Research Highlight

F-ZrO₂ Based, Solar Driven Photocatalytic Production of High-Purity CO from Formic Acid

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Received: 2 December 2024; Accepted: 6 December 2024; Available online: 13 December 2024

ABSTRACT: High-purity carbon monoxide is crucial for various industrial applications, but current production methods are costly and require complex purification steps. A photothermal approach has been explored for producing high-purity carbon monoxide from formic acid, optimizing conditions to favor the dehydration pathway and minimizing hydrogen contamination. Using zirconium dioxide-based catalysts and sunlight-driven processes enhances efficiency, achieving high-purity carbon monoxide with reduced hydrogen by-products. The photothermal technique offers a promising, sustainable method for high-purity carbon monoxide production from formic acid, which could significantly reduce industrial costs and environmental impact.

Keywords: CO; Formic acid decomposition; Photothermal catalysis; ZrO_2

Carbon monoxide (CO) with a purity exceeding 99.999% is essential in industries such as CO lasers, environmental monitoring, integrated circuits, and electronics. Conventionally, high-purity CO is produced by separating it from gas mixtures like CO, H_2, and CH_4. Still, this process requires multiple purification steps, making CO one of the most expensive industrial gases [1]. Formic acid (HCOOH) presents a promising alternative for CO production through dehydration ($HCOOH \rightarrow CO + H_2O$), offering a high output-to-input value ratio [2]. However, formic acid can decompose via two different pathways: dehydration, which yields CO and water, and dehydrogenation, which produces CO_2 and hydrogen. To achieve high-purity CO, it is crucial to favor the dehydration pathway. Traditional catalysts have shown promise by reducing the hydrogen content to as low as 0.2%, but trace amounts of hydrogen remain, necessitating additional purification steps [3]. A critical challenge remains to improve catalyst efficiency to minimize hydrogen formation and explore methods for removing hydrogen during CO production.

The study of Li et al. [4] aims to address this challenge by exploring sunlight-driven methods for CO production (Figure 1). Theoretical calculations were utilized to identify suitable catalysts for formic acid dehydrogenation, revealing that pure fluorite-structured ZrO_2 could effectively exclude formic acid dehydrogenation intermediates. A synthesis method was developed to produce pure fluorite ZrO2 nanomaterials capable of directly generating high-purity CO from formic acid. The pure fluorite ZrO_2 nanosheets exhibited a stable thermal formic acid CO production rate of 55 mmol g^{-1} h^{-1} at 250 °C, with no hydrogen impurity. Furthermore, assisted by a TiC/Cu-based photothermal reactor, the pure fluorite ZrO_2 nanosheets achieved a photothermal CO production rate of 83 mmol g^{-1} h^{-1}, along with an exceptionally high solar-to-chemical efficiency of 12.3% under 0.5 sun irradiation. In situ testing further validated their theoretical predictions, demonstrating that the pure fluorite ZrO_2 surface effectively excludes all formic acid dehydrogenation intermediates. In addition, under ambient solar irradiation, the system achieved 1538 L m^{-2} of pure CO production per day, corresponding to an estimated input-output profit of US$18,714 m^{-2} per year.

