

Supporting Information

Elegant Z-scheme-Dictated g-C₃N₄ Enwrapped WO₃ Superstructures: A Multifarious Platform for Versatile Photoredox Catalysis

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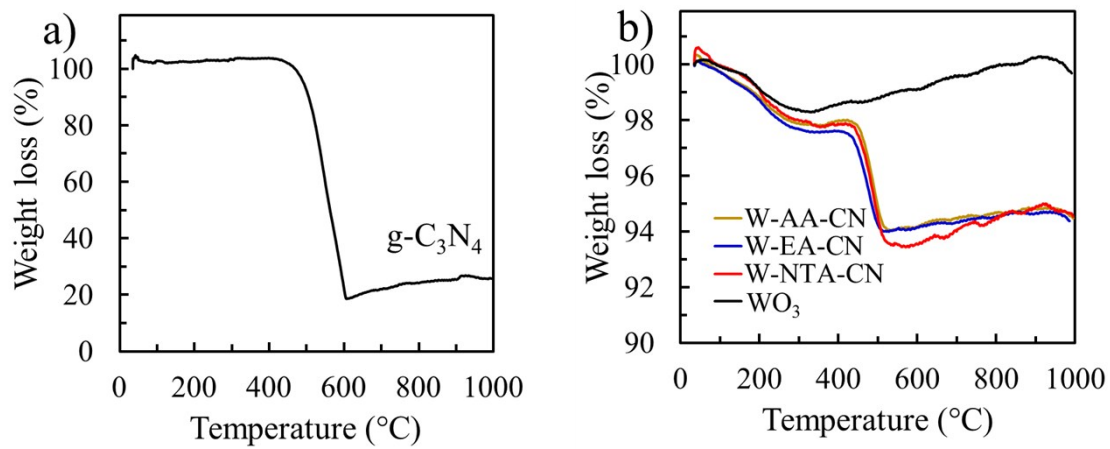
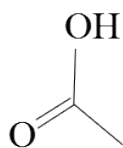
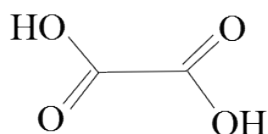


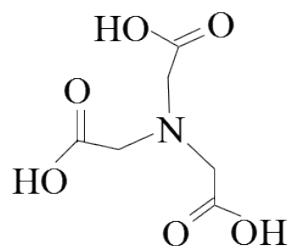
Fig. S1. TGA results of (a) g-C₃N₄ and (b) W-AA-CN, W-EA-CN, W-NTA-CN, WO₃.



acetic acid



ethanedioic acid



nitrilotriacetic acid

Fig. S2. Molecular structures of acetic acid (AA), ethanedioic acid (EA) and nitrilotriacetic acid (NTA) used for the synthesis of different WO_3 superstructures.

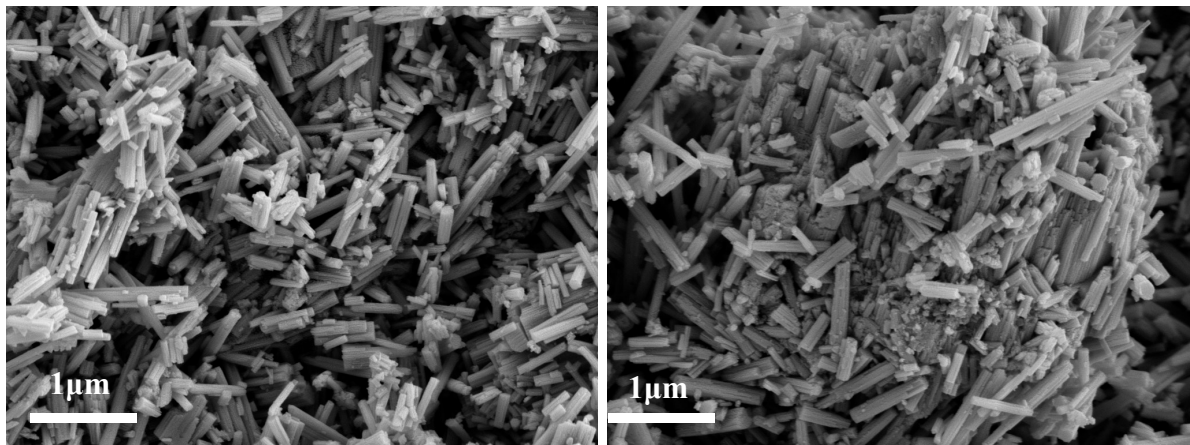


Fig. S3. FESEM images of WO_3 prepared without using organic acids.

