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Atomic indium oxide domains redirect zinc selectivity for exclusive CO₂-to-formate conversion

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Abstract

The electrochemical reduction of CO₂ (CO₂RR) to formic acid (HCOOH) is both economically viable and technically promising for industrial applications. However, current catalysts for HCOOH production exhibit substantial overpotentials to achieve industrial production rates. This limitation stems from the relatively low activity for solvent–water activation of high HCOOH-selective catalysts, e.g., Bi and Sn, which in turn leads to a high energy barrier for the hydrogenation of CO₂-to-*HCOO intermediates. Here, we report the exclusive CO₂-to-formate conversion on Zn, a well-known CO-selective catalyst with moderate hydrogen evolution activity, via atomic indium oxide domain (In₁O₆) functionalization. The catalyst demonstrates Faradaic efficiencies for HCOOH exceeding 90% across a wide voltage range. Impressively, it required merely −1.49 V vs. RHE to deliver an activity of −1000 mA cm^{−2} with current efficiency of ~94%, showing much improved cathodic energy efficiency (~45%) compared with that of conventional alternatives. Mechanistic studies revealed that the incorporation of atomic In₁O₆ domains into Zn shifts the CO₂ adsorption configuration on the surface from bent to linear, thereby driving the selectivity inversion from CO to HCOOH. In₁O₆ domains further modulate the electronic structure of Zn and its adsorption properties, resulting in highly active Zn^{δ+} sites, which are conducive to the stabilization of *HCOO intermediates and yield enhanced activity. This work establishes the concept of bridging-atom-mediated single-atom modulation, offering new insights into the design of efficient and sustainable systems for CO₂ electrolysis and beyond.

Keywords CO₂ reduction reaction, Formate/formic acid, Single-atom modulation, Porous solid electrolyte reactor

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1 Introduction

The electrochemical reduction of CO₂ (CO₂RR) represents a promising avenue for sustainable chemical synthesis, enabling the transformation of a greenhouse gas into valuable fuels and feedstocks [1]. Among the wide spectrum of potential CO₂RR products, formic acid (HCOOH) stands out for its economic feasibility and scalability in industrial applications [2]. In this context, substantial efforts have been devoted to designing catalysts that can selectively convert CO₂ into HCOOH. Early studies empirically classified catalysts into categories, identifying gold (Au), silver (Ag) and zinc (Zn) as CO-selective, whereas lead (Pb), bismuth (Bi) and indium (In) were associated with HCOOH selectivity [3–5]. While this empirical framework provided a foundation for catalyst development, it also imposed rigid boundaries that constrained further exploration. Recent studies on single-atom alloy (SAA) catalysts have demonstrated that selectivity on a host metal can be fundamentally redirected by isolated dopant atoms that serve as electronic modulators rather than active sites, as exemplified by Pb₁Cu for formate and Sb₁Cu for CO production in our previous reports [6, 7]. However, in the reported SAA systems, the dopant atom directly bonds to the host metal, and modulation is confined to the nearest-neighbor shell. A question thus arises: can single-atom modulation be extended beyond direct metal–metal contact to achieve selectivity control through indirect electronic coupling?

To address this question, it is instructive to first consider the mechanistic basis of selectivity. Advances in theory and spectroscopy have revealed that the selectivity for CO or HCOOH is governed by the stabilization of specific intermediates: *COOH for CO and *HCOO for HCOOH [8]. A significant challenge in optimizing catalysts for HCOOH production lies in the fact that metals with favorable *HCOO binding strengths often exhibit low activity in solvent–water activation [4, 9], thus limiting the overall efficiency. For example, conventional formate-producing metals, such as Pb and In, possess relatively inert surfaces for hydrogen adsorption, such that negligible amounts of hydrogen can adsorb at potential where CO₂ is reduced [3], consequently resulting in substantial overpotentials in the CO₂RR [5, 10, 11]. These outcomes have, therefore, inspired new approaches focused on shifting the balance between CO₂ and water activation. Previous studies have shown that the sulfur doping strategy plays a role in accelerating water activation among traditional formate-producing catalysts during the CO₂RR [12, 13]. Nevertheless, owing to the weak binding strength of sulfur–metal bonds, atom leaching still occurs and subsequently leads to destructive structural collapse and stability attenuation [14, 15]. An alternative strategy is to redirect CO-selective catalysts that

already possess moderate hydrogen evolution reaction (HER) activity, rather than attempting to accelerate water activation on intrinsically sluggish formate-producing metals. We therefore turn our focus to Zn, a prototypical CO-selective catalyst that is abundant, cost-effective, and widely studied for the CO₂RR [3, 5, 16]. Moreover, Zn (with negative $\Delta H^* - \Delta \text{COOH}^*$) also has advantages in water activation, which might realize energy-efficient HCOOH production under high production rates [4, 16, 17].

Herein, we report a HCOOH-selective Zn catalyst by introducing atomic indium oxide domains (In₂O₃) into a Zn matrix (Fig. 1a), denoted In₁(O)Zn. Unlike conventional single-atom alloys in which the dopant directly contacts the host metal, here we establish abundant Zn^{δ+} active sites in In₁(O)Zn catalysts through the incorporation of atomic indium oxide domains [6, 7, 18]. Since In-based species are prone to oxidation, they can preserve an oxygen-coordinated In_xO_y environment under cathodic potentials, thereby enabling an indirect modulation pathway through In–O–Zn bridging bonds [19–21], leading to enhanced structural stability during operation conditions. The resultant catalyst shows impressive performance, achieving a Faradaic efficiency (FE) for HCOOH production above 90% across a wide voltage range (−1.01 to −1.49 V vs. RHE), with a peak efficiency of 94% at a current density of −1000 mA cm^{−2}. Spectroscopies and theoretical simulations revealed that the incorporation of the atomic In₂O₃ domain modulates the electronic structure of the Zn matrix, lowers the energy barrier for *HCOO formation, and thus facilitates formate desorption. When integrated in a porous solid electrolyte (PSE) reactor, it demonstrates stable performance for producing pure formic acid, maintaining an FE_{HCOOH} of ~92% for over 260 h at −50 mA cm^{−2}. This work establishes the concept of bridging-atom-mediated single-atom modulation, wherein a dopant atom tunes the host metal indirectly through a heteroatom bridge, offering new insights into the design of efficient and sustainable systems for CO₂ reduction.

2 Results and discussion

2.1 Zinc catalyst fabrication and characterization

The zinc catalyst was synthesized via the co-reduction of a Zn²⁺ and In³⁺ precursor (see *Methods*). X-ray diffraction (XRD) analysis revealed a pure ZnO crystal structure (PDF 89–0510, Fig. S1), excluding the formation of In nanoparticles. The incorporation of In was verified by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which revealed that the In content was 4.7 at% (labeled as ~5% In content sample, Table S1). This result is consistent with the X-ray photoelectron spectroscopy (XPS) data, which further validated the

