Unveiling hydrocerussite as an electrochemically stable active phase for efficient carbon dioxide electroreduction to formate

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For most metal-containing CO2 reduction reaction (CO2RR) electrocatalysts, the unavoidable self-reduction to zero-valence metal will promote hydrogen evolution, hence lowering the CO2RR selectivity. Thus it is challenging to design a stable phase with resistance to electrochemical self-reduction as well as high CO2RR activity. Herein, we report a scenario to develop hydrocerussite as a stable and active electrocatalyst via in situ conversion of a complex precursor, tannin-lead(II) (TA-Pb) complex. A comprehensive characterization reveals the in situ transformation of TA-Pb to cerussite (PbCO3), and sequentially to hydrocerussite (Pb3(CO3)2(OH)2), which finally serves as a stable and active phase under CO2RR condition. Both experiments and theoretical calculations confirm the high activity and selectivity over hydrocerussite. This work not only offers a new approach of enhancing the selectivity in CO2RR by suppressing the self-reduction of electrode materials, but also provides a strategy for studying the reaction mechanism and active phases of electrocatalysts.
Electrocatalysis has emerged as a promising technology for renewable energy conversion and storage,[1–3], where a key factor is the development of electrocatalysts with higher activity, better selectivity, longer stability, and lower cost.[4–6]. While the activity and stability are the two ends of a seesaw, the high activity of electrocatalysts often cannot be sustained for a long time, mainly because of the undesirable reconstruction of electrode surfaces. With the development of in situ characterization techniques, researchers have observed the structural transformation of electrocatalysts during the electrolysis.[7]. Many efforts have been devoted to exploring the real active species derived from the pre-catalysts. For instance, metal oxyhydroxides, derived from the oxidative transformation of metal chalcogenides and pnictides, are found to be the active species for the oxygen evolution reaction (OER), promoting the rapid developments of highly efficient electrocatalytic materials for OER.[8–10]. Thus the exploration of the real active species is of great importance for the rational design and synthesis of advanced electrocatalysts with high intrinsic activity.

Electrochemical CO₂ reduction reaction (CO₂RR) can convert the greenhouse gas (CO₂) to various value-added chemicals.[11–16], while the competing hydrogen evolution reaction (HER) is usually more favorable on many metallic electrodes. Although many high-valence metal electrocatalysts are proved to be reduced to zero-valence metal at CO₂RR condition, such as BiO,[17] PbO₂,[18] SnO₂,[19] CuO,[20] In₂O₃,[21] it was found the residual metastable metal oxides are tightly correlated with the high selectivity towards CO₂RR.[22–24]. However, with the self-reduction occurring, HER becomes more and more dominant, leading to a diminished CO₂RR efficiency. Besides, many complex electrocatalysts also undergo unavoidable dissociation and self-reduction under cathodic working conditions. For example, a Ni(II) benzenedithiol complex was revealed to be completely transformed to Ni nanosheets under cathodic conditions.[25]. A Cu(II) phthalocyanine complex undergoes reversible conversion to metallic Cu clusters, which acts as the active species in CO₂RR.[26]. The self-reduction of electrocatalysts and the desirable CO₂RR are actually competitive processes. To achieve high selectivity, developing electrocatalysts with predominant CO₂RR over self-reduction is highly desirable.

Herein, we report a scenario to make effective use of the electrochemical structure evolution of a complex pre-catalyst, tannin–lead(II) (denoted as TA–Pb), toward high formate selectivity in CO₂RR. The TA–Pb pre-catalyst performs a formate Faradaic efficiency (FE) of up to 96.4 ± 0.9%. Through a set of comprehensive characterizations, it is identified that TA–Pb is transformed to cerussite (PbCO₃, denoted as PCO) at first, then sequentially to hydrocerussite (Pb₂(CO₃)₂(OH)₂, denoted as PCOH) at steady state, which essentially serves as the active phase for highly selective formate production. In addition, we also synthesize pure cerussite nanoparticles and hydrocerussite nanoplates to confirm the transformation mechanism and the key role of hydrocerussite in CO₂RR, respectively. The density functional theory (DFT) calculations also reveal the high formate selectivity, which can be attributed to the appropriate binding strength with HCOO⁻ on hydrocerussite. All the results unveil hydrocerussite as a highly selective and stable phase for formate production in CO₂RR.

