Supplementary Materials

UiO66-NH₂@In₂O₃ Heterostructures for Improved Photocatalytic CO₂ Reduction

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Samples	Sacrificial agent	Products	Productivity (µmol/g/h)	Ref.
UiO66-NH ₂ @In ₂ O ₃	H_2O	СО	69.30	This work
Ag/GaOOH/CaTiO ₃	H ₂ O	CO	0.04	1
UiO66 with Defects	H ₂ O	CO	1.33	2
UiO68-NH ₂ -ML100	TEOA	CO	21.3	3
Ni-MOF (H ₂ O)	Ru(bpy) ₃ Cl ₂ ·6H ₂ O TEOA	СО	9610	4
Co-MOF/Cu ₂ O	H_2O	CO	3.83	5
PCN222-Cu@TpPa1	H ₂ O	CO CH ₄	0.6 21.3	6
PCN-224(Cu)/TiO ₂	H ₂ O	CO	37.21	7

Table S1. A brief survey of CO₂ reduction performances of reported photocatalysts.

1. H.X. Qiu, A. Yamamoto, H. Yoshida, *Sustainable Energy Fuels*, 2024,8, 1287-1294.

- Y.Q. He, C.G. Li, X.B. Chen, Z. Shi, S.H. Feng, ACS Appl. Mater. Interfaces 2022, 14, 25, 28977–28984.
- 3. S.Q. Wang, X.Z. Wang, X.M. Cheng, J. Ma, W.Y. Sun, J. Mater. Chem. A, 2022, 10, 16396-16402.
- 4. K.N. Song, S.J. Liang, X.H. Zhong, M.Y. Wang, X.F. Mo, X.Q. Lei, Z. Lin, *Applied Catalysis B: Environmental*, 2022, 309,121232.
- W.W. Dong, J. Jia, Y. Wang, J.R. An, O.Y. Yang, X.J. Gao, Y.L. Liu, J. Zhao, D.S. Li, *Chem. Eng. J.*, 438, 2022,135622.
- 6. Z.L. Wu, W. Li, L.L. Hou, Q.M. Wei, H.X. Yang, Y.Y. Jiang, D.Y. Tang, Sep. Purif. Technol., 311, 2023, 123322.
- 7. L. Wang, P.X. Jin, J.W. Huang, H.D. She, Q.Z. Wang, ACS Sustain. Chem. Eng, 18, 2019, 7, 15660-15670.



Figure S1. The standard XRD pattern of In_2O_3 and UiO66-NH₂ shows that the main In_2O_3 peaks around 30° and 35° overlap with the diffraction peaks of UiO66-NH₂, making it difficult to distinguish the In_2O_3 phase in the heterostructure.



Figure S2. (a, b) The estimated band gap of UiO66-NH₂ and In₂O₃ from Tauc plots. (c, d) Mott-Schottky curves of samples tested at 1000 Hz and 1500Hz in 0.5 mol L^{-1} Na₂SO₄ solution.



Figure S3. XRD patterns of $InN_3O_9 \cdot xH_2O$ (a) and $InN_3O_9 \cdot xH_2O$ calcined at 250 °C (b), 280 °C (c), and 300 °C (d). XRD analysis confirmed that calcination at 250 °C, 280 °C, and 300 °C for 4 hours consistently produced pure In_2O_3 , as no diffraction peaks corresponding to indium nitrate were observed.



Figure S4. XRD patterns of UiO66-NH₂@In³⁺ calcined at 300 °C (a) and 350 °C (b). Increasing the calcination temperature to 300 °C resulted in significantly weakened XRD diffraction peaks, though they remained assignable to UiO66-NH₂, indicating partial structural collapse (**Figures S4a**). At 350 °C, the XRD peaks corresponding to UiO66-NH₂ disappeared entirely, and only ZrO₂ and In₂O₃ diffraction peaks were observed, signaling complete framework decomposition. Specifically, the main diffraction peaks of In₂O₃ overlap with the peaks of ZrO₂ at around 30° and 35° (2θ), which makes it difficult to distinguish the In₂O₃ phase in the XRD pattern. The standard XRD pattern of In₂O₃ is for reference (PDF#06-0416). To provide a clearer view of the phase conversion of UiO66-NH₂@In³⁺, the bottom of Figure S4 provides a detailed description of the product transformation as the calcination temperature increases from 250°C to 350°C. Initially, the product is UiO66-NH₂@In₂O₃ (250°C), which gradually transitions into a partially collapsed structure, UiO66-NH₂(ZrO₂)/In₂O₃ (300°C). Ultimately, the structure fully collapses, resulting in a ZrO₂/In₂O₃ composite (350°C).



Figure S5. SEM images of UiO66-NH₂@In³⁺ calcined at 300 °C (a) and 350 °C (b). SEM analysis revealed that samples calcined at 300 °C exhibited partially collapsed structures with traces of octahedral morphology and the emergence of numerous nanoparticles (**Figures S5a**). At 350 °C, the structure collapsed entirely, leaving only aggregated nanoparticles (**Figures S5b**).



Figure S6. Photoelectrochemical measurements of UiO66-NH₂, In_2O_3 , and UiO66-NH₂@In₂O₃ confirm enhanced photocatalytic activity, as evidenced by the significantly higher photocurrent observed for UiO66-NH₂@In₂O₃.