https://doi.org/10.70322/prp.2024.10012

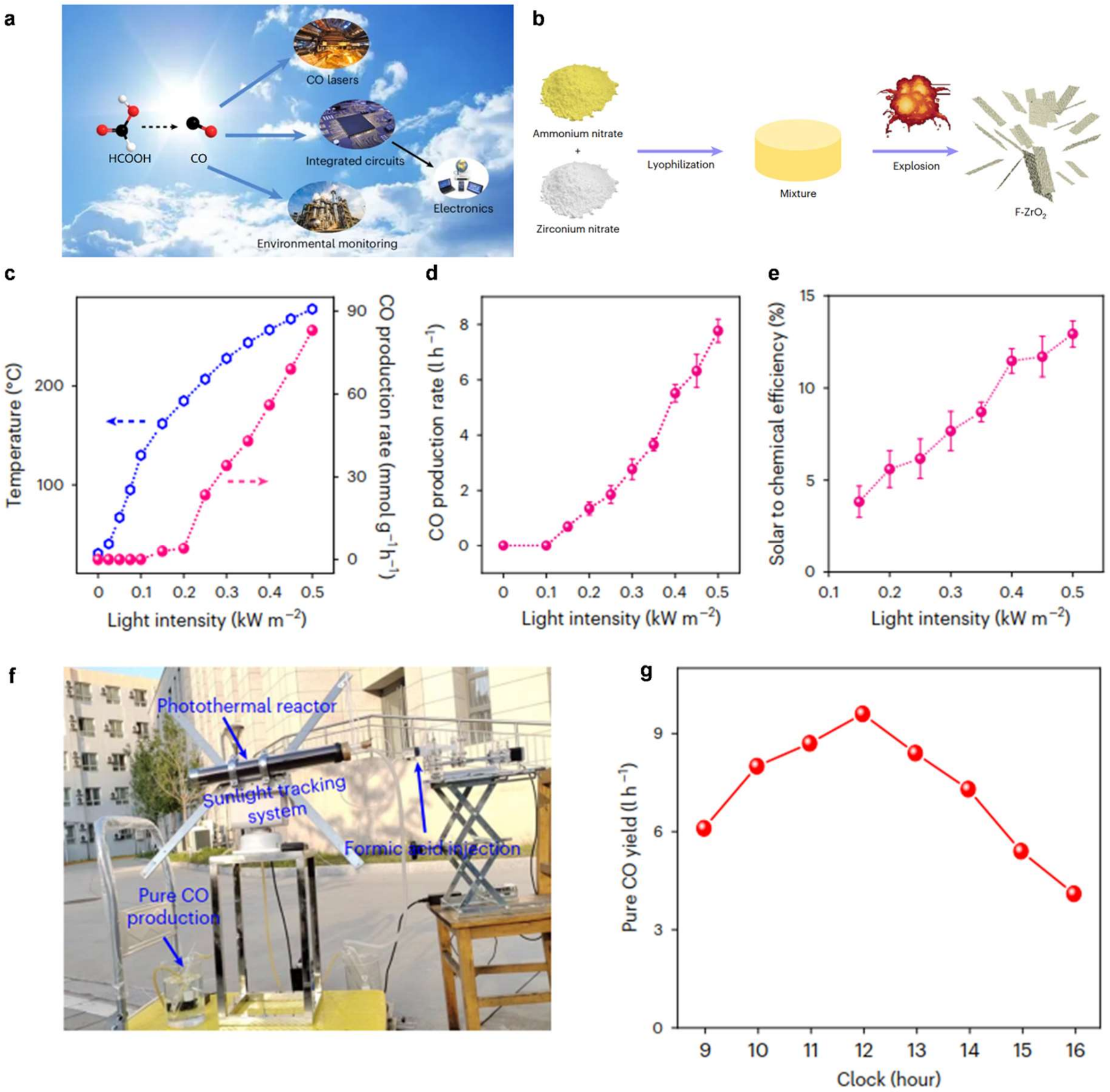

Figure 1. (**a**) Applications of high-purity CO produced through photothermal decomposition of formic acid in various industries such as CO lasers, integrated circuits, electronics, and environmental monitoring. Black, red, and white colors represent C, O, and H atoms, respectively. (**b**) Synthesis process of pure fluorite ZrO_2 (F-ZrO_2) using an explosion method. (**c**) Temperature (blue line) and CO production rate (red line) of F-ZrO_2 combined with a TiC/Cu-based reactor under sunlight irradiation. Test conditions: 30 mg catalyst; formic acid flow rate: 0.02 mL/min. (**d**) CO production rate and (**e**) corresponding solar-to-chemical efficiency of scalable photothermal formic acid dehydration. Test conditions (**d**,**e**): 40 g catalyst; formic acid flow rate: 0.15 to 14 mL/h. Error bars represent standard deviations (s.d.) from n = 3 independent tests. Data are presented as mean values ± s.d. (**f**) Outdoor photothermal formic acid dehydration at Hebei University. (**g**) CO production rate of outdoor scalable photothermal formic acid dehydration. Test conditions: 40 g catalyst; formic acid flow rate: 12 to 36 mL/h. (adapted with permission from Li et al. [4], copyright 2024, Springer Nature).

Overall, the study of Li et al. [4] represents a groundbreaking innovation in high-purity CO production, showcasing the remarkable use of a sunlight-driven system for CO generation. The clever integration of pure fluorite-structured ZrO_2, produced through an explosion method, ensures exceptional stability and hydrogen-free CO output, pushing the boundaries of scientific ingenuity. With outstanding solar-to-chemical efficiency and scalability, this work offers a transformative, eco-friendly solution that reshapes the future of industrial CO production. While this study represents a significant breakthrough, there are a few areas for further enhancement. On one hand, enhancing the long-term stability and anti-poisoning ability of the catalyst is crucial for sustained and efficient operation. On the other hand, conducting a comprehensive life cycle assessment to evaluate the system's environmental impact and overall performance would provide valuable insights for further improvements. Despite the challenges, the solar-driven formic acid dehydration technology for high-purity CO production holds promising potential, with the prospect of achieving more efficient, cost-effective, and environmentally friendly industrial applications in the future.

Acknowledgments

Y. Zheng is grateful for support from the Academy of Advanced Carbon Conversion Technology, Huaqiao University. G. Li is grateful for support from the State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University.

Author Contributions

Y.Z. wrote the paper. Y.C., G.L. and S.W. revised the paper. All authors assisted during the manuscript preparation.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Funding

This work was financially supported by the Natural Science Foundation of Xiamen, China (3502Z202372027 and 3502Z202373050), Fujian Provincial Natural Science Foundation of China (2023J01115 and 2023J01117), the National Natural Science Foundation of China (21902051), the Open Research Fund of Academy of Advanced Carbon Conversion Technology, Huaqiao University (AACCT0005) and the Open Project Program of the State Key Laboratory of Photocatalysis on Energy and Environment (SKLPEE-KF202209), Fuzhou University.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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