

Promoting electrocatalytic CO₂ reduction to CO via Sulfur-Doped Co-N-C Single-Atom Catalyst

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Abstract

Electrocatalytic reduction of CO₂ to fuels and chemicals possesses huge potential to alleviate current environmental crisis. Heteroatom doping in metal-nitrogen-carbon (M-N-C) single-atom catalysts (SACs) has been found capable to promote the electrocatalytic CO₂ reduction reaction (CO₂RR). However, the origin of the enhanced activity is still elusive. Here, we report that sulfur-doped cobalt-nitrogen-carbon single-atom catalyst (Co1-SNC) exhibits superior CO₂RR performance compared to sulfur-free counterpart (Co1-NC). On the basis of in situ attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS), kinetic isotope effect (KIE) and theoretical calculation, it is demonstrated that sulfur doping can promote water activation, elevate the d-band center of Co active site, and reduce the free energy of *COOH intermediate formation. This work deepens the understanding of the CO₂RR chemistry over heteroatom-doped SACs for designing efficient CO₂RR processes.

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Promoting Electrocatalytic CO₂ Reduction to CO via Sulfur-Doped Co-N-C Single-Atom Catalyst⁺

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Keywords

Electrocatalytic | CO₂RR | Sulfur-doped | Metal-nitrogen-carbon | ATR-SEIRAS

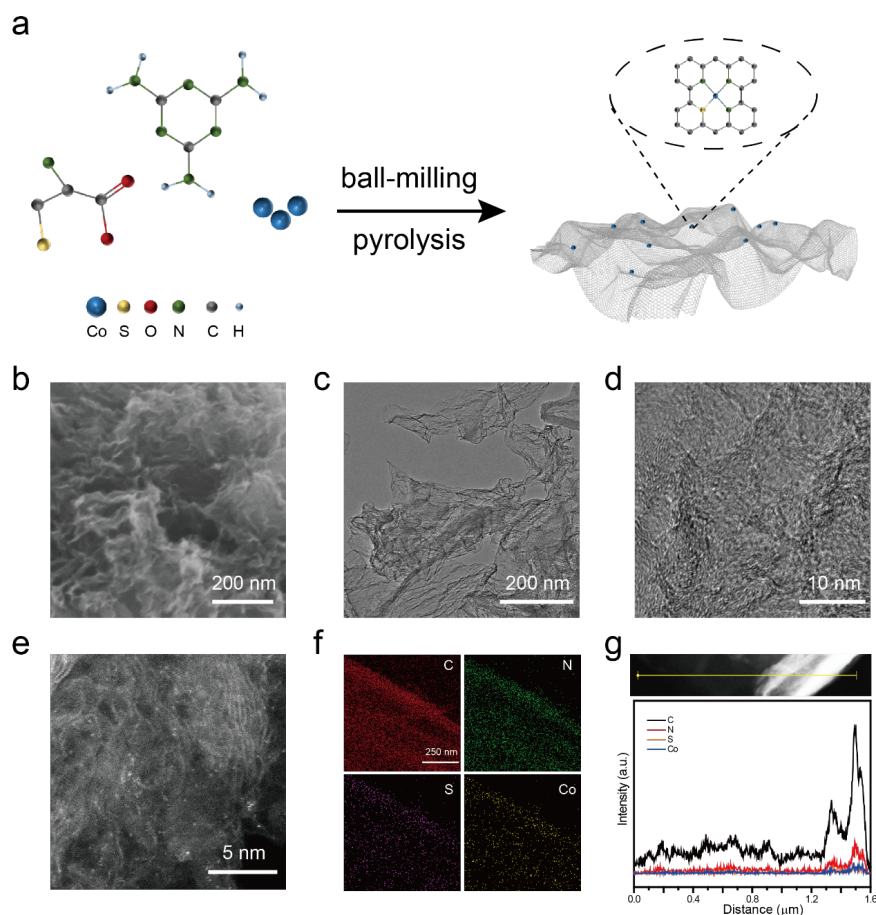
Comprehensive Summary

Electrocatalytic reduction of CO₂ to fuels and chemicals possesses huge potential to alleviate current environmental crisis.

Background and Originality Content

Electrocatalytic CO₂RR affords a promising route to address the current environmental and energy issues by converting CO₂ into carbon-based fuels^[1, 2]. Among the different electrochemical CO₂RR products, CO is regarded as one of the most promising industrial targets due to its high energy efficiency^[3, 4]. Tremendous efforts have been devoted to developing efficient electrocatalysts with high activity and selectivity to favor CO production^[5, 6]. Recently, single-atom catalysts have aroused increasing interests owing to their high atomic utilization efficiency and tunable coordination structure^[7, 8]. Metal-nitrogen-carbon catalysts as one of the most typical SACs have attracted extensive attention for the CO₂RR to produce CO^[9, 10]. However, M-N-C catalysts usually exhibit poor CO₂RR performance without further modification. Therefore, developing

