Efficient electroreduction of carbon dioxide to multcarbon products in aqueous solution is of great importance and challenging. Unfortunately, the low efficiency of the production of C₂ products limits implementation at scale. Here, we report reduction of carbon dioxide to C₂ products (acetic acid and ethanol) over a 3D dendritic copper-cuprous oxide composite fabricated by in situ reduction of an electrodeposited copper complex. In potassium chloride aqueous electrolyte, the applied potential was as low as −0.4 V vs reversible hydrogen electrode, the overpotential is only 0.53 V (for acetic acid) and 0.48 V (for ethanol) with high C₂ Faradaic efficiency of 80% and a current density of 11.5 mA cm⁻². The outstanding performance of the electrode for producing the C₂ products results mainly from near zero contacting resistance between the electrocatalysts and copper substrate, abundant exposed active sites in the 3D dendritic structure and suitable copper(I)/copper(0) ratio of the electrocatalysts.
Carbon dioxide (CO₂) is an abundant C₁ resource. As a cheap resource, it is a suitable electrochemical reaction medium and hydrogen source. In the quest for developing techniques for CO₂ utilization, electrochemical reduction offers a potential route to economical conversion of CO₂ and water into value-added chemicals and fuels. Until now, extensive efforts have been devoted to the development of catalysts for electrocatalytic reduction of CO₂ in water. Despite the notable progress, it is still highly desirable to develop efficient electrocatalysts to steer the reaction pathways toward higher value products and reduce reaction overpotential.

Products with two or more carbons (C₂₊ product), such as acetic acid and ethanol, are very useful chemicals or fuels. Efficient electrochemical reduction of CO₂ to C₂₊ products is of great importance. Literature survey shows that Cu-based catalysts are the most efficient material for electrocatalytic reduction of CO₂, and Cu is a key component for forming multichain products. On Cu-derived oxide electrocatalysts, C₂ or C₂₊ products could be formed with Faradaic efficiency (FE) of ~70%. Cu nanoparticles, Cu nanocubes, and Cu nanocatalysts show selectivity up to 60% for transformation of CO₂ to C₂₊ products. Plasma-activated Cu or Cu nanocube catalysts exhibit high FE to ethylene (60%) or ethylene/ethanol (45%/22%). Recent study indicates that the FE of ethylene on Boron-modified Cu-based electrocatalysts could reach 79%. Cu gas diffusion electrode was found to be efficient for CO₂ reduction to ethylene with a FE of 70% at high current density. Besides, Cu₃S–Cu core–shell–vacancy catalyst could boost CO₂ reduction to C₂ product with a FE of 32% at −0.95 V vs RHE. Metal-free catalysts, such as nitrogen-doped mesoporous carbon, are also used as efficient catalysts for CO₂ reduction to ethanol (44%). It was also demonstrated that bimetallic catalysts have improved activity and selectivity for CO₂ reduction to hydrocarbons. Comparing with production of C₁ chemicals or fuels, the reports on electrochemical reduction of CO₂ to C₂₊ products is very limited. Especially, exploration of electrochemical systems to mediate multiple proton transfers with low overpotential is still a challenge for CO₂ reduction to C₂₊ products because the C–C coupling is difficult. It is both scientifically and practically appealing to explore efficient electrolysis systems for CO₂ reduction to C₂₊ product under heterogeneous catalysis conditions in aqueous media.

Designing robust electrocatalysts is very important for efficient CO₂ reduction. Previous reports indicate that heterogeneous metal-based catalysts derived from molecular complexes can be favorable electrocatalysts. The catalytic properties of the catalysts can be tailored by adjusting and regulating the composition of the complexes, and they exhibit excellent catalytic activity toward water splitting and oxygen reduction. So far, it is also an approach toward the fabrication of electrocatalysts, such as additive controlled electrodeposited Cu catalysts for CO₂ reduction. However, as a precursor, the complex was generally prepared ex situ or used as a homogeneous additive in decomposition of the new structure in CO₂ electroreduction. Electrodeposition is a very useful technique that requires simple equipment with precise control of the growth processes, purity, structures, and morphologies of the deposits. The deposits are well suited for many applications, such as fuel cells, batteries, and sensors. This method has also been used to prepare electrocatalysts for CO₂ reduction. For example, electrodeposited In or Bi electrode can promote CO₂ reduction to CO with high selectivity. Cu₂O prepared by electrodeposition method can control the catalytic selectivity of CO₂ to hydrocarbons. In situ deposited Cu nanodendrites as gas diffusion layer can reach high FE for C₂ products. In general, it is easy to produce two-dimensional (2D) materials using the direct electrodeposition method. While an electrodeposition process can also create a 3D material, it is difficult to control the microstructure with desired features. Therefore, it is very interesting to explore more practical methods for obtaining stable 3D structures with desirable structures for CO₂ electrocatalytic reduction.

The immobilization of molecular catalysts onto surfaces provides some obvious advantages over heterogeneous catalysts, such as controllable 3D structure, fast electron transfer rate, etc. Recently, an electrosynthesis method has been used to prepare metal organic complex films supported on conducting substrates. This route constructs the metal organic complex films by assembling the reduced organic linkers and oxidized metal ions on a conductive substrate. The synthetic method is currently emerging as a promising approach for producing films of specific configurations, particularly in sensors and electric devices.

Herein, we report a more direct and facile method to electrodeposi a high-surface area Cu-complex film onto conductive substrates. A 3D dendritic Cu–Cu₂O composite catalyst (denoted as Cu–Cu₂O/Cu) can be obtained via in situ growth and decomposition of the corresponding Cu-complex film. By using the Cu-complex electrodes as precursors and templates, the Cu–Cu₂O/Cu electrode shows unique characteristics, such as dendritic 3D structure as well as near zero contact resistance between the catalyst and the substrate. The in situ synthesized electrode has outstanding catalytic performance for CO₂ reduction to C₂ products in KCl aqueous electrolyte. At −0.4 V vs RHE, the FE of C₂ products could reach 80% with a current density of 11.5 mA cm⁻². The respective overpotentials for acetic acid and ethanol are 0.53 and 0.48 V, respectively.

