Boosting proton reduction via isolated Cu atoms in Bi lattice for efficient electroreduction of CO₂ to formate

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Abstract

Current Bi-based catalysts suffer from low current density for electroreduction of CO₂ to formate due to the high energy barrier of H⁺ reduction to *H on Bi sites. Here we report a unique BiCu single-atom alloy catalyst (SAAC) that can deliver a ultrahigh formate partial current density (j_{formate}) of 434 mA cm⁻², the highest among the reported Bi-based electrocatalysts to date, with a formate Faradaic efficiency (FE_{formate}) of 96.5% at -0.55 V (vs. RHE) in a flow cell, while BiCu alloy catalyst containing Cu nanoclusters can only deliver a j_{formate} of 48.5 mA cm⁻² with a FE_{formate} of 37.3% under an identical condition. Mechanism investigations reveal that the isolated single-atom Cu in BiCu SAAC can dramatically reduce the energy barrier of H⁺ reduction to *H on Cu site for boosting the reduction of CO₂ to formate. Our work provides a new strategy for engineering unfavourable energy barrier of electrocatalysts to promote CO₂ reduction.

Introduction

The excessive emission of carbon dioxide (CO₂) has caused severe climate problems. To alleviate the global warming and fossil fuel depletion, an appealing route is to convert CO₂ into fuels and industrial feedstocks with renewable electricity^{1,2}. Among the various products in electrocatalytic CO₂ reduction reaction (CO₂RR), formate/formic acid (HCOO⁻/HCOOH) has received growing concern due to its competitive economic value for its excellent hydrogen storage capacity in fuel cell applications and extensive demands in chemical and pharmaceutical industries^{3,4}. To date, several metals, such as Pd, In, Sn, Pb and Bi, have been reported for efficient electroreduction of CO₂ into formate in aqueous solution⁵⁻⁸. In particular, by virtue of the low cost, low toxicity and high Faradaic efficiencies for formate (FE_{formate}), Bi-based electrocatalysts have attracted increasing interest^{9,10}. Benefiting from the semi-metal feature of Bi, the surface electron accessibility is significantly limited in aqueous solution, thus suppressing the competing hydrogen evolution reaction (HER)¹¹. However, the semi-metal feature of Bi also leads to low current density (low production rate) for electroreduction of CO₂ to formate, which greatly hinders the commercial application of Bi-based electrocatalysts. To solve this problem, several strategies such as integrating catalysts with conductive substrates¹⁰, increasing the density of active sites by optimizing the morphology of catalyst or raising catalyst loading^{12,13}, have been reported. Alloying strategy has also been proved to be an effective pathway to regulate the unsatisfactory intrinsic activity of Bi via introducing another component with complementary characters, thereby realizing better catalytic performance than that of the individual constituent¹⁴. For example, a bimetallic catalyst featuring BiSn alloy core with BiSnO_x shell shows a formate partial current density (j_{formate}) as high as 74.6 mA cm⁻² at -1.38 V versus reversible hydrogen electrode (vs. RHE), with a FE_{formate} of 72.1% in a gas diffusion electrolyser (GDE), whereas monometallic Sn/SnO_x core/shell structure can only achieve a j_{formate} of 15 mA cm⁻² under identical conditions¹⁵. Compared with pure Bi, the Bi-SnO_x surface structure can effectively lower the energy barrier of *HCOO formation, whereas the energy barrier of H* formation on Bi-

SnO_x is even higher than that on SnO_x , contributing to a more effective suppression of HER. However, the j_{formate} significantly decreases to 20.9 mA cm^{-2} with the $\text{FE}_{\text{formate}}$ over 90%. Therefore, simultaneously achieving high $\text{FE}_{\text{formate}}$ and high j_{formate} still remains a great challenge for Bi-based catalysts.

As an intersection of single-atom catalysts (SACs) and alloy catalysts, single-atom alloy catalysts (SAACs) have shown exceptional performances in various catalytic reactions, such as selective hydrogenation^{16,17}, O_2 activation¹⁸, selective oxidation¹⁹, CO oxidation²⁰, C–H activation²¹, and electrocatalytic water oxidation²². The precise surface structures of SAACs provide excellent platforms for understanding the structure–performance relationship in heterogeneous catalytic process on atomic scale. Moreover, unlike the single metal atoms anchored on the metal oxides or carbon materials which usually serve as supports only (although the charges of the metal centres are significantly influenced by the supports)²³, the isolated metal in SAAC may catalyse reactions synergistically with the neighbouring metal atoms in the metal support²⁴. This feature endows SAACs with unique behaviours in the adsorption and activation of reactants or key intermediates, thereby contributing to enhanced catalytic performance. Taking a deep insight into the process of CO_2 -to- HCOO^- conversion, the reduction of H^+ plays a significant role in the formation of the key intermediate $^*\text{HCOO}$ ²⁵, which is, however, often ignored in Bi-based catalysts. The H^+ reduction is very difficult on metallic Bi because of its low affinity to H^+ , and thus greatly reduces the j_{formate} for Bi-based catalysts. According to the volcano plot of the exchange current density as a function of the Gibbs free energy of adsorbed atomic hydrogen for various metals²⁶, the non-noble metal Cu has a suitable hydrogen adsorption energy that enables not only a favourable hydrogen adsorption compared with Bi, Ag and Au, but also an easier hydrogen desorption than that on Pt, Ir and other metals for the subsequent H transfer to $^*\text{CO}_2$. However, aggregation of Cu atoms would lead to undesired HER and lower the selectivity for the formation of formate. Therefore, constructing BiCu SAACs, in which the isolated Cu atoms are embedded in Bi lattice, would effectively promote the H^+ reduction and the formation of $^*\text{HCOO}$, with an efficient suppression of HER, and eventually achieve both high $\text{FE}_{\text{formate}}$ and high j_{formate} .

