

# Hydrophobicity-controlled CuO Electrode for Enhanced Electrochemical CO<sub>2</sub> Reduction to Ethylene

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## ABSTRACT

Cu-based materials are effective electrocatalysts for converting carbon dioxide to ethylene. However, the hydrogen evolution reaction (HER) in aqueous solutions competes with the desired carbonaceous product, leading to poor selectivity. To overcome this issue, a PVDC coating was applied to a CuO electrode to regulate surface hydrophobicity, suppressing HER and promoting ethylene production. The influence of the PVDC layer on proton transfer and electrocatalyst stabilization was thoroughly investigated by varying the coating amount and order. The modified CuO electrode with a coating layer of only 50  $\mu\text{g}/\text{cm}^2$  induced an optimal surface hydrophobicity (WCA=122°). It exhibited a highly efficient and selective ethylene production ( $\text{FE}_{\text{C}_2\text{H}_4}$ =41.4%,  $|j|_{\text{C}_2\text{H}_4}$ =6.8mA/cm<sup>2</sup>) and suppressed hydrogen evolution ( $\text{FE}_{\text{H}_2}$ =22.7%) at a low potential of -0.89V vs. RHE. The spent modified CuO electrode exhibited an increased presence of Cu<sup>+</sup>, facilitating the C-C coupling process. The stable hydrophobic properties and good electrical conductivity of PVDC-modified electrodes offer a simple and successful approach for advanced electrocatalyst development.

**Keywords:** Electrochemical CO<sub>2</sub> reduction; Ethylene production; Copper catalyst; Enhanced Faraday efficiency; Hydrophobicity control; Polymer coating.

## NOMENCLATURE

### Abbreviations

eCO <sub>2</sub> RR	Electrochemical CO <sub>2</sub> reduction reaction
HER	Hydrogen evolution reaction
FE	Faraday efficiency
PVDC	Polyvinylidene chloride
PVDF	Polyvinylidene fluoride
WCA	Water contact angle

### Symbols

$j$	Current density
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## 1. INTRODUCTION

While powered by renewable energy, electrochemical CO<sub>2</sub> reduction is one of the promising ways to mitigate the greenhouse effect as it's a carbon-neutral or carbon-negative process. Value-added carbonaceous products including CO, HCOOH, CH<sub>4</sub>, and C<sub>2+</sub> could all be generated. Ethylene is distinguished by its higher economic value and the superior ability for carbon sequestration as a lower-carbon product that might be utilized directly as a raw material in the chemical industry[1]. It continues to be challenging to develop highly active and selective catalysts for the electrochemical production of ethylene owing to the intricate reaction pathways of the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR)[2-4].

Research on copper-based catalysts with various crystal planes, sizes, structures, and roughness has already achieved impressive results in the current stage of electrocatalytic reduction of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub>[5-7]. The oxide-derived Cu electrode exhibited more excellent selectivity and activity in CO<sub>2</sub>RR to ethylene as compared to a pure Cu electrode. The presence of protons is essential to the equilibrium of the electron in the entire ethylene process, and, as a consequence, it's hard to inhibit the major side reaction, the hydrogen evolution reaction [8]. It's essential to carry out studies on HER reduction strategies. Among them, polymer coating for the hydrophobicity modification on the electrodes was one of the most effective and generally applicable approaches.

In this work, a cheap and accessible polymer Polyvinylidene chloride(PVDC) was used to create a hydrophobic layer on the surface of CuO electrodes by physical deposition. The hydrophobicity of the electrode is altered by modifying the thickness of the PVDC layer, which is accomplished by varying the PVDC coating's thickness. A three-phase reaction zone of gas, liquid and solid is created to moderately limit proton transfer. This simple wettability adjustment measure would not only improve the catalytic activity and selectivity of CuO electrodes for ethylene production but could also be useful as a general technique to suppressing HER for other electrocatalysts to their desired products.