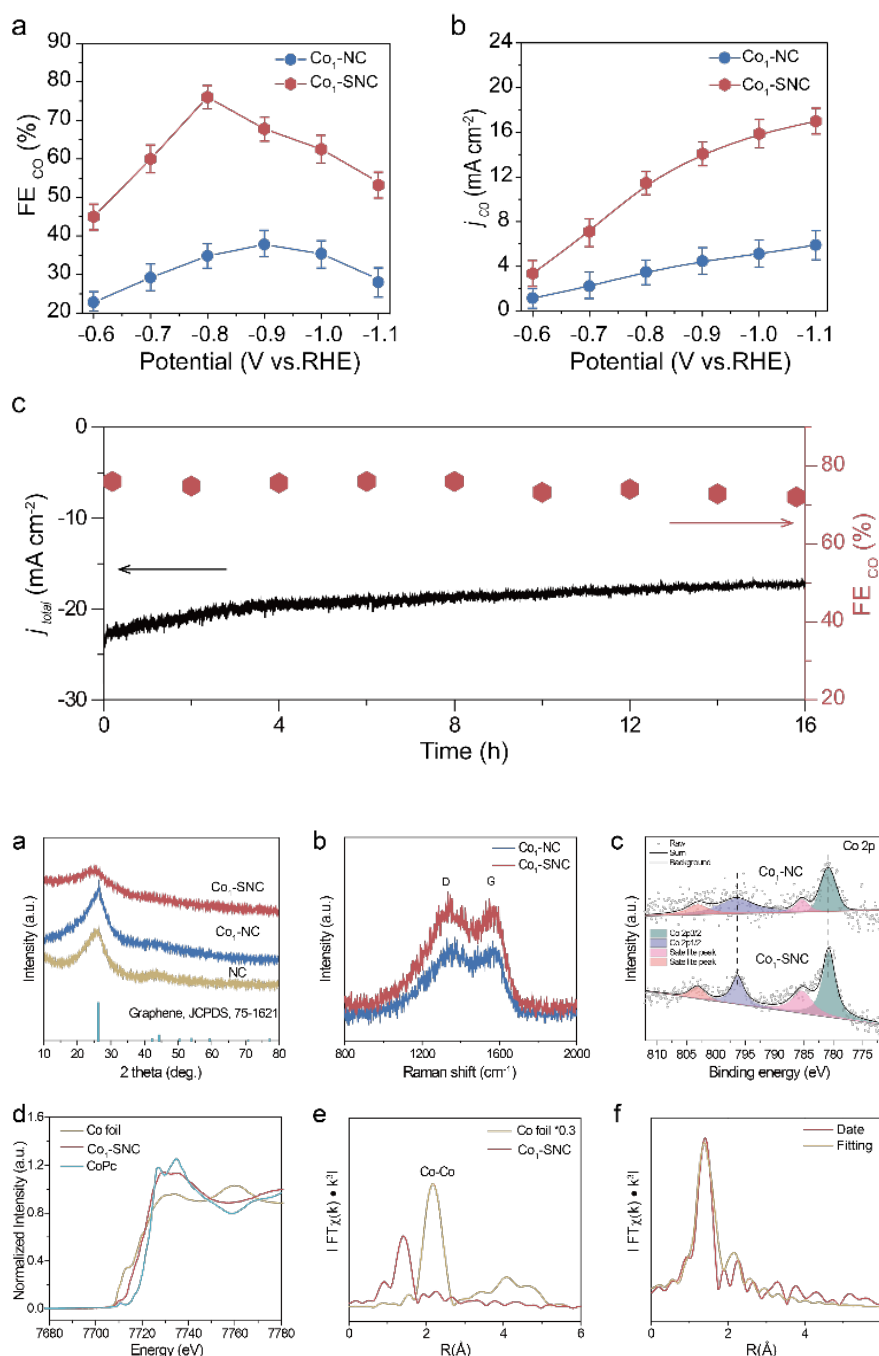
effective M-N-C catalysts for highly active CO₂RR remains challenging yet urgent.



The introduction of heteroatoms (such as B, P, S and Se) into M-N-C catalysts provides a useful strategy to further enhance its catalytic activity due to the optimized electronic structure^[11-14]. For example, Yang et al. developed S doped NiNC catalyst for robust CO₂RR due to the formation of low-valent Ni(I)^[15]. Besides, P doped FeNC catalyst also exhibited impressive performance owing to the moderate adsorption energy^[16]. According to the previous reports, the formation of *COOH intermediate via the proton-electron transfer process is the rate-determining step (RDS) for CO₂RR to CO^[17, 18]. However, few studies have scrutinized the water activation and proton transfer.

In this work, we develop a Co₁-SNC catalyst with S doped in the first shell of CoN₄. The Co₁-SNC exhibits superior CO₂RR performance compared to Co₁-NC. *In situ* ATR-SEIRAS and KIE studies indicate that Co₁-SNC owns better water affinity and superior capability for water activation. Theoretical analyses further show that S doping can upshift the d-band center of Co active site and reduce the free energy of *COOH intermediate formation. This work enriches the understanding of CO₂RR chemistry over heteroatom doping M-N-C SACs and offers new insights for developing high-performance catalysts for various important electrochemical reactions.

