Photocatalytic Water-Donating Transfer Semi-hydrogenation of Alkynes Coupled with Glycerol Oxidation over Pd-TiO_2

En Zhao[a,b,c], Shaokang Zhai[a,b], Jingyuan Su[a,b], Hehe Fan[a,b], Zhaohui Chen[a,b], Ziyi Fan[a,b], Wenjun Zhang[a,b], Haijiao Lu[c,*], and Zupeng Chen[a,b,*]

[a]State Key Laboratory for Development and Utilization of Forest Food Resources, Nanjing Forestry University, Nanjing 210037, China

[b]Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, Nanjing Forestry University, Longpan Road 159, Nanjing 210037, China

[c]Nanomaterials Centre, School of Chemical Engineering, and Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, 4072 St Lucia, Brisbane, Australia

Table of Contents

Supplementary Figures

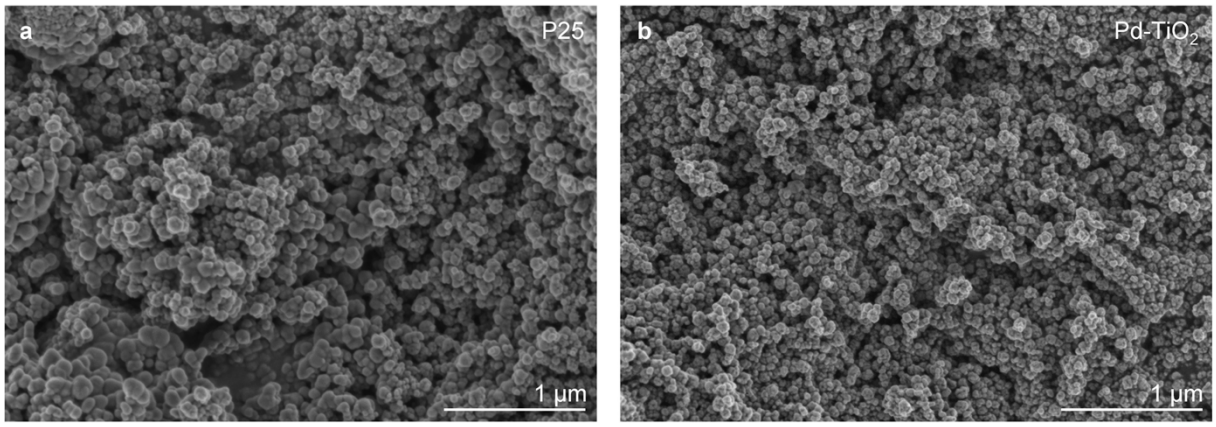

Figure S1. SEM images of (a) P25 and (b) Pd-TiO_2.

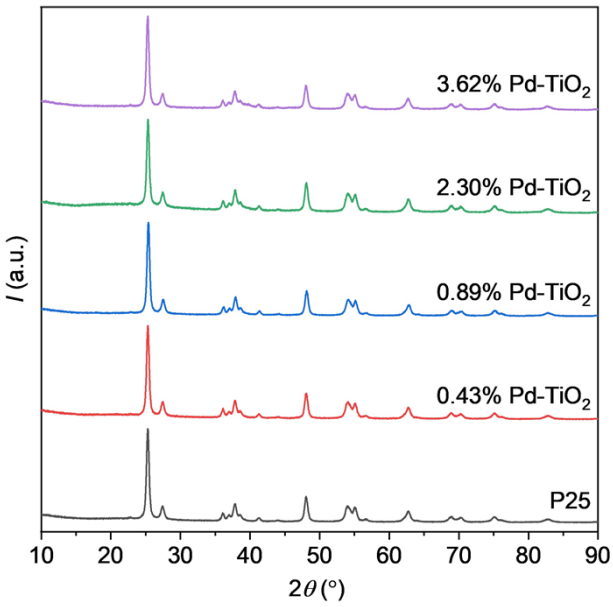

Figure S2. XRD patterns of P25 and Pd-TiO_2 with different Pd loadings.

