Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Material

Photocatalytic CO_2 Reduction to CH_4 by Iron Porphyrin Supported on Atomically Thin Defective Titanium Dioxide

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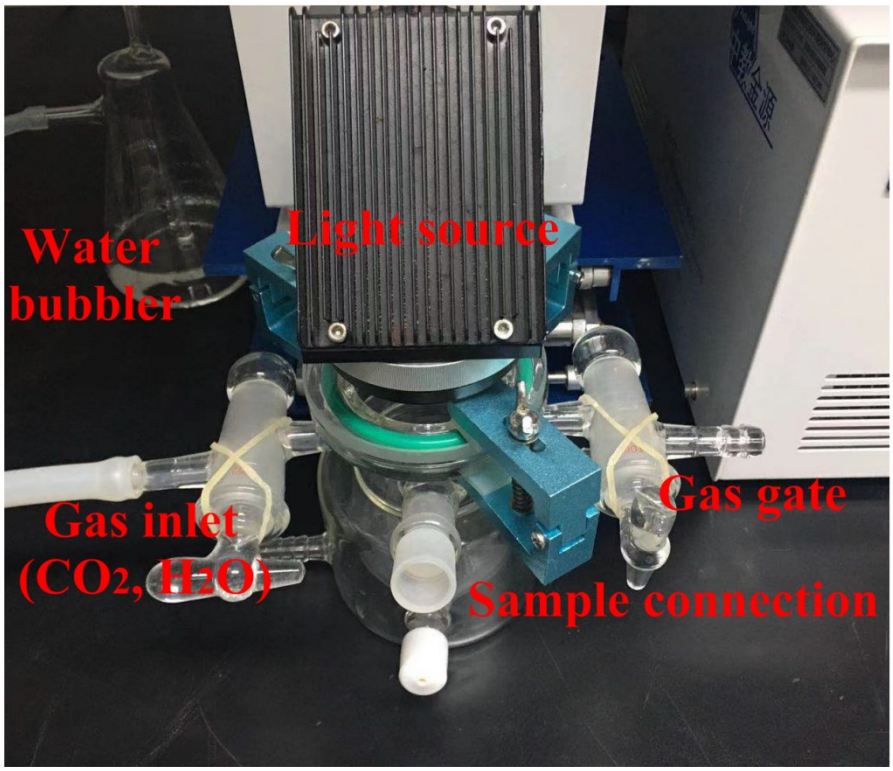

Figure S1. The design of photocatalytic reactor system.

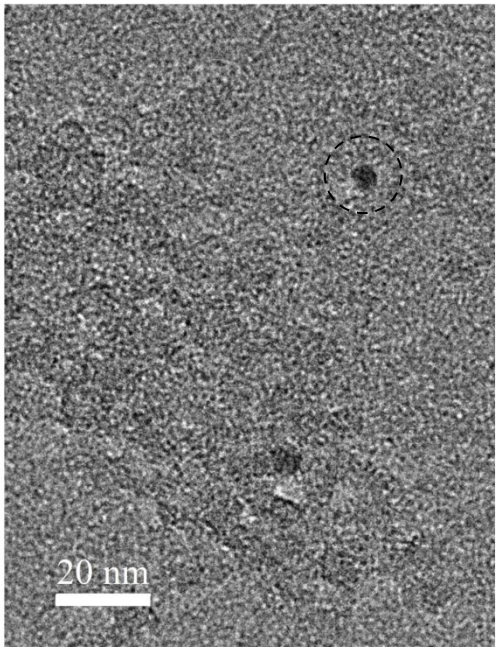

Figure S2. TEM image of pure FeTPP.