Results and Discussion



The Co₁-SNC catalyst was synthesized by ball-milling a mixture of melamine, L-cysteine and CoCl₂, followed by a two-step calcination in argon atmosphere (Figure 1a). Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and aberration-corrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM) were applied to investigate the morphology and structure of Co₁-SNC and Co₁-NC. As shown in Figure 1b-d, the typical morphology of Co₁-SNC is sheet-like thin layer with no obviously observed nanoparticles. In Figure 1e, the bright dots can be assigned to the monodispersed Co atoms^[19]. Moreover, the elemental mapping and line scan further reveal the uniform distribution of C, N, S, and Co elements on the Co₁-SNC catalyst (Figures 1f and g). The Co content (1.04 wt.% and 0.98 wt.% for Co₁-NC

and Co₁-SNC, respectively) was estimated by the inductively coupled plasma optical emission spectrometry (ICP-OES). More morphological characterizations of the Co₁-NC are shown in Figure S1.

Figure 2. (a) XRD patterns of Co₁-SNC, Co₁-NC and NC. (b) Raman spectra of Co₁-NC and Co₁-SNC. (c) Co 2p XPS spectra of Co₁-NC and Co₁-SNC. (d) Co k-edge XANES spectra. (e) R space EXAFS spectra of Co₁-SNC and Co foil reference. (f) The fitting curve of Co₁-SNC.

As shown in Figure 2a, the XRD patterns only show diffraction peaks at 26.2° and 43.6°, which are assigned to (002) and (101) plane of graphitic carbon, respectively. The XRD results further indicate that Co nanoparticles are absent in both Co₁-NC and Co₁-SNC. Compared to Co₁-NC, the XRD peaks for Co₁-SNC become broader and weaker, suggesting that S doping results in low crystallinity and defective structure, which is further proved by a higher I_D/I_G ratio of Co₁-SNC in the Raman measurement (Co₁-NC:1.02; Co₁-SNC:1.10) in Figure 2b^[20]. Besides, the Brunauer–Emmett–Teller (BET) specific surface area was measured to be 113.12 and 299.66 m² g⁻¹ for Co₁-NC and Co₁-SNC, respectively (Figure S2).

Next, we performed XPS measurements to explore more detailed surface structure of Co₁-NC and Co₁-SNC catalysts. As shown in Figure S3, N 1s XPS spectra can be deconvoluted into pyridinic-N (398.13 eV), pyrrolic-N (399.79 eV), graphitic-N (400.93 eV) and oxidized N species (402.76 eV) for both Co₁-NC and Co₁-SNC^[21]. Besides, the S 2p XPS spectrum for the Co₁-SNC catalyst displays a peak at 165.16 eV, which can be attributed to S-Co bond^[22]. Figure 2c displays the Co 2p XPS spectra, where the peaks at 780.89 eV and 796.3 eV correspond to the Co 2p_{3/2} and Co 2p_{1/2} orbitals of Co²⁺, respectively. Noteworthily, compared to Co₁-NC, the binding energy of Co₁-SNC is blue-shifted, suggesting that the incorporation of S can enrich electron density on the Co site, which expects to boost the adsorption of CO₂. X-ray absorption near-edge structure (XANES) spectroscopy was performed to examine the coordination structure of Co₁-SNC (Figure 2d). The pre-edge of Co₁-SNC is observed higher than that of Co foil but lower than that of cobalt phthalocyanine (CoPc), indicating that the cobalt valence state in Co₁-SNC is between 0 and +2^[23]. Moreover, extended X-ray absorption fine structure (EXAFS) was analyzed to further get information on the local structure of Co₁-SNC. As displayed in Figure 2e, the Co₁-SNC exhibits the characteristic peaks of the Co-N bond at 1.4 Å and no Co-Co bond (2.1 Å) can be found, which further confirms the existence of atomically dispersed Co. In addition, the fitting result discloses that the coordination number of the Co atom in the first shell is near four with the proposed CoN₃S structure (Figure 2f and Table S1).

Figure 3. Electrochemical CO₂RR performance of Co₁-NC and Co₁-SNC. (a) FE_{CO} of Co₁-NC and Co₁-SNC at different potentials. (b) Partial current density of CO (j_{CO}) over Co₁-NC and Co₁-SNC. (c) Stability test of Co₁-SNC at -0.8 V (vs. RHE) in CO₂saturated 0.5 M KHCO₃ solution.

The CO₂RR performance of the as-prepared catalysts was evaluated in CO₂-saturated 0.5 M KHCO₃ electrolyte (details can be found in the Supporting Information). All potentials here are relative to the reversible hydrogen electrode (RHE) scale unless stated otherwise. According to the linear sweep voltammetry (LSV) curves (Figure S4), Co₁-SNC shows comparable hydrogen evolution activity to Co₁-NC in Ar-saturated electrolyte. It is worth noting that Co₁-SNC exhibits a much higher current density and smaller onset potential compared to Co₁-NC in the CO₂-saturated electrolyte, indicating a superior CO₂RR performance^[24]. Furthermore, according to Figures 3a and b, Co₁-SNC exhibits a much higher FE_{CO} and larger j_{CO} than those of Co₁-NC across all testing potentials. The maximum FE_{CO} of Co₁-SNC reaches 75.6 ± 2% at -0.8 V. Besides, no liquid products can be detected (Figure S5). Furthermore, the durability of Co₁-SNC for CO₂RR was assessed at a constant applied potential of -0.8 V (Figure 3c). The Co₁-SNC catalyst can maintain a stable cathodic current density at 17.5 mA cm⁻² and an average FE_{CO} of 76%, suggesting excellent catalytic stability of Co₁-SNC in the CO₂RR.

