Solar reduction of carbon dioxide on copper-tin electrocatalysts with energy conversion efficiency near 20%

Copper catalysts modified with tin have been demonstrated to be selective for the electroreduction of carbon dioxide to carbon monoxide. However, such catalysts require the precise control of tin loading amount. Here, we develop a copper/tin-oxide catalyst with dominant tin oxide surface being formed via a spontaneous exchange reaction between sputtered tin and copper oxide. Even though the surface of this catalyst is tin-rich, it achieves an excellent performance towards carbon monoxide production in a flow cell. This contrasts with copper/tin-oxide prepared via atomic layer deposition since it yields selectivity to carbon monoxide on a copper-rich surface. Mechanism studies reveal that the tin sites on the tin-rich copper/tin-oxide surface achieve a suitable binding with adsorbed carbon monoxide under the presence of copper. Powered by a triple-junction solar cell, the copper/tin-oxide based electrolyzer sets a new benchmark solar-to-chemical energy conversion efficiency of 19.9 percent with a Faradaic efficiency of 98.9 percent towards carbon monoxide under simulated standard air mass 1.5 global illumination.
work (CuO-SnO$_2$ ALD). In order to avoid this unwanted change in selectivity towards HCOO formation, the thickness of the SnO$_2$ overlayer has to be less than 2.7 nm.

Here, we develop a new Cu-SnO$_2$ catalyst where the SnO$_2$ species are formed via spontaneous exchange reaction (SER) between CuO substrate and sputtered Sn particles (Cu-SnO$_2$ SER). In spite of its Sn-rich nature as evidenced by X-ray photoelectron spectroscopy (XPS) and lead underpotential deposition (Pb UPD), Cu-SnO$_2$ SER achieves nearly exclusive production of CO with the thickness of the Sn overlayer varying from 40 to 160 nm. Using X-ray absorption spectroscopy (XAS), electrochemical analysis and CO adsorption/stripping experiments, we reveal that the Cu-regulated SnO$_2$ SER sites have a suitable binding for forming C-bound CO species, rendering its selectivity and activity for CO generation. Finally, we directly wire a III-V InGaP$_2$/InGaAs/Ge triple-junction solar cell to a custom-built two-electrode flow electrolyzer, setting a new record for solar-to-CO energy conversion efficiency.

**Results**

**Synthesis and characterization of CuO, CuO-SnO$_2$ SER and CuO-SnO$_2$ ALD**

CuO nanowires (NWs) were prepared by electrochemical anodization of a Cu film supported on a gas diffusion electrode (GDE) in 3 M KOH, followed by annealing at 150 °C for 1 h under ambient condition (Fig. 1a)\textsuperscript{19}. Metallic Sn with expected thickness of 60 nm was then sputtered onto CuO NWs. The spontaneous oxygen transfer from CuO to metallic Sn leads to the formation of SnO$_2$ (Supplementary Note 1) and the sample is denoted as CuO-SnO$_2$ SER. On the other hand, ultrathin layers of SnO$_2$ were coated onto CuO via atomic layer deposition for the preparation of CuO-SnO$_2$ ALD. Three samples...
including CuO, CuO-SnO2 SER and CuO-SnO2 ALD were characterized by X-ray diffraction (XRD), XPS, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) (Fig. 1b-i).

To avoid the interference from GDE, XRD of three samples that deposited on glass was performed (Fig. 1b). For all three samples, XRD reveals the existence of CuO. The detected peaks for metallic Cu are partially attributed to the underlying electrode sputter. CuO-SnO2 SER exhibits visible peaks at 2θ = 30.8°, 32.9° and 44.9° that are assigned to diffractions from Sn(200), Sn(101) and Sn(211) facets, respectively (Fig. 1b). CuO-SnO2 ALD shows no other peak than those from the diffractions of CuO and Cu even if the number of cycles for ALD was increased to 300 (Fig. 1b and Supplementary Fig. 1), indicating that the SnO2 layer prepared by the ALD is amorphous. The XRD patterns of all the samples prepared on the GDE are also provided in Supplementary Fig. 1.

As expected, CuO shows a Cu 2p peak at 934.1 eV in the XPS spectrum, representing its dominant Cu(II) species (Supplementary Fig. 2). CuO-SnO2 SER shows Cu(0) 2p peaks at 932.6 and 952.3 eV as well as two intense peaks at 486.6 and 495.0 eV for Sn(IV) 3d5/2 and 3d3/2, respectively (Fig. 1c). This demonstrates that the spontaneous reaction between CuO and Sn leads to the formation of SnO2 with trace amount of metallic Sn remaining. Note that the possible atmospheric oxidation of the sample surface was minimized by immediately vacuum packing after sputtering. CuO-SnO2 ALD shows only Sn(IV) 3d5/2 and 3d3/2 at 486.7 and 495.1 eV, respectively, confirming the purity of Sn (IV) prepared by ALD (Fig. 1c and Supplementary Fig. 2). XPS survey spectra of three samples are shown in Supplementary Fig. 2.

SEM reveals a nanowire structure of CuO with diameters of 200–400 nm and lengths of several micrometers (SupplementaryFig. 3). Nanoparticles with sizes of 60–90 nm are observed on the surface of CuO-SnO2 SER (Fig. 1d). The high-angle annular dark field (HAADF) image and energy dispersive X-ray (EDX) spectroscopic mapping of CuO-SnO2 SER show a mixture of Cu/CuO and Sn/SnO2 particles on the sample surface (Supplementary Fig. 4), visualizing the oxygen exchange between Sn and CuO. For CuO-SnO2 ALD, a 5-cycle ALD SnO2 coating is invisible under SEM (Fig. 1e), while HAADF-EDX mapping, high resolution (HR)TEM images and SEM-EDX mapping demonstrate the distribution of SnO2 on the surface of CuO NWs (Supplementary Figs. 5-7). The thickness of SnO2 with 5-ALD-cycle is estimated to be 1.35 nm by a linear fitting between thickness and number of ALD cycles (Supplementary Figs. 8-9).

