Selective CO-to-acetate electroproduction via intermediate adsorption tuning on ordered Cu-Pd sites

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Article

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Abstract

Electrochemical reduction of carbon monoxide (CO) has recently been emerging as a potential alternative for converting carbon emission into high-value multi-carbon products such as acetate. Nonetheless, the activity and selectivity for producing acetate have remained low. Herein, we developed an atomically ordered copper-palladium intermetallic compound (CuPd-IC) structure that achieved a high Faradaic efficiency of $70 \pm 5\%$ for CO-to-acetate production with a partial current density of $425 \text{ mA}\cdot\text{cm}^{-2}$. This corresponded to an acetate production rate of $4.0 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$, and 5.3 times of enhancement in acetate production compared to pure Cu. Structural characterizations and density functional theory calculations suggested that CuPd-IC presents a high density of Cu-Pd pairs that act as the active sites to enrich the surface CO coverage, stabilize the surface ethenone as a key acetate-path intermediate, and inhibit hydrogen evolution reaction, thus promoting acetate formation. Using a membrane electrode assembly device, the CuPd-IC catalyst enabled 100 hours of CO-to-acetate operation at $500 \text{ mA}\cdot\text{cm}^{-2}$ and an average acetate Faradaic efficiency of 43%, producing $\sim 2 \text{ mol}$ acetate.

Introduction

Acetic acid is a common chemical reagent for manufacturing various polymers, solvents, medicals, and foods. The global acetic acid market has reached ~ 17.3 million tons (MT) in 2019 and is projected to hit ~ 24.5 MT by 2025¹. Approximately 75% of acetic acid in chemical industry today is produced from the carbonylation process, in which methanol and carbon monoxide (CO) react to produce acetic acid, while also causing CO₂ emission^{2, 3}. Renewable-energy-powered electrocatalysis offers a unique net-zero-emission approach to produce acetic acid (in the form of acetate) by directly utilizing the CO₂-derived CO^{4, 5}.

However, the present Faradaic efficiency (FE) of electrochemical CO reduction reaction (CORR) for producing acetate remains below 50%⁵⁻⁷, far lower than the demanding profitable requirement modelled by techno-economic assessments⁴. Recent reports from Jiao and co-workers revealed that ethenone (*CH₂-C=O) is a key intermediate for acetate formation from CO electroreduction^{7, 8}. Given that ethenone interacts with Cu surfaces rather weakly⁷, the low acetate selectivity on Cu catalysts is likely to arise from the lack of sites that strongly adsorb the ethenone intermediate and promote acetate formation. To promote the formation of ethenone intermediate and subsequent acetate, we proposed that introducing palladium (Pd), a heteroatom that binds carbon-based species more strongly than Cu⁹, can greatly strengthen the interaction between catalysts and ethenone, modulate the reaction thermodynamics, and thereby favor acetate formation.

We began by developing an atomically-ordered CuPd-IC as an efficient CORR electrocatalyst toward acetate. Structural characterizations revealed that the obtained CuPd-IC structure featured alternately aligned rows of Cu and Pd atoms, providing a high density of Cu-Pd pairs without forming large-area Cu or Pd aggregations (Fig. 1a-c). This CuPd-IC catalyst was found to enable a high-selectivity-at-high-

current-density electrocatalytic CORR-to-acetate performance, with a corresponding FE of $70 \pm 5\%$ and a partial current density of $425 \text{ mA}\cdot\text{cm}^{-2}$. Compared to pure Cu, the CuPd-IC catalysts achieved 5.3 times of increase in acetate activity at -1.03 V vs. reversible hydrogen electrode (RHE). Furthermore, we operated a 100-hour CO electroreduction using the CuPd-IC catalyst in a membrane electrode assembly (MEA) device and obtained $\sim 2 \text{ mol}$ acetate production, equivalent to an average acetate FE of 43%. Moreover, density functional theory (DFT) calculations revealed that the Cu-Pd-constructed pair sites with ordered arrangements allowed to avoid either too weak or too strong ethenone adsorption on pure Cu or pure Pd sites, respectively. Compared to pure Cu sites, the Cu-Pd pairs enabled to increase the adsorption and coverage of surface CO, stabilize the ethenone intermediate, and thus promote acetate production (Fig. 1d).

