Exploring dopant effects in stannic oxide nanoparticles for CO₂ electro-reduction to formate

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The electrosynthesis of formate from CO₂ can mitigate environmental issues while providing an economically valuable product. Although stannic oxide is a good catalytic material for formate production, a metallic phase is formed under high reduction overpotentials, reducing its activity. Here, using a fluorine-doped tin oxide catalyst, a high Faradaic efficiency for formate (95% at 100 mA cm⁻²) and a maximum partial current density of 330 mA cm⁻² (at 400 mA cm⁻²) is achieved for the electroreduction of CO₂. Furthermore, the formate selectivity (≈90%) is nearly constant over 7 days of operation at a current density of 100 mA cm⁻². In-situ/operando spectroscopies reveal that the fluorine dopant plays a critical role in maintaining the high oxidation state of Sn, leading to enhanced durability at high current densities. First-principle calculation also suggests that the fluorine-doped tin oxide surface could provide a thermodynamically stable environment to form HCOO⁻ intermediate than tin oxide surface. These findings suggest a simple and efficient approach for designing active and durable electrocatalysts for the electrosynthesis of formate from CO₂.
The catalytic conversion of CO₂ to fuels or valuable chemical products provides a carbon-neutral cycle that can mitigate the rapid consumption of fossil resources and increasing CO₂ emissions. Recently, in accordance with global CO₂ reduction regulations, carbon capture utilization and storage (CCUS) technology for large-scale greenhouse gas reduction and conversion to high-value-added products has been intensively researched. In particular, the electrocatalytic reduction of CO₂ has attracted interest owing to recent developments in electricity production from renewable energy sources such as solar and wind. As a widely used raw material in the pharmaceutical, tanning, and textile industries that can also act as a hydrogen carrier for fuel cells, formate is a very attractive product of the CO₂ reduction reaction (CO₂RR). Furthermore, given the hydrogen evolution reaction (HER; Eq.2), inhibiting the HER is essential for obtaining a high selectivity for formate. According to spectroscopy and suggested that the oxidized Sn surface is a key factor in achieving high CO₂RR activity over a wide range of current densities but also maintained its performance for more than a week. The electrochemical CO₂RR performance is significant affected by the device design and the type of purged CO₂. Therefore, it is necessary to develop alternative Sn-based electrocatalysts to ensure stability at high current densities. This phenomenon can be suppressed under strongly alkaline conditions. The SnO₂ and doped-SnO₂ samples consist of very small oxide clusters (<5 nm) with uniform distributions. All the catalysts had similar average particle sizes [2.567 nm (SnO₂), 2.121 nm (FTO), 2.391 nm (ITO), and 2.154 nm (ATO)], and the dopants were uniformly distributed in the doped-SnO₂ particles (Supplementary Figs. 2–4). On the contrary, while the SnO₂ catalyst without tetradecylamine (TDA) surfactant has a similar particle size compared to SnO₂ with TDA surfactant (2.603 nm, Supplementary Fig. 5), it aggregated to show a disordered mesoporous structure. The SnO₂ and doped-SnO₂ nanoparticles all exhibited rutile tetragonal crystal structures, as identified by analyzing the zone axis of the images. Furthermore, the crystal structures and average particle sizes of the synthesized nanoparticles were analyzed using X-ray diffraction (XRD) (Fig. 1d). In the XRD patterns, the (110), (101), and (211) reflections of tetragonal SnO₂ were observed at 20 values of 26.3°, 33.6°, and 51.9°, respectively. The quality of the synthesized SnO₂ and doped-SnO₂ catalysts was analyzed by thermogravimetric analysis (TGA) (Supplementary Fig. 6). All the catalysts showed a weight loss of ~20% from 30 to 500 °C owing to the removal of adsorbed water molecules and stable oxygen functional groups in the carbon support. Under flowing O₂, the catalyst weight slightly increased and then decreased rapidly, which was attributed to complete oxidation of the carbon support to CO₂ gas after the formation of oxygen functional groups. The SnO₂ and doped-SnO₂ catalysts were both found to have oxide contents of approximately 40 wt%. The similarities in the morphologies, crystal structures, and oxide contents of the SnO₂ and doped-SnO₂ nanoparticles allowed comparisons of their catalytic activities and efficiencies for CO₂ reduction to formate under the same conditions. CO₂-to-formate conversion performance. The electrochemical CO₂RR activities of the SnO₂-based catalysts were evaluated in a homemade flow cell using gaseous CO₂ to accelerate the CO₂RR while minimizing the mass transfer resistance. A detailed schematic of the flow cell is shown in Fig. 2a and Supplementary Fig. 7. The SnO₂-based catalysts were loaded onto a gas diffusion layer (GDL) and gaseous CO₂ was supplied to the cathode. An electrolyte of 1 M KOH or 1 M KHCO₃ was used in both the
cathode and anode flow channels, which were physically separated using an anion exchange membrane (AEM). Supplementary Figure 8a shows the linear sweep voltammetry (LSV) curves for SnO2/C and SnO2/C without tetradecylamine (TDA) using 1 M KOH as the electrolyte. SnO2/C exhibited significantly lower overpotentials than SnO2/C without TDA. At current densities below 300 mA cm\(^{-2}\), SnO2 showed a faradaic efficiency for formate (FEformate) of more than 70% (Supplementary Fig. 8b). In contrast, for SnO2/C without TDA, FEformate was reduced to 28.6% at 200 mA cm\(^{-2}\). The maximum formate production rate of SnO2/C (4.11 mmol h\(^{-1}\) cm\(^{-2}\)) was almost three times higher than that of SnO2/C without TDA (1.44 mmol h\(^{-1}\) cm\(^{-2}\)). The effect of TDA on the SnO2 particle size before and after CO2RR is not substantial. However, without TDA, the SnO2 particles are agglomerated (Supplementary Fig. 9: HR-TEM images of the SnO2 catalyst with and without TDA). These results show that the uniformity of the SnO2 particles significantly affects their CO2RR activity.

