Orbital Interactions in Bi-Sn Bimetallic Electrocatalysts for Highly Selective Electrochemical CO₂ Reduction toward Formate Production

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A highly selective and durable electrocatalyst for carbon dioxide (CO₂) conversion to formate is developed, consisting of tin (Sn) nanosheets decorated with bismuth (Bi) nanoparticles. Owing to the formation of active sites through favorable orbital interactions at the Sn-Bi interface, the Bi-Sn bimetallic catalyst converts CO₂ to formate with a remarkably high Faradaic efficiency (96%) and production rate (0.74 mmol h⁻¹ cm⁻²) at −1.1 V versus reversible hydrogen electrode. Additionally, the catalyst maintains its initial efficiency over an unprecedented 100 h of operation. Density functional theory reveals that the addition of Bi nanoparticles upshifts the electron states of Sn away from the Fermi level, allowing the HCOO⁺ intermediate to favorably adsorb onto the Bi-Sn interface compared to a pure Sn surface. This effectively facilitates the flow of electrons to promote selective and durable conversion of CO₂ to formate. This study provides sub-atomic level insights and a general methodology for bimetallic catalyst developments and surface engineering for highly selective CO₂ electroreduction.

1. Introduction

The conversion of carbon dioxide (CO₂) gas into value-added chemicals by electrochemical CO₂ reduction reactions (CO₂RR) is considered as a promising strategy for recycling CO₂ with economic and environmental benefits.[1–7] This can be performed efficiently in the future by coupling CO₂RR to overcome large energy barriers and shift reaction pathways toward formate formation.

Based on previously reported studies, most metal-based catalysts such as Au,[17,18] Ag,[19–21] and Ni,[22,23] were shown to demonstrate a low selectivity toward the formation of formate, favoring the conversion of CO₂ to CO, while Cu was demonstrated to produce a variety of hydrocarbons and alcohols at low Faradaic efficiencies (FE).[24–28] Interestingly, Pd,[29–31] Sn,[32–36] Bi,[37–40] In,[41] and Pb,[28] on the other hand, have demonstrated relatively high selectivity for formate production. Pd shows high selectivity with relatively low overpotentials, but it is too expensive for large-scale CO₂ reduction systems. Meanwhile, In and Pb are known to be toxic and not environmentally friendly, which leaves Sn and Bi as good candidates for formate producing catalysts. These metals, being comparatively inexpensive and environmentally benign, are also interesting as electrode materials for large-scale CO₂ reduction systems to be integrated into smart energy-grids.[42,43] In terms of catalyst composition, combining more than one element in the form of binary or multicomponent catalysts has shown to be an effective approach to tune the selectivity of CO₂RR catalysts.[44–49] However, a wide range of Faradaic efficiencies for formate production (FEformate) from 40% to 99% have been reported on various binary Sn-based electrodes. Improved FEformate has been observed with binary Sn-based catalysts containing Pd.[44]
Ag,[46] Cu,[45] and S[42] as the secondary metal, while reduction in FE_{formate} has been observed with Cd- and Zn,[50] containing catalysts. These results indicate that the formation of formate is sensitive to the electronic structure of Sn-based bimetallic surfaces modified by the secondary atom. As such, understanding the synergetic interaction[51] between binary components is of significant importance in designing catalysts that can perform the conversion of CO₂ to formate at high FE. In addition, other ways to enhance the activity and selectivity of catalysts for CO₂RR include morphology engineering[52–54] and tuning of oxidation states at the surface of catalysts.[8,36,38,55] In general, high surface area catalysts increase the active sites exposure and allow for specific crystal edge and step sites to interact with reactants.[18,56] The results from the literature suggest that by appropriately combining concepts from the compositional and morphological studies, a formate producing CO₂RR catalyst with high activity and selectivity can be produced.

