Constructing Fecal-derived Electrocatalysts for CO₂ Upcycling: Simultaneously Tackling Waste and Carbon Emissions

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Methodology

Materials and synthesis

Materials

The hydrothermal biochar processed at 300°C (35%~40% productivity from dry pig manure) used in this study was sourced from the Nanjing Zhongshan Botanical Garden at the Jiangsu Institute of Botany, Chinese Academy of Sciences. The KOH (≥99.99%) was purchased from Aladdin; copper acetylacetonate (97%) was purchased from Meryer; Nafion solution (5 wt.% in a mixture of lower aliphatic alcohols and water, containing 45% water) was from Macklin; ethanol (AR, ≥99.7%) and urea (AR, ≥99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd.; activated carbon (specifically for raw pharmaceuticals) was purchased from ACMEC.

Sythesis of Cu-biochar catalyst

We added varying amounts of copper acetylacetonate (100 mg, 200 mg, 300 mg, 400 mg, 500 mg, 800 mg, 1000 mg, 1200 mg, 1500 mg, 2000 mg, and 4000 mg), along with 1.0 g KOH and 0/1.5/3 g urea, to 0.5 g of 300°C hydrothermally treated pig manure biochar. The mixture was thoroughly ground and then calcined at 800°C for 2 hours under a nitrogen atmosphere at a heating rate of 5°C/min. After calcination, the catalyst powder was washed with ultrapure water, filtered, and dried, yielding the catalyst powder Cu-NB-x (where x represents the amount of copper acetylacetonate in mg). The group with 3 g urea added was labeled as Cu-3NB-x. We also substituted pig manure biochar with activated carbon to prepare the activated carbon comparison group, labeled Cu-NC-x, and an unmodified control group without urea, labeled Cu-B-x.

Characterization

SEM was performed on a JEOL JSM-7800F. TEM was conducted on a JEOL JEM-2800 at 200 kV. XRD data was collected using a Shimadzu XRD-6000 with Cu Kα (λ = 1.5418 Å). XPS was performed using a PHI5000 Versaprobe. Specific surface area measurements were conducted on a Micromeritics ASAP 2460 analyzer.

Preparation of electrodes

To prepare the working electrode, We dispersed 2.5 mg of catalyst in 250 μL of ethanol, then added 7.5 μL of Nafion solution, and ultrasonicated the mixture for 1 hour to form a uniform ink. Then, 250 μL of catalyst ink was evenly drop-cast on a 2.5 cm x 1 cm carbon paper (SGL Sigracet 29BC) and dried at room temperature. The Cu-UB-x group was replaced with the Cu-UC-x and Cu-B-x groups for control measurements using the same preparation method. The geometric area of contact between the working electrode and the electrolyte was 1 cm², and the catalyst loading on the carbon paper was 1 mg/cm². Nickel foam (Alfa Aesar, 20 ppi) was used as the counter electrode, and an Ag/AgCl electrode (40 mm long, Innovative Instruments) served as the reference electrode.

Electrochemical Measurements

We conduct electrochemical measurements in a flow cell. The electrolysis cell consisted of an anode and a cathode flow chamber, separated by a hydroxide exchange membrane (Fumatech, FAA-3-PK-130), with the gas diffusion layer cathode and nickel foam anode. A 1 M KOH aqueous solution was used as both the catholyte and anolyte. The electrolyte flow rate was controlled by a piston pump (Agilent 1260 series). The cathode potential was measured against an external Ag/AgCl reference electrode (CHI, 3 M KCl) and converted to the RHE value using the formula: E(RHE)=E(Ag/AgCl)+0.197V+0.0592×pH. The gas flow rate into the flow cell was set to 40 sccm using an Alicat MC mass flow controller. The gas products were quantified using a gas chromatograph (GC) with a Molsieve 5 Å column connected to a thermal conductivity detector (TCD) and an HP-PLOT Q column connected to a flame ionization detector (FID). Liquid-phase products, including formic acid, ethanol, acetic acid, and propanol, were measured using Nuclear Magnetic Resonance (NMR, Bruker AVANCE III 500 MHz). FE was calculated using the formula:

$$E_{faradaic} = \frac{-\alpha nF}{Q}$$

Where:
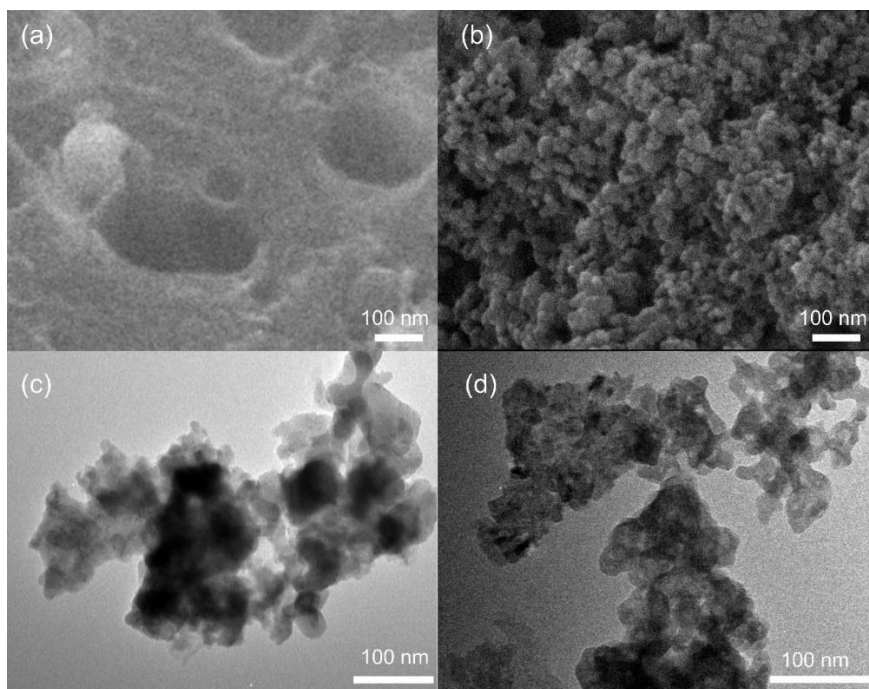
α: the number of electrons transferred to produce a particular product;

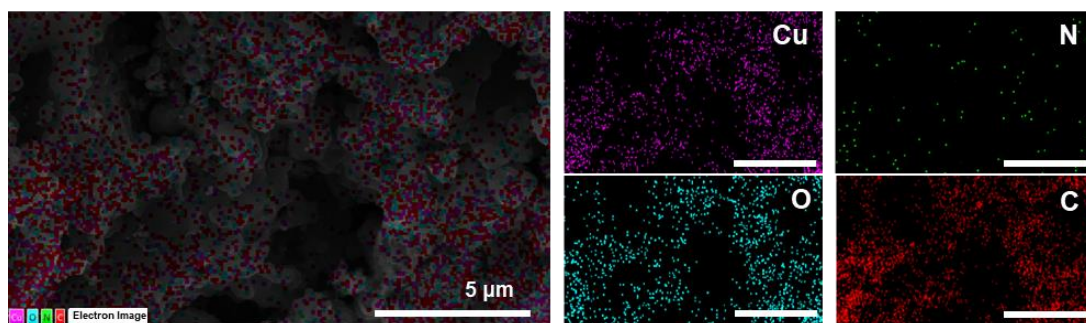n : the molar amount of the resulting product,

