

Supporting information

Double charge carrier mechanism through 2D/2D interface assisted ultrafast water reduction and antibiotic degradation over architecting S, P co-doped g-C₃N₄/ZnCr LDH photocatalyst

Dipti Prava Sahoo, Kundan Kumar Das, Sulagna Patnaik, Kulamani Parida*

**Centre for Nano Science and Nano Technology, Siksha O Anusandhan (Deemed to be)
University, Bhubaneswar-751030**

*Corresponding Author: K.M. Parida

E-mail: kulamaniparida@soauniversity.ac.in & paridakulamani@yahoo.com Tel. No: +91-674-2351777; Fax: +91-674-2350642

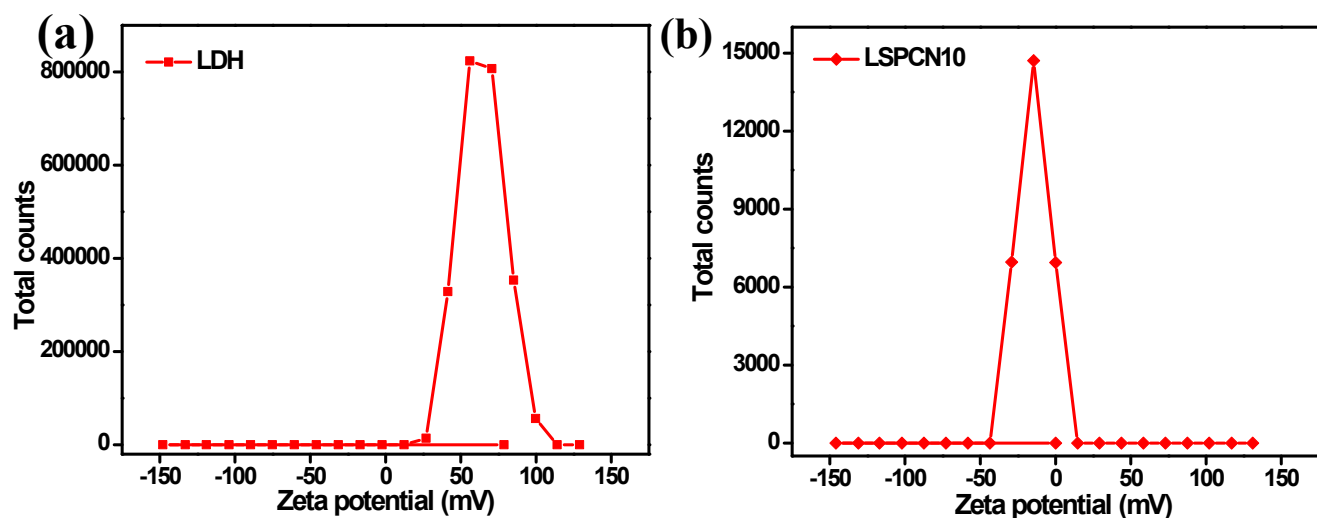


Fig. S1 Zeta potentials of (a) LDH and (b) LSPCN10 samples.

