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7 Sn-decorated Cu for Selective Electrochemical CO₂
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ABSTRACT

Sn-decorated Cu (Cu-Sn) electrodes were proposed as an alternative to Ag- and Au-based electrocatalysts for the selective reduction of CO₂ to CO. Here we demonstrate that selectivity does not only depend on catalyst surface composition, but is strongly affected by the electrode morphology. At current densities above 10 mA·cm⁻², we find that morphology can control the CO₂ reduction pathways to CO and other products, including the competing H₂ evolution, on the Cu-Sn surface. An electrode design with dendritic morphological features yields the highest CO partial current density of 11.5 mA·cm⁻² at -1.1 V vs. RHE, avoiding the significant loss of CO selectivity observed for an electrode with less sharp, rounder morphological features. Efficient CO₂ mass transport to the catalyst surface and a high local CO₂ concentration, promoted by the dendritic structure, stabilize the Cu-SnO overlayer, suppress the competing H₂ evolution reaction, and maintain CO selectivity above 85% over a wide potential range.

1. Introduction

Electrocatalysts facilitate the electrochemical CO₂ reduction reaction (CO₂RR) to valuable products. The great challenge consists in developing an electrocatalyst with low overpotential to achieve high reaction rates and to maximize its selectivity for the desired products. The CO₂RR to carbon monoxide (CO) or formate/formic acid (HCOO⁻/HCOOH) are considered to be the economically most favorable processes to compete with conventional production routes ¹. High selectivity and high stability for the CO₂RR to CO in aqueous electrolyte were reported for bimetallic Cu-Sn catalysts ²⁻⁹. Due to the lower cost of Cu and Sn compared to Au or Ag, Cu-Sn catalysts are better suited for large-scale deployment compared to *e.g.* nanostructured Au- ¹⁰⁻¹³ and Ag-based ¹⁴⁻¹⁵ catalysts. The highest selectivity for CO production is achieved at an optimal Cu/Sn ratio at the catalyst surface ^{3-4, 6, 8}. High CO faradaic efficiencies above 90 % were reported at low-to-moderate overpotentials resulting in CO partial current densities of 1.9 to 4.6 mA·cm⁻² at -0.7 V (vs. RHE) ^{3, 6, 8}.

However, with the improvement of the CO₂RR kinetics, the electrode surface encounters CO₂ mass-transport limitations ¹⁶⁻¹⁷. CO₂ depletion near the electrodes at high current densities, due to both the CO₂RR and unfavorable high local pH ¹⁷, limits the maximum CO partial current density. The mass transport of CO₂ and products can be improved by tuning the electrode architecture on the micro- and nanometer scale. Sharp morphologies were shown to lead to field-induced reagent concentration ¹³ and morphology-enhanced gas evolution ¹⁶ for Au catalysts, which improve the maximum CO partial current density significantly.

Here we demonstrate the impact of catalyst morphology on the selectivity and stability of Cu-Sn catalysts for CO production. For a Cu-Sn catalyst with a morphology consisting of aggregated Cu-Sn particles, we observe high selectivity for CO production at intermediate potentials ($\geq 70\%$

at -0.7 to -0.9 V), resulting in the highest CO partial current density of $6.1 \text{ mA} \cdot \text{cm}^{-2}$. However, at more negative potentials, CO production is strongly suppressed. Simultaneously, the hydrogen (H_2) evolution reaction (HER) dominates, and the CO_2RR tends to produce more reduced C_2 chemicals (ethylene (C_2H_4) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)). We show that by growing the Cu-Sn catalyst with a dendrite morphology, the high selectivity for CO production is maintained at high overpotentials (74% at -1.1 V), resulting in a high CO partial current density of $11.5 \text{ mA} \cdot \text{cm}^{-2}$.

2. Experimental Section

Nanostructured Cu electrodes are prepared by electroplating polycrystalline Cu in acidic CuSO_4 solution on a Cu mesh¹⁸⁻¹⁹. The morphology is controlled by adapting the CuSO_4 concentration and the plating current density. In a second step, the freshly deposited Cu structures are decorated electrochemically by Sn atoms in basic $\text{KSn}(\text{OH})_3$ solution.

Morphology, crystalline structure, and surface composition are characterized by field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured in a three-electrode cell with N_2 - or CO_2 -saturated 0.1 M KHCO_3 aqueous solutions. CO_2 electrolysis was performed in a custom-built two-compartment electrolysis cell in a three-electrode configuration. Unless otherwise specified, all potentials refer to the reversible hydrogen electrode (RHE). The volume fraction (concentration) of gaseous products was measured by gas chromatography (GC) with a Plot Q (Ar carrier gas) and a Plot U (He carrier gas) column. Liquid phase products were quantified using ^1H nuclear magnetic resonance (NMR).

