

Supporting Information

Building Z-scheme Heterojunction with Keggin-type Heteropolymers Modified Two-dimensional g-C₃N₄ for Significantly Photocatalytic Performance

Huimin Han^a, Jinyuan Liu^{b,*}, Bin Wang^b, Shumin Zhu^b, Shihao Jia^a, Qi Tang^a, Yingjie Hua^{a,*},
Huaming Li^b, Chongtai Wang^a, Hui Xu^{b,*}

^a School of Chemistry and Chemical Engineering of Hainan Normal University, Key Laboratory of Electrochemical Energy Storage and Energy Conversion of Hainan Province, Key Laboratory of Electrochemical Energy Storage and Light Energy Conversion Materials of Haikou City, Haikou, 571158, P.R. China.

^b Institute for Energy Research, Jiangsu University, Zhenjiang 212013, Jiangsu, P. R. China

***Corresponding author:** jyliu@ujs.edu.cn; 521000hua282@sina.com; xh@ujs.edu.cn

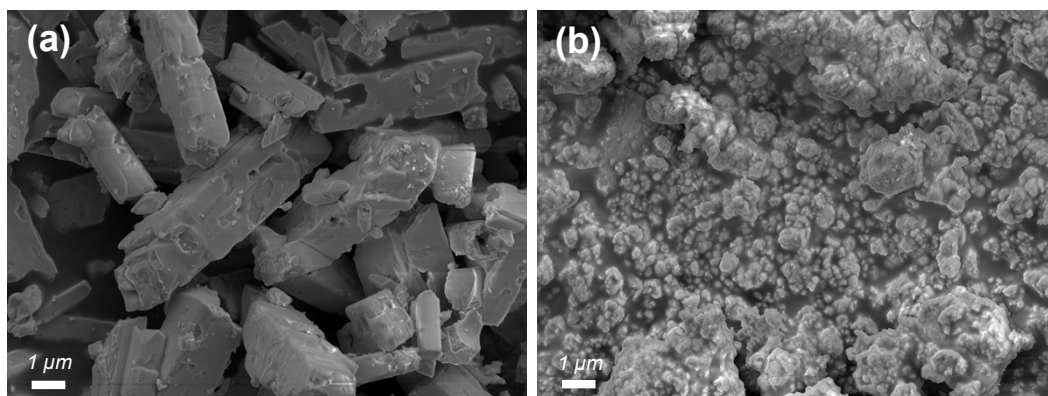


Fig. S1. SEM images of (a) $\text{Cs}_5\text{PW}_{11}\text{Co}$ and (b) $\text{Cs}_4\text{PW}_{11}\text{Fe}$

