Copper Sulfide as the Cation Exchange Template for Synthesis of Bimetallic Catalysts for CO2 Electroreduction

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Among metals used for CO2 electroreduction in water, Cu appears to be unique in its ability to produce C2+ products like ethylene. Bimetallic combinations of Cu with other metals have been investigated with the goal of steering selectivity via creating a tandem pathway through the CO intermediate or by changing the surface electronic structure. Here, we demonstrate a facile cation exchange method to synthesize Ag/Cu electrocatalysts for CO2 reduction using Cu sulfides as a growth template. Beginning with Cu2−xS nanosheets (C?nano-0, 100 nm lateral dimension, 10 nm thick), varying the Ag+ concentration in the exchange solution produces a gradual change in crystal structure from Cu7S4 to Ag2S, as the Ag/Cu mass ratio varies from 0.1 to 10 (CA-nano-x, x indicating increasing Ag fraction). After cation exchange, the nanosheet morphology remains but with increased shape distortion as the Ag fraction is increased. Interestingly, the control (C-nano-0) and cation exchanged nanosheets have very high Faradaic efficiency for producing formate at low overpotential (−0.2 V vs. RHE). The primary effect of Ag incorporation is increased production of C2+ products at −1.0 V vs. RHE compared with C-nano-0, which primarily produces formate. Cation exchange can also be used to modify the surface of Cu foils. A two-step electro-oxidation/sulfurization process was used to form Cu sulfides on Cu foil (C-foil-x) to a depth of a few 10s of microns. With lower Ag+ concentrations, cation exchange produces uniformly dispersed Ag; however, at higher concentrations, Ag particles nucleate on the surface. During CO2 electroreduction testing, the product distribution for Ag/Cu sulfides on Cu foil (CA-foil-x-y) changes in time with an initial increase in ethylene and methane production followed by a decrease as more H2 is produced. The catalysts undergo a morphology evolution towards a nest-like structure which could be responsible for the change in selectivity. For cation-exchanged nanosheets (CA-nano-x), pre-reduction at negative potentials increases the CO2 reduction selectivity compared to tests of as-synthesized material, although this led to the aggregation of nanosheets into filaments. Both types of bimetallic catalysts are capable of selective reduction of CO2 to multi-carbon products, although the optimal configurations appear to be metastable.
| File list (2)                                                                                           |                                                                 |
|--------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| Cation exchange E-CO2R ChemRxiv Final.pdf (1.42 MiB)                                                    | [view on ChemRxiv](#) • [download file](#)                   |
| Cation exchange E-CO2R ESI ChemRxiv Final.pdf (2.46 MiB)                                               | [view on ChemRxiv](#) • [download file](#)                   |
Copper sulfide as the cation exchange template for synthesis of bimetallic catalysts for CO$_2$ electroreduction

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Among metals used for CO$_2$ electroreduction in water, Cu appears to be unique in its ability to produce C2+ products like ethylene. Bimetallic combinations of Cu with other metals have been investigated with the goal of steering selectivity via creating a tandem pathway through the CO intermediate or by changing the surface electronic structure. Here, we demonstrate a facile cation exchange method to synthesize Ag/Cu electrocatalysts for CO$_2$ reduction using Cu sulfides as a growth template. Beginning with Cu$_2$S$_4$ nanosheets (C-nano-0, 100 nm lateral dimension, 10 nm thick), varying the Ag$^+$ concentration in the exchange solution produces a gradual change in crystal structure from Cu$_7$S$_4$ to Ag$_2$S, as the Ag/Cu mass ratio varies from 0.1 to 10 (CA-nano-x, x indicating increasing Ag fraction). After cation exchange, the nanosheet morphology remains but with increased shape distortion as the Ag fraction is increased. Interestingly, the control (C-nano-0) and cation exchanged nanosheets have very high Faradaic efficiency for producing formate at low overpotential (~0.2 V vs. RHE). The primary effect of Ag incorporation is increased production of C2+ products at ~1.0 V vs. RHE compared with C-nano-0, which primarily produces formate. Cation exchange can also be used to modify the surface of Cu foils. A two-step electro-oxidation/sulfurization process was used to form Cu sulfides on Cu foil (C-foil-x) to a depth of a few 10s of microns. With lower Ag$^+$ concentrations, cation exchange produces uniformly dispersed Ag; however, at higher concentrations, Ag particles nucleate on the surface. During CO$_2$ electroreduction testing, the product distribution for Ag/Cu sulfides on Cu foil (CA-foil-x-y) changes in time with an initial increase in ethylene and methane production followed by a decrease as more H$_2$ is produced. The catalysts undergo a morphology evolution towards a nest-like structure which could be responsible for the change in selectivity. For cation-exchanged nanosheets (CA-nano-x), pre-reduction at negative potentials increases the CO$_2$ reduction selectivity compared to tests of as-synthesized material, although this led to the aggregation of nanosheets into filaments. Both types of bimetallic catalysts are capable of selective reduction of CO$_2$ to multi-carbon products, although the optimal configurations appear to be metastable.

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Introduction

CO$_2$ electroreduction (CO$_2$R) has become one of the most promising strategies towards achieving a carbon-neutral environment. Provided that it is powered by a renewable energy source, it can sustainably convert the greenhouse gas CO$_2$ into fuels like methanol and ethanol, and commodity chemicals such as ethylene.\(^1,^2\) Cu has been of intense interest as an electrocatalyst for this reaction, as it is selective for CO$_2$ reduction over water reduction and can produce C2+ products, due to its positive adsorption energy for H* and more optimal binding energy for CO$_2$ and related intermediates, compared to other metals.\(^3^–^6\) Still, it has been difficult to control selectivity to a single CO$_2$ reduction product. To this end, many research groups investigated alloys and bimetallic configurations of Cu with other metals to attempt to tune the overall catalyst performance.\(^3\)

There are two main conceptual strategies for Cu-based alloy and bimetallic electrocatalysts. One approach is to create a tandem catalyst mechanism via combining Cu with other CO-producing elements like Ag or Au. In this concept, the crucial intermediate CO made on the second metal surface can transfer to Cu to be further reduced.\(^7^–^1^2\) For example, polycrystalline copper foil with Au nanoparticles favors the generation of oxygenates over hydrocarbons at low overpotentials.\(^1^3\) Increased CO concentration achieved by Ag nanoparticles on oxide-derived Cu nanowires may also open another pathway, namely *CO + *CH$_4$ coupling towards increased ethanol generation.\(^1^4\) A second approach is to change the local electronic structure of Cu by alloying with the other elements in order to tune the binding strength towards intermediates.\(^1^5^–^1^9\) For example, Ag atoms in the bimetallic Cu-Ag catalyst create a diversity of binding configurations compared with pure Cu that facilitates the production of ethanol.\(^2^0\) The compressive surface strain induced by Ag reduces the H* adsorbates, leading to the selective suppression of HER and favors the production of multi-carbon oxygenates.\(^2^1\) Ag$_2$Cu$_2$O$_3$, with a 1:1 stoichiometric ratio between Ag and Cu, can be used to produce bimetallic catalysts with a known composition and uniform distribution on the atomic scale. When applied to CO reduction, catalysts of this type can achieve 92% Faradaic efficiency towards C2+ products at 600 mA cm$^{-2}$.\(^2^2\)

