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Influence of transition metal modification of oxide-derived Cu electrodes in electroreduction of CO₂

Li Liu, Na Tian [#], Long Huang, Yu-Hao Hong, Ai-Yun Xie, Feng-Yang Zhang, Chi Xiao, Zhi-You Zhou, Shi-Gang Sun ^{*}

State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China

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ABSTRACT

The modification of oxide-derived Cu electrode with Ni, Zn, and Au was examined to improve the catalytic activity of CO₂ electroreduction. The experimental results showed that Ni modification increased the Faraday efficiency of the formation of formic acid and *n*-propanol. The Faraday efficiency relating to the formation of the liquid products was as high as 34.3% at −1.5 V versus the saturated calomel electrode reference potential. In contrast, modification with Zn reduced the formic acid formation efficiency but enhanced the alcohol formation efficiency. Finally, modification with Au suppressed the selectivity toward the formation of both formic acid and alcohols.

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1. Introduction

The overconsumption of fossil fuels is a cause of increased CO₂ emission in the atmosphere, which presents numerous environmental problems such as increasing sea levels and environmental degradation. Considering that the consumption of fossil fuels remains necessary at present, it is worth looking into the recycling of the emitted CO₂ by reducing the latter to useful organics or liquid fuels, which can then be used as alternative clean energy resources [1–3]. In recent years, photochemical [4,5] and electrochemical methods [6,7] have been

primarily examined toward the reduction of CO₂. The electrochemical method is the most promising approach owing to its convenient large-scale application capability and simple tuning possible at room temperature. Various electrode materials have extensively been investigated to obtain different reduction products such as carbon monoxide, formic acid, methane, and methanol [6–8]. Metal electrodes are readily available and can provide satisfactory current density in aqueous media.

Specifically, extensive studies have been conducted on Cu electrodes [9,10] because Cu has the unique ability to catalyze the formation of hydrocarbons [7,8,11]. Efforts have been de-

^{*} Corresponding author. Tel/Fax: +86-592-2180181; E-mail: sgsun@xmu.edu.cn

[#] Corresponding author. Tel/Fax: +86-592-2180181; E-mail: tnsd@xmu.edu.cn

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voted to alloying Cu with other different metals [12,13] and modifying the Cu electrode surface [14] to improve the catalytic performance of Cu. Kanan et al. [15] examined the modification of Cu electrode by annealing Cu foil in air and electrochemically reducing the resulting Cu_2O layers. The modified Cu required a lower overpotential than polycrystalline Cu toward catalyzing the reduction of CO_2 owing to the exposed crystal facets on the Cu electrode after annealing and electroreduction. Thus, modifying the surface of electrodes with certain metals is an efficient method to promote the activity toward CO_2 reduction. For instance, Zhao et al. [16] modified Co_3O_4 nanotubes with Cu nanoparticles. Modification with the Cu nanoparticles influenced the adsorption of intermediate products, resulting in high selectivity toward the formation of formic acid. Moreover, the yield and selectivity toward the formation of formic acid are the highest to date among other previously reported results. In another study, Rudnev et al. [17] modified single crystal platinum with copper and reported that the resulting Cu/Pt (110) electrode is currently the most active among all electrodes examined to date. Although some studies have focused on the modification on polycrystalline Cu, the modification of oxide-derived Cu with transition metals has not been investigated to date.

In this work, an oxide-derived Cu electrode was modified with Ni, Zn, or Au for application in CO_2 reduction and detailed insights into the effect of modification of these transition metals on Cu electrode were presented.

2. Experimental

2.1. Materials and instruments

Copper foil (0.025 mm thickness, 99.999% metals basis, Alfa Aesar), Na_2CO_3 ($\geq 99.999\%$, Sigma-Aldrich), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (99.995%, Aladdin), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (analytical reagent grade, Sinopharm Chemical Reagent Co., Ltd.), $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (analytical reagent grade, Sinopharm Chemical Reagent Co., Ltd.), and KCl (guaranteed reagent grade, Xilong Scientific Co., Ltd.) were used in the present study.

The electrochemical experiments were conducted on a PAR-263A potentiostat (EG&G)—a three-electrode system was used for the experiments. Copper foil was used as the working electrode. Platinum plate served as the counter electrode. All data presented in this work are relative to the saturated calomel electrode (SCE).

The electrolysis experiments were performed in a glass H-cell. Naphthol membrane was used to separate the working and counter electrode compartments to prevent oxidation of the reduced CO_2 products. The volume of the cathode chamber was 5.5 mL.

The liquid-phase products were quantified using solvent-suppressed 1D ^1H NMR spectroscopy (500 MHz, Avance III). For the NMR analysis, a 500- μL electrolyte sample was mixed with 100 μL of 14.1 mmol/L dimethyl sulfoxide in D_2O as an external standard. The charge of the liquid products was calculated from the NMR data, and the Faraday efficiency was obtained by dividing the charge by the total reduction charge.