Herein, we have designed and synthesized a bimetallic Bi-Sn catalyst for efficient production of formate. The combined effect of Sn and Bi components along with unique morphology control results in high formate partial current density as well as long durability, showing almost exclusively formate production over 100 h of operation. On the basis of our physicochemical, electrochemical, and density functional theory (DFT) analyses, these excellent traits of the catalyst are ascribed to four factors: i) the interface between Sn and Bi is highly favorable for charge transport due to the higher electronegativity of Bi, allowing electron density to easily flow from Sn to Bi. The sub-atomic orbital interaction therefore strengthens the interaction at the active site with the HCOO* intermediate, boosting the selectivity of SnO₂ nanosheets for CO₂RR. ii) the Bi-Sn nanosheet structure is observed to be very robust based on electron microscopic images in Figure 1d,e, small Bi particles attached to the surface of SnO₂ nanosheets are observed to be 3 nm in average diameter and with a d-spacing of 0.329 nm that corresponds to the (102) plane of SnO₂ in both Bi-decorated and Bi-free samples. iii) the nanosheet structure with enhanced edge site exposure promotes mass transport of CO₂ and formate ions during the reactions; iv) the fabrication of the CO₂RR electrode is possible without the use of a binding material, significantly reducing the electronic resistance. In summary, these advantages lead to the development of a catalyst system that can efficiently convert CO₂ to formate at high current densities for extended time periods, which will be demonstrated in the following sections.

2. Results and Discussion

2.1. Fabrication of Bimetallic Bi-Sn Electrodes

A schematic diagram illustrating the structure of Bi-Sn bimetallic catalyst deposited on a flexible carbon fabric substrate is shown in Figure 1a, which is used as a CO₂RR electrode without further modification. As described in the Experimental Section, SnO₂ nanosheets were deposited on a flexible carbon substrate by a facile and scalable hydrothermal reaction technique, followed by the electrodeposition of Bi nanoparticles uniformly onto the surface of SnO₂ nanosheets. High surface area carbon fabric was used as the growth substrate during the hydrothermal reaction, which allowed SnO₂ nanosheets to grow vertically without any addition of polymer binders, such as polytetrafluoroethylene or Nafion, which usually lower the overall electronic conductivity of the electrode. Additionally, this method can be deployed for gas diffusion electrode fabrication for future gas phase CO₂ electrolyzer applications. Prior to testing for CO₂RR activity, the as-synthesized catalyst was exposed to an in situ electrochemical reduction conditioning step by applying a constant potential of −1.14 V versus reversible hydrogen electrode (RHE) for 20 min to reduce SnO₂ to Sn nanosheets, similarly to previously reported methods in the literature.[46,57] Therefore, a portion of the current observed during the in situ electrochemical reduction is ascribed to the reduction of SnO₂ to Sn (Figure S1, Supporting Information). To prevent reoxidation of the freshly prepared surface, the electrode was tested immediately in the same electrolyte without exposing to the open environment, which allowed CO₂RR to occur over the Bi-Sn surface.[46,58,59]

As revealed by scanning electron microscopy (SEM), 2D vertically standing Bi-SnO₂ nanosheets are observed to successfully grow directly on the porous carbon substrate as shown in Figure 1b and Figure S2a in the Supporting Information. This structure is very advantageous for increasing the surface area since unsupported 2D nanostructures tend to agglomerate and lose active surface area. No obvious morphological change is observed after the in situ electroreduction of Bi-SnO₂ nanosheets as shown in Figure 1c. The surface of the nanosheets may have reoxidized during the SEM characterization, but this image is still indicative of no significant morphological change resulting from the in situ electroreduction. The SEM images of various electrodes fabricated using varying Bi deposition times (SnO₂/CF, Bi(0.1)-SnO₂/CF, Bi(0.5)-SnO₂/CF, Bi-Sn/CF, and Bi(3)-SnO₂/CF) show similar vertically standing nanosheet morphology (Figure S2b–f, Supporting Information, respectively). As shown by the scanning transmission electron microscopy (STEM) and high-resolution TEM (HRTEM) images in Figure 1d,e, small Bi particles attached to the surface of SnO₂ nanosheets are observed to be 3 nm in average diameter and with a d-spacing of 0.329 nm that corresponds to the (102) plane of Bi.[56] In comparison, SnO₂ nanosheets show lattice fringes with a d-spacing of 0.335 nm which corresponds to the (110) plane of SnO₂ in both Bi-decorated and Bi-free samples (Figure 1f, respectively).[13] The elemental constituents of the electrodes are revealed by energy dispersive X-ray spectroscopy as shown in Figure S3 in the Supporting Information, which clearly indicate the presence of both Bi and Sn. It is important to carefully control the Bi deposition time as excessive current passed during this step leads to aggregation and formation of relatively large Bi clusters as shown by SEM and TEM images (Figures S2g,h and S4, Supporting Information).