Herein, we report the design, synthesis and electrocatalytic performance for the reduction CO_2 to formate of a BiCu nanosheet SAAC, with the isolated Cu atoms embedded in Bi lattice. As expected, the optimized pathway for the reduction of CO_2 to formate enables BiCu nanosheet SAAC achieving both high j_{formate} and high $\text{FE}_{\text{formate}}$ in CO_2RR , with a j_{formate} of 77 mA cm^{-2} and a $\text{FE}_{\text{formate}}$ of 91.6% in an H-type cell, as well as a j_{formate} as high as 434 mA cm^{-2} and a $\text{FE}_{\text{formate}}$ of 96.5% in a GDE. Moreover, the $\text{FE}_{\text{formate}}$ can still remain over 80% even in 10% CO_2 , where the CO_2 concentration is close to that of the industrial CO_2 emissions without energy-consuming CO_2 capture process. Our results strongly demonstrate the great potential of the BiCu SAAC for CO_2RR in commercial applications.

Results

Fabrication and characterization of BiCu SAAC. The BiCu-x alloy nanosheets were obtained by *in situ* electroreduction of BiOI-Cu-x nanosheets in Ar-saturated 0.5 M NaHCO₃ (Supplementary Fig. 1). BiOI-Cu-x precursors with a sheet-like morphology were synthesised via a hydrothermal method (Supplementary Figs. 2-4). The molar ratios of Bi/Cu were carefully tuned by controlling the amount of CuCl₂ during the synthesis of BiOI-Cu-x nanosheets, and inductively coupled plasma-optical emission spectrometry (ICP-OES) results reveal that the molar contents of Cu in BiCu-x alloy catalysts are 0.2%, 0.5%, 1% and 3% (denoted as BiCu-0.2, BiCu-0.5, BiCu-1, and BiCu-3, respectively), close to those for the corresponding BiOI-Cu-x precursors (Supplementary Table 1). For comparison, metallic Bi nanosheets were also prepared by *in situ* electroreduction of BiOI nanosheets under the same conditions as those of BiCu-x nanosheets. X-ray diffraction (XRD) patterns show only metallic Bi crystallographic phase in BiCu-x nanosheets (Supplementary Fig. 5), suggesting the total conversion of BiOI-Cu-x precursors to metallic Bi and BiCu-x alloys, which is further verified by the X-ray photoelectron spectroscopy (XPS) results (Supplementary Fig. 6).

Scanning electron microscopy (SEM) images show that the Bi and BiCu-x samples remain the two-dimensional morphology with rough surfaces (Fig. 1a and Supplementary Fig. 7). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of BiCu-0.5 shows small nanoparticles with an average size of ~5 nm dispersed uniformly over the surface of the nanosheet, indicating abundant boundaries and interfaces in BiCu-0.5 (Fig. 1b). High-resolution transmission electron microscopy (HRTEM) image for BiCu-0.5 displays clear lattice fringes of rhombohedra Bi (012) facet, with an interplanar spacing of 0.33 nm for both nanoparticle and substrate (Fig. 1c). Fast Fourier transform (FFT) pattern further demonstrates the polycrystallinity of the BiCu-0.5 nanosheets (Supplementary Fig. 8). High-resolution energy-dispersive X-ray spectroscopy (EDS) analysis for BiCu-0.5 shows that Bi and Cu elements are homogeneously distributed over the catalyst (Fig. 1d), suggesting the formation of BiCu alloy. Notably, no distinguishable aggregation of Cu signals was observed in the XRD pattern (Supplementary Fig. 5), the HRTEM image (Fig. 1c) or the EDS elemental mapping image (Fig. 1d), indicating the possible atomic dispersion of Cu atoms in BiCu-0.5 nanosheets.

