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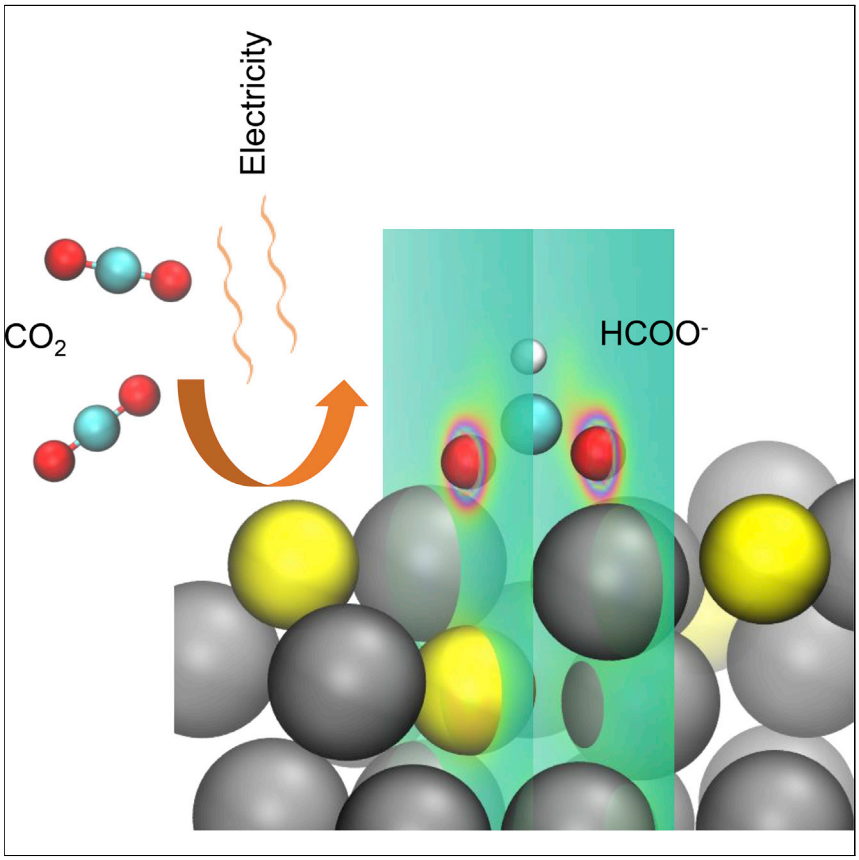

The electrochemical reduction of carbon dioxide (CO_2RR) offers a compelling route to energy storage and high-value chemical manufacture. The presence of sulfur atoms in catalyst surfaces promotes undercoordinated sites, thereby improving the electrochemical reduction of CO_2 to formate. The resulting sulfur-modulated tin catalysts accelerate CO_2RR at geometric current densities of 55 mA cm^{-2} at −0.75 V versus RHE with a Faradaic efficiency of 93%.

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HIGHLIGHTS

Electrochemical reduction of CO_2 to renewable fuels is urgently needed

The incorporation of sulfur into tin favors formate generation

Sulfur-modulated tin increases the CO_2 reduction current density

Sulfur-modulated tin provides excellent stability

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Sulfur-Modulated Tin Sites Enable Highly Selective Electrochemical Reduction of CO_2 to Formate

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SUMMARY

Electrochemical reduction of carbon dioxide (CO_2RR) to formate provides an avenue to the synthesis of value-added carbon-based fuels and feedstocks powered using renewable electricity. Here, we hypothesized that the presence of sulfur atoms in the catalyst surface could promote undercoordinated sites, and thereby improve the electrochemical reduction of CO_2 to formate. We explored, using density functional theory, how the incorporation of sulfur into tin may favor formate generation. We used atomic layer deposition of SnS_x followed by a reduction process to synthesize sulfur-modulated tin (Sn(S)) catalysts. X-ray absorption near-edge structure (XANES) studies reveal higher oxidation states in Sn(S) compared with that of tin in Sn nanoparticles. Sn(S)/Au accelerates CO_2RR at geometric current densities of 55 mA cm^{-2} at −0.75 V versus reversible hydrogen electrode with a Faradaic efficiency of 93%. Furthermore, Sn(S) catalysts show excellent stability without deactivation (<2% productivity change) following more than 40 hours of operation.

INTRODUCTION

The electrochemical reduction of carbon dioxide (CO_2RR) offers a compelling route to energy storage and high-value chemical manufacture.[1–4] It enables the use of increasingly abundant renewable energy sources, such as solar and wind, to drive the conversion of CO_2 to renewable fuels and feedstocks. This approach stands to reduce present-day dependence on conventional fuels and also help mitigate net CO_2 emissions. Despite recent breakthroughs, the energy efficiency of CO_2RR is still far from being a viable alternative to fossil energy sources.[4–7] Improvements in selectivity and partial current density with robust and stable long operating times are of crucial importance to continue advances in the direction of commercial viability.