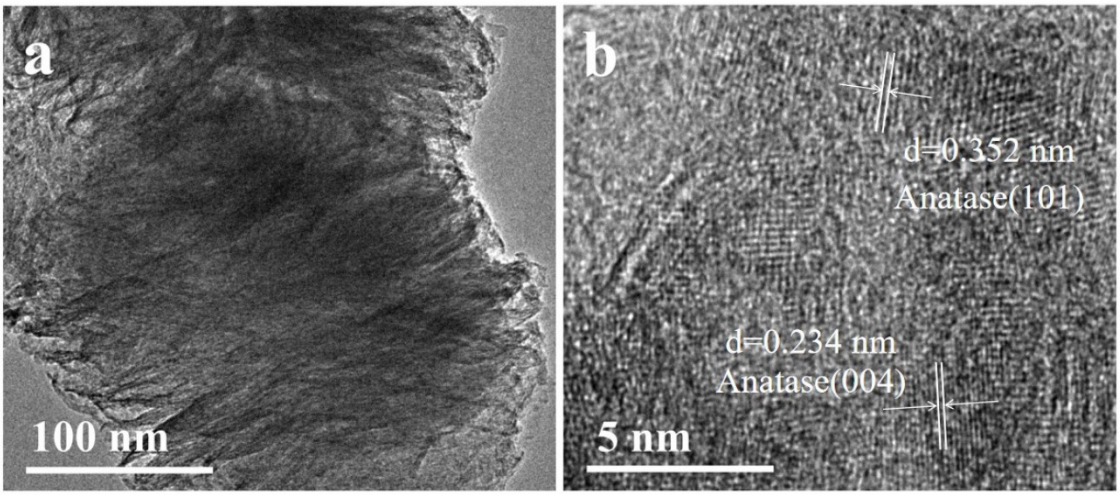

Figure S3. (a) TEM spectra and (b) HRTEM spectra of B-TiO_2-350.

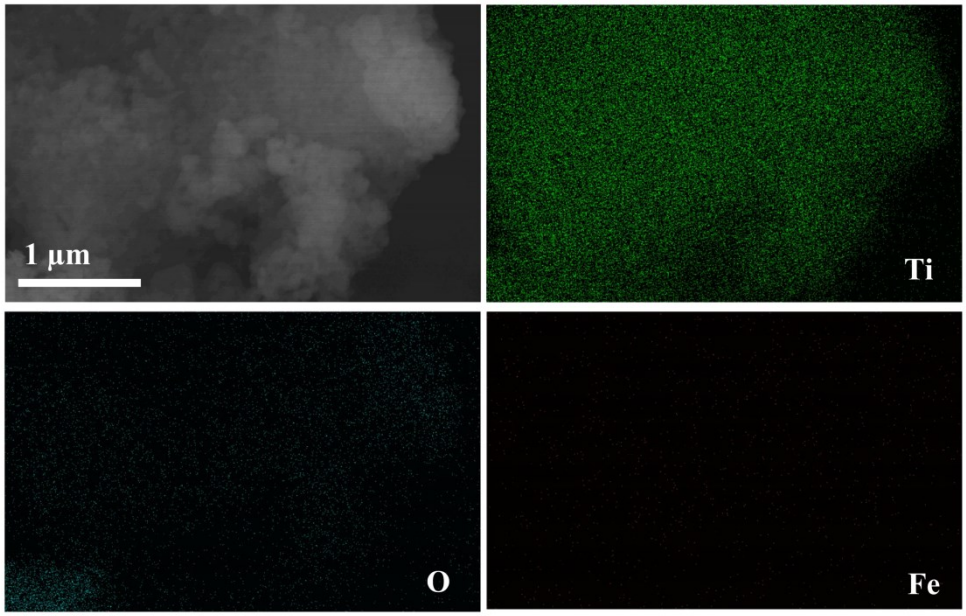

Figure S4. EDS elemental maps of B-TiO_2-350.

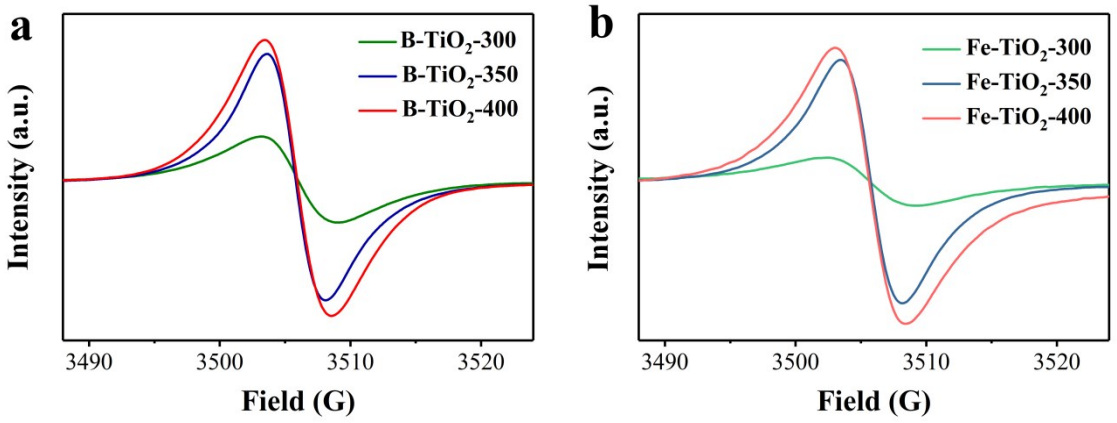

Figure S5. EPR spectra of (a) B-TiO_2-x and (b) Fe-TiO_2-x.

