## Supporting Information

## Hierarchically Porous WO<sub>3</sub>/CdWO<sub>4</sub> Fiber-in-Tube Nanostructures Featuring Readily Accessible Active Sites and Enhanced Photocatalytic Effectiveness for Antibiotic Degradation in Water

Feng Rong<sup>†</sup>, Qifang Lu<sup>\*†</sup>, Haoxin Mai<sup>‡</sup>, Dehong Chen<sup>\*‡</sup>, Rachel A. Caruso<sup>\*‡</sup>

<sup>†</sup>School of Material Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, P. R. China; E-mail: luqf0110@126.com (Q. F. Lu)

<sup>‡</sup>Applied Chemistry and Environmental Science, School of Science, RMIT University, Melbourne, Victoria 3000, Australia; E-mail: dehong.chen@rmit.edu.au (D. H. Chen), rachel.caruso@rmit.edu.au (R. A. Caruso)



Figure S1. The photocatalytic reaction set-up used in this study.



Figure S2. XRD patterns of the WO<sub>3</sub> and CdWO<sub>4</sub> nanofibers calcined at 550 °C.



Figure S3. (a and b) SEM images of the precursor fibers used to fabricate the

WO<sub>3</sub>/CdWO<sub>4</sub> FITNs.



**Figure S4.** Raman spectra of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs and WO<sub>3</sub>/CdWO<sub>4</sub> compounds I, II, and III. All these samples have been calcined at 550 °C in air.

The peaks associated with WO<sub>3</sub> at 260, 716, and 807 cm<sup>-1</sup> (shown in blue text) increase in intensity with the increase of WO<sub>3</sub> content from 5.91 wt% in WO<sub>3</sub>/CdWO<sub>4</sub> compound I to 38.59 wt% in compound III.



**Figure S5.** TGA curves of the WO<sub>3</sub>/CdWO<sub>4</sub> FITNs, and WO<sub>3</sub>/CdWO<sub>4</sub> compounds I, II, and III after calcination.



Figure S6. TEM images of the (a) WO3 and (b) CdWO4 nanofibers calcined at 550 °C in

air.



**Figure S7.** N<sub>2</sub> sorption isotherms of the WO<sub>3</sub>/CdWO<sub>4</sub> FITNs, WO<sub>3</sub>, and CdWO<sub>4</sub>. These samples have been calcined at 550 °C in air.



**Figure S8.** (a) Adsorption of CIP over different catalysts in the dark and (b) kinetics curves of CIP degradation over WO<sub>3</sub>, CdWO<sub>4</sub>, and WO<sub>3</sub>/CdWO<sub>4</sub> FITNs.



**Figure S9.** (a-c) The evolution of the UV absorbance spectra of CIP over time in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs, WO<sub>3</sub>, and CdWO<sub>4</sub> as labeled.



**Figure S10.** Relative TOC content during the decomposition of CIP in the presence of WO<sub>3</sub>, CdWO<sub>4</sub>, and WO<sub>3</sub>/CdWO<sub>4</sub> FITNs under simulated sunlight illumination.



**Figure S11.** (a) XRD patterns of the WO<sub>3</sub>/CdWO<sub>4</sub> FITNs before and after six cycles of the CIP photodegradation reaction and (b) SEM image of the WO<sub>3</sub>/CdWO<sub>4</sub> FITNs after six cycles of the CIP photodegradation reaction.



**Figure S12.** (a) Adsorption of tetracycline (TC) over WO<sub>3</sub>, CdWO<sub>4</sub>, and WO<sub>3</sub>/CdWO<sub>4</sub> FITNs in the dark, (b) photocatalytic degradation efficiency of TC, and (c) relative TOC content during the decomposition of TC in the presence of WO<sub>3</sub>, CdWO<sub>4</sub>, and WO<sub>3</sub>/CdWO<sub>4</sub> FITNs under simulated sunlight illumination. (d-f) The evolution of the UVvis absorbance spectra of TC over time in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs, WO<sub>3</sub>, and CdWO<sub>4</sub>.



