Supplementary Information (SI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2025

## Photocatalytic norfloxacin degradation enabled by dual S-scheme nanocellulose-based

## Ag2WO4/NiO/MoO3 tertiary heterojunction

Shabnam Sambyal<sup>a</sup>, Vinay Chauhan<sup>a</sup>, Pooja Shandilya<sup>b,d</sup>\*, Aashish Priye<sup>b,c</sup>\*

<sup>a</sup>School of Advanced Chemical Sciences, Shoolini University, Solan, HP 173229, India

<sup>b</sup>Department of Chemical and Environmental Engineering, University of Cincinnati,

Cincinnati, OH 45221, USA

<sup>c</sup>Digital Futures, University of Cincinnati, Cincinnati, OH 45221, USA

<sup>d</sup>Department of Chemistry, MMEC, Maharishi Markandeshwar (Deemed to be University),

Mullana-Ambala, Haryana 133207, India

\*Corresponding Authors: Aashish Priye and Pooja Shandilya

*E-mail: priyeah@ucmail.uc.edu and shandipj@ucmail.uc.edu* 

Photocatalyst	Pollutants	Photodegradation efficiency	Irradiation time	Migration	Recyclability	References	
		(In %)	(In min)				
ZnTiO <sub>3</sub> -nanocellulose	Tetrahydrochloride	98.27	120	-	5	[1]	
Cellulose/x-Fe <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	Congo Red	98.5	35	Type-II	4	[2]	
MrGO/Ag <sub>2</sub> WO <sub>4</sub>	Lomefloxacin	93.62	120	Z-scheme	4	[3]	
	degradation						
Ag <sub>2</sub> WO <sub>4</sub> /ZIF-8	MB degradation	98.3	120	Z-scheme	5	[4]	
Ag <sub>2</sub> WO <sub>4</sub> /BiOBr	Lanasol Red	98	15	Z-scheme	4	[5]	
$g-C_3N_4/Ag_2WO_4/Bi_2S_3$	Congo Red	98	60	S-scheme	5	[6]	
g-C <sub>3</sub> N <sub>4</sub> /BiOI/Ag <sub>2</sub> WO <sub>4</sub>	Sudan Red III	89	90	Z-scheme	5	[7]	
NiO@Bi2MoO6-MoS2	Indigo carmine	98.8	120	-	5	[8]	
NiO/BiOI	Rhodamine B	-	-	S-scheme	5	[9]	
NiO/BiOBr	Oxytetracycline and 2-	72.6 and 97.7	120 and 9	Z-scheme	4	[10]	
	Mercaptobenzothiazole						
Bi <sub>2</sub> WO <sub>6</sub> /NiO	Ciprofloxacin	92.5	90	S-scheme	-	[11]	

**Table S1:** Previous reports on nanocellulose, Ag<sub>2</sub>WO<sub>4</sub>, NiO and MoO<sub>3</sub> based heterojunction for photodegradation application.

3D-Bi2MoO6@MoO3/PU	Oxytetracycline	88.89	20	Z-scheme	9	[12]
$ZnIn_2S_4@MoO_3\\$	Tetracycline	99.2	90	Z-scheme	4	[13]
	hydrochloride					
ZnO/CuO/MoO <sub>3</sub>	Rhodamine B and	97 and 79	120	Type-II	5	[14]
	alizarin yellow					

**Table S2:** Comparative analysis of contemporary literature in recent years regarding the photocatalytic efficiency of NFX.