Formate is one interesting product among the variety that can be synthesized via CO_2RR. It can be directly used as a fuel, as a means of H_2 storage, or as a feedstock in the synthesis of fine chemicals of interest to the pharmaceutical industry.[8,9] A recent paper utilizing a gross-margin model for defining technoeconomic benchmarks for CO_2 reduction showed that formate and carbon monoxide may offer paths to economically viable products.[10] Unfortunately, in the case of formate, high selectivity has been achieved only at the expense of low current density, yielding

Context & Scale

With rapid advances in the efficient and cost-effective conversion of sunlight to electrical power, the development of storage technologies for renewable energy is even more urgent. Using renewable electricity to convert CO_2 into formate simultaneously addresses the need for storage of intermittent renewable energy sources and the need to reduce greenhouse gas emissions. We report an increase of greater than 4-fold in the current density (hence the rate of reaction) in formate electrosynthesis compared with relevant controls. Our catalysts also show excellent stability without deactivation (<2% productivity change) following more than 40 hours of operation.

impractically low partial current densities (j_{HCOO^-}). In addition, many catalysts exhibit rapid deactivation within hours.[4,11–15]

Metal surfaces have been widely used for the heterogeneous electroreduction of CO_2 due to their robustness and superior catalytic activity.[6,14,16] Different strategies have been explored to control selectivity, reduce overpotentials, and increase energy efficiency.[17–26] From a materials perspective, the choice of metals can be used to tailor CO_2RR selectivity. For example, metals such as Pd, Pb, Co, Hg, In, Bi, Cd, or Sn have been reported to favor selectivity toward formate over carbon monoxide or hydrogen.[4,13,17–24] On the other hand, it has been shown that the presence of high-index facets, undercoordinated sites, and adatoms can improve CO_2RR energetics as the energy required for the intermediate steps in the electroreduction of CO_2 is lowered.[25–27]

The use of metal-oxide-derived catalysts has been found to increase performance in CO_2 reduction when compared with their fully reduced counterparts.[4,12,21] Metal electrodes obtained from the reduction of metal oxides exhibit a prominent increase in selectivity and provide lower overpotentials in the electrosynthesis of CO and ethylene.[28] This is ascribed to a combination of an increased number of undercoordinated sites, the presence of oxygen promoters in metal oxides, and the synergetic effect between remaining oxide species and native metal atoms.[4,21,28]

Here, we demonstrate the use of sulfide-derived metal catalysts to promote a high number of favorable catalytic sites. We obtain, as a result, high selectivity and high partial current density for CO_2RR to formate. We hypothesized that sulfur-modulated tin catalysts (Sn(S)) could offer superior catalytic selectivity, since the removal of sulfur atoms incorporated in the Sn slab leads to a surface lattice distortion, thereby generating undercoordinated active Sn sites. We developed a materials strategy based on atomic layer deposition that combines ultra-sharp features—which enable exploitation of field-induced reagent concentration (FIRC)[3]—with the benefits of a tin sulfide-derived catalyst. As a result, we report high current density to geometric formate (~55 mA cm^{-2}). The new catalysts exhibit excellent stability over the course of a 40-hr initial study.

RESULTS AND DISCUSSION

Computational Studies

We first sought to model the effect on the catalytic activity of CO_2RR to formate provided by doping sulfur atoms into Sn slabs. To this end, we carried out a computational study in which we systematically varied the sulfur content from pure tin to tin(II) sulfide. Density functional theory (DFT) calculations were used to probe the energetics along the different CO_2RR pathways toward formate, carbon monoxide, and hydrogen. Different sulfur contents are expected to modify the surface morphology and electronic structure thereby affecting the CO_2RR activity (Figure S1). The electrochemical reduction of CO_2 to formate is known to proceed via an initial proton-coupled electron transfer to form a bound formate intermediate (HCOO*).[25] Other competing reaction pathways have different predominant intermediates. Carbon monoxide evolution, for example, typically proceeds via a bound carboxylate intermediate (COOH*).[3,29] The hydrogen evolution reaction (HER), on the other hand, requires a bound proton (H*) intermediate.[30]

A highly selective catalyst for the production of formic acid will favor the formation of formate over carboxylate and proton intermediates. To assess the selectivity and

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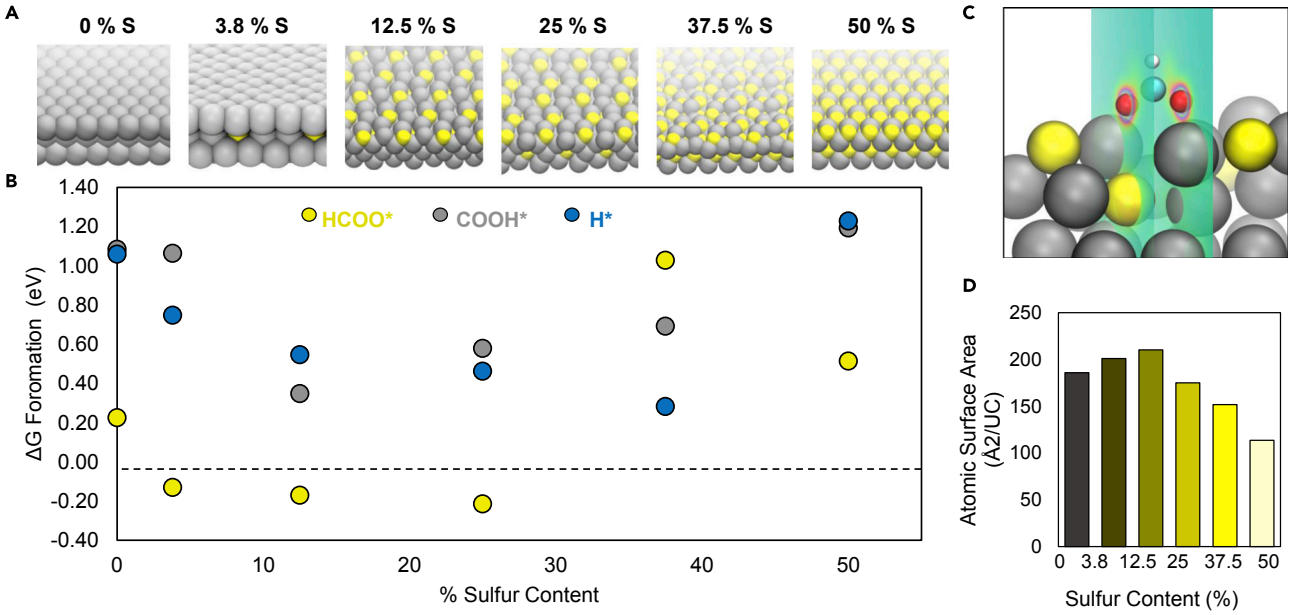

Figure 1. Computational Investigation of Sulfur-Modulated Tin System

(A) Optimized surface slab structures of pure Sn, S-modulated Sn, and SnS.