**Figure S13.** TEM images of the (a)  $WO_3/CdWO_4$  compound I (molar ratio of W:Cd = 1.10:1.00), (b)  $WO_3/CdWO_4$  compound II (molar ratio of W:Cd = 1.50:1.00), and (c)  $WO_3/CdWO_4$  compound III (molar ratio of W:Cd = 2.00:1.00) obtained after calcination at 550 °C.



**Figure S14.** (a) Adsorption of CIP over different catalysts in the dark, (b) photocatalytic degradation efficiency of CIP under simulated sunlight illumination, and (c, d and e) the evolution of the absorbance spectra of CIP over time in the presence of the WO<sub>3</sub>/CdWO<sub>4</sub> compound I (molar ratio of W:Cd = 1.10:1.00), WO<sub>3</sub>/CdWO<sub>4</sub> compound II (W:Cd = 1.50:1.00), and compound III (molar ratio of W:Cd = 2.00:1.00).



**Figure S15.** Rietveld refinement from 10° to 120° in 2 theta of (a) WO<sub>3</sub>/CdWO<sub>4</sub> compound I (molar ratio of W:Cd = 1.10:1.00), (b) WO<sub>3</sub>/CdWO<sub>4</sub> FITNs (molar ratio of W:Cd = 1.25:1.00), (c) WO<sub>3</sub>/CdWO<sub>4</sub> compound II (molar ratio of W:Cd = 1.50:1.00), and (d) WO<sub>3</sub>/CdWO<sub>4</sub> compound III (molar ratio of W:Cd = 2.00:1.00).



**Figure S16.** (a) Survey XPS spectra and high-resolution XPS spectra of (b) W 4f, (c) Cd 3d, and (d) O 1s of the WO<sub>3</sub>/CdWO<sub>4</sub> compounds I, II, and III, as labeled. All these samples have been calcined at 550 °C.

Only slight shifts (within experimental error) in binding energy were observed for all these samples.



**Figure S17.** (a) UV-vis DRS and (b) steady-state PL spectra of the WO<sub>3</sub>/CdWO<sub>4</sub> compound I, II, and III.

The band edge of the sample is red shifted slightly with the increase of WO<sub>3</sub> content from WO<sub>3</sub>/CdWO<sub>4</sub> compound I (5.91 wt%), compound II (23.63 wt%) to III (38.59 wt%).



**Figure S18.** EPR spectra of the photodegradation systems kept in the dark in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs (labeled as dark) and under irradiation for 5 minutes in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs and WO<sub>3</sub>/CdWO<sub>4</sub> compounds I, II, and III: (a) DMPO- $\cdot$ OH and (b) DMPO- $\cdot$ O<sub>2</sub><sup>-</sup>.

The signals of DMPO- $\cdot$ O<sub>2</sub><sup>-</sup> and DMPO- $\cdot$ OH are much weaker for WO<sub>3</sub>/CdWO<sub>4</sub> compounds I, II, and III compared with measurement in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs as photocatalyst, suggesting WO<sub>3</sub>/CdWO<sub>4</sub> compounds I, II, and III are less effective for photocatalytic degradation under the same reaction conditions.



**Figure S19.** Mass spectra of the intermediates formed during the photodegradation of CIP after (a) 0, (b) 30, (c) 60, and (d) 90 min irradiation in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITN photocatalyst.



**Figure S20.** Spectra obtained from HPLC-MS of the TC intermediates eluted at different reaction time of (a) 0, (b) 40, (c) 80, and (d) 120 min in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs.