In this context, a facile strategy to introduce another element of specific concentration mixed with Cu on a variety of catalyst morphologies would be beneficial. This motivated us to investigate the cation exchange method, whereby a guest metal is introduced in the ion-form to replace the host metal ion in the compounds partially or entirely. This chemical conversion method has been widely employed to metal sulfides and oxides to achieve metastable facets, heteroatom doping, and introducing defect and strain, thus can be used to make multi-metal catalysts.\(^2^3\) Specific to CO$_2$ reduction, the choice of the parent compound used for cation exchange may influence catalyst performance. We note here the reported enhancement in C2+ product selectivity for oxide-derived copper as compared to metallic copper, some of which has been attributed to increased roughness and grain boundaries which form as a result of \textit{in-situ} reduction of the oxide starting material.\(^2^4^–^2^7\) Bearing this in mind, we hypothesized that Cu sulfide could serve as a convenient cation exchange template for the formation of bimetallic CO$_2$R electrocatalysts. We further hypothesized that the depletion of sulfur which occurs at the negative potential used to drive CO$_2$R could lead to morphology changes which could be beneficial for control of selectivity.\(^1^1^,^2^8\)

To test these hypotheses, we developed a cation exchange method to accommodate two commonly catalyst designs for CO$_2$ reduction: nanoparticles and foil electrodes. Ag was selected as the second metal as it is selective for the production of CO, which is believed to be the key intermediate for the formation of C2+ products. For creating nanoscale catalysts, we prepared Cu sulfide nanosheets (C-nano-0) by colloidal synthesis, while for modifying Cu surfaces, Cu sulfides were directly grown on Cu foil using electro-oxidation followed by sulfurization. In both cases, the Ag/Cu mass ratio of the catalysts could be controlled at the cation exchange step. For nanosheets, the Ag/Cu mass ratio can reach 10 with the original structure remaining nearly intact. Cation
exchange on surface-modified Cu foils (C-foil-x) produces well-dispersed Ag at low concentrations but leads to Ag particle nucleation at higher concentrations. Compared with C-nano-0 controls, CO₂ reduction on moderately cation exchanged Ag/Cu sulfide nanosheets (CA-nano-2) increases the selectivity to C2+ products at −1.0 V vs. RHE. The selectivity for CO₂ reduction of cation exchanged foils increases and then decreases over a period of 16 hours. Both the nanosheets and copper foil catalysts undergo noticeable morphology changes during the CO₂ reduction, which may explain why the product distributions change as the CO₂ reduction proceeds.

**Synthesis procedures**

The synthesis methods are summarized here; full details are in Electronic Supplementary Information (ESI).

**Cu sulfide nanosheets (C-nano-0)**

C-nano-0 was synthesized with a modified colloidal synthesis recipe ([Scheme 1a](#Scheme1a), see also Table 1 for sample nomenclature). Typically, 257 mg copper (I) thiocyanate (CuSCN) was dispersed in 25 mL oleylamine (OAM). The mixture was first degassed and heated in N₂ to 240°C for 30 min. The synthesized nanosheets were then washed with hexanes and ethanol to remove the surface ligands and dispersed in hexanes for storage.

**Cu sulfides on Cu foil (C-foil-x)**

Cu sulfides on Cu foil (C-foil-x) were synthesized with a two-step electro-oxidation/sulfurization process ([Scheme 1b](#Scheme1b)). Cu foil was first cleaned and etched by 4 M HCl. After that, Cu(OH)₂ was grown on the Cu foil by electro-oxidation in 1 M NaOH to produce an oxide layer of a few 10s of microns thick followed by sulfurization with 0.1 M Na₂S. After cation exchange where Ag⁺ replaces the Cu⁺ in the Cu sulfides, Ag/Cu sulfide nanosheets (CA-nano-x) remain nanosheet structure with some distortion in shape as the Ag/Cu mass ratio ranges from 0.1 to 10; while for C-foil-x, Ag nucleates at higher Ag concentration, that impedes the uniform distribution of Ag and Cu.

**Scheme 1** Synthetic strategies for Ag/Cu sulfide catalysts. (a) Cu sulfide nanosheets (C-nano-0, 100 nm lateral dimension, 10 nm thick) were obtained through colloidal synthesis with CuSCN in oleylamine (OAM). (b) Cu sulfides on Cu foil (C-foil-x) were obtained through electro-oxidation in 1 M NaOH to produce an oxide layer of a few 10s of microns thick followed by sulfurization with 0.1 M Na₂S. After cation exchange where Ag⁺ replaces the Cu⁺ in the Cu sulfides, Ag/Cu sulfide nanosheets (CA-nano-x) remain nanosheet structure with some distortion in shape as the Ag/Cu mass ratio ranges from 0.1 to 10; while for C-foil-x, Ag nucleates at higher Ag concentration, that impedes the uniform distribution of Ag and Cu.

**Cu sulfides on Cu foil (C-foil-x)**

Cu sulfides on Cu foil (C-foil-x, see Table 2 for sample nomenclature) were synthesized with a two-step electro-oxidation/sulfurization process ([Scheme 1b](#Scheme1b)). Cu foil was first cleaned and etched by 4 M HCl. After that, Cu(OH)₂ was grown on the Cu foil by electro-oxidation in 1 M NaOH. The electrode was then immersed in 0.1 M Na₂S at 90°C for 12 h to obtain Cu sulfides. The current density set during the electro-oxidation process affects the grain size, as will be discussed later. Carbon substrates including carbon paper and carbon cloth with deposited Cu as the Cu source and chemical oxidation for the growth of Cu(OH)₂ were also tried but were less successful; see ESI for details ([Figure S1–6](#FigureS1–6)).
Cation exchange method

For nanosheet samples, the hexanes dispersion containing C-nano-0 was added to an OAM solution (7 mL) containing the Ag precursor AgNO$_3$. The solution was first degassed and heated to 50°C in N$_2$ and kept for another 30 min to complete the cation exchange reaction. The nanosheets were then washed with ethanol and hexanes and dispersed in hexanes for storage. The samples are denoted CA-nano-x as shown in Table 1.

