

Comparison study of CO₂ electroreduction to formate fuel on Cu_xO nanocatalysts synthesized with different reducing agent in hydrothermal method

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Abstract. In this study, novel kinds of Cu_xO nanocatalysts have been successfully synthesized with different reducing agents (aniline, O-methoxyaniline and 3,5-dimethoxyaniline) by a facile hydrothermal method. The catalytic performances of the as-prepared Cu_xO nanocatalysts were investigated systematically for the electroreduction of CO₂, and compared with the one which has been produced in our previous work using 2,5-dimethoxyaniline as catalyst's synthetic reducing agent. The experiments show that the catalytic activity of Cu_xO nanocatalysts largely depends on the molecular structure of the reducing agent used for the catalyst's synthesis. Using 3,5-dimethoxyaniline as an effective reducing agent, the obtained Cu_xO nanocatalyst gives the best catalytic activity in terms of both reduction current density and Faradaic efficiency. A high current density larger than 20 mA cm⁻² was observed at -1.25V. The Faradaic efficiency of formate production with a maximum value of 36% was obtained at low potential of -0.7 V vs. SHE.

Introduction

Currently, a lot of researchers have explored valuable conversion methods to control the content of CO₂ in the atmosphere such as chemical reduction, radiation reduction, electrochemical reduction and photochemical reduction [1]. Among these methods, electrochemical reduction of CO₂ is considered as a pretty appropriate technology because of its simple, environmentally friendly and well controllable specialties [2,3]. However, the CO₂ electroreduction kinetics is extremely sluggish, and the focal point is to develop efficient catalysts which can increase the activity and selectivity, especially for room-temperature CO₂ reduction in aqueous solutions [4]. In this regard, the single crystal copper (Cu) electrode has been studied for CO₂ electroreduction owing to its advantage of low cost and abundant. Nevertheless, there are some fatal weaknesses for the electrochemical reduction method. For example, many researchers reported that copper electrode has the characters of poisoning and deactivation [5,6]. Moreover, pure Cu electrode is easy to be corroded in alkaline electrolyte, which will shorten its service life [7].

In order to avoid these disadvantages and improve the performance of CO₂ reduction, with 2,5-dimethoxyaniline as the reducing agent, we have prepared efficient Cu_xO nanocatalysts with special 3D hierarchical nanosphere structure by a hydrothermal method, which showed high catalytic performance for CO₂ electroreduction [8,9]. As a continuing effort in improving Cu_xO catalyst's activity and selectivity, in this paper, using aniline, O-methoxyaniline and 3,5-dimethoxyaniline as the effective reducing agents, we prepared novel three kinds of Cu_xO nanoparticles to investigate the effects of different reducing agents on the obtained catalysts' catalytic performances for CO₂ electroreduction.

Experiment

Cu_xO nanocatalysts preparation. Cu_xO nanocatalysts were prepared using the same synthesis conditions as reported in our previous work [8], except by applying different reducing agents such as aniline, O-methoxyaniline and 3,5-dimethoxyaniline. Fig. 1 illustrates the molecular structure of these three reducing agents. In order to analysis the catalytic performances for Cu_xO nanocatalysts, the three samples synthesized using different reducing agents were labeled with Cu_xO_a (the reducing agent is aniline), Cu_xO_b (the reducing agent is O-methoxyaniline) and Cu_xO_c (the reducing agent is 3,5-dimethoxyaniline), respectively.

Cu_xO/GDL Electrode preparation. 15 mg Cu_xO nanoparticles was suspended in 1mL isopropyl alcohol (Sinopharm Chemical Reagent Co.) and moderate Nafion® solution (5 wt%) was added to the mixture solution to increase adhesion of catalyst ink. The loading of catalyst was 3 mg cm⁻².