To further characterize Bi-Sn electrodes, X-ray diffraction (XRD) was conducted to study the crystal structure of the Bi-SnO₂/CF electrode, which clearly showed peaks that matched Bi (joint committee on powder diffraction standards (JCPDS) No. 44-1246) and SnO₂ (JCPDS No. 41-1445) (Figure 1g). Even though no morphological change was observed before and after the in situ reduction of the electrodes based on the SEM analysis above, the XRD patterns of Bi-SnO₂/CF and Bi-Sn/CF in Figure 1g clearly show disappearance of the SnO₂ peaks, and emergence of Sn peaks at 30.6° and 32.0° which correspond to the (200) and (101) planes (JCPDS No. 04-0673). The same trend was observed with...
other Bi(x)-SnO2/CF and oxide-derived Bi-Sn/CF electrodes as shown by their XRD patterns (Figure S5, Supporting Information). Further composition and valence state analyses of the Bi(x)-SnO2/CF electrodes have been conducted by X-ray photoelectron spectroscopy (XPS). The obtained XPS spectra are calibrated via alignment of the C(sp2) peak position in the C 1s spectrum to its reference value of 284 eV. The survey XPS spectrum (Figure S6a, Supporting Information) clearly confirms that the samples consist of the elements Bi, Sn, O, and C. Moreover, the high-resolution core spectrum of Sn 3d5/2 and Sn 3d3/2 (Figure S6b, Supporting Information) show that the two main peaks (486.77/495.18 eV in Bi-SnO2/CF and 486.70/495.11 eV in Bi-Sn/CF, respectively) correspond to Sn4+ in SnO2. The transition from SnO2 to Sn after the in situ electroreduction is observed by the negative shift in the binding energy of 0.07 eV from Bi-SnO2/CF to Bi-Sn/CF as shown in Figure S6b in the Supporting Information. Despite the electrode having undergone reoxidation due to the air exposure during sample transport to XPS, the electrode still maintained this shift indicative of the robustness of the in situ reduction process. As shown in Figure S6c in the Supporting Information, the peak profile of Bi 4f (159.27/164.58 eV and 158.57/163.85 eV for Bi-SnO2/CF and Bi-Sn/CF, respectively) indicates that Bi3+ species dominate as the main component of bismuth oxide. The small peaks at 156.22/161.70 eV are ascribed to Bi04f on the surface. The XRD patterns only show the metallic Bi phase in both Bi-SnO2/CF and reduced Bi-Sn/CF samples as it is a bulk probing technique, while the surface sensitivity of XPS allows characterization of the oxidation states of Bi nanoparticles. The binding energies of Sn3d5/2 and Sn3d3/2 peaks shift to larger energies with increasing amounts of Bi as shown in Figure 2a. Specifically, Bi(0.1)-SnO2/CF has the lowest Sn3d5/2 and Sn3d3/2 peaks shift to larger energies with increasing amounts of Bi as shown in Figure 2a. Specifically, Bi(0.1)-SnO2/CF has the lowest Sn3d5/2 and Sn3d3/2 peaks shift to lower binding energies. In addition, the Bi(3)-SnO2/CF has the lowest Bi 4f7/2/Bi 4f5/2 binding energy (Figure 2b). These results are clear indications of the transfer of electrons from Sn to Bi atoms, which modifies the overall electronic structure of
the active sites at the Bi-Sn interface. The interaction of Sn and Bi orbitals and how it affects the formation of formate during CO₂RR will be discussed with both experimental and computational results in the following sections.