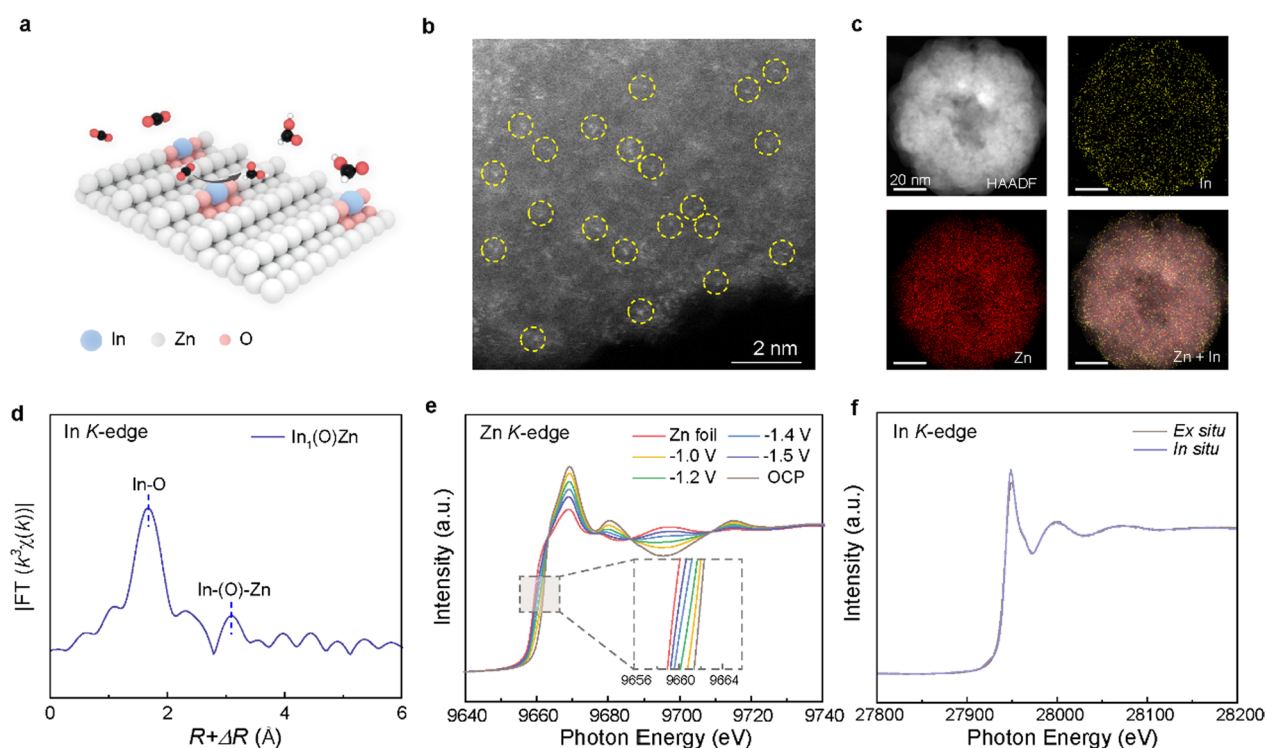


Fig. 1 Structural characterization of the $\text{In}_1(\text{O})\text{Zn}$ catalyst. **a** Schematic illustration of CO_2 -to-formate conversion over the catalyst surface. **b, c** HAADF-STEM image and STEM-EDS mapping of In and Zn. The yellow circles highlight In single atoms. **d** *Ex situ* EXAFS spectra at the In K-edge of the $\text{In}_1(\text{O})\text{Zn}$ catalyst. **e** *Operando* Zn K-edge XAS spectra of the $\text{In}_1(\text{O})\text{Zn}$ catalyst under applied potentials during the CO_2RR . The Zn foil is shown as a reference. All potentials were calibrated to the RHE scale. **f** *In situ* and *ex situ* In K-edge XANES profiles of the $\text{In}_1(\text{O})\text{Zn}$ catalyst. Owing to the low content of In, the *in situ* In K-edge signal quality was unsatisfactory. Here, we compared only the XANES profiles to analyze the degree of oxidation

successful doping of In into the Zn matrix (Fig. S2). Transmission electron microscopy (TEM) revealed spherical Zn nanoparticles with diameters of approximately 50–60 nm (Fig. S3). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with energy-dispersive X-ray spectroscopy (EDS) provided insights into the atomic structure of the catalyst. HAADF-STEM images (Fig. 1b) revealed the atomic dispersion of In single atoms within the Zn matrix, highlighted by yellow circles. STEM-EDS mapping (Fig. 1c) further confirmed the uniform distribution of In within the ZnO spheres, with no evidence of aggregation. Moreover, large-scale EDS mapping ruled out the presence of In particles (Fig. S4). Together, these analyses suggested the successful incorporation of atomically dispersed In into the Zn matrix.

To gain a detailed understanding of the coordination environment of the In dopant in the as-prepared Zn catalyst, extended X-ray absorption fine structure (EXAFS) measurements were conducted at the In K-edge. Previous structural data for the In_2O_3 crystal revealed an In–O contribution at ~ 2.15 Å, and a 2nd-shell In–In bond distance of ~ 3.34 Å which is typical

of In–(O)–In coordination [22]. As shown in Fig. 1d, the dominant peak at approximately 2.14 Å corresponds to the In–O bond. The absence of a signal at around 2.7 Å [23], characteristic of In–In bonds in clusters, indicates that In dopants should exist as single atoms within the Zn matrix. In addition, a notable contribution at ~ 3.24 Å was observed, which was attributed to the In–Zn interactions in the 2nd-shell, distinctly shifted from the 2nd-shell In–In interaction. This observation unambiguously established the formation of In–(O)–Zn bridging coordination in the catalyst, which was further supported by the wavelet transform (WT) of the In K-edge EXAFS (Fig. S5). Detailed EXAFS simulations and fitting results, summarized in Table S2, accurately revealed the formation of atomic indium oxide domains (In_1O_6 in average) within the Zn catalyst, denoted $\text{In}_1(\text{O})\text{Zn}$.

In an effort to elucidate the electronic structure and monitor the dynamic evolution of the catalysts under CO_2RR conditions, we conducted *operando* X-ray absorption spectroscopy (XAS) studies. *Operando* Zn K-edge XAS profiles (Fig. 1e) revealed that the Zn matrix in the $\text{In}_1(\text{O})\text{Zn}$ catalyst underwent gradual reduction under increasingly negative cathodic potentials.

However, the Zn matrix retained partially electron-deficient states throughout the reaction, presumably attributed to its electronic interaction with the atomic In_1O_6 domains (Figs. 1e and S6). In stark contrast, pristine-Zn was fully reduced to a metallic state during the CO_2RR (Fig. S7). To further elucidate the changes in the electronic state of the In dopants during the CO_2RR , an *operando* XAS study was performed at the In *K*-edge. A comparison of the *in situ* and *ex situ* XANES profiles (Fig. 1f) revealed that the electronic state of the In single atoms in the $\text{In}_1(\text{O})\text{Zn}$ catalyst remained largely unchanged and was sustained in an oxidized state after one hour of electroreduction. Additionally, the profiles of *in situ* and *ex situ* $\chi(k)$ data in the *k*-space (Fig. S8) were basically matched, except for the signal quality during *in situ* experiment. These findings align with the *operando* Zn *K*-edge XAS results (Fig. 1e), confirming the robustness of the atomic In_1O_6 domain under electrochemical conditions.

Considering that the as-obtained $\text{In}_1(\text{O})\text{Zn}$ was mainly oxidized during synthesis (Figs. S1–2), temperature-programmed reduction with hydrogen (TPR- H_2) was conducted (Fig. S9) to monitor the initial oxygen content of the pristine-Zn and $\text{In}_1(\text{O})\text{Zn}$ samples. The results revealed that the initial oxygen content of the $\text{In}_1(\text{O})\text{Zn}$ catalyst was ~ 18.9 wt%, which was slightly greater than that of Zn (~ 17.8 wt%). We further employed an *in situ* electrochemical quartz crystal microbalance (EQCM) to quantitatively analyze the changes in the oxygen content of different catalysts during the electroreduction process [24]. Under cathodic potentials, these catalysts undergo a reduction process during which oxygen atoms leach out, resulting in gradual weight loss [25]. As shown in Fig. S10, the weight loss for the $\text{In}_1(\text{O})\text{Zn}$ catalyst (6044.2 Hz, ~ 7 wt%) was significantly smaller than that for pristine-Zn (19573.6 Hz, ~ 20 wt%). The much lower weight loss observed for $\text{In}_1(\text{O})\text{Zn}$ during the EQCM analysis indicates its greater stability against reduction, and further corroborated the *operando* XAS study in which the atomic In_1O_6 domains remained stable during the CO_2RR .

