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# Solvothermally-Prepared Cu<sub>2</sub>O Electrocatalysts for CO<sub>2</sub> Reduction with Tunable Selectivity by the Introduction of p-Block Elements

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Abstract: The electroreduction of CO2 to fuels and chemicals is an attractive strategy for valorizing CO2 emissions. In this study, we show that a Cu<sub>2</sub>O electrocatalyst prepared by a simple and potentially scalable solvothermal route effectively targeted CO evolution at low to moderate overpotentials ( $CE_{co}$  ca. 60% after 12 h at -0.6 V vs. RHE), and that the introduction of p-block elements (In, Sn, Ga, Al) into the catalyst can be employed to tune its selectivity. SEM, HRTEM, and voltammetric analyses revealed that the Cu<sub>2</sub>O catalyst undergoes extensive surface restructuring (favorable for CO evolution) under reaction conditions. Modification of Cu<sub>2</sub>O with Sn and In further enhanced the current efficiency for CO (ca. 75% after 12 h at -0.6 V). On the other hand, the introduction of AI significantly altered the selectivity profile of the catalyst, decreasing the selectivity toward CO but promoting the reduction of CO<sub>2</sub> to ethylene (CE ca. 7%), n-propanol, and ethanol (CE ca. 2% each) at -0.8 V vs. RHE. We relate this result to a decreased reducibility of Al-doped Cu<sub>2</sub>O which might preserve Cu<sup>+</sup> species (favorable for C<sub>2</sub>H<sub>4</sub> production) under reaction conditions, as supported by XRD, XPS and H<sub>2</sub>-TPR observations.

### 1. Introduction

The development of technologies able to transform waste materials into valuable products is a key pillar for sustainable growth. Owing to its scalability and facile coupling with renewable energies, the electroreduction of  $CO_2$  (e $CO_2RR$ ) is an attractive approach to utilize anthropogenic  $CO_2$  emissions as a resource for the synthesis of fuels and chemicals under ambient conditions.<sup>[1]</sup> However, the lack of inexpensive and stable electrocatalysts that are also sufficiently active and selective at low overpotentials is a major barrier toward its practical implementation.<sup>[2,3]</sup> The efficient reduction of  $CO_2$  to CO, which along with HCOOH is the most commonly observed e $CO_2RR$  product at the lower overpotential range (i.e. below -0.8 V vs. RHE), would provide a versatile compound for the

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[c] Dr. Roland Hauert Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf (Switzerland) production of liquid fuels and plastics by well-established processes in industry. On the other hand, the direct conversion of  $CO_2$  into more reduced products with greater economic value (such as hydrocarbons and alcohols) is very promising, although this route has been hindered so far by the high overpotentials required and the difficulty of targeting the production of a single compound.<sup>[4]</sup>

Noble metal electrocatalysts, such as Au-<sup>[5-7]</sup> and Ag-based electrodes,<sup>[8-11]</sup> and Pd nanoparticles,<sup>[12]</sup> are among the best performing materials for CO<sub>2</sub> reduction to CO known so far. Nevertheless, their large-scale application would be hindered by their scarcity and high price. Copper, which is abundant and inexpensive, has been widely studied due to its unique ability to reduce CO<sub>2</sub> to hydrocarbons and oxygenates at high overpotentials,<sup>[4,13,14]</sup> but regular polycrystalline Cu electrodes perform poorly at milder conditions because the eCO2RR is outcompeted by the hydrogen evolution reaction (HER). In contrast, Cu electrodes prepared from the reduction of thick oxide films (oxide-derived Cu) showed much better eCO2RR performance at low overpotentials, producing a mixture of CO and COOH (i.e. ca. 35% current efficiency each at -0.5 V vs. RHE).<sup>[15]</sup> Subsequent efforts have demonstrated the ability of oxidized Cu films to yield more reduced products, such as ethylene and ethanol,<sup>[16-19]</sup> and the production of n-propanol from  $CO_2$  was recently reported by Ren et al. over a Cu<sub>2</sub>O/Cu(OH)<sub>2</sub> foil.<sup>[20]</sup> Although the irregular structure of these OD Cu materials is commonly acknowledged to play an important role, a precise rationalization of their catalytic behavior particularly in regard to the production of highly reduced compounds, has remained elusive. It has been postulated that thicker Cu<sub>2</sub>O layers favor the formation of C<sub>2</sub>H<sub>4</sub> due to local pH effects on the (rougher) electrode surface,<sup>[16,21]</sup> whereas grain boundary sites that bind CO strongly have been associated with the reduction of CO to C2 compounds.<sup>[22,23]</sup> Based on operando spectroscopic studies, Mistry et al. recently postulated that Cu<sup>+</sup> species that are resistant to reduction under eCO<sub>2</sub>RR conditions are key for driving the formation of  $C_2H_4$  over OD Cu electrodes.[24]

Another route for the design of better  $eCO_2RR$  catalysts is to develop multicomponent systems able to break the linear relationship between the binding energies of CO and COOH intermediates on transition metal surfaces.<sup>[25,26]</sup> For example, early studies by Watanabe et al. demonstrated changes in the selectivity patterns of electrodeposited Cu alloys compared to bare copper.<sup>[27]</sup> More recently, Takanabe and co-workers showed that the electrodeposition of indium<sup>[28]</sup> and tin<sup>[29]</sup> on thermally oxidized Cu foils yielded electrodes with outstanding selectivity for CO in the lower overpotential range (e.g.  $CE_{CO}$  ca. 90% at –0.6 V vs. RHE), and similar observations were reported ChemSusChem

by Zhao et al. over Sn-decorated Cu<sub>x</sub>O nanowires (NWs) anchored to a Cu substrate.<sup>[30]</sup> These findings have been ascribed to the formation of alloys on the surface and the inhibiting effect of In and Sn on the HER,<sup>[28,29]</sup> although high selectivities for CO have only been observed when oxidized substrates are used as starting materials. In contrast, bulk Cu-Sn<sup>[29]</sup> and Ag-In<sup>[31]</sup> alloy electrodes have shown comparatively poor performance at similar potentials, indicating that nanostructure plays a key role in the emergence of synergistic effects in multicomponent electrocatalysts.

