

**A novel nano-sized red phosphorus decorated borocarbonitride heterojunction  
with enhanced photocatalytic performance for tetracycline degradation**

Yi Wang<sup>a,b</sup>, Xing Zhao<sup>a</sup>, Lan Wang<sup>c,\*</sup>, Yu Yang<sup>b</sup>, Limin Jiao<sup>a</sup>, Zhihao Wu<sup>a</sup>, Xuan Gao<sup>a</sup>, Sheng Cheng<sup>d</sup>, Mingzhang Lin<sup>a,\*</sup>

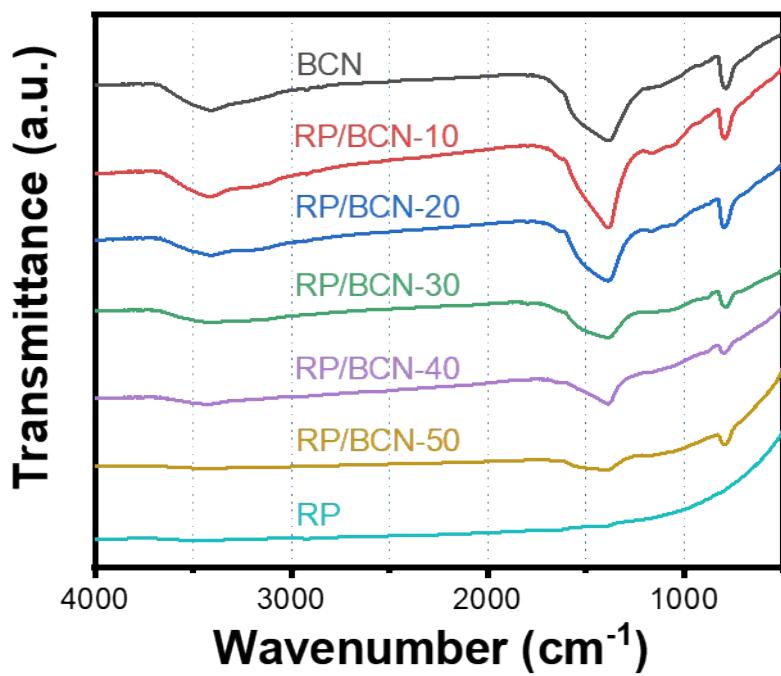
<sup>a</sup> School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, Anhui 230026, China

<sup>b</sup> Reactor Operation and Application Research Sub-Institute, Nuclear Power Institute of China, Chengdu, Sichuan 610041, China

