

Article

Highly Efficient Electrocatalytic Carboxylation of 1-Phenylethyl Chloride at Cu Foam Cathode

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Abstract: A simple and efficient electrocatalytic carboxylation of benzyl chloride with CO₂ is described. The reaction operates under 1 atm CO₂ and room temperature in a single chamber electrolysis cell with Cu foam cathode and Mg sacrificial anode. No additional catalyst is needed, and noble metal is not necessary. The effects of cathode material, solvent current density, charge amount, and temperature were studied using 1-phenylethyl chloride as a model compound. Under optimal conditions, 99% yield of 2-phenylpropionic acid could be obtained. Moreover, reasonable yields were also achieved with other benzyl chlorides.

Keywords: electrocatalytic; carboxylation; carbon dioxide; benzyl chlorides; Cu foam

1. Introduction

CO₂ reutilization is considered to be a plausible strategy to recycle the waste CO₂ emissions from energy-intensive industrial activities [1,2]. Therefore, a number of strategies for CO₂ fixation are being developed, despite its thermodynamic stability and kinetic inertness [3–7]. CO₂ can be used as a simple renewable feedstock for various high-value-added chemicals such as methanol, formic acid, methane, urea, organic carbonates, and carboxylic acid derivatives [3]. Among them, carboxylic acids have widespread applications, which are widely used in the synthesis of bioactive compounds and value-added chemicals [8].

Conventionally, organometallic nucleophiles such as Grignard reagents were used to synthesize carboxylic acids from CO₂. However, such reaction processes utilize toxic or hazardous reducing agents, as well as generate a large amount of waste reagents [6,7]. Electrocatalytic carboxylation may use clean electricity for the synthesis of carboxylic acids, providing a worthy alternative [9–22]. The electroreduction of organic halides on different cathodes (Zn, Hg, Cu, Ag, Au, Pt, Sn, Pb, and Bi) have been studied by Bellomunno and coworkers [23], who showed that the group 11 metals have good catalytic properties towards this reduction process. Many researchers also demonstrated that a silver electrode has extraordinary electrocatalytic effect for carboxylation of halogenated compounds [14–20], which was also confirmed by our previous work [14,15]. In the subsequent research, it was found that silver nanoparticles (Ag NPs) exhibit better electrocatalytic activity than silver flakes [16]. On the other hand, Cu, being low cost compared to noble metals, is one of the most effective electrodes for CO₂ reduction

reaction [24,25]. The potential use of Cu electrode for the electrocarboxylation of organic chlorides has not been demonstrated before.

In this work, we report the electrocatalytic carboxylation of 1-phenylethyl chloride (1a) with Cu foam electrode, avoiding the use of noble metals and catalysts (Figure 1). We showed that CO₂ can be converted into carboxylic acids on the Cu foam electrode under mild conditions. In addition, Ag–Cu dendrite electrode was used for the first time in the electrocarboxylation of 1-phenylethyl chloride to study the effect of cathode material.



Figure 1. Electrocatalytic carboxylation of 1-phenylethyl chloride at Cu foam.

2. Results and Discussion

2.1. Characterization of Electrode Materials

The Cu foam and bimetallic Ag–Cu electrode were characterized by many methods. Figure 2b displays the XRD patterns of Cu foam, the (111), (200) and (220) crystal faces were observed. It is notable that no trace of any other substance such as copper oxide or cuprous oxide was contained in this material. The FE–SEM patterns (Figure 2a) of the Cu foam revealed that this electrode has a porous network structure, indicating large active area. The SEM pattern of bimetallic material Ag–Cu obtained at 10 mM AgNO₃ for 10 min was shown in Figure 2c; the dendrites uniformly formed and almost covered the whole electrode surface, which had been confirmed by energy dispersive X-Ray fluorescence spectrometer (EDX, Figure 2d).