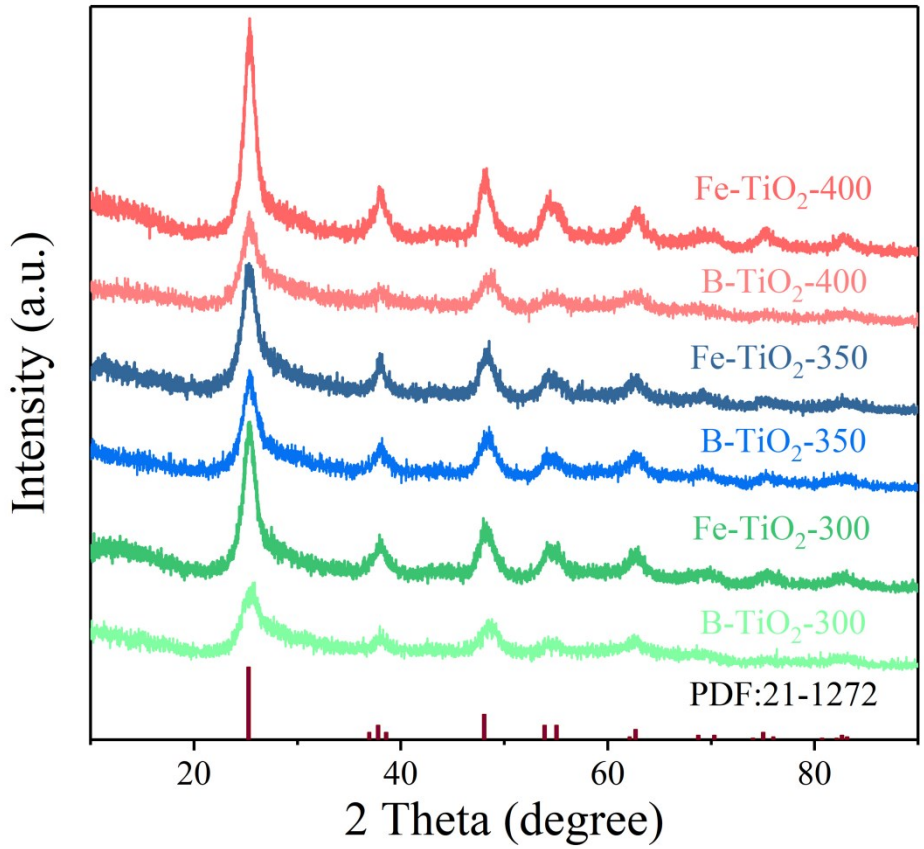

Figure S6. XRD pattern of B-TiO_2-x and Fe-TiO_2-x.

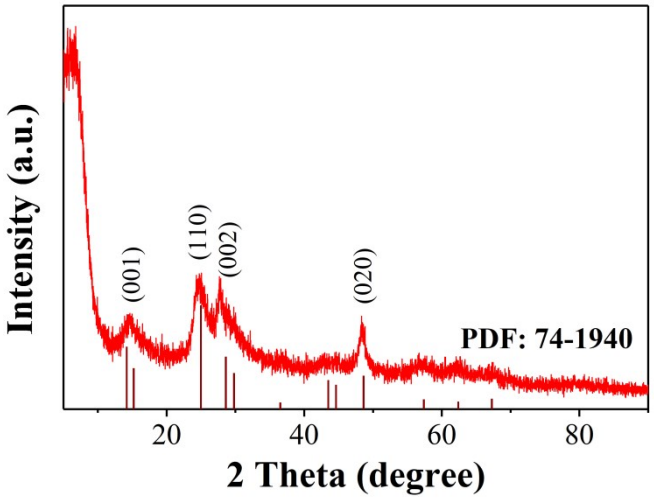

Figure S7. XRD pattern of 2D TiO_2.