Photocatalyst	Photocatalyst	Pollutant	pН	Light source	Reactive	Degradation	Time	Cycles	References
	Dosages	concentration			species	efficacy	(In min)		
	(In mg/L)	(In mg/L)				(In %)			
NiO	10	50	10	Xe lamp	$\dot{O}H$ and $h^+$	-	40	-	[15]
MoO <sub>3</sub>	50	20	-	300 W Xe lamp	${}^{\bullet}\!OH$ and $h^+$	100	40	5	[16]
TiO <sub>2</sub>	1000	-	1	Hg lamp	-	-	80	-	[17]
Mn:ZnS Quantum Dots	60	15	10	Hg lamp	$e^-$ , $O_2^-$ and $OH$	86	60	4	[18]
Ce-TiO <sub>2</sub> and B-TiO <sub>2</sub>	500 and 1000	10	7	Under sunlight	h <sup>+</sup> and e <sup>-</sup>	93	180	5	[19]
Ag <sub>3</sub> PO <sub>4</sub> /graphene oxide	-	15	-	250 W Xe lamp	$h^+$ and $O_2^-$	83.68	100	4	[20]

$Bi_2Sn_2O_7/g$ - $C_3N_4$	20	20	-	500 W Xe lamp	$e^-$ and $h^+$	94	3 h	5	[21]
LaOCI/LDH	20	10	7	300 W Xe lamp	·O <sub>2</sub> -	90	150	3	[22]
ZnFe <sub>2</sub> O <sub>4</sub> /BiOBr	-	50	-	300 W Xe lamp	$h^+$ and $O_2^-$	91.70	60	5	[23]
NiWO <sub>4</sub> @g-C <sub>3</sub> N <sub>4</sub>	50	10	-	W lamp	${}^{\circ}\!OH$ and $h^+$	97	60	5	[24]
In <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	30	20	-	500 W Xe lamp	ЮH	100	10	45	[25]
ZnO/ZnS	25	25	7	UV lamp	'O <sub>2</sub> -	95	3 h	5	[26]
NiO/ZnO	30	10 µM	-	W lamp	$O_2^-$ and $h^+$	96.73	80	5	[27]
GDQ-MoS <sub>2</sub> @Co <sub>3</sub> O <sub>4</sub>	20	20	9	150 W Xe lamp	$e^{-}$ and $O_2^{-}$	99.3	90	4	[28]
NC-ANM	15	50	6	LED bulb 50W	<b>OH and O2</b>	99.6	30	7	Present
									work



**Scheme 1.** Schematic diagram for the formation of (a) nanocellulose, (b) Ag<sub>2</sub>WO<sub>4</sub>, (c) NiO, (d) MoO<sub>3</sub>, and (e) NC-ANM heterojunction.



**Figure S1**. HRTEM result of (a) nanocellulose, (b) Ag<sub>2</sub>WO<sub>4</sub>, (c) NiO,(d) MoO<sub>3</sub>, (e) NC-ANM heterojunction, and (f) SAED pattern of NC-ANM. Nanocellulose, Ag<sub>2</sub>WO<sub>4</sub>, NiO, and MoO<sub>3</sub> are granular, irregular-size rods, block sheets, and rod-like morphology with size 10-50 nm and NC-ANM, indicating its polycrystalline nature.



**Figure S2.** BET analysis of (a) nanocellulose, (b) Ag<sub>2</sub>WO<sub>4</sub>, (c) NiO, (d) MoO<sub>3</sub>, (e) NC-ANM heterojunction, and (f) pore size distribution of NC-ANM. N<sub>2</sub> adsorption-desorption isotherm and pore size distribution of the NC-ANM composite, revealing its mesoporous structure with a high surface area and a narrow pore size distribution, beneficial for photocatalytic applications.



**Figure S3.** FTIR spectra of (a) nanocellulose, Ag<sub>2</sub>WO<sub>4</sub>, NiO, MoO<sub>3</sub>, and (b) NC-ANM heterojunction.



Figure S4. XPS survey of (a) nanocellulose, (b) Ag<sub>2</sub>WO<sub>4</sub>, (c) NiO, and (d) MoO<sub>3</sub>.



**Figure S5.** Mott-Schottky plots for bare (a) n-type Ag<sub>2</sub>WO<sub>4</sub>, (b) p-type NiO, (c) n-type MoO<sub>3</sub>, and (d) Band structure of ANM heterojunction.



