Spontaneously Sn Doped Bi/BiO$_x$ Core–shell Nanowires Toward High-Performance CO$_2$ Electroreduction to Formate

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Electrochemical CO$_2$ reduction to formate using renewable electricity provides a promising strategy to product value-added carbon-based fuels and feedstocks. However, it still remains a grand challenge to further reduce the cathodic potentials and increase current density for the large-scale practical applications of formate. Herein, we report that spontaneously Sn doped Bi/BiO$_x$ nanowires (denoted as Bi/Bi(Sn)O$_x$ NWs) are prepared from electrochemical dealloying strategy. The Bi/Bi(Sn)O$_x$ NWs exhibit impressive CO$_2$ electroreduction activity to formate with a Faradaic efficiency (FE) > 92% from -0.5 to -0.9 V versus reversible hydrogen electrode (RHE), and achieve a current density of 301.4 mA cm$^{-2}$ at -1.0 V vs. RHE
under gas diffusion cell configuration. In-situ Raman spectroscopy and theory calculations reveal that the incorporation of Sn atoms into BiO$_x$ species modulates the electron states of Bi, allowing the $^*$OCHO intermediate to favorably adsorb onto the reconstructed Bi(Sn)O$_x$ surface while promotes formate generation by suppressing the competitive hydrogen evolution reaction. This work provides effective in-situ construction of the metal/metal oxide hybrid composites with heteroatom doping and offers insights in promoting practical CO$_2$ conversion technology.

Electrochemical reduction of CO$_2$ into value-added chemicals or fuels provides a promising strategy to alleviate the excessive combustion of fossil fuels and greenhouse effects, especially driven by renewable energy$^{1,2}$. The nontoxic formate is an important liquid product of electrochemical CO$_2$ conversion, which has been widely applied to various energy and industrial fields, such as hydrogen storage and fuel cells$^{3-5}$. However, the inevitable bottleneck in electrochemical CO$_2$ reduction reaction leads to the poor selectivity and low efficiency for the production of desired formate because of the large energy barrier required for activating CO$_2$ to $^*$OCHO intermediate and the inevitably competing hydrogen evolution reaction (HER) in aqueous media$^6$. Therefore, it is immensely significant yet challenging to exploit high-activity, selectivity, and stability catalysts for the large-scale practical formate applications.

Recently, various heterogeneous electrocatalysts including metals (such as Pd, Bi, In, Sn, etc.) and their derivatives have shown recent progress in electrochemical CO$_2$ reduction to formate$^7$-$^9$. Among them, Bi-based oxide nanostructures generally prefer...
to convert CO$_2$ into formate due to their strong adsorption of CO$_2$ intermediates and poor activity for HER$^{10-13}$. Unfortunately, various Bi-based oxides usually suffer from undesirable activity in a low and wide cathodic potential window owing to their relatively low intrinsic electrical conductivity and low selectivity toward formate production$^{14-16}$. One feasible strategy for promoting electrical conductivity is to prepare core–shell nanostructured catalysts with a highly conductive metal core and thin metal oxide shell, which can potentially modulate the electronic properties and tune the binding strength of the intermediates$^{17-19}$. To further promote the activity of electrocatalysts, engineering new Bi-based materials by incorporating other components has emerged as an efficient strategy to modulate the reactant adsorption, activation and product desorption, such as Bi$_2$O$_3$ nanosheets modified by nitrogen-doped graphene quantum dots or multi-channel carbon matrix$^{13,20}$, Sn-Bi eutectic alloys$^{21-23}$, hybrids of Sn nanosheets and Bi nanoparticles$^{24}$, Bi@Sn core–shell nanoparticles$^{17}$, which are promising candidates for the electrochemical reduction of CO$_2$ to formate. Obviously, the problems of low formate selectivity and high competition with hydrogen evolution at low overpotentials remain unsolved even by using flow cell reactors.