Results
Electrosynthesis and characterization of Cu-complex/Cu. The electrodes were fabricated via two steps, including in situ electrodeposition of Cu-complex film on Cu substrate (denoted as Cu-complex/Cu) and in situ electroreduction of the CuII in Cu-complex film to obtain Cu–Cu₂O/Cu electrode, which are discussed in the following.

In this work, six Cu-complexes with different ligands, which are denoted as Complex-1 to Complex-6 (Supplementary Scheme 1), were in situ deposited on Cu substrate by electrosynthesis method, where the numbers correspond to that of the ligands shown in Supplementary Scheme 1. The procedures to prepare the Cu-complex/Cu is shown schematically in Fig. 1a taking Complex-1 (pyromellic acid, 1,2,4,5-H₄BTC) as the example. Briefly, the electrosynthesis of Complex-1/Cu was carried out in a two-electrode system, which consisted mainly of Cu foil anode, Cu foil cathode, ligand, and electrolyte solution. The CuII ions produced from electro-oxidation of the Cu anode (Cu substrate) coordinated with the electro-deprotonated organic ligands generated at the cathode, and then the complex film grew in situ on Cu substrate surface.

The growth of Complex-1 film on Cu substrate at different electrodeposition times were investigated using scanning electron microscopy (SEM, Fig. 1b). It is demonstrated that Complex-1 film with 3D hierarchical structure was formed with increasing electrodeposition time. The side-view SEM image of the Complex-1/Cu with electrodeposition time of 60 min is also given (Fig. 1b, Supplementary Figs. 1–6), indicating that the complex film of about 60 µm compacted tightly with the Cu substrate without any noticeable crack. This is understandable because the Cu ions were generated from the Cu substrate and the complexes grew on the substrate surface.
The complex with electrodeposition time of 60 min was further characterized by Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) methods (Supplementary Figs. 7 and 8). The results show that the complexes were synthesized successfully and there was no evident impurity in the complexes. The X-ray photoelectron spectroscopy (XPS) spectra indicate that CuII was the major metallic species in the complex (Supplementary Fig. 9). N2 adsorption/desorption method was used to determine the surface areas and porous properties of the complex, and the results (Supplementary Fig. 10 and Supplementary Table 1) demonstrate that the complex has porous structure, and the molar ratio of Cu and ligand in the complex was 2.69, which was obtained from the Cu and C contents in the complexes determined by induced coupled plasma (ICP) methods (Supplementary Table 2) and the complex loading was 0.67 mg cm\(^{-2}\) after 60 min deposition (Supplementary Table 3). Small angle X-ray scattering (SAXS) technique was used to analyze the fractal structure. The surface fractal (\(D_f\)) values were obtained from the \(\ln(I)/\ln(h)\) vs \(\ln(h)\) plots (Supplementary Fig. 11). It can be seen that the surface of the complexes was coarse. The roughness factors of the complex film and Cu substrate were also determined by measuring the double layer capacitance using the reported method\(^{44,42}\). The results (Supplementary Fig. 12 and Supplementary Table 4) indicate that the surface of the complex film was much rougher than that of Cu substrate. All the results above confirm that the Cu-complex was successfully synthesized on the Cu substrate by the electrodeposition method. This is understandable because multibenzenecarboxylates are commonly used ligands in preparation of metal complexes\(^{43-48}\). The formation of the complexes was further proved by successful synthesis of the single crystal with 3D supramolecular structure (Supplementary Figs. 13–18 and Supplementary Tables 15–21) using interface growth method.

Decomposition and characterization of Cu–Cu2O/Cu. We found that the CuII in Cu-complex/Cu electrode was reduced quickly in N\(_2\) or CO\(_2\)-saturated 0.1 M KCl aqueous electrolyte at applied potential of \(-0.4\) V vs RHE. The current density at different electroreduction times are given in Fig. 2a. The current density was reduced to near zero after 5 min in N\(_2\)-saturated electrolyte. The current density in CO\(_2\)-saturated electrolyte became constant after 5 min, and the current after 5 min was originated from the CO\(_2\) electroreduction, which will be discussed in detail in the following sections. The change of electrode properties with electroreduction times was studied by SEM, XRD, XPS, and X-ray absorption fine structure spectroscopy (XAFS) methods. SEM images (Fig. 2b and Supplementary Fig. 19) show clearly that the 3D flower-like morphology of the complex was transformed into the dendritic 3D structure completely in initial 5 min of electroreduction. The morphology did not change notably after 5 min, and the thickness of the dendritic layer was about 40 µm. The XPS spectra of the catalyst film at different electroreduction times given in Fig. 2c, d indicate that the valence states of Cu changed from CuII to CuI and Cu0 during the initial stage of electroreduction. The film after electroreduction was composed of Cu and Cu2O as can be known from the XRD patterns (Supplementary Fig. 20). The ratio of CuI/Cu0 became constant after 5 min of electroreduction (Supplementary Fig. 21 and Supplementary Table 5). The XAFS modeling and analysis results (Supplementary Figs. 22, 23 and Supplementary Table 6) further revealed the existence of Cu–O and Cu–Cu in the catalyst after electroreduction, and the CuI/Cu0 ratio was unchanged after 5 min, which is consistent with the results of XPS study (Supplementary Fig. 21 and Supplementary Table 5). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images of the catalyst with an electroreduction time of 5 min are presented in Fig. 2e–g, demonstrating that high density of grain boundaries (GBs) exist between Cu and Cu2O. The oxygen vacancies on the interface of Cu and Cu2O create new defect states located in the band gap, and the electrons on the defect states are easily excited, leading to the enhanced conductivity\(^{49-51}\). All the results above show that the Complex-1 changed into Cu and Cu2O composite denoted as Cu–Cu2O-1 (the number corresponds to the number of the complex) on Cu substrate after electroreduction, and the composition and morphology were stable after 5 min of reduction. As expected, the Cu–Cu2O-1 film and Cu substrate in the Cu–Cu2O-1/Cu also compacted tightly without any noticeable crack (Fig. 2b). In this work, the Cu-complexes on the Cu substrate acted as the precursor and template for the formation of the Cu–Cu2O-1 catalyst with 3D structure on the Cu substrate.