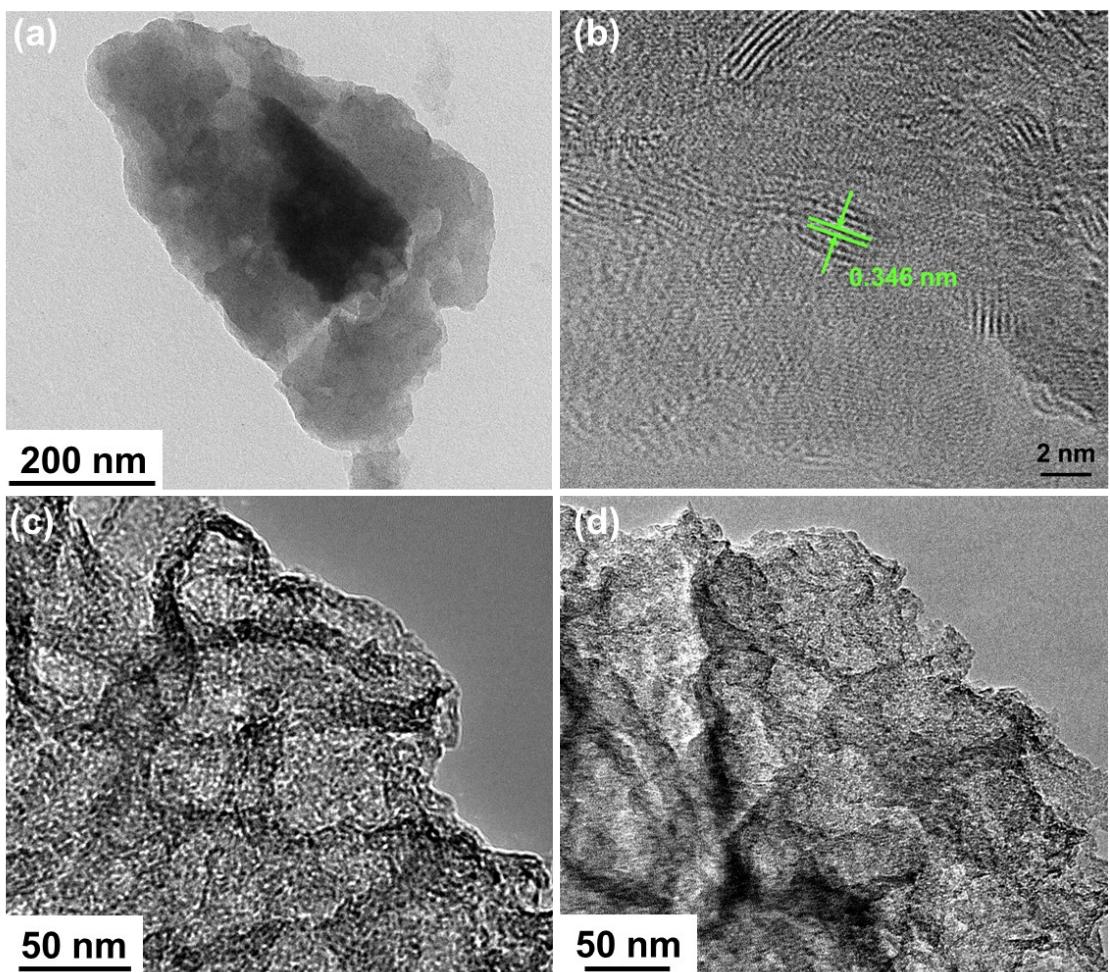
<sup>c</sup> School of Materials, Sun Yat-sen University, Guangzhou, Guangdong 510275, China

<sup>d</sup> Instrumental Analysis Center, Hefei University of Technology, Hefei, Anhui 230009, China

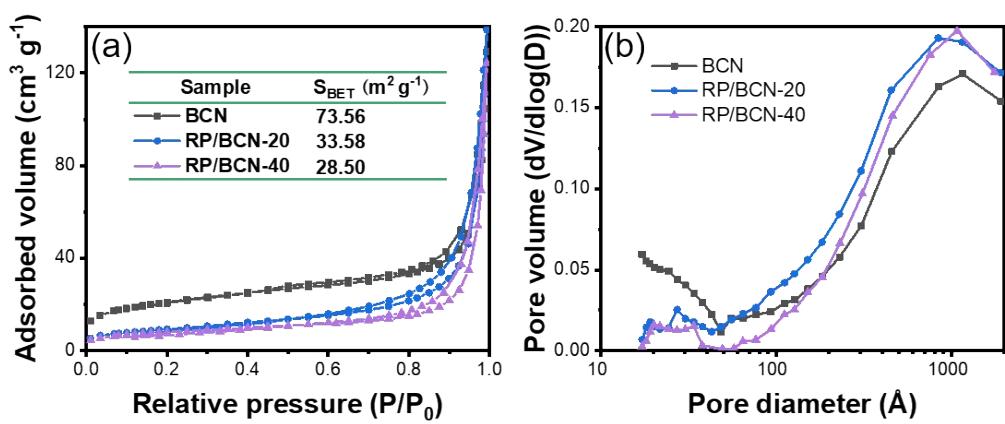
\* To whom correspondence should be addressed. E-mail: [wanglan\\_only@163.com](mailto:wanglan_only@163.com) (L. Wang), [gelin@ustc.edu.cn](mailto:gelin@ustc.edu.cn) (M. Z. Lin).



