Tin nanoparticles decorated copper oxide nanowires for selective electrochemical reduction of aqueous CO2 to CO

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Tin Nanoparticles Decorated Copper Oxide Nanowires for Selective
Electrochemical Reduction of Aqueous CO$_2$ to CO†

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Abstract

A low-cost electrocatalyst comprising tin nanoparticles on copper oxide nanowires selectively converts CO$_2$ to CO. A facile and cost-effective surface modification method, electroless deposition, is used to prepare the electrode. The hybrid electrode exhibits excellent selectivity, activity and durability at modest overpotentials. Notably, the CO faradaic efficiency can reach 90% and the CO partial current density approaches 4.5 mA cm$^{-2}$ at an overpotential of 690 mV. This is comparable to some noble metal catalysts.
Introduction

Continued intense use of fossil fuels has given rise to an accumulation of atmospheric CO$_2$ which is considered to be a major contributor to global warming.$^1$ Electrochemical reduction is an intriguing and promising method to convert CO$_2$ into useful fuels or industrial chemicals under ambient conditions.$^{2-4}$ However, the viability of this approach is currently restricted by the lack of inexpensive, efficient, selective and stable electrocatalysts required for large-scale industrial application.$^5$

To date, a number of heterogeneous catalysts have been investigated for electrochemical conversion of CO$_2$ into value-added products such as CO, HCOOH, CH$_4$ and other hydrocarbons.$^{6-8}$ Among all the possible CO$_2$ electroreduction (CO$_2$ER) reactions, the generation of CO according to $CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$ is a process of fundamental significance.$^5, 9-11$ The product, CO, is a precursor for synthesis of methanol$^{12, 13}$ and other organic compounds$^{10}$ that can act as fuels. Moreover, this two-electron reduction process of aqueous CO$_2$ is accompanied by a hydrogen evolution reaction (HER). These two products (H$_2$ and CO) also known as syngas, is a critical feedstock for the Fischer-Tropsch process to produce synthetic fuels such as liquid hydrocarbons.$^{14-16}$ It is highly desirable to develop electrocatalysts capable of efficiently converting CO$_2$ to CO.

Some nanostructured noble metals such as Au$^{17-20}$, Ag$^{21-24}$ and Pd$^{25-27}$ have been demonstrated to promote this process with faradaic efficiencies (FEs) above 80% and high current densities at modest overpotentials. They are among the most efficient electrocatalysts for CO formation. However, their high cost and low abundance in nature limit large-scale application. Some earth-abundant and inexpensive metals such as Zn and Cu are promising alternatives.$^{8, 9}$ Dendrite-like Zn$^{28}$, reduced nanoporous ZnO$^{29}$ and nanoscale Zn$^{30}$ have been developed for aqueous CO$_2$ electroreduction. However, they require large overpotentials (>
900 mV) to achieve high FEs (> 80%) for CO production. Oxide-derived copper catalysts\textsuperscript{31,32} can drive this process at low overpotentials (< 500 mV), but suffer from low FEs (< 60%) for CO production and low current densities (< 1 mA cm\textsuperscript{-2}).

