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Article

Efficient CO₂ Electroreduction on Tin Modified Cuprous Oxide Synthesized via a One-Pot Microwave-Assisted Route

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Abstract: Bimetallic copper-tin catalysts are considered cost-effective and suitable for large-scale electrochemical conversion of CO₂ to valuable products. In this work, a class of tin (Sn) modified cuprous oxide (Cu₂O) is simply synthesized through a one-pot microwave-assisted solvothermal method and thoroughly characterized by various techniques. Sn is uniformly distributed on the Cu₂O crystals showing a cube-within-cube structure, and CuSn alloy phase emerges at high Sn contents. The atomic ratio of Cu to Sn is found to be crucially important for the selectivity of the CO₂ reduction reaction, and a ratio of 11.6 leads to the optimal selectivity for CO. This electrode shows a high current density of 47.2 mA cm⁻² for CO formation at −1.0 V vs. the reversible hydrogen electrode and also displays good CO selectivity of 80–90% in a wide potential range. In particular, considerable CO selectivity of 72–81% is achieved at relatively low overpotentials from 240 mV to 340 mV. During the long-term tests, satisfactory stability is observed for the optimal electrode in terms of both electrode activity and CO selectivity. The relatively low price, the fast and scalable synthesis, and the encouraging performance of the proposed material implies its good potential to be implemented in large-scale CO₂ electrolyzers.

Keywords: carbon dioxide conversion; electrocatalysis; cuprous oxide; tin; overpotential



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1. Introduction

Electrochemical conversion of carbon dioxide (CO₂) can create a bridge between the carbon capture/storage process and the renewable energy technology. By utilizing clean electricity as energy input and captured CO₂ as raw material, the CO₂ reduction reaction (CO₂RR) can directly produce valuable chemical feedstocks, including C₁ products such as carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), and formic acid (HCOOH), C₂ products such as ethylene (C₂H₄), ethane (C₂H₆) and ethanol (C₂H₅OH), C₂₊ products such as n-propanol (CH₃CH₂CH₂OH) and so on [1]. Among these products, the simple and small building-block molecules, CO and HCOOH, are considered to be techno-economic convenient and comparable with the conventional chemical synthesis [2]. CO plays a vital role in the chemical industry and is considered to be the most important and versatile C₁-building block [3]. Its utilization is intensive in processes such as Fischer-Tropsch synthesis of hydrocarbons and Monsanto/Cativa acetic acid synthesis at large industrial scales [4].

A tremendous effort has been dedicated to the CO₂RR, mainly focusing on the catalyst materials and processes [5,6]. State-of-the-art catalysts for the CO₂RR to CO are gold (Au) and silver (Ag), allowing excellent selectivity of over 95% [7,8]. Other materials, such as palladium (Pd), zinc (Zn), metal (Ni, Zn, Sb, and Co)-nitrogen-carbon complexes and copper alloys, also showed satisfactory CO selectivity [5,9,10]. Bimetallic Cu-Sn catalysts

have attracted the most intensive attention due to the high selectivity and good stability for the CO₂RR to CO in aqueous electrolyte [11–15]. In addition, compared with Au and Ag, Cu and Sn are much more abundant and more cost-effective, making Cu-Sn catalysts more suitable for the large-scale implementation. Hence, further study on the Cu-Sn catalysts is expected to bring benefits to both the academic and industrial sectors related to the CO₂ valorization. In most previous works, Cu-Sn catalysts were obtained by deposition methods and tested as free-standing electrodes in a batch reactor [11–17]. Despite the outstanding selectivity for the CO₂RR to CO, these free-standing electrodes suffer from severe mass diffusion limitations at relatively higher current densities ($>15\text{ mA cm}^{-2}$), making it commercially unfeasible [6]. One of the critical causes is the low solubility and diffusivity of CO₂ in aqueous electrolytes [18]. The electrolysis process with gas-fed CO₂ in a flow reactor is considered an effective strategy to mitigate the CO₂ transport limitation, resulting in current densities as high as tens to hundreds of milliamperes. In such an approach, the gas diffusion electrode (GDE) is the key component [19,20]. It is usually composed of a catalyst layer and a hydrophobic substrate. The high porosity and hydrophobicity of the GDE can ensure high CO₂ diffusion rates and shorten the diffusion distance from the substrate to the catalyst layer.

To enable the fabrication of GDEs, we fabricated a class of Sn-Cu material through a simple microwave-assisted solvothermal route, using tin acetate and copper acetate as Sn and Cu precursors, respectively. Ethylene glycol (EG) was used as both the solvent and the reducing agent. The Sn modified Cu₂O catalyst containing a nominal Cu:Sn atomic ratio of 12.0 is denoted as Sn-Cu₂O, and it is characterized by good CO selectivity (70–80%) at low overpotentials (240–340 mV) and encouraging performance in a wide potential range for the CO₂RR. Various samples with different atomic ratios of Cu to Sn have been synthesized and studied for comparison and they are denoted as CuSn0.5, CuSn1.0, and CuSn2.0 with nominal Cu:Sn ratios of 36.0, 18.0, and 9.0, respectively.

2. Results and Discussion

2.1. Physical and Chemical Characterizations of the As-Prepared Catalysts

X-ray diffraction (XRD) analysis was firstly performed to study the crystalline phase composition of the samples. As shown in Figure 1a, the peaks of the Cu₂O sample correspond to the reflections related to the (110), (111), (200), (211), (220), (311), and (222) planes of crystalline Cu₂O (cubic, space group Pn-3m) [21]. No peaks for impure crystalline phases are observed for this sample. The Sn-Cu₂O sample shows a similar XRD pattern with peaks for only Cu₂O phase (Figure 1b). However, careful inspection of the pattern reveals a clear shoulder in the (200) peak (see Figure 1c). In the literature, some CuSn alloys with various stoichiometry show XRD patterns that mainly consist of only one dominant peak in the 42–43° 2 θ range [22,23]. Other samples with different Cu:Sn atomic ratios have also been characterized by XRD. As shown in Figure S1, the samples with lower Sn contents show only crystalline Cu₂O phase, and the sample which contains more Sn also displays a CuSn alloy peak in the 42–43° 2 θ range at notable intensity.