Evaluation of CO₂RR performances. CO₂RR performances of the Bi and BiCu-x catalysts were evaluated in an H-type cell filled with 0.5 M NaHCO₃ aqueous solution, and the liquid product was analysed by ¹H-NMR and ion chromatograph (Supplementary Fig. 9). As revealed by the linear sweep voltammetry curves (Fig. 2a and Supplementary Fig. 10), at low potential (below -1.0 V), all the current densities in CO₂-saturated solution are higher than those in Ar-saturated solution, indicating the occurrence of CO₂RR on each catalyst. With the potential more negatively shifted, the current density of BiCu-0.5 in CO₂-saturated solution keeps higher than that in Ar-saturated solution (Fig. 2a), whereas reverse results were observed for the other catalysts (Supplementary Fig. 10). A total current density of 63.6 mA cm⁻² was achieved by BiCu-0.5 at -1.58 V vs. RHE in CO₂ atmosphere, surpassing the current densities of all the other Bi and BiCu-x alloy catalysts. These results highlight the best electrocatalytic performance of BiCu-0.5 for CO₂RR among the Bi and BiCu-x catalysts, especially under high current density. The FE_{formate} of Bi and BiCu-x catalysts at different potentials are shown in Fig. 2b and Supplementary Fig. 11. For the Bi nanosheets,

the FE_{formate} reaches a maximum value of 84.7% at -1.18 V, and quickly decreases to less than 50% at the potentials negative than -1.48 V, where HER becomes dominant. On the contrary, the BiCu-0.5 catalyst keeps high selectivity for formate with FE_{formate} reaching above 94.0% in a wide potential window (-0.88 V to -1.28 V), and the maximum FE_{formate} reaches 95.7% at -0.98 V. The FE_{formate} can maintain over 85.0% even at -1.48 V, indicative of the efficient suppression of HER on BiCu-0.5. Notably, the maximum FE_{formate} of BiCu-3 decreases to 89.7% at -1.08 V and sharply drops to 39.9% at -1.28 V. A volcano-type relationship between FE_{formate} and the Cu content was observed, and BiCu-0.5 displays the maximum FE_{formate} . Fig. 2c presents the j_{formate} for Bi and BiCu-0.5 at various potentials. Distinctly, as the overpotential increases, the disparity in j_{formate} between Bi and BiCu-0.5 becomes increasingly significant, and a j_{formate} of 45.1 mA cm^{-2} was achieved at -1.48 V for BiCu-0.5, which is 3.2 times higher than that for Bi. The Tafel slop of formate production for BiCu-0.5 is 107 mV dec^{-1} , much lower than that for Bi (133 mV dec^{-1}), which confirms the favourable CO_2RR kinetics for BiCu-0.5 (Supplementary Fig. 12). To further explore the intrinsic activity of the BiCu-0.5, electrochemically active surface area (ECSA) was estimated (Supplementary Fig. 13), and used to normalize the geometrical current density. The ECSA-corrected j_{formate} of BiCu-0.5 still shows the highest value among the five catalysts, 2.8 times higher than that of Bi at -1.48 V (Supplementary Fig. 14). Thus, it can be concluded that incorporating Cu in Bi can actually enhance the catalytic current for CO_2RR , and 0.5% is the optimal molar percentage of Cu.

To eliminate the overpotential caused by the resistance of the electrolyte and show the accurate electrocatalytic performance, ohmic resistance compensation was conducted. The maximum FE_{formate} of 98.3% was achieved with a j_{formate} of 27.0 mA cm^{-2} at an overpotential of only 680 mV, and j_{formate} reaches a maximum value of 76.6 mA cm^{-2} with a FE_{formate} of 91.6% at -1.13 V (Supplementary Fig. 15), further confirming the outstanding CO_2RR performance of BiCu-0.5. Long-term stability test was also conducted for BiCu-0.5. As shown in Fig. 2d, BiCu-0.5 delivers a steady current density of about 40 mA cm^{-2} with FE_{formate} kept over 90% during the 40 h CO_2RR measurement. Besides, neither phase transformation nor morphology change was observed for the BiCu-0.5 after 40 h electrolysis, as revealed in Supplementary Fig. 16.

Insight of the enhanced CO_2RR performance. It is natural to ask what factors enable the outstanding CO_2RR performance of BiCu-0.5. The result of Nyquist plots reveals that the incorporation of Cu in BiCu-0.5 contributes to an improved mass transportation over the catalyst/electrolyte interface during the CO_2RR (Supplementary Fig. 17)²⁷. Another key parameter that greatly influences the CO_2RR performance is the pH at the surface of catalyst, since the reduction of H^+ to *H plays an important role in both formation of formate and H_2 ²⁸. During the electrolysis, the pH near the cathode would arise owing to the rapid consumption of proton. To monitor the pH change during electrolysis, we conducted *in situ* Raman spectroscopy measurements, where the Raman signals of HCO_3^- (the peak at 1015 cm^{-1}) and CO_3^{2-} (the peak at 1068 cm^{-1}) can act as indicators to reflect the change in pH^{29, 30}. The spectra were recorded after 600 s electrolysis at each potential in CO_2 -saturated 0.5 M NaHCO_3 solution (Fig. 3a,b). Evidently, the

peak intensities of CO_3^{2-} for both Bi and BiCu-0.5 gradually increase as the potential negatively shifts, indicative of the increase in pH value. Besides, a more pronounced enhancement in the peak intensities of CO_3^{2-} was observed for BiCu-0.5, implying that the pH value is more elevated at the surface of BiCu-0.5 catalyst, which can be attributed to its higher current densities and more rapid consumption of the proton. Concurrently, a stronger peak at 2713 cm^{-1} corresponding to HCOO^- was observed for BiCu-0.5, suggesting the promoted production of formate (Fig. 3c,d)³¹.

