

Research Highlight

Open Access



Spin polarization effect enhances photocatalytic CO₂ reduction

Lijie Wang¹, Shiqun Wu^{1,2,*}, Jinlong Zhang^{1,2,*}

¹Key Laboratory for Advanced Materials, Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, Shanghai Engineering Research Center for Multimedia Environmental Catalysis and Resource Utilization, East China University of Science and Technology, Shanghai 200237, China.

²Shanghai Engineering Research Center for Multimedia Environmental Catalysis and Resource Utilization, East China University of Science and Technology, Shanghai 200237, China.

***Correspondence to:** Prof. Shiqun Wu, Prof. Jinlong Zhang, Key Laboratory for Advanced Materials, Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, Shanghai Engineering Research Center for Multimedia Environmental Catalysis and Resource Utilization, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. E-mail: wushiqun@ecust.edu.cn; jlzhang@ecust.edu.cn

How to cite this article: Wang, L.; Wu, S.; Zhang, J. Spin polarization effect enhances photocatalytic CO₂ reduction. *Chem. Synth.* **2025**, *5*, 46. <https://dx.doi.org/10.20517/cs.2025.24>

Received: 20 Feb 2025 **First Decision:** 2 Apr 2025 **Revised:** 3 Apr 2025 **Accepted:** 9 Apr 2025 **Published:** 22 Apr 2025

Academic Editor: Jun Xu **Copy Editor:** Ting-Ting Hu **Production Editor:** Ting-Ting Hu

Keywords: CO₂ photoreduction, spin polarization, charge separation, Co₃O₄

Efficient CO₂ conversion to high-value hydrocarbons such as CH₄ is crucial for carbon neutrality but is hindered by sluggish proton-coupled electron transfer and charge recombination. Enhancing electron density at active sites has been a key strategy, with approaches such as defect engineering, noble metal loading, and heterojunction construction yielding significant progress. However, inherent charge carrier limitations necessitate alternative strategies to further improve photocatalytic efficiency^[1].

Spin polarization, defined as the unequal distribution of spin-up and spin-down electrons within a system, has recently garnered significant attention as an effective strategy to modulate charge carrier dynamics in photocatalytic processes. This spin asymmetry can be induced via the incorporation of magnetic metal dopants (e.g., Mn, Fe), the introduction of cationic vacancies, or through structural asymmetry, and can be further amplified under the application of an external magnetic field. During the transport of



© The Author(s) 2025. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.



photogenerated electrons, spin flipping may occur as a result of spin-orbit coupling and hyperfine interactions. In conventional, non-spin-polarized systems, such spin-flipped electrons can still recombine readily with holes of opposite spin. By contrast, in spin-polarized systems, flipped electrons are less likely to encounter spin-compatible holes [Figure 1A], thereby effectively suppressing charge recombination. This mechanism prolongs the lifetime of photogenerated carriers and facilitates enhanced spatial separation of charges. In addition to reinforcing spin polarization, an external magnetic field also induces Lorentz forces that drive photogenerated electrons and holes in opposite directions [Figure 1B], thereby accelerating carrier migration and further diminishing recombination probability. The synergistic effects of spin-selective recombination suppression and magnetically induced charge separation ultimately lead to significantly enhanced photocatalytic efficiency^[2].

The spin polarization effect has achieved considerable advancements in photocatalytic hydrogen production and has recently emerged as a promising strategy for CO₂ photoreduction. For instance, Lin *et al.* investigated the role of spin polarization in manganese-ion (Mn²⁺)-doped halide perovskite nanoplates (CsPbBr₃ NPLs)^[3]. Their study demonstrated that Mn doping, in conjunction with an external magnetic field, enabled precise modulation of spin-polarized electrons, significantly enhancing the efficiency of photocatalytic CO₂ reduction. However, while this work highlighted the role of spin polarization in promoting charge carrier separation, it had a negligible impact on product selectivity in CO₂ reduction.

Building upon this strategy, we incorporated Mn dopants into Co₃O₄ to induce spin polarization. The Mn sites functioned as hole-enriching centers adjacent to Co, forming spatially proximate redox-active sites^[4]. The Mn-induced spin polarization effect, further amplified by an external magnetic field, effectively suppressed charge recombination between these neighboring redox sites. Therefore, the spatial confinement of redox centers facilitated efficient proton transfer, which not only led to a remarkable 28.8-fold increase in CO₂ reduction efficiency but also promoted multi-electron-proton coupling [Figure 1C-E], thereby enhancing methane selectivity from 30.7% to 94.2%^[4].

