Surface Oxygen Injection in Tin Disulfide Nanosheets for Efficient CO₂ Electroreduction to Formate and Syngas

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HIGHLIGHTS

• A surface oxygen-injection strategy is proposed to synergistically modulate the electronic structure of the SnS₂ nanosheets, thereby regulating the oxophilicity of the catalyst surface.

• The surface oxygen doping facilitates the CO₂ activation and enhances the affinity for HCOO* species.

• The oxygen-injection SnS₂ nanosheets exhibit a remarkable Faradaic efficiency of 91.6% for carbonaceous products with a current density of 24.1 mA cm⁻² at -0.9 V vs RHE.

ABSTRACT

Surface chemistry modification represents a promising strategy to tailor the adsorption and activation of reaction intermediates for enhancing activity. Herein, we designed a surface oxygen-injection strategy to tune the electronic structure of SnS₂ nanosheets, which showed effectively enhanced electrocatalytic activity and selectivity of CO₂ reduction to formate and syngas (CO and H₂). The oxygen-injection SnS₂ nanosheets exhibit a remarkable Faradaic efficiency of 91.6% for carbonaceous products with a current density of 24.1 mA cm⁻² at -0.9 V vs RHE, including 83.2% for formate production and 16.5% for syngas with the CO/H₂ ratio of 1:1. By operando X-ray absorption spectroscopy, we unravel the in situ surface oxygen doping into the matrix during reaction, thereby optimizing the Sn local electronic states. Operando synchrotron radiation infrared spectroscopy along with theoretical calculations further reveals that the surface oxygen doping facilitated the CO₂ activation and enhanced the affinity for HCOO* species. This result demonstrates the potential strategy of surface oxygen injection for the rational design of advanced catalysts for CO₂ electroreduction.

KEYWORDS

Oxygen injection; Tin disulfide; CO₂ electroreduction; Formate; Syngas

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1 Introduction

Electroreduction of carbon dioxide (CO$_2$RR) into high-value fuels and feedstocks offers a compelling pathway not only to meet the increasing energy demand, but also to alleviate the environmental crisis caused by CO$_2$ emissions [1–3]. According to the gross-margin model, formate is considered to be one of the most economically feasible products in the CO$_2$RR, which can be widely used as an important raw material in the chemical and pharmaceutical industries, as well as a potential hydrogen carrier and the liquid fuel for proton-exchange membrane fuel cell [4–6]. Up to now, various metal-based electrocatalysts, such as Pd, In, Hg, Pb, Cd, and Sn, have been exploited to achieve the CO$_2$ electroreduction to formate [7–13]. Among these electrocatalysts, Sn-based materials have attracted considerable attention due to their advantages of earth abundance, non-toxicity, and low cost. Unfortunately, the catalytic performance of most Sn-based materials is still limited by the high energy barrier for CO$_2$ activation, which is usually attributed to the poor stabilization of CO$_2^*$− intermediates [14–18]. To this end, it is of great significance to develop an efficient and durable Sn-based catalysts for the CO$_2$ electroreduction to formate.

Given that the CO$_2$ molecule activation is closely related to the number and inherent activity of active sites, many effective strategies have been employed to tailor the active sites of electrocatalysts for enhancing the efficiency of the CO$_2$ electroreduction to formate [19–21]. The surface chemistry modification, as a powerful strategy, has attracted great interest in adjusting electronic properties of active sites to target intermediate adsorption energy as well as harvest high selectivity [22–25]. For example, Xie et al. developed a general amino acid modification approach on Cu electrodes for the selective electroreduction of CO$_2$ toward hydrocarbons [26]. Previous theoretical calculations have confirmed that the *OCHO binding energy is closely associated with the oxophilicity of the catalyst surface, which can be achieved by modifying the surface of the electrocatalyst with oxygen atom [27]. For instance, Gao et al. reported a phenomenon that partially oxidized atomic cobalt layers effectively adjusted the electronic structure, promoted the activation of CO$_2$, and stabilized the relevant key intermediates, thereby enhancing the efficiency of the CO$_2$ electroreduction to liquid fuel [28]. As another example, Won et al. prepared hierarchical Sn dendrites and found that the natural oxygen content is closely related to the stability of CO$_2^*$− intermediates and the selectivity of formate [29]. To improve the catalytic performance of Sn-based materials, oxygen modification is a promising strategy to regulate the surface oxophilicity of the catalysts and further manipulate their electronic structure. In fact, most of the catalysts with surface chemical modification have undergone structural evolution of the active phase under operation conditions, leading to deviations in the understanding the nature of the active site. Therefore, monitoring the structural evolution of Sn-based catalysts with surface oxygen modification under realistic working conditions is crucial for understanding the nature of the active phase and the rational design of targeted CO$_2$RR catalysts.