Experimental\textsuperscript{33-36} and theoretical\textsuperscript{37-39} studies have revealed that alloying copper with other metals is an effective way to improve CO\textsubscript{2}-to-CO conversion. By alloying, the binding strength of the *CO intermediate can be tuned to enhance the reaction kinetics, and thus enhance the CO production.\textsuperscript{35} For example, Akihiro et al.\textsuperscript{34} demonstrated that electroplated Cu-Sn alloy could deliver a CO faradaic efficiency of 67% and a CO partial current density of 0.6 mA cm\textsuperscript{-2} at an applied potential of ~ -0.87 V vs reversible hydrogen electrode (RHE). Takanabe et al.\textsuperscript{36} developed a Cu-In alloy catalyst by electrodepositing expensive In on reduced oxide-derived Cu surface, which selectively converted CO\textsubscript{2} to CO with a FE of 95% at -0.7 V vs RHE. Very recently, they reported a similar Cu-Sn alloy catalyst by electrodepositing Sn on the Cu surface, demonstrating high FE\textsubscript{CO} values > 90% over a broad potential range from - 0.5 V to - 0.8 V vs RHE.\textsuperscript{40} Their density functional theory (DFT) calculations suggested that the presence of In or Sn greatly affected the adsorption ability of neighbouring Cu. The H adsorption became unfavourable while the CO adsorption energy was nearly unchanged, leading to higher selectivity toward CO. However, the alloys usually contains large amount of bulk components without access to electrolyte, greatly reducing the materials utilization efficiency in electrochemical interfacial catalysis such as CO\textsubscript{2}ER and HER. Moreover, the alloying methods are generally highly time- and energy-consuming processes, requiring either state-of-the-art synthesis methods\textsuperscript{35,41} or large amounts of energy (i.e. thermal energy\textsuperscript{42} and electricity\textsuperscript{34,36}) to form desirable atomic arrangements. To realize the large-scale electrochemical conversion of CO\textsubscript{2} to CO, it is extremely crucial to explore a cost-effective fabrication method to produce copper-based hybrid catalysts.
Herein, we have developed tin nanoparticle-decorated copper oxide nanowire (Cu$_x$O-Sn) catalysts for efficient conversion of aqueous CO$_2$ to CO. The Cu$_x$O nanowires (NWs) are anchored on Cu foil and modified by inexpensive Sn nanoparticles (NPs) via a facile, scalable and low-cost electroless deposition method. After a five-second deposition of Sn NPs, the resulting hybrid nanowires demonstrated a significantly improved CO faradaic efficiency from 6% to 82%, and a CO partial current density increase from 0.3 to 4.5 mA cm$^{-2}$ at an overpotential of 690 mV. Its selectivity and activity towards CO formation can be easily tuned by the Sn deposition time. This highly selective Cu$_x$O-Sn NWs electrocatalyst and its facile fabrication method may provide one step forward to the efficient electroreduction of CO$_2$ on a large scale.

**Experimental Section**

**Materials.** Copper foil (99.9%, 0.127 mm thick, Alfa Aesar) was used as a substrate for the catalyst. Tin (II) sulphate (SnSO$_4$, 95%, Sigma-Aldrich), sodium hydroxide (NaOH, 99.0%, Chem-Supply), sodium citrate dihydrate (C$_6$H$_5$Na$_3$O$_7$·2H$_2$O, 99%, Sigma-Aldrich), sodium dihydrogen orthophosphate (NaH$_2$PO$_4$, 99.0%, Chem-Supply) were used in the anodization of Cu foil and deposition of Sn NPs. HAuCl$_4$·3H$_2$O (99.9%, Sigma-Aldrich) was used to deposit Au NPs on Cu NWs. Potassium bicarbonate (KHCO$_3$, 99.7%, Sigma-Aldrich) was used for electrolyte.

**Catalyst Preparation.**

Synthesis of Cu$_x$O NWs: Cu(OH)$_2$ NWs were first synthesized on Cu foils by an electrochemical anodization method in an alkaline solution. The Cu foil (1 cm × 1 cm) with a rectangular tip (0.3 cm × 0.5 cm) cut by a laser engraver was polished to a mirror-like finish
using sand paper (Grit 1200), while the back side was fully covered with commercial tape (3M Company). After being cleaned with DI water and dried by N₂, the Cu foil was immediately immersed into a 1 M NaOH solution for the anodization at a current density of 2 mA cm⁻² for 10 min with an Ag/AgCl (3 M KCl) reference electrode and a platinum gauze (2 cm × 2 cm) counter electrode. The resultant Cu foil with a cyan layer of Cu(OH)₂ NWs was rinsed with copious amounts of DI water and dried by N₂, followed by peeling off the tape. The Cu(OH)₂ NWs were dehydrated by annealing them at 200°C for 2 h in an air atmosphere. The brown dehydrated Cu(OH)₂ NWs were electrochemically reduced to dark red CuₙO NWs in a 0.1 M KHCO₃ solution at a constant potential of -1.4 V vs Ag/AgCl (3 M KCl) for 10 min. The related electrochemical anodization and reduction curves are shown in Supporting Information (Figure S1).

