

Bifunctional Cu-Based Catalyst for Electrochemical Conversion of Carbon Dioxide into CO and Formate

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Abstract - Electrocatalytic conversion of CO₂ into value-added products is increasingly becoming one of the most viable approaches for mitigating the negative impacts of anthropogenic CO₂ emissions and alleviating the impact of these emissions on global warming. However, the effectiveness of the electrocatalytic conversion technique is highly dependent on the type of electrocatalyst used and at times limited by the selectivity of the catalyst towards one specific product. In this work, CuO nanocatalysts were synthesized using sol-gel technique and applied for the electrochemical conversion of carbon dioxide into CO and formate. The synthesized catalysts were characterized using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Transmission electron microscopy (TEM), and X-ray powder diffraction (XRD) techniques. A homogenous mixture of the synthesized nanocatalysts with PTFE was uniformly deposited on carbon electrode through the drop-casting technique. The electrochemical activity of the prepared electrodes was then investigated using Linear sweep voltammetry, cyclic voltammetry, and chronopotentiometry techniques. The results indicated that electrodes prepared using the synthesized CuO catalyst can be effectively applied to convert carbon dioxide into both CO and formate at different current densities. At a high current density of 50 mA.cm⁻², the CuO-doped carbon electrodes could simultaneously produce 470 ppm of CO and 273 ppm of formate. Furthermore, the CuO nanocatalyst doping exhibited high stability on the carbon electrodes, which indicates that the electrodes can be effectively applied for large-scale applications.

Keywords: CuO catalyst; Electrochemical conversion; CO; Formate; CO₂ reduction.

1. Introduction

The increase in atmospheric CO₂ levels coupled with the necessity for discovering alternative pathways for producing commercially valuable carbon-based products has sparked an interest among the scientific community for developing technologies for effective capture and conversion of CO₂[1]. In this regard, electrochemical conversion has emerged as the one of the most viable technologies that can effectively serve the purpose repurposing CO₂ into valuable chemicals and fuel, known as electrofuels. These electrofuels are readily storable, distributable, and usable, with CO₂ being the primary waste product that can be captured and reintroduced into the reactor to complete the cycle. This technology facilitates the recycling of CO₂, mitigating CO₂ emissions and combating global warming. Moreover, the chemical feedstocks and fuels produced through electrochemical CO₂ reduction offer a means to reduce reliance on traditional fossil resources.

Depending on the type of catalyst used, the electrochemical reduction offers different pathways for different products. The electroreduction of CO₂ to CO is a promising reaction pathway. Carbon monoxide exists as a gas at ambient pressure; therefore, it can be easily separated from the aqueous solution for further application [2]. Additionally, CO is quite robust and is required by a wide range of industries including chemicals, metallurgy and medicine. More importantly, it is one of crucial component of syngas (CO and H₂) which is widely applied in the industries for the synthesis of various organic chemical products and intermediates through the Fischer-Tropsch process [3]. The traditional process for production CO is through CO₂ hydrogenation otherwise known as the reverse water gas shift reaction. This is reaction is limited by the equilibrium and is only favored at high temperature (typically above 400 °C) [4]. Whereas the CO₂ electroreduction can be easily performed under ambient conditions with higher CO₂-to-CO activity and selectivity.

Out of the numerous other products derived from CO₂ reduction, Formate is another product that stands out in particular for several intriguing reasons. Firstly, the economic viability of large-scale electrochemical conversion of carbon dioxide into formate has been deemed economically feasible as it ranks among the highest value-added chemicals attainable through

CO₂ reduction [5]. The market price for formic acid hovers around 1300 USD per ton, comparable to that of carbon monoxide but significantly surpassing that of methanol and ethylene [6]. Additionally, formic acid holds significance as the most basic naturally occurring carboxylic acid, witnessing a continual surge in demand each year owing to its diverse array of applications. Projections indicate that the global formic acid market is poised to reach an estimated value of 620 million dollars [7].

The potential for obtaining CO and Formate from electrochemical reduction CO₂ process for the storage and conversion of CO₂ is undeniable. However, the reduction process is at times limited by the effectiveness of the catalysts used and at times limited by the selectivity of the catalyst towards one product. In this work, a bifunctional copper oxide nanocatalyst was synthesized using sol-gel technique. The synthesized catalyst was then deposited on carbon electrodes using drop-casting method. The electrodes were then tested to evaluate the effectiveness of the synthesized CuO nanocatalyst for simultaneous production of CO and formate.