Figure S21. Mass spectrum of the CIP solution irradiated for 90 min in the absence of



**Figure S22.** Photocatalytic degradation pathways of TC in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs.

According to the detected intermediates and the related reports,<sup>1-3</sup> two possible degradation pathways of TC were proposed and are illustrated in Figure S22. The first pathway is the primary degradation by the addition of hydroxyl with the attack of the •OH radicals to generate the intermediate with m/z=475, which is further fragmented to the product G (m/z=396) via the deprivation of methyl from the tertiary amine and amide group. Pathway II is successive fragmentation induced by reactive species. Intermediates A then B with m/z of 416 and 362 are generated via the loss of the N-dimethyl group due to the relatively low bond energy of C–N and the deamidation reaction. Subsequently, the product C with m/z 340 is generated through the detachment of a hydroxyl group. Finally, the intermediate D (m/z=318) is changed to E (m/z=274) and H (m/z=186) via deacetylation and oxidation reactions. These intermediates derived from TC are gradually decomposed into CO<sub>2</sub> and H<sub>2</sub>O in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs.

Materials	Weight (mg)	Antibiotic solution	Irradiation time	Degradation efficiency	Ref.
WO <sub>3</sub> /CdWO <sub>4</sub>	40 mg	20 mg/L, CIP	90 min	93.4%	This work
WO <sub>3</sub> /CdWO <sub>4</sub>	40 mg	10 mg/L, TC	120 min	91.8%	This work
g-C <sub>3</sub> N <sub>4</sub> /CdWO <sub>4</sub>	50 mg	10 mg/L, TC	300 min	78%	4
WO <sub>3</sub> /Bi <sub>2</sub> WO <sub>6</sub>	40 mg	10 mg/L, CIP	120 min	79.5%	5
WO <sub>3</sub> /Bi <sub>2</sub> MoO <sub>6</sub>	50 mg	20 mg/L, TC	120 min	77.3%	6
g-C <sub>3</sub> N <sub>4</sub> /WO <sub>3</sub> /NCDs	20 mg	10 mg/L, TC	60 min	$\sim 80\%$	7
ZnWO <sub>4</sub> -CdS	50 mg	15 mg/L, CIP	60 min	~ 85%	8

**Table S1.** Comparison of the photocatalytic performance of WO<sub>3</sub>/CdWO<sub>4</sub> FITNs with other reported tungstate-based photocatalysts.

**Table S2.** WO<sub>3</sub> content and degradation efficiency of CIP in the presence of samples with varied WO<sub>3</sub> content.

Sample	molar ratio of W:Cd	CdWO4 (wt%)	WO3 (wt%) <sup>#</sup>	Degradation efficiency^
WO <sub>3</sub> /CdWO <sub>4</sub> compound I	1.10:1.00	94.09	5.91	81.5%
WO <sub>3</sub> /CdWO <sub>4</sub> FITNs	1.25:1.00	85.23	14.77	93.4%
WO <sub>3</sub> /CdWO <sub>4</sub> compound II	1.50:1.00	76.37	23.63	76.9%
WO <sub>3</sub> /CdWO <sub>4</sub> compound III	2.00:1.00	61.41	38.59	71.6%

Note: <sup>#</sup>WO<sub>3</sub> contents were calculated using Rietveld refinement.

<sup>^</sup>CIP (20 mg/L aqueous solution) was used and degradation efficiency was measured after 90 min irradiation.

Intermediate products	Molecular formula	m/z	Structural formula
CIP	C <sub>17</sub> H <sub>18</sub> FN <sub>3</sub> O <sub>3</sub>	332	Б Н Х С С С С С С С С С С С С С С С С С С
A	$C_{17}H_{16}FN_{3}O_{5}$	362	
В	C <sub>16</sub> H <sub>16</sub> FN <sub>3</sub> O <sub>4</sub>	334	
С	$C_{15}H_{16}FN_3O_3$	306	
D	C <sub>14</sub> H <sub>11</sub> FN <sub>2</sub> O <sub>4</sub>	291	
E	C <sub>13</sub> H <sub>11</sub> FN <sub>2</sub> O <sub>3</sub>	263	
F	$C_{13}H_{12}N_2O_3$	245	
G	$C_{13}H_{10}N_2O_5$	274	

**Table S3.** Identification of CIP degradation products in the presence of WO<sub>3</sub>/CdWO<sub>4</sub> FITN photocatalyst.