In this work, we present novel Sn doped Bi/BiO$_x$ nanowires with high electrical conductivity Bi metallic core and amorphous Sn-doped BiO$_x$ shell through electrochemical dealloying. The Bi/Bi(Sn)O$_x$ NWs exhibits an excellent catalytic activity and selectivity for electrochemical CO$_2$ reduction to formate over a wide negative potential range, with a Faradaic efficiency (FE) $>$ 92% from -0.5
to -0.9 V versus reversible hydrogen electrode (RHE), and a maximum FE value of 98 ± 2 % at −0.7 V under gas diffusion cell configuration. The impressive performance is attributable to the incorporation of Sn atoms into BiO\textsubscript{x} species, which can modulate the electron states of Bi, allowing the *OCHO intermediate to favorably adsorb onto the Bi(Sn)O\textsubscript{x} surface while promotes formate production by suppressing the competitive hydrogen evolution reaction.

**Results**

**Material synthesis and characterization.** A schematic illustration of the fabrication process toward novel Bi/Bi(Sn)O\textsubscript{x} NWs is shown in **Figure 1a**. By utilizing the disparity in electrochemical stability of the Bi and Sn phases, the Sn atoms were priority dissolved from the arc-melt spinning Bi\textsubscript{1−x}Sn\textsubscript{x} (at%) alloy ribbons by galvanic corrosion in 0.25 M H\textsubscript{2}SO\textsubscript{4} solution at the applied potential of -0.3 V versus Ag/AgCl (**Supplementary Fig. 1**)\textsuperscript{25,26}. During the dealloying of the Bi-Sn alloys, as the Sn atoms are continuously dissolved into the electrolyte from the Sn phase, the Bi atoms would be released and reorganized into well-arranged single-phase Bi-based nanowires along the direction of etching (**Fig. 1b**)\textsuperscript{27,28}. Scanning electron microscopy (SEM) image (**Fig. 1c**) displays the continuous nanowire structure of the etched ribbons. The corresponding energy dispersive X-ray spectroscopy (EDS) analysis provides a chemical composition of Bi/Sn atom ratio is ∼95:5 (**Supplementary Fig. 2**). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image clearly shows that crystalline range of Bi/Bi(Sn)O\textsubscript{x} NWs with
diameter of ~30 nm is surrounded by thick amorphous-like shells (Fig. 1d). The selected-area electron diffraction (SAED) exhibits a single diffraction pattern, which could be indexed as a rhombohedral Bi structure (JCPDS No. 44-1246) with a growth direction of [101] (Fig.1e). The lattice distance measured from fast Fourier transformation (FFT) of HAADF-STEM image (Fig. 1f) exhibits the interface of Bi (101) core and amorphous oxide shell. The distribution of different elements in the nanowires is revealed by STEM-EDS element maps (Fig. 1g), where Bi is homogeneously present in the central region, while coexistence of Bi, Sn and O on the surface of the metallic Bi core.