2. Experimental Methods

2.1. Materials

Analytical-grade chemical reagents were used to perform all experimental work. Copper (II) nitrate, Sulphuric acid, Nafion membrane 117, acetone, ethanol, and perchloric acid were purchased from Sigma-Aldrich. Liquid Chromatography grade formate (99%, Sigma Aldrich) was used to develop the standard calibration curve in the HPLC. All chemicals were used as is without further purification and deionized water (DI) was used to prepare each solution.

2.2. CuO Nanoparticles Synthesis

Copper oxide nanoparticles were prepared using a facile sol-gel technique. Briefly, about 3 grams of Copper (II) nitrate were dissolved in 100 ml of ethanol and heated to 50 °C under continuous stirring. Concurrently, a solution of oxalic acid containing 3 grams of oxalic acid in 50 ml of ethanol was also heated to under 50 C under continuous stirring. The prepared oxalic acid solution was then added slowly into Copper (II) nitrate solution while stirring for another 1 hour. The obtained solution was dried overnight in an oven at 80 °C and then calcined under air at 400 °C for 2 hours to obtain the CuO nanoparticles [8, 9].

2.3. Characterization

The X-ray diffraction (XRD) patterns of the synthesized CuO nano-catalysts were examined on a German-made Bruker-D8 Advance (Cu-Ka 40 mA, 40 kV), in the 2θ range 20–80°. The surface morphologies of the nano-catalysts were observed using Scanning electron microscopy (FEI Nova Nano SEM 450). The internal composition of CuO nano-catalysts were observed using a transmission electron microscope (TEM, FEI, TALOS F200X). A PerkinElmer Pyris 1 TGA was used to investigate the thermal stability of the catalysts by performing a thermogravimetric analysis within a temperature range of 30 – 850 °C at heating rate of 10 °C /min under N₂ atmosphere. Finally, X-ray photoelectron spectroscopy (XPS) analysis of the CuO samples was conducted on an AXIS Ultra DLD, KRATOS XPS apparatus.

2.4. Electrode Preparation

Firstly, a 0.5 mm thick carbon electrode was divided into 1×1 cm tiny electrodes and cleaned with DI water. Then the required quantity of CuO nano-catalyst was dissolved in a PTFE solution (50 µl PTFE and 300 µl DI water) to create a uniform ink-like emulsion and sonicated in an ultra-sonication instrument for 90 minutes. The CuO nano-catalyst containing emulsion was then drop-casted onto a carbon electrode, dried in an oven at 160 °C for three hours, and then allowed to cool to room temperature for one hour. It is important to note that the CuO catalysts were doped to ensure the catalyst covers the entire surface of the carbon electrode. The obtained final CuO-doped carbon electrodes were then used to perform the experimental works.

2.5. Experimental Set-up

An H-type cell was used to perform electrochemical CO₂ reduction experiments. A schematic diagram of the H-type cell is shown in Figure 1. The cell consisted of a cathodic and an anodic chamber, and Nafion 117 membrane was employed

to divide the two compartments in the cell. The reference (Ag/AgCl) and working electrodes consisting of the CuO-nanocatalyst doped carbon electrodes were both placed in the cathodic compartment of the electrochemical cell. The cathodic chamber was filled with 40 mL of NaHCO₃ solutions of different concentrations to serve as the cathodic electrolyte or catholyte. Furthermore, this chamber also contained an inlet, where CO₂ was fed into the cell during the experimental runs. The Pt-based counter electrode was placed in the cell's anodic compartment. The chamber was filled with 40 mL of 1 molar KOH solution to act as the analytic electrolyte or anolyte. A CS2150 potentiostat from Corrtest (China) was used to perform the electrochemical studies. The chronopotentiometry experiments were conducted for 60 minutes at a steady current. Before each experimental run, the solution was purged with carbon dioxide gas (99.999%). The gas leaving the H-Cell was analyzed using a Bosean K-600 gas detector to detect the CO product formed, and liquid samples were taken from the cathodic compartment of the H-cell and tested in an HPLC (Shimadzu, LC-2050C LT) to analyze the formate product formed.