Despite the promising results achieved with modified oxidederived Cu electrodes, these materials display modest current densities and require elaborate synthetic procedures combining thermal and electrochemical steps on bulk substrates. Comparatively few efforts have been geared toward transferring the performance of such systems to powdered catalysts that can be synthesized in large scale and easily integrated into a gas diffusion electrode (GDE) of a practical electrolyzer. A step in this direction was recently demonstrated through the in situ formation of Cu-In alloys from the reduction of the CuInO<sub>2</sub> delafossite,<sup>[32]</sup> resulting in high selectivity for CO (i.e.  $CE_{CO}$  ca. 60% at -0.6 V vs. RHE) following the generation of a heterogeneous nanostructure after successive CO<sub>2</sub> reduction cycles.<sup>[33]</sup>

In this contribution, we adopted a simple and potentially scalable solvothermal route for preparing Cu<sub>2</sub>O catalysts in powdered form, and evaluated their performance at low to moderate overpotentials (i.e. up to -0.80 V vs. RHE) in 0.1 M KHCO<sub>3</sub>. This approach enabled us to assess in a comparable basis the effect of introducing different p-block elements (Sn, In, Ga, and Al) into Cu<sub>2</sub>O by adding the corresponding precursor to the synthesis medium. While the performance of the unmodified Cu<sub>2</sub>O catalyst compared favorably to a commercial sample and to OD Cu electrodes reported in the literature, marked improvements in selectivity and stability for CO production were attained by the addition of Sn and In to Cu<sub>2</sub>O. On the other hand, the introduction of Al into the Cu<sub>2</sub>O catalyst promoted the production of C2 and C3 compounds, such as ethylene, ethanol and n-propanol, at moderate overpotential.

### 2. Results and Discussion

#### 2.1. CO<sub>2</sub> electroreduction over pristine Cu<sub>2</sub>O

The unmodified Cu<sub>2</sub>O catalyst (Cu<sub>2</sub>O-ud) was prepared by the solvothermal reduction in ethylene glycol of a Cu(II) precursor. Figure 1 shows the performance of Cu<sub>2</sub>O-ud over a long 12hour electrolysis at -0.6 V in CO2-saturated 0.1 M KHCO3. A commercial sample of Cu<sub>2</sub>O (Cu<sub>2</sub>O-cs) was evaluated as a benchmark at the same conditions. Both catalysts showed an increase of the total current density over the first hour of the reaction followed by a plateau. Nevertheless, the commercial sample showed stable (and low, ca. 10%) selectivity for CO throughout the whole run, whereas the selectivity profile of the Cu<sub>2</sub>O-ud catalyst evolved significantly during the experiment. Initially, the Cu<sub>2</sub>O-ud catalyst showed a preference for the HER which gradually shifted toward CO evolution even as the total current remained stable. Electrolyses performed at other potentials revealed a similar evolving behavior of the current efficiency for CO, although more reducing potentials resulted in a faster equilibration of the catalyst (Figure 1b). Compared to any other reported Cu<sub>2</sub>O-derived electrodes, either prepared by the thermal oxidation of Cu foils<sup>[15]</sup> or by the electrodeposition of Cu<sub>2</sub>O films on Cu substrates,<sup>[16]</sup> the evolved Cu<sub>2</sub>O-ud catalyst shows higher selectivity for the reduction of CO<sub>2</sub> to CO over a range of potentials (i.e. ca. 55%, compared to ca. 30% at -0.6 V) and a much lower production of formate. This observation suggests that the solvothermal synthesis (followed by equilibration) might be more effective than other treatments in generating OD Cu catalysts with highly active sites for CO evolution while avoiding the "dead-end" formate pathway. However, we remark that this comparison is limited by the fact that tests reported in the literature are usually much shorter and might not be fully representative of the final catalytic performance of such oxide-derived Cu electrodes. Nonetheless, the high initial selectivity for CO and low production of formate over Cu2O-ud contrast markedly with available works. The results in Figure 1 highlight the suitability of a simple and potentially scalable solvothermal synthesis for preparing a Cubased powder catalyst with solid performance for this reaction.



**Figure 1**. (a) Current efficiency (*CE*) and total current density (*j*) in CO<sub>2</sub> reduction electrolyses at -0.6 V vs. RHE in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> (pH 6.75) over a commercial Cu<sub>2</sub>O sample (Cu<sub>2</sub>O-cs, left) and the unmodified Cu<sub>2</sub>O catalyst (Cu<sub>2</sub>O-ud, right) prepared by solvothermal reduction. (b) Average current efficiency for CO (bars) and partial current density for CO (diamonds) during the final 2 hours of 12-hour electrolyses at different potentials. The dashed horizontal lines indicate the average *CE*<sub>CO</sub> during the first 2 hours of each electrolysis, evidencing the catalyst evolution toward higher CO selectivity. The difference between the starting and final points becomes less pronounced at more cathodic potentials.

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**Figure 3**. Scanning electron (SEM) and high-resolution transmission electron (HRTEM) micrographs of solvothermally-prepared Cu<sub>2</sub>O (Cu<sub>2</sub>O-ud, top row) and a commercial Cu<sub>2</sub>O sample (Cu<sub>2</sub>O-cs, bottom row), before and after CO<sub>2</sub> reduction electrolyses at -0.6 V vs. RHE. The insets show the selected area electron diffraction (SAED) patterns of the used catalysts, evidencing their polycrystalline nature and the presence of Cu and Cu<sub>2</sub>O (diffraction rings associated to the corresponding (111) crystallographic planes are highlighted). The black arrows point to some of the steps and edges present on the surface of the used Cu<sub>2</sub>O-ud catalyst, while the blue dashed box highlights a region of overlapping lattice fringes leading to a Moiré pattern.

Figure 2 shows the XRD patterns of the pure Cu<sub>2</sub>O electrodes before and after electrolyses at -0.6 V for 12 h (the corresponding patterns of the powders are shown in Figure S1). The diffractogram of the fresh Cu<sub>2</sub>O-ud electrode confirms that Cu<sub>2</sub>O was obtained from the solvothermal synthesis, albeit a fraction of the precursor was reduced to metallic Cu. The Cu<sub>2</sub>O-cs electrode shows only Cu<sub>2</sub>O, as expected. The average crystallite size calculated with the Scherrer equation (based on the (111) peak of the Cu<sub>2</sub>O powders) was found to be 14 and 37 nm for the prepared and commercial Cu<sub>2</sub>O samples, respectively. The diffractrograms of both electrodes after the electrolysis are practically identical and evidence the almost complete bulk reduction of Cu<sub>2</sub>O to metallic Cu under eCO<sub>2</sub>RR conditions. In addition, the change of the peak shape in the Cu LMM Auger spectra of the Cu<sub>2</sub>O-ud electrode (taken after 4 min of sputtering with  $Ar^{\dagger}$ ) confirm the formation of  $Cu^{0}$  (**Figure S2**).

