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Article

Copper-indium bimetallic catalysts for the selective electrochemical reduction of carbon dioxide

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ABSTRACT

Copper-indium bimetallic catalysts with a dendritic structure are fabricated by a two-step electro-deposition method using a hydrogen evolution template for the CO₂ electroreduction reaction (CO₂RR). The dendritic Cu-In-30 catalyst electrodeposited for 30 min shows the highest specific surface area and exposes the most active sites, resulting in improved CO₂RR activity. The dendritic Cu-In-30 catalyst exhibits distinctly higher formate partial current density (42.0 mA cm⁻²) and Faradaic efficiency (87.4%) than those of the In-30 catalyst without the dendritic structure (the formate partial current density and Faradaic efficiency are 4.6 mA cm⁻² and 57.0%, respectively) at -0.85 V vs. reversible hydrogen electrode, ascribed to the increased specific surface area. The Cu-In-30 catalyst can maintain stable performance for 12 h during the CO₂RR. In addition, the intrinsic current density of Cu-In-30 with the dendritic structure (4.8 mA cm⁻²) is much higher than that of In-30 without the dendritic structure (2.1 mA cm⁻²), indicating that the dendritic structure promotes the CO₂RR, possibly due to additional coordination unsaturated atoms.

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1. Introduction

With the excessive consumption of fossil fuels, global warming caused by carbon dioxide (CO₂) is receiving increasing attention [1–7]. The CO₂ electroreduction reaction (CO₂RR), which utilizes renewable energy sources, is a feasible strategy for converting CO₂ into useful fuel and chemicals, such as carbon monoxide, formate, and methane [8–14]. Particularly, formate with a high hydrogen content is usually used as liquid fuel

in fuel cells. Moreover, formate can also be directly used for fabric processing, tanning, textile printing, and silage storage, as well as metal surface treatment agents, rubber additives, and industrial solvents [5,15–18]. Nonetheless, the CO₂RR process is generally accompanied by high energy consumption owing to the sluggish kinetics and low selectivity toward formate production. Therefore, the design of efficient catalysts is crucial for promoting the CO₂RR current density and selectivity toward formate at low overpotentials.

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Currently, precious metals such as gold and palladium can effectively convert CO₂ into CO or formate [19–22]; however, their high cost greatly limits their application in CO₂RR. Indium and its alloys have already been proven to possess high catalytic properties for CO₂RR to afford formate with a low cost [23–29]. However, the current density and selectivity of these catalysts are unsatisfactory at low overpotentials. Furthermore, copper-based catalysts exhibit appropriate selectivity toward formate production, although they usually suffer from poor stability in a short duration. Thus, the current density and stability of indium and copper require further enhancements [30,31]. One promising solution involves combining copper with indium to construct a bimetallic catalyst, which can increase the current density and stability for the selective CO₂RR to form formate at low overpotentials, owing to the synergistic effect between indium and copper.

In this work, we fabricated the copper-indium bimetallic catalysts with a dendritic structure by a two-step electrodeposition method for CO₂RR. The electrochemical deposition using a hydrogen evolution template could effectively form the dendritic structure, which was able to increase the specific surface area and activity of the catalysts due to the superior three-dimensional (3D) open structure [16,32]. Moreover, the unique copper-indium double-layer structure could also improve the stability of CO₂RR. The relationship between the electrodeposition time of indium and the electrochemically active surface areas (ESAs) was investigated. The Cu-In-30 catalyst with the electrodeposition time of 30 min had the most electrochemical active sites; therefore, it could greatly enhance the catalytic activity for CO₂RR. The Cu-In-30 catalyst exhibited a formate partial current density of 42.0 mA cm⁻² and formate Faradaic efficiency of 87.4% at -0.85 V vs. reversible hydrogen electrode (RHE) and maintained a stable performance for 12 h during the CO₂RR test in a 0.1 mol L⁻¹ KHCO₃ solution. In addition, the ESA-corrected current density of Cu-In-30 with the dendritic structure for formate (4.8 mA cm⁻²) was much higher than that of In-30 without the dendritic structure (2.1 mA cm⁻²), indicating that the dendritic structure could increase the intrinsic activity.

2. Experimental

2.1. Materials

Indium sulfate (In₂(SO₄)₃, 99.0%), boric acid (H₃BO₃, 99.5%), potassium sulfate (K₂SO₄, 99.0%), and potassium bicarbonate (KHCO₃) were purchased from Sinopharm Chemical Reagent Co. Copper sulfate (CuSO₄, 99.0%), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), and acetone (CH₃COCH₃) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd.