(B) Gibbs free energies of formation ($\Delta G_{formation}$) for HCOO* (yellow), COOH* (gray), and H* (blue) intermediates, which are the rate-limiting intermediates along the reaction pathway to produce formate, carbon monoxide, and hydrogen gas, respectively.

(C) Volume slice of the charge densities through the middle of the oxygen atom of a bound HCOO* intermediate.

(D) Atomic accessible surface area of the metal slab normalized to the number of tin atoms as a function of sulfur content.

limiting potentials for each product, we calculated the Gibbs free energy of formation (ΔG_f) for HCOO*, COOH*, and H* intermediates on the (100) surface of Sn(S) as a function of sulfur content (Figure 1B and Table S3). The bound HCOO* intermediate visualized with a volume slice of the electronic charge densities through the center of the oxygen atoms is shown in Figure 1C. Here, the free energy of formation is the reaction free energy necessary to electrochemically reduce CO_2 to a surface intermediate species at 0 V versus reversible hydrogen electrode (RHE) at pH 0, 298 K, and 1 atm. In the majority of cases, the Gibbs free energy of formation for HCOO* is lower than that of COOH*. This suggests that the production of formic acid is the energetically preferred pathway. The reaction energy diagram for electroreduction of CO_2 to formic acid with catalysts of various sulfur content is shown in Figure S2. For both formate and carboxylate intermediates, the same trend is observed whereby a slight doping of S into Sn drastically lowers ΔG_f and, as the content of S increases, so does the free energy of formation. An opposite trend was observed for H*, whereby the free energy of formation increases upon S incorporation.

Interestingly, the ΔG_f for HCOO* was found to be negative for 3.8% (−0.13 eV), 12.5% (−0.17 eV), and 25% (−0.21 eV) S-doped Sn. This suggests that the formation of the rate-limiting formate intermediate is thermodynamically downhill when sulfur is slightly doped into tin.

The theoretical limiting potential for CO_2RR—the calculated minimum thermodynamic potential necessary to drive the electrochemical reaction forward—was found to be closest to zero for 3.8% S with a value of −0.07 V versus RHE at pH 0, 298 K, and 1 atm (Table S4). The limiting potential is taken from the reaction energy diagram (Figure S2) and is the largest ΔG along the reaction pathway. For this same composition, the limiting potentials for CO production and HER were much more negative

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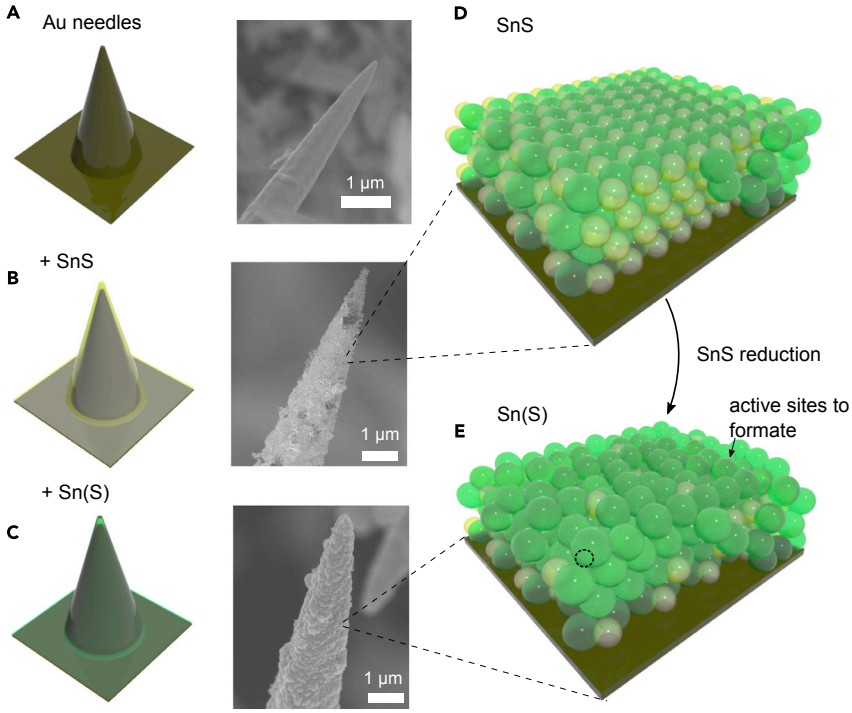

Figure 2. Fabrication of Nanostructured Sn(S) Catalysts

(A–C) Schematic and SEM images of the process leading to the fabrication of Sn(S) nanostructured electrodes. (A) Au needles. (B) Au needles after SnS deposition by ALD process. (C) Au needles coated with sulfur-modulated-tin films.

(D) A SnS_x slab is conformally deposited by ALD on top of the nanostructured metal backbone.

(E) The selective reduction of SnS_x leads to Sn(S) films, which promotes CO_2RR toward formate. The dashed circle means active sites for formate generation.

(−1.06 V and −0.75 V, respectively). These results suggest that the onset potential for formate production may be lower than that of CO or H_2, highlighting the beneficial effects of S incorporation on the energetics of formate generation.