2.2. Preparation of oxide-derived Cu electrode and modification

The oxide-derived Cu electrode was prepared using the method by Kanan et al. [15]. After cleaning the Cu foil (1 cm $\times$ 1 cm) in phosphoric acid, the foil was annealed in air at 300 $^\circ\text{C}$ for 5 h. The resulting copper oxide electrode was then electrochemically reduced at -0.9 V for 1 h in 0.1 mol/L NaHCO_3 obtained by blowing CO_2 in Na_2CO_3 solution. The reduction of the copper oxide layers was complete when the reduction current was nearly zero.

Modification of the prepared oxide-derived Cu electrode was performed by potentiostatic deposition. To achieve efficient deposition, the latter was conducted at potentials more negative than the thermodynamic potentials. Specifically, the deposition potentials of Ni, Zn, and Au on the oxide-derived Cu electrode were set at -0.9 , -1.2 , and -0.5 V in 1 mmol/L NiSO_4 , 1 mmol/L ZnSO_4 , and 1 mmol/L HAuCl_4 , respectively. The deposition charges were 0.29, 0.28, and 0.29 C for Ni, Zn, and Au, respectively. The deposition charge was optimized accordingly. For example, modification of the oxide-derived Cu electrode with Ni was performed at 0.10, 0.29, and 0.50 C Ni, and the Faraday efficiencies of the reduction products on the different electrodes were compared. The 0.29 C Ni-modified electrode showed the highest Faraday efficiency toward the formation of formic acid. Hence, 0.29 C was chosen as the deposition charge for Ni. It should be pointed out that an accurate deposition charge cannot be determined because hydrogen evolution simultaneously occurs on the electrode during modification.

The microstructure of the electrode raw material and unmodified and modified electrodes was characterized by scanning electron microscopy (SEM; Hitachi-S4800).

2.3. Electrolysis experiments

For the electrolysis experiments, 5 mL of 0.1 mol/L NaHCO_3 was introduced in the cathode chamber of the H-cell and CO_2 was continuously blown throughout the experiment to ensure the saturation of CO_2 in solution. The reduction of CO_2 was performed under constant potential at -1.2 , -1.3 , -1.4 , -1.5 , and -1.6 V. Electrolysis lasted for 2 h to enrich the reduction products. To normalize the current density, the double-layer capacitances were measured to determine the active surface areas of the electrodes.

3. Results and discussion

3.1. Characterization of the electrodes

Fig. 1(a), (b) shows the SEM images of the annealed Cu and annealed Cu after reduction (oxide-derived Cu), respectively. The annealed copper foil had a rough surface; however, the surface of the oxide-derived Cu was rougher. This could be attributed to the formation of smaller crystal domains upon reduction. The oxide-derived Cu feature more exposed (100) and (110) sites that can bind strongly with the intermediate product COOH_{ads} and realize a low overpotential [18]. In a study by Kanan et al. [19], grain boundaries were considered as

Fig. 1. SEM images of annealed Cu (a), annealed Cu after reduction (oxide-derived Cu) (b), and oxide-derived Cu modified by Ni (d), Zn (e), and Au (f). (c) Variations in the reduction current of the annealed Cu as a function of time at -0.9 V in 0.1 mol/L NaHCO_3 purged with N_2 .

the reason for high catalytic CO_2 reduction activity. Fig. 1(c) shows the changes in the reduction current upon annealed Cu (copper oxide) layers as a function of time. The reduction current decreased to nearly zero after 1 h, indicating that the reduction of the copper oxide layers was complete. Comparison of the SEM images in Fig. 1(d)–(f) and Fig. 1(b) revealed that modification with Ni, Zn, or Au minimally changed the morphology of the oxide-derived Cu; the morphology of the modified oxide-derived Cu was rough and not well defined.

3.2. Electrochemical experiments

As linear sweep voltammetry (LSV) experiments can be easily performed and allow complete measurement of the reduction current during CO_2 reduction in a wide potential region,

Fig. 2. Linear sweep voltammetry (LSV) curves of CO_2 reduction on different electrodes in CO_2 -saturated 0.1 mol/L NaHCO_3 solution. For comparison, the LSV curve of CO_2 reduction performed on oxide-derived Cu in N_2 -saturated 0.1 mol/L NaHCO_3 solution is also given. Sweep rate 10 mV/s.