2.2. Materials preparation

The catalyst was prepared by a two-step electrodeposition method. The copper foam was cut into a square with an area of 1 cm² (1 cm × 1 cm) and placed into the acetone and ethanol mixed solution for 30 min to clean the grease on the surface by

ultrasonic treatment. The copper foam was immersed into the 6 mol L⁻¹ hydrochloric acid solution for 15 min to etch off the oxides on the surface. The cleaned copper foam was used as the working electrode, and platinum wire and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrodes were immersed in a 0.1 mol L⁻¹ copper sulfate and 1 mol L⁻¹ sulfuric acid mixed solution that was constantly stirred to maintain the balance of electrolyte concentration. Dendritic copper was produced by the hydrogen template method that involves applying a current of -2.5 A cm⁻² to the working electrode for 20 s, which can cause the electrodeposited copper to assume an irregular shape. Subsequently, the copper foam with the dendritic copper on its surface served as the working electrode; the counter electrode was platinum wire, and Ag/AgCl served as the reference electrode. The electrodes were placed into the electrolyte containing 3 mmol L⁻¹ indium sulfate, 0.1 mol L⁻¹ potassium sulfate, and 15 mM boric acid. The current on the working electrode was -30 mA cm⁻², applied for 1.5, 7.5, 15, 30, and 60 min, and the obtained electrodes were denoted as Cu-In-1.5, Cu-In-7.5, Cu-In-15, Cu-In-30, and Cu-In-60, respectively. The Cu-In-30 catalyst exhibited the best performance in ensuring that indium completely covers the surface of dendritic copper. For comparison, indium electrodeposited on non-dendritic copper was prepared by electrodeposition in the solution containing 3 mmol L⁻¹ indium sulfate, 0.1 mol L⁻¹ potassium sulfate, and 15 mmol L⁻¹ boric acid with a current of -30 mA cm⁻² for 30 min on the copper foam, which was denoted as In-30. The prepared catalysts were washed with water and ethanol to remove the residual impurities, after which they were dried in a vacuum oven.

2.3. Physicochemical characterizations

X-ray diffraction (XRD Empyrean-100) measurement was used to detect the change in indium crystallinity as the electrodeposition time increased in the range of 10°–90°. The process of indium gradually covering the dendritic copper surface and the distribution of copper and indium on the surface of the catalyst was observed by scanning electron microscopy (SEM, JSM-7800F). After ultrasonic dispersion in ethanol, the catalyst was dropped onto a molybdenum mesh carbon film for observing the microstructure of the catalyst sample using high-resolution transmission electron microscopy (HRTEM, JEM-2100). The catalysts were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) that used the C 1s peak located at 284.6 eV to calibrate the binding energy positions to analyze the valence state of the catalyst. The actual loading of indium was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, 7300DV).

2.4. Electrochemical measurements

An H-cell filled with 40 mL of the 0.1 mol L⁻¹ KHCO₃ solution was used for the CO₂RR measurements, and the compartments were separated by a Nafion 115 membrane. In the two compartments of the H-cell, 95% CO₂-5% N₂ gas was purged at a

flow rate of 20 mL min⁻¹ for 30 min to saturate the electrolyte. The pH of the saturated electrolyte was 6.8. The electrolyte was continuously stirred for a maximum mass transfer rate. The prepared catalyst was used as the working electrode, Ag/AgCl was placed in the vicinity of the working electrode as the reference electrode, and platinum was placed in the compartment of the cell as the counter electrode. All potential calculations are obtained by *iR* compensation and are represented with RHE. Prior to the CO₂RR test, a potential of -0.75 V vs. RHE was applied for 20 min to reduce the indium oxide on the catalyst surface to metallic indium.