To further understand the electrochemical properties of electrocatalysts, the electrochemically active surface area (ECSA) was investigated. The electrochemical double-layer capacitance (C_{dl}) of Co₁-SNC (0.75 mF cm⁻²) is higher than that of Co₁-NC (0.25 mF cm⁻²), indicating the more active sites for CO₂RR on Co₁-SNC catalyst (Figure S6). However, the CO partial current densities normalization by ECSA of Co₁-SNC and Co₁-NC are -15.28 and -13.92 mA cm⁻², respectively, demonstrating that the intrinsic activity for CO

production of the Co₁-SNC electrocatalyst is higher than Co₁-NC (Figure S7).

In situ ATR-SEIRAS was performed to investigate the mechanism of CO₂RR on Co₁-NC and Co₁-SNC catalysts. The IR spectra were collected from 0 to -1.0 V (vs. RHE) with a step of 0.1 V in a CO₂saturated 0.5 M KHCO₃ solution. As shown in Figures 4a and b, the peak at 3400 cm⁻² and 1950 cm⁻² can be assigned to the O-H stretching band of surface water and adsorbed *CO intermediate, respectively^[25, 26]. The frequency and intensity of the vibrations are strongly dependent on the electrode potential, indicating that the obtained ATR-SEIRAS signals are mainly from the electrode from the electrode interface^[27]. Compared to Co₁-NC, the O-H stretching band shifts to lower wavenumbers, suggesting a stronger affinity between water molecules and Co₁-SNC (Figure 4c)^[28].

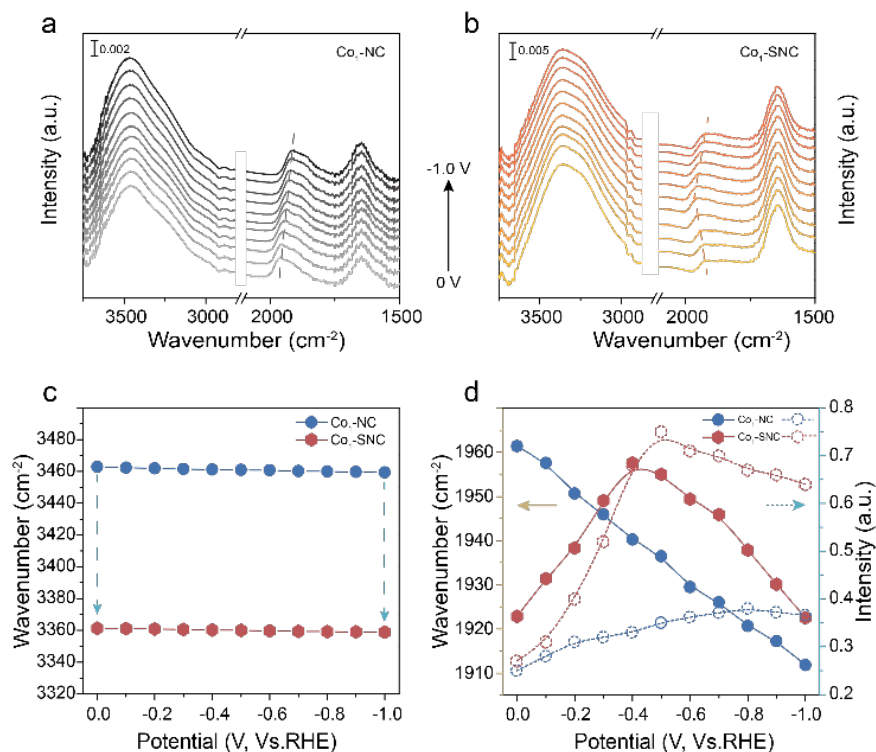


Figure 4. *In situ* ATR-SEIRAS spectra of Co₁-NC (a) and Co₁-SNC (b) at different applied potentials. (c) O-H stretching wavenumbers of interfacial water at different applied potentials. (d) Potential-dependent *CO wavenumbers and peak-integrated intensities on Co₁-NC and Co₁-SNC catalysts, respectively. Solid and dotted lines represent *CO wavenumbers and peak intensities, respectively.

Furthermore, Figure 4d shows that the *CO band frequencies increase initially and then decrease with increasing the cathodic potential over Co₁-SNC. Besides, there are no obvious *CO peaks on the surfaces of both catalysts in an Ar-saturated 0.5 M KHCO₃ solution (Figure S8). According to previous reports, the Stark effect could cause the frequency shift of *CO band to a lower wavenumber with decreasing cathodic potential, and a higher *CO coverage would induce the frequency shift to a higher wavenumber due to the dipole-dipole coupling effect^[29]. The *CO peak-integrated intensities further show a higher *CO coverage over Co₁-SNC, explaining the superior CO₂RR to CO performance over Co₁-SNC^[30].

Additionally, as proton-feeding is important for the formation of the crucial intermediate (*COOH) during CO₂RR, kinetic isotope effect (KIE) of H/D over Co₁-NC and Co₁-SNC catalysts was performed to explore the water activation process. As shown in Figure 5a, the KIE of Co₁-NC and Co₁-SNC are close to 2, indicating that the activation of water was involved in the RDS of CO₂RR, which was further demonstrated

by the effect of pH of electrolyte that a higher local pH environment favored the formation of CO (Figure 5b)^[31]. Besides, compared to Co₁-NC (1.98), the decreased KIE value (1.72) indicates accelerated H₂O dissociation over Co₁-SNC^[32]. Furthermore, electrochemical impedance spectroscopy (EIS) was preformed to evaluate the interfacial charge-transfer process, and the Co₁-SNC shows a smaller charge transfer resistance, corresponding to a faster charge-transfer process to form reactive intermediates (Figure 5c)^[33].