In order to gain further insight into the crystalline structure of both samples, the XRD patterns are fitted by Rietveld refinement using the structural models reported in the experimental section, and the refined parameters are shown in Table 1. It is interesting to note that there is no significant change in the lattice parameter and the coherent scattering domain size for the Cu₂O phase in both samples. Concerning the Sn-Cu₂O sample, this outcome means that eventual incorporation of Sn atoms in the Cu₂O phase (thus labeled Cu₂O:Sn) is not causing distortion of the unit cell if we assume that the Sn content is not limited only to the CuSn alloy phase.

The morphology and particle size of the as-prepared catalysts were studied by Field emission scanning electron microscopy (FESEM). As shown in Figure 2a,b, the Cu₂O sample is composed of flower-like particles that resemble eight-petal-shaped crystals. Four petals are present in each plane and are highly symmetric in the structure. This eight-pod framework is likely due to the crystal branching along all $\langle 111 \rangle$ directions of Cu₂O [24].

Similar branching was also observed in ethanol-water solvents with formic acid as the reducing agent [25]. In some particles, the pods are significantly amplified and each pod has a cubic shape. These particles tend to form a big cube and they are called “cube-within-cube” or “crystal-within-crystal” arrangements [25]. Some particles eventually grow into single symmetric cubes with a small space in the center, due to the faster growth of the eight petals. The addition of a small number of Sn^{4+} ions leads to faster growth of the eight petals into small cubes that are packed in a cubic aggregate, as shown in Figure 2d,e. In most particles, the center space is significantly narrowed and even eliminated, generating single symmetric cubes. Despite the difference in the morphology, most particles in both samples show a similar average particle size of 8–10 μm and have a rough surface (Figure 2c,f). Moreover, it is worth noting the presence of a second class of structures with irregular lamellar morphology, with variable lateral size in the micrometer range.

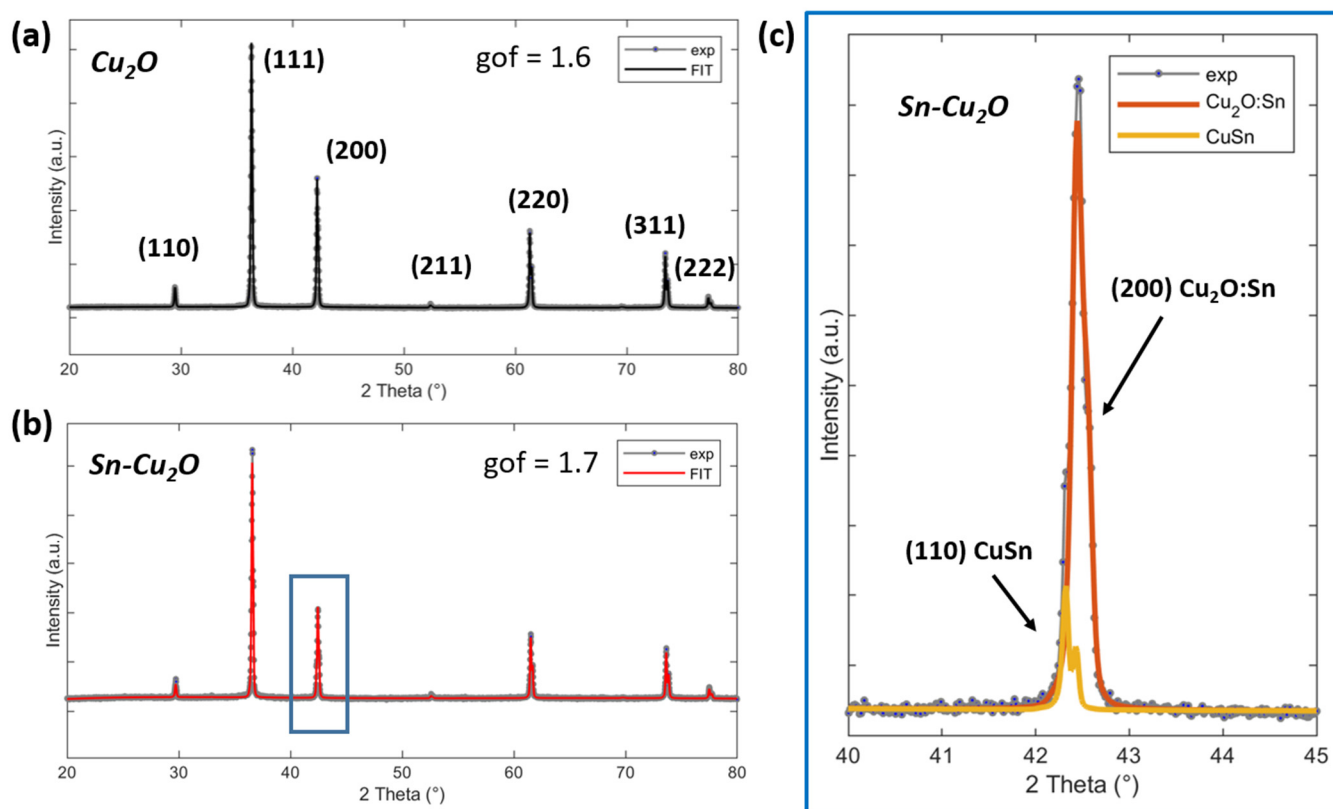


Figure 1. XRD patterns of Cu_2O (a) and $\text{Sn-Cu}_2\text{O}$ (b) catalysts with corresponding Rietveld refinement fit and goodness-of-fit (gof) values. Panel (c) provides a view of the (200) peak of the XRD pattern from $\text{Sn-Cu}_2\text{O}$ sample, showing contributions from two different phases.

Table 1. Parameters obtained from Rietveld refinement for the Cu_2O and $\text{Sn-Cu}_2\text{O}$ samples.