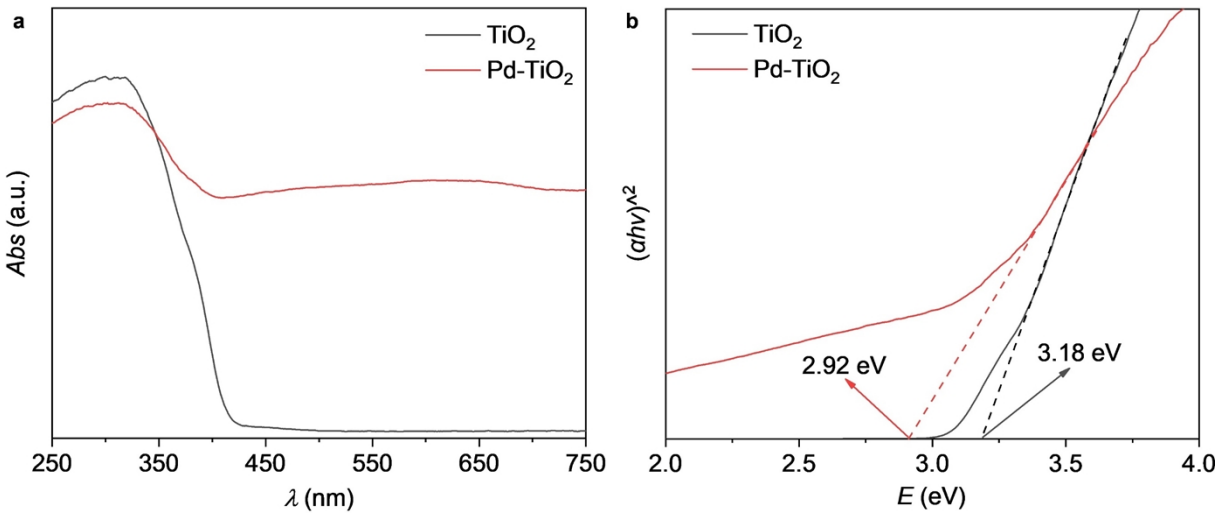

Figure S3 (a) UV-vis absorption spectra and (b) Tauc plots of P25 and Pd-TiO_2.

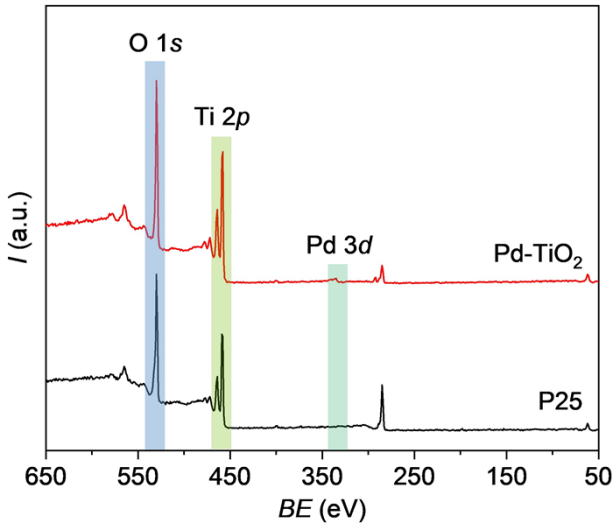

Figure S4 XPS survey spectra of P25 and Pd-TiO_2.

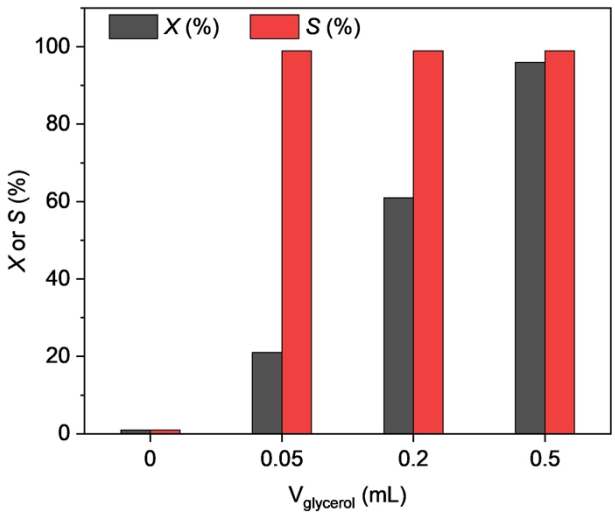

Figure S5 Effect of the amount of glycerol on the photocatalytic semi-hydrogenation performance of phenylacetylene.

