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Supplementary Materials

Insight on the rapid degradation of antibiotic rifampicin by W-doped O-bridged g-C_3N_4 via coupling effect of electron replenishment effect in dark degradation stage and electrophilic attack in photocatalytic stage: experiments and DFT simulation calculation

Panpan Li[1], Jingde Luan[1]*, Longde Jiang[1], Yu Zhang[1], Wengang Liu[2], Zheng Yan[1], Xin Ke[1]

1 College of Energy and Environment, Shenyang Aerospace University,No.37 Daoyi South Avenue, Shenbei New Area, Shenyang 110136, P.R.China

2 School of Resources and Civil Engineering, Northeastern University, 11 Wenhua Road, Heping District, Shenyang, 110819, China

Corresponding authors: Jingde Luan*

mail address: jdluan@sau.edu.cn (Jingde Luan)

S1 Electrochemical test

The current i-t curve and electrochemical impedance spectroscopy (EIS) were measured in 0.1 mol/L Na_2SO_4 electrolyte by CHI660E electrochemical workstation. A three-electrode system was adopted in the test, with platinum wire electrode (Pt) as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The sample was dissolved in anhydrous ethanol and evenly coated on 1×1 cm^2 glass carbon sheet (GCE) as the working electrode. In the frequency range of 0.01-10^5 Hz, the Mott-Schottky plot was measured. The current i-t curve is tested using 300W xenon lamp with filter ($\lambda \geq 400$ nm) as light source, tin foil plate as a shading plate, 30 s darkness and 30 s illumination alternately.

S2 LC-HRMS test

LC-HRMS test was performed on Shimadzu 30A using waters C18 Column (120A, 1.7 μm, 2.1 mm × 100 mm) at a temperature of 35℃. The mobile phase consisted of 0.1% formic acid water (A) and acetonitrile (B), and the injection volume was 10 μL.

High-resolution mass spectrometry was performed on the AB SCIEX Triple Tof 5600 (time-of-flight mass spectrometry) mass spectrometer, using Analyst TF 1.8 Software for information acquisition and SCIEX OS software for data analysis. The species structure was determined by reference to AB's small molecule database. The test was performed in positive/negative mode (TOF MS IDA) with a scanning range of 40-1000 DA.

The liquid to be detected is the clarified liquid that reacts for 8 minutes (the end of dark reaction), 20 minutes and 40 minutes (the end of photodegradation reaction) under the optimal working condition. 400 nm < λ < 800 nm; catalyst amount 10 mg; C_0 = 150 mg/L; volume

100 mL.

S3 The construction of computational model

(1) SEM images confirmed that the as-prepared CN and WOCN in this work exhibit as stacked block structure with flakes, rather than a stripped monolayer structure. Therefore, it is more reasonable to use a double-layer structure to investigate the effect of modification on the interlayer charge transfer, according to the relevant researches [1, 2].

(2) By calculating the peak area of each valence in the W 4f spectrum of WOCN sample, it can be found that the proportion of W^{6+} (42.0%) and W^{5+} (46.9%) is far higher than that of W^{4+} (11.1%), revealing that W^{5+} and W^{6+} are the main valence states of W element [3, 4]. Thus, the valence states of two W atoms in the model are set to be +6 (W1) and +5 (W2) in DFT calculation, respectively.

S4 Regeneration performance of as-prepared photocatalyst

(1) As shown in Fig. 3h, the characteristic peaks of W-O and W-N bonds in regenerated $WOCN_6$-2 are obviously blue-shifted compared to the original $WOCN_6$-2, indicating a decrease in electron density near the two functional groups, corresponding to the change of W valence state [5, 6]. The W-O absorption peaks at 878 cm^{-1} and 737 cm^{-1} are significantly weakened, which is caused by the conversion of some O atoms into CO, CO_2 and other gases in the regeneration calcination.

