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Engineering Oxygen vacancy mediated Step-scheme charge carrier dynamic coupling $WO_{3-X}/ZnFe_2O_4$ heterojunction towards robust photo-Fenton driven Levofloxacin detoxification

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Synthesis of $ZnFe_2O_4$ (ZnF)

A combination of hydrothermal and calcination techniques were being employed to fabricate ZnF nanoparticles. At first, calculated amount of zinc nitrate and iron nitrate were dissolved in distilled water under vigorous magnetic stirring to form a homogeneous solution at room temperature. Then after, aqueous solution KOH was added to the homogenised solution in order to maintain the pH=13 of the solution. The resulting solution was transferred into a 100 mL Teflon-lined autoclave and the container was closed and maintained at 190 °C for 8 h. The container was cooled to room temperature after the completion of reaction. The as-obtained product was washed with distilled water and ethanol and finally dried in an oven at 80 °C. Then the solid material was heated at 550 °C for 5 h in a muffle furnace and brown-coloured ZnF nanoparticles were obtained.[1]

Synthesis of WO_{3-x}

Tungsten trioxide was prepared as per literature with small modification. Initially, some amount of $Na_2WO_4 \cdot 2H_2O$ was dispersed in distilled water under vigorous magnetic stirring to obtain a homogeneous solution. Soon after complete dissolution, 4.8 M of HNO_3 was added to the homogenised tungsten solution and the mixture was left stirring for 36 h at room temperature. After the reaction, the tungsten trioxide was collected by filtration and washed continuously to neutral pH and dried for 12 h. The collected solid powder was finally calcined at 500 °C for 5 h to obtain desired material $WO_{3-X.}$ [2]

Synthesis of WO_{3-X}/ZnF (WZF)

WO_{3-X}/ZnF heterojunction was prepared as follows: initially different amounts of as prepared WO_{3-X} were dispersed in 40 mL ethanol which was followed by the addition of 0.5 g of fumaric acid and subjected to stirring for 2 h. To the above suspension, 1 g of ZnF nanoparticles was added and stirred for 12 h at 60 °C. The obtain powders were collected by centrifugation, dried and then heat-treated at 550 °C for 4 h to remove organics. The prepared composites are named according to the weight percentage of WO_{3-X} taken during the time of preparation i.e. 10WZF (10wt% WO_{3-X}), 15WZF (15wt% WO_{3-X}) and 20WZF (20wt% WO_{3-X}).

Sl. No	**Instrument**	**Description**	**Model**
1	X-Ray Diffraction (XRD)	CuKα radiation source (λ=0.154nm), scanning window 2θ =5°-70° and 40 KV and 40 mA	Rigaku-Ultima IV
2	UV–Visible (UV–Vis) diffuse reflectance spectra (DRS)	Deuterium UV lamp and Xe visible light, $BaSO_4$ as standard	JASCO V-750
3	Fourier Transform Infrared spectrometer (FTIR)	KBr pellet as reference	JASCO FTIR-4600
4	Photoluminescence Spectrofluorometer (PL)	Deuterium UV lamp and Xe visible light	JASCO FP-8300 spectrofluorometer
5	Raman spectrometer	332nm laser	RENISHAW InVia Raman spectrometer
6	Electrochemical analyser	Three electrode-based system, Pt counter, Ag/AgCl reference and sample coated FTO as working. 0.1M NaSO4 electrolyte.	IVIUMnSTAT Multichannel electrochemical analyser
7	Transmission electron microscopy (TEM)	Acceleration voltage-200 kV	TEM,JEOL-2100

Photo-Fenton Levofloxacin (LVX) degradation

Levofloxacin was selected as a typical pollutant for photocatalytic application. At first 0.015 g of catalyst along with 20 mL of Levofloxacin (LVX) solution was taken in a conical flask and allowed to stir for 15 min under dark conditions to establish adsorption-desorption equilibrium prior to exposure of sunlight for 30 min. Certain amount of H_2O_2 was added to the reaction medium before irradiation with sunlight. The suspension was centrifuged and the concentration of LVX present in solution was analysed by using JASCO V-750 UV-Vis spectrophotometer in between the wavelength of 200-400 nm.

