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Efficient Infrared-Light-Driven CO₂ Reduction Over Ultrathin Metallic Ni-doped CoS₂ Nanosheets

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Abstract: Converting CO_2 and H_2O into carbon-based fuel by IR light is a tough task. Herein, compared with other singlecomponent photocatalysts, the most efficient IR-light-driven CO₂ reduction is achieved by an element-doped ultrathin metallic photocatalyst-Ni-doped CoS_2 nanosheets (Ni-CoS₂). The evolution rate of CH_4 over Ni-CoS₂ is up to $101.8 \,\mu molg^{-1}h^{-1}$. The metallic and ultrathin nature endow $Ni-CoS_2$ with excellent IR light absorption ability. The PL spectra and Arrhenius plots indicate that Ni atoms could facilitate the separation of photogenerated carriers and the decrease of the activation energy. Moreover, in situ FTIR, DFT calculations, and CH₄-TPD reveal that the doped Ni atoms in CoS_2 could effectively depress the formation energy of the *COOH, *CHO and desorption energy of CH_4 . This work manifests that element doping in atomic level is a powerful way to control the reaction intermediates, providing possibilities to realize high-efficiency IR-light-driven CO₂ reduction.

t is extremely meaningful to convert CO₂ and H₂O into carbon-based fuels by solar energy, holding great promise to solve the energy crisis and environmental problems.^[1,2] Though great efforts have been put into this area, CO₂ photoreduction efficiency is still very low. One of the reasons is the insufficient solar energy utilization. Previously, CO₂ photoreduction mainly focused on the ultraviolet and visible range,^[3] while the infrared light (ca. 50 % of solar spectrum) driven CO₂ reduction has been rarely reported. Considering the band edges matching and overpotential issues, the band gaps of photocatalysts often need to be larger than 1.8 eV, which theoretically hinders the utilization of infrared light ($h\nu < 1.55$ eV).^[4] Therefore, it is difficult for traditional single-

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202017041. component photocatalyst to achieve IR-light-driven CO_2 reduction without sacrificial agent. In this context, to maximize the use of solar energy, it is imperative to design novel photocatalysts that can fulfill the efficient IR-light-driven CO_2 reduction.

Metallic photocatalysts are expected to be promising candidates for IR-light-driven CO_2 reduction. Compared with semiconductor photocatalysts, the small (or even no) band gaps of metallic photocatalysts ensure their excellent absorption of IR light;^[5] more importantly, the partially-filled conduction band of metallic photocatalysts could act as the intermediate band and allows them to satisfy the redox potentials for IR-light-driven CO_2 reduction.^[6] However, their high carrier concentration often causes severe recombination of electron-hole pairs;^[7] moreover, the CO_2 reduction activity is still very low and CO_2 could only be converted into CO in those systems.^[4,8] Thus, it remains a tough task to efficiently convert CO_2 and H_2O into carbon-based fuels by metallic photocatalysts under IR light irradiation.

Herein, we designed an element-doped ultrathin metallic photocatalyst to achieve high-efficiency IR-light-driven CO₂ reduction. The ultrathin morphology could reduce carrier diffusion length and is beneficial to decrease the electron-hole recombination rates; meanwhile, it also benefits the implementation of element doping at atomic level, which is an effective way to regulate their CO₂ reduction activity and selectivity simultaneously. CoS₂ were taken as an example, and ultrathin Ni-doped CoS₂ nanosheets (called Ni-CoS₂ nanosheets or Ni-CoS₂ for short) were fabricated by a modified salt-mediated strategy (Supporting Information, Figure S1).^[9] XRD pattern (Supporting Information, Figure S3) and Raman spectra (Supporting Information, Figure S4) could be indexed to pure cubic-CoS₂^[10] while the XPS spectra (Supporting Information, Figure S5A,B) clearly verified the introducing of Ni $(3.69 \operatorname{atomic} \%)$ into CoS₂. More defects might also be introduced in Ni-CoS₂ during the doping processes (Supporting Information, Figure S5C,D). TEM image (Figure 1A) manifested their ultrathin morphology, while the annular dark-field TEM image and the corresponding element mappings (Figure 1B) revealed the homogeneous distribution of Co, S, and Ni elements. The lattice plane spacings of Ni-CoS₂ (Figure 1 C) were 0.28 nm with a dihedral angle of 90°, implying their [0 0 1] orientation. Furthermore, AFM image and the height profiles (Figure 1D) showed that the average thickness of Ni-CoS $_2$ were ca. 1.0 nm, which corresponds to 2-unit cells (Supporting Information, Figure S10). Above results verified the successful synthesis of Ni-CoS₂ nanosheets. For comparison, pristine CoS₂ nanosheets



Figure 1. Characterizations for Ni-CoS₂ nanosheets: A) TEM image; B) annular dark-field TEM image and the corresponding element mappings, the scale bar is 100 nm; C) HRTEM image; D) AFM image.