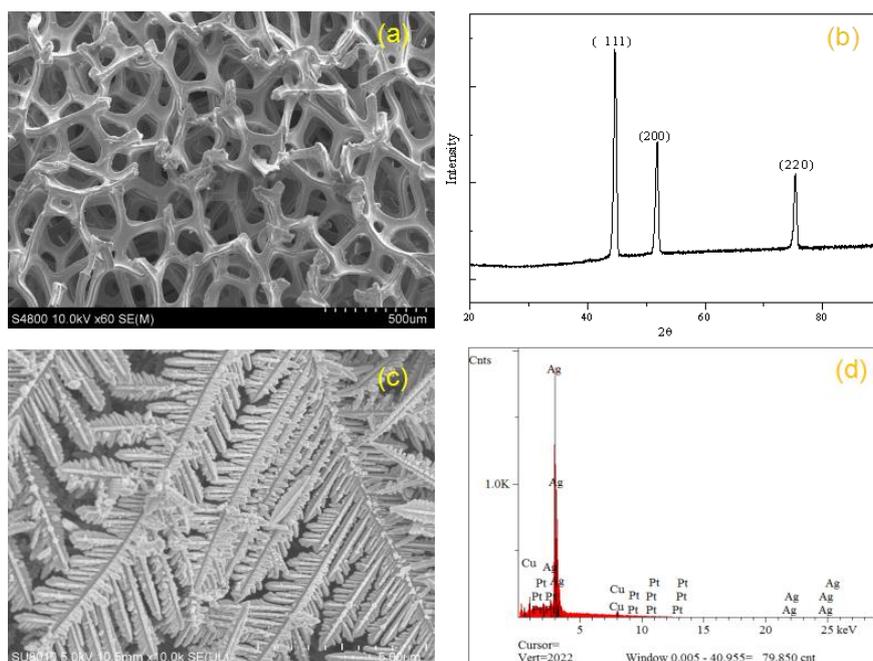


Figure 2. Characterization of Cu foam and Ag–Cu: SEM of Cu foam (a) and Ag–Cu (c); XRD of Cu foam (b); EDX of Ag–Cu (d).

2.2. Electrocarboxylation of 1-Phenylethyl Chloride

The typical electrocatalytic carboxylation was conducted in 0.05 M 1-phenylethyl chloride (1a) in 10 mL CO₂-saturated tetraethylammonium iodide–acetonitrile (TEAI–MeCN) solution, with Cu foam cathode and sacrificial magnesium (Mg) anode (Figure 1). The effects showed that 2-phenylpropionic acid (2a) was the main product. The effects of various parameters such as cathode material, solvent, current density (J), the charge amount (Q), and temperature (T) were analyzed and investigated.

To study the effect of the electrode material, the reaction was firstly carried out at Cu foam electrode. 73% yield of 2a could be obtained (Table 1, entry 1). Since it is reported that Ag-based nanocatalysts [26–31] were efficient in the one-electron reductive cleavage of C–X bonds [31], the Ag–Cu dendrite electrode was synthesized and applied to the reaction. The yield of 2a obtained with Ag–Cu dendrite electrode was higher than that with Ag flake electrode (Table 1, entries 2, 3), which is consistent with our previous study [16]. However, it is lower than that with Cu foam electrode (Table 1, entries 1, 2), and even lower than that with Cu flake (Table 1, entry 4). In order to explore the reasons for this phenomenon, cyclic voltammetry (CV) was used to study the reaction.

The cyclic voltammograms were recorded in 0.1 M tetraethyl ammonium tetrafluoroborate–acetonitrile TEABF₄–MeCN solution at a sweep rate of 0.1 V s^{−1} (Figure 3). Firstly, the background was scanned on the Ag electrode, and oxidation–reduction peaks have not been found (curve a). Then, 1-phenylethyl chloride (1a, 4 mM) was added into the electrolyte solution, an irreversible reduction peak appeared which corresponds to 2e[−] reduction of 1a [17]. Compared to the reduction of 1a on Ag disk electrode (curve b), a more positive onset potential was observed on Cu disk (curve c), which indicates that the reduction occurs more easily at Cu electrode. The results might be able to explain the higher yield obtained with Cu electrode than that with Ag. As for the lower yield on the Ag–Cu electrode, it may be considered from the following. The surface of Ag–Cu electrode was covered by Ag dendrites, and the reaction at Ag–Cu electrode may be equivalent to the reaction at Ag electrode. If so, the yield on the Ag–Cu electrode would be lower. However, the specific reasons for the above phenomenon are still being studied.

