Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2024

Supporting Information for

Modulation of d-Band Electron Enables Efficient CO₂

Electroreduction towards CO on Ni Nanoparticles

Lei Wang^{1,2}, Yan Kong¹, Huizhu Cai², Jianju Sun², Xingxing Jiang², Xuan Li¹, Qi Hu², Hengpan Yang^{2,*}, Chuanxin He^{2,*}

 ¹ Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, 230026, China
 ² College of Chemistry and Environmental Engineering, Shenzhen University,

² College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, Guangdong, 518060, China

* Corresponding author. E-mail: <u>hpyang@szu.edu.cn</u> (H. Y.); <u>hecx@szu.edu.cn</u> (C. H.)

Contents:

Supplementary Fig. S1 to S25 Supplementary Table S1 to S3

1. Chemicals

Nickel nitrate hexahydrate (Ni(NO₃)₂-6H₂O), zinc nitrate hexahydrate (Zn(NO₃)₂-6H₂O, AR), 2-methylimidazole (C₄H₆N₂, AR), polyacrylonitrile (PAN, AR), N,Ndimethylformamide (DMF, AR), sodium hydroxide (NaOH), anhydrous ethanol (C₂H₅OH) and potassium bicarbonate (KHCO₃, AR) were purchased from Shanghai Aladdin Biochemical Technology Co. All the chemical reagents and materials were used in an as-received manner without further purification. Nickel nanopowder (20 nm-100 nm, 99.9%) was purchased from Shanghai McLean Biochemical Technology Co. Nafion (117solutions, 5 wt%) was purchased from DuPont. Carbon dioxide and N₂ with 99.99% purity were purchased from Shenzhen Huatepeng Special Gas Co. Deionized water with an electrical conductivity of 0.057 μ S cm⁻¹ was used for the experiments.

2. Catalyst synthesis

Synthesis of ZIF-8. ZIF-8 was synthesized by co-precipitation. First, 10 mmol of zinc nitrate hexahydrate was dissolved in 200 mL of methanol. In addition, 80 mmol of 2-methylimidazole was dissolved in 200 mL of methanol. After dissolving with sufficient stirring, the solution containing 2-methylimidazole was poured into the zinc nitrate solution and stirred rapidly for 30 min. after which it was centrifuged and washed, and the resulting white product was vacuum dried overnight.

Synthesis of Ni-ZIF-8. 1.5 g of ZIF-8 was dispersed in 150 ml of ethanol and sonicated for 10 min. 3 mL of a 100 mg mL⁻¹ aqueous nickel nitrate solution was added dropwise into the dispersed ZIF-8 at room temperature and stirred vigorously for 24 h to enable ZIF-8 to fully adsorb the nickel salt. After stirring was completed, it was collected by centrifugation and vacuum dried overnight.

Synthesis of Ni-PCNF. 2 g of Ni-ZIF-8 was dispersed in 12 g of DMF and 1g of PAN was added and stirred until PAN was dissolved. Then the mixed spinning solution was poured into a syringe and electrostatic spinning was carried out at a voltage of 18 KV. After the spinning was completed, the obtained pristine nanofibers were vacuum

dried at 60 °C, after which they were heated in a muffle furnace at an elevated temperature rate of 2 °C min⁻¹ to 240 °C in order to stabilize their structure. Finally, the spun filaments were carbonized by heating to 900 °C under N₂ atmosphere with a heating rate of 5 °C min⁻¹ for 2 h. The desired catalysts were obtained by cooling to room temperature and removing them. In contrast, PCNF was obtained by replacing Ni-ZIF-8 with 1.5 g of ZIF-8 and performing the same procedure, while Ni-CNF was synthesized by adding 1 g of PAN and 300 mg of nickel nitrate hexahydrate to 12 g of DMF and performing the above procedure.

3. Materials characterization

The crystalline phases of all samples were determined by X-ray diffraction (XRD) experiments in the 2θ range from 10° to 80° (Empyrean diffractometer). Morphological properties of the samples were observed with a field emission scanning electron microscope (FE-SEM) (JSM-7800F and TEAM Octane Plus), a transmission electron microscope (TEM) (JEOL JEM 2100), and a high-resolution transmission electron microscope (HR-TEM) with SADE spectroscopy (JEM-2100 and X-Max80). The chemical states of different elements were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo K-Alpha+ X-ray photoelectron spectrometer. N₂ adsorption-desorption experiments were carried out by Micromeritics BELSORP-max instrument at 77 K and the deflated samples were tested at 423 K under vacuum conditions for 15 hours.

