

Electronic Supplementary Information for
Synergistic Effects of Pd and Cu for Production of Hydrogen and Formate via
Electrocatalytic Formaldehyde Oxidation

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1. Experimental section

1.1 Materials and chemicals

All chemical reagents were of analytical grade and used without further purification. Potassium hydroxide (KOH, 96%), sodium tetrachloropalladate(II) (Na_2PdCl_4), formic acid, acetylacetone (99.5%), and acetic acid (99.5%) were obtained from Aladdin Chemical Co. A formaldehyde aqueous solution (HCHO, 37 wt.% in H_2O , containing 10~15% stabilizer) was sourced from McLean Biochemical Co. Ethanol was procured from Shanghai Lingfeng Chemical Reagent Co.

1.2. Synthesis of Pd-Cu/ Cu_2O /CF

Synthesis of Cu/ Cu_2O /CF: The copper foam (CF) substrate was initially cut into $1 \times 1.5 \text{ cm}^2$ and immersed in 3 M HCl for 20 min to remove surface oxides and organic impurities. For Cu/ Cu_2O /CF synthesis, pretreated CF was immersed in 30 mL of 30 wt% H_2O_2 solution under ambient conditions for 12 h to facilitate surface oxidation. The resulting Cu/ Cu_2O /CF was washed with deionized water and ethanol washes, followed by vacuum drying at 60 °C.

Synthesis of Pd-Cu/ Cu_2O /CF: The Cu/ Cu_2O /CF was transferred into a glass vial containing 20 mL of 1 mM Na_2PdCl_4 aqueous solution. The reaction system was maintained at 80 °C in an oil bath for 1 h to facilitate Pd deposition. After natural cooling to room temperature, the resulting Pd-Cu/ Cu_2O /CF composite was thoroughly washed with deionized water and ethanol three times. Finally, the product was dried under vacuum at 60 °C for 12 h before structural and catalytic characterization. We also prepared various catalysts by adjusting the concentration of the Na_2PdCl_4 to investigate its effects on catalyst performance. The Pd-Cu/ Cu_2O /CMS was synthesized following the Pd-Cu/ Cu_2O /CF preparation procedure, except using a copper sheet instead of copper foam.

1.3. Characterizations

The ZEISS Gemini 500 Scanning Electron Microscope (SEM) was used to characterize the sample morphology. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained from a JEM-2100F. The crystal structure of the catalyst was obtained using a DX-2700 x-ray diffractometer (XRD). The elemental composition and electronic states of the catalyst were measured using an X-ray photoelectron spectroscopy (XPS) model ULVAC PHI quantimeter. UV-Vis absorption was obtained using a TU-1900 spectrophotometer. The gas phase products were analyzed using a gas chromatograph (GC-2014 Shimadzu). Liquid products were analyzed by collecting nuclear magnetic resonance (NMR) using an Avance III HD 500 (Bruker).

1.4. Electrochemical experiments

All electrochemical tests were done on a Koster electrochemical workstation CorrTest.CSSstudio. A three-electrode electrolytic system was constructed using an H-type electrolyzer with an anion-exchange membrane, where the working electrode was the prepared catalyst, and the counter and reference electrodes were graphite rods and Hg/HgO, respectively. The cathode and anode electrolytes were 1 M KOH and 0.3 M HCHO in 1 M KOH, respectively. Linear Scanning Voltammetry (LSV) curves were recorded after repeating the test until stabilization, at a scan rate of 5 mV/s. All FOR and HER tests were compensated with 95% iR to counteract the resistance of the electrolyte, and stirring was switched on to rapidly vent the gases generated on the catalyst surface. The i -t cycling stability test of FOR was carried out in 50 mL of electrolyte with 0.3 M HCHO in 1 M KOH. The two-electrode bipolar hydrogen production electrolysis system was carried out with Pd-Cu/Cu₂O/CF as the anodic catalyst and Pt/C/CF as the cathodic catalyst in a $1 \times 1 \text{ cm}^2$ flow cell

with a volume of 400 mL of electrolyte.