Table 1. Electrocarboxylation of 1-phenylethyl chlorides under different conditions. ^a

Entry	Cathode	<i>J</i> (mA/cm ²)	<i>Q</i> (F/mol)	<i>T</i> (°C)	Yield ^b (%)
1	Cu foam	5	2.0	18	73
2	Ag–Cu	5	2.0	18	64
3	Ag flake	5	2.0	18	57
4	Cu flake	5	2.0	18	69
5 ^c	Cu foam	5	2.0	18	6
6	Cu foam	7	2.0	18	77
7	Cu foam	8	2.0	18	84
8	Cu foam	9	2.0	18	87
9	Cu foam	11	2.0	18	78
10	Cu foam	13	2.0	18	75
11	Cu foam	9	1.0	18	45
12	Cu foam	9	1.5	18	68
13	Cu foam	9	2.5	18	92
14	Cu foam	9	3.0	18	93
15	Cu foam	9	2.5	35	83
16	Cu foam	9	2.5	0	94
17	Cu foam	9	2.5	−10	99

^a Electrolyses conducted in a single chamber electrolysis cell, Mg anode, electrolyte solution: MeCN(10 mL)-TEAI(0.1 M)-substrate(0.05 M). ^b Chemical yield based on **1a**, determined by HPLC. ^c Dimethylformamide (DMF) as solvent.

The CVs also showed a slightly higher current at Ag electrode, indicating a greater electroreduction rate at Ag electrode. In order to speed up the reaction rate at Cu electrode, Cu foam with a larger specific surface area instead of Cu flake was used. Greater reaction rate on Cu foam than that on Cu flake has been confirmed by potentiostatic electrolysis. The electrolysis was carried out under peak potential of 1-phenylethyl chloride reduced on Cu electrode (ca. −1.18 V) with Cu foam and Cu flake as working electrode, respectively. After the depletion of 70 C charges, the current was turned off. The resulting *Q*–*t* curves (Figure 4) show that the time required on the Cu foam is shorter, about 4/5 of that on the Cu flake electrode. In addition, a slightly higher yield of the target product was obtained on the Cu foam electrode (Table S1). Hence, Cu foam was used as cathode in the next study.

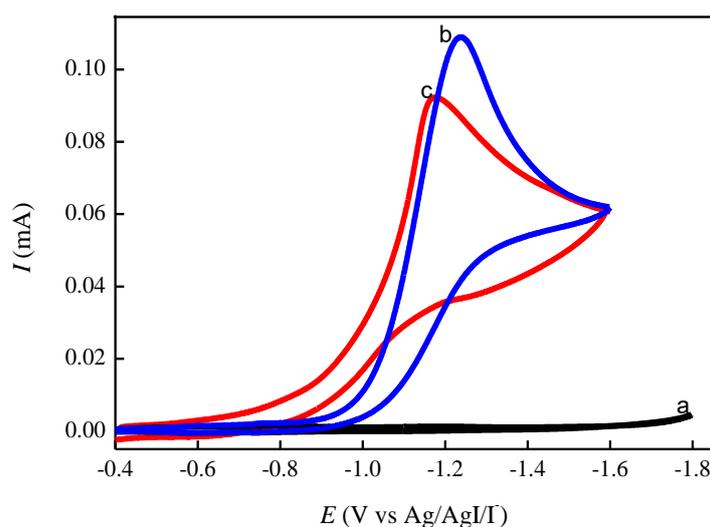


Figure 3. Cyclic voltammograms of 4 mM 1-phenylethyl chloride recorded at different cathodes in 0.1 M TEABF₄-MeCN solution at a sweep rate of 0.1 V s^{−1} at 18 °C saturated with N₂ (a) background; (b) Ag disk; (c) Cu disk.

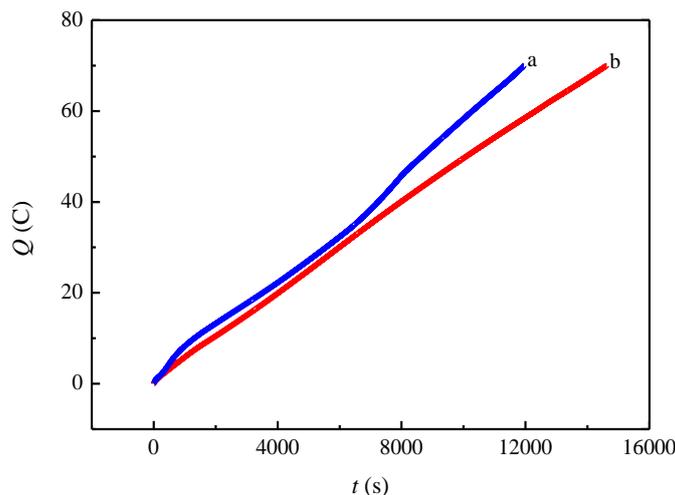


Figure 4. Q - t curve on different cathode (a) Cu foam, (b) Cu flake.