To observe the effects of doping on the CO2RR activity, the electrochemical CO2RR activities of FTO/C, ATO/C, and ITO/C were compared with that of SnO2/C (Fig. 2b, c and Supplementary Figs. 8 and 9). All the SnO2-based electrodes exhibited similar LSV curves, but the electrochemical reaction products differed (Supplementary Fig. 10a). In 1 M KOH solution, FTO/C exhibited an excellent FEformate value of 95% at 100 mA cm\(^{-2}\), which is higher than that of ITO/C (85%), ATO/C (80%), and SnO2/C (80%). Moreover, FTO/C maintained a FEformate value of more than 90% up to a current density of 300 mA cm\(^{-2}\). The maximum partial current density and formate production rate of FTO/C were 330 mA cm\(^{-2}\) and 6.31 mmol h\(^{-1}\) cm\(^{-2}\), respectively, which are superior to those of ITO/C (272 mA cm\(^{-2}\), 5.20 mmol h\(^{-1}\) cm\(^{-2}\)), ATO/C (242 mA cm\(^{-2}\), 4.62 mmol h\(^{-1}\) cm\(^{-2}\)), and SnO2/C (215 mA cm\(^{-2}\), 4.11 mmol h\(^{-1}\) cm\(^{-2}\)). These results indicate that F doping of SnO2 promotes the catalytic activity for the CO2RR to formate.

To test the stabilities of FTO/C and SnO2/C, 1 M KHCO3 was used as the electrolyte. In 1 M KOH, the anolyte is neutralized during the electrochemical CO2RR, leading to a high overpotential for OER (Supplementary Fig. 11). Considering the stability of the whole system, the CO2 electrolyzer was optimized for neutral media. At 100 mA cm\(^{-2}\), the FEformate value of FTO/C was ~90%, whereas that of SnO2/C was ~75% (Supplementary Fig. 12). During the stability tests at a current density of 100 mA cm\(^{-2}\), the FEformate value of SnO2/C decreased significantly after several hours and the cell potential decreased slightly, showing the low stability of SnO2/C. In contrast, the cell potential of FTO/C remained stable for 7 days and a FEformate value of ~90% was maintained (Fig. 2e, f). X-ray photoelectron spectroscopy (XPS), HAADF-STEM, and EDS after the stability tests demonstrated that the structure and chemical state of FTO/C...
remained the same even after the exposure to long-term cathodic conditions (Supplementary Figs. 13 and 14). These results indicate that F doping of SnO$_2$ provides excellent long-term stability for formate production in a gaseous CO$_2$-fed flow cell. To evaluate the level of developed catalysts, the activity and stability of the FTO/C catalysts were compared with that of other Sn-based literature catalysts (Fig. 2e, f and Supplementary Table 1). The FTO/C catalysts exhibits comparable FE$_{\text{formate}}$ and current density to other best-reported catalysts, indicating enhanced intrinsic catalytic properties for CO$_2$ electro-reduction to formate. Remarkable durability of FTO/C compared to other literatures suggests that F doping improves stability of Sn catalysts required for real electrochemical formate production.

