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Selective and stable electroreduction of CO₂ to CO at the copper/indium interface

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ABSTRACT. Electrochemical reduction of CO₂ using renewable energy is a promising strategy to mitigate the CO₂ emissions and to produce valuable chemicals. However, the lack of highly selective, highly durable and non-precious-metal catalysts impedes the applications of this reaction. In this work, copper nanowires supported indium catalysts are proposed as advanced electrocatalysts for the aqueous electroreduction of CO₂. The catalysts are synthesized by a facile method, which combines In³⁺ deposition on Cu(OH)₂ nanowires, mild oxidation and *in situ* electroreduction procedures. With a thin layer of metallic In deposited on the surface of the Cu nanowires, the catalyst exhibits a CO Faradaic efficiency of ~93% at -0.6 to -0.8 V vs. RHE; additionally, an unprecedented stability of 60 hours is achieved. The characterization results combined with density functional theory (DFT) calculations reveal that the interface of Cu and In plays an essential role in determining the reaction pathway. The calculation results suggest that the Cu-In interface enhances the adsorption strength of *COOH, a key reaction intermediate for CO production, while destabilizes the adsorption of *H, an intermediate for H₂ evolution. We believe that these findings will provide guidance on the rational design of high performance bimetallic catalysts for CO₂ electroreduction by creating the metal-metal interface structure.

KEYWORDS: CO₂ electrochemical reduction, catalysis, Copper, Indium, Interface, DFT

1. INTRODUCTION

The electrochemical reduction of carbon dioxide (CO₂RR) is a promising process to reduce the excess CO₂ levels in the atmosphere and at the same time, recycle CO₂ into valuable chemicals and fuels. More importantly, this reaction can be conducted under ambient conditions, and the input electricity can be generated from solar, wind or hydropower. However, due to the competition between the CO₂ reduction and the hydrogen evolution reactions, as well as the

several proton-assisted multiple-electron transfer processes that occur during the reaction, it is highly challenging to develop highly efficient catalysts with high selectivity and stability. Previous research has shown that the selectivity of the CO₂ electroreduction products, such as CO, HCOOH, CH₄ and other hydrocarbons, has been found to strongly depend on the nature of the metal electrodes.¹ Recent efforts have been devoted towards engineering the morphology, the crystal structure and the particle size of the metals, as well as the composition of the metal alloys to enhance the CO₂RR activity to yield a certain product.^{2,3} Among all of the reduction products, CO, as an important feedstock used in the chemical industries such as Fischer-Tropsch synthesis, has attracted much attention. Excellent CO₂ to CO performances have been achieved on noble metals, e.g., Au,⁴⁻⁸ Ag⁹⁻¹² and Pd^{13,14}. For example, ~100 % selectivity of CO at an overpotential of only 0.24 V was observed on nanostructured Au catalysts,^{4,8} however, the high cost of noble metals remains a significant disadvantage in regard to their large-scale applications. Non-noble metals, such as Zn, are considered to be alternatives due to their high abundance on Earth and good CO selectivity. Nanostructured Zn electrodes, such as Zn dendrite,^{15,16} nanoporous Zn,¹⁷ and hierarchical hexagonal Zn¹⁸ have shown CO Faradaic efficiencies (FEs) of greater than 90 %; however, the high selectivity can only be achieved at very negative potentials relative to the equilibrium potential.

Recent studies have proposed that alloying Cu with other metals, such as Au,^{19,20} In²¹⁻²⁵ and Sn^{26,27}, is an effective approach to enhancing the CO selectivity at a relatively low overpotential, at the same time reducing the use of precious metals. For example, Kim et al showed that alloying Au with Cu at different compositions can selectively reduce CO₂ to CO, and that Au₃Cu showed even better CO mass activity than Au.¹⁹ Takanabe et al. developed Cu-In and Cu-Sn alloy catalysts by electrodeposition of In or Sn onto the oxide-derived Cu, and both catalysts

showed ~90 % CO FE at -0.6 V (versus a reversible hydrogen electrode, RHE; all potentials in this paper are versus RHE unless otherwise specified).^{23,26} Through alloying, the catalysts are believed to be capable of tuning the binding strength of the key reaction intermediates, such as *COOH and *H, so as to produce CO at high selectivity. However, similar alloy catalysts could lead to distinct reaction pathways due to a different atomic structure, morphology and/or composition.^{20,28} Very recently, Kim et al synthesized a series of Au-Cu alloy nanoparticles with identical morphology and composition but different atomic ordering degree and managed to show that, through ordering transformation, a highly selective CO catalyst (highly ordered Au-Cu) can be turned to an H₂ selective catalyst (disordered Au-Cu).²⁰ Moreover, Hoffman et al found that Cu-In alloy catalysts with varied compositions preferentially reduced CO₂ to formate rather than CO, which was previously observed to be the major products from Cu-In alloy catalysts.²⁵ These results indicate that rational design of highly selective alloy catalysts can be complicated by various of factors. Furthermore, surface segregation of bimetallic catalysts induced by the potential during the electrocatalytic reaction, which could lead to the deactivation of the catalysts, is also a critical issue.²⁹⁻³² In addition, since only surface atoms are utilized in catalytic reactions, the surface-to-mass ratio of the bulk alloyed catalysts should be improved to reduce the catalyst cost.³³ Therefore, it is desirable to design a bimetallic catalyst with a high ratio of active centers on the surface, less surface segregation potential, and advanced CO₂RR performance.