Determination of gas-phase products: The gas products were collected in the anode and cathode chambers of the H-type electrolyzer with Pd-Cu/Cu₂O/CF as the anode, Pt/C/CF as the cathode, and Hg/HgO as the reference electrode, respectively. The anodic electrolyte was 50 ml of 0.3 M HCHO in 1 M KOH, and the cathodic electrolyte was 50 ml of 1 M KOH; the test voltage was 0.1 V (RHE). The gas-phase products were analyzed using a gas chromatograph (GC-2014 Shimadzu).

Analysis of liquid phase products: 500 μ l of the electrolyte after anodic testing was added to 200 μ l of heavy water (D₂O) and mixed well, and then 520 μ L was removed and analyzed by nuclear magnetic resonance (NMR) using Avance III HD 500 (Bruker).

Faraday Efficiency: The Faraday efficiency is calculated from the volume of H₂ and the number of charges transferred Q obtained by the drainage method, with a laboratory ambient temperature of 25 °C. The formula is as follows:

$$FE\% = \frac{nF \times N}{Q} \times 100\%$$

where n is the number of electrons transferred per product molecule, F is the Faraday constant (96,485 C mol⁻¹), N is the number of moles of product, and Q is the total transferred charge.

Calculation formula for HCHO conversion:

$$\text{Conversion}\% = \frac{\text{HCHO consumed (mol)}}{\text{Total HCHO (mol)}} \times 100\%$$

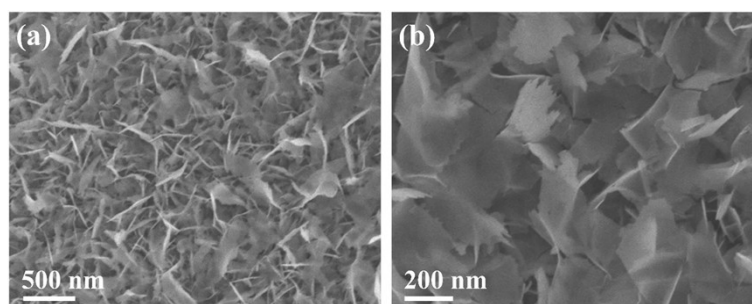


Fig. S1. (a) Low- and (b) high-magnification SEM images of Cu/Cu₂O/CF.

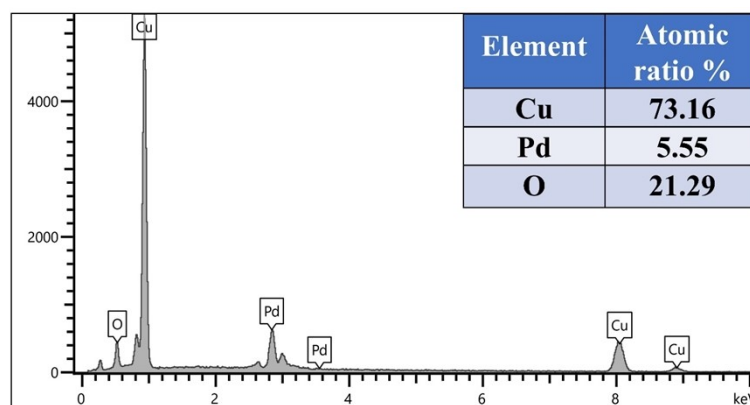


Fig. S2. EDS spectra and the atomic ratio for the elements of the Pd-Cu/Cu₂O/CF.

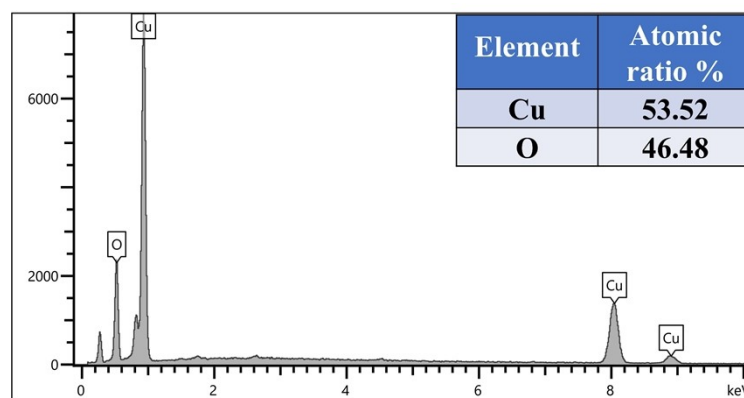


Fig. S3. EDS spectra and the atomic ratio for the elements of the Cu/Cu₂O/CF.