**Theoretical investigation of CO$_2$-formate conversion on the SnO$_2$ and FTO surface.** The enhanced FE$_{\text{formate}}$ of FTO was investigated through density functional theory (DFT) calculations. As the XRD patterns of the as-prepared SnO$_2$ and FTO nanoparticles did not reveal any preferred orientations, the SnO$_2$ and FTO surfaces were modeled using a four-layer slab composed of the tetragonal (110) plane. To build the FTO (110) supercell, 15% of the oxygen atoms in the SnO$_2$ (110) supercell were randomly replaced with fluorine atoms. The elementary steps of the electrochemical conversion reaction of CO$_2$ to HCOOH involving two electron pathways were described in three steps (Method).

CO$_2$ adsorption on the catalyst surface was performed to consider the onset potential difference between water and CO$_2$ reduction. The adsorbed CO$_2$ (CO$_2^*$) is then converted to the HCOO$^*$ intermediate and HCOOH (g) in sequence with two proton-coupled electron transfers. A recent study demonstrated that, in CO$_2$ reduction current densities higher than 35 mA cm$^{-2}$, the proton can be supplied to CO$_2^*$ on the electrode surface by the dissociation of water molecules. At these current density regions, a huge amount of unused hydroxide ions is rapidly generated as a by-product, which results to the increase of the local interfacial pH to values above 12. This is regardless of the type of the buffering agent used. In this regard, the proton for the CO$_2$ reduction reaction is assumed to be predominantly supplied by the local electrolyte.

For both the SnO$_2$ and FTO (110) surfaces, the CO$_2$ molecule was gently adsorbed on the Sn atoms. Then, the HCOO$^*$ intermediate was formed as the oxygen atoms of CO$_2$ were tightly bound to the Sn atoms. The difference between the CO$_2$ adsorption energies on the SnO$_2$ and FTO surfaces was not substantial. However, approximately, a 1-eV difference was observed on the free energies for the HCOO$^*$ formation. The FTO surface could provide thermodynamically favorable conditions for HCOO$^*$ formation compared to the SnO$_2$ surface, whereas the conditions on the SnO$_2$ surface favors the HCOOH$_{(g)}$ formation (Fig. 3 and 4).
Fig. 3 DFT calculation results of Sn-based catalysts for electrochemical CO₂ conversion to formate. Free energy diagram of CO₂ to HCOOH conversion reaction on the a SnO₂ (110) and b FTO (110) surface (yellow: Sn, red: O, white: H, green: F). The strained supercells were used to simulate the structural change on SnO₂ and FTO nanoparticles at an applied potential of 1.0 V under CO₂ reduction reaction.

Supplementary Table 2). From the computational hydrogen electrode model, a minimum potential of −2.05 V was required for SnO₂ to overcome the activation barrier of HCOO* formation, whereas −1.79 V was needed for FTO to complete HCOOH formation. Identical free energy calculations using strained SnO₂ and FTO supercells were performed to simulate the structural changes on the SnO₂ and FTO electrodes during CO₂ reduction. The in-situ EXAFS data demonstrated that the bonding distance between Sn and Sn (or O) was slightly decreased by applying a potential of −1.0 V. Consequently, the lattice constants of the SnO₂ and FTO supercells decreased uniformly by 1.37% and 0.33%, respectively. The observed changes in the lattice constants correspond to the average change of each bonding distance at −1.0 V (Supplementary Fig. 15 and Supplementary Table 3). Although the strained SnO₂ (110) surface registered a lower energy for the formation of HCOOH at 0.42 eV, the energies for CO₂ adsorption and HCOO* formation were almost identical to those recorded for the SnO₂ surface. As such, the free energy for the HCOOO* formation, which is the potential-limiting step, was not affected by the compression of the SnO₂ (110) crystal. In consequence, a potential of more than 2 V was still required for the strained SnO₂. In contrast, the strained FTO (110) surface showed a 0.27-eV lower free energy for the HCOOH formation, while the energies for CO₂ adsorption and HCOO* formation slightly increased compared to that on the SnO₂ surface. Since the HCOO* formation is the potential-limiting step for the FTO electrode, the minimum potential to complete the CO₂-to-HCOOH conversion reaction decreased from −1.79 V to −1.65 V as the FTO crystal was compressed. The DFT studies suggest that doping fluorine to SnO₂ could alter the chemical environment of the oxide surface, making it thermodynamically stable for HCOO* intermediate formation, which is an important step in the CO₂-to-HCOOH conversion reaction. In addition, the compression of the crystal through the application of an external bias rendered an effective contribution only for FTO. Therefore, these factors are assumed to facilitate formate production in the FTO electrode.