(2) Seen from Fig.S5, the transient current signal of the regenerated sample shows a significant decrease under light irradiation, indicating that the electron transfer ability was weakened compared to the original $WOCN_6$-2. However, the current intensity of the

regenerated sample is still higher than that of CN, suggesting a stronger charge transfer ability and catalytic activity [3].

S5 Figures

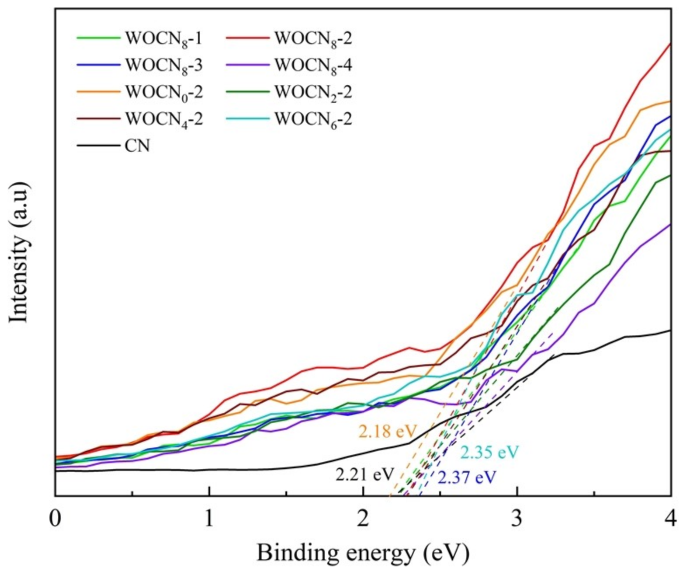


Figure S1 XPS-VB spectra of asprepared catalysts.

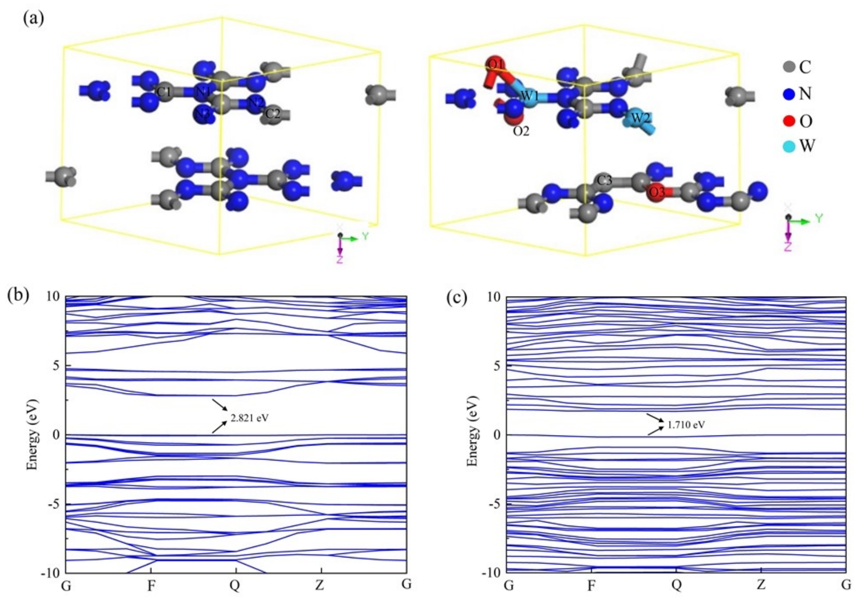


Figure S2 (a) The structure models and (b) - (c) calculated band structures of the CN and $WOCN_6$-2.