Solvents have their own physicochemical and electrochemical properties, and many electrochemical reactions are affected by the nature of the solvents. Thus, the influence of solvent has been studied. The electrolysis was performed in both MeCN and DMF (Table 1, entries 1, 5). We observed that when the reaction was carried out in MeCN using 5 mA cm^{-2} current density and 2.0 F mol^{-1} charge, the expected product 2a was obtained in 73% yield. In contrast, only 6% yield of 2a was obtained in DMF under the same conditions. This may be due to the larger solubility of CO_2 in MeCN compared with DMF [32].

The current density (J) and charge passed in electrolyses (Q) also affected the yield of 2a. In fact, lower yields were obtained at both low and high current densities compared with the result at 9 mA/cm^2 (87%, Table 1, entry 8). The results at low current densities 5 mA/cm^2 and 7 mA/cm^2 (73% and 77%, Table 1, entries 1, 6) can probably be ascribed to side reactions such as the reduction of CO_2 to C1 or C2 compounds [33,34], while the results at high current densities 11 mA/cm^2 and 13 mA/cm^2 (78% and 75%, Table 1, entries 9, 10) can be ascribed to lower current efficiency with increased ohmic component. The highest yield of 2a was achieved with 9 mA/cm^2 current density and 2.5 F mol^{-1} charge of 1a (92%, Table 1, entry 13). With further increase of consumed charge, the yield of 2a was not significantly improved (Table 1, entry 14). The results indicate that the best charge amount is 2.5 F/mol .

Temperature is one of the important factors for the reaction, which mainly affects the thermodynamics and kinetics of the reaction, as well as the solubility of CO_2 [32]. Therefore, the effect of the temperature on the reaction was studied (Table 1, entries 12, 13, 15–17). As the temperature increased from $-10 \text{ }^\circ\text{C}$ to $35 \text{ }^\circ\text{C}$, the yield of 2a decreased. The highest yield of 2a was obtained at $-10 \text{ }^\circ\text{C}$ (99%, Table 1, entry 17), a relatively low temperature. That is mainly because carbon dioxide is one of the raw materials of the reaction, and its solubility increases as the temperature of the solution decreases. It is worth emphasizing that the Cu foam, a highly efficient cathode, generated very good results for electrocarboxylation carboxylation of 1-phenylethyl chloride. Even at room temperature $18 \text{ }^\circ\text{C}$, normal pressure, 92% yield of 2a was obtained (Table 1, entry 13).

The results of this work may be comparable with literature data on the electrocarboxylation of $\text{ArCH}(\text{CH}_3)\text{Cl}$. We have previously reported that the electrocatalytic carboxylation of 1-phenylethyl bromide with CO_2 at a Ag NP electrode [16]. Best yield (98%) of 2a was obtained at 273 K using 5 mA cm^{-2} current density and 2.5 F mol^{-1} charge. Under the optimized conditions, with 1-phenylethyl chloride as substrate, the yield of 2a was 86%. Isse and coworkers studied the electroreduction reduction of arylethyl chlorides at Ag cathode in the presence of CO_2 , the acid yields were 70–81% at 273.15 K [18]. They also reported electrochemical carboxylation of arylethyl chlorides catalysed either by nickel(I) Schiff base complexes or by radical anions derived from aromatic esters, and yielded acids in the range of 26–88% [22]. Tateno and coworkers developed a novel electrochemical carboxylation system for CO_2 fixation to benzyl halides using a microreactor. In this system, 52–98% yield of acids

was obtained with Pt anode [12]. The acid yields reported in this work are well comparable with these data. On the other hand, the use of noble metals and catalysts were avoided.