## 2. MATERIAL AND METHODS

### 2.1 Preparation of CuO-polymer electrodes

CuO nanoparticles(<50 nm, Sigma Aldrich) were cleaned ultrasonically in acetone and then rinsed with DI water. The cleaned CuO was dried in a drying oven at 120 °C overnight. 10 mg of cleaned CuO NPs were dispersed in 2 ml DMF by sonication for 25 minutes[9]. A volume of 200 μL of the resulting dispersion was drop-casted on each side (2 × 2 cm<sup>2</sup>) of carbon paper and thoroughly dried at 105 °C. Then, the prepared CuO electrode was cut into 1 × 1 cm<sup>2</sup> pieces. The CuO loading of 0.25 mg/cm<sup>2</sup>.

To prepare CuO-PVDC electrodes, 5/10/20/30 μL 5 mg/ml PVDC/DMF solution was drop-casted onto each side of previously prepared CuO electrodes and dried on a heating plate at 80 °C for 1 hour. As the polymer loading was 25, 50, 100, and 150 μg/cm<sup>2</sup>, the electrodes were named CuO-PVDC 25, CuO-PVDC 50, CuO-PVDC 100 and CuO-PVDC 150, respectively.

### 2.2 Electrochemical CO<sub>2</sub> reduction reaction

CO<sub>2</sub> electroreduction test was conducted in the conventional 50 ml H-cell at room temperature and ambient pressure, with a proton-exchange membrane (Nafion 117). 50 mL 0.1 mol/L KHCO<sub>3</sub> solution was used as the electrolyte in each compartment. Ag/AgCl electrode and a 1 × 1 cm<sup>2</sup> platinum plate were used as a reference and counter electrode. Catholyte was first saturated with 99.999% CO<sub>2</sub> before the test. In the electrolysis, 30 sccm CO<sub>2</sub> flow was continuously bubbled into the catholyte with magnetic stirring at around 700 rpm. The CHI660e electrochemical workstation (CH instrument Inc.) was used to perform all the electrochemical tests. All the potentials have been manually corrected for Ohmic loss (iR<sub>s</sub>) based on  $E_{corrected} = E_{applied} - 85\% iR_s$  (where *i* is the current in the potentiostatic process, *R<sub>s</sub>* is solution resistance determined by electrochemical impedance spectroscopy, which is around 30 Ω) and converted to reversible hydrogen electrode scale using  $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.21$  (pH=6.8). After 20-minute CO<sub>2</sub>RR at a constant potential, the gas product was analyzed online using a gas chromatography instrument (GC 8890, Agilent) equipped with two flame ionization detectors (FID) and one thermal conductivity detector (TCD). The detector temperature was held at 275 °C and the oven at 60 °C. The content of gas products was quantified according to the calibration curves obtained by injecting known volumes of the pure gas mixed in Ar[10-12].

## 3. CALCULATION

The maximum CO<sub>2</sub> consumption rate could be determined from the current density at the working potential. Here, we take a current density of 10 mA/cm<sup>2</sup> as an example, the PVDC-modified electrodes reach the specified current at the potential of ~-1.66 V vs. RHE. Due to the complexity of the CO<sub>2</sub>RR products and the interference of H<sub>2</sub> by-products, the electron consumption rate can hardly be transferred to the CO<sub>2</sub> consumption rate. The ratio of electron consumption to CO<sub>2</sub> consumption was predicted to be around 3.5 referring to the actual product distribution. Therefore, for the PVDC-modified CuO electrode, the CO<sub>2</sub> consumption rate on the CuO-PVDC electrode at the current density of 10 mA/cm<sup>2</sup>, is  $2.97 \times 10^{-8}$  mol/cm<sup>2</sup>·s[13]. The permeability of CO<sub>2</sub> in PVDC was around 0.95 cm<sup>3</sup>·mm/m<sup>2</sup>·day·atm[14]. In this case, the thickness of the PVDC layer could not be precisely measured due to the irregular electrode surface. We assume it to be 0.1 μm, and the flux of CO<sub>2</sub> through the

polymer layer is calculated to be  $4.9 \times 10^{-10}$  mol/cm<sup>2</sup>·s, which is much less than the theoretical CO<sub>2</sub> consumption rate. These results indicate that CO<sub>2</sub> mass transport might be one of the limiting factors when the PVDC thickness is over 1.65 nm. Besides, the increased PVDC loading with the wider and deeper range of coverage on CuO electrodes would lead to decreased current density and affect ethylene production. Thus, CuO electrodes with a spot of PVDC layer would stand out for its moderate proton transfer rate and sufficient CO<sub>2</sub> supply at the electrode-polymer interface.