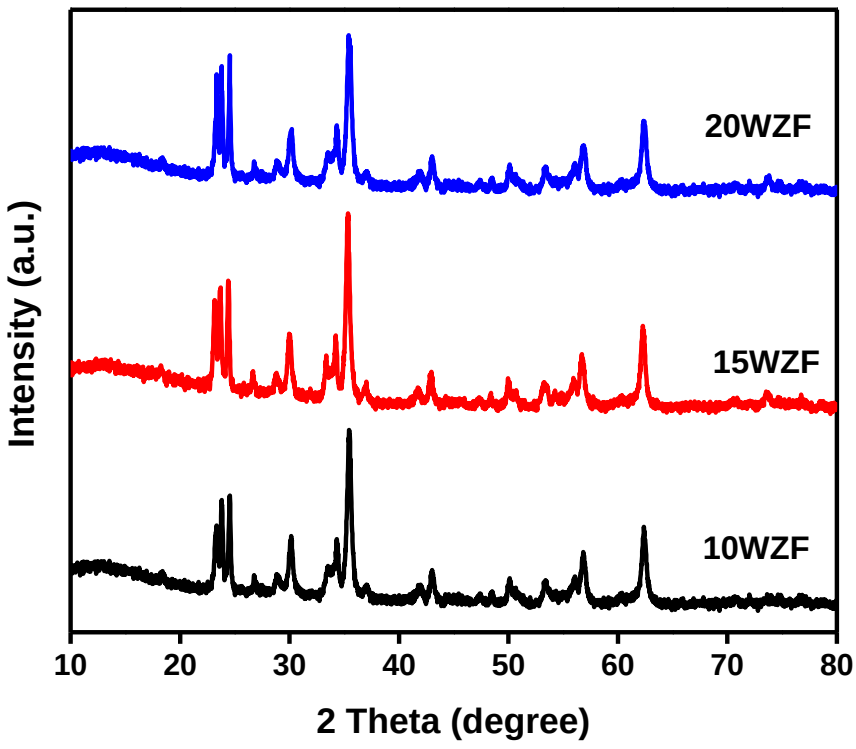

Figure S1. XRD patterns of 10WZF, 15WZF and 20ZWF composite materials

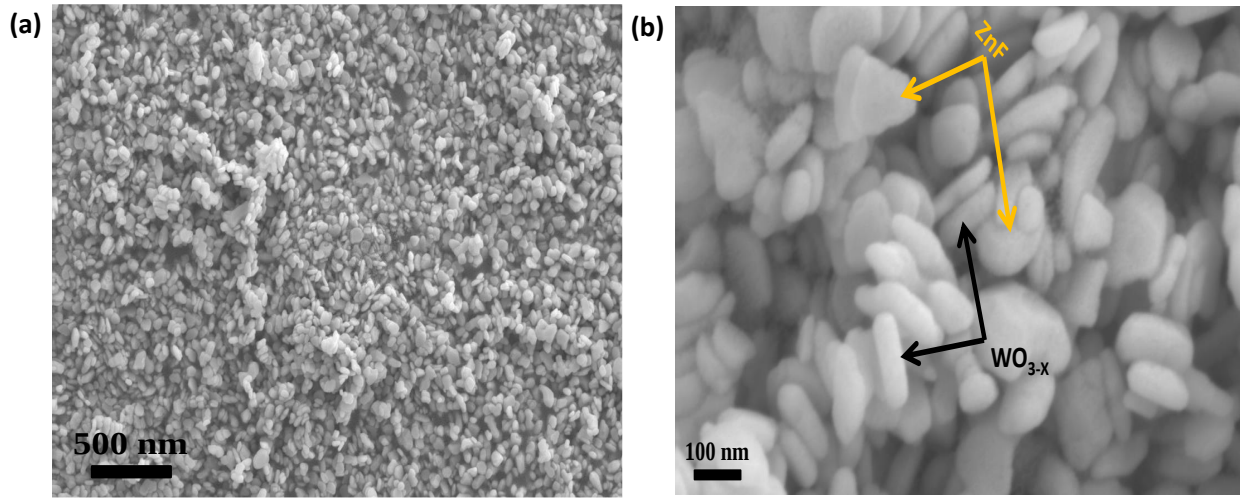

Figure S2. (a) low and (b) enlarged SEM images of 15WZF

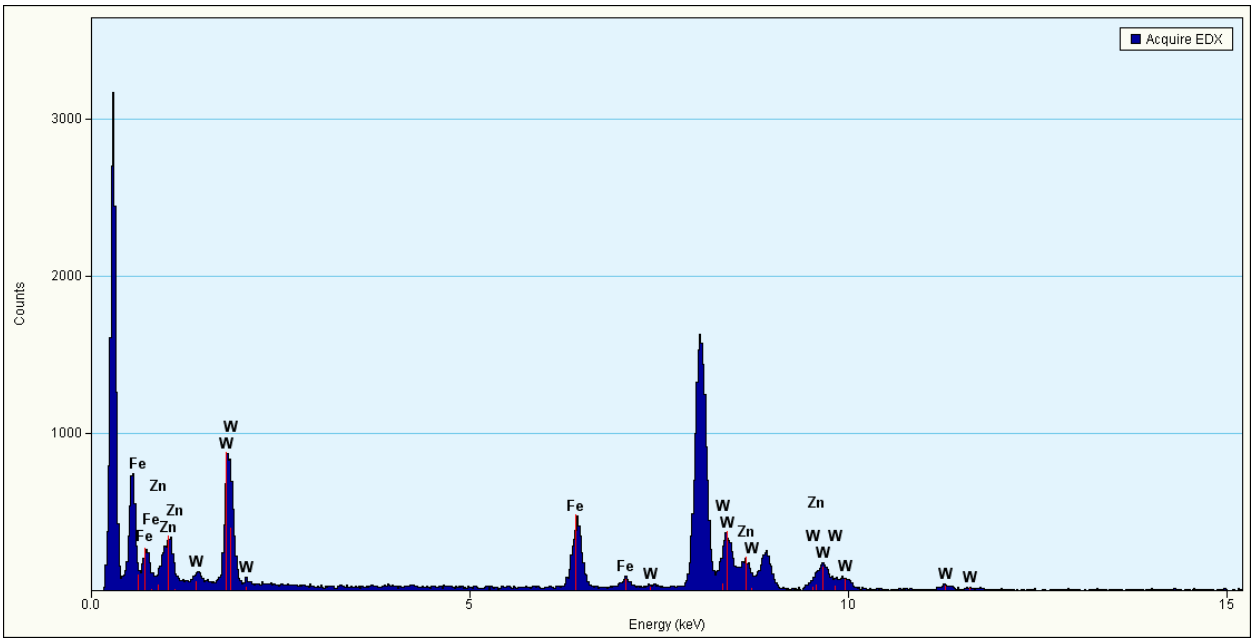