Herein, we discuss the fabrication of a Cu-In catalyst with a thin layer of In supported on the surface of Cu nanowires (NWs). Investigated in a 0.1 M KHCO₃ electrolyte at -0.6 V, the resulting Cu-In catalyst displayed high selectivity (> 90%) for CO production and long-term stability (60 h). The characterization results indicate that the metallic In nanoparticles are mainly

deposited on the surface of the Cu NWs, which provides a high density of Cu-In interfaces that barely changes after the stability test. The density functional theory (DFT) calculations confirm the essential role of the Cu-In interface in tuning the stability of key reaction intermediates (*COOH, *H and *OCHO) and, ultimately, the CO selectivity. The high selectivity and stability offered by the Cu NWs supported In catalyst indicates that the formation of bulk Cu-In alloy is not prerequisite for the high CO₂RR performance. This study also highlights the potential of engineering metal-metal interfaces for enhanced catalytic performance.

2. EXPERIMENTAL SECTION

2.1 Materials. Cu foils of 0.125-mm thicknesses (99.9% purity) were purchased from Goodfellow, UK. An Ag/AgCl reference electrode (3 M NaCl) was purchased from ALS Corporation, Japan. InCl₃ (99.999% trace-metal basis) and KHCO₃ (99.95%, trace metal basis) were obtained from Sigma-Aldrich. HNO₃ (2.0 N standardized solution) was obtained from Alfa Aesar. High purity CO₂ (99.999%) and N₂ (99.999%) were from Cabagas, Switzerland. All chemicals were used as purchased without further purification.

2.2 Preparation of Cu(OH)₂ NWs. The Cu(OH)₂ NWs were first synthesized on the surface of a Cu foil using a facile chemical oxidation method.^{11,34} The pristine Cu foil (1 x 1 cm²) was ultrasonically cleaned with acetone and water for 5 min. Then, it was further cleaned with 2 M HNO₃ under sonication for 5 min to remove the surface copper oxides and other impurities. Next, it was fully rinsed in Milli-Q water and dried with an N₂ flow. The foil was then immersed in an as-prepared solution containing 2.5 M NaOH and 0.125 M (NH₄)₂S₂O₈ for 10 min to grow Cu(OH)₂ nanowires. The growth process was accompanied by a change of color from reddish to dark cyan, indicating the formation of Cu(OH)₂ NWs.³⁴ Afterwards, the Cu foil with a layer of Cu(OH)₂ NWs was thoroughly rinsed with Milli-Q water and dried with an N₂ flow.

2.3 Synthesis of Cu NWs supported In catalysts. Indium was deposited on Cu by a very simple wetting method, which involved dipping the as-prepared Cu foil with Cu(OH)₂ NWs into an InCl₃ solution for 30 seconds. After that, the foil was dried with N₂ and annealed in air at 150°C for 2 h. InCl₃ solutions of various concentrations (2 mM, 5 mM, 10 mM, 20 mM, 50 mM and 100 mM) were prepared with Milli-Q water, and the corresponding catalysts prepared with these InCl₃ solution were named as CuIn2, CuIn5, CuIn10, CuIn20, CuIn50 and CuIn100, respectively.

2.4 Characterization. The ICP-OES measurements were taken using an Agilent 5110 inductively coupled plasma optical emission spectrometry (ICP-OES) system. Samples after InCl₃ deposition but before oxidation were dissolved in 2% HNO₃ for 1 min to prepare the solution for ICP measurements. In this way, all the Cu(OH)₂ nanowires and the deposited InCl₃ were dissolved but the bulk Cu foil is barely dissolved (as indicated by the control experiment, the Cu substrate contributed ca. 2.5% of the total discovered Cu, which was subtracted during the calculation of bulk In/Cu ratio). Cu and In standard solutions with different concentrations were prepared by dissolving Cu(NO₃)₂ and InCl₃ in 2% HNO₃, respectively. All measurements were performed three times, and the average values were reported. Scanning electron microscopy (SEM) images were collected on an FEI Teneo system. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analyses were performed on an FEI Tecnai Osiris at an acceleration voltage of 200 kV. This microscope is equipped with a high brightness X-FEG gun and silicon drift Super-X EDX detectors. High-angle annular dark-field (HAADF) images and EDX elemental maps were acquired in scanning TEM (STEM) mode. X-ray diffraction (XRD) patterns were obtained from a Bruker D8 Advance equipped with a Cu K α X-ray source at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) analyses were performed using a Mg

K α X-ray source (1253.6 eV) and Phoibos 100 (SPECS) hemispherical electron analyzer with a multichanneltron detector. The XPS spectra were recorded in fixed analyzer transmission mode using pass energies of 90 eV for the survey and 20 eV for the narrow scans. All the spectra were calibrated using C 1s spectra at the binding energy of 285.0 eV.

2.5 Electrochemical reduction of CO₂. The electrochemical measurements were conducted using a customized, airtight, two-compartment cell and an ALS 2352 potentiostat. A piece of platinum gauze (2.5 x 2.5 cm²) and an Ag/AgCl (3 M NaCl) electrode were applied as the counter and reference electrodes, respectively. The working and counter electrode compartments were separated with a Nafion membrane (212, DuPont). The electrolyte was a 0.1 M KHCO₃ aqueous solution prepared with Milli-Q water. Each compartment of the cell was filled with 32 mL of KHCO₃ solution and with 13 mL of dead volume. CO₂ was introduced into the cathodic compartment and was controlled by a mass flow controller (EL-Flow, Bronkhorst) at a flow rate of 21 mL/min during the experiments. It was allowed to saturate the solution for at least 30 min before the start of each experiment (the pH value was measured to be 6.8), while the anodic compartment was bubbled with N₂ at 20 mL/min. All potentials were recorded against the Ag/AgCl (3 M NaCl) reference electrode and then converted to reversible hydrogen electrode (RHE) values using the Nernst equation: $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.21 \text{ V} + 0.0591 \text{ V} * \text{pH}$.