The generated gases during the CO₂RR, such as CO, entered into an on-line micro gas chromatograph (GC) (Agilent 490) equipped with a thermal conductivity detector and Molsieve 5A column to analyze the gas product. Electrolysis was carried out for 30 min at each potential. At the end of the constant potential electrolysis, the electrolyte was collected and the liquid-phase product was detected using a Bruker AVANCE III 400 MHz nuclear magnetic resonance spectrometer. The concentration of the liquid product (only formate in this work) was determined from the linear relationship of the area ratio between the known concentration of sodium 3-(trimethylsilyl)-1-propanesulfonate (Sigma-Aldrich) and the product to be measured. Therefore, the corresponding Faradaic efficiency can be calculated according to the following formula:

$$F_f = C \times V \times N \times F \times I^{-1} \times t^{-1},$$

where F_f is the Faradaic efficiency of formate (%), C is the concentration of formate (mol L⁻¹), V is the volume of the electrolyte (40 mL), N is the number of reaction transfer electrons (2), F is the Faradaic constant (96485 C mol⁻¹), I is the current density (mA cm⁻²), and t is the total duration of the reaction at a single potential (1800 s).

After each constant potential electrolysis test, the two compartments were cleaned with water, after which a fresh 0.1 mol L⁻¹ KHCO₃ electrolyte was poured and CO₂ gas was purged for 30 min to saturate the electrolyte.

The ESAs of different samples were determined by cyclic voltammetry (CV) in 5 mmol L⁻¹ K₃Fe(CN)₆ and 0.1 mol L⁻¹ KCl solution, with the prepared catalyst employed as the working electrode and the platinum wire as the counter electrode;

Ag/AgCl was employed as the reference electrode. The ESA was obtained using the Randles-Sevcik equation [33,34]:

$$I_p = (2.36 \times 10^5) n^{3/2} \times A \times D^{1/2} \times C \times \nu^{1/2},$$

where I_p is the peak current, n is the number of reaction transfer electrons (1), D is the reaction-diffusion coefficient (4.34×10^{-6} cm² s⁻¹), A is the electrochemical surface area (cm²), C is the concentration of K₃Fe(CN)₆ (5×10^{-6} mol cm⁻³), and ν is the CV scan rate (5 mV s⁻¹).

3. Results and discussion

Figure 1a shows the XRD patterns of Cu-In-1.5, Cu-In-7.5, Cu-In-15, Cu-In-30, and Cu-In-60. Metallic copper on the surface of the copper foam can be observed at 43.2°, 50.5°, and 74.1° (PDF 04-0836). As the electrodeposition time on the copper foam increases, it can be clearly observed that the diffraction peaks of indium at $2\theta = 33.0^\circ$, 36.3° , and 39.2° (PDF 05-0642) gradually increase, which indicates that the content of indium is increased. Since indium is rapidly oxidized in the air, a diffraction peak of In₂O₃ (PDF 06-0416) is observed in the XRD patterns. Similarly, the XRD patterns of In-30 show diffraction peaks of indium and In₂O₃ (Fig. S1). When the dendritic copper is deposited in the first step, the copper on the surface is oxidized spontaneously to CuO (PDF 44-0706) and is reflected in the XRD patterns. For Cu-In-1.5, indium is formed by electrodeposition, which cannot completely cover the surface of the dendritic copper; therefore, a small amount of Cu₂O (PDF 05-0667) is formed. To determine the valence state of the indium surface, XPS analysis was carried out. Figure 1b shows the XPS spectra of Cu-In-30; the binding energy of the In 3d_{5/2} orbital is 444.7 eV, and the binding energy of the In³⁺ 3d_{5/2} orbital is 445.7 eV, which are consistent with the previously reported values [35,36].

Figure 2 shows the SEM images of bare copper, Cu-In-1.5, Cu-In-7.5, Cu-In-15, Cu-In-30, Cu-In-60, and In-30. The structure of the dendritic copper can be clearly seen in Fig. S2, which is made up of many small copper particles. Figures 2a and 2b indicate that the bare copper foam surface is smooth. Figure 2c shows that Cu-In-1.5 still maintains a good dendritic structure because the electrodeposition time is only 1.5 min at -30 mA

Fig. 1. XRD patterns of the electrode-electrodeposited indium metal on the dendritic copper for various periods (a), and the In 3d XPS spectra of Cu-In-30 (b).