Table 1 Cation-exchanged nanosheet samples with precursor and reagent contents and mass ratios as measured by SEM-EDS.

| Label     | C-nano-0 (mg) | AgNO$_3$ (mg) | Ag/Cu mass ratio |
|-----------|---------------|---------------|------------------|
| C-nano-0  | -             | 0             | 0                |
| CA-nano-1 | 30            | 15            | ~0.1             |
| CA-nano-2 | 30            | 30            | ~0.5             |
| CA-nano-3 | 30            | 45            | ~1               |
| CA-nano-4 | 30            | 90            | ~10              |

To perform cation exchange for the Cu sulfides on Cu foil (C-foil-x), AgNO$_3$ was added to OAM with N$_2$ bubbled to the solution in small petri-dish. After the solution was heated to 50°C and well mixed, C-foil-x was placed in the solution and kept for another 30 min. The electrode was then cleaned with ethanol and hexanes and dried with N$_2$ flow. The Ag/Cu sulfides on Cu foil were named CA-foil-x-y with x denoting the current density and y the relative Ag fraction (Table 2). As discussed later, the concentration of Ag$^+$ in the cation exchange solution affected the dispersion of Ag, with uniform distributions being formed at low concentrations and Ag particles nucleating on the surface at high concentrations.

Table 2 Sulfides on Cu foil with electro-oxidation and cation exchange parameters.

| Label         | Current density (mA cm$^{-2}$) | AgNO$_3$ (mg) |
|---------------|-------------------------------|---------------|
| C-foil-10     | 10                            | -             |
| C-foil-20     | 20                            | -             |
| C-foil-30     | 30                            | -             |
| C-foil-40     | 40                            | -             |
| CA-foil-20-10 | 20                            | 10            |
| CA-foil-20-20 | 20                            | 20            |
| CA-foil-20-30 | 20                            | 30            |
| CA-foil-20-40 | 20                            | 40            |
| CA-foil-40-40 | 40                            | 40            |

Electrochemical characterization and product analysis

Electrode preparation and CO$_2$ reduction

For nanosheet samples (C-nano-0 and CA-nano-x), the catalysts were first anchored on carbon black at a 1:1 mass ratio of catalyst to carbon. The catalyst was dispersed in ethanol and water, and Nafion was added as the binder. After sonication, the homogeneous catalyst ink was drop cast on glassy carbon substrates (GC) followed by drying overnight at room temperature. Typically, the catalysts were tested with the loading of 0.6 mg on an electrode area of 0.785 cm$^2$. Sulfides on Cu foil (C-foil-x and CA-foil-x-y) were tested directly without further modification. The CO$_2$ reduction was conducted in a three-electrode system with 0.05 M K$_2$CO$_3$ as the electrolyte and Pt and Ag/AgCl
(saturated KCl) as the reference and counter electrode, respectively. The cathodic and anodic chambers were separated by a cation exchange membrane. CO₂ was purged at 5 sccm to the cathodic chamber, and the test started after 15 min CO₂ purging to ensure complete saturation. We note that the freshly prepared electrodes are not active for CO₂R and initially favour H₂ production. The time evolution of the catalysts and the induced changes in the product profiles under CO₂ electroreduction conditions are thus discussed in detail.

Product detection
The gas products, including H₂, CO, methane, ethylene, and ethane, were detected by online gas chromatography (GC) using methods reported previously. Typically, GC sampling was started 5 min after the test began, and the results were given by the average of the second to the last sample. The electrolyte was collected after each test and analysed by nuclear magnetic resonance (NMR) for liquid products, including formate, methanol, ethanol, n-propanol, and other low-concentration C2+ products such as acetate, glycolaldehyde, allyl alcohol, acetaldehyde, acetone, and propionaldehyde.

Results and discussion
Cu sulfide nanosheets (C-nano-0)
TEM images of C-nano-0 made by colloidal synthesis are presented in Figure 1. The nanosheets have a hexagonal shape with a lateral size of 100 nm and a thickness of 10 nm, as marked in Figures 1a and 1b (side view of stacked nanosheets). As shown in the HRTEM image (Figure 1c), the planes with the spacing of 1.95 Å and a 60° angle in between can be assigned to the (0 16 0) and (0 8 6) planes of monoclinic Cu₇S₄. In addition, the 3.28 Å lattice spacing in the side view HRTEM image matches the (16 0 0) plane (Figure 1d). Some areas exhibit less contrast with no clear lattice; these areas may have a high defect concentration or be amorphous. The nanosheets have a large specific surface area which could be beneficial for catalytic activity.

![TEM characterization of C-nano-0](image)

**Figure 1** TEM characterization of C-nano-0. (a) C-nano-0 has a hexagonal shape with a lateral size of 100 nm. (b) Side-view of a stack of nanosheets, showing the thickness of 10 nm. (c, d) High-resolution TEM (HRTEM) image shows the lattice structure of monoclinic Cu₇S₄.

XPS spectra of C-nano-0 provide information about the surface condition of the nanosheets (Figure S7, 8). The S/Cu atomic ratio was 0.67, slightly higher than the stoichiometric ratio of Cu₇S₄, supporting the Cu₇S₄ lattice structure with a sulfur-rich surface of C-nano-0. Most Cu in the
nanosheets has the valence state of 1+, the deviation of the spectrum may result from the defects in the nanosheets and Cu\(^{2+}\). The existence of N, the peaks at 163 eV in the S\(_{2p}\) spectrum, and the peak at 286 eV in the C\(_{1s}\) spectrum indicate the presence of a small amount of residual ligand-SCN from the precursor CuSCN. It is also possible that OAM is present despite the washing steps designs to remove it; however, prior studies have shown that it does not block active sites for CO\(_2\) electroreduction.

**Bimetallic sulfide nanosheets (CA-nano-x)**

![Figure 2](image)

**Figure 2** Lattice structure, morphology, and composition of sulfide nanosheets. (a) XRD spectra for C-nano-0 and CA-nano-x. Lattice structure evolves from Cu\(_7\)S\(_4\) to Ag\(_2\)S with increased Ag concentration. (b) SEM image for CA-nano-4, nanosheet structure remains with shape distortion. (c) Side-view TEM of stacked CA-nano-2, morphology, also shown in Figure S13a. (d) SEM and EDS mapping shows uniform distribution of Cu, Ag, and S within the nanosheets. (e) HRTEM image of CA-nano-2 shows the lattice structure of Ag\(_2\)S viewed from direction [1 0 0]. (f, g) HRTEM images for the basal surface. Yellow and white marks denote the defect and boundary-rich surface.

The mass ratio of Ag/Cu concentration was well controlled from 0.1 (CA-nano-1) to 10 (CA-nano-4), roughly determined by the EDS results (Figures S9–12). As shown in the XRD spectra (Figure 2a), the crystal structure of the nanosheets undergoes a noticeable change as the Ag concentration increases. Prior to cation exchange, the nanosheets have the crystal structure of Cu\(_7\)S\(_4\) (PDF #23-0958),\(^{38}\) in agreement with TEM. For a small amount of cation exchange (CA-nano-1), the crystal structure remains the same as the C-nano-0 with the most prominent peak in the XRD pattern at
\(\sim 48^\circ\) being assigned to \(\text{Cu}_2\text{S}_4\) (0 1 6 0). At higher Ag concentrations, a shift of the peak near \(\sim 32^\circ\) is observed from the yellow marked position for \(\text{Cu}_2\text{S}_4\) to the purple marked \(\text{Ag}_2\text{S}\) position. The appearance (CA-nano-2) and shift of the peak pointed by the arrow as Ag concentration increases support the gradual structural change. With the ratio of Ag/Cu reaches 10 (CA-nano-4), the structure completely changes to \(\text{Ag}_2\text{S}\), demonstrated by the peak at \(\sim 34^\circ\), which can be assigned to (1 2 1) planes. The morphology also undergoes obvious change with large shape distortion and the nanosheet structure remains (Figure 2b), while with Ag/Cu ratio less than 1, the hexagonal shape remains with only minor changes in shape or thickness (Figure S9–12).