#### 4. RESULTS&DISCUSSION

The CuO electrodes were prepared by directly drop-casting CuO NPs/DMF dispersion liquid onto carbon paper. After thorough drying, the CuO layer was covered with various amounts of PVDC by drop-casting the PVDC/DMF solution onto the as-prepared CuO electrodes. The CuO nanoparticle is a cylindrical structure with a section diameter of around 50 nm and a length of 100-200 nm. Due to the high temperature (105 °C) in the drying process, CuO nanoparticles are not uniformly dispersed and have apparent agglomeration on the surface of carbon paper, resulting in the partial exposure of carbon fiber (Fig. 1a, b). From Figure 1b, a

establishes the connection between CuO nanoparticles and carbon paper.

There is thereby an urgent need to figure out whether the characteristics of electrocatalysts were sacrificed by hydrophobic materials and elucidate their influence on product distribution. The PVDC effect on electrochemical behaviour has been investigated by linear sweep voltammograms(LSV) recorded at CuO electrode and CuO-PVDC electrodes from 0.5 V to -2 V in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> aqueous solutions at a scan rate of 0.01 V/s. The LSV for the first cycle is presented in Fig.1c. On the first cycle, Cu<sup>2+</sup> was reduced to Cu<sup>0</sup> or Cu<sup>+</sup>, which could be proved by the irreversible reductive wave between 0.2 V and -1 V vs. RHE and further XPS test[9]. It should be noted that there is no significant difference in the overall trends of curves for the CuO electrode and CuO-PVDC electrodes. With more PVDC coating, the enhancement in current density was less noticeable, and the curves were close to that of the bare CuO electrode. Besides, the onset potential for PVDC-modified carbon paper and PVDC-modified CuO electrodes shifted negatively compared with the bare carbon paper and CuO electrodes, which suggests that proton transfer from electrolyte was hindered in the presence of PVDC polymer[15].