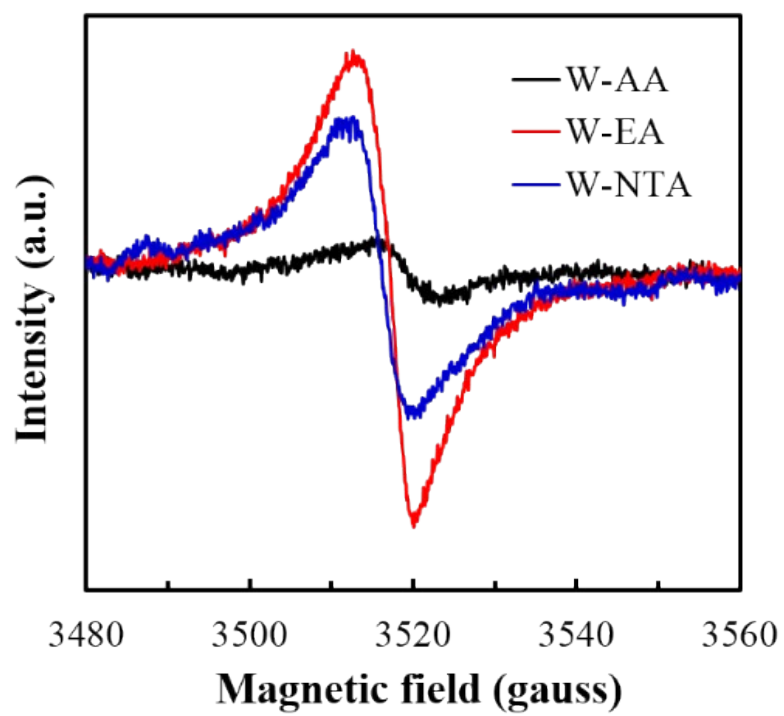


Fig. S4. ESR spectra of oxygen vacancy for W-AA, W-EA and W-NTA.

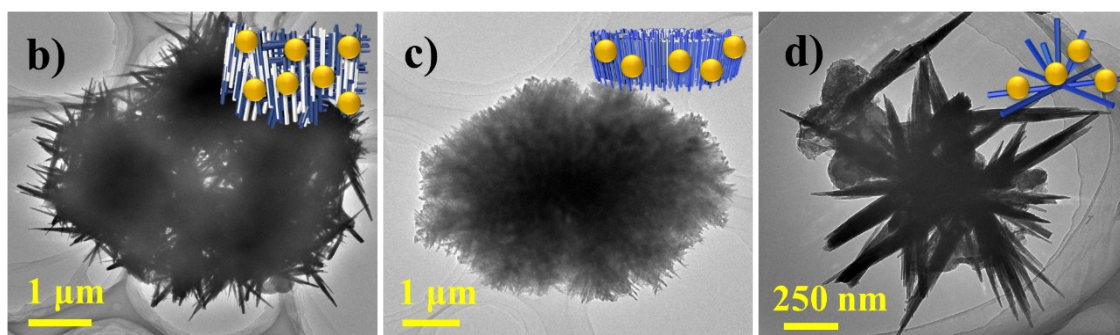
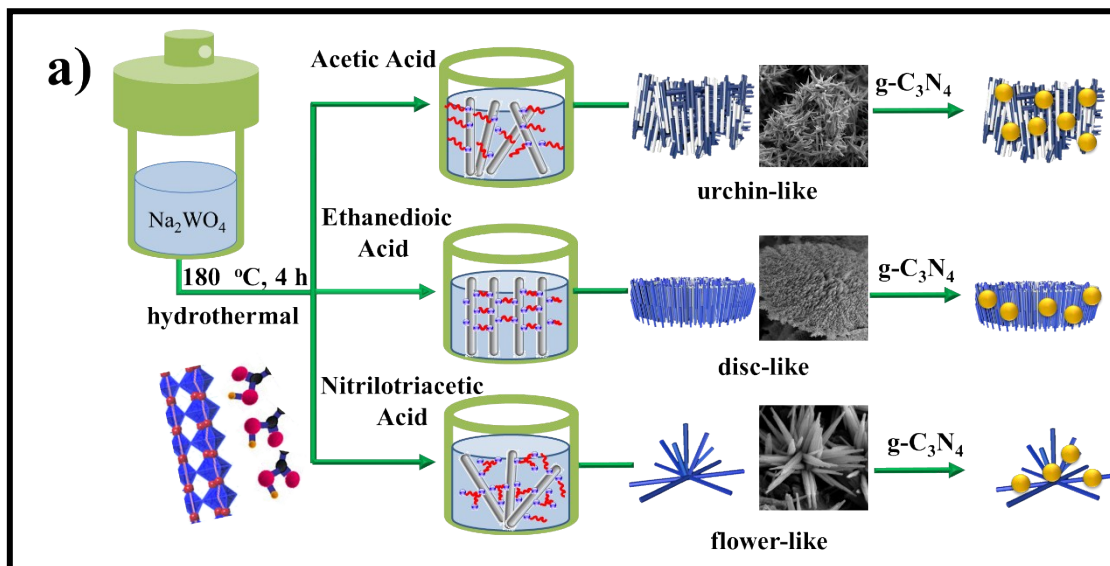


Fig. S5. (a) Possible growth mechanism of WO_3 superstructures induced by organic acids. TEM images of (b) W-AA-CN, (c) W-EA-CN and (d) W-NTA-CN heterostructures.