Fig. 2. SEM images of bare copper before electrodeposition (a, b), the electrodes with electrodeposited indium on the dendritic copper structure for 1.5 min (c), 7.5 min (d), 15 min (e), 30 min (f), and 60 min (g), and the electrode with directly electrodeposited indium on the copper foam (h).

cm^{-2} , and the electrodeposited indium does not cover the structure of the dendritic copper completely. However, as the deposition time increases, the content of the metallic indium increases and the electrodeposited indium fills the gap between the dendritic copper particles [16]; thus, the graininess of the catalyst gradually decreases, as shown in Fig. 2c–2g. For Cu-In-30, indium completely covers the surface of the dendritic copper and maintains a dendritic structure well with maximizing the active site [37–39]. In the Cu-In-60 catalyst, since the amount of indium is sufficiently large to slightly destroy the dendritic structure, the active site cannot be fully utilized. By firstly depositing a dendritic copper structure and subsequently electrodepositing the metallic indium, the specific surface area can be maximized. As shown in Fig. 2h, In-30 is obtained only by electrodepositing indium, which does not have a dendritic structure and is formed by stacking many small particles on the flat copper foam surface.

To survey the microstructure of the Cu-In-30 catalyst, the TEM image of the Cu-In-30 catalyst was obtained and is shown in Fig. 3a. The characteristic space of the lattice in indium is affected by HRTEM and destroyed immediately; therefore, the

Fig. 3. HRTEM images of the Cu-In-30 catalyst (a), SEM image of the Cu-In-30 catalyst (b), and corresponding EDX elemental maps (c, d).

local area can only be enlarged to observe the characteristic space of the lattice, which is 0.27 nm and conforms well to the (101) plane of indium. Figures 3b–3d show the energy dispersive X-ray (EDX) elemental maps of the Cu-In-30 catalyst, indicating that indium is evenly distributed on the dendritic copper structure. The EDX elemental maps of Cu-In-1.5, Cu-In-7.5, Cu-In-15, Cu-In-60, and In-30 are shown in Fig. S3, and it can be clearly seen that as the electrodeposition time increases, the indium coverage on the dendritic copper surface gradually increases, while in the In-30 catalyst, indium is simply laid flat on the surface of the copper foam. Compared with the In-30 catalyst, the Cu-In-30 catalyst has a higher specific surface area and also exposes more active sites.

To understand the effect of the electrodeposition time of indium on the CO_2RR performance, the Faradaic efficiencies of all the catalysts at different potentials were determined and are shown in Fig. 4a. All the catalysts start to produce formate at -0.65 V vs. RHE in a CO_2 -saturated $0.1 \text{ mol L}^{-1} \text{ KHCO}_3$ solution. The Faradaic efficiency of Cu-In-1.5 for formate is only 21.5% at -0.65 V vs. RHE, and with the prolongation of the electrodeposition for indium, the Faradaic efficiencies of Cu-In-7.5, Cu-In-15, Cu-In-30, and Cu-In-60 for formate correspond to 31.0%, 40.8%, 46.3%, and 31.4%, respectively. When the potential is negatively shifted from -0.65 to -1.05 V vs. RHE, the Faradaic efficiency for formate of each sample gradually increases and reaches the highest value at -0.85 V vs. RHE. When the potential continues to shift negatively, the Faradaic efficiency for formate of each sample basically remains unchanged. Moreover, the formate Faradaic efficiency of Cu-In-30 is always the highest under each potential condition. Thus, the Cu-In-30 catalyst shows the highest formate Faradaic efficiency that reaches 87.4% at -0.85 V vs. RHE. The formate Faradaic efficiency of Cu-In-60 under each potential condition is slightly lower than that of Cu-In-30, because an overly high amount of indium is electrodeposited so the gaps between the small particles of dendritic copper are filled, and the active sites are less

Fig. 4. Faradaic efficiency (a) and partial current density for formate (b) on the dendritic Cu-In electrodes with various electrodeposition times; Faradaic efficiencies (c) and partial current densities (d) for formate on the Cu-In-30, In-30, copper foil, and indium foil electrodes.

than those in the Cu-In-30 catalyst. From -0.65 to -1.05 V vs. RHE, the Faradaic efficiencies of the by-products, such as H_2 and CO , are shown in Fig. S4, which further explains that the metallic indium on the dendritic copper can selectively convert CO_2 to formate and effectively prevent the production of CO and H_2 .

The partial current densities of H_2 and CO by the other catalysts from -0.65 to -1.05 V vs. RHE are shown in Fig. S5. All the catalysts show low partial current densities of formate (<2 mA cm^{-2}) at -0.65 V vs. RHE. As the potential continues to shift negatively, the conversion of CO_2 to formate gradually becomes the dominant reaction. The partial current density of formate provided by Cu-In-30 reaches 42.0 mA cm^{-2} . Interestingly, at each potential, the partial current density of formate displays a volcano shape, and Cu-In-30 always maintains the highest value. Therefore, the conversion of CO_2 to formate can be effectively promoted by electrodepositing indium on the dendritic copper for 30 min.