The chemical state and electronic structure of the Bi/Bi(Sn)Ox NWs were further investigated by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) measurements. Figure 2a–c show Bi/Bi(Sn)Ox NWs survey spectra and typical XPS fitting curves of the Bi 4f, Sn 3d, and O 1s spectra before and after Ar⁺ etching (5 keV, 3 min), along with the Bi₂O₃ and SnO₂ nanoparticles as references. The Bi 4f spectrum of the Bi/Bi(Sn)Ox NWs in Figure 2a could be deconvoluted into Bi⁰ and Bi³⁺ components. This suggests that Bi⁰ and Bi³⁺ species co-exist on the surfaces of Bi/Bi(Sn)Ox NWs. More importantly, the intensity of the Bi⁰ peak was increased after the Ar⁺ etching, which could be associated with the expose of the inner metallic Bi core while the decrease of the outer layer of oxide shell. Moreover, the Sn 3d XPS spectrum of Bi/Bi(Sn)Ox NWs dramatically decreases in intensity in the etched XPS spectra (Fig. 2b). The surface adsorbed oxide (531.8 eV) was also removed after the Ar⁺ etch (Fig. 2c). Specifically, the surface compositions obtained from XPS
agree with the SEM-EDS results (Supplementary Table 1). The Bi L3-edge X-ray absorption near edge structure (XANES) spectra of the Bi/Bi(Sn)Ox NWs in Figure 2d reveal visible similarities with that of the Bi and Bi2O3 reference. These similarities are to be expected, given that Sn atoms in both Bi2O3 and BiOx lattices are expected to be octahedrally coordinated by oxygen atoms, leading to similarities in their structural and electronic properties. Meanwhile, the XANES spectra apparently reveal that Bi L3-edge position of the Bi/Bi(Sn)Ox NWs is located between the Bi foil and Bi2O3, indicating coexistence of metallic Bi and oxidation state Bi species in the core-shell structure. The corresponding Fourier-transformed extended x-ray absorption fine structure (FT-EXAFS) spectra and inversed FT-EXAFS are presented in Figure 2e, f, respectively. The similar positions of the metallic Bi peak positions suggest that these bonds lengths in the Bi/Bi(Sn)Ox NWs are similar to those in the Bi reference, strongly indicating the metallic Bi-core structure. In stark contrast, the observed Bi–O peaks appear at distinctly positions in the Bi/Bi(Sn)Ox NWs spectra, revealing a distinct structural difference relative to the pure Bi reference. Interestingly, the formation of Bi2O3, SnO2 can be predicted from the Bi–Sn–O ternary phase diagram at low Sn content (region iii, Supplementary Fig. 3)\textsuperscript{23}, which is consistent with our XPS and XAS results. According to the above-mentioned surface and bulk sensitive techniques, we can conclude that the prepared Bi-based nanowires display a core-shell structure with metallic Bi cores and amorphous Bi(Sn)Ox shells. In fact, the synergetic effect of the metallic core and the amorphous oxide shell in providing both good bulk conductivity and surface activity is beneficial to high performance CO2 electroreduction.
**Electrochemical CO$_2$ reduction performance.** The electrocatalytic CO$_2$ reduction performance of the Bi/Bi(Sn)O$_x$ NWs were evaluated in a gas diffusion flow cell with 1.0 M KOH electrolyte (Supplementary Fig. 4), along with commercial Bi, Bi$_2$O$_3$, and SnO$_2$ as references (Supplementary Fig. 5, 6). Figure 3a shows linear sweep voltammetry (LSV) curves of the Bi/Bi(Sn)O$_x$ NWs with commercial Bi, Bi$_2$O$_3$, and SnO$_2$ nanopowder catalysts. The cathodic current density of the Bi/Bi(Sn)O$_x$ NWs sharply increases and markedly reaches −301.4 mA cm$^{-2}$ at −1.0 V vs. RHE under CO$_2$ flow, suggesting its superior CO$_2$ reduction activity. Resultant gaseous products were periodically sampled and examined using gas chromatography (GC), and the liquid products were analyzed by nuclear magnetic resonance (NMR) spectroscopy (Supplementary Fig. 7, 8). Faradaic efficiency of Bi/Bi(Sn)O$_x$ NWs and commercial Bi, Bi$_2$O$_3$, SnO$_2$ nanopowders were calculated and summarized in Figure 3b and Supplementary Figure 9. Bi/Bi(Sn)O$_x$ NWs possess the highest selectivity towards formate, with above 92% Faradaic efficiency in a wide potential range (from −0.5 to −0.9 V) and a maximum FE of nearly 100% at −0.7 V versus RHE (Fig. 3c). In contrast, Bi, Bi$_2$O$_3$, and SnO$_2$ catalysts show lower selectivity towards formate, while CO or H$_2$ dominates in the low potential range (Supplementary Fig. 9). In addition, the partial current density of formate on Bi/Bi(Sn)O$_x$ NWs is significantly higher than that of commercial Bi, SnO$_2$, and Bi$_2$O$_3$ nanopowders (Fig. 3d), showing a desirable formate current density of ~100 mA cm$^{-2}$ at a maximum formate FE of −0.7 V. Compared with reported Bi-based catalysts for electrochemical CO$_2$ reduction, Bi/Bi(Sn)O$_x$ NWs maintain the highest formate selectivity over a wide potential range (Supplementary
The energy efficiency (EE) of the Bi/Bi(Sn)Oₓ NWs is further evaluated, which shows a high EE over 60% in a wide potential range (Supplementary Fig. 10). Tafel analysis is indispensable for understanding the kinetics of CO₂ electroreduction. The Bi/Bi(Sn)Oₓ NWs exhibit a much lower Tafel slope of 124 mV dec⁻¹, suggesting that the chemical rate-determining step (RDS) is the first electron transfer step to generate surface adsorbed CO₂●⁻ species (Supplementary Fig. 11)²⁹-³¹. Furthermore, the Bi/Bi(Sn)Oₓ NWs displays remarkably higher CO₂ adsorption capability compared with commercial Bi and Bi₂O₃ (Supplementary Fig. 12). This could lead to CO₂ enrichment on the local working electrode surface, which is beneficial for CO₂ activation and reduction³²,³³. Electrochemical impedance spectroscopy (EIS) analysis further verifies that the Bi/Bi(Sn)Oₓ NWs catalyst with metallic core-shell structure could generate small internal resistance and rapid charge transfer behavior for a low onset potential and fast CO₂ reduction reaction (CO₂RR) kinetics (Supplementary Fig. 13). To evaluate the intrinsic activity of the catalysts, we measured the electrochemically active surface area (ECSA) for Bi/Bi(Sn)Oₓ NWs, Bi, Bi₂O₃, and SnO₂ (Supplementary Fig. 14) and evaluated their ECSA-normalized partial current densities for formate production, hydrogen evolution, and CO production (Supplementary Fig. 15). Strikingly, Bi/Bi(Sn)Oₓ NWs show lower HER and CO production rates, which results in it having higher selectivity for formate production than pure Bi, Bi₂O₃, and SnO₂. These results confirm that the presence of metallic Bi core in the hybrid catalysts could decrease the energy barrier and facilitate the charge-transfer process from the electrode to the adsorbed CO₂, contributing to excellent
selectivity and ultrahigh current density. In addition, a long-term stability testing on the Bi/Bi(Sn)Oₓ NWs catalyst shows a negligible current decay and a steady FE of formate over 10 h at an operated potential of -0.7 V. Furthermore, no detectable compositions and morphology changes were observed on Bi/Bi(Sn)Oₓ NWs after the long-term operation, implying the superior structural stability (Supplementary Fig. 16, 17).