Investigations have been done into the impact of

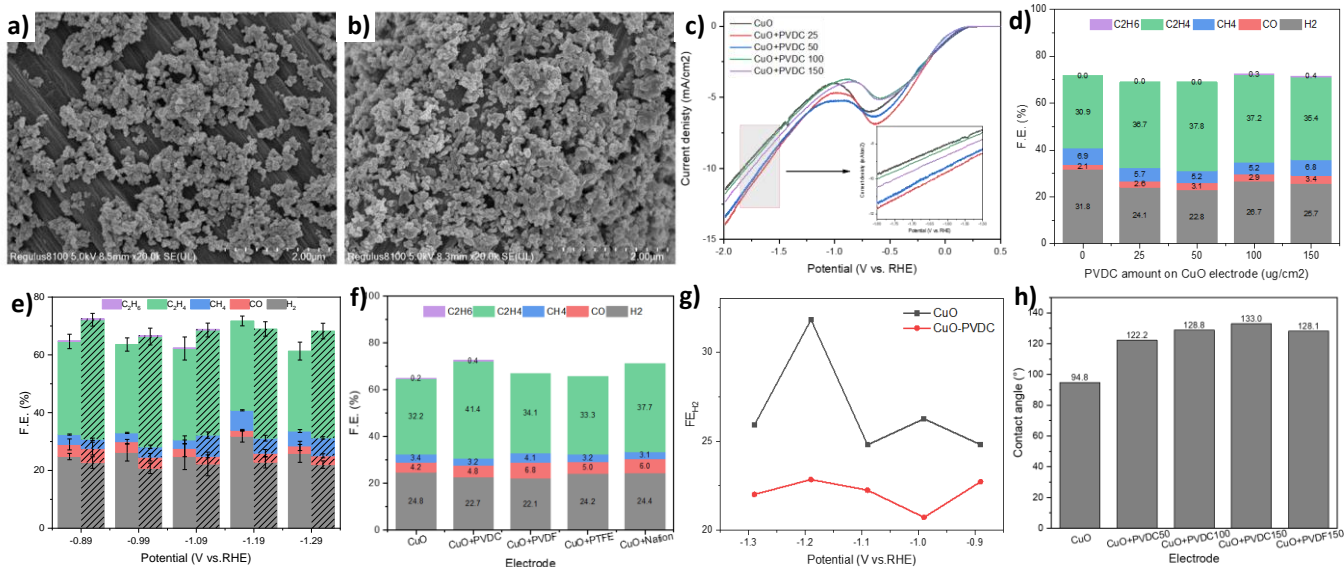


Fig. 1. SEM images of a) CuO electrode; b) CuO-PVDC50 electrode; c) LSV of CuO electrodes and CuO-PVDC electrodes at a scan rate of 10 mV/s without iR-corrected; the product distribution of d)CuO and CuO-PVDC electrodes at -1.19V; e) bare CuO electrode(left column with no pattern) and CuO-PVDC50 (right column with oblique line); g) faradaic efficiencies of H<sub>2</sub> for bare CuO electrode and CuO-PVDC50 under different working potentials with 85% iR-corrected; h) water contact angle of electrodes.

film could be found covering CuO particles and carbon paper. The film bonds the particles together and

PVDC on the selectivity and activity of electrochemical carbon dioxide reduction. The CO<sub>2</sub> reduction performance test reveals that the PVDC modification

does have a significant improvement in HER suppression and ethylene formation. Without polymer modification, the bare CuO electrode showed FE of  $\sim 31.8\%$  for H<sub>2</sub> evolution and FE of  $\sim 30.9\%$  for ethylene production, and gaseous products predominated. With various PVDC coating amounts, all the FEs of H<sub>2</sub> decreased by over 5%, meanwhile, FE<sub>ethylene</sub> increased by at least 4.5%. CuO electrode reached optimal performance with only 50  $\mu\text{g}/\text{cm}^2$  coating of PVDC. The hydrogen evolution was significantly inhibited from 31.8% to 22.8%, while FE<sub>C<sub>2</sub>H<sub>4</sub></sub> increased from 30.9% to 37.8%. The incremental PVDC coating amount didn't show any positive correlation tendency with the selectivity of products. Instead, excessive PVDC loading would suppress CO<sub>2</sub> reduction while limiting the proton transfer. Overall, it could be concluded that the partial current density of ethylene was optimized on the CuO-PVDC electrode and that of hydrogen was decreased to a certain extent.

The CO<sub>2</sub>RR performances of bare CuO and CuO-PVDC50 electrodes were tested under the working potential range from -0.89 V to -1.29 V vs. RHE (with 85% iR-corrected) in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> electrolyte to investigate the product selectivity variation induced by the gas/liquid/solid triple-phase contact interface difference. The bare CuO electrodes showed the Faraday efficiency of H<sub>2</sub> fluctuated between 24.8% and 31.8%, FE<sub>C<sub>2</sub>H<sub>4</sub></sub> was around 30%, and the Faraday efficiency of all gaseous products was over 61% under the whole working potential range (Fig. 1e). CuO electrode reached the optimal performance with only 50  $\mu\text{g}/\text{cm}^2$  coating of PVDC when the hydrogen evolution was greatly inhibited to 22.8%, which is 2.1-9% less than that on the bare CuO electrode under the same working potentials (Fig. 1g). After 50  $\mu\text{g}/\text{cm}^2$  PVDC modification, the production of CO and CH<sub>4</sub> (FE<sub>CO+CH<sub>4</sub></sub> <10%) was similar with that on CuO electrode, C<sub>2</sub>H<sub>4</sub> formation was greatly facilitated, the FEs of ethylene on CuO-PVDC electrode were 4.7-9.3% higher than that on the unmodified CuO electrode at the same potential. Notably, at -0.89 V vs. RHE, with a total current density of 16.5 mA/cm<sup>2</sup>, the highest FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of 41.4% was achieved on the CuO-PVDC electrode, evidently higher than that of the CuO electrode (FE<sub>C<sub>2</sub>H<sub>4</sub></sub> = 32.2%), the partial current density of ethylene reached 6.8 mA/cm<sup>2</sup>, which is among the highest yield in the reported electrocatalytic CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> conversion with CuO derived electrodes.