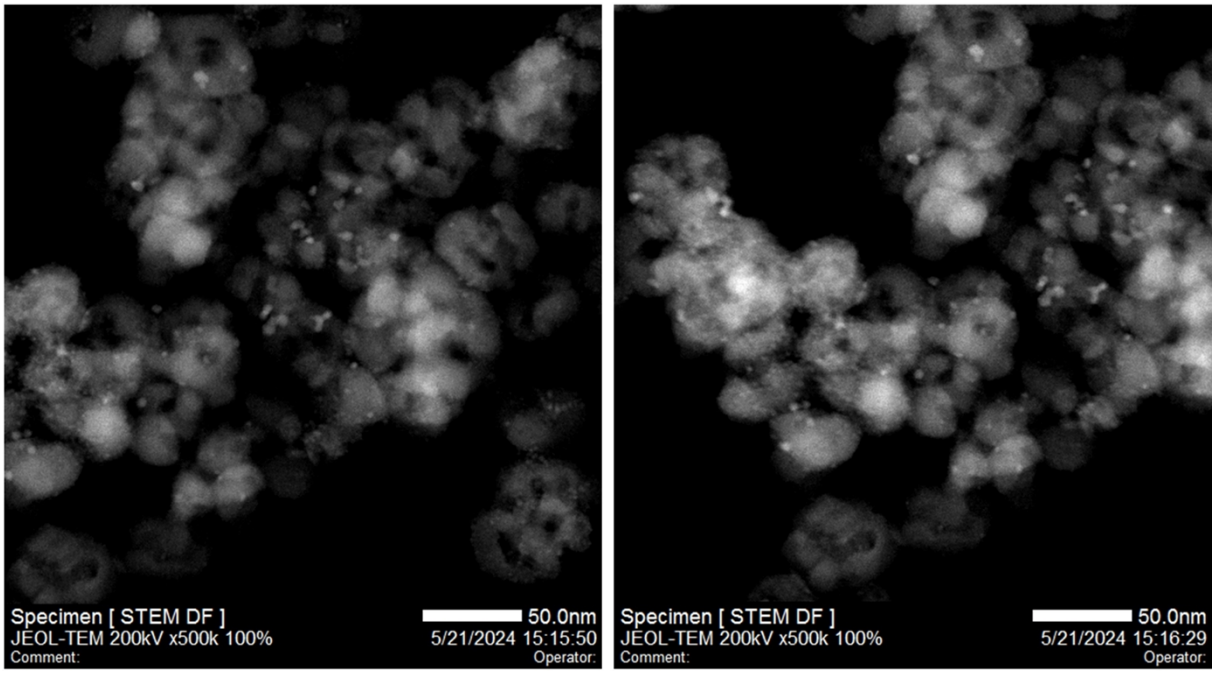

Figure S6. STEM images of the used Pd-TiO_2 after five consecutive reaction runs.

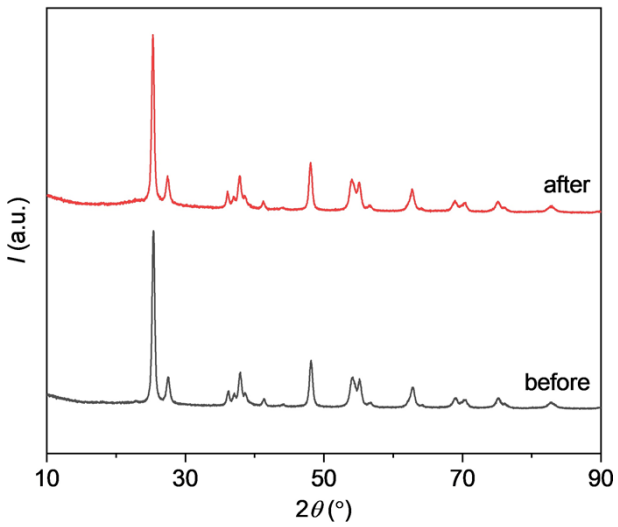

Figure S7. XRD patterns of Pd-TiO_2 before and after five consecutive reaction runs.