HER performance of Bi and BiCu-0.5 was also evaluated in Ar-saturated 0.5 M Na_2SO_4 solution (Supplementary Fig. 18). Distinctly, a decrease of 80 mV in overpotential was achieved by BiCu-0.5 at an ECSA-corrected current density of 0.1 mA cm^{-2} , indicating that Cu atoms are more favourable for H^+ reduction than Bi atoms. Accordingly, we deduce that the introduction of Cu atoms would accelerate the H^+ reduction, and the consequent higher pH around the cathode would in turn contribute to a more effective suppression of HER, thereby promoting the formate production. This was further verified by the comparison of the CO_2RR performances for both catalysts in three different electrolytes (Supplementary Fig. 19; buffer capacity: $\text{Na}_2\text{SO}_4 < \text{NaHCO}_3 < \text{Na}_2\text{HPO}_4$). Notice that the pH near the catalyst surface would increase more significantly in the electrolyte with weaker buffer capacity. The $\text{FE}_{\text{formate}}$ increases as the buffer capacity decreases for both BiCu-0.5 and Bi, evidencing that a higher pH environment favours the formation of formate, which can be attributed to the lower sensitivity of proton concentration for CO_2RR owing to its sluggish and complex kinetics³⁰. Besides, the BiCu-0.5 delivers a substantially higher $\text{FE}_{\text{formate}}$ than Bi in the same electrolyte, and a more pronounced enhancement was achieved by BiCu-0.5 when NaHCO_3 was replaced by Na_2SO_4 . This result strongly demonstrates that the Cu atoms can mainly serve as the catalytic sites for reducing H^+ to $^*\text{H}$, and this feature is essential especially for formate production under high current densities when the amount of H^+ is limited. HCO_3^- concentration dependence experiment reveals that there is no obvious correlation between the j_{formate} and the HCO_3^- concentration for BiCu-0.5 (Supplementary Fig. 20), indicating that the H^+ comes from H_2O rather than HCO_3^- .

For BiCu-x alloy catalysts, the arrangements of the surface atoms play a critical role in the catalytic performance. To further understand the outstanding CO_2RR performance of BiCu-0.5, atomic resolution aberration-corrected HAADF-STEM was performed (Fig. 4a). The darker dots marked by red circles can be assigned to Cu atoms according to the disparity in Z-contrast between Cu and Bi atoms³². The line intensity profile in Fig. 4b also validates the isolated Cu atom in Bi lattice. As a step further, synchrotron radiation-based X-ray absorption fine structure (XAFS) spectroscopy was conducted to resolve the local structure of Cu atoms. Fig. 4c shows the Cu K-edge X-ray absorption near-edge structure (XANES) spectra for BiCu-x nanosheets ($x = 0.5, 1$ and 3), as well as the spectra for standard Cu foil, Cu_2O and CuO as references. The absorption edge positions of three BiCu-x catalysts situate between those of Cu and CuO , suggesting that the Cu atoms in BiCu-x are partially oxidized¹⁴. The Fourier-transformed extended XAFS (EXAFS) spectra are shown in Fig. 4d. The BiCu-0.5 displays a dominant peak of Cu–O at $1.94\text{ \AA}$, and a