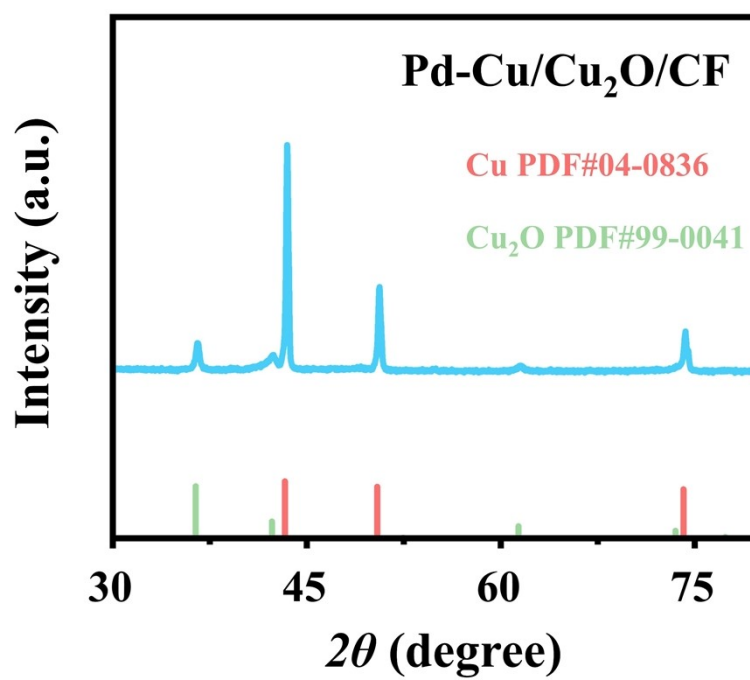


Fig. S4. XRD pattern of Pd-Cu/Cu₂O/CF.

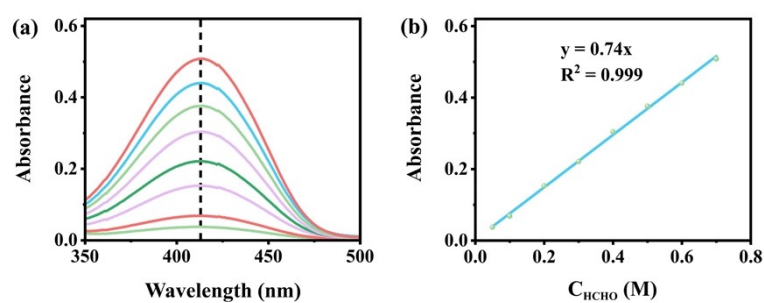


Fig. S5. (a) UV-vis absorption spectra of the product from the reaction between acetyl acetone and HCHO of different known concentrations. (b) The calibration curve was obtained by plotting the HCHO concentration against absorption peak intensity at $\lambda = 413$ nm.

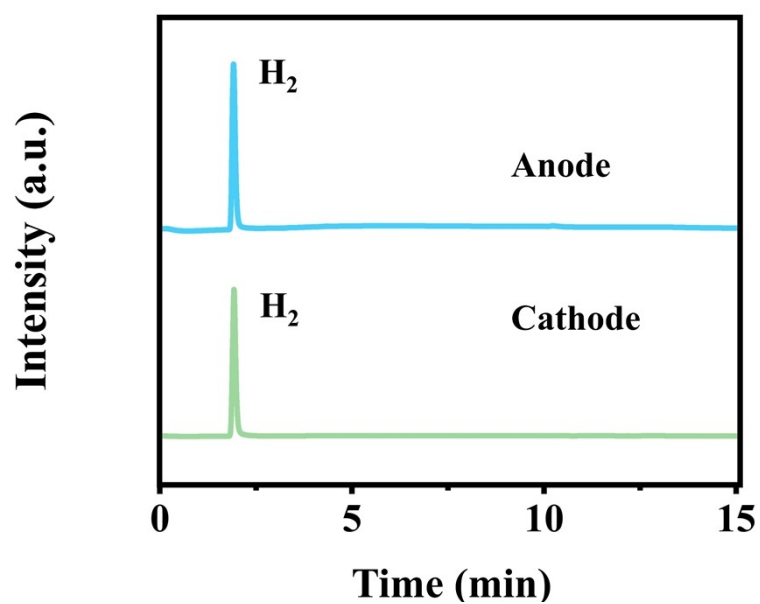


Fig. S6. GC spectra of gas phase products at cathode and anode.