Change of morphology and chemical composition after electrochemical reduction

The three samples were pre-reduced at a constant geometric current density of –30 mA cm−2 for ~100 s in a custom-designed flow cell with 0.5 M KHCO3 and CO2 being separately infused at flow rates of 0.25 and 20 cm3 min−1, respectively (Supplementary Fig. 10). They were then characterized by XRD, XPS, SEM, TEM and EDX.

For all three samples, disappearance of XRD peaks from CuO demonstrates the reduction of CuO substrate to Cu (Fig. 1b and Supplementary Fig. 11). Thus, the three samples after pre-reduction are denoted as Cu, Cu-SnO2 SER and Cu-SnO2 ALD afterwards. No alloy phase is observed by XRD on either Cu-SnO2 SER or Cu-SnO2 ALD.

High-resolution XPS spectrum of Cu shows dominant metallic Cu features for Cu-SnO2 SER and Cu-SnO2 ALD (Fig. 1c). Sn(IV) 3d peaks for Cu-SnO2 SER remain almost identical with the ones of CuO-SnO2 SER. However, the binding energy of Sn(IV) 3d peaks on Cu-SnO2 ALD surface is 0.4 eV lower as compared to CuO-SnO2 ALD, which is attributed to the partial reduction of Sn4+ to Sn2+. The persistence of SnOx species on both samples is consistent with previous reports. According to our XPS analysis, Cu-SnO2 SER Shows a Sn-rich surface with a Sn-to-Cu ratio of 58:42, while the ratio on Cu-SnO2 ALD surface is around 10:90 (Supplementary Table 1). This is consistent with Pb UPD measurement, showing a 7-fold decrease in the number of Cu active sites on Cu-SnO2 SER as compared to Cu (Supplementary Fig. 12 and Table 2).

CuNWs reconstruct into flakes after pre-reduction (Supplementary Fig. 11), resulting in a highly rough surface (Supplementary Fig. 13 and Supplementary Table 3). For Cu-SnO2 SER Catalyst, Sn/SnO2 nanoparticles remain on the surface of Cu NWs (Fig. 1f). For Cu-SnO2 ALD, SnO2 nanoparticles with size of around 10 nm are dispersed on the surface (Fig. 1g). SEM-EDX analysis reveals that the bulk concentration of Sn remains unchanged on both catalysts after pre-reduction (Supplementary Fig. 14).

HRTEM images and the selected area electron diffraction patterns show lattice fringe of 0.294 nm that is assigned to metallic Sn(200) on Cu-SnO2 SER (Fig. 1h and i and Supplementary Fig. 15). The lattice fringe of metallic Cu(111) with a spacing of 0.208 nm is also visible on both Cu-SnO2 SER (Fig. 1j and m). The observation of Cu2O(111) facet is likely due to the oxidation of Cu during the preparation of TEM sample (Fig. 1j and k). HAADF-EDX analysis shows an even distribution of Sn on the surface of Cu NWs on both pre-reduced catalysts (Supplementary Fig. 16).

Additional characterizations of the catalysts after 50 min electrolysis at –50 mA cm−2 are shown in Supplementary Figs. 17-18. Both Cu-SnO2 catalysts show a noticeable decrease in Sn content after 50 min-reaction, mainly due to the partial dissolution of Sn into electrolyte. This is further corroborated by the ICP-OES analysis of the electrolyte that was collected after electrolysis on Cu-SnO2 SER catalyst (Supplementary Table 4). However, the amount of Sn dissolved from Cu-SnO2 ALD is not detectable by ICP-OES since the loading of SnO2 is extremely low.

Selective and durable electrolysisis of CO on Cu-SnO2 SER and Cu-SnO2 ALD

The catalytic performances of Cu-SnO2 SER and Cu-SnO2 ALD as well as Cu catalysts were analyzed in 0.5 M KHCO3 using a custom-designed flow reactor. Linear sweep voltammograms reveal that Cu-SnO2 SER and Cu-SnO2 ALD exhibit lower cathodic geometric current density than Cu (Supplementary Fig. 19). For example, the cathodic current density on Cu reaches ~195 mA cm−2 at -0.80 V vs. reversible hydrogen electrode (RHE), which is ca. 2.2x and 1.5x larger than the ones on Cu-SnO2 SER and Cu-SnO2 ALD, respectively.

We performed chronopotentiometric measurements at different current densities from ~20 to ~250 mA cm−2 with gaseous products being analyzed by an online gas chromatography and liquid products being evaluated by a high-performance liquid chromatography (Supplementary Note 2, Supplementary Tables 5-12). The total Faradaic efficiency (FE) of products on Cu is well below 100% at current densities from ~20 to ~100 mA cm−2 (Supplementary Table 5), which is due to the crossover of liquid products in ionic form from the catholyte to the anolyte (Supplementary Table 6). Cu catalyzes the production of a mixture of carbonaceous products, with H2 being dominant if the applied cathodic current density is less than 60 mA cm−2 (Supplementary Fig. 20). Once the cathodic current density reaches 250 mA cm−2, C2+ products are favored with a peak FE of 75%.

Cu-SnO2 ALD delivers a remarkable FE of 99% for CO generation at ~40 mA cm−2 (Fig. 2a). On Cu-SnO2 SER, FE for CO production increases from 64% at ~20 mA cm−2 to 98% at ~50 mA cm−2 and remains >83% till the current density reaches ~100 mA cm−2 (Fig. 2b). Notably, the Faradaic yield of H2 is suppressed by up to an order of magnitude on both catalysts as compared to Cu (Supplementary Tables 9 and 11). As the cathodic current density further increases to 150–250 mA cm−2, C2+ products including ethylene, ethanol and n-propanol are formed on both Cu-SnO2 catalysts. A FE of 12.5–14.6% is observed on Cu-SnO2 SER, while ethanol and trace amount of ethylene are produced by Cu-SnO2 ALD with a maximum FE of ~2.3% (Supplementary Fig. 20). The FE of different products on Cu-SnO2 ALD and Cu-SnO2 SER are also
analyzed as a function of potential (Supplementary Fig. 21). Briefly, Cu-SnO$_2$ALD displays the highest FE of CO of 98% at -0.63 V vs. RHE, with the FE maintaining at >90% from -0.59 to -0.77 V. As compared to Cu-SnO$_2$ALD, Cu-SnO$_2$SER requires 60 mV larger overpotential, -0.69 V vs. RHE to reach the best selectivity of 98% towards CO generation. At potential that is < -0.75 V, FE for H$_2$ and HCOO$^-$ production starts to increase. C$_2$H$_4$ products are largely suppressed on both catalysts, suggesting inhibition of further reduction of CO. Additionally, the pH of electrolyte and the nanostructure of Cu substrate have little impact on the maximum selectivity of CO on both catalysts (Supplementary Figs. 22–24).