(called CoS₂) were also synthesized (Supporting Information, Figures S3–S10).

Experimental characterizations and theoretical calculations were utilized to disclose the electrical properties and band structures of Ni-CoS2 and CoS2. Both Ni-CoS2 and CoS2 possessed superp electrical transport ability (Figure 2A); more importantly, the resistivities of Ni- CoS₂ and CoS₂ increased along with the elevating temperature verified their metallic nature. Meanwhile, their metallic nature was further confirmed by the valence-band spectra (Supporting Information, Figure S11). Hence, the partially occupied band is considered as the conduction band (CB) for the metallic conductor.^[6] Theoretical calculations were applied to further illustrate their electronic structures (Figure 2B.C: Supporting Information, Figure S12A,B). It was found that their Fermi level located within the conduction band and their metallic nature was validated once again. Notably, metallic materials could generate electrons and holes through interband and intraband transitions.^[4,6] For instance, photon absorption could lead to the electrons transition from $E_{\rm F}$ to lowest unoccupied band (B1) in metallic materials. Herein, UV/Vis-NIR diffuse reflectance spectra and synchrotron-radiation photoelectron spectra were used to further analyze their band structures. The average absorbance for Ni-CoS₂ and CoS₂ were around 1.63 and 1.78 ranging from UV to near infrared region (Figure 2D), which meant 97.7% and 98.3% of incident light was absorbed. And the energy gaps (Eg) of Ni-CoS₂ and CoS₂ (Figure 2D) were 1.15 and 1.05 eV. Meanwhile, secondary electron cutoff (Figure 2E) revealed the E_{F} of Ni-CoS₂ and CoS₂ were -5.04 and -4.81 eV (vs. vacuum), respectively. Ultimately, the electronic band structures of metallic Ni-CoS₂ and CoS₂ were obtained (Figure 2F; Supporting Information, Figure S13). The intraband transitions in



Figure 2. A) Temperature dependence of resistivities; B) density of states (the upper part is spin-up and lower part is spin-down) and C) calculated band structure of Ni-CoS₂ nanosheets (spin-up is red and spin-down is gray); D) UV/Vis-NIR diffuse reflectance spectra, the inset denotes the energy gaps; E) secondary electron cutoff acquired by synchrotron-radiation photoemission spectra; F) diagram of the electronic band structures for Ni-CoS₂ and CoS₂ nanosheets. The B₁, CB, B₋₁, E_F, and E_g represent the lowest unoccupied band, conduction band, the highest fully occupied band, Fermi level, and energy gap, respectively.

the highest fully occupied band (B_{-1} , transitions in B_{-1} from the lower level to the top), and interband transitions from B_{-1} to $E_F E_F$ to B_1 for both Ni-CoS₂ and CoS₂ could be realized by IR light, where the generated holes in the B_{-1} could oxidize H_2O to O_2 and the photoinduced electrons in the B_1 could reduce CO₂ to CH₄ and CO (Figure 2F; Supporting Information, Figure S13).

Infrared-light-driven CO₂ reduction experiments were conducted to investigate their performance (Supporting Information, Figure S15). The temperature of samples will increase under irradiation, and the increased temperature might enhance the CO₂ reduction rate. However, in many cases, photocatalysts are dispersed in liquid solvent (such as water, acetonitrile), in which photoinduced heat is easily wasted.^[11,12] To make better use of photoinduced heat, a quartz tray was used to separate water and photocatalyst, where photoinduced heat could be efficiently retained (Supporting Information, Figure S16A). As expected, both Ni-CoS₂ and CoS₂ could enable CO₂ reduction under IR light to form CH₄ and CO as the main reduction products (Figure 3A; Supporting Information, Figures S26, S27). The evolution rates of CH₄ and CO over Ni-CoS₂ were up to101.8 and 37.5 μ molg⁻¹h⁻¹, which were roughly 3.3 and 2.8 times