2.2 Zinc-catalyzed CO_2 -to-formate conversion

The CO_2RR catalytic performance of the $\text{In}_1(\text{O})\text{Zn}$ catalyst was evaluated using a standard three-electrode flow cell system with 0.5 M KHCO_3 as the electrolyte (see *Methods*). Gas chromatography (GC) was employed to analyze the gas products, whereas ion chromatography (IC) and nuclear magnetic resonance (NMR) spectroscopy were used to quantify the liquid products. As shown in Fig. 2a, b, the $\text{FE}_{\text{formate}}$ remained above 90% across a wide potential range from -1.01 to -1.49 V vs. RHE. At merely -1.49 V vs. RHE, the $\text{In}_1(\text{O})\text{Zn}$ catalyst

could deliver a very high activity of -1000 mA cm^{-2} with an impressive $\text{FE}_{\text{formate}}$ of $\sim 94\%$. Notably, the competing hydrogen evolution reaction (HER) and CO generation were suppressed to below 7% throughout the CO_2RR process. In stark contrast, without atomic In_1O_6 domains, pristine-Zn behaves as a typical CO-selective catalyst (Fig. 2a, b), which is in complete agreement with previous reports [3, 5, 14, 15]. The In catalyst delivered notably inferior performance for electrochemical CO_2 -to- HCOOH conversion than did $\text{In}_1(\text{O})\text{Zn}$ (Fig. 2a, b).

We thus sought to link such a selectivity reversal and activity enhancement directly to the impact of the atomic In_1O_6 domains formed in the $\text{In}_1(\text{O})\text{Zn}$ catalyst. First, to rule out contributions from the electrochemically active surface area (ECSA), we measured the ECSAs of all the catalysts (Fig. S11). The ECSA-normalization result (Fig. 2c) revealed that the significantly increased performance for CO_2 -to- HCOOH conversion on $\text{In}_1(\text{O})\text{Zn}$ stemmed from its intrinsic properties. To further explore the influence of the atomic In_1O_6 domains, we synthesized two controls with In contents of 2% and 13% (Table S1). As shown in Fig. S12, both samples exhibited inferior CO_2 -to- HCOOH conversion performance than $\text{In}_1(\text{O})\text{Zn}$ (5% In content), with lower formate selectivity and catalytic activity, as evidenced by the *j*-V curves (Fig. S12c). Under the same cathodic potentials, $\text{In}_1(\text{O})\text{Zn}$ delivers higher activities up to -937 mA cm^{-2} with an impressive $\text{FE}_{\text{formate}}$ of $\sim 94\%$, while the others merely achieved -834 and -918 mA cm^{-2} current densities with 83% and 90% formate selectivity (separately for 2% and 13% samples). Moreover, when applying -1 A cm^{-2} current density, the overpotentials on 2% and 13% $\text{In}(\text{O})\text{Zn}$ samples were 180 mV and 140 mV larger than $\text{In}_1(\text{O})\text{Zn}$, respectively. We inferred that the reduced performance of the 2%-In sample was attributed to insufficient active sites due to limited atomic In_1O_6 domains, whereas the 13%-In sample experienced metal segregation (Fig. S13), which disrupted the uniform geometric structure within $\text{In}_1(\text{O})\text{Zn}$. These comparisons, taken together, highlight the critical role of the atomic In_1O_6 domains in the $\text{In}_1(\text{O})\text{Zn}$ catalyst.

We further investigated the water activation ability of the as-obtained catalysts by monitoring their HER behaviors. As shown in Fig. 2d, pristine-Zn exhibited outstanding HER catalytic performance compared with the other two, indicating its superiority in water activation. We also observed lower onset potential and higher HER activity for $\text{In}_1(\text{O})\text{Zn}$ compared to In catalysts, suggesting that $\text{In}_1(\text{O})\text{Zn}$ is more capable of water activation. After ECSA normalization (Fig. S14), the above conclusion remained unchanged. Together, these results indicate that our strategy of utilizing Zn as a substrate is feasible, and the

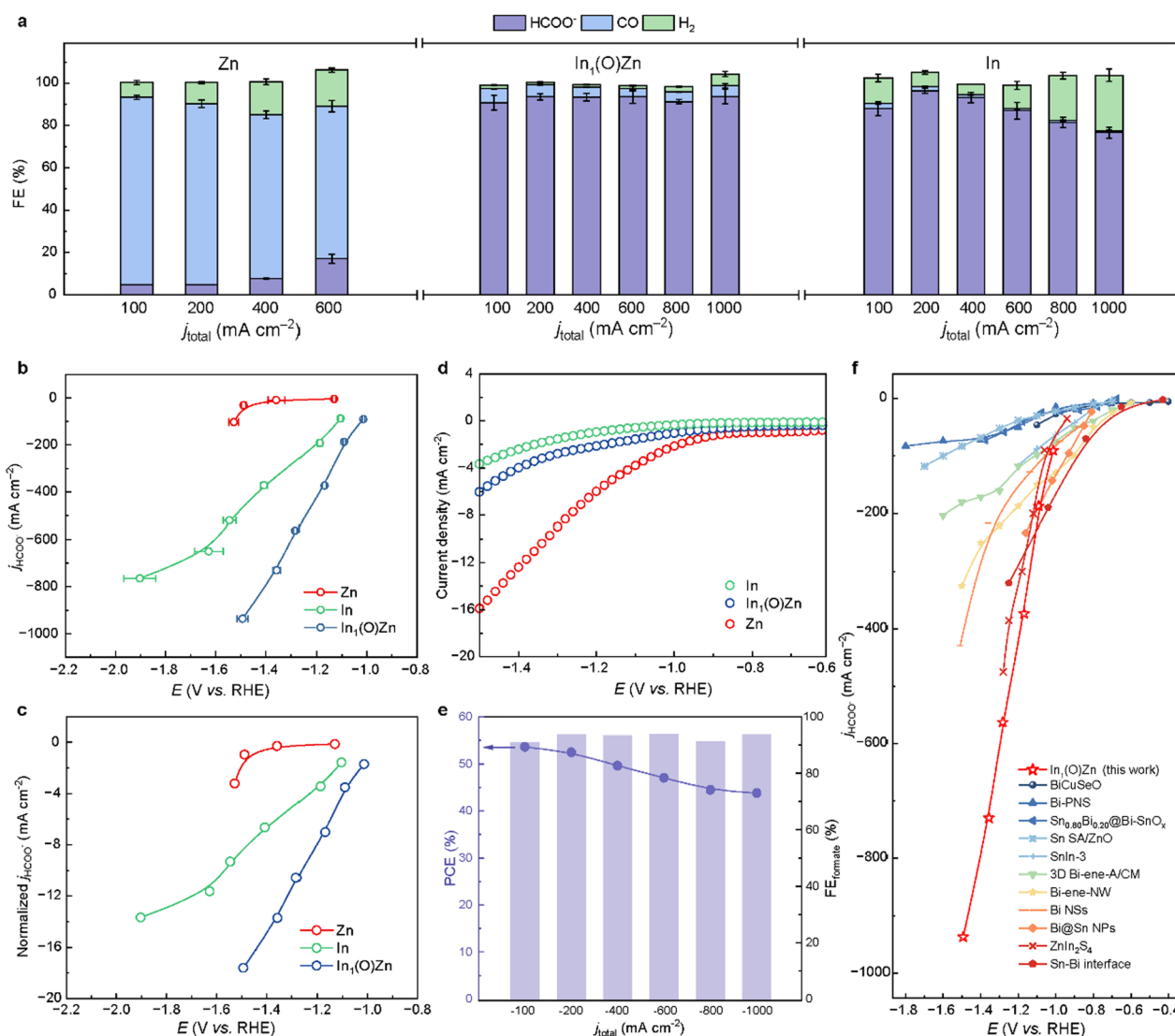


Fig. 2 CO₂RR performance over In₁(O)Zn, Zn and In catalysts. **a** FEs of all CO₂RR products at different current densities. **b, c** j_{formate} -V and ECSA normalized j_{formate} -V curves of three as-synthesized catalysts. The error bars in **a** and **b** correspond to the standard deviation of three independent measurements with 0.5 M KHCO₃ as the electrolyte. **d** LSV curves of three as-synthesized catalysts during the HER. **e** Half-cell PCE for CO₂-to-formate conversion on In₁(O)Zn catalyst. **f** j_{formate} -V curves of the state-of-the-art In/Bi/Sn-based catalysts in flow cell systems during the CO₂RR compared with In₁(O)Zn catalyst. References reproduced from BiCuSeO (0.5 M KHCO₃), Bi-PNS (0.5 M KHCO₃), Sn_{0.80}Bi_{0.20}@Bi-SnO_x (0.5 M KHCO₃), Sn SA/ZnO (0.5 M KHCO₃), SnIn-3 (1 M KHCO₃), 3D Bi-ene-A/CM (1 M KHCO₃), Bi-ene-NW (1 M KHCO₃), Bi NSs (1 M KHCO₃), Bi@Sn NPs (2 M KHCO₃), ZnIn₂S₄ (1 M KHCO₃) and the Sn-Bi interface (0.5 M KHCO₃) [26–36]

In₁(O)Zn catalyst successfully stimulated the activation of water. Through the optimization of water activation, the overpotential for CO₂-to-formate conversion was significantly reduced, while the half-cell power conversion efficiency (PCE) across various current densities was greatly enhanced (Fig. 2e). Of note, the PCE remained at ~45% at –1000 mA cm^{–2} with an FE_{formate} above 90%, outperforming a wide range of reported catalysts (Table S3) [34, 35, 37–39]. We also evaluated the CO₂RR performance of the In₁(O)Zn catalyst against reported state-of-the-art

Sn/Bi/In-based catalysts in typical flow cell systems with a KHCO₃ electrolyte. As shown in Fig. 2f, the In₁(O)Zn catalyst achieved significantly higher formate current densities at moderate overpotentials, demonstrating its superior performance [26–36].