To computationally investigate the morphological changes that doping induced on the tin, accessible surface areas were calculated using Connolly surface areas (Figure S3 and Table S6). It was found that slight doping of sulfur atoms increased the atomic surface area (normalized to the number of tin atoms in the slab) compared with tin sulfide or pure tin by 13% (Figure 1D). The 12.5% sulfur-doped Sn(S) structure had the largest accessible surface area of 210 $Å^2$ per unit cell, whereas the close-packed pure tin structure had the lowest accessible surface area of 186 $Å^2$ per unit cell. This high surface area suggests the surface has a greater degree of accessibility and is more likely to have undercoordinated sites due to the imperfect packing caused by the slight doping of sulfur. This result was validated by comparing the electrochemically active surface area (ECSA) of Sn(S) and Sn nanoparticles (NPs) as described later in the text.

Synthesis and Characterization of Sulfur-Modulated Tin Catalysts

A method to achieve a controllably sulfur-doped Sn surface was then required to successfully implement these findings. We took the view that atomic layer deposition (ALD) could provide precise control over both S content and film thickness (Figures 2 and S4). SnS_x thin films were deposited from the reaction of tetrakis(dimethylamino)tin(IV) (TDMA-Sn) and H_2S. The resulting films were then electrochemically

Table 1. Comparison of Catalytic Parameters of Sulfur-Modulated Tin Catalysts and Controls

Samples	Electrolyte	Potential (V versus RHE)	Current Density (mA cm^{-2})	Faradaic Efficiency (%)	Reference
Sn(S)/Au	0.1 M $KHCO_3$	−0.75	55	93.3	This work
Sn nanoparticles/Au	0.1 $MKHCO_3$	−0.75	42	30.2	This work
SnO_x-derived Sn	0.5 M $KHCO_3$	−1.05	12	19	Lu et al.[11]
SnO_2 nanoparticles	0.1 M $KHCO_3$	−1.05	9.5	90	Kim et al.[14]
SnO_x/Sn	0.1 M $KHCO_3$	−1.05	11	70	Pander et al.[22]
Oxide-derived Pb	0.5 M $KHCO_3$	−1.05	1	95	Hollingsworth et al.[23]
SnS_2-derived Sn/rGO	0.5 M $KHCO_3$	−1.05	11.75	85	Li et al.[31]
Sn quantum sheets/GO	0.1 M $KHCO_3$	−1.05	12	60	Lei et al.[32]
Partial oxidized Co	0.1 M Na_2SO_4	−0.24	10	90	Gao et al.[4]
Pd nanoparticles	0.5 M $KHCO_3$	−0.20	22	97	Klinkova et al.[13]
Pd nanoparticles	0.5 M $KHCO_3$	−0.35	8	90	Won da et al.[18]
Sn	$[Bmim]PF_6$	−1.05	15	95	Lee et al.[16]

reduced to partially remove S atoms (see Experimental Procedures for details), thereby increasing the density of active sites. *In situ* Raman spectra at −1.0 V versus RHE confirmed that the bulk and vast majority of SnS_x is reduced to Sn metal at high potentials (Figure S5). As discussed later, the catalytic activity of Sn(S)/Au shows significantly superior performance than pure Sn nanoparticles/Au samples, which is in agreement with DFT calculations (Table 1).

Morphological strategies have been shown to dramatically increase the rate for CO_2RR toward a given product. Field-induced reagent concentration (FIRC) is a catalytic phenomenon that was first reported on nanostructured gold nanoneedles for the reduction of CO_2 to CO (Figure 2A).[3] Simply, high-curvature nanostructures exhibit a high local negative electric field, which concentrates proximate positively charged cations that help to stabilize CO_2 reduction intermediates, promoting CO_2RR. Computational studies have since shown that strong local electric fields and the presence of cations proximate to the surface promote CO_2RR.[33] The concept of sharp nanostructures promoting CO_2RR activity and boosting current densities has since been demonstrated for CO_2 reduction to formate[13] and formic acid oxidation[15] on branched Pd NPs and CO_2 reduction to ethylene on copper nanodendrites.[17]

We sought to explore the synergy between FIRC and sulfur-modulated tin catalysts, building hybrid electrodes that combine the best nanostructured FIRC morphologies of Au nanoneedles with Sn(S), which improves formate evolution energetics (Figure 2). This required that the sulfur-modulated tin film be conformally deposited over the Au nanoneedles, maximizing activity toward the desired products and otherwise blocking CO active Au facets. We optimized the ALD process by controlling substrate preparation, pulse duration, and the number of cycles (Figures 2B and 2D). We achieved homogeneously dispersed sulfur elements into the Sn metal by ALD of SnS_x followed by an *in situ* reduction process to give the active Sn(S) catalyst (Figures 2C and 2E). We have found that regardless of starting Sn:S composition (1:1 or 1:2), the majority of the sulfur is removed during the reduction step. These results imply a limitation to the amount of sulfur that can remain after the initial reduction to SnS_x (Figure S13).

High-resolution transmission electron microscopy (HRTEM) studies were performed to provide greater insight into the surface structure and morphology of the catalyst