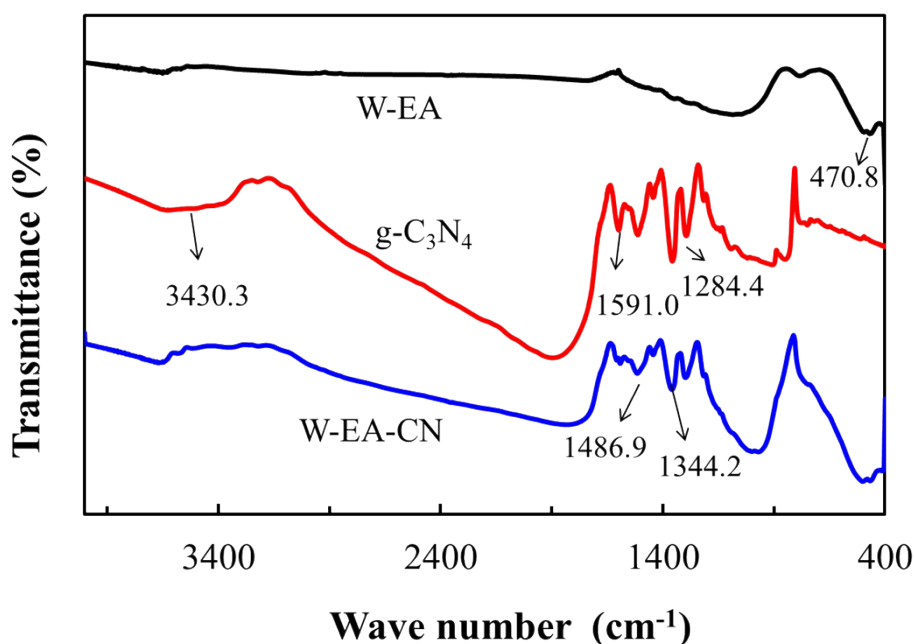


Fig. S6. FTIR spectra of W-EA, g-C₃N₄, and W-EA-CN.

Note: Fig. S6 shows the FTIR spectra of W-EA, g-C₃N₄ and W-EA-CN. The FTIR spectra of W-EA and W-EA-CN illustrate the characteristic absorption bands at 450–760 cm⁻¹, which are attributed to the W-O stretching and W-O-W bridging stretching modes^{1,2}. FTIR spectrum of g-C₃N₄ is featured by the presence of several peaks located between 1200 and 1650 cm⁻¹, which can be assigned to the stretching vibration mode of aromatic C-N heterocycles containing either trigonal N(-C)₃ or bridging C-NH-C units, indicating the formation of C-N-C bonds^{3,4}. Additionally, a broad band at around 3430 cm⁻¹ was clearly seen in the FTIR spectrum of g-C₃N₄, indicative of the stretching vibration mode of N-H groups^{5,6}. Noteworthy, all characteristic peaks of g-C₃N₄ can be clearly observed in the FTIR spectrum of W-EA-CN, verifying successful attachment of g-C₃N₄ on the WO₃ framework.

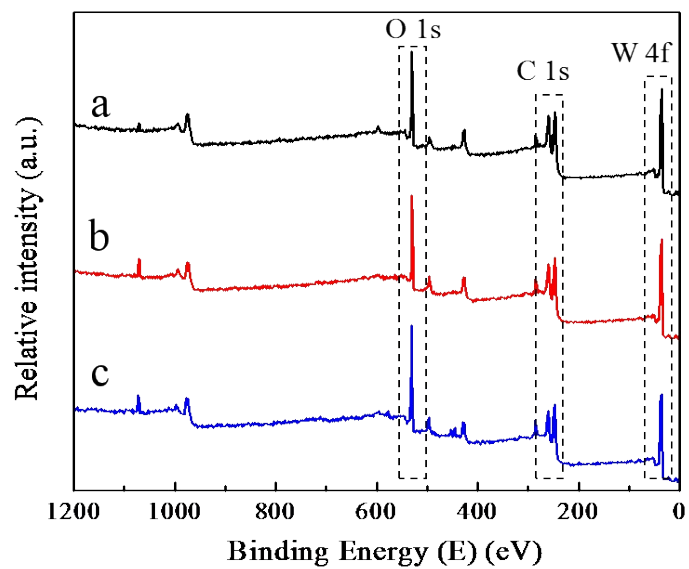


Fig. S7. Survey XPS spectra of (a) W-AA, (b) W-EA and (c) W-NTA.

Tab. S1. E_g , E_{CB} and E_{VB} of WO_3 and $g-C_3N_4$ in blank sample and heterostructures.