Origin of excellent durability with high current density under highly reduction potential. In addition to the high FEformate of FTO/C, the high partial current density for formate at high cathodic overpotentials with excellent stability is another major advantage of this catalyst. To reveal the origin of this behavior, in-situ/operando X-ray absorption near-edge structure (XANES) spectroscopy at the Sn k-edge and Raman spectroscopy were performed for SnO₂-based electrodes under gaseous CO₂RR conditions in a customized electrochemical cell with a GDL (Supplementary Figs. 16 and 17). XANES is a bulk-sensitive technique that can reveal the oxidation state of materials, whereas Raman spectroscopy is a surface-sensitive technique that can identify the chemical structure of materials. Therefore, the combination of in-situ/operando spectroscopies can be used to reveal the state of materials during the CO₂RR. The ex-situ Sn k-edge XANES spectrum showed that both catalysts were predominantly in the quadrivalent (+4) oxidation state (Figs. 4a, b). The in-situ/operando XANES spectrum of SnO₂ exhibited a strong electrolyte-induced energy shift and fitting revealed a large fraction of metallic Sn. In contrast, the spectrum of FTO showed only a small energy shift at the reduction potential, indicating that the change in the oxidation state is extremely small. The linear combination fitting (LCF) results visually represent this trend more clearly (Fig. 4c, d).

The in-situ/operando Raman spectra, which show the chemical states of the surface, are shown in Fig. 4e, f. Carbon supports for the catalysts were not used for the in-situ/operando experiments to improve the peak intensity. The Raman peak at 630 cm⁻¹, which is associated with the symmetric stretching of Sn–O bonds (A₁g modes), was identical for SnO₂ and FTO, confirming the presence of oxide phase (Fig. 4a–d). This peak was observed for both SnO₂ and FTO at applied potentials above −0.8 V. However, for SnO₂, the Raman peak disappeared at a potential of −1 V, whereas for FTO, the Raman peak was still present at a potential of −1.2 V. These findings demonstrate that the surface of SnO₂ is converted to metallic Sn but the oxidized state of the FTO surface is maintained under high cathodic overpotentials, which is consistent with the in-situ/operando XANES results. Despite their similar radii, F ions have a higher electronegativity than O ions. This property would make F–Sn bonds stronger than O–Sn bonds, leading to enhanced stability of FTO. The behavior of SnO₂ and FTO catalysts for CO₂RR are summarized in Fig. 4e. SnO₂ catalysts exhibit good performance for CO₂ electro-reduction to formate by improving interaction with
HCOO\(^{-}\). Furthermore, oxidation state of FTO stabilized by strong F–Sn bonds under high cathodic overpotentials contributes the enhanced current density and durability. Thus, we expect that the enhanced current density and durability of FTO could allow the development of economically feasible CO\(_2\)RR technology.

**Discussion**

In summary, we obtained insights into the performance of doped-SnO\(_2\) catalysts for the CO\(_2\)RR to formate using a combination of flow-type single-cell experiments, in-situ/operando spectroscopy, and DFT calculations. Compared with traditional SnO\(_2\) catalysts, the nanoparticles synthesized using TDA were much smaller because this surfactant prevents particle agglomeration during SnO\(_2\) growth via micelle formation. The high dispersion of our catalysts allowed for a large number of oxide species to act as electrochemically active centers. The FTO/C catalyst exhibits higher performance than other doped catalysts, achieving partial faradaic efficiency (95% at 100 mA cm\(^{-2}\)) compared with traditional SnO\(_2\) catalysts, which signifi- cantly affects the CO\(_2\)RR activity, did not change significantly under an applied potential. These findings suggest that fluorine dopant played an important role in increasing the selectivity for formate on the FTO catalyst by modulating electronic structure of Sn and enhancing the durability by preventing reduction under reduction potentials. Our study provides insights for designing highly active and durable electrocatalysts for the electrochemical conversion of CO\(_2\)RR to formate.