Synthesis of CuₙO-Sn NWs: CuₙO NWs on Cu foil with the backside covered with epoxy was immersed into a Sn electroless plating bath⁴³ to deposit Sn NPs at 80°C. After the deposition, it was rinsed thoroughly with ethanol and DI water to remove any residue and dried by N₂. The plating bath was composed of 0.3 M SnSO₄, 2.8 M NaOH, 0.9 M NaH₂PO₄ and 0.6 M sodium citrate. An elapsed time of 5 s, 10 s, 20 s or 80 s was applied. The corresponding samples are referred as CuₙO-Sn5, CuₙO-Sn10, CuₙO-Sn20 or CuₙO-Sn80.

Synthesis of CuₙO-Au-Sn NWs: Gold was coated on the surfaces of CuₙO NWs by the simple displacement reaction between Cu metal and AuCl₄⁻ ions. The freshly-prepared dark red CuₙO NWs were immersed into a 0.5 mM HAuCl₄ aqueous solution for 20 s. The as-obtained samples, referred to as CuₙO-Au20, were rinsed with copious amounts of DI water and dried by N₂. Tin NPs were finally deposited onto these CuₙO-Au20 NWs following the same method as that on CuₙO NWs.

Structural Characterization.
The microstructure of the catalysts was analysed by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu Kα radiation at a scan rate of 4 degree min⁻¹. The morphology of the samples was investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-7500FA) and scanning transmission electron microscopy (STEM, JEOL ARM200F) in conjunction with energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) was measured on a SPECS PHOIBOS 100 Analyser with X-ray excitation provided by Al Kα radiation (hv = 1486.6 eV) at a high voltage of 12 kV and a power of 120 W. The XPS binding energy spectra were recorded at a pass-energy of 20 eV in the fixed analyser transmission mode. All the spectra were calibrated by C 1s = 284.6 eV.

**Electrochemical Measurements.**

A potentiostat (CH Instrument 650D) was used for all the experiments. A piece of platinum gauze (2 cm × 2 cm) and an Ag/AgCl (3 M KCl, BASi) electrode served as counter electrode and reference electrode respectively. The 0.1 M KHCO₃ aqueous solution was used as electrolyte directly without any purification. All the potentials were corrected using the automatic iR compensation function on the potentiostat. The potentials were measured against the reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale by the following equation, E_{RHE} = E_{Ag/AgCl} + 0.21 + 0.0591×pH. The pH value of CO₂-saturated 0.1 M KHCO₃ aqueous solution is 6.78. The current density reported in this work was normalized to the geometric surface area.

**CO₂ Reduction and Products Analysis.**

A two-compartment gastight glass H-cell was used for CO₂ electrochemical reduction. The cathodic and anodic compartments were separated by a Nafion membrane (Nafion® 117, Alfa-Aesar). Each compartment contained 30 mL of 0.1 M KHCO₃ electrolyte. The volume of the headspace is approximately 20 mL. Prior to the CO₂ reduction, the working electrodes were
reduced at a constant potential of -1.4 V (vs Ag/AgCl) for 30 min with an Ar flow of ~20 mL min\(^{-1}\) to reduce the oxides on the catalysts surface. Then the electrolyte in the cathodic compartment was purged with CO\(_2\) (99.99%, BOC) for 30 min, before the CO\(_2\) reduction was carried out at different potentials each for 70 min. The catholyte was magnetically stirred at 1000 rpm to enhance the mass transport of CO\(_2\). During the electrolysis, CO\(_2\) was continuously bubbled into the cathodic compartment at a rate of 20.0 mL min\(^{-1}\) controlled by a mass flow controller (GFC17, Aalborg\(^{®}\)) and vented directly into the gas-sampling loop (1 mL) of a gas chromatograph (GC) (8610C, SRI Instruments). The GC was equipped with a packed MolSieve 5A column and a packed Haysep D column. Argon was used as the carrier gas. A flame ionization detector (FID) with methanizer was used to quantify CO, CH\(_4\), C\(_2\)H\(_4\) and C\(_2\)H\(_6\), and a thermal conductivity detector (TCD) was used to quantify H\(_2\). External standard method was adopted with a standard gas mixture (BOC) composed of H\(_2\), CO, CH\(_4\), C\(_2\)H\(_4\), C\(_2\)H\(_6\) and CO\(_2\). The first GC run was initiated at the 20th min, and thereafter re-initiated every 16 min for three times. The average of the results from these four measurements was used in the data analysis.