Even though the solvothermally-prepared Cu<sub>2</sub>O catalyst and the commercial sample are chemically similar, their microstructures are markedly different, as evidenced by the SEM micrographs of the electrodes (**Figure 3**). The Cu<sub>2</sub>O-ud catalyst is comprised by large irregular aggregates (with a size of ca. 1  $\mu$ m) with a jagged surface. In contrast, the particles of the fresh Cu<sub>2</sub>O-cs catalyst are much finer and have a smoother surface, and do not form large aggregates on the electrode surface. The electrolysis leads to a roughening of both catalysts, as reflected by the appearance of more defined nanometric polyhedral features on the surface of the particles, which are particularly abundant in the used Cu<sub>2</sub>O-ud catalyst. This roughening conceivably results in a growth of the electrochemically active surface area (ECSA), as reflected by the increase of the double-layer (DL) capacitance of the electrodes (**Table S1**) and of the total current density in



**Figure 2.** XRD patterns of fresh and used (i.e. after 12-hour  $CO_2$  reduction electrolyses)  $Cu_2O$ -ud and  $Cu_2O$ -cs electrodes. The fresh electrodes are comprised mainly of ( $\mathbf{\nabla}$ )  $Cu_2O$  and are mostly reduced to ( $\nabla$ ) metallic Cu under e $CO_2RR$  conditions. Reflections from the carbon gas diffusion layer (GDL) used as substrate are marked with ( $\mathbf{\star}$ ).

the early stages of the electrolysis (**Figure 1a**). HRTEM analysis of the used Cu<sub>2</sub>O-ud catalyst (scraped off a glassy carbon substrate after 4 h of electrolysis at -0.6 V) showed a very irregular surface populated by nanoparticles, causing numerous steps and edges (**Figure 3**). Moreover, the used Cu<sub>2</sub>O-ud catalyst is characterized by an abundance of Moiré fringes, with the overlapping lattices possibly being a consequence of the faulted layering of platelet-like structures upon restructuring under eCO<sub>2</sub>RR conditions (HRTEM of the fresh catalyst is shown in **Figure S3**). It is reasonable to postulate that this restructuring leads to a highly stepped surface. Similar features are present to a more limited extent in the used benchmark sample, suggesting that Cu<sub>2</sub>O-cs does not undergo such extensive surface transformation when exposed to eCO<sub>2</sub>RR



**Figure 4.** Cyclic voltammograms (scan rate 20 mV s<sup>-1</sup>) in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> of fresh Cu<sub>2</sub>O-ud and Cu<sub>2</sub>O-cs electrodes, and following 12-hour CO<sub>2</sub> reduction electrolyses at -0.6 V vs. RHE.

conditions, likely as a result of its higher crystallinity and larger crystallite size (as evidenced by XRD patterns of the fresh powders, **Figure S1**), and of its significantly lower total surface area  $(0.9 \text{ m}^2 \text{ g}^{-1} \text{ vs. } 5.4 \text{ m}^2 \text{ g}^{-1}$  in the Cu<sub>2</sub>O-ud catalyst, as determined by N<sub>2</sub> physisorption). Moreover, this observation is consistent with the lower ECSA (after the reaction) of the Cu<sub>2</sub>O-cs electrode compared to Cu<sub>2</sub>O-ud, as reflected by DL capacitance measurements (**Table S1**) and by its overall lower activity. These results suggest that only Cu<sub>2</sub>O powders which are initially quite irregular would undergo in situ a deep restructuring process favorable for CO<sub>2</sub> reduction, mirroring the differences commonly observed between smooth polycrystalline Cu electrodes and oxide-derived electrodes prepared by treating Cu bulk substrates.<sup>[15,16]</sup>

Cu<sub>2</sub>O-ud The catalyst after the reaction showed electrochemically active sites that are not originally present in the fresh material, as extracted from the cyclic voltammograms (CVs) shown in Figure 4. The oxidation features at -0.13 and 0.25 V seem to be correlated to overlapping reduction features forming the broad peak at -0.21 V. None of these peaks are detectable in the CVs of the fresh Cu<sub>2</sub>O-ud or the used Cu<sub>2</sub>O-cs electrodes, suggesting a possible fingerprint of sites that are particularly active for CO evolution. Though the exact nature of these sites cannot be determined at this stage, similar features have been previously associated to the presence of defects,<sup>[34]</sup> which is consistent with the HRTEM analysis of the used Cu<sub>2</sub>O-ud catalyst (Figure 3).

#### 2.2. Evaluation of p-block elements as modifiers

After identifying Cu<sub>2</sub>O-ud as a promising and potentially scalable catalyst for CO<sub>2</sub> reduction, we assessed the catalytic effect of incorporating p-block elements as modifiers. Previous reports have shown that the electrodeposition of small amounts of indium<sup>[28]</sup> and tin<sup>[29]</sup> on oxidized Cu foils leads to enhanced selectivity for CO at low overpotentials. In this context, we hypothesized that a similar effect could be achieved via a solvothermal synthesis. Consequently, the modified Cu<sub>2</sub>O catalysts were prepared by the reduction in ethylene glycol of the Cu(II) precursor along with an appropriate amount of the chloride of the second element. In addition to indium and tin, this synthetic approach allowed us to evaluate the effect of gallium and aluminum on Cu<sub>2</sub>O, which would be more difficult to incorporate into the catalyst via electrochemical methods.



**Figure 5**. Average current efficiency (bars), total current density (circles) and partial current density for CO in CO<sub>2</sub> reduction electrolyses (2 h duration each) at different potentials over doped Cu<sub>2</sub>O catalysts.

The elemental analysis of the thus prepared catalysts showed that the foreign elements were mostly added to Cu<sub>2</sub>O in the intended amounts, but that only little aluminum could be incorporated, resulting in an Al-doped Cu<sub>2</sub>O catalyst (Table 1). We remark that the optimization of the synthetic procedure might improve the control of the modifier content in the resulting Cu<sub>2</sub>O catalysts. In particular, additional experiments showed that by switching to Al(NO<sub>3</sub>)<sub>3</sub> as the aluminum source (without any other changes to the synthetic procedure), it was possible both to increase the amount of modifier introduced into the Cu2O catalyst (up to similar ratios present in the In- and Sn-modified materials) and to more precisely target lower loadings. However, these variations did not alter significantly the catalytic behavior in the investigated potential range (Figure S4), so that Cu<sub>2</sub>O:Al-140 can be reasonably assumed to be representative of the behavior of Al-modified Cu<sub>2</sub>O catalysts prepared by the herein presented method.

 $\label{eq:constraint} \mbox{Table 1. Target and actual loadings of the modified $Cu_2O$ catalysts expressed as the atomic ratio of $Cu$ to the second element (Cu/M). $$$ 

Modifier	Catalyst	Target Cu/M	Actual Cu/M <sup>[a]</sup>	M content (wt.%)
Sn	Cu <sub>2</sub> O:Sn-20	20	28.1	5.6
In	Cu <sub>2</sub> O:In-20	20	20.8	7.2
Ga	Cu <sub>2</sub> O:Ga-20	20	30.5	3.1
AI	Cu <sub>2</sub> O:Al-140	20	139.4	0.3

[a] X-ray fluorescence (XRF) spectroscopy

As an initial assessment, we compared the electrocatalytic performance of the modified catalysts in short (2 h)  $eCO_2RR$  electrolyses in 0.1 M KHCO<sub>3</sub> at -0.6 V and -0.8 V (Figure 5).

