

Supplementary material

Upcycling Textile White Mud to Fabricate MIL-125-Derived Amorphous TiO₂@C: Effective Electrocatalyst for Cathodic Reduction of Antibiotics

Jinmei Zhu ¹, Xiaofei Wen ², Yuanhui Feng ², Shuaibing Ren ², Zimo Lou ^{1,2,3,*} and Jiansheng Li ^{3,*}

¹ Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, Hangzhou 310014, China; zhujinmei@zjut.edu.cn

² College of Environment, Zhejiang University of Technology, Hangzhou 310014, China; wenxiaofei18@163.com (X.W.); yuanhuifeng0105@163.com (Y.F.); renshuaibing1026@163.com (S.R.)

³ Key Laboratory of Jiangsu Province for Chemical Pollution Control and Resources Reuse, School of Environment and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

* Correspondence: louzimo@zjut.edu.cn (Z.L.); lijsh@njust.edu.cn (J.L.)

ORCID; <https://orcid.org/0000-0001-8070-5091>

Table of Contents

Text S1. Working electrode preparation

Figure S1. H-type cell for cathodic reduction test

Figure S2. Cathodic reduction test of FLO under Air, O₂ and N₂ atmospheres

Figure S3. Adsorption of FLO by different electrocatalysts

Figure S4. Effect of molar ratio of BDC: Ti on the electro-reductive degradation efficiency of FLO

Figure S5. Effect of temperature calcination of TiO₂ and NaBH₄ mixtures during TiO₂@C-W fabrication on the electro-reductive degradation efficiency of FLO

Figure S6. TOC removal efficiency

Figure S7. Proposed pathways of the cathodic degradation of nitrofurazone (NFZ) and metronidazole (MNZ)

Table S1 Comparison of elimination rate and degradation efficiency with the previous reports

Text S1. Working electrode preparation

Carbon papers (20 × 20 mm) were firstly soaked into 0.5 M H₂SO₄ solution for 5 h to improve their hydrophilicity, and were washed in ultrasonic bath with DI water and ethanol for 20 min in sequence to remove impurities. For a specific working electrode, 7.5 mg sample (e.g. TiO₂@C-W) was added into a solution of 5 mL ethanol and 1.5 mL isopropanol containing 7.5 μL Nafion[®] (5 wt.%) to form a mixture. The mixture was ultrasonicated for 10 min to form an ink. The ink was transferred onto the pretreated carbon paper on a heating plate using a brush. Aforementioned steps were repeated to coat uniform films on both sides of the carbon paper

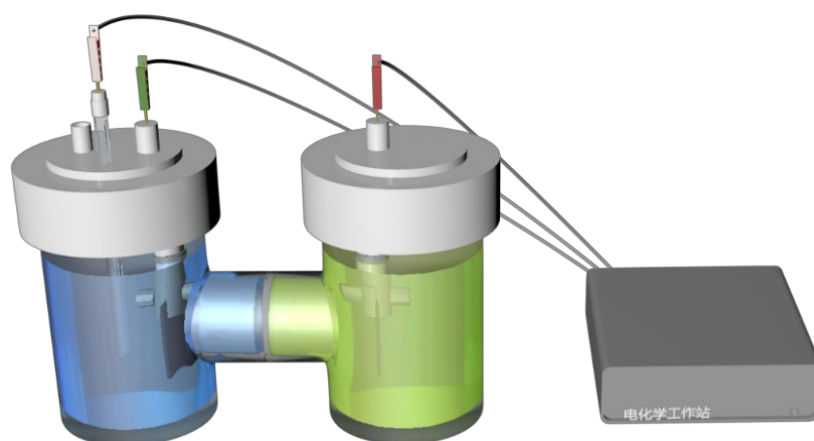


Figure S1. H-type cell for cathodic reduction test

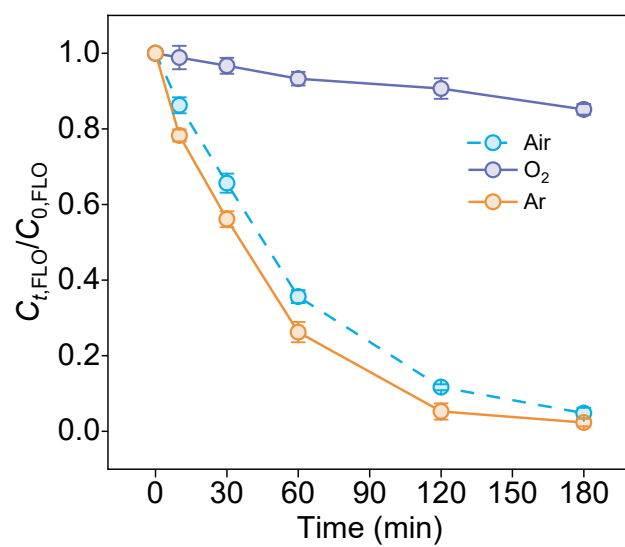


Figure S2. Cathodic reduction test of FLO under Air, O_2 and N_2 atmospheres (reaction conditions: $[FLO]_0=20 \text{ mg L}^{-1}$, applied bias=0 V, $[Na_2SO_4]=50 \text{ mM}$).

