁻, H₂O, CO₂+ H₂O + OH⁻ replaced seven, eight, and eight water molecules, respectively. The negative charge (·) of the ion was neutralized by a uniform background charge. We did not consider the hydroxide ions and protons in the electrolyte during simulation. Total energy of the above four possible intermediates was calculated by AIXM at a constant temperature of 300 K (using Nose-Hoover thermostat with a time step of 0.5 fs) as implemented in the Vienna ab initio simulation program (VASP)34. Perdew-Burke-Ernzerhof (PBE) functional31 and DFT-D35 methods were used to describe the exchange and correlation energies and the van der Waals interactions, respectively. All plane wave cutoff energy of 400 eV and Gamma centered k-mesh of 1 x 1 x 1 were set in MD simulations. Considering the calculation cost, we ran 7 ps for each structure. From these AIMD calculations, we analyzed the arithmetic average of their total energies using different averaging time windows from 0.5 ps to 2.0 ps. It is found that averaging within a time window of 2.0 ps gives a value fluctuates around the final value by ±0.1 eV, less than other time windows. Therefore, average energy was evaluated from last 2.0 ps AIMD trajectory, as shown in Supplementary Table 3. The formation of CO₂+ and HCO₃⁻ are electrochemical oxidation steps. Supplementary Table 4 shows inorganic standard electrode potentials42. The reaction between H₂O and CO₂ was calculated by two separated processes including H₂O ↔ OH⁻ + H⁺ and CO₂ + OH⁻ ↔ HCO₃⁻ because the energy of H⁺ + e⁻ in CO₂+ ↔ H⁺ + CO₂ gas transformation step is difficult to accurately calculate by MD simulations. Therefore, we deal with this step by adding the above two steps together. To better match the results of the experiment, we convert the standard electrode potential into a reversible hydrogen electrode (U_RHE = U_EFF + 0.059 × pH, pH = 12). Take CO₂ + OH⁻ ↔ HCO₃⁻ reaction as an example, the standard electrode potential for this reaction E_f = 1.175 + 0.03 V and the potential corresponding to conversion to RHE is 2.278 V (pH = 12, U_RHE = 1.175 + 0.059 × 12 = 2.278 V), corresponding to the reaction free energy of 0 eV. When the electrode potential is increased to 3 V, the reaction is exothermic with an energy of −0.72 eV. 

Gibbs free energies on the SnO₂(110) surface calculations. The exchange-correlation potential is described by a general gradient approximation (GGA) with spin polarized revised Perdew-Burke-Ernzerhof (PBE)31 functional due to that it is more adept at describing chemisorption on metals. The projector augmented wave (PAW) is applied to describe the electron-ion interaction and the plane-wave energy cutoff is set to 400 eV. All structures are optimized with a convergence criteria of 1 × 10⁻⁶ eV/Å for the energy and 0.02 eV/Å for the forces. The SnO₂(110) surface is the most common form of tin oxide (Space group: P4/mmm, No. 136)34. Therefore, the SnO₂(110) surface is modeled using a slab with a (4 x 2) supercell consisting of 3 trilayers and containing 144 atoms. The vacuum spacing is set to more than 15 Å for surface isolation to prevent interaction between two neighboring surfaces. The top two trilayers are fully relaxed during the structural optimization and geometry optimizations for SnO₂(110) are performed with 1 x 1 x 1 k-mesh. The Poisson-Boltzmann (PB) implicit solvation model, Vaspolv32, was used to describe the effect of solution as implemented in VASP 5.4.4, with a dielectric constant ε = 80 for water. All molecules were performed with a 15 × 15 × 15 k-point grid sampling. Computational hydrogen electrode (CHE)46 model was used to calculate the Gibbs free energy change for OER elementary reactions. At electrode potential U = 0 V (vs. reversible hydrogen electrode, RHE), the Gibbs free energy change (ΔG) can be calculated by

$$\Delta G = \Delta E + \Delta E_{ringe} - T\Delta S + \Delta G_{gs}$$

where ΔE is the energy difference between the products and reactants from DFT computations; ΔE_{ringe} and ΔS are the changes in zero-point energy and entropy, respectively, which are obtained from the vibrational frequency calculations; T is the temperature at 298 K. The energy corrections of gas-phase species in this work, including zero point energies (ZPE) and entropies (TS), are listed in Supplementary Table 5. ΔG_{gs} = −nE, where U is the electrode applied potential relative to RHE, ε is the elementary charge transferred and n is the number of proton–electron pairs transferred. 2e⁻−WOR path is calculated in alkaline condition. We calculated the chemical potential of hydroxides and electrons with reference to previous work43, μH₂O/H₂O = −ε₇ = 9.81 eV, μ⁻½ = 9.81 eV, μCO₂/CO₂ = −ε₁₂ = 12 eV, CO₂−/HCO₃⁻/H₂CO₃ and CO₂−/OH⁻/H₂O reversible hydrogen electrode potential (U_{RHE} = 1.173 V) at T = 298.15 K. The accuracy of the above DFT methodology applied in our work is mainly based on published work. More details can be found in the Supporting Information.

Data availability
The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions
L.F., X.B. and C.X. contributed equally. L.F. and H.W. conceived the project and designed the experiments. H.W. supervised the project. L.F., C.X., Xiao Zhang, Y.X., and Z.W. perform the experimental study. X.B., Xunhua Zhao, and Yuanyue Liu performed the theoretical study. L.F., X.B, Yingying Lu, Yuanyue Liu, and H.W. wrote the manuscript with support from all authors.

Competing interests
The authors declare no competing interests.

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