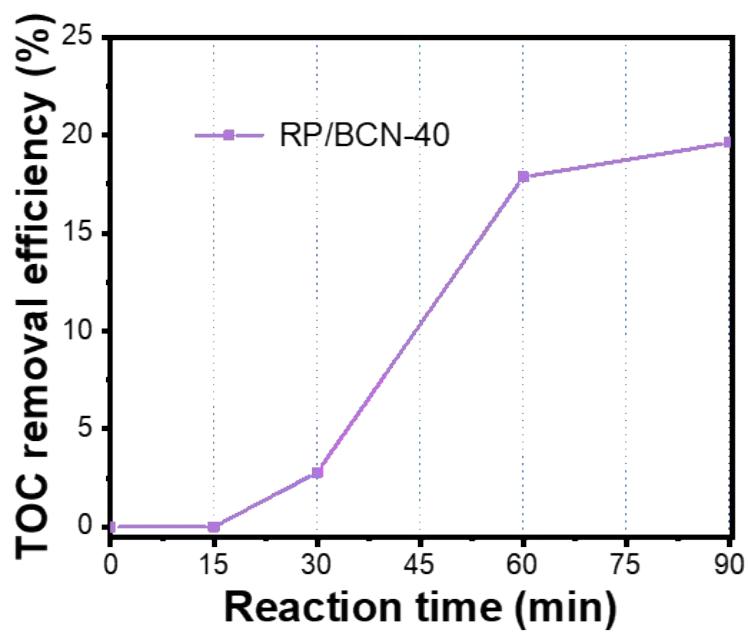
**Fig. S1** FT-IR spectra of BCN, RP/BCN, and RP samples.



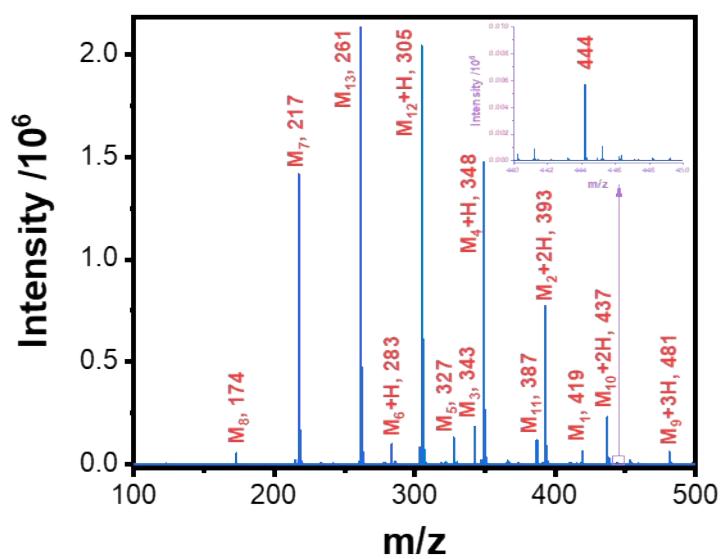
**Fig. S2** TEM (a) and HR-TEM (b) images of BCN. FE-TEM images of BCN (c) and RP/BCN-40 (d).



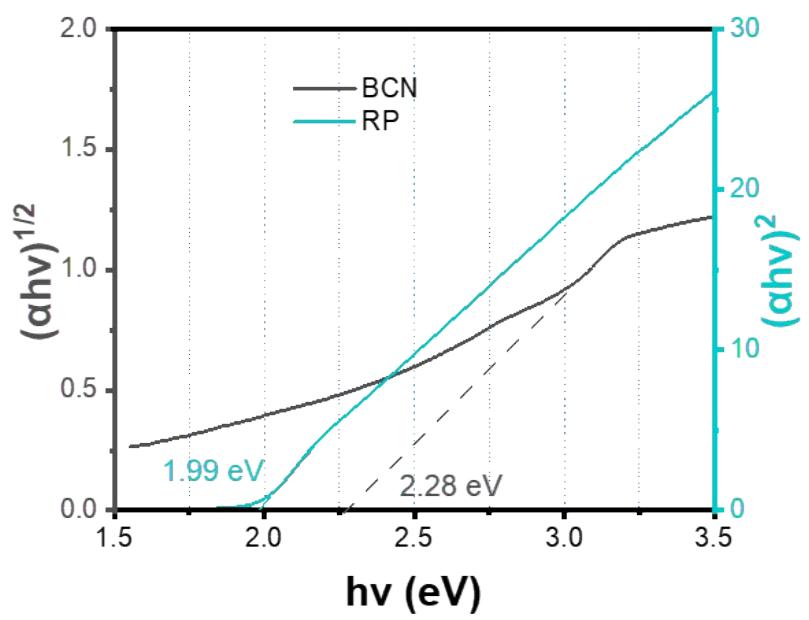
**Fig. S3** N<sub>2</sub> adsorption–desorption isotherms **(a)** and BET specific surface area in the inset, and the corresponding BJH pore size distribution **(b)** of BCN, RP/BCN-20 and RP/BCN-40 samples.