The gas-phase products were detected online with a gas chromatograph (GC, SRI instruments 8610C) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID with a methanizer). The CO₂ gas flow with the products from cathodic compartment was vented directly into the sampling loop of the GC. Aliquots were collected every 20 min during the reaction, and at least three injections were measured per potential. Liquid products were

detected by high-performance liquid chromatography instrument (HPLC, Thermo Scientific, Dionex UltiMate 3000 Standard System) according to the procedure described before.³⁵

2.6 DFT models and calculations. All plane-wave DFT calculations were carried out with the Vienna ab initio Simulation Program (VASP)³⁶ using the generalized gradient approximation (GGA) and Perdew, Burke and Ernzerhof (PBE)³⁷ exchange-correlation functional. The Cu(111) and Cu(211) surfaces were modeled using a three-layer (6 x 6) Cu (111) and a three-layer (3 x 2) Cu(211) periodic unit cell, respectively. The Cu supported In surface was modeled using a (2 x 2) monolayer In island on a three-layer (6 x 6) Cu(111) surface. In all cases, the bottom layer was fixed during optimization, while the remaining atoms were relaxed until the forces in the system were less than 0.05 eV/ Å. The projector augmented wave pseudopotentials³⁸ were used to describe the interactions between the ions and electrons in expanding plane waves with a 400 eV cutoff energy and employing a 5 x 5 x 1 Monkhorst-Pack mesh³⁹ for k-point sampling. The fermi-level smearing was set at 0.1 eV, and spin polarization was included in all DFT calculations. In determining the adsorption energies, all sites on Cu(111) and Cu(211), as well as the sites on and near the In island, were considered. Only the most stable sites and adsorption configurations are reported here.

All thermodynamic properties were calculated based on the molecular vibration analysis from the DFT calculations. The free energies of the adsorbates were treated with 3N degrees of freedom for the vibrational calculations. In our study, all vibrations were treated as harmonic oscillator approximations. The Gibbs free energies were calculated at 298 K and 1 atmosphere according to $G = E_{\text{DFT}} + E_{\text{ZPE}} + \int_0^{298} C_V dT - T\Delta S$, where E_{DFT} is the DFT total energy, E_{ZPE} is the zero-point vibrational energy, $\int_0^{298} C_V dT$ is the heat capacity, T is the temperature and ΔS is the entropy. Gas-phase molecules were treated as an ideal gas, corrections for molecules (CO₂,

CO and HCOOH) have been applied using the values for the PBE function to accurately describe the reaction free energy for CO₂RR.⁴⁰ An approximate solvation correction to account for the effect of water has been applied for *COOH and *CO, which were stabilized by 0.25 and 0.1 eV, respectively. Free energy diagrams were established using the computational hydrogen electrode (CHE) method, following the seminal work of Nørskov et al.⁴¹ Additional details of the DFT calculations are provided in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization. A facile method with mild preparation conditions was used to prepare the Cu-In catalysts. Firstly, the Cu(OH)₂ NWs were grown on a Cu foil surface *via* chemical oxidation in a NaOH and (NH₄)₂S₂O₈ solution for 10 min.^{11,34} Then, In was deposited by simply dipping the Cu(OH)₂ NWs/Cu into the InCl₃ aqueous solution for 30 s. Taking the advantage of the super-hydrophilic property of the Cu(OH)₂ NWs,⁴² the InCl₃ solution can immediately wet the Cu(OH)₂ layer leading to the homogeneous dispersion of In³⁺ on the Cu(OH)₂ NWs (Figure S1). Afterwards, the obtained material was dehydrated at 150°C for 2 h in an air atmosphere and the final catalyst was obtained by the *in situ* electroreduction prior to the CO₂ electroreduction experiments.

Figure 1a-d shows SEM images of the typical CuIn20 catalyst evolution process according to the sample preparation steps (see Figure S2 for additional SEM images). After chemical oxidation, the Cu(OH)₂ NWs homogeneously cover on the surface of the Cu foil with an average length of ca. 10 μm (Figure 1a). The crystal structure is confirmed by XRD to be Cu(OH)₂ (JCPDS 13-0420) while the high intensity peaks at 43.4 ° (111) and 50.4 ° (110) are attributed to the Cu foil substrate (PDF 01-071-3645) (Figure 1e). XPS was used to investigate the surface

chemical states of the samples. As shown in Figure 1f, the peaks at 934.7 eV and 954.6 eV can be assigned to the Cu 2p_{3/2} and Cu 2p_{1/2} peaks while the other two peaks are shown as satellite peaks. The high intense satellite peaks are characteristic of Cu²⁺, and the Cu 2p_{3/2} peak position (934.7 eV) agrees well with that of Cu(OH)₂.⁴³

Figure 1 Morphology, crystal structure and surface oxidation state evolution of the CuIn20 catalyst characterized by SEM, XRD and XPS. (a) As prepared Cu(OH)₂ NWs, (b) after immersing into 20 mM InCl₃ solution for 30 s, (c) after oxidation at 150 °C for 2 h and (d) after electrochemical reduction at -0.6 V for 20 min in CO₂ saturated 0.1 M KHCO₃. Corresponding XRD patterns (e) and XPS spectra (f) of the sample after each preparation step, spectra from bottom to top represent of step (a) to (d).

After dipping the NWs into a 20 mM InCl₃ solution, they become less sharp but also rougher due to the corrosive nature of the acidic solution (Figure 1b). No significant differences in the XRD patterns were observed after this step, indicating that the crystal structure of the Cu(OH)₂ NWs was left unchanged. The absence of diffraction peaks from the In species could be due to the small amount of In and/or its amorphous structure. Nevertheless, the presence of In peaks (445.2 eV for In 3d_{5/2} and 452.8 eV for In 3d_{3/2}) in the XPS spectra confirms that In³⁺ ions have been deposited on the Cu(OH)₂ NWs (Figure 1f). Interestingly, the peak positions are in

accordance with those of $\text{In}(\text{OH})_3$ rather than InCl_3 (see Figure S3 for XPS spectra of standard InCl_3 and $\text{In}(\text{OH})_3$), implying that the In exists mainly in the form of $\text{In}(\text{OH})_3$.