Details of chemicals, experiments, and analysis are provided in the Supporting Information (SI).

3. Results and Discussion

3.1 Cu electrodes with two morphologies

Fig. 1a and b show typical SEM images comparing two very different electrode morphologies. The dendrites shown in the inset of Fig. 1a consist of a vertical stem from which horizontal branches grow into six symmetry-related directions. Branches are typically a few 100 nm long ending in a relatively sharp tip. Randomly oriented dendrites are arranged in larger clusters several micrometers in size. In contrast, the morphology in Fig. 1b shows much more rounded features arranged in larger clusters. For simplicity, we refer to this morphology as the particle morphology, although the ‘particles’ did not grow individually.

Fig. 1c compares cyclic voltammograms for the two morphologies of Cu before Sn deposition in N₂-saturated 0.1 M KHCO₃ (pH 8.8). The voltammogram of the particle morphology shows a first oxidation peak at -0.1 V and a second oxidation peak at 0.2 V, which were assigned by Schouten *et al.*²⁰ to the oxidation of lower-coordinated Cu (e.g. on (100) facets or at steps) and the oxidation of higher-coordinated Cu on close-packed (111) facets, respectively. In contrast, the dendrite morphology shows only one oxidation peak at 0.2 V indicating predominant Cu(111) surface orientation.

In Fig. 1d and e, we compare the partial and total current densities (normalized to the specific surface area of Cu determined by double layer capacitances²¹) for the two Cu electrode morphologies in CO₂-saturated electrolyte. Partial current densities were calculated by

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3 multiplying the total current density by the corresponding faradaic efficiencies determined by GC
4 for gaseous products and by ^1H NMR for liquid products (see procedures in SI). For both
5 morphologies, HER dominates for Sn-free Cu electrodes at potentials from -0.4 to -0.9 V (Fig.
6 S3), in agreement with previous studies ²²⁻²³. The H_2 partial current densities measured on the two
7 morphologies are similar at all selected potentials, indicating the independence of the HER
8 activity on morphology. Interestingly, the minor CO_2RR products evolving from the dendrite
9 morphology consist of CO and HCOO^- only, while the products from the particle morphology
10 include in addition C_2 products (C_2H_4 and C_2H_6), indicative for a relatively high ratio of (100)
11 facets and grain boundaries ²⁴⁻²⁶.
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25 3.2 Characterization of Sn-decorated Cu electrodes

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28 Dendrite and particle morphology retain their initial Cu morphologies after Sn decoration (see
29 Fig. 2a and Fig. S4 for SEM images after Sn decoration). A high-resolution scanning TEM image
30 of the tip of a Cu-Sn dendrite branch is shown in Fig. 2b. High-resolution elemental mapping by
31 energy dispersive X-ray spectroscopy (EDS) indicates that Sn distributes homogeneously on both
32 electrode morphologies (Fig. S5 and S6). The enhanced EDS signal of Sn along the edge of the
33 dendrite in Fig. 2c is due to geometrical effects. Direct evidence for the coexistence of Cu and Sn
34 sites at the surface of the catalyst from cyclic voltammetry will be discussed in Fig. 3. From the
35 high-resolution TEM image in Fig. 2d, the polycrystalline nature of the dendrite branch becomes
36 apparent, covered by a 2-3 nm thin amorphous layer. In the electron diffraction pattern in Fig. 2e
37 from the region in Fig. 2d, reflections from Cu(111), Cu(200), and Cu(220) can be identified
38 along with Cu_2O (111) reflections. Cu_2O forms during the transfer in air of the sample to the TEM.
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54 Since the synergistic effect of Cu and Sn for CO production is expected to strongly depend on the
55 surface Cu/Sn ratio ^{3-4, 6}, the optimal value to reach the highest CO faradaic efficiency at -0.8 V
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was characterized for both morphologies independently. We employ XPS to determine the Cu/Sn ratio at the surface of both morphologies. It turns out that for the samples with the highest CO selectivity at -0.8 V, the resulting ratio of the maximum intensity for the Cu 2p_{3/2} and Sn 3d_{5/2} peaks after subtraction of a Shirley background is about 12 for both morphologies (Fig. S7). Thus neglecting shadowing effects, the Sn surface content is about the same for both morphologies. Higher-resolution photoelectron spectra of the Cu 2p peaks, Cu LMM Auger peaks and Sn 3d peaks are shown in Fig. S8, indicating partial oxidation of Cu and Sn, which is due to the exposure in air.