## REFERENCES

- Jiang, D.; Wang, T.; Xu, Q.; Li, D.; Meng, S.; Chen, M. Perovskite Oxide Ultrathin Nanosheets/g-C<sub>3</sub>N<sub>4</sub> 2D-2D Heterojunction Photocatalysts with Significantly Enhanced Photocatalytic Activity Towards the Photodegradation of Tetracycline. *Appl. Catal. B: Environ.* 2017, 201, 617-628.
- (2) Yang, Y.; Zeng, Z.; Zhang, C.; Huang, D.; Zeng, G.; Xiao, R.; Lai, C.; Zhou, C.; Guo, H.; Xue, W.; Cheng, M.; Wang, W.; Wang, J. Construction of Iodine Vacancy-Rich BiOI/Ag@AgI Z-Scheme Heterojunction Photocatalysts for Visible-Light-Driven Tetracycline Degradation: Transformation Pathways and Mechanism Insight. *Chem. Eng. J.* 2018, *349*, 808-821.
- (3) Ren, L.; Zhou, W.; Sun, B.; Li, H.; Qiao, P.; Xu, Y.; Wu, J.; Lin, K.; Fu, H. Defects-Engineering of Magnetic Fe<sub>2</sub>O<sub>3</sub> Ultrathin Nanosheets/Mesoporous Black TiO<sub>2</sub> Hollow Sphere Heterojunctions for Efficient Charge Separation and The Solar-Driven Photocatalytic Mechanism of Tetracycline Degradation. *Appl. Catal. B: Environ.* 2019, 240, 319-328.
- (4) Huang, K.; Hong, Y.; Yan, X.; Huang, C.; Chen, J.; Chen, M.; Shi, W.; Liu, C. Hydrothermal Synthesis of g-C<sub>3</sub>N<sub>4</sub>/CdWO<sub>4</sub> Nanocomposite and Enhanced Photocatalytic Activity for Tetracycline Degradation under Visible Light. *CrystEngComm* 2016, *18*, 6453-6463.
- (5) Zhang, M.; Lai, C.; Li, B.; Huang, D.; Liu, S.; Qin, L.; Yi, H.; Fu, Y.; Xu, F.; Li, M.; Li, L. Ultrathin Oxygen-Vacancy Abundant WO<sub>3</sub> Decorated Monolayer Bi<sub>2</sub>WO<sub>6</sub> Nanosheet: a 2D/2D Heterojunction for the Degradation of Ciprofloxacin under Visible and NIR Light Irradiation. *J. Colloid Interface Sci.* **2019**, *556*, 557-567.
- (6) Li, S.; Hu, S.; Jiang, W.; Zhang, J.; Xu, K.; Wang, Z. In Situ Construction of WO<sub>3</sub> Nanoparticles Decorated Bi<sub>2</sub>MoO<sub>6</sub> Microspheres for Boosting Photocatalytic Degradation of Refractory Pollutants. *J. Colloid Interface Sci.* **2019**, *556*, 335-344.
- (7) Jia, J.; Jiang, C.; Zhang, X.; Li, P.; Xiong, J.; Zhang, Z.; Wu, T.; Wang, Y. Urea-

Modified Carbon Quantum Dots as Electron Mediator Decorated g-C<sub>3</sub>N<sub>4</sub>/WO<sub>3</sub> with Enhanced Visible-Light Photocatalytic Activity and Mechanism Insight. *Appl. Surf. Sci.* **2019**, *495*, 143524.

(8) Huo, P.; Tang, Y.; Zhou, M.; Li, J.; Ye, Z.; Ma, C.; Yu, L.; Yan, Y. Fabrication of ZnWO<sub>4</sub>-CdS Heterostructure Photocatalysts for Visible Light Induced Degradation of Ciprofloxacin Antibiotics. *J. Ind. Eng. Chem.* **2016**, *37*, 340-346.