Liquid products were analysed on a 400 MHz NMR spectrometer (Bruker Avance) at 30°C and quantified according to a previous report\(^{25}\). A 0.5 mL of product-containing electrolyte was syringed out from the cathodic compartment after CO\(_2\) electroreduction. It was mixed with 100 µL internal standard (1-Propanesulfonic acid 3-(trimethylsilyl) sodium salt, DSS, 99.7%, Sigma-Aldrich) and 100 µL D\(_2\)O (99.9 %, Cambridge Isotope Lab), and then transferred to a NMR sample tube. The 1D \(^1\)H spectra were measured with water suppression by a pre-saturation method. The area ratio of the formate peak or ethanol peak to the DSS peak was compared to the standard curves to quantify the concentration of formate and ethanol. Standard curves of formate and ethanol were made by using sodium formate
(99.999%, Sigma-Aldrich) and ethanol (99.5%, Sigma-Aldrich) together with the internal standard and D$_2$O, as shown in Figure S2 (Supporting Information).

**Results and discussion**

The Cu$_x$O-Sn hybrid nanowires (NWs) were fabricated on the Cu foil using a facile and scalable method, as illustrated in Figure 1a. Briefly, Cu(OH)$_2$ NWs were synthesized on Cu foil via electrochemical anodization. They were transformed to Cu$_x$O NWs via a dehydration process and a subsequent electrochemical reduction process. The electroless deposition of Sn nanoparticles (NPs) on Cu$_x$O NWs resulted in the final product, Cu$_x$O-Sn hybrid nanowires. Figure 1b shows four representative X-ray diffraction (XRD) patterns of the materials used or formed during this fabrication process. They can be assigned to the standard substances, Cu (JCPDS 04-0836), Cu(OH)$_2$ (JCPDS 13-0420), Cu$_2$O (JCPDS 65-3288) and CuO (JCPDS 48-1548). It is clear that a mixture of Cu$_2$O and CuO, denoted Cu$_x$O, was formed after the dehydration of Cu(OH)$_2$ and the subsequent reduction. The colour of the material changed concomitantly from cyan to brown and finally to dark red (Supporting Information, Figure S3). After the tin deposition, a sharp peak appeared at 51.9º corresponding to the (211) plane of SnO$_2$ (JCPDS 41-1445), indicating the successful deposition of tin on the Cu$_x$O nanowires. The corresponding morphology changes were investigated by scanning electron microscopy (SEM) as shown in Figure 1c and Figure S4. The Cu$_x$O-Sn20 (Sn deposition for 20 s) electrode exhibited a three-dimensional open porous structure composed of nanowires. These hybrid nanowires typically have a diameter of 50~100 nm with a length of several microns. They have a slightly rough surface. With increased tin deposition time, this architecture remained unchanged, however, a rougher surface was observed on the nanowires (Figure S5).
Figure 1 (a) Illustration of the fabrication process of Cu₃O-Sn NWs; (b) XRD patterns of Cu foil, Cu(OH)₂, Cu₃O and Cu₃O-Sn20; (c) Typical SEM images of Cu₃O-Sn20 NWs under various magnifications.

The morphology and structure of these hybrid nanowires were further investigated by transmission electron microscopy (TEM). Figure 2a shows a typical high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Cu₃O-Sn20 hybrid nanowires. These nanowires have rough surface, and their diameters range from 50 nm to 100 nm, consistent with SEM observations. In addition, pores or gaps are observed in the bulk or at the edges of these nanowires. This may arise from the collapse of the Cu(OH)₂ crystals during dehydration. Figure 2b shows a typical bright-field TEM image of these hybrid nanowires with tin or tin oxide nanoparticles (small black dots, ~ 20 nm) deposited on the surface. In the high-resolution TEM (HRTEM) image (Figure 2c), two different sets of lattice spacing, 0.175 nm and 0.211 nm, were observed and these can be assigned to the (211) and (210) planes of SnO₂ (JCPDS 41-1445). In addition to those relatively big SnO₂ NPs (~
20 nm, Figure 2b), the CuₓO NWs were also decorated with irregular small SnO₂ nanocrystals with a size of less than 10 nm (Figure 2c). The presence of tin species can be verified by the selected area electron diffraction (SAED) analysis as well. In the SAED pattern (Figure 2d), the obvious diffraction rings were derived from Cu₂O and CuO, indicating the polycrystalline structure of CuₓO NWs. Those four selected bright spots were indexed to the various planes of standard SnO₂. They are consistent with the XRD and HRTEM analyses. The dark-field image in Figure 2e derived from the selected diffraction spot provides further evidence for the presence and particular shape of the SnO₂ on the nanowires. In addition, the element mapping results of CuₓO-Sn20 (Figure 2f) clearly reveal the uniform and conformal deposition of Sn on the surface of Cu NWs. The mapping results of CuₓO-Sn40 and CuₓO-Sn80 are provided in Figure S6. The Sn coverage on the surface of CuₓO NWs gradually increases with the prolonged deposition time.
**Figure 2** (a) HAADF-STEM and (b) bright-field TEM image of Cu$_x$O-Sn$_{20}$ NWs; (c) HRTEM image of the hybrid NWs; (d) SAED pattern of the hybrid NWs in figure (b); (e) Dark-field image from the bright spot pinpointed by the red arrow in (d); (f) STEM elemental mapping results of Cu$_x$O-Sn$_{20}$ hybrid NWs, the bottom right image is acquired by overlaying the element Cu and Sn.