Figure S3 EDAX spectrum of 15WZF

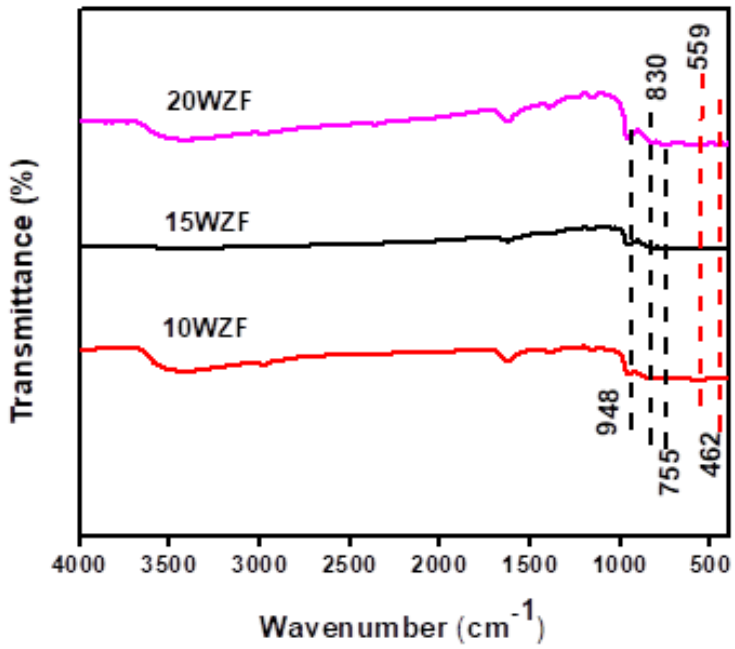

Figure S4. FTIR spectra of 10WZF, 15WZF and 20WZF composites

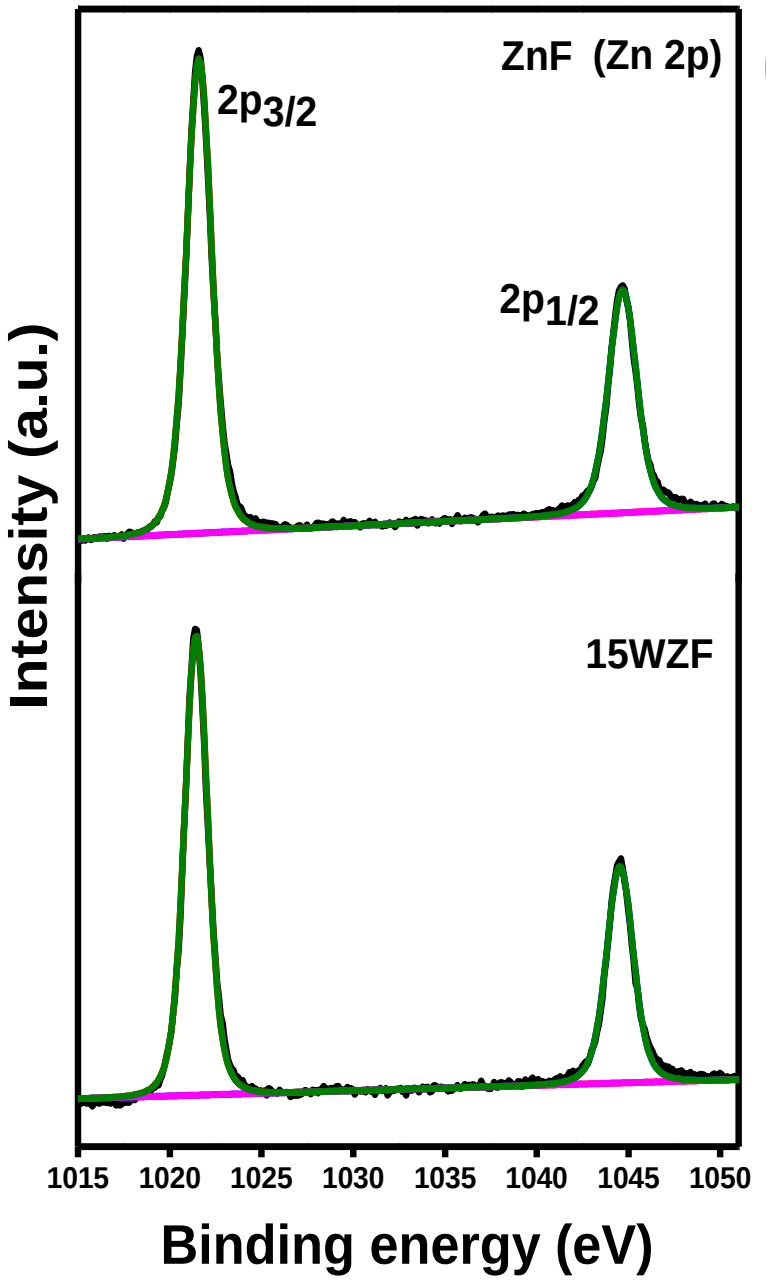

Figure S5. XPS peak of Zn 2p of ZnF and 15WZF

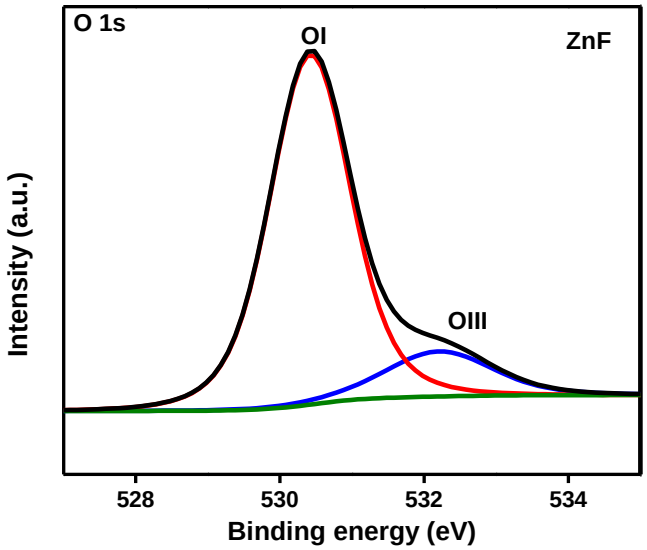