The cyclic voltammograms of the Cu-Sn electrode with dendrite morphology (Fig. 3a) are compared with those of polycrystalline Sn (Fig. 3b) and Cu electrodes (Fig. 3c) in both N₂- and CO₂-saturated 0.1 M KHCO₃ solutions. The corresponding data for the Cu-Sn electrode with particle morphology are shown in Fig. S9. By comparison with Fig. 3b, the reduction peak from 0.0 to -0.4 V in Fig. 3a is attributed to the reduction of SnO₂ to a mixed Sn(II) oxide/hydroxide²⁷⁻²⁸, and it couples to the reoxidation peak from 0.05 to 0.5 V. The reduction peaks from 0.6 to 0.1 V in Fig. 3a can be identified by comparison with Fig. 3c as related to CuO_x reduction to Cu²⁰. Combining information from TEM, XPS, and cyclic voltammetry, we conclude that the electrode surface consists of Cu, Sn and O. At the potentials for CO₂RR (< -0.4 V), SnO₂ is reduced to Sn(II) oxide/hydroxide, for simplicity denoted as SnO. Thus, the electrodes investigated in this work consist of a Cu core decorated with a Cu-SnO overlayer whose precise atomic structure is not yet to be determined.

The detailed mechanism for CO₂RR to CO on Cu-Sn electrodes is still under debate. Takanabe's group³ suggested that substitution of Sn atoms on Cu surfaces weakens the H adsorption on Cu and in turn enhances the selectivity exclusively for CO. An alternative scenario was proposed by

Li *et al.* ⁶ suggesting that the synergistic effect observed on the Cu-doped SnO₂ surface is due to the uniaxial compression of SnO₂ and Cu doping on the SnO₂ surface or subsurface. The debate focuses on the oxidation state of Sn: The former one suggests the existence of metallic Sn in the Cu-Sn surface alloys ³, while the later one proposes SnO₂ as the catalytically active species ⁶. Operando measurements by Baruch *et al.* ²⁸ and Dutta *et al.* ²⁹ exclude the existence of metallic Sn under the experimental conditions for selective CO₂RR, even though the Pourbaix diagram ³⁰ suggests that metallic Sn is thermodynamically stable under such highly reductive conditions. Moreover, Baruch *et al.* ²⁸ compared the CO₂RR on Sn⁰, Sn^{II}₆O₄(OH)₄, and Sn^{IV}O₂ electrodes, and suggested that a Sn^{II} oxyhydroxide surface is the catalytically active species. Density functional theory calculations, performed by Luc *et al.* ³¹, indicate that the thermally neutral formation of adsorbed CO₂ negative ion (*CO₂⁻) at the oxygen vacancy of SnO (101) precedes the formation of *COOH and *OCHO intermediates, corresponding to the production of CO and HCOO⁻, respectively ³². Following Baruch *et al.* ²⁸ and Dutta *et al.* ²⁹, a Cu-SnO overlayer is considered in this work to provide the catalytically active sites for CO₂RR. In contrast to the high HCOO⁻ selectivity of SnO, Cu-SnO is more selective for CO.

3.3 Electrolytic performance

The performance of the two Cu-Sn electrode morphologies for the CO₂RR is assessed in CO₂-saturated electrolyte. CO₂ gas bubbles flow continuously into the cathodic compartment with a flow rate of 30 sccm to maintain efficient CO₂ supply and mechanical convection. Fig. 4a and c present the faradaic efficiencies for the dominant products as a function of applied potential for the dendrite and particle morphology. The sum of all measured faradaic efficiencies is also given and falls close to 100% indicating that no significant amounts of other reaction products are formed. Corresponding partial and total current densities are reported in Fig. 4b and d. Strikingly,

the dendrite morphology exhibits very high faradaic efficiency of above 85% for CO evolution at potentials between -0.7 V and -1.0 V, peaking even at 91% at -0.7 V. The faradaic efficiency for H₂ evolution remains below 20% even at high overpotentials, resulting in a high CO partial current density of up to 11.5 mA·cm⁻² at -1.1 V, 170% of the maximum value measured for the particle morphology. Moreover, this is the first study reporting a CO partial current density higher than 10 mA·cm⁻² for the Cu-Sn system^{2-3, 6-9}. The situation is very different for the particle morphology in Fig. 4c and d. Here the HER starts to dominate abruptly at potentials more negative than -0.9 V with faradaic efficiencies above 50%. Consequently the faradaic efficiency for CO evolution drops below 25%.