After dipping, the sample was oxidized in air, and open pores were introduced along the nanowires due to the dehydration of $\text{Cu}(\text{OH})_2$ (Figure 1c).²⁷ As a result, the CuO phase (JCPDS 45-0937) was detected by XRD, as shown in Figure 1e. The XPS spectra confirm the Cu^{2+} valence state, while the slightly lower binding energy shift of the peak indicates the formation of CuO.⁴³ At the same time, $\text{In}(\text{OH})_3$ was also oxidized to In_2O_3 , as indicated by the shift of the In $3d_{5/2}$ peak to 444.8 eV.

The electrochemical reduction was performed at -0.6 V in CO_2 saturated 0.1 M KHCO_3 , and the current reaching a steady state after the complete reduction (Figure S4). The CuO NWs become less homogeneous but still retain their form as nanowires (Figure 1d). The XRD pattern shows that the CuO peaks are disappeared and the diffraction peaks from the reduced Cu are hardly noticeable due to the strong background peaks from the Cu foil. In the XPS spectrum, a shift of the Cu 2p peak to a lower binding energy, accompanied by the disappearance of the satellite peaks, is a reliable indicators of the reduction of CuO to $\text{Cu}^0/\text{Cu}^{1+}$. Although it is difficult to distinguish Cu_2O from metallic Cu due to their similar binding energy values,²⁶ the Cu LMM Auger spectra (See Figure S5) confirms the presence of Cu on the sample surface. In the case of In, again, no diffraction peak arises from In species, but the XPS spectrum of In shows a slight broadening and a shifting to a lower binding energy. Deconvolution of the In $3d_{5/2}$ peak reveals that it consists of two peaks at the binding energies of 444.8 eV and 443.8 eV which can be assigned to In_2O_3 and metallic In, respectively.⁴⁴ According to the cyclic voltammogram (CV) results (Figure S6), In is in the metallic state at the potentials lower than -0.4 V, which is

consistent with the Pourbaix diagram as well as the previously reported results.^{24,31} Thus presence of In_2O_3 can be ascribed to the air oxidation before the XPS measurement.

The detailed morphology, crystal structure and elemental distribution of the CuIn20 catalyst were examined by TEM coupled with EDX. Figure 2a shows the bright-field TEM image of a CuIn20 NW. As can be seen, the NW has a porous structure and is composed of nano-sized grains ranging from 10 to 30 nm. EDX elemental maps (Figure 2b-e) reveal the homogeneous distribution of the Cu in the entire nanowire structure, forming Cu nano grains that are covered with a thin layer (< 5 nm) of In on the surface. To assess the crystal structure of these phases, selected area electron diffraction (SAED) patterns and dark-field TEM images were also collected and these are shown in Figure 2. Experimental SAED patterns of the NW and a region close to its surface are compared with simulated patterns of Cu and In in Figure 2f. The clear diffraction rings at 4.8, 5.6, 7.9 and 9.3 nm^{-1} correspond to the (111), (200), (220) and (311) reflections of Cu, while an additional weak and diffuse ring at 3.7 nm^{-1} is from the (101) reflection of In. Dark-field TEM images using the In(101) (Figure 2g) and Cu(111) (Figure 2h) reflections show that the nanowire is composed of Cu grains of ~ 10 to 20 nm in size and that the covering layer is made of ~ 1 to 3 nm sized In nanoparticles. Combining the morphology, surface state and crystal structure measurements, we can conclude that a thin layer of metallic In was successfully deposited on the surface of the Cu NWs and the highly dispersed In nanoparticles could provide abundant Cu-In interfaces.

Figure 2 (a) Bright-field TEM image of the CuIn₂₀ sample. (b) HAADF-STEM image and the corresponding EDX elemental maps of (c) Cu + In, (d) In and (e) Cu. (f) SAED patterns of the CuIn₂₀ wire (upper part) and simulated diffraction pattern of In and Cu (bottom part). Dark-field TEM images formed using (g) In(101) and (h) Cu(111) reflections.

3.2 CO₂ eletroreduction performance. Cyclic voltammetry, performed in an N₂ and CO₂ saturated 0.1 M KHCO₃ electrolyte, was used to provide an initial, qualitative assessment of the electrocatalytic performance of the Cu NWs as well as the CuIn₂₀ catalyst. The current densities (geometric current density, all current density in this work are versus geometric surface area unless otherwise specified) recorded during N₂ purge are due to the hydrogen evolution reaction (HER), where the Cu NWs sample shows much higher current density than that of CuIn₂₀, indicative of a strong suppression of H₂ evolution on the CuIn₂₀. In CO₂ saturated electrolyte, the current densities acquired on the Cu NWs (at potentials between -0.6 to -0.8 V) are less than

a half of those occurring under a N_2 atmosphere. The decreased current density in the CO_2 atmosphere is in agreement with the previously reported results for Cu electrodes,^{1,45} and has been proposed to be due to the adsorption of reaction intermediates (e.g. CO) on the Cu surface, which blocks the Cu active sites and therefore decreases the current density. However, purging of CO_2 does not lead to this decrease of current density for CuIn20; on the contrary, a slightly increase can be observed in this case. This result, along with the fact that the CuIn20 shows higher current density than the Cu NWs in the presence of CO_2 , is already an indication of the distinct performance of the CuIn20 catalyst in regard to CO_2 reduction.⁴⁶