Results And Discussion

Materials synthesis and characterization

The CuPd-IC catalyst was first synthesized by chemically reducing copper and palladium salts in a sodium borohydride solution, followed by annealing in argon gas to accelerate atomic displacement and form the atomically ordered structure (Methods in the Supplementary Information)¹⁰. For comparison, Cu_3Pd , disordered CuPd (d-CuPd), CuPd_3 alloys, and pure Cu and Pd nanoparticles, were also prepared in a similar approach using solutions containing metal species with corresponding ratios and concentrations. The X-ray diffraction (XRD) pattern of CuPd-IC exhibited a body-centred cubic phase with a series of distinctive diffraction peaks at 2θ of 29.88° , 42.77° , 53.05° , 62.09° , 70.42° , and 78.34° (Fig. 2a), corresponding to the (100), (110), (111), (200), (210) and (211) crystal planes of the ordered CuPd-IC structure (ICSD 181913). In contrast, the XRD spectra of Cu_3Pd , CuPd_3 , and disordered CuPd (d-CuPd) alloys presented broadened peaks between the (111) diffractions of pure Cu and Pd (Fig. 2b), confirming the formation of Cu-Pd alloys¹¹. The composition of each Cu-Pd alloy was conducted by scanning electron microscope energy-dispersive X-ray spectroscopy. The Cu/Pd molar ratios were determined as 1:1, 1:1, 3:1, and 1:3, for CuPd-IC, d-CuPd, Cu_3Pd , and CuPd_3 , respectively (**Supplementary Table 1**).

Transmission electron microscopy (TEM) images confirmed that the CuPd-IC sample had an average particle size of $\sim 50 \text{ nm}$ (**Supplementary Fig. 1**). In contrast, Cu, Pd, d-CuPd, Cu_3Pd , and CuPd_3 nanoparticles had similar particle sizes of $\sim 10 \text{ nm}$. TEM mapping analyses identified the co-existence and uniform distributions of Cu and Pd elements in those particles (**Supplementary Fig. 2–3**). The atomic structure of the CuPd-IC sample was further investigated by aberration-corrected high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The entire lattice presented highly ordered rectangular arrays with alternating bright and dark columns of atoms (Fig. 2c). Due to the difference of atomic numbers of Cu ($Z = 29$) and Pd ($Z = 46$), the Pd atom columns appeared much brighter than those of Cu atoms. The two perpendicular orientations of unit cells were highlighted and labelled (Fig. 2d). The (100) direction contained both Cu and Pd atoms in an alternating order, while the

(110) direction only had the same kind of atoms within each row. The intensity profile measured from the STEM images presented a periodic oscillation pattern (Fig. 2e), and the average peak-to-peak distances were 0.211 and 0.298 nm, corresponding to the Pd – Pd distances at (110) and (100) directions, respectively.

The chemical states of Cu and Pd species of the CuPd-IC were studied using X-ray photoelectron spectroscopy (XPS). Compared to pure Cu nanoparticles, the Cu 2p_{3/2} and 2p_{1/2} peaks of CuPd-IC upshifted 0.31 and 0.15 eV toward higher binding energy, respectively (**Supplementary Fig. 4a**), owing to the larger electron negativity of Pd than that of copper¹². Correspondingly, the Pd 3d_{5/2} and 3d_{3/2} peaks of CuPd-IC downshifted 0.28 and 0.25 eV, compared to pure Pd nanoparticles (**Supplementary Fig. 4b**). Besides, the surface valence band spectra of those Cu-Pd alloys showed that with the increase of the Pd fraction, the d-band center position of these samples exhibited an upshift toward the Fermi-level (**Supplementary Fig. 5**), which was beneficial for enhancing the adsorption of intermediate species^{13, 14}.

To precisely resolve the local structural information for Pd and Cu atoms, the samples were further characterized by X-ray absorption fine structure (XAFS) spectroscopy. For different Cu-Pd alloys, the Cu and Pd K-edge X-ray absorption near-edge structure (XANES) spectra were displayed, compared to those of the standard Cu and Pd foils. The Cu K-edge spectrum of the Cu-Pd alloys presented an absorption edge at 8979.0 eV (Fig. 3a, b), indicating a dominant metallic Cu feature. The Pd K-edge spectra of the Cu-Pd alloys were also examined and presented an absorption edge at 24,370.0 eV, indicating the feature of metallic Pd (**Supplementary Fig. 6**). Structural information about local atomic coordination was derived by fitting the extended X-ray adsorption fine structure (EXAFS) spectra, and the fitted structural parameters were summarized in **Supplementary Table 2**. The main peaks in both the Cu K-edge and Pd K-edge spectra of CuPd-IC fit well with the characteristics of the Cu – Pd bond, suggesting that the Cu – Pd bonds dominate the coordination environments of Cu and Pd atoms in CuPd-IC (**Supplementary Fig. 7**).