2.2. Electrochemical CO₂ Reduction Studies

As mentioned above, the oxide-derived Bi(x)-Sn/CFs electrodes are tested immediately following the in situ precondition reduction step to prevent surface reoxidation. The CO₂RR activity of the prepared electrodes (Bi-Sn/CF, Sn/CF, and CF) are measured by linear sweep voltammetry (Figure 3a). Under N₂ bubbling of 0.5 mKHCO₃ electrolyte, the increase in the current past −0.7 V is ascribed to the HER, which is the main competing reaction during the CO₂RR. With the CO₂-purged electrolyte, however, a dramatic current increase is observed which indicates that the CO₂RR occurs readily on the Bi-Sn catalyst.[45] A series of constant potential electrolysis measurements are performed to investigate potential dependence of the electrode on FE formate as shown in Figure 3b. With increasing overpotential, FE formate was found to continuously increase for all electrodes tested, reaching a maximum at −1.14 V versus RHE, then decreasing slightly after this point. This might be due to mass transport limitations of CO₂. Oxide-derived Bi-Sn/CF bimetallic catalyst demonstrated the highest FE formate of 94% ± 2% at −1.14 V versus RHE, while FE formate was 78% ± 2% on the Sn/CF electrode at −1.14 V versus RHE. Although a wide range of FE formate from 40% to 99% has been reported on various Sn-based electrodes (Table S1, Supporting Information), the Bi-Sn/CF electrode presented in this study, which has the advantages of a nonprecious metal composition and a practically viable fabrication method, demonstrates both very high FE and current density. These excellent performance metrics are attributed to the unique Sn nanosheet structures which consist of many edge and corner sites that lead to a strong local electric field as depicted in Figure S7 in the Supporting Information. According to the field-induced reagent concentration theory,[18] high-curvature structures concentrate electric fields which can affect local ion concentrations and in turn lead to a high local concentration of CO₂ close to the active CO₂ reduction reaction surface.[18,56,61] The Bi/CF electrode exhibits an FE formate of 78% ± 2% (Figure S8a, Supporting Information), which is slightly lower than the reported literature values obtained with Bi dendrites,[40] nanoflakes,[50] and nanosheets.[37,38] This is likely due to the agglomeration of Bi particles into clusters during the electrodeposition in the absence of SnO₂ nanosheets (Figure S5h, Supporting Information), resulting in the loss of active sites.

![Figure 2. a) Sn 3d and b) Bi 4f core level XPS spectra of Bi(3)-SnO₂/CF, Bi-SnO₂/CF, Bi(0.1)-SnO₂/CF, and SnO₂/CF.](image)

![Figure 3. a) CO₂RR activities of the prepared electrodes (Bi-Sn/CF, Sn/CF, and CF) in a N₂-(dotted line) and CO₂-purged (solid line) 0.5 mKHCO₃ electrolyte at a scan rate of 20 mV s⁻¹. b) FE of formate generated on electrodes (Bi-Sn/CF, Sn/CF, and CF) at a series of potentials from −0.64 to −1.34 V. c) FE of formate, CO and H₂ on oxide-derived Bi-Sn/CF electrodes at a series of potentials from −0.64 to −1.34 V. d) FE of formate with varying ratios of Bi and Sn at −1.14 V versus RHE. The error bars represent the standard deviations of three independent measurements of the same sample.](image)
of high-index planes,\cite{40} corner and edge sites,\cite{56} and under-coordinated Bi sites\cite{38} which are responsible for high CO\textsubscript{2}RR activity in Bi dendritic and nanoflake structures. The decreasing FE\textsubscript{formate} at high overpotentials is indicative of the formation of hydrogen and CO outcompeting the reduction of CO\textsubscript{2} to formate, as shown by the production distribution in Figure 3c. This competition between the production of formate, hydrogen, and CO is commonly observed and reported in the literature.\cite{39} However, it is important to note that the optimized Bi-Sn catalyst composition and morphology in this study highly favors the production of formate, as FE of CO is kept below 10\% and the rest being hydrogen at all potentials tested. No other products aside from CO, H\textsubscript{2} and formate are observed, which significantly simplifies product separation since CO and H\textsubscript{2} gases can be easily separated out from the liquid phase that contains formate. This allows the electrolyte to be readily refined and used as the hydrogen carrier\cite{12–14,62} or as the fuel for formic acid fuel cells.\cite{15,16}

The effect of Bi deposition on the selectivity of CO\textsubscript{2}RR has been explored by varying the electrodeposition time of Bi on SnO\textsubscript{2} nanosheets, resulting in the different compositions of Bi-Sn bimetallic catalysts. The electrochemical testing reveals the 1:1 ratio of Bi:Sn to demonstrate the highest FE\textsubscript{formate} as shown in Figure 3d, with either increasing or decreasing amounts of Bi leading to the reduction of FE\textsubscript{formate}. Structurally, these electrodes are observed to be different as shown in Figures S2 and S4 in the Supporting Information, with the best performing Bi-Sn electrode displaying a uniform distribution of 3 nm Bi nanoparticles on Sn nanosheets surfaces, greatly increasing the exposure of the active Bi-Sn interface. In comparison, electrodes with a Bi:Sn ratio lower than 1 are observed to be absent of Bi nanoparticles (Figure S4b, Supporting Information), while electrodes with a Bi:Sn ratio larger than 1 lead to the formation of relatively larger Bi clusters due to the agglomeration of Bi nanoparticles (Figure S4d, Supporting Information). Interestingly, all electrodes fabricated and tested still show considerably favorable CO\textsubscript{2}RR activity toward formate production resulting in FE\textsubscript{formate} of over 75\%. Regardless, these results obtained from different Bi-Sn compositions indicate that the amounts of each element have a strong influence on the structure of the catalyst which in turn dictate the product selectivity during CO\textsubscript{2}RR. Based on this optimized Bi-Sn bimetallic composition and morphology, the electrode fabrication can be readily scaled up to produce highly efficient CO\textsubscript{2} reduction active gas diffusion electrodes for high conversion rate devices such as CO\textsubscript{2} electrolyzers.

