Supporting Information

For

An Acid-Alkaline Furfural Hybrid Battery for Furoate and Bipolar Hydrogen Production

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Experimental section

Materials. Commercial Cu foam (thickness: 2 mm) was purchased from Kunshan Xingzhenghong Electronic Materials Co., Ltd. Carbon paper (thickness: 0.19 mm, porosity: 78%) were purchased from Toray Industries, Inc. Potassium hydroxide (KOH, AR), sodium hydroxide (NaOH, AR), ammonium persulfate ($(NH_4)_2S_2O_8$, AR), sulfuric acid (H_2SO_4, AR), and sodium sulfate (Na_2SO_4, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Furfural (98%) and commercial 20 wt% Pt/C powder were obtained from Shanghai Macklin Biochemical Co., Ltd. Chloroplatinic acid ($H_2PtCl_6 \cdot xH_2O$, AR), dimethylsulfoxide (DMSO, 99.9%) and deuterated water (D_2O, 99.9%) were purchased from Sigma Aldrich Co., Ltd. Dupont proton exchange membrane (PEM, Nafion N115 and N117) and 5 wt% Nafion solution were purchased from Suzhou Sinero Technology Co. Ltd. The distilled water (10-15 MΩ·cm) used throughout all experiments was purified through a Millipore system.

Preparation of Cu(OH)$_2$ on Cu foam. Cu(OH)$_2$ nanorods self-supported on Cu foam were prepared by a wet chemical oxidation method. To be specific, a piece of Cu foam (1 cm × 2 cm) was ultrasonically cleaned in acetone and 1 M H_2SO_4 for respective 15 min in sequence. The pretreated Cu foam was then immersed in 10 mL solution containing 0.34 g $(NH_4)_2S_2O_8$ and 1 g NaOH for 15 min. The resulted Cu(OH)$_2$ nanorods on Cu foam were finally washed by distilled water and then dried under an infrared heating lamp.

Preparation of Pt-Cu on Cu foam. The Pt-Cu nanorods on Cu foam were prepared by an electrochemical co-reduction approach (similar as our previous work, *Chem. Eng. Sci*. **2022**, *258*, 117769). Specifically, the electroreduction process was conducted at a constant voltage of 3 V for 30 min at ambient temperature in a two-electrode system, wherein the obtained Cu(OH)$_2$ on Cu foam, a Pt sheet and 50 mL of 1 M KOH/0.1 mM H_2PtCl_6 mixed solution were used as the cathode, anode and electrolyte, respectively. After the reaction, the obtained Pt-Cu nanorods on Cu foam were washed by distilled water and subsequently preserved in ethanol. The mass loadings of Pt and Cu were *ca.* 0.32 and 9.02 mg cm^{-2}, respectively, determined by inductively coupled plasma optical emission spectrometer (ICP-OES).

Preparation of Cu on Cu foam. The synthesis of Cu metal nanorods on Cu foam was the same as that of the Pt-Cu, except for the absence of H_2PtCl_6.

Preparation of commercial 20 wt% Pt/C on carbon paper. 1.6 mg commercial 20 wt% Pt/C powder was dispersed in a mixed solution containing 100 µL distilled water, 100 µL isopropanol and 10 µL 5 wt% Nafion solution with an ultrasonic powder of 40 kHz for at least 1 h to form the homogeneous ink. The whole ink was then drop-casted onto a piece of carbon paper (1 cm × 1 cm) under the infrared heating lamp. Finally, the commercial Pt/C catalyst which the mass loading of Pt was *ca.* 0.32 mg cm^{-2} was obtained.

Physical characterization. Scanning electron microscopy (SEM) images were recorded on a HITACHI S-4800. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were collected on a FEI Tecnai F30. X-ray diffraction (XRD) patterns were recorded by Rigaku Ultima-IV XRD with Cu-Kα radiation ($\lambda = 1.5405$ Å). X-ray photoelectron spectroscopy (XPS) analysis was performed on Thermo Fisher ECSALAB Xi+ with Al-Kα as radiation source. ICP-OES was conducted on Agilent 7800. Nuclear magnetic resonance (NMR) spectra were collected by Bruker Avance III 500 MHz.