2.3. Electrocarboxylation of Other Benzyl Chlorides

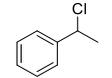
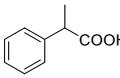
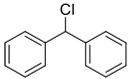
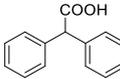
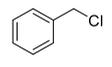
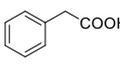
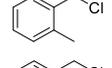
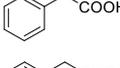
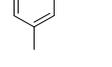
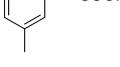
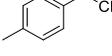
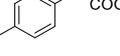
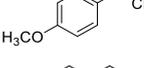
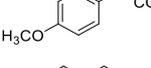
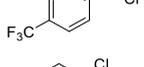
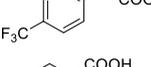
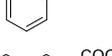
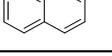
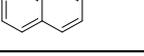
To explore the substrate scope of the reaction, the procedure was carried out under the conditions of Table 1 entry 12, with the following organic halides: chlorodiphenylmethane (1b), benzyl chloride (1c), 2-methylbenzyl chloride (1d), 3-methylbenzyl chloride (1e), 4-methylbenzyl chloride (1f), 4-methoxybenzylchloride (1g), 4-trifluoromethylbenzyl chloride (1h), chlorobenzene (1i) and 2-chloronaphthalene (1j). The results are reported in Table 2.

In the case of 1b, 80% yield of 2b was obtained (Table 2, entry 2), lower than that of 2a (Table 2, entry 1). That is mainly due to the larger steric hindrance of the phenyl group as compared to a methyl group. When the methyl group of 1a was substituted by a H atom, namely 1c, 83% yield of 2c was achieved (Table 2, entry 3). The lower yield of 2c might be attributed to a side reaction (e.g., dimerization) of 1c.

To study the effect of different substituted positions on the reaction, three isomers of *o*-, *m*- and *p*-methylbenzyl chloride (1d–1f) were used as substrate, and the corresponding carboxylic acid yields were 85%, 88% and 72%, respectively (Table 2, entries 4–6). The yields of 2d (entry 4) and 2e (entry 5) are comparable to that of 2c (entry 3), whereas the yield 2f (entry 6) is lower than that of 2c. This indicates that the electron-donating group located at the ortho and meta positions of the halo group has little effect on the reactivity of the C–X bond, while it has a passivation effect on the reactivity of the C–X bond at the para-position. In order to confirm this conclusion, benzyl chlorides substituted by an electron-donating group (–OCH₃) and an electron-withdrawing group (–CF₃) at the para positions have been studied (entries 7, 8). Low yield was obtained with the electron-donating group (–OCH₃), while high yield was achieved with the electron-withdrawing group (–CF₃). The results are consistent with the above conclusion.

As for chlorobenzene (1i) and 2-chloronaphthalene (1j), no supposed carboxylic acid (2i, 2j) could be detected (entries 9, 10). That is mainly because the C–X bonds of 1i and 1j were not easily broken (*p*, π -conjugate effect), and because of the unfavourable reaction to form carboxylic acid.

Table 2. Electrocatalytic carboxylation of other benzyl chlorides on Cu foam cathode ^a.

Entry	Substrate	Product	Yield ^b (%)
1			92
2			80
3			83
4			85
5			87
6			72
7			76
8			88
9			–
10			–

^a Electrolysis were performed under the same conditions as Table 1, entry 13. ^b Chemical yields based on substrates, determined by HPLC.

3. Materials and Methods

3.1. Materials and Instruments

All benzyl chlorides and acids were purchased from J&K Chemical Co. (Beijing, China). Cu foam was purchased from Kunshan Jiayisheng Electronics Co. (Jiangsu, China). MeCN and DMF were kept over 4-Å molecular sieves. Other reagents were used as received. Galvanostatic electrosynthesis was performed using a digital direct current-regulated power supply (HY3005MT, Hangzhou, China). Voltammetric measurements were conducted using the CHI650C electrochemical station (Chenhua, Shanghai, China) in a conventional three-electrode cell. The product yield was determined by high-performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) (Thermo Scientific, Germering, Germany) equipped with a UV (RS Variable Wavelength) (Thermo Scientific, Germering, Germany) detector. Microstructure and morphology of Cu foam and Ag–Cu were analyzed using Hitachi SU8000/S4800 field-emission scanning electron microscope (FE–SEM) (Hitachi, Tokyo, Japan) equipped with an energy dispersive X-Ray fluorescence spectrometer (Ametek, Oxford, UK). X-ray diffraction (XRD) (Rigaku Corporation, Tokyo, Japan) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu K α radiation ($k = 1.5406 \text{ \AA}$).

3.2. General Procedure of Electrode Treatment and Preparation

Cu foam was cut into a circle ($d = 2 \text{ cm}$) by mould and then cleaned successively with HCl (2 M), acetone and deionized water in an ultrasound reactor for 5 min. After drying, the Cu foam could be used as working electrode.