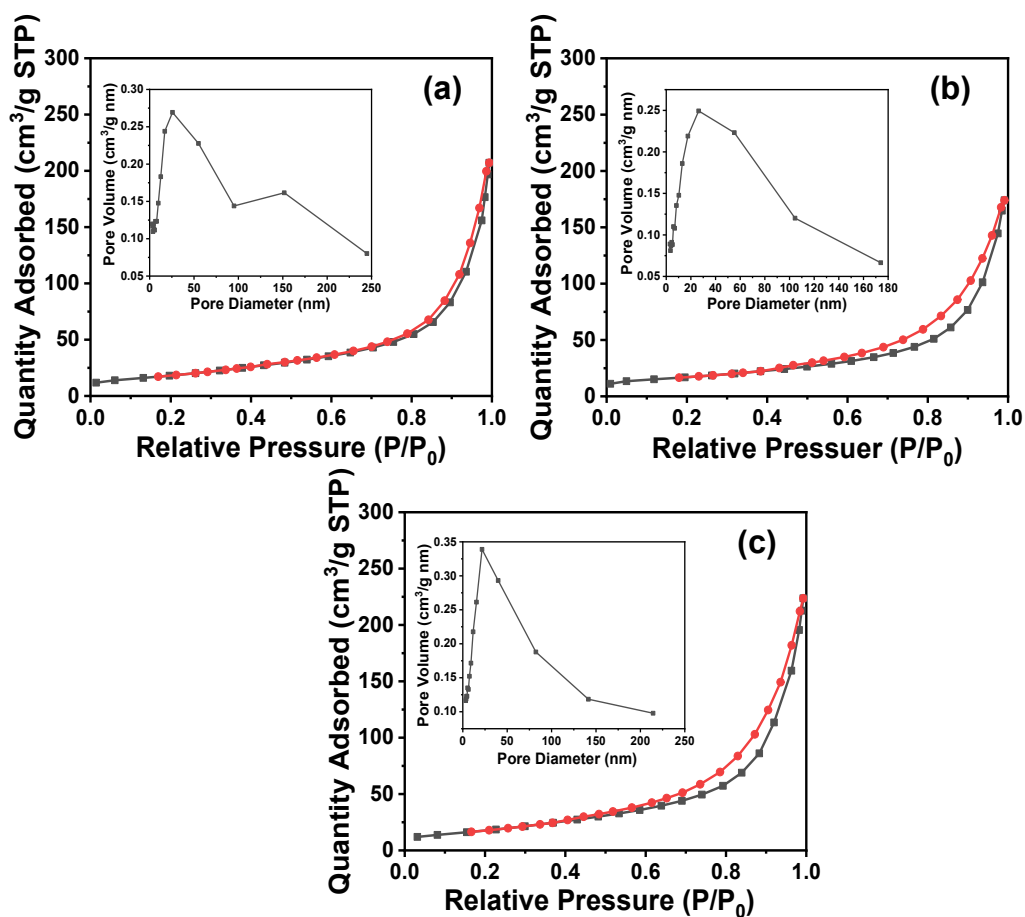


Fig. S2. N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves of (a) $\text{g-C}_3\text{N}_4$, (b) 3 wt.% $\text{Cs}_5\text{PW}_{11}\text{Co}/\text{g-C}_3\text{N}_4$, (c) 3 wt.% $\text{Cs}_4\text{PW}_{11}\text{Fe}/\text{g-C}_3\text{N}_4$

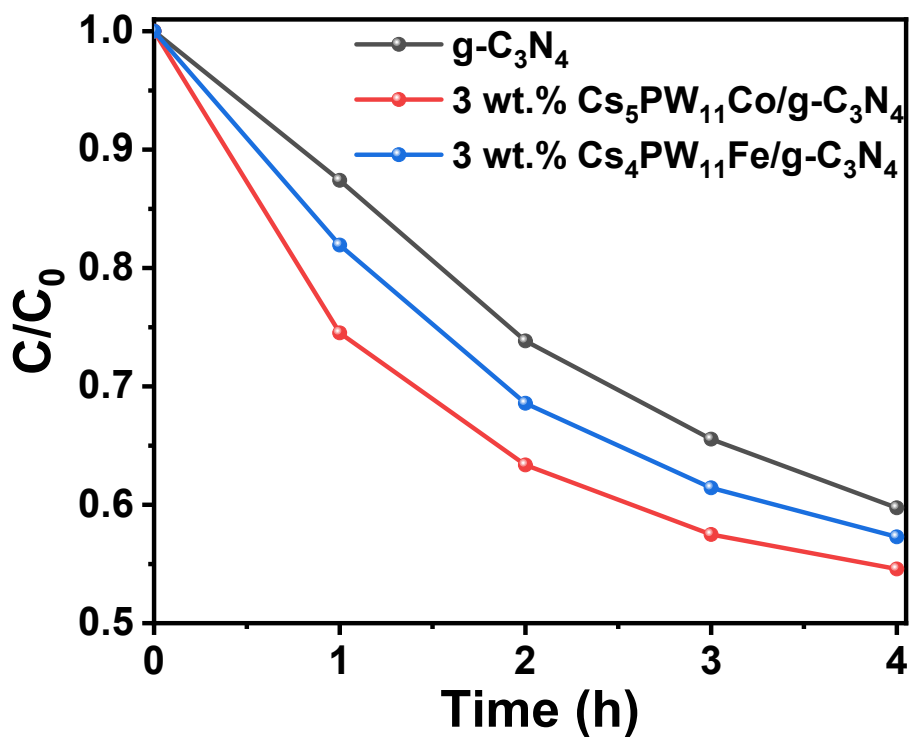


Fig. S3. Trapping experiment of active species during the photocatalytic degradation of BPA over 3 wt.% Cs₅PW₁₁Co/g-C₃N₄ and 3 wt.% Cs₄PW₁₁Fe/g-C₃N₄ under visible light irradiation