To investigate the reduction products and to determine the catalyst selectivity of both the Cu NWs and CuIn20, potentiostatic CO_2 electrolysis was carried out in CO_2 saturated 0.1 M $KHCO_3$ solution. Figures 3b and c present the FEs of the reduction products in a potential range of -0.4 V to -1.0 V on the Cu NWs and CuIn20. As shown in Figure 3b, the Cu NWs sample shows a typical volcano-shaped evolution of CO selectivity over the studied potential range, which increases from 18% at -0.4 V to 47% at -0.6 V and then decreases after -0.7 V, reaching 16% at -1.0 V. In agreement with previous studies of oxidized Cu-derived catalysts, CO is the predominant reaction product at low to medium overpotentials.^{7,23,26,27,47,48} Formic acid ($HCOOH$) is another product reduced from CO_2 ; its selectivity increased linearly with a decrease in the applied potential to -0.8 V, and it then decreased slightly at -1.0 V. This trend is also consistent with the results in the literature for polycrystalline Cu^{1,49} and some oxide-derived Cu catalysts.^{48,50} HER, as a competitive reaction of CO_2RR , produces H_2 in the whole investigated potential window, with high FE (> 50%) at less negative potentials (-0.4 V and -0.5 V). In contrast, for the CuIn20 catalyst, CO is the only major reduction product in the entire studied potential range. Its FE approaches 95% in the range of -0.6 to -0.8 V which is even higher than

that of other state-of-the-art Cu alloy catalysts (CuIn, CuSn, etc.) and some noble metals under similar experimental conditions.^{21–24} The distinct preference for CO formation in combination with the suppression of H₂ and HCOOH formation implies a change in the catalytic nature after In deposition. The total current density (j_{tot}) and CO partial current density (j_{CO}) of the Cu NWs and CuIn20, measured under potentiostatic conditions, are plotted in Figure 3d. The j_{tot} of CuIn20 is systematically higher than that of the Cu NWs catalyst, in agreement with the CV results (Figure 3a), and indicative of an improved overall activity. The enhanced j_{tot} can be mainly attributed to the increased surface roughness (Figure S7 and Table S1) during the CuIn20 sample preparation, as well as the distinct nature of the catalytic centers. Since j_{tot} also includes the current from HER, j_{CO} provides a better understanding of the catalytic CO₂-to-CO performance. As shown in Figure 3d, a dramatic difference can be observed between CuIn20 and Cu NWs, such that the j_{CO} from CuIn20 are on average more than 5 times higher than those of the Cu NWs.

Figure 3 (a) Cyclic voltammograms obtained for Cu NWs and CuIn20 in N₂ or CO₂ saturated 0.1 M KHCO₃ electrolyte (scan rate: 50 mV/s). Faradaic efficiency analysis of (b) Cu NWs and (c) CuIn20 at various potentials (error bars represent the standard deviation of three independent measurements). (d) Comparison of the total current density and CO partial current density profiles for Cu NWs and CuIn20. (e) Stability test of Cu NWs and CuIn20. Data in (b)-(e) were acquired in CO₂ purged 0.1 M KHCO₃ solution. (f) Overview of various reported Cu based bimetallic catalysts' performance for CO₂-to-CO in aqueous electrolyte, including Cu-In²¹⁻²⁵, Cu-Sn^{26,27}, Cu-Au^{19,20,51}, Cu-Pd^{52,53}, and Cu-Ag⁵⁴ (the details are summarized in Table S2 and Table S3 in the Supporting Information).

Long-term electrolysis was performed at an applied potential of -0.6 V to test the stability of the Cu NWs and CuIn20 (Figure 3e). Although the Cu NWs catalyst shows a ~50 % CO FE during the first hour of electrolysis, that value declines to ~37 % over 5 h and reaches to 32 % after 12 h of operation. In stark contrast, the CuIn20 catalyst exhibits an unprecedented stability. During a 60 h stability test, the total current density is stable at ~1.7 mA/cm², and the CO FE maintains a value of over 90 % (an average of fluctuating values) with negligible decay. Deactivation of Cu electrodes during CO₂RR has been investigated in previous studies and different mechanisms for this phenomenon proposed,^{1,55-60} in light of which, some insight into the improved stability of CuIn20 can also be provided. One of the reasons for Cu electrodes deactivation is the deposition of metal impurities, such as Fe, Zn etc., from the electrolyte onto the Cu surface,^{55,56} so that the observed long-term stability of the CuIn20 catalyst may be attributed to its low sensitivity to the metal impurities. According to the previous report,²¹ In suppresses HER of the pure metal electrodes (e.g. Fe, Co, Ni, Cu and Zn) when it forms alloys with those metals. Therefore, deposition of impurities onto the surface of the In covered Cu

(CuIn20) instead of pure Cu (Cu NWs) may lead to the formation of an In-based bimetallic structure which is likely to slow down the deactivation. Formation of graphitic carbon due to the decomposition of reaction intermediates (e.g. CO), which accumulated on the surface over time, was also proposed as an explanation of the degradation of Cu electrodes.^{1,57–60} As it is evident in Figure 3a that the Cu NWs electrode loses its catalytic activity in the CO₂ saturated electrolyte, while such a process is not observed in the case of CuIn20. It is reasonable to suggest that the formation of graphitic carbon from catalytic intermediates decomposition is more plausible with the Cu NWs than CuIn20. In addition, the stable Cu supported In structure should also play an important role in the long-term performance. For bimetallic systems, surface segregation of one metal onto the other driven by various forces, such as heat, potential and adsorbates etc., has been found to cause the degradation of the catalysts.^{29,30} However, in our case, most of the In is originally deposited on the surface of the Cu NWs instead of the bulk (Figure 2). Therefore, further segregation of In onto the surface during the CO₂RR, as observed in other In-based alloy systems,^{25,31} is not expected. This is confirmed by the SEM, XRD and XPS characterizations, from which no significant change of the sample property is observed after the 60 h test (Figure S7).