LSV of CO_2 reduction on the different electrodes was performed, and the results are shown in Fig. 2. CO_2 reduction occurred at potentials lower than -0.9 V by comparing the curves recorded in CO_2 -saturated 0.1 mol/L NaHCO_3 solution and in N_2 -saturated solution. The electrodes modified with Zn and Au showed higher current densities than the oxide-derived Cu electrode, whereas the electrode modified with Ni showed a lower current density than the Cu electrode. It should be noted that the currents obtained from both hydrogen evolution and CO_2 reduction contribute to the total voltammetric current. The catalytic performance toward CO_2 reduction on the different electrodes can be quantitatively evaluated by determining the Faraday efficiency of the formation of the different products detected by NMR and gas chromatography.

The liquid-phase products of CO_2 reduction at constant potential were analyzed by NMR spectroscopy. Fig. 3 shows the Faraday efficiency of the formation of formic acid in the potential range of -1.2 to -1.6 V, and Table 1 lists the Faraday effi-

Fig. 3. Faraday efficiency (FE) of the formation of formic acid upon CO_2 reduction on the different electrodes.

Table 1FE (%) of the formation of ethanol and *n*-propanol upon CO₂ reduction on the different electrodes.

<i>E</i> (V vs. SCE)	Oxide-derived Cu		Modified by Ni		Modified by Zn		Modified by Au	
	Ethanol	<i>n</i> -Propanol	Ethanol	<i>n</i> -Propanol	Ethanol	<i>n</i> -Propanol	Ethanol	<i>n</i> -Propanol
–1.2	—	—	—	—	—	—	—	—
–1.3	—	—	—	—	—	—	—	—
–1.4	1.0	0.5	0.5	0.9	1.0	0.5	0.3	—
–1.5	0.8	1.0	1.6	2.7	1.2	1.6	0.2	—
–1.6	0.9	1.0	1.4	2.3	1.6	2.0	0.8	1.0

ciency of the formation of ethanol and *n*-propanol. On oxide-derived Cu, at potentials of –1.2 and –1.3 V, formic acid was the only liquid-phase product detected, and the corresponding Faraday efficiencies were 5.6% and 15.0%. At more negative potentials (–1.4 to –1.6 V), the Faraday efficiency of the formation of formic acid generally increased with increasing potentials, and small amounts of ethanol and *n*-propanol were detected.

Ni modification of the oxide-derived Cu electrode increased the Faraday efficiency of the formation of formic acid and *n*-propanol. The alcohol products were detected at applied reduction potentials ranging from –1.4 to –1.6 V. At –1.5 V, the Faraday efficiency of the formation of formic acid was 30.0%, and those of ethanol and *n*-propanol were 1.6% and 2.7%, respectively. These values were higher than the corresponding values obtained on the unmodified oxide-derived Cu electrode.

To understand the rationales for the high Faraday efficiency obtained for the Ni-modified electrode, the gas-phase products of CO₂ reduction on the oxide-derived Cu and Ni-modified oxide-derived Cu electrodes were analyzed by online gas chromatography. As shown in Table 2, Ni modification significantly increased the yield of CO. Ni has a smaller atomic radius ($r = 0.1246$ nm) than Cu ($r = 0.1278$ nm). Hence, modification of Cu with Ni is expected to instigate lattice contraction when compared with pure Cu. Such a geometric strain will result in a downshift of the *d*-band center, which decreases the binding energy of CO [13]. As a result, the Ni-modified Cu will yield more low-degree reduced products (CO and HCOOH) than pure Cu. Previously, Todoroki and coworkers [14] have also reported that monolayer and sub-monolayer Ni on the Cu(111) surface increase the yield of CO. As for the increase of multi-carbon alcohols, the addition of Ni may promote coupling of C–C bonds.

Zn modification of the oxide-derived Cu electrode decreased the Faraday efficiency of the formation of formic acid in the potential range studied. In the potential range of –1.4 to –1.6 V, small amounts of alcohols, including ethanol and *n*-propanol, were detected, and the Faraday efficiencies of the formation of the alcohols were slightly higher than those obtained on the unmodified oxide-derived Cu electrode. These results indicate that the introduction of Zn facilitates the hydrogenation of intermediate products slightly.

Also, Au modification of the oxide-derived Cu electrode decreased the Faraday efficiency of the formation of both formic acid and alcohols in the potential range studied. At –1.5 V, the Faraday efficiencies for the formation of formic acid and ethanol were only 20.5% and 0.2%, respectively. As previously reported [7], the main reduction product on the Au-modified

Table 2

Faraday efficiency (%) of the formation of gas products on the oxide-derived Cu and Ni-modified oxide-derived Cu electrodes.

<i>E</i> (V vs. SCE)	Oxide-derived Cu			Modified by Ni		
	H ₂	CO	C ₂ H ₄	H ₂	CO	C ₂ H ₄
–1.3	27.5	39.7	5.7	32.5	31.6	4.6
–1.4	36.7	17.4	8.2	37.6	44.6	1.0
–1.5	49.9	6.6	14.2	57.0	8.4	2.9

electrode was CO owing to its weak bond with CO. Once CO₂ is reduced to CO, CO easily desorbs from the surface; therefore, further reduction is difficult [20].