The electrocatalytic performance of Cu–Cu2O/Cu. The linear sweep voltammograms (LSVs) over Cu–Cu2O-1/Cu electrode in CO\(_2\) or N\(_2\) saturated 0.1 M KCl aqueous electrolyte were determined (Supplementary Fig. 24), which shows reduction of CO\(_2\) clearly. The dependence of current density on concentration of KCl solution saturated by CO\(_2\) over Cu–Cu2O-1/Cu electrode is provided in Supplementary Fig. 25, demonstrating that 0.1 M KCl solution was the optimal electrolyte.

The electrocatalytic performance of the Cu–Cu2O-1/Cu electrode was further investigated by electrolysis of CO\(_2\) at different applied potentials in 0.1 M KCl aqueous solution using a typical H\(^+\) type cell, in which water acted as a proton source\(^{56,52}\).
and the results are given in Fig. 3. The experiment at each condition was repeated three times and the average values are used. In this work, the applied potential is referencing to the reversible hydrogen electrode (RHE) and the current density is calculated by geometric surface area. Under the reaction conditions, acetic acid and ethanol were the only liquid products detected by NMR spectroscopy, and H2, CO and CH4 were the gaseous product determined using gas chromatography (GC) (Supplementary Fig. 26 and Supplementary Table 7). The electrocatalytic performances of neat Cu foil, Cu foam obtained by direct electrodeposition without using ligand, Cu2O and CuO electrodes prepared using reported method11,40,41,53 were also studied for comparison (Supplementary Fig. 27), and the results are also given in Fig.3. Clearly, Cu–Cu2O-1/Cu electrode had much better performance for C2 product (acetic acid and ethanol) generation than other Cu-based electrodes. The applied potential and the overpotential over the Cu–Cu2O-1/Cu electrode were much lower (Fig. 3a), and the FE was much higher (Fig. 3b). At applied potential of −0.4 V vs RHE, the overpotential on Cu–Cu2O-1/Cu electrode was as low as 0.53 V (for acetic acid) and 0.48 V (for ethanol) (Fig. 3c, d). The current density and FE for the C2 product were 11.5 mA cm−2 and 80.7% (48% for acetic acid and 32% for ethanol), respectively. Supplementary Table 8 presents the recent advances in reduction of CO2 to C2+ products. Previous report indicates that dendritic Cu catalysts are capable of reducing CO2 to C2 products. These desired structures can be synthesized through different methods7,38,54. However, the characteristics of the catalyst such as structure and oxidation state are difficult to be controlled, which lead to high overpotential of the C2 products. Using molecular complex as an additive is another method to promote reduction of CO2 to C2 product30–32. However, as a precursor, the complex was generally prepared ex situ and used as a homogeneous additive in decomposition of the new structure. Compared with these methods, the Cu–Cu2O catalyst synthesized in this work through in situ deposition/decomposition method exhibited controllable 3D structure, high charge transfer rate and lower overpotential toward liquid C2 products. By comparing with the data reported (Supplementary Table 8), it can be known that this in situ electro.synthesized Cu–Cu2O-1/Cu electrode had significantly lower applied potential and overpotential, higher current density, and higher FE for liquid C2 products, especially in aqueous
were collected at room temperature and ambient pressure; electrolyte, 0.1 M KCl; CO2 stream, 5 sccm.

The result in Supplementary Table 9 indicates that the amounts of the C2 products changes with applied potential and the amounts of the generated C2 products increased almost linearly with increasing of electrolysis time (Supplementary Fig. 28). The turnover frequency (TOF) for CO2 reduction reaction over the catalysts at different applied potentials are provided in Supplementary Table 10. The Cu–Cu2O–1/Cu electrode exhibited the TOFs of acetic acid and ethanol were 17.0 and 15.6 h⁻¹, respectively.

Electrolyte also plays an important role in the CO2 reduction. Recently, researchers have reported the reduction of CO2 to C2+ products in KCl aqueous electrolyte, and it was found to decrease the overpotential and increase the C2 selectivity. The rise in local pH facilitated a higher amount of adsorbed *CO, which promotes their C–C coupling to C2 products, and it was found to decrease the overpotential and increase the C2 selectivity. The rise in local pH facilitated a higher amount of adsorbed *CO, which promotes their C–C coupling to C2 products.

To confirm that CO2 was carbon source of the product, we also conducted the blank experiments using N2 to replace CO2 in the electrolysis. The experiments showed that no product was formed in the electrolysis when using N2. To further verify that the product was derived from CO2 reduction, isotope–labeled 13CO2 was used to study the reaction over Cu–Cu2O–1/Cu. From 1H NMR spectra in Supplementary Figs. 33 and 34, we can only see the H signal of 13CH3 group on the acetic acid and ethanol, which splits into two peaks by the coupling with 13C atom. Moreover, the 13C NMR spectra showed strong 13C signals as 13CO2 was used as the feedstock (Supplementary Fig. 35). The results further confirm that all the carbon atoms in the product were from CO2, which is consistent with the conclusion obtained from the blank experiment using N2.