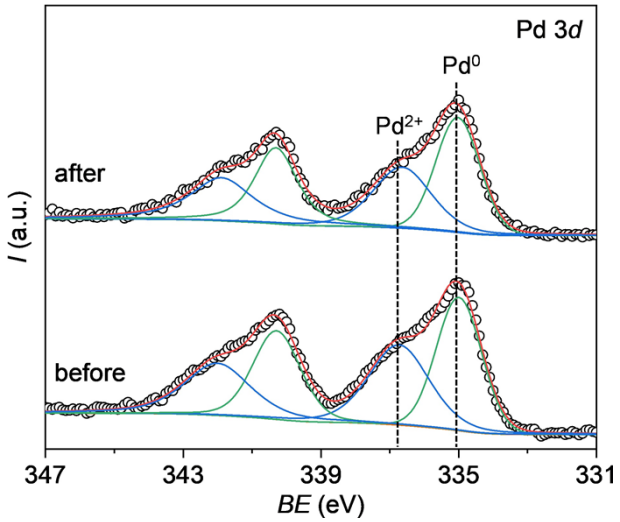

Figure S8. Pd 3*d* XPS spectra of Pd-TiO_2 before and after five consecutive reaction runs.

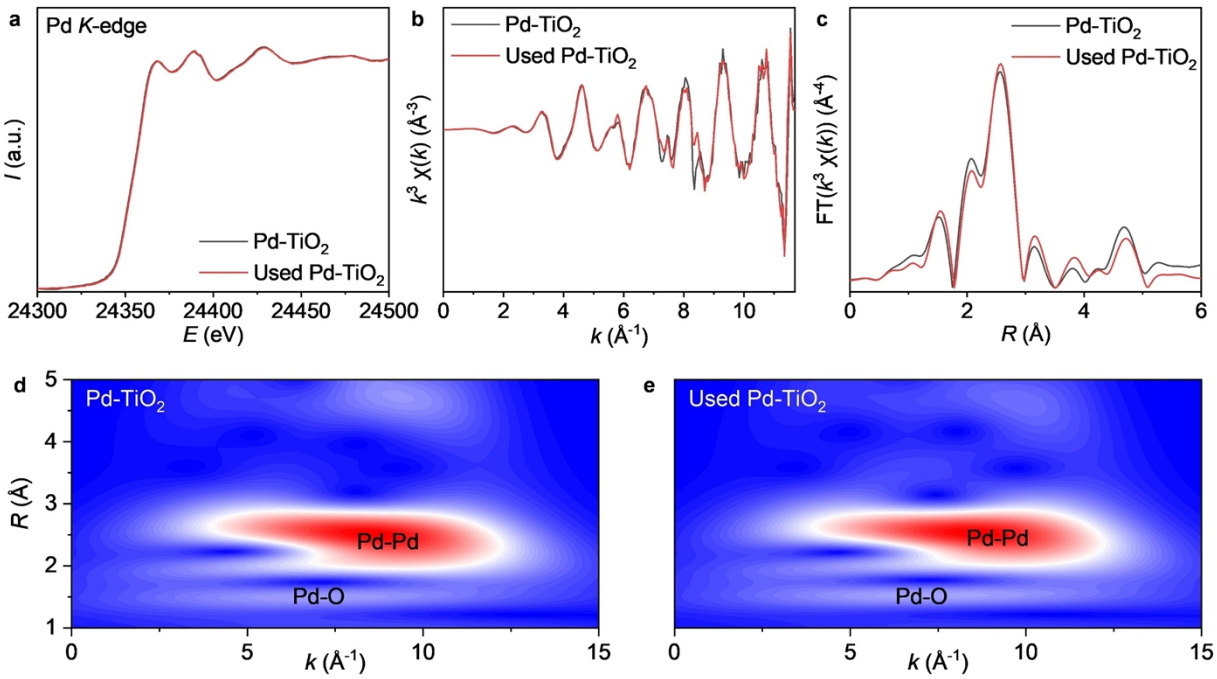

Figure S9. (a) Pd *K*-edge XANES spectra, (b) k^3-weighted Pd *K*-edge EXAFS spectra, and (c) Fourier transform of k^3-weighted Pd *K*-edge EXAFS spectra of Pd-TiO_2 and the used Pd-TiO_2. Wavelet transform EXAFS spectra of (d) Pd-TiO_2 and (e) used Pd-TiO_2.