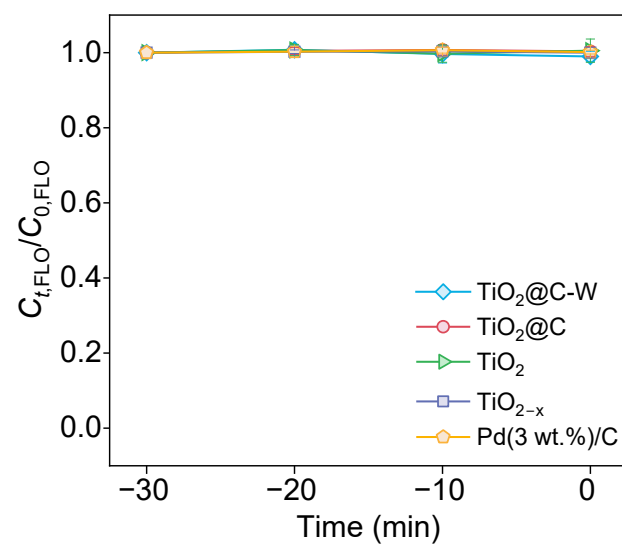


Figure S3. Adsorption of FLO by different electrocatalysts (reaction conditions: $[\text{FLO}]_0 = 20 \text{ mg L}^{-1}$, applied bias = 0 V, $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$)

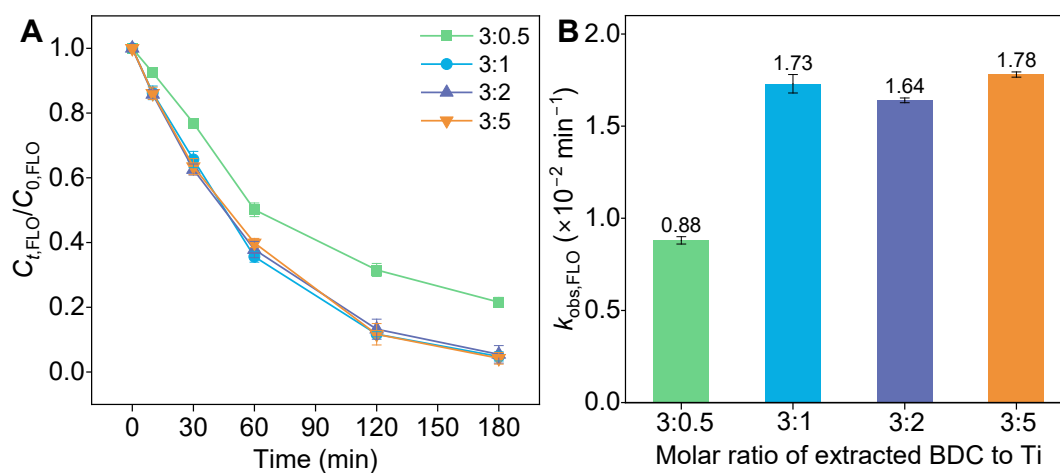


Figure S4. Effect of molar ratio of BDC: Ti on the electro-reductive degradation efficiency of FLO; (A) $C_{t,FLO}/C_{0,FLO}$ and (B) $k_{obs,FLO}$ of dechlorinating. (reaction conditions: $[FLO]_0=20 \text{ mg L}^{-1}$, applied bias=-1.2 V, $[Na_2SO_4]=50 \text{ mM}$).