### Investigation into the catalytic ability of Cu–Cu2O/Cu

There are several reasons for the outstanding performance of the Cu–Cu2O–1/Cu electrode in the electrocatalytic reduction of CO2 to the C2 products. First, the Cu–Cu2O–1 catalyst and Cu substrate contacted very well in the electrode. This structure can reduce or eliminated the contacting resistance between the catalyst and the Cu substrate, which is favorable to reducing the overpotential and applied potential. In order to get some evidence to support this point, some control experiments were designed. We prepared Complex-1 by solvothermal method using the same ligand and fabricated the complex electrode by loading the complex suspension onto the carbon paper (CP) using conventional drop-casting method (Supplementary Figs. 36 and 37), and the complex was also reduced to Cu–Cu2O composite by electroreduction to obtain Cu–Cu2O–1/CP electrode as known from the XPS characterization (Supplementary Fig. 38). Supplementary
Mechanism. With the aim to understand the mechanistic pathway toward the formation of acetic acid and ethanol by CO₂ reduction, some control experiments were conducted in the presence of the possible reaction intermediates, such as CO, formic acid, formaldehyde, acetaldehyde, and acetic acid. Supplementary Table 14 presents the production rates of acetic acid and ethanol in these experiments. The results indicate that CO, formaldehyde and acetaldehyde are three important intermediates in the C₂ product pathway. Supplementary Fig. 46A shows the IR spectra of the electrolyte after different electrolysis times. The intensity of acetic acid and ethanol increased with increasing electrolysis time, indicating that the amount of C₂ products generated increased with electrolysis time, suggesting the formation of acetic acid and ethanol from electroreduction of CO₂. We also conducted the IR study in the presence of possible reaction intermediates (Supplementary Fig. 46B). The result indicates that CO₂, formic acid, and acetaldehyde are the possible intermediate in the mechanistic pathway. This conclusion is consistent with the result in Supplementary Table 14. Supplementary Scheme 2 gives the possible mechanistic pathway for the electrocatalytic production of acetic acid and ethanol. The three key steps are (i) CO₂ activation; (ii) C₂ product formation, which was found to compete with C₂ products; (iii) C₂ dimerization, which can be important for CO⁺CH₂ intermediate. For acetic acid, the intermediate COCH₂⁻ is further reduced at the electrode surface to form CH₃COO⁻ species. This tentative mechanistic pathway is able to explain the experimental observations discussed above.

Discussion

In summary, 3D dendritic Cu–Cu₂O/Cu electrodes for CO₂ reduction can be prepared by electroreduction of in situ deposited Cu-complex film on Cu substrate successfully. They had outstanding performance for electrochemical reduction of CO₂ to C₂ product in KCl aqueous solution. The results show that reducing contacting resistance between the catalysts and the substrate in the electrodes, increasing exposed active sites in the 3D structure and chemical composition of Cu–Cu₂O composition are favorable to enhance the efficiency for the reduction of CO₂ to C₂.

The electrocatalytic performance of other Cu–Cu₂O/Cu electrodes.

In order to verify the versatility of the method, we also prepared Cu–Cu₂O/Cu electrodes using other ligands, including 1,2-H₂BTC, 1,3,5-H₂BTC, and 1,2,3,4,5-H₂BTC. The complexes on Cu substrate are denoted as Complex-1, Complex-2, Complex-3, Complex-4, Complex-5, and Complex-6, respectively. The complexes were also characterized using different methods, and the results are given in Supplementary Figs. 1–11, Supplementary Figs. 13–18, and Supplementary Tables 1–4. Supplementary Tables 1–4. The corresponding electrodes are represented by Cu–Cu₂O/Cu, Cu–Cu₂O/Cu, Cu–Cu₂O/Cu, Cu–Cu₂O/Cu, Cu–Cu₂O/Cu, and the characterization results are provided in Supplementary Figs. 19–21 and Supplementary Table 5. All the results showed that 3D dendritic Cu₂O/Cu films on Cu electrodes could also be prepared using these ligands, and the detailed discussion on this are provided in the supporting information. Subsequently, the as-prepared Cu–Cu₂O/Cu electrodes were used for CO₂ reduction in 0.1 M KCl aqueous electrolyte, and the results are given in Fig. 4. Supplementary Figs. 43–45. Generally, these Cu–Cu₂O/Cu electrodes could also provide CO₂ electroreduction to C₂ products at very low applied potential and overpotential with high selectivity in the aqueous electrolyte. At ~0.4 V vs RHE, the FE of C₂ products over Cu–Cu₂O/Cu electrodes is ~45. Generally, these Cu–Cu₂O/Cu electrodes could also provide CO₂ electroreduction to C₂ products at very low applied potential and overpotential with high selectivity in the aqueous electrolyte. At ~0.4 V vs RHE, the FE of C₂ products over Cu–Cu₂O/Cu electrodes is ~45.
products. This work opens a simple way to efficient transformation of CO₂ into valuable chemicals or liquid fuels, and the findings are helpful for designing other electrodes for efficient electroreduction of CO₂. We believe that this work will trigger many interesting work in the future.

**Methods**

**Materials.** CO₂ (Beijing Beiwen Gas Chemical Industry Co., Ltd., research grade) had a purity of 99.999% and used as received. ¹³CO₂ (99 atom% ¹³C, <1 atom%) was purchased from Beijing Gaishi Chemical Gas Center. Pyromellic acid (1,2,4,5-H₄BTC, 96%), 1,2,4-benzenetricarboxylic acid (1,2,4-H₃BTC, 98%), 1,3,5-benzenetricarboxylic acid (1,3,5-H₃BTC, purity > 99%), 1,2,3-benzenetricarboxylic acid (1,2,3-H₃BTC, 95%), 2,6-pyrindinedicarboxylic acid (2,6-H₂PyDC, 99%), tetramethylammonium bromide (TMAB, 99%), and tetrabutyl ammonium perchlorate (TBAP, 99%) were obtained from J&K Scientific Ltd. 1,4-Benzedicarboxylic acid (1,4-H₂BDC, 99%) was purchased from TCI. Cu(NO₃)₂·3H₂O (A. R. grade), acetonitrile (AcN, A. R. grade), methanol (A. R. grade), and Cu foil (0.2 mm in thickness, purity > 99.99%) were provided by Sinopharm Chemical Reagent Co., Ltd, China. Potassium chloride (KCl, 99.997%) was purchased from Alfa Aesar China Co., Ltd, which was purified by recrystallization three times before use. Toray carbon paper (CP, TGP-H-60, 19 × 19 cm) and Nafion N-117 membrane (0.180 mm thick, ≥0.90 mg/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Polytetrafluoroethylene (PTFE, 60 wt% aqueous solution) was purchased from Sigma-Aldrich Co. LLC. Tetraethylammonium hexafluorophosphate (TBAPF₆, >98%) was provided by the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

**In situ electrosynthesis of the Complex-1 to 5 on Cu substrate.** The structures of the ligands are shown in Supplementary Scheme 1. The procedures were similar to that used for preparing HKUST-1. Copper acetate (Cu(NO₃)₂·3H₂O (2.6 g, 10.7 mM) was dissolved in 30 mL of H₂O in a flask. 1,3,5-H₃BTC·3H₂O solution was slowly added to the 1,2,4,5-H₂BTC solution with stirring at room temperature. Then 2 mL of DMF was added to the mixture solution with stirring. The mixture was transferred into a Teflon-lined autoclave and the reaction occurred at 90 °C under hydrothermal condition for 48 h. After cooling to room temperature, the solid was collected and washed with H₂O and ethanol. The obtained Cu-Complex-1 was dried in a vacuum oven at 80 °C for 24 h.