Cu_2O				$\text{Sn-Cu}_2\text{O}$			
Phase	Cu_2O	a (Å)	Size (nm)	Phase	$\text{Cu}_2\text{O:Sn}$	a (Å)	Size (nm)
-	cubic	4.268	108	-	cubic	4.269	88
-	$Pn-3m$	-	-	-	$Pn-3m$	-	-
-	-	-	-	-	-	-	-
-	-	-	-	phase	CuSn	a (Å)	size (nm)
-	-	-	-	-	cubic	3.027	285
-	-	-	-	-	$Im-3m$	-	-

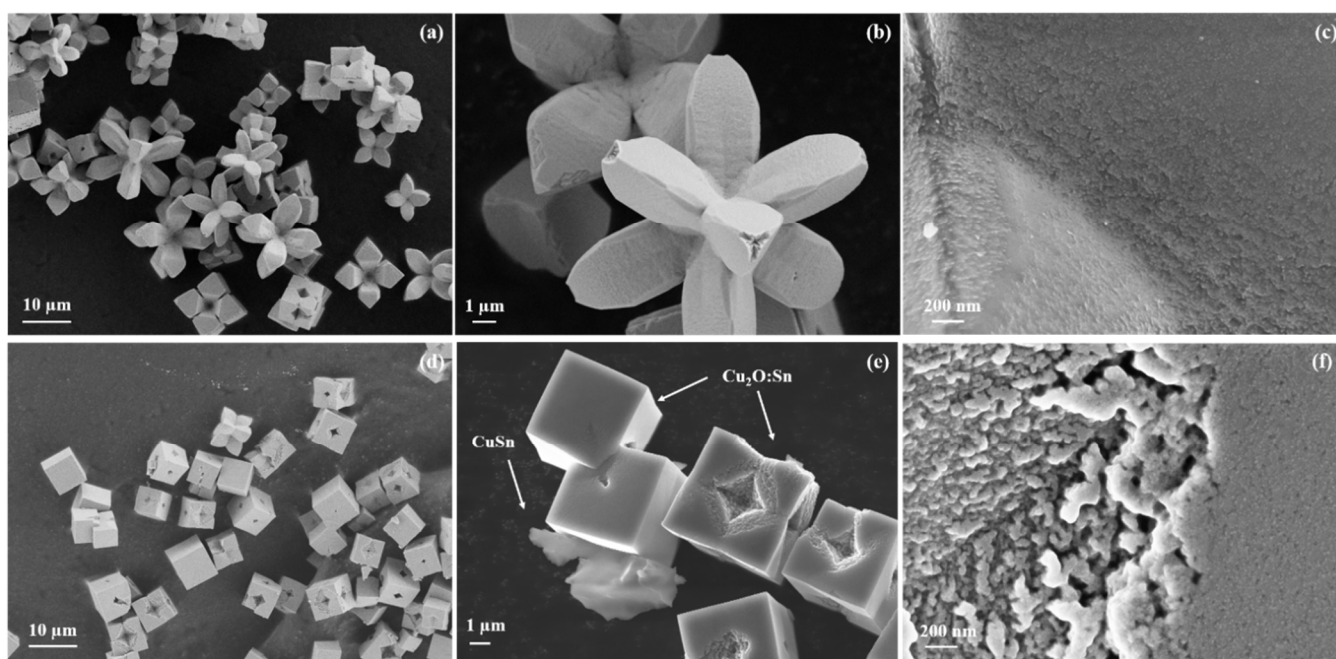


Figure 2. FESEM images of the samples. (a–c) Cu_2O , (d–f) $\text{Sn-Cu}_2\text{O}$.

Energy dispersive X-ray (EDX) analysis provides useful information on these two classes of structures, as shown in Figure S2. Specifically, EDX mapping proves two important points: (1) Sn is homogeneously distributed in both cubic and lamellar structures; (2) a higher Sn/Cu at % ratio is present in the lamellar structures. Combining EDX and XRD results, it is reasonable to ascribe the $\text{Cu}_2\text{O}:\text{Sn}$ crystalline phase to the cubic morphology, while the CuSn crystalline phase is associated with the lamellar structures with a higher Sn content.

FESEM analysis has also been performed on other samples with various Cu:Sn ratios, as shown in Figure S3. It is likely that a higher Sn^{4+} concentration in the precursor solution promotes the growth of the eight petals into an entire cube. In addition, the sample with the highest Sn content (Cu:Sn = 9.0) shows significant irregular and lamellar structures associated with the CuSn alloy phase, in agreement with the XRD result (Figure S1).

Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed in order to quantify the Cu and Sn elements. It is found that the Cu_2O sample contains 85 wt.% of Cu element, and the $\text{Sn-Cu}_2\text{O}$ sample consists of 70 wt.% of Cu and 11 wt.% of Sn. By stoichiometric calculation, the Cu_2O percentage is 96 wt.% in the Cu_2O sample, and the $\text{Sn-Cu}_2\text{O}$ sample contains 79 wt.% of Cu_2O and 11 wt.% of Sn (about 14 wt.% of O-Sn-O). The atomic ratio of Cu to Sn is calculated to be 11.6, which is in good agreement with the nominal one of 12.0 in the precursor solution. The remaining weight could be attributed to the surface adsorbed species. By ICP analysis, it is further confirmed that other samples with various Cu:Sn ratios are composed of the desired Cu and Sn contents.

X-ray photoelectron spectroscopy (XPS) measurements have been performed on Cu_2O and $\text{Sn-Cu}_2\text{O}$ samples in order to examine their surface physicochemical properties. From surveys spectra in Figure 3a, we can verify the presence of Cu, O, and C on both samples and the Sn signal only from the $\text{Sn-Cu}_2\text{O}$ one. $\text{C}1\text{s}$ peak, on both samples, is mainly due to the environmental exposure (spectra not reported). From the HR spectra, we can distinguish different oxidation states, thanks to the evaluation of chemical shifts in the binding energy (BE) scales. From $\text{Cu}2\text{p}$ HR doublets (Figure 3b), we can clearly see that both samples show typical spectra related to Cu^+ oxidation state, with a very small and weak satellite due to Cu^{2+} state [26]. To further confirm this attribution, we also checked the $\text{CuL}_3\text{M}_{4.5}\text{M}_{4.5}$ Auger peaks, from which the modified Auger parameter can

be calculated [27]. This parameter also allows us to distinguish between Cu^+ and Cu^0 , which show almost the same chemical shift in the $\text{Cu}2\text{p}$ doublet. We thus obtained two values equal to 1849.3 eV and 1849.4 eV for Cu_2O and $\text{Sn-Cu}_2\text{O}$ samples, respectively, in accordance with the reported value of 1849.2 ± 0.3 eV for Cu^+ average oxidation state [26]. A final check has been reserved to the $\text{Sn}3\text{d}$ doublet for $\text{Sn-Cu}_2\text{O}$ sample (Figure 3d). A typical spectrum due to Sn^{2+} oxidation state is clearly observed [12], with $\text{Sn}3\text{d}_{5/2}$ peak located at 486.3 eV and its counterpart $\text{Sn}3\text{d}_{3/2}$ at 494.7 eV ($\Delta_{\text{doublet}} = 8.4$ eV).