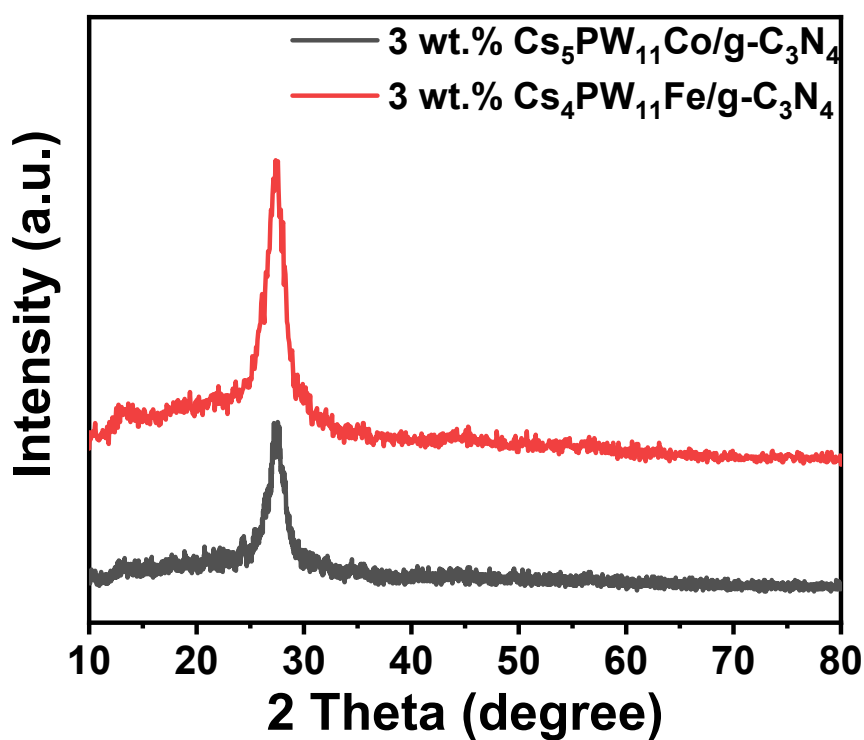


Fig. S4. XRD patterns of the 3 wt.% Cs₅PW₁₁Co/g-C₃N₄ and 3 wt.% Cs₄PW₁₁Fe/g-C₃N₄ materials after the cycling photocatalytic experiments.