Cu<sub>2</sub>O-ud was tested under the same conditions and is shown as a benchmark. The addition of Sn and In had a marked enhancing effect on the selectivity for CO, which is most pronounced in the In-modified catalyst at -0.6 V, while at -0.8 V the addition of Sn and In resulted in very similar behavior. The addition of Ga had a small positive effect at -0.6 V but significantly decreased the  $CE_{CO}$  at -0.8 V. It is interesting to note that the addition of AI to Cu<sub>2</sub>O (even at the small loading that resulted from the synthesis) had a large effect on the selectivity profile, significantly decreasing the selectivity for CO but increasing the current efficiency for ethylene at -0.8 V (no ethylene was detected over any catalyst at -0.6 V). Apart from the gaseous products shown in Figure 5, only trace amounts of methane and ethane were observed at -0.8 V, comprising a negligible share of the current efficiency (i.e. less than 0.1% in all cases).

#### 2.3. Stability of Sn- and In-modified Cu<sub>2</sub>O catalysts

Since the 2-hour electrolyses showed that the addition of tin and indium had the largest effect in enhancing the selectivity of Cu<sub>2</sub>O for CO at -0.6 and -0.8 V, the Cu<sub>2</sub>O:Sn-20 and Cu<sub>2</sub>O:In-20 catalysts were selected for additional experiments. Their stability was assessed by performing 12-hour electrolyses at -0.6 V and -0.8 V (**Figure 6**). At -0.6 V, the Sn- and In-modified catalysts equilibrated more rapidly and achieved a considerably higher selectivity for CO (> 70%) compared to pristine Cu<sub>2</sub>O. The In-modified catalyst performed better than its Sn counterpart, although this might be a reflection of the slightly higher amount of the modifier in Cu<sub>2</sub>O:In-20.

In terms of stability, a different picture emerges at -0.8 V. The current efficiency for CO over both catalysts is very high in the

early stages of the electrolysis (ca. 80% in the first 2 h) but then decreases steadily. In fact, at the end of each run the selectivity for CO over the modified catalysts was slightly lower than over pristine Cu<sub>2</sub>O, but with opposite temporal trends. This initially suggests a gradual deactivation of the In- and Sn-containing catalysts. Previous reports have linked the eCO2RR activity of In and Sn electrodes to oxidic species that are stable at the cathodic potentials of the electrolysis.[35,36] Based on these observations, we have postulated that the synergistic effect in Ag-In<sup>[31]</sup> and Cu-In<sup>[33]</sup> electrocatalysts might be based on the interaction of non-reducible species, such as In(OH)<sub>3</sub>, with the metallic components. In this context, a possible cause for deactivation at -0.8 V could be the gradual reduction of such oxidic species. Nevertheless, the partial current density for CO over the Cu<sub>2</sub>O:Sn-20 and Cu<sub>2</sub>O:In-20 catalysts remains fairly stable after 4 h, implying that the decrease of the selectivity is not caused by a loss of preferential active sites for CO evolution (sites that are possibly located at the interfaces between Cu and oxidic Sn/In species) but rather by the generation of new "unmodified" sites more favorable for hydrogen evolution. Considering that Cu<sub>2</sub>O has been reported to show unexpected resistance to reduction even at -1.0 V vs. RHE,<sup>[24]</sup> it is possible that new HER sites appear from the reduction of Cu<sub>2</sub>O that was not reducible at -0.6 V but is transformed to Cu<sup>0</sup> as the potential is increased. It is interesting to note that the Cu-Sn NWs catalyst developed by Zhao et al.<sup>[30]</sup> showed an even higher selectivity for CO at -0.8 V (initial CE<sub>co</sub> ca. 90%) compared to Cu<sub>2</sub>O:Sn-20 However, the CE<sub>co</sub> also decreased steadily throughout a 12hour run along an increase of the current efficiency for H<sub>2</sub> and of the total current density (although the increase of the current density was less pronounced than in Cu<sub>2</sub>O:Sn-20). This observation suggests that this catalyst might also suffer from a similar effect as  $Cu_2O:Sn-20$ . On the other hand, the  $CE_{CO}$  and



**Figure 6**. Current efficiency (*CE*) and partial current density for CO ( $j_{CO}$ ) in 12-hour CO<sub>2</sub> reduction electrolyses at (a) –0.6 V vs. RHE and (b) –0.8 V vs. RHE over Sn- (left) and In-modified (right) Cu<sub>2</sub>O catalysts with Cu/M = 20. The arrows between the plots indicate the evolved  $CE_{CO}$  (i.e. average over the last 2 h in 12 h electrolyses) over the unmodified Cu<sub>2</sub>O catalyst at each corresponding potential.



Figure 7. (a) Current efficiency (CE<sub>C2H4</sub>) and partial current density for ethylene (j<sub>C2H4</sub>) in 12-hour CO<sub>2</sub> reduction electrolyses at -0.8 V vs. RHE over unmodified (left) and Al-doped Cu<sub>2</sub>O (right) catalysts. (b) Average current efficiencies for different products in 12-hour electrolyses. The inset shows the distribution of minor liquid phase products obtained over the Cu<sub>2</sub>O:Al-140 catalyst.

the current density at -0.6 V over the electrodeposited Cu-Sn and Cu-In catalysts demonstrated by Takanabe and coworkers<sup>[28,29]</sup> appears to be rather stable at -0.6 V. Along with the data in Figure 6, these results suggest that the generation of HER sites on these catalysts can be minimized at -0.6 V (and at even less cathodic potentials), thus preserving the high selectivity for CO.

Overall, the enhancement of the current efficiency for CO following the addition of In and Sn to Cu<sub>2</sub>O is in line with recent results from Cu-In and Cu-Sn electrodes prepared by electro-<sup>[28,29]</sup> and electroless<sup>[30]</sup> deposition. Consequently, we show that a simpler and more scalable synthesis is capable of effectively transferring the outstanding current efficiencies for CO observed over these model materials to Cu<sub>2</sub>O catalysts in a form more amenable to practical implementation. However, it is important to note that the aforementioned electrodes generally achieved even higher selectivities for CO. Compared to the solvothermal synthesis presented in this contribution, it is likely that electroand electroless deposition achieve a finer dispersion of Sn and In on the Cu surface, resulting in a larger amount of sites that benefit from the interaction between Cu and Sn/In species. Nevertheless, the exploratory nature of this work leaves an open space for optimization efforts that might close the performance gap in future developments.