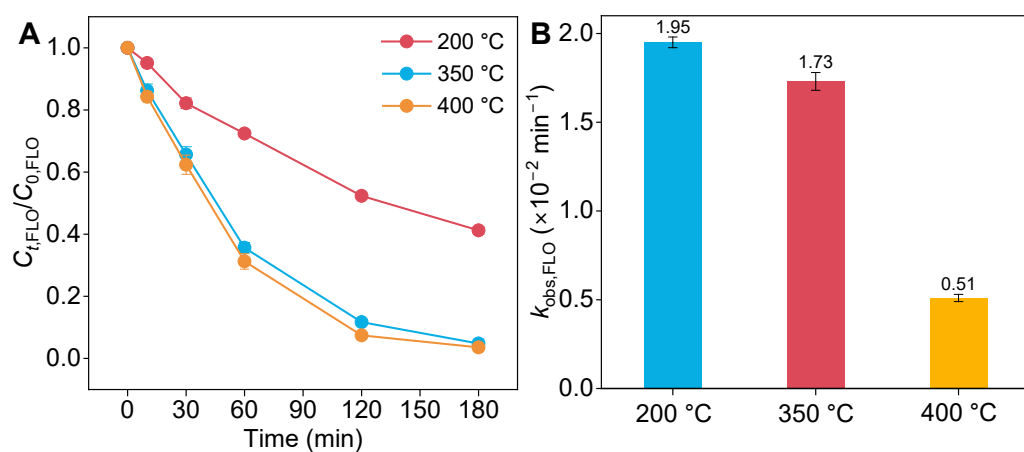


Figure S5. Effect of temperature calcination of TiO_2 and NaBH_4 mixtures during $\text{TiO}_2@\text{C-W}$ fabrication on the electro-reductive degradation efficiency of FLO (reaction conditions: $[\text{FLO}]_0 = 20 \text{ mg L}^{-1}$, applied bias = -1.2 V , $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$).

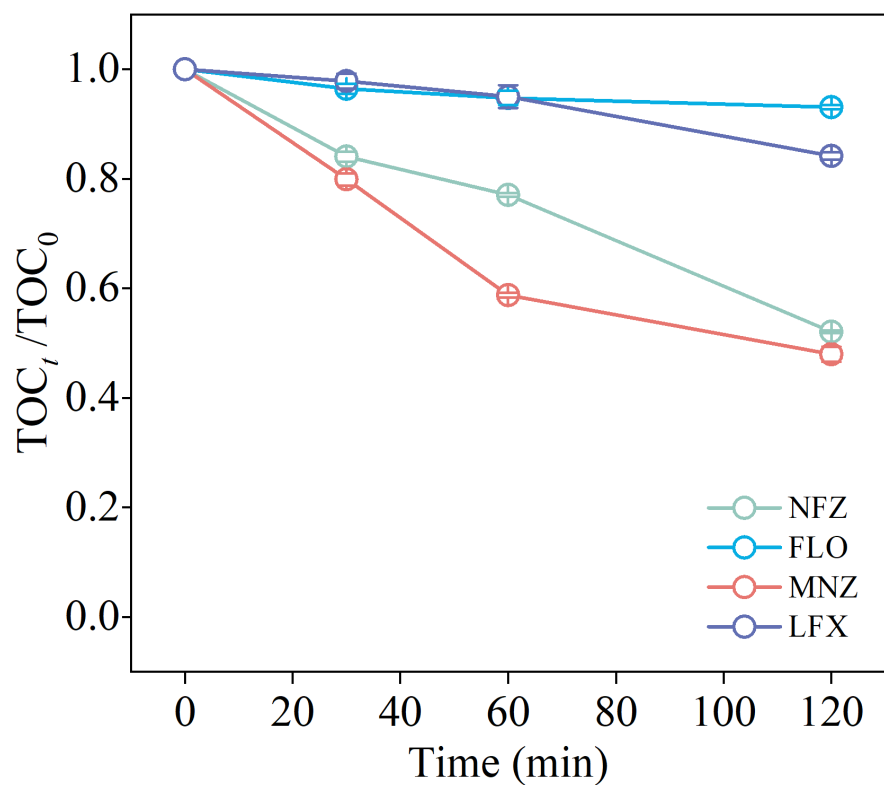


Figure S6. Evolution of solution TOC removal (as mineralization efficiency) as a function of treatment time in cathodic reduction process for florfenicol (FLO), nitrofurazone (NFZ), metronidazole (MNZ) and levofloxacin (LFX) removal by $TiO_2@C-W$ (reaction conditions: $[NFZ]_0=[MNZ]_0=[FLO]_0=20 \text{ mg L}^{-1}$, applied bias= -1.2 V , $[Na_2SO_4]=50 \text{ mM}$).