To further understand the superior CO₂RR performance of Co₁-SNC, we performed density functional theory (DFT) calculations. Typical CoN₄ and CoN₃S model were constructed (Figure 5d), with match well with the EXAFS fitting results. As shown in Figure 5e, the formation of *COOH intermediate via the proton-electron transfer process is the rate-determining step for CO₂RR to CO^[34]. Moreover, the reaction free energy of the RDS reduces from 1.88 eV over CoN₄ to 1.54 eV over CoN₃S. Furthermore, the density of states (DOS) and Bader charge analysis were performed to reveal the electronic structure of CoN₄ and CoN₃S. As displayed in Figure 5f, the S doping elevates the d-band center of cobalt from -1.02 eV to -0.79 eV, which benefit the CO₂ activation^[35]. Besides, differential charge density distribution analysis shows that the Co₁-N₃S possesses a stronger electronic interaction with *COOH intermediate, facilitating the CO₂ adsorption (Figure 5g, Figure S9). Therefore, S doping can optimize the adsorption and activation of CO₂ on the Co active site.

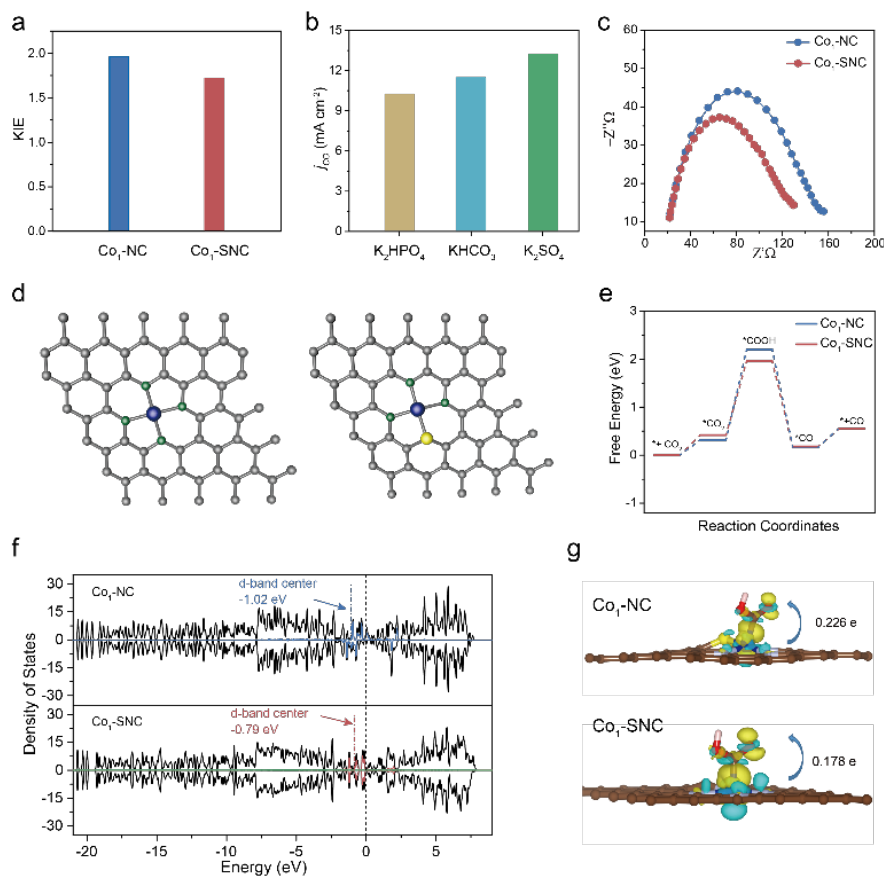


Figure 5. (a) KIE of Co₁-NC and Co₁-SNC measured at -0.8 V (vs. RHE). (b) Effect of electrolyte pH on CO₂RR performance over the Co₁-SNC at -0.8 V (vs. RHE). (c) EIS Nyquist plot of the Co₁-NC and Co₁-SNC catalysts. (d) Theoretically computed model of CoN₄ and CoN₃S. (e) The calculated free energy diagrams of CO₂-to-CO conversion. (f) The calculated density of states for Co 3d orbital of CoN₄ and CoN₃S. (g) Differential charge density distribution between the catalyst (CoN₄ and CoN₃S) and *COOH

intermediate.

Conclusions

In summary, Co₁-SNC catalyst with a Co₁-N₃S structure has been successfully prepared through a facile pyrolysis method, which exhibits a greatly enhanced CO₂RR to CO performance compared to Co₁-NC. *In situ* ATR-SEIRAS and KIE analyses demonstrate accelerated water dissociation over the Co₁-SNC catalyst. Furthermore, DFT calculations indicate that the introduction of S into Co₁-NC can adjust the electronic structure of Co active center, facilitating the adsorption and activation of CO₂.