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Figure 3. A) Formation rates of CH_4 and CO under infrared light irradiation as well as at 45 °C in the dark; synchrotron-based vacuum UV photoionization mass spectrometry of the gas products for the B) ¹³C and C) ¹⁸O isotope labeling experiments; D) cycling measurements of IR-light-driven CO₂ reduction; E) CO₂ adsorption isotherms; F) photoluminescence spectra. The error bars in A represent the standard deviations of three independent measurements.

higher than those of the CoS₂. Notably, the formation rate of CH₄ over Ni-CoS₂ is so far the highest records among the reported single-component photocatalysts (Supporting Information, Table S1).^[13–20] Meanwhile, the electron selectivity (carbon-based products) of CH₄ for Ni-CoS₂ (90.6%) was also higher than that of CoS₂ (88.2%). The control experiments showed that no CH4 or CO was detected when photocatalysts, IR light or CO₂ was removed (Supporting Information, Figure S4), verifying the crucial role of both the photocatalysts and IR light in transforming CO₂ to CH₄ and CO. ¹³CH₄ and ¹³CO were generated in the ¹³CO₂ labeling experiment (Figure 3B; Supporting Information, Figure S18), which ambiguously proved that CH₄ and CO originated from CO₂. Meanwhile, the presence of ¹⁶O¹⁸O in the ¹⁸O labeling experiment verifies that O₂ originated from H₂O (Figure 3C; Supporting Information, Figure S18). Interestingly, the CO₂ photoreduction performance of Ni-CoS₂ could be further enhanced under full-spectrum irradiation, and the formation rates of CH₄ and CO could reach 243.2 and 63.5 μ mol g⁻¹ h⁻¹ (Supporting Information, Figure S19), respectively. Cycling measurements showed that both Ni-CoS₂ and CoS₂ were of excellent stability and their activities did not show obvious drop even after 24 hours (Figure 3D; Supporting Information, Figure S20).

To evaluate the photothermal effect, the result of thermographic photographs showed that the temperature of $Ni\text{-}CoS_2$

could rise from 17.2°C to 43.2°C under IR light irradiation (Supporting Information, Figure S21A,B). The control experiments depicted that there was negligible amount of gas product at 45 °C in the dark, and the reaction temperature needed to be around 180°C in pure thermocatalysis to obtain comparable CH₄ formation rates (Supporting Information, Figure S22A, Table S2). When photoinduced heat was deliberately excluded (Supporting Information, Figure S23B, S24), the performance of Ni-CoS₂ declined sharply. The result suggested the photoinduced heat was also significant for CO₂ reduction.^[21] These similar phenomena can also be observed when full-spectrum light was applied (Supporting Information, Figures S23C, S25). Therefore, it is a good strategy to make full use of the IR-light-induced heat and a landmark activity for IR-light-driven CO2 reduction was achieved over metallic Ni-CoS2 nanosheets.

To unveil the origin of the boosted IR-light-driven CO₂ reduction performances, fundamental steps were analyzed. The BET surface area of Ni-CoS₂ was 17.75 m²g⁻¹ (Supporting Information, Figure S28), which was almost double that of CoS_2 (8.89 m²g⁻¹). This might be attributed to Ni-CoS₂'s higher degree of disorder (Supporting Information, Figure S3) or more defects (introduced by doping processes simultaneously; Supporting Information, Figures S5, S28). The enlarged surface area could facilitate the CO₂ adsorption in return. As expected, Ni-CoS₂ possessed a CO₂ adsorption capacity of 5.16 cm³g⁻¹, roughly 1.85 times larger than that of CoS_2 (Figure 3E). Then, photoinduced charge carriers were needed to reduce the adsorbed CO₂. Due to the strong photoabsorption ability, almost all the incident light could be absorbed by Ni-CoS₂, which benefited the generation of charge carriers. Meanwhile, the photoluminescence intensity of Ni-CoS₂ was weaker than that of CoS_2 (Figure 3F), suggesting the introducing of Ni atoms facilitated the separation of photogenerated carriers. More importantly, the activation energy to reduce CO2 into CH4 and CO over Ni-CoS₂, measured by Arrhenius plots, was lower than that over CoS₂ [Supporting Information, Figure S22D, Eq. (S4)]. It indicted that the introducing of Ni atoms could enhanced their reactive activity.^[22] Furthermore, both the higher desorption temperature of CO and lower desorption temperature of CH₄ over Ni-CoS₂ than these over CoS₂ (Figure 4A; Supporting Information, Figure S29) were beneficial to further reduce the adsorbed CO into CH₄. In situ FTIR measurements were conducted to detect the reaction intermediates. As for Ni-CoS₂ (Figure 4B), the new peaks at 1643 and 1528 cm⁻¹ could be indexed to *COOH, while those located at 1157 cm⁻¹ and 1080 cm⁻¹ could be assigned to *CH₃O and *CHO, respectively.^[4,14,23] Thus, the IR-lightdriven CO2 reduction processes might be suggested as follows:

 $* + CO_2 + H^+ + e^- \rightarrow *COOH \tag{1}$

$$*COOH + H^+ + e^- \rightarrow H_2O + *CO$$
⁽²⁾

$$^{*}CO + H^{+} + e^{-} \rightarrow ^{*}CHO \text{ or } ^{*}CO \rightarrow ^{*} + CO \uparrow$$
(3)

$$^{*}CHO + H^{+} + e^{-} \rightarrow ^{*}CH_{2}O$$
⁽⁴⁾

Communications



Figure 4. A) CH₄-TPD measurements; B) in situ FTIR for Ni-CoS₂ nanosheets; free energy diagrams of IR-light-driven CO₂ reduction to CO and CH₄ for C) Ni-CoS₂ nanosheets and D) CoS₂ nanosheets.

$$^{*}\mathrm{CH}_{2}\mathrm{O} + \mathrm{H}^{+} + \mathrm{e}^{-} \to ^{*}\mathrm{CH}_{3}\mathrm{O}$$

$$\tag{5}$$

$$^{*}\mathrm{CH}_{3}\mathrm{O} + \mathrm{H}^{+} + \mathrm{e}^{-} \rightarrow ^{*}\mathrm{O} + \mathrm{CH}_{4} \uparrow$$

$$\tag{6}$$

$$^{*}O + H^{+} + e^{-} \rightarrow ^{*}OH \tag{7}$$

$$^{*}OH + H^{+} + e^{-} \rightarrow H_{2}O \tag{8}$$

where the * denotes active sites.

Some important information during the CO₂ reduction processes was obtained with DFT calculations. As displayed in Figure 4C,D and the Supporting Information, Tables S3–5 and Equations (S16)–(S24), the formation of *COOH was the rate-determining step for two photocatalysts, while Ni-CoS₂ possessed a lower *COOH formation energy. The fact that Ni-COOH bonds (1.95 Å) on Ni-CoS₂ were shorter than Co-COOH bonds (1.97 Å) on CoS₂, suggesting the stronger bonding between Ni and *COOH benefited the stabilization of *COOH. In addition, the formation energy of *CHO was much more negative than the desorption energy of CO over Ni-CoS₂ (Figure 4C), implying Ni-CoS₂ were apt to further reduce CO to form CH₄. Moreover, the lower desorption energy of CH₄ over Ni-CoS₂ indicated CH₄ could be easier desorbed from their surface.

In conclusion, high-efficiency IR-light-driven CO₂ reduction has been achieved by Ni-CoS₂ nanosheets. The CH₄ evolution rates were 101.8 μ mol g⁻¹ h⁻¹, which is the highest record for IR-light-driven CO₂ reduction among all singlecomponent photocatalysts. The metallic and ultrathin nature endowed Ni-CoS₂ nanosheets with excellent IR light absorption ability, while their band structures were able to fulfill CO₂ reduction and H_2O oxidation simultaneously by IR light with the partially occupied conduction band acting as the mediator. In situ FTIR and DFT calculations showed that the formation of *COOH intermediate was the rate-determining step, and Ni-CoS₂ nanosheets possessed a lower *COOH formation energy due to the stronger bonding between Ni atoms and *COOH. Furthermore, the introducing of Ni atoms could depress the formation energy of *CHO and desorption energy of CH₄, so that their selectivity and catalytic activity were improved simultaneously.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CO_2 conversion \cdot infrared photocatalysis \cdot metallic photocatalyst \cdot ultrathin 2D materials