**Results**

**Electrochemical performances and transformation of TA-Pb.** The tannin–lead(II) (TA–Pb) complex film is prepared by simply mixing Pb(II) and tannin aqueous solution in the presence of carbon fiber paper (CP) as the substrate (Fig. 1a). By examining with a high-resolution transmission electron microscope (HRTEM), the coordination of TA and Pb(II) forms a layer of amorphous film contacting closely to the substrate with the thickness of ~20 nm for single-layer TA–Pb with CP as the substrate (inset in Fig. 1a, Supplementary Fig. 1 and Supplementary Note 1). The extended X-ray absorption fine structure (EXAFS) exhibits clear coordination of Pb–O and Pb–C for a five-membered ring in a chelate ligand (Fig. 1b)[27], suggesting the 6-coordinated Pb(II) ions as reported before[28].

The electrochemical activity was tested in a standard three-electrode system with 0.5 M NaHCO₃ as the electrolyte (Supplementary Fig. 2). Before CO₂RR tests, all the samples were pre-treated under ~0.92 V for 30 min to reach the steady state. Liquid products were detected by nuclear magnetic resonance (NMR), while the gaseous ones were detected by gas chromatography (GC). The products in CO₂RR with single-layer TA–Pb as pre-catalyst are formate, CO₂, and H₂, which is in accordance with other reported Pb-based electrocatalysts[29–31]. And ~0.92 V vs. reversible hydrogen electrode (RHE) is the optimum potential to achieve the highest formate FE (Supplementary Fig. 3 and Supplementary Note 2). The formate FE can be further improved by increasing the layers of the TA–Pb, and the 3-layer TA–Pb complex shows the highest formate FE of 96.4 ± 0.9% at the optimum potential of ~0.92 V with a small amount of H₂,atable CO₂RR measurements (Fig. 2d).
The X-ray photoelectron spectra (XPS) of TA-Pb clearly show the organic functional groups of tannin molecules in the C 1s and O 1s spectra (Fig. 2e and Supplementary Fig. 7). However, these peaks of organic functional groups completely disappear in the t-PCO, suggesting the decomposition of the TA-Pb complex in stage I. The symmetric O 1s peak of t-PCO at 532.7 eV suggests the O element only exists in the form of CO\textsubscript{3}\textsuperscript{2−}. However, in t-PCOH, the appearance of a new peak represented OH\textsuperscript{−} confirms the formation of hydrocerussite. Similarly, the symmetric peak at 138.8 eV is attributed to PbCO\textsubscript{3} in the Pb 4f 7/2 spectra of t-PCO (Fig. 2f), while the peak at 138.3 eV in t-PCOH represents the formation of Pb-OH\textsuperscript{3−}. It should be pointed out that no Pb(0) is found throughout the whole process. And the cyclic voltammetry (CV) curve of t-PCOH shows no redox peak in the tested range, firmly verifying the stability of hydrocerussite in CO\textsubscript{2}RR (Supplementary Fig. 8).