In Fig. 4e, the CO₂ conversion rate, *i.e.* the amount of CO₂ converted to reduced carbon products per second per geometric surface area, is shown as a function of potential. At low overpotentials (-0.5 V to -0.8 V), the conversion rates are very similar for both morphologies, confirming that catalyst surfaces with optimized Cu/Sn ratio exhibit identical activity for CO₂RR independent of morphology and preferential crystal facets, in agreement with Sarfraz's work³. However, at potentials $\leq$ -0.9 V, the conversion rate reaches a ceiling at 39 nmol·s⁻¹·cm⁻² for the particle morphology, and decreases to 33 nmol·s⁻¹·cm⁻² at -1.1 V. In contrast, the conversion rate continues to increase for the dendrite morphology, reaching a value of almost 70 nmol·s⁻¹·cm⁻², *i.e.* about twice as high as for the particle morphology, at -1.1 V. A similar trend is also observed for the CO₂ conversion rate to CO shown in Fig. S10c.

To understand the impact of morphology on selectivity at high overpotentials, it is instructive to inspect the evolution of minor reaction products. For the dendrite morphology, the main product besides CO and H₂ is HCOO⁻ reaching 7.5% in faradaic efficiency at -1.1 V, while C₂ products (C₂H₄ and CH₃CH₂OH) contribute only 5.5% in total. For the particle morphology, the situation

is again very different as the C₂ products are detected at -0.9 V, dominating HCOO⁻ evolution at -1.0 V and -1.1 V. The C₂ products indicate that the Cu-Sn surface retains some of the original features of pure Cu, since C₂H₄ and CH₃CH₂OH are the major C₂ products of Cu-catalyzed CO₂RR³³. Moreover, H₂ is a byproduct for both morphologies at low overpotentials, at which CO is the main product. At high overpotentials H₂ becomes the main product on the particle morphology, indicating the ineffectiveness of the electrode in suppressing the HER. Extensive EIS analyses (see Fig. S11) show a reduced charge transfer resistance (R_{CT}) at the electrode/electrolyte interface for the dendrite morphology in the presence of CO₂, confirming the high selectivity for CO₂RR versus HER. On the contrary, R_{CT} values are found to be similar in both atmospheres for particle morphology, indicating the poor selectivity.

Local electric field induced reagent concentration by sharp morphological features was invoked by Liu *et al.* to explain the enhanced selectivity and activity of Au nano-needles for CO₂RR to CO¹³. An alternative scenario was suggested by Burdyny *et al.*¹⁶, in which sharp dendritic electrodes are capable of nucleating and releasing gas bubbles at smaller sizes, thereby enhancing effective mass transport by convective flow particularly at current densities > 10 mA·cm⁻². Both effects result in an increase of the local reagent concentration through the dendrite morphology, leading to an enhanced selectivity for CO₂RR rather than HER. Our results indicate that these mechanisms may also apply to Cu-Sn systems.

The exact amount of CO₂ transported to the Cu-Sn electrode surface cannot be measured directly. Instead, we estimate the amount of CO₂ efficiently transported to the surface by the amount of carbon detected in all final products, which is proportional to the CO₂ conversion rate. For the particle morphology, the decrease of the CO₂ conversion rate at high overpotentials indicates less efficient transport of CO₂ to the electrode surface. In contrast, no saturation of the CO₂ conversion

rate is observed on the dendrite morphology, indicating more efficient CO₂ transport. Here the dendrite morphology promotes a high CO₂ concentration at the electrode surface, and maintains a high selectivity for CO₂RR to CO. Due to the relatively lower local CO₂ concentration, CO selectivity at potentials ≤ -0.9 V decreases for the Cu-Sn electrodes with particle morphology.

To understand the decrease in CO selectivity on Cu-Sn electrodes at high overpotentials, we investigate the potential-dependent surface composition. As mentioned before, a Cu-SnO overlayer is considered to be the catalytically active species for CO₂RR to CO. The reduction of the Cu-SnO overlayer to a metallic Cu and Sn (mCu-Sn) surface may explain the decrease in CO selectivity. Metallic Sn is selective for HER rather than CO₂RR²⁸⁻²⁹, consistent with the observed abrupt increase of the H₂ partial current density and the formation of C₂ products catalyzed by metallic Cu. The reduction of Cu-SnO to mCu-Sn on the particle morphology happens at potentials ≤ -0.9 V, while on the dendrite morphology it happens at potentials ≤ -1.1 V. Considering the relatively higher CO₂ concentration near dendrites, CO₂ appears to stabilize the Cu-SnO overlayer under a reductive condition. The mechanism requires further study.