Electrochemical test. Furfural oxidation reaction (FOR) was tested *via* a Chenhua electrochemical workstation (CHI660E) in a H-type electrolytic cell, wherein a Cu foam with catalyst loading, a Pt sheet and a Hg/HgO electrode were used as working, auxiliary and reference electrodes, respectively. Catholyte was 1 M KOH while anolyte was 1 M KOH/0.2 M furfural mixed solution. They were separated by a Nafion 117 PEM. The anolyte was continuously stirred with 1000 rpm throughout the tests to minimize mass transport limits. The potential with regard to Hg/HgO reference electrode was converted to reversible hydrogen electrode (RHE) by cyclic voltammetry in H$_2$-saturated electrolytes using Pt sheets as both the working and auxiliary electrodes (*Adv. Mater.* **2019**, *31*, 1806296). All the linear sweep voltammetry (LSV) curves were recorded at 10 mV s^{-1} and converted to RHE with 100% iR_s compensation. The R_s was obtained by electrochemical impedance spectroscopy (EIS). Tafel plots were derived from LSV curves. Chronopotentiometry and chronoamperometry tests were used to evaluate the FOR stability.

Assembly of an acid-alkaline furfural hybrid battery. The acid-alkaline furfural hybrid battery was assembled in a membrane electrode flow reactor, wherein the Pt-Cu on Cu foam (1 cm × 1 cm) and commercial 20 wt% Pt/C on carbon paper (1 cm × 1 cm) were used as the anode and cathode, respectively. They were separated by a K$^+$ exchange membrane (transformed from a Nafion N115 PEM in 1 M KOH at 60 °C beforehand).

Catholyte was 1 M H_2SO_4 while anolyte was 1 M KOH/0.2 M furfural, and their flow rates were controlled to be 150 mL min^{-1} by a peristaltic pump. Two pieces of TA1-type titanium metal, engraved with single serpentine flow channel, were used as bipolar plates. Chronopotentiometry was employed to evaluate the stability. Discharging power densities were equal to current densities times voltages. Internal resistance of the battery was measured by EIS. In the **Movie S1**, we use two organic glass plates with single serpentine flow channel as bipolar plates and copper tape as wires.

Quantification of H_2. The generated H_2 *via* FOR or hydrogen evolution reaction (HER) was quantified by a water drainage method (see digital photographs in Fig. S10, S14 and S15, *Energy Environ. Sci*. **2020**, *13*, 86). Specifically, the generated H_2 in the sealed H-type electrolytic cell or acid-alkaline furfural hybrid battery was flowed into an inverted cylinder with saturated distilled water or electrolytes through connected silicone tubes. The volume of H_2 can thus be read timely.

Quantification of furoate. The generated furoate were quantified by ^1H NMR using DMSO as an internal standard. 500 µL anolyte was added into 100 µL DMSO/D_2O (0.1 vol%) in the NMR tube. We have subtracted the produced furoate (equivalent to furfuryl alcohol) *via* Cannizzaro disproportionation when furoate Faradaic efficiencies were calculated.

Faradaic efficiency calculation. Faradaic efficiencies of furoate and H_2 were calculated on the basis of the following equation.

$$FE = nzF/It \times 100\% \tag{1}$$

where n is the mole number of products, z is the number of transferred electrons of FOR or HER, F is Faraday constant (96485 C mol^{-1}), I is current and t is time.

Electricity consumption calculation. Electricity consumption (kWh Nm^{-3} H_2) was calculated based on the following equation.

$$W = UnzF/3600000 \tag{2}$$

where W is the electricity consumed for 1 m^3 H_2 production at the normal temperature and pressure (kWh Nm^{-3} H_2), U is the input/output voltage at 100 mA cm^{-2}.