**Active sites identification and mechanisms of CO₂RR.** To survey the detailed structure of the Bi/Bi(Sn)Oₓ NWs surface during CO₂RR, in situ electrochemical Raman spectroscopy analysis was performed to identify the dynamic evolution of the Bi/Bi(Sn)Oₓ NWs surface (Supplementary Fig. 18). As Figure 4a shown, three typical Raman peaks at 97 cm⁻¹, 128 cm⁻¹ and 314 cm⁻¹ are presented under open circuit potential (OCP), which are assigned to the Bi-Bi and Bi-O stretching mode. When the cathodic potential is gradually increasing from -0.4 V to -0.8 V vs. RHE in the CO₂-saturated electrolyte, the peaks of the Bi-O are still remained under the actual CO₂RR condition. It is worth noting that the scattering intensity of Bi-O peak weakens but preserves strength to some extent at -0.8 V vs. RHE, indicative of partial reduction of the Bi(Sn)Oₓ shell in the Bi/Bi(Sn)Oₓ NWs catalyst during CO₂RR. Nevertheless, the Bi–O structure can be reconstructed when the potential is removed, which in accordance with previous reports. These results indicate that Bi-O structure is stable under the maximum formate Faradaic efficiency, while it was being partial reduced to metallic Bi at high overpotential.