**Synthesis of Complex-3 by solvothermal method.** The procedures to synthesize the Complex-3 with organic linker 1,3,5-H₃BTC were similar to that reported previously. In a typical experiment, Cu(NO₃)₂·3H₂O (2.6 g, 10.7 mM) was dissolved in 30 mL of H₂O in a flask. 1,3,5-H₃BTC·3H₂O solution was slowly added to the 1,2,4,5-H₂BTC solution with stirring at room temperature. The solution became turbid with formation of precipitate. DMF (2 mL) was added to the mixture, and then the combination was transferred to a Teflon-lined autoclave and allowed to be reacted at 90 °C for 24 h. After cooling to room temperature, the solid was collected and washed with H₂O and ethanol. The obtained Cu-Complex was dried in a vacuum oven at 80 °C for 24 h.

**Fabrication of the electrodes using Cu-Complexes synthesized by solvothermal method.** The complex electrodes were prepared by loading Cu-Complex suspension onto the carbon paper (CP) using drop-casting method. Briefly, the as-prepared Cu-Complex was dispersed in acetone, then suitable amount of 6.0 wt% PTFE aqueous solution was added to the as prepared Cu-Complex dispersion. The final mixture contained 10 mg/mL complex and 0.6 wt% PTFE, which was ultrasonicated for 30 min to form a uniform suspension. Then 0.1 mL of the suspension was sonicated for 30 min to form a uniform suspension. Then 0.1 mL of the suspension was applied to the carbon paper using a microsyringe. After application, the carbon paper was dried at room temperature. The active mass loading was approximately 1.5 mg/cm². The working and counter electrode with a gap of 1 cm and the electrochemical experiments could be controlled by a DC mode on a galvanostat/potentiostat (CS310, Wuhan Corrett Instrument Co., China). The electrolyte consisted of 25 mL of ethanol/water (75:25 vol%) solution, 5–15 mg MTAB (99.9%, supporting electrolyte), and 5 mg Cu-complex-1 or 15 mg Complex-2, or 10 mg Complex-3, or 5 mg Complex-4, or 15 mg Complex-5, or 15 mg Complex-6. The electro-synthesis was performed by applying a potential difference of 9.0 V between the Cu foil electrodes in 70 °C electrolyte. Cu-Complex was in situ formed at the anode.

**Fig. 4** Carbon dioxide reduction over copper-cuprous oxide electrodes prepared using ligands two to six. a The total current density at different applied potentials; b Faradaic efficiencies of the C₂ products at applied potential of –0.4 V vs RHE. c, d Dependence of partial current density of acetic acid and ethanol on overpotential, respectively. Data were collected at room temperature and ambient pressure; electrolyte, 0.1 M KCl; CO₂ stream, 5 sccm.
Electrodeposition of CuO on Cu foil. Electrochemical growth of CuO film was accomplished by using a conventional three-electrode cell using the method reported. The copper foil substrate was used as working electrode, a platinum sheet as counter electrode, and Ag/AgCl as reference electrode. The electrodeposition was carried out cathodically using the solution containing 0.02 M CuSO4 and 0.34 M DL-Lactic acid (85%) at pH 9 adjusted using 2 M NaOH. Deposition were carried out at 70 °C and −0.95 V vs Ag/AgCl for 30 min.

Electrodeposition of CuO on Cu foil. CuO thin films were grown by electrodeposition technique using potentiostatic method reported. A standard three-electrode cell was used for the electrodeposition. The copper foil substrate was used as working electrode, a platinum sheet as counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrodeposition of CuO was carried out cathodically from an aqueous bath composed of CuSO4 (0.03 M) and Li(+) tartaric acid (0.03 M). The deposition of CuO thin film was carried out at a deposition potential of −650 mV vs SCE. The solution pH was adjusted to 10−12 by the addition of 2 M NaOH solution. The deposition was carried out at 75 °C for 30 min.

Direct electrodeposition of Cu foam on Cu foil. The method was similar to that for synthesis of Cu-Complex40,41, and the main difference was that the ligand was not used. A Cu foam on Cu foil was electrodeposited in a solution containing 0.25 M CuSO4 and 0.34 M DL-Lactic acid (85%) at pH 9 adjusted using 2 M NaOH solution. The deposition was carried out at 75 °C for 30 min.

Material characterization. Powder X-ray diffraction (XRD) patterns were acquired with a X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-Kα radiation, and the scan speed was 5°/min. X-ray photoelectron spectroscopy (XPS) analysis was conducted on the Thermo Scientific ESCALAB 250Xi (USA) using 200 W monochromatic Al Kα radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3 × 10−10 mbar. The contents of Cu and C in the complex were determined by induced coupled plasma optical emission spectrometer (ICP-OES, VARIO VISTA-MPX). The morphologies of materials were characterized by a HITACHI S-4800 scanning electron microscope (SEM) and a JOEL JEM-2100F high-resolution transmission electron microscope (HR-TEM). The porosity properties and surface areas of the materials were obtained from nitrogen adsorption−desorption isotherms determined using a Micromeretics ASAP 2020 M system. For XRD, ICP-OES, gas adsorption−desorption measurements, in order to get enough sample, at least 10 electrodes were prepared at the same conditions and the catalytic films were scraped and collected for characterization.