shoulder peak at 2.24 Å probably to Cu–Cl introduced by the CuCl₂ precursor³³. For BiCu-3, however, the peak of Cu–Cu at 2.57 Å becomes dominant, and the Cu–O peak significantly declines. In BiCu-1, both peaks of Cu–O at 1.94 Å and Cu–Cu at 2.57 Å can be observed, and the peak of Cu–O is dominant (Fig. 4d). The wavelet transform (WT) plots for BiCu-0.5 and BiCu-1 both show the maximum value at 5 Å⁻¹, which corresponds to Cu–O bond, whereas the maximum of the WT plot for BiCu-3 is at 8 Å⁻¹, close to that for Cu foil, which corresponds to Cu–Cu bond (Fig. 4e). The absence of Cu–Cu bond in BiCu-0.5 demonstrates that the Cu atoms are single-atom isolated, whereas the Cu atoms in BiCu-1 are mainly single-atom isolated accompanying with small amount of Cu clusters, and the Cu atoms in BiCu-3 are mainly in aggregation state. The Cu aggregation would lead to the promoted H₂ evolution³⁴, accounting for the poor formate selectivity of BiCu-3 (Supplementary Fig. 11c). Besides, the XAFS data of the BiCu-0.5 after 40 h electrolysis suggests that the fine structure of BiCu-0.5 is well retained (Supplementary Fig. 21). Notably, the Bi L₃-edge XANES spectra show that the Bi atoms in BiCu-x are also severely oxidized (Supplementary Fig. 22), which is consistent with the results of XPS and *ex situ* Raman spectrum (Supplementary Fig. 23). The existence of oxidized Cu and Bi in BiCu-0.5 can be attributed to the high susceptibility of Bi and isolated Cu to O₂³⁵. To unearth the actual valence states of the metal elements during CO₂RR, *in situ* Raman spectroscopy was carried out (Fig. 4f). For BiOI-Cu-0.5 precursor, the peaks at 87 and 151 cm⁻¹ can be assigned to the A_{1g} and E_g stretching modes of Bi–I bond, respectively³⁶. After cyclic voltammetry (CV) treatment, only peaks at 71 and 97 cm⁻¹ were observed for BiCu-0.5, which are known as the E_g and A_{1g} modes for metallic Bi³⁷. This result strongly demonstrates the total conversion of BiOI-Cu precursor to metallic Bi in BiCu-0.5. Moreover, a similar metallic Bi Raman spectrum was recorded at -0.88 V in CO₂-saturated NaHCO₃ solution, which confirms the maintenance of Bi⁰ during CO₂RR. According to the standard reduction potentials (E^0 (Bi³⁺/Bi) = 0.317 V; E^0 (Cu²⁺/Cu) = 0.340 V; E^0 (Cu⁺/Cu) = 0.520 V)³⁸, the reduction of Cu²⁺ and Cu⁺ to Cu⁰ is more thermodynamically favoured than the reduction of Bi³⁺ to Bi⁰. Fig. 4g displays the CV curves for Bi and BiCu-x catalysts. The reduction peak at 0.08 V can be assigned to the reduction of Bi³⁺ to Bi⁰³⁵. Owing to the extremely low concentration of Cu elements in BiCu-0.5, no extra reduction peak was observed. Nonetheless, a new peak at 0.15 V emerged in BiCu-3, corresponding to the reduction of Cu²⁺ to Cu⁰³⁹. Therefore, we can deduce that both Cu and Bi atoms in BiCu-x are in zero valence state during the CO₂RR. With all the analysis above, we can finally confirm the successful fabrication of BiCu SAAC with atomically dispersed Cu atoms in Bi lattice for CO₂RR.

Theoretical study on the mechanism for enhanced formate production. To shed light on the correlation between the isolated Cu atom and the enhanced CO₂RR performance, density functional theory (DFT) calculations were carried out. The (012) surface is adopted to construct the theoretical model. On the basis of our experimental results, we reasonably proposed a reaction mechanism involving H⁺ reduction for the formate generation on the surface of Bi and BiCu-0.5 catalysts, as illustrated in Fig. 5a, b, respectively. The corresponding free energy diagrams are shown in Fig. 5c. The maximum free energy barrier (ΔG) on Bi surface is from H⁺ to adsorbed *H (0.66 eV), indicating that the H⁺ reduction is the rate-

determining step (RDS). In contrast, the ΔG of H^+ reduction is reduced to 0.25 eV on the isolated Cu sites in BiCu-0.5. The projected density of states (PDOS) calculation results reveal that the d -band centre of the isolated Cu atoms (-2.42 eV) is closer to the Fermi level than that of Bi (-2.75 eV), which is beneficial to the hydrogen adsorption (Supplementary Fig. 24). The above results were confirmed by the experiments of the kinetic isotope effect (KIE) of H/D over Bi and BiCu-0.5 catalysts. As shown in Supplementary Fig. 25, when D_2O was used as an electrolyte, a remarkable decrease in the formation rate of formate was observed for Bi catalyst, with the corresponding KIE value of 1.82, suggesting that the reduction of H^+ to *H is indeed a RDS on Bi catalytic site. In contrast, for BiCu-0.5, the KIE value was calculated to be only 1.08, indicating that the H^+ reduction is no longer involved in the RDS on the Cu site in BiCu-0.5⁴⁰.

To gain in-depth information for the *H transfer step, the transition state (*TS) for the formation of *HCOO from adsorbed *H and *CO_2 was further simulated. As shown in Fig. 5c, the formation of *TS becomes the RDS on BiCu-0.5, with a maximum ΔG value of 0.42 eV, which can be attributed to the stronger interaction between *H and Cu atoms. Nonetheless, it is still lower than the ΔG of the RDS on Bi (0.66 eV for H^+ reduction to *H). Moreover, the overall ΔG for the *TS drops to 0.97 eV on BiCu-0.5 compared with the value on Bi (1.18 eV), further indicating the favourable formation of *HCOO intermediate on BiCu-0.5. These results demonstrate that incorporating single-atom Cu in Bi lattice can indeed boost the reduction of H^+ to *H , and the synergistic catalysis of Cu and Bi can reduce the energy barrier of the RDS, and thus promotes the formation of *HCOO . On the basis of the above-mentioned analysis, the overall CO_2 -to- $HCOO^-$ process on the surface of BiCu-0.5 was proposed in Fig. 5d.