To gain further insights into the CO₂RR activity and selectivity toward formate production on the reconstructed Bi/Bi(Sn)Oₓ NWs, density functional theory (DFT)
calculations were carried out to analyze the thermodynamic reaction process. The structural models for the DFT calculations were built based on a Bi$_2$O$_3$ layer deposited on the Bi surface according to the above structural identifications (Supplementary Fig. 19). The binding strength of *OCHO intermediates could be inferred from the position of the highest p-electronic states ($E_p$) and the charge density distribution. In Figure 4b, the $E_p$ of Bi/Bi(Sn)O$_x$ moves more closely to the Fermi level ($E_f$) and displays a stronger electronic interaction between *OCHO, which also consistent with the stronger electronic interaction between *OCHO and the substrate (Fig. 4b, inset). We also explored the reaction pathways for CO$_2$ reduction to HCOOH and HER. In Figure 4c, the Bi/Bi(Sn)O$_x$ catalyst shows a lower energy barrier ($\Delta G$) for *OCHO formation, which indicate that the doped of Sn atom can greatly stabilize *OCHO. In addition, the calculated Gibbs free energies for H$_2$ pathway on Bi/Bi(Sn)O$_x$ (0.6 eV) surfaces is higher than that of Bi/BiO$_x$ (0.32 eV), indicating the superior inhibition of HER. Hence, according to the above results, we speculate the possible mechanism of the CO$_2$RR processes in Bi/Bi(Sn)O$_x$ surface, where the CO$_2$ molecules can been fast adsorption and proton-coupled electron transfer to form *OCHO intermediates. The incorporation of Sn atoms into Bi-O structure can facilitate the stabilizing *OCHO, and eventually accelerate the production of formate (Fig. 4d).

Conclusions

In summary, we demonstrated a facile route to synthesis the Bi/Bi(Sn)O$_x$ NWs with a metallic Bi core and amorphous Sn-doped BiO$_x$ shells by electrochemical
dealloying method. The resultant Bi/Bi(Sn)Ox NWs yielded excellent electrochemical CO₂ reduction activity with FE over 92% at a wide potential range (-0.5 ~ -0.9 V vs. RHE) and a high current density (> 300 mA cm⁻² at -1.0 V) in the gas diffusion cell. Moreover, Bi/Bi(Sn)Ox NWs showed stable current density and FE_{HCOOH} without significant decay during chronoamperometry test over 10 h. In-situ Raman and DFT calculations suggested that the incorporation of Sn atoms into BiOx surfaces that stabilizes the *OCHO intermediate and suppresses the HER. The present work opens a new avenue to develop new core/shell catalysts with the desired control on reaction pathways and target products for highly efficient CO₂RR, but offers a facile and economic strategy to create new atom doped oxide catalysts reconstructed from bimetallic surfaces for boosting other chemical reactions.
Methods

Materials synthesis. The Bi$_{1}$Sn$_{99}$ (at%) precursor alloy ribbon was prepared by arc melting and copper roller spinning technique under an argon atmosphere. The alloy ribbons with the dimensions of ~3 mm wide and 40 μm thick were cut into thin plates with dimensions of 5 mm wide and 20 mm long for the subsequent dealloying process. Bi/Bi(Sn)O$_{x}$ NWs catalysts was fabricated by electrochemically etching the Bi$_{1}$Sn$_{99}$ precursors in a 0.25 M H$_{2}$SO$_{4}$ solution configuration with a Ag/AgCl and graphite sheet as the reference and counter electrode, respectively. The selective Sn phase dissolution process was determined by the critical oxidation potentials of the Sn in Bi$_{1}$Sn$_{99}$ alloy ribbon. In our experiments, Bi/Bi(Sn)O$_{x}$ NWs was obtained at a dealloying voltage of -0.3 V (vs. Ag/AgCl) for 3000 s after the almost dissolution of the Sn. The dealloyed samples were rinsed by deionized water for more than three times still the solution became neutral. Commercial Bi (~200 mesh, 99.999%) was purchased from Alfa Aesar. Bismuth (III) oxide (Bi$_{2}$O$_{3}$, 99.999%), Stannic (IV) Oxide (SnO$_{2}$, 99%) were purchased from Adamas.

Characterizations: XRD patterns of the samples were taken by using a Bruker D8 Advance X-ray diffraction with Cu Kα radiation ($\lambda$=1.5418 Å). Microstructure and chemical composition were inspected with a MIR3 TESCAN SEM (at 10 kV and 5.5 mm work distance.) equipped with an Oxford energy dispersive X-ray spectroscopy. The TEM, HAADF-STEM and EDS mapping were taken by a JEM-ARM 200F with double spherical aberration (Cs) correctors for both the probe-forming and image-forming objective lenses at an accelerating voltage of 200 kV. The chemical state and
composition of the samples were characterized using X-ray photoelectron spectroscopy (XPS, AXIS SUPRA) with a Al Kα monochromatic. The CO₂ adsorption isotherms were measured by a Micromeritics ASAP2460. Raman spectra were obtained by Witec alpha300 R confocal Raman microscopes with He/Ne laser of λ = 532 nm and 20 mW. In-situ electrochemical/Raman spectra were achieved in a commercial Raman cell using 1 M KOH electrolyte and CO₂ is flowing at 5 mL min⁻¹ under different applied potential. X-ray absorption spectra, including the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), were obtained at the Bi L₃-edge at the beamline 01C1 (National Synchrotron Radiation Research Center: NSRRC, Hsinchu, Taiwan). All spectra were obtained in the fluorescence mode at room temperature. The spectra were normalized with respect to the edge height after subtracting the pre-edge and post-edge backgrounds using Athena software.