	E_g /eV	E_{VB} /eV	E_{CB} /eV
W-AA	2.75	+3.37	+0.62
W-EA	2.56	+3.27	+0.71
W-NTA	2.67	+3.33	+0.66
$g-C_3N_4$	2.68	+1.57	-1.11
W-AA-CN	2.70	-	-
W-EA-CN	2.61	-	-
W-NTA- CN	2.66	-	-

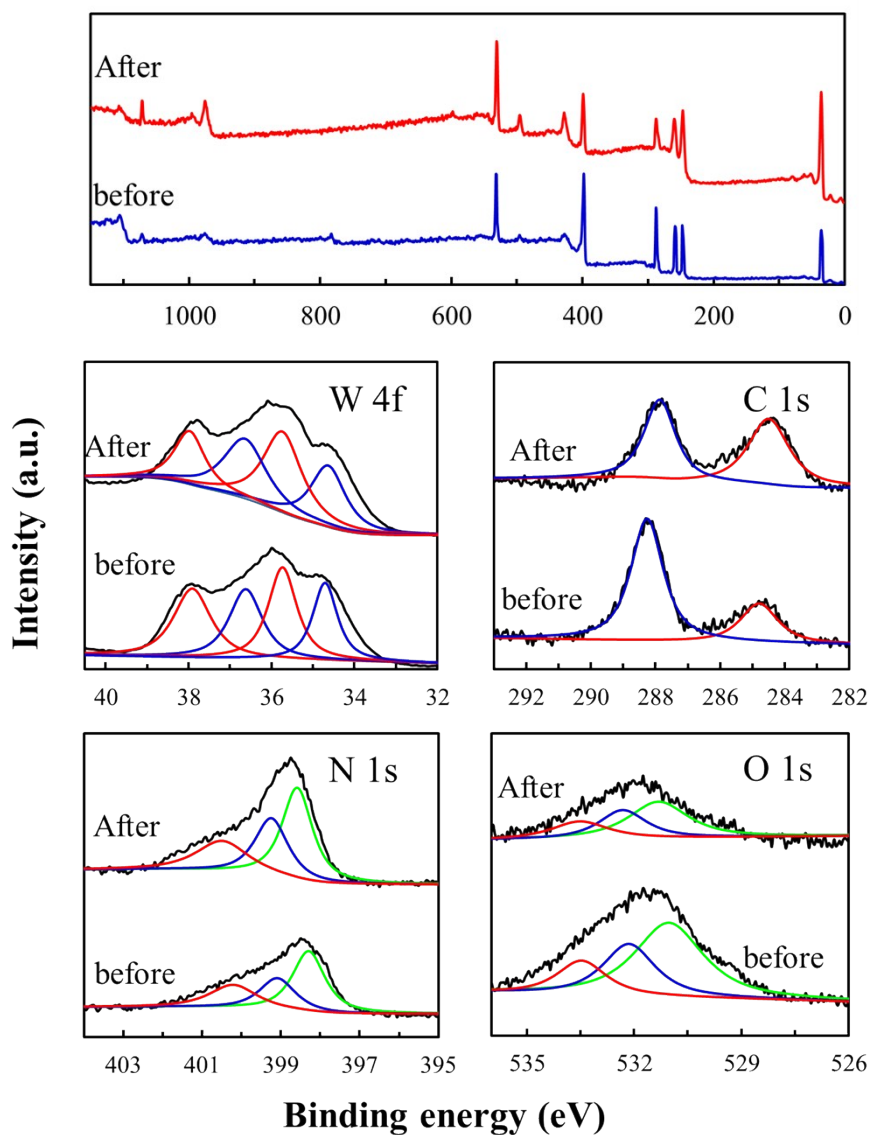


Fig. S8. Survey and high-resolution XPS spectra of W-EA-CN heterostructure before and after five successive cyclic photocatalytic reactions.