Figure 2c–g show the morphology, elemental distribution, and typical lattice structure of CA-nano-2 (Ag/Cu = 0.5) as determined by SEM and TEM. The morphology uniformity of the nanosheets decreases compared with that before cation exchange (Figure S13a), but the enlarged SEM image with elemental mapping still provides evidence of the uniform distribution of Ag, Cu, and S, without any spatial separation (Figure 2d).

HRTEM images obtained from the side-view demonstrate the existence of crystalline \(\text{Ag}_2\text{S}\). In Figure 2e, observed from direction (1 0 0), the plane with the spacing of 1.77 Å and 2.4 Å can be assigned to the planes (0 4 0) and (0 1 3), respectively. Besides, it shows a composition of small crystals with different facets on the basal surface (Figure 2f, g). The yellow line marks the boundary between two crystals that possess different structures, the white lines show the tilt of the lattice, and the yellow circles mark less-contrast areas indicating defect and amorphous regions. Combined with HRTEM images showing different lattices and the corresponding FFT patterns obtained from CA-nano-2 (Figure S13), one conclusion can be made is that crystal structure becomes more complicated due to the introduction of Ag and that the cation exchange does not have a simple outcome, a single crystal \(\text{Ag}_2\text{S}\) or dominant exposed facets, for instance.

The complicated surface outcome from cation exchange might arise from a number of factors: the hexagonal shape of C-nano-0 triggers cation exchange from the corners and form separate grains connected by grain boundaries; the intrinsic poor crystallinity of the template leads to inconsistent reaction tendencies at different areas; the energy imposed by the low temperature (50°C) for cation exchange is not enough for atoms to move towards the more crystalline structure. Therefore, as expected, CA-nano-2 has a complicated defect and boundary-rich structure.

**Sulfide nanosheets for CO\(_2\) reduction**

SEM analysis shows that the nanosheets were evenly dispersed on porous carbon before CO\(_2\)R (Figure S14). Prior in-situ work with copper oxide pre-catalysts has shown that under CO\(_2\)R conditions, reduction of oxides to metallic Cu occurs prior to the formation of gas phase products. We thus expected that sulfide nanosheets could have a similar behaviour, with the initial current being due to non-faradaic processes as the catalyst is reduced. Therefore, pre-reduction at negative potentials may increase selectivity for CO\(_2\) reduction. Additionally, the pre-reduction may facilitate the removal of the surface ligands -SCN, which might block or change the activity of the catalytic sites. Previous research show such anionic ligands could be removed under negative potentials and may induce reconstruction of the nano-scale catalysts, which further influence the performance. Thus, for a consistent comparison, the electrodes were evaluated in the same potential sequence. All samples were tested for the same 1.5 h duration from the most positive potential (−0.2 V vs. RHE) to the most negative potential (−1.6 V vs. RHE), as shown in Figure 3 where two different cation-exchanged samples CA-nano-2 and CA-nano-4 are evaluated and compared with C-nano-0 control. Cyclic voltammetry (CV) measurements were conducted for the electrodes to show both Ag and Cu in the nanosheets are electrochemical active (Figure S15). It is worth mentioning that the current densities between the three samples are of similar values and trends, such that all catalysts had similar mass transfer limits for CO\(_2\) availability at a given potential (Figure S16).
Interestingly, at −0.2 V vs. RHE, Figure 3a, all nanosheet catalysts produced formate exclusively before the production of other potential 2e\(^-\) products: CO and by-product \(\text{H}_2\) from HER. However, we note that the Faradaic efficiency at −0.2 V vs. RHE cannot be measured precisely since the potentiostat current at this potential, ~0.01 mA, is very small. Also, the larger current measured at the beginning of a run due to the non-Faradic reduction of the catalyst surface sulfide or oxide layers, where not all the electrons were used for the formation of electrocatalytic CO\(_2\) reduction products, can lead to inaccuracy, especially for small negative potential regions, where large current fluctuations were observed as shown by the error bars (Figure 3b). To assess whether formate was made just at the start or throughout the run, we tested CA-nano-2 again at −0.2 V vs. RHE after the electrode has been tested at more negative potentials (Figure S17). Formate was still the only product detected, although the initial current density was smaller compared with as-synthesized material. One explanation is the initial current was from the reduction of the surface oxidation layer formed in the environment after the previous test instead of the reduction of the catalyst as for fresh electrode.\(^{43}\) Formate was also the only product detected at −0.1 V and −0.3 V vs. RHE for nanosheets (Figure S18).

For all nanosheets, \(\text{H}_2\) appears as a product at −0.4 V vs. RHE. At larger negative potentials its FE decreases and FE for formate increases. For C-nano-0, CO appears at −1.0 V vs. RHE (FE\(_{\text{CO}}\) = 6%). C2+ products, including ethylene, ethanol, and C3 products like n-propanol, appear at −1.0 V vs. RHE in trace amounts and dominate at −1.2 V vs. RHE with the ratio of C2+ to C1 products of 3.51. This ratio further increases when a more negative potential is applied, 7.57 and 8.19 for −1.4 V and −1.6 V vs. RHE, respectively (Figure 3c). However, this increase comes from the decrease of formate.
and methane, rather than increased production in C2+ products, and an increase in H2 production is also clearly shown since −1.0 V vs. RHE (Figure S19).