The transformation of the TA-Pb complex was further investigated by Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The time-dependent in situ Raman spectra are shown in Fig. 2g. It is clearly shown that the fluorescent intensity from the ligand tannin ascends at first and then descends with the time prolonging (Supplementary Fig. 9,10), indicating the TA-Pb complex undergoes a part-to-whole dissociation. A small peak at 1065 cm\textsuperscript{−1} appears after electrolysis for 210s, which is attributed to C–O symmetric stretching vibration of CO\textsubscript{3}\textsuperscript{2−} 35, indicating the formation of t-
hydrocerussite. As shown in Fig. 2h, with the applied potential decreasing, the intensity of bands at ~1360 cm\(^{-1}\) transforms into cerussite and hydrocerussite sequentially, in total reflecting the phase change from cerussite to hydrocerussite (Supplementary Fig. 13). No obvious band associating with CO\(^2\)\(^{-}\) appears as early as the ascending process of fluorescence, which means that the dissociation of TA-Pb and the formation of t-PCO are accompanying rather than separate and sequential. Moreover, in ex situ FTIR spectra, the disappearance of the complex peaks again confirms the dissociation of the complex (Supplementary Fig. 11). In situ attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was employed to investigate the reaction path of hydrocerussite. As shown in Fig. 2h, with the applied potential decreasing, the intensity of bands at ~1360 cm\(^{-1}\) gradually increases (Supplementary Fig. 12 and Supplementary Note 3), which can be associated with the vibration of O–C–O in the two-oxygen bridge-bonded formate species (*HCOO\(^3\))\(^{-}\), confirming the *HCOO pathway of hydrocerussite (Supplementary Fig. 13). No obvious band associating with CO\(^4\)\(^+\) can be found in the region of 1900–2100 cm\(^{-1}\), indicating that the formation of CO on hydrocerussite is almost inhibited\(^3\), which is consistent with the above experimental FE results. All the above results confirm that the TA-Pb complex electrochemically dissociates and transforms into cerussite and hydrocerussite sequentially, in which the valence state of Pb remains +2 during the whole electrolysis, suggesting hydrocerussite to be the active species for electrochemical CO\(_2\)RR via the pathway of *HCOO as the intermediate.

Performances of as-prepared cerussite and hydrocerussite. To further investigate the transformation of cerussite to hydrocerussite, we prepared cerussite nanoparticles (denoted as c-PCO) and studied their behavior under the same conditions of CO\(_2\)RR. The TEM image of the as-prepared c-PCO shows the irregular nanoparticles (Fig. 3a and Supplementary Fig. 14a). After tested at −0.92 V in the presence of CO\(_2\) for 30 min, it is found that the c-PCO nanoparticles completely transform to monocristalline hexagonal nanosheets (Fig. 3b and Supplementary Fig. 14b). The corresponding selected area electron diffraction (SAED) pattern shows the dominant exposed facet of (0001) (inset in Fig. 3b). XRD pattern of the hexagonal nanosheets matches well with hexagonal hydrocerussite without any impurity (Fig. 3c), and the nanosheets is named as c-PCOH. XPS and ex situ Raman spectra also confirm the phase change from cerussite to hydrocerussite (Supplementary Figs. 15, 16). By studying the transformation process, it is found that the c-PCO nanoparticles first convert to cerussite nanoparticles via an Ostwald ripening process\(^3\), then to hexagonal hydrocerussite nanosheets through the selective etching of CO\(_2\) and the insertion of OH\(^–\) (see more details in Supplementary Figs. 17–20 and Supplementary Notes 4–7).

The hydrocerussite nanoparticles (shorted as h-PCOH) were also fabricated to estimate their CO\(_2\)RR performance. The SEM image of the as-prepared hydrocerussite nanoparticles performs quasi-hexagonal nanowires with the diameter of several microns (Fig. 3d). After the CO\(_2\)RR measurements, all the results of SEM images (Supplementary Fig. 21), XRD patterns (Fig. 3e), XPS...
spectra (Supplementary Fig. 22) and ex situ Raman spectra (Supplementary Fig. 23) indicate that the morphology, structure, and composition of the h-PCOH remain unchanged, confirming that hydrocerussite is stable and the active species for CO$_2$RR. When compared the CO$_2$RR performances of h-PCOH with t-PCOH, it is found that h-PCOH generates the similar products of dominant formate, a small amount of H$_2$, and trace CO (Supplementary Fig. 24a). Specifically, h-PCOH performs the formate FE of 90.1 ± 0.8% at −0.92 V with the stability of over 10 h (Fig. 3f and S24b). The slightly lower FE of h-PCOH may originate from the poor coverage of in situ formed t-PCOH. Moreover, limited by the high mass loading of h-PCOH (4.01 mg cm$^{-2}$ for Pb), its TOF is calculated to be only 6.8 × 10$^{-4}$ s$^{-1}$, which is 80 times lower than that of t-PCOH, further indicating a high catalytic efficiency of the complex-derived hydrocerussite.