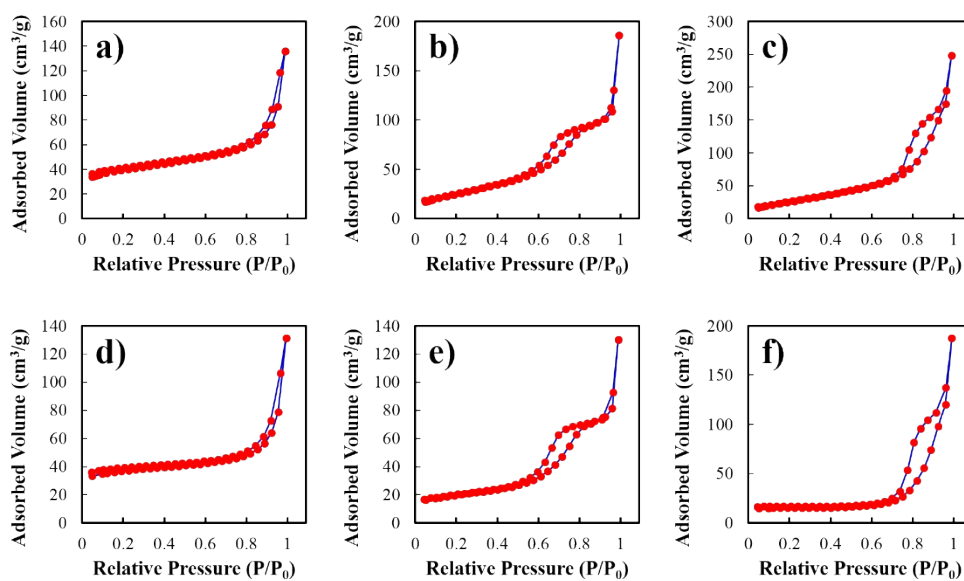


Fig. S9. Specific surface areas of (a) W-AA, (b) W-EA, (c) W-NTA, (d) W-AA-CN, (e) W-EA-CN and (f) W-NTA-CN heterostructures.

Tab. S2. Specific surface area, pore volume and pore size of different samples.

	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
W-AA	97.5	0.385	6.2
W-AA-CN	44.2	0.291	10.3
W-EA	128.9	0.200	5.3
W-EA-CN	65.6	0.175	8.4
W-NTA	167.6	0.488	10.4
W-NTA-CN	112.7	0.154	11.2

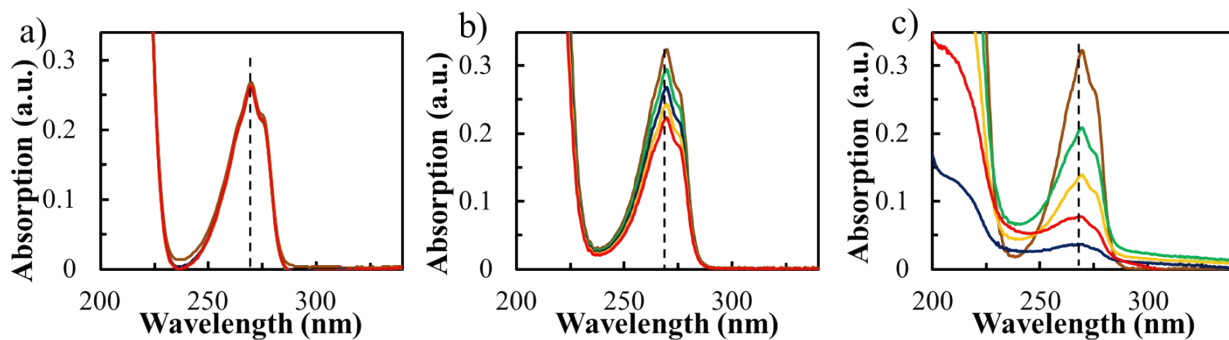


Fig. S10. UV-vis spectra of phenol (270 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

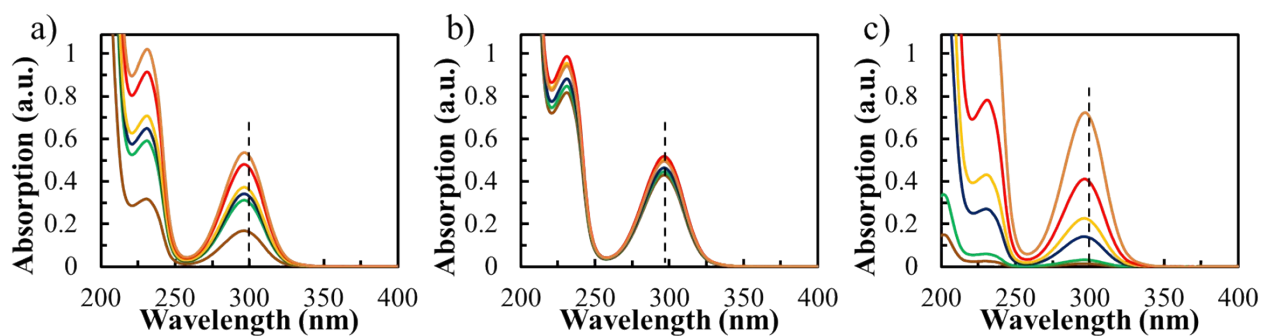


Fig. S11. UV-vis spectra of salicylic acid (300 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

