Modulating electric field distribution by alkali cations for CO₂ electroreduction in strongly acidic medium

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The reaction of carbon dioxide with hydroxide to form carbonate in near-neutral or alkaline medium severely limits the energy and carbon efficiency of CO₂ electroreduction. Here we show that by suppression of the otherwise predominant hydrogen evolution using alkali cations, efficient CO₂ electroreduction can be conducted in acidic medium, overcoming the carbonate problem. The cation effects are general for three typical catalysts including carbon-supported tin oxide, gold and copper, leading to Faradaic efficiency as high as 90% for formic acid and CO formation. Our analysis suggests that hydrated alkali cations physiosorbed on the cathode modify the distribution of electric field in the double layer, which impedes hydrogen evolution by suppression of migration of hydronium ions while at the same time promoting CO₂ reduction by stabilization of key intermediates.

Electrochemical reduction of CO₂ to produce chemicals and fuels is widely studied as a potential solution for renewable energy storage and CO₂ recycling. Because the hydrogen evolution reaction (HER) dominates in acidic aqueous solutions, CO₂ electroreduction is conducted in an alkaline or near-neutral medium. These reaction media, however, create one of the key obstacles regarding high-efficiency, steady-state CO₂ electroreduction: the facile reaction of CO₂ with hydroxide (OH⁻) to form carbonate (CO₃²⁻). In alkaline medium, although the overpotentials of many catalysts are minimized, the carbonate problem obliges continuous refreshment of OH⁻ electrolytes in a flow cell configuration to obtain stable performance. The regeneration of CO₂ and 2OH⁻ from aqueous carbonate is energy demanding and leads to low or even negative energy efficiency for CO₂ electroreduction. In near-neutral media such as bicarbonate solutions, although steady-state CO₂ electrolysis is possible, CO₂ is still consumed by OH⁻ anions electrochemically generated by CO₂ electroreduction. In near-neutral media both the high resistance of the solution and higher over-potential for oxygen evolution reaction (OER) lead to high cell voltage and low energy efficiency. In strongly acidic media the resistance and over-potential for OER are lower, and the carbonate problem can be solved since carbonate will not cross the medium to the anode. An acidic medium is also essential to obtaining formic acid from CO₂ reduction. In near-neutral and alkaline media the same reduction leads to formate, which requires energy-intensive downstream processes for separation and conversion.

Efficient CO₂ electroreduction in an acidic medium is challenging because the HER is normally more facile than CO₂ reduction. It was reported that, in CO₂-saturated 0.1 M HClO₄ solution (pH 1.0), the Faradaic efficiency of HER was nearly 100% on Fe-N-C and Au catalysts, both of which are efficient CO₂-reduction catalysts in near-neutral and alkaline media. CO₂ reduction to CO was feasible in mildly acidic media (pH ≥ 3.0) such as mixed HClO₄/NaClO₄ (ref. 11) and K₃HPO₄ solutions. Bondue et al. proposed that HER is suppressed by OH⁻ anions generated from CO₂ reduction. During the preparation of our publication, Huang et al. reported efficient CO₂ electroreduction on Cu catalysts in strongly acidic solutions (pH 0.67) with mixed H₃PO₄/KCl electrolytes. In both studies, alkali cations are essential for CO₂ reduction but the mechanism of cation promotion remains unclear. The very recent work of Monteiro et al. demonstrated that alkali cations are indispensable for the stabilization of CO₃⁻ species, a key intermediate in CO₂ reduction. However, it remains unclear how alkali cations suppress the predominant HER in acidic media.

Here we demonstrate efficient CO₂ electroreduction, with Faradaic efficiency as high as 90%, in strongly acidic solutions (pH 1.0) by suppression of HER with alkali cations. This approach can be applied for three representative classes of catalyst, namely carbon-supported SnO₂, Au and Cu nanoparticles (SnO₂/C, Au/C and Cu/C; Supplementary Fig. 1), which yield formic acid, CO and hydrocarbons, respectively, as the main CO₂ reduction products. Our simulation and analysis indicate that alkali cations in the double layer of the cathode effectively shield the electric field in the diffusion layer and suppress the migration of hydronium ions towards the cathode, which lowers the concentration of hydronium ions in the outer Helmholtz plane (OHP) and thus suppresses HER. Meanwhile cations strengthen the field in the Stern layer and stabilize key intermediates in CO₂ reduction.