The CO production rate is considerably improved on Cu-SnO$_2$ALD and Cu-SnO$_2$SER (Fig. 2c and Supplementary Fig. 25). Remarkable geometric partial current densities of ~177 mA cm$^{-2}$ at -0.99 V vs. RHE and ~207 mA cm$^{-2}$ at -0.89 V vs. RHE for CO production are achieved on Cu-SnO$_2$SER and Cu-SnO$_2$ALD, respectively (Fig. 2c). Specific current density normalized against electrochemical active surface area (Supplementary Table 3) shows little difference between two Cu-SnO$_2$ catalysts at potential > -0.9 V vs. RHE (Fig. 2d).

The effect of the sputtered Sn thickness on the catalytic performance of Cu-SnO$_2$SER is investigated at a constant current density of ~50 mA cm$^{-2}$ (Fig. 2e). By reducing the thickness of Sn from 60 nm to 20 nm, the production of CO remains dominant (Supplementary Fig. 26). Surprisingly, growing the thickness further to 160 nm still results in the selective formation of CO on Cu-SnO$_2$SER catalyst (Fig. 2e), even though the Cu surface is mostly covered by nanoparticles that are mainly consisted of SnO$_2$SER (Supplementary Fig. 27). Thus we assume that the SnO$_2$SER could also be active for CO generation in the presence of Cu. By contrast, the selectivity of Cu-SnO$_2$ALD catalyst dramatically shifts to HCOO$^-$ if the thickness increases from 2.7 to 5.4 nm (Fig. 2f, Supplementary Figs. 28–29). Note that both sputtered Sn and ALD-SnO$_2$ on GDE deliver a favorable HCOO$^-$ formation in our reaction system (Supplementary Fig. 29).

Excellent stability of Cu-SnO$_2$ALD and Cu-SnO$_2$SER towards CO production is demonstrated by long-term electrolysis. With periodic removal of precipitated salt (Supplementary Fig. 30), both catalysts exhibit outstanding durability, with a steady FE of CO over 85% after ~130 h at a current density of ~40 mA cm$^{-2}$ and over 80% after ~120 h at a current density of ~100 mA cm$^{-2}$ (Fig. 2g, Supplementary Fig. 31).

Structure-activity relationship as revealed by X-ray absorption spectroscopy

To interrogate the relationship between activity and the local structures of Cu-SnO$_2$SER and Cu-SnO$_2$ALD, we performed XAS at the Cu K-edge and Sn K-edge (Fig. 3, Supplementary Figs. 32–34). From the Cu K-edge, the conversion of CuO to metallic Cu after pre-treatment confirms the reduction process (Fig. 3a, b), consistent with our XPS analysis. In contrast, the Sn K-edge results show that most Sn species in both catalysts retain a Sn(IV) feature even after pre-reduction of the catalysts (Fig. 3c, d), which is in a good agreement with the XPS analysis.

We then fitted the post-edges of the Sn K-edge XAS for both catalysts after reduction (Fig. 3e, Supplementary Fig. 34 and Table 3). On Cu-SnO$_2$ALD, we find the presence of Sn-Cu bond in addition to Sn-O and Sn-O-Sn bonds. According to previous studies, Sn-Cu sites could contribute to the selective CO production. However, these Sn-Cu...
sites are not found in the Cu-SnO2 SER. Instead, Sn-Sn bond formation is resolved in addition to Sn-O and Sn-O-Cu bonds. Taken together, while both Cu-rich and Sn-rich catalysts share a similar Cu-supported SnO2 configuration, they hold different local structures for their respective production of CO from CO2 reduction.

**Binding of key intermediates as probed by electrochemical CO adsorption and in situ Raman spectroscopy**

Electrochemical cyclic voltammograms of three catalysts in both He and CO flowing conditions are shown in Fig. 4a and Supplementary Fig. 35. The voltammograms have a slightly slanted baseline due to the reduction of the unavoidable residual oxygen molecules inside the pores of GDE substrate. Even though substitution of GDE by a rigid substrate, i.e. glass, renders a flat baseline, we choose to use GDE as the flow cell. As compared to the CV curve of Cu, the peaks at 0.30–0.39 V on Cu-SnO2 SER and ~0.41–0.50 V on Cu-SnO2 ALD originate from Sn/SnO2 redox reactions (Fig. 4a and Supplementary Fig. 36)31. CO adsorption/stripping features were further characterized by cyclic voltammetry within a narrow potential window from −0.5 to 0.1 V vs. RHE under the flow of CO (Fig. 4b). The peaks at −0.35/0.21 V and −0.24 V on Cu substrate are attributed to the CO stripping and adsorption on the Cu active site, respectively, as confirmed by the linearity between the cathodic peak current and the scan rate (Supplementary Figs. 37–38)31,32. These peaks are in excellent agreement with previous CO adsorption studies on polycrystalline Cu reported by Horii et al.31,32.

The CO stripping peaks shift positively to −0.32 V and −0.16 V on Cu-SnO2 ALD surface as compared to Cu, indicating the modified binding energy of CO on Cu sites with SnO2 coating (Fig. 4b). Note that CO adsorption peak at −0.24 V becomes faint on Cu-SnO2 ALD as compared to the one of Cu, due to the decreased amount of Cu sites with SnO2 ALD overlayer. Surprisingly, a shoulder for the cathodic peak at −0.33 V and a broad anodic peak at −0.17 V, representing the CO adsorption and stripping at the SnO2 SER active site respectively, appear on the Cu-SnO2 SER (Fig. 3b and Supplementary Fig. 39). The cathodic peak becomes more intense in the presence of Cu as compared to the non-modified Sn to CO on Cu-SnO2 SER catalyst. Based on the fact that the Sn-rich surface still shows remarkable CO production rate (Supplementary Table 1 and Fig. 2c–d), we believe that surface SnO2 SER is the essential active site for CO production.