The FT-IR spectra were collected at a resolution of 4 cm−1 on a Bruker Vector 27 spectrophotometer in the 400−4000 cm−1 region. The IR spectra of samples were measured by the conventional KBr pellet method. To get enough sample, at least 10 electrodes were prepared at the same conditions and the complex films were scraped and collected. The Quasi in situ X-ray photoelectron spectra (XPS) were measured on an AXIS ULTRA DLD spectrometer with AlKα resource (hv = 1486.6 eV). The protective sample transfer procedure was similar to that reported in the literature. For investigating the evolution of Cu species in the reaction process, catalysts were electrolyzed with different times in the CO2-saturated electrolytes. After that, the samples were immediately immersed in Ar-prepurged acetone and then transferred into an Ar-filled glove box to protect the catalyst from direct contacting of air. Then, the samples were cleaned, dried and cut into 3 × 3 mm and glued on a stage with a double sided adhesive. The stage was evacuated into vacuum to prevent the sample to be oxidized in the air. The subsequent testing processes were the same as that of the common X-ray photoelectron spectroscopy. The contaminated carbon C 1s signal at 289.8 eV was used to calibrate binding energies. The spectra were deconvoluted with XPS PEAK 4.1 software by subtracting the Shirley background and applying the Lorentzian−Gaussian function. The modified Auger parameter (αcu) was calculated according to the following equation:

$$\alpha_{cu} = E_b + E_K$$

where $E_b$ is the binding energy of the Cu 2p1/2 core level and $E_K$ is the kinetic energy of the Cu Auger electron.

X-ray absorption fine structure spectroscopy (XAFS) measurements were taken at 1W2B beamline of Beijing Synchrotron Radiation Facility (BSRF), China. The Cu K-edge (8979 eV) XAFS spectra were collected under electrochemical environment using the fluorescence detection method. The EXAFS data were processed according to the standard procedure including the ATHENA module implemented in the IFEFFIT software package. The Cu K-edge X-ray absorption spectra of the catalysts were collected after reaction at different times. The Cu K-edge X-ray absorption spectra of Cu-complexes, CuO, Cu2O, and Cu foil were collected for reference.

Small angle X-ray scattering (SAXS) experiments were carried out at Beamline 1W2A at the Beijing Synchrotron Radiation Facility. The apparatus and the procedures were similar to that used in previous work. The data were collected using a CCD detector (MAR) with maximum resolution of 3450 × 3450 pixels. The wavelength of the X-ray was 1.54 Å, and the distance of the sample to detector was 1.31 m. In a typical experiment, the sample was added into the sample cell, and the X-ray scattering data were recorded. The 2-D SAXS images were obtained from the detector and then transformed into the profiles of intensity (I) vs wavevector (q) by the software FIT2D. To get enough sample, at least 10 electrodes were prepared at the same conditions and the complex films were scraped and collected for characterization.

Crystal data and structure refinement for Complex-1, Complex-4, and Complex-5. In total, 0.05 mmol of 1,2,4,5-H4BTC, or 1,2,3-H3BTC, or 2.6-H2PyDC was dissolved in 20 mL ethanol, and then a solution of 0.05 mmol Cu(NO3)2 in 5 mL H2O was added to the mixture. As the solvent evaporating, blue crystals were obtained after solvent evaporation. Then, it was washed with acetone and air dried. The product was recrystallized from ethanol-H2O (4:1).

The model was similar to that used in previous work. The Cu K-edge X-ray absorption spectra of Cu-complexes, CuO, Cu2O, and Cu foil were collected for reference. The EXAFS data were obtained from the detector and then transformed into the profiles of intensity (I) vs wavevector (q) by the software FIT2D. To get enough sample, at least 10 electrodes were prepared at the same conditions and the catalyst films were scraped and collected for characterization.
in aqueous solution at pH 7.0 vs standard hydrogen electrode (SHE) (Eq. (6)) is:

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad E = -0.41 \text{ V vs SHE at pH 7.0} \] (5)

\[ 2\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \quad E^{\text{Acetic acid}} = 0.125 \text{ V vs SHE at pH 7.0} \] (6)

Applying the Nernst equation (Eq. (7)), the equilibrium potential is estimated to be:

\[ E^\circ = -0.289 \text{ V} + \frac{R \text{ln}[10]}{F} \text{pH} = 0.125 \text{ V vs RHE at pH 7.0} \] (7)

Therefore, using the same method, \( E^\circ \) for the half reaction of \( \text{CO}_2 \) to acetic acid and \( \text{CO}_2 \) to ethanol are:

\[ 2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{CH}_3\text{OH} + 2\text{H}_2\text{O} \quad E^{\text{Ethanol}} = 0.084 \text{ V vs RHE} \] (9)

Electrochemical impedance spectroscopy measurements. The experimental apparatus was the same as that for LSV measurements. The experiment was carried out in \( \text{CO}_2 \) saturated 0.1 M KCl solution. The impedance spectra was recorded at open circuit potential (OCP) with an amplitude of 5 mV of \( 10^2 \text{ to } 10^5 \text{ Hz} \). The data obtained from the electrochemical impedance spectroscopy (EIS) measurements were fitted using the Zview software (Version 3.1, Scriber Associates, USA).