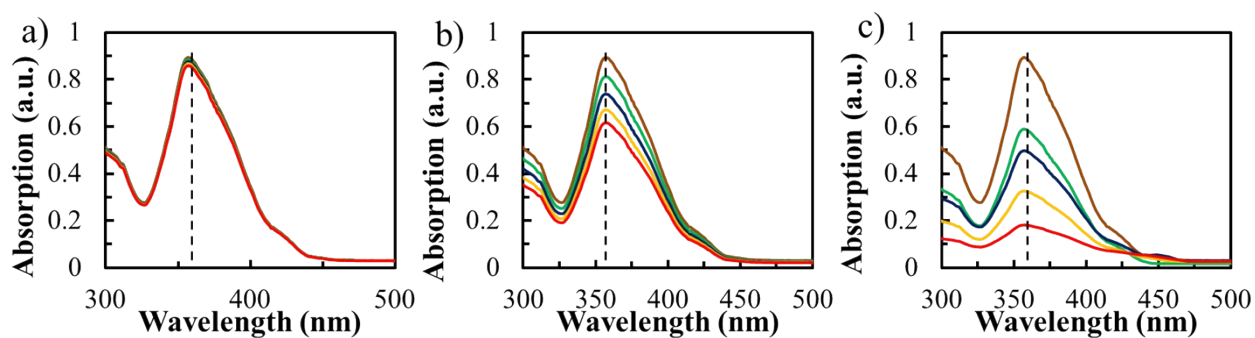


Fig. S12. UV-vis spectra of Cr(VI) (364 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

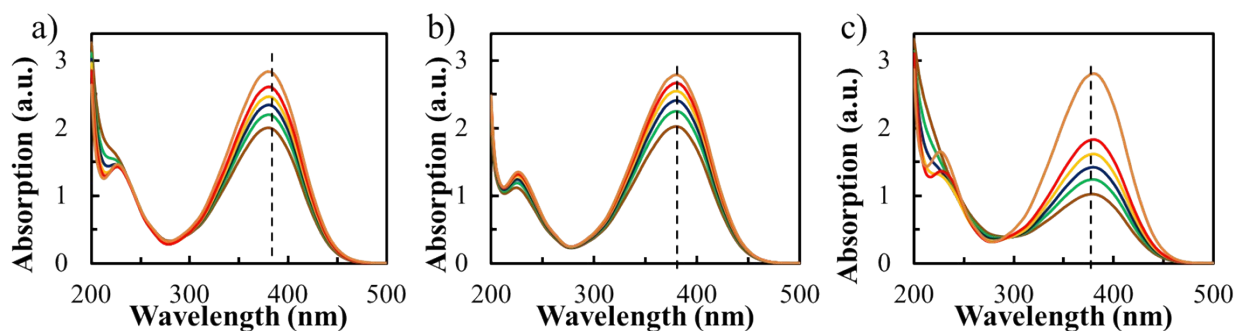


Fig. S13. UV-vis spectra of 4-nitroaniline (380 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

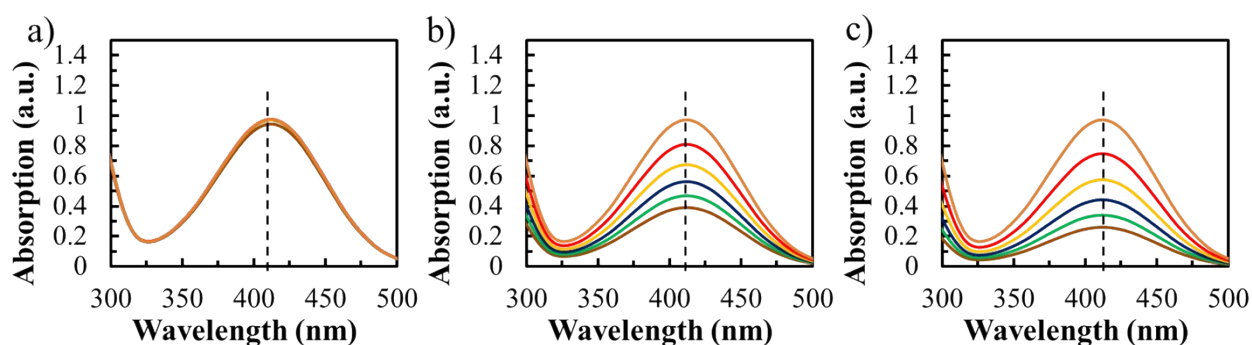


Fig. S14. UV-vis spectra of 2-nitroaniline (412 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

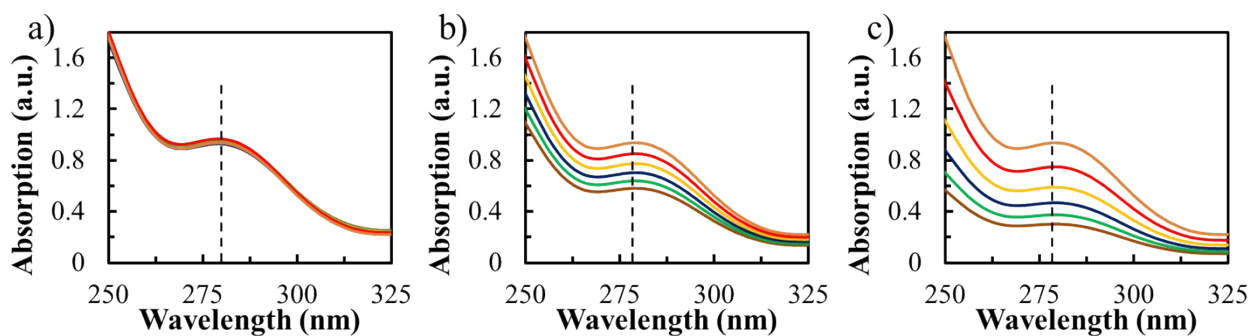


Fig. S15. UV-vis spectra of 3-nitroaniline (279 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