**Electrochemical CO₂RR measurements:** All CO₂ reduction experiments were performed in a commercial gas-diffusion flow cell separated by anion exchange membrane (Sustainion X37-50). The two compartments were each filled with ~35 mL of 1 M KOH electrolyte. A Pt foil and Hg/HgO (1M KOH) electrode were used as the counter electrode and reference electrode, respectively. Electrode potentials were converted to the reversible hydrogen electrode (RHE) reference scale using $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \text{ V} + 0.059 \times \text{pH}$. The linear sweep voltammetry (LSV) curves were recorded with a CHI-760E electrochemical workstation with a scan rate of 5 mV s⁻¹. For clarity, all LSV data were not corrected for a negligible ohmic drop. The chronoamperometry tests were conducted at each potential for 40 min. The long-term
stability measurement was operated at the potential of \(-0.7\) V versus RHE for 10 h. The current densities were normalized to the geometric surface area. CO\(_2\) gas was delivered into the cathodic compartment at a rate of 10 ml/min and was routed into a gas chromatograph (Shimadu, GC-2010 Plus). The catalyst was sprayed on a gas diffusion layer of Sigracet 29 BC with a surface area of 1 cm\(^2\), the eventually loading mass is \(\sim 1\) mg cm\(^{-2}\).

The gaseous products from CO\(_2\) electroreduction were quantified by a gas chromatograph equipped with a flame ionization detector (FID) for CO and a thermal conductivity detector (TCD) for H\(_2\) quantification. Before the FID, a methanizer is equipped for the detection of CO. High-purity Argon (99.999\%) was used as the carrier gas. The Faradaic efficiency of each gas product was calculated by the equation:

\[
\text{FE} (\%) = \frac{neF}{Q} \times 100\%
\]

where \(e\) is the number of electrons transferred, \(F\) is Faraday constant, \(n\) is the mole fraction of the product, and \(Q\) is the total charge.

Liquid products were quantified on Bruker 400 MHz NMR spectrometer. Typically, 500 \(\mu\)l of collected catholyte exiting the reactor was mixed with 100 \(\mu\)l D\(_2\)O containing 20 ppm (m/m) dimethyl sulphoxide (\(\geq 99.9\%\); Alfa Aesar) as the internal standard. The faradic efficiency for HCOOH generation was calculated as follows:

\[
\text{FE}_{\text{HCOOH}} (\%) = \frac{Q_{\text{HCOOH}}}{Q_{\text{total}}} \times 100\% = \frac{n_{\text{HCOOH}}eF}{l \times t} \times 100\%
\]

where \(n\) (mol) is the generated amount of formate; \(e\) (= 2) is the number of transferred electrons for 1 mol of formate generation; and \(t\) (s) is the electrolysis time.

The cathode energy efficiency was calculated to define the energy utilization
toward the HCOOH product using the following formula:

\[
EE = \frac{1.23 - E_{HCOOH}}{1.23 - E_{applied}} \times FE_{HCOOH} \times 100\%
\]

where \(E_{HCOOH} = -0.2\) V vs. RHE is the thermodynamic potential for HCOOH formation, 1.23 V is the thermodynamic potential for the oxygen evolution reaction, and \(E_{applied}\) is the applied potential vs. RHE\(^{14}\).