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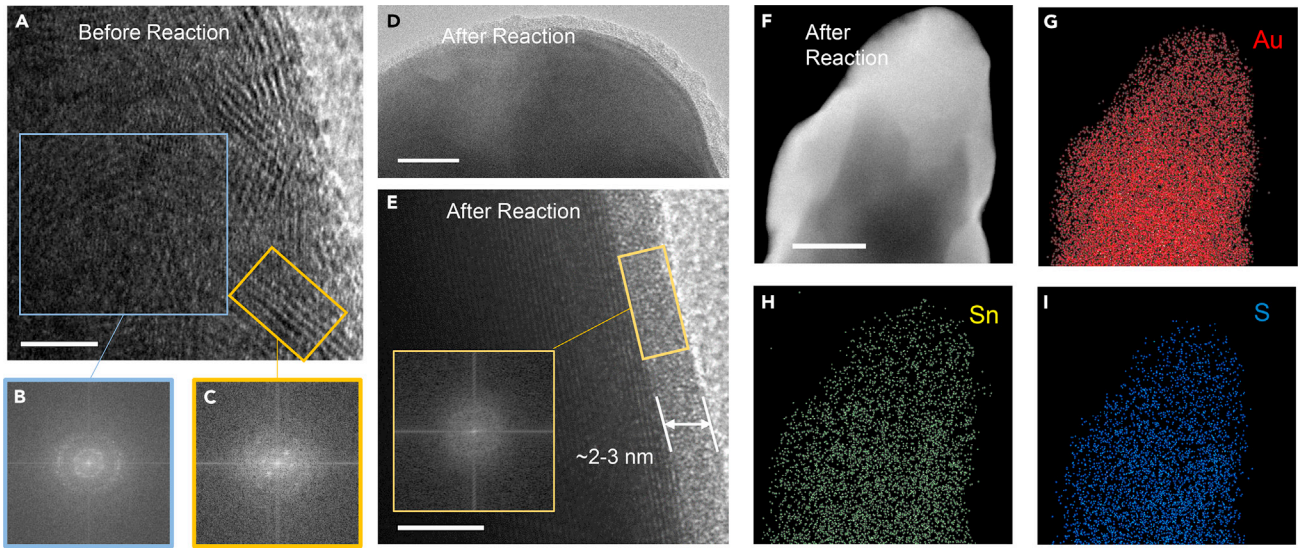

Figure 3. Characterization of Sulfur-Modulated Tin Catalysts

(A) High-resolution transmission electron microscope (HRTEM) image of the ALD SnS_x before reaction showing a highly polycrystalline surface. Scale bar represents 5 nm.

(B and C) Fast Fourier transform (FFT) of the polycrystalline region (B) and one specific crystalline grain (C).

(D and E) HRTEM image of the reduced Sn(S) active catalyst after reaction showing a uniform amorphous layer on the surface. Scale bar represents 20 nm for (D); scale bar represents 5 nm for (E). Inset is the FFT of the amorphous region.

(F–I) STEM image (F) of Sn(S)/Au and the corresponding EDS mapping to show homogeneously dispersed Au (G), Sn (H), and S (I). Scale bar represents 100 nm.

before and after reaction (Figure 3). It was found that, before reaction, highly polycrystalline tin sulfide is formed with extremely small grain sizes of ~5 nm (Figures 3A–3C). After reaction, a thin layer of amorphous tin-based material about 2–3 nm thick forms on the surface (Figures 3D and 3E). Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) elemental mapping showed a conformal coating of Sn(S) on Au needles, and a uniform, uncorrelated spatial distribution of Au, Sn, and S (Figures 3F–3I), consistent with the EDS line scan (Figure S6).

To elucidate the electronic configuration of the resulting Sn(S) layer in the final structure, we performed X-ray absorption spectroscopy (XAS) on Sn(S) and Sn NPs before, *in situ*, and after reaction (Figure 4). Sn NPs were used as a control of Sn(S). We analyzed the edge position of each compound as it shifts to higher energies with increasing oxidation of Sn.[34,35] *In situ* Sn L_3-edge spectra at −0.7 V versus RHE indicate that the reduction of SnS_x to Sn(S) resulted in an oxidation state between Sn^0 and Sn^{2+}, while Sn NPs do not change oxidation state (Figure 4A).[36,37] This suggests Sn(S) at −0.7 V versus RHE was more oxidized than Sn metal, which agreed with the *in situ* S K-edge spectra[38] (Figure S11). The trend observed from the Sn L_3-edge (Figure 4B) indicates that sulfur-doped Sn possessed a higher oxidation state than Sn NPs after reaction (edge shift indicated by a red arrow),[36,37] consistent with Sn K-edge measurements (Figure 4C).[35] Sn(S) exhibited a higher oxidation state than Sn NPs after reaction because Sn(S) was more readily oxidized to high valence after exposure to the open circuit potential and air. We propose that Sn(S) may have more undercoordinated Sn sites than the Sn NP control.

The surface chemical compositions of SnS_x, Sn(S) after reaction, and Sn NPs after reaction were further probed by X-ray photoelectron spectroscopy (XPS). The S 2p spectra of Sn(S) after reaction revealed the survival of sulfur throughout the reaction (Figure 4D). Based on the results from XPS analysis, the content of S in the Sn(S)