To confirm the surface chemical states of Cu$_x$O-Sn hybrid nanowires, X-ray photoelectron spectroscopy (XPS) analysis was performed. XPS spectra for Cu$_x$O and Cu$_x$O-Sn were obtained (Figure S7). Figure 3a shows the high-resolution Cu 2p spectra of three different Cu$_x$O samples. They all exhibited two main peaks at or near the binding energies of 932.6 eV and 952.4 eV that can be assigned to the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks of Cu$^{0/1+}$, respectively.\textsuperscript{31,32} The surface layer (< 10 nm) of the dehydrated Cu(OH)$_2$ NWs was mainly dominated by CuO, as evidenced by the presence of the characteristic Cu$^{2+}$ satellite peaks and the shift of Cu 2p$_{3/2}$ peak towards higher binding energy\textsuperscript{31}. After the reduction, only the peaks of Cu$^{0/1+}$ were detected. Taking the XRD and SAED results into consideration, it can be concluded that only the surface of dehydrated Cu(OH)$_2$ NWs were reduced to Cu$_2$O and/or Cu, while CuO still persisted within the core of the nanowires. In addition, the Cu 2p peaks were nearly unchanged after Sn deposition, manifesting that the presence of tin species does not significantly affect the electronic structure of the copper. Figure 3b shows the detailed Sn 3d$_{5/2}$ XPS spectrum of the hybrid nanowires. It consists of two peaks at the binding energies of 486.5 eV and 484.8 eV corresponding to Sn$^{4+}$ and Sn$^0$, respectively.\textsuperscript{44} The Sn$^{4+}$ can be ascribed to SnO$_2$ formed by the spontaneous oxidation of Sn NPs in air.
Figure 3 (a) Cu 2p XPS spectra of Cu₄O-Sn₂O, Cu₄O and dehydrated Cu(OH)₂; (b) High resolution Sn 3d XPS spectra and the corresponding fitting results.

Electrochemical reduction of CO₂ using the Cu₄O-Sn NW electrode was evaluated. Prior to CO₂ reduction, the surface oxides were electrochemically reduced by holding the electrodes at -0.8 V (vs RHE) for 30 min in Ar-purged electrolyte (Figure S8). Copper oxide and tin oxide might still persist beneath the catalyst surface, however, the residual oxides presumably do not contribute to CO₂ reduction due to the limited access afforded to the electrolyte. To simplify, Cu₄O-Sn nanowire catalysts are cited as Cu-Sn NWs in the following discussion.