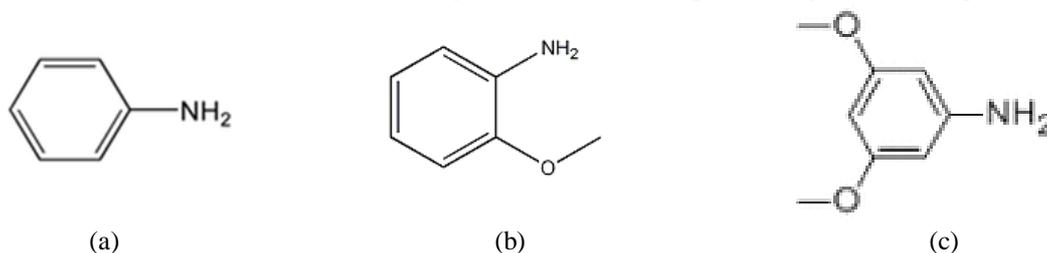


Fig. 1 Molecular structure of aniline (a), O-methoxyaniline (b) and 3,5-dimethoxyaniline (c) used for Cu_xO nanocatalysts synthesis.

Electrochemical test. All electrochemical measurements were tested in a conventional three-electrode electrochemical cell as shown in Fig. 2, in which cation exchange membrane (Nafion® 117, Dupont) was used as a separator to allow proton (H⁺) through from the anode chamber to cathode chamber. A Pt foil electrode and a saturated calomel electrode (SCE) were used as the counter electrode(CE) and the reference electrode(RE), respectively. Carbon paper (4 cm², used as GDL) coated with Cu_xO nanoparticles was used as working electrode(WE). 0.5 M KHCO₃ aqueous solution was used as electrolyte. All measured potentials were referenced to a standard hydrogen electrode (SHE) at ambient temperature and pressure.

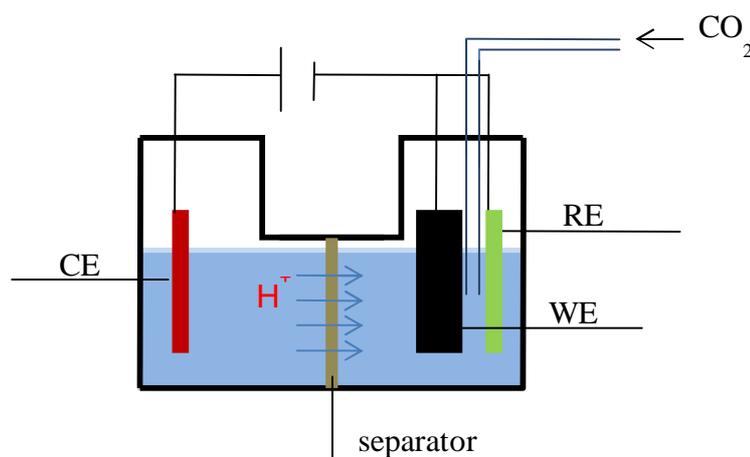


Fig. 2 The electrochemical reduction cell of CO₂.

The electrocatalytic activity and kinetics of Cu_xO/GDL electrode were tested using cyclic voltammetry (CV) at potential scan rates of 50 mV s⁻¹, in a potential range of 1.25 V to -1.25 V vs. SHE. The controlled potential electrolysis was carried out using a CHI660E electrochemical analyzer in the same standard H-type cell. Before each electrolysis process, the electrolyte was bubbled with N₂ for at least 30 minutes to exhaust the dissolved air in the electrolyte, and CO₂ gas was continuously

bubbled to maintain the saturation during the following electrolysis. For soluble product measurements, the electrolysis time was controlled for 60 minutes with a constant potential of -0.7 V vs. SHE was imposed for 1 hour for analysis reduction products test, where the electrolysis currents were continuously recorded.

The produced formate was determined and analyzed by ion chromatography (IC). The faradaic efficiency for the formation of formate (FE) was calculated according to eqn. (1) [8]:

$$FE = N \cdot n \cdot F / Q \quad (1)$$

where N is the moles of formate produced; n represents the number of electrons exchanges for reduction of carbon dioxide to formate ($n = 2$ here); F is Faraday's constant (96485 C mol⁻¹) and Q is the total charge during the electrolysis. All the measurements were performed under room temperature and ambient pressure.