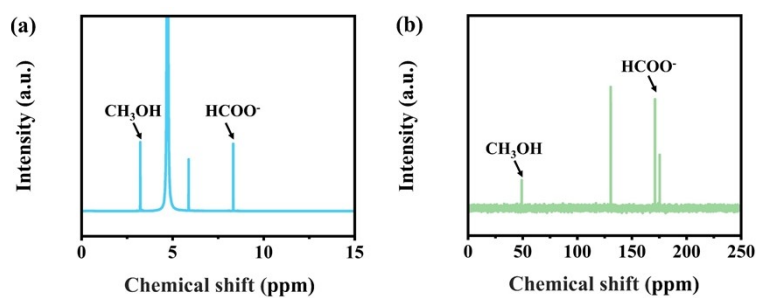


Fig. S7. (a) ^1H NMR and (b) ^{13}C NMR spectra of the anodic electrolyte after reaction at 0.1 V.

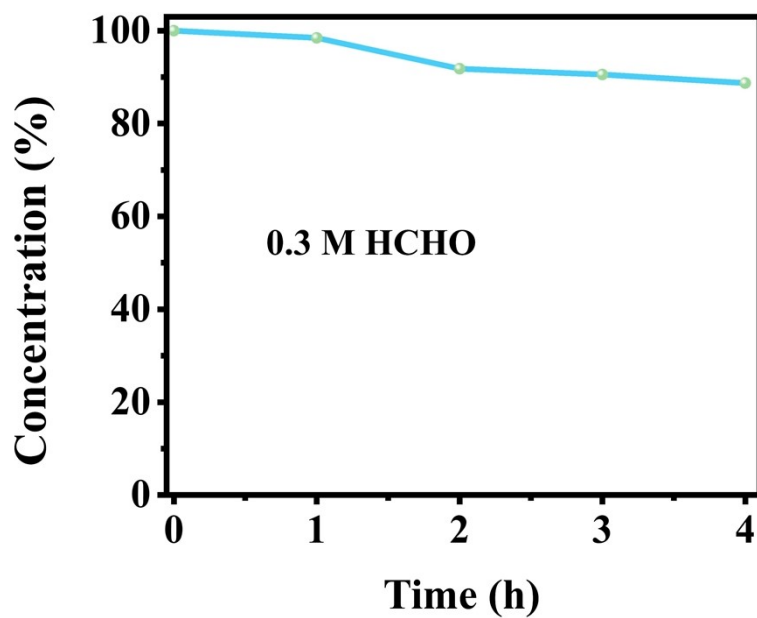


Fig. S8. Concentration change curve of 0.3M HCHO solution under standard conditions.