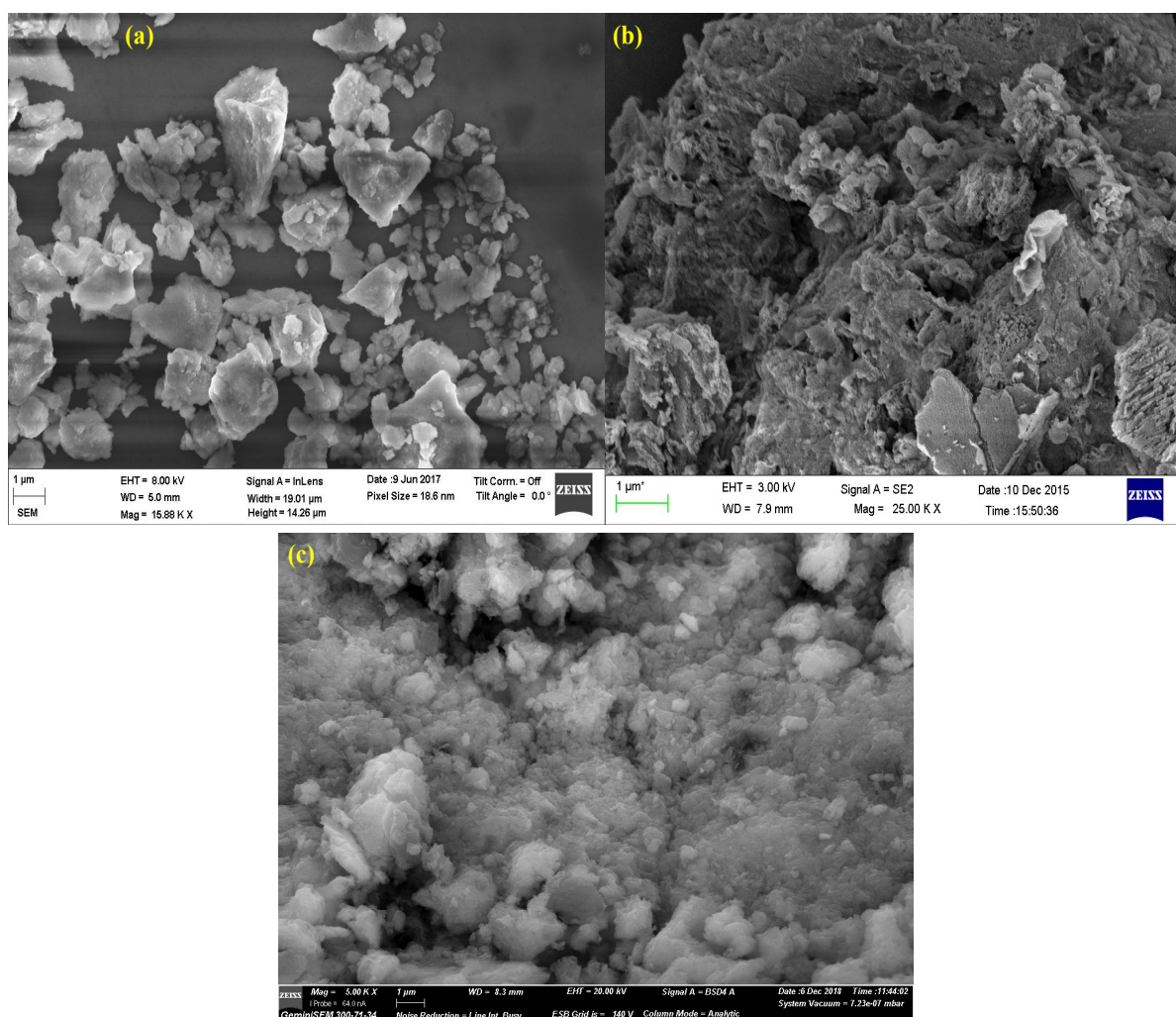


Fig. S2 SEM images of (a) LDH, (b) SPCN (c) LSPCN10 material.

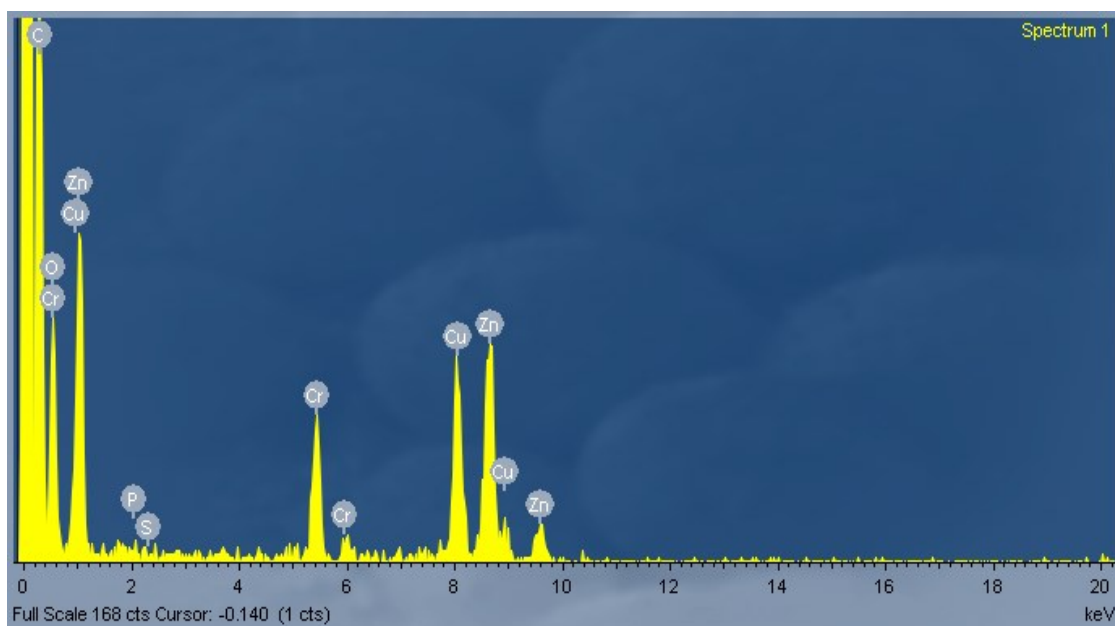


Fig. S3 EDX elemental analysis of LSPCN10 material.

