Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Fenton reaction by H_2O_2 produced on magnetically recyclable $Ag/CuWO_4/NiFe_2O_4$ photocatalyst

by

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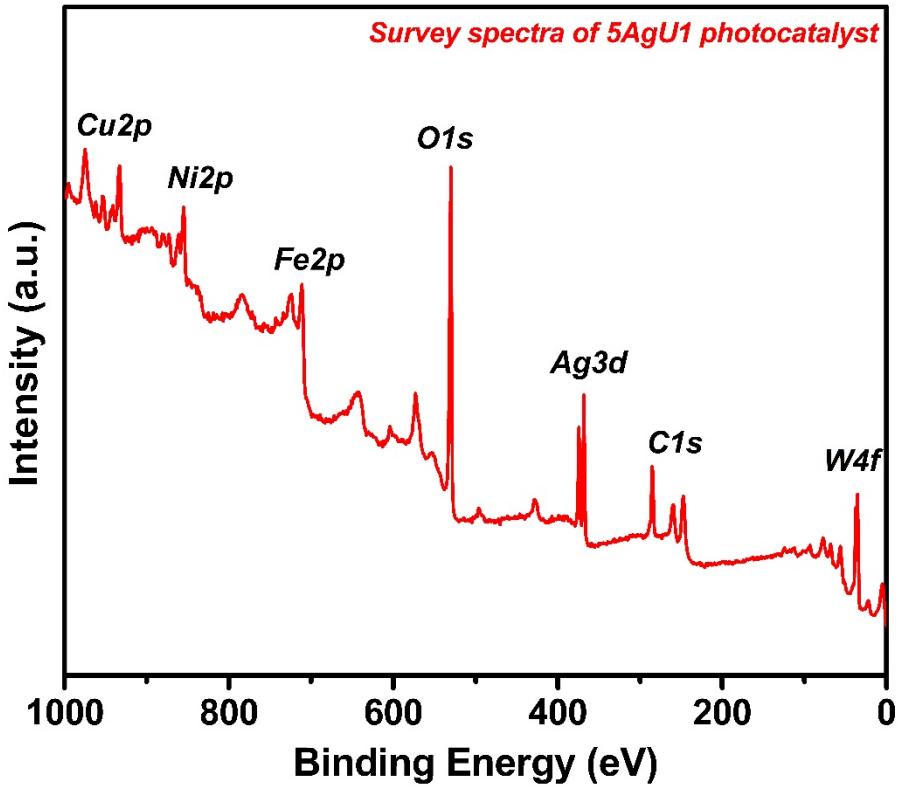

Figure S1. Survey spectra of 5AgU1 composite photocatalyst

Experimental details for H_2O_2 determination

The H_2O_2 amount produced (after photocatalyst separation) was determined by a redox titration of 2 ml of the sample solution with standard acidified (using 1M H_2SO_4) 0.2mM (aqueous) $KMnO_4$ solution. The solution turning pink indicated the endpoint of the (H_2O_2 – $KMnO_4$) titration. Additionally, an iodometric method using absorbance spectroscopy [30,31] was also employed to quantitatively verify the H_2O_2 production over the photocatalyst exhibiting the best activity. In brief, colorless KI gets oxidized by H_2O_2 to liberate I_2. The I_2 formed reacts with excess I^- (or KI) to form yellow-colored I_3^- anions, showing intense absorption at a characteristic ~ 352 nm wavelength. Ammonium molybdate (as a catalyst) can accelerate the slow KI oxidation by H_2O_2 for yellow I_3^- anion formation by reaction with excess KI. Thus, 0.1M potassium iodide (2ml) and 0.01M ammonium molybdate hexahydrate (50 μL) were

added to the reaction mixture (obtained after magnetic removal of photocatalyst nanoparticles). The reaction mixture was allowed to stand for 30 minutes. The absorbance of I_3^- at 352 nm was measured by a UV−vis spectrophotometer. The concentration of H_2O_2 formed was calculated by interpolating the absorbance intensity in a calibration plot prepared previously using known H_2O_2 concentrations.