To convincingly explain why the dendritic copper structure can effectively convert CO_2 to formate, the Faradaic efficiency of formate produced by the Cu-In-30 catalyst is compared with those toward formate shown by the In-30, copper foil, and indium foil catalysts from -0.65 to -1.05 V vs. RHE in Fig. 4c. The Faradaic efficiencies of formate produced by In-30, copper foil, and indium foil are only 11.0%, 2.2%, and 2.1% at -0.65 V vs. RHE, respectively, which are much lower than that of formate

produced by Cu-In-30. As the potential shifts continuously to more negative values, the formate Faradaic efficiency of Cu-In-30 is always higher than those of In-30, copper foil, and indium foil at each potential. The Faradaic efficiency of 87.4% toward formate is shown by Cu-In-30 at -0.85 V vs. RHE, while the formate Faradaic efficiencies of In-30, copper foil, and indium foil are only 57.0%, 9.6%, and 19.2%, respectively, which highlights the importance of the dendritic structure. The difference between the four catalysts is not only reflected in the Faradaic efficiency of formate, but also in the partial current density of formate, as shown in Fig. 4d. At each potential, the Cu-In-30 electrode provides a higher current density than the In-30, copper foil, and indium foil catalysts between -0.65 V to -1.05 V vs. RHE. The difference between the four catalysts reaches a maximum at -0.85 V vs. RHE. The partial current density of Cu-In-30 is 42.0 mA cm^{-2} , but the partial current densities of the In-30, copper foil, and indium foil are 4.6 mA cm^{-2} , 0.4 mA cm^{-2} , and 0.7 mA cm^{-2} , respectively, which is because the dendritic structure enables the catalyst to have a relatively high specific surface area and additional active sites.

The ESAs were used to explain why the Cu-In-30 electrode exhibits the highest CO_2RR performance (Fig. 5). CV measurement was employed for the ESA tests from 0.55 V to 1.25 V vs. RHE. According to the Randles-Sevcik equation, the ESAs of Cu-In-1.5, Cu-In-7.5, Cu-In-15, Cu-In-30, and In-30 were determined and are listed in Table 1. It can be clearly seen that as the

Fig. 5. Cyclic voltammograms of different catalysts for ESA measurement in 5 mmol L⁻¹ K₃Fe(CN)₆ and 0.1 mol L⁻¹ KCl solution.

Table 1

ESA values for each catalyst measured by CV.

Catalyst	In-30	Cu-In-1.5	Cu-In-7.5	Cu-In-15	Cu-In-30
ESA (cm ²)	2.4	5.7	6.3	6.4	8.7

electrodeposition time for indium on the dendritic copper increases, the ESA of the catalyst also gradually increases, and Cu-In-30 reaches the highest value of 8.7 cm², whereas In-30 only reaches 2.4 cm². In addition, Table S1 shows that the ESA-corrected current density of the Cu-In-30 catalyst with the dendritic structure for formate (4.8 mA cm⁻²) was also much higher than that of In-30 without the dendritic structure (2.1 mA cm⁻²), indicating that the dendritic structure improves the intrinsic activity, possibly due to the additional coordination unsaturated atoms.

To further emphasize the superiority of the Cu-In-30 electrode, we performed a stability test for 12 h (Fig. 6). The stability test was carried out in an H-cell, and the concentration of formate in the electrolytic cell was increased continuously with the test time. Consequently, the pH was gradually decreased, resulting in the continuously increased current density and Faradaic efficiency of H₂. We replaced the electrolyte with a fresh one at hourly intervals to avoid the effect of these negative factors on the test results. During the 12 h test, the Faradaic

Fig. 6. Stability test of the Cu-In-30 catalyst measured at -0.85 V vs. RHE for CO₂RR.

ic efficiency of formate did not significantly decrease and maintained a value around 82.3%, which further indicates the excellent catalytic performance of the Cu-In-30 catalyst.