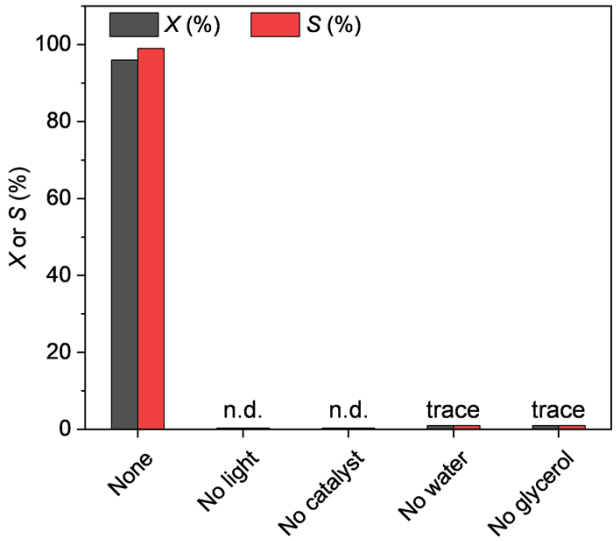

Figure S10. Photocatalytic water-donating transfer semi-hydrogenation with the oxidation of glycerol reactions under various conditions.

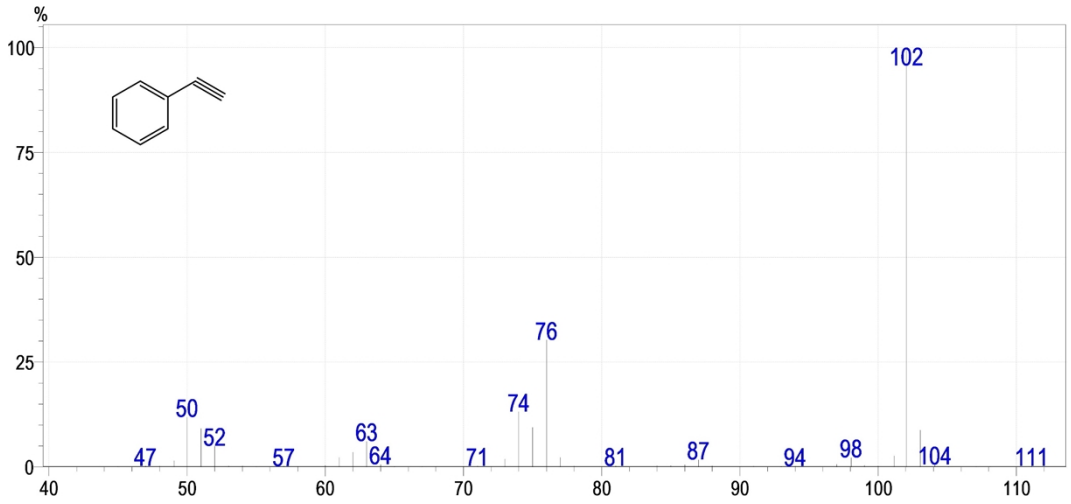

Figure S11. Mass spectrum of phenylacetylene.

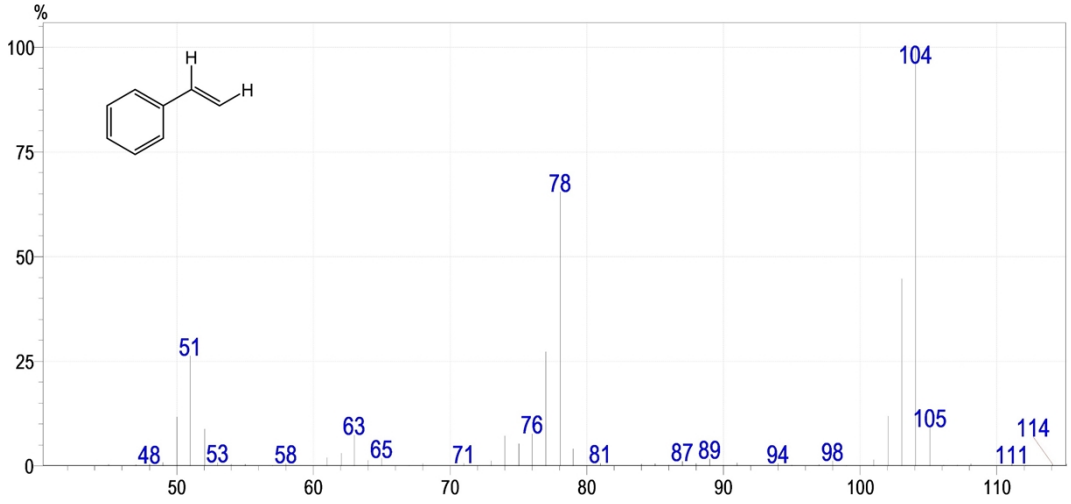

Figure S12. Mass spectrum of styrene.