4. Electrochemical measurements

H-type cell. H-type cell electrochemical measurements were performed in a threeelectrode system on an electrochemical workstation. A saturated calomel electrode and a platinum foil were used as reference and counter electrodes in all measurements, and the reference electrode was standardized as a reversible hydrogen electrode. N_2 saturated 0.1 M KHCO₃ (pH=7.2) and CO₂ saturated 0.1 M KHCO₃ (pH=6.8) solutions were used as electrolytes. The potentials mentioned below are derived from comparison with the reversible hydrogen electrode. For the preparation of the working electrode, 200 μ L of catalyst ink (10 mg mL⁻¹ catalyst) was prepared by dispersing 2 mg of catalyst in a mixture of 950 μ L of ethanol and 50 μ L of 5% Nafion, and then dropping the ink onto 1 cm² of carbon paper. The catalyst loading was 1 mg cm⁻².

Flow cell. CO_2 electroreduction measurements were performed in a customized flow cell with an electrochemical workstation. Proton exchange membranes were used to separate the anionic solution from the cation, facilitating ion transfer while attenuating product crossover. Prepared gaseous diffusion electrodes, nickel foam, and calibrated Ag/AgCl (saturated KCl) were used as working, counter, and reference electrodes, respectively. During the test, 1 M KOH was injected into the anode and cathode chambers by a peristaltic pump at a constant flow rate of 10 mL min⁻¹. A mass flow meter fed CO_2 gas at a flow rate of 20 mL min⁻¹ into the gas chamber.

5. Production rate and mass activity of CO

The production rate of CO was calculation as follows:

Production rate =
$$Q_{total} \times FE_{CO} / (F \times z_{CO} \times t \times S)$$

Where Q_{total} is the total charge consumed in the electrolysis, t is the electrolysis time of the CO2 reduction reaction, z is the number of transfer electrons (2 for H₂ or CO), F is the Faraday constant (96485 C mol⁻¹) and S is the geometric area of the electrode. The yield rate was calculated through normalizing production rate by the metal mass load.^[1] The mass activity for CO production was defined as the partial current density for CO normalized by the Ni metal mass load, and calculated by the following formula:

Mass activity =
$$j_{\text{total}} \times \text{FE}_{\text{CO}}/\text{m}_{\text{Ni}}$$

where j_{total} is the total current density (mA cm⁻²), m_{Ni} is the specific load of Ni metal on the working electrode contacted with catholyte, which can be obtained according to the ICP. ^[2]

6. Theoretical calculation

Computational investigations were performed utilizing the Vienna Ab-initio

Simulation Package (VASP) to execute density functional theory (DFT) computations, as outlined in references.^[3, 4] These calculations employed the Projector Augmented-Wave (PAW) method to characterize the effective nuclear potential, with the valence electrons being represented by a plane wave basis limited by an energy ceiling of 500 eV.^[5, 6] To facilitate the fractional population of Kohn-Sham orbitals, we applied a Gaussian smearing technique with a smearing width of 0.05 eV. Our study focused on a carbon surface (C (002)) model consisting of a quartet of layers, isolated by a vacuum expanse measuring 20 Å. The substrate's lowest bi-layers were immobilized in their bulk crystalline configurations, whereas relaxation was permitted for the atoms in the two uppermost layers. Adatom configurations included three nitrogen atoms affixed to the initial layer atop the substrate, with two additional nitrogen atoms bonded to the subsequent layer. Self-consistent electronic energies were determined based on the criterion of an energy variation below 10^{-5} eV. Convergence in geometric optimization was adjudged to be achieved when the alteration in energy was less than 0.03 eV Å⁻¹.



Fig. S1. SEM images of (a) Ni-PCNF, (b) Ni-CNF, (c) PCNF, (d) NiNPs.



Fig. S2. TEM image of Ni-CNF



Fig. S3. TEM image of PCNF.



Fig. S4. TEM image of NiNPs



Fig. S5. N₂ adsorption/desorption isotherms and pore size distributions of (b) Ni-CNF, (c) Ni-CNF, (d) PCNF.

Sample	Specific surface area	Adsorption volume	Total pore volume
	$(m^2 \cdot g^{-1})$	$(cm^{3} \cdot g^{-1})$	$(cm^{3} \cdot g^{-1})$
Ni-PCNF	246.3	56.6	0.2228
Ni-CNF	80.4	18.5	0.2062
PCNF	277.8	63.8	0.2595

Table S1. Specific surface area and pore volume content of the three samples.



Fig. S6. C 1s XPS spectra of (a) Ni-PCNF, (b) Ni-CNF, (c) PCNF, (d) NiNPs.



Fig. S7. LSV measurement curves in N_2 and CO_2 saturated 0.1 M KHCO₃ electrolyte on (a) Ni-PCNF, (b) Ni-CNF, (c) PCNF, (d) NiNPs.