To further elucidate the role of spin polarization in photocatalytic CO₂ reduction, we designed cobalt oxide with engineered Co vacancies. Through comprehensive experimental and theoretical investigations, we demonstrated that spin polarization not only enhances charge separation kinetics but also optimizes the energy landscape of CO₂ reduction [Figure 1F]^[2]. Notably, for the first time, we provided a thermodynamic framework to explain how spin polarization facilitates photocatalytic CO₂ reduction, offering profound mechanistic insights into its fundamental role in guiding charge dynamics and reaction thermodynamics. Although the application of spin polarization in CO₂ photoreduction remains limited, existing studies collectively suggest that its promotional effects can be primarily attributed to two aspects: first, the suppression of charge carrier recombination and the enhancement of carrier migration, which improve the reaction kinetics; second, the modulation of energy barriers in key reaction steps, thereby favorably influencing reaction thermodynamics. These combined effects not only enhance the overall catalytic activity but may also steer the reaction pathway, potentially altering product selectivity.

Despite the significant potential of spin polarization in CO₂ photoreduction, research in this field remains in its early stages. Notably, in electrocatalysis and other photocatalytic domains, the modification of materials with chiral molecules or the fabrication of spin-polarized materials has emerged as a growing research focus. For example, Ai *et al.* utilized chiral methionine molecules as symmetry-breaking agents to synthesize chiral ZnO [Figure 1G]^[5]. Their study revealed that the chiral structure functions as a spin filter, inducing spin polarization, which not only prolongs carrier lifetimes but also increases the population of triplet species, ultimately enhancing photocatalytic oxygen evolution efficiency by more than twofold.