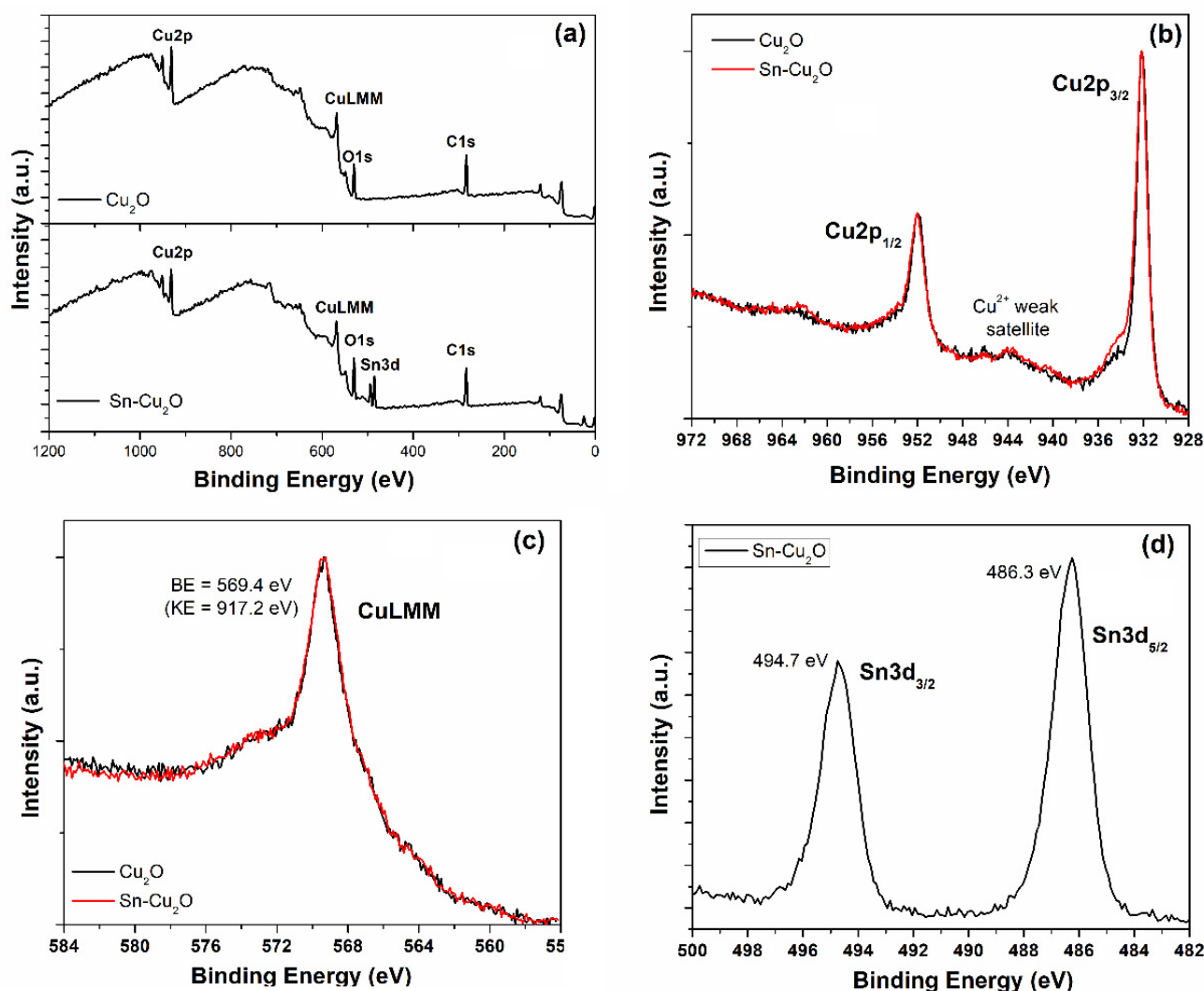


Figure 3. XPS analyses on the prepared samples: (a) survey spectra, (b) $\text{Cu}2\text{p}$ doublet HR spectra, (c) $\text{CuL}_3\text{M}_{4.5}\text{M}_{4.5}$ Auger peaks, and (d) $\text{Sn}3\text{d}$ doublet HR spectrum.

2.2. Comparison of the CO_2RR Performance on Various Samples

In order to compare the activity and selectivity of Cu_2O and Cu-Sn materials for the CO_2RR , chronoamperometric (CA) measurements were carried out in a batch cell (Scheme S1a) in a CO_2 -saturated 0.1 M KHCO_3 solution. All potentials are reported versus the reversible hydrogen electrode (RHE) in this work. The i - t curves and product analyses are shown in Figure 4. At each potential, the Cu_2O electrode (Figure 4a) shows a higher current density than the $\text{Sn-Cu}_2\text{O}$ one (Figure 4c). On both electrodes, the current density increases while negatively shifting the applied potential. In the investigated potential range, the Cu_2O electrode shows poor selectivity for the CO_2RR , with faradaic efficiency for CO (FE_{CO}) lower than 7% and FE_{HCOOH} smaller than 15% (Figure 4b). In contrast, the Sn -modified Cu_2O sample shows significantly enhanced CO_2RR selectivity, with CO as

the dominant product (Figure 4d). The CO selectivity reaches a good value of about 87% at -0.6 V and -0.7 V, and it decreases at -0.8 V and -0.9 V. The partial current densities for CO formation (j_{CO}) are calculated to be 1.3 mA cm^{-2} , 2.0 mA cm^{-2} , 3.0 mA cm^{-2} , and 3.7 mA cm^{-2} at -0.6 V, -0.7 V, -0.8 V, and -0.9 V, respectively, which are typically low at such potentials in a batch reactor [4,11,28]. The CO_2RR performance of other samples with various Cu:Sn ratios is shown in Figure S4. A very low amount of Sn addition (Cu:Sn = 36.0) can significantly increase the CO selectivity of the Cu_2O electrode, and the CO selectivity is enhanced with further increase of the Sn content until the Cu:Sn reaches about 12.0 in the Sn- Cu_2O . Further raising the Sn amount leads to the decrease of CO selectivity and the increase of HCOOH selectivity. Hence, the Sn- Cu_2O sample is optimal for the CO_2RR to CO in this study.