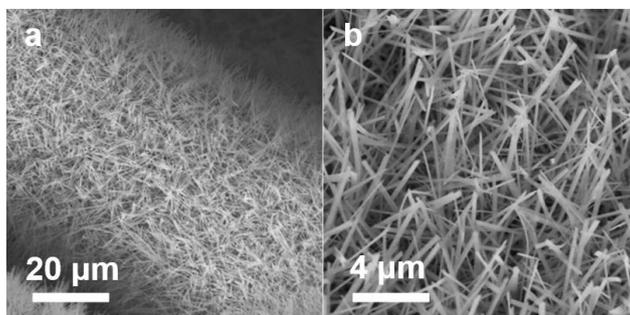**Additional figures**

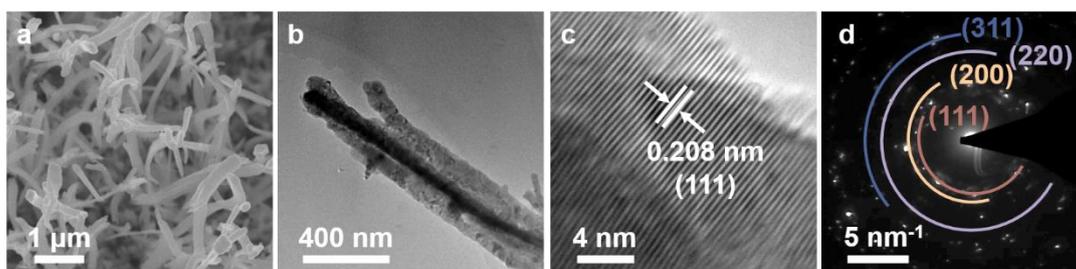**Fig. S1** SEM images of Cu(OH)$_2$ nanorods.

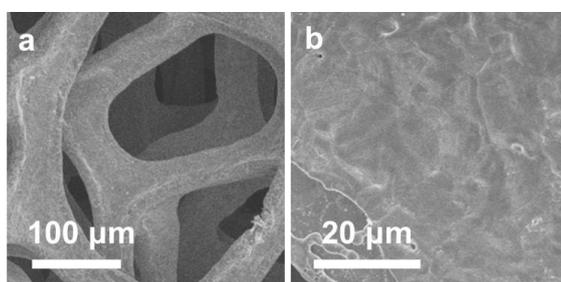**Fig. S2** (a) SEM, (b) TEM, (c) HRTEM images and (d) SAED pattern of Cu nanorods.

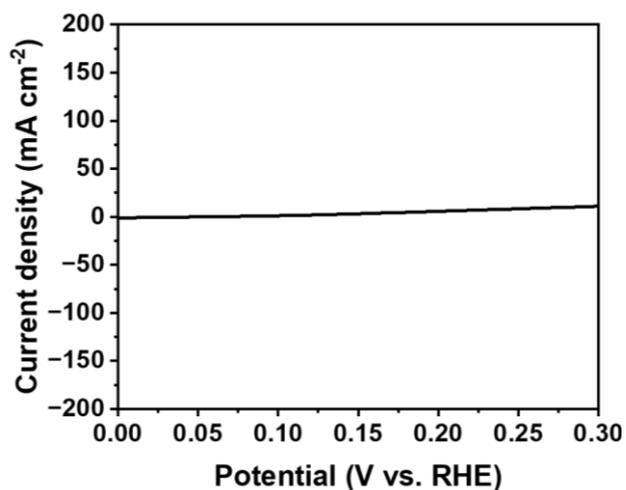**Fig. S3** SEM images of the bare Cu foam substrate.