Herein, the SnS$_2$ nanosheets arrays on the carbon paper with surface oxygen modification were rationally designed under the guidance of density function theory (DFT) to effectively electroreduce CO$_2$ into formate and syngas (CO and H$_2$). The introduction of oxygen into the surface of SnS$_2$ nanosheets achieved the exposure of Sn active sites and optimal Sn electronic states, thereby enhancing the adsorption and activation of CO$_2$. Specifically, the SnS$_2$ nanosheets with surface oxygen modification exhibit a remarkable Faradaic efficiency of 91.6% for carbonaceous products at −0.9 V vs RHE, including 83.2% for formate production and 16.5% for syngas with the CO/H$_2$ ratio of 1:1. Operando X-ray absorption spectroscopy unravels that the in situ surface oxygen doping into the matrix under working conditions effectively changes the local electronic state of Sn, thereby providing an optimized electronic structure to improve CO$_2$RR performance. In addition, operando synchrotron radiation infrared spectroscopy and DFT calculations further confirm that the local electronic state of Sn is manipulated through surface oxygen modification, thereby promoting the CO$_2$ activation and enhancing the affinity for HCOO* species.

2 Experimental Section

The experimental details are provided in Supporting Information (SI). This section briefly summarizes the synthesis measurements.

In a typical synthesis of SnS$_{2-x}$O$_x$/CC, 5 mmol of SnCl$_4$·5H$_2$O and 15 mmol of thioacetamide were dissolved in 40 mL of deionized water. The mixture and carbon paper (2 × 2) were then transferred into a Teflon-lined
stainless-steel autoclave, followed by being heated to 190 °C for 8 h. After the mixture was cooled down naturally to room temperature, the SnS₂/CC was washed by water three times and ethanol twice to remove any possible ions, followed by being dried under vacuum at 60 °C for 12 h. The SnS₂-xOₓ/CC was prepared by placing the SnS₂/CC in the muffle furnace that had been heated at 300 °C for several minutes.

3 Results and Discussion

3.1 Preparation and Characterization of SnS₂-xOₓ/CC

At first, to gain insight into the effect of surface oxygen-injection engineering on electronic properties of SnS₂ nanosheets, we conducted DFT calculations by using the SnS₂ slab with/without oxygen injection as the models (Fig. 1a, b). Compared with the pristine SnS₂, the surface oxygen injection leads to a new additional state near the Fermi level (Fig. 1c, d), which is beneficial to manipulate the local electronic structure of Sn and expose the active site of Sn at the edges. Notably, O 2p states also contributed the unoccupied part of these levels, making them serve as the highly catalytically active sites. Furthermore, the electronic localization functions (ELF) exhibit that the charge density is mainly derived from the S atoms for both the SnS₂ with/without oxygen injection (Fig. S1). Owing to the introduction of oxygen atoms, the electron density of the whole system has undergone distinctly change, further indicating surface oxygen injection effectively tailors the local electronic structure of Sn.