Figure S6. XPS peak of O 1s of ZnF

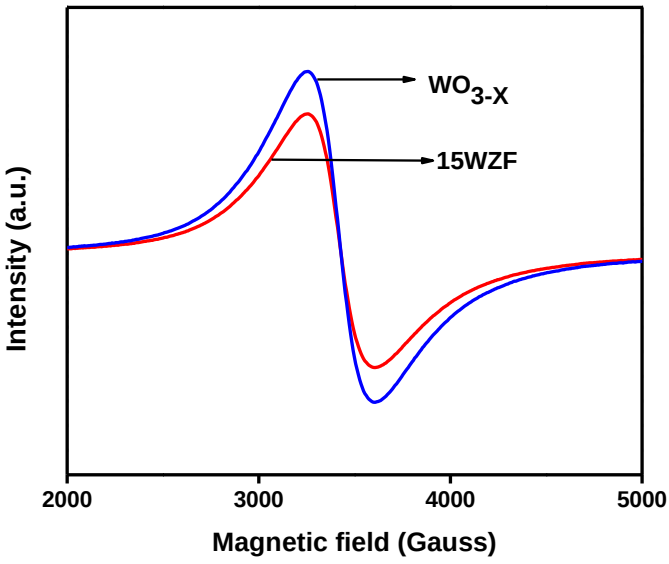

Figure S7 EPR patterns of WO_{3-X}, and 15WZF

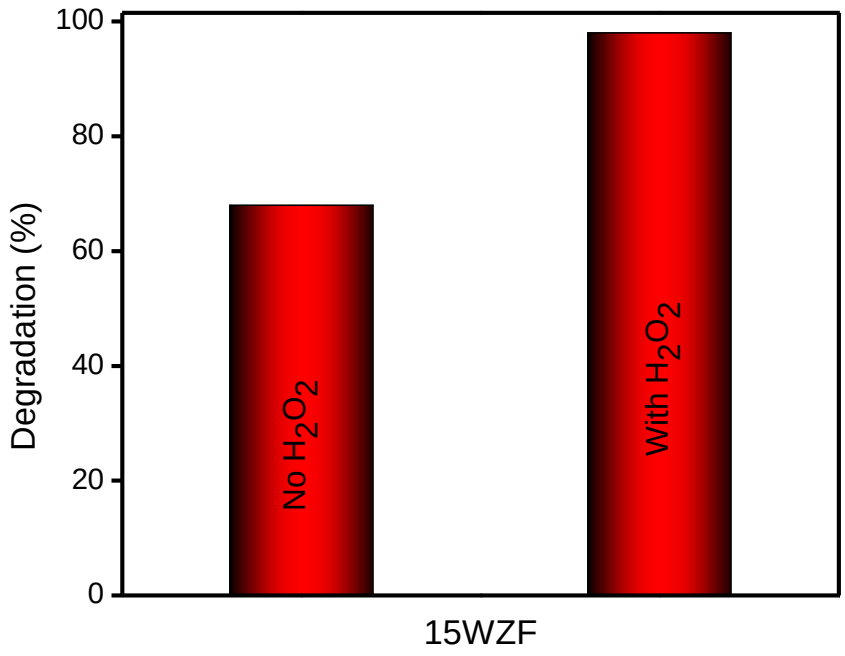

Figure S8. Levofloxacin degradation over 15WZF photocatalyst in absence and presence of H_2O_2