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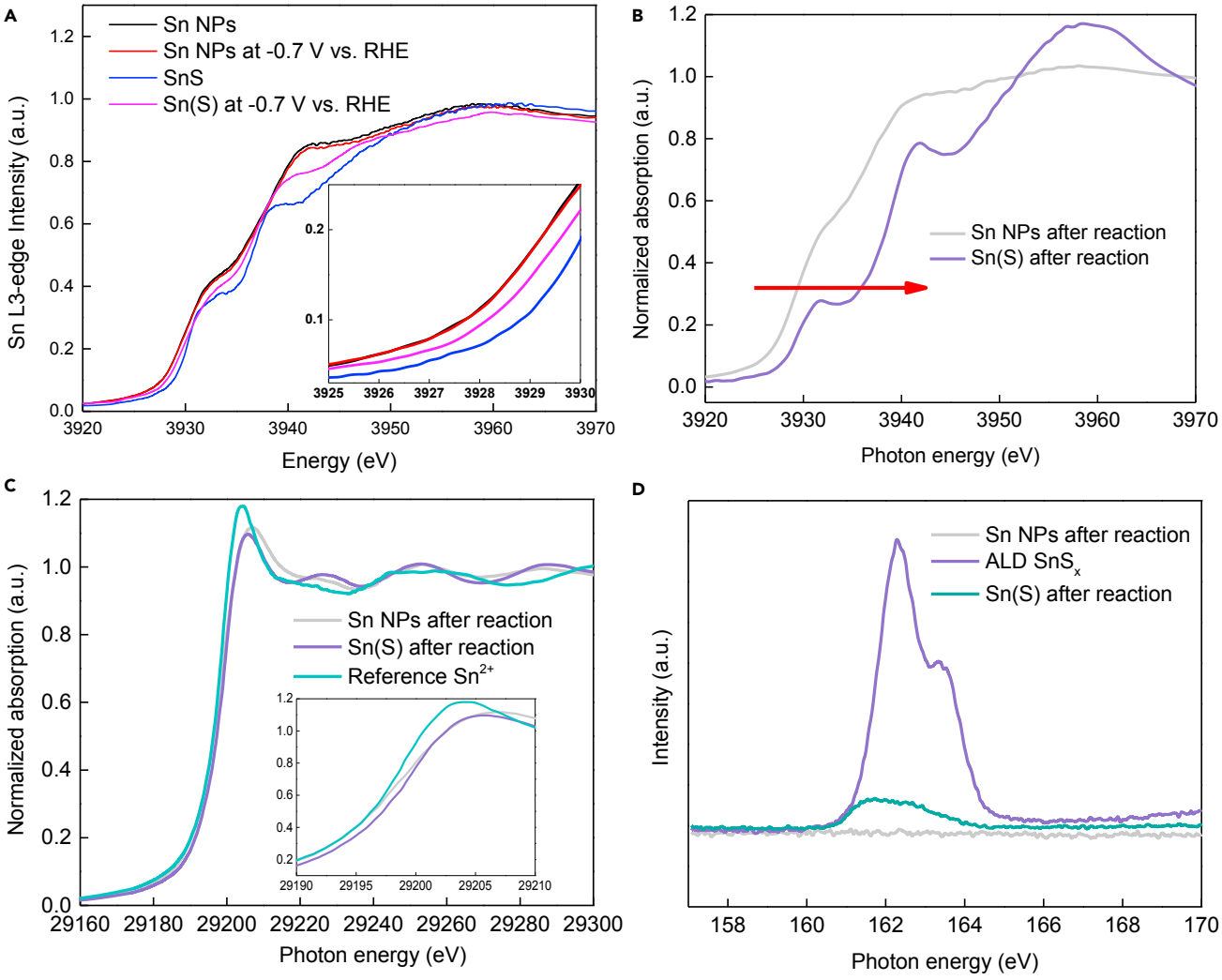

Figure 4. Electronic Structure of Sn(S) and Sn

(A) *In situ* Sn L_3-edge XANES spectra of Sn NPs, SnS, Sn NPs at −0.7 V versus RHE, and Sn(S) at −0.7 V versus RHE. Inset shows zoom in of the pre-edge energy range.

(B) Sn L_3-edge spectra of Sn(S) and Sn NPs on carbon paper after reaction (edge shift indicated by a red arrow).

(C) Sn K-edge of Sn(S) and relevant controls. Inset shows zoom in of the pre-edge energy range.

(D) XPS spectra of Sn(S), Sn NPs, and ALD SnS_x.

catalyst was calculated to be 3.2 at %. To avoid the effect of Au substrates and thus the potential increased sulfur content adhering to gold, we deposited Sn(S) on carbon paper (Figure S14) and found the content of S in the Sn(S)/carbon paper after reaction to be 4.6% (Figure S15).

Evaluation of Activity for Electrochemical Reduction of CO_2

We then proceeded to evaluate the catalytic performance of the Sn(S)-FIRC hybrid electrodes. Linear sweep voltammetry traces reveal the superior current density of S-modulated Sn samples over bare Sn NPs (Figure 5A). The Faradaic efficiency of S-modulated Sn samples approaches 100% for potentials more negative than −600 mV versus RHE. The resulting partial current density is significantly higher than that of Sn samples (Figures 5B and S12). We have also synthesized Sn film on Au needles by sputtering as a control (Figure S19). A record Faradaic efficiency of 93%