One other point to highlight in this study is the use of flexible and porous carbon fabric as a high surface area growth substrate, which directs the uniform growth of Sn nanosheets and increases the active sites exposure. The porous nature of the electrode significantly promotes diffusion of the dissolved CO\textsubscript{2} into the active sites and the products out of the electrode by the freely flowing electrolyte.\cite{31,39,63} Therefore, the interactions between the catalyst and the surrounding fluid are enhanced. As Figure S8b in the Supporting Information shows, the production rate of formate can be as high as 0.74 mmol h\textsuperscript{−1} cm\textsuperscript{−2} for oxide-derived Bi-Sn/CF electrode at the optimum potential, which is remarkable in comparison to 0.2 mmol h\textsuperscript{−1} cm\textsuperscript{−2} as reported in a previous study of a tin-based CO\textsubscript{2}RR catalyst.\cite{43} The easily scalable composite oxide-derived Bi-Sn/CF electrodes can be sandwiched with a hydrophobic gas diffusion layer to compose a gas diffusion electrode, which is a good candidate for industrial CO\textsubscript{2}-consuming flow electrolyzers.\cite{64}

### 2.3. Stability of Oxide-Derived Bi-Sn/CF Electrode

The durability of the oxide-derived Bi-Sn/CF electrode is demonstrated by conducting CO\textsubscript{2}RR at the optimum potential for an extended period of time of up to 100 h. The resulting current density and FE toward formate are observed to slightly fluctuate due to increasing concentrations of formate in the electrolyte, which is a common phenomenon observed in batch type reactors.\cite{43} In order to eliminate the effect of variation of formate concentration in the electrolyte, it is replaced with fresh electrolyte every 20 h. The durability testing proceeds by applying a constant potential of −1.14 V versus RHE, where the highest FE\textsubscript{formate} is observed, without changing any other cell component. The FE\textsubscript{formate} is calculated every 20 h of operation, and the concentration of formate is found to be as high as 180 × 10\textsuperscript{−3} M. The oxide-derived Bi-Sn/CF electrode exhibits excellent stability over 100 h of operation without any obvious degradation in FE or partial current density of formate as shown in Figure 4 and Figure S9 in the Supporting Information, which is likely attributed to the strong anchoring effect between the active Bi-Sn structure and the carbon fabric substrate which are observed to be unchanged even after long-term durability testing (Figure 4, inset).

### 2.4. Computational Analysis

Periodic DFT calculations have been conducted to support the experimental results obtained above for high CO\textsubscript{2} reduction activity toward formate production on the Bi-Sn bimetallic catalyst. The computational analysis considers two main pathways for CO and HCOO\textsuperscript{−} production from the adsorption of bicarbonate (CO\textsubscript{3}H\textsuperscript{−}) species (Figure S10, Supporting Information),
which is reported as the primary carbon source for formate production during CO2 electroreduction in the literature.\cite{17,44,65} Figure S10c in the Supporting Information shows the binding of CO2H* to the electrode surface during the initial electrochemical step to the carbon atom ((1)) or the oxygen atom ((3)) resulting in the formation of the COOH* or HCOO* intermediates, respectively.\cite{46,66,67} The second electrochemical step (R2) results in the production of CO ((2)) or HCOOH ((4)).\cite{67}

\[
\begin{align*}
\text{CO}_3\text{H}^* + \text{H}^+ + e^- &\rightarrow \text{COOH}^* + \text{OH}^* \quad \text{(R1a)} \\
\text{COOH}^* + \text{H}^+ + e^- &\rightarrow \text{CO}^* + \text{H}_2\text{O}^* \quad \text{(R2a)} \\
\text{CO}_3\text{H}^* + \text{H}^+ + e^- &\rightarrow \text{HCOO}^* + \text{OH}^* \quad \text{(R1b)} \\
\text{HCOO}^* + \text{H}^+ + e^- &\rightarrow \text{HCOOH}^* \quad \text{(R2b)}
\end{align*}
\]