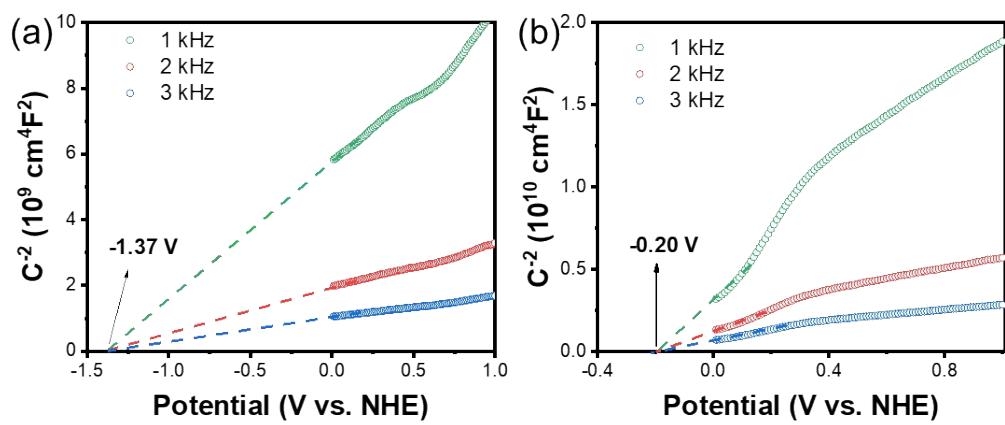
**Fig. S4** TOC removal efficiency of TC over RP/BCN-40 under visible exposure.



**Fig. S5** The UPLC-MS spectra of TC using RP/BCN-40 as the photocatalysts after 120-min exposure.



**Fig. S6** The band gaps of pure BCN and RP determined by the Tauc plot.



**Fig. S7** The electrochemical Mott-Schottky curves for BCN (**a**) and RP (**b**).

**Table S1** Elemental analysis from XPS for BCN, RP/BCN, and RP samples.

Sample	B (at%)	C (at%)	N (at%)	P (at%)
<b>BCN</b>	51.59	10.73	37.33	—
<b>RP/BCN-20</b>	50.70	11.04	35.42	2.84
<b>RP/BCN-40</b>	49.51	11.28	34.63	4.59
<b>RP</b>	—	13.34	—	86.66