CA-nano-2 starts to produce noticeable C2+ products, including ethylene (10%), ethanol (4%), and n-propanol (3%) at −1.0 V vs. RHE, more positive than for C-nano-0. Also, the overall CO2 reduction products dominate at −1.4 V vs. RHE (77.7%), which is shifted from −1.2 V for C-nano-0; this may be attributed to better HER suppression at more negative potentials as a result of the Ag content.18 For CA-nano-2 at −1.4 V vs RHE, the Faradaic efficiency for C2+ products is 68.6%, and the ratio of C2+ over C1 products is 7.53. The C2+/C1 ratio is similar to that of the control (Figure 3c), but with a smaller FE for H2. The introduction of Ag leads to an increase in CO production compare to the control, with the maximum FE reached −1.0 V vs. RHE. When a more negative potential is applied, the FE for CO decreases, which could be a result of CO diffusion to Cu where it is further reduced to C2+ products.8 At −1.6 V vs. RHE, where Ag has less contribution to reducing CO2 to CO but instead increases HER, methane becomes the dominant product.44

For CA-nano-4, where Ag/Cu ratio is 10, CO production from Ag becomes the primary product, especially at −1.2 V vs. RHE (53%), much higher than that of CA-nano-2 (8%). Also, methane is a dominant product at negative potentials (25% at −1.4 V vs. RHE). One explanation for the large increase in C1 products might be that the increased concentration of Ag breaks up the continuous Cu surface, making the CO-CO binding difficult.45 Thus, instead of making C2 products like ethylene and ethanol, conversion of the CO intermediate forms methane. Indeed, for this catalyst, the highest C2+/C1 ratio was only 1.33 (Figure 3c). Similar to the other nanosheet samples, with more negative potential applied, H2 became the dominant product, which also caused a decrease in the current density for overall CO2 reduction at −1.6 V vs. RHE where more surface has been occupied by the H absorbent for H2, instead of performing CO2 reduction.

Sulfides on Cu foil. (C-foil-x and CA-foil-x-y)

For bimetallic sulfides on Cu foil, the crystal size of the Cu sulfide template (C-foil-x, x denoting current density, Table 2) can be controlled by the current density during the electro-oxidation process. Larger and more defined grains are produced at higher current densities (Figure 4a). For cation-exchanged samples (CA-foil-x-y), the Ag/Cu mass ratio increases as more Ag precursor is added during the cation exchange (Figure S20). With lower Ag concentrations (CA-foil-20-10), the Ag and S were uniformly distributed across the surface. (Figure 4b, c). SEM image from the side view indicates the thickness of 10s of microns, consistent with the calculated modified Cu thickness (Figure 4d, SEI). Also, compared with C-foil-20, the surface of the cation-exchanged counterpart CA-foil-20-10 transformed into a rippled structure composed of finer grains, with empty spaces between layers, demonstrated by zoomed-in images, that might be beneficial for the transport of reactants and products (Figure 4e, f). However, with further increased Ag precursor AgNO3, Ag nucleation on the surface through the reduction of Ag+ to metallic Ag instead of exchanging Cu+ can be observed (CA-foil-20-40). Ag concentration at the newly merged flower-like flakes is clearly shown in Figure 4g and Figure S21. When the particle size of Cu sulfides was too large (C-foil-40), the cation-exchanged counterpart CA-foil-40-40 with enough Ag precursor (40 mg) grow into a triangle structure (Figure S22).
Evolution of sulfide catalysts during the CO₂ reduction

Bimetallic sulfides on Cu foil (CA-foil-x-y) with a variety of Ag concentrations were tested in the potential range from −0.8 V to −1.4 V vs. RHE. If considering ethylene as the target product, CA-foil-20-40 with high surface Ag concentration at −1.2 V vs. RHE gave the best performance (FEethylene = 34%, Figure 5a, S23). However, results of different runs show large variations in terms of both FE and current density, with selectivity to ethylene and liquid C2+ products initially improving and then declining (3 tests at −1.0 V vs. RHE and then 3 at −1.2 V vs. RHE, Figure S24). The morphology after reduction also shows obvious change from the fresh sample, which may come from the reaction between active surface and the reactant and intermediates (Figure 5b).

To further investigate this performance change, as-synthesized CA-foil-20-40 was directly tested at −1.0 V vs. RHE for 16 h. The current was in the range of 8–12 mA cm⁻² during the test, Figure S25. Faradaic efficiency for the gas products is plotted in Figure 5c. CO was the first gas product of CO₂ reduction to be observed and reaches a maximum in FE at 2 hours. Ethylene and methane increased with the consumption of CO, and FE for ethylene rose from 0% at first to 17% at 8 h. As the plot
shows, the product profile undergoes continuous change during CO$_2$ reduction, with the optimal working region for ethylene being between 6 to 10 h.

![Sulfides on Cu foil](image)

**Figure 5** Evolution of catalysts and corresponding products change during CO$_2$ reduction. (a) Faradaic efficiency plot for CA-foil-20-40 at $-1.2$ V vs. RHE. Morphology of CA-foil-20-40 after CO$_2$ reduction. Corresponding current plot is in Figure S23. (c) Faradaic efficiency for gas products. Sample: CA-foil-20-40. Test condition: $-1.0$ V vs. RHE for 16 h. Corresponding current plot is in Figure S25. (d) SEM image of CA-foil-20-40 after test. (e) Comparison of sulfide nanosheet CA-nano-0 and C-nano-2 between directly tested at $-1.4$ V vs. RHE (left bar plot) and tested after pre-reduction at other negative potentials (right bar plot). (f) Faradaic efficiency for gas products. Sample: CA-nano-4. Test condition: $-1.4$ V vs. RHE for 13 h. Corresponding current plot is in Figure S28. (g) SEM image of CA-nano-4 after test.

The evolution of the catalyst surface may explain the performance change. **Figure 5d** is the SEM image of the catalyst after the 16 h reduction. The surface morphology changes from the particle shape into the nest structure composed of filaments with a diameter of ~20 nm, which appears to have a higher surface area compared with the fresh sample. The increased roughness of the catalyst during the CO$_2$ reduction might be one reason for the change of gas product distribution since the nest composed of the 1D filament structure possesses both high surface area and good electrical conductivity derived from the interconnected nature and structural stability compared with nanoparticle counterparts.

C-foil-x also undergoes similar morphology change under CO$_2$R condition, with smaller grains (C-foil-10), the surface evolved into nest structure composed of filaments (diameter: 40 nm). The time evolution of the catalyst is also influenced by the particle size of Cu sulfides on Cu foil, as the grain size increases as a higher current applied in the electro-oxidation step, the nest structure evolved from CO$_2$R that possess high roughness and sufficient gas pathway, which might be beneficial gradually disappears and is replaced by large particles (Figure S26). According to the research on oxide-derived copper, the surface copper oxide may be reduced to metallic copper under negative potential, while other groups have reported that the residual underlying oxygen is beneficial for
The sulfides on Cu foil may also go through a similar process, but will eventually be depleted such that the catalyst will be metallic copper, thus the depletion of sulfur may result in the evolution of morphology and performance.

Besides, as previously mentioned, for sulfides on the Cu foil electrode, there is a limit for the introduction of Ag because the cation exchange of Cu\(^+\) by Ag\(^+\) competes with the direct nucleation on the electrode surface. Thus, in order to create an Ag-rich surface by other means, we deposited 100 nm Ag by an E-beam evaporator onto the Cu sulfides layer. However, when tested at −1.1 V vs. RHE, the potential most beneficial for Ag foil to produce CO,\(^{48}\) the morphology change from the flat overlayer to more complex nest structures during the CO\(_2\) reduction still occurred and exposed the underlying Cu sites. As result, the product distribution was very different from that expected from a Ag-rich surface.\(^{49}\) (Figure S27).