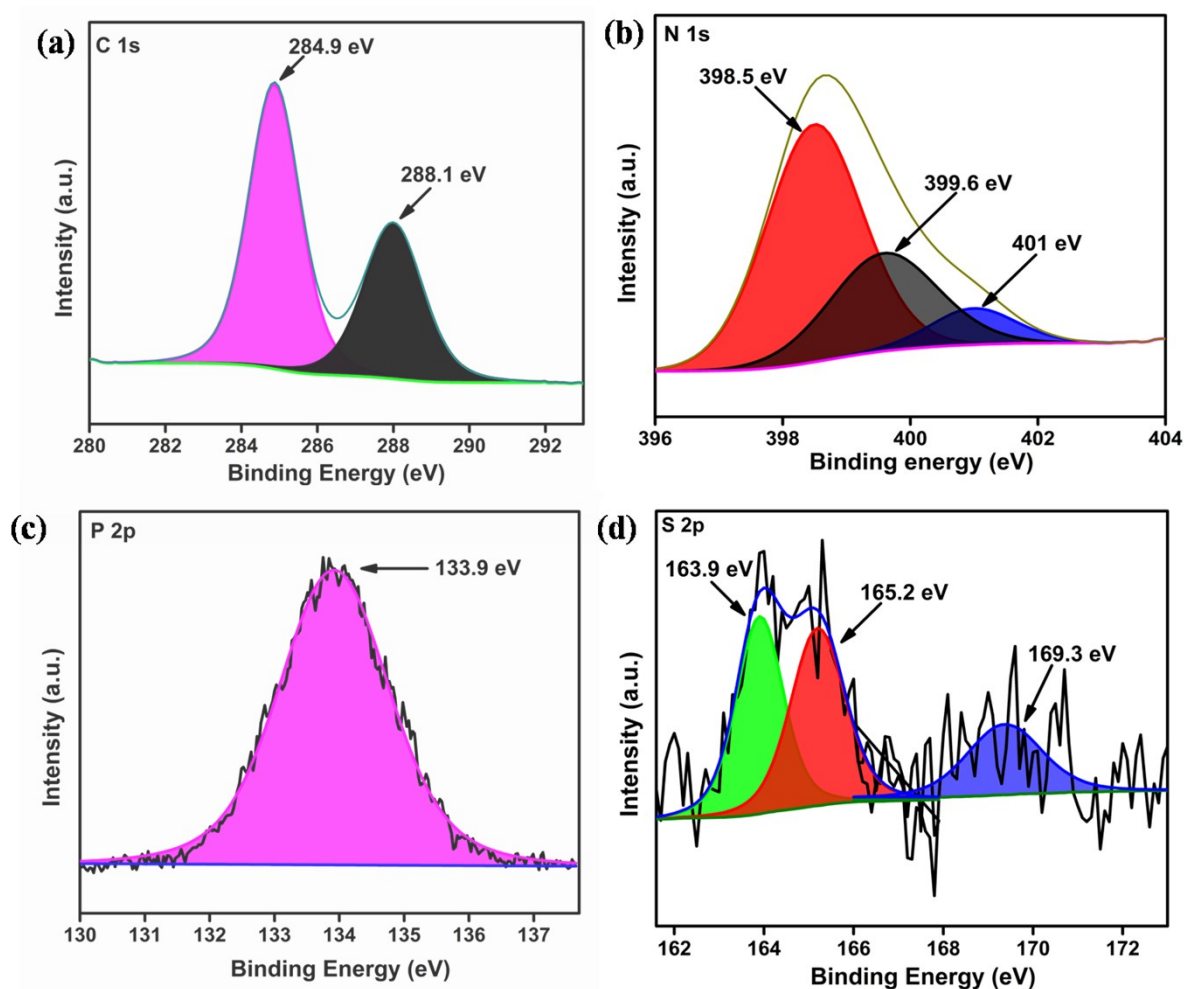


Fig. S4 High resolution deconvoluted XPS spectra of SPCN: (a) C 1s, (b) N 1s, (c) P 2p and (d) S 2p.