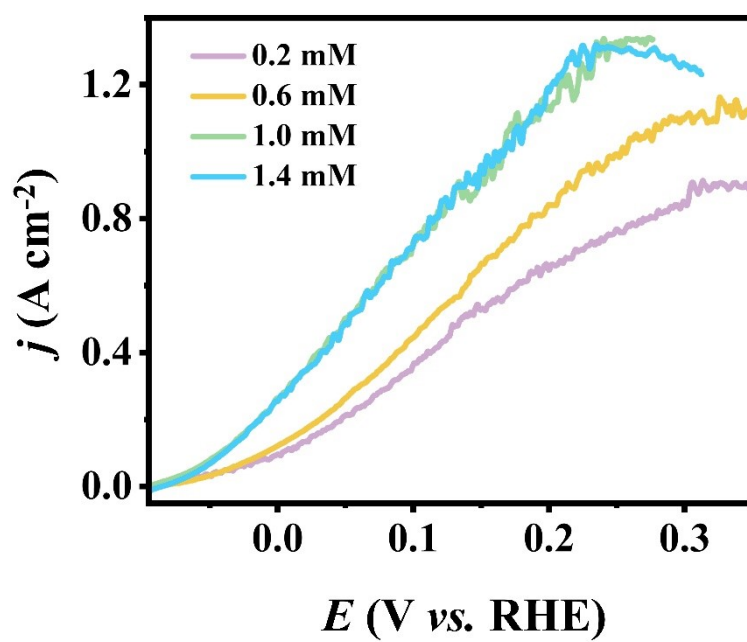


Fig. S9. LSV curves of catalysts prepared in Na_2PdCl_4 solution under different concentration conditions.

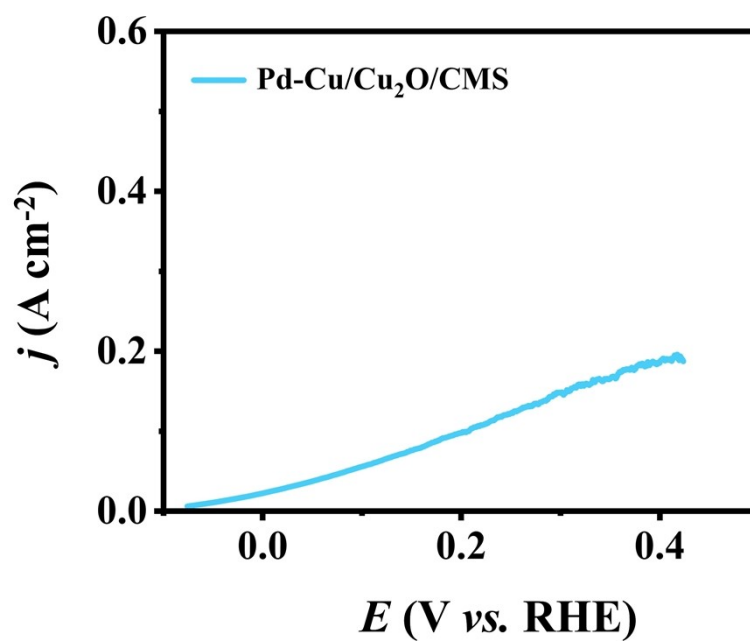


Fig. S10. LSV curve of $\text{Pd-Cu/Cu}_2\text{O/CMS}$.

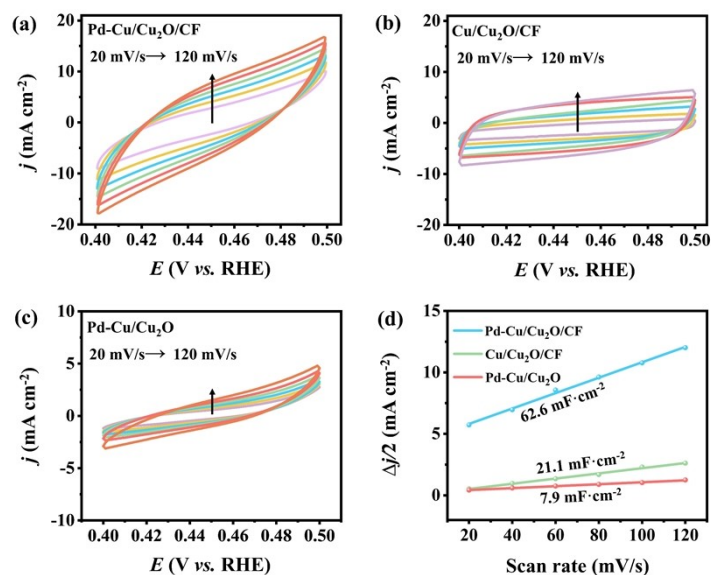


Fig. S11. (a-c) CV curves of Pd-Cu/Cu₂O/CF, Cu/Cu₂O/CF, and Pd-Cu/Cu₂O with scan rates from 20 mV/s to 120 mV/s and potentials between 0.4 V and 0.5 V (RHE) in 1.0 M KOH. (d) C_{dl} values of Pd-Cu/Cu₂O/CF, Cu/Cu₂O/CF, and Pd-Cu/Cu₂O.