As was the case for the aforementioned Cu-In and Cu-Sn electrodes, the performance of the catalysts changed with the amount of Sn and In added. At very low contents (Cu/M = 250), the Sn-modified catalyst was very similar to pristine Cu<sub>2</sub>O (with the advantage of faster stabilization), whereas the In-modified catalyst had a significantly worse selectivity for CO than Cu<sub>2</sub>Oud (Figure S5). Increasing the loading in the synthesis medium beyond Cu/M = 20 resulted in very heterogeneous materials (i.e. Cu<sub>2</sub>O alongside the oxides of In and Sn, as well as CuCl), which prevented a straightforward comparison with the catalysts with lower loadings. Nevertheless, an interesting 'high loading scenario' occurs in mixed equimolar oxides in which the distribution of Cu and the second element are expected to be completely homogeneous. We have previously shown that the in situ reduction of CuInO<sub>2</sub> followed by its exposure to successive CO2 reduction cycles results in the gradual segregation of Cu and In and the formation of In(OH)3, alongside an increase of the activity and selectivity for CO.[33] In light of these results, we attempted a similar approach using Cu-Sn mixed (hydr)oxides, namely CuSnO<sub>3</sub> and CuSn(OH)<sub>6</sub>. These materials were very poor CO<sub>2</sub> reduction catalysts at -0.6 V and at more cathodic potentials formate (and not CO) was the favored eCO2RR product by a large margin. Exposing of these catalysts to successive electrolytic runs did not alter much their selectivity, suggesting that neither CuSnO<sub>3</sub> nor CuSn(OH)<sub>6</sub> undergo a restructuring process favorable for CO evolution as CuInO<sub>2</sub> does (Figure S6). In fact, the performance of these materials was practically identical to that of pure SnO<sub>2</sub>, particularly at higher overpotentials (Figure S7). This effect might occur if a surface enrichment of Sn in the mixed (hydr)oxides 'masks' the activity of Cu, in an analogous manner to Cu-Sn electrodes when the amount of Sn electrodeposited exceeded a monolayer coverage.[29]

#### 2.4. CO<sub>2</sub> reduction to C<sub>2</sub>H<sub>4</sub> over Al-doped Cu<sub>2</sub>O

The introduction of AI had a significant influence on the selectivity pattern of Cu<sub>2</sub>O. Even though it negatively affected the production of CO at -0.8 V, a beneficial effect was the increase in the current efficiency for ethylene at this potential (Figure 5). This observation was particularly intriguing because this behavior was not observed in any of the other modified Cu<sub>2</sub>O catalysts. In a 12-hour run the Al-doped Cu<sub>2</sub>O catalyst showed a stable current efficiency for C<sub>2</sub>H<sub>4</sub> of ca. 7% following an initial equilibration phase. In contrast, the selectivity for C<sub>2</sub>H<sub>4</sub> over pristine  $Cu_2O$  (max. ca. 3.5%) was lower than over Cu<sub>2</sub>O:Al-140 and then decreased steadily as the run progressed (Figure 7a). Both the partial current density for C<sub>2</sub>H<sub>4</sub> and the total current density over Al-modified Cu<sub>2</sub>O were significantly higher than over the unmodified catalyst, which is probably linked to a higher ECSA as shown by the DL capacitance measurements (Table S1). The Al-doped catalyst also produced more formate, as well as several highly reduced products in the liquid phase that were not detected over undoped Cu<sub>2</sub>O, although the presence of these products at amounts below the detection limit of the NMR analysis cannot be discounted (Figure 7b). Out of this fraction, the presence of n-propanol and ethanol (CE ca. 2% each) are noteworthy, alongside smaller amounts of methanol and acetate. In comparison, a recent study by Ren et al.<sup>[20]</sup> demonstrated a current efficiency for n-propanol of ca. 10% over Cu<sub>2</sub>O/Cu(OH)<sub>2</sub> foils biased at -0.95 V vs. RHE.



**Figure 8.** XRD patterns of fresh and used (i.e. after 12-hour CO<sub>2</sub> reduction electrolyses) modified Cu<sub>2</sub>O electrodes. The fresh electrodes are comprised mainly of ( $\mathbf{\nabla}$ ) Cu<sub>2</sub>O and are mostly reduced to ( $\nabla$ ) metallic Cu under eCO<sub>2</sub>RR conditions except for the case of Cu<sub>2</sub>O:Al-140, where reflections from the oxide phase are still apparent. Reflections from the carbon GDL are marked with ( $\mathbf{\star}$ ).

The production of small amounts of ethylene at comparable potentials over unoptimized Cu electrodes has been previously reported (e.g. CE around 2% over polycrystalline Cu<sup>[4]</sup> and the original oxide-derived Cu electrode at -0.8 V).<sup>[15]</sup> The low selectivity for C<sub>2</sub>H<sub>4</sub> over Cu<sub>2</sub>O-ud (and over the Sn- and Inmodified catalysts) is in line with these results. On the other hand, the increased selectivity for C2H4 over the Al-doped catalyst mimics to some extent the performance of materials that have been tailored to target the production of C<sub>2</sub>H<sub>4</sub>, such as thick Cu<sub>2</sub>O films on Cu sheets,<sup>[16,18]</sup> plasma-activated Cu foils,<sup>[24]</sup> and nanocubes formed from the reduction in the presence of halides of Cu(I) oxide formed on Cu electrodes.<sup>[37]</sup> In addition, the appearance of n-propanol alongside ethylene in the Cu<sub>2</sub>O:Al-140 catalyst is consistent with previous reports proposing a C-C coupling mechanism of carbon monoxide and ethylene precursors. Moreover, ex situ measurements, discussed in more detail in the following section, point toward a stabilizing role from Al on Cu<sup>+</sup> species, which has been previously linked to increased selectivity for  $C_2H_4$  over OD Cu electrodes.<sup>[24,38]</sup>

#### 2.5. Structural characterization of modified Cu<sub>2</sub>O catalysts

Considering that the effect of adding Sn and In to Cu<sub>2</sub>O (i.e. enhanced selectivity for CO) was different from the effect of doping with Al (i.e. lower  $CE_{CO}$  but increased selectivity for C<sub>2</sub>H<sub>4</sub> and alcohols), we evaluated whether the structural changes underwent by these catalysts might be associated with the diverging effect of the modifiers.

The XRD patterns of the modified catalysts in their fresh state confirm the presence of  $Cu_2O$  as the main phase alongside a small fraction of metallic Cu, as was the case in the pristine  $Cu_2O$  catalyst (**Figure 8**, and the corresponding powders shown

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Figure 9. SEM micrographs of the fresh and used electrodes following 12-hour electrolyses over Sn-, In- and Al-modified Cu<sub>2</sub>O catalysts (Sn- and In at -0.6 V, Al at -0.8 V). The scale bar in the insets represents 200 nm.

in **Figure S1**). The formation of other oxides (e.g. In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) was not observed, although the XRD patterns of the fresh powders indicate the existence of CuCl in trace amounts (**Figure S1**). Although the presence of halides in large amounts has been reported to influence the eCO<sub>2</sub>RR performance<sup>[39]</sup> and the nanostructure of Cu electrodes,<sup>[17,37]</sup> we remark that intensity of the peak from CuCl (which is proportional to the content) is small and comparable in all the modified catalysts. Consequently, the presence of trace amounts of CuCl is unlikely to greatly influence the catalytic behavior of the modified Cu<sub>2</sub>O catalysts, or be the reason behind the divergent influence of Sn and In compared to Al.

The diffractograms of the used In- and Sn-modified catalysts evidenced the bulk reduction of the materials to metallic Cu under  $eCO_2RR$  conditions, as expected (**Figure 8**). No intermetallic Cu-In and Cu-Sn compounds were detected after the reaction, although their formation cannot be completely disregarded due to their expectedly low concentration and the large background signal from the carbon GDL.