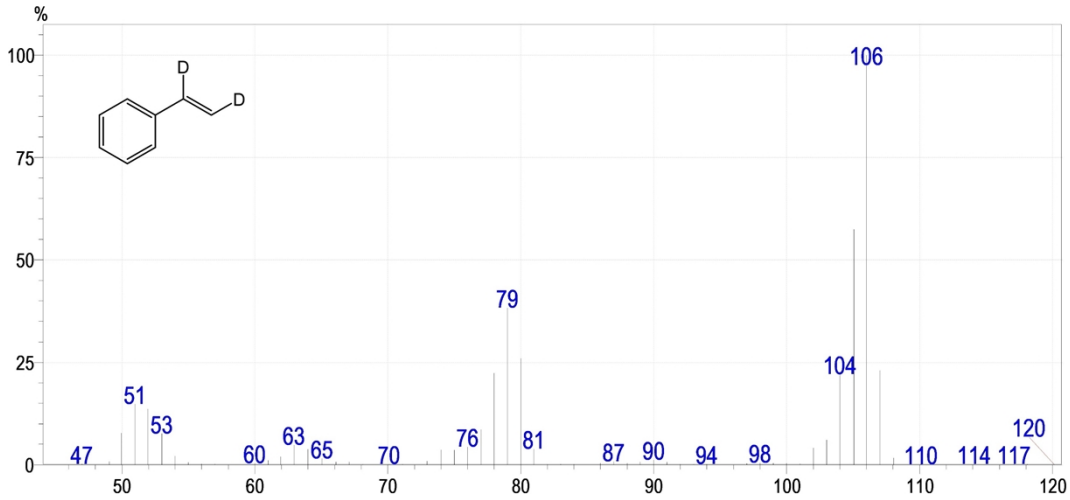

Figure S13. Mass spectrum of deuterated styrene.

Supplementary Table

Table S1. Metal loading for different photocatalysts.

Sample	M[a] (wt.%)
Pd-TiO_2	0.43 (0.50)
	0.89 (1.00)
	2.30 (2.50)
	3.62 (5.00)
Pt-TiO_2	0.72 (1.00)
Au-TiO_2	0.86 (1.00)
Ru-TiO_2	0.61 (1.00)
Ni-TiO_2	1.05 (1.00)
Used Pd-TiO_2	0.80

[a] ICP-OES (in parentheses, theoretical loading).

Table S2. Comparison of the photocatalytic water-donating hydrogenation systems for semi-hydrogenation of alkynes reported in the literature with that of the present system.

Catalyst	Hydrogen source	Hole sacrificial agent	Additive	X (%)	S (%)	Reference
Pd-TiO_2	**Water**	**Glycerol**	**None**	**96**	**99**	**This work**
Cu/TiO_2	Water	Glycerol	NaOH	99	63	Ref. S1
TiO_2-$Pd_{0.5}Pt_{0.5}$	Water	Methanol	None	100	94	Ref. S2
Pd/TiO_2	Water	Methanol	None	99	99	Ref. S3
Ni/C_3N_4	Water	Triethylamine	None	100	97	Ref. S4
Ni-N/CN	Water	Triethylamine	None	100	92	Ref. S5

Supplementary References

1. H. Kominami, R. Akamata, and A. Tanaka, *Appl. Catal. A-Gen.*, **2024**, 675, 119635.
2. M. Li, N. Zhang, R. Long, W. Ye, C. Wang and Y. Xiong, *Small*, **2017**, 13, 1604173.
3. Q.-C. Wei, Y. Chen, Z. Wang, D.-Z. Yu, W.-H. Wang, J.-Q. Li, L.-H. Chen, Y. Li, B.-L. Su, *Angew. Chem. Int. Ed.*, **2022**, 61, e202210573.
4. T. Jia, D. Meng, H. Ji, H. Sheng, C. Chen, W. Song and J. Zhao, *Appl. Catal. B Environ.*, **2022**, 304, 121004.
5. T. Jia, D. Meng, R. Duan, H. Ji, H. Sheng, C. Chen, J. Li, W. Song and J. Zhao, *Angew. Chem. Int. Ed.*, **2023**, 62, e202216511