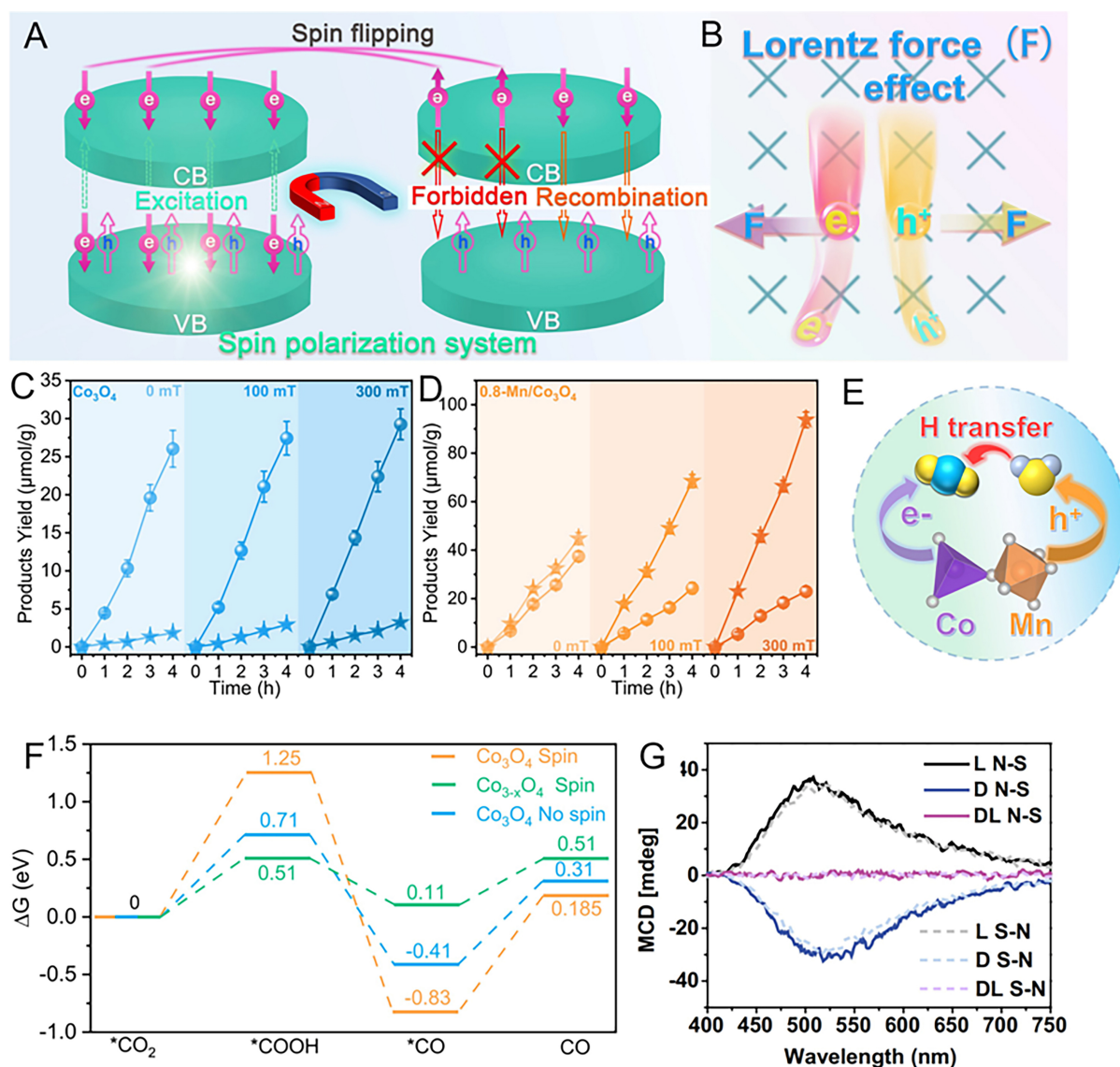


Figure 1. (A) Mechanism for spin polarization inhibiting photoinduced carrier recombination^[2]; (B) Illustration of the influence of the Lorentz force on the transport of photogenerated charge carriers^[2]. Reproduced with permission from^[2]. Copyright 2024 American Chemical Society; Photocatalytic CO₂ reduction performance of Co₃O₄ (C) and Mn/Co₃O₄ (D) under external magnetic field (from 0 to 300 mT), catalyst: 5 mg, light intensity: 80 mW·cm⁻²^[4]; (E) Photocatalytic CO₂ methanation mechanism of Mn/Co₃O₄^[4]. Reproduced with permission from^[4]. Copyright 2024 American Chemical Society; (F) Computed free energy profiles for CO₂ photoreduction to CO on Co₃O₄ and Co_{3-x}O₄, comparing results with and without incorporating spin polarization in the calculations^[2]. Reproduced with permission from^[2]. Copyright 2024 American Chemical Society; (G) MCD spectra measured under parallel (solid lines) and antiparallel (dashed lines) magnetic fields^[5]. Reproduced with permission from^[5]. Copyright 2023 Springer Nature. MCD: Magnetic circular dichroism; CB: conduction band; VB: valence band.

Looking ahead, the incorporation of chiral molecular modification or the development of intrinsically spin-polarized materials is expected to advance the design of highly efficient spin-polarized materials for CO₂ photoreduction. Moreover, such approaches will provide deeper mechanistic insights into the intrinsic role of spin polarization in governing charge dynamics and reaction pathways in CO₂ photoreduction.

Beyond CO₂ photoreduction, spin polarization has demonstrated significant potential in various catalytic applications, including electrocatalysis and other photocatalytic reactions, suggesting that spin polarization

may serve as a universal strategy for improving charge dynamics across diverse catalytic systems. However, challenges remain in precisely controlling spin polarization effects in non-magnetic materials, as well as in designing stable spin-polarized interfaces under reaction conditions. Developing advanced characterization techniques and theoretical models will be critical for further elucidating these mechanisms and guiding material design.

In summary, spin polarization represents a groundbreaking advancement in photocatalytic CO₂ reduction, addressing critical challenges in charge carrier dynamics and product selectivity. The rational design of spin-polarized materials, particularly through chiral modifications and defect engineering, will be key to unlocking new levels of efficiency in CO₂ photoreduction. Future research should focus on deepening the mechanistic understanding of spin polarization at the atomic level and exploring synergistic strategies that combine spin-selective effects with advanced photocatalytic architectures.

DECLARATIONS

Authors' contributions

Wrote the draft manuscript: Wang, L.