Electrochemical capacitance measurements. Cyclic voltammetry (CV) was used for the electrochemical capacitance measurements. The experiments were performed by collecting cyclic voltammograms in 0.1 M TRAPF, in McCN solution at scan rates from 50 to 400 mV/s. The experiment was performed in three-electrode configurations, in which a silver wire was used as quasi-reference electrode and Pt gauze was used as counter electrode. Data obtained over a potential range of 40 mV around the open circuit potential of Cu-Cu2O-V/Cu electrode is shown in Fig. S13. Plot of the current density from the quasi-square CV curves, calculated at the open circuit potential, as a function of scan rate. The surface roughness factor was calculated from the capacitance data.42

\( \text{CO}_2 \) reduction electrolysis and product analysis. Controlled potential electrolysis (CPE) was carried out. The electrolysis experiments were conducted at 25 °C in a typical H-type cell, which was similar to that used in our previous works for \( \text{CO}_2 \), electrochemical reduction.42 The as synthesized Cu-Complex electrodes were used as the working electrode. The Ag/AgCl (saturated KCl) was used as the reference electrode and the Pt gauze was used as counter electrode. The cathode and anode compartments were separated through a Na2SO4 aqueous solution (0.5 M) was used as anodic electrolyte. Electrochemical reduction of \( \text{CO}_2 \) was carried out at ambient temperature. Under the continuous stirring, \( \text{CO}_2 \) was bubbled into the catholyte (25 mL/min) for 60 min before electrolysis. After that, potentiostatic electrochemical reduction of \( \text{CO}_2 \) was carried out with \( \text{CO}_2 \) bubbling (5 mL/min). The gaseous product was collected and analysed by gas chromatography (GC, HP 4890D), which was equipped with FID and TCD detectors using helium as the internal standard.41 4H NMR spectroscopy was carried out to quantify the liquid products after electrolysis of desired time at each given potential. The current density and Faradaic efficiencies (FEs) of the products were calculated using the amounts of the products obtained from GC and 4H NMR analysis.

Similarly, all potentials were referencing to RHE using the pH of the \( \text{CO}_2 \)-saturated KCl solution.

After the quantification, the Faradaic efficiency (FE) toward each product were calculated as follows:48

\[ \text{FE(%) = \frac{\text{amount of the product} \times n \times F}{C} \times 100} \] (10)

where \( n \) is number of moles of electrons to participate in the Faradaic reaction, \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), and \( C \) is the amount of charge passed through the working electrode.

Turnover frequency measurements. TOF for \( \text{CO}_2 \) reduction reaction over the catalysts was calculated on the basis of amounts of products, electrolysis time, the moles of \( \text{Cu} \) species on the electrode determined gravimetrically. The moles of \( \text{Cu} \) species were assumed to be the same as that in the complexes precursors. To get the reliable amount of the complex, at least 10 Cu-complex/Cu electrodes were prepared, and the mass of the complex was calculated from the mass difference before and after electrodeposition. The moles of \( \text{Cu} \) was known from the molar weight of the complex (Supplementary Table 15) and mass of the complex in the complex/Cu electrode (Supplementary Table 3).

Tafel analysis. The Tafel plots were constructed from the partial current density and the overpotential. The overpotential was the difference between the applied potential and the thermodynamic potential for the reaction of interest.4 As mentioned above thermodynamic potentials for the reactions of \( \text{CO}_2 \) to acetic acid and \( \text{CO}_2 \) to ethanol are 0.125 and 0.084 V, respectively.

Reporting summary. Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability. All data supporting the findings of this study are available from the corresponding author on request.