Conclusion

Sn-decorated Cu electrodes with optimal Cu/Sn ratios are investigated for the electrochemical conversion of CO₂ to CO. A Cu-SnO overlayer is considered to be the catalytically active species for this reaction. We investigated the effect of morphology on the selectivity and reaction pathways of CO₂RR at high current densities. On the electrode with particle morphology, a saturation followed by a decrease in CO partial current density is observed when going to higher overpotentials. This result is understood in terms of Cu-SnO reduction to metallic Cu-Sn. No

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3 such saturation is observed for an electrode with dendrite morphology in the same potential range.
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5 The dendrite morphology promotes a high CO₂ concentration at the electrode surface and
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7 maintains a high CO faradaic efficiency over a broad potential range. Our results emphasize the
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9 importance of subtle variations in electrode morphology that control mass transport and regulate
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11 the local concentration of reagent or reaction intermediates at the catalyst surface. Future studies
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13 on enhancing CO₂RR selectivity can thus not be limited only on catalyst surface and subsurface
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15 composition, but very importantly must also take into account the electrode morphology.
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Figure 1. Typical SEM images of Cu electrodes with the dendrite (a) and particle (b) morphologies, and their cyclic voltammograms (c) in the Cu-redox potential range. Partial current densities for all products during the electrochemical CO₂ reduction on the Cu electrodes with the dendrite (d) and particle (e) morphologies.

Figure 2. (a) SEM image of Cu-Sn dendrites. Scanning TEM image (b) and high-resolution scanning TEM-EDS elemental mapping (c) of a single Cu-Sn dendrite. (d) High-resolution TEM image of a nanostructure at the tip of a Cu-Sn dendrite. (e) Electron scattering pattern from the region in (d).

Figure 3. Cyclic voltammograms of Cu-Sn dendrite (a), polycrystalline Sn (b), and polycrystalline Cu (c) electrodes measured in the metal redox potential range at a scan rate of 10 mV·s⁻¹.

Figure 4. Faradaic efficiencies of Cu-Sn electrodes with the dendrite (a) and particle (c) morphologies for dominant products during the CO₂ reduction reaction, and their corresponding partial current densities shown in (b) and (d), respectively. (e) Comparison of CO₂ conversion rates for both morphologies.

ASSOCIATED CONTENT

Supporting Information

Chemicals, materials and deposition procedures; Materials characterization; Electrolysis and product analysis; XRD patterns, CO₂RR selectivity of Cu electrodes; Morphology, element mapping, surface composition, cyclic voltammograms, electrochemical impedance spectra of Cu-Sn electrodes; Electrolytic performance of Cu-Sn electrodes for CO₂RR (PDF)

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ABBREVIATIONS

Cu-Sn, Sn-decorated Cu; CO₂RR, CO₂ reduction reaction; HCOO⁻/HCOOH, formate/formic acid; RHE, reversible hydrogen electrode; HER, hydrogen evolution reaction; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; EDS, energy dispersive X-ray spectroscopy; CV, cyclic voltammetry; EIS, electrochemical impedance spectroscopy; GC, gas chromatography; NMR, nuclear magnetic resonance; SnO, Sn(II) oxide/hydroxide; *CO₂⁻, adsorbed CO₂ negative ion; R_{CT}, charge transfer resistance; mCu-Sn, metallic Cu and Sn.

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Table of Content

Figure 1. Typical SEM images of Cu electrodes with the dendrite (a) and particle (b) morphologies, and their cyclic voltammograms (c) in the Cu-redox potential range. Partial current densities for all products during the electrochemical CO₂ reduction on the Cu electrodes with the dendrite (d) and particle (e) morphologies.

84x136mm (300 x 300 DPI)

Figure 2. (a) SEM image of Cu-Sn dendrites. Scanning TEM image (b) and high-resolution scanning TEM-EDS elemental mapping (c) of a single Cu-Sn dendrite. (d) High-resolution TEM image of a nanostructure at the tip of a Cu-Sn dendrite. (e) Electron scattering pattern from the region in (d).

84x62mm (300 x 300 DPI)

Figure 3. Cyclic voltammograms of Cu-Sn dendrite (a), polycrystalline Sn (b), and polycrystalline Cu (c) electrodes measured in the metal redox potential range at a scan rate of 10 $\text{mV}\cdot\text{s}^{-1}$.

Figure 4. Faradaic efficiencies of Cu-Sn electrodes with the dendrite (a) and particle (c) morphologies for dominant products during the CO_2 reduction reaction, and their corresponding partial current densities shown in (b) and (d), respectively. (e) Comparison of CO_2 conversion rates for both morphologies.