We also applied in situ Raman spectroscopy to investigate the adsorption of CO on three catalysts using a custom-made flow cell (Fig. 4c–e and Supplementary Figs. 40–42). The spectrum of Cu-SnO2 SER catalyst is almost featureless since surface-enhanced Raman scattering (SERS) effect from Cu is largely inhibited by the thick Sn layer33. Cu and Cu-SnO2 ALD show Raman peaks at wavenumbers of ~288, ~510 and ~604 cm−1 at open circuit potential, representing oxides of Cu. When we change the current density from −20 to −100 mA cm−2 on Cu, features associated with frustrated rotation of *CO, CO-CO stretching and C≡O stretching appear at ~265, ~348 and ~2065 cm−1, respectively34. Interestingly, Cu-SnO2 ALD shows a blue-shift of *CO rotation peak from ~265 to ~284 cm−1, indicating a higher excitation energy of the *CO restricted rotation on Cu active sites after coating SnO2 overlayer. The upward shift of this rotational frequency is likely attributed to the electrochemical Stark effect34, which is caused by the more negative potential of Cu-SnO2 ALD required for selective CO formation as compared to Cu at the same current density (Supplementary Fig. 19). We further scrutinized the Raman signal of the C≡O stretching mode at ~2000–2100 cm−1 observed on Cu and Cu-SnO2 ALD cathodes. In accordance with previous in-situ Raman investigations35,36, we assign these peaks to the linearly adsorbed CO on atop Cu sites (*CO atop). On Cu-SnO2 ALD catalyst, the *CO atop peak appears more intense as compared to *CO atop on Cu at all current densities (Fig. 4d). As *CO atop coverage is in dynamic equilibrium with local CO concentration35,36.

**Fig. 3** X-ray absorption spectroscopy analysis. The Cu K-edge XAS features of two as-prepared CuO-SnO2 samples, two pre-reduced Cu-SnO2 catalysts and two Cu standards (Cu foil and CuO) at the (a) near-edge and (b) post-edge after Fourier transform. The Sn K-edge XAS features of two as-prepared CuO-SnO2 samples, two pre-reduced Cu-SnO2 catalysts and two Sn standards (Sn foil and SnO2) at the (c) near-edge and (d) post-edge after Fourier transform. (e) Fitting of the post-edge of Sn K-edge XAS of both Cu-SnO2 catalysts after pre-reduction.
the increase of peak intensity is consistent with the high current density of CO production on the Cu-SnO2 catalyst (Fig. 2a). In addition, the observed slight red-shift of the *CO peak is attributed to the weaker binding of CO on SnO2-doped Cu defect sites.

The C≡O stretching band is further decoupled into two peaks with a low wavenumber (LW) of ~2010 and a high wavenumber (HW) of 2055 cm⁻¹ (Supplementary Fig. 41). It has been well-established that the adsorbed HCOO⁻ on Cu active sites. Moreover, a small peak appears with a Raman shift of 510 cm⁻¹, which might be related to the hydroxyl intermediates adsorbed on Cu. The hydroxyl species favors CO₂ adsorption in the form of H₂CO₃, which in turn will be transformed to HCOO⁻ species, promoting the formation of formate.

In overall, the Raman features on Cu-SnO₂ ALD catalysts are consistent with its high selectivity towards formate formation, indicating that SnO₂ overlayers with different thickness successfully tune the adsorption energy of different intermediates on the Cu active sites.

Photosynthesis of CO from CO₂ on Cu-SnO₂ ALD catalyst

We developed an integrated PV-EC system to perform unbiased synthesis of CO from CO₂ and water, which provides a route to recycling CO₂ into a valuable chemical feedstock using renewable electricity.

2CO₂ ⇌ 2CO + O₂ (∆G = -1.32 V, under ambient pressure and temperature)

Both FE_CO and the cell voltage (V_cell) necessary to drive the uphill conversion are the key factors affecting the efficiency of electrolyzer as well as the overall solar to fuel (STF) energy conversion efficiency (Supplementary Note 3). We first designed a two-electrode flow cell based on Cu-SnO₂ ALD cathode for nearly exclusive production of CO (Fig. 5a and Supplementary Fig. 43). Further we optimized the electrolyzer including refining electrolyte by replacing KHCO₃ with KOH to decrease cathode overpotential, excluding the membrane and selecting electrodeposited IrO₃ as an appropriate anode (Supplementary Fig. 44), to minimize the cell voltage. As a result, an overall cell voltage of only ~2.0 V is required for maintaining a 95% faradaic efficiency for CO generation at a current density of ~40 to ~60 mA cm⁻² (current normalized by geometric surface area of cathode, 0.25 cm²).
On the basis of this electrolysis requirement, a III-V semiconductor, InGaP2/InGaAs/Ge triple-junction photovoltaic cell was employed and directly connected with our flow electrolyzer via copper wire to provide the required cell voltage as well as necessary current for driving the CO2 conversion to CO (Fig. 5a). The effective illumination area of the selected InGaP2/InGaAs/Ge solar cell is 0.92 cm2. Under simulated air mass 1.5 G irradiation, the triple-junction cell delivers an open-circuit photovoltage (Voc) of 2.57 V, a short-circuit current density of 14.96 mA cm−2 and a fill factor of 92.0%, representing a power conversion efficiency (PCE) of 31.52% (Fig. 5b). By intersecting the J–V curves of the electrolyzer and the solar cell, we predict the operating point to be at 2.02 V and 14.83 mA cm−2 (Fig. 5b). Note that here the electrolysis current is normalized against the effective illuminated area of the solar cell (0.92 cm2). The unassisted PV-EC system delivers an average solar current density of 14.80 mA cm−2 (Fig. 5c), with an average FE of 98.9% for CO production (Fig. 5d). This is a new benchmark for solar-to-CO conversion with a peak STF efficiency of 19.7% and an average value of 19.6% during 2-hr electrolysis (Fig. 5d, Supplementary Note 3). We note here that switching electrolyte from KHCO3 to KOH is advantageous for driving the CO2 conversion to CO (Fig. 5a). The effective illumination leads to a significant drop in the current density after ~2 hr electrolysis (Supplementary Figs. 47-48). The dissolution of Sn is also observed (Supplementary Table 14). But neither the dissolved Ir nor Sn was re-deposited on their counterparts, as indicated by the absence of corresponding signals in the EDX spectrum (Supplementary Figs. 47-48). Further investigation on replacing IrOx by a stable and earth-abundant catalyst for oxygen evolution reaction is currently in progress.