As depicted by the energy profiles (Figure 5a,b), the energy differences (\(\Delta E_1\)) between the adsorption of two competing intermediates (COOH* and HCOO*) on the Sn (101) and Bi-Sn (101) surfaces are 0.55 and 0.81 eV, respectively. The energy differences of corresponding adsorbed products (\(\Delta E_2\)) are 0.43 and 0.85 eV, respectively. The higher values of \(\Delta E_1\) and \(\Delta E_2\) on the Bi-Sn (101) surface indicate that the pathway involving the HCOO* intermediate leads to more favorable formation of formate due to the changes in the electronic structure caused by interfacing with Bi nanoparticles, consistent with the experimental results discussed above.

To better understand the reason for the higher values of \(\Delta E_1\) and \(\Delta E_2\) on the Bi-Sn (101) surface, the projected density of states (PDOS) of the O atom in adsorbed HCOO* and surface Sn atoms in Sn (101) and Bi-Sn (101) are analyzed by decomposing the electron density and the wave function into the atomic orbital contributions. As shown in Figure 6a, there are harmonic p-p and p-s overlaps between the O-2p and Sn-5s, Sn-5p states at energy levels from 0 to \(-10\) eV in Sn (101). In contrast, for Bi-Sn (101), there are three new harmonic overlaps (\(\alpha, \beta, \) and \(\gamma\)) showing the strong interaction between the O and Sn atoms for Bi-doped Sn (101) surface.\cite{68} Especially for the \(\alpha\) and \(\gamma\) areas, large overlaps between O-2p and Sn-4d are observed, indicating strong O–Sn bonding. The density of states at the Fermi energy level (\(E_F\)) roughly determines the availability of electrons for a given reaction.\cite{69} Comparing the PDOS of the p orbitals (Figure 6b) and d orbitals (Figure 6c) of an Sn atom on Sn (101) and Bi-Sn (101) surfaces before HCOO* adsorption, both p and d orbitals of Sn electron states are upshifted away from the Fermi level after interfacing with Bi deposits. Although Sn is not a transition metal, the d orbitals of Sn electron states is still important and needs to be considered for studying the changes in electronic structures.\cite{70} Therefore, the electron density from more electronegative O atoms is readily transferred to the p and d orbitals of Sn atoms, boosting the adsorption energy of the HCOO* intermediate to the Bi-Sn (101) surfaces and leading to the improved selectivity of CO2RR toward formate production.\cite{49,71,72} This finding is consistent with and can be used to explain other reported bimetallic component catalysts (Table S1, Supporting Information) which have shown improved formate selectivity when secondary atoms such as Pd,\cite{44} Ag,\cite{46} Cu,\cite{45} and S\cite{42} were incorporated into Sn, which all have a stronger electronegativity than Sn. On the other hand, the selectivity toward formate was found to decrease with the incorporation of Cd and Zn\cite{50} due to their lower electronegativity compared to Sn (Figure S11, Supporting Information). Strategic combination of binary components will thus lead to the optimum binding energy on the volcano plot, with the electron density shifting between bimetallic components due to their contrasting electronegativity values being the significant contributor.

3. Conclusion

In summary, a bimetallic Bi-Sn catalyst was synthesized and investigated for highly efficient conversion of CO2 into formate. Due to the orbital interaction of Bi-Sn and Sn-O, the composition and morphology optimized electrode (Bi-Sn/CF) led to FEformate of 96% at \(-1.14\) V versus RHE with a high production rate of 0.74 mmol h\(^{-1}\) cm\(^{-2}\). Additionally, the electrode demonstrated an excellent durability of 100 h of continuous operation with no degradation in current density and FE. Furthermore, DFT simulation showed that Bi nanoparticles that formed an interface with the underlying Sn nanosheet resulted in both the p and d orbitals of Sn electron states to be upshifted away...
from the Fermi level. This in turn led to the shifting of the electron density from more electronegative O atoms to the p and d orbitals of Sn atoms, thereby better stabilizing HCOO* intermediates on Bi-Sn(101) than on an undecorated pure Sn(101) surface. The present work sheds light on rational design of catalysts for future CO2RR studies by presenting a facile synthesis technique for nanostructured bimetallic catalysts and providing sub-atomic insights into electronic structure changes at the bimetallic interfaces.