Notably, although stability is crucial for practical applications, evaluations of Cu-based catalysts, for example, oxide-derived Cu and Cu-based alloys, were performed only for ~ 10 h in the previous studies^{23,26,27,50} and deactivation could already be observed in some works after several hours of operation.^{23,26,27} To place the CuIn20 catalyst in the context of the CO₂-to-CO catalysis literature, we compared the CO selectivity and catalyst stability of CuIn20 with the state-of-the-art Cu-based alloy catalysts in which CO₂RR is also performed in aqueous electrolytes and at atmospheric pressure (Figure 3f) (details are given in Table S2 and S3). It is

obvious that the CuIn20 catalyst in this work is promising as it is among the most selective Cu-based electrocatalysts, active at low over potential and exhibits exceptional operational stability.

Catalysts prepared by immersing Cu NWs in InCl_3 solutions with different concentrations were also employed to study the effects of the In-deposition amount on the CO_2RR performance. Prior to the activity test, the amount of deposited In was determined by ICP-OES analysis. As shown in Figure 4a, the In deposition amount is linearly related to the concentration of InCl_3 , which indicates that the amount of In can be simply tailored by manipulating the concentration of InCl_3 . The CO_2 electrolysis campaign was then carried out at a constant potential of -0.6 V on these Cu-In catalysts. The significant difference in the FE and current density values (shown in Figure 4b) implies that the amount of deposited In plays an essential role in the catalytic performance during the CO_2RR . Interestingly, both the current density and the CO FE follow a similar trend that first increases with the In amount, reaching a maximum at the CuIn20 catalyst, and then decreases for a higher amount of In. The change in the j_{tot} is mainly correlated to the evolution of the surface morphology. As shown in the SEM results (Figure 1 and Figure S2), the slight etching of the $\text{Cu}(\text{OH})_2$ NWs with a low-concentration InCl_3 solution (5 to 20 mM) increases the surface roughness while higher concentration solutions (50 to 100 mM) cause severe corrosion of $\text{Cu}(\text{OH})_2$ and lead to the reduced surface area. This is confirmed by a similar trend in the double-layer capacitance results, which reflect a change in the electrochemically active surface area (Table S1). Moreover, the adsorption of reaction intermediates may also play an role in decreasing the j_{tot} , particularly for the sample with a small amount of In on the surface (Figure S9).

Figure 4 The effect of InCl_3 concentration on (a) the In-deposition amount, (b) total and CO partial current densities, (c) Faradaic efficiencies and (d) the In/Cu atomic ratio of the obtained catalysts. CO_2RR were performed at -0.6 V in CO_2 saturated 0.1 M KHCO_3 . The error bars represent the standard deviation from at least three independent measurements.

Concerning the catalytic selectivity, H_2 , CO and HCOOH are the only products detected by GC and HPLC, with the total FEs of 97.6 ± 3.6 %. As shown in Figure 4c, for all of the Cu-In catalysts, the FEs of H_2 and HCOOH are suppressed but the formation of CO is preferred, emphasizing the importance of In decoration. The CO FE, however, depends strongly on the In-deposition amount and reaches a maximum ($\sim 93\%$) for the CuIn20 catalyst (with an In deposition amount of $0.52 \mu\text{mol}/\text{cm}^2$). At values below $0.52 \mu\text{mol}/\text{cm}^2$, the CO FE shows an increasing trend with the amount of In, while an excess of In (higher than $0.52 \mu\text{mol}/\text{cm}^2$) leads to a decrease in the CO selectivity. This variation in selectivity should be attributable to the changes in the number of catalytic centers, which will be further discussed later. To demonstrate the profoundly high surface-to-mass ratio of In in our Cu-In catalysts, In/Cu atomic ratios

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3 derived from ICP-OES and XPS results are plotted in Figure 4d, representing the bulk and
4 surface In/Cu ratios, respectively. Both profiles display a good positive linear relationships with
5 the InCl_3 concentrations. However, the surface In/Cu ratios are approximately 20-fold higher on
6 average than the bulk ratios. Taking the CuIn20 sample as an example, although the In/Cu ratio
7 calculated from the ICP-OES results is only 0.031, the surface ratio obtained from XPS is 0.86.
8 This is also in agreement with the TEM results (Figure 2), where the In nanoparticles are
9 distributed on the surface of Cu grains.

10
11 Since the dramatic difference between Cu NWs and CuIn20 regarding the CO selectivity is
12 clearly evidenced by the experimental data, the origin of this difference needs to be understood.
13 The selective production of CO on the Cu NWs (47% at -0.6 V) can be attributed to the high
14 surface area and high density of the grain boundary structure that forms during the
15 electrochemical reduction of Cu oxides, as previously proposed for other oxide-derived Cu
16 catalysts.^{47,50} In addition, the higher local pH around the Cu NWs cathode, which is raised due to
17 the production of OH^- from HER and CO_2RR , could also suppress the H_2 production.^{1,61} For the
18 CuIn20 catalyst, since a small amount of In was deposited on the $\text{Cu}(\text{OH})_2$ NWs precursor and
19 identical oxidation/electroreduction treatments were applied as those for Cu NWs catalyst, it can
20 well inherit the morphological and structural advantages of the Cu NWs. However, these features
21 are not sufficient to provide a long-term (60 h) high CO selectivity (> 90%), as demonstrated by
22 the fast deactivation of Cu NWs electrode (Figure 3e). Thereby, the superior CuIn20
23 performance should be originated from the unique synergy between Cu and In. Previous works
24 have shown some evidence for such the Cu-In synergistic effects in CO_2RR , however, the
25 intrinsic active sites have still not been definitively determined. According to the work of the
26 Takanabe group,^{22,23} the active sites are ascribed to the Cu-In alloys, where the In atoms