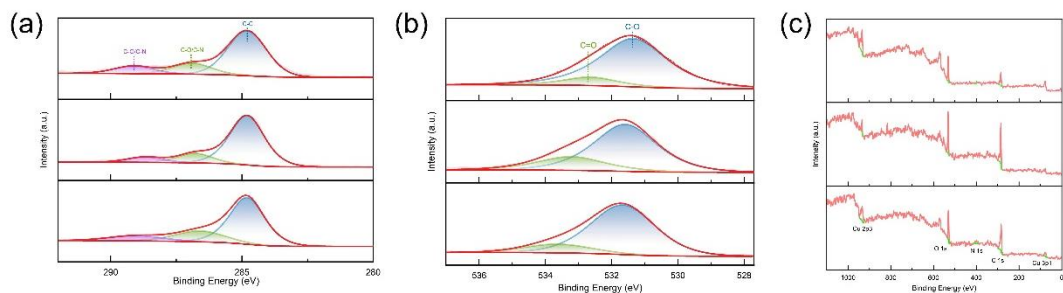F : Faraday's constant (value of 96,485 C-mol^{-1})
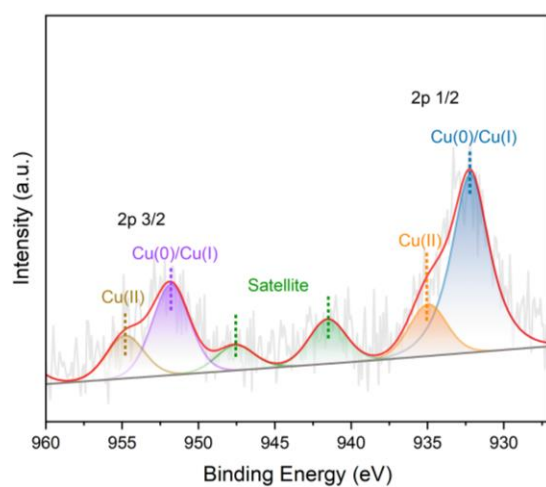
Q : the total amount of charge transferred.

Figure S1: SEM images of (a) Cu-B-2000 (b) Cu-NC-2000; TEM images of (c) Cu-B-2000 (d) Cu-NC-2000.
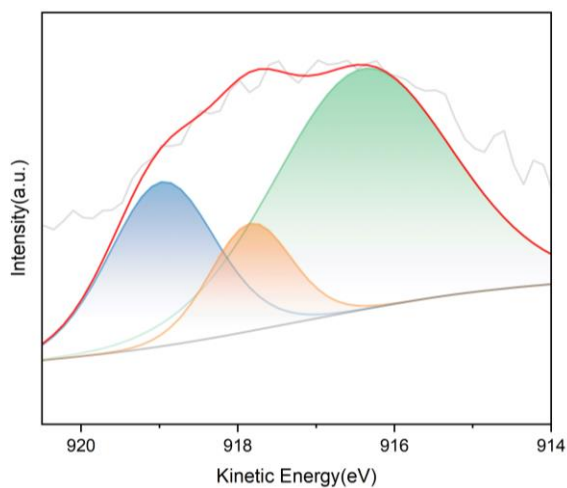

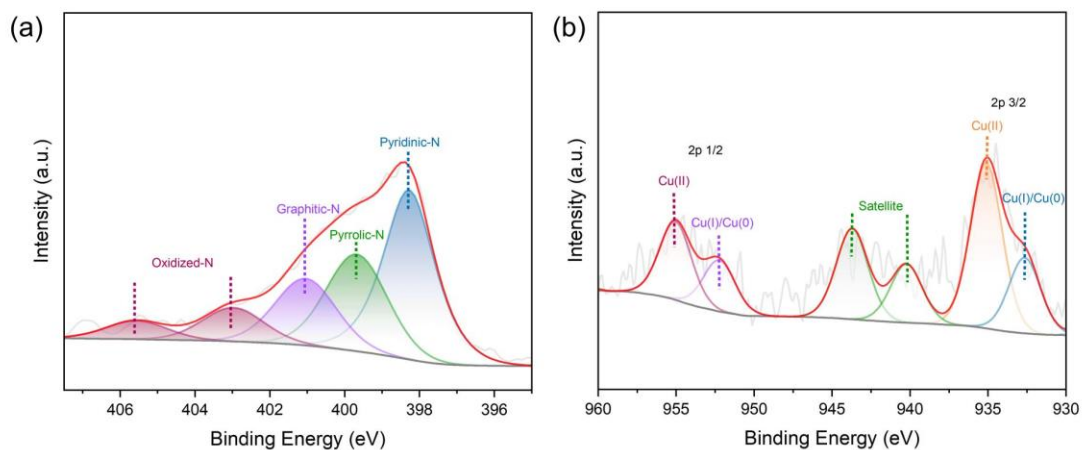**Figure S2: EDS-mapping (Cu,C,O,N) of Cu-NC-2000.**

Figure S3: XPS images of Cu-NB-2000, Cu-B-2000, Cu-NC-2000 of C1s, O1s and full spectrum.