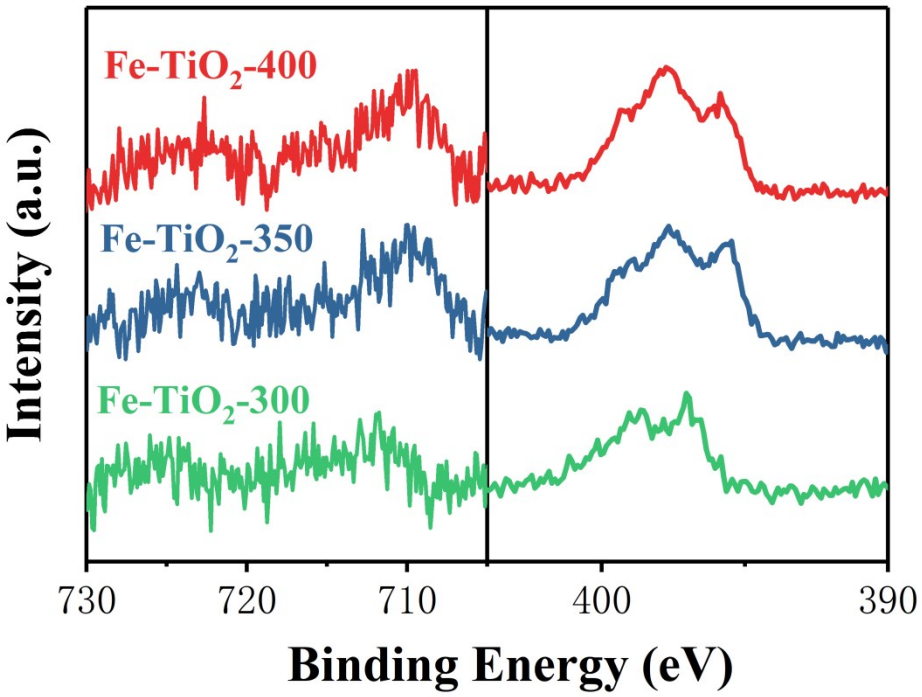

Figure S8. Fe 2p and N 1s XPS spectra of Fe-TiO_2-x.

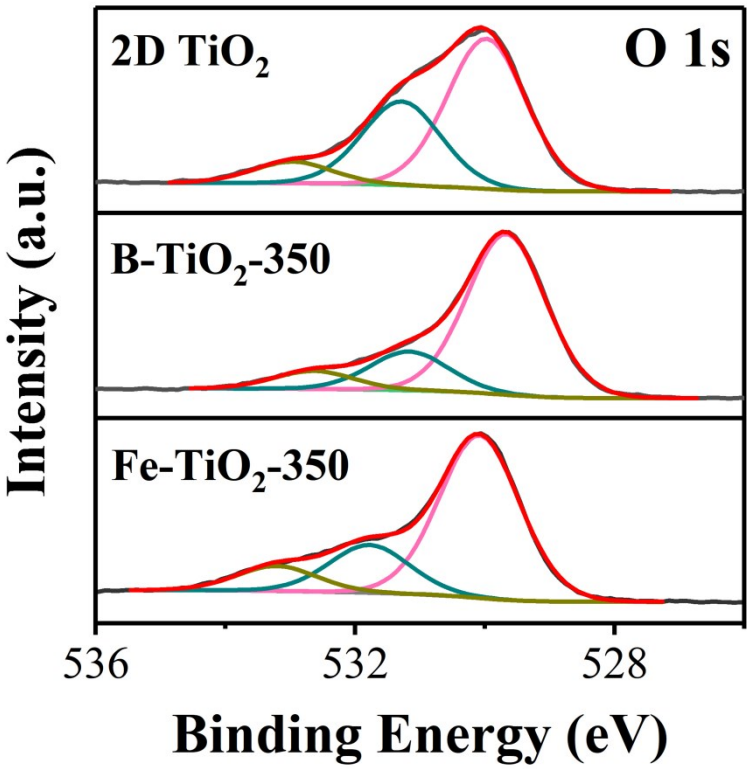

Figure S9. O 1s XPS spectra of 2D TiO_2, B-TiO_2-350, and Fe-TiO_2-350.

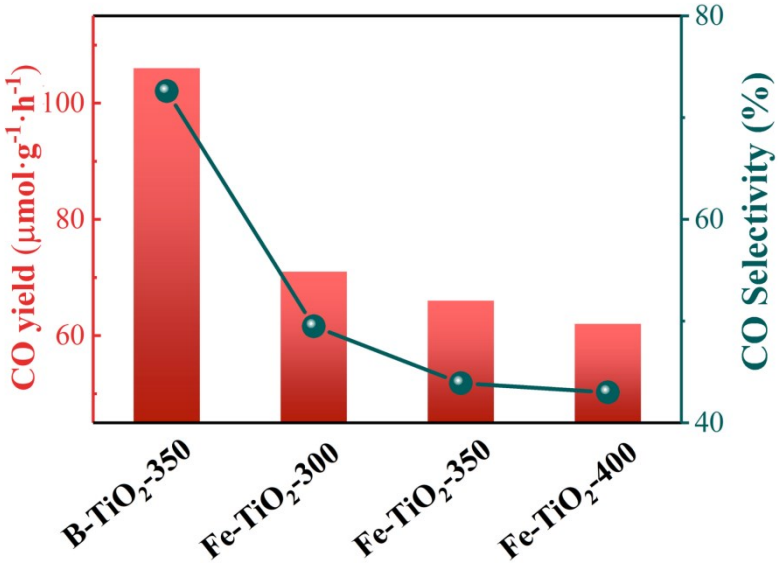

Figure S10. CO generation rate and selectivity of B-TiO_2-350 and Fe-TiO_2-x.