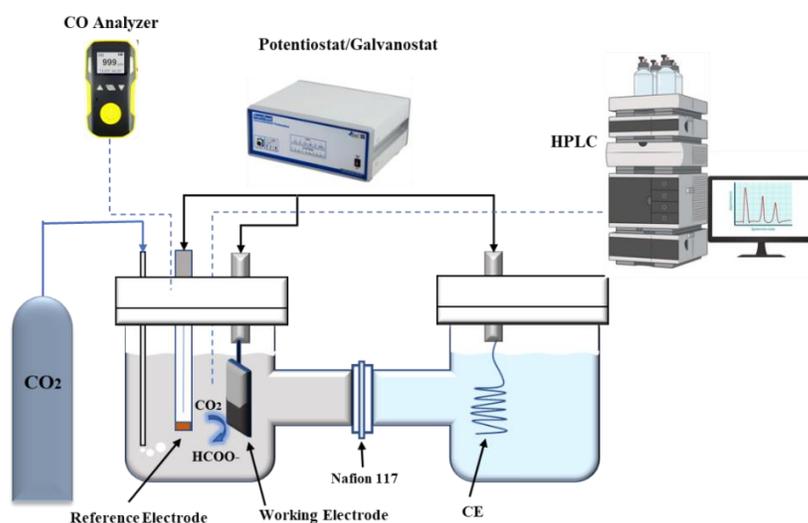


Fig. 1: A Schematic Diagram of the H-Cell used for the Electrochemical Reduction of CO₂ [1]

3. Results and Discussion

3.1. XRD, TGA and XPS analysis

The X-ray diffraction spectrum of the synthesized copper oxide nanoparticles is illustrated in Figure 2A. distinct peaks appear at 2θ values of 31.72°, 35.40°, 37.89°, 48.88°, 53.34°, 58.10°, 61.49°, 66.34°, 67.99°, 72.45°, and 74.88°, corresponding to crystal planes (110), (-111), (111), (-202), (020), (202), (113), (311), (221), (311), and (-222) respectively. These peaks align closely with those expected from the JCPDS card No. 01.080.0076 for CuO nanoparticles of the monoclinic phase [10]. The thermogravimetric analysis of the CuO nano-catalysts is shown in Figure 2B. Initially, the samples exhibited a gradual weight loss until it reached a temperature of around 350 °C, where the sample lost about 60% of its initial weight. This loss was due to loss of the physical absorbed water [11-13]. The surface morphology of the nano-catalysts was further analyzed using the XPS technique and the obtained spectrum is shown in Figure 3. The characteristic peak of Cu_{2p} could be clearly observed from the figure. The peaks observed at 933.7 eV and 953.4 eV are attributed to the binding energies of Cu2p_{3/2} and Cu2p_{1/2} for Cu (II). Owing to influence of the oxide layers, the intensity difference between the peaks of Cu2p_{3/2} and Cu2p_{1/2} is minimal within the CuO nano-catalysts. The spectrum also exhibited the characteristic peak for O_{1s} with the peak attributed to C-O being observed at binding energy of 532 eV [12, 14, 15]. All in all, all three analyses clearly affirm the formation of pure copper oxide nano-catalysts through the sol-gel technique adopted in this work.