4. Conclusions

Copper-indium bimetallic catalysts with a dendritic structure were prepared by a two-step electrodeposition method using hydrogen evolution as a template. The Cu-In-30 catalyst with the electrodeposition time of 30 min had the most electrochemical active sites; therefore, it could effectively improve the conversion of CO₂ to formate. The Cu-In-30 catalyst exhibited a formate partial current density of 42.0 mA cm⁻² and formate Faradaic efficiency of 87.4% at -0.85 V vs. RHE, and maintained a stable performance for 12 h during the CO₂RR measurement. The ESA-corrected formate partial current density of Cu-In-30 with the dendritic structure (4.8 mA cm⁻²) was higher than that of In-30 without the dendritic structure (2.1 mA cm⁻²), suggesting that the dendritic structure could increase the intrinsic activity. This work provides a feasible strategy to improve the selectivity and current density of CO₂RR toward formate production.

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Graphical Abstract

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Copper-indium bimetallic catalysts for the selective electrochemical reduction of carbon dioxide

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Due to the three-dimensional dendritic structure, the Cu-In-30 catalyst shows high performance in the CO₂ electroreduction reaction with a formate partial current density of 42.0 mA cm⁻² and Faradaic efficiency of 87.4%.

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Cu-In二元金属催化剂上CO₂电化学还原邵加奇^{a,b}, 王毅^b, 高敦峰^b, 叶克^{a,b,*}, 王琪^{c,#}, 汪国雄^b^a哈尔滨工程大学材料科学与化学工程学院超轻材料与表面技术教育部重点实验室, 黑龙江哈尔滨150001^b中国科学院大连化学物理研究所催化基础国家重点实验室, 洁净能源国家实验室(筹), 辽宁大连116023^c大连交通大学材料科学与工程学院辽宁省轨道交通关键材料重点实验室, 辽宁大连116028

摘要: 石油、天然气和煤等化石能源的转化利用不可避免排放大量的CO₂, 造成一系列生态和环境问题。CO₂电化学还原可以在温和反应条件下将CO₂转化为CO或甲酸等, 近年来受到研究者广泛关注, 但因CO₂具有很稳定的化学结构, CO₂电化学还原要求催化剂具有高的活性, 选择性和稳定性。贵金属如金和钯可以有效地将CO₂转化为相应的燃料如CO和甲酸等, 但

贵金属昂贵的价格限制了其大规模应用, 所以迫使人们寻找非贵金属催化剂来替代它们。铜及其合金被应用于 CO_2 电化学还原生成甲酸, 但在低过电位下, 这些催化剂的电流密度和选择性都不理想。铜基催化剂也能催化 CO_2 电化学还原生成甲酸, 但在短时间内稳定性较差。因此, 需要进一步提高In和Cu催化剂上 CO_2 电化学还原的电流密度和稳定性。一种可能的解决方案是构建Cu-In双金属催化剂, 通过两者的协同作用, 有望提升在低过电位下 CO_2 电化学还原生成甲酸的电流密度和稳定性。

在本工作中, 我们通过氢气模板法制备出具有树枝状结构的Cu, 然后在其表面均匀电沉积金属In。通过两步电沉积法制备出一种具有树枝状结构的Cu-In二元金属催化剂。控制电沉积In的时长分别为1.5, 7.5, 15, 30和60 min。根据SEM及EDX元素分布图谱可知, 随着电沉积In时间的增加, In在Cu表面的覆盖率逐渐增高。我们还研究了In的电沉积时间与其电化学活性表面积(ESA)之间的关系。结果表明, In的电沉积时间与其电化学活性表面积成正比, 且当电沉积时间达到30 min时, 电极具有最大的电化学活性表面积。具有树枝状结构的Cu-In-30催化剂ESA数值为 8.7 cm^2 , 而不具备树枝状结构的In-30催化剂的ESA数值仅为 2.4 cm^2 。在 -0.65 V vs. RHE 至 -1.05 V vs. RHE 电位窗口中, 与其它催化剂相比, Cu-In-30催化剂上 CO_2 电化学还原生成甲酸的法拉第效率最高可达87.4%。树枝状结构的Cu-In-30催化剂由于具有开放的三维结构, 所以能够暴露出更多的活性位, 从而提高了催化剂的电化学性能。在 -0.85 V vs. RHE 电位下, 甲酸分电流密度可达 42.0 mA cm^{-2} , 且具有较高的电化学稳定性(12 h)。而不具有树枝状结构的In-30催化剂生成甲酸的法拉第效率为57.0%, 且甲酸分电流密度为 4.6 mA cm^{-2} 。

关键词: CO_2 电还原; 铜; 铟; 电沉积; 甲酸

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