To elucidate the reaction mechanism for CO₂-to-formate conversion, kinetic analysis was conducted. Tafel analysis (Fig. S15) revealed a slope of 127.3 mV dec^{–1} for the In₁(O)Zn catalyst, indicating that the first electron transfer of *CO₂ was the

rate-determining step (RDS, Table S4) [40]. This value, which is significantly lower than the $270.3 \text{ mV dec}^{-1}$ observed for pristine-Zn, highlights the enhanced

electron transfer efficiency for $\text{In}_1(\text{O})\text{Zn}$ [41]. Fourier-transform alternating current voltammetry (FTacV) measurements (Fig. 3a, b) provided further insights

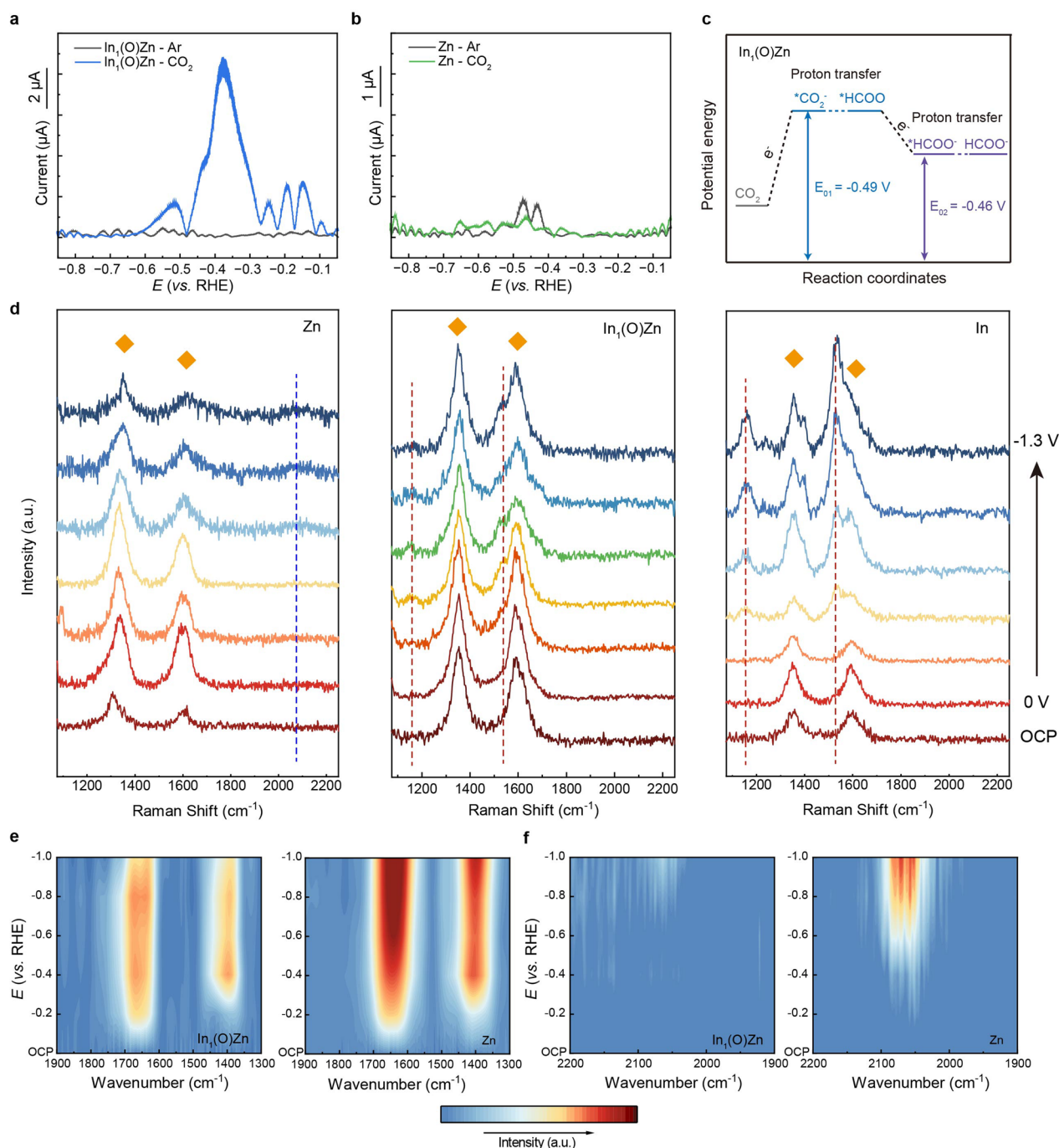


Fig. 3 Mechanistic studies of the effects of electrochemical CO_2 -to-formate conversion on the $\text{In}_1(\text{O})\text{Zn}$ catalyst. **a, b** FTacV measurements of the $\text{In}_1(\text{O})\text{Zn}$ and Zn catalysts under Ar and CO_2 atmospheres, respectively. **c** Schematic illustration of the electron transfer and chemical reaction steps deduced from the FTacV simulation of the $\text{In}_1(\text{O})\text{Zn}$ catalyst. **d** *In situ* Raman spectra of $\text{In}_1(\text{O})\text{Zn}$, pristine-Zn and In catalysts at different potentials during the CO_2RR . **e, f** *In situ* ATR-IR spectra of $\text{In}_1(\text{O})\text{Zn}$ and pristine-Zn catalysts during the CO_2RR . All potentials were calibrated to the RHE scale

into the electron transfer kinetics [42, 43]. The 5th harmonic component, which is highly sensitive to fast heterogeneous electron transfer [44], exhibited a complex response from 0 to -0.9 V vs. RHE corresponding to CO₂RR activity under CO₂-saturated conditions on the In₁(O)Zn catalyst. Interestingly, however, no signals related to HER were observed in the argon environment (Fig. 3a), implying that the H₂ generation on In₁(O)Zn was significantly inhibited. In contrast, pristine-Zn showed a negligible response under CO₂ but a distinct signal under Ar (Fig. 3b), linking it to its inferior CO₂RR ability but superior HER activity. These results suggested that the atomic In₁O₆ geometry suppresses the HER while promoting CO₂-to-formate conversion on In₁(O)Zn. To further probe the electron transfer process, stepwise simulations were conducted (Fig. S16) [45]. The standard rate constant for the one-electron CO₂-to-^{*}CO₂[−] step was calculated to be one-seventh that of the ^{*}COOH-to-^{*}COOH[−] step, identifying the former as the RDS. On the basis of the fitting transfer coefficient ($\alpha=0.45$) for CO₂-to-^{*}CO₂[−], the calculated Tafel slope of 131 mV dec^{−1} closely matched the experimental value of 127.3 mV dec^{−1}, validating the simulation. In addition, the formation potentials for the first ($E_{01}=-0.49$ V) and second ($E_{02}=-0.46$ V) electron transfer steps confirmed that the first step is more energetically demanding, reinforcing its identification as the RDS (Fig. 3c).