Results
CO₂ electroreduction in acidic media. Both the activity and selectivity of the CO₂ reduction reaction are sensitive to alkali metal cations in near-neutral bicarbonate solutions. Several hypotheses, including local pH effect and electrostatic interaction, have been offered to explain these cation effects. Inspired by these studies, we decided to explore the potential influence of alkali cations in CO₂ reduction vis-à-vis HER in strongly acidic media. We first probed the effect of K⁺ in CO₂ reduction on SnO₂/C at pH 1.0. We used a three-electrode flow cell with a gas diffusion electrode (GDE) as the working electrode (Supplementary Fig. 2) for...
electrocatalytic tests. Figure 1a shows the cyclic voltammetry (CV) curves of SnO2/C in two different electrolyte solutions: an aqueous solution of formic acid and CO2 (light pink). Scan rate was 20 mV s−1. b–g, Faradaic efficiency (b,d,f) and partial current density (c,e,g) of different reduction products in 0.1 M H2SO4 + 0.4 M K2SO4. The catalysts used were SnO2/C (b,c), Au/C (d,e) and Cu/C (f,g). Partial current densities of minor products on Cu/C are not shown. Error bars were s.d. based on testing of three individual working electrodes.

Figure 1b–g shows the performance of SnO2/C, Au/C and Cu/C in electrolyte solutions containing 0.1 M H2SO4 + 0.4 M K2SO4 (pH1.5). This combination of electrolytes is more practicable than that of HOTf+ KOTf, even though the addition of K+ ions changed the pH of H2SO4 solutions marginally. For SnO2/C, formic acid was the major product of CO2 reduction, with maximum Faradaic efficiency and partial current density of 88% and 314 mA cm−2, respectively (Fig. 1b,c). These performance metrics are comparable to state-of-the-art results for formic acid production from a solid-state electrolyser21 and formate formation in near-neutral solutions 22. An aqueous solution of formic acid could be separated from the electrolyte solution by distillation (Supplementary Fig. 4), demonstrating the advantage of an acidic reaction medium for formic acid generation compared with a near-neutral or alkaline medium where only formate would be generated. For Au/C, CO was the major product, with maximum Faradaic efficiency and partial current density of 91% and 227 mA cm−2, respectively (Fig. 1d,e). For Cu/C, formic acid, CO, methane, ethylene, propene, acetic acid, ethanol and 1-propanol were detected as the products of CO2 reduction (Supplementary Fig. 5). The minimum Faradaic efficiency of HER was 16%, lower than that of the Cu/perfluorosulfonic acid (PFSA) catalyst in H3PO4/KCl medium (Faradaic efficiency of HER, 36%)
reported by Huang et al.16. Among products of >2-electron reduction, ethylene was the major product with a partial current density of 136 mA cm$^{-2}$ (Fig. 1g). Its Faradaic efficiency was 25% (Fig. 1f), similar to the highest level recorded for ethylene production on Cu/PFSA in H$_2$PO$_4$/KCl medium reported by Huang et al.1. The maximum partial current densities of CO formation on Au/C and ethylene formation on Cu/C in acidic media were comparable to those for state-of-the-art catalysts in near-neutral and alkaline media1,12,13.