4. Conclusions

The effect of modification of Ni, Zn, and Au of oxide-derived Cu electrode on CO₂ reduction was investigated. Formic acid was obtained as the main liquid product on all electrodes. The Ni-modified electrode showed the highest Faraday efficiency toward the formation of formic acid and *n*-propanol among all the electrodes studied.

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Graphical Abstract

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Influence of transition metal modification of oxide-derived Cu electrodes in electroreduction of CO₂Li Liu, Na Tian*, Long Huang, Yu-Hao Hong, Ai-Yun Xie, Feng-Yang Zhang, Chi Xiao, Zhi-You Zhou, Shi-Gang Sun*
Xiamen University

Oxide-derived Cu electrode was modified with Ni, Zn, or Au, and the Ni-modified electrode showed the highest Faraday efficiency toward formation of formic acid: at -1.5 V (SCE), the Faraday Efficiency of liquid products is 34.3%; besides, the Zn-modified electrode slightly facilitated the formation of alcohols.

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厦门大学化学化工学院, 福建厦门361005

摘要: CO₂还原是一种解决温室效应以及能源短缺问题的有效方式。目前对于水溶液体系中的CO₂还原, 主要有光催化、电催化以及光电催化等方法, 其中还原CO₂法可在室温下进行, 并较易实现大规模应用。由于金属电极在CO₂电催化还原过程中表现较高电流密度和催化性能, 使得目前研究的热点集中于金属电极的修饰改性。金属Cu与H₂, CO结合能力适中, 并且对生成碳氢化合物具有较好的催化性能, 因此其在催化CO₂还原中具有较大潜力。以往对于Cu的研究主要集中在表面修饰、调控表面结构以及制备合金等方向, 其中对金属进行氧化后再还原的处理也是提高其催化活性的一种有效手段。氧化后还原得到的铜具有较大的粗糙度, 且暴露的活性位点更多, 对CO₂还原具有较好的催化活性。我们对铜箔在空气氛围下、300 °C焙烧5 h, 然后恒电位还原, 再进行过渡金属Ni、Zn、Au的修饰, 研究所得样品电催化还原CO₂性能。电极的表面形貌用扫描电镜表征, CO₂还原的液相和气相产物分别用核磁和在线气相色谱进行检测。

修饰后电极的形貌没有发生太大变化, 仍具有十分粗糙的表面结构。通过线性扫描伏安曲线可以看出, 修饰Zn、Au后电流密度较未修饰前有明显增加, 但是由于CO₂还原过程中不可避免地伴随析氢副反应, 因此, 我们通过计算产物的法拉第效率来表征修饰后的电极对产物选择性的改变: 未修饰时, 在-1.2至-1.6 V均可检测到甲酸的生成, 电位负于-1.4 V时可以检测到乙醇和正丙醇。Ni的修饰明显提高了甲酸的法拉第效率, 也促进了正丙醇的生成。-1.3 V时甲酸的法拉第效率为26.0%, -1.5 V时液相产物的法拉第效率为34.3%。在线气相色谱结果发现, Ni的修饰也明显提高了CO的法拉第效率, 在-1.4 V下, CO的法拉第效率为44.6%。这可能是由于Ni ($r = 0.1246$ nm)的原子半径比Cu ($r = 0.1278$ nm)更小, 因此Ni的修饰会使Cu发生晶格收缩、导致 d 带中心下移而降低了CO的结合能, 从而更易生成CO和HCOOH; 而修饰Ni后对CO₂还原产物正丙醇的提高可能是由于Ni的引入促进了C-C键的形成。修饰Zn后, 甲酸的产率明显下降, 在-1.6 V下甲酸的法拉第效率

只有14.8%,但是乙醇与正丙醇的法拉第效率分别为1.6%与2.0%,相较于未修饰的电极略有提高.修饰Au后,液相产物甲酸及醇类的法拉第效率明显下降,在-1.5 V下,甲酸的法拉第效率只有7.9%,且只检测到少量的乙醇,未检测到正丙醇的生成,这可能与Au修饰后的电极对CO₂还原中间体CO的吸附较弱有关,生成的CO中间体更易从表面脱附,而难以被进一步还原.

关键词: 二氧化碳还原; 氧化后还原铜箔; 恒电位沉积; 法拉第效率; 过渡金属修饰

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*通讯联系人. 电话/传真: (0592)2180181; 电子信箱: sgsun@xmu.edu.cn

#通讯联系人. 电话/传真: (0592)2180181; 电子信箱: tnsd@xmu.edu.cn

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