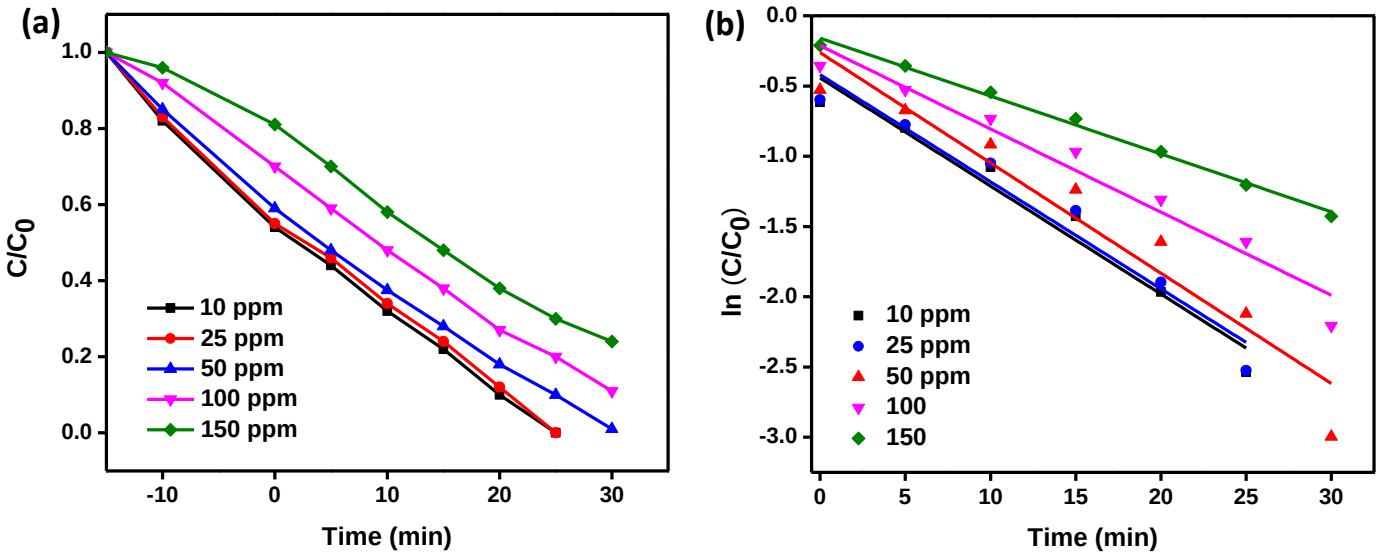

Figure S9. Effect of operation parameters on LVX degradation by 15WZF photocatalyst (a) LVX concentration (b) kinetics

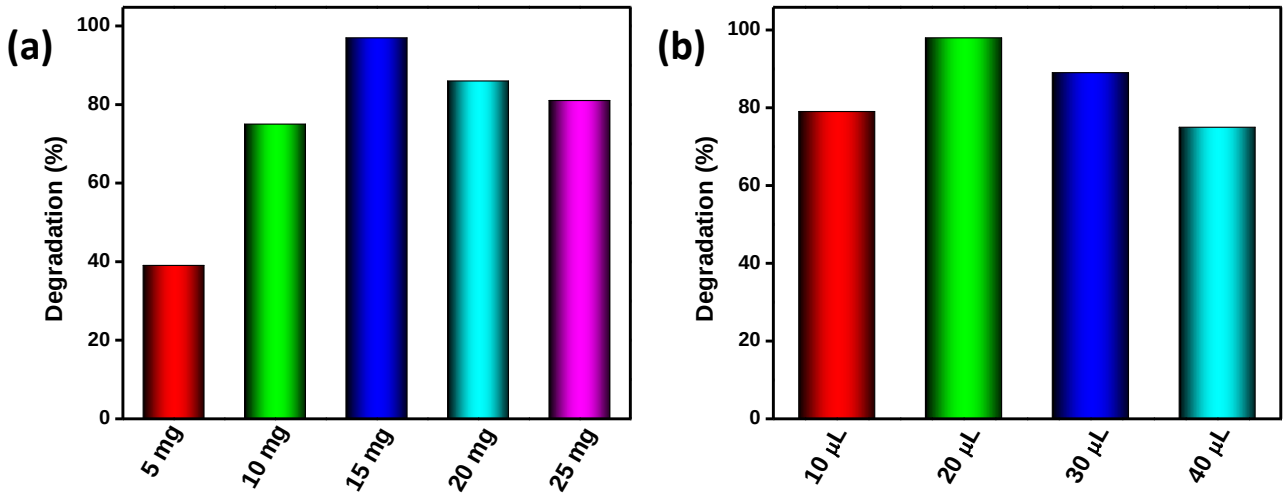

Figure S10. Effect of operation parameters on LVX degradation by 15WZF photocatalyst (a) catalyst dose and (b) H_2O_2 concentration