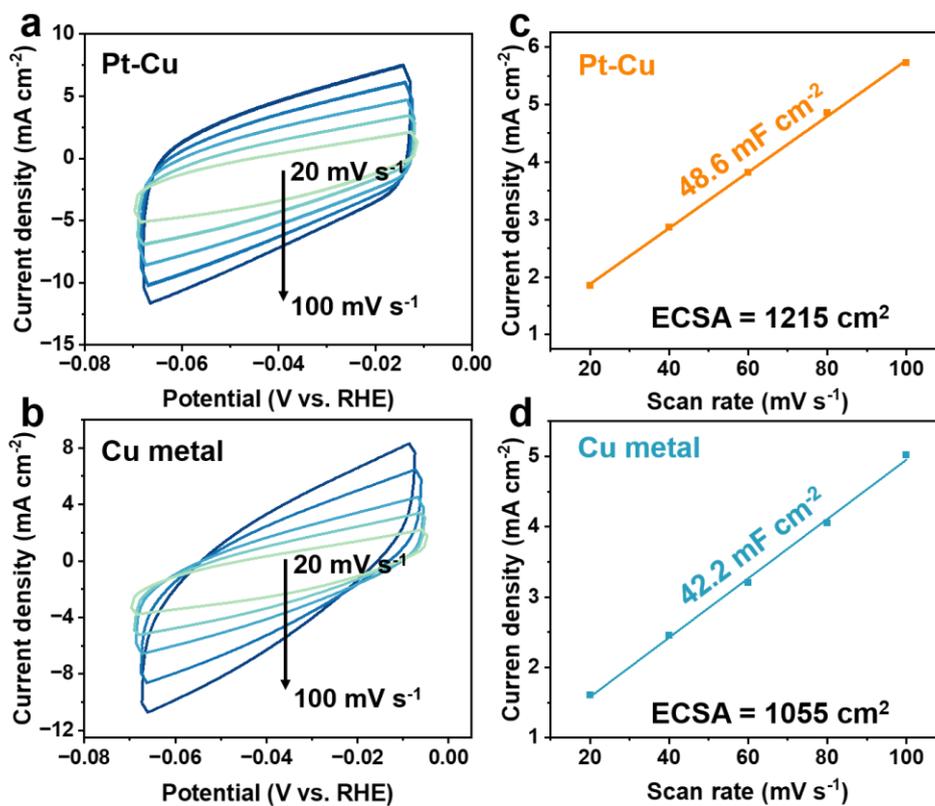**Fig. S4** The LSV curve of the bare Cu foam substrate in 1 M KOH and 0.2 M furfural mixed electrolyte.

Fig. S5 (a, b) CV curves within non-Faradaic regions and (c, d) the calculated specific C_{dl} of the Pt-Cu and Cu catalysts.
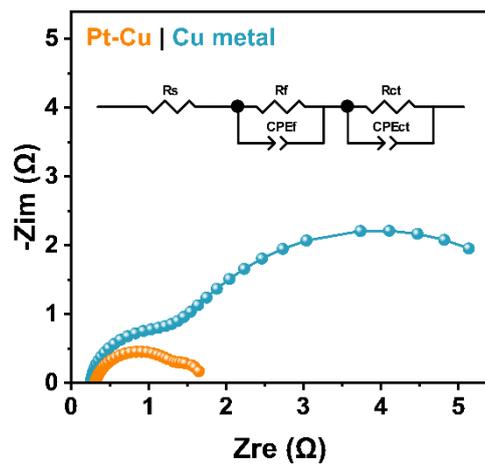
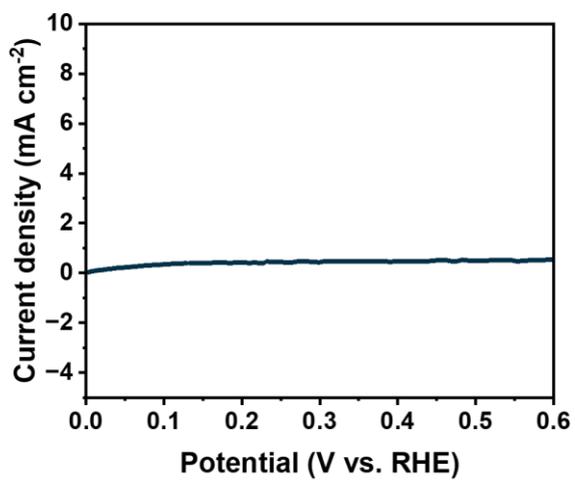**Fig. S6** EIS spectra of the Pt-Cu and the Cu catalysts at 0.02 V *vs.* RHE.