Figure 4a shows the iR-corrected potential dependent total current densities ($j_{\text{total}}$) and CO partial current densities ($j_{\text{CO}}$) for Cu NWs and Cu-Sn20 NWs electrodes, which were measured and averaged based on the steady-state currents from the chronoamperometry (Figure S9). The Cu NWs exhibited higher total current densities at a potential region from -0.5 to -1.0 V (vs RHE), and a more positive onset potential for CO₂RR compared to Cu-Sn20 NWs. These results indicate that the electron transfer rate and the overall catalytic activity are
depressed after introducing Sn NPs onto Cu NWs. The longer the Sn deposition lasted, the more obvious this effect was (Figure S10). Nevertheless, this hybrid catalyst demonstrates a much more efficient CO$_2$-to-CO conversion. The CO partial current densities of Cu-Sn20 NWs significantly surpassed that of Cu NWs at all the potentials, and reached a maximum of ~ 6.7 mA cm$^{-2}$ at -1.1 V (vs RHE) compared to that only 0.24 mA cm$^{-2}$ for Cu NWs. The Tafel plot of Cu-Sn20 electrode (Figure S11) exhibited a slope of greater than 120 mV per decade over the range of -0.3 to -0.7 V (overpotential), indicating that an initial single-electron transfer to CO$_2$ forming surface adsorbed $CO_2^-$ intermediates is the rate-determining step.\textsuperscript{31,32}

Detailed product analysis for CO$_2$ reduction on these two electrodes at various applied potentials is shown in the Supporting Information (Figure S12). The products for Cu NWs included H$_2$, HCOOH, CO, CH$_4$, C$_2$H$_4$, C$_2$H$_6$ and C$_2$H$_5$OH, consistent with the previous reports\textsuperscript{32}, while only H$_2$, HCOOH and CO were detected for Cu-Sn20 catalysts; clearly demonstrating the change of catalytic nature after the Sn decoration. The potential dependent CO and H$_2$ selectivity for these two catalysts were compared and displayed in Figure 4b and 4c, respectively. The Cu NWs showed low faradaic efficiencies for CO (FE$_{CO}$ < 20%), while primarily generating H$_2$ (FE$_{H_2}$ > 60%) and HCOOH (FE ~ 30%, Figure S12) at the potential from -0.6 V to -1.0 V. In contrast, Cu-Sn20 electrode demonstrated a much higher CO selectivity and a suppressed H$_2$ evolution, especially at the middle cathodic region (-0.7 to -1.0 V vs RHE). The CO selectivity exhibited a typical volcano shape over the potential range of -1.0 V to -0.5 V, reaching a maximum FE$_{CO}$ value of 82% at -0.7 V vs RHE (corresponding to an overpotential of 590 mV relative to the CO$_2$/CO equilibrium potential, -0.11 V vs RHE). Notably, at -0.8 V vs RHE (an overpotential of 690 mV) the FE$_{CO}$ reached ~ 80% but with a significantly enhanced CO current density of 2.74 mA cm$^{-2}$, nearly three times higher than that at -0.7 V vs RHE (0.96 mA cm$^{-2}$). This indicates that an applied
overpotential of 690 mV is optimum to drive the conversion of CO$_2$ to CO with excellent selectivity and activity.

The durability of Cu-Sn20 hybrid catalyst was then evaluated under the optimal overpotential, as shown in Figure 4d. During the first 6 h of electrolysis, the current density was nearly steady, and the real-time CO faradaic efficiency fluctuated around 82%, consistent with the quasi-steady-state FE$_{CO}$ (80%, averaged over 70 min) in Figure 4b. The FE$_{H2}$ gradually increased from ~10% to ~20%. Although the FE$_{CO}$ exhibited a slight decay with further electrolysis, it still reached 78% after 12 h of electrolysis, revealing its excellent stability towards aqueous CO$_2$ reduction. This slight decline of FE$_{CO}$ and increase of FE$_{H2}$ might arise from a small amount of sintering$^{20}$ that occurred during the electrolysis as displayed in the SEM images (Figure S13) after the prolonged CO$_2$ reduction.
**Figure 4** (a) Total current densities (dashed line) and CO partial current densities (solid line) for stationary CO$_2$ electroreduction on Cu NWs (navy blue) and Cu-Sn20 NWs (red) at various potentials in 0.1 M KHCO$_3$; lines to guide the eye. (b, c) Comparison of the faradaic efficiency of CO and H$_2$ at different potentials between Cu NWs and Cu-Sn20 NWs; (d) Long-term stability test of Cu-Sn20 catalyst at -0.8 V (vs RHE) for 12 h in CO$_2$-saturated 0.1 M KHCO$_3$ solution. The error bars in (b) and (c) represent one standard deviation based on three independent sample measurements.