**DFT calculations.** To understand the chemical origin of high formate selectivity in CO$_2$RR over hydrocerussite, DFT calculations were performed. The hydrocerussite models are structured, and the optimized lattice parameters of 5.28 × 5.30 × 23.68 Å are in good agreement with the experiments (Supplementary Fig. 25a)\(^\text{41}\). As observed above, hydrocerussite prefers to expose the (0001) surface. In this way, there are three possible terminations of hydrocerussite (0001), denoted with Layer A, B, and C, as shown in Supplementary Fig. 25b. The B-termination is thermodynamically most stable with the surface energies ($E_s$) of −0.24 eV nm$^{-2}$ relative to A ($E_s = −0.04$ eV nm$^{-2}$) and C ($E_s = 2.64$ eV nm$^{-2}$). Besides, since hydrocerussite is in situ produced from the complex pre-catalyst, two kinds of vacancies (CO$_3^{2−}$ or OH$^−$ removal) are considered herein. As a consequence, six possible active sites on hydrocerussite are examined to compared with the reference metallic Pb(111), including perfect A, B, and C terminations, denoted as A-p, B-p, and C-p, and defected A, B, and C ones, denoted as A-d, B-d, and C-d (Supplementary Fig. 25b). Then we calculated the adsorption energies of all the possible intermediates in CO$_2$RR to producing H$_2$, CO, and formate, respectively. According to the result of in situ ATR-FTIR spectra, *HCOO adsorption energy is chosen as the descriptor to establish the correlation between different active sites and adsorbates, as shown in Supplementary Fig. 26.

The reaction free energies ($\Delta G$) of all possible elementary steps are calculated and plotted versus the adsorption free energy of *HCOO [G$_{ad}$(*HCOO)] (Fig. 4a), where the solid lines represent the $\Delta G$-determining steps of HCOOH, CO, and H$_2$ production. The HCOOH production can follow two paths via either *COOH or *HCOO, crossed at about −1.3 eV. On A-p, B-p, and C-p, the $\Delta G$ for HCOOH production is unfavored (about 2.0 eV), which means at least −2.0 V is needed to produce HCOOH on the perfect surfaces. On the contrary, the $\Delta G$-determining step on defected surfaces is smaller than 0.5 eV. On A-d and C-d, HER is more favorable than HCOOH and CO. However, HCOOH is most preferred over B-d via the *HCOO pathway, and the product selectivity preference obeys the order of HCOOH > H$_2$ > CO, which is exactly consistent with our experiments. Besides, B-d is the most stable termination and should be the dominant site of hydrocerussite. In comparison, the HCOOH activity and selectivity on Pb(111) are lower than the B-d of hydrocerussite, in agreement with the low HCOOH FE of Pb foil about 40% (Supplementary Fig. 4b). The explicit reaction free energy diagrams under 0 V vs. RHE on B-d of hydrocerussite and Pb (111) are displayed in Supplementary Fig. 27. On B-d, HCOOH is more favorable than H$_2$ and CO in thermodynamics due to the stronger adsorption of *HCOO than *H and *COOH by 0.61 and 1.24 eV, respectively. On Pb(111), although *HCOO is also more preferred than *H, their small energy difference of only 0.17 eV together with the higher concentration of proton than
CO₂ in an electrolyte, can actually reverse the preference of HCOOH and H₂. Figure 4b is the two-dimensional map of activity and selectivity of the sites of hydrocerussite, where \( G_{ad}(*\text{HCOOH}) \) is introduced as another dimension and varying independently with \( G_{ad}(*\text{HCOO}) \). The map contains four regions, which represent different products. Only B-d shows an obvious HCOOH preference and activity, further confirming B-d as the active site.