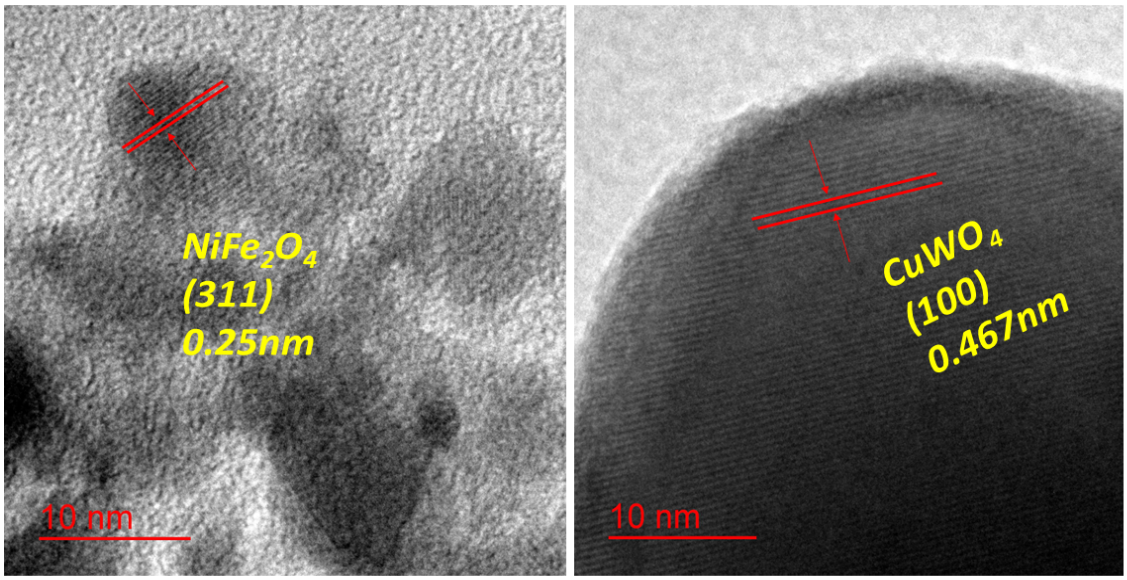

Figure S2. HR-TEM images of pristine $NiFe_2O_4$ and $CuWO_4$

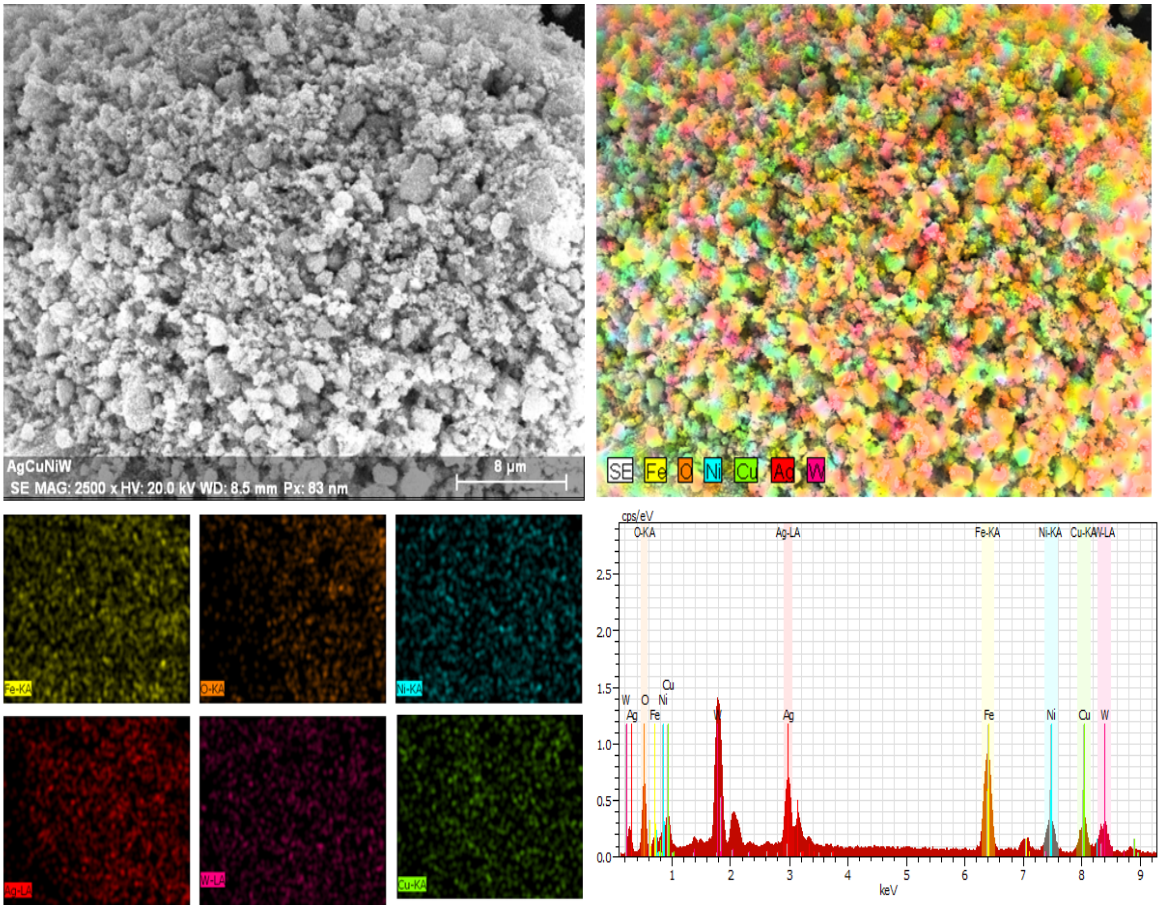

Figure S3. represents the elemental mapping and EDX of 5AgU1 photocatalyst.

