

Supporting Information

Metal–organic complex derived 3D porous carbon supported g-C₃N₄/TiO₂ as photocatalysts for efficient degradation of antibiotic

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1. Experimental section

1.1 Materials

Melamine, 2,6-pyridine diformaldehyde, p-methoxyaniline, melamine sponge and solvents were purchased from commercial sources and were used without further purification. All other reagents used in this research were analytically pure and used without further purification.

1.2 X-ray crystallography

The single-crystal X-ray diffraction data for the two compounds were collected on a Rigaku R-AXIS RAPID IP or a Siemens SMART 1000 CCD diffractometer using

graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structures were resolved by direct methods and refined on F^2 by the full-matrix least squares using the SHELXTL-2014 crystallographic software. Anisotropic thermal parameters were refined to all of the non-hydrogen atoms. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode included water molecules. Topological analyses were performed with ToposPro software.

1.3 Preparation and characterization of catalysts

The morphologies of the g-C₃N₄/TiO₂/CNOT-0 (termed as g-C₃N₄/TiO₂ in the following part), g-C₃N₄/TiO₂/CNOT-5, g-C₃N₄/TiO₂/CNOT-10, and g-C₃N₄/TiO₂/CNOT-15 samples were performed by the field emission scanning electron microscope (FESEM, Hitachi SU-8010), transmission electron microscope (TEM, Hitachi HT-7700) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100F). The BET surface area measurements were recorded by a Micrometrics surface area and porosity analyzer (ASAP 2020) at liquid nitrogen temperature (77 K). The X-ray diffraction (XRD) patterns were obtained on X-ray diffractometer (Rigaku D/max-2400) using a Cu K α_1 radiation ($\lambda = 0.15418 \text{ nm}$) at 40 kV and 200 mA. In order to minimize re-absorption effects absorbencies in the 10 mm fluorescence cuvette were kept under 0.05 at the excitation wavelength. The emission properties were recorded with Edinburgh FLS 920 fluorescence spectrometer. A Perkin–Elmer Lambda 35 spectrometer was used to measure the UV–vis absorption spectra of g-C₃N₄/TiO₂, g-C₃N₄/TiO₂/CNOT-5, g-C₃N₄/TiO₂/CNOT-10, and g-C₃N₄/TiO₂/CNOT-15. The photo-electrochemical measurements were measured on a CHI-660B electrochemical workstation. The active species of degradation were detected based on the electron paramagnetic resonance spectrometer (EPR, JEOL JES-FA200 spectrometer).

1.4 Chlortetracycline hydrochloride adsorption and photocatalytic experiments

Chlortetracycline hydrochloride (CTC-HCl) adsorption was conducted in the dark in a 50 mL Erlenmeyer flask. The as-prepared samples (0.02 g) were respectively added to 100 mL CTC-HCl (10 mg/L) seawater solution and shaken at a speed of 200 r/min at 25 °C. A 2 mL aliquot of the suspension was taken at intervals. The CTC-HCl concentration was analyzed by a high performance liquid chromatography (HPLC, SHIMADZU LC-16) with a UV detector at 344 nm. The mobile phase was composed of acetonitrile and 0.05 mol/L KH_3PO_4 (volume ratio: 30:70), and the flow rate was 1 mL/min.

The photocatalytic performance of the as prepared samples were evaluated by removing CTC-HCl. A 300 W Xenon lamp (PLSSXE300UV, Beijing Perfect Light Co., Ltd.) with a 420 nm cut-off filter used as the visible-light source. Typically, 20 mg photocatalyst was dispersed in a quartz reactor containing 100 mL CTC-HCl (10 mg/L) solution. Prior to visible-light irradiation, the suspensions were stirred in the dark for 1 h to reach the adsorption-desorption equilibrium. During the process, 2 mL of the suspension was extracted at given intervals. Finally, the concentration of