To analyze the effect of applied potential on CO₂RR into HCOOH, the potential-dependent barriers and reaction energies under different experimental potentials are calculated (Fig. 4c). At \(-0.82\) V vs. RHE, the elementary reactions \( \text{CO}_2(g) + (\text{H}^+ + e^-) \rightarrow *\text{HCOO} \) and \( *\text{HCOO} + (\text{H}^+ + e^-) \rightarrow \text{HCOOH} \) are both exothermic, with a barrier of 0.82 and 0.57 eV, respectively. In kinetics, CO₂ protonation is still more difficult than the formation of HCOOH and can be considered as the rate-determining step (RDS). As the potential decreases, the activation energy of CO₂ protonation becomes lower gradually, which will increase the reaction rate and HCOOH partial current density in the experiment according to the transition state theory. Therefore, we further perform a microkinetic simulation to calculate the charge transfer rate of a single active site \( (k) \) at different applied potentials. Figure 4d shows the experimental HCOOH partial current density \( (j_{\text{exp}}) \) plotted versus our theoretical charge transfer rate \( k \). A nice linear correlation has been established, confirming our calculations and analysis above regarding the active site and reaction mechanism.

Stability of hydrocerussite. In the whole electrolysis, we attribute the high formate FE and electrochemical stability of hydrocerussite to its dominant CO₂RR. In this sense, both the electrochemical reduction from hydrocerussite to metal Pb and the competing HER are suppressed. It can be evidenced by the comparison of linear scan voltammetry (LSV) curves in Ar and CO₂ (Supplementary Fig. 28). All the redox peaks under Ar completely disappear in CO₂, suggesting the inhibition of Pb reduction under CO₂ bubbling. Another controlled experiment is to test the stability of h-PCOH at \(-0.92\) V under Ar for 5 h. Different from the results under CO₂, the FE of hydrogen dramatically rises to over 80%, and the formate FE decreases to around 5% (Fig. 5a and Supplementary Fig. 29). Besides, with the electrolysis time prolonging, the hydrogen FE becomes larger and larger, while the formate FE goes smaller. And no CO can be detected under this condition. It should be noted that the total FE of all the products is obviously smaller than 100%, suggesting that parts of the provided electrons are used to reduce the hydrocerussite. This conjecture can be further confirmed by the XRD pattern of this sample after electrolysis for 5 h. As shown in Fig. 5b, the appearance of XRD peaks from PbO and metal Pb clearly demonstrates the decomposition and reduction of hydrocerussite under this condition, which is in accordance with the Pourbaix diagram of lead in the presence of CO₂. In addition, when the reduced hydrocerussite is tested in CO₂ again, obvious decay of formate FE (~60%) can be found just as our expectation (Fig. 5c). From the above results, it is sure that the
presence of CO₂ is of great importance to maintain the stability of hydrocerussite under cathodic conditions. Without CO₂, hydrocerussite is gradually decomposed and finally reduced to metal Pb, accompanying with enhanced hydrogen evolution and weakened selectivity of formate production (Fig. 5d). In other words, the preference of CO₂RR on hydrocerussite can effectively suppress the self-reduction of the electrocatalyst and the accompanying enhanced HER.

Discussion

In summary, we have revealed the dynamic change of TA–Pb complex film as a model pre-catalyst under the conditions of CO₂RR, and finally unveiled hydrocerussite as the new active species for formate generation. The rapid transformation of TA–Pb to cerussite (t-PCO) and subsequent conversion to hydrocerussite (t-PCOH) are revealed during the electrochemical CO₂RR conditions. t-PCOH is found to be the active species to produce formate with an optimum FE of 96.4 ± 0.9%. In addition, cerussite nanoparticles are prepared to verify the phase transformation to hydrocerussite. The hydrocerussite nanoplates are also directly fabricated, and perform similar high formate FE and self-reduction properties compared with t-PCO. The high formate FE of hydrocerussite originates from its dominance of CO₂RR, thus the reduction of the electrocatalyst itself and consequent HER is blocked. This work not only opens a facile avenue to improve the CO₂RR selectivity by suppressing the reduction of the electrocatalysts, but also establishes a guideline for fundamentally understanding the transformation process and active species of metal-complex catalytic materials for cathodic reactions.