**Table S2** Comparison of TC degradation efficiency and apparent rate constant with previously reported photocatalysts.

Photocatalyst	Reaction condition	Degradation efficiency	Apparent rate constant	References
Ag <sub>3</sub> PO <sub>4</sub> -PN photocatalyst	TC, 0.03 mg mL <sup>-1</sup> ; catalyst, 2 mg mL <sup>-1</sup>	85.0%, 120 min	0.0023 min <sup>-1</sup>	[1]
LaFeO <sub>3</sub> /SnS <sub>2</sub> hybrid	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 0.33 mg mL <sup>-1</sup>	28.8%, 120 min	0.0028 min <sup>-1</sup>	[2]
BiOI/MIL-125(Ti) composite	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 0.25 mg mL <sup>-1</sup>	70.0%, 240 min	0.0048 min <sup>-1</sup>	[3]
Polyaniline/Perylene diimide organic heterojunction	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 0.5 mg mL <sup>-1</sup>	~70%, 120 min	0.0088 min <sup>-1</sup>	[4]
AgI/Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub> heterojunction	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 0.33 mg mL <sup>-1</sup>	45.4%, 60 min	0.0097 min <sup>-1</sup>	[5]
Porous hollow cube ZnFe <sub>2</sub> O <sub>4</sub>	TC, 0.04 mg mL <sup>-1</sup> ; catalyst, 0.5 mg mL <sup>-1</sup>	85.0%, 70 min	0.0118 min <sup>-1</sup>	[6]
Ag/g-C <sub>3</sub> N <sub>4</sub> plasmonic photocatalyst	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 1.7 mg mL <sup>-1</sup>	83.0%, 120 min	0.0120 min <sup>-1</sup>	[7]
Cu <sub>2</sub> O-TiO <sub>2</sub> -Pal heterojunction	TC, 0.03 mg mL <sup>-1</sup> ; catalyst, 1 mg mL <sup>-1</sup>	71.5%, 240 min	0.0129 min <sup>-1</sup>	[8]
ZnSnO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub> heterojunction	TC, 0.01 mg mL <sup>-1</sup> ; catalyst, 0.5 mg mL <sup>-1</sup>	85.0%, 120 min	0.0131 min <sup>-1</sup>	[9]
Sludge-TiO <sub>2</sub> photocatalysts	TC, 0.005 mg mL <sup>-1</sup> ; catalyst, 0.01 mg mL <sup>-1</sup>	76.3%, 120 min	0.0142 min <sup>-1</sup>	[10]
BiOCl microflowers co-modified with oxygen vacancies and Mn <sup>2+</sup>	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 1 mg mL <sup>-1</sup>	~79%, 15 min	0.0146 min <sup>-1</sup>	[11]
BiOCl/Bi <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> nanorod	TC, 0.05 mg mL <sup>-1</sup> ; catalyst, 1 mg mL <sup>-1</sup>	90.0%, 120 min	0.0158 min <sup>-1</sup>	[12]
Mn-doped SrTiO <sub>3</sub> nanocubes	TC, 0.01 mg mL <sup>-1</sup> ; catalyst, 1 mg mL <sup>-1</sup>	66.7%, 60 min	0.0166 min <sup>-1</sup>	[13]
γ-In <sub>2</sub> Se <sub>3</sub> nanoparticles	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 1 mg mL <sup>-1</sup>	91.5%, 120 min	0.0175 min <sup>-1</sup>	[14]
Cl-doped porous g-C <sub>3</sub> N <sub>4</sub> nanosheets	TC, 0.01 mg mL <sup>-1</sup> ; catalyst, 0.5 mg mL <sup>-1</sup>	92.0%, 120 min	0.0201 min <sup>-1</sup>	[15]
Carbon dots modified ZnSnO <sub>3</sub>	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 1 mg mL <sup>-1</sup>	81.8%, 60 min	0.0231 min <sup>-1</sup>	[16]
RP/BCN-40	TC, 0.02 mg mL <sup>-1</sup> ; catalyst, 0.5 mg mL <sup>-1</sup>	73.8%, 90 min	0.0224 min <sup>-1</sup>	This work