The polymer coating has a considerable impact on ethylene production. To further investigate the polymer effect on the selectivity and activity of CuO electrodes, a series of control experiments were conducted using other hydrophobic materials such as polyvinylidene

fluoride (PVDF), polytetrafluoroethylene (PTFE) and Nafion. When polymers were coated on CuO electrodes, the CO<sub>2</sub>RR performance of electrodes was enhanced with an increase in ethylene selectivity and a reduction in hydrogen evolution (Fig. 1f). At the same potential, the sum of faradaic efficiency of H<sub>2</sub>, CO and CH<sub>4</sub> for each polymer-modified electrode was nearly 32%, the hydrogen evolution was slightly inhibited. The enhancement of ethylene yield varies from polymer to polymer. PVDC- and Nafion-modified CuO electrodes display a significant increase from 32.2% to 41.4% and 37.7%, respectively. For the same coating amount, PVDC modification is outstanding, probably because it has adequate limitations on proton transfer.

The water contact angle, as an indicator of surface hydrophobicity, has been measured for the CuO with various PVDC and PVDF coating amounts. The results confirm that the PVDC layer could introduce hydrophobicity and the strength of which is positively correlated with the coating amount. With different hydrophobicity, the electrical conductivity and porosity of electrodes might be affected. The modified CuO electrodes showed higher hydrophobicity than unmodified ones, and even a 50  $\mu\text{g}/\text{cm}^2$  PVDC layer could increase the water contact angle from 94.8° to 122.2°. In the experimental range, the water resistance was slightly enhanced with the increase in PVDC coverage. Notably, the hydrophobicity of CuO-PVDC (133.0°) was higher than that of CuO-PVDF (128.1°) with the same loading amount of 150  $\mu\text{g}/\text{cm}^2$ . 100  $\mu\text{g}/\text{cm}^2$  PVDC modification could introduce a similar hydrophobicity with 150  $\mu\text{g}/\text{cm}^2$  PVDF, which means the hydrophobic effect of the PVDC layer was better than that of PVDF. The comparison of the eCO<sub>2</sub>RR performance of PVDF- and PVDC-modified CuO electrodes is shown in Fig. 1f). The CuO-PVDF electrode shows a suppression in H<sub>2</sub> evolution and an increase in CH<sub>4</sub> production, but the effect is not as good as the PVDC-modified electrode with the same hydrophobicity or coating amount. This result indicates that the hydrophobicity of the electrode does influence the hydrogen evolution, but it is not the determining factor for the product selectivity.

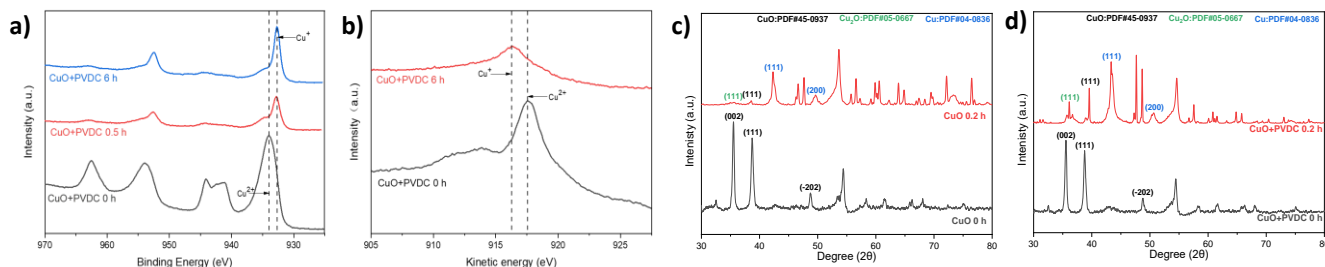


Figure 2. a) The high-resolution XPS Cu 2p and b) Cu LMM on CuO electrode with 50  $\mu\text{g}/\text{cm}^2$  PVDC coating; XRD for c) CuO electrode; d) CuO-PVDC50 electrode.