The hybrid Cu-Sn NWs electrodes exhibited strikingly different CO$_2$ reduction activities at -0.8V (vs RHE) depending on the coverage of Sn NPs. The faradaic efficiencies and the partial current densities of CO, H$_2$ and HCOO$^-$ significantly changed with the increase of Sn deposition time (Figure 5a, 5b). Both FE$_{\text{HCOO}}$ and FE$_{\text{H2}}$ increased with the increasing Sn deposition time. FE$_{\text{CO}}$ experienced a sharp increase within a deposition time of 10 s, and a decrease with the prolonged deposition time. When the deposition time was longer than 40 s, the evolution of HCOO$^-$ and H$_2$ prevailed. The electrochemical surface areas of these Cu-Sn hybrid NWs can be reflected by their double-layer capacitance. The capacitance experienced an increase within a Sn deposition time of 60 s (Figure S14). This trend is consistent with that for FE$_{\text{H2}}$, FE$_{\text{HCOO}}$, $j_{\text{H2}}$ and $j_{\text{HCOO}}$, but contrary to that of FE$_{\text{CO}}$ and $j_{\text{CO}}$. It indicates that the increased surface area mainly consists of active interfaces for H$_2$ and HCOO$^-$ formation. For Cu-Sn120, the FE$_{\text{HCOO}}$ reached a maximum of ~ 54% with a FE$_{\text{H2}}$ of ~32%, whereas the FE$_{\text{CO}}$ was only ~17%. This result is very close to that on a Sn electrode with a native 3.5 nm SnO$_x$ layer$^{44}$. Notably, the highest FE$_{\text{CO}}$ of ~90% was achieved on Cu-Sn10 electrode. A maximum CO partial current density of 4.5 mA cm$^{-2}$ together with a FE$_{\text{CO}}$ of 82% was reached on the Cu-Sn5 NWs. The catalytic performance is much better than that from Cu-Sn.
alloy or N-doped carbon nanotubes, Cu-Pd alloy, and even comparable to polycrystalline gold and Pd NPs.

All the above evidence suggests that the intrinsic activity for CO$_2$-to-CO conversion on Cu-Sn hybrid nanowires most likely arises from the synergistic interaction between Sn NPs and Cu NWs. This effect may be explained by reference to the recently reported DFT calculations for Cu-Sn catalysts. The Sn atom can disrupt the multifold sites on the surface of pure Cu, disfavoring the adsorption of H and leaving the adsorption of CO relatively unperturbed. Thus the hydrogenation processes (H$_2$ and HCOO$^-$ formation) are inhibited while CO productivity is hardly affected, resulting in an improved FE$_{CO}$. This effect can be optimized by tuning the density of Cu-Sn interfaces to an optimal value (corresponding to a deposition time of ~ 10 s in this work). When the active sites on Cu NWs are fully covered by Sn NPs (~ 80 s), the effect from Sn metal prevails. As revealed in Figure 5c, when the deposition time was 10 s, only a small amount of Sn species was scattered on the surfaces of Cu NWs. When the time increased to 40 s, a sparse thin Sn layer (~ 3 nm) was formed, and the Sn content concomitantly increased from 2.0 wt% to 5.6 wt%. The FE$_{CO}$ suffered from a sharp drop from 90% to 33%. These results clearly demonstrate that the improved CO selectivity is from the Cu-Sn interface. When the Sn coverage increased from 2.0 wt% to 5.6 wt%, the Cu sites responsible for CO production might mostly get occupied by Sn NPs, resulting in the significant decline of FE$_{CO}$. When the deposition time was prolonged to 80 s, the Sn layer became denser and fully covered the Cu NWs. Therefore it exhibited the prevailing catalytic performance of pristine Sn metal with a FE$_{HCOO^-}$ of ~50%.

It should be noted that the performance of our optimized Cu$_x$O-Sn electrode (high FE$_{CO}$ of ~ 90% only at -0.8 V vs RHE) is not as excellent as that of the recently reported Cu-Sn alloy catalyst (FE$_{CO}$ > 90% in a broad potential range from -0.5 to -0.8 V). This difference can be
attributed to the microstructure of Cu₃O-Sn electrode. Compared with the uniform Cu-Sn atomic arrangement in the alloy, the nanoscale non-uniform distribution of Sn NPs from electroless deposition may leave some Cu sites unaffected by Sn species. The catalytic behaviour of pristine Cu or Sn still persists in the Cu₃O-Sn electrode, leading to its relatively low performance compared with the Cu-Sn alloy catalyst. Nevertheless, the electroless deposition method applied in this work can well preserve the Cu₃O nanowires morphology to achieve a high current. For example, the Cu₃O-Sn5 electrode (5s deposition of Sn) demonstrated a \( j_{\text{CO}} \) of 4.5 mA cm\(^{-2}\) at -0.8 V, surpassing that \( \sim 3.1 \) mA cm\(^{-2}\) for the reported Cu-Sn catalyst (~15 min electrodeposition of Sn).