**Methods**

**Preparation of SnO\(_2\) and doped-SnO\(_2\) catalysts.** To synthesize the SnO\(_2\) and doped-SnO\(_2\) catalysts, TDA (Sigma-Aldrich) was dissolved ultrasonically in a mixture of deionized water and ethanol. Then, SnCl\(_4\) (Sigma-Aldrich) was added, and the mixture was stirred for 3 h. The suspension was centrifuged, filtered, and washed several times with an ethanol solution. To remove excess TDA, the as-prepared SnO\(_2\) catalyst was transferred to a glass-lined stainless-steel autoclave and hydrothermally treated at 120 °C for 24 h. A detailed description of the formation of tin ethbutoxide intermediate in the ethanol solution and the formation of SnO\(_2\) through the hydrolysis reaction is described in Supplementary Note 1. ATO, FTO, and ITO were synthesized using the same procedure, except that the composition of the metal precursor was varied by adding antimony acetate (C\(_6\)H\(_9\)O\(_6\)Sb, Sigma-Aldrich), ammonium fluoride (NH\(_4\)F, Sigma-Aldrich), and indium chloride (InCl\(_3\), Sigma-Aldrich), respectively. Varying amounts of the dopant salts were added to 712 mg of SnCl\(_4\) to synthesize the doped-SnO\(_2\) sample. In ATO, 25.0 mg C\(_6\)H\(_5\)O\(_5\)Sb was used, in FTO, 19.48 g NH\(_4\)F, and in ITO, 109.6 g InCl\(_3\). Antimony and indium were doped in the form of mixing Sb\(_2\)O\(_3\) or In\(_2\)O\(_3\) with SnO\(_2\) during hydrolysis and condensation, respectively. On the other hand, fluorine was incorporated through oxygen substitution\(^{54}\).

**Preparation of SnO\(_2\)-based catalyst electrodes for the CO\(_2\)RR.** A catalyst ink was prepared by ultrasonically mixing 5 wt% of ionomer solution (Dowicide, 15 wt% target of catalyst) and SnO\(_2\)-based catalyst powder (30 mg) with ethanol (2 mL). The SnO\(_2\)-based catalyst electrodes were fabricated by spraying the prepared catalyst ink onto a GDL (Sigracet 39 BB, SGL Carbon) at 70 °C. The electrode area was 2 cm\(^2\) and the loading of SnO\(_2\) was fixed at 0.5 mg cm\(^{-2}\).

**Preparation of Fe-Ni foam electrodes for the oxygen evolution reaction (OER in alkaline).** Fe-Ni foam electrodes for the OER were fabricated by a simple dip-
coating method. The Ni foam was washed with deionized water and dried under nitrogen. After dipping in a 0.125 M FeCl$_3$ solution, the Ni foam was removed and dried in a convection oven at 70°C. The FeCl$_3$-coated Ni foam was then activated using a three-electrode system in 1 M KOH at a current density of 100 mA cm$^{-2}$ for 10 min. A graphite rod and Hg/HgO electrode were used as the counter and reference electrodes, respectively.

**Preparation of IrO$_2$/Pt coated Ti-foam electrodes for the oxygen evolution reaction (OER in neutral).** A catalyst ink was prepared by ultrasonically mixing 5 wt% of sonomer solution (Nafion, 10 wt% target of catalyst) and commercial iridium oxide catalyst powder (Alfa Aesar, 30 mg) with ethanol (2 mL). The electrodes were fabricated by spraying the prepared catalyst ink onto a Pt coated Ti foam at 70°C. The electrode area was 2 cm$^2$ and the loading of IrO$_2$ was fixed at 1 mg cm$^{-2}$. The reason of IrO$_2$ catalyst for OER in neutral electrolyte was described in Supplementary Note 2.