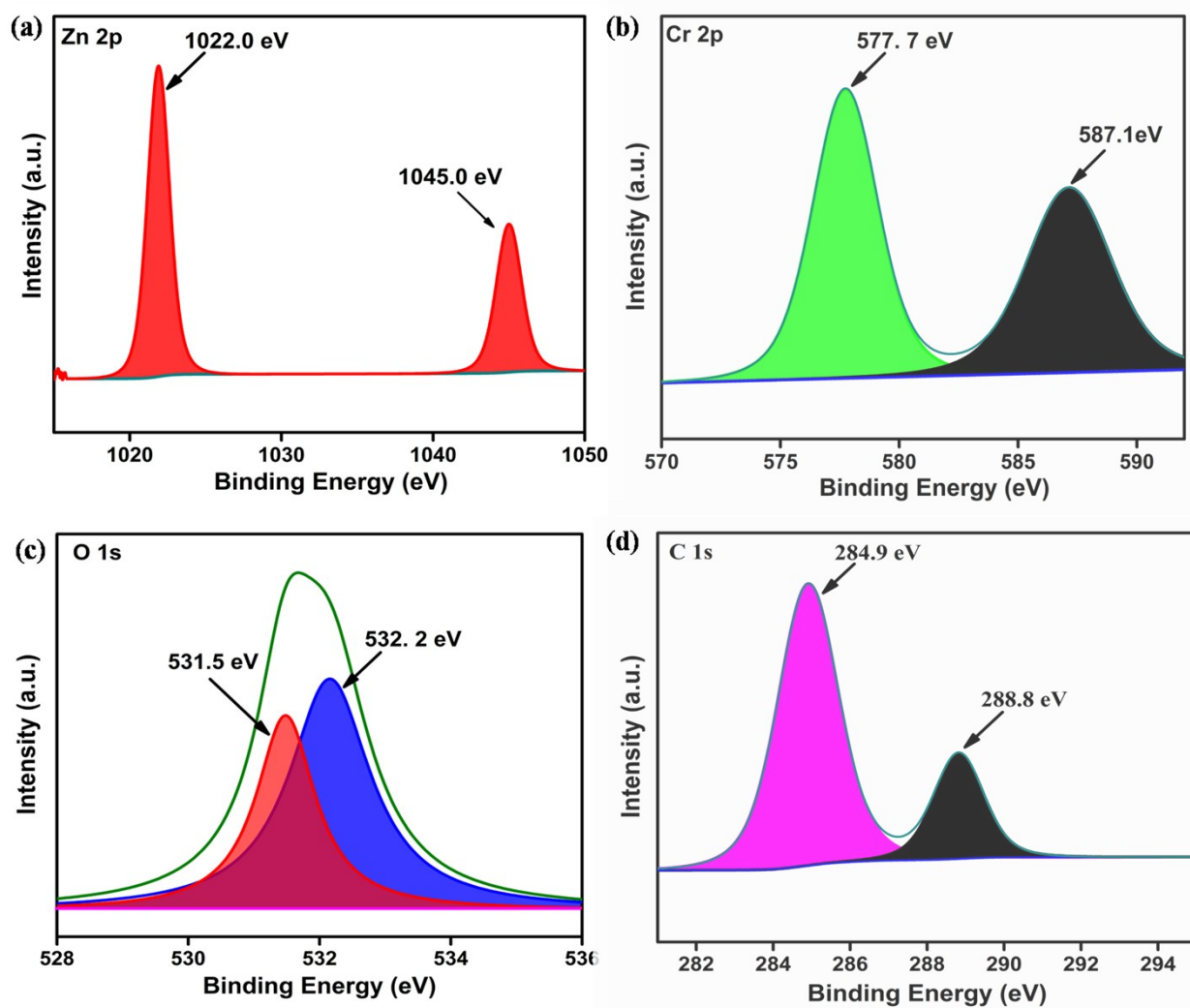
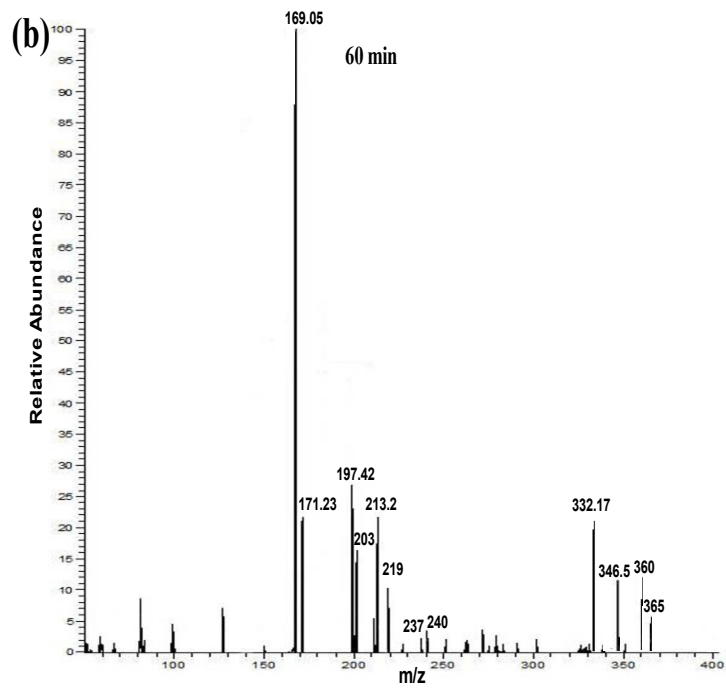
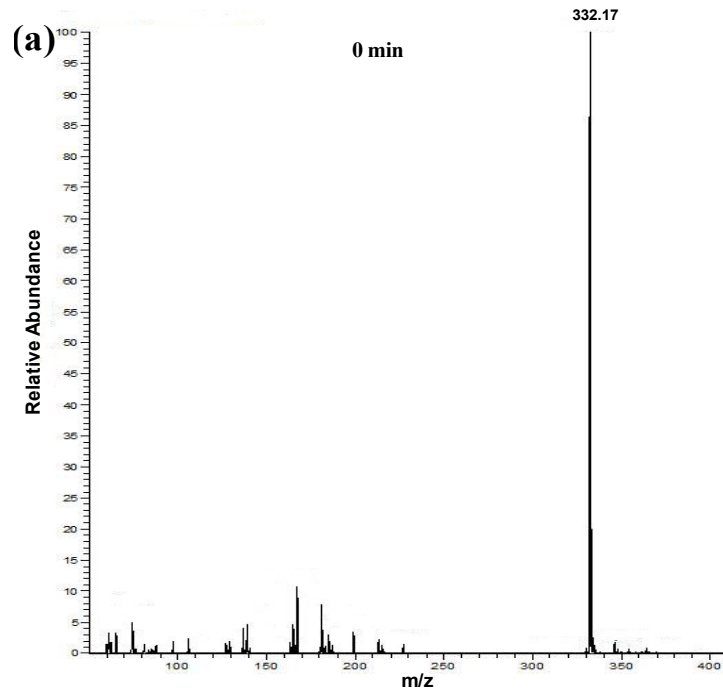


Fig. S5 High resolution deconvoluted XPS spectra of LDH: (a) Zn 2p, (b) Cr 2p, (c) O 2p and (d) C 1s.