Fig. S8. Faradaic efficiencies for CO₂RR products at different applied potentials on (a) Ni-PCNF,(b) Ni-CNF, (c) PCNF, (d) NiNPs.



Fig. S9. The partial current densities for CO.



Fig. S10. ¹H NMR spectrum for qualitative characterization of the liquid phase product.



Fig. S11. (a) LSV curves of Ni-PCNF, Ni-PCNF with KSCN in CO_2 -saturated 0.1 M KHCO₃ solutions; (b) FE_{CO} of Ni-PCNF, Ni-PCNF with KSCN.



Fig. S12. (a) LSV curves of Ni-PCNF, Ni-PCNF on flow-cell; (b) FE_{CO} of Ni-PCNF, Ni-PCNF on flow-cell.



Fig. S13. Cyclic voltammetry curves of (a) Ni-PCNF, (b) Ni-CNF, (c) PCNF, and (d) NiNPs at different scan rates.



Fig. S14. Differences in charging current density at 0.71 V_{RHE} for all samples before catalysis against scan rate for determining double–layer capacitance (C_{dl}).



Fig. S15. Current density vs. time for (a) Ni-PCNF, (b) Ni-CNF, (c) PCNF, and (d) NiNPs at different CO_2RR potentials.



Fig. S16. SEM images of Ni-PCNF after the long-time $\rm CO_2RR$ stability test.



Fig. S17. TEM images of Ni-PCNF after the long-time CO_2RR stability test.

Catalyst	$E\left(\mathrm{V}_{\mathrm{RHE}} ight)$	FE _{CO} (%)	J _{CO} (mA cm ⁻²)	electrolyte
Ni-PCNF	-1	94	18.8	0.1 M KHCO ₃
Ni-N-C ⁷	0.80	69	1	0.1 M KHCO ₃
ACP/S-N-Ni ^[8]	-0.77	80	3.4	0.5 M KHCO ₃
Ni-Nx-C2 ^[9]	-0.7	85	9.5	0.1 M KHCO ₃
FeN4/C ^[10]	-0.6	97	6.87	0.1 M KHCO ₃
NC-CNTs (Ni) ^[11]	-1	90	10	0.1 M KHCO ₃
NiSA-N-CNTs ^[12]	-0.7	90	31.5	0.5 M KHCO3
h-Ni/N/C ^[13]	-0.8	96	21.6	0.5 M KHCO3
Ni-N3-V SAC ^[14]	-0.8	94	48	0.5 M KHCO3
Ni-N4/C-NH ^[15]	-0.8	89	40	0.5 M KHCO3
CoCu-DASC ^[16]	-0.9	93	25	0.5 M KHCO3
Ni(NC)-1 ^[17]	-0.8	99	12	0.5 M KHCO3

Table S2. Comparison of Ni-PCNF with other reported CO₂RR preparations for CO performance in the H-cell.

Table S3. Comparison of Ni-PCNF with other reported CO_2RR preparations for CO performance in the flow-cell.

Catalyst	$E\left(\mathrm{V}_{\mathrm{RHE}} ight)$	FE _{CO} (%)	$J_{CO} (mA \; cm^{-2})$	electrolyte
Ni-PCNF	-1.3	96	164.6	1.0 M KOH
A-Fe@NG-Li ₁ K ₃ ^[18]	-0.2	91	73	1.0 M KOH
Ni-N ₄ /C-NH ₂ ^[19]	-0.8	89	327.8	1.0 M KOH
Zn/NC-NSs ^[20]	-1.06	84	67	0.5 M KHCO ₃
Ni@NiNCM ^[21]	-0.92	84	126	0.5 M KHCO ₃
CALF-20 ^[22]	-0.97	94.5	32.8	1.0 M KOH
P-Zn ^[23]	-0.68	83.6	167.2	1.0 M KOH



Fig. S18. (a) side and (b) top view of the theory Ni-PCNF model.



Fig. S19. (a) side and (b) top view of the theory NiNPs model.



Fig. S20. (a) side and (b) top view of *COOH adsorption on the surface of theory Ni-PCNF models



Fig. S21. (a) side and (b) top view of *CO adsorption on the surface of theory Ni-PCNF models



Fig. S22. (a) side and (b) top view of *COOH adsorption on the surface of theory NiNPs models



Fig. S23. (a) side and (b) top view of *CO adsorption on the surface of theory NiNPs models



Fig. S24. (a) side and (b) top view of *H adsorption on the surface of theory Ni-PCNF models



Fig. S25. (a) side and (b) top view of *H adsorption on the surface of theory NiNPs models

Reference

[1] J. Bi, P. Li, J. Liu, Y. Wang, X. Song, X. Kang, X. Sun, Q. Zhu, B. Han, Angew. Chem. Int. Ed, 2023, 62, e202307612.