**Activation of cation-exchanged nanosheets**

For CA-nano-x nanosheets, when put directly under CO\(_2\) reduction conditions, the performance is far from ideal. Thus we tried to employ pre-reduction under other negative potentials as an activation method to improve CO\(_2\)R selectivity. As shown in Figure 5e, freshly prepared C-nano-0 and CA-nano-2 were directly placed at −1.4 V vs. RHE, and the results are compared with that after pre-reduction at other negative potentials. For direct, much more H\(_2\) was produced compared with the pre-reduced electrode results, the FE for H\(_2\) was 76% for CA-nano-0 and 39% for C-nano-2, while for pre-reduced samples, the number was only 50% and 30%, respectively. The product distribution of CO\(_2\) reduction also varies from the pre-reduced electrodes. For example, for fresh C-nano-0, the major CO\(_2\) reduction products are C1 species, including formate (10%) and methane (6%). In contrast, when the sample was tested at the same potential after pre-reduction, there were mainly C2+ products. The situation was similar for cation exchanged nanosheets. The total FE for C2+ products for fresh CA-nano-2 was 38.02%, only half the C2+ products observed for the pre-reduced electrode (69%).

After CO\(_2\) reduction, as expected, the adjacent nanosheets were evolved into a filament structure with a diameter of ~100 nm, similar to the diameter of the synthesized nanosheets, and the product profile changes accordingly (Figure 5f, g). The change might be related to the surface ligands, which may affect electrochemical behavior and the stability of nanomaterials, yet more characterizations need to be done to confirm this.\(^{41,50,51}\) Additionally, for C-nano-0, the Cu transformed into large clusters (~500 nm, Figure S29), different from the filament structure of CA-nano-2. This might come from the difference in the CO/CO\(_2\) binding energy on Cu and Ag.\(^{52}\) With higher binding energy between the Cu and CO/CO\(_2\) facilitate the mobility of the anchored Cu, thus resulting in the aggregation. However, the Ag added to the system in the CA-nano-2 products has smaller binding energy with CO/CO\(_2\) and confined the mobility, and the spatial separation of the nanosheets prevents further agglomeration.

**Conclusions**

We have demonstrated that Cu sulfides can be used as a template for cation exchange to achieve bimetallic Ag/Cu sulfide catalysts with a well-controlled Ag/Cu mass ratio by changing the concentration of Ag precursor AgNO\(_3\). For nanosheets, the Ag/Cu ratio can reach 10 with the nanosheet structure remaining, while it is difficult to produce an Ag-rich surface beginning with sulfides on Cu foil. Formate was the only product detected at small negative potentials (~0.2 V vs. RHE), and with the introduction of moderate Ag, nanosheet catalysts showed increased C2+ product generation for CO\(_2\) reduction. The product profiles appear to be influenced by CO availability controlled by Ag concentration, suggesting a possible tandem catalytic mechanism. The reconstruction of the catalyst during CO\(_2\) reduction increased the production of multi-carbon products.
The cation exchange method can be further applied to other bimetallic or trimetallic chalcogenides like phase segregated Cu-Au sulfides, Cu-Ni selenides, Cu-Co sulfides nanoboxes, and CuInS2-doped ZnS, and could potentially be used for multifunctional photo/electrocatalysis. With modifications of ligands or additives during the cation exchange method, may realize the control of even vs. uneven distribution of two elements with the same overall concentration that can be employed as a great test field for mechanism investigation.

**Conflicts of interest**

There are no conflicts to declare.

**Author contributions**

Jinghan Li and JWA conceptualized the study, and JWA acquired funding for it. Jinghan Li and Junrui Li developed synthesis methodology and analytical chemistry methods. Jinghan Li performed all syntheses and conducted the electrochemical, XRD, XPS, and SEM characterization and data interpretation. Chaochao Dun performed TEM characterization using funding acquired by Jeffrey J. Urban. Di Zhang and Jiajun Gu provided advice on data analysis and mentorship. Jinghan Li and JWA wrote the original draft of the manuscript and all authors contributed to its final editing.

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Copper sulfide as the cation exchange template of bimetallic catalysts for CO$_2$ electroreduction

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Synthesis methods

Materials
Potassium carbonate (99.995% metals basis), nitric acid (70%), hydrochloric acid (37%), silver nitrate (99%), sodium hydroxide (98%), ammonium hydroxide solution (30%), sodium sulfate decahydrate (99%), oleylamine (70%), hexanes (98%), ethanol (100%), copper (I) thiocyanate (99%) were purchased from Sigma-Aldrich. Carbon black was purchased from AkzoNobel. Selemion AMV cation exchange membranes were purchased from Asahi Glass Co., Ltd. Substrates used here were carbon paper (Sigracet 39 BB, FuelCellStore), carbon cloth (WOS1009, Phychemi), glassy carbon plate (type 2, Alfa Aesar), and Cu foil (99.999%, Alfa Aesar). 18.2 MΩ deionized (DI) water was produced by a Millipore system. The solutions mentioned in this paper are aqueous if there is no specific description. All chemicals were used without further purification. Carbon dioxide (99.999%), argon (99.999%), and hydrogen (99.999%) were purchased from Praxair and used for electrochemical tests and gas chromatography.

Colloidal synthesis for Cu sulfide nanosheets (C-nano-0)
The Cu sulfide nanosheets (C-nano-0) were synthesized through the process modified from a previously reported recipe.1,2 Specifically, 257 mg copper(I) thiocyanate (CuSCN) was dispersed in 25 mL oleylamine (OAM). The mixture was degassed at room temperature for 10 min. The flask was then heated to 100°C (5°C min⁻¹), then degassed for another 10 min. After that, N₂ was added to the flask before the temperature raised at the speed of 5°C min⁻¹ until 240°C, and held for another 30 min. The synthesized nanosheets were then transferred with hexane from the flask to centrifuge tubes and were cleaned with ethanol (added to the hexanes dispersion for centrifuge), and hexanes (for redispersion of nanosheets with sonication) 3 times (8000 rpm, 5 min). The nanosheets were then dispersed in hexanes, and the concentration of the hexane dispersion was determined by weighing the mass of a small volume of the dispersion after hexanes evaporated. The dispersion was sonicated for 10 min before use.

Synthesis of Cu(OH)₂ on Cu foil
Two methods have been used to grow Cu(OH)₂ on Cu foil: (1) electro-oxidation and (2) chemical oxidation.4 Cu foil was first cleaned and etched by sonication in 4 M HCl for 15 min, rinsed with DI water, and dried under N₂ flow. The electro-oxidation was conducted in a two-electrode system, where the Cu foil was used as the working electrode, Pt as the counter electrode, and 1 M NaOH as the electrolyte. For chemical oxidation, the Cu foil was immersed into 0.33 M ammonium hydroxide for 3 to 24 h, rinsed with DI water, and dried under N₂ flow.