Revised and rewrote some parts of the manuscript: Wu, S.; Zhang, J.

Availability of data and materials

Not applicable.

Financial support and sponsorship

This work was supported by the National Natural Science Foundation of China (22202070), the Chenguang Program of Shanghai Education Development Foundation and Shanghai Municipal Education Commission (24CGA30), National Key R&D Program of China Program of China (2022YFE0107900, 2022YFB3803600), the Innovation Program of Shanghai Municipal Education Commission (2021-01-07-00-02-E00106), the Science and Technology Commission of Shanghai Municipality (22230780200, 20DZ2250400, 2018SHZDZX03), the Shanghai Rising-Star Program (22YF1410200), and Fundamental Research Funds for the Central Universities (222201717003).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2025.

REFERENCES

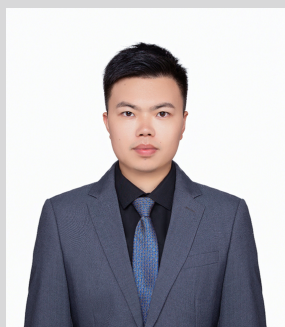
1. Pan, L.; Ai, M.; Huang, C.; et al. Manipulating spin polarization of titanium dioxide for efficient photocatalysis. *Nat. Commun.* **2020**, *11*, 418. [DOI](#) [PubMed](#) [PMC](#)
2. Li, M.; Wu, S.; Liu, D.; et al. Optimizing reaction kinetics and thermodynamics for photocatalytic CO₂ reduction through Spin polarization manipulation. *ACS. Catal.* **2024**, *14*, 14098-109. [DOI](#)

3. Lin, C. C.; Liu, T. R.; Lin, S. R.; et al. Spin-polarized photocatalytic CO₂ reduction of Mn-doped perovskite nanoplates. *J. Am. Chem. Soc.* **2022**, *144*, 15718-26. DOI PubMed
4. Li, M.; Wu, S.; Liu, D.; et al. Engineering spatially adjacent redox sites with synergistic spin polarization effect to boost photocatalytic CO₂ methanation. *J. Am. Chem. Soc.* **2024**, *146*, 15538-48. DOI PubMed
5. Ai, M.; Pan, L.; Shi, C.; et al. Spin selection in atomic-level chiral metal oxide for photocatalysis. *Nat. Commun.* **2023**, *14*, 4562. DOI PubMed PMC



Lijie Wang

Lijie Wang received his B.Sc. degree in Materials Chemistry from Anqing Normal University in 2022. He is currently pursuing his M.Sc. in Applied Chemistry at the School of Chemistry and Molecular Engineering, East China University of Science and Technology, under the supervision of Prof. Jinlong Zhang. His research focuses on the design and application of catalysts for photocatalytic reduction of carbon dioxide to value-added carbon-based compounds.



Shiqun Wu

Shiqun Wu received his Ph.D. in 2021 from East China University of Science and Technology under the supervision of Prof. Jinlong Zhang, and subsequently continued his postdoctoral research at the same institution. In 2024, he was appointed as an Associate Researcher at East China University of Science and Technology. His research interests focus on the design and modulation of atomically dispersed active sites in photocatalysts, with applications in the photocatalytic conversion of methane and carbon dioxide. He is currently a Youth Committee Member of the Photochemistry Division of the Chinese Renewable Energy Society, a Youth Editorial Board Member of *Carbon Neutralization*, and a Member of the Working Group of Youth Editor of *Chemical Synthesis*.



Jinlong Zhang

Jinlong Zhang received his Ph.D. in Fine Chemicals from East China University of Science and Technology in 1993. He subsequently conducted postdoctoral research at Osaka Prefecture University. In 2000, he was appointed full professor at East China University of Science and Technology. In recognition of his academic contributions, he was elected a Member of Academia Europaea in 2019.

Professor Zhang currently serves on the Editorial Board of *Applied Catalysis B: Environmental* and is an Associate Editor of *Research on Chemical Intermediates*. His research focuses on photocatalysis, environmental science, and materials science. He has been recognized as one of Elsevier's "Most Cited Chinese Researchers" annually from 2014 to 2024 and has been named a "Highly Cited Researcher" by Clarivate Analytics from 2018 to 2024.