To decipher the reaction pathway on the catalysts, *in situ* Raman spectroscopy was conducted to track the evolution of the reactive intermediates. Figure 3d shows the *in situ* Raman spectra acquired for the In₁(O)Zn, pristine-Zn and In catalysts under negative sweep potentials from 0 to -1.3 V vs. RHE. Two peaks at 1350 and 1580 cm^{−1} associated with D and G bands from the gas diffusion layer were observed on all catalysts (marked with orange squares above). The intensities of these two peaks were slightly interfered by H₂ gas bubbles from the HER on both pristine-Zn and In catalysts. For the In₁(O)Zn catalyst, peaks at 1160 and 1540 cm^{−1} (marked with red dashed lines), associated with carboxylate species that form formate [46–48], were observed. Both peaks were also observed for the In catalyst but continuously increased with overpotential. Notably, at -1.3 V vs. RHE, the peak intensity of carboxylate species at 1540 cm^{−1} was strikingly prominent on In catalyst. Such over-accumulation of intermediates would result in the poisoning of active sites on catalyst surface, consequently lowering the overall catalytic activity and inhibiting formate generation. By contrast, for In₁(O)Zn, these peaks at 1160 and 1540 cm^{−1} initially increased but then gradually decreased, reflecting the swift desorption of intermediates on atomic In₁O₆ domains modified Zn matrix. The above comparisons indicate the distinct adsorption

behaviors of formate intermediates on In₁(O)Zn versus In catalyst. In comparison, pristine-Zn merely showed a peak at 2000–2100 cm^{−1} related to CO^{*} intermediates (marked with the blue dashed line) [49, 50], whereas no formate-related signals were observed, consistent with predominant CO formation. To corroborate these findings, *in situ* attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was also employed to examine the adsorption of chemical intermediates. As shown in Fig. 3e, both Zn and In₁(O)Zn exhibited peaks at ~ 1650 and 1450 cm^{−1}, corresponding to H–O–H species and ^{*}COOH/^{*}HCOO, respectively [51–53]. The more intense peak at ~ 1650 cm^{−1} for Zn indicates superior H₂O activation [54], which aligns with its greater H₂ formation during the CO₂RR. For In₁(O)Zn, the ^{*}HCOO peak at 1450 cm^{−1} decreased with increasing overpotential, suggesting easier desorption of this intermediate. Additionally, the ATR-SEIRAS spectra (Fig. 3f) revealed a strong CO signal (2000–2100 cm^{−1}) for Zn [55], whereas this signal was negligible for In₁(O)Zn, which was correlated with CO production from Zn and formate generation from In₁(O)Zn. These findings confirm that the atomic In₁O₆ domain alters the adsorption behavior of intermediates on Zn, suppressing CO and H₂ production while promoting formate selectivity.

3 Theoretical simulation

Density functional theory (DFT) calculations were performed to further elucidate the atomistic origin of the selectivity difference between pristine-Zn and In₁(O)Zn. The Zn (101) facet (Fig. S17a) was chosen to model the pristine-Zn catalyst, as it has been identified as the active surface for the CO₂RR [56, 57]. For In₁(O)Zn, experimental EXAFS characterization revealed an In–O coordination number (CN) of approximately 6 (5.8) (Table S2). Accordingly, a single In atom coordinated with six oxygen atoms (In₁O₆) was embedded into the Zn (101) surface to model In₁(O)Zn (Fig. S17b). After geometry optimization, the average bond lengths of In–O and In–Zn in the In₁(O)Zn model are 2.24 and 3.24 Å (Table S5), respectively, which are consistent with the experimental results (2.14 and 3.24 Å). Bader charge analysis revealed that the Zn atoms adjacent to oxygen exhibited positive charges ($q=0.43\sim 0.65$) (Fig. 4a), echoing the experimentally observed Zn^{δ+} species.

To further investigate the catalytic properties of pristine-Zn and In₁(O)Zn for the CO₂RR, we conducted DFT calculations to analyze the adsorption energies (E_{ads}) of the intermediates and the corresponding transition states (Figs. 4b, c and S18–19). Under explicit solvent and electric field conditions, the E_{ads} values for In₁(O)Zn are more positive than those for pristine-Zn, indicating weaker adsorption strengths for intermediates on In₁(O)

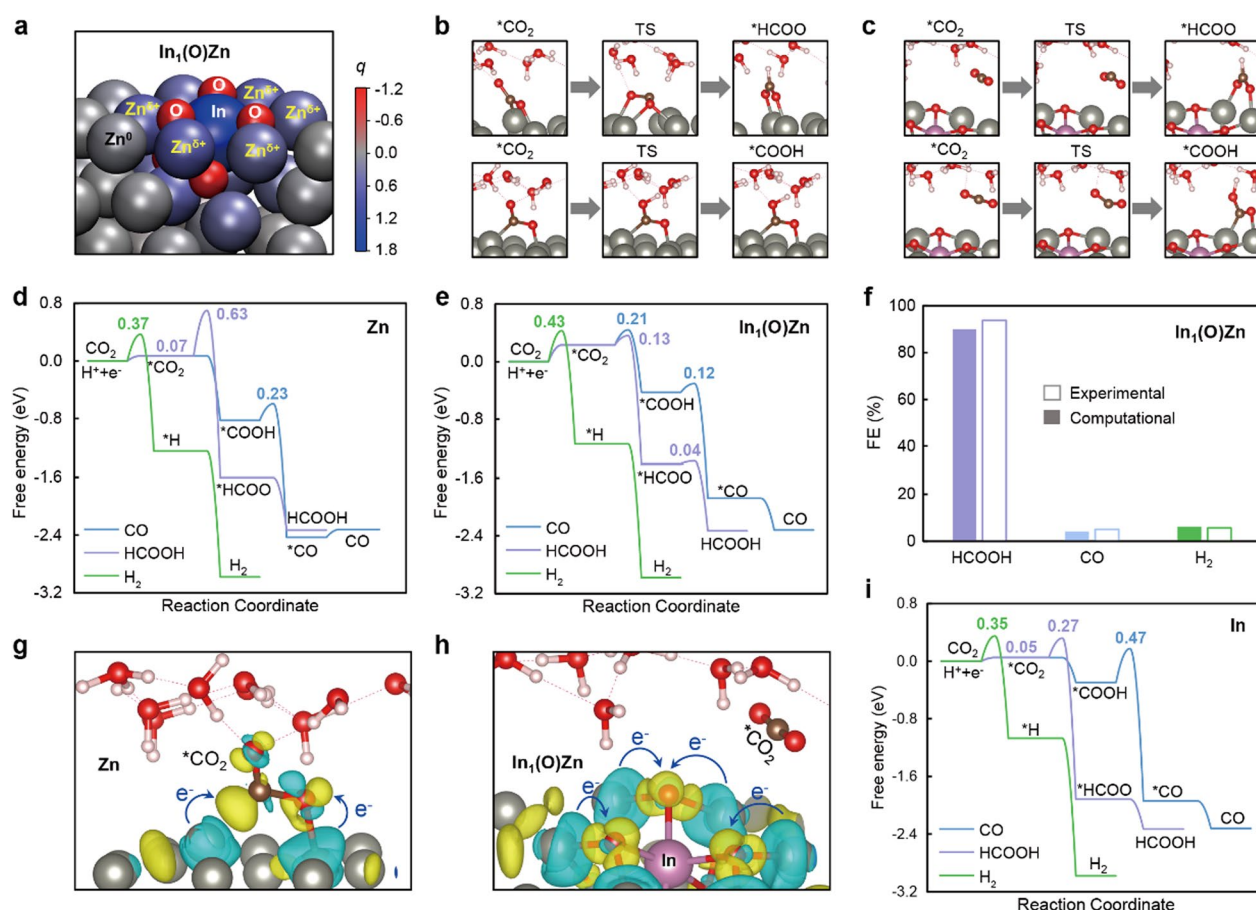


Fig. 4 Density functional theory studies of the CO₂RR on Zn, In, and In₁(O)Zn catalysts. **a** Bader charge analysis of the In₁(O)Zn surface. The color of the atom represents the charge; refer to the color bar on the right. **b, c** Optimized structures of *CO₂, *HCOO, *COOH and the corresponding transition state (TS) on Zn and In₁(O)Zn, respectively. **d, e** Free energy diagrams of the CO₂RR to HCOOH and CO and the HER on Zn and In₁(O)Zn at -1.49 V vs. RHE, respectively. **f** Computational and experimental FEs of HCOOH, CO, and H₂ on In₁(O)Zn at -1.49 V vs. RHE. **g, h** Charge density difference analysis for *CO₂ adsorption on Zn and In₁(O)Zn, respectively. The electron accumulation and depletion are shown in yellow and cyan, respectively, with an isosurface of 0.006 e/Bohr³. **i** Free energy diagrams of the CO₂RR to HCOOH and CO and the HER on In at -1.49 V vs. RHE