Then, the SnS₂ nanosheets arrays with partially oxidized surface on the carbon paper (denoted as SnS₂-xOₓ/CC) were prepared, as schematically illustrated in Fig. 2a. Specifically, the pristine SnS₂ nanosheets arrays were directly grown on the carbon paper by a simple hydrothermal method. Afterward, the SnS₂-xOₓ/CC was further synthesized by the low-temperature calcination of the as-prepared SnS₂/CC under the air atmosphere. The morphology of the SnS₂-xOₓ/CC was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 2b, the final products present a hierarchical nanosheets arrays composed of SnS₂-xOₓ nanosheets and flexible carbon paper. The TEM images of the SnS₂ and SnS₂-xOₓ took the nanosheet morphology (Figs. 2c and S2a), whereas the SnS₂ nanosheets were completely oxidized into SnO₂ nanoplatelets (Fig. S3). The high-resolution transmission electron microscopy (HRTEM) image in Fig. 2d shows that the SnS₂-xOₓ lattice fringes with an interplanar distance of 0.32 nm indexed to the (002) facets of SnS₂, confirming the as-obtained SnS₂-xOₓ nanosheets retain its pristine crystal structure (Fig. S2b, c) [30]. Besides, there is an obvious circle of amorphous layer at the edge of the SnS₂-xOₓ nanosheet, which is attributed to the partial oxidation on the surface of the SnS₂ nanosheet. In addition, the homogeneous fast Fourier transform (FFT) pattern indicates the SnS₂ phase recorded from [002] orientation (inset in Fig. 2e).

The element of O was uniformly distributed on the whole SnS₂-xOₓ nanosheet which can be further confirmed by the high-angle annular dark-field energy-dispersive X-ray spectroscopy (HAADF-EDS) elemental mapping and EDS spectrum (Figs. 2f and S4).

To further investigate the phase composition and electronic structure of the SnS₂-xOₓ/CC, we performed X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurement. As evidenced by the XRD patterns in Fig. S5, the SnS₂/CC and SnS₂-xOₓ/CC exhibited the diffraction peaks at 30.74°, 32.09°, and 44.98°, which were indexed to the (200), (101), and (211) planes of hexagonal SnS₂ (JCPDS No. 23–0677) [31]. Remarkably, no additional peaks corresponding to the phases of SnO₂ could be found, indicating that the surface oxygen injection did not change the crystalline phase of SnS₂. We further carried out the XPS measurements to clarify the form of O existing in SnS₂-xOₓ/CC. As disclosed by XPS survey spectra, a weak signal of O was recorded in SnS₂-xOₓ/CC, further confirming successful introduction of O (Figs. S6 and S7). In addition, the peaks at 495.3 and 486.8 eV were attributed to Sn 3d₃/₂ and Sn 3d₅/₂ of SnS₂-xOₓ/CC, respectively (Fig. S8) [32]. Compared with the SnS₂/CC, the Sn 3d₃/₂ and 3d₅/₂ peaks for SnS₂-xOₓ/CC shifted to higher binding energies, due to the larger electronegativity of O than that of S.

The surface-sensitive synchrotron radiation soft X-ray absorption structure (XAS) was further employed to investigate the changes in the local electronic structure of SnS₂ caused by surface oxygen-injection engineering. As shown in Fig. S9, O K-edge XAS spectra for SnS₂-xOₓ/CC and pure SnO₂/CC displayed similar shapes, implying SnO₂ species were formed on the surface of SnS₂-xOₓ/CC, further confirming the surface oxygen injection successfully replaced the S atoms. In addition, S L-edge XAS spectra exhibited the two characteristic peaks located at 163.3 eV (S-Sn π⁺
peak) and 166.6 eV (S-Sn σ* peak) observed in pure SnS$_2$/CC and the SnS$_{2-x}$O$_x$/CC (Fig. S10). Compared with pristine SnS$_2$/CC, the relative strength of S-Sn for SnS$_{2-x}$O$_x$/CC was slightly reduced, which was attributed to the substitution of partial S atoms on the surface of SnS$_{2-x}$O$_x$/CC by O atoms. Meanwhile, the X-ray absorption near-edge structure (XANES) measurement was employed to further investigate the effect of surface oxygen injection. Compared with pristine SnS$_2$/CC, the white line peak of the SnS$_{2-x}$O$_x$/CC shifted to the high-$E$ region, due to the electronegativity of O being greater than that of S, in consistent with the results of Sn 3d XPS spectrum (Fig. S11). Given that the white line peak of Sn K-edge intensity originating from the transition of the 1s to 5p orbital, the increase in the white line peak intensity after surface oxygen injection indicates the increases in the possibility of electron transition from the 1s-5p orbital. The above results reveal the surface oxygen injection effectively manipulates the local electronic structure of Sn.