Results and Discussion

The electrochemical activities of CO₂ reduction. The influences of three different reducing agents (aniline, O-methoxyaniline, 3, 5-dimethoxyaniline) on the synthesized catalyst's activity for CO₂ electroreduction have been investigated and the results are shown in Fig. 3. The CV curves of Cu_xO nanoparticles in 0.5M N₂-bubbled (black line) and CO₂-bubbled (red line) KHCO₃ aqueous solution were recorded with potential range from 1.25 V to -1.25 V. From Fig. 3(a-c), it can be seen that under N₂ gas atmosphere, there is no obvious current occurred in the whole tested potential range. The current density of 5 mA cm⁻² produced at -1.25 V vs. SHE can be ascribed to the hydrogen evolution reaction under N₂ gas atmosphere. However, when purged with CO₂ instead of N₂ for all three as-prepared Cu_xO catalysts, a sharp increase in current density was clearly observed. The above results suggest that the electroreduction of CO₂ was occurred on these three electrodes. Further from Fig. 3(c), one can see that the highest reduction current density of about -20 mA cm⁻² can be achieved for Cu_xO_c catalyst, i.e., with 3,5-dimethoxyaniline as reducing agent. This result is consistent with our previous work [8]. For an detailed observation, the reduction current density produced by Cu_xO_c nanocatalyst is 2 times higher than that of Cu_xO_a nanocatalyst, that is, with aniline as reducing agent (Fig. 3(a)). These results indicate that the presence of methoxy functional group is very important, which may facilitate the reduction of CO₂ dramatically. To our interest, it was found that the amount of methoxy functional groups also has great effect on the catalytic performance of the as-prepared Cu_xO nanocatalyst. From Fig. 3(d), it can be observed that the reduction current density of Cu_xO_c catalyst is also 2 times larger than that of Cu_xO_b catalyst, where Cu_xO_b was synthesized using O-methoxyaniline as the reducing agent. It was noted that the reduction current density of Cu_xO_b catalyst is even slightly lower than that of Cu_xO_a, further verifying that the amount of methoxy functional group plays a key role in synthesizing the high performance Cu_xO nanocatalyst for CO₂ reduction process.

Faradaic efficiency of CO₂ reduction. Fig. 4 shows the Faradaic efficiency of formate formation of Cu_xO nanocatalysts at -0.7V vs. SHE. From Fig. 4, it can be seen that the highest Faradaic efficiency was obtained for Cu_xO_c catalyst reaching to 36%. However, this value is much lower than our previous reported Cu_xO nanocatalyst, where 2,5-dimethoxyaniline was used as the reducing agent [8]. It should be noted that the Cu_xO_c catalyst synthesized using 3,5-dimethoxyaniline as reducing agent shows the same electrocatalytic activity as in the case for Cu_xO one synthesized with 2,5-dimethoxyaniline as reducing agent, however, very different selectivity was obtained. This may be resulting from the location of methoxy functional group in the dimethoxyaniline molecule, which controls the morphology formation of the as-prepared Cu_xO nanocatalyst, and thus the formate formation selectivity. Further from Fig. 4, the Faradaic efficiency of formate formation of Cu_xO_a (without methoxy functional group) is 25%, higher than that of Cu_xO_b (17%) catalyst. This is in a well agreement with the electrochemical activity as shown in Fig. 3. The above results further suggest that not only the presence of methoxy functional group is the one that affects the as-prepared catalyst's

activity for CO₂ reduction, but also the amount and the location of methoxy functional group in dimethoxyaniline molecule also play the important role in electrolytic CO₂ reduction process.