**Figure 5** Comparison of (a) product selectivity and (b) partial current density of CO (red squares), H\(_2\) (blue triangles) and HCOO\(^-\) (green circles) for the Cu-Sn catalysts with different Sn deposition time ranging from 0 s to 120 s at -0.8 V (vs RHE) in CO\(_2\)-saturated 0.1 M KHCO\(_3\) solution. The error bars represent one standard deviation based on three independent
measurements. (c) STEM mapping results of three typical Cu-Sn samples with various Sn deposition time (10 s, 40 s and 80 s).

The synergistic effect between adsorbed Sn NPs and Cu NWs can be further evidenced by changing the properties of Cu NWs. With this purpose, Au NPs were in situ anchored on the surfaces of Cu NWs, as an interference factor, via a facile redox reaction between copper and chloroauric acid. Cu-Au20 NWs (Au deposition for 20 s) and Cu-Au20-Sn20 NWs were prepared and investigated under the same conditions in comparison to Cu NWs and Cu-Sn20 NWs. The structural characterization of Cu-Au20 NWs is shown in Figure S15. Detailed product analysis of Cu-Au20 and Cu-Au20-Sn20 NWs can be found in the Supporting Information (Figure S16). Figure 6 highlights the potential dependent $\text{FE}_{\text{CO}}$ and $j_{\text{CO}}$ of these four electrodes. It is clear that Cu-Au20 NWs displayed similar $\text{CO}_2$-to-CO behaviour as Cu NWs. The introduction of Au does not obviously change the $\text{FE}_{\text{CO}}$. However, the $\text{FE}_{\text{CO}}$ changed dramatically after introducing Sn (20s) onto Cu-Au20 NWs, as observed for Cu NWs. It can be deduced that the introduction of Sn is the key to improve the CO selectivity. It is also noticed that Cu-Au20-Sn20 shows slightly higher $\text{FE}_{\text{CO}}$ and $j_{\text{CO}}$ values compared with Cu-Sn20, which may be ascribed to the intrinsic high activity of gold for $\text{CO}_2$-to-CO conversion, decreased electron transfer resistance (Figure S17) and increased surface area (Figure S18). Moreover, the Cu-Au20-Sn20 electrode exhibits an obvious change of the $\text{FE}_{\text{CO}}$ and the $j_{\text{CO}}$ trend at the potential region between -1.0 V and -1.2 V (vs RHE). These results clearly demonstrate that the addition of a third element Au can further alter the CO selectivity and activity.
Figure 6 Potential dependent CO faradaic efficiency (a) and partial current density (b) for Cu (orange upside down triangles), Cu-Sn20 (green triangles), Cu-Au20 (navy blue squares) and Cu-Au20-Sn20 NWs (red diamonds).

Conclusion

In summary, a novel kind of tin nanoparticles decorated copper oxide hybrid nanowire catalysts has been developed via a facile, scalable and low-cost procedure. The Cu-Sn hybrid catalyst exhibited excellent selectivity, activity and durability at moderate overpotentials towards the electrochemical reduction of CO$_2$ to CO. The enhanced performance arose from the synergistic interaction between the Sn NPs and Cu NWs, which could be easily tuned by changing the coverage of Sn NPs. Particularly, a highest FE$_{CO}$ of 90% and a maximum $j_{CO}$ of 4.5 mA cm$^{-2}$ were reached under an overpotential value of 690 mV with a Sn decoration of 10 s and 5 s, respectively. The introduction of a third metal Au between Cu and Sn can further enhance the CO selectivity and activity of these Cu-Sn hybrid nanowire catalysts. The origin of such improved catalytic performance requires further detailed studies. We believe
that our work paves a new way to fabricate non-precious Cu-based hybrid materials at a large scale for efficient reduction of CO$_2$.

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