We also compared the performances of Au/C for CO$_2$ electroreduction in acidic (0.1 M H$_2$SO$_4$ + 0.4 M KHCO$_3$) and near-neutral (0.8 M KHCO$_3$) and alkaline (0.8 M KOH) media in a two-electrode cell (Supplementary Fig. 6). As expected, the carbonate problem was severe in an alkaline medium: while the initial cell voltage was low, it increased substantially (by 34%) after 2.5 h (Fig. 2a). Meanwhile, the pH of the solution decreased from 13.5 to 8.1 due to the reaction of C$_2$H$_3$O$_2$H with CO$_2$ (Fig. 2b). In near-neutral and acidic media, cell voltages were largely stable (Fig. 2a) because no net reaction between electrolyte and CO$_2$ occurred in these media. The pH of the solutions remained stable after 4 h of electrolysis (Fig. 2b). The overall cell voltage with the acidic medium was about 0.3 V lower than that with the near-neutral medium for 200 mA cm$^{-2}$ at 4 h. For catalysts SnO$_2$/C and Cu/C, inductively coupled plasma–mass spectrometry (ICP–MS) was used to measure the dissolution of metal into the electrolyte solution during electrolysis (Supplementary Table 1). After 4 h of electrolysis at 200 mA cm$^{-2}$, 1.70% of Sn and 0.27% of Cu were dissolved in acidic medium. Although dissolution ratios were lower in near-neutral and alkaline media (Supplementary Table 1), the majority of SnO$_2$/C and Cu/C remained stable. The size distributions of Sn and Cu nanoparticles after electrolysis were similar to those of the as-prepared catalysts (Supplementary Fig. 7).

**Carbon and energy efficiency.** Table 1 summarizes the theoretical carbon efficiency of CO$_2$ electroreduction in generating different products in a flow cell in acidic, near-neutral or alkaline medium, and a membrane-electrode-assembly (MEA) set-up with an anion exchange membrane. In alkaline medium, the constant reaction of CO$_2$ with OH$^-$ led to carbon efficiency of around 10% or lower$^{2,25,26}$. In near-neutral medium and in an MEA set-up, CO$_2$ reacts with OH$^-$ generated at the cathode (CO$_2$ reduction), forming carbonate ions; the latter cross the electrolyte solution or the membrane to the anode where they react with H$^+$ generated by OER (Supplementary Fig. 8b). When CO or formate is the product, 50% of CO$_2$ is consumed to form carbonate but, in the case of ethylene production, 75% of CO$_2$ is consumed to form carbonate$^{11}$. Indeed, in the reduction of CO$_2$ to CO on Au in near-neutral medium, a large amount of CO$_2$ was detected in the gas generated at the anode (Supplementary Fig. 9), in agreement with the above analysis. In contrast, the theoretical carbon efficiency in acidic medium is as high as 100%, which is supported by the fact that CO$_2$ was not detected in the gas product at the anode in CO$_2$ electroreduction on Au in acidic medium (Supplementary Fig. 9). Note that a crossover of formate through an anion exchange membrane in a flow cell in neutral or alkaline medium would further decrease carbon efficiency. This issue can be avoided by using a proton exchange membrane-based flow cell in acidic medium (Supplementary Fig. 10).

Figure 3 shows the estimated energy consumption of a sustainable system required to produce 1 mole of CO and ethylene assuming a current density of 200 mA cm$^{-2}$ (for the methods used see Supplementary Note 1). One-electron reduction of CO$_2$, the first step in CO$_2$ reduction without the involvement of protons, has been shown to be the rate-determining step (RDS) in CO formation on Au$^{14,16}$ and single-atom catalysts$^{7}$. Consequently, the formation rate of CO was pH independent on the standard hydrogen electrode (SHE) scale. The CO–CO coupling step was found to be the RDS of the reactions that led to C$_2$ products on Cu-based catalysts$^{26,27,28}$. Over a long potential window, CO coverage is relatively saturated$^{28}$, leading to a pH-independent formation rate of C$_2$. 

### Table 1 | Theoretical carbon efficiency (%) of CO$_2$ reduction to generate CO, formic acid (or formate) and ethylene in a flow cell in acidic, near-neutral or alkaline medium, and an MEA set-up with an anion exchange membrane

| Product                  | Acidic | Neutral | Alkaline* | MEA |
|--------------------------|--------|---------|-----------|-----|
| CO                        | 100    | 50      | 11.7      | 50  |
| Formic acid (or formate)  | 100    | 50      | 11.7      | <50 |
| Ethylene                 | 100    | 25      | 4.2       | 25  |