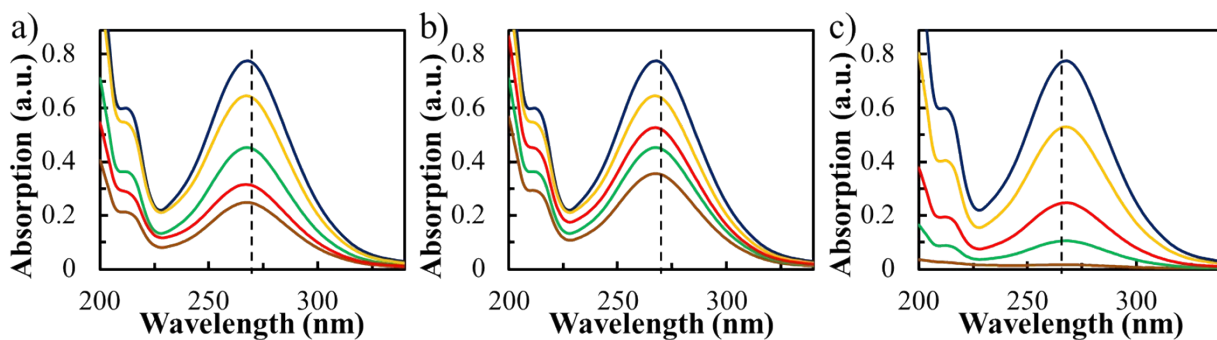


Fig. S16. UV-vis spectra of nitrobenzene (268 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

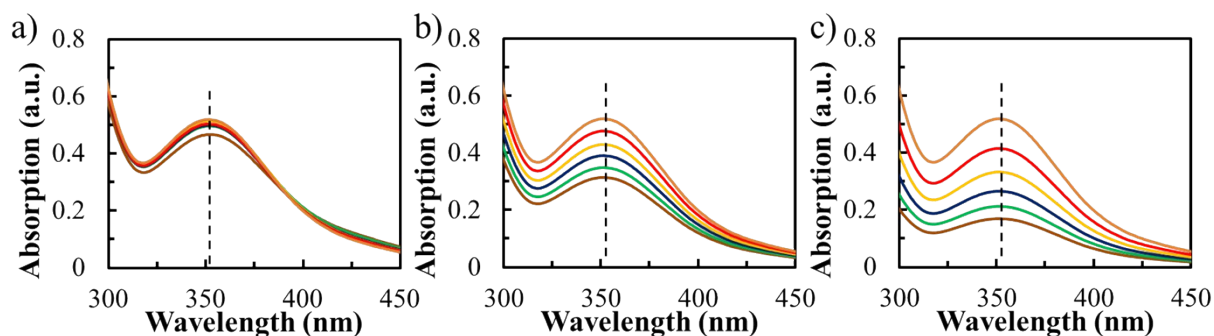


Fig. S17. UV-vis spectra of 2-nitrophenol (352 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

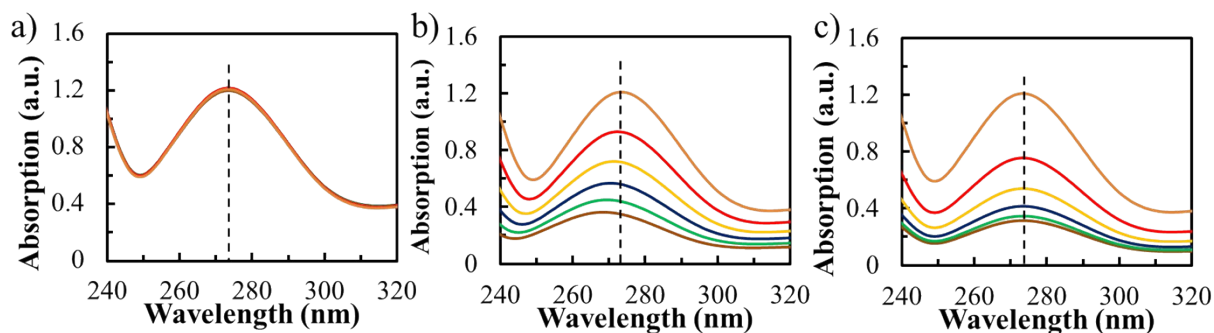


Fig. S18. UV-vis spectra of 3-nitrophenol (272 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