occupied the Cu step sites and hindered the adsorption of H thus inhibiting the HER. While through the evolution of different Cu-In catalysts (CuInO_2 , $\text{Cu/In}_2\text{O}_3$ and Cu/In(OH)_3) under CO_2RR conditions, Larrazábal et al. noted that the presence of an In(OH)_3 shell-like matrix surrounding the Cu-rich regions was essential for the high performance.²⁴ Nevertheless, these findings cannot explain our results, since neither Cu-In alloys nor an In(OH)_3 phase was detected from the fresh (Figures 1e and 2) and used CuIn20 catalyst (Figure S7). Therefore, a different type of Cu-In synergy must be responsible for the enhanced CO_2RR performance.

3.3 DFT modeling. The characterization results have shown that instead of forming Cu-In alloys, the In nanoparticles are adsorbed on the Cu NWs in the metallic state, providing abundant Cu-In interfaces. This suggests that the synergistic effects between metallic Cu and In could be the main factors in enhancing the CO selectivity. In order to understand and assess the influence of synergistic effects on the CO_2RR performance, DFT calculations were conducted. Whilst it remains a computational challenge to directly simulate the CO_2 reduction over real nanoparticles (several nm size) by means of DFT calculations,¹³ it is nonetheless possible to simulate the process on a Cu-supported small In island, representing as the model of the Cu NWs supported In nanoparticles. This simplification can be made based on the calculated results that (1) increases in the number of In atoms and (2) increases in the number of layers of the In island do not substantially change the electronic structure of Cu and In (Figure S10 – S12), which is also in agreement with the previous findings.³³ In addition, a two-dimensional In island is found to be more stable than a three-dimensional island under the simulation condition (details in Figure S11). Therefore, a four-atom mono-layer In island supported on a Cu(111) surface (referred to In@Cu) was constructed as a DFT model to illustrate the Cu-In synergistic effects. For comparison, DFT simulations were also performed on Cu(111) and Cu(211) facets, representing

the Cu NWs. The Cu(111) facet was selected because it shows the most intense diffraction ring in SAED (Figure 2) and it is also the most stable low-index facet among the planes, while the Cu(211) facet represents the stepped facet and is suggested to be more energetically favorable for CO₂RR than terrace sites.⁴⁰

Figure 5 shows the calculated Gibbs free energy (ΔG) diagrams (details in Table S4 and S5) for CO₂ reduction to CO through three proposed elementary reaction steps:⁶²

where the asterisk (*) indicates either a surface-bound species or a vacant catalytically active site. As shown in Figure 5a, the activation of CO₂ through the formation of a COOH* intermediate is the potential-determining step (PDS) for all three facets and is shown as an uphill energy barrier for the first proton-coupled electron-transfer step. Apparently, the ΔG required to form *COOH is lower for the In@Cu surface as compared to the Cu(111) and the stepped Cu(211) surfaces, suggesting a lower onset potential requirement for CO₂RR on the In@Cu surface. The binding configurations of *COOH on In@Cu shown in the top panel of Figure 5a and the corresponding density of states (DOS) (details in Figure S13) could help in understanding the origin of the decreased ΔG for *COOH on In@Cu. It is noticeable that, with a more oxygen affinitive metal In on the surface of Cu, C in *COOH binds to Cu, whereas O binds to In. This binding configuration shifts the DOS of the adsorbed *COOH to a lower energy level compared with that on the Cu(111) surface, indicative of an improved *COOH stabilization. Furthermore, since the electronic structures of Cu and In are not significantly influenced by each other (Figure S10), geometric effects rather than electronic effects probably play a dominant role

to enhance the adsorption strength of $^*\text{COOH}$.^{33,63} The subsequent step to generate adsorbed $^*\text{CO}$ proceeds downhill in free energy on all three surfaces. After $^*\text{CO}$ formation, desorption of CO from In@Cu is more difficult than that for Cu(111), even though, CO desorption is expected since the energy barrier is only 0.17 eV, while the further protonation of $^*\text{CO}$ to $^*\text{CHO}$ should not occur because of the much higher energy barrier (0.8 eV, Figure S14). In the case of Cu(211), the surface binds to CO even strongly, thus the catalytic activity could be suppressed due to the large CO desorption energy.^{40,64} This explains the experimental observation in CV (Figure 3a) that Cu NWs shows lower current density in CO_2 saturated electrolyte. Moreover, as we discussed earlier, further reduction of the strongly bound $^*\text{CO}$ may also lead to the accumulation of carbon and therefore the poisoning of the Cu NWs electrode.

It is also worth noting here that, when compared with the previously reported DFT calculations for a Cu-In alloy catalyst,²³ a significant difference between the two systems is observed regarding the stabilization of the intermediates. In particular, the presence of In in the Cu-In alloy improves the stability of $^*\text{COOH}$ by less than 0.1 eV while barely changing the CO adsorption energy.²³ However, the distinct trends shown in our system (significantly improved $^*\text{COOH}$ stability and moderately enhanced $^*\text{CO}$ stability) indicate that the Cu-In interface behaves differently to the Cu-In alloy in the CO_2RR process. These differences are also in agreement with the recently reported results for Au-Cu interfaces and Au-Cu alloys, where the Au-Cu interface is more effective than the Au-Cu alloys in stabilizing the $^*\text{COOH}$ and $^*\text{CO}$.³³