Extended assessment on CO_2RR performances. Encouraged by the unique surface structure and outstanding CO_2RR performance of BiCu-0.5, we move forward to investigate its potential in commercial utilization. Gas diffusion electrolyser (GDE) was employed to overcome the mass-transfer limitation at the electrode/solution interface (Supplementary Fig. 26), thereby producing high current density to meet the industrial requirements⁴. As shown in Fig. 6a, b, a current density of 150 mA cm^{-2} with a FE_{formate} of 94.8% was achieved at -0.48 V vs. RHE , and the current density and FE_{formate} remained virtually unchanged after electrolysis 240 min, suggesting the remarkable stability of BiCu-0.5 under high current density. Moreover, both an extremely high current density of 450 mA cm^{-2} and a high FE_{formate} of 96.5% can be achieved at -0.55 V vs. RHE . In sharp contrast, BiCu-3 only achieved a current density of 130 mA cm^{-2} with a FE_{formate} as low as 37.3% at -0.55 V vs. RHE ; the FE_{formate} was further reduced to 30.6% at -0.70 V vs. RHE , accompanied with a current density of 320 mA cm^{-2} (Supplementary Fig. 27). The low FE_{formate} of BiCu-3 can be attributed to the existence of Cu nanoclusters on the surface of Bi nanosheets, which are favourable for H_2 rather than formate production. This result further demonstrates the crucial role of single-atom Cu in BiCu-0.5 for promoting CO_2 electroreduction to formate with both high FE_{formate} and high j_{formate} . Fig. 6c displays a comparison of BiCu-0.5 with the reported state-of-the-art Bi-based electrocatalysts for reduction of CO_2 to formate (detailed information is listed in Supplementary Table 2). To our knowledge, the BiCu-0.5 SAAC exhibits the highest j_{formate} values among the reported Bi-based

electrocatalysts with excellent FE_{formate} in both H-type cell and GDE. Another issue that hinders the utilization of the electrocatalytic technique is the requirement of high-purity CO_2 as a feedstock for achieving high Faradaic efficiency, whereas the concentration of CO_2 in flue gas is only about 10%^{41, 42}. With this in mind, we performed the CO_2 RR using 10% CO_2 as the feedstock. As shown in Fig. 6d, the FE_{formate} can even approach over 80% in a wide potential window, and a value as high as 86.9% is achieved at -0.98 V, highlighting the great potential of BiCu-0.5 SAAC for CO_2 RR in commercial applications.

Discussion

In summary, we have successfully synthesized the BiCu nanosheets SAAC featuring isolated Cu atoms in Bi lattice. Benefiting from the unique surface structure, the BiCu-0.5 exhibits an outstanding electrocatalytic activity toward CO_2 reduction to formate with a current density up to 450 mA cm^{-2} and a FE_{formate} of 96.5% at -0.55 V in GDE, the highest j_{formate} value among the reported Bi-based electrocatalysts (Supplementary Table 2). Moreover, a high FE_{formate} over 80% can be achieved by BiCu-0.5 using a flue gas containing only 10% CO_2 . Experimental and theoretical studies reveal that the isolated Cu sites in BiCu-0.5 catalysts can dramatically reduce the energy barrier for H^+ reduction to $^*\text{H}$, a rate-determining step on Bi sites. The synergistic catalysis of Cu site for H^+ reduction and Bi site for CO_2 fixation and activation can promote the formation of $^*\text{HCOO}$, achieving both high j_{formate} and high FE_{formate} for electroreduction of CO_2 to formate. As for the BiCu-3 containing Cu clusters, a lower FE_{formate} was achieved owing to the promoted H_2 production on Cu clusters, in contrast to $^*\text{H}$ formation on isolated Cu sites in BiCu-0.5. Our work provides an ideal platform to understand the roles of both metals of “isolated single-atom” and support in SAACs during catalytic process, and opens up new perspectives for rational design of SAACs for highly efficient electroreduction of CO_2 to value-added products.