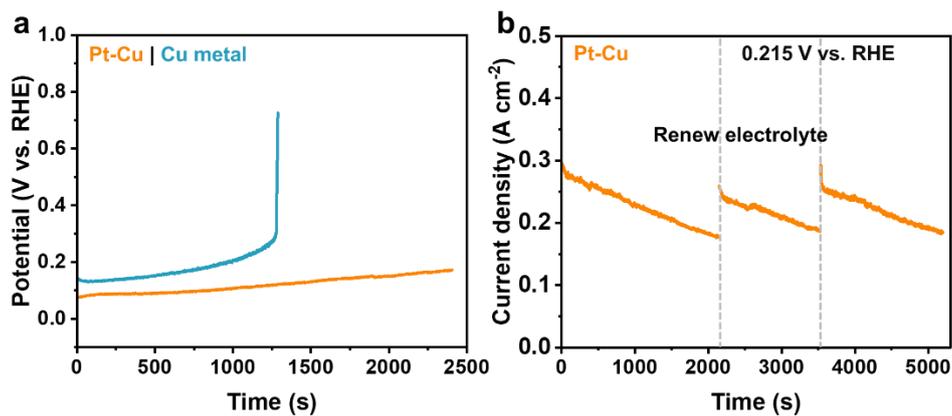**Fig. S7** FOR LSV curve of the commercial Pt/C catalyst on carbon paper.

Fig. S8 (a) Chronopotentiometry curves of the Pt-Cu and Cu catalysts at 100 mA cm^{-2} and (b) chronoamperometry curves of the Pt-Cu catalyst at 0.215 V *vs.* RHE.
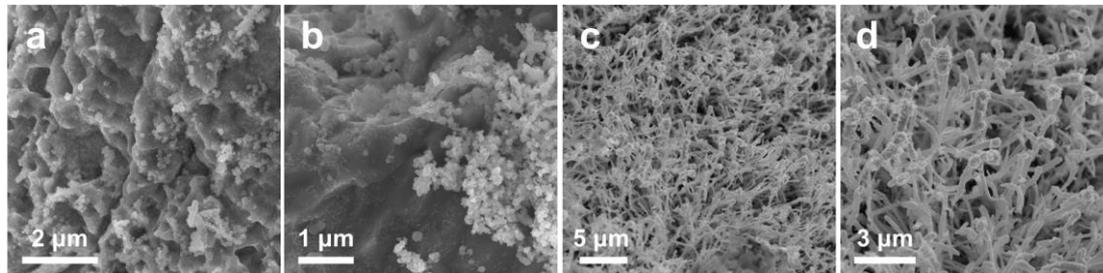