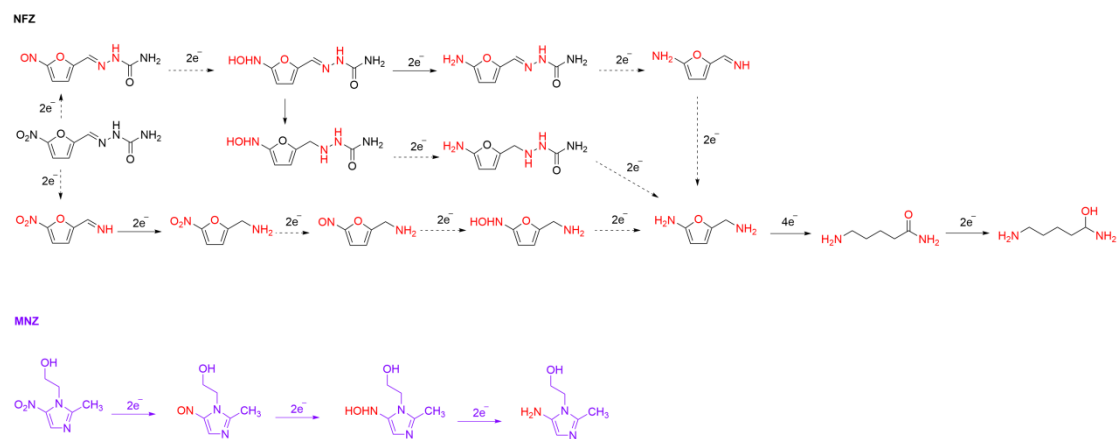


Figure S7. Proposed pathways of the cathodic degradation of nitrofurazone (NFZ) and metronidazole (MNZ)

Table S1 Comparison of removal efficiency and k_{obs} with the previous reports

Antibiotic	Elimination Technology	removal efficiency	k_{obs} (min^{-1})	Ref.
NFZ	cathodic reduction with $\text{TiO}_2@\text{C-W}$ as electrode	95% (3h)	0.019	This study
	Cathodic degradation Graphite fiber brushtwisted by titanium wire	98.8% (9 h)	0.016	[1]
	Biocathodic degradation	70% (1 h)	0.020	[2]
	Zr(IV)-Based Metal-Organic Frameworks	95%	-	[3]
MNZ	cathodic reduction with $\text{TiO}_2@\text{C-W}$ as electrode	93%	0.015	This study
	Cathodic degradation Graphite fiber brushtwisted by titanium wire	98% (9 h)	0.013	[1]
	reduction reaction by nanoscale zero-valent iron particles	95% (1.5 h)	-	[4]
	Oxidative degradation by granular activated carbon	80% (4 h)	0.023	[5]
	UV/ TiO_2 photocatalysis	88% (0.5 h)	0.052	[6]
LFX	cathodic reduction with $\text{TiO}_2@\text{C-W}$ as electrode	68% (3 h)	0.006	This study
	sonochemical degradation using carbon tetrachloride	99% (15 min)	-	[7]
	Photocatalytic degradation using highly crystalline TiO_2 nanoparticles	90% (2 h)	-	[8]
	Electrochemical degradation by PbO_2 electrode	100% (160 min)	0.028	[9]

Reference

1. Kong, D.; Liang, B.; Yun, H.; Cheng, H.; Ma, J.; Cui, M.; Wang, A.; Ren, N. Cathodic degradation of antibiotics: characterization and pathway analysis. *Water Res.* **2015**, *72*, 281-292.
2. Kong D.; Yun H.; Cui D.; Qi, M.; Shao C.; Cui D.; Ren N.; Liang B.; Wang A. Response of antimicrobial nitrofurazone-degrading biocathode communities to different cathode potentials. *Bioresource Technology*. **2017**, *241*:951-958.
3. Wang B.; Lv X.; Feng D.; Xie L.; Zhang J.; Li M.; Xie Y.; Li J.; Zhou H. Highly Stable Zr(IV)-Based Metal-Organic Frameworks for the Detection and Removal of Antibiotics and Organic Explosives in Water. *J Am Chem Soc.* **2016** *138*(19):6204-6216.
4. Chen, J.; Qiu, X.; Fang, Z.; Yang, M.; Pokeung, T.; Gu, F.; Cheng, W.; Lan, B.. Removal mechanism of antibiotic metronidazole from aquatic solutions by using nanoscale zero-valent iron particles. *Chem. Eng. J.* **2012**, *181-182*: 113-119.
5. Forouzesheh, M.A.; Ebadi, A.; Aghaeinejad-Meybodi. Degradation of metronidazole antibiotic in aqueous medium using activated carbon as a persulfate activator. *Purif. Technol.* **2019**, *240*:145-151.
6. Tran, M.; Fu, C.; Juang, R. Effects of water matrix components on degradation efficiency and pathways of antibiotic metronidazole by UV/TiO₂ photocatalysis. *J. Mol. Liq.* **2019**, *276* 32-38.
7. Guo, W.; Shi, Y.; Wang, H.; Yang, H.; Zhang, G. Intensification of sonochemical degradation of antibiotics levofloxacin using carbon tetrachloride. *Ultrason Sonochem.* **2010**, *17*(4):680-684.
8. Kansal, S.; Kundu, P.; Sood, S.; Lamba, R.; Umar A.; Mehta, S. K. Photocatalytic degradation of antibiotic levofloxacin using well-crystalline TiO₂ nanoparticles, *New J. Chem.* **2014**, *38*, 3220-3226.
9. Xia, Y.; Dai, Q. Electrochemical degradation of antibiotic levofloxacin by PbO₂ electrode: Kinetics, energy demands and reaction pathways. *Chemosphere.* **2018**, *205*:215-222.