The Ag–Cu dendrite was prepared according to literature [35]. The treated Cu foam was immersed in 10 mM AgNO₃ solution without any surfactant for 10 min in the dark avoiding Ag photoreduction.

The resulting dendritic Ag–Cu was washed with deionized water and ethanol 3 times, then dried for 24 h at 35 °C under vacuum. After that, dendritic Ag–Cu was used as the cathode for electrolysis.

3.3. General Process of Cyclic Voltammetry

Cyclic voltammetric studies were undertaken with CHI650C electrochemical workstation (Chenhua, Shanghai, China). A conventional three-electrode cell was employed with Cu ($r = 1$ mm) and Ag ($r = 1$ mm) disk working electrode, a platinum sheet (1 cm \times 2 cm) counter electrode and a Ag/AgI/0.1 mol L⁻¹ TBAI reference electrode. The electrochemical behavior of 1-phenylethyl chloride (4 mM) was scanned at different cathodes in TEABF₄-MeCN solution with a sweep rate of 0.1 V s⁻¹ in a nitrogen atmosphere. For a clear understanding of the potentials, we report the CV curves versus the oxidation (E^0) of ferrocene (Figure S1). The E^0 of Fc/Fc⁺ couple versus Ag/AgI/I⁻ in MeCN is 0.93 V in this work.

3.4. General Electrolysis Procedure

A typical galvanostatic electrolysis was carried out in a mixture of 1-phenylethyl chloride (50 mM), supporting electrolyte TEAI (0.1 M) and MeCN 10 mL saturated with CO₂ (1 atm) in an undivided glass cell equipped with a (Mg) rod anode and Cu foam cathode ($r = 1$ cm). Continuous CO₂ flow was maintained during the whole electrolysis process. After consuming a charge of 2.0 F mol⁻¹, the current was turned off. MeCN was removed by rotary evaporation, then the rest was hydrolyzed with HCl (0.2 M, 15 mL) and extracted with Et₂O (20 mL) 3 times. The organic layers were dried with MgSO₄, and then evaporated. The main features of the target products were identified by HP 6890/5973N GC/MS (Agilent, USA) and the yields were determined by high-performance liquid chromatography (HPLC).

3.5. General Process of Constant-Potential Electrolysis

The potentiostatic electrolysis was carried out in a mixture of 1-phenylethyl chloride (50 mM), supporting electrolyte TEAI (0.1 M) and MeCN 10 mL saturated with CO₂ (1 atm) in an undivided glass cell equipped with a sacrificial magnesium (Mg) rod counter electrode, Cu flake (1.5 cm \times 2 cm) and Cu foam working electrode ($r = 1$ cm), and Ag/AgI/0.1 mol L⁻¹ TBAI reference electrode, under the peak potential of 1-phenylethyl chloride on Cu electrode (ca. -1.18 V). Continuous CO₂ flow was maintained during the electrolysis process. After the consumption of 70 C charges, the current was turned. Post-processing and detection are the same as galvanostatic electrolysis.

4. Conclusions

In conclusion, a Cu foam electrode was effective for the electrocatalytic carboxylation of 1-phenylethyl chloride. 99% yield of 2-phenylpropionic acid was obtained under optimized conditions. Moderate-to-good yields were also achieved with other benzyl chlorides. Considering the high effectiveness, the economic benefits and the bigger availability of Cu foam cathode, we believe that the synthesis method described in this study has good potential for practical applications.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/7/273/s1>: Figure S1: Cyclic voltammograms versus Fc/Fc⁺ of 4 mM 1-phenylethyl chloride recorded at different cathodes in 0.1 M TEABF₄-MeCN solution at a sweep rate of 0.1 V s⁻¹ at 18 °C saturated with N₂ (a) background, (b) Ag disk, and (c) Cu disk. Table S1: Constant potential electrolysis on different cathodes.

Author Contributions: Author contributions: Conceptualization, J.-X.L.; data curation and investigation: L.-X.W. and Q.-L.S.; formal analysis: Y.-B.G. and H.W.; methodology: M.-P.Y., Y.-G.Z., and H.W.; resources: Y.-B.G., H.W., and J.-X.L.; supervision and visualization: J.-X.L.; validation: M.-P.Y. and Y.-G.Z.; writing—original draft: L.-X.W.

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Conflicts of Interest: The authors declare no conflict of interest.

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