Theoretical carbon efficiency was estimated by assuming that (1) all CO$_2$ is consumed at the cathode to form reduction products or carbonate and (2) the Faradaic efficiency of the desired product is 100%. *Assuming a constant reaction rate between CO$_2$ and OH$^-$ ions at the gas–electrolyte interface and a current density of 200 mA cm$^{-2}$. Supplementary Note 1 describes the methods used. Formate ions penetrate the membrane and may be oxidized at the anode, leading to a decrease in carbon efficiency.
products on the SHE scale. In our experiments, the partial current density-potential (versus SHE) plots of these products at different pH values were indeed close to each other (within the range of 100 mV; Supplementary Fig. 11). Because the equilibrium potentials of CO$_2$/CO and CO$_2$/ethylene are constant on the RHE scale, the overpotential increases as pH decreases. Thus, energy consumption due to overpotential loss at the cathode is in the order acidic > near neutral > alkaline. Despite this, the overall energy consumption is lowest in acidic medium (Fig. 3) owing to lower losses in other categories. In alkaline medium the regeneration of KOH electrolyte is most energy demanding, leading to an overall energy consumption threefold higher than that in acidic medium. In near-neutral medium, ohmic (Supplementary Fig. 12a) and anode energy losses (Supplementary Fig. 12b) were higher than those in acidic medium, leading to an overall energy consumption about 14% higher than that in acidic medium.

Cation effect. To understand how K$^+$ further suppressed HER on SnO$_2$, Au and Cu under strongly acidic solutions, we measured linear sweeping voltammetry (LSV) curves of a polycrystalline Au rotating-disk electrode (RDE) in different electrolyte solutions (Fig. 4a). The onset potential of HER in 0.1 M HOTf +0.4 M KOTf was close to that in HOTf solution (0.1 or 0.5 M), while in the K$^+$-containing solution a diffusion-limitation feature was observed as a plateau of current density appeared at −0.6 V versus SHE. The current density increased again at about −1.3 V versus SHE, close to the onset potential of HER in 0.4 M KOTf, indicating that reduction of water molecules started at this potential. The plateau was about 6% higher than the limiting diffusion current density of hydronium reduction calculated according to the Levich equation. In sharp contrast, in 0.1 M HOTf no plateau of HER current density was observed. To probe the possibility that some unknown impurities contained within KOTf had suppressed HER$^+$, we prepared a 0.1 M HOTf +0.4 M KOTf solution by partial neutralization of HOTf with electronic-grade KOH (99.999% pure). The LSV curves collected in this solution (Supplementary Fig. 13) overlapped well with those in Fig. 4a, supporting the idea that K$^+$ ions, rather than unknown impurities, had suppressed HER. LSV curves of SnO$_2$/C on glassy carbon RDE (Supplementary Fig. 14) and CV curves of SnO$_2$/C on GDE in a N$_2$ atmosphere (Fig. 1a) show similar trends to those in Fig. 3a, indicating that suppression of HER by K$^+$ in strongly acidic medium is a universal effect.

We next probed whether other alkali cations, such as Li$^+$, Na$^+$ and Cs$^+$, would have an effect on competition between HER and CO$_2$ reduction similar to that of K$^+$. Indeed, in 0.1 M HOTf +0.4 M MOTf (Li, Na, Cs), plateaux of similar current density were observed (Supplementary Fig. 14), indicating that these alkali cations also suppressed the migration of hydronium ions. We then measured CO$_2$ electroreduction on SnO$_2$/C and Cu/C under acidic solutions containing these alkali cations (Supplementary Figs. 15–17). All alkali cations promoted CO$_2$ reduction by inhibition of HER, but the effects were variable. On SnO$_2$/C, the Faradaic efficiency of CO$_2$ reduction increased in the order Li$<$ Na$<$ K$<$ Cs (Fig. 4b), and the partial current densities of formic acid and CO increased in the same order (Fig. 4c). On Cu/C, the partial current density of ethylene increased in a similar order, Li$<$ Na$<$ K$<$ Cs (Supplementary Fig. 17).

Mechanistic study of cation effect. To probe how alkali cations suppress the reduction of hydronium ions, we conducted a simulation based on the Poisson–Nernst–Planck (PNP) model, which includes migration as one of the mechanisms for mass transport$^{32}$. Hydronium ions, K$^+$ and OTf$^-$ were considered, and reduction of hydronium ions was regarded as the only source of HER in strongly acidic media. HER current density was assumed proportional to the concentration of hydronium ions in the OHP and exponential to the electrode potential. The simulation reproduced the features of HER at potentials more positive than for the onset of reduction of water (Supplementary Fig. 18): in a K$^+$-free solution, the current density of hydronium reduction increased, with no limitation, as the potential moved cathodically; and in a K$^+$-containing solution, a plateau with a limiting current appeared. The limiting current density was slightly higher (~18%) than the plateau of current density observed in our RDE experiment (Fig. 4a), this small difference being attributed to omission of the steric effect of cations in our PNP model.