4. Experimental Section

Direct Growth of SnO2 Nanosheets on Carbon Fabrics (SnO2/CF): SnO2 nanosheets were grown on a conductive high surface area carbon fabric (CF, Fuel Cell Earth). The synthesis of SnO2/CF electrode was conducted according to previous work in our lab. Specifically, 0.5646 g of tin(II) chloride dihydrate (SnCl2∙2H2O, Alfa), 0.4508 g of urea (NH2CONH2, Sigma-Aldrich), and 0.1122 g of ammonium fluoride (NH4F, Sigma-Aldrich) were completely dissolved in distilled de-ionized (DDI) water (60 mL) under stirring, then hydrochloric acid (HCl, 37%, Sigma-Aldrich) was added dropwise until the solution turned transparent. One piece of CF (5.0 × 5.0 cm) with the solution were transferred into a 100 mL Teflon-lined autoclave and kept at 180 °C for 10 h. After the hydrothermal process, the obtained CF was rinsed with DDI water and ethanol repeatedly and dried under vacuum at 80 °C overnight.

Bismuth Decoration on SnO2/CF (Bi-SnO2/CF): The as-grown SnO2/CF was used as the substrate to electrodeposit Bi, forming Bi-SnO2/CF. First, an aqueous bismuth solution was prepared by dissolving 0.9700 g of bismuth (III) nitrate pentahydrate (Bi(NO3)3∙5H2O, Sigma-Aldrich) in 60 mL of DDI water; then hydrochloric acid (HCl, 37%, Sigma-Aldrich) was added dropwise to make the solution transparent. One piece of SnO2/CF (1.0 × 1.0 cm) was immersed in the deposition solution as the working electrode, while a saturated calomel electrode (SCE) and a platinum foil were used as reference electrode and counter electrode, respectively. The electrodeposition was conducted by applying −0.1 V versus SCE until a desired amount of electron charge was passed to obtain the composite electrodes with different ratios of Sn and Bi (Table S2, Supporting Information). Pure CF also served as a substrate for the direct deposition of Bi as a comparison, which was denoted as Bi/CF. After electrodeposition, Bi(x)-SnO2/CF and Bi/CF electrodes were cleaned with DDI water and dried in an oven at 80 °C overnight.

In Situ Electrochemical Reduction of Bi-SnO2/CF (Oxide-Derived Bi-Sn/CF) Electrode: In situ electrochemical reduction of the bimetallic electrode was conducted in CO2-saturated 0.5 m KHCO3 electrolyte at −1.8 V versus SCE to electrochemically reduce the as-grown SnO2 during the hydrothermal reaction to Sn. This preconditioning step is consistent with methods mentioned in the literature for tin-based catalysts.

Materials Characterization: The complex oxide-derived Bi-Sn composite electrodes synthesized in this study were characterized by the following techniques. XRD (Rigaku Miniflex 600) and XPS (X-ray Photoelectron Spectrometer, Thermo Scientific K-Alpha XPS spectrometer) were used to confirm the crystal structure and elemental composition, respectively. SEM (LEO field emission scanning electron microscope (FESEM) 1530) and TEM (JEOL 2010F) were employed to observe the morphology of the electrodes.

Electrochemical Measurements: Electrochemical CO2 reduction was conducted in a gas-tight H-type cell with Nafion 117 membrane to separate the two compartments and prevent reoxidation of CO2RR products at the anode (Figure S12, Supporting Information). One platinum wire and an SCE were used as the counter and reference electrodes, respectively. The calibration of the reference electrode was checked against an RHE and the measured potentials (vs SCE) were converted to RHE using the formula

\[
E_{(RHE)} = E_{(SCE)} + 0.235 V + 0.0591 m \times pH.
\]

The electrolyte was 0.5 m potassium bicarbonate (KHCO3, ≥99.95%, Sigma-Aldrich) saturated with CO2 (pH = 7.2). Before electrolysis, the electrolyte was purged with CO2 gas (99.998%, Praxair Gas) for at least 30 min. Each compartment contained 30 mL of electrolyte with a 20 mL headspace. The electrolyte in the cathodic compartment was stirred at a rate of 600 rpm to enhance the electrochemical reaction rate.
mass transport of CO$_2$ and products around the surface of the working electrode. The working electrodes for electrolysis experiments consisted of 0.5 × 1.0 cm oxide-derived Bi(x)-Sn/CF held by a clamp made of platinum. The CO$_2$ reduction was performed for 1 h at various potentials in the electrolyte. The electrochemical measurements were carried out using a potentiostat (BioLogic VSP300). The current densities reported in this work were normalized to the geometric surface area. The CO$_2$ electroreduction test was repeated three times and the results presented are the averaged values. All the experiments were conducted under ambient pressure and at room temperature (23 °C).