**Electrochemical CO$_2$RR flow cell tests.** A detailed schematic of the flow cell used for evaluating the electrochemical CO$_2$RR performance is shown in Supplementary Fig. 7. The fabricated SnO$_2$-based catalyst electrodes were used as the cathode. The active area of each electrode was 2 cm$^2$, and CO$_2$ as the reactant gas was fed into the serpentine flow field channel on the cathode side at a flow rate of 50 sccm. The electrolyte solution of 1 M KOH or 1 M K$_2$CO$_3$ was supplied to both the anode and cathode sides using a pump. An AEM (Dioxide Materials, X37-50 Grade RT) was used to separate the anode and cathode flow channels. All electrochemical tests were conducted using a VSP potentiostat (BioLogic, VMPSB-10), which was suitable for measurements up to 10 A. The reference electrode (Ag/AgCl, 3.5 M KCl) was inserted in the cathode flow line to measure and control the cathode potential.

The Faradaic efficiency of the catalyst was measured using GC and IC where points were taken at 18 min-intervals. The formate concentrations on the catholyte entering the GC, was connected to the cathode outline. Ultrahigh-purity helium gas conductivity detector were used to detect carbon-based gases (CO, CH$_4$, and C$_2$H$_4$) for the van der Waals dispersion correction. A kinetic energy cutoff of 500 eV was used with a plane-wave basis set. Gaussian smearing was applied with a smearing width of 0.1 eV. The geometries were fully relaxed until the residual force on the atoms converged to 0.01 eV/Å. The SnO$_2$ (110) supercell was modeled with a unit cell of the tetragonal space group (mp-856) obtained from the Materials Project. The four layers of the primitive unit cell that are cleaved to the (110) plane were expanded six times (2 × 3 × 4), yielding a supercell of 24 Sn and 48 O atoms with a constant lattice parameter of 6.83 Å × 9.73 Å × 13.67 Å. For the FTO (110) supercell, seven O atoms (−15%) were randomly replaced with F atoms. To simulate the SnO$_2$ and FTO crystal conditions under an applied potential of −1.0 V, the lattice constants of strained SnO$_2$ and FTO (110) bulk supercell were 6.74 Å × 9.60 Å × 13.48 Å and 6.81 Å × 9.70 Å × 13.62 Å, respectively. The Brillouin zone was sampled with a Monkhorst–Pack k-point mesh of (5 × 4 × 2) for bulk SnO$_2$ and FTO (110) supercells. To build the slab structure, a 20-Å vacuum gap was added along the c-axis of the stabilized supercells. The bottom two layers of the slab were fixed, while the top two layers were allowed to relax during geometry optimization. The Brillouin zone was sampled with a Monkhorst–Pack k-point mesh of (5 × 3 × 1) for SnO$_2$ and FTO (110) slab supercells.

The elementary steps of the electrochemical conversion reaction of CO$_2$ to HCOOH involving 2 electron pathway are described as follows:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{H}_2$$

$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\text{O}$

$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_2$ (HCOOH)

where $\text{R}$ represents the surface sites for molecule adsorption. The change in Gibbs free energy ($\Delta G$) at 298 K and 1 atm was calculated thorough $\Delta G = \Delta H - T \Delta S$, where $\Delta H$ is the total electronic energy obtained from the DFT optimization, $\Delta S$ is the change in the zero-point energies, $T$ is the temperature, and $\DeltaS$ is the change in entropy. The computational hydrogen electrode model$^{62}$ was applied to calculate the chemical potential of proton/ electron pairs, which scale to the half of the chemical potential of H$_2$ gas under standard conditions and electrons with an applied bias of $U$ ($-eU$). The pH contribution is considered by adding $k_B T \ln 10 \times pH$ to $\Delta G$, where $k_B$ is the Boltzmann constant. The $ZPE$ and $S$ of the molecules and adsorbates were determined from the calculated vibrational frequencies and NIST database$^{63,64}$, where all vibrations were treated in the harmonic oscillator approximation. The $ZPE$ and $S$ data are listed in Supplementary Tables 2 and 5, respectively.

**Data availability**

Source data are provided with this paper.

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Author contributions
H.-S.O. and Y.-J.K. conceived the idea, designed the experiments, and supervised the work. D.K.L. designed/simulated the DFT calculations. J.-Y.K. synthesized the catalysts, analyzed the data, and wrote the manuscript. W.H.L. conducted the electrochemical and in-situ experiments and wrote the manuscript. M.G.K. performed XANES analysis. J.P., Y.J., and B.K.M. contributed to the electrochemical analysis. T.-Y.S. and W.-S.L. contributed to the catalyst synthesis. All authors reviewed the manuscript and agreed with its content.

Competing interests
The authors declare no competing interests.

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