**Figures S6.** (a) Degradation percentage for binary heterojunction in possible combination and NC-ANM heterojunction, and (b) The kinetic analysis indicates that the reaction follows a pseudo-first-order model where NC-ANM heterojunction exhibits the highest rate constant.



**Figure S7.** (a) Zero-point charge of NC-ANM heterojunction, (b) Trapping experiment for photodegradation of NFX using bare Ag<sub>2</sub>WO<sub>4</sub>, (c) NiO, and (d) MoO<sub>3</sub>.



**Figure S8.** Liquid chromatography-mass spectrometry (LC-MS) chromatograms of NFX degradation at (a) time = 0 mins, and (b) time = 15 mins.

## References

- Gogoi, J. and D. Chowdhury, *Photodegradation of emerging contaminant tetracycline* using a zinc titanate nanocellulose composite as an efficient photocatalyst. Materials Advances, 2023. 4(9): p. 2088-2098.
- Helmiyati, H., et al., Green hybrid photocatalyst containing cellulose and γ–Fe2O3– ZrO2 heterojunction for improved visible-light driven degradation of Congo red. Optical Materials, 2022. 124: p. 111982.
- 3. Sun, Y., et al., *Efficient removal of lomefloxacin by Z-scheme MrGO/Ag2WO4 heterojunction recyclable composite under visible light: Mechanism of adsorption and photodegradation.* Journal of Environmental Chemical Engineering, 2022. **10**(1): p. 107120.
- Mohammed, R.O., et al., *Enhanced photocatalytic degradation activity of ZIF-8 doped with Ag2WO4 photocatalyst*. Journal of the Taiwan Institute of Chemical Engineers, 2023. 151: p. 105141.
- Fu, S., et al., Facile fabrication of Z-scheme Ag2WO4/BiOBr heterostructure with oxygen vacancies for improved visible-light photocatalytic performance. Journal of Science: Advanced Materials and Devices, 2023. 8(2): p. 100561.
- Jabbar, Z.H., et al., Photocatalytic destruction of Congo red dye in wastewater using a novel Ag2WO4/Bi2S3 nanocomposite decorated g-C3N4 nanosheet as ternary Sscheme heterojunction: Improving the charge transfer efficiency. Diamond and Related Materials, 2023. 133: p. 109711.
- Liao, Y., et al., A novel g-C3N4/BiOI/Ag2WO4 heterojunction for efficient degradation of organic pollutants under visible light irradiation. Ceramics International, 2021.
   47(18): p. 26248-26259.
- Nandisha, P. and S. Yallappa, Synthesis and characterization of ternary NiO@ Bi2MoO6–MoS heterojunction with enhanced photodegradation efficiency towards indigo carmine dye. Solid State Sciences, 2023. 139: p. 107157.
- 9. Hu, X., et al., *Step-scheme NiO/BiOI heterojunction photocatalyst for rhodamine photodegradation*. Applied Surface Science, 2020. **511**: p. 145499.
- Dong, J., et al., Construction of Z-scheme NiO/BiOBr heterojunction for facilitating photocatalytic degradation of oxytetracycline and 2-mercaptobenzothiazole. Journal of Alloys and Compounds, 2024. 976: p. 172920.