**Figure 10.**, Cyclic voltammograms (scan rate 20 mV s<sup>-1</sup>) in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> following 12 h CO<sub>2</sub> reduction electrolyses at -0.6 V vs. RHE. of (a) In-modified Cu<sub>2</sub>O and (b) Sn-modified Cu<sub>2</sub>O, at two different loadings and (c) at -0.8 V vs. RHE of Al-doped Cu<sub>2</sub>O. (d) H<sub>2</sub>-TPR profiles of fresh Cu<sub>2</sub>O-ud and Cu<sub>2</sub>O:Al-140.

The addition of p-block elements to Cu<sub>2</sub>O seemed to have only minor effects on the microstructure of the resulting catalysts, as examined by SEM (Figure 9, lower magnification micrographs are shown in Figure S8). The introduction of indium and aluminum appeared to favor the formation of micrometric particles with sparsely dispersed cubes, while the addition of tin favored the formation of smaller, spherical aggregates. Nevertheless, the surface of the particles in the modified catalysts appears jagged and irregular (as in Cu<sub>2</sub>O-ud material) and the small differences in morphology evidenced in the micrographs do not seem to reflect a change of the preferred growth orientation of the crystallites, as can be deduced from the predominance of the (111) peak of Cu<sub>2</sub>O in the XRD patterns. As in the Cu<sub>2</sub>O-ud catalyst, post-reaction micrographs of the modified materials showed a roughening of the surface due to the formation of fine polyhedral features, particularly on the spherical particles. These features appear to be more dense and abundant in Cu<sub>2</sub>O:Al-140, although this is most likely a result of its exposure to a more aggressive potential (i.e. -0.8 V compared to -0.6 V for the In- and Sn-doped samples), as reflected by the more pronounced relative increase of the current density (Figure 7).

The cyclic voltammograms unveiled stark differences in the electrochemically active sites of the catalysts. Remarkably, the presence of indium led to similar (though better defined) redox features as in the parent material (**Figure 10a**). The lack of any detectable signal from In contrasts with its clear presence on the catalyst surface, as shown by the elemental mapping (**Figure 11**). XPS measurements did not provide evidence of metallic In

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Figure 11. Elemental maps over fresh and used Sn-, In- and Al-doped  $Cu_2O$  catalysts following 12-hour electrolyses. The scale bar in the inset represents 200 nm.

after the reaction, but rather indicates that it is present as In<sup>3+</sup> (Figure S2). These observations strongly suggest that indium exists in the Cu<sub>2</sub>O:In-20 catalyst as an electrochemically silent oxidic species, such as In(OH)<sub>3</sub>, as observed previously on anodized In electrodes<sup>[35]</sup> and Cu-In catalysts.<sup>[33]</sup> On the other hand, the presence of Sn has a clear effect on the voltammetric response (Figure 11b). Since redox features labeled "1" and "3" correspond respectively to the oxidation and reduction of the Sn<sup>0</sup>/SnO<sub>2</sub> pair,<sup>[40]</sup> it is inferred that isolated Sn must exist in the used catalyst, as confirmed by the elemental mapping. However, the oxidation feature "2" likely corresponds to stabilized (i.e. less oxidizable) Sn<sup>0</sup> species associated with Cu-Sn intermetallic compounds. These compounds would be formed by the interdiffusion of metallic Cu and Sn<sup>[41,42]</sup> formed in situ under reaction conditions, which is consistent with the redistribution of Sn after the reaction as observed by EDX mapping. In the case of the Al-doped catalyst, the CV lacks the redox features that were associated to CO evolution in the undoped catalyst. This fact, together with the low selectivity for CO observed over the Al-doped catalyst, reinforces the premise of fingerprint peaks associated to defect sites particularly active for CO evolution.

In contrast to Sn and In, Al appears to be very finely dispersed in the fresh catalyst (**Figure 11**). An indication that Al affects  $Cu_2O$  in a different way to In and Sn is provided by the XRD diffraction



**Figure 12.** (a) Cu LMM Auger spectra of Cu<sub>2</sub>O-ud and Cu<sub>2</sub>O:Al-140 electrodes after eCO<sub>2</sub>RR electrolyses (12 h, -0.8 V) following successive cycles of Ar<sup>\*</sup>-sputtering (indicated by the black arrow). The unsputtered surfaces (bottom, red curve) show only (▼) Cu<sub>2</sub>O, whereas characteristic features from (▽) metallic Cu become apparent after sputtering. (b) Variation of the atomic concentration of Cu<sup>0</sup> (on a Cu basis) with increasing depth, as obtained by peak fitting of the Cu LMM Auger spectra after each sputter cycle. As a reference, the sputter yield on Ta<sub>2</sub>O<sub>5</sub> was found to be 4 nm min<sup>-1</sup>.

patterns (Figure 8), since reflections from Cu<sub>2</sub>O are still visible in the Al-doped material after 12 hours of electrolysis at -0.8 V. This result initially suggests that the presence of AI hinders the bulk reduction of Cu<sub>2</sub>O to metallic Cu at the evaluated potentials. The Cu LMM Auger spectra of unmodified and Al-doped Cu<sub>2</sub>O electrodes following the electrolysis (Figure 12a) shows only Cu<sub>2</sub>O at the surface, although this is possibly a consequence of surface oxidation upon exposure to air following the reaction.[43] Nevertheless, depth profiling reveals the presence of metallic Cu in both electrodes, as shown by the appearance of characteristic features in the Cu LMM Auger peak. From a qualitative point of view, these features are more prominent in the spectra of the used Cu<sub>2</sub>O-ud electrode, suggesting a more metallic character in comparison to the Al-doped material. Figure 12b shows the Cu<sup>0</sup> content (based on the total Cu content) as determined by peak fitting of Cu<sup>0</sup> and Cu<sub>2</sub>O contributions to the Auger spectra after each sputtering cycle employing experimentally-derived line shapes (Figure S9). The fraction of metallic copper in both electrodes shows an increasing trend versus the sputter time (and hence versus depth) after the removal of the surface oxide layer with 30 s of sputtering (depth ca. 2 nm). Nevertheless, it is interesting to note that the Cu<sup>0</sup> content is significantly higher in the Cu<sub>2</sub>O-ud electrode than in its Al-doped counterpart at all points, matching the qualitative observations from the Auger spectra in Figure 12a. Although it is difficult to directly extrapolate these ex situ measurements to the actual state of the surface under reaction conditions, the lower Cu<sup>0</sup> content in the Cu<sub>2</sub>O:AI-140 electrode after the electrolysis is consistent with the proposition that doping with Al endows Cu<sub>2</sub>O with a higher

degree of resistance to reduction under  $eCO_2RR$  conditions compared to the unmodified catalyst.