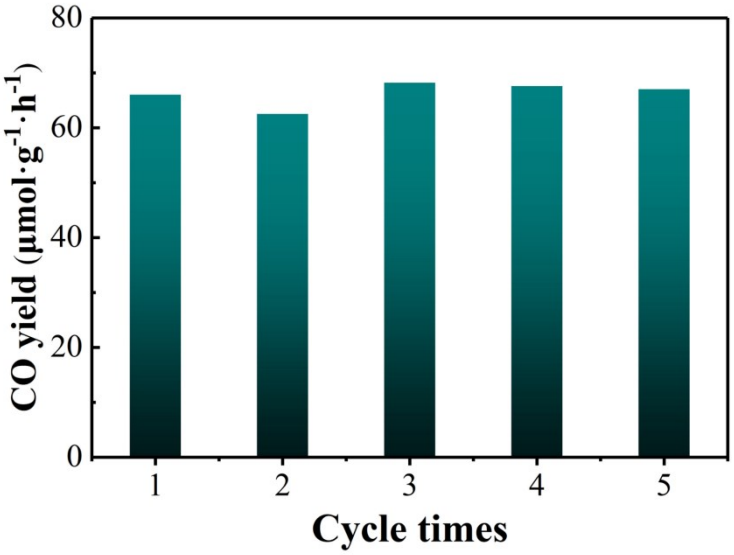

Figure S11. CO cycle experiments of Fe-TiO_2-350 in CO_2 photoreduction.

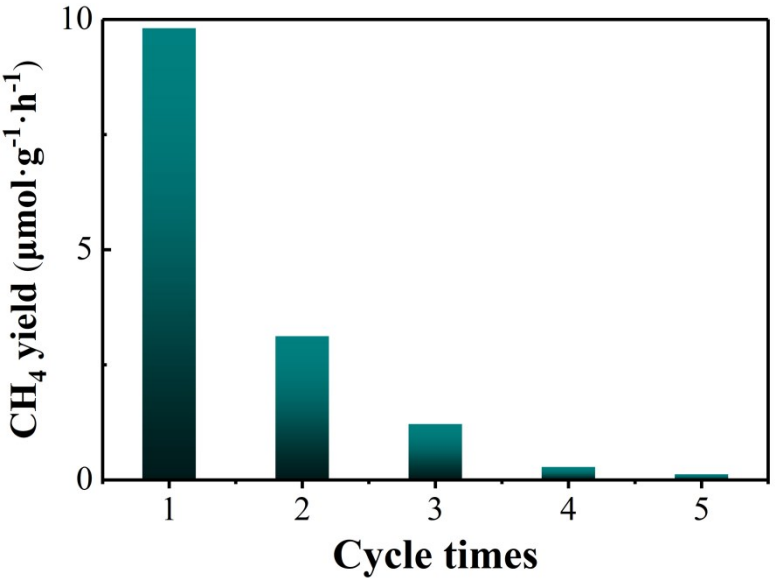

Figure S12. Cycle experiments of Fe-2D TiO_2 in CO_2 photoreduction. The synthesis of 2D TiO_2 coated by FeTPP without OVs (Fe-2D TiO_2) catalysts was similar to that of Fe-TiO_2-x. Briefly, 50 mg 2D TiO_2 and 2.5 mg Fe-porphyrin were added to 50 mL DMF. The other procedures were same as the synthesis of Fe-TiO_2-x.

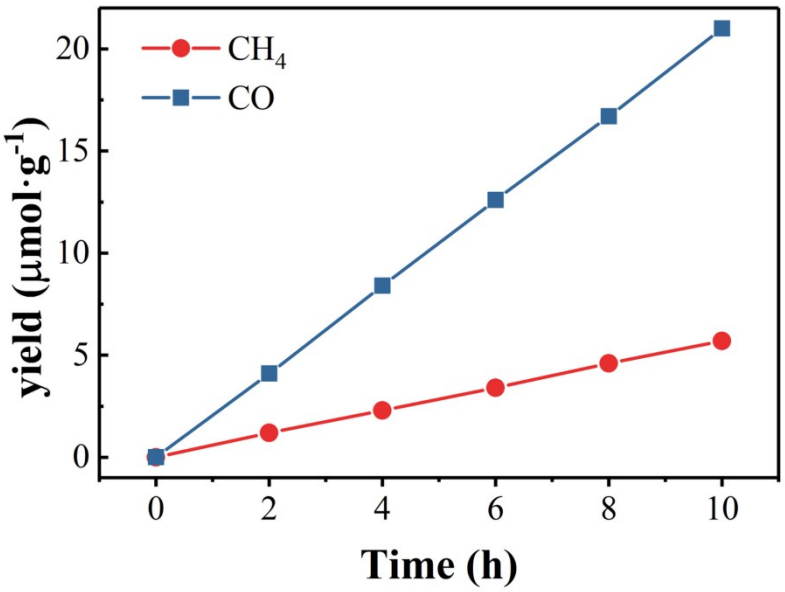

Figure S13 CO and CH_4 yield of pure FeTPP.