- Li, Z., et al., *Bi-functional S-scheme S-Bi2WO6/NiO heterojunction for photocatalytic ciprofloxacin degradation and CO2 reduction: Mechanisms and pathways.* Separation and Purification Technology, 2023. 310: p. 123197.
- Liu, Y., et al., Stable photodegradation of antibiotics by the functionalized 3D-Bi2MoO6@ MoO3/PU composite sponge: High efficiency pathways, optical properties and Z-scheme heterojunction mechanism. Chemosphere, 2023. 332: p. 138911.
- Ouyang, C., et al., Direct Z-scheme ZnIn2S4@ MoO3 heterojunction for efficient photodegradation of tetracycline hydrochloride under visible light irradiation. Chemical Engineering Journal, 2021. 424: p. 130510.
- Hussain, M.K., et al., Enhanced visible light-driven photocatalytic activity and stability of novel ternary ZnO/CuO/MoO3 nanorods for the degradation of rhodamine B and alizarin yellow. Materials Science in Semiconductor Processing, 2023. 155: p. 107261.
- PARIMALA, L. and J. SANTHANALAKSHMI, Synthesis, Characterisation and Catalytic Behaviour of NiO Nanoflowers for the Photo Degradation of Norflaxacin in Aqueous Medium. Chemical Science, 2019. 8(1): p. 70-76.
- Huang, Y., et al., Molybdenum oxide nanorods decorated with molybdenum phosphide quantum dots for efficient photocatalytic degradation of rhodamine B and norfloxacin. Research on Chemical Intermediates, 2022. 48(7): p. 2887-2901.
- 17. Haque, M. and M. Muneer, *Photodegradation of norfloxacin in aqueous suspensions of titanium dioxide*. Journal of Hazardous materials, 2007. **145**(1-2): p. 51-57.
- Patel, J., A.K. Singh, and S.A. Carabineiro, Assessing the photocatalytic degradation of fluoroquinolone norfloxacin by Mn: ZnS quantum dots: Kinetic study, degradation pathway and influencing factors. Nanomaterials, 2020. 10(5): p. 964.
- Manasa, M., P.R. Chandewar, and H. Mahalingam, *Photocatalytic degradation of ciprofloxacin & norfloxacin and disinfection studies under solar light using boron & cerium doped TiO2 catalysts synthesized by green EDTA-citrate method.* Catalysis today, 2021. 375: p. 522-536.
- Ji, B., et al., *Immobilized Ag 3 PO 4/GO on 3D nickel foam and its photocatalytic degradation of norfloxacin antibiotic under visible light*. RSC advances, 2020. 10(8): p. 4427-4435.

- 21. Zhu, Z., et al., *Facile Construction of Bi2Sn2O7/g-C3N4 Heterojunction with Enhanced Photocatalytic Degradation of Norfloxacin*. Inorganics, 2022. 10(9): p. 131.
- Zhang, W., et al., Boosted photocatalytic degradation of norfloxacin on LaOCl/LDH: Synergistic effect of Z-scheme heterojunction and O vacancies. Journal of Environmental Chemical Engineering, 2022. 10(3): p. 107812.
- 23. Meng, X., et al., *Preparation and visible light catalytic degradation of magnetically recyclable ZnFe2O4/BiOBr flower-like microspheres*. Journal of Alloys and Compounds, 2023. **954**: p. 169981.
- 24. Muthuraj, V., Superior visible light driven photocatalytic degradation of fluoroquinolone drug norfloxacin over novel NiWO4 nanorods anchored on g-C3N4 nanosheets. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2019. 567: p. 43-54.
- 25. Yu, H., et al., Enhanced photocatalytic degradation of norfloxacin under visible light by immobilized and modified In2O3/TiO2 photocatalyst facilely synthesized by a novel polymeric precursor method. Journal of Materials Science, 2019. 54(14): p. 10191-10203.
- Liu, W., et al., Synergistic adsorption-photocatalytic degradation effect and norfloxacin mechanism of ZnO/ZnS@ BC under UV-light irradiation. Scientific Reports, 2020. 10(1): p. 11903.
- Arunpandian, M., et al., Visible-Light Induced Degradation of Norfloxacin and Methylene Blue Using Easily Recoverable NiO/ZnO Heterostructures: Analysis of Efficacy, Stability, Reaction Mechanism and Degradation Pathway. Journal of Inorganic and Organometallic Polymers and Materials, 2023: p. 1-14.
- Adhikari, S., S. Mandal, and D.-H. Kim, pn Junction catalysis in action: Boosting norfloxacin photodegradation with ZIF-67-based Co3O4 wrapped in MoS2 with surface functionalized graphene quantum-dot. Applied Surface Science, 2024. 653: p. 159374.