Figure 5a,b shows the profiles of potential and electric field strength with and without K$^+$ ions. The addition of K$^+$ ions led to a stronger electric field in the Stern layer and a weaker electric field >2 nm away from the cathode (Fig. 5b, inset). Hydrated K$^+$ ions and hydronium ions showed competitive adsorption at OHP of the cathode. The electric fields generated by the cathode and by these cations at OHP were in the same direction in the Stern layer while opposite in the diffuse layer (Fig. 5c). Although hydronium ions accumulated at OHP had a similar effect to K$^+$ on electric field distribution, the effect was weak since hydronium ions at OHP were consumed in HER (Fig. 5d). Hence, in K$^+$-free medium the electric field was not sufficiently confined within a few nanometres from the cathode, and migration of hydronium ions under electric field facilitated the refilling of hydronium ions to OHP. The concentration of hydronium ions at OHP did not change notably as the electrode potential shifted cathodically (Supplementary Fig. 19a,b), indicating that hydronium ions would not be depleted as current density increased. In K$^+$-containing medium, due to the competitive adsorption of hydrated K$^+$ ions against hydronium ions at OHP, a chemically inert hydrated K$^+$ layer formed at OHP and shielded the electric field from the cathode in a long potential window. Thus, migration of hydronium ions was dramatically suppressed. As the electrode potential moved negatively, more hydrated K$^+$ ions...
accumulated at OHP while the concentration of hydronium ions at OHP decreased (Supplementary Fig. 19c,d). Therefore, only in an alkali cation-containing medium would depletion of hydronium ions occur near the cathode, leading to diffusion limitation similar to the LSV curves in Fig. 4a.

For CO2 reduction in aqueous media, adsorbed CO2 (CO2ad) is regarded as a key intermediate7,14,20,33,34. Stabilization of CO2ad on the surface of catalysts promotes the production of CO and formate7,14,20,33,34. The two C=O bonds of CO2ad bend away from the surface, endowing CO2ad with a large dipole moment oriented outwards18,37. Thus, the electric field in the Stern layer stabilizes CO2ad at OHP (Fig. 5c). Similarly the OCCO intermediate, a key intermediate in CO2 electroreduction, is generated from CO2 reduction. These interactions between electric field and dipole moment of adsorbed intermediates.

The cation effect on pH near the cathode was further explored by PNP modelling. Hydronium ion reduction, OH− generation from CO2 reduction, homogeneous reaction between hydronium ions and OH− ions and the dissociation of water molecules were included in the simulation. Figure 6a compares the pH profiles in 0.1 M HOTf and 0.1 M HOTf + 0.4 M KOTf at −0.7 V versus PZC in K+−containing medium. The pH at OHP in K+−free medium was <0, ascribed to the fact that the electric field was not effectively shielded in the absence of inert cations in the diffuse layer. Figure 6b further compares pH profiles in two media when reduction current densities were both around 200 mA cm−2. In K+−containing medium we observed the increase in pH approaching OHP. The pH reached maximum (6.3) at 2 nm from OHP and dropped when further approaching it. Nevertheless, the pH at OHP (5.1) was still considerably higher than that for the bulk medium (1.0). In K+−free medium, pH did not vary as much when approaching OHP, and dropped steeply when the distance to OHP was <5 nm. Although several studies have proposed that local pH increase at the cathode–electrolyte interface is essential to the promotion of CO2 reduction over HER14–16,19,40, our simulation results indicate that inert alkali cations are indispensable for interfacial pH increase at high current densities.