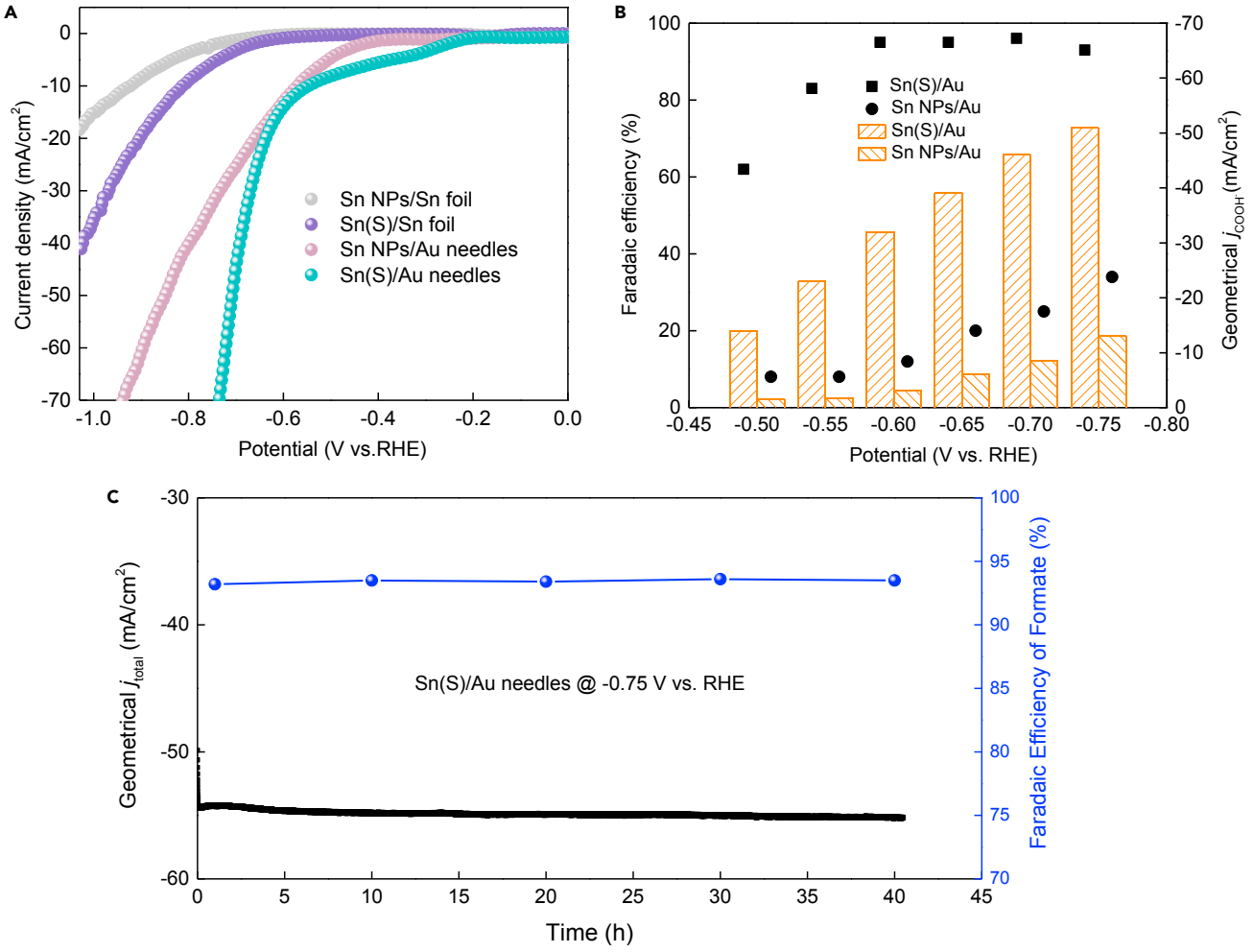

Figure 5. Performance of Sulfur-Modulated Tin Catalysts and Controls in a Three-Electrode Configuration in CO_2 Saturated 0.1 M $KHCO_3$ Aqueous Electrolyte

(A) The CO_2RR polarization curve of catalysts loaded on Au needles and Sn foil, respectively.

(B) Potential dependence (with iR corrected) of Faradaic efficiencies and current densities for CO_2RR on Sn(S)/Au (squares) and Sn NPs/Au (circles).

(C) Stability test of Sn(S) at −0.75 V versus RHE (iR corrected).

with a total current density of 55 mA cm^{-2} (normalized to geometric surface area) is obtained at −0.75 V versus RHE for Sn(S)/Au. This formate partial current density on Sn(S)/Au represents higher than that of the best non-noble metal (Tables 1 and S8). To evaluate the effect of surface area, we measured the ECSA for Sn(S)/Au, Sn NPs/Au, and sputtered Sn/Au from the electrochemical double-layer capacitance of the catalytic surface (Figure S8). From ECSA normalized performance of CO_2 reduction to formate, the high catalytic activity of Sn(S)/Au includes an appreciable intrinsic (not surface-area-related) contribution. The partial current density for formate on Sn(S)/Au, normalized by ECSA, is between 1.2 and 3 times higher than that of Sn NPs/Au and sputtered Sn/Au (Figure S9 and Table S9). To experimentally probe the reaction intermediates, we observed formate in the interfacial region (1,300–1,400 cm^{-1}) by *in situ* attenuated total reflection mode Fourier transform infrared (ATR-FTIR) (Figure S18).[39,40] We note that a bound intermediate formate species (HCOO*) has been reported before in the literature,[39] but unfortunately we were not able to detect this species. While our *in situ* ATR-FTIR was inconclusive for bound HCOO* intermediates, there were no peaks that could be attributed to

the bound or interfacial carboxylate intermediate (COOH*). These results qualitatively agree well with our simulations, whereby the reaction pathways are based on prior literature.[13,25]

One of the most critical aspects of formate production from CO_2RR is the deactivation of the catalyst over time. Although Pd catalysts only require low potential for CO_2 to formate (Table 1), CO poisoning has limited its potential practical application.[13] To characterize the performance stability of the Sn(S) catalysts, we performed CO_2 reduction with the Sn(S) catalyst under a constant potential of −0.75 V versus RHE continuously for 40 hours. We observed no appreciable decrease (<2%) in current (Figure 5C) during this time interval. Furthermore, we performed potential-cycling experiments that showed no degradation in activity over five 1-hr cycles (Figure S20). We also confirmed the Faradaic efficiency for formate generation was nearly quantitative (>93%) throughout the electrocatalytic process. This formate partial current density on Sn(S)/Au is higher than the previously reported non-noble metal catalysts in aqueous solution (Table 1),[2,30] confirming that the undercoordinated tin sites greatly increased the catalytic activity of CO_2 to formate.

EXPERIMENTAL PROCEDURES

DFT Calculations

Initially, we started by simulating a SnS slab.[41] It is characterized by an orthorhombic herzenbergite structure where the Sn^{2+} ion adopts a tetrahedral geometry coordinating three S^{2-} ions with the Sn $5s^2$ lone pair occupying the fourth position.[42] We then gradually increased the Sn content in the SnS crystal structure by randomly replacing S atoms with Sn atoms such that the resultant structures had 37.5%, 25%, and 12.5% sulfur content. The atomic positions and unit cell parameters of all structures were relaxed and fully optimized using DFT (Figure S17). The optimized structural parameters for SnS (Tables S1 and S2) served as a benchmark for the validity of further calculations. The {100} facet was used for all slabs with a 4 × 4 × 4 atom slab and 20 Å between mirror images in the z axis in the unit cell. To justify the facet choice, we calculated the surface energies for the {100}, {110}, {111}, {211}, and {311} facets of SnS (Table S7). It was found that the {100} facet has the lowest surface energy and is thus expected to be the most stable surface. Bader charge analysis shows electron density of the bound oxygen atoms is slightly higher on slightly doped Sn(S), suggesting a stronger Sn–O intermediate bond (Table S5).