With the deployment of gas-diffusion-electrode based flow cell, the production rate of CO in our system shows a 1 to 2 orders of magnitude improvement over previously reported systems using H-cell configuration (Supplementary Table 15). Besides an unprecedented solar-to-fuel energy conversion efficiency of our system, the usage of earth-abundant cathode as well as a 3 times enhancement of CO production rate over state of the art present a critical step towards further scale-up applications of this technology. Meanwhile, it is noted that strategies for long-term operation with affordable components of the integrated system are still required to make PV-EC system competitive with the fossil fuel derived alternatives.

In summary, earth-abundant electrocatalysts with metallic Sn as well as SnO2 being introduced onto CuO nanowires are developed for the efficient synthesis of CO from CO2 reduction. In the custom-made flow cell with gas diffusion electrode supported catalysts, we achieve almost unit selectivity towards CO formation on both Cu-SnO2 SER and Cu-SnO2 ALD catalysts in 0.5 M KHCO3 electrolyte. Partial current densities of ~177 and ~207 mA cm−2 for CO generation are delivered by Cu-SnO2 SER and Cu-SnO2 ALD catalysts, respectively. On the basis of catalytic performance of Cu-SnO2 SER with different Sn thickness as well as CO adsorption behavior on Cu-SnO2 SER surface, we propose that the SnO2 sites on Cu surface is selectively catalyzing CO generation. The intermediate adsorption configuration on the Cu-SnO2 ALD catalyst observed by in situ Raman spectroscopy explains its excellent CO selectivity. Based on our highly efficient system for electrochemical...
CO₂ reduction, a triple-junction InGaP/InGaAs/Ge photovoltaic is chosen to provide the needed energy for unassisted solar-driven CO₂ reduction. Direct coupling of solar device and flow electrolyzer enables a peak solar-to-CO conversion efficiency of 19.7% and average one of 19.6% during 2 hr-electrolysis under standard AM 1.5 G illumination. Our work serves as a guide for future design of artificial photosynthesis configuration, which is a promising strategy to produce commodity chemicals and fuels directly with only CO₂ and water as reactant and renewable energy as power source.

Methods
Preparation of electrodes

Preparation of CuO nanowires substrate. Polycrystalline Cu layer with a thickness of around 900 nm was first sputtered (DP650, AllianCe-Concept) on the surface of gas diffusion electrode (GDE, Sigracet 38 BC, Fuel Cell Store). During sputtering, Cu target with high purity (99.99%) was bombarded under a direct current (DC, Hüttinger TruPlasma 3002) power of 400 W with a sputtering rate of 2.65 nm s⁻¹. The pressure of the chamber was kept at 5.0 × 10⁻² mbar using both a dry pump (Pfeiffer-Adixen ACP 40) and a cryogenic pump (CTI ON-BOARD 8). The Cu/GDE substrate was then anodized using both a dry pump (Pfeiffer-Adixen ACP 40) and a cryogenic window from 0.32 to 1.48 V vs. RHE at a scan rate of 1 mV s⁻¹ and 100 potential values used in this work are scaled to RHE scale as follows: $V_{\text{RHE}} = V_{\text{Ag/AgCl(KCl sat)}} + 0.197 V + 0.059 V \times \text{pH}$.

Catalyst characterization

The surface morphology of the catalyst was characterized using a field emission scanning electron microscope (FE-SEM, Merlin, Zeiss), and elemental mappings were obtained from energy-dispersive X-ray (EDX) analysis. Cross-section of atomic layer deposited SnO₂ layer on planar CuO surface was measured by focus ion beam (FIB, Merlin, Zeiss). The samples were first protected by carbon film and then a hole was milled in front of it, creating a flat surface perpendicular to the sample surface. Transmission electron microscopy (TEM) was conducted on Talos, equipped with a high-angle annular dark field (HAADF) detector (FEI). The crystalline structure of the catalysts was analyzed by X-ray diffraction (XRD) on a Bragg-Brentano instrument coupled with a monochromated Cu Kα radiation (λ = 1.5409 Å) and a grazing incident beam. Diffractograms were recorded between 20 – 10 to 70° with a slow scan rate of 0.25° min⁻¹ and a step size of 0.026°. The surface chemical compositions of the sample were measured by X-ray photoelectron spectroscopy (XPS) on a PHI VersaProbe II scanning microprobe (Physical Instrument AG, Germany). Analysis was carried out using a monochromatic Al Kα X-ray source of 24.8 W power. The Cu K- and Sn K-edges XAS spectra were recorded at the 20 BM beamline of the Advanced Photon Source in Argonne National Laboratory (Leomne, IL, US), in which fluorescence signals were collected. XAS data were processed with Demeter (v.0.9.26)⁴⁹. For data analysis, we applied the same structure (Sn-doped Cu₅Sn₄O₇) for the EXAFS fittings of both Cu-SnO₂ ALD and Cu-SnO₂ SER catalysts. Note that we have a pre-caution process of removing possible residual electrolyte ions on the electrode for all the samples after pre-treatment. Right after reduction, the catholyte chamber was infused with DI water to remove the residual ions to prevent the possible reaction between the ions with the catalyst. The sample was then removed from the cell. Both the front and back of the GDE were washed with DI water thoroughly for several times, followed by drying with air gun. For the XPS and XAS characterizations, the as-synthesized Cu-SnO₂ SER as well as all the samples after pre-treatment and 50-min reduction were immediately packed in vacuum after cleaning. The vacuum packaging helps to minimize the impact of atmospheric oxidation at the catalyst surface.