In our experiment, the partial current density of CO2 reduction on SnO2/C in 0.1 M HOTf + 0.4 M KOTf largely exceeded the plateau of HER current density under this condition (Supplementary Fig. 20), implying that water is the proton source for CO2 reduction and that OH− ions are generated from CO2 reduction. These OH− ions were expected to react with hydronium ions near the
The effect of different alkali cations on CO₂ reduction has been extensively studied in near neutral and alkaline media. In alkali-containing media, the activity of CO₂ reduction to CO and ethylene was highest with Cs⁺ and lowest with Li⁺, similar to our observation in acidic media. The size of hydrated cations decreased from Li to Cs. As the size of hydrated cations decreases, more alkali cations can accumulate at the OHP, resulting in a further increase in local pH and a decrease in the current density of hydronium reduction. Fig. 6c shows the pH at OHP, and Fig. 6d shows the simulated partial current densities of hydronium reduction and CO₂ reduction at different potentials in K⁺-containing medium. As CO₂ reduction started to occur, hydronium reduction became suppressed due to the generation of OH⁻ from CO₂ reduction. This result agrees with our experimental observation (Supplementary Fig. 20). Owing to this local pH effect in the presence of an inert cation, the Faradaic efficiency of CO₂ reduction could reach as high as 90% for SnO₂/C and Au/C catalysts (Fig. 1b,d). Supplementary Fig. 21c compares the simulated pH profiles in K⁺-containing medium at −1.26 V versus PZC with and without OH⁻ generation from CO₂ reduction. The maximum pH appeared at 2 nm from OHP in both cases, with pH values of 6.3 and 5.5, respectively. This result indicates that local pH increase in K⁺-containing medium was mainly due to the effective shielding of the electric field by alkali cations while the generation of OH⁻ ions from CO₂ reduction further increased local pH by 0.8 units.

The effect of different alkali cations and quaternary ammonium cations on CO₂ reduction has been studied extensively in near neutral and alkaline media. In alkali-containing media, the activity of CO₂ reduction to CO and ethylene was highest with Cs⁺ and lowest with Li⁺, similar to our observation in acidic media. The size of hydrated cations decreased from Li to Cs. As the size of hydrated cations decreases, more alkali cations can accumulate at the OHP. According to the model shown in Fig. 5c, the electric field was more confined in the Stern layer as the concentration of cations in OHP increased, and thus CO₂ad and the OCCO intermediate were more effectively stabilized and the formation of CO and ethylene further promoted.

Under N₂, the onset potential and plateau current density for HER were similar with different alkali cations (for example, Supplementary Fig. 14 for SnO₂/C). Under CO₂, HER current density was higher with Li⁺ or Na⁺ than with K or Cs (Fig. 4c and Supplementary Fig. 22). This trend is due to the influence of CO₂ reduction on HER. CO₂ reduction generates OH⁻ ions, which then neutralize hydronium ions. As shown in Fig. 6d, a higher CO₂ reduction current density leads to a lower hydronium reduction current density. The current density of CO₂ reduction increases, from Li⁺ to Cs⁺. Thus, the current density of hydronium reduction should decrease from Li⁺ to Cs⁺. This trend was observed on SnO₂/C at −1.14 and −1.24 V (Supplementary Fig. 22). At −1.34 V, the reduction of water in addition to hydronium contributes to HER, which led to the trend shown in Fig. 4c.

Previous studies have shown that methane production and HER followed the same trend for CO₂ reduction on Cu in near-neutral and alkaline media, which was attributed to the involvement of water (as a proton source) in the RDS of methane formation. For CO₂ reduction on Cu/C in acidic medium containing alkali cations, this trend did not hold when the potentials were increased (Fig. 1g). This result can be understood considering the change of proton source in HER at different potentials. At potentials more positive
than −1.2 V versus RHE, hydronium ions are the proton source for HER; at more negative potentials, water becomes an additional proton source. On the other hand, water is the proton source for CO₂ reduction at all potentials (see above).

Double-layer effects in electrokinetics have long been studied. Earlier work proposed that alkali cations accumulated at OHP shielded the electric field, decreasing the force for outward migration of anions from the cathode. We show here that a similar effect can suppress migration of hydronium towards the cathode, thereby disfavoring HER. This effect can be exploited to conduct efficient CO₂ electroreduction in strongly acidic media. Our work is a further demonstration that electrocatalysis can be controlled by modulation of the electric field near the electrode.