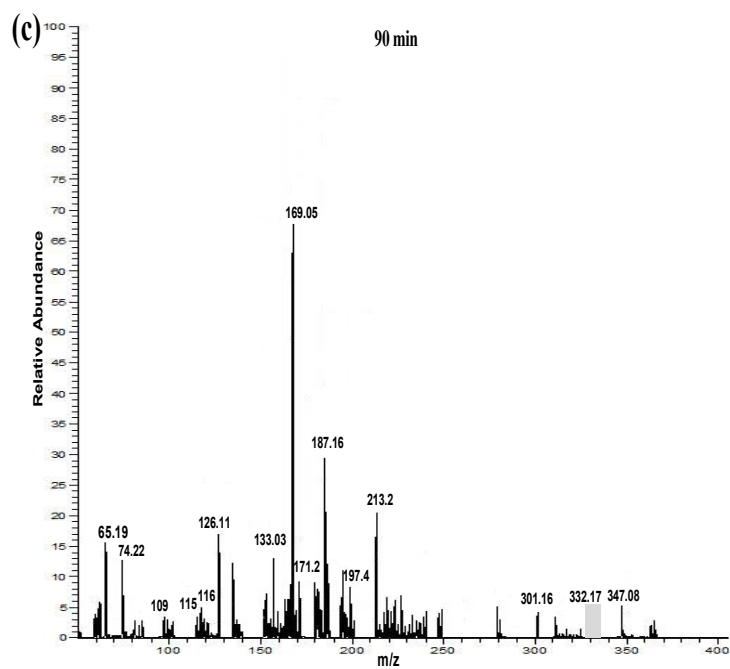


Fig. S6 LC-MS of CPX solution during degradation process over LSPCN10 heterostructure: (a) 0 min, (b) 60 min and (c) 90 min.

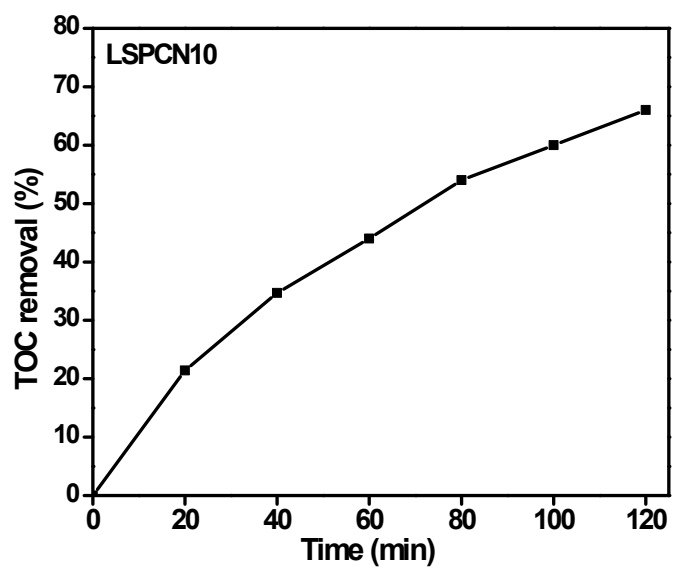


Fig. S7 TOC removal of photocatalytic CPX degradation over LSPCN10.