CO$_2$RR Products Analysis: The concentration of reaction products in the liquid electrolyte was detected using a 500 MHz $^1$H liquid NMR spectrometer (Bruker Advance) with the water suppression method. The standard solution consisted of 4.61 × 10$^{-3}$ m N,N-dimethylformamide (99.99%, Sigma-Aldrich) and D$_2$O (99.99%, Sigma-Aldrich). N,N-dimethylformamide was used as an internal reference for the chemical shifts. Typically, NMR samples were prepared by mixing 630 µL of the product-containing electrolyte and 70 µL standard solution. Formate calibration curves (Figure S13, Supporting Information) were generated using a stock solution of sodium formate (Sigma-Aldrich). Assuming that two electrons are needed to produce one formate molecule, the FE can be calculated as follows: $FE = 2F \times \text{mol}_{\text{formate}}/Q = 2F \times \text{mol}_{\text{formate}}/(\mathcal{F} t)$, where $F$ is the Faraday constant.$^{[18]}$

Gas products were quantified by gas chromatography (GC, Inficon Micro 3000 GC). The GC has two channels, one equipped with a packed Molecular Sieve column and the other with a packed Plot U column. Each channel was connected to a thermal conductivity detector. Argon (Praxair Gas, 99.9999%) and helium (Praxair Gas, 99.999%) were used as the carrier gases, separately. The gases from the outlet of the cathodic compartment were collected by a 50 CC gas-tight syringe (Perfektron), then injected into the GC. Every gas sample was measured three times. The FEs of both CO and H$_2$ production resulting from the electrolysis were calculated by methods reported in the literature.$^{[44,73]}

DFT Calculation Methods: In order to investigate the origin of the high performance of Bi-Sn bimetallic catalysts, calculations were carried out using periodic DFT implemented in the Vienna Ab initio Simulation Package (VASP 5.2).$^{[76,77]}$ The projector-augmented wave method was applied to solve the ion-electron interactions in a periodic system.$^{[73]}$ The generalized gradient approximation$^{[79]}$ with Perdew–Burke–Ernzerhof$^{[80]}$ functionals was used to treat the exchange-correlation interactions in the Kohn–Sham equations.$^{[76]}$ Spin-polarized calculations were carried out with an energy cutoff for the plane waves of 400 eV.

The convergence criteria for optimization of the atomic structure were set at 5 × 10$^{-6}$ eV and a Hellmann–Feynman$^{[81]}$ force of 0.01 eV Å$^{-1}$. The Gaussian smearing method ($\sigma = 0.1$ eV) was used. A Monkforst–Pack k-point mesh of $2 \times 2 \times 1$ k-points was employed.$^{[82–84]}$ By increasing the cutoff energy to 450 eV and the number of k-points to $4 \times 4 \times 1$, a negligibly small change was observed in adsorption energies ($\sim$0.01 eV) of surface species, which indicates that adsorption energy values are well converged with respect to these parameters. As previously reported,$^{[84]}$ CO$_2$ reduction occurs at a metallic Sn site and the (101) facet of Sn can be detected by HRTEM; therefore, a Sn (101) surface with four atomic layers and $2 \times 2$ unit cells was used as the model system. The interface of Bi-Sn bimetallic electrode is important for highly selective CO$_2$RR. In order to simulate the role of Bi on this bimetallic catalyst, a Bi-Sn (101) surface was built by docking one Bi atom onto the surface of pure Sn (101) surface (Figure S10, Supporting Information). Although there were no explicit alloy peaks observed in the XRD pattern, Bi atoms at the surface of Sn can still be inserted into the underlying lattice to form a bimetallic Bi-Sn interface.$^{[43]}$ A vacuum layer of 15 Å was added to separate neighboring slabs to avoid possible interaction. An $8 \times 8 \times 1$ k-points mesh was used for the density of states calculation.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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