Furthermore, the Fourier transform (FT) $k^2$-weighted extended XAFS (EXAFS) spectrum of the Sn K-edge was employed to further reveal the effect of surface oxygen injection on the local electronic structure of Sn at the atomic level. Considering the surface oxygen injection into the SnS$_2$ nanosheets, we performed out least-squares EXAFS curve fitting analysis for Sn by considering two backscattering paths, including Sn–S and Sn–O. Compared with the SnS$_2$/CC, the Sn K-edge FT-EXAFS curve for SnS$_{2-x}$O$_x$/CC presented a new peak at 1.49 Å, which is ascribed to the Sn–O coordination (Fig. 2a) [33]. By quantitative EXAFS curve fitting analysis, the coordination number of Sn-S for

Fig. 1 Top view and side view of the model for a pristine SnS$_2$ and b SnS$_{2-x}$O$_x$. Calculated DOS of c SnS$_2$ and d SnS$_{2-x}$O$_x$ slabs.
SnS$_{2-x}$O$_x$/CC is confirmed to be 4.3, smaller than that of pristine SnS$_2$/CC (6.0), and the coordination number of Sn–O is verified to be 2.1, further confirming surface oxygen injection successfully replaced the S atoms (Table S1 and Fig. S12). Moreover, the wavelet transform (WT) of Sn K-edge EXAFS oscillations exhibited the intensity maxima at 4.3 Å$^{-1}$ and around 8.2 Å$^{-1}$ of SnS$_{2-x}$O$_x$/CC, which associate with Sn–O and Sn–S contributions, respectively (Fig. S13). Taken together, the successful injection of surface oxygen effectively manipulated the local electronic structure of SnS$_2$.

3.2 Electrocatalytic CO$_2$RR Performances of the SnS$_{2-x}$O$_x$/CC

Surface oxygen-injection engineering provides a potential prospect for enhancing the CO$_2$ electroreduction. The electrocatalytic CO$_2$ reduction activities of the three Sn-based catalysts were evaluated using a three-electrode H-cell in CO$_2$-saturated 0.5 M KHCO$_3$. The linear sweep voltammetric (LSV) curves in Fig. S14 revealed that the SnS$_{2-x}$O$_x$ nanosheets exhibited higher current density than that of pristine SnS$_2$ nanosheets, confirming the injection
of oxygen effectively enhanced the electrocatalytic activity of SnS$_2$/CC. Particularly, the geometrical current density of SnS$_{2-x}$O$_x$/CC achieved 19.68 mA cm$^{-2}$, which was 2.7 times higher than that of pristine SnS$_2$/CC at overpotential of −0.8 V vs RHE (Fig. 2a). For these three Sn-based catalysts, H$_2$, CO, and formate were the main catalytic products, which are quantified by online gas chromatography and $^1$H NMR analysis (Fig. S15). Figure 2b exhibits partial current density for carbonaceous products (CO and formate), respectively. At all applied potentials, the SnS$_{2-x}$O$_x$/CC presented the largest current density among the three electrocatalysts, demonstrating the high activity for CO$_2$ electroreduction. As shown in Fig. 2c, the SnS$_{2-x}$O$_x$/CC displayed the highest Faradaic efficiency (FE) for carbonaceous products among the three electrocatalysts, while the pristine SnS$_2$/CC exhibited the lowest FE value. At −0.9 V vs RHE, the SnS$_{2-x}$O$_x$/CC exhibited the FE of 91.8% for carbonaceous products, including the FE of 83.5% for formate production and the FE of 16.5% for syngas with the H$_2$/CO ratio of 1:1. It is worth noting that such syngas ratio is optimal for multiple chemical synthesis (e.g., Fischer–Tropsch synthesis, fermentation and alcohol synthesis, and hydroformylation processes). Furthermore, the as-prepared SnS$_{2-x}$O$_x$/CC displayed an excellent durability for 10-h potentiostatic test with the less than 3% decay in current density, together with the FE for formate and CO keeping steady at −0.9 V vs RHE (Fig. 2d). The above results demonstrate that the SnS$_{2-x}$O$_x$/CC represents a promising catalyst for persistently producing formate and syngas toward CO$_2$RR.