Electrochemical measurements with a flow cell

Electrochemical flow cell. A custom-built flow cell was used for performing galvanostatic CO₂ reduction and conducting cyclic voltammetry. The cathodic and anodic chambers were separated by an anion exchange membrane (AEM, Fumasep FKS-50, Fumatech), or a cation exchange membrane (CEM, Fumasep FKE-50, Fumatech) when the catalyst delivers a high selectivity towards HCOO.

Chronopotentiometric measurement and product quantification. Aqueous KHCO₃ (99.999%, Sigma-Aldrich) with a concentration of 0.5 M (pH = 8.36) or KOH (Reactolab, S.A.) with a concentration of 1.0 M (pH = 13.82) was pumped inside two electrolyte chambers using a peristaltic pump with a rate of 0.25 cm³ min⁻¹. Gaseous CO₂ with high purity (99.98%, Garbagas) was flowed into cathodic and anodic chambers with flow rates of 20 and 5 cm³ min⁻¹, respectively, controlled by mass flow controllers (MFC, Alicat Scientific). Three-electrode configuration was used for characterizing catalytic performance of Cu and both Cu-SnO₂ catalysts towards CO₂ reduction. A 200 nm-thick platinum film sputtered on the surface of GDE was used as the counter electrode (CE) and a KCl saturated Ag/AgCl (Pine) was used as the reference electrode (RE). The Ag/AgCl electrode was calibrated by a reversible hydrogen electrode (RHE, HydroFlex) before each-day measurement and the potential values used in this work are scaled to RHE scale as follows: $V_{\text{RHE}} = V_{\text{Ag/AgCl(KCl sat)}} + 0.197 V + 0.059 V \times \text{pH}$.
All the chronopotentiometric (CP) measurements were conducted using a Gamry potentiostat (Interface 1000). The potential at each applied current density was determined by linear sweep voltammmograms (LSV) measured on different catalysts. The voltage was recorded with IR drop being automatically corrected via a current interrupt mode. Each CP measurement employed a fresh working electrode and the electrolysis last 40–50 min. During each electrolysis, four gas aliquots were automatically sampled into an online gas chromatography (GC, Trace ULRTA, Thermo). A micropacked shi n carbon column (Restek) was used to separate the gas products and a pulse discharge detector (PDD, Vici) was used to quantify the products, coupled with a calibration curve obtained using standard gas mixtures (Carbagas) with all the reference gases (H2, CO, CH4, C2H4, C2H6, and C2H5). The electrolyte was collected during electrolysis and the dissolved liquid products were analyzed using high performance liquid chromatography (HPLC, Agilent Infinity II) after reaction. An organic acid analysis column (AMINEX HPX-87H) was used to separate the liquid products. A refractive index detector (RID) was used to quantify HCOO- and CH3COO-. A variable wavelength detector (VWD) was used to quantify the C2H4OH and C2H5OH. Standard solution including HCOONa (for HCOO- > 99.0%, Fluka Analytical), CH3COONa (for CH3C2O2– > 99.0%, Sigma-Aldrich), C2H5OH (>99.8%, Sigma Scientific) and C2H4OH (>99.8%, Fisher Scientific) with known concentrations was used for calibration.

CO adsorption on catalyst surface. Aqueous 0.5 M KHC2O3 with pH of 8.36 was pumped into both catholyte and anolyte chambers at a rate of 0.25 cm³ min⁻¹ and gaseous CO (99.998%, Carbagas) or He (99.9999%, Carbagas) was purged into cathodic gas chamber at a rate of 50 cm³ min⁻¹. GDE-supported Pt and Ag/AgCl were used as the CE and RE, respectively. All the catalysts were pre-reduced at a constant current density for ~100 s before measurement. For each test, at least three cycles of cyclic voltammograms were conducted to ensure a steady state of the electrode surface. A potential window from -1.5 V to +2.2 V vs. RHE was chosen to measure all the oxidation and reduction peaks on Cu and both Cu-SnO2 catalysts. Then the potential was carefully tuned from -0.6 V to 0.2 V vs. RHE to avoid the significant surface change, such as Cu oxidation, for the observation of the CO adsorption and stripping features on the surface active site.

Pb underpotential deposition on Cu active site. Evaluation of the surface Cu active sites was carried out by Pb underpotential deposition in an aqueous solution containing 0.1 M HClO4 (70%, Merck) and 0.001 M Pb(OAc)2 (≥99.99%, Sigma-Aldrich). The electrolyte and gaseous He (99.9999%, Carbagas) were flowed into cathode chamber and cathodic gas chamber at a rate of 0.25 cm³ min⁻¹ and 20 cm³ min⁻¹, respectively. GDE-supported Pt and Ag/AgCl were used as the CE and RE, respectively. All the catalysts were pre-reduced at a constant current density of ~30 mA cm⁻² for ~100 s before measurement. The applied potential was first held at the initial potential, -0.21 V or -0.24 V vs. RHE, for 5 min before each scan, and voltammograms were recorded from -0.21 V to 0.29 V vs. RHE for Cu and Cu-SnO2 ALD and -0.24 V to 0.19 V for Cu-SnO2 SER. All the voltammograms were measured at a scan rate of 50 mV s⁻¹. The charge consumed for Pb stripping (oxidation) was determined by integrating the oxidation peak area and was used for analyzing the number of surface Cu active sites. Background curves were also measured using bare 0.1 M HClO4 electrolyte under the identical condition. Each experiment was repeated using at least two fresh samples and an average of stripping charge was reported.