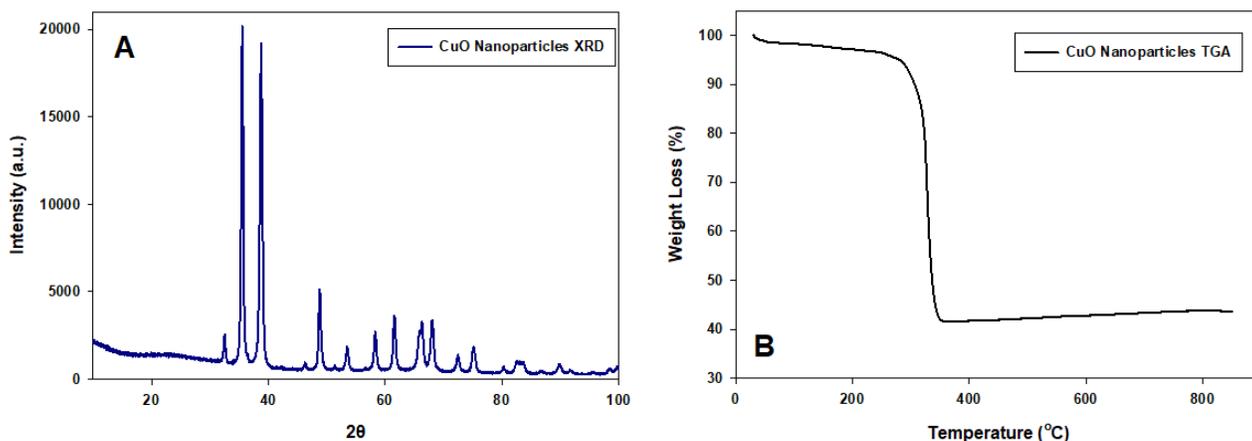


Fig. 2: XRD (A) and TGA (B) of the Copper Oxide Nano-catalysts

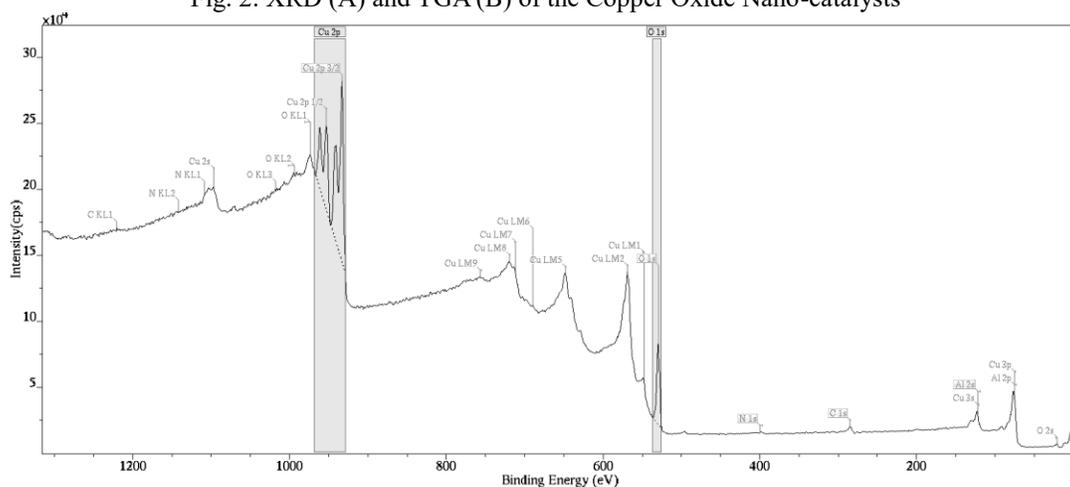


Fig. 3: XPS of the Copper Oxide Nano-catalysts

3.2. SEM and TEM

SEM was utilized to investigate the surface morphology of CuO nanoparticles, and the resulting image is depicted in Figure 4A. The low-magnification image reveals a significant level of agglomeration, resulting in the formation of larger solid structures where smaller particles are dispersed randomly across the surface [11]. TEM image of the CuO samples is shown in Figure 4B. The image shows the CuO synthesized from the sol-gel technique were nearly spherical in shape. The figure also show that together this spherical CuO nano-catalysts formed of aggregates [16].