Zn (Table S6). A notable distinction in *CO₂ adsorption behavior is observed: *CO₂ adopts a bent configuration on pristine-Zn but remains linear on In₁(O)Zn, which constitutes the structural origin of the selectivity inversion from CO to formate (Fig. 4b, c). For Zn, bent *CO₂ bonds through one C atom and one O atom, imposing steric constraints that kinetically hinder *HCOO formation, resulting in a high energy barrier ($E_a=0.63$ eV) (Fig. 4d). In contrast, *COOH formation on Zn is barrierless (Fig. 4d), with subsequent protonation to *CO ($E_a=0.23$ eV) and *CO desorption ($E_a=0.11$ eV) being more favorable, leading to CO as the dominant product. For In₁(O)Zn, linear *CO₂ avoids steric hindrance, enabling facile formation of both *HCOO and *COOH (Fig. 4c). However, *HCOO formation is more exothermic, with a lower energy barrier ($E_a=0.13$ eV) than *COOH formation ($E_a=0.21$ eV), favoring formate production. The barrier for the HER was also calculated.

In₁(O)Zn showed a greater HER barrier (0.43 eV) than did pristine-Zn (0.37 eV), which is consistent with the reduced HER FE for In₁(O)Zn. Microkinetic simulations were used to quantify the CO₂RR selectivity of In₁(O)Zn, yielding Faradaic efficiencies of 89.9% for HCOOH, 4.1% for CO, and 6.0% for H₂, which closely aligns with the experimental results (Fig. 4f). To understand the electronic origin of this contrasting adsorption geometry, charge density difference analyses were performed. On Zn, remarkable electron transfer occurs from the catalyst surface to adsorbed *CO₂ (Fig. 4g), rendering *CO₂ bent and thus bonding to Zn with C atoms. In contrast, on In₁(O)Zn, electrons are transferred primarily to adjacent oxygen atoms, inducing Zn^{δ+} species and stabilizing linear *CO₂, which favors formate production (Fig. 4h). For comparison, the CO₂RR on In electrode was also modeled (Fig. S20). Although *COOH formation is more kinetically facile than *HCOO, the subsequent protonation to

*CO is hindered by a high barrier of 0.47 eV, resulting in low activity and selectivity for CO production (Fig. 4i). Microkinetic simulations revealed that the In surface is blocked by *COOH during the CO₂RR (Fig. S21) because of the fast production ($E_a=0$ eV) but sluggish conversion ($E_a=0.47$ eV) of *COOH, explaining the experimentally observed continuous accumulation of carboxylate species (Fig. 3d).

4 Practical application

Having established the mechanistic basis for the selectivity inversion, we next assessed the stability of the as-synthesized In₁(O)Zn catalyst for practical applications. A 4 cm² electrode device with a proton-conducting PSE was utilized to produce pure HCOOH solution (Fig. S22). At a current density of -50 mA cm⁻², the In₁(O)Zn-based solid-state reactor exhibited stable operation for over 260 h, maintaining an average FE_{HCOOH} above 90% (Fig. S23). An average concentration of ~59 mM pure formic acid solution was demonstrated in the PSE reactor at approximately 3.7 V (Fig. S24). In addition, the In₁(O)Zn catalyst delivered a maximum full-cell energy efficiency of 51% from electricity to generate pure formic acid solution. This performance surpasses that of many reported bulk Sn/Bi/In-based catalysts for CO₂-to-HCOOH conversion (Table S7), demonstrating the superiority of our In₁(O)Zn catalyst in terms of selectivity and stability for further practical applications [27, 29, 30, 58–64]. Moreover, the absence of significant potential drops during the 260-h stability test highlights the robust durability of the In₁(O)Zn catalyst under catalytic conditions. Post-catalysis microscopic analysis further confirmed the robustness of the atomic In₁O₆ structure (Figs. S25–26), along with post-reaction XPS analysis (Fig. S27). The above characterization results, taken together, showcased the enduring structural stability of In₁(O)Zn catalyst after long-term electrolysis.

5 Conclusion

In summary, we have demonstrated that the selectivity of Zn, a prototypical CO-producing catalyst, can be completely inverted to exclusive formate production through the incorporation of atomic In₁O₆ domains. *In situ* XAS and EQCM analyses revealed the presence and stability of Zn^{δ+} sites, which play pivotal roles in enhancing CO₂RR performance. The In₁(O)Zn catalyst demonstrated high formate selectivity, maintaining Faradaic efficiencies above 90% across a wide potential range, with a maximum FE_{formate} of 94% at a current density of -1000 mA cm⁻². Mechanistic studies suggested that this selectivity shift was induced by the incorporation of atomic In₁O₆ domains, which modulate the electronic structure of Zn to favor *HCOO formation.

More broadly, this work introduces the concept of bridging-atom-mediated modulation, in which a single dopant atom tunes the host metal indirectly through a heteroatom bridge: a fundamentally different paradigm from conventional single-atom alloys that rely on direct metal–metal contact. This strategy may offer a general approach for redirecting selectivity in electrocatalytic systems beyond CO₂ reduction.

Supplementary Information

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Supplementary material 1.

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Author contributions

The project was conceptualized by C.X. and was supervised by C.X. and J.X. Jing X. conducted all the experiments with the help of the following co-authors. Y.C. and X.L. helped with the XAS data processing. R.Z. conducted the FTacV simulation. C.-W.P. performed the *ex situ* XAS measurements. S.H. carried out the HAADF-STEM characterizations. Y.W., Chun.L., Cheng.L. and Y.J. assisted with research advice and discussions. Q.L., J.Z. and T.Z. contributed to paper preparation. J.L. and J.X. performed the DFT calculations. Jing X., J.L., C.X., and J.X. wrote the paper with input from all the authors. All the authors discussed the results and commented on the manuscript.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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References

1. Xiao H, Goddard WA, Cheng T, Liu Y (2017) Cu metal embedded in oxidized matrix catalyst to promote CO₂ activation and CO