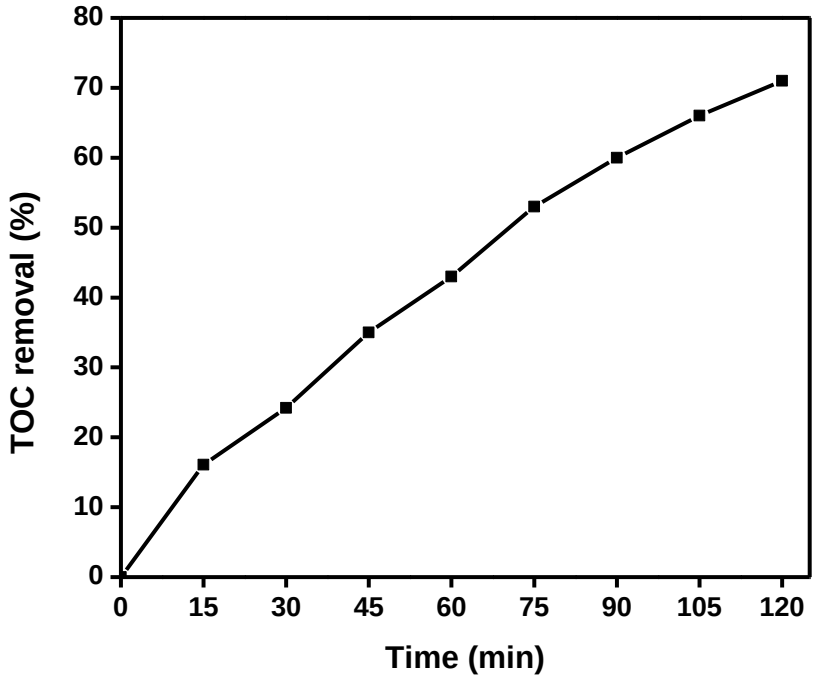

Figure S11. TOC removal percentage of LVX over 15WZF

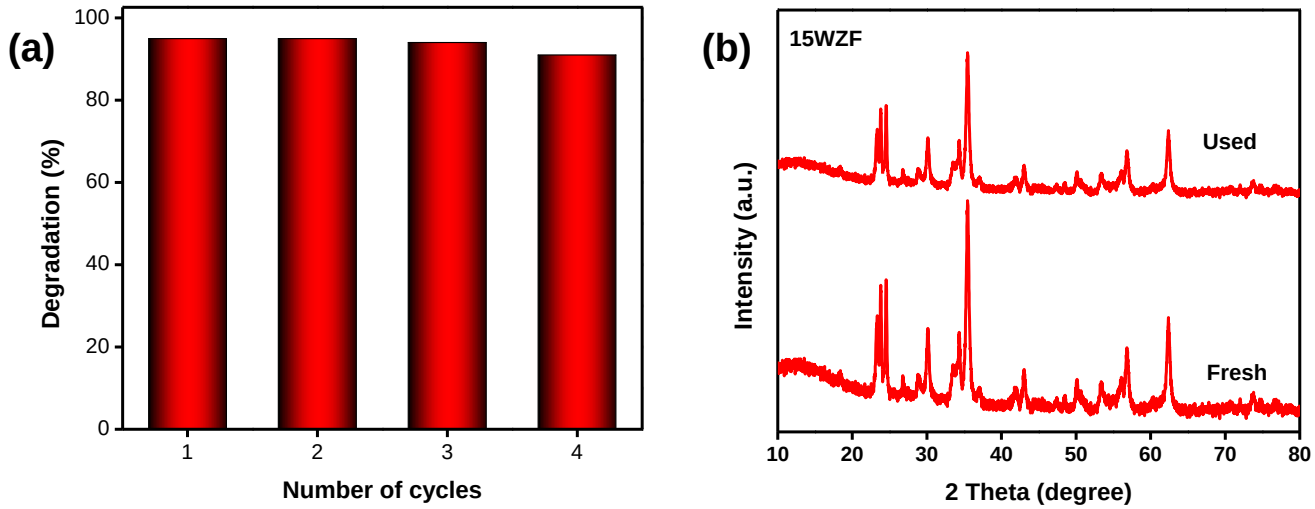

Figure S12. (a) Recyclability test toward LVX degradation over 15WZF and (b) post-XRD characterization of 15WZF