Inspired by surface oxygen injection to improve the CO$_2$ electroreduction performance of SnS$_2$/CC, we studied the microscopic reaction kinetics of the pristine SnS$_2$/CC and SnS$_{2-x}$O$_x$/CC. Based on cyclic voltammogram measurements at different scan rates, the double-layer capacitance ($C_{dl}$) value increased from 3.27 mF cm$^{-2}$ of the pristine SnS$_2$/CC to 3.75 mF cm$^{-2}$ of the SnS$_{2-x}$O$_x$/CC, indicating that surface oxygen injection effectively increases the electrochemical active surface area (ECSA) of the electrocatalysts (Figs. S16 and S17). Given that the ECSA of the electrocatalysts is positively correlated with the active sites, we have reason to believe that the surface oxygen modification effectively exposes the active site of Sn. The Tafel plots were further employed to verify the rate-limiting step of the Sn-based catalysts in the CO$_2$RR process. The Tafel slopes of the Sn-based catalysts were all close to 118 mV dec$^{-1}$, demonstrating that the activation of CO$_2$ served as the rate-limiting step (Fig. S18) [34,35]. In addition, the Nyquist plots were used to confirm the facilitated electron transfer process [36]. The SnS$_{2-x}$O$_x$/CC displayed the charge transfer resistance ($R_{CT}$) of 12.1 Ω, which was smaller than that (15.8 Ω) of SnS$_2$/CC (Fig. S19). Therefore, surface oxygen injection effectively accelerates the charge transfer process of SnS$_2$/CC during the CO$_2$RR (Fig. 3).

### 3.3 Operando X-ray Absorption Spectroscopy Study

Given that the bulk phase stability of transition metal chalcogenides with heat treatment is destroyed, the bulk phase is in a relatively unstable state [37]. Based on the equilibrium theory of crystalline chemistry, the catalyst in the electrolyte driven by both energetical and kinetical force will tend to freely optimize the structure of the entire bulk, so that the bulk tends to a relatively stable state [38–41]. Therefore, we employed operando XAFS measurements to monitor the structural evolutions of the SnS$_{2-x}$O$_x$/CC under realistic working conditions. Figure 4a shows the operando Sn $K$-edge XANES spectra at different applied potentials, along with the data for Sn foil, SnS$_2$, and SnO$_2$ as references. When cathodic potentials were applied, the absorption edge of Sn $K$-edge XANES spectra shifted toward low-$E$ side compared to the case of the open-circuit condition, indicating the decrease in the Sn valence state during CO$_2$RR process. Furthermore, when a cathodic potential of −0.9 V versus RHE was applied, the white line peak intensity was significantly increased in relation to the case (−0.4 V versus RHE), indicating more 5$p$ electrons participate in the reaction. After the reaction, the white line peak approximately returned to the state (−0.4 V versus RHE), further confirming that the SnS$_{2-x}$O$_x$/CC catalyst undergone in situ reconstruction during the reaction and tended to form a relatively stable state.

Furthermore, the EXAFS was further employed to reveal the atomic reconstruction of the SnS$_{2-x}$O$_x$/CC catalyst under working conditions (Figs. 4b and S20). At first sight, the Fourier transform curves of SnS$_{2-x}$O$_x$/CC displayed a significantly dampening in the Sn–S coordination peak and a heightening in the Sn-nonmetallic coordination peak under working condition. Specifically, at the applied potential of −0.4 V versus RHE before the occurrence of CO$_2$RR, the
EXAFS fitting results showed that the Sn–O coordination number increased from 2.5 to 3.6, which may be ascribed to the further doping of surface oxygen into the SnS$_2$ lattice during the reaction. To further verify the above conjecture, we performed XRD on the SnS$_{2-x}$O$_x$/CC after reaction. As expected, the intensity of the diffraction peaks of SnS$_2$ was significantly reduced after the reaction, and the characteristic peak of SnO$_2$ appeared in the SnS$_{2-x}$O$_x$/CC after reaction (Fig. S21). Moreover, at the potential of -0.9 V versus RHE during CO$_2$RR, Sn–O coordination number arose from 3.6 to 4.2 and the Sn–S coordination number remained unchanged, which may be attributed to the adsorption of the reaction intermediate species. When the cathode potential was removed, the Sn–O coordination number recovered to the state at -0.4 V, while the coordination number of Sn–S remained unchanged (Table S2). The above results indicated that the SnS$_{2-x}$O$_x$/CC had undergone dynamic surface reconstruction and surface oxygen doping plays a critical role under reaction conditions.