Experimental

Synthesis of catalysts

Synthesis of Co₁-SNC : 6 g melamine, 2 g L-Cysteine and 10 mg Cobalt chloride were first grounded into a homogeneous precursor by ZrO₂ mortar ball. Subsequently, the fine powder mixture was undergone a two-stage pyrolysis and carbonization process at the Ar atmosphere (first stage: from 25 °C to 580 °C, maintain at 580 °C for 2 h and then heated to 900 °C for 1.5 h). The heating rate of the whole process was 2 °C/min. After cooling down to room temperature, the product was leached at 80 °C in 0.5 M HCl for 24 h to remove the unstable species. Afterwards, the sample was heated at 700 °C again to eliminate the residual Cl⁻.

Synthesis of Co₁-NC : The same method was used for the synthesis of Co₁-NC (For Co₁-NC, L-alanine was used instead of L-Cysteine. For detail: 6 g melamine, 2 g L-alanine and 10 mg Cobalt chloride was used).

Electrochemical measurements

All electrochemical CO₂ reduction experiments were performed at room temperature and normal pressure on a three-electrode system in an H-type cell (separated by a Nafion 117 membrane) with a CHI 760e potentiostat. The catalyst coated carbon fiber paper (1 × 1 cm²), Ag/AgCl electrode and platinum slice were used as working, reference and counter electrode, respectively. The electrolyte was 0.5 M KHCO₃ aqueous solution. The potential was converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.059 × pH + 0.198 V. The gaseous products (i.e., H₂ and CO) were quantified by a gas chromatography (GC-2014, SHIMADZU) equipped with a flame ionization detector (FID) for CO and a thermal conductivity detector (TCD) for H₂ quantification. The flow rate of CO₂ was controlled at 20 cc/min at the inlet of electrochemical cell. The liquid-phase products were quantified on a nuclear magnetic resonance spectroscopy (NMR, Bruker Avance III 600 MHz) with dimethyl sulfoxide (DMSO) as the internal standard.

Other experimental details and characterization data are available in Supporting Information.

Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.2023xxxxx>.

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References

- [1] Gu, J.;Hsu, C. S.;Bai, L.;Chen, H. M.; Hu, X. Atomically dispersed Fe (3+) sites catalyze efficient CO₂electroreduction to CO. *Science* **2019** , *364* , 1091-1094.
- [2] Jiao, J.;Lin, R.;Liu, S.;Cheong, W. C.;Zhang, C.;Chen, Z.;Pan, Y.;Tang, J.;Wu, K.;Hung, S. F.;Chen, H. M.;Zheng, L.;Lu, Q.;Yang, X.;Xu, B.;Xiao, H.;Li, J.;Wang, D.;Peng, Q.;Chen, C.; Li, Y. Copper atom-

pair catalyst anchored on alloy nanowires for selective and efficient electrochemical reduction of CO₂. *Nat. Chem.***2019** , *11* , 222-228.

[3] Wang, Q.;Liu, K.;Hu, K.;Cai, C.;Li, H.;Li, H.;Herran, M.;Lu, Y. R.;Chan, T. S.;Ma, C.;Fu, J.;Zhang, S.;Liang, Y.;Cortes, E.; Liu, M. Attenuating metal-substrate conjugation in atomically dispersed nickel catalysts for electroreduction of CO₂ to CO. *Nat. Commun.* **2022** , *13* , 6082.

[4] Ou, H.;Ning, S.;Zhu, P.;Chen, S.;Han, A.;Kang, Q.;Hu, Z.;Ye, J.;Wang, D.; Li, Y. Carbon Nitride Photocatalysts with Integrated Oxidation and Reduction Atomic Active Centers for Improved CO₂ Conversion. *Angew. Chem. Int. Ed.***2022** , *61*, e2022065.

[5] Wei, Z.;Ding, J.;Duan, X.;Chen, G.-L.;Wu, F.-Y.;Zhang, L.;Yang, X.;Zhang, Q.;He, Q.;Chen, Z.;Huang, J.;Hung, S.-F.;Yang, X.; Zhai, Y. Enhancing Selective Electrochemical CO₂ Reduction by In Situ Constructing Tensile-Strained Cu Catalysts. *ACS Catal.***2023** , *13*, 4711–4718.

[6] Huang, J. R.;Qiu, X. F.;Zhao, Z. H.;Zhu, H. L.;Liu, Y. C.;Shi, W.;Liao, P. Q.; Chen, X. M. Single-Product Faradaic Efficiency for Electrocatalytic of CO₂ to CO at Current Density Larger than 1.2 A cm⁻² in Neutral Aqueous Solution by a Single-Atom Nanozyme. *Angew. Chem. Int. Ed.* **2022** ,*61* , e202210985.

[7] Qiao, B.;Wang, A.;Yang, X.;Allard, L. F.;Jiang, Z.;Cui, Y.;Liu, J.;Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt₁/FeOx. *Nat. Chem.* **2011**, *3*, 634-641.

[8] Wang, A.;Li, J.; Zhang, T. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* **2018**, *2*, 65-81.

[9]Zhu, J.;Xiao, M.;Ren, D.;Gao, R.;Liu,X.;Zhang,Z.;Luo,D.;Xing,W.;Su, D.;Yu, A.; Chen, Z. Quasi-Covalently Coupled Ni-Cu Atomic Pair for Synergistic Electroreduction of CO₂. *J. Am. Chem. Soc.***2022** , *144* , 9661-9671.