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References

1. He, M. Y., Sun, Y. H. & Han, B. X. Green carbon science: scientific basis for integrating carbon resource processing, utilization, and recycling. Angew. Chem. Int. Ed. 52, 9620–9633 (2013).
2. Qiao, J. L., Liu, Y. Y., Hong, F. & Zhang, J. J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. Chem. Soc. Rev. 43, 631–675 (2014).
3. Gao, S. et al. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. Nature 529, 68–71 (2016).
4. Li, C. W. & Kanan, M. W. CO2 Reduction at low overpotential on Cu electrodes resulting from the reduction of thick CuO films. J. Am. Chem. Soc. 134, 7231–7234 (2012).
5. Lin, S. et al. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO2 reduction in water. Science 349, 1208–1213 (2015).
6. Zhou, Y. S. et al. Dopant-induced electron localization drives CO2 reduction to CH2, hydrocarbons. Nat. Chem. 10, 974–980 (2018).
7. Luna, P. D. et al. Catalyst electro-redoposition controls morphology and oxidation state for selective carbon dioxide reduction. Nat. Catal. 1, 103–118 (2018).
8. Dinh, C. T. et al. CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 360, 783–787 (2018).
9. Louidice, A. et al. Tailoring copper nanocrystals towards C2 products in electrochemical CO2 reduction. Angew. Chem. Int. Ed. 55, 5789–5792 (2016).
10. Hori, T., Takahashi, I., Koga, O. & Hoshii, N. Electrochemical reduction of carbon dioxide at various series of copper single crystal electrodes. J. Mol. Catal. A: Chem. 199, 39–47 (2003).
11. Ren, D. et al. Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper(II) oxide catalysts. ACS Catal. 5, 2814–2821 (2015).
12. Lum, Y., Yue, B., Lobaccaro, P., Bell, A. T. & Ager, J. W. Optimizing C-C coupling on oxide-derived copper catalysts for electrochemical CO2 reduction. J. Phys. Chem. C. 121, 14191–14203 (2017).
13. Roberts, F. S., Kuhl, K. P. & Nilsson, A. High selectivity for ethylene from carbon dioxide reduction over copper nanocube electrocatalysts. Angew. Chem. Int. Ed. 54, 5179–5182 (2015).
14. Song, Y. et al. High-selectivity electrochemical conversion of CO2 to ethanol using a copper nanoparticle/N-doped graphene electrode. Chem. Sel. 1, 6055–6061 (2016).
15. Jiang, K. et al. Metal ion cycling of Cu foil for selective C-C coupling in electrochemical CO2 reduction. Nat. Catal. 1, 111–119 (2018).
16. Mistry, H. et al. Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. Nat. Commun. 7, 12123 (2016).
17. Gao, D. F. et al. Plasma-activated copper nanocube catalysts for efficient carbon dioxide electroreduction to hydrocarbons and alcohols. ACS Nano 11, 4825–4831 (2017).
18. Zhuang, T. T. et al. Steering post-C-C coupling selectivity enable high efficiency electroreduction of carbon dioxide to multi-carbon alcohols. Nat. Catal. 1, 421–428 (2018).
19. Song, Y. et al. Metal-free nitrogen-doped mesoporous carbon for electroreduction of CO2 to ethanol. Angew. Chem. Int. Ed. 56, 10840–10844 (2017).
20. Clark, E. L., Hahn, C., Jaramillo, T. F. & Bell, A. T. Electrochemical CO2 reduction over compressively strained CuAg surface alloys with enhanced multi-carbon oxygenate selectivity. J. Am. Chem. Soc. 139, 15848–15857 (2017).
21. Costentin, C., Robert, M. & Savaist, J. M. Catalysis of the electrochemical reduction of carbon dioxide. Chem. Soc. Rev. 42, 2423–2436 (2013).
22. Zhu, D. D., Liu, J. L. & Qiao, S. Z. Recent advances in inorganic heterogeneous electrocatalysts for reduction of carbon dioxide. Adv. Mater. 28, 3423–3452 (2016).
23. Andreiadis, I. S. E. et al. Molecular engineering of a cobalt-based electrocatalytic nanomaterial for H2 evolution under fully aqueous conditions. Nat. Chem. 5, 488–493 (2013).
24. Blasco-Ahitar, Soriano-Lopez, Z., Carbo, J. B., Poblet, J. M. & Galan-Mascaros, G. Polyoxometalate electrocatalysts based on earth-abundant metals for efficient water oxidation in acidic media. Nat. Chem. 10, 24–30 (2018).
25. Schley, N. D. et al. Distinguishing homogeneous from heterogeneous catalysis in electrode-driven water oxidation with molecular iridium complexes. J. Am. Chem. Soc. 133, 10473 (2011).
26. Stracke, J. J. & Finke, R. G. Electrocatatytic water oxidation beginning with the cobalt polyoxometalate [Co6(OH)6(WO4)3]10–: Identification of heterogeneous CoOx as the dominant catalyst. J. Am. Chem. Soc. 133, 14872–14875 (2011).
27. Cobo, S. et al. A Janus cobalt-based catalytic material for electro-splitting of water. Nat. Mater. 11, 802–807 (2012).
28. Kaeffer, N. et al. The dark side of molecular catalysis: Diimine-dioxime cobalt complexes are not the actual hydrogen evolution electrocatalyst in acidic aqueous solutions. ACS Catal. 6, 3727–3737 (2016).
29. Kanan, M. W. & Nocera, D. G. In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co2+. Science 321, 1072–1075 (2008).
30. Huan, T. N. et al. From molecular copper complexes to composite dendritic copper catalysts at high current density. Adv. Mater. 29, 3901–3907 (2015).
31. Han, Z., Kortlever, R., Chen, H. Y., Peters, J. C. & Agapie, T. CO2 reduction catalysis. ACS Catal. 7, 3313–3323 (2017).
32. Shin, H. C., Dong, J. & Liu, M. Nanoporous structures prepared by an electrochemical deposition process. Adv. Mater. 15, 1610–1614 (2003).
33. Lu, X. Y. & Zhao, C. Electrodeposition of hierarchically structured three-dimensional nickel-iron electrodes for efficient oxygen evolution at high current densities. Nat. Commun. 6, 6616 (2015).
34. Sun, Y. J. et al. Electrodeposited cobalt-sulfide catalyst for electrochemical and photoelectrochemical hydrogen generation from water. J. Am. Chem. Soc. 135, 17699–17702 (2013).
35. Medina-Ramos, J., DiMeglio, J. L. & Rosenhal, J. Efficient reduction of CO2 to CO with high current density using in situ or ex situ prepared Bi-based materials. J. Am. Chem. Soc. 136, 8361–8367 (2014).
36. Ding, C. M., Li, A. L., Lu, S. M., Zhang, H. F. & Li, C. In situ electrodeposition indium nanocrystals for efficient CO2 reduction to CO with low overpotential. ACS Catal. 6, 6438–6443 (2016).
37. Reller, C. et al. Selective electroreduction of CO2 toward ethylene on nano dendritic copper catalysts at high current density. Adv. Energy Mater. 7, 1600114 (2017).
38. Chen, Y. H. & Kanan, M. W. Tin oxide dependence of the CO2 reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts. J. Am. Chem. Soc. 134, 1986–1989 (2012).
39. Li, W. J., Tu, M., Cao, R. & Fischer, R. A. Metal-organic framework thin films: electrochemical fabrication techniques and corresponding applications & perspectives. J. Mater. Chem. A 4, 12336–12360 (2016).
40. Yadum, S. et al. Site-selective synthesis of Janus-type metal-organic framework composites. Angew. Chem. Int. Ed. 53, 4001–4005 (2014).
41. Yang, J. et al. A multifunctional biphasic water splitting catalyst tailored for integration with high-performance semiconductor photoanodes. Nat. Mater. 16, 335–341 (2017).
42. Köferstein, R. & Robl, C. Synthesis and crystal structure of two CuII-benzene-1,2,4,5-tetracarboxylates with three-dimensional open frameworks. Z. Anorg. Allg. Chem. 640, 310–316 (2014).
43. Qin, C., Wang, X. L., Wang, E. B., Hu, C. W. & Xu, L. [Cu2(HBTC)2(H2O)2][Cu2(H2O)2]2Cl2·H2O: a new arm-shaped two-dimensional copper coordination polymer having both transverse and helical-like channels. Inorg. Chem. Commun. 7, 788–791 (2004).
44. Jeong, N. C., Samanta, B., Lee, C. Y., Farha, O. K. & Hupp, J. T. Coordination-chemistry control of proton conductivity in the iconic metal-organic-framework material HKUST-1. J. Am. Chem. Soc. 134, 51–54 (2011).
45. Ma, L. F., Li, C. P., Wang, L. Y. & Du, M. CuII and ZrII coordination frameworks with benzene-1,2,4,5-tetracarboxylate tetracationic and flexible dipyridylic coligand: a new type of entangled architecture and a unique 4-connected topological network. Cryst. Growth Des. 11, 3309–3312 (2011).
46. van Albada, G. A., Ghazalli, M., Al-Farhan, K., Bouwman, E. & Reedej, J. Three new pyridine-2,6-dicarboxylate copper(II) compounds with coordinated pyrimidine-based ligands: synthesis, characterization and crystal structures. Polyhedron 52, 1059–1064 (2013).
Additional information

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