**Fig. 3**  
(a) Geometrical current densities over SnS$_2$/CC, SnS$_{2-x}$O$_x$/CC, and SnO$_2$/CC.  
(b) Current densities for carbonaceous product (C-product) over SnS$_2$/CC, SnS$_{2-x}$O$_x$/CC, and SnO$_2$/CC.  
(c) Faradaic efficiencies for formate, H$_2$, and CO production over SnS$_2$/CC, SnS$_{2-x}$O$_x$/CC, and SnO$_2$/CC.  
(d) Plot of geometrical current density ($j$) and Faradaic efficiencies for C-product versus time over the SnS$_{2-x}$O$_x$/CC at a constant potential of -0.9 V vs RHE.
3.4 *Operando* Synchrotron Radiation Fourier Transform Infrared Spectroscopy Study

*Operando* synchrotron radiation Fourier transform infrared spectroscopy (SR-FT-IR) was further employed to investigate the catalytic mechanism for the well-designed SnS$_{2-x}$O$_x$/CC during the CO$_2$RR. All SR-FTIR spectra were recorded with the electrocatalysts at CO$_2$RR catalytic process (open circuit, −0.6, −0.7, −0.8, and −0.9 V) to reveal the production and transformation of key intermediates. As displayed in Fig. 4c, the monodentate carbonate groups (m-CO$_3^{2−}$) appeared at the peaks of ~1520 cm$^{-1}$, demonstrating that more CO$_2$ was adsorbed on the surface of electrocatalyst with the decrease in applied voltage. Meanwhile, a new characteristic peak appeared in the SR-FTIR spectra of ~1694 cm$^{-1}$ (CO$_2$·− radicals) and the intensity of peak continually increased as the applied potentials decreased, indicating that the CO$_2$ molecules adsorbed on the catalyst surface were activated to CO$_2$·− radicals during the reaction $^{[42]}$. Meanwhile, as the cathode potential decreases, the peak intensity at ~1541 cm$^{-1}$ (HCOO$^-$) increased further confirming the excellent proton trapping ability of CO$_2$·− radicals $^{[33]}$. The peaks at ~1354 cm$^{-1}$ and ~1660 cm$^{-1}$ is ascribed to the symmetry vibration of the HCOO$^*$ intermediates, which corresponds to the key intermediates or the products for CO$_2$ electroreduction $^{[43]}$. Based on the above-mentioned operando SR-FTIR analysis, the pathway of electroreduction from CO$_2$ to HCOOH conversion by the SnS$_{2-x}$O$_x$/CC could be proposed as the following reactions (Fig. 4d):

\begin{align*}
\text{Step 1:} & \quad \text{CO}_2(g) + e^{-} + \rightarrow \text{CO}_2^* \quad \text{(Activation process)} \quad (1) \\
\text{Step 2:} & \quad \text{CO}_2^* + \text{HCOO}^- (aq) \rightarrow \text{HCOO}^* + \text{CO}_2^{2+} \quad \text{(Surface reaction)} \quad (2)
\end{align*}
Step 3: \[
\text{HCOO}^- + \text{HCO}_2^- + e^- \rightarrow \text{HCOOH} (l) + \text{CO}_3^{2-} (\text{Desorption process})
\] (3)