Based on operando studies, Mistry et al. have recently proposed that Cu<sup>+</sup> species that are resistant to reduction are behind the very high selectivity for ethylene (i.e. CE ca. 40% at -0.8 V vs. RHE) observed over plasma-activated Cu electrodes.<sup>[24]</sup> In accordance with this result, it is possible that the preserved Cu<sub>2</sub>O in the Al-doped catalyst drives its increased selectivity for C<sub>2</sub>H<sub>4</sub>. It is interesting to note that we also observed a stabilizing effect of AI on Cu<sub>2</sub>O in temperature-programmed reduction (TPR) experiments with H<sub>2</sub> over the fresh catalyst (Figure 10d). In this case, the addition of AI clearly decreased the reducibility of Cu<sub>2</sub>O, as evidenced by the shift of the reduction peak by ca. 100 °C in Cu<sub>2</sub>O:Al-140 compared to the undoped sample. This result suggests at least some degree of parallelism between the gas-phase and the electrochemical reducibility. Nevertheless, we remark that elucidating the mechanism through which AI might hinder the reduction of Cu<sub>2</sub>O requires further studies.

### 3. Conclusions

In this work, we employed a simple and potentially scalable onepot solvothermal route for preparing Cu<sub>2</sub>O catalysts for the electrochemical reduction of CO<sub>2</sub>, and studied the catalytic effect of introducing Sn, In, Ga, and Al into the Cu<sub>2</sub>O material by adding the corresponding precursors to the synthesis medium. The pristine Cu<sub>2</sub>O catalyst showed enhanced selectivity for CO and high activity at reduced overpotentials relative to a commercial sample and to oxide-derived Cu electrodes described in the literature, while inhibiting the reduction of CO<sub>2</sub> to formate. The addition of Sn and In to Cu<sub>2</sub>O was found to have a promotional effect on the reduction of CO<sub>2</sub> to CO, in line with previous results obtained over Cu-In and Cu-Sn electrodes but with the advantage of a more practical catalyst. In contrast to Sn and In, AI was incorporated only at low amounts and had a detrimental effect on the current efficiency for CO. Instead, the catalyst was driven toward ethylene production, as it showed a sevenfold increase of the current efficiency for  $C_2H_4$  at -0.8 V vs RHE compared to pristine Cu<sub>2</sub>O and to the Sn- and In-modified catalysts. Ex situ characterization of the catalysts showed that the Sn- and In modified catalysts were mostly reduced to metallic Cu after the electrolysis conditions, as was the case of the parent material. However, the Al-doped catalyst showed a clearer presence of Cu<sub>2</sub>O even after 12 h of reaction, suggesting that the reduction of the oxide matrix was hindered. In this context, we postulate that the increased selectivity for C<sub>2</sub>H<sub>4</sub> observed over the Al-doped Cu<sub>2</sub>O catalyst might be linked to a stabilizing effect of AI on Cu<sup>+</sup> species under reaction conditions. We foresee that the optimization of these catalysts might close the performance gap compared to electrodes prepared by less practical synthetic methods.

### **Experimental Section**

Catalyst synthesis. Copper(I) oxide catalysts were prepared from the reduction of a Cu(II) precursor by a one-pot solvothermal route based on the procedure described by Deng et al.<sup>[44]</sup> For the synthesis of the pristine Cu<sub>2</sub>O catalyst (Cu<sub>2</sub>O-ud), the Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O precursor (4 mmol, Sigma-Aldrich, purum p.a.) was dissolved in ethylene glycol (40 ml, Sigma-Aldrich, 99%) under vigorous magnetic stirring (750 rpm for at least 15 min) and the solution was then transferred to a 50 ml Teflonlined autoclave. The sealed autoclave was heated at 140 °C for 10 h and then allowed to cool down to room temperature. The precipitate was collected by centrifugation, washed and centrifuged three times with ultrapure water, and dried overnight at 80 °C in a vacuum oven. The modified catalysts were prepared in a similar manner by dissolving an appropriate amount of chloride salt of the second element in ethylene glycol along with the Cu(II) precursor in the first step of the synthesis (e.g. 0.2 mmol for a target Cu:modifier atomic ratio of 20). The employed precursors were  $SnCl_4 \cdot 5H_2O$  (Sigma-Aldrich, 98%),  $InCl_3$  (ABCR, 99.99%), GaCl<sub>3</sub> (Acros Organics, 99.99%) and AlCl<sub>3</sub> 6H<sub>2</sub>O (Fluka, 99.99%). Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Fluka, 99%) was also evaluated as an Al source. A commercial sample of Cu2O (Sigma-Aldrich, 99.99%) was employed as a benchmark catalyst (Cu<sub>2</sub>O-cs). The catalysts are coded as  $Cu_2O:M-N$ , where M denotes the introduced p-block element (M = Sn, In, Ga, AI) and N is the Cu/M atomic ratio. CuSn(OH)<sub>6</sub> and CuSnO<sub>3</sub> powders were prepared according to a previously reported procedure.<sup>[45]</sup> Briefly, concentrated ammonia solution (1.5 ml, Sigma-Aldrich, 25%) was added dropwise under stirring to an aqueous solution of  $Cu(SO_4)_2 \cdot 5H_2O$ (25 ml, 50 mM, Sigma-Aldrich, puriss.), followed by the addition of an aqueous solution of Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O (25 ml, 75 mM, Sigma-Aldrich, 95%) over ca. 5 min. The precipitate was aged for 15 min and then collected by centrifugation, washed with water and ethanol, and dried overnight at 80 °C in a vacuum oven to obtain CuSn(OH)<sub>6</sub>. Amorphous CuSnO<sub>3</sub> was obtained by calcination of this material in static air at 400 °C for 3 h.

Electrode preparation. Electrodes were prepared by airbrushing a catalyst ink on a gas diffusion layer (GDL). The ink was prepared by dispersing the catalyst (50 mg) in a mixture of ultrapure water (5 ml), 2propanol (5 ml, Sigma-Aldrich, 99.8%) and Nafion solution (50 µl, 5 wt.%, Sigma-Aldrich) for 15 minutes with an ultrasonic processor (VibraCell VCX130). This dispersion was then painted with an airbrush (Iwata Eclipse HP-SBS) on the microporous laver of a GDL (Sigracet 35BC. SGL Group, 12 cm<sup>2</sup> cross-sectional area) which had been mounted on a hot plate at a temperature of 90 °C. A catalyst loading of 1 to  $2 \text{ mg cm}^{-2}$ was typically achieved in this manner. The electrodes were produced by cutting the GDL into L-shaped pieces and attaching them through the protrusion to a flat silver contact soldered to a copper wire. The resulting joint and the wire were covered with abundant PTFE tape to avoid contact with the electrolyte, yielding square electrodes with an area of 1 cm<sup>2</sup> or 2.25 cm<sup>2</sup> (larger electrodes were used for tests at lower potentials). Current densities reported in this work are referred to the geometric area of the corresponding electrode.