Conclusions

By using alkali cations to suppress hydronium reduction and promote CO₂ reduction, we demonstrated efficient CO₂ electroreduction in strongly acidic media. We showed that this approach is universal for various catalysts and cations, and we revealed cation-induced modulation of electric field as the origin of the catalytic effects. This work provides a promising strategy to avoid the carbonate problem associated with CO₂ electroreduction, which is one of the main roadblocks for low-temperature CO₂ electrolysis.

Methods

Preparation of catalysts. Carbon black (Vulcan XC-72R), anhydrous tin(II) chloride (SnCl₂, 98%, Acros), sodium oxalate (Na₂C₂O₄, 99.5%, Sigma-Aldrich), hydrochloric acid (HCl, 37%, VWR International), borane tert-butyamine complex (BTB, 97%, Sigma-Aldrich), copper(II) acetylacetonate (Cu(acac)₂, 98%, Acros), and trioctylphosphine oxide (TOPO, 99%, Sigma-Aldrich) were used as received, without further purification. Hydrochloric acid (HCl, 37%, VWR international), gold(III) chloride hydrate (SnCl₂·H₂O, 99.9%, Sigma-Aldrich), oleylamine (approximate C₁₈-content 80–90%, Acros), and trioctylphosphine oxide (TOPO, 99%, Sigma-Aldrich) were used as received, without further purification. Deionized water (18 MΩ, Deionized water purification system (Merck Millipore Corporation), was used for all experiments.

Synthesis of SnO₂/C was performed using a method modified from ref. 50: 120 mg of nitric acid-treated carbon black was dispersed in 10 ml of deionized water, and 200 μl of HCl (37%) was added followed by 190 mg of anhydrous SnCl₂ under vigorous stirring. After 30 s, 10 ml of 0.2 M Na₂C₂O₄ solution was added immediately and dispersion maintained under stirring at 25 °C for 30 min. SnC₂O₄/C was then collected by centrifugation, washed with deionized water three times and dried under vacuum at 25 °C. The as-synthesized SnC₂O₄/C was then loaded in a corundum crucible and placed in a muffle. The sample was heated to 400 °C in air at a ramping rate of 5 °C min⁻¹ and kept at 400 °C for 4 h. After the sample had cooled naturally to room temperature, SnO₂/C was obtained.

Synthesis of Cu/C was performed using a method modified from ref. 52: 0.196 g Cu(acac)₂ and 2.90 g of TOPO were dissolved in 35 ml of oleylamine, and 100 mg of carbon black added to this solution. The mixture was stirred at 600 r.p.m. for 10 min under a N₂ atmosphere. Next, 22.5 mg of BTB was dissolved in 2.5 ml of oleylamine and this solution was rapidly injected into the above-mentioned mixture. The resulting mixture was stirred at 25 °C under N₂ for 1 h, then 15 ml of ethanol was added. A black powder was separated from the reaction mixture by centrifugation, washed twice with toluene/ethanol solvent (v:v 1:1) and dried at 70 °C. Finally, the powder was heated at 185 °C in air overnight to give the final sample of Au/C. Supplementary Fig. 1c,d shows the HAADF–STEM image and PXRD pattern of SnO₂/C.

Synthesis of Au/C was performed using a method modified from ref. 51: 50 mg of HAuCl₄·H₂O, 125 μl of toluene and 30 mg of carbon black were added to 10 ml of oleylamine, and the mixture was stirred for 600 min. The reaction was maintained at 200 °C for 1 h and then cooled naturally to room temperature. Next, 40 ml of ethanol was added to the mixture and a black solid separated from the reaction mixture by centrifugation. This crude product was washed twice with n-hexane/ethanol solvent (v:v 1:1) and dried under vacuum at room temperature to give the final sample of Au/C. Cu/C was stored in a glovebox with N₂ to prevent oxidation of Cu. Supplementary Fig. 1e,f shows the HAADF–STEM image and PXRD pattern of Cu/C.