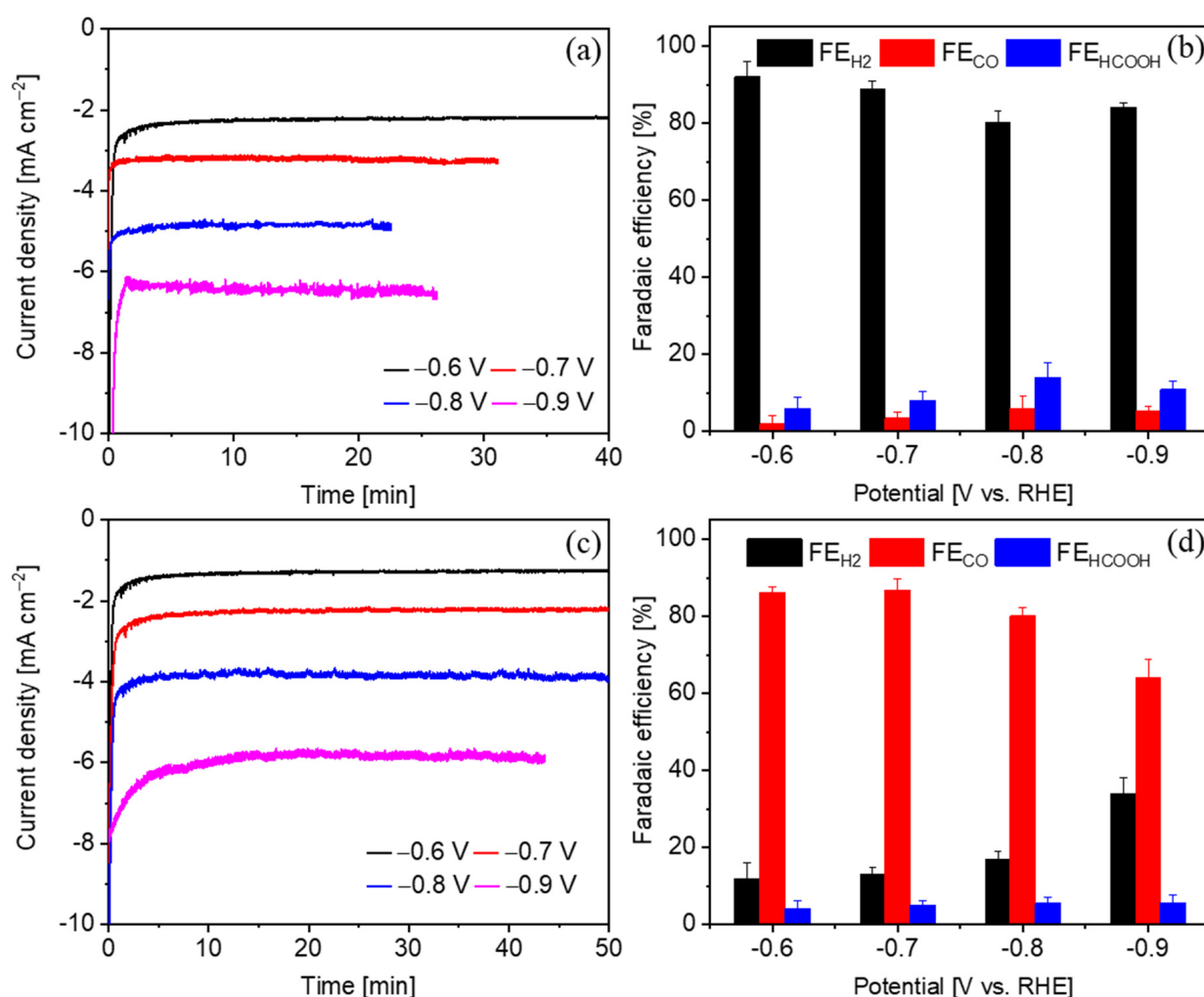


Figure 4. CA measurements and product analyses in a CO_2 -saturated 0.1 M KHCO_3 aqueous solution in a batch cell. (a) i-t curves at various potentials on Cu_2O electrode and (b) the corresponding product analyses, (c) i-t curves at various potentials on Sn- Cu_2O electrode and (d) the corresponding product analyses.

Many studies have explored the role of Sn in the CO_2RR and the electronic properties of the Cu-Sn bimetallic materials by density functional theory (DFT) calculation. Qiao et al. reported that Sn can donate electrons to Cu, causing the charge redistribution on the surface [29]. The Sn sites that are positively charged can hinder nucleophilic attack on the carbon atoms, increasing the thermodynamic barrier to $^*\text{COOH}$ adsorption. Hence, a high Sn content can promote the formation of HCOOH . However, a large amount of works demonstrate that a relatively low Sn percentage prefers to produce CO [11–14]. Wang et al. [30] reported that the increased electron density on the Cu sites, assisted by

the adjacent SnO_x sites, can weaken the binding of $^*\text{CO}$, and thus can favor the CO_2RR to CO. Takanabe et al. [11] suggested that H adsorption on the Sn modified Cu facets is much lower compared to that on the pure Cu structure, explaining the high selectivity for the CO_2RR on the Sn modified Cu materials. These results suggest that Sn modification can increase the CO_2RR selectivity of Cu, and a high amount of Sn in the Cu-Sn materials favors the production of HCOOH , while a relatively low Sn content prefers the CO formation, in good agreement with the results presented herein.