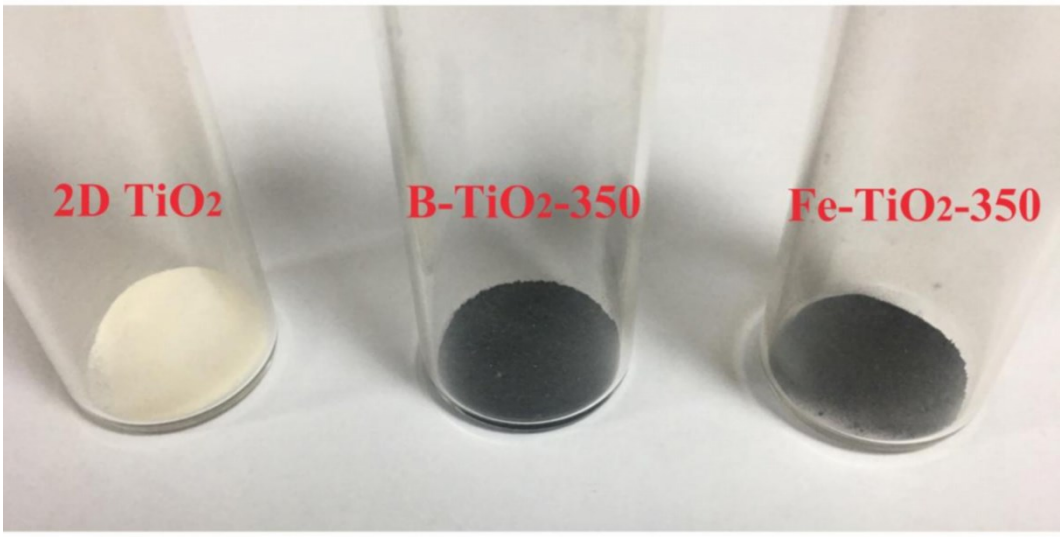

Figure S14. Color of sample of 2D TiO_2, B-TiO_2-350, and Fe-TiO_2-350.

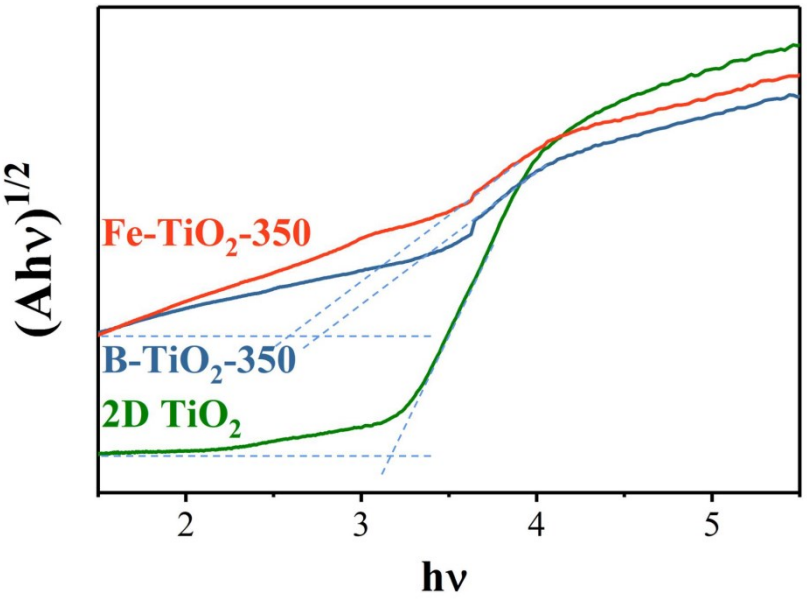

Figure S15. The transformed Kubelka-Munk functions of 2D TiO_2, B-TiO_2-350, and Fe-TiO_2-350.