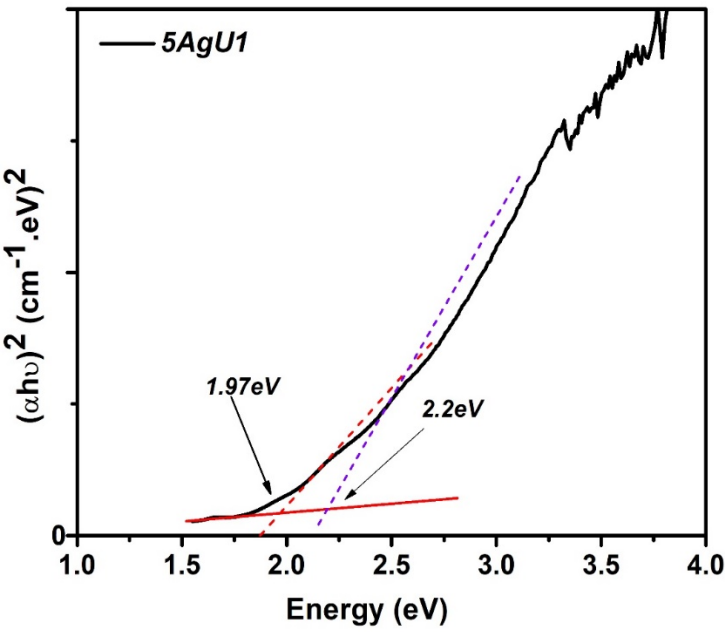

Figure S4. Tauc plot of 5AgU1 sample

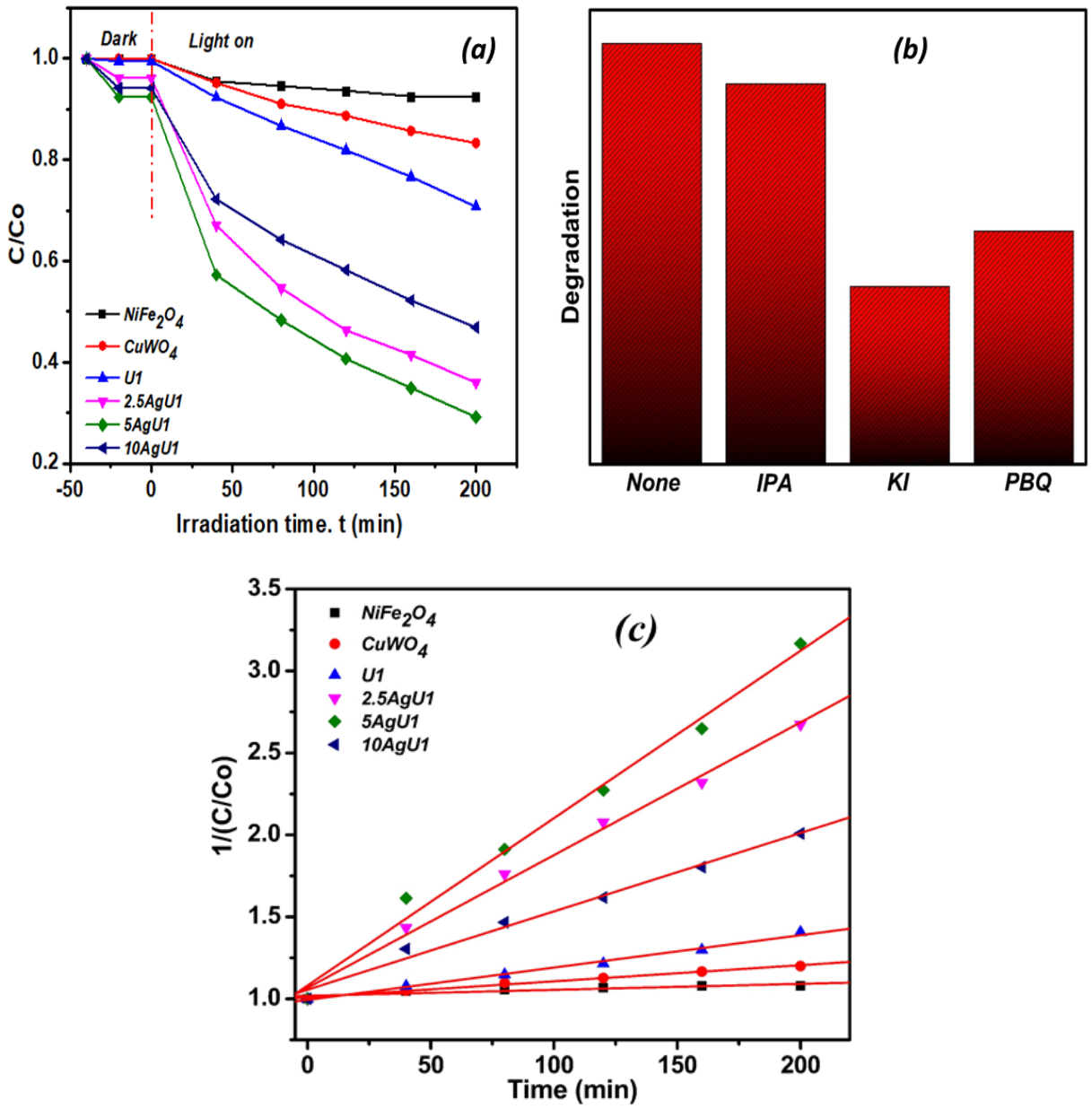

Figure S5 (a). Comparison plot of tetracycline degradation with time overall prepared photocatalyst **(b)** Trapping experiment for degradation of tetracycline on 5AgU1 photocatalyst **(c)** Second order reaction kinetics plot for tetracycline degradation on different photocatalyst (without oxygen purging).