2.3. Study of the CO_2RR on the Sn- Cu_2O Electrode in a Semi-Flow Cell

Further investigations have been carried out at the Sn- Cu_2O electrode in a semi-flow cell fed with gas phase CO_2 . In 0.1 M KHCO_3 , the Sn- Cu_2O electrode performs better in a flow cell (Figure 5a) than in a batch cell (Figure 4c,d) in terms of both the reaction rate and the selectivity toward the CO_2RR to CO. The FE_{CO} is about 45% at -0.35 V and it becomes dominant at lower potentials. It reaches 79% at -0.45 V and surpasses 80% from -0.5 V to -1.0 V. The FE_{CO} is peaked at about 90% from -0.6 V to -0.8 V. The j_{CO} is 1.8 mA cm^{-2} at -0.6 V and it rapidly increases to 9.9 mA cm^{-2} at -0.9 V. The total current densities are 2.0 mA cm^{-2} , 3.5 mA cm^{-2} , 5.5 mA cm^{-2} , and 12.2 mA cm^{-2} at -0.6 V, -0.7 V, -0.8 V, and -0.9 V, respectively, which are much higher than those obtained in the batch cell and are superior to the reported results at similar test conditions [12,14]. In addition, no significant CO_2 diffusion limitation has been observed in the flow cell since the CO formation rate increases rapidly with raising the electrochemical driving force even at very negative potentials. More concentrated KHCO_3 electrolytes have further been utilized for the CO_2RR on the Sn- Cu_2O electrodes. The HCO_3^- ions can not only enhance the ionic conductivity, but also increase the local CO_2 availability near the electrode surface [31,32]. As shown in Figure 5 and Table S1, the partial current density for CO formation increases with raising the KHCO_3 concentration at each potential, particularly at more negative ones (≤ -0.8 V). The CO formation rate raises with negatively shifting the potential in each electrolyte and it reaches a highest current density of 47.2 mA cm^{-2} at -1.0 V in 2.0 M electrolyte. No CO_2 diffusion limitation is noticed, indicating that the CO_2 availability is indeed enhanced in the flow cell with respect to that in the batch one. The CO selectivity of the electrode is also affected by the KHCO_3 concentration. As displayed in Figure 5 and Table S2, the FE_{CO} shows a higher value in the 0.1 M KHCO_3 electrolyte compared to those obtained in other concentrations at most of the low potentials (≤ -0.5 V). At higher potentials (> -0.5 V), the electrolyte with 1.0 M KHCO_3 leads to the highest CO selectivity with FE_{CO} values of 72%, 79%, and 81% at -0.35 V, -0.4 V, and -0.45 V, respectively. Such potentials are more positive than the reported ones where similar CO selectivity was obtained in the literatures [11–14,33–36]. It is further worth noticing that the CO_2RR performance of the Sn- Cu_2O electrode represents one of the best outcomes among those obtained with CuSn-based electrocatalysts recently proposed in the literatures for the CO_2 conversion to CO (see Table S3).

The stability of the Sn- Cu_2O electrode has been evaluated in various CO_2 -saturated KHCO_3 electrolytes, as shown in Figure 6. At relatively low current density ($< 10 \text{ mA cm}^{-2}$), the electrode displays very good stability in terms of both reactivity and CO selectivity (Figure 6a,b). As the KHCO_3 concentration in the electrolyte increases, the current density increases and its retention during the long-term electrolysis remains excellent, while the CO selectivity slightly decreases as a function of time (Figure 6c,d). Nevertheless, at the end of 10-h tests, the CO selectivity retains good values of about 90% in the 0.1 M and 0.5 M KHCO_3 electrolytes and 80% and 70% in the 1.0 M and 2.0 M electrolytes, respectively.

Concisely, the Sn- Cu_2O electrode shows good activity and selectivity for the CO_2RR to CO in a wide potential range. In particular, it achieves considerable CO selectivity at relatively low overpotentials from 240 mV to 340 mV. From the long-term tests, the Sn- Cu_2O demonstrates encouraging stability during the CO_2RR in various concentrated KHCO_3 electrolytes. Hence, it is possible to anticipate that the facilely synthesized material could be a promising candidate for the CO_2 valorization at large scales.

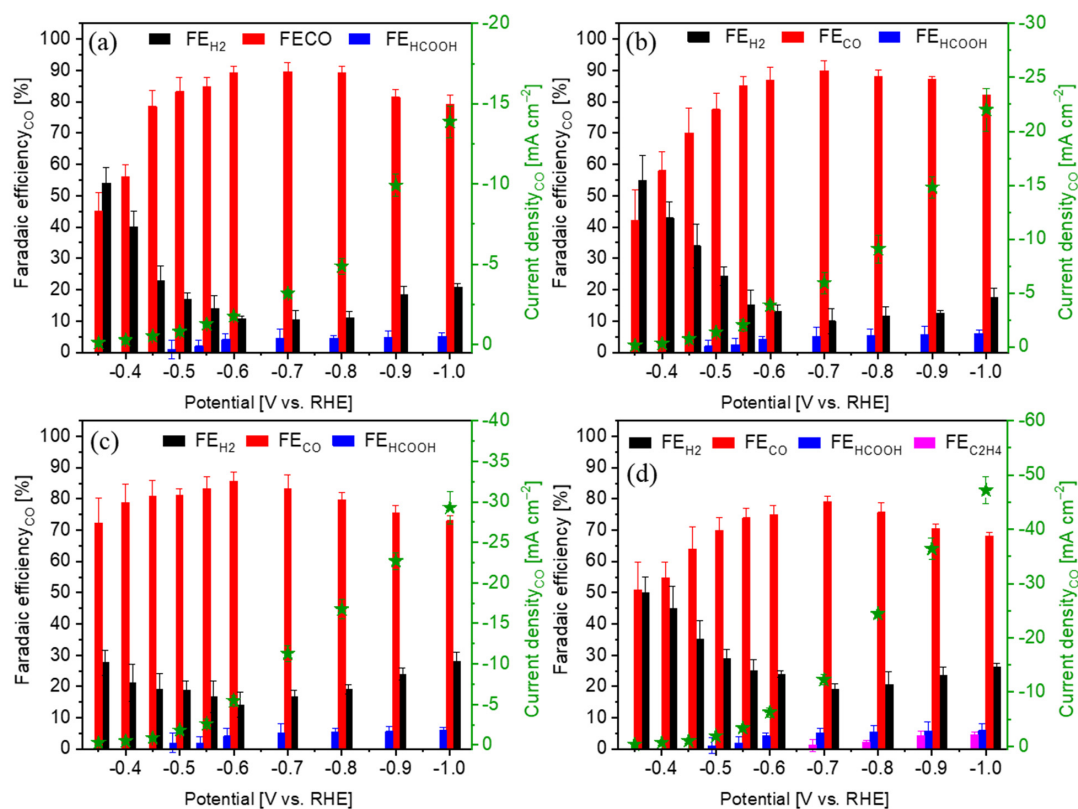


Figure 5. Product analyses and CO current density at a Sn-Cu₂O electrode in a semi-flow cell with various CO₂-saturated KHCO₃ electrolytes: (a) 0.1 M, (b) 0.5 M, (c) 1.0 M, and (d) 2.0 M.