Fig. S9 SEM images of the (a, b) Cu, and (c, d) Pt-Cu catalysts after the FOR.
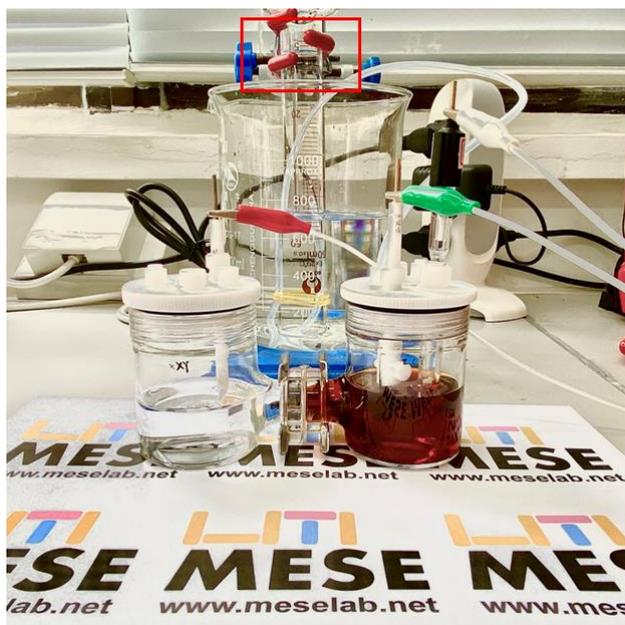
Fig. S10 Digital photograph of the set-up of an H-type electrolyzer to measure H_2 Faradaic efficiency at the anode.
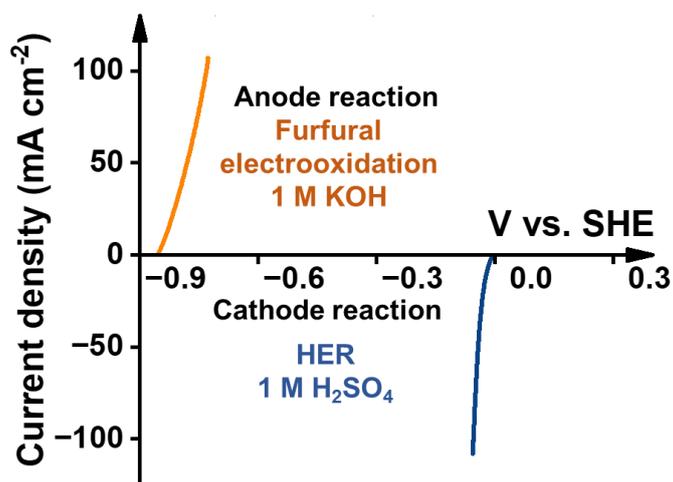

Fig. S11 Half-electrode LSV curves of the acid-alkali furfural hybrid battery by using Pt-Cu catalyst as the anode and commercial Pt/C as the cathode.
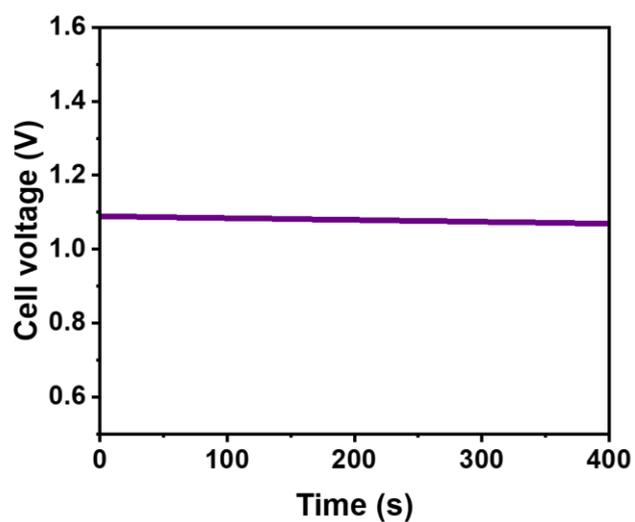
Fig. S12 The open circuit voltage curve of the acid-alkaline furfural hybrid battery.
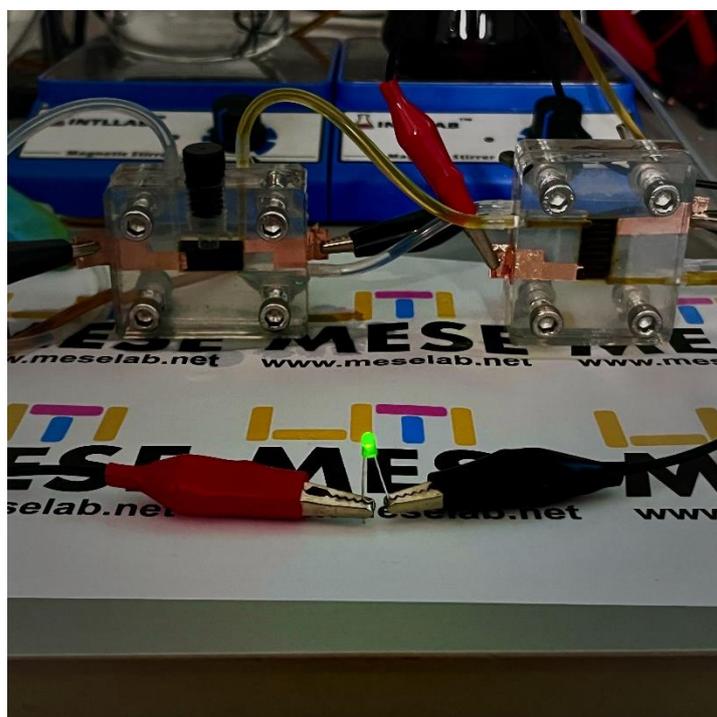