[10] Han, S. G.;Ma, D. D.; Zhu, Q. L. Atomically Structural Regulations of Carbon-Based Single-Atom Catalysts for Electrochemical CO₂ Reduction. *Small Methods* **2021** ,*5* , e2100102.

[11] Ma, X.;Du, J.;Sun, H.;Ye, F.;Wang, X.;Xu, P.;Hu, C.;Zhang, L.; Liu, D. Boron, nitrogen co-doped carbon with abundant mesopores for efficient CO₂ electroreduction. *Appl. Catal. B Environ.* **2021** , *298* .

[12] Chen, S.;Li, X.;Kao, C. W.;Luo, T.;Chen, K.;Fu, J.;Ma, C.;Li, H.;Li, M.;Chan, T. S.; Liu, M. Unveiling the Proton-Feeding Effect in Sulfur-Doped Fe-N-C Single-Atom Catalyst for Enhanced CO₂ Electroreduction. *Angew. Chem. Int. Ed.***2022** , *61* , e202206233.

[13] Zhuang, Z.;Xia, L.;Huang, J.;Zhu, P.;Li, Y.;Ye, C.;Xia, M.;Yu, R.;Lang, Z.;Zhu, J.;Zheng, L.;Wang, Y.;Zhai, T.;Zhao, Y.;Wei, S.;Li, J.;Wang, D.; Li, Y. Continuous Modulation of Electrocatalytic Oxygen Reduction Activities of Single-Atom Catalysts through p-n Junction Rectification. *Angew. Chem. Int. Ed.* **2023** , *62* , e202212335.

[14] Chen, Z.;Su, X.;Ding, J.;Yang, N.;Zuo, W.;He, Q.;Wei, Z.;Zhang, Q.;Huang, J.; Zhai, Y. Boosting oxygen reduction reaction with Fe and Se dual-atom sites supported by nitrogen-doped porous carbon. *Appl. Catal. B Environ.* **2022** , *308* .

[15] Yang, H. B.;Hung, S.-F.;Liu, S.;Yuan, K.;Miao, S.;Zhang, L.;Huang, X.;Wang, H.-Y.;Cai, W.;Chen, R.;Gao, J.;Yang, X.;Chen, W.;Huang, Y.;Chen, H. M.;Li, C. M.;Zhang, T.; Liu, B. Atomically dispersed Ni(i) as the active site for electrochemical CO₂ reduction. *Nat. Energy* **2018** ,*3* , 140-147.

[16] Li, K.;Zhang, S.;Zhang, X.;Liu, S.;Jiang, H.;Jiang, T.;Shen, C.;Yu, Y.; Chen, W. Atomic Tuning of Single-Atom Fe-N-C Catalysts with Phosphorus for Robust Electrochemical CO₂ Reduction. *Nano Lett* **2022** , *22* , 1557-1565.