Synthesis of Cu(OH)₂ on the carbon substrate
The Cu(OH)₂ on the carbon substrate was prepared with a modified electro-oxidation method.3 The carbon paper or carbon cloth was first cleaned with sonication, 15 min in 1 M HNO₃ followed by 15 min in DI water, then dried with N₂ flow. 50 nm layer of Cu was deposited on each side using an e-beam evaporation system (Angstrom Engineering Inc., Nexdep). The region other than the testing area was sheltered to block the deposition. The electro-oxidation method used is similar to that used for Cu foil.

Sulfurization for Cu sulfides on Cu foil (C-foil-x)
The Cu(OH)₂ electrode was cut into a 2 cm × 2 cm square and was immersed in 0.1 M Na₂S at 90°C for 12 h. The electrode was taken out from the Teflon reactor after the temperature decreased to room temperature. The electrode was dried under N₂ flow after thoroughly rinsing with DI water.
Cation exchange for bimetallic sulfides

The bimetallic sulfide nanosheets (CA-nano-x) were obtained by a cation exchange method. The previous prepared hexanes dispersion of C-nano-0 was used for cation exchange and the volume added was calculated from the concentration. Typically, the dispersion containing 30 mg C-nano-0 was added to 7 mL OAM, Ag precursor silver nitrate (AgNO₃) was then added to the mixture (Table 1 in the main text for sample nomenclature). The solution was degassed and distilled (hexanes) at room temperature for 20 min, the temperature was then increased to 50°C, and N₂ was added back to the flask. The flask was then kept at 50 °C for another 30 min. The nanosheets were then cleaned with the same process as C-nano-0. For bimetallic sulfides on Cu foil (CA-foil-x-y), the AgNO₃ was first added to 7 mL OAM in a small petri-dish, N₂ gas was bubbled into the solution for 10 min before the temperature is raised to 50°C, the electrode was then put into the dish, and shake for another 30 min. The electrode was then taken out and sonicated in hexanes for 15 min, and ethanol for another 15 min, and dried under N₂ flow.

The estimation of thickness for modified surface layer on Cu foil

The number was estimated assuming all the electrons in electro-oxidation contributed to the formation of Cu(OH)₂, specifically, one atom of Cu⁺ achieved from Cu counts one electron. The calculation here is for CA-foil-20-y/C-foil-20, with the electro-oxidation at a current density of 20 mA cm⁻² for 30 min to obtain Cu(OH)₂ layer, based on the parameters below.

The density of Cu: 8.92 g cm⁻³, molar mass: 63.546 g mol⁻¹.

Thus, \( \frac{63.546 \text{ g mol}^{-1}}{8.92 \text{ g cm}^{-3}} = 7.124 \text{ cm}^2 \text{ mol}^{-1} \)

Total electrons consumed:

\[ 20 \text{ mA cm}^{-2} \times 30 \text{ min} \times 2 \text{ cm} \times 2 \text{ cm} = 144 \text{ C} = 8.99 \times 10^{20} \text{ electrons} = 0.00149 \text{ mol electrons}. \]

That means the volume of Cu modified:

\[ 0.00149 \text{ mol} \times 7.124 \text{ cm}^2 \text{ mol}^{-1} = 0.0106 \text{ cm}^3 \]

The thickness was obtained by the volume divided by the total area of both sides of the Cu foil. \( \frac{0.0106 \text{ cm}^3}{8 \text{ cm}^2} \approx 13.25 \mu \text{m} \)

Electrochemical measurement details

Electrode preparation for nanosheet samples (C-nano-0 and CA-nano-x)

The nanosheets samples were first mixed with carbon black (mass ratio, 1:1) and then drop cast on the glassy carbon plate. To anchor catalysts on carbon, the carbon black was first dispersed in hexanes and sonicated for 30 min to reach a homogenous suspension. The catalyst dispersion was then added in drops to the carbon suspension under sonication. The mixed solution was sonicated for another 30 min. The catalyst was then washed and centrifuged with ethanol (8000 rpm, 5 min) for 3 times. The catalyst-carbon mix was then ground before use. For catalyst ink, typically, 60 mL of Nafion solution (5 wt.%, DuPont Co.) was added into 1 mL catalyst suspension that contains 3 mg catalyst (volumetric ratio of ethanol/water is 3:1). The electrode was dried overnight at room temperature. The absence of ethanol detected at ~0.2 V vs. RHE demonstrates no ethanol contaminants exist before CO₂ reduction.

Electrochemical measurements

The Biologic SP-300 potentiostat was used for electrochemical analysis. The CO₂ reduction was carried out in 0.05 M K₂CO₃ using a three-electrode system with Ag/AgCl (saturated KCl) as reference and Pt plate as the counter electrode. The working electrode and counter electrode with an area of 0.785 cm² were placed facing each other in the cathodic and anodic chamber (2.4 mL electrolyte in each), respectively, separated by the cation exchange membrane. The CO₂ gas was purged at 5 sccm to the cathodic chamber, and the test started after 15 min purging when the solution was saturated with CO₂.

The potential was converted to the RHE scale using the following equation:
$E_{\text{vs. RHE}} = E_{\text{vs. Ag/AgCl}} + 0.197 \, \text{V} + 0.0591 \times \text{pH}$

85% of solution resistance was corrected during the electrochemical experiments.

**Products analysis**

All gas products including H₂, CO, methane, ethylene, ethane, were detected by MG#3 Gas Chromatography from SRI Instruments, equipped with a 12” long HaySep D column and Ar as the carrier gas. H₂ was detected by a TCD detector, others were detected by an FID equipped with a methanizer. The outlet of the electrochemical cell was linked to the GC during the whole run, and for a typical 1.5 h test, 6 results can be obtained, and the average of the last 5 runs gives the gas product results. The GC was calibrated with 3 calibration gas cylinders with different concentrations.

All liquid products were detected by NMR (Bruker Avance III 500 MHz). Typically, 700 mL of electrolyte, containing CO₂ reduction products, were mixed with 35 mL internal standard solution: 10 mM dimethyl sulfoxide (DMSO) and 50 mM phenol in D₂O. The products were analyzed mainly according to a well-organized table in the reference.

The Faradaic efficiency (FE) for each product was calculated by $FE = \frac{znF}{Q}$, where $z$ is the number of exchanged electrons, $n$ is the moles of the product produces, $F$ is the Faraday constant, $Q$ is the charge passed.

**Supplemental catalyst characterization and CO₂ reduction performance**

**Cu(OH)₂ on the carbon substrate**

Cu(OH)₂ grown on the carbon paper have a nanosheet structure, however not uniformly distributed because of the shadowing effect during Cu deposition, the randomly aligned nanofibers, and the uneven soaking of the electrolyte of carbon paper. The electro-oxidation process was conducted in 1 M NaOH, at the current density of 10 mA cm⁻² for 5 min.

![Figure S1 SEM images of Cu(OH)₂ on the carbon paper obtained by the electro-oxidation method.](image)

To have more control on the Cu(OH)₂ distribution, carbon cloth composed with aligned nanofibers was used as the carbon substrate. Small current density achieves large thin nanosheets, while larger current density achieves small thick sheets.