Figure S4: XPS image of Cu-NB-2000 of Cu 2p after 10-minute electrolysis

Figure S5: XPS image of Cu LMM

Figure S6: XPS image of Cu-3NB-2000 of (a) N 1s and (b) Cu 2p

Materials	BET Surface Area/m^2·g^{-1}
Cu-NB-2000	421.9095
Cu-NC-2000	325.525
Cu-B-2000	257.2448
Biochar	2.4001

Table S1: BET surfaces Area of prepared samples

Materials	Potential (V vs. RHE)	FE	j_{C2+} (mA/cm^3)	Ref
PDI-Cu/Cu	-1.9	FE$_{C2H4}$=31.4%	~76	[1]
PDI@Cu cluster	-2.1	FE$_{C2H4}$=31.3%	82.6	[2]
NC-Cu	-0.93	FE$_{EtOH}$=31%	22	[3]
CuTCPP	-1.2	FE$_{C2H4}$=40.6%	~3	[4]
Cu-CuO/P-CCDL-600	-1.5	FE$_{EtOH}$=38.9%	~19	[5]
char-Cu-N	-1.2	-	j_{tot}=34.6	[6]
Cu$_x$O@C-2	-1.08V	FE$_{C2H4}$=41.3%	21.5	[7]

Cu$_x$O@C-3	-1.08V	FE$_{C2H4}$=38.3%	15.4	[7]
Cu$_x$O@C-1	-1.08V	FE$_{C2H4}$=31.0%	10.2	[7]
Cu$_x$O	-1.08	FE$_{C2H4}$=24.1	7.7	[7]

Table S2: ECR performances of different materials.

Materials	Cu-NB-4000	Cu-NB-2000	Cu-NB-1000
Cu wt%	27.59%	19.28%	15.95%

Table S3: Cu concentration by inductively coupled plasma spectrometer

Element	Cu	Zn	Fe	Mn	Ca	Mg	K	Na
Concentration (mg/kg)	8.90	286.51	1400681.21	93.92	6896.22	6382.33	12252,80	4755.55

Table S4: Concentration (mg/kg) of metal species in pig manure

1.   Y. Zhang, J. Gui, D. Wang, J. Mao, C. Zhang and F. Li, *Nanoscale*, 2023, **15**, 1092-1098.

2.   J. Gui, L. Li, B. Yu, D. Wang, B. Yang, Q. Gu, Y. Zhao, Y. Zhu and Y. Zhang, *ACS Applied Materials & Interfaces*, 2023, **15**, 25516-25523.

3.   Y. Sun, H. Jing, Z. Wu, J. Yu, H. Gao, Y. Zhang, G. He, W. Lei and Q. Hao, *ChemistrySelect*, 2022, **7**, e202200557.

4.   M. Sun, Z. Tao, X. Xu, S. Min and L. Kang, *Applied Catalysis A: General*, 2023, **666**, 119406.

5.   Z. Yu, M. Gu, H. Wang, L. Jiang, P. Sun, X. Liu, Y. Pei, G. Wang and X. Zhang, *The Journal of Physical Chemistry C*, 2024, **128**, 4171-4179.

6.   L. Dong, D. Feng, Y. Zhang, Z. Wang, Y. Zhao, Q. Du, J. Gao and S. Sun, *Carbon Capture Science & Technology*, 2024, **13**, 100250.

7.   C. Chen, J. Zhang, Y. Qi, J. Zhang, T. Guo and H. Wang, *Fuel*, 2024, **372**, 132245.