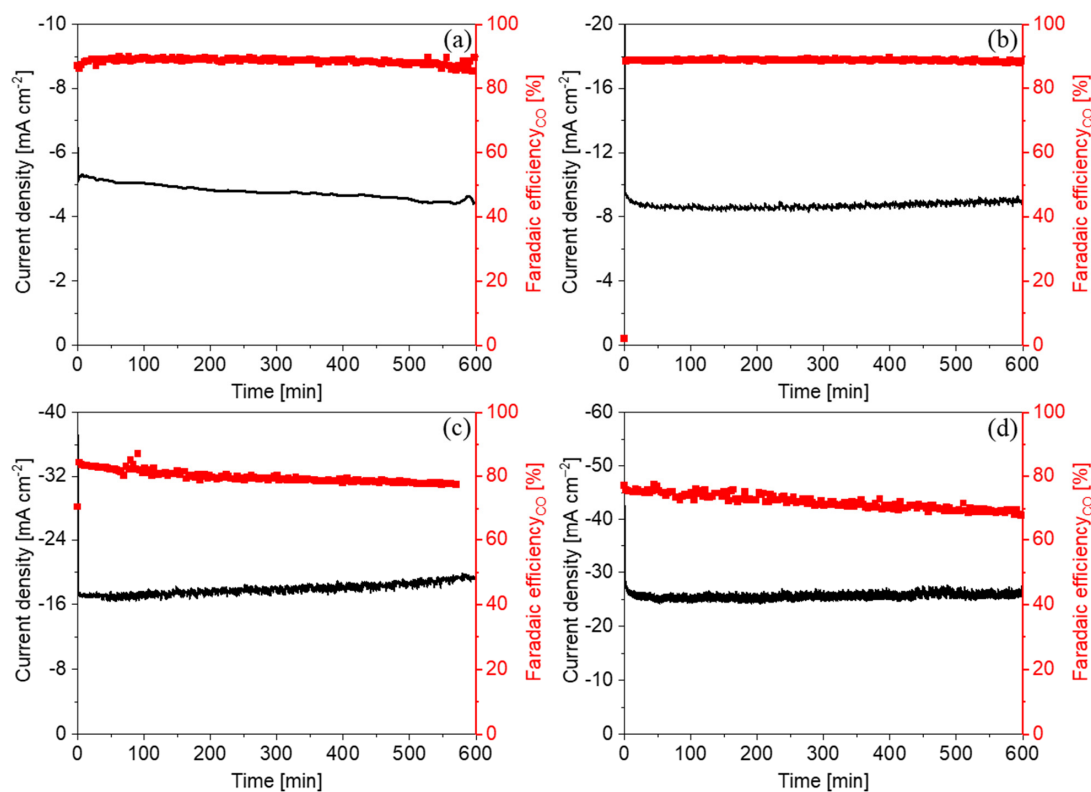


Figure 6. Geometric current density and CO selectivity at a Sn-Cu₂O electrode during 10-h tests in various CO₂-saturated KHCO₃ electrolytes: (a) 0.1 M, (b) 0.5 M, (c) 1.0 M and (d) 2.0 M.

3. Materials and Methods

3.1. Materials

Nafion[®] 117 solution (5 wt.%), isopropanol, copper(II) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$, 99.9%), tin(IV) acetate ($\text{Sn}(\text{CH}_3\text{COO})_4$, 99.9%), sodium hydroxide (NaOH, 98%), potassium bicarbonate (KHCO_3 , 99.7%), ethylene glycol (EG, 99.8%), and acetic acid (CH_3COOH , 99.8%, anhydrous) were purchased from Sigma-Aldrich (Merck, Germany). All the chemicals were used as received.

3.2. Synthesis

For the preparation of the Sn modified Cu_2O catalyst containing a nominal Cu:Sn atomic ratio of about 12.0 (denoted as Sn- Cu_2O), 150 mg of $\text{Sn}(\text{CH}_3\text{COO})_4$ was dissolved in 2 mL of CH_3COOH . Meanwhile, 920 mg of $\text{Cu}(\text{CH}_3\text{COO})_2$ was dissolved in 40 mL EG and 5 mL of H_2O . Then, the $\text{Sn}(\text{CH}_3\text{COO})_4$ solution was added into $\text{Cu}(\text{CH}_3\text{COO})_2$ solution drop by drop. After vigorous agitation for 5 min, the mixture was transferred into a microwave oven (Milestone STARTSynth, Milestone Inc., Italy). The irradiation lasted for 2 min at 900 W with a T_{Max} of 220 °C. After cooling down to room temperature, the precipitate was separated by centrifuge, washed twice with H_2O and once with ethanol, and then dried at 60 °C overnight under vacuum. Other samples with different atomic ratios of Cu to Sn, namely CuSn0.5, CuSn1.0, and CuSn2.0 with a Cu:Sn ratio of 36.0, 18.0, and 9.0, respectively, were prepared for comparison by changing the amounts of precursors. The Cu_2O sample was also prepared with the same procedure except that the precursor solution was 920 mg of $\text{Cu}(\text{CH}_3\text{COO})_2$ dissolved in 40 mL of EG, 2 mL of CH_3COOH , and 5 mL of H_2O .

3.3. Physical and Chemical Characterizations

ICP-OES, with an iCAP 7600 DUO (Thermo Fisher Scientific, Waltham, MA, USA), was used to analyze the Cu and Sn elements.

The crystalline phases of the powder samples were analyzed by XRD measurements, which were performed on a PANalytical X'Pert Pro instrument (Cu-K α radiation, 40 kV and 30 mA) with a PANalytical X'Celerator detector. The XRD patterns were analyzed by means of Rietveld refinement with the software TOPAS-Academic [37]. The structural model used for Cu_2O is Crystallography Open Database (COD) ID: 9007497, while for the CuSn the reference model is COD ID: 1524713. The diffractometer instrumental function was determined by analyzing the XRD pattern of the LaB_6 standard provided by the National Institute of Standards and Technology. Peak broadening due to coherent scattering domain size was modelled by using Gaussian and Lorentzian contributions implemented in the CS_G and CS_L functions in TOPAS-Academic.

To analyze the morphology of the materials, FESEM (ZEISS Auriga, Eggenstein-Leopoldshafen, Germany) was performed on the powder samples. EDX spectroscopy was carried out with an Oxford Instruments X-max detector based on Silicon drift technology with a 50 mm² active area.

XPS was performed on the powder samples to examine the surface compositions. A PHI 5000 VersaProbe (Physical Electronics, Chanhassen, MN, United States) system with an X-ray source of a monochromatic Al K α radiation (1486.6 eV) was employed for the analysis and the spectra were analyzed with MultiPak Version 9.0 dedicated software. C1s peak at 284.5 eV was used as reference for all core-level peak energies and the background contribution was subtracted by means of a Shirley function in the high resolution (HR) spectra.