To further elucidate the high CO selectivity on the In@Cu surface, the free energies for the HER reaction steps were also calculated and are plotted in Figure 5b. As a much higher free energy (0.67 eV) is required for $^*\text{H}$ adsorption on In@Cu compared to Cu(111) (0.12 eV) and Cu(211) (0.08 eV), the In@Cu surface is predicted to be less active than the Cu facets for H_2

1 evolution. Likewise, the production of formic acid as a competitive reaction was also calculated
2
3 with DFT. Recent results have suggested that formate (*OCHO) is the key intermediate for CO₂-
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5 to-HCOOH,⁶⁵⁻⁶⁸ thus the free energy diagrams for this pathway are summarized in Figure 5c; as
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7 shown, formation of *OCHO is thermodynamically favorable on the Cu(211) and In@Cu
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9 surfaces while a 0.28 eV energy cost is needed for the Cu(111) surface. Additionally, on all three
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11 surfaces while a 0.28 eV energy cost is needed for the Cu(111) surface. Additionally, on all three
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13 surfaces, the *OCHO intermediate is much more stabilized than *COOH. However, instead of
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15 HCOOH, CO is the major product experimentally observed in the low overpotential range (< -
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17 0.7 V) on Cu NWs and CuIn₂₀ catalysts. This indicates that although the employed
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19 thermodynamic model explains well the favoring of CO production over *CHO and HER and the
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21 advantages of In@Cu over Cu(111) and (211), it cannot straightforwardly explain the
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23 predominance of CO over HCOOH. This is likely due to the additional activation barrier needed
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25 for the production of HCOOH which is not captured in the electronic energy calculations, as
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27 proposed previously in other systems.^{65,69-72} For example, the hydronium and/or the metal
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29 cations in the system could lower the activation barrier for *COOH, and therefore, limit the
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31 production of HCOOH and lead to the high selectivity of CO.^{65,69,70} Nevertheless, the too strong
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33 *OCHO adsorption strength on In@Cu is still a limiting factor for HCOOH production.⁶⁵ Taken
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35 together, the theoretical calculations suggest that the enhanced CO selectivity of CuIn₂₀ should
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37 be mainly attributed to the Cu-In interfacial sites, which significantly decrease the energy barrier
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39 for the formation of *COOH but can still readily release the adsorbed *CO. Moreover, the
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41 weakly adsorbed *H and strongly adsorbed *OCHO at the Cu-In surface could also suppress the
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43 selectivity of the competitive reactions.
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Figure 5 Free energy diagrams for (a) CO₂ to CO, (b) H₂ evolution and (c) CO₂ to HCOOH on Cu(111), Cu(211) and In@Cu surfaces, at 0 V vs. RHE. The upper panels show the DFT-optimized geometries for each reaction step on In@Cu (geometries on the other two facets are summarized in the Supporting Information). Cu: reddish-orange, In: yellow, C: dark-gray, O: red, and H: white.

The critical role of the In content on the CO₂RR performance, therefore, can also be correlated with the Cu-In interfaces since the interfacial area is linked to the surface In coverage. It is challenging to quantitatively determine the interfacial area of the Cu and In with an experimental method (Figure S15), however, the XPS results along with the simulation, carried out with the Simulation of Electron Spectra for Surface Analysis (SESSA) software, can provide an appropriate estimation (details in the Supporting Information).^{73–76} The simulation results (Figure S16 and S17) show that, for all the Cu-In samples, both of the Cu and In surfaces are exposed to the electrolyte, demonstrating that the Cu-In interfaces are accessible for CO₂RR. Additionally, increasing the In deposition amount gradually decreases the Cu exposure area (from ~87 % to ~23%), while an optimized amount of In (CuIn20 sample) leads to a medium coverage of the Cu surface and provides the highest number of Cu-In interfacial sites (Figure S18b). More importantly, we found that the number of interfacial sites follows the same volcano-shaped trend

as the CO₂-to-CO activity (j_{CO} , Figure 4b), which again confirms the active role of the Cu-In interfaces and the importance of surface In coverage.

4. CONCLUSIONS

In summary, we report a high performance CO₂RR catalyst with a thin layer of In covering on the surface of the Cu NWs, which is fabricated by dipping Cu(OH)₂ NWs into InCl₃ solution in order to deposit a small amount of In³⁺ on the surface, followed with a mild oxidation and *in situ* electroreduction treatments. By tuning the concentration of the InCl₃ solution, the In deposition amount can be easily manipulated. All of the studied Cu-In catalysts show enhanced CO₂RR performance compared to that of the Cu NWs, in particular, with an optimized amount of In (0.52 μmol/cm²), the CuIn20 catalyst reaches a CO Faradaic efficiency of ~93% at -0.6 V and has an unprecedented stability over a 60 h period. Detailed characterizations, including SEM, XRD, XPS, TEM and ICP-OES, prove that a high density of metallic In nanoparticles are deposited mostly on the surface of the Cu NWs, providing abundant Cu-In interfaces. The DFT calculations reveal that the interface of the two metals significantly decreases the free energy barrier for the formation of the key reaction intermediate (*COOH) of CO₂ to CO. Concurrently, the weakly adsorbed *H and strongly adsorbed *OCHO are suggested to suppress the activity of competitive H₂ and HCOOH production reactions. This study shows that Cu-In interfaces derived from a simple synthetic approach can be highly selective and stable for CO₂ to CO reaction, which could inspire the further development of advanced bimetallic catalysts through the creation of a high density of metal-metal interfaces.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Further SEM/XPS/XRD characterization of the as prepared and used Cu-In catalysts, chronoamperometry curve for the pre-reduction of the CuIn₂₀ catalyst, measurement of the double layer capacitance, activity and stability comparisons with other CO₂ electroreduction catalysts, cyclic voltammogram results, details of DFT calculations and details of the Cu-In interface determination.

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Notes

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