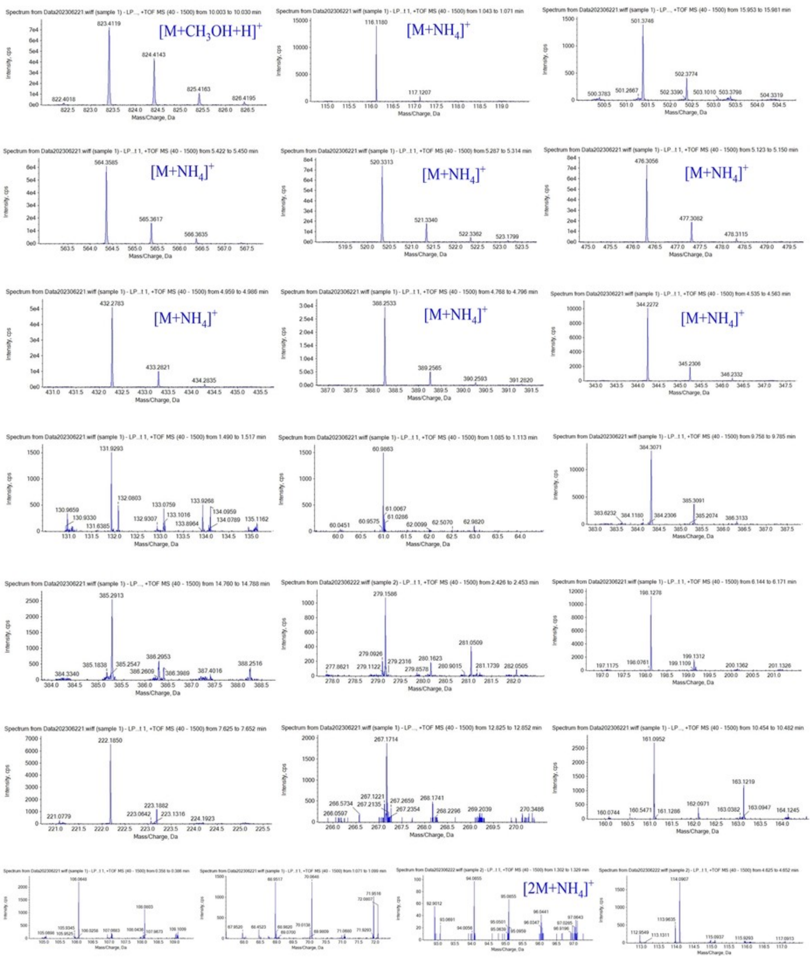


Figure S3 LC-HRMS analysis results of dark degradation of RIF by $WOCN_6$-2 for 8 minutes.

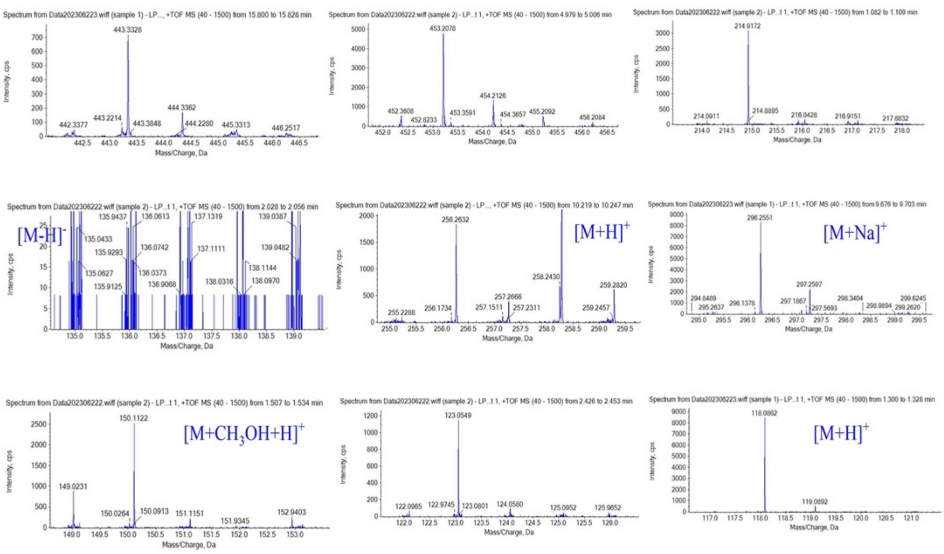


Figure S4 LC-HRMS analysis results of photodegrades of RIF by $WOCN_6$-2 for 20 minutes and 40 minutes.