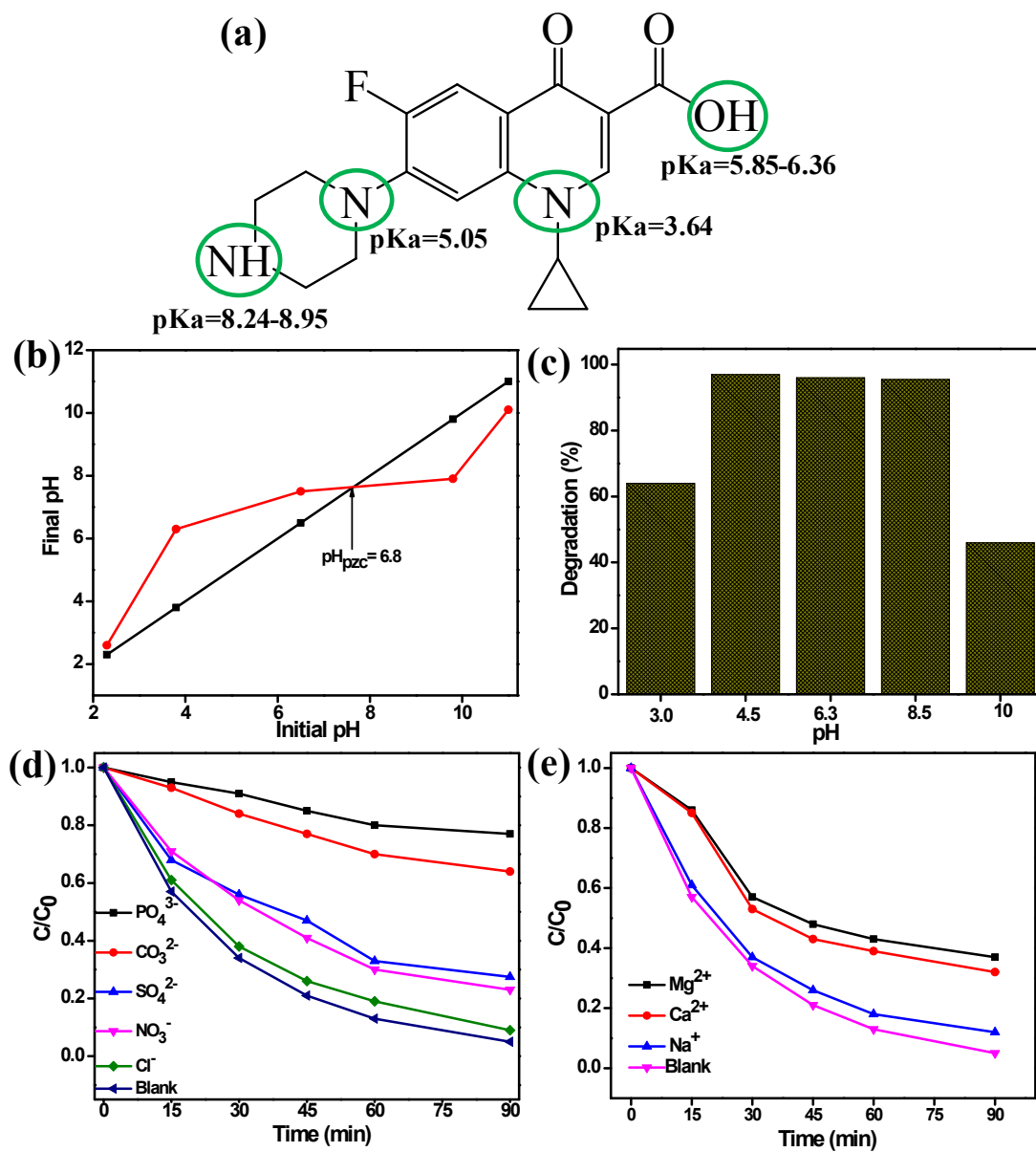


Fig. S8 (a) Molecular structure of CPX ($C_{17}H_{18}FN_3O_3$), (b) PZC plot of LSPCN10 heterostructure, photocatalytic degradation of CPX under (c) different pH, various (d) anions and (e) cations.

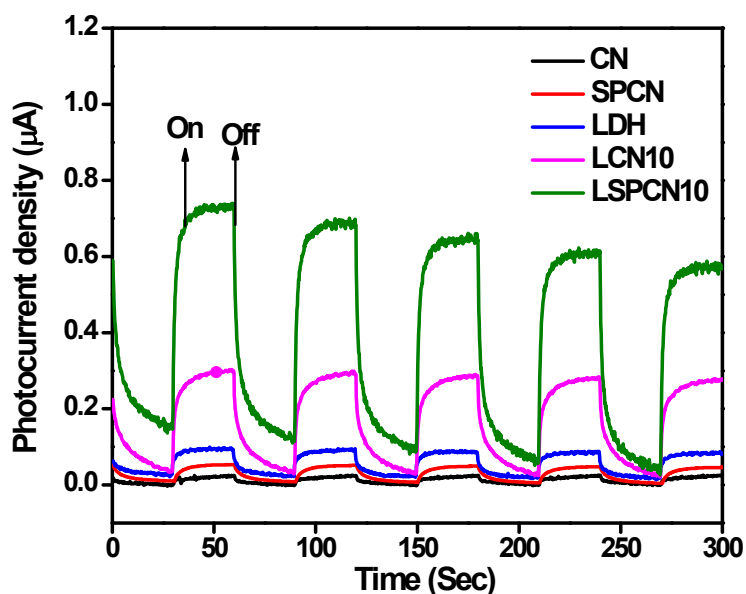


Fig. S9 Transient Photocurrent response analysis of CN, SPCN, LDH, LCN10 and LSPCN10 under discontinuous visible light irradiation.