3.5 Density Functional Theory (DFT) Calculations

DFT calculations were employed to elucidate the catalytic contribution from partial oxidation at SnS$_{2-x}$O$_x$ for CO$_2$RR. The models for pristine SnS$_2$ and SnS$_{2-x}$O$_x$ were chosen for the simulation. Figure S22 shows optimized adsorption configurations of HCOO$^*$ intermediates on the armchair edges of the pristine SnS$_2$ slab and SnS$_{2-x}$O$_x$ slab with distinguishable Sn-O distances, from the material [44]. Specifically, the Sn–O bond length ($d_{\text{Sn-O}}$) is 2.28 Å for SnS$_2$, while the bond length $d_{\text{Sn-O}}$ for SnS$_{2-x}$O$_x$ is reduced to 2.24 Å, implying that the surface oxygen injection effectively enhances the binding to the HCOO$^*$ intermediate. Besides, DFT calculations were further conducted on the Gibbs free energy ($\Delta G$) with multiple elementary reaction steps over SnS$_2$ with/without oxygen injection. As exhibited in Fig. 4e, for both SnS$_2$ and SnS$_{2-x}$O$_x$, the formation of HCOO$^*$ is further confirmed to be the rate-limiting step for formate, which is consistent with the results of Tafel slopes. For the SnS$_{2-x}$O$_x$ slab, the $\Delta G$ for HCOO$^*$ formation ($\Delta G_{\text{HCOO}^*}$) was calculated to be 0.97 eV, which is much lower than that for pristine SnS$_2$ slab (1.31 eV), indicating surface oxygen injection enhanced the activation of CO$_2$ and correspondingly facilitated the formation of HCOO$^*$. To gain an in-depth insight into the nature of surface oxygen doping enhancing the intrinsic activity of SnS$_2$, we calculated the projected density of state of HCOO$^*$ absorbed SnS$_2$ and SnS$_{2-x}$O$_x$ (Fig. 4f). In the HCOO$^*$ PDOS, the dominant features are that HCOO$^*$ exhibits strong interaction with the valence band region of SnS$_2$ and SnS$_{2-x}$O$_x$, which leads to strong chemical adsorption. Notably, the state density of HCOO$^*$ overlaps more with the orbital of Sn (5p) in SnS$_{2-x}$O$_x$ with regard to that in SnS$_2$, and the higher occupied state of HCOO$^*$ is near the Fermi level, indicating that HCOO$^*$ has a stronger interaction with SnS$_{2-x}$O$_x$, which is consistent with the calculation result of $\Delta G_{\text{HCOO}^*}$. Furthermore, the charge density differences calculations also show that more electrons gather around the adsorption site in SnS$_{2-x}$O$_x$, indicating that the surface oxygen injection makes the SnS$_2$ edges exhibit a stronger affinity for HCOO$^*$ species (Fig. S23). The above results confirm that surface oxygen injection alters the local electronic structure of Sn atom with optimal $\Delta G_{\text{HCOO}^*}$ to effectively facilitate the production of formate over CO$_2$RR. Particularly, the above theoretical calculation results are consistent with the previous experimental results.

4 Conclusions

In conclusion, we developed SnS$_2$ nanosheets with surface oxygen modification for CO$_2$ electroreduction to formate and syngas (CO and H$_2$). The surface oxygen-injection engineering achieved exposure of Sn active site and optimal Sn electronic states, thereby enhancing the adsorption and activation of CO$_2$. Surface oxygen injection on SnS$_2$ nanosheets significantly improved electrocatalytic activity and selectivity of CO$_2$ reduction to formate and syngas (CO and H$_2$). Specifically, at −0.9 V vs RHE, the SnS$_{2-x}$O$_x$/CC exhibits the highest FE of 91.6% for carbonaceous products, including the FE of 83.2% for formate production and the FE of 16.5% for syngas with the H$_2$/CO ratio of 1:1. Moreover, the as-prepared SnS$_{2-x}$O$_x$/CC displays an excellent durability for 10-h potentiostatic test with less than 4% decay in current density. Operando XAS unravels that the in situ surface oxygen doping into the matrix under working conditions effectively modulates the Sn local electronic state. Operando SR-FTIR and DFT calculations reveal that the surface oxygen doping enhanced the affinity for HCOO$^*$ species by manipulating the Sn electronic states and accelerated the CO$_2$ activation. This work opens a span-new door for the design of advanced catalysts for CO$_2$ electroreduction.

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Author Contributions TC, TY, and WZ developed the idea and designed experiments. TC, XS, WZ, LW, and TD performed the catalyst synthesis and characterizations and FTIR measurements and electrochemical experiments. LC and TD performed the TEM characterization. WZ and XL made the XAFS calculation and commented on the manuscript. All authors discussed the results and commented on the manuscript.
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