Electronic Supplementary Material

Nanostructured MnO_x/g-C_3N_4 for photodegradation of Sulfamethoxazole under visible light irradiation

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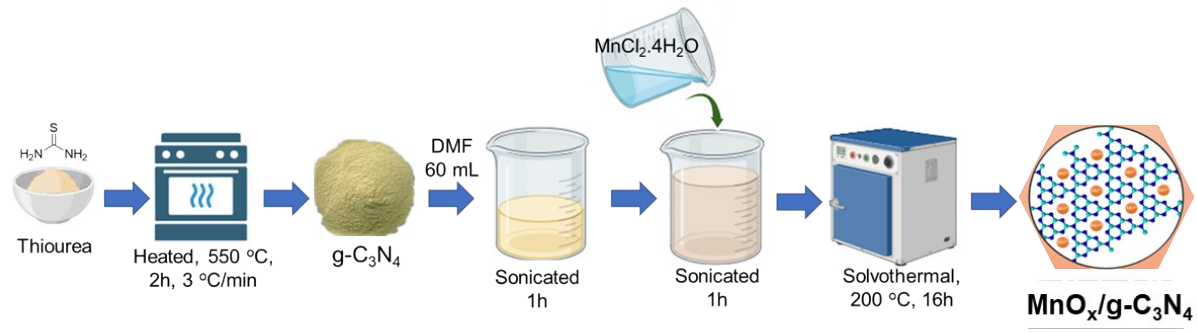

Figure S1. Schematic diagram of the synthesis of Mn modified on the CN.

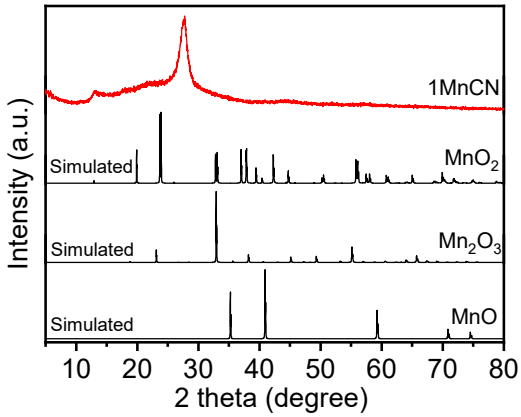

Figure S2. XRD pattern of the 1MnCN sample and simulated samples (from the Crystallography Open Database) of MnO, MnO_2, and Mn_2O_3.

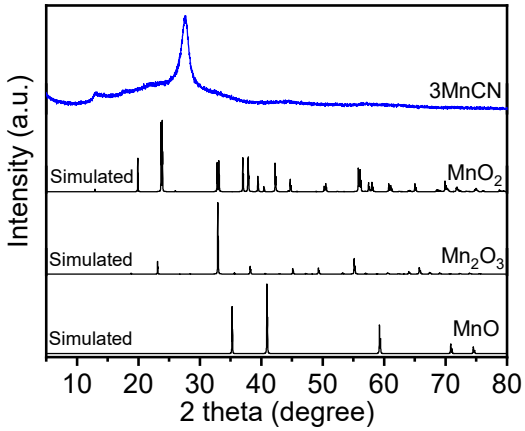

Figure S3. XRD pattern of the 3MnCN sample and simulated samples (from the Crystallography Open Database) of MnO, MnO_2, and Mn_2O_3.

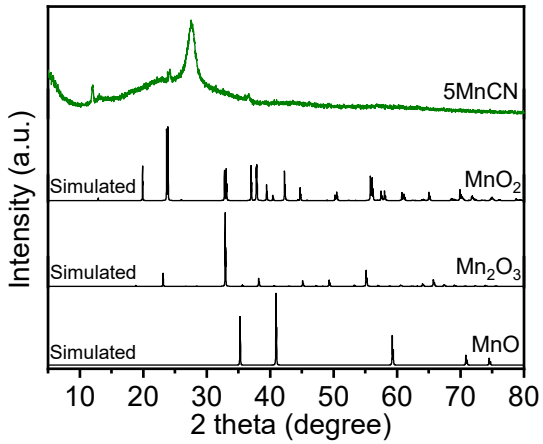

Figure S4. XRD pattern of the 5MnCN sample and simulated samples (from the Crystallography Open Database) of MnO, MnO_2, and Mn_2O_3.

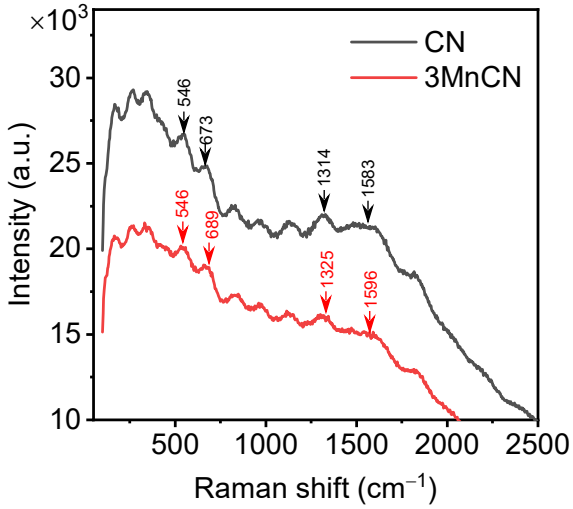

Figure S5. Raman spectroscopy of CN and 3MnCN samples.

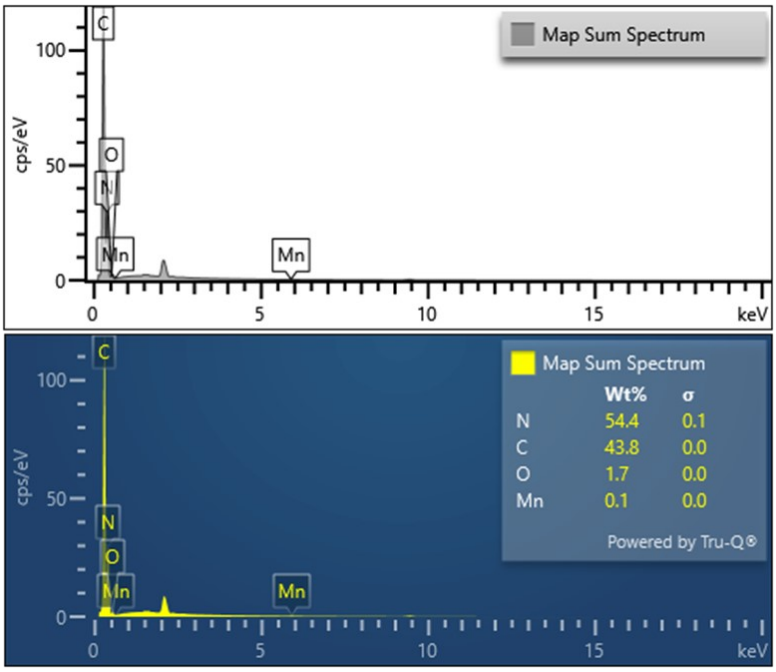

Figure S6. EDX analysis of the synthesized 3MnCN.

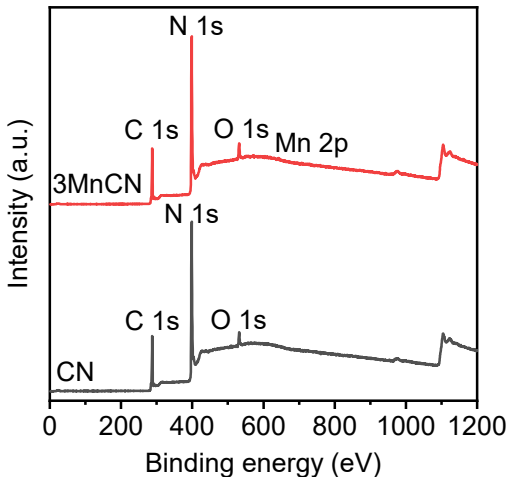

Figure S7. Survey XPS of CN and 3MnCN.

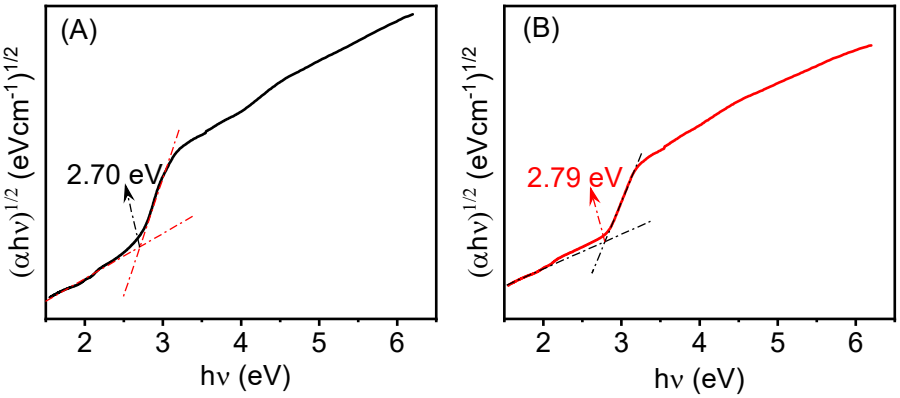

Figure S8. Bandgap energy of CN (A) and 3MnCN (B)

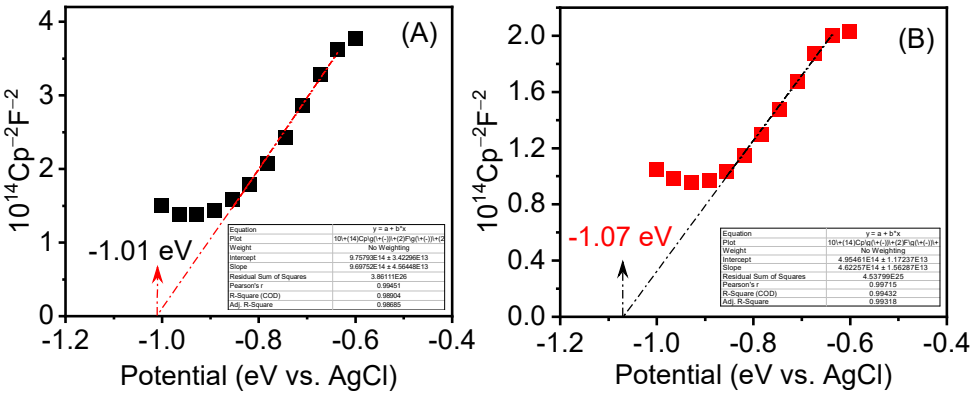

Figure S9. Mott-Schottky plots of the CN (A) and 3MnCN (B) samples.

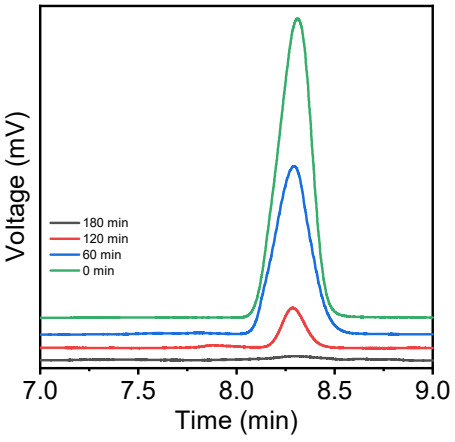

Figure S10. HPLC results of SMX photodegradation catalyzed by the 3MnCN after 180 minutes of irradiation.

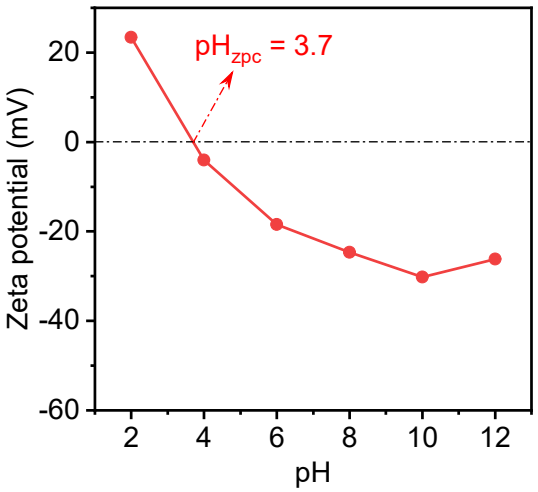

Figure S11. Zeta potential at different pH of the as-synthesized 3MnCN.

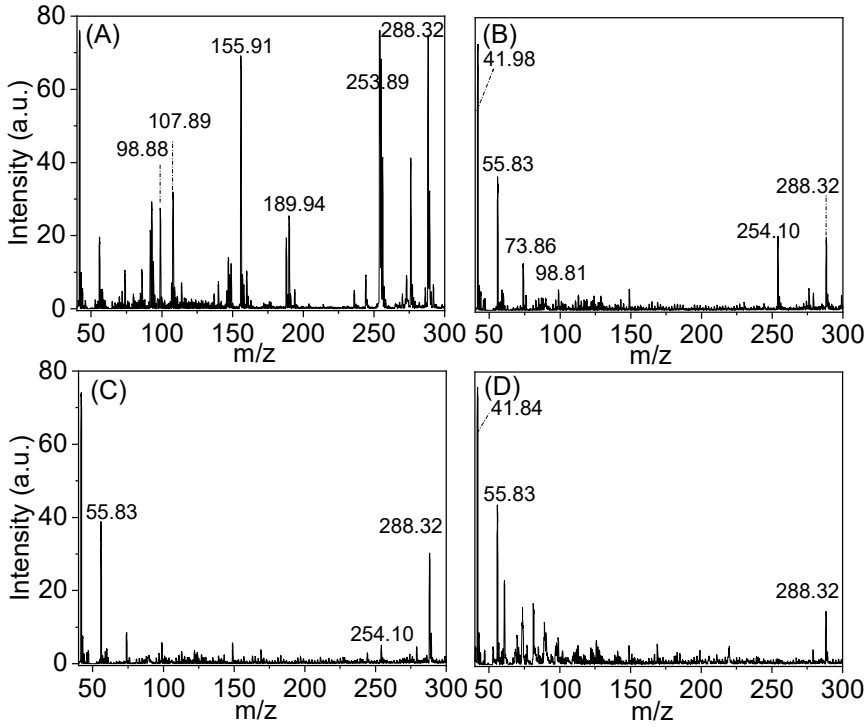

Figure S12. LC-MS spectra of the (A) initial SMX solution and (B) – (D) degradation intermediate products by the 3MnCN photocatalyst at different photodegradation time points.

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Số/*Code*: IER-N2409.0446/1

BẢNG KẾT QUẢ PHÂN TÍCH
ANALYSIS RESULTS

Tên khách hàng : **NGUYỄN THỊ KIM OANH**
Customer's name ***NGUYEN THI KIM OANH***
Tên mẫu : 3MnCN – Before
Name of sample *3MnCN – Before*
Mô tả mẫu : Mẫu được chứa trong ống nhựa
Described sample *Sample is contained in centrifuge tube*
Đơn vị lấy mẫu : Khách hàng gửi mẫu
Sampling Agency *Sampled by Customer*

Ngày lấy mẫu : 19.09.2024
Sampling date:
Ngày gửi mẫu : 19.09.2024
Date of receipting:

TT **No.**	THÔNG SỐ PHÂN TÍCH ***PARAMETERS***	ĐƠN VỊ ***UNITS***	KẾT QUẢ ***RESULTS***	GIỚI HẠN PHÁT HIỆN ***LOD***	TIÊU CHUẨN SO SÁNH ***STANDARD VALUES*** [a]	PHƯƠNG PHÁP THỬ ***ANALYSE METHODS***
1.	Mangan (Mn) *Manganese (as Mn)*	g/kg	1,131	-	-	SMEWW 3111B:2017

Ghi chú/ *Notes*:

1. Giấy chứng nhận đủ điều kiện hoạt động dịch vụ quan trắc môi trường số hiệu: VIMCERTS 138 (GCN số 04/GCN-BTNMT)/*The Certificate of eligible for service activities in environmental monitoring, code: VIMCERTS 138.*
2. Các kết quả phân tích chỉ có giá trị trên mẫu thử /*The results are valid only on the tested sample.*
3. Thông tin tên khách hàng và tên mẫu thử được ghi trên phiếu kết quả này theo yêu cầu của khách hàng/ *Customer's name and sample information are provided by customer.*
4. KPH: Không phát hiện/ *KPH: Non-detectable,* LOD: Giới hạn phát hiện/*LOD: Limit of detection.*
5. Dấu (-): Không chứa giá trị, thông tin/*Items with remark (-): Not available or No information.*
6. [a] Khách hàng không yêu cầu quy chuẩn so sánh/ *Customers do not require standards.*

Ho Chi Minh City, 27/09/2024

Đại diện nhóm phân tích *Representative of Test Group*	Phụ trách PTN. CLMT *The lab's administrator*	Viện Trưởng *Director*
Nguyễn Văn Sang	ThS. Nguyễn Thành Trung	GS.TS Lê Thanh Hải

ĐẠI HỌC QUỐC GIA TP. HỒ CHÍ MINH
VIỆN MÔI TRƯỜNG VÀ TÀI NGUYÊN

Figure S13. Result of ICP-MS analysis of 3MnCN before.

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BẢNG KẾT QUẢ PHÂN TÍCH
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Sampling Agency *Sampled by Customer*

Ngày lấy mẫu : 19.09.2024
Sampling date:
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Date of receipting:

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1.	Mangan (Mn) *Manganese (as Mn)*	g/kg	1,128	-	-	SMEWW 3111B:2017

Ghi chú/ *Note*:

1. Giấy chứng nhận đủ điều kiện hoạt động dịch vụ quan trắc môi trường số hiệu: VIMCERTS 138 (GCN số 04/GCN-BTNMT)/*The Certificate of eligible for service activities in environmental monitoring, code: VIMCERTS 138.*
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Ho Chi Minh City, 27/09/2024

Đại diện nhóm phân tích *Representative of Test Group*	Phụ trách PTN. CLMT *The lab's administrator*	Viện Trưởng *Director*
Nguyễn Văn Sang	ThS. Nguyễn Thành Trung	GS.TS Lê Thanh Hải

VIỆN MÔI TRƯỜNG VÀ TÀI NGUYÊN

Figure S14. Result of ICP-MS analysis of 3MnCN after.

Table S1. SEM-EDS mapping and surface elemental composition (XPS) of 3MnCN; BET surface areas, pore volume, and average pore of CN and 3MnCN; Band gap energy (Eg) and reaction rate constant (k) of CN, 1MnCN, 3MnCN, and 5MnCN.

Samples	% wt. Mn		S_{BET} (m^2/g)	Pore volume (x 10^{-3} cm^3/g)	Average pore width (nm)	Eg (eV)	CB/VB	k (10^{-3} min^{-1})	R^2
	EDS	XPS							
CN	-	-	44	79	7.1	2.42	-0.29/2.13	0.5	0.9361
1MnCN	-	-	-	-	-	2.45	-	2.6	0.9979
3MnCN	0.1	0.1	8	17	8.3	2.39	-0.06/2.33	3.5	0.9961
5MnCN	-	-	-	-	-	2.49	-	2.1	0.9984

Table S2. Surface elemental compositions of the catalysts.

Catalyst (Sample)	**Mn^{2+} (%)**	**Mn^{3+} (%)**	**Mn^{4+} (%)**
3MnCN	26.4	35.8	37.8

Table S3. Raw data for control experiments assessing the degradation of the SMX antibiotic using other MnO_x modified g-C_3N_4 samples. Experimental conditions: $[SMX]_0$ = 15 mg L^{-1}, $[catalyst]_0$ = 20 mg, pH = 5, V = 100 mL, light source: 40 W white LED lamp. C and C_0 (mol L^{-1}) represent the concentrations of SMX at the current time (t min) and the initial time (0 min), respectively. The standard deviation (σ) was calculated based on data from three samples

Sample	Time (min)	$C/C_0 \pm \sigma$	$-\ln(C/C_0)$
CN	-60	1 ± 0	--
	0	1.04123 ± 0.01324	0
	60	1.07134 ± 0.0121	-0.02853
	120	1.03451 ± 0.00745	0.00642
	180	1.06063 ± 0.02022	-0.01836
	240	1.04053 ± 0.02317	8.39682E-4
1MnCN	-60	1 ± 0	--
	0	1.04395 ± 0.0764	0
	60	0.8274 ± 0.03946	0.24359
	120	0.59861 ± 0.02933	0.56733
	180	0.37225 ± 0.02065	1.04268
	240	0.24986 ± 0.01619	1.4419
3MnCN	-60	1 ± 0	--
	0	1.03292 ± 0.03091	0
	60	0.47588 ± 0.04655	0.77938
	120	0.23014 ± 0.02011	1.50486
	180	0.17858 ± 0.01916	1.76016
	240	0.15418 ± 0.00759	1.9028
5MnCN	-60	1 ± 0	--
	0	1.13153 ± 0.03498	0
	60	0.97626 ± 0.03137	0.14762
	120	0.81096 ± 0.02225	0.33301
	180	0.63663 ± 0.04697	0.57747
	240	0.48044 ± 0.05854	0.86393

Table S4. Raw data for control experiments assessing the degradation of the SMX antibiotic at other pH conditions using 3MnCN catalyst. Experimental conditions: $[SMX]_0$ = 15 mg L^{-1}, $[catalyst]_0$ = 20 mg, V = 100 mL, light source: 40 W white LED lamp. C and C_0 (mol L^{-1}) represent the concentrations of SMX at the current time (t min) and the initial time (0 min), respectively. The standard deviation (σ) was calculated based on data from three samples.

Sample	Time (min)	$C/C_0 \pm \sigma$	$-\ln(C/C_0)$
pH = 9	-60	1 ± 0	--
	0	0.988051 ± 0.06767	0
	60	0.858807 ± 0.055803	0.139946
	120	0.798238 ± 0.067208	0.214467
	180	0.739968 ± 0.049053	0.288979
	240	0.701295 ± 0.049817	0.343025
pH = 7	-60	1 ± 0	--
	0	1.007844 ± 0.05461	0
	60	0.907956 ± 0.043681	0.104092
	120	0.820211 ± 0.018275	0.20479
	180	0.72055 ± 0.020963	0.334513
	240	0.632697 ± 0.066846	0.469528
PH = 5	-60	1 ± 0	--
	0	1.032923 ± 0.030906	0
	60	0.475878 ± 0.04655	0.779377
	120	0.230144 ± 0.020108	1.504856
	180	0.178582 ± 0.019163	1.760155
	240	0.154178 ± 0.007591	1.902802
pH = 3	-60	1 ± 0	--
	0	1.086844 ± 0.077185	0
	60	0.725153 ± 0.029288	0.402997
	120	0.411477 ± 0.043006	0.974404
	180	0.308843 ± 0.034709	1.261838
	240	0.270841 ± 0.015516	1.388666

Table S5. Raw data for control experiments assessing the degradation of the SMX antibiotic with other photocatalytic doses using 3MnCN sample. Experimental conditions: $[SMX]_0$ = 15 mg L^{-1}, V = 100 mL, light source: 40 W white LED lamp. C and C_0 (mol L^{-1}) represent the concentrations of SMX at the current time (t min) and the initial time (0 min), respectively. The standard deviation (σ) was calculated based on data from three samples

Sample	Time (min)	$C/C_0 \pm \sigma$	$-\ln(C/C_0)$
No catalyst	-60	1 ± 0	--
	0	0.979092 ± 0.026516	0
	60	1.0002 ± 0.006777	-0.02168
	120	0.985879 ± 0.000769	-0.00728
	180	0.98424 ± 0.015453	-0.00549
	240	0.985099 ± 0.017033	-0.00634
10 mg	-60	1 ± 0	--
	0	1.06178 ± 0.03047	0
	60	0.88256 ± 0.02483	0.18486
	120	0.72431 ± 0.03797	0.38345
	180	0.58521 ± 0.05225	0.59925
	240	0.45554 ±0.05394	0.85272
20 mg	-60	1 ± 0	--
	0	1.03292 ± 0.03091	0
	60	0.47588 ± 0.04655	0.77938
	120	0.23014 ± 0.02011	1.50486
	180	0.17858 ± 0.01916	1.76016
	240	0.15418 ± 0.00759	1.9028
30 mg	-60	1 ± 0	--
	0	1.01288 ± 0.02224	0
	60	0.80374 ± 0.02187	0.2314
	120	0.54174 ± 0.03266	0.6274
	180	0.37104 ± 0.0676	1.02067
	240	0.28552 ± 0.04315	1.27679

Table S6. Raw data for scavenger trapping experiments assessing the degradation of the SMX antibiotic using 3MnCN sample. Experimental conditions: $[SMX]_0$ = 15 mg L^{-1}, $[catalyst]_0$ = 20 mg, pH = 5, V = 100 mL, light source: 40 W white LED lamp. C and C_0 (mol L^{-1}) represent the concentrations of SMX at the current time (t min) and the initial time (0 min), respectively. The standard deviation (σ) was calculated based on data from three samples

Scavenger	Time (min)	$C/C_0 \pm \sigma$	Scavenger	Time (min)	$C/C_0 \pm \sigma$
$K_2Cr_2O_7$	-60	1 ± 0	TBA	-60	1
	0	0.979227 ± 0.041439		0	1.0427 0.017849
	60	0.901536 ± 0.032514		60	0.63046 0.05273
	120	0.908846 ± 0.034115		120	0.337111 0.054284
	180	0.871698 ± 0.035059		180	0.262858 0.032863
	240	0.810111 ± 0.046817		240	0.234774 0.03058
$Na_2C_2O_4$	-60	1 ± 0	BQ	-60	1
	0	1.083876 ± 0.012506		0	0.995192 0.036679
	60	0.627045 ± 0.004858		60	1.104673 0.052611
	120	0.34797 ± 0.023054		120	1.097346 0.071742
	180	0.247658 ± 0.019485		180	1.122792 0.099219
	240	0.215765 ± 0.026142		240	1.142558 0.104452

Table S7. Toxicity of SMX and its intermediates using the ECOSAR program[a].

Compounds	m/z	Acute toxicity (mg. L^{-1})			Chronic toxicity (mg. L^{-1})			Hazard category
		Fish (LC_{50})	Daphnid (LC_{50})	Green Algea (EC_{50})	Fish (ChV)	Daphnid (ChV)	Green Algea (ChV)	
SMX	253	893.69	2.10	9.24	1.10	0.13	13.96	Toxic
P1	288	8446.54	2.21	20.22	4.87	0.333	26.68	Toxic
P2	190	5822.62	14.96	262.29	1473.69	5.08	229.05	Not Harmful
P3	99	443.43	0.74	3.64	2.59	0.05	5.38	Harmful
P4	156	18.21	179.06	-	10.93	69.33	0.62	Harmful
P5	109	4.81	0.55	94.01	0.62	0.07	25.66	Toxic
P6	56	-	-	-	-	-	-	Harmful
P7	42	67.23	37.06	24.41	6.34	3.33	5.98	Harmful
P8	74	255.91	2252.58	1591.09	147.85	172.85	272.59	Not Harmful

[a]The predicted toxicity values are classified according to the system established by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (United Nations, 2011). Not harmful: LC_{50}/EC_{50}/ChV greater than 100 mg. L^{-1}; harmful: 10 mg. L^{-1}< LC_{50}/EC_{50}/ChV <100 mg. L^{-1}; toxic: 1 mg. L^{-1} <LC_{50}/EC_{50}/ChV < 10 mg. L^{-1}; very toxic: LC_{50}/EC_{50}/ChV< 1 1mg. L^{-1}. The lowest acute toxicity values between and within the different trophic levels (fish, daphnid, and green algae) were used to define the appropriate hazard category of the compounds.

Table S8. Summary of the photocatalytic properties of other MnO_x/g-C_3N_4 nanostructures towards degradation of pollutants.

Sample	Amount	Pollutants	Concentration and Usage	Power source	Time	Efficiency	Ref.
MnOx/g-C_3N_4	20 mg	Sulfamethoxazole	15 mg L^{-1}, 100 mL	White light LED lamp, 40W	240 min	85%	This work
2D-2D g-C_3N_4/MnO_2	50 mg	Rhodamine (RhB)	10 mg L^{-1}, 50 mL	Xenon lamp, 300 W	60 min	91.3%	1
Mn-adsorbed g-C_3N_4	200 mg	Rhodamine (RhB)	4 mg L^{-1}, 100 mL	Xe-lamp, 300 W	160 min	99%	2
g-C_3N_4-Mn-H	50 mg	Rhodamine (RhB)	10 mg L^{-1}, 100 mL	Xe arc lamp, 300W	60 min	88.9%	3
Mn-doped g-C_3N_4 nanoribbon	50 mg	Methylene Blue (MB)	10 mg L^{-1}, 200 mL	Xe-lamp, 300 W	180 min	96%	4
Mn/O co-doped g-C_3N_4	20 mg	Malachite green (MG)	20 mg L^{-1}, 50 mL	Xenon lamp, 350 W	30 min	91.7%	5
g-C_3N_4/diatomite/MnO_2	30 mg	Rhodamine (RhB)	10 mg L^{-1}, 100 mL	Xe lamp, 300 W	50 min	94%	6
MnO_x/g-C_3N_4	20 mg	Methyl orange (MO)	20 mg L^{-1}, 50 mL	Xenon lamp, 300 W	20 min	94%	7
MnO_2/g-C_3N_4	50 mg	Rhodamine (RhB)	20 mg L^{-1}, 50 mL	Xenon lamp, 300 W	100 min	99%	8
MnO_2/g-C_3N_4	50 mg	Methylene Blue (MB)	20 mg L^{-1}, 100 mL	Xe lamp, 500 W	150 min	94%	9

References

1 P. Xia, B. Zhu, B. Cheng, J. Yu and J. Xu, *ACS Sustain. Chem. Eng.*, 2018, **6**, 965–973.

2 W. Zhang, Z. Zhang, S. Kwon, F. Zhang, B. Stephen, K. K. Kim, R. Jung, S. Kwon, K.-B. Chung and W. Yang, *Appl. Catal. B Environ.*, 2017, **206**, 271–281.

3 J.-C. Wang, C.-X. Cui, Y. Li, L. Liu, Y.-P. Zhang and W. Shi, *J. Hazard. Mater.*, 2017, **339**, 43–53.

4 J.-C. Wang, C.-X. Cui, Q.-Q. Kong, C.-Y. Ren, Z. Li, L. Qu, Y. Zhang and K. Jiang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 8754–8761.

5 X. Xu, S. Wang, T. Hu, X. Yu, J. Wang and C. Jia, *Dye. Pigment.*, 2020, **175**, 108107.

6 R.-R. Chen, Q.-F. Ren, Y.-X. Liu, Y. Ding, H.-T. Zhu, C.-Y. Xiong, Z. Jin and W.-C. Oh, *J. Korean Ceram. Soc.*, 2021, **58**, 548–558.

7 W. Gong, Q. Wu, L. Ma, W. Zhang, X. Li, A. Xu and S. Zhao, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2023, **659**, 130812.

8 K. Ahmad, A. Chaudhary, W. Raza, A. Alsulmi and H. Kim, *Opt. Mater. (Amst).*, 2023, **140**, 113857.

9 M. Abdullah, S. D. Alahmari, F. F. Alharbi, S. R. Ejaz, M. S. Waheed, S. Aman, A. G. Al-Sehemi, A. M. A. Henaish, Z. Ahmad and H. M. T. Farid, *J. Mater. Sci. Mater. Electron.*, 2024, **35**, 517.