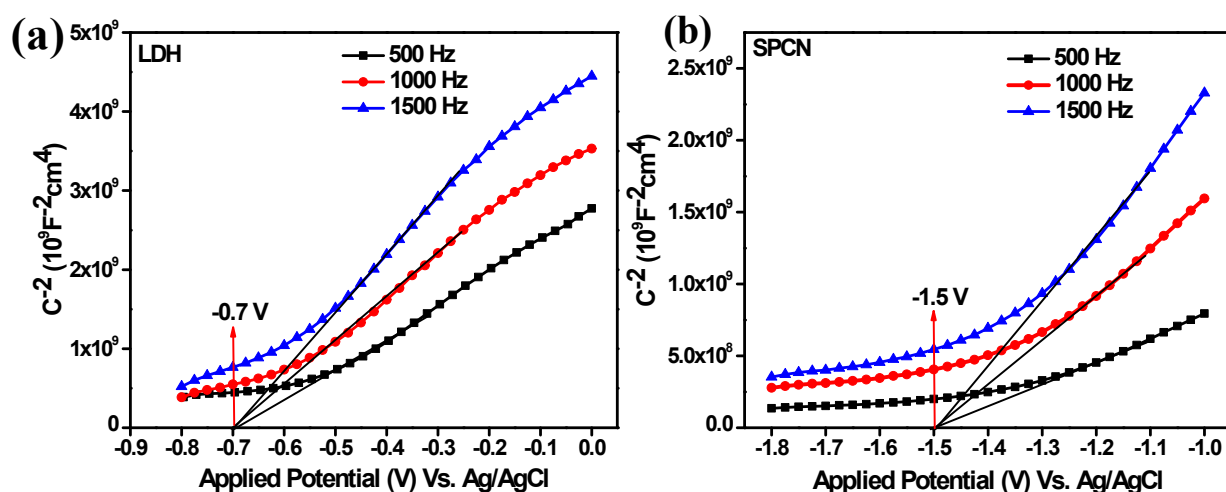


Fig. S10 Mott-Schottky plot of (a) LDH and (b) SPCN at different frequencies.

Table S1 A comparison study for photocatalytic ciprofloxacin degradation over present heterostructure with the reported $g\text{-C}_3\text{N}_4$ and LDH based system.

Photocatalysts	Reaction condition (visible light source, CPX concentration, catalyst dosage and time period)	CPX degradation efficiency	Ref
NiAl LDH/ Fe_3O_4 -RGO	500 W Xe, ($\lambda \geq 420$), 10 ppm CPX solution, (40 ml) 10 mg, 150 min	91%	1

NiAlFe LDH/RGO	500W Xe, ($\lambda \geq 420$), 10 ppm CPX solution (40 mL), 10 mg, 120 min	92%	2
SO ₄ ²⁻ -g-C ₃ N ₄ /Ag ₃ PO ₄	400W Xe, ($\lambda \geq 420$), 20 ppm CPX solution (50mL), 20 mg, 50 min	>90%	3
Ag@P-g-C ₃ N ₄ /BiVO ₄	300W Xe, ($\lambda \geq 420$), 10 ppm CPX solution (50mL), 25mg, 120 min	93 %	4
C-dot@ nitrogen deficient g-C ₃ N ₄	300W Xe, ($\lambda \geq 420$), 10 ppm CPX solution (20mL), 20mg, 360 min	3.5 times more than g- C ₃ N ₄	5
g-C ₃ N ₄ -TiO ₂	300W Xe, ($\lambda \geq 420$), 10 ppm CPX solution (80mL), 30mg, 180 min	85%	6
NiAg/ g- C ₃ N ₄ /Cd ₂ Sb ₂ O _{6.8}	Sun light, 20 ppm CPX solution (50mL), 50mg, 70 min	82%	7
LSPCN10 (Present research)	250 wt medium pressure Hg ($\lambda \geq 420$ nm), 20 ppm CPX solution (20 mL), 20 mg, 90 min	95%	

Table S2 A comparison study for photocatalytic H₂ evolution over present heterostructure with the reported g-C₃N₄ and LDH based system.

Photocatalyst	Visible light source and sacrificial agents	H ₂ evolution ($\mu\text{mol g}^{-1}\text{h}^{-1}$)	Ref
CdSe/ZnCr LDH	450 W Xe ($\lambda \geq 420$), Na ₂ SO ₄ /Na ₂ S /Pt	1560	8
CdZnS/ZnCr LDH	300 W Xe, ($\lambda \geq 420$), CH ₃ OH	18320	9
g-C ₃ N ₄ /NiFe LDH	125 W Hg ($\lambda \geq 420$), CH ₃ OH	24800	10

RGO/La ₂ Ti ₂ O ₇ /NiFe LDH	100 mW AM 1.5, ($\lambda \geq 420$), TEOA	532	11
ZnCr LDH/g-C ₃ N ₄	300 W Xe ($\lambda \geq 420$), TEOA	156	12
1 wt% Pt/ NiS/P-S g-C ₃ N ₄	125 W Hg ($\lambda \geq 420$), TEOA,	1805	13
3 wt% Pt/g-C ₃ N ₄ /Ti ₃ C ₂	250 W Hg, ($\lambda \geq 420$), TEOA	72.3	14
CoAl LDH/ g-C ₃ N ₄	300 W Xe, ($\lambda \geq 420$), TEOA	680	15
Co(OH) ₂ /ZnCr LDH	125 W Hg, ($\lambda \geq 420$), CH ₃ OH	27875	16
WO _{3-x} /Ag/ZnCr LDH	150 W Xe ($\lambda \geq 420$), CH ₃ OH	29375	17
LSPCN10 (Present research)	150 W Xe ($\lambda \geq 420$), CH ₃ OH	32975	