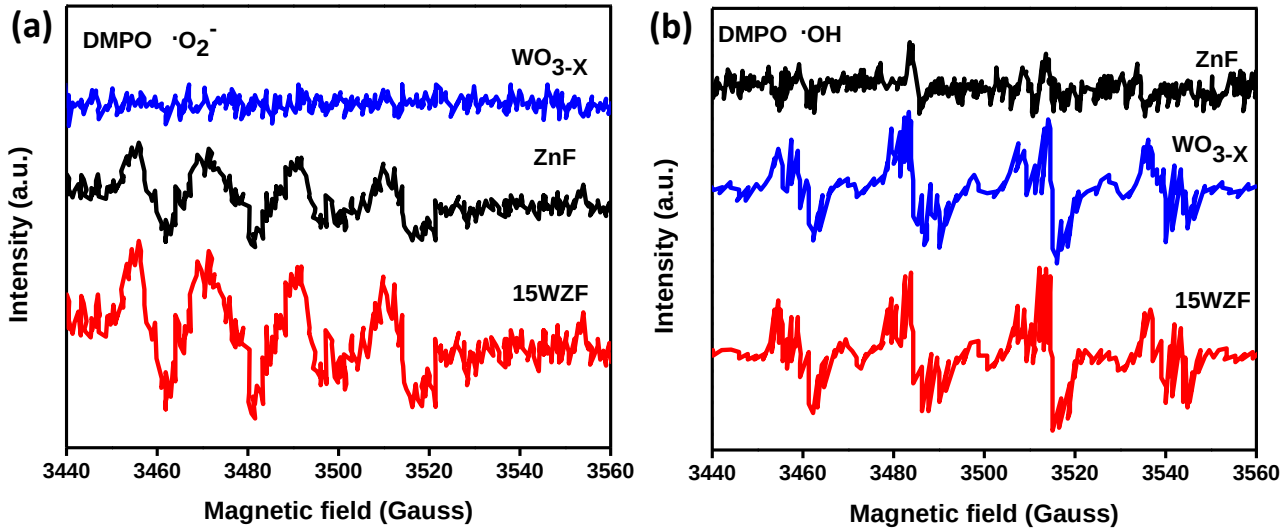

Figure S13. EPR spectra of (a) DMPO- $^{\bullet}O_2^-$ in methanol and (b) DMPO- $^{\bullet}OH$ in aqueous dispersion in presence of WO_{3-X}, ZnF and 15WZF

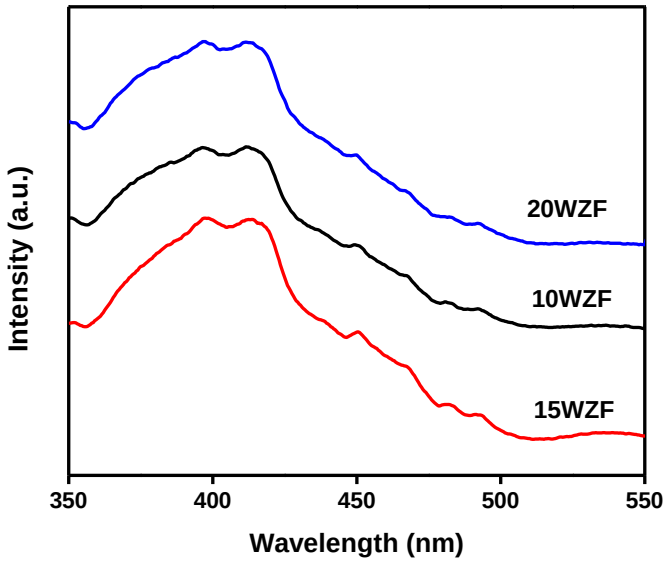

Figure S14. PL spectra of 10WZF, 15WZF and 20WZF specimens

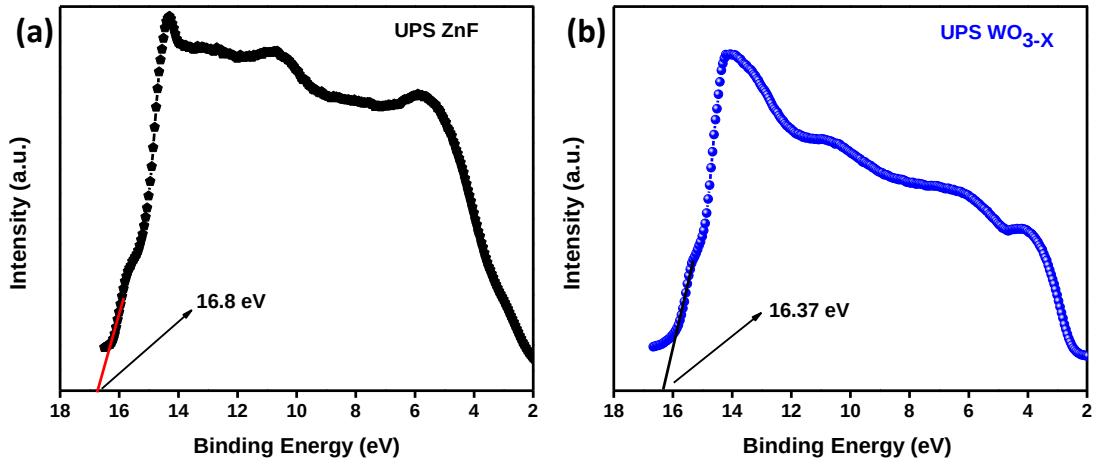

Figure S15. Ultraviolet photoemission spectroscopy (UPS) spectra of ZnF and WO_{3-X}