X-Ray Absorption Measurements

The Sn K-edge spectra were collected at the 06ID-1 Hard X-ray MicroAnalysis (HXMA) beamline and soft X-ray Microcharacterization (SXMRB) beamline from Canadian Light Source. *In situ* Sn-L_3 edge and S K-edge XANES spectra were collected at the soft X-ray Microcharacterization (SXMRB) beamline from Canadian Light Source. *Ex situ* Sn L_3-edge spectra were collected at Beamline 10.3.2 from the Advanced Light Source.

Preparation of Sn(S) on Au Needles

Gold electrodes were prepared through an electrodeposition process using a solution containing $HAuCl_4$ (99.99%, Sigma) and HCl (TraceSELECT) solution.[3] SnS_x was deposited at 90°C using tetrakis(dimethylamino)-tin(IV) (TDMASn, 99.99% Sn; Strem Chemicals) and H_2S at a constant growth rate of 0.035 nm per cycle measured by ellipsometry. TDMASn was held at 65°C. Nitrogen was used as a carrier gas (99.9999% pure, Carbagas) with a flow rate of 10 sccm.[43–45] Cyclic voltammetry measurements from 0.4 V to −1.0 V versus RHE at 50 mV/s were performed in CO_2 saturated 0.1 M $KHCO_3$ electrolyte for three cycles to activate and partially remove sulfur atoms from

the as-prepared SnS_x/Au electrode. The CO_2 reduction performance was then carried out in the same electrolyte.

Preparation of Sn Nanoparticles on Au Needles

Electrophoretic deposition was implemented to uniformly deposit Sn NPs on nanostructured Au electrode.[34,46,47] Specially, 10 mg/L Sn NPs in ethanol were placed in the ultrasonic bath for 50 min and centrifuged for 30 min at 4,000 rpm to remove large NPs from the suspension. Finally, a DC power supply of 20 V was applied for 20 min to deposit Sn NPs (Figure S7).

Electrocatalytic Reduction of CO_2

All CO_2 reduction experiments were performed using a three-electrode system connected to an electrochemical workstation (Autolab PGSTAT302N). Ag/AgCl (with saturated KCl as the filling solution) and platinum mesh were used as reference and counter electrodes, respectively. Electrode potentials were converted to the RHE reference scale using $E_{RHE} = E_{Ag/AgCl} + 0.197\ V + 0.0591 \times pH$. The potentials were iR corrected using electrochemical impedance spectroscopy (Figure S16).

The electrolyte was 0.1 M $KHCO_3$ saturated with CO_2. Formate was quantified on gas chromatography with mass spectrometry (PerkinElmer Clarus 600 GC-MS System). Assuming that two electrons are needed to produce one formate molecule, the Faradaic efficiency was calculated as follows: Faradaic efficiency = $2F \times n_{formate}/Q = 2F \times n_{formate}/(I \times t)$, where F is the Faraday constant, I is the current, t is the running time, and $n_{formate}$ is the total amount of formate produced (in moles).

Characterization

High-resolution TEM (HRTEM) images were taken on an FEI monochromated F20 UT Tecnai microscope operated at 200 kV. STEM elemental mapping of samples were taken on a FEI Titan 80–300 environmental (scanning) electron microscope (E(S) TEM), with a spot size of 6 and a C2 aperture size of 70 μm. Scanning electron microscopy (SEM) was performed on a Hitachi SU8230 scanning electron microscope operated at 1.0 kV. Powder X-ray diffraction patterns were obtained with a MiniFlex600 instrument. XPS measurements were carried out on a Thermo Scientific K-Alpha system, with a 300 μm spot size, 75 eV pass energy, and energy steps of 0.05 eV, and aluminum anode X-ray excitation. The Shirley algorithm was used to fit the background. Then the atomic ratio was computed by summing over the curves over the background and taking into account the absorption cross-section of Sn and S to determine relative ratios from their intensities (Figure S10). The *in situ* spectroelectrochemical (ATR-FTIR) measurements were performed on a Bruker IFS 66/S spectrometer. For the *in situ* technique, a sealed electrochemical cell (Figure S18) with Pt as counter electrode, Sn(S) as working electrode, and Ag/AgCl reference electrode was mounted in the spectrometer. The system was continuously flushed with CO_2 saturated 0.1 M $KHCO_3$. Sn(S) was deposited onto a germanium crystal (1 × 1 × 0.2 cm parallelepiped, angle 45°C) as reflection element. During the spectroscopic recording, a constant potential was applied (−0.3 V, −0.5 V, and −0.7 V versus RHE, respectively) (Figure S18).

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 20 figures, and 9 tables and can be found with this article online at https://doi.org/10.1016/j.joule.2017.09.014.

AUTHOR CONTRIBUTIONS

E.H.S. and P.Y. supervised the project. X.Z. designed the experiments. P.D.L. carried out the simulation parts. X.Z., P.D.L., N.B., and M.N.B. performed the X-ray measurements. M.B.R. carried out *in situ* Raman measurements. Yifan Li and Yuzhang Li performed the TEM measurements. O.V. carried out the XPS measurements. X.Z., F.P.G.d.A., B.Z., M.L., T.Z., and C.T.D. performed electrochemical measurements. P.S. carried out *in situ* FTIR measurements. Y.C. and X.D. revised the manuscript. All authors discussed the results and assisted during manuscript preparation.

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