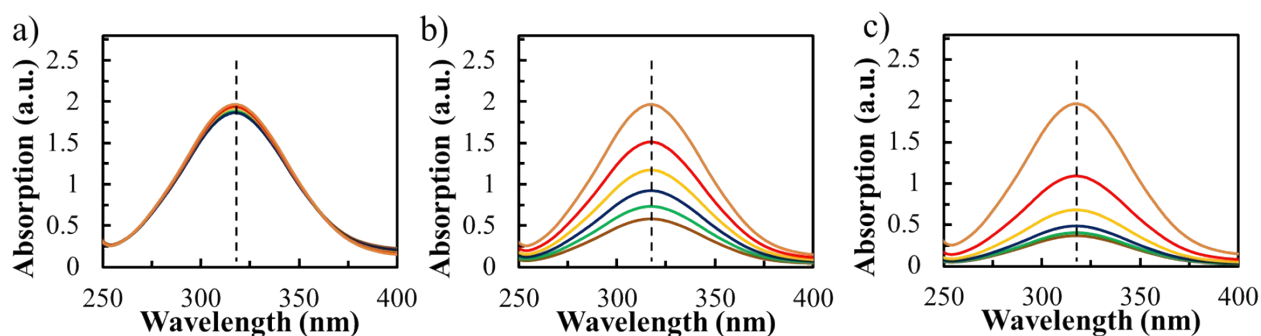


Fig. S19. UV-vis spectra of 4-nitrophenol (317 nm) degraded by (a) W-EA, (b) g-C₃N₄ and W-EA-CN.

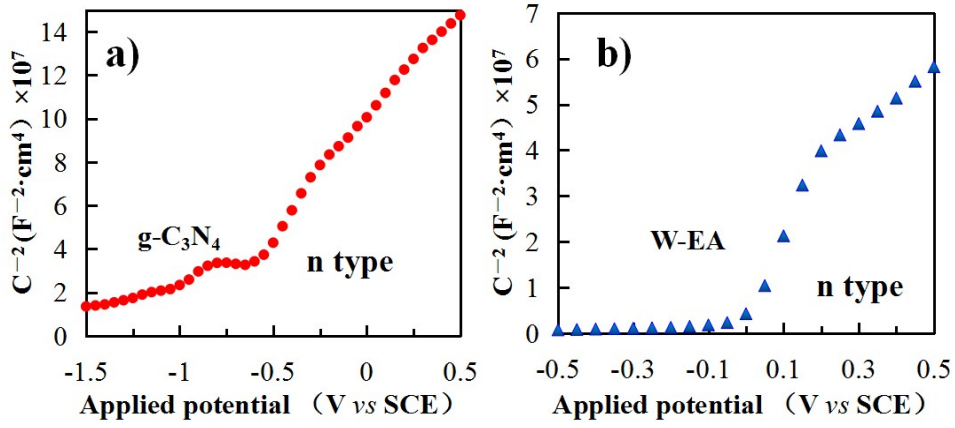


Fig. S20. Mott–Schottky results of (a) g-C₃N₄ and (b) W-EA.

Appendix: bandgap energy calculation

The bandgap energy of the photocatalysts is calculated based on the following equations ^{7, 8}:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where h , ν , A , and E_g are absorption coefficient, Planck constant, light frequency, proportionality and bandgap energy, respectively.

The band edge positions of CB and VB for semiconductors can be determined by the following equations:

$$E_{VB} = X - E_e + 0.5E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

where X is the absolute electronegativity of the semiconductor, X are 4.73 and 6.49 eV for g-C₃N₄ and WO₃ and E_e is the energy of free electrons on the hydrogen scale (ca. 4.5 eV).

References

1. K. Katsumata, R. Motoyoshi, N. Matsushita and K. Okada, *J. Hazard. Mater.*, 2013, **260**, 475-482.
2. J. Li, H. Hao and Z. Zhu, *Mater. Lett.*, 2016, **168**, 180-183.
3. Z. W. Zhao, Y. J. Sun and F. Dong, *Nanoscale*, 2015, **7**, 15-37.
4. Y. Zheng, L. H. Lin, B. Wang and X. C. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 12868-12884.
5. S. W. Cao, J. X. Low, J. G. Yu and M. Jaroniec, *Adv. Mater.*, 2015, **27**, 2150-2176.
6. J. J. Zhu, P. Xiao, H. L. Li and S. A. C. Carabineiro, *Acs Appl. Mater. Interfaces*, 2014, **6**, 16449-16465.
7. S.F. Chen, Y.F. Hu, S.G. Meng, X.L. Fu, *Appl. Catal. B-Environ.*, 2014, **150**, 564-573.
8. H.F. Li, H.T. Yu, X. Quan, S. Chen, Y.B. Zhang, *Acs Appl. Mater. Interfaces*, 2016, **8**, 2111-2119.