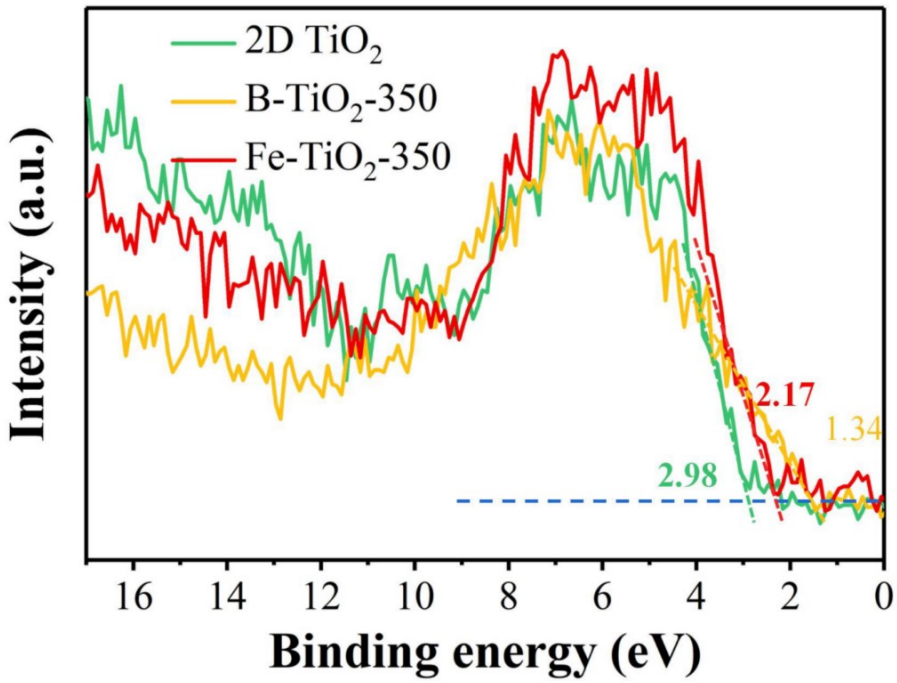

Figure S16. The VB-XPS spectra of 2D TiO_2, B-TiO_2-350, and Fe-TiO_2-350.

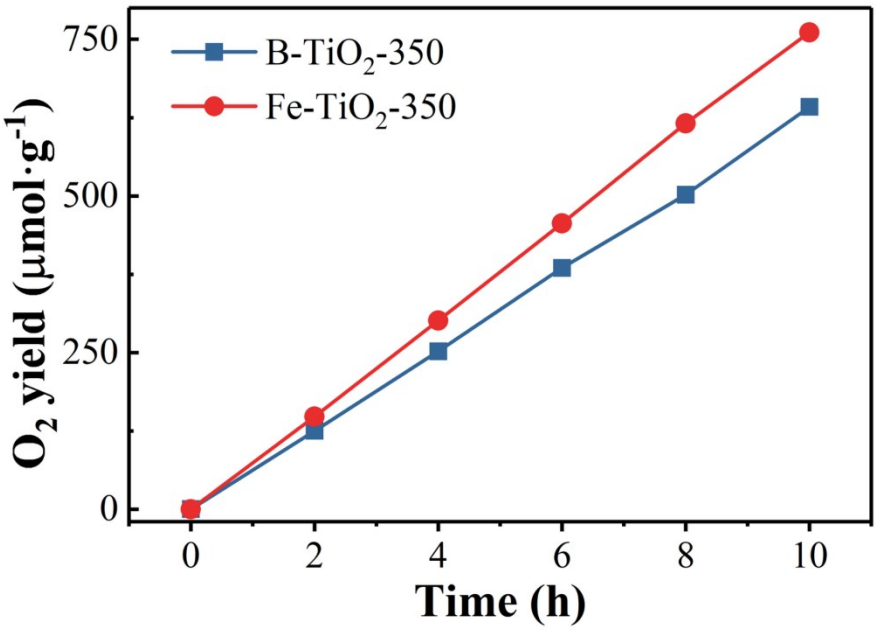

Fig. S17 O_2 yield of B-TiO_2-350, and Fe-TiO_2-x.

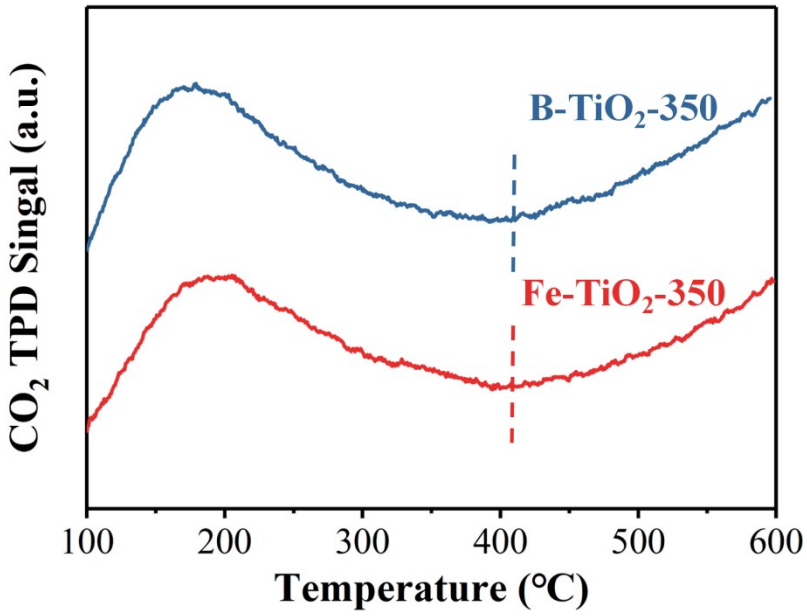

Figure S18. The CO_2-TPD profiles of B-TiO_2-350, and Fe-TiO_2-350.