In addition, the Cu K-edge EXAFS spectra and fitting results were compared with those of different Cu-Pd alloys and standard Cu foil (Fig. 3c). The bond lengths of the Cu–Pd and Cu–Cu bonds were determined as ~ 2.58 and ~ 2.51 Å, respectively. For all the Cu-Pd alloys, the Cu coordination numbers (CNs) were calculated as ~ 8, while the CN ratios between Cu–Pd and Cu–Cu for were 7.2:0.5 (CuPd-IC), 4.8:3.1 (d-CuPd), 2.2:5.7 (Cu₃Pd), and 6.6:1.9 (CuPd₃), respectively (Fig. 3c). The highest ratio for CuPd-IC suggests its highest density of Cu-Pd pairs. Similar conclusion was also drawn from the Pd K-edge. The CuPd-IC showed the largest CN ratio between Pd–Cu and Pd–Pd bonds as 6.6:1.6 (**Supplementary Fig. 8** and **Supplementary Table 2**), confirming the existence of high-density Cu-Pd pairs within the CuPd-IC.

Further investigation using wavelet-transform EXAFS (WT-EXAFS) of Cu K-edge and Pd K-edge also confirmed the ordered Cu-Pd atomic arrangement in the CuPd-IC sample (Fig. 3d). WT-EXAFS analysis is useful for separating backscattering atoms, providing a radial distance and the k-space resolution¹⁵. For the Cu–Cu path, the WT maximum was at 7.53 Å⁻¹ for the copper foil, which rose to higher k-values of 8.55 for d-CuPd, and 9.80 Å⁻¹ for CuPd-IC, respectively. This increased k-value and intensity of CuPd-IC

suggested its higher Cu-Pd mixing degree compared to d-CuPd. Similarly, compared to d-CuPd ($8.39 \text{ \AA}^{-1}$) and pure Pd foil ($9.86 \text{ \AA}^{-1}$), the CuPd-IC presented a WT maximum at a k-value of $8.62 \text{ \AA}^{-1}$ (**Supplementary Fig. 9**), indicating a higher structural order around Pd sites of CuPd-IC than d-CuPd^{15, 16}.

CO electroreduction performance

The electrochemical CORR measurements of different Cu-Pd alloys were then conducted to investigate their catalytic performances. A flow-cell electrolyzer was used to break the low solubility limitation of CO in aqueous electrolytes for a high CO conversion rate (Methods in the Supplementary Information)^{17, 18}. For CuPd-IC (Fig. 4a, **Supplementary Table 3**), the total current density increased rapidly with increasing applied potential and reached $\sim 650 \text{ mA}\cdot\text{cm}^{-2}$ at -1.03 V vs. RHE, with a partial current density of $425 \text{ mA}\cdot\text{cm}^{-2}$ and a corresponding FE of $\sim 70 \pm 5\%$ for producing acetate (**Supplementary Table 3**), substantially superior to the state-of-the-art electrocatalysts for CO-to-acetate reduction⁵⁻⁷. A representative ¹H-NMR spectrum of the electrolyte after electrochemical CORR was displayed (**Supplementary Fig. 10**). In comparison, for pure Cu nanoparticles (Fig. 4b, **Supplementary Table 4**), although the total current density was over $800 \text{ mA}\cdot\text{cm}^{-2}$ at -0.88 V vs. RHE, the major reduction products were C_2H_4 and ethanol, with corresponding FE values of $43 \pm 2\%$ and $27 \pm 3\%$, respectively. The FE of acetate production was below 10% in the entire range of applied voltage.

To further explore the catalytic function of the Cu-Pd pairs, the CO electroreduction performances of CuPd-IC and other Cu-Pd alloys with different compositions and structures were measured and compared (**Supplementary Fig. 11–13** and **Supplementary Table 5–7**). The acetate selectivity showed a volcano type with the Pd content (Fig. 4c), in which the CuPd-IC presented the highest acetate selectivity compared to other Cu-Pd alloys. The excellent CORR performance of the CuPd-IC catalyst with high-selectivity-at-high-current-density was further translated to a high acetate production rate of $\sim 1.1 \text{ }\mu\text{mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ (Fig. 4d). In contrast, pure Pd was inactive for CO electroreduction due to its too strong CO adsorption^{12, 19}, and thus only H_2 evolution was observed (**Supplementary Fig. 14**).