Methods

Depositing TA–Pb complex on substrates. For a typical synthesis of a single-layer TA–Pb complex, a piece of the substrate was put in a clean and empty 20 mL vessel with the addition of 10 mL 10 mM Pb(NO₃)₂. After sufficient adsorption for 15 min, 10 mL 9 mg mL⁻¹ tannic acid (TA) solution was quickly added. 2 M NaOH was then added to adjust pH to ~7. Then the vessel was gently shaken and stood at room temperature without disturbance for 6 h. At last, the product was washed with water and dried naturally. To prepare multiple-layer TA–Pb, this procedure was repeated for suitable times. For instance, if this procedure was repeated for three times, the as-prepared products are named as the 3-layer TA–Pb. For environmental concerns, the Pb-containing residual reaction solution was collected and stored in a dedicated container. CP was used as the substrate in electrochemical measurements. Before deposition, CP was cut into rectangular pieces with a size of 1 × 3 cm² and immersed in acetone and water for 15 min in sequence. Rutile TiO₂ nanorod arrays supporting on F-doped tin oxide (FTO) glass were used as the substrate for TEM observation and ex situ FTIR spectroscopy. FTO glass was cut into a rectangular shape with a size of 1 × 2.5 cm², and sonicated in diluted HCl, acetone, and water for 15 min in sequence. To prepare rutile TiO₂ nanorod arrays, 15 mL water, 15 mL concentrated HCl, and 0.5 mL tetrabutyl titanate were added to a Teflon-lined stainless-steel autoclave and stirred for 15 min. A piece of clean FTO glass was put into the autoclave with the conductive side facing down. Then the autoclave was sealed and treated at 180 °C for 1 h. After the reactor cooled down naturally, the FTO with the white product was washed with water and alcohol, respectively, and dried naturally. Then the product was calcined in air at 500 °C for 2 h with the heating rate of 5 °C min⁻¹ to finally obtain the rutile TiO₂ nanorod arrays.

Synthesis of c-PCO nanoparticles. c-PCO nanoparticles were prepared by a simple precipitation method. Briefly, 5 mL 1.2 M Na₂CO₃, and 5 mL 1.2 M Pb (OAc)₃·3H₂O were mixed and stirred for 5 min. Then 10 mL water was added and stirred for another 1 h at room temperature. The white product was collected by centrifugation and washed with water and ethanol several times, then dried in a vacuum oven for 6 h.

Synthesis of h-PCOH nanoparticles. 2.50 g Pb(NO₃)₂, 2.25 g urea, 0.073 g polyethylene glycol with the molecular weight of 2000 (PEG-2000), and 200 mL water were added in a flask. The flask was vigorously stirred and refluxed at 105 °C for 5 h. The product was collected by centrifugation and washed with water and ethanol several times, then dried in a vacuum oven for 6 h.
Characterization. The transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were carried out with a JEOl JEM-2100F microscope. The scanning electron microscopy images were taken with a Hitachi S-4800 microscope. The X-ray absorption fine structure (XAFS) were performed at the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF). All the XAFS spectra were analyzed with the ATHENA software package. The k-weighting was set to 1 for the Fourier transforms. Fourier transforms of (k) were performed in the k-range of 0.2 Å⁻¹ with the Hanning window function. All the EXAFS spectra were without phase correction. The gaseous products of electrochemical CO₂RR were detected by a GC (Shimadzu GC-2010). All the formate was measured by a 400 MHz NMR spectrometer (Bruker AVANCE III HD). All the potentials were referred to the normal hydrogen electrode (NHE). A Gaussian smearing with a width of 0.2 eV was used. All the total energy calculations were performed at 0.05 eV/Å. The hydrocerussite (001) surface with a vacuum of 20 Å was used to model experimental hydrocerussite samples. Six layers were contained in the slab, with the top three relaxed and the rest fixed. A (4 x 4) P6(11) slab with 4 layers was used to model Pb foil, where the top two were allowed to be relaxed. To calculate the protonation barriers, a layer of H₂O with a density of ~1 g cm⁻² was introduced upon the surface of catalysts.