Changes in the active species on the electrode before and after the reaction have been demonstrated by LSV and SEM measurements. X-ray photoelectron spectroscopy (XPS) was used to characterize the Cu oxidation state on CuO and CuO-PVDC electrodes before and after the 30-minute and 6-hour electrocatalytic CO<sub>2</sub>RR test. The existence of Cu (II) on unused CuO-PVDC electrodes is evidenced by a shoulder observed on the main peak at 933.9 eV (Fig. 2a). The active species on the carbon paper before the reaction should be CuO which is also supported by XRD. After the short-term and long-term reactions, the peak shifted to 932.8 eV, which should be associated with Cu<sup>+</sup> based on both Cu 2p and Cu LMM spectra (Fig. 2a, 2b). It could be concluded that this change of oxidation state from Cu<sup>2+</sup> to Cu<sup>+</sup> may occur in the first half hour of the reaction, and Cu<sup>+</sup> would not be further reduced to Cu<sup>0</sup> during the 6-hours reaction. There is no evident effect of PVDC on holding back the reduction of CuO. XRD analysis was conducted to gain insight into the valence stage change of Cu in electrocatalysis. The CuO electrode was tested before and after a 20-minute CO<sub>2</sub>RR test at -0.89 V vs. RHE in CO<sub>2</sub>-saturated 0.1M KHCO<sub>3</sub>. Figure 2a,b shows significant variations in the overall peak pattern. Peaks at 43.3° and 50.4° correspond to the crystal phase of (111) and (200) of Cu (JCPDS: 04-0836), while peaks at 36.4° correspond to the crystal phase of (111) of cuprite. This suggests that CuO was likely reduced to a mixture of Cu and Cu<sub>2</sub>O, which contradicts the XPS results. The discrepancy may be due to the limited detection depth (less than 10 nm) of XPS. A small amount of CuO was found on both spent electrodes, which did not participate in the reaction or reoxidize before the XRD test. Reviews on the phase of surface Cu species indicate that due to the presence of strongly oxidative species in electrolytes, cathodic reduction and reoxidation occur simultaneously, resulting in a dynamic equilibrium. The most active species are expected to be in the form of zero-valent copper, with some remaining as stable Cu<sup>+</sup> [16, 17]. The relative ratio of Cu<sup>2+</sup>, Cu<sup>+</sup>, and Cu<sup>0</sup> can be estimated from

the peak areas of their corresponding (111) plane. Notably, the Cu<sup>+</sup> content on the PVDC-modified electrode is almost three times higher than that on the unmodified electrode, which explains the higher ethylene yield of the CuO-PVDC electrode.

## 5. CONCLUSIONS

In conclusion, the amount of PVDC coating can be regulated to make the hydrophobic CuO electrode. A PVDC coating of only 50  $\mu\text{g}/\text{cm}^2$  over the CuO layer with a surface water contact angle of 122° has the best synergistic effect on the suppression of hydrogen and the formation of ethylene ( $\text{FE}_{\text{C}_2\text{H}_4}=41.4\%$ ,  $\text{FE}_{\text{H}_2}=22.7\%$ ,  $|j|_{\text{C}_2\text{H}_4}=6.8\text{mA}/\text{cm}^2$ , at a low potential of -0.89V vs. RHE), with the conductivity unaffected. We have confirmed that a small amount of PVDC coating could help to regulate the proton transfer rate and bind Cu electrocatalysts without affecting CO<sub>2</sub> permeability. Moreover, the ratio of Cu<sup>+</sup> and Cu<sup>0</sup> was larger on the spent CuO-PVDC electrode, resulting in the enhanced production of multicarbon products. This strategy could be useful for optimizing efficient catalysts for electrochemical reactions that are prone to electrolyte overflow.

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#### DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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