Fig. S13 Digital photograph showing the LED light bulb lit by two tandem acid-alkaline furfural hybrid batteries.

Fig. S14 Digital photograph of the set-up of the acid/alkaline furfural hybrid battery to measure H$_2$ Faradaic efficiency at both the cathode and anode.

Fig. S15 Digital photograph of the set-up of the two acid/alkaline furfural hybrid battery in series to measure H$_2$ Faradaic efficiency at both the cathode and anode by directly connecting the cathode and anode.
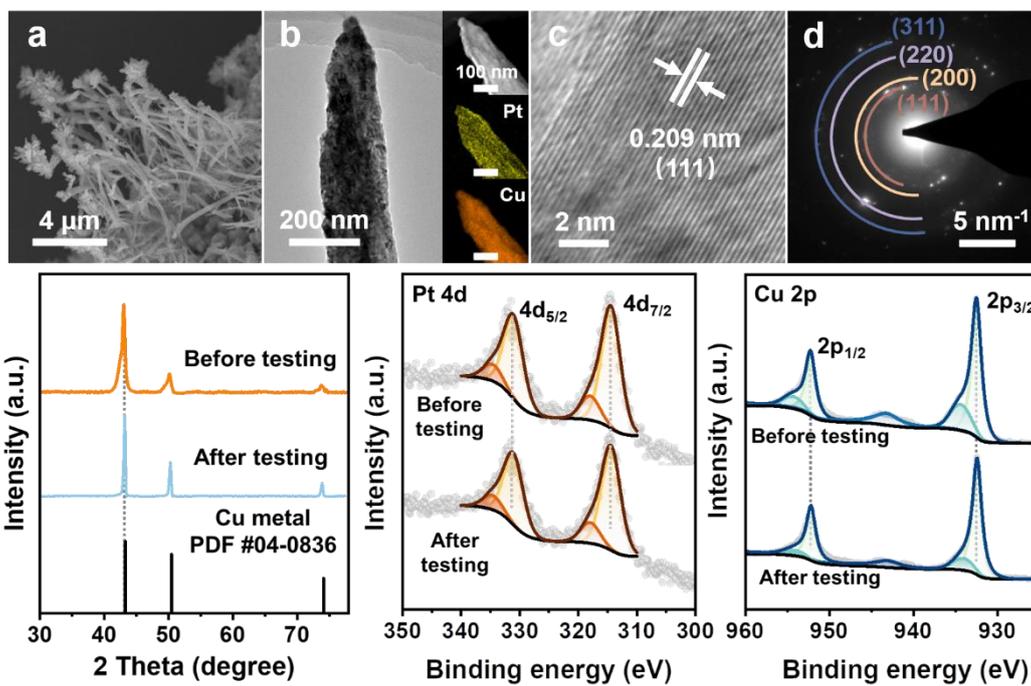
Fig. S16 Post physical characterizations of the Pt-Cu catalyst. (a) SEM, (b) TEM, (c) HRTEM images, (d) SAED, (e) XRD patterns, (f) Pt 4d and (g) Cu 2p XPS spectra.