## References

1. Q. Yan, M. Xu, C. Lin, J. Hu, Y. Liu and R. Zhang, Efficient photocatalytic degradation of tetracycline hydrochloride by  $\text{Ag}_3\text{PO}_4$  under visible-light irradiation, *Environ. Sci. Pollut. R.*, 2016, **23**, 14422-14430.
2. L. Jin, L. Rong, Y. Chen, X. Zhou, X. Ning, Z. Liang, M. Lin, X. Xu, L. Xu and L. Zhang, Rational design of Z-scheme  $\text{LaFeO}_3/\text{SnS}_2$  hybrid with boosted visible light photocatalytic activity towards tetracycline degradation, *Sep. Purif. Technol.*, 2019, **210**, 417-430.
3. W. Jiang, Z. Li, C. Liu, D. Wang, G. Yan, B. Liu and G. Che, Enhanced visible-light-induced photocatalytic degradation of tetracycline using  $\text{BiOI}/\text{MIL}-125(\text{Ti})$  composite photocatalyst, *J. Alloys Compd.*, 2021, **854**, 157166.
4. W. Dai, L. Jiang, J. Wang, Y. Pu, Y. Zhu, Y. Wang and B. Xiao, Efficient and stable photocatalytic degradation of tetracycline wastewater by 3D Polyaniline/Perylene diimide organic heterojunction under visible light irradiation, *Chem. Eng. J.*, 2020, **397**, 125476.
5. J. Luo, X. Ning, L. Zhan and X. Zhou, Facile construction of a fascinating Z-scheme  $\text{AgI}/\text{Zn}_3\text{V}_2\text{O}_8$  photocatalyst for the photocatalytic degradation of tetracycline under visible light irradiation, *Sep. Purif. Technol.*, 2020, **255**, 117691.
6. Y. Cao, X. Lei, Q. Chen, C. Kang, W. Li and B. Liu, Enhanced photocatalytic degradation of tetracycline hydrochloride by novel porous hollow cube  $\text{ZnFe}_2\text{O}_4$ , *J. Photoch. Photobio. A*, 2018, **364**, 794-800.
7. W. Xu, S. Lai, S. C. Pillai, W. Chu, Y. Hu, X. Jiang, M. Fu, X. Wu, F. Li and H. Wang, Visible light photocatalytic degradation of tetracycline with porous Ag/graphite carbon nitride plasmonic composite: degradation pathways and mechanism, *J. Colloid Interface Sci.*, 2020, **574**, 110-121.
8. Y. Shi, Z. Yang, B. Wang, H. An, Z. Chen and H. Cui, Adsorption and photocatalytic degradation of tetracycline hydrochloride using a palygorskite-supported  $\text{Cu}_2\text{O}-\text{TiO}_2$  composite, *Appl. Clay Sci.*, 2016, **119**, 311-320.
9. Xiliu, Huang, Feng, Guo, Mingyang, Li, Hongji, Ren and Yu, Hydrothermal synthesis of  $\text{ZnSnO}_3$  nanoparticles decorated on  $g\text{-C}_3\text{N}_4$  nanosheets for accelerated photocatalytic degradation of tetracycline under the visible-light irradiation, *Sep. Purif. Technol.*, 2020, **230**, 115854.
10. X. Zhu, W. Yuan, M. Lang, G. Zhen, X. Zhang and X. Lu, Novel methods of sewage sludge

utilization for photocatalytic degradation of tetracycline-containing wastewater, *Fuel*, 2019, **252**, 148-156.

11. H. Yu, D. Ge, Y. Liu, Y. Lu, X. Wang, M. Huo and W. Qin, One-pot synthesis of BiOCl microflowers co-modified with Mn and oxygen vacancies for enhanced photocatalytic degradation of tetracycline under visible light, *Sep. Purif. Technol.*, 2020, **251**, 117414.
12. Y. Xu, D. Lin, X. Liu, Y. Luo, H. Xue, B. Huang, Q. Chen and Q. Qian, Electrospun BiOCl/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> nanorod heterostructures with enhanced solar light efficiency in the photocatalytic degradation of tetracycline hydrochloride, *ChemCatChem*, 2018, **10**, 2496-2504.
13. G. Wu, P. Li, D. Xu, B. Luo, Y. Hong, W. Shi and C. Liu, Hydrothermal synthesis and visible-light-driven photocatalytic degradation for tetracycline of Mn-doped SrTiO<sub>3</sub> nanocubes, *Appl. Surf. Sci.*, 2015, **333**, 39-47.
14. X. Wei, H. Feng, L. Li, J. Gong, K. Jiang, S. Xue and P.K. Chu, Synthesis of tetragonal prismatic γ-In<sub>2</sub>Se<sub>3</sub> nanostructures with predominantly {110} facets and photocatalytic degradation of tetracycline, *Appl. Catal. B*, **260**, 118218-118218.
15. F. Guo, M. Li, H. Ren, X. Huang, K. Shu, W. Shi and C. Lu, Facile bottom-up preparation of Cl-doped porous g-C<sub>3</sub>N<sub>4</sub> nanosheets for enhanced photocatalytic degradation of tetracycline under visible light, *Sep. Purif. Technol.*, 2019, **228**, 115770.
16. F. Guo, X. Huang, Z. Chen, H. Sun and W. Shi, Investigation of visible-light-driven photocatalytic tetracycline degradation via carbon dots modified porous ZnSnO<sub>3</sub> cubes: Mechanism and degradation pathway, *Sep. Purif. Technol.*, **253**, 117518.