Table S1: Comparison of photocatalytic H_2O_2 generations of prepared photocatalyst in this study with other previously reported photocatalytic system in recent years.

Photocatalyst	***Reaction Condition***	***Light Source***	***H_2O_2 production ($\mu molg^{-1}h^{-1}$)***	***References***
Benzene/K^+/CN	Water with molecular oxygen (O_2)	300W Xe lamp (λ > 420 nm)	287.5	[1]
3F-BN	5% IPA / distilled water mixture	Visible light (λ > 420 nm)	729	[2]
SPCN	10% IPA / distilled water mixture	Visible light (λ > 420 nm)	323.6	[3]
WO_3/CN-SUP	5% EtOH / distilled water mixture//O_2 purging	AM 1.5G	322	[4]
5% $ZnIn_2S_4$/FTCN50	10% EtOH / distilled water mixture	Visible light (λ > 420 nm)	135.98	[5]
SN-GQD-TiO_2	5% IPA / distilled water mixture	Visible light (λ > 420 nm)	902	[6]
K_2HPO/GCN	10% EtOH / distilled water mixture	Visible light (λ > 420 nm)	505	[7]
FeOOH/UPCN	Only water	Visible light (λ > 420 nm)	29.89	[8]
CdS/Fe_3O_4/N-doped C	Only water	300W Xe lamp (λ > 420 nm)	47.28	[9]
Ag@U-g-C_3N_4-NS	Only water	300W Xe lamp (λ > 420 nm)	67.50	[10]
$CoWO_4$@Bi_2WO_6	Water with molecular oxygen (O_2)	300W Xe lamp (λ >	40	[11]

		420 nm)		
$Fe_2(MoO_4)_3/Ag/Ag_3PO_4$	Only water	UV-visible light	273.6	[12]
	Methanol/water mixture		400.8	
HDMP grafted gC_3N_4	10% IPA / distilled water mixture with O_2 bubbling	300W Xe lamp (λ > 420 nm)	174	[13]
TiO_2 /In_2S_3	O_2 saturated water/ 10% EtOH	300W Xe lamp (28 mW/cm2)	752	[14]
E-MoS_2/FeS_2	Pure water	300W Xe lamp	75	[15]
Fe_2O_3/MoS_2@Ag	Pure water	Visible	15	[16]
(Fe)NCQDs/MIL-101	Pure water	500W Xe lamp (λ > 420 nm)	80	[17]
Ag_3PO_4@$NiFe_2O_4$	75 vol% MeOH/ water mixture	300W Xe lamp (λ > 420 nm)	130	[18]
5AgU1	Water with molecular oxygen (O_2)	Cool white LED (1070 W/m^2)	930	This work
	5% EtOH / distilled water mixture		1380	
	5% IPA / distilled water mixture		1410	

Table S2: A Comparison table of self-Fenton degradation system on 5AgU1 photocatalyst prepared in this study with other previously reported photocatalytic system

Photocatalyst	***Pollutant amount***	***Light source***	***Degradation % and time***	***Ref***
FeOCl/CDots	5ppm (p-chlorophenol)	150W Xe lamp ($\lambda > 420$ nm)	90.1%(180min)	[19]
HDMP grafted gC_3N_4	20ppm (Oxytetracycline hydrochloride)	300W Xe lamp ($\lambda > 420$ nm)	79.8 % (120min)	[13]
g-C_3N_4 /PDI/Fe	10ppm (p-nitrophenol)	300W Xe lamp ($\lambda > 420$ nm)	80% (60min)	[20]
FeOOH/UPCN	20ppm (Oxytetracycline)	300W Xe lamp ($\lambda > 420$ nm)	86.23%(120min)	[8]
Fe_2O_3/MoS_2@Ag	10ppm (2,4Dichlorophenol)	Visible	99% (150min)	[16]
(Fe)NCQDs/MIL-101	10ppm (Tetracycline)	500W Xe lamp ($\lambda > 420$ nm)	100% (180min)	[17]
Ag@ s-(Co_3O_4/$NiFe_2O_4$)	10ppm (Tetracycline)	Cool white LED (1070 W/m^2)	~99% (400min)	[21]
5AgU1	10ppm (Tetracycline)	Cool white LED (1070 W/m^2)	93% (60min)	**This work**