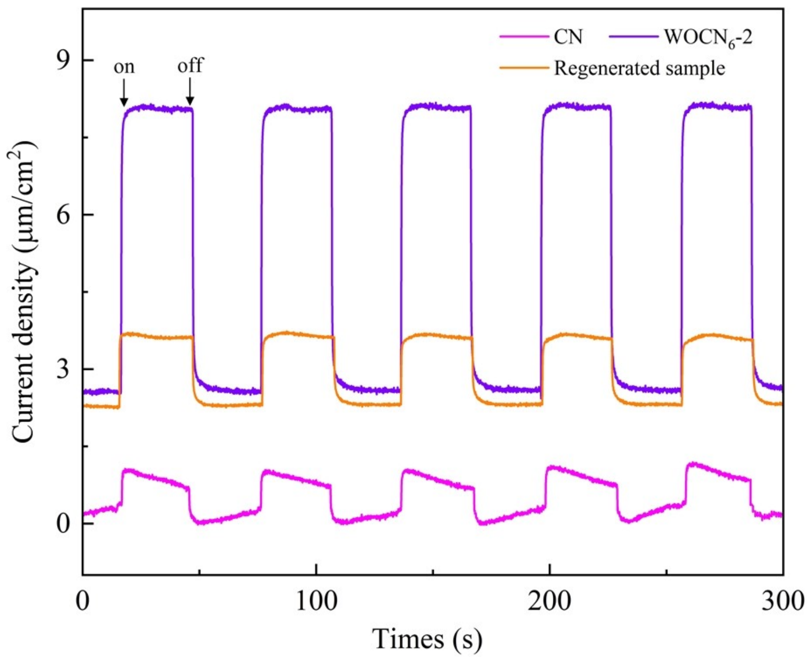


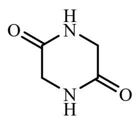
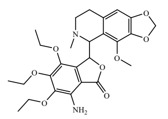
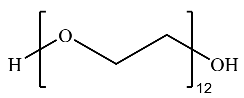
Figure S5 i-t spectra of original $WOCN_6$-2 and regenerated samples

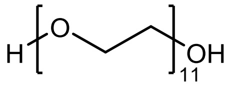
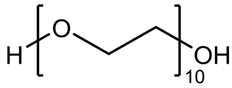
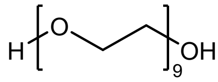
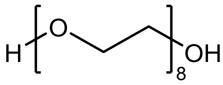
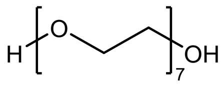
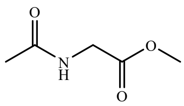
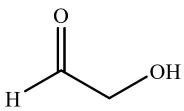
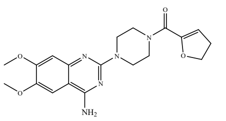
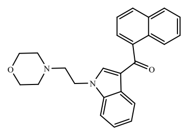
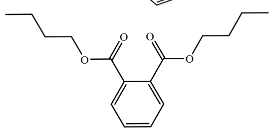
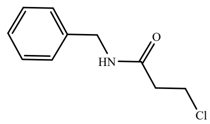
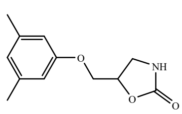
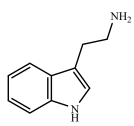
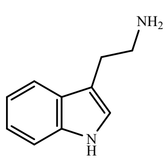
S6 Tables