**DFT Calculations.** The calculations were performed with the VASP package\(^{36}\), using Perdew-Burke-Érnzerhof (PBE) of exchange correlation energy functional based on a generalized gradient approximation (GGA) method\(^{37,38}\). After testing the energy cutoff and k-points convergence, we chose 450 eV as our cutoff energy, and used a 5 × 5 × 1 k-points grid to sample the unit cell Brillouin zone\(^{39}\). The convergence thresholds were set as \(1 \times 10^{-5}\) eV/atom for the energy, and atomic relaxation was performed until all components of the residual forces were less than 0.02 eV/Å. The spin polarization is considered for magnetic atoms in all simulations and DFT-D3 correction is used to deal with van der Waals interactions. A Bi\(_2\)O\(_3\) layer is deposited on two layer Bi (111) substrate as Bi/BiO\(_x\) model. For Bi/Bi(Sn)O\(_x\) simulation, we adopted Sn replace the partial Bi atom in Bi\(_2\)O\(_3\).

The Gibbs free energy of formation \((\Delta G)\) for each step is calculated by the following formula:

\[
\Delta G = \Delta DFT + \Delta ZPE - T\Delta S
\]

Where \(\Delta DFT\), \(\Delta ZPE\) and \(T\Delta S\) are DFT energy change, the zero-point energy change and entropy change between the product and reactant, and temperature T is set as 298.15 K.
The D-band center calculation is based on J. K. Nørskov’s works and uses the following formula\textsuperscript{40}:

\[
\Delta \varepsilon_d = \frac{\int_{-\infty}^{+\infty} x \rho(x) dx}{\int_{-\infty}^{+\infty} \rho(x) dx}
\]

Where \( \int_{-\infty}^{+\infty} x \rho(x) dx \) is the integral of the product of the energy level and the density of states from negative infinity to positive infinity and \( \int_{-\infty}^{+\infty} \rho(x) dx \) is the integral of the density of states from negative infinity to positive infinity.
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Data availability. The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Figure Legends

Figure 1. Structural characterizations of Bi/Bi(Sn)Oₓ nanowires. (a) Schematic illustration for the preparation of the Bi/Bi(Sn)Oₓ NWs. (b) XRD patterns, (c) SEM image. (d) STEM-HAADF image. (e, f) Corresponding SAED pattern and enlarge image. (g) STEM-EDS element mapping of Bi, Sn, and O. Scale bars: (c) 1 μm, (d) 10 nm, (e) 5 1/nm, (f) 2 nm, (g) 20 nm.

Figure 2. X-ray photoelectron spectroscopy and X-ray absorption spectroscopy characterizations of Bi/Bi(Sn)Oₓ NWs. (a) Bi 4f, (b) Sn 3d, and (c) O 1s XPS spectra of the Bi/Bi(Sn)Oₓ NWs before and after Ar⁺ etching. (d) Bi L₃-edge XANES spectra of the Bi/Bi(Sn)Oₓ NWs, Bi₂O₃, and Bi foil. (e, f) Corresponding FT-EXAFS and inversed FT-EXAFS spectra.

Figure 3. Electrochemical CO₂ reduction performance of Bi/Bi(Sn)Oₓ NWs in a flow cell. (a) LSV curves of the Bi/Bi(Sn)Oₓ NWs, Bi, Bi₂O₃, and SnO₂ catalysts in Ar- or CO₂-saturated 1.0 M KOH aqueous solution. (b) H₂, CO, and formate FEs of the Bi/Bi(Sn)Oₓ NWs. (c, d) Potential-dependent FE (c) and partial current density (d) of Bi/Bi(Sn)Oₓ NWs, Bi, Bi₂O₃, and SnO₂. (e) Long-term stability test of the Bi/Bi(Sn)Oₓ NWs at −0.7 V vs. RHE.

Figure 4. In-situ Raman and DFT calculations. (a) In-situ electrochemical Raman spectra of Bi/Bi(Sn)Oₓ NWs. (b) Projected p-orbital DOS of the Bi site with *OCHO
adsorbate, insert is charge density differences calculations of *OCHO bonded to Bi/BiOx and Bi/Bi(Sn)Ox. (c) Free-energy diagrams for HCOOH, and H2 formation on Bi/BiOx and Bi/Bi(Sn)Ox. (d) The schematic illustration of CO2 reduction processes on the Bi/Bi(Sn)Ox.
Figure 1.
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