**Characterization of catalysts and electrodes.** The chemical composition of the modified catalysts (i.e. the Cu/M atomic ratio *N*) was determined by X-ray fluorescence (XRF) spectroscopy in an Orbis Micro-XRF analyzer equipped with a 35 kV Rh anode and a silicon drift detector. X-ray diffraction (XRD) patterns of the powder catalysts and the electrodes were obtained with a PANalytical X'Pert PRO-MPD diffractometer with Bragg-Brentano geometry using Ni-filtered Cu Ka radiation ( $\lambda = 0.1541$  nm). The instrument was operated at 40 mA and 40 kV, and the patterns were recorded in the 10–70° 2 $\theta$  range with an angular step size of 0.05° and a counting time of 180 s per step. The used electrodes were analyzed after rinsing them copiously with ultrapure water following removal from the cell, and drying them in a

vacuum desiccator at ca. 3 mbar for at least 60 min prior to the measurement. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Physical Electronics (PHI) Quantum 2000 photoelectron spectrometer using monochromated AI Ka radiation (1486.6 eV) generated from an electron beam operated at 15 kV and 32.3 W and a hemispherical capacitor electron energy analyzer equipped with a channel plate and a position-sensitive detector. The binding energy (BE) scale was calibrated with the Au 4f signal being at 84.0 ± 0.1 eV. Compensation of surface charging during spectra acquisition was obtained by simultaneous operation of an electron and an argon ion neutralizer. Depth profiles were recorded by employing alternating cycles of XPS analysis and sputtering with a focused 2 kV Ar<sup>+</sup> beam rastered over an area of 4 mm<sup>2</sup>. The sputter yield was determined to be 4 nm min<sup>-1</sup> in a 100 nm Ta<sub>2</sub>O<sub>5</sub> reference film. Peak fitting of the Cu LMM Auger spectra was carried out in the CasaXPS software using experimentally-derived line shapes from reference Cu and Cu<sub>2</sub>O samples.[46,47] A detailed description of the peak fitting procedure is provided in the Supporting Information. Scanning transmission electron (STEM) micrographs in high-angle annular dark field (HAADF) mode, as well as energy-dispersive x-ray spectroscopy (EDX) element maps of the electrocatalysts, were obtained in a FEI Talos instrument operated at 200 kV, while high-resolution transmission electron microscopy (HRTEM) analyses were carried out in a FEI Tecnai F30 microscope operated at 300 kV. For these analyses, the samples were ultrasonically dispersed in a few drops of ethanol and then dropcasted onto lacev-carbon-coated Ni grids. Samples of the used electrocatalysts were obtained by scratching the catalyst off the electrode with a utility knife. Standard scanning electron microscopy (SEM) of the fresh and used electrodes was carried out in a FEI Quanta 200F instrument operated at 15 kV. Temperatureprogrammed reduction with hydrogen (H2-TPR) experiments were carried out in a Thermo Scientific TPDRO 1100 unit equipped with a thermal conductivity detector. The H2-TPR experiments over the fresh catalysts comprised an isothermal drying step in He (150 °C, 1 h) followed by a temperature ramp from 50 to 900 °C (10 °C min<sup>-1</sup>) in a flow of 5 vol.% H<sub>2</sub> in  $N_2$  (20 cm<sup>3</sup> STP min<sup>-1</sup>).

Electrochemical tests. A custom gastight glass cell with two compartments separated by a Nafion® 212 membrane (Alfa Aesar, 0.05 mm thickness) was employed for all electrochemical experiments. A 0.1 M KHCO<sub>3</sub> solution (Sigma-Aldrich, 99.95% trace metals basis) prepared with 18.2 M $\Omega$  cm ultrapure water was used as the electrolyte. Each compartment contained 45 ml of the electrolyte that was saturated with CO<sub>2</sub> (PanGas, purity 4.5), with a resulting pH of 6.75, and CO<sub>2</sub> was bubbled continuously into the catholyte during the electrolysis at a flow rate of 20 cm<sup>3</sup> min<sup>-1</sup>. All electrochemical measurements were carried out at room temperature with an Autolab PGSTAT302N potentiostat, using a Pt wire as the counter electrode and a Ag/AgCl reference electrode (3 M NaCl, model RE-1B, ALS). The GDL-based working electrodes were completely dipped into the electrolyte, and a new electrode was used for each test unless indicated otherwise. All potentials reported in this work are referenced to the reversible hydrogen electrode (RHE) scale. The potentiostatic electrolyses were carried out with the iR compensation function set at 85% of the uncompensated resistance  $R_{u}$ , which was determined before the start of the electrolysis and updated every 7.5 min by electrochemical impedance spectroscopy measurements at the electrolysis potential. Following each electrolysis, the recorded potentials were converted to the RHE scale after manually correcting for the remaining uncorrected  $R_{\rm u}$ , as described by Kuhl et al.<sup>[4]</sup> Double-layer (DL) capacitances of the electrodes (normalized to the geometric area) in the reaction medium (CO2-saturated 0.1 M KHCO3) before and after 12hour electrolyses at -0.8 V were estimated by performing CVs at different scan rates (range: 2 to 40 mV s<sup>-1</sup>) narrowly centered (30 mV) on the open circuit potential (OCP), following stabilization of the full CV response.

Product analysis. The outlet gas from the cathodic compartment flowed continuously through a sample loop and was periodically injected into an SRI 8610C gas chromatograph (Multi-Gas #3 configuration) for analysis, using Ar (PanGas, purity 5.0) as the carrier gas at a head pressure of 2.3 bar. The GC was equipped with packed HayeSep D and Molecular Sieve 13X columns, a methanizer, and thermal conductivity and flame ionization detectors. GC runs were initiated 10 min after the start of the electrolysis and thereafter every 15 min. Following the electrolysis, a sample of the catholyte was taken for liquid-phase analysis. The concentration of formate was determined by high-performance liquid chromatography (HPLC) in a Merck LaChrom system equipped with a Bio-Rad Aminex HPX-87H column heated at 35 °C and a refractive index detector (Hitachi Chromaster 5450) set at 30 °C. An aqueous solution of H<sub>2</sub>SO<sub>4</sub> (5 mM, flowing at 0.6 ml min<sup>-1</sup>) served as eluent. Selected samples were also analyzed for additional liquid-phase products by <sup>1</sup>H NMR in a Bruker Avance III HD 500 MHz spectrometer in a similar manner to Kuhl et al.<sup>[4]</sup> Finally, the current efficiency for the liquid-phase products was calculated by relating the amount produced to the total charge passed during the electrolysis. Additional details are provided in the Supporting Information.

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# Entry for the Table of Contents

### ARTICLE

One way or another. The selectivity in  $CO_2$  reduction over  $Cu_2O$ electrocatalysts prepared by a simple and potentially scalable solvothermal route can be tuned by the introduction of p-block elements. The addition of tin and indium further enhances the selectivity for CO, while the introduction of aluminum promotes the formation of valuable C2 and C3 products at moderate overpotential.



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Solvothermally-Prepared Cu<sub>2</sub>O Electrocatalysts for CO<sub>2</sub> Reduction with Tunable Selectivity by the Introduction of p-Block Elements