![Figure S2 SEM images of Cu(OH)₂ on the carbon cloth obtained by the electro-oxidation method. (a, b) were obtained with the current density of 1.25 mA cm⁻² for 10 min; (c, d) were obtained with the current density of 2.5 mA cm⁻² for 10 min.](image)

However, after the sulfurization process, most of the Cu-containing nanosheets detached from the carbon fibers because of the weak binding between the deposited copper and the carbon fibers as well as the harsh sulfurization condition.
Figure S3 Cu(OH)$_2$ on carbon cloth after sulfurization.

Cu(OH)$_2$ on Cu foil by chemical oxidation
Considering the detachment of Cu-containing nanosheets from the carbon substrate during the sulfurization, chemical oxidation directly on Cu foil substrate was tried.

Figure S4 Cu(OH)$_2$ grown on Cu foil by chemical oxidation. The deposition time from (a) to (d) is 3 h, 6 h, 9 h, and 24 h, respectively.

Figure S5 Cu(OH)$_2$ grown on Cu foil after chemical oxidation for 9 h.
After sulfurization, the Cu sulfide nanosheets can be clearly seen from the SEM images; however, the nanosheets tend to gather instead of uniformly distribute through the whole surface.

Figure S6 Cu sulfides on Cu foil obtained by hydrothermal sulfurization from chemical oxidation derived Cu(OH)$_2$. (a, b) were from Cu(OH)$_2$ obtained by 9 h chemical oxidation. (c, d) were from 24 h chemical oxidation.
Cu sulfide nanosheets (C-nano-0)

**Figure S7** Full XPS spectrum of C-nano-0. The S/Cu atomic ratio (0.67) was determined from the Cu 2p and S 2p peak areas with appropriate sensitivity factors.

**Figure S8** High-resolution XPS spectra of Cu 2p, S 2p, C 1s, and N 1s for C-nano-0. The existence of N, the doublet at 163 eV in the S 2p spectrum, and the peak at 286 eV in the C 1s spectrum indicate a small amount of residual ligand -SCN from the precursor CuSCN.

Bimetallic sulfide nanosheets (CA-nano-x)

SEM images and the Ag/Cu mass ratio obtained from EDS data demonstrated successful replacement of Cu with Ag during the cation exchange process (Figures S9–12). For nanosheets with ultra-high Ag concentration (CA-nano-4), the regular hexagonal shape distorted to irregular ones with the nanosheet structure remains. The Ag/Cu ratios ranging from ~0.1 to ~10 obtained from EDS results are provided in the figure captions. HRTEM images and corresponding FFT patterns of basal planes show that crystal structure becomes more complex after cation exchange.
**Figure S9** Morphology and composition of CA-nano-1. Ag/Cu ratio is ~0.1. (a, b) SEM images. (c) EDS spectrum. (d) SEM images with elemental mapping.

**Figure S10** Morphology and composition of CA-nano-2. Ag/Cu ratio is ~0.5. (a) SEM image. (b) EDS spectrum. (c) SEM image with elemental mapping.

**Figure S11** Morphology and composition of CA-nano-3. Ag/Cu ratio is ~1. (a, b) SEM images. (c) EDS spectrum.
Figure S12 Morphology and composition of CA-nano-4. Ag/Cu ratio is \( \sim 10 \). (a) SEM image with elemental mapping. (b, c) EDS spectra show uniform distribution.

Figure S13 Characterization of CA-nano-2 nanosheets. (a) TEM images. HRTEM images (b, d, f) and corresponding FFT patterns (c, e, g) of basal planes show each nanosheet may contain several small crystals with completely different exposed facets or even composition, although the shape does not vary much.

Nanosheets anchored on carbon substrate for tests

Figure S14 Morphology of C-nano-0 nanosheets and their uniform distribution on porous carbon. (a) SEM image for C-nano-0 nanosheets. (b) SEM image for C-nano-0 dispersed on carbon black.
Figure S15 CV plot for CA-nano-2 compared with C-nano-0 control. The curves suggest both Cu and Ag are catalytically active for bimetallic nanosheets. Sweeping speed: 10 mV s$^{-1}$.

Figure S16 Chronoamperometry (CA) plot of sulfide nanosheet with applied potential in the range from $-0.2$ V to $-1.6$ V vs. RHE.

Figure S17 Current density for nanosheet samples at $-0.2$ V vs. RHE. CA-nano-2 second time represents the electrode tested at $-0.2$ V vs. RHE after previously tested at more negative potentials.

Figure S18 Current density for sulfide nanosheets at small negative potentials. Inset: Faradaic efficiency plot, the only product detected was formate, although the Faradaic efficiency may not be the accurate number due to testing limit.
Cation exchange for bimetallic sulfides on Cu foil (CA-foil-x-y)

Ag concentration can be well controlled by the amount of Ag precursor AgNO\textsubscript{3} added. With a low concentration in OAM, Cu can be uniformly exchanged by Ag throughout the electrode. As the precursor increased, Ag nucleation started to appear, see the bright spot in Figure S20c. Since the Cu foil can also contribute to the Cu concentration in the EDS result, no quantitative Ag/Cu mass ratio is provided. However, the comparison between areas of Cu and Ag peaks in EDS results still demonstrates the control.

Figure S20 Morphology and elemental concentration of CA-foil-x-y. The Ag precursor AgNO\textsubscript{3} added for (a) to (c) was 10, 20, 30 mg, respectively.

The extra silver added during cation exchange resulted in Ag nucleation on the surface.

Figure S21 Morphology of CA-foil-20-40 as-synthesized.
Figure S22 Morphology of Cu sulfides on Cu foil C-foil-40 (a, b), and its cation exchanged counterpart CA-foil-40-40 (c, d) when the original particle size was large (100 nm).

Catalyst evolution and corresponding performance change

Figure S23 (a) Current density plot of CA-foil-20-40 at −1.2 V vs. RHE. (b) Morphology of CA-foil-20-40 after CO₂ reduction.

Figure S24 Product profile changes with the testing sequence. FE and current density bar plots for CA-foil-20-40. The columns in the plot represent different tests with the testing sequence from left to right.

Figure S25 Current density plot of CA-foil-20-40 for 16 h CO₂ reduction at −1.0 V vs. RHE.
Figure S26 Morphology of C-foil-x after CO$_2$ reduction.

Figure S27 CO$_2$ reduction performance at −1.1 V vs. RHE (FE and current density bar plots) for C-foil-20 and Cu foil with 100 nm deposited Ag layer on top.

Figure S28 Current density plot of CA-nano-4 for 13 h CO$_2$ reduction at −1.4 V vs. RHE.
Figure S29  Morphology of nanosheets samples anchored on carbon after CO$_2$ reduction. SEM images for CA-nano-4 (a, b) and C-nano-0 (c) after CO$_2$ reduction.

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