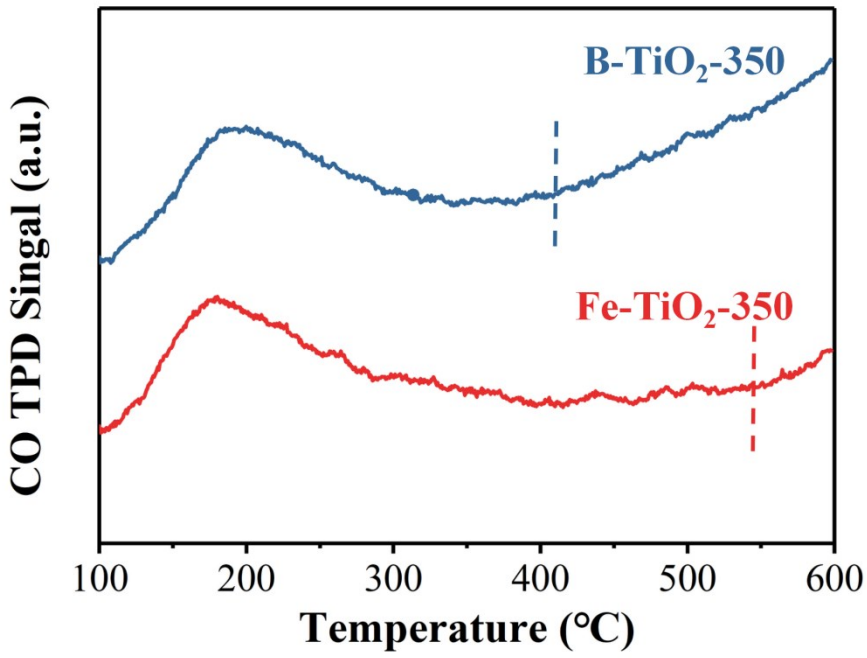

Figure S19. The CO-TPD profiles of B-TiO_2-350, and Fe-TiO_2-350.

Table S1. Photoreduction performance of Fe-TiO_2-350 composites in this work and related TiO_2-based photocatalysts reported in the literatures.

Catalyst	Light source	Products yield ($\mu mol \cdot g^{-1} \cdot h^{-1}$)	Products selectivity	Reference
Fe-TiO_2-350	Visible light	CH_4: 20.45, CO: 66	CH_4: 56.1%	This work
0.5Au/mT-H6	300W Xe lamp	CH_4: 10.07, CO: 6.71	CH_4: 60%	[1]
Ir-TiO_2	300W Xe lamp	CH_4: 2.88, CO: 8.13	CH_4: 58%	[2]
TiO_2@TiO_2-x	Visible light	CH_4: 2.7, CO: 0.9	CH_4: 73%	[3]
TiO_2-rGO	500W Xe lamp	CH_4: 2.37, MeOH: 3.07	CH_4: not metioned	[4]
TiO_2-graphene	UV light	CH_4: 27.4, CO: 70.8	CH_4: 28%	[5]
g-C_3N_4/TiO_2	300W Xe lamp	CH_4: 5.21, CO: 0.84	CH_4: 96%	[6]
Cu-TiO_2	300W Xe lamp	CO: 3.2	CO: 100%	[7]

Reference

1. S. Cai, J. Chen, Q. Li and H. Jia, *ACS applied materials & interfaces*, 2021, DOI: 10.1021/acsami.0c23036.

2. K. Tang, Z. Wang, W. Zou, H. Guo, Y. Wu, Y. Pu, Q. Tong, H. Wan, X. Gu, L. Dong, J. Rong and Y.-W. Chen, *Acs Applied Materials & Interfaces*, 2021, **13**, 6219-6228.

3. G. Yin, X. Huang, T. Chen, W. Zhao, Q. Bi, J. Xu, Y. Han and F. Huang, *Acs Catalysis*, 2018, **8**,

1009-1017.

4. S. Liu, T. Jiang, M. Fan, G. Tan, S. Cui and X. Shen, *Journal of Alloys and Compounds*, 2021, **861**.
5. Z. Xiong, Y. Luo, Y. Zhao, J. Zhang, C. Zheng and J. C. S. Wu, *Physical Chemistry Chemical Physics*, 2016, **18**, 13186-13195.
6. K. Li, B. Peng, J. Jin, L. Zan and T. Peng, *Applied Catalysis B-Environmental*, 2017, **203**, 910-916.
7. Z. Jiang, W. Sun, W. Miao, Z. Yuan, G. Yang, F. Kong, T. Yan, J. Chen, B. Huang, C. An and G. A. Ozin, *Advanced Science*, 2019, **6**.