Characterizations. PXRD patterns were collected on an Aeris diffractometer (Panalytical) with monochromatic Cu Kα radiation. HAADF–STEM images were collected on a FEI Talos transmission electron microscope (TEM) operated at 200 kV with a high-brightness XFEG gun. X-ray photoelectron spectroscopy (XPS) characterizations were performed on a PHI5000 VersaProbe II XPS system from Physical Electronics (PHI), with a detection limit of 1 at%. Monochromatic X-rays were generated by an Al Kα source (1,486.7 eV). ICP–MS results were obtained from a NexION 350 unit (PerkinElmer).

Electrochemical measurements. All electrochemical measurements were carried out on a Gamry Reference 3000 electrochemical instrument. Current-interrupt iR compensation was used, unless otherwise noted. An Ag/AgCl saturated KCl electrode was used as the reference electrode. The potential of the working electrode versus SHE was calculated according to:

\[
E \text{ (versus SHE)} = E \text{ (versus Ag/AgCl)} + 0.197 \text{ V} \tag{1}
\]

Potential versus RHE was calculated according to:

\[
E \text{ (versus RHE)} = E \text{ (versus SHE)} + 0.0592 \text{ V} \times pH \tag{2}
\]

Electrolyte pH values were measured by pH meter (HI 991002, Hanna instruments).
The performance of CO2 reduction was tested in a home-made flow cell, shown in Supplementary Fig. 2. The left part, made of stainless steel, was used as the current collector of the working electrode and the gas chamber of CO2 stream behind it. The two parallel perforated metal tube (PEEK) parts were the chambers holding electrolyte solutions for the working and counter electrodes. The window for the effective area was set to 1 × 1 cm² and the thickness of each chamber was 1 cm. Each chamber has an inlet and an outlet for electrolytes; the reference electrode was inserted in the chamber of the working electrode. A Nafion 211 membrane was used to separate the counter electrode from the chamber of the working electrode. Titanium plate with a window (1 × 3 cm²) was used as the current collector for the counter electrode. Polytetrafluoroethylene films were used as gaskets. All parts were pressed together by four sets of screws and nuts.

To prepare the catalyst ink of SnO2/C, Au/Cu and Cu/C, 20 mL of catalyst, 4 mL of ethanol and 200 μL of Nafion dispersion (5%, ABCR) were mixed and sonicated for 30 min. Tech carbon cloth with a micropore layer on one side (WS1S1009) was used as the GDE. The carbon cloth was cut into squares (1.5 × 1.5 cm²) as the working electrodes. Iridium (IV) oxide (IrO2, 99%, ABCR) sprayed on ELAT hydrophilic carbon cloth was used as the catalyst for the counter electrode. The ink of IrO2 contained 20 mg of IrO2, 4 mL of ethanol and 40 μL of Nafion dispersion. When we tested Cu/C in 0.1 M H2SO4 + 0.4 M K2SO4 and 0.1 M H2SO4 + 0.4 M CaSO4, half of the electrode was covered by Kapton tape and its effective area was 0.5 cm². The effective electrode area in other cases was 1 cm².

Potential dependent CO2 reduction properties were tested in the three-electrode flow cell using the chronoamperometry method. The volume of both catholyte and anolyte solutions was 14 ml, and both were circulated at a flow rate of 5 ml min⁻¹. The flow rate was controlled by a peristaltic pump (REGLO Digital MS-4/8, Ismatec). Humidified CO2 was connected to the inlet of the gas chamber, with the outlet connected to gas chromatography (GC) for online detection of gas-phase products. The flow of CO2 was controlled by a mass flow controller (Red-y smart outlet connected to gas chromatography (GC) for online detection of gas-phase products. The flow rate was controlled by a peristaltic pump (REGLO Digital MS-4/8, Ismatec). Humidified CO2 was connected to the inlet of the gas chamber, with the outlet connected to gas chromatography (GC) for online detection of gas-phase products. The flow of CO2 was controlled by a mass flow controller (Red-y smart

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Author contributions
J.G. performed the majority of synthesis, characterization and electrochemical tests. S.L. performed simulations. W.N. performed Au RDE tests. W.R. performed electrochemical tests in near-neutral and alkaline media. J.G., S.L., S.H. and X.H. analysed data. J.G. and X.H. wrote the paper, with input from all other co-authors. S.H. and X.H. directed the research.

Competing interests
The authors declare no competing interests.

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