To assess the potential toward commercially-relevant acetate manufacture, we conducted a long-term electrochemical test using a 5 cm^2 MEA electrolyzer equipped with CuPd-IC catalyst (Methods in the Supplementary Information). The MEA allowed to reduce the electrolyte ohmic losses and avoid electrolyte flooding through gas diffusion layer²⁰. The full cell voltage was well maintained between $-3.6 \pm 0.1 \text{ V}$ during a 100-hour continuous operation at a constant current density of $500 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 4e). The total acetate production was $\sim 2 \text{ mol}$, corresponding to an average acetate production FE of $\sim 43\%$.

Density functional theory calculations

Density function theory (DFT) calculations were conducted to obtain an atomic insight into the enhanced acetate activity and selectivity on the CuPd-IC catalyst. As CuPd(110) is the most stable surface of the ordered body-centered-cubic (BCC) CuPd alloy, while Cu(111) and Pd(111) are the most stable surfaces for the face-centered-cubic (FCC) Cu and Pd, respectively, these surfaces were employed as the model

systems. In order to examine the coverage effect, the adsorption free energies of various reaction intermediates were also calculated at a low coverage (0.06 monolayer, ML) and a high coverage (0.50 ML), respectively.

We started by checking the adsorption free energies of CO on CuPd(110), Cu(111) and Pd(111). The adsorption of CO on CuPd(110) is stronger than that on pure Cu (-0.06 eV), but weaker than that on pure Pd (-1.01 eV). For CuPd(110), it was found that CO prefers to locate on a hollow site consisting of two Pd atoms and one Cu atom, rather than that of a Pd atom and two Cu atom (i.e., CuPd₂ hollow site vs. Cu₂Pd hollow site, Fig. 5a). As shown in **Supplementary Table 8**, the adsorption free energies of CO on CuPd(110) are more negative as compared to that on the Cu(111) surface both at the low coverage (-0.78 eV vs. -0.06 eV) and at the high coverage (-0.49 eV vs. 0.02 eV), showing that CuPd-IC can bind CO more strongly to enrich CO on its surfaces as compared to pure Cu.

Then, the formation of acetate on CuPd(110) at both low and high surface coverages of *CO was examined. The reaction energetics were calculated based on the standard hydrogen electrode (SHE) model^{21, 22}, in which one-half of the chemical potential of hydrogen was used as the chemical potential of the proton-electron pair. The initial step was the formation of *CO–COH, which is a common intermediate proposed in the literature for the formation of the C₂₊ products^{23–26}. Afterwards, the acetate formation pathway, proposed by Luc *et. al.* for Cu(111)⁷, was employed. The free energy changes for the acetic acid formation on CuPd(110) at 0 V (vs. SHE) at the low coverage (blue curve in Fig. 5b) and the high coverage (red curve in Fig. 5b) are both presented (data in **Supplementary Table 9**), and the adsorption configurations of the intermediates are summarized (**Supplementary Fig. 15–16**). The results show that the ΔG for the C–C coupling is uphill by 1.53 eV at the low coverage, which is significantly decreased to 0.87 eV at the high coverage. For all the following steps, the ΔG values are more negative at the high coverage than those at the low coverage, and thus they shall overcome lower barriers according to the Brønsted–Evans–Polanyi relations^{27, 28}. In particular, for ethenone (*CH₂–C = O) that is considered as the key intermediate on the acetate formation pathway, the ΔG for the ethenone formation at the high coverage is -0.61 eV, significantly lower than that at the low coverage (-0.22 eV). Thus, a high coverage of *CO can further accelerate the acetate formation.

In addition to a stronger CO adsorption, the role of Pd in CuPd-IC in enhancing the acetate formation was also studied by comparing the acetate formation pathways on both CuPd(110) and Cu(111) surfaces (Fig. 5c), where only the results of free energy changes at the low coverage were presented. Starting from the CO–COH*, it was found that the ΔG of the ethenone formation is 0.04 eV on Cu(111) surface, but is -0.22 eV on CuPd(110) (Fig. 5c, **Supplementary Table 10**), suggesting that the introduction of Pd can stabilize ethenone, the key intermediate on the acetate formation pathway proposed in the literature^{7, 29}.

In addition, for alloys with Pd/Cu > 1, the aggregation of Pd atoms leads to more severe hydrogen evolution reaction. As shown in **Supplementary Table 11**, under 298.15 K and 105 kPa H₂ pressure, the hydrogen binding free energy was calculated to be 0.16 eV on Pd(111) with *CO coverage as high as 0.69

ML, much lower than that of 0.32 eV for *H on CuPd(110) with *CO coverage reaching 0.50 ML. Thus, we hypothesized that the highly ordered CuPd-IC presents a high density of the Cu–Pd pairs to minimize the Pd–Pd clustering, which allows to enrich the CO adsorption, stabilize ethenone and depress hydrogen evolution, thus leading to an efficient production of acetate.