Table S1: Degradation efficiency, R^2, K_{app} and $t_{1/2}$ values of all synthesized samples towards LVX photo-Fenton degradation

Photocatalyst	**Degradation Efficiency (%)**	**(R^2)**	**(k_{app}) ($10^{-4}min^{-1}$)**	**$t_{1/2}$ (min)**
Blank	3	0.98	29	0.023
WO_{3-X}	42	0.97	141	0.0049
ZnF	61	0.96	256	0.0027
10WZF	92	0.98	618	0.0011
15WZF	99	0.95	898	0.0007
20WZF	87	0.98	487	0.0014

Table S2 A comparative table showing the rate of LVX degradation by various photocatalytic systems as compared to 15WZF photocatalyst

Photocatalyst	**Light source**	**Levofloxacin concentration**	**Catalyst dosage**	**Time**	**Degradation Efficiency (%)**	**Ref**
30 wt% MoS_2 /$Ag_2Mo_2O_7$	150 W Xe lamp	5 ppm	100 mg	90 min	97	3
$ZnFe_2O_4$/NCDs/Ag_2CO_3	300 W Xe lamp ($\lambda > 420$ nm)	10 ppm	30 mg	90 min	88.75	4
Ag_2CO_3/CeO_2/AgBr	300 W Xe lamp	10 ppm	25 mg	40 min	87.3	5
Bi_2WO_6 nanocuboids	Visible light	10 ppm	0.75g	150 min	80	6
$SrTiO_3$/(Ag/Fe_3O_4) /g-C_3N_4	500 W Xe lamp ($\lambda > 420$ nm)	10 ppm	30 mg	90 min	99.3	7
3%Ta_3N_5/TiO_2	250 W Xe lamp	10 ppm	50 mg	120 min	92.79	8
10% Ag/AgCl@ZIF-8	150 W Xe lamp	10 ppm	50 mg	60 min	87.3	9

/g-C_3N_4	(λ > 420 nm)					
MoS_2/C	30 mWXe lamp (λ > 420 nm)	10 ppm	10 mg	180 min	86.9	10
500-MnO@MnO_x	500 W Xe lamp	30 ppm	5 mg	30 min	98.1	11
$(BiOBr)_{0.75}$- $(Bi_7O_9I_3)_{0.25}$-U	400 W halogen bulb	50 ppm	0.2g	120 min	95.4	12
15% $WO_{3-X}/ZnFe_2O_4$	Sunlight	50 ppm	15 mg	30 min	99	This work

References

1. S.B. Rawal, H.J. Kang, D.I. Won and W.I. Lee, *Appl. Catal. B: Environ.*, 2019, **256**, 117856.
2. J. Fu, Q. Xu, J. Low, C. Jiang and J. Yu, *Appl. Catal. B: Environ.*, 2019, **243**, 556-565.
3. S. Adhikari, S. Mandal and Do-H. Kim, Chem. Eng. J., 2019, **337**, 31-43
4. L. Li, C-G. Niu, H. Guo, J. Wang, M. Ruan, L. Zhang, C. Liang, H-Y. Liu and Y-Y. Yang, Chem. Eng. J., 2020, **383**, 123192.
5. X-J. Wen, C-G. Niu, H. Guo, L. Zhang, C. Liang and G-M. Zeng, J. Catal., 2018, **385**, 211-223.
6. A. Kaur and S. K. Kansal, Chem. Eng. J., 2016, **302**, 194-203.
7. A. Kumar, A. Rana, G. Sharma, M. Naushad, A. H. Al-Muhtaseb, C. Guo, A. I. Juez and F. J. Stadler, ACS Appl. Mater. Interfaces, 2018, **10**, 40474-40490.

8. Y. Jiang , X. Jing, K. Zhu, Z. Peng, J. Zhang, Y. Liu, W. Zhang, L. Ni and Z. Liu, Dalton Trans., 2018, **47**, 13113-13125.
9. J. Zhou, W. Liu and W, Cai, Sci. Total Environ., 2019, 696, 133962.
10. L. Zeng, S. Li, X. Li, J. Li, S. Fan, X. Chen, Z. Yin, M. Tadé and S. Liu, Chem. Eng. J., 2019, 378, 122039.
11. A. Wang, Z. Chen, Z. Zheng, H. Xu, H. Wang, K. Hu and K. Yan, Chem. Eng. J.,2020, 379, 122340.
12. S. G.Fard, M.Haghighi and M.Shabani, Appl. Catal. B: Environ., 2019, 248, 320-331.