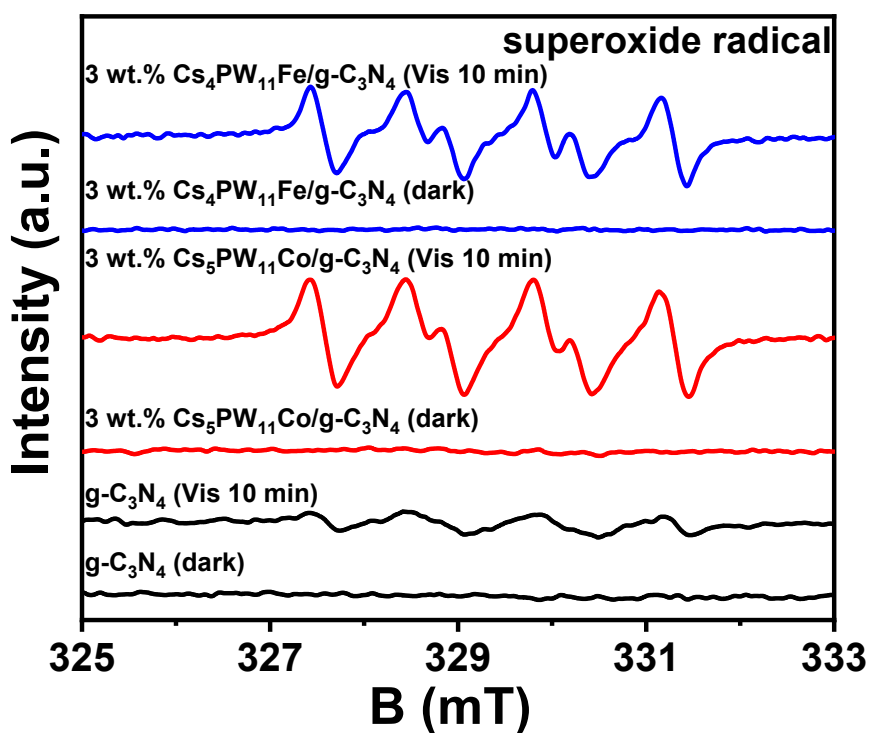


Fig. S5. ESR spectrum of 3 wt.% $\text{Cs}_x\text{PW}_{11}\text{M/g-C}_3\text{N}_4$ ($\text{M}=\text{Co}, \text{Fe}$) and 2D $\text{g-C}_3\text{N}_4$ radical trapped by DMPO: $\cdot\text{O}_2^-$ radical species under visible light irradiation and in dark

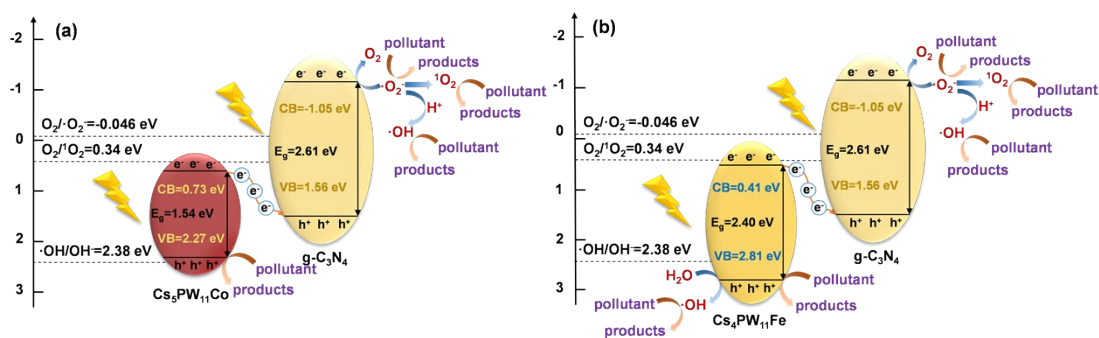


Fig. S6. The possible photocatalytic mechanism in (a) $\text{Cs}_5\text{PW}_{11}\text{Co/g-C}_3\text{N}_4$ system and (b) $\text{Cs}_4\text{PW}_{11}\text{Fe/g-C}_3\text{N}_4$ system.

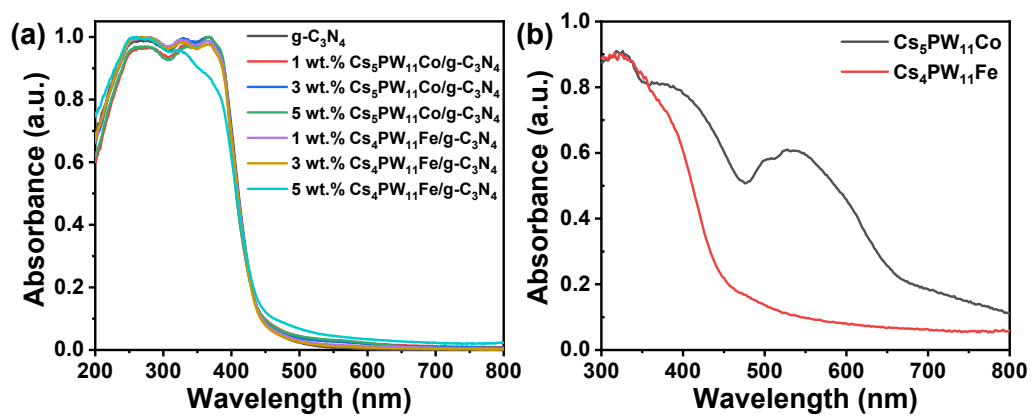


Fig. S7. UV-vis spectra (a) g-C₃N₄ and Cs_xPW₁₁M/g-C₃N₄ at different contents, (b) Cs_xPW₁₁M (M=Co, Fe).