References

1. J. Ni, J. Xue, L. F. Xie, J. Shen, G. He and H. Chen, Construction of magnetically separable NiAl LDH/Fe₃O₄-RGO nanocomposites with enhanced photocatalytic performance under visible light, *Phys. Chem. Chem. Phys.*, 2018, **20**, 414-421.
2. J. Liang, Y. Wei, Y. Yao, X. Zheng, J. Shen, G. He and H. Chen, Constructing high-efficiency photocatalyst for degrading ciprofloxacin: Three-dimensional visible light driven graphene based NiAlFe LDH, *J Colloid Interf Sci.*, 2019, **540**, 237-246.
3. Z. Liu, J. Tian, C. Yu, Q. Fan, X. Liu, K. Yang, J. Zeng and H. Ji, Ultrasonic fabrication of SO₄²⁻ doped g-C₃N₄/Ag₃PO₄ composite applied for effective removal of dyestuffs and antibiotics, *Mater. Chem. Phys.*, 2020, **240**, 122206.
4. Y. Deng, L. Tang, C. Feng, G. Zeng, J. Wang, Y. Zhou, Y. Liu, B. Peng and H. Feng, Construction of plasmonic Ag modified phosphorous-doped ultrathin g-C₃N₄ nanosheets/BiVO₄ photocatalyst with enhanced visible-near-infrared response ability for ciprofloxacin degradation, *J. Hazard. Mater.*, 2018, **344**, 758-769.
5. H. Zhang, W. Wu, Y. Li, Y. Wang, C. Zhang, W. Zhang, L. Wang, and L. Niu, Enhanced photocatalytic degradation of ciprofloxacin using novel C-dot@ Nitrogen deficient g-C₃N₄: synergistic effect of nitrogen defects and C-dots. *Appl. Surf. Sci.*, 2019, **465**, 450-458.
6. Z. Yang, J. Yan, J. Lian, H. Xu, X. She and H. Li, g-C₃N₄/TiO₂ Nanocomposites for Degradation of Ciprofloxacin under Visible Light Irradiation, *Chemistry Select*, 2016, **1**, 5679-5685.
7. V. Jayaraman and A. Mani, Ag, Ni bimetallic supported g-C₃N₄ 2D/Cd₂Sb₂O_{6.8} pyrochlore interface photocatalyst for efficient removal of organic pollutants, *J. Mater. Sci-Mater. El.*, 2020, **31**, 11247-11267.
8. G. Zhang, B. Lin, Y. Qiu, L. He, Y. Chen and B. Gao, Highly efficient visible-light-driven photocatalytic hydrogen generation by immobilizing CdSe nanocrystals on ZnCr-layered double hydroxide nanosheets, *Int. J. Hydrogen Energ.*, 2015, **40**, 4758-4765.
9. L. Yao, D. Wei, D. Yan and C. Hu, ZnCr Layered Double Hydroxide (LDH) Nanosheets Assisted Formation of Hierarchical Flower-Like CdZnS@LDH Microstructures with Improved Visible-Light-Driven H₂ Production, *Chem. Asian J.*, 2015, **10**, 630-636.
10. S. Nayak, L. Mohapatra and K. M. Parida, Visible light-driven novel g-C₃N₄/NiFe-LDH composite photocatalyst with enhanced photocatalytic activity towards water oxidation and reduction reaction, *J. Mater. Chem. A*, 2015, **3**, 18622-18635.

11. R. Boppella, C. H. Choi, J. Moon and D. H. Kim, Spatial charge separation on strongly coupled 2D-hybrid of rGO/La₂Ti₂O₇/NiFe-LDH heterostructures for highly efficient noble metal free photocatalytic hydrogen generation, *Appl. Catal., B: Environ.*, 2018, **239**, 178–186.
12. J. M. Lee, J-H. Yang, N. H. Kwon, Y. K. Jo, J-H. Choy and S-J. Hwang, Intercalative Hybridization of Layered Double Hydroxide Nanocrystal with Mesoporous g-C₃N₄ for Enhancing Visible Light-Induced H₂ Production Efficiency, *Dalton Trans.*, 2018, **47**, 2949-2955.
13. L. Liu, X. Xu, Z. Si, Z. Wang and R. Ran, Y. He and D. Weng, Noble metal-free NiS/P-S codoped g-C₃N₄ photocatalysts with strong visible light absorbance and enhanced H₂ evolution activity, *Catal. Commun.*, 2018, **106**, 55-59.
14. T. Su, Z. D. Hood, M. Naguib, L. Bai, S. Luo, C. M. Rouleau, I. N. Ivanov, H. Ji, Z. Qin and Z. Wu, 2D/2D heterojunction of Ti₃C₂/g-C₃N₄ nanosheets for enhanced photocatalytic hydrogen evolution, *Nanoscale*, 2019, **11**, 8138-8149.
15. J. Zhang, Q. Zhu, L. Wang, M. Nasir, S. -H. Cho and J. Zhang, g-C₃N₄/CoAl-LDH 2D/2D hybrid heterojunction for boosting photocatalytic hydrogen evolution, *Int. J. Hydrogen Energ.*, 2020.
16. D. P. Sahoo, S. Nayak, K. H. Reddy, S. Martha and K. Parida, Fabrication of a Co(OH)₂/ZnCr LDH “p–n” heterojunction photocatalyst with enhanced separation of charge carriers for efficient visible-light-driven H₂ and O₂ evolution, *Inorg. chem.*, 2018, **57**, 3840-3854.
17. D. P. Sahoo, S. Patnaik and K. Parida, Construction of a Z-Scheme Dictated WO_{3-x}/Ag/ZnCr LDH Synergistically Visible Light-Induced Photocatalyst towards Tetracycline Degradation and H₂ Evolution. *ACS Omega*, 2019, **4**, 14721-14741.