Methods

Preparation of BiCu-x catalysts. BiOI-Cu-x nanosheets were first synthesized according to a modified reported method as following⁹. 0.97 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and a certain amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 20 mL acetic acid aqueous solution (1.2 M), and the mixture was vigorously stirred for 20 min to get a homogeneous solution. Then 5 mL KI aqueous solution (2 M) was added dropwise to the above solution, followed by the addition of NaOH aqueous solution (3 M) for adjusting the solution pH to 6 to form an orange suspension. After stirring for another 30 min, the solution was then transferred into a 50 mL Teflon-lined autoclave and heated at 433 K for 2 h. The product was washed twice with water and dried in vacuum under 333 K. The samples with different Cu/Bi molar ratios were denoted as BiOI-Cu-x ($x = 0.2, 0.5, 1, 3$). The pure BiOI nanosheets were synthesized by the same procedure, except for the absence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

The as-prepared BiOI-Cu-x nanosheets were converted into BiCu-x alloy nanosheets by *in situ* electrochemical reduction prior to CO₂RR test. Typically, 5 mg BiOI-Cu-x sample and 2.5 mg carbon black (Cabot Vulcan XC-72) were well dispersed in 1 mL solution containing 750 μ L of ethanol, 200 μ L of H₂O, and 50 μ L 5% Nafion by ultrasonication for 1 h. Then 100 μ L of the above ink was uniformly dropped onto a carbon cloth ($0.5 \times 1 \text{ cm}^2$, WOS1009, CeTech) and dried naturally, reaching a catalyst mass loading of 1 mg cm^{-2} . The electrochemical conversion was performed in Ar-saturated 0.5 M NaHCO₃ aqueous solution, during which 200 cycles of cyclic voltammetry (CV) ranging from -0.6 V to -1.5 V vs. Ag/AgCl were carried out with a scan rate of 0.1 V s^{-1} . After that, the electrode was rinsed in water for 3 times and dried by N₂ flow, and the BiCu-x alloy-loaded working electrode (WE) was finally obtained.

Electroreduction of CO₂ in H-type cell. The electrochemical measurements were performed at ambient pressure and temperature in an H-type cell connected to a CHI 760E electrochemical workstation (Shanghai ChenHua Instruments), in which a platinum plate and a Ag/AgCl electrode (filled with saturated KCl aqueous solution) were employed as the counter and reference electrodes, respectively. The two compartments were separated by a proton exchange membrane (Nafion 117) and filled with 16 mL 0.5 M NaHCO₃ solution each. Before CO₂RR test, the electrolyte was first purged with Ar to remove O₂ and then CO₂ for at least 30 min to obtain CO₂-saturated 0.5 M NaHCO₃ solution. For the electrocatalytic reduction of 10% CO₂, similar procedure was applied except that the pure CO₂ was replaced by 10% CO₂/Ar. Unless otherwise specified, all potentials in this work are converted into reversible hydrogen electrode (RHE) scale by $E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 \text{ V} + 0.0591 \times \text{pH}$. A gas chromatograph (SHIMADZU GC-2014) equipped with two Porapak N columns and dual detectors (FID and TCD) was employed to quantify the gas products. The liquid products were first qualitatively analysed by ¹H-NMR (Bruker 400 MHz), and the production of formate was further quantified by the ion chromatograph (IC, Metrohm ECO).

Electroreduction of CO₂ in gas diffusion electrolyser. A customized gas diffusion electrolyser (GDE) system connected to an Autolab PGSTAT302N electrochemical workstation (Metrohm) was employed to evaluate the CO₂RR performance of the BiCu-0.5 sample at high current density under ambient pressure and temperature (Supplementary Fig. 26). The gas diffusion electrode (GDE) was fabricated by depositing BiOI-Cu-0.5 sample onto a $3 \times 3 \text{ cm}^2$ gas diffusion layer (Sigracet 29 BC) with a mass loading of 1 mg cm^{-2} , followed by the *in situ* electrochemical reduction as described above. During the CO₂RR test, the exposed area of GDE was fixed to 1 cm^2 by a shaped gasket. A Ag/AgCl electrode and a $3 \times 3 \text{ cm}^2$ Pt foil were used as the reference electrode and the counter electrode, respectively. KOH aqueous solution (1.0 M) was used as the electrolyte with a flow rate of 2.5 mL min^{-1} , and the flow rate of CO₂ was fixed at 30 sccm by a mass flow controller. Ohmic resistance compensation with a level of 80% was applied for the electrolysis.

***In situ* Raman spectroscopy measurements.** *In situ* Raman spectroscopy measurements were performed using a WITec alpha300 R confocal Raman imaging system with a 633 nm laser as the excitation source.

A standard silicon wafer (520 cm^{-1}) was employed to calibrate the Raman system. A CCD camera with 1650×1650 pixels was used to photograph the sample surface and collect the spectra. In a specially designed two-compartment cell, the sample was spread on a glassy carbon electrode with its planar surface perpendicular to the incident laser. The electrode surface was covered by a thin layer of electrolyte (0.5 M NaHCO_3). Each compartment of the cell was sealed with a quartz window, and equipped with two channels for gas flow.