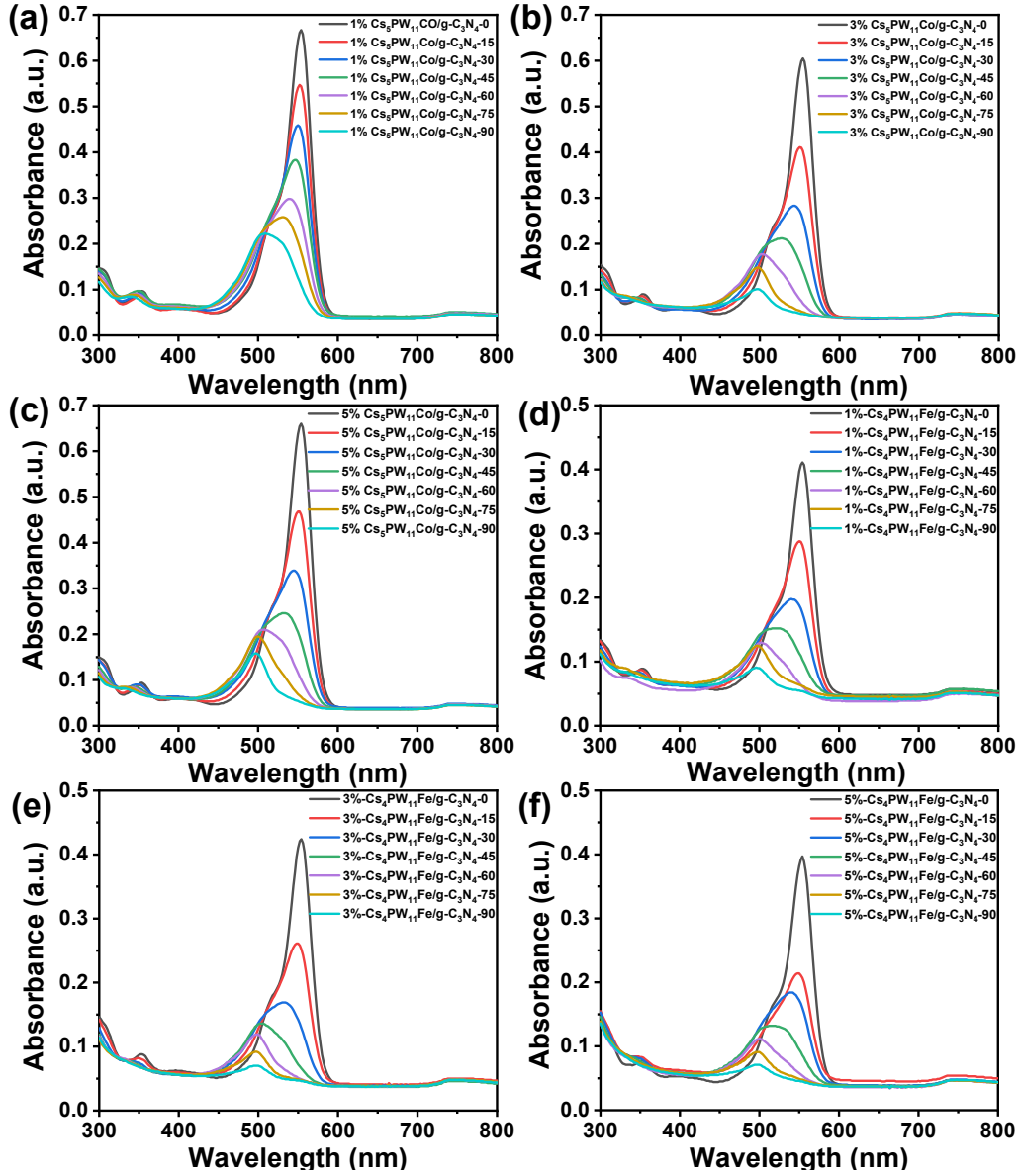


Fig. S8. (a-f) absorption spectral of RhB by $\text{Cs}_x\text{PW}_{11}\text{M/g-C}_3\text{N}_4$.