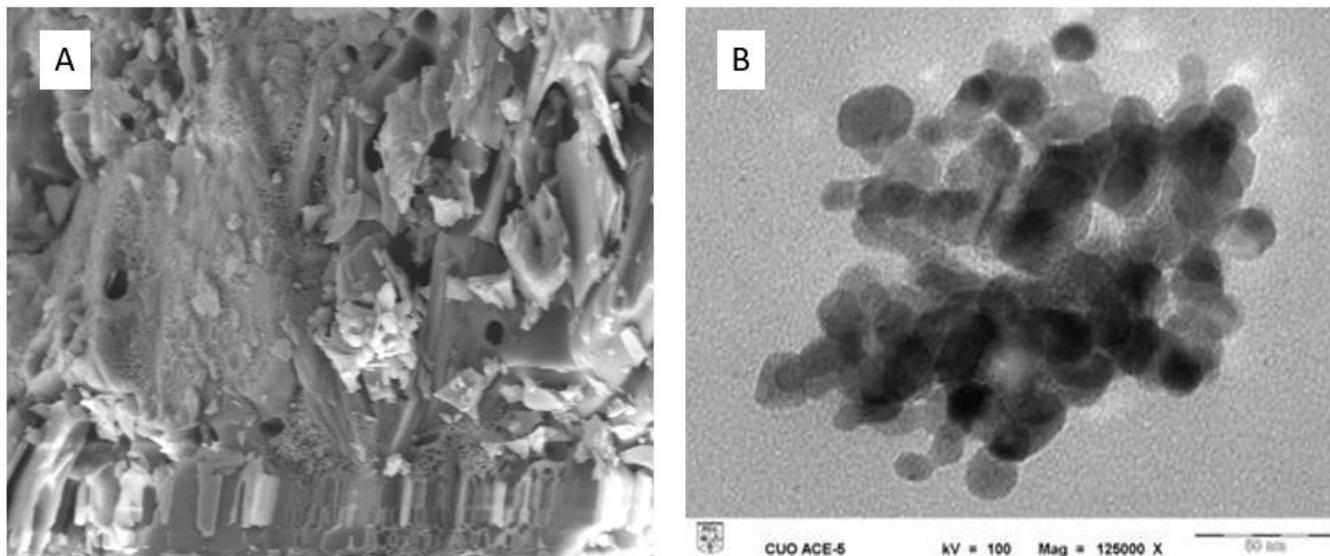


Fig. 4: SEM (A) and TEM (B) of the Copper Oxide Nano-catalysts

3.3. Electrocatalytic reduction of CO₂

A series of electrochemical reduction experiments were performed to investigate the faradic efficiency and concentration of CO and formate using CuO-doped carbon electrodes in the H-type electrochemical cell. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronopotentiometry tests were performed to analyze the performance of the electrodes. First, the chronopotentiometry experiments were performed to test the effectiveness of the catalysts to convert carbon dioxide into CO and formate. During the chronopotentiometry tests, the applied potential values were varied, and the current value constant was kept constant. To maintain consistency and for the purpose of comparison, all chronopotentiometry trials were carried out at a specific time. Using an HPLC and a CO detector both the liquid and gaseous products were analyzed and the FE% of the intended product (formate and carbon monoxide) was determined.

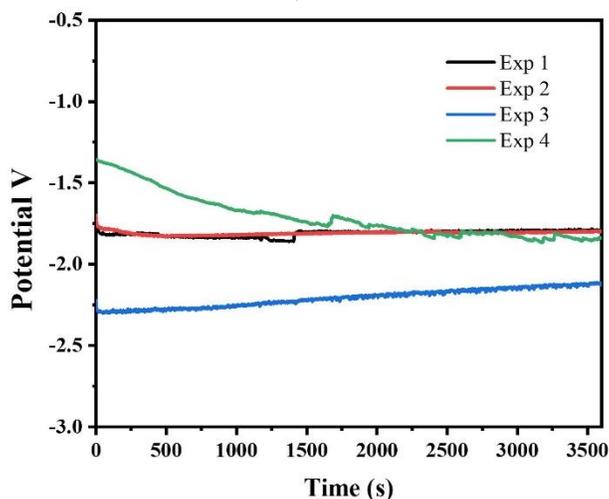


Fig. 5: The chronopotentiometry spectra of CuO electrodes in different NaHCO₃ catholyte and 0.1M KOH anolyte solution for fixed time of 1 hour.

Four different sets of chronopotentiometry experiments were conducted at different conditions (Figure 5) and details for each experimental run along with the obtained results are shown in Figure 5. The chronopotentiometry experiments results confirm the conversion of carbon dioxide into CO and formate. The detailed experimental results are shown in table 1. At

low catholyte concentration (0.4 M NaHCO₃), the increase in the CuO dosage from 1.64 mg to 5 mg increased the CO concentration from 315 ppm to 470 ppm. The same effect was observed in terms of Formate production with the concentration increasing from 117 to 273 ppm. Interestingly, At a current -70 mA.cm⁻², and catholyte concentration of 0.6 M, the increase in CuO doping from 3 to 7 mg, decreased the CO concentration from 453 ppm to 427 ppm. This behavior was also observed in terms of formate production as well. These results clearly indicate the system needs to be further optimized in terms of the applied current, catholyte concentration and CuO dosage to ensure the generation of the maximum amount CO along with formate. The maximum CO concentration of 470 ppm and Formate concentration of 273 ppm were obtained at Current of -50 mA.cm⁻², Catholyte Concentration 0.4 M with carbon electrodes containing 5 mg of CuO doping.