3.4. Electrode Preparation

For the fabrication of the electrode, 15 mg of a synthesized catalyst, 1.5 mg of acetylene carbon black (CB, Shawinigan Black AB50), 67.5 μL of Nafion[®] 117 solution, and 400 μL of isopropanol were mixed and sonicated for 40 min until a uniform slurry was obtained. The slurry was then casted onto a carbon paper with a microporous layer (GDL; SIGRACET

28BC, SGL Technologies, Germany). The obtained electrode was dried at room temperature overnight to evaporate the solvents. The catalyst loading of each electrode is approximately 3.0 mg cm^{-2} .

3.5. CO₂ Electrolysis and Product Analysis

The CO₂RR was performed by using chronoamperometric technique on a CHI760D potentiostat (CH Instruments, Inc., 3700 Tenneson Hill Drive Austin, TX, USA). The potential was corrected by compensating the ohmic potential drop, of which 85% by the instrument (iR-compensation) and 15% by manual calculation.

For the comparison of various electrodes, CA experiments were conducted in a customized two-compartment three-electrode batch cell, as shown in Scheme S1a. A proton exchange membrane (NafionTM Membrane N117, Ion Power, München, Germany) was used to separate the anodic and cathodic sides. The reference electrode was a mini Ag/AgCl (1 mm, leak-free LF-1) and the counter was a Pt foil. A catalyst-coated carbon paper (geometric area: 1.35 cm^2) was used as the working electrode. A 0.1 M KHCO₃ aqueous solution was used as the electrolyte for both sides. During the CA tests, a constant CO₂ flow was maintained at 15 mL min^{-1} to saturate the electrolyte and to bring out the gaseous products.

The Sn-Cu₂O electrode was then evaluated in a customized three-compartment three-electrode semi-flow cell, as shown in Scheme S1b. In the flow cell, the cathode separated the cathodic side into two compartments: one was the catholyte and the other was the CO₂ gas feed. Both catholyte and anolyte were 25 mL of KHCO₃ aqueous solution with the same concentration (0.1 M, 0.5 M, 1.0 M, or 2.0 M) and were circulated at 2 mL min^{-1} during the test. A constant CO₂ flow of 5 mL min^{-1} was purged through the anolyte in order to maintain a constant pH. A CO₂ flow of 15 mL min^{-1} was maintained in the gas compartment of the cathodic side in order to supply the CO₂ reactant and bring out the products.

A micro gas chromatograph (μ GC, Fusion[®], INFICON, Bad Ragaz, Switzerland) was used to analyze the gas-phase products in real time. The μ GC was equipped with two modules, one with a 10 m Rt-Molsieve 5A column and the other with an 8 m Rt-Q-Bond column, and both with a micro thermal conductivity detector (micro-TCD). The products in liquid phase were detected through a high-performance liquid chromatograph (Thermo Scientific Ultimate3000 HPLC, Waltham, MA, United States). The detector was a UV-Vis one set at 210 nm and the column is a ReproGel ($300 \times 8 \text{ mm}$). An aqueous solution of 9.0 mM H₂SO₄ (flow rate of 1.0 mL min^{-1}) was used as the mobile phase.

Faradaic efficiency (FE), namely current efficiency, is the key parameter for determining the selectivity of the electrode toward a specific product. The FE for a specific product was calculated by applying Equation (1),

$$FE = \frac{nNF}{Q} \quad (1)$$

where n is the number of electrons required to obtain 1 molecule of this product ($n = 2$ for CO, HCOOH, and H₂ formation); N is the amount of an identified product (number of moles, mol); Q is the total charge passed through the system during the electrolysis (coulombs, C); F is the Faraday constant ($96,485 \text{ C mol}^{-1}$).

Partial current density for CO formation, j_{CO} , was calculated via Equation (2),

$$j_{\text{co}} = j_{\text{total}} * FE_{\text{CO}} \quad (2)$$

where FE_{CO} is the FE for CO formation and j_{total} is the total geometric current density.

The production rate of CO ($\mu\text{mol h}^{-1} \text{ cm}^{-2}$) was calculated through Equation (3),

$$\text{Production rate}_{\text{co}} = \frac{j_{\text{CO}} * t}{2F} * 10^3 \quad (3)$$

where t is a constant of 3600.

4. Conclusions

In this work, powder-like Sn-Cu bimetallic materials have been synthesized and studied for the electrochemical CO₂ conversion. Assisted by microwave, the solvothermal synthesis process was found to be fast, simple, and energetically convenient. All obtained powder samples are mainly composed of Cu₂O crystals that are uniformly modified by Sn, and some of them with high Sn contents also consist of a CuSn alloy. The catalytic performance of the optimal Sn-Cu₂O electrode toward the CO₂RR has been investigated in KHCO₃ electrolyte with various concentrations, showing good selectivity, activity, and stability. Based on the encouraging results, future work will be focused on the improvement of the GDEs in order to further increase the CO₂ conversion rate and the CO selectivity, aiming at facilitating the application of the herein proposed material in the large-scale electrosynthesis of valuable chemicals from CO₂ feedstock.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11080907/s1>. Scheme S1: Electrochemical cells for the CO₂ electrolysis: (a) batch cell and (b) semi-flow cell. Figure S1: XRD patterns of Cu₂O, CuSn0.5, CuSn1.0 and CuSn2.0 samples (a) and a view of (200) peak (b). Figure S2: EDX characterization of the region of sample Sn-Cu₂O depicted in the FESEM image, consisting of an EDX spectrum, Cu K α and Sn L α elemental maps. Figure S3: FESEM images of the samples. (a) Cu₂O, (b) CuSn0.5, (c) CuSn1.0, (d) Sn-Cu₂O and (e) CuSn2.0. Figure S4: CO₂RR in a batch cell in a CO₂-saturated 0.1 M KHCO₃ aqueous solution on various samples. The dark green line is a guide to the eye for CO partial current density. Table S1: Current density for CO formation on the Sn-Cu₂O electrode at various potentials in different electrolytes. Table S2: Faradaic efficiency for CO formation on the Sn-Cu₂O electrode at various potentials in different electrolytes. Table S3: Comparison of different CuSn-based electrocatalysts in liquid-phase CO₂ electrolysis.

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