Double layer capacitance measurement. Electrochemical surface active area of Cu, Cu-SnO2 SER and Cu-SnO2 ALD was assessed by measuring their double layer capacitance. The experiments were carried out under almost identical condition as the one for performing CO2 reduction, with 0.5 M KHC2O3 being flowed into cathode chambers at a flow rate of 0.25 cm³ min⁻¹ and He being flowed into gas compartments at a flow rate of 20 cm³ min⁻¹, respectively. In order to establish the potential window without Faradaic current, the voltammograms were first scanned within a wide potential range from 0.35 to 0.85 V vs. RHE for Cu and 0.25 to 0.95 V vs. RHE for Cu-SnO2 SER and Cu-SnO2 ALD catalysts. Then the curves were collected within a non-faradaic current window at different scan rates of 20, 40, 60, 50 to 100 mV s⁻¹ for Cu and 10, 20, 40, 50, 60 mV s⁻¹ for Cu-SnO2 SER and Cu-SnO2 ALD catalysts.

In situ Raman spectroscopy
In situ Raman spectra were measured using a Horiba confocal Raman microscope equipped with a 638 nm-diode laser, a water immersion (WI) objective (100×, Olympus), a monochromator (600 grooves/mm grating) and a charge coupled device (CCD) detector. The WI objective was protected from the electrolyte by a Teflon film with thickness of 0.0005-inch (FEP, American Durafilm) and a layer of DI water between the objective and the protective film. The electrochemical CO2 reduction was carried out in a home-made spectro-electrochemical flow cell, and aqueous 0.5 M KHCO3 being purged into catholyte chamber at a rate of 0.25 cm³ min⁻¹ and CO2 being flowed into the cathodic gas chamber at a rate of 20 cm³ min⁻¹, respectively. A biologic SP-200 potentiostat was used to apply a constant current density for pre-reduction as well as CO2 reduction. For experiments performed on different catalysts, the electrode was first pre-reduced at -30 mA cm⁻², followed by the measurements under applying constant current densities. Each current density was applied for at least 5 min before the collection of the spectra to ensure a steady-state condition of the catalyst surface. All the spectra in the main text were shown as collected without baseline correction or any other post-treatment.

Solar-driven CO2 reduction
Electrolyzer. The catalyst for measurement of solar-driven CO2 reduction was prepared in the same way as described above. In order to optimize the CO production in aqueous 2 M KOH electrolyte, the number of ALD cycles of deposited SnO2 was adjusted to 10. A film of electrodeposited IrOx was used as the counter electrode. A custom built two-electrode flow electrolyzer was used for measuring linear sweep voltammetry (LSV) and conducting CO2 reduction. The LSV curve was recorded in the applied potential from 1.0 to 2.5 V at a scan rate of 25 mV s⁻¹.

Solar cell. A triple-junction InGaP2/InGaAs/Ge photovoltaic cell with a masked area of 0.92 cm² was measured under standard AM 1.5 G illumination using the Oriel LCS-100 Class ABB solar simulator (Newport). The measurement was carried out in air at room temperature. A certified silicon solar cell (Newport) was used to calibrate the light intensity before measurement. J-V characteristic of the device was assessed in both forward and backward directions within a potential range from 2.6 to 0 V with a scan rate of 25 mV s⁻¹ and a step time of 40 ms.

Integrated device. The solar cell was then wired to our two-electrode electrolyzer and the performance of the integrated PV-EC system was measured via chronamperometry without applying bias under AM 1.5 G illumination. The produced gas products were periodically sampled into GC every ~11.25 min and the average current density during 1.5 min before each injection was used to quantify the faradaic efficiency of dominant products, H2 and CO. The generated liquid products that dissolved in electrolyte was analyzed by HPLC after electrosynthesis.

Reporting summary
Further information on research design is available in the Nature Research Reporting Summary linked to this article.
Data availability
The authors declare that all data supporting the results of this study are available within the paper and its supplementary information files or from the corresponding authors upon reasonable request.