[2] S. Yuan, J. Peng, B. Cai, Z. Huang, A. T. Garcia-Esparza, D. Sokaras, Y. Zhang, L. Giordano,

K. Akkiraju, Y. Zhu, R. Hübner, X. Zou, Y. Román-Leshkov, Y Shao-Horn, Nat. Mater., 2022, 21, 673-680.

- [3] G. Kresse, J. Furthmüller, Phys. Rev. B, 1996, 54, 11169-11186.
- [4] G. Kresse, J. Hafner, Phys. Rev. B, 1994, 49, 14251.
- [5] P.E. Blöchl, Phys. Rev. B, 1994, 50, 17953-17979.
- [6] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
- [7] B.J. Park, Y. Wang, Y. Lee, K.J. Noh, A. Cho, M.G. Jang, R. Huang, K.S. Lee, J.W. Han, Small, 2021, 17, 2103705.
- [8] S. Li, M. Ceccato, X. Lu, S. Frank, N. Lock, A. Roldan, X.M. Hu, T. Skrydstrup, K. Daasbjerg,J. Mater. Chem., A, 2021, 9, 1583-1592.
- [9] W. Ju, A. Bagger, G.P. Hao, A.S. Varela, I. Sinev, V. Bon, B. Roldan Cuenya, S. Kaskel, J. Rossmeisl, P. Strasser, Nat. Commun., 2017, 8, 1-9.
- [10] C. Liu, Y. Wu, K. Sun, J. Fang, A. Huang, Y. Pan, W. Cheong, Z. Zhuang, Z. Zhuang, Q. Yuan,H. Xin, Chem., 2021, 7, 1297-1307.
- [11] Q. Fan, P. Hou, C. Choi, T.S. Wu, S. Hong, F. Li, Y.L. Soo, P. Kang, Y. Jung, Z. Sun, Adv. Energy Mater., 2020, 10, 1903068.
- [12] Y. Cheng, S. Zhao, B. Johannessen, J.P. Veder, M. Saunders, M.R. Rowles, M. Cheng, C. Liu,M.F. Chisholm, R. De Marco, H.M. Cheng, Adv. Mater., 2018, 30, 1706287.
- [13] Y. Chen, J. Zhang, J. Tian, Y. Guo, F. Xu, Y. Zhang, X. Wang, L. Yang, Q. Wu, Z. Hu, Adv. Funct. Mater., 2023, 33 2214658.
- [14] L. Yuan, S. Zeng, G. Li, Y. Wang, K. Peng, J. Feng, X. Zhang, S. Zhang, Adv. Funct. Mater., 2023, 33, 2306994.
- [15] Z. Chen, X. Zhang, W. Liu, M. Jiao, K. Mou, X. Zhang, L. Liu, Energy Environ. Sci., 2021, 14, 2349-2356.
- [16] J.D. Yi, X. Gao, H. Zhou, W. Chen, Y. Wu, Angew. Chem. Int. Ed., 2022, 61, e202212329.
- [17] C. Wen, F. Mao, Y. Liu, X. Zhang, H. Fu, L. Zheng, P. Liu, H. Yang, ACS Catal., 2019, 10,

1086-1093.

[18] D. Zhao, K. Yu, P. Song, W. Feng, B. Hu, W. Cheong, Z. Zhuang, S. Liu, K. Sun, J. Zhang, C. chen, Energy Environ. Sci., 2022, 15, 3795-3804.

[19] Z. Chen, X. Zhang, W. Liu, M. Jiao, K. Mou, * Zhang, L. Liu, Energy Environ. Sci., 2021, 14, 2349-2356.

- [20] J. Chen, Z. Li, X. Wang, X. Sang, S. Zheng, S. Liu, B. Yang, Q. Zhang, L. Lei, L. Dai, Y. Hou, Angew. Chem. Int. Ed., 2022, 61, e202111683.
- [21] X. Wang, X. Sang, C. Dong, S. Yao, L. Shuai, J. Lu, B. Yang, Z. Li, L. Lei, M. Qiu, L. Dai, Y. Hou, Angew. Chem., 2021, 133, 12066-12072.
- [22] T. Al-Attas, N. Marei, X. Yong, N. Yasri, V. Thangadurai, G. Shimizu, S. Siahrostami, M.
- Kibria. ACS Catal., 2021, 11, 7350-7357.

[23] W. Luo, J. Zhang, M. Li, A. Züttel, ACS Catal., 2019, 9(5): 3783-3791.