Reaction phase diagram. All the adsorption free energies of intermediates were first calculated, referenced to CO₂(g), H₂(g), and H₂O(g). All the adsorption free energies could be correlated with that of HCOO, in the format of $G_{\text{ads}}(X) = a \times G_{\text{ads}}(\text{HCOO}) + b$, where $G_{\text{ads}}(X)$ was the adsorption free energy of intermediate X and $G_{\text{ads}}(\text{HCOO})$ was that of HCOO, used as descriptor herein. Then, the reaction free energy ($\Delta G$) of all involved elementary steps, such as *COOH + (H⁺ + e⁻) → HCOO⁻, can be calculated by $\Delta G = G(\text{HCOO}) - G(\text{H³⁺ + e⁻}) - G_{\text{ads}}(\text{COOH})$, where G(\text{HCOO}) was the chemical potential of formic acid and G(\text{H³⁺ + e⁻}) was referred to 1/2 H₂ under $U=0$ V vs. RHE, respectively, referenced to the same criterion with adsorption energies. Obviously, G(\text{HCOO}) and G(\text{H⁺ + e⁻}) were constants, and $G_{\text{ads}}(\text{COOH})$ was linearly correlated with $G_{\text{ads}}(\text{HCOO})$. Therefore, the reaction free energy as a linear function of $G_{\text{ads}}(\text{HCOO})$ could be obtained (Fig. 4a), which was defined as the reaction phase diagram in our previous report. Besides, a two-dimensional map of activity and selectivity (Fig. 4b) could be obtained by making $G_{\text{ads}}(\text{COOH})$ vary independently with $G_{\text{ads}}(\text{HCOO})$ and analytically calculating the corresponding reaction free energy at every pair of $G_{\text{ads}}(\text{COOH})$ and $G_{\text{ads}}(\text{HCOO})$, which can give a more accurate description on the activity and selectivity. Potential-dependent barrier and reaction energy. The potential effect on thermodynamic reaction free energy was considered by changing the chemical potential of (H⁺ + e⁻) by -\text{eV}, as suggested in the computational hydrogen electrode approximation. The potential-dependent kinetic barriers of electrochemical reaction (\text{A} + \text{H⁺ + e⁻} + 4\text{AH}) were calculated by using an equivalent analogous non-electrochemical reaction (\text{A} + \text{H⁺ + e⁻}) combined with Marcus theory, an effective method developed by Janik et al.

Microkinetics simulations. The rate of CO₂ protonation is considered as the total reaction rate since it is the RDS. The rate constant (a) was determined by:

$$a = A e^{-\frac{E_a}{RT}}$$

(3)

where $g_a$ is the activation free energy, $\xi$ is the Boltzmann constant and $T$ is temperature. $A$ is the prefactor and calculated by:

$$A = \frac{k_B T Q_\text{f}}{h^\frac{1}{2}}$$

(4)

where $h$ is the Planck constant; $Q_f$ and $Q_r$ refer the partition functions of the transition and initial states, respectively. $A$ was approximated to be $10^{13}$ s⁻¹ for surface reactions in this work. The forward rate of CO₂ protonation [CO₂(g) + (H⁺ + e⁻) + $\epsilon$ → HCOO⁻] was calculated by:

$$r = a c(\text{CO}_2) c(\text{H}^\text{+}) \theta^4$$

(5)

where $c(\text{CO}_2)$, $c(\text{H}^\text{+})$ and $\theta^4$ are the concentration of CO₂ and proton in electrolyte and coverage of the free active site, respectively. The charge transfer rate on a single active site (k) is:

$$k = rz^2F$$

(7)

where $z$ is the total number of electrons transferred in the overall reaction, for $F = 1.6 \times 10^{-19}$. In principle, $c(\text{CO}_2)$, $c(\text{H}^\text{+})$ and $\theta^4$ are constant at different potentials, hence the term $|z(\text{CO}_2)c(\text{H}^\text{+})\theta^4|$ is assumed to be 1 in this study. By this approximation, the charge transfer rate $k$ under different potentials can be estimated.

Data availability. The source data underlying Figs. 1–5 are provided as a Source Data file. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
B.Z. conceived and directed the project. B.Z. and Y.S. designed the experiments. Y.S. and Y.J. carried out the experiments. J.L. and J.X. performed and analyzed the DFT calculations. Y.L. carried out the in situ Raman spectroscopy. Y.S. and Y.L. conducted the in situ ATR-FTIR spectroscopy. Y.S. and J.L. wrote the paper. Y.Y., J.X., and B.Z. revised the paper. All authors discussed the results and commented on the paper.

Competing interests
The authors declare no competing interests.