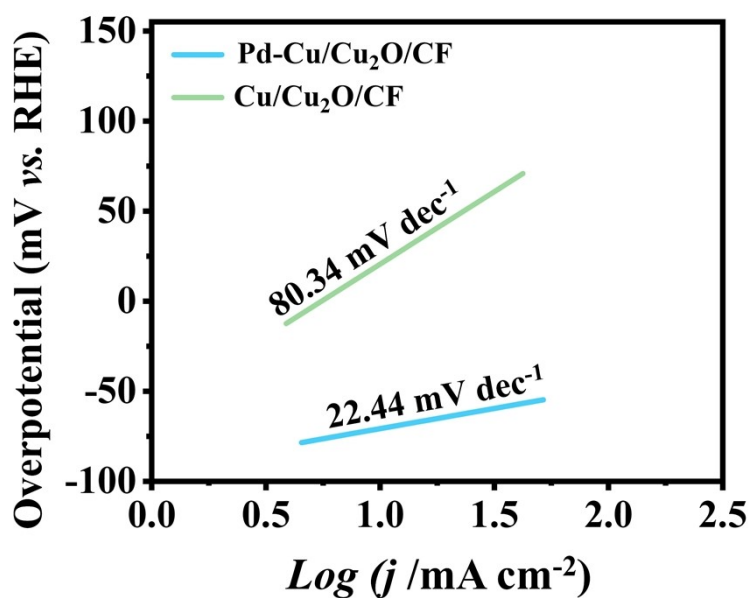


Fig. S12. Tafel curves of Cu/Cu₂O/CF and Pd-Cu/Cu₂O/CF.

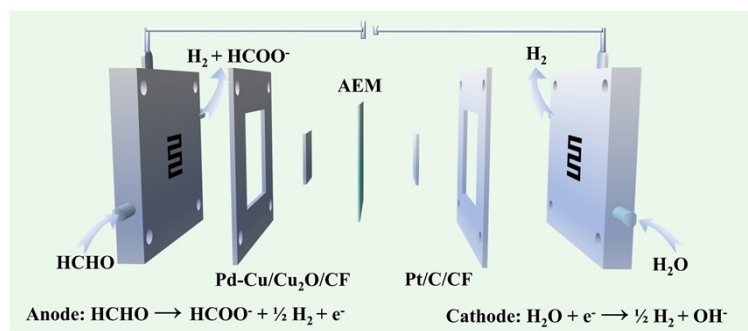


Fig. S13. Schematic illustration of the flow cell of the dual hydrogen production system.

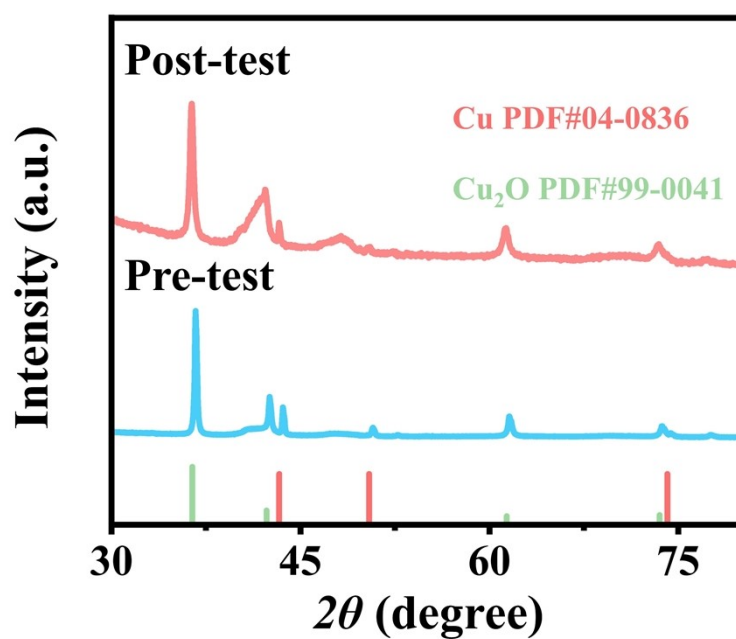


Fig. S14. XRD plots of catalysts before and after a long period of testing.