- [17] Ding, T.;Liu, X.;Tao, Z.;Liu, T.;Chen, T.;Zhang, W.;Shen, X.;Liu, D.;Wang, S.;Pang, B.;Wu, D.;Cao, L.;Wang, L.;Liu, T.;Li, Y.;Sheng, H.;Zhu, M.; Yao, T. Atomically Precise Dinuclear Site Active toward Electrocatalytic CO₂ Reduction. *J. Am. Chem. Soc.* **2021** , *143* , 11317-11324.
- [18] Kong, X.;Ke, J.;Wang, Z.;Liu, Y.;Wang, Y.;Zhou, W.;Yang, Z.;Yan, W.;Geng, Z.; Zeng, J. Co-based molecular catalysts for efficient CO₂ reduction via regulating spin states. *Appl. Catal. B Environ.* **2021** , *290* .
- [19] Ding, J.;Teng, Z.;Su, X.;Kato, K.;Liu, Y.;Xiao, T.;Liu, W.;Liu, L.;Zhang, Q.;Ren, X.;Zhang, J.;Chen, Z.;Teruhisa, O.;Yamakata, A.;Yang, H.;Huang, Y.;Liu, B.; Zhai, Y. Asymmetrically coordinated cobalt single atom on carbon nitride for highly selective photocatalytic oxidation of CH₄ to CH₃OH. *Chem.***2023** , *9*, 1017.
- [20] Chen, Z.;Niu, H.;Ding, J.;Liu, H.;Chen, P. H.;Lu, Y. H.;Lu, Y. R.;Zuo, W.;Han, L.;Guo, Y.;Hung, S. F.; Zhai, Y. Unraveling the Origin of Sulfur-Doped Fe-N-C Single-Atom Catalyst for Enhanced Oxygen Reduction Activity: Effect of Iron Spin-State Tuning. *Angew. Chem. Int. Ed.* **2021** , *60* , 25404-25410.
- [21] Liu, Y.;Ding, J.;Li, F.;Su, X.;Zhang, Q.;Guan, G.;Hu, F.;Zhang, J.;Wang, Q.;Jiang, Y.;Liu, B.; Yang, H. B. Modulating Hydrogen Adsorption via Charge Transfer at Semiconductor-Metal Heterointerface for Highly Efficient Hydrogen Evolution Catalysis. *Adv. Mater.***2023**, *35*, 2207114.
- [22] Huang, Y.;Jiang, L.-W.;Liu, H.; Wang, J.-J. Electronic structure regulation and polysulfide bonding of Co-doped (Ni, Fe)_{1+x}S enable highly efficient and stable electrocatalytic overall water splitting. *Chem. Eng. J.***2022** , *441* .
- [23] Ghorai, U. K.;Paul, S.;Ghorai, B.;Adalder, A.;Kapse, S.;Thapa, R.;Nagendra, A.; Gain, A. Scalable Production of Cobalt Phthalocyanine Nanotubes: Efficient and Robust Hollow Electrocatalyst for Ammonia Synthesis at Room Temperature. *ACS Nano* **2021** , *15* , 5230-5239.
- [24] Liu, J.;Li, P.;Bi, J.;Wang, Y.;Zhu, Q.;Sun, X.;Zhang, J.;Liu, Z.; Han, B. Sm and S Co-doping to Construct Homo-hetero Cu Catalysts for Synergistic Enhancing CO₂ Electroreduction+. *Chin. J. Chem.* **2023** , *41* , 1443-1449.
- [25] Gunathunge, C. M.;Li, J.;Li, X.;Hong, J. J.; Waegle, M. M. Revealing the Predominant Surface Facets of Rough Cu Electrodes under Electrochemical Conditions. *ACS Catal.* **2020** , *10* , 6908-6923.
- [26] Cui, R.;Yuan, Q.;Zhang, C.;Yang, X.;Ji, Z.;Shi, Z.;Han, X.;Wang, Y.;Jiao, J.; Lu, T. Revealing the Behavior of Interfacial Water in Te-Doped Bi via Operando Infrared Spectroscopy for Improving Electrochemical CO₂ Reduction. *ACS Catal.***2022** , *12* , 11294-11300.
- [27] Dunwell, M.;Yang, X.;Setzler, B. P.;Anibal, J.;Yan, Y.; Xu, B. Examination of Near-Electrode Concentration Gradients and Kinetic Impacts on the Electrochemical Reduction of CO₂ using Surface-Enhanced Infrared Spectroscopy. *ACS Catal.* **2018** ,*8* , 3999-4008.
- [28] Sun, K.;Yu, K.;Fang, J.;Zhuang, Z.;Tan, X.;Wu, Y.;Zeng, L.;Zhuang, Z.;Pan, Y.; Chen, C. Nature-inspired design of molybdenum-selenium dual-single-atom electrocatalysts for CO₂ reduction. *Adv. Mater.* **2022** , *34*, 2206478
- [29] Li, H.;Jiang, T.-W.;Qin, X.;Chen, J.;Ma, X.-Y.;Jiang, K.;Zhang, X.-G.; Cai, W.-B. Selective Reduction of CO₂ to CO on an Sb-Modified Cu Electrode: Spontaneous Fabrication and Physical Insight. *ACS Catal.* **2021** , *11* , 6846-6856.
- [30] Li, Y.;Wei, B.;Zhu, M.;Chen, J.;Jiang, Q.;Yang, B.;Hou, Y.;Lei, L.;Li, Z.;Zhang, R.; Lu, Y. Synergistic Effect of Atomically Dispersed Ni-Zn Pair Sites for Enhanced CO₂ Electroreduction. *Adv. Mater.* **2021** , *33* , e2102212.
- [31] Ma, W.;Xie, S.;Zhang, X. G.;Sun, F.;Kang, J.;Jiang, Z.;Zhang, Q.;Wu, D. Y.; Wang, Y. Promoting electrocatalytic CO₂reduction to formate via sulfur-boosting water activation on indium surfaces. *Nat. Commun.* **2019** , *10* , 892.

- [32] Wang, X.;Sang, X.;Dong, C. L.;Yao, S.;Shuai, L.;Lu, J.;Yang, B.;Li, Z.;Lei, L.;Qiu, M.;Dai, L.; Hou, Y. Proton Capture Strategy for Enhancing Electrochemical CO₂ Reduction on Atomically Dispersed Metal-Nitrogen Active Sites*. *Angew. Chem. Int. Ed.***2021** , 60 , 11959-11965.
- [33] Zhang, J.;Yin, R.;Shao, Q.;Zhu, T.; Huang, X. Oxygen Vacancies in Amorphous InOx Nanoribbons Enhance CO₂ Adsorption and Activation for CO₂ Electroreduction. *Angew. Chem. Int. Ed.* **2019** , 58 , 5609-5613.
- [34] Li, S.;Lu, X.;Zhao, S.;Ceccato, M.;Hu, X.-M.;Roldan, A.;Liu, M.; Daasbjerg, K. p-Block Indium Single-Atom Catalyst with Low-Coordinated In–N Motif for Enhanced Electrochemical CO₂ Reduction. *ACS Catal.* **2022** ,12 , 7386-7395.
- [35] Han, G.;Zhang, X.;Liu, W.;Zhang, Q.;Wang, Z.;Cheng, J.;Yao, T.;Gu, L.;Du, C.;Gao, Y.; Yin, G. Substrate strain tunes operando geometric distortion and oxygen reduction activity of CuN₂C₂ single-atom sites. *Nat. Commun.* **2021** , 12 , 6335.

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