- dimerization for electrochemical reduction of CO₂. *Proc Natl Acad Sci USA* 114(26):6685–6688
2. Jouny M, Luc W, Jiao F (2018) General techno-economic analysis of CO₂ electrolysis systems. *Ind Eng Chem Res* 57(6):2165–2177
 3. Bagger A, Ju W, Varela AS, Strasser P, Rossmeisl J (2017) Electrochemical CO₂ reduction: a classification problem. *ChemPhysChem* 18(22):3266–3273
 4. Nitopi S, Bertheussen E, Scott SB, Liu X, Engstfeld AK, Horsch S, Seger B, Stephens IEL, Chan K, Hahn C, Nørskov JK, Jaramillo TF, Chorkendorff I (2019) Progress and perspectives of electrochemical CO₂ reduction on copper in aqueous electrolyte. *Chem Rev* 119(12):7610–7672
 5. Vasileff A, Xu C, Jiao Y, Zheng Y, Qiao S-Z (2018) Surface and interface engineering in copper-based bimetallic materials for selective CO₂ electroreduction. *Chem* 4(8):1809–1831
 6. Zheng T, Liu C, Guo C, Zhang M, Li X, Jiang Q, Xue W, Li H, Li A, Pao C-W, Xiao J, Xia C, Zeng J (2021) Copper-catalysed exclusive CO₂ to pure formic acid conversion via single-atom alloying. *Nat Nanotechnol* 16(12):1386–1393
 7. Li J, Zeng H, Dong X, Ding Y, Hu S, Zhang R, Dai Y, Cui P, Xiao Z, Zhao D, Zhou L, Zheng T, Xiao J, Zeng J, Xia C (2023) Selective CO₂ electrolysis to CO using isolated antimony alloyed copper. *Nat Commun* 14(1):340
 8. Feaster JT, Shi C, Cave ER, Hatsukade T, Abram DN, Kuhl KP, Hahn C, Nørskov JK, Jaramillo TF (2017) Understanding selectivity for the electrochemical reduction of carbon dioxide to formic acid and carbon monoxide on metal electrodes. *ACS Catal* 7(7):4822–4827
 9. Xue J et al (2026) Promoted CO₂ electrolysis to formic acid using single atom cobalt alloyed tin. *Adv Mater*. <https://doi.org/10.1002/adma.72719>
 10. Nankya R, Xu Y, Elgazzar A, Zhu P, Wu TU, Qiu C, Feng Y, Che F, Wang H (2024) Cobalt-doped bismuth nanosheet catalyst for enhanced electrochemical CO₂ reduction to electrolyte-free formic acid. *Angew Chem Int Ed* 63(36):e202403671
 11. Ma W, Xie S, Zhang X-G, Sun F, Kang J, Jiang Z, Zhang Q, Wu D-Y, Wang Y (2019) Promoting electrocatalytic CO₂ reduction to formate via sulfur-boosting water activation on indium surfaces. *Nat Commun* 10(1):892
 12. Peng B, She H, Wei Z et al (2025) Sulfur-doping tunes *p*-*d* orbital coupling over asymmetric Zn-Sn dual-atom for boosting CO₂ electroreduction to formate. *Nat Commun* 16:2217
 13. Chen S, Li X, Kao CW, Luo T, Chen K, Fu J, Ma C, Li H, Li M, Chan TS, Liu M (2022) Unveiling the proton-feeding effect in sulfur-doped Fe-N-C single-atom catalyst for enhanced CO₂ electroreduction. *Angew Chem Int Ed*. <https://doi.org/10.1002/anie.202206233>
 14. Zheng Q, Luan S, Feng Y, Lv S-W, Zhang Y, Cong Y (2024) Introduction of sulfur in Bi₂O₃ to boost water activation for enhancing the reduction of CO₂ to formate. *J Power Sources* 601:234298
 15. Liu F, Ren X, Zhao J, Wu H, Wang J, Han X, Deng Y, Hu W (2022) Inhibiting sulfur dissolution and enhancing activity of SnS for CO₂ electroreduction via electronic state modulation. *ACS Catal* 12(21):13533–13541
 16. Kuhl KP, Hatsukade T, Cave ER, Abram DN, Kibsgaard J, Jaramillo TF (2014) Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces. *J Am Chem Soc* 136(40):14107–14113
 17. Lee CW, Cho NH, Yang KD, Nam KT (2017) Reaction mechanisms of the electrochemical conversion of carbon dioxide to formic acid on tin oxide electrodes. *ChemElectroChem* 4(9):2130–2136
 18. Xue J, Dong X, Liu C et al (2024) Turning copper into an efficient and stable CO evolution catalyst beyond noble metals. *Nat Commun* 15:5998
 19. Wang Z, Zhou Y, Liu D, Qi R, Xia C, Li M, You B, Xia BY (2022) Carbon-confined Indium oxides for efficient Carbon dioxide reduction in a solid-state electrolyte flow cell. *Angew Chem Int Ed*. <https://doi.org/10.1002/anie.202200552>
 20. Wei Z, Ding J, Wang Z, Wang A, Zhang L, Liu Y, Guo Y, Yang X, Zhai Y, Liu B (2024) Enhanced electrochemical CO₂ reduction to formate over phosphate-modified In: water activation and active site tuning. *Angew Chem Int Ed*. <https://doi.org/10.1002/anie.202402070>
 21. Li J, Li J, Liu X, Chen J, Tian P, Dai S, Zhu M, Han Y-F (2021) Probing the role of surface hydroxyls for Bi, Sn and In catalysts during CO₂ reduction. *Appl Catal B Environ*. <https://doi.org/10.1016/j.apcatb.2021.120581>
 22. The Materials Project. Materials Data on In₂O₃ by Materials Project. United States: N. Web. 2020. <https://doi.org/10.17188/1675933>
 23. Pardoe JAJ, Downs A (2007) Development of the chemistry of indium in formal oxidation states lower than +3+. *Chem Rev* 107(1):2–45
 24. Singh V, Tiwari A, Nagaiah TC (2018) Facet-controlled morphology of cobalt disulfide towards enhanced oxygen reduction reaction. *J Mater Chem A* 6(45):22545–22554
 25. Lin G, Zhang Z, Ju Q, Wu T, Segre CU, Chen W, Peng H, Zhang H, Liu Q, Liu Z, Zhang Y, Kong S, Mao Y, Zhao W, Suenaga K, Huang F, Wang J (2023) Bottom-up evolution of perovskite clusters into high-activity rhodium nanoparticles toward alkaline hydrogen evolution. *Nat Commun* 14(1):280
 26. Duan J, Liu T, Zhao Y, Yang R, Zhao Y, Wang W, Liu Y, Li H, Li Y, Zhai T (2022) Active and conductive layer stacked superlattices for highly selective CO₂ electroreduction. *Nat Commun* 13(1):2039
 27. Yu ZL, Wu SQ, Chen LW, Hao YC, Su X, Zhu Z, Gao WY, Wang B, Yin AX (2022) Promoting the electrocatalytic reduction of CO₂ on ultrathin porous bismuth nanosheets with tunable surface-active sites and local pH environments. *ACS Appl Mater Interfaces* 14(8):10648–10655
 28. Yang Q, Wu Q, Liu Y, Luo S, Wu X, Zhao X, Zou H, Long B, Chen W, Liao Y, Li L, Shen PK, Duan L, Quan Z (2020) Novel Bi-doped amorphous SnO(x) nanoshells for efficient electrochemical CO₂ reduction into formate at low overpotentials. *Adv Mater* 32(36):e2002822
 29. Zhang Y, Jang H, Ge X, Zhang W, Li Z, Hou L, Zhai L, Wei X, Wang Z, Kim MG, Liu S, Qin Q, Liu X, Cho J (2022) Single-atom Sn on tensile-strained ZnO nanosheets for highly efficient conversion of CO₂ into formate. *Adv Energy Mater*. <https://doi.org/10.1002/aenm.202202695>
 30. Wang J, Ning S, Luo M, Xiang D, Chen W, Kang X, Jiang Z, Chen S (2021) In-Sn alloy core-shell nanoparticles: in-doped SnOx shell enables high stability and activity towards selective formate production from electrochemical reduction of CO₂. *Appl Catal B Environ*. <https://doi.org/10.1016/j.apcatb.2021.119979>
 31. He YC, Ma DD, Zhou SH, Zhang M, Tian JJ, Zhu QL (2022) Integrated 3D open network of interconnected bismuthene arrays for energy-efficient and electrosynthesis-assisted electrocatalytic CO₂ reduction. *Small* 18(1):e2105246
 32. Zhang M, Wei W, Zhou S, Ma D-D, Cao A, Wu X-T, Zhu Q-L (2021) Engineering a conductive network of atomically thin bismuthene with rich defects enables CO₂ reduction to formate with industry-compatible current densities and stability. *Energy Environ Sci* 14(9):4998–5008
 33. Yang J, Wang X, Qu Y, Wang X, Huo H, Fan Q, Wang J, Yang LM, Wu Y (2020) Bi-based metal organic framework derived leafy Bismuth nanosheets for Carbon dioxide electroreduction. *Adv Energy Mater*. <https://doi.org/10.1002/aenm.202001709>
 34. Xing Y, Kong X, Guo X, Liu Y, Li Q, Zhang Y, Sheng Y, Yang X, Geng Z, Zeng J (2020) Bi@Sn core-shell structure with compressive strain boosts the electroreduction of CO₂ into formic acid. *Adv Sci* 7(22):1902989
 35. Chi LP, Niu ZZ, Zhang XL, Yang PP, Liao J, Gao FY, Wu ZZ, Tang KB, Gao MR (2021) Stabilizing indium sulfide for CO₂ electroreduction to formate at high rate by zinc incorporation. *Nat Commun* 12(1):5835
 36. Ren B, Wen G, Gao R, Luo D, Zhang Z, Qiu W, Ma Q, Wang X, Cui Y, Ricardez-Sandoval L, Yu A, Chen Z (2022) Nano-crumpled induced Sn-Bi bimetallic interface pattern with moderate electron bank for highly efficient CO₂ electroreduction. *Nat Commun* 13(1):2486
 37. Whipple DT, Finke EC, Kenis PJ (2010) Microfluidic reactor for the electrochemical reduction of carbon dioxide: the effect of pH. *Electrochem Solid-State Lett* 13(9):B109–B111
 38. Li H, Oloman C (2006) Development of a continuous reactor for the electro-reduction of carbon dioxide to formate - Part 1: process variables. *J Appl Electrochem* 36:1105–1115
 39. Wen G, Ren B, Park MG, Yang J, Dou H, Zhang Z, Deng Y, Bai Z, Yang L, Gostick J, Botton GA, Hu Y, Chen Z (2020) Ternary Sn-Ti-O electrocatalyst boosts the stability and energy efficiency of CO₂ reduction. *Angew Chem Int Ed* 59(31):12860–12867
 40. Li C, Zhong X, Ji Y, Hong Y, Li J, Wang Y, Zeng H, Liu C, Chen Z, Li X, Jiang Q, Zheng T, Peng H-J, Liu X, Xia C (2025) Surface amorphization of bismuth for efficient acidic CO₂ electrolysis. *ACS Nano* 19(22):21095–21104
 41. Zhang S, Kang P, Ubnoske S, Brennaman MK, Song N, House RL, Glass JT, Meyer TJ (2014) Polyethylenimine-enhanced electrocatalytic reduction of CO₂ to formate at nitrogen-doped carbon nanomaterials. *J Am Chem Soc* 136(22):7845–7848
 42. Zhang Y, Chen L, Li F, Easton CD, Li J, Bond AM, Zhang J (2017) Direct detection of electron transfer reactions underpinning the tin-catalyzed electrochemical reduction of CO₂ using Fourier-Transformed ac voltammetry. *ACS Catal* 7(7):4846–4853