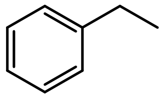
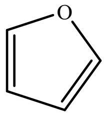
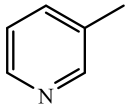
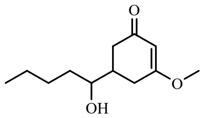
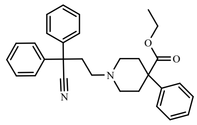
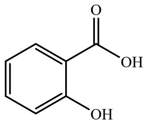
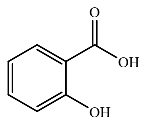
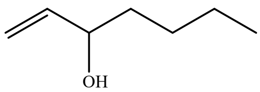
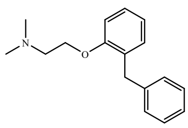
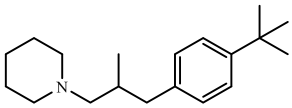
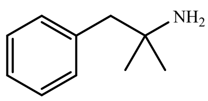
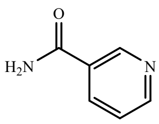
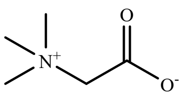
Table S1 The specific surface area and average aperture of CN and $WOCN_6$-2.

	BET Surface Area (cm^2/g)	average pore diameter (nm)
CN	70.90	7.78
$WOCN_6$-2	51.52	9.61

Table S2 Number and structure of possible intermediates in RIF degradation.

number	m/z	structural formula	name
A	116 $[M+NH_4]^+$		piperazine-2,5-dione
B	501		Tritoqualine
C	564 $[M+NH_4]^+$		PEG-12

C1	520 $[M+NH_4]^+$		PEG-11
C2	476 $[M+NH_4]^+$		PEG-10
C3	432 $[M+NH_4]^+$		PEG-9
C4	388 $[M+NH_4]^+$		PEG-8
C5	344 $[M+NH_4]^+$		PEG-7
D	133		methyln - acetylglycinate
E	61		Glycolaldehyde
F	384		prazosin
G	385		JWH-200
H	279		dibutyl phthalate
I	198		beclamide
J	222		metaxalone
K	267		Zinniol
L	161		tryptamine

M	106		ethylbenzene
N	69		furan
O	94		3-methylpyridine
P	443		epicatechin-gallate
Q	453		Diphenoxylate
R	215		Pestalotin
S	137[M-H] $^-$		Salicylic acid
T	114		hept-1-en-3-ol
U	256 [M+H] $^+$		phenyltoloxamine
V	296 [M+Na] $^+$		enpropidin
W	150 [M+ CH_3OH +H] $^+$		phentermine
X	123		nicotinamide
Y	118 [M+H] $^+$		betaine

76 **Table S3** Comparison of photocatalytic performance between W-doped O-bridged $g-C_3N_4$ and the previously reported carbon nitride

Photocatalyst	Light source	Pollutant	Dosage	Reaction time	Removal rate	References
rh-In_2O_3 Nanocrystals	UV lamp Light (intensity Iinc 0.82 mW/cm^2)	10 mg/L Rifampin	0.1 g/L	120 minutes	94%	[7]
TiO_2/graphene composite nanofiber photocatalysts	UVC-Philips lamp	30 mg/L Rifampin	0.5 g/L	300 minutes	87%	[8]
CdS-ZnS coupled system	100 W W-lamp	8 mg/L Rifampin	0.5 g/L	120 minutes	98%	[9]
$ZnIn_2S_4$	100 W iodogallium lamp (350-450 nm)	10 mg/L Rifampin	0.05 g/L	90 minutes	100%	[10]
$MoSe_2$ -polypyrrole nanocomposite	In dark	10 mg/L Congo Red	0.2 g/L	30 minutes	50%	[11]
6%-CuS/$g-C_3N_4$	In dark (0.5 mL 30% H_2O_2)	30 mg/L RhB	0.4 g/L	60 minutes	74%	[12]
W-doped O-bridged $g-C_3N_4$	In dark + 300 W Xenon lamp (≥ 400nm)	150 mg/L Rifampin	0.1 g/L	dark 8 minutes light 40 minutes	91%	in this work
	In dark	10 mg/L Rifampin	0.1 g/L	5 minutes	100%	

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