Table 1: The comparative chronopotentiometry results CuO electrodes at different conditions.

Experimental Run	Current (mA)	Catholyte (M)	Dosage (mg)	CO concentration (ppm)	Formate concentration (ppm)
1	-45	0.4	1.64	315	117
2	-70	0.6	3	453	213
3	-50	0.4	5	470	273
4	-70	0.6	7	427	178

Next, the cyclic voltammetry experiment was initially performed under experimental conditions in which the maximum CO and Formate production was achieved (Experimental Run 3) to check the activity of the prepared electrodes and the obtained CV curve is shown in Figure 6A. The CV curve shows the prominent reduction peak. The activity of the electrode was further tested using linear sweep voltammetry and the LSV was also applied to activate the electrode for the electrochemical carbon dioxide reduction experiments (Figure 6B). Similar to the CV curve, shows the prominent reduction peak was also observed for the LSV curve. LSV curve also shows a good current density value of 60 mA/cm². Overall, these results clearly show the promises of CuO-doped carbon electrodes for effective electrochemical conversion of CO₂ to CO and Formate.

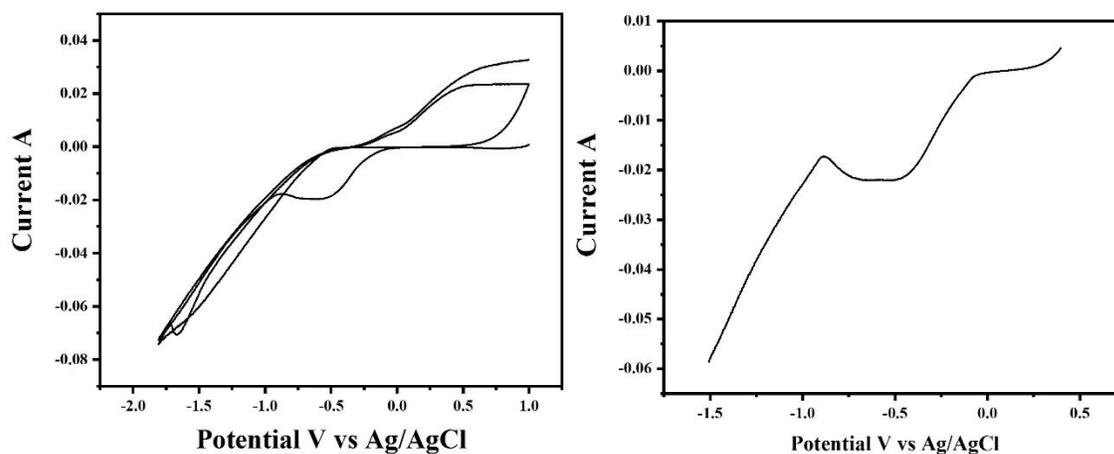


Fig. 6: The cyclic voltammetry spectra of CuO on carbon electrode at 20mV scan rate and Linear sweep voltammetry spectra of CuO electrode was shown.

4. Conclusions

Copper oxide nanoparticles were synthesized using facile sol-gel technique. The synthesized catalysts were analyzed using XRD, TGA, XPS, SEM and TEM techniques. XRD, TGA and XPS analysis of the samples confirmed the formation of CuO nano-catalysts with results from all three analyses exhibiting good consistency with the analyses reported in the literature. SEM images showed the formation of large solid structure formed from the agglomeration of the smaller particles, while the TEM images of the samples revealed that the synthesized CuO nano-catalysts were spherical in shape. Following that, the CuO catalysts were doped onto carbon electrodes and the activity of the electrodes were investigated in terms of CO and Formate products formed. At a high current density of 50 mA.cm⁻², the CuO-doped carbon electrodes could simultaneously produce 470 ppm of CO and 273 ppm of formate. Moreover, the CV and LSV curves obtained for the electrodes affirmed the stability of the CuO-doped electrodes. Overall, the results clearly show the potential of applying CuO as bifunctional catalyst for effect electrochemical conversion CO₂ into CO and Formate. However, further optimization experiments are required to elucidate the intricacies of the CuO based electrode and improve its activity for large-scale applications.

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