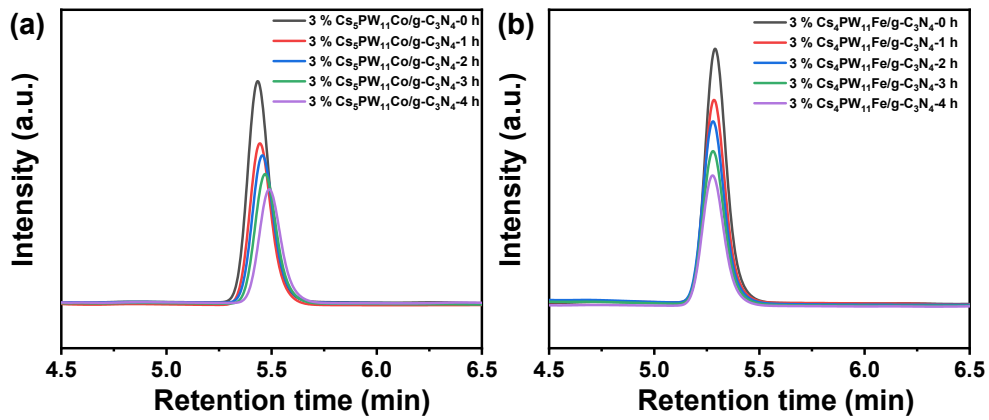


Fig. S9. (a, b) HPLC spectrums of BPA solution degraded by 3 wt.% $\text{Cs}_x\text{PW}_{11}\text{M/g-C}_3\text{N}_4$.

Table S1. Absolute electronegativity of each constituent element

Atom	Cs	P	W	O	Fe	Co
X (eV)	2.18	5.62	4.40	7.54	4.06	4.30

Table S2. Comparison of RhB degradation among different catalysts.

Photocatalysts	Initial concentration	Light source and irradiation time	Removal efficiency	Ref.
Bi ₂ WO ₆ /ZnWO ₄	10 mg/L	500 W Xe lamp 4 h	89%	S1
NiS/ZnO	2.01×10 ⁻⁵ mol/L	8W UV-light 2h	93%	S2
CeO ₂ /CdS quantum dots	10 mg/L	300 W Xe lamp 3 h	96.16%	S3
g-C ₃ N ₄ /H-TiO ₂	10 mg/L	300 W Xe lamp 2 h	65%	S4
Bi ₃ O ₄ Cl/Bi ₅ O ₇ I	17 ppm	300 W Xe lamp 90 min	97%	S5
AgIO ₃ /WO ₃	2×10 ⁻⁵ mol/L	300 W Xe lamp 140 min	100%	S6
BiOCl/H ⁺ TiNbO ₅ ⁻	10 mg/L	250 W Xe lamp 90 min	99%	S7
g-C ₃ N ₄ /CQDs/CC	5 mg/L	250 W Xe lamp 90 min	92%	S8

Table S3. Comparison of RhB degradation among g-C₃N₄ based materials.

Photocatalysts	Initial	Light source and	Removal	Ref.
----------------	---------	------------------	---------	------

	concentration	irradiation time	efficiency	
GQDs/mpg-C ₃ N ₄	10 mg/L	300 W Xe lamp 2 h	97%	S9
Ultrathin g-C ₃ N ₄	30 ppm	300 W Xe lamp 90 min	100%	S10
Thin porous amino-rich g-C ₃ N ₄	10 mg/L	500 W Xe lamp 1 h	99%	S11
g-C ₃ N ₄ /H-TiO ₂	10 mg/L	300 W Xe lamp 2 h	65%	S12
S-g-C ₃ N ₄	10 mg/L	500W Xe lamp 2 h	90%	S13
g-C ₃ N ₄ /CNTs	10 mg/L	300 W Xe lamp 1 h	98.1%	S14
Ag/AgCl-CN	5 mg/L	300 W Xe lamp 120 min CEL-LED 100lamp 70	98.5%	S15
P-Cl/g-C ₃ N ₄	10 mg/L	W 120 min	99.62%	S16