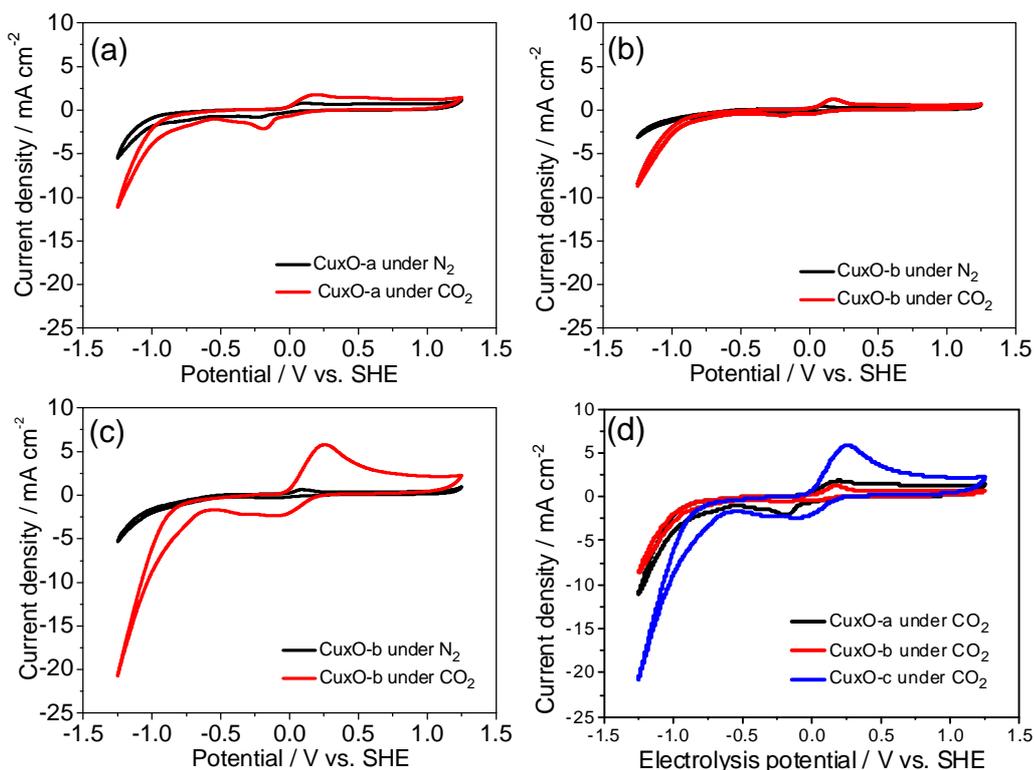


Fig. 3 The CV curve of Cu_xO_{-a} (a), Cu_xO_{-b} (b), Cu_xO_{-c} (c) nanocatalysts, which was measured in 0.5M KHCO₃ aqueous solution with N₂ gas (black line) and CO₂ gas (red line) atmosphere, respectively. (d) The comparison of CV curves for three Cu_xO nanocatalysts under CO₂ gas atmosphere.

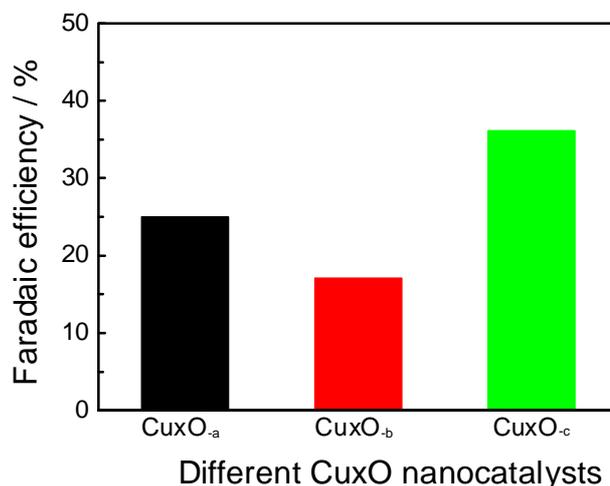


Fig. 4 Faradaic efficiency of formate formation of Cu_xO nanocatalysts at -0.7V vs. SHE.

Conclusions

In short, the catalytic activity of Cu_xO nanocatalysts depends largely on the structure of the reducing agent used for the catalyst's synthesis in hydrothermal method. Also, the amount of methoxy functional groups and the location in the molecular have great effect on the finally obtained Cu_xO catalysts' activity. In terms of both reduction current density and Faradaic efficiency, Cu_xO nanocatalyst with 3,5-dimethoxyaniline performs the best. The current density is larger than 20 mA cm⁻² and the Faradaic efficiency of formate is up to 36%.

Acknowledgments

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