Additional tables

Table S1. Performance comparison of aldehyde oxidation reaction of the Pt-Cu catalyst with other recently reported catalysts.

Catalyst	Aldehyde	Activity (V *vs.* RHE @ 100 mA cm^{-2})	Reference
Pt-Cu	Furfural	0.076	*This work*
Cu$_x$O	Formaldehyde	0.136	*Chem*, **2023**, 10.1016/j.chempr.2022.12.008.
CuAg	Furfural	0.210	*Energy Environ. Sci.* **2022**, 15, 4175.
Cu$_3$Ag$_7$	Formaldehyde	0.220	*Nat. Commun.* **2023**, 14, 525.
Cu	Furfural	0.381	*Angew. Chem. Int. Ed.* **2022**, 61, e202115636.
Cu	HMF	0.115	*Nat. Catal.* **2022**, 5, 66.
Pd	Formaldehyde	0.67	*Nat. Catal.* **2023**, 10.1038/s41929-023-00923-6.

Table S2. The comparison of cell voltage and electricity consumption of energy-saving hydrogen production systems at 100 mA cm^{-2}. Note: Negative values represent cell voltage output or electricity generation.

Reaction type	Voltage input (V)	Electricity consumption (kWh Nm^{-3} H$_2$)	Reference
Acid-alkali furfural hybrid battery	-0.47	-0.56	*This work*
Alkaline furfural fuel cell	-0.74	-1.77	*Angew. Chem. Int. Ed.* **2022**, 134, e202115636
Alkaline water electrolyzer	1.58	3.78	*Energy Environ. Sci.* **2021**, 14, 6546.
	1.73	4.14	*Energy Environ. Sci.* **2022**, 15, 4048.
	1.72	4.11	*Energy Environ. Sci.* **2022**, 15, 185.
Alkaline hydrazine electrolyzer	0.23	0.55	*Angew. Chem. Int. Ed.* **2022**, 61, e202113082.
	0.24	0.57	*Nat. Commun.* **2021**, 12, 4182.
	0.21	0.50	*Sci. Adv.* **2020**, 6, eabb4197.
Alkaline low-voltage-driven aldehyde electrolyzer	0.21	0.50	*Energy Environ. Sci.* **2022**, 15, 4175.
	0.13	0.31	*Nat. Commun.* **2023**, 14, 525.
	0.27	0.65	*Nat. Catal.* **2022**, 5, 66.
Alkaline HMF electrolyzer	1.67	3.99	*Adv. Mater.* **2020**, 32, 2000455.
	1.63	3.90	*Angew. Chem. Int. Ed.* **2016**, 55, 9913.
	1.64	3.92	*J. Am. Chem. Soc.* **2016**, 138, 13639.
Alkaline urea electrolyzer	1.55	3.71	*Energy Environ. Sci.,* **2018**, 11,1890.
	1.54	3.68	*Adv. Funct. Mater.* **2021**, 31, 2104951.
	1.35	3.23	*Nat. Energy,* **2021**, 6, 904.
Alkaline sulfide electrolyzer	0.58	1.39	*Adv. Mater.* **2022**, 34, 2109321.
	0.64	1.53	*Green Chem.* **2021**, 23, 6975.
	0.62	1.48	*Energy Environ. Sci.* **2020**, 13, 119.
Alkaline alcohol electrolyzer	1.46	3.49	*Energy Environ. Sci.* **2022**, 15, 5300.
	1.78	4.26	*Adv. Funct. Mater.,* **2017**, 27, 1704169.
	1.08	2.58	*Nat. Commun.* **2022**, 13, 147.