Computational details. The Vienna *ab initio* simulation package (VASP) combined with the projected augmented wave (PAW) method was used to perform all the calculations. The generalized gradient approximation (GGA) was adopted, with the Perdew-Burke-Ernzerh (PBE) chosen as the exchange-correlation functional. An energy cutoff of 450 eV was set for the plane wave basis set. The van der Waals interactions were described using the DFT-D3 method with Becke-Jonson damping. A $3 \times 3 \times 1$ Monkhorst-Pack *k*-point was employed. The convergence thresholds for energy and force were set to 10^{-5} eV and $0.02\text{ eV \AA}^{-1}$, respectively.

In this work, a 2×2 supercell of bismuth bulk was optimized and the (012) surface with six atomic layers was constructed as the surface slab. During the calculations, the top two layers were fully relaxed. To avoid the interaction between two units, the vacuum layers were set to be 15 Å. The Gibbs free energy of each intermediate in the simulated pathway was calculated as follows:

$$G = E_{\text{DFT}} + E_{\text{ZPE}} + \int C_V dT - TS$$

Where E_{DFT} is the electronic energy directly obtained from DFT calculations, E_{ZPE} is the zero-point vibrational energy, $\int C_V dT$ is the heat capacity, T is the temperature (298.15 K), and S is the entropy.

Declarations

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

Y. L. and T. L. conceived and designed the experiments. P. L. prepared the materials and performed the characterizations. Y. L. carried out the *in situ* Raman spectroscopy measurements. L. L., B. N. and Y. L. analysed the XANES and EXAFS data. H. W. carried out the computational investigations and provided theoretical analysis. Y. L., T. L., and P. L. wrote the manuscript. T. L. was responsible for the overall direction of the project. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Structure characterizations of BiCu-0.5 alloy nanosheets. a SEM, b STEM and c HRTEM images for BiCu-0.5. The inset in panel b is the size distribution of surface BiCu alloy nanoparticles. d HAADF-STEM-EDX elemental mapping images of BiCu-0.5. Scale bar for d is 2 nm.

Figure 2

Assessment of CO_2RR performance of BiCu-0.5 and Bi. a Linear sweep voltammetry curves of BiCu-0.5 and Bi in Ar- or CO_2 -saturated 0.5 M NaHCO_3 aqueous solution (scan rate: 10 mV s^{-1}). b $\text{FE}_{\text{formate}}$ and c j_{formate} of formate for BiCu-0.5 and Bi under different potentials. d Long-term stability test with 40 h electrolysis and corresponding $\text{FE}_{\text{formate}}$ for BiCu-0.5. The error bars represent the standard deviation based on at least triplicate tests.

Figure 3

In situ Raman spectroscopy of Bi and BiCu-0.5 catalysts. In situ Raman spectra for Bi (a and c) and BiCu-0.5 (b and d) during electrochemical reduction of CO₂ at different potentials in CO₂-saturated 0.5 M NaHCO₃.

Figure 4

Atomic-scale structure analysis of BiCu- x alloy nanosheets. a, Atomic-resolution aberration-corrected HAADF-STEM image and b corresponding intensity line profile for BiCu-0.5. c Normalized Cu K-edge XANES and d EXAFS spectra of BiCu- x alloy catalysts with different Cu contents (0.5, 1 and 3%), with Cu foil, Cu₂O and CuO as references. e Wavelet transform plots of BiCu-0.5, BiCu-1, BiCu-3 and Cu foil. f In situ Raman spectra of BiOI-Cu-0.5, fresh-made BiCu-0.5 and BiCu-0.5 under electrolysis at -0.88 V. g Cyclic voltammograms of Bi, BiCu-0.5 and BiCu-3 alloy catalysts.

Figure 5

Density functional theory calculations and reaction route. Optimized adsorption configurations of (II) $\ast\text{H}$, (III) $\ast\text{H}+\ast\text{CO}_2$, (IV) $\ast\text{TS}$, and (V) $\ast\text{HCOO}$ on (012) facets of a Bi and b BiCu-0.5. c Free energy diagrams for HCOOH formation on BiCu-0.5 and Bi. d Schematic illustration for the reduction of CO_2 to formate on the Bi–Cu synergistic sites of BiCu-0.5. The magenta, blue, grey, red, and green balls represent Bi, Cu, C, O, and H, respectively.

Figure 6

CO_2RR performance of BiCu-0.5 in a gas diffusion electrolyser (GDE) and in dilute CO_2 atmosphere. a Current-time curves for BiCu-0.5 at different potentials (-0.48 V , -0.52 V and -0.55 V vs. RHE) in 1.0 M KOH aqueous solution (pH = 13.5), and corresponding $\text{FE}_{\text{formate}}$. b Stability test for BiCu-0.5 with a current density of 150 mA cm^{-2} for 240 min. c Comparison of j_{formate} and $\text{FE}_{\text{formate}}$ for BiCu-0.5 with recently reported Bi-based materials. Note: the corresponding references are listed in the Supplementary References. d $\text{FE}_{\text{formate}}$ and corresponding j_{formate} at various potentials for BiCu-0.5 in an H-type cell containing 0.5 M NaHCO_3 aqueous solution under 10% CO_2 atmosphere.

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