References
1. Ran, J., Jaroniec, M. & Qiao, S.-Z. Cocatalysts in semiconductor-based photocatalytic CO2 reduction: achievements, challenges, and opportunities. Adv. Mater. 30, 1704649 (2018).
2. Yu, S., Wilson, A. J., Kumari, G., Zhang, X. & Jain, P. K. Opportunities and challenges of solar-energy-driven carbon dioxide to fuel conversion with plasmonic catalysts. ACS Energy Lett. 2, 2058–2070 (2017).
3. Zhou, X. & Xiang, C. Comparative analysis of solar-to-fuel conversion efficiency: a direct, one-step electrochemical CO2 reduction reactor versus a two-step, cascade electrochemical CO2 reduction reactor. ACS Energy Lett. 3, 1892–1897 (2018).
4. Centi, G. & Perathoner, S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. Catal. Today 148, 191–205 (2009).
5. Lewis, N. S. Toward cost-effective solar energy use. Science 315, 759–761 (2007).
6. Kondratenko, E. V., Mul, G., Baltrusaitis, J., Larrazábal, G. O. & Pérez-Ramírez, J. Status and perspectives of CO2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. Energy Environ. Sci. 6, 3132–3135 (2013).
7. Schreier, M. et al. Solar conversion of CO2 to CO using Earth-abundant electrocatalysts prepared by atomic layer modification of CuO. Nat. Energy 2, 17087 (2017).
8. Zhang, G. et al. Efficient CO2 electroreduction on facet-selective copper films with high conversion rate. Nat. Commun. 12, 5745 (2021).
9. Gao, J. et al. Selective C–C coupling in carbon dioxide electroreduction via efficient spillover of intermediates as supported by operando Raman spectroscopy. J. Am. Chem. Soc. 141, 18704–18714 (2019).
10. Dinh, C.-T. et al. CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 360, 783–787 (2018).
11. Weekes, D. M., Salvatore, D. A., Reyes, A., Huang, A. & Berlinguette, C. P. Electrolytic CO2 Reduction in a Flow Cell. Acc. Chem. Res. 51, 910–918 (2018).
12. Cheng, W.-H. et al. Monolithic photoelectrochemical device for direct water splitting with 19% efficiency. ACS Energy Lett. 3, 1795–1800 (2018).
13. Li, Q. et al. Tuning Sn-catalysis for electrochemical reduction of CO2 to CO via the core/shell Cu/SnO2 structure. J. Am. Chem. Soc. 139, 4290–4293 (2017).
14. Sarfraz, S., Garcia-Esparza, A. T., Jedidi, A., Cavallo, L. & Takanabe, K. Cu–Sn bimetallic catalyst for selective aqueous electroreduction of CO2 to CO. ACS Catal. 6, 2842–2851 (2016).
15. Ren, W. et al. Isolated copper–tin atomic interfaces tuning electrocatalytic CO2 conversion. Nat. Commun. 12, 1449 (2021).
16. Zhang, M. et al. Tunable selectivity for electrochemical CO2 reduction by bimetallic Cu–Sn catalysts: Elucidating the roles of Cu and Sn. ACS Catal. 11, 11003–11108 (2021).
17. Dong, W. J. et al. Evidence of local corrosion of bimetallic Cu–Sn Catalysts and its effects on the selectivity of electrochemical CO2 reduction. ACS Appl. Energy Mater. 3, 10568–10577 (2020).
18. Pardo Pérez, L. C. et al. Determining structure-activity relationships in oxide derived Cu-Sn catalysts during CO2 electroreduction using X-ray spectroscopy. Adv. Energy Mater. 12, 2103328 (2022).
19. Ren, D. et al. Atomic layer deposition of ZnO on CuO enables selective and efficient electroreduction of carbon dioxide to liquid fuels. Angew. Chem. Int. Ed. 58, 15036–15040 (2019).
20. Oehl, N. et al. In situ X-ray diffraction study on the formation of α-Sn in nanocrystalline Sn-based electrodes for lithium-ion batteries. CrystEngComm 17, 8500–8504 (2015).
21. Xie, M. et al. Amorphous ultrathin SnO2 films by atomic layer deposition on graphene network as highly stable anodes for lithium-ion batteries. ACS Appl. Mater. Interfaces 7, 27735–27742 (2015).
22. Kwoka, M. et al. XPS study of the surface chemistry of L-CVD SnO2 thin films after oxidation. Thin Solid Films 490, 36–42 (2005).
23. Chen, Y. & 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).
24. Vasileff, A. et al. Selectivity control for electrochemical CO2 reduction by charge redistribution on the surface of copper alloys. ACS Catal. 9, 9411–9417 (2019).
25. Trasatti, S. & Pettiri, O. A. Real surface area measurements in electrochemistry. Pure Appl. Chem. 63, 711–734 (1991).
26. Zhang, J., Luo, W. & Züttel, A. Crossover of liquid products from electrochemical CO2 reduction through gas diffusion electrode and anion exchange membrane. J. Catal. 385, 140–145 (2020).
27. Zhang, S., Kang, P. & Meyer, T. J. Nanostructured tin catalysts for selective electrochemical reduction of carbon dioxide to formate. J. Am. Chem. Soc. 136, 1734–1737 (2014).
28. Won, D. H. et al. Rational design of a hierarchical tin dendrite electrode for efficient electrochemical reduction of CO2. Chem. SusChem 8, 3092–3098 (2015).
29. Mandal, L. et al. Investigating the role of copper oxide in electrochemical CO2 reduction in real time. ACS Appl. Mater. Interfaces 10, 8574–8584 (2018).
30. Tang, W. et al. The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO2 electroreduction. Phys. Chem. Chem. Phys. 14, 76–81 (2012).
31. Hori, Y. et al. Adsorption of carbon monoxide at a copper electrode accompanied by electron transfer observed by voltammetry and IR spectroscopy. Electrochim. Acta 39, 2495–2500 (1994).
32. Hori, Y., Koga, O., Yamazaki, H. & Matsuo, T. Infrared spectroscopy of adsorbed CO and intermediate species in electrochemical reduction of CO2 to hydrocarbons on a Cu electrode. Electrochim. Acta 40, 2617–2622 (1995).
33. Ren, D., Gao, J., Zakeeruddin, S. M. & Grätzel, M. New insights into the interface of electrochemical flow cells for carbon dioxide reduction to ethylene. J. Phy. Chem. Lett. 12, 7583–7589 (2021).
34. Chernyshova, I. V., Somasundaran, P. & Ponnamaram, G. On the origin of the elusive first intermediate of CO2 electroreduction. Proc. Natl Acad. Sci. 115, E9261–E9270 (2018).
35. Chou, T.-C. et al. Controlling the oxidation state of the Cu electrode and reaction intermediates for electrochemical CO2 reduction to ethylene. J. Am. Chem. Soc. 142, 2857–2867 (2020).
36. Gunathunge, C. M., Ovalle, V. J., Li, Y., Janik, M. J. & Waeghele, M. M. Existence of an electrochemically inert CO population on Cu electrodes in alkaline pH. ACS Catal. 8, 7507–7516 (2018).
37. Salimón, J., Hernández-Romero, R. M. & Kalaji, M. The dynamics of the conversion of linear to bridge bonded CO on Cu. J. Electroanal. Chem. 538-539, 249–257 (2005).
38. Malkani, A. S., Dunwell, M. & Xu, B. Operando spectroscopic investigations of copper and oxide-derived copper catalysts for electrochemical CO reduction. ACS Catal. 9, 474–478 (2019).
39. Eren, B., Liu, Z., Stacchiola, D., Somorjai, G. A. & Salmeron, M. Structural changes of Cu(110) and Cu(110)-(2 × 1)-O surfaces under carbon monoxide in the torr pressure range studied with scanning tunneling microscopy and infrared reflection absorption spectroscopy. J. Phys. Chem. C. 120, 8227–8231 (2016).
40. Hollins, P., Davies, K. J. & Pritchard, J. Infrared spectra of CO chemisorbed on a surface vicinal to Cu(110): The influence of defect sites. Surf. Sci. 138, 75–83 (1984).
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Author contributions
J.G. J.L. and Y.L contributed equally. J.G. and D.R. conceived the idea. J.G. designed and carried out all the electrochemistry experiments. D.R. performed TEM analysis and M.X. assisted in XRD characterization. J.L. and Y.F. helped with the XAS measurement and relative data analysis. Y.L. proposed the implementation of III-V solar cell to the electrolysis system for solar-driven CO₂ reduction. S.M.Z coordinated the project. J.G., D.R. and M.G. supervised the project. J.G. and D.R wrote the manuscript which was finalized by all the other co-authors.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Jing Gao, Dan Ren or Michael Grätzel.

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