- J. L. White, M. F. Baruch, J. E. Pander III, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* 2015, *115*, 12888–12935.
- [2] M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* 2014, 114, 1709-1742.
- [3] X. Chang, T. Wang, J. Gong, Energy Environ. Sci. 2016, 9, 2177– 2196.
- [4] X. Li, L. Liang, Y. Sun, J. Xu, X. Jiao, X. Xu, H. Ju, Y. Pan, J. Zhu, Y. Xie, J. Am. Chem. Soc. 2019, 141, 423–430.
- [5] Y. L. Wang, T. Nie, Y. H. Li, X. L. Wang, L. R. Zheng, A. P. Chen, X. Q. Gong, H. G. Yang, *Angew. Chem. Int. Ed.* **2017**, *56*, 7430–7434; *Angew. Chem.* **2017**, *129*, 7538–7542.
- [6] X. Xu, C. Randorn, P. Efstathiou, J. T. Irvine, Nat. Mater. 2012, 11, 595–598.
- [7] Z. Hu, G. Liu, X. Chen, Z. Shen, J. C. Yu, Adv. Funct. Mater. 2016, 26, 4445–4455.
- [8] L. Liang, X. Li, J. Zhang, P. Ling, Y. Sun, C. Wang, Q. Zhang, Y. Pan, Q. Xu, J. Zhu, Y. Luo, Y. Xie, *Nano Energy* **2020**, 69, 104421.
- [9] X. Xiao, H. Song, S. Lin, Y. Zhou, X. Zhan, Z. Hu, Q. Zhang, J. Sun, B. Yang, T. Li, L. Jiao, J. Zhou, J. Tang, Y. Gogotsi, *Nat. Commun.* 2016, *7*, 11296.
- [10] S. G. Lyapin, A. N. Utyuzh, A. E. Petrova, A. P. Novikov, T. A. Lograsso, S. M. Stishov, J. Phys. Condens. Matter 2014, 26, 396001.
- [11] S. Sun, M. Watanabe, J. Wu, Q. An, T. Ishihara, J. Am. Chem. Soc. 2018, 140, 6474–6482.

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- [12] X. K. Wang, J. Liu, L. Zhang, L. Z. Dong, S. L. Li, Y. H. Kan, D. S. Li, Y. Q. Lan, ACS Catal. 2019, 9, 1726–1732.
- [13] Z. B. Fang, T. T. Liu, J. Liu, S. Jin, X. P. Wu, X. Q. Gong, K. Wang, Q. Yin, T. F. Liu, R. Cao, H. C. Zhou, J. Am. Chem. Soc. 2020, 142, 12515–12523.
- [14] X. Li, Y. Sun, J. Xu, Y. Shao, J. Wu, X. Xu, Y. Pan, H. Ju, J. Zhu, Y. Xie, *Nat. Energy* **2019**, *4*, 690–699.
- [15] S. Zhu, S. Liang, J. Bi, M. Liu, L. Zhou, L. Wu, X. Wang, Green Chem. 2016, 18, 1355–1363.
- [16] Y. Bai, J. Zhao, S. Feng, X. Liang, C. Wang, Chem. Commun. 2019, 55, 4651–4654.
- [17] J. Li, Y. Ye, L. Ye, F. Su, Z. Ma, J. Huang, H. Xie, D. E. Doronkin, A. Zimina, J. D. Grunwaldt, Y. Zhou, *J. Mater. Chem. A* **2019**, *7*, 2821–2830.
- [18] J. Yu, J. Low, W. Xiao, P. Zhou, M. Jaroniec, J. Am. Chem. Soc. 2014, 136, 8839–8842.

- [19] Q. Liu, Y. Zhou, J. Kou, X. Chen, Z. Tian, J. Gao, S. Yan, Z. Zou, J. Am. Chem. Soc. 2010, 132, 14385–14387.
- [20] S. Sorcar, Y. Hwang, C. A. Grimes, S. I. In, *Mater. Today* 2017, 20, 507–515.
- [21] Y. X. Li, M. M. Wen, Y. Wang, G. Tian, C. Y. Wang, J. C. Zhao, Angew. Chem. Int. Ed. 2021, 60, 910–916; Angew. Chem. 2021, 133, 923–929.
- [22] L. Wang, W. Zhang, X. Zheng, Y. Chen, W. Wu, J. Qiu, X. Zhao, X. Zhao, Y. Dai, J. Zeng, *Nat. Energy* **2017**, *2*, 869–876.
- [23] G. E. Ewing, W. E. Thompson, G. C. Pimentel, J. Chem. Phys. 1960, 32, 927–932.

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