References

- S1 Y. Rao, H. Liu, B. Zhong, Z. Li, In-situ construction of Bi₂WO₆/ZnWO₄ heterojunctions with enhanced photocatalytic performance toward RhB degradation. *Mater. Lett.*, 2022, **312**, 131707.
- S2 S.K.Pandey, P. K. Mishra, D. Tiwary, Enhanced photocatalytic performance of NiS/ZnO nanocomposite for the remediation of PNP and RhB dye. *J. Environ. Chem. Eng.*, 2022, **10**, 107459.
- S3 H. Pei, Q. Jia, R. Guo, T. Zhang, N. Liu, Z. Mo, Flower-like CeO₂/CdS quantum dots heterojunction nanocomposites with high photocatalytic activity for RhB degradation. *Colloids Surf., A*, 2022, **648**, 129256.
- S4 B. Yu, C. Miao, D. Wang, H. Li, D. Sun, W. Jiang, C. Liu, G. Che, Preparation of visible light responsive g-C₃N₄/H-TiO₂ Z-scheme heterojunction with enhanced photocatalytic activity for RhB degradation. *J. Mater. Sci.: Mater. Electron.*, 2022, **33**, 17587-17598.
- S5 S. T. U. Din, H. Lee, W. Yang, Z-Scheme Heterojunction of 3-Dimensional Hierarchical

- Bi₃O₄Cl/Bi₅O₇I for a Significant Enhancement in the Photocatalytic Degradation of Organic Pollutants (RhB and BPA). *Nanomaterials*, 2022, **12**, 767.
- S6 Q. Cao, Y. Zheng, X Song. Enhanced visible-light-driven photocatalytic degradation of RhB by AgIO₃/WO₃ composites. *J. Taiwan Inst. Chem. Eng*, 2017, **70**, 359-365.
- S7 C. Liu, X. Gao, C. Zhang, T. Cheng, Y. Wang, Layered BiOCl/H⁺ TiNbO₅⁻ heterojunctions for boosting visible-light-driven photocatalytic RhB degradation. *Sustainable Energy Fuels*, 2021, **5**, 4680-4689.
- S8 B Zhu, X Li, Y Wang, N. Liu, Y. Tian, Visible-light-driven photocatalytic degradation of RhB by carbon-quantum-dot-modified g-C₃N₄ on carbon cloth. *CrystEngComm*, 2021, **23**, 4782-4790.
- S9 J. Liu, H. Xu, Y. Xu, Y. Song, Graphene quantum dots modified mesoporous graphite carbon nitride with significant enhancement of photocatalytic activity. *Appl. Catal. B*, 2017, **207**, 429-437.
- S10 S. Gao, X. Wang, C. Song, S. Zhou, F. Yang and Y. Kong, Engineering carbon-defects on ultrathin g-C₃N₄ allows one-pot output and dramatically boosts photoredox catalytic activity, *Appl. Catal. B*, 2021, **295**, 120272.
- S11 T. Huang, J. Chen, L. Zhang, Precursor-modified strategy to synthesize thin porous amino-rich graphitic carbon nitride with enhanced photocatalytic degradation of RhB and hydrogen evolution performances. *Chinese J. Catal.*, 2022, **43**, 497-506.
- S12 M. Ge, X. Li, Z. Liu, M. Zhang, Enhanced photocatalytic degradation performance of cyano groups-modified carbon nitride nanosheets synthesized by magadiite template-assisted thermal treatment. *Mater Sci Semicond Process*, 2022, **141**, 106420.
- S13 Q. Fan, J. Liu, Y. Yu, A simple fabrication for sulfur doped graphitic carbon nitride porous rods with excellent photocatalytic activity degrading RhB dye. *Appl. Surf. Sci.*, 2017, **391**, 360-368.
- S14 G. Liu, M. Liao, Z. Zhang, Enhanced photodegradation performance of Rhodamine B with g-C₃N₄ modified by carbon nanotubes. *Sep. Purif. Technol.*, 2020, **244**, 116618.
- S15 H. Xu, Y. Chang, X. Shen, Construction of Ag/AgCl-CN heterojunctions with enhanced photocatalytic activities for degrading contaminants in wastewater. *J. Colloid Interface Sci.*, 2019, **543**, 25-33.
- S16 Y. Yang, H. Jin, C. Zhang, Nitrogen-deficient modified P-Cl co-doped graphitic carbon nitride with enhanced photocatalytic performance. *J. Alloys Compd.*, 2020, **821**, 153439.