Conclusion

In this work, we demonstrated that the atomically ordered CuPd-IC catalysts can substantially enhance the activity and selectivity for the CO-to-acetate electroreduction. Using the CuPd-IC catalysts, we achieved a record-high acetate-production partial current density of $425 \text{ mA}\cdot\text{cm}^{-2}$ and a corresponding acetate FE of $70 \pm 5\%$, substantially exceeding different disordered Cu-Pd alloys, pure Cu and Pd nanoparticles. An acetate production rate of $4.0 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ was obtained, indicating 5.3 times of improvement in acetate production activity compared to pure Cu. Our theoretical studies demonstrated that the Cu-Pd pair sites act as the active sites to enhance the CO adsorption, stabilize the ethenone intermediate, and depress hydrogen evolution, thereby substantially enhancing the acetate production pathway. This work suggests that introducing heteroatom dopants with well-controlled active-site structure can strongly affect the intermediate adsorption and reaction energy of an electrocatalytic process, which offers to produce more value-added chemicals from carbon emissions at commercially-relevant performance metrics.

Declarations

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Author contributions

G.Z. and X.X. proposed, designed, and supervised the project. G.Z., X.X., Y.J., Z.C. and Y.W. wrote the manuscript. Y.J., C.Y., J.X., A.G., J.C., T.-K.S., and J.L. performed the experiments and analyzed the data. Z.C. and X.X. performed the theoretical calculations. All the authors discussed, commented on, and revised the manuscript.

Competing interests

The authors declare no competing interests.

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Data availability

The data described in this paper are available from the authors upon reasonable request.

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Figures

Figure 1

Schematic illustration of the CuPd-IC with appropriate CO adsorption energy to enhance CO electroreduction to acetate. (a-c) CO adsorption on (a) pure Cu, (b) CuPd-IC and (c) pure Pd. (d) Schematic showing the proposed mechanism for CO reduction on CuPd-IC with the stabilization of ethenone ($^*CH_2-C=O$).

Figure 2

Structural characterizations of the Cu-Pd alloys. (a) XRD patterns of Cu (blue curve), Pd (green curve), and CuPd-IC (red curve). Inset: the corresponding crystal structure of CuPd-IC. (b) XRD patterns of Cu₃Pd, d-CuPd and CuPd₃ alloys. (c) Aberration-corrected HAADF-STEM images of CuPd-IC. (d) Magnified STEM images of the blue box in c. Inset: the schematics of CuPd-IC structure, where atoms in red and green

color represent Cu and Pd, respectively. (e) Intensity profiles measured from the HADDF-STEM images of CuPd-IC, corresponding to (110) and (100) directions, respectively.

Figure 3

XAS analysis of the Cu-Pd alloys. (a) Cu K-edge XANES spectra of Cu nanoparticles, Pd nanoparticles, CuPd-IC, d-CuPd, Cu₃Pd, and CuPd₃ alloys, in reference of Cu foil and Cu₂O. (b) The first derivatives of the spectra in a. (c) FT-EXAFS spectra fitting results (left panels) and coordination numbers (right panels)

of the Cu-Pd alloys at Cu K-edge. (d) WT-EXAFS spectra of CuPd-IC, d-CuPd, and Cu foil reference at Cu K-edge.

Figure 4

CO electroreduction performances. (a, b) Partial current densities and FE of each CORR product and H₂ of (a) CuPd-IC and (b) Cu, as a function of the applied potential in 1 M KOH. (c) FE values of acetate (upper panel), ethanol (middle panel), and C₂H₄ (lower panel) for Cu, Pd, and different Cu-Pd alloys at -0.98V

vs. RHE without iR-correction. (d) Comparison with reported literatures on current densities, FEs, and corresponding acetate production rates. Data of this work are indicated by red stars. (e) Continuous 100-h measurement using a 5 cm² MEA electrolyzer with a total current density of 500 mA·cm⁻². The electrolyte was 0.5 M KHCO₃.

Figure 5

DFT calculations. (a) Adsorption configurations and adsorption energies of *CO at Cu(111), CuPd(110) and Pd(111) surface. (b) Free energy evolution for acetic acid formation on CuPd(110) at 0 V (vs. RHE) at low coverage and at high coverage respectively. The energies of two *CO at low coverage (0.12 ML) and at high coverage (0.50 ML) are chosen as the references for LC and HC respectively. (c) Free energy evolution for acetic acid formation on Cu(111) and CuPd(110) at 0 V (vs. RHE).

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