43. Zhang X, Sun X, Guo S-X, Bond AM, Zhang J (2019) Formation of lattice-dislocated bismuth nanowires on copper foam for enhanced electrocatalytic CO₂ reduction at low overpotential. *Energy Environ Sci* 12(4):1334–1340
44. Zhang Y, Zhang X, Ling Y, Li F, Bond AM, Zhang J (2018) Controllable synthesis of few-layer bismuth subcarbonate by electrochemical exfoliation for enhanced CO₂ reduction performance. *Angew Chem Int Ed* 57(40):13283–13287
45. Kennedy GF, Bond AM, Simonov AN (2017) Modelling ac voltammetry with MECSim: facilitating simulation-experiment comparisons. *Curr Opin Electrochem* 1(1):140–147
46. Chernyshova IV, Somasundaran P, Ponnuram S (2018) On the origin of the elusive first intermediate of CO₂ electroreduction. *Proc Natl Acad Sci U S A* 115(40):E9261–E9270
47. Mao Y, Yang H, Wang G, Xu Y, Liu J, Li W, Li Q, He Y, Yip S, Liang X (2024) Functional polymers-coated Cu hollow microspheres for CO₂ conversion in primary Zn-CO₂ batteries. *Chem Eng J*. <https://doi.org/10.1016/j.cej.2024.152856>
48. Pohl M, Pieck A, Hanewinkel C, Otto A (1996) Raman study of formic acid and surface formate adsorbed on cold-deposited copper films. *J Raman Spectrosc* 27:805–809
49. Li H, Wei P, Gao D, Wang G (2022) In situ Raman spectroscopy studies for electrochemical CO₂ reduction over Cu catalysts. *Curr Opin Green Sustain Chem*. <https://doi.org/10.1016/j.cogsc.2022.100589>
50. Jiang S, Klingan K, Pasquini C, Dau H (2019) New aspects of operando Raman spectroscopy applied to electrochemical CO₂ reduction on Cu foams. *J Chem Phys* 150(4):041718
51. Jiang K, Wang H, Cai W-B, Wang H (2017) Li electrochemical tuning of metal oxide for highly selective CO₂ reduction. *ACS Nano* 11(6):6451–6458
52. Zhu S, Jiang B, Cai WB, Shao M (2017) Direct observation on reaction intermediates and the role of Bicarbonate anions in CO₂ electrochemical reduction reaction on Cu surfaces. *J Am Chem Soc* 139(44):15664–15667
53. Firet NJ, Smith WA (2016) Probing the reaction mechanism of CO₂ electroreduction over Ag films via operando infrared spectroscopy. *ACS Catal* 7(1):606–612
54. Dai Y, Li H, Wang C, Xue W, Zhang M, Zhao D, Xue J, Li J, Luo L, Liu C, Li X, Cui P, Jiang Q, Zheng T, Gu S, Zhang Y, Xiao J, Xia C, Zeng J (2023) Manipulating local coordination of copper single atom catalyst enables efficient CO₂-to-CH₄ conversion. *Nat Commun* 14(1):3382
55. Hao J, Zhu H, Zhao Q, Hao J, Lu S, Wang X, Duan F, Du M (2023) Interatomic electron transfer promotes electroreduction CO₂-to-CO efficiency over a CuZn diatomic site. *Nano Res* 16(7):8863–8870
56. da Won H, Shin H, Koh J, Chung J, Lee HS, Kim H, Woo SI (2016) Highly efficient, selective, and stable CO₂ electroreduction on a hexagonal Zn catalyst. *Angew Chem Int Ed Engl* 55:9297–9300
57. Long J, Luan D, Fu X, Li H, Xiao J (2024) Theoretical design of the electrocatalytic urea synthesis from carbon dioxide and nitric oxides. *ACS Catal*. <https://doi.org/10.1021/acscatal.4c03785>
58. Mohamed AGA, Zhou E, Zeng Z, Xie J, Gao D, Wang Y (2022) Asymmetric oxo-bridged ZnPb bimetallic electrocatalysis boosting CO₂-to-HCOOH reduction. *Adv Sci* 9(4):e2104138
59. Fan L, Xia C, Zhu P, Lu Y, Wang H (2020) Electrochemical CO₂ reduction to high-concentration pure formic acid solutions in an all-solid-state reactor. *Nat Commun* 11(1):3633
60. Ma W, Bu J, Liu Z, Yan C, Yao Y, Chang N, Zhang H, Wang T, Zhang J (2020) Monoclinic scheelite bismuth vanadate derived bismuthene nanosheets with rapid kinetics for electrochemically reducing carbon dioxide to formate. *Adv Funct Mater*. <https://doi.org/10.1002/adfm.202006704>
61. Wu Z, Wu H, Cai W, Wen Z, Jia B, Wang L, Jin W, Ma T (2021) Engineering Bismuth-Tin interface in bimetallic aerogel with a 3D porous structure for highly selective electrocatalytic CO₂ reduction to HCOOH. *Angew Chem Int Ed Engl* 60(22):12554–12559
62. Li F, Gu GH, Choi C, Kolla P, Hong S, Wu T-S, Soo Y-L, Masa J, Mukerjee S, Jung Y, Qiu J, Sun Z (2020) Highly stable two-dimensional bismuth metal-organic frameworks for efficient electrochemical reduction of CO₂. *Appl Catal B-Environ*. <https://doi.org/10.1016/j.apcatb.2020.119241>
63. Li N, Yan P, Tang Y, Wang J, Yu X-Y, Wu HB (2021) In-situ formation of ligand-stabilized bismuth nanosheets for efficient CO₂ conversion. *Appl Catal B-Environ*. <https://doi.org/10.1016/j.apcatb.2021.120481>
64. Lv L, Lu R, Zhu J, Yu R, Zhang W, Cui E, Chen X, Dai Y, Cui L, Li J, Zhou L, Chen W, Wang Z, Mai L (2023) Coordinating the edge defects of Bismuth with Sulfur for enhanced CO₂ electroreduction to Formate. *Angew Chem Int Ed Engl* 62(25):e202303117

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