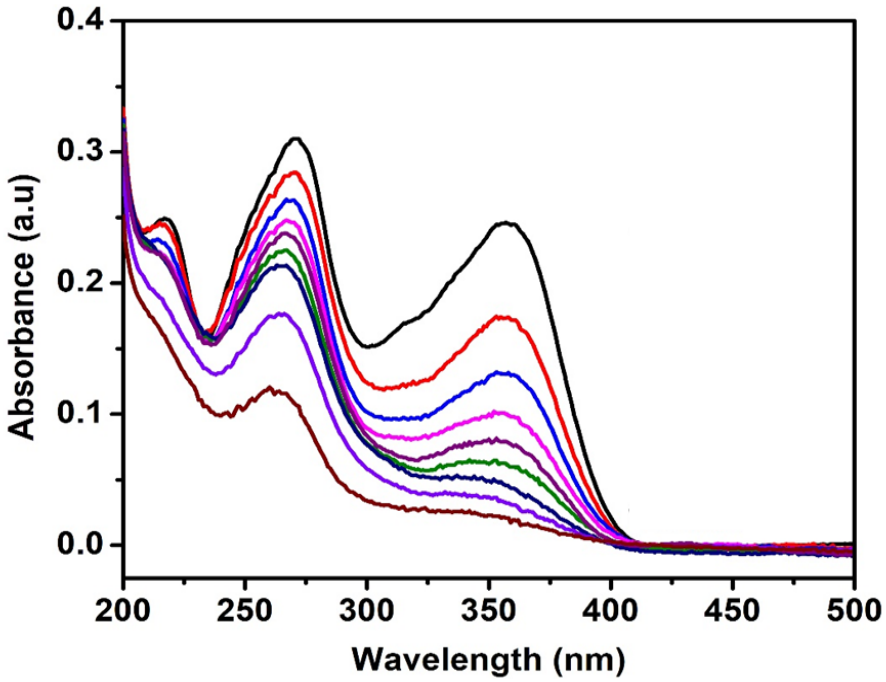

Figure S6. UV-visible absorbance vs wavelength plot of tetracycline degradation

Experiment procedure of NBT Test:

The nitroblue tetrazolium (NBT) test was used to spectrophotometrically determine the superoxide radicals in the aqueous solution of 5AgU1 photocatalyst. Experiments were conducted under i) a continuous flow of O_2 and ii) without any oxygen flow. In a typical experiment, 500uL of the dispersed photocatalyst nanoparticles were added to the 6ml of 2.5×10^{-5} mol/L NBT solution in a quartz vial. The vial, which was otherwise sealed with the silicon rubber septum, was continuously subjected to O_2 gas purging through the solution and visible light irradiation from a cool white LED (1070W/m^2) for 160min. The dispersed photocatalyst was separated by magnetic decantation and the 2ml of the supernatant was analyzed by UV-Vis spectrophotometer to measure the rate of production of formazan derivatives.

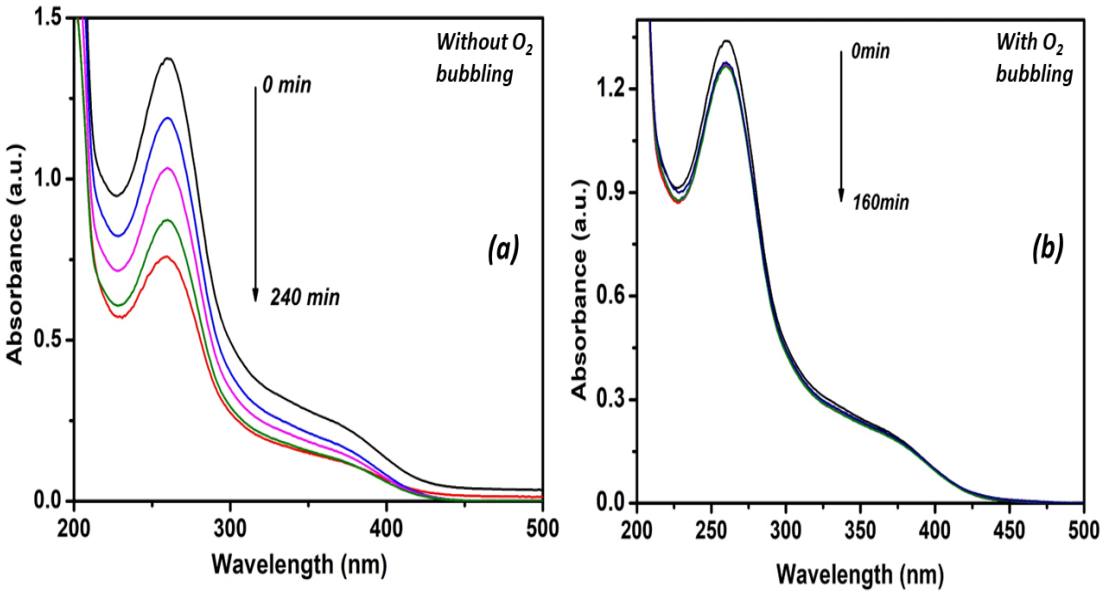

Figure S7. UV-vis absorbance spectra of 2.5x 10^{-5} mol/L NBT aqueous solution containing 5AgU1 photocatalyst (a) without O_2 bubbling (b) with O_2 bubbling

Statement of tetracycline degradation pathway

In an in-situ Fenton-like reaction, the generated •OH radical plays a major role in the degradation of tetracycline. The tetracycline molecule has phenolic and amine groups and double bonds. These have relatively high electron density and can be easily attacked by the reactive oxygen groups like $^{\cdot}OH$ and $^{\cdot}O_2^-$, resulting in several intermediate products [49-53]. Previous investigations of heterogeneous Fenton-catalyzed degradation of tetracycline suggest the following possible pathways. Figure S10 describes these pathways that were possibly followed during the degradation of tetracycline ($C_{22}H_{24}N_2O_8$) by 5AgU1 photocatalyst.

In the first pathway, an attack by hydroxyl radicals on the tetracycline molecule produced product 1 (P1) by dehydroxylation and N-demethylation [49,51]. Products 2, 3, and 4 were generated after consecutive dehydroxylation and demethylation. At last, smaller fragments and molecules (CO_2, H_2O, N-fragments) could be generated via

occurring of a ring-opening reaction. In the second pathway, product 1 was further attacked by the •OH radicals. Consequently, product 5 and product 6 were generated via dihydroxylation, and demethylation followed by a benzene ring opening reaction.

In the third pathway, initially, carbon ring opening occurred, resulting in product 7 and product 8. Further, these products lost the hydroxyl, carbonyl, and two N-methyl groups followed by cleavage of the aromatic ring. Finally, these organic molecules eventually keep breaking down into smaller and smaller compounds until they are fully mineralized into CO_2, H_2O, and N-minerals.

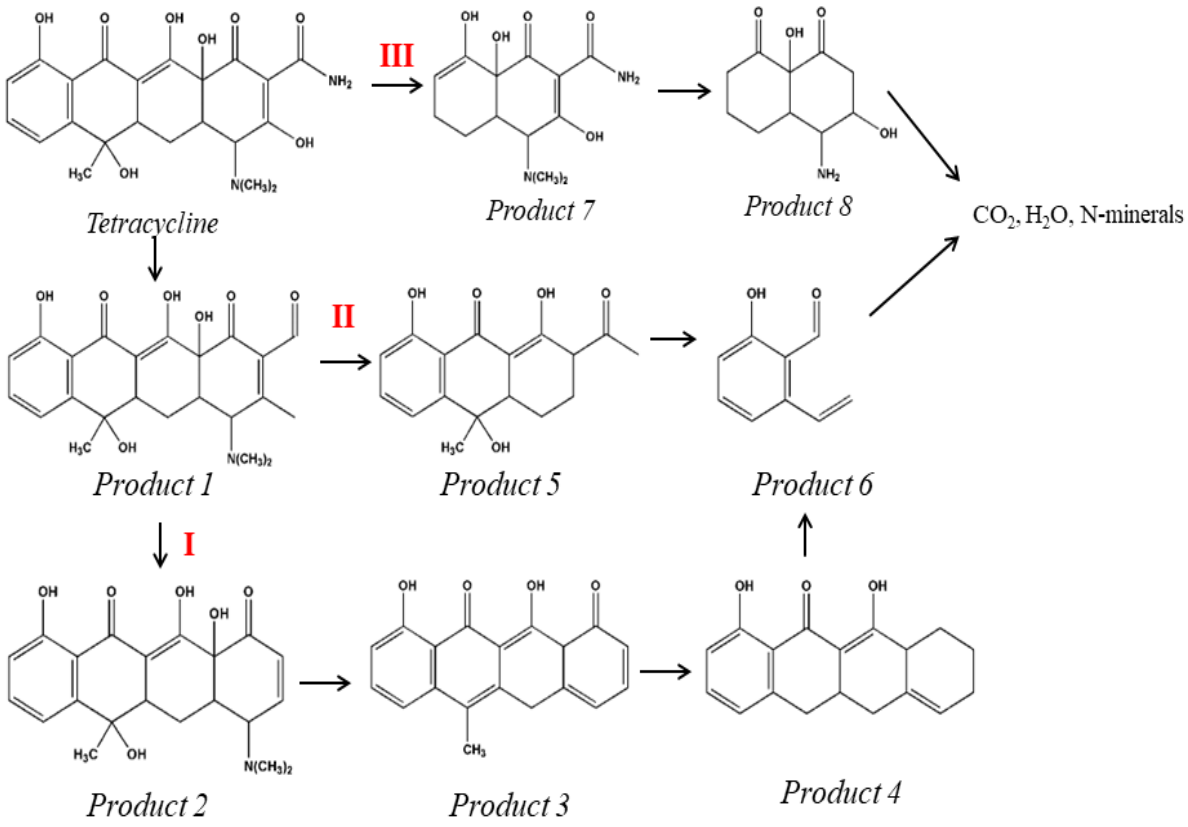

Figure S8. Proposed degradation pathway of in-situ Fenton degradation of tetracycline molecules.

Experimental details of TOC Method

Initially, 10 mg of the photocatalyst sample was mixed with 10 ml of the tetracycline solution in a 250 ml beaker. Then, 10 ml of 1N potassium dichromate ($K_2Cr_2O_7$) was added to the antibiotic solution. The resulting solution was left to stand for 30 minutes. The next step was the addition of 20 ml of 98% H_2SO_4. The mixture was allowed to stand for 30 minutes more. After that, 100ml of distilled water was added to the reaction mixture, and the mixture was allowed to cool for 10 minutes. The resultant mixture was filtered and the absorbance of the supernatant was determined at 600 nm (to estimate Cr^{3+}) by UV-visible spectroscopy.

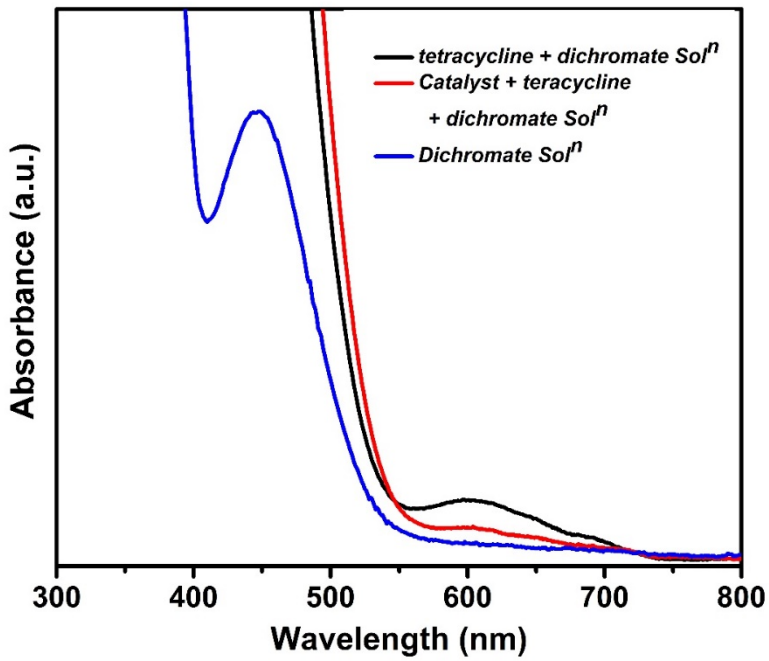

Figure S9. TOC analysis of tetracycline solutions degraded on the 5AgU1 photocatalyst.

References

(1) Chen, Y.; Yan, X.; Lin, H.; Wang, C.; Xu, J. Enhanced Fenton-like Degradation of Rhodamine B and Congo Red by Benzene and K+ Co-Doped Carbon Nitride with in Situ-Generated H_2O_2. *J Taiwan Inst Chem Eng* 2022, ***131***.

(2) Das, K. K.; Mansingh, S.; Mohanty, R.; Sahoo, D. P.; Priyadarshini, N.; Parida, K. 0D–2D Fe_2O_3 /Boron-Doped g-C_3N_4 S-Scheme Exciton Engineering for Photocatalytic H_2O_2 Production and Photo-Fenton Recalcitrant-Pollutant Detoxification: Kinetics, Influencing Factors, and Mechanism. *The Journal of Physical Chemistry C* 2022.

(3) Miao, W.; Wang, Y.; Liu, Y.; Qin, H.; Chu, C.; Mao, S. Persulfate-Induced Three Coordinate Nitrogen (N_3C) Vacancies in Defective Carbon Nitride for Enhanced Photocatalytic H_2O_2 Evolution. *Engineering* 2022.

(4) Jourshabani, M.; Yun, S. –H; Razi Asrami, M.; Lee, B. –K. Superior Photodegradation of Organic Compounds and H_2O_2 Production over Tungsten Oxide/Carbon Nitride Heterojunction with Sizable Heptazine Units: Dual Polycondensation and Interface Engineering. *Chemical Engineering Journal* 2022, ***427***.

(5) Liang, Q.; Liu, X.; Shao, B.; Tang, L.; Liu, Z.; Zhang, W.; Gong, S.; Liu, Y.; He, Q.; Wu, T.; Pan, Y.; Tong, S. Construction of Fish-Scale Tubular Carbon Nitride-Based Heterojunction with Boosting Charge Separation in Photocatalytic Tetracycline Degradation and H_2O_2 Production. *Chemical Engineering Journal* 2021, ***426***, 130831.

(6) Zheng, L.; Su, H.; Zhang, J.; Walekar, L. S.; Vafaei Molamahmood, H.; Zhou, B.; Long, M.; Hu, Y. H. Highly Selective Photocatalytic Production of H_2O_2 on Sulfur and Nitrogen Co-Doped Graphene Quantum Dots Tuned TiO2. *Appl Catal B* 2018, ***239***, 475–484.

(7) Tian, J.; Wu, T.; Wang, D.; Pei, Y.; Qiao, M.; Zong, B. One-Pot Synthesis of Potassium and Phosphorus-Doped Carbon Nitride Catalyst Derived from Urea for Highly Efficient Visible Light-Driven Hydrogen Peroxide Production. *Catal Today* 2019, ***330***, 171–178.

(8) Shi, W.; Sun, W.; Liu, Y.; Zhang, K.; Sun, H.; Lin, X.; Hong, Y.; Guo, F. A Self-Sufficient Photo-Fenton System with Coupling in-Situ Production H_2O_2 of Ultrathin Porous g-C_3N_4 Nanosheets and Amorphous FeOOH Quantum Dots. *J Hazard Mater* 2022, ***436***.

(9) Zhang, J.; Lin, L.; Wang, B.; Zhang, Y.; Wang, Y.; Zhang, L.; Jiang, Y.; Chen, H.; Zhao, M. Efficient Charge Separation of Photo-Fenton Catalyst: Core-Shell CdS/Fe_3O_4@N-Doped C for Enhanced Photodegradation Performance. *Colloids Surf A Physicochem Eng Asp* 2021, ***625.*** 126974.

(10) Cai, J.; Huang, J.; Wang, S.; Iocozzia, J.; Sun, Z.; Sun, J.; Yang, Y.; Lai, Y.; Lin, Z. Crafting Mussel-Inspired Metal Nanoparticle-Decorated Ultrathin Graphitic Carbon Nitride for the Degradation of Chemical Pollutants and Production of Chemical Resources. *Advanced Materials* 2019, *31* (15).

(11) Wang, J.; Yang, L.; Zhang, L. Constructed 3D Hierarchical Micro-Flowers $CoWO_4$@Bi_2WO_6 Z-Scheme Heterojunction Catalyzer: Two-Channel Photocatalytic H_2O_2 Production and Antibiotics Degradation. *Chemical Engineering Journal* **2021**, ***420***.127639.

(12) Ma, S.; Yang, Y.; Li, J.; Mei, Y.; Zhu, Y.; Wu, J.; Liu, L.; Yao, T.; Yang, Q. Z-Scheme Fe2(MoO4)3/Ag/Ag3PO4 Heterojunction with Enhanced Degradation Rate by in-Situ Generated H2O2: Turning Waste (H_2O_2) into Wealth (•OH). *J Colloid Interface Sci* 2022, ***606***, 1800–1810.

(13) Yang, Y.; Zeng, G.; Huang, D.; Zhang, C.; He, D.; Zhou, C.; Wang, W.; Xiong, W.; Li, X.; Li, B.; Dong, W.; Zhou, Y. Molecular Engineering of Polymeric Carbon Nitride for Highly Efficient Photocatalytic Oxytetracycline Degradation and H_2O_2 Production. *Appl Catal B* 2020, ***272***. 118970.

(14) Yang, Y.; Cheng, B.; Yu, J.; Wang, L.; Ho, W. TiO_2/In_2S_3 S-Scheme Photocatalyst with Enhanced H_2O_2-Production Activity. *Nano Res* 2021.

(15) Yang, Y.; Yu, H.; Wu, M.; Zhao, T.; Guan, Y.; Yang, D.; Zhu, Y.; Zhang, Y.; Ma, S.; Wu, J.; Liu, L.; Yao, T. Dual H_2O_2 Production Paths over Chemically Etched MoS_2/FeS_2 Heterojunction: Maximizing Self-Sufficient Heterogeneous Fenton Reaction Rate under the Neutral Condition. *Appl Catal B* 2023, ***325***, 122307.

(16) Guo, M.; Xing, Z.; Zhao, T.; Qiu, Y.; Tao, B.; Li, Z.; Zhou, W. Hollow Flower-like Polyhedral α-Fe_2O_3/Defective MoS_2/Ag Z-Scheme Heterojunctions with Enhanced Photocatalytic-Fenton Performance via Surface Plasmon Resonance and Photothermal Effects. *Appl Catal B* 2020, ***272***, 118978.

(17) Xie, Y.; Liu, C.; Li, D.; Liu, Y. In Situ-Generated H_2O_2 with NCQDs/MIL-101(Fe) by Activating O_2: A Dual Effect of Photocatalysis and Photo-Fenton for Efficient Removal of Tetracyline at Natural PH. *Appl Surf Sci* 2022, ***592***. 153312.

(18) Huang, S.; Xu, Y.; Zhou, T.; Xie, M.; Ma, Y.; Liu, Q.; Jing, L.; Xu, H.; Li, H. Constructing Magnetic Catalysts with In-Situ Solid-Liquid Interfacial Photo-Fenton-like Reaction over Ag_3PO_4@$NiFe_2O_4$ Composites. *Appl Catal B* 2018, ***225***, 40–50.

(19) Zhang, J.; Zhang, G.; Ji, Q.; Lan, H.; Qu, J.; Liu, H. Carbon Nanodot-Modified FeOCl for Photo-Assisted Fenton Reaction Featuring Synergistic in-Situ H2O2 Production and Activation. *Appl Catal B* 2020, ***266***.118665.

(20) Xiong, Z.; Wang, Z.; Muthu, M.; Zhang, Y. Construction of an In-Situ Fenton-like System Based on a g-C_3N_4 Composite Photocatalyst. *J Hazard Mater* 2019, ***373***, 565–571.

(21) Kumar, U.; Kuntail, J.; Kumar, A.; Prakash, R.; Pai, M. R.; Sinha, I. In-Situ H_2O_2 Production for Tetracycline Degradation on Ag/s-(Co_3O_4/$NiFe_2O_4$) Visible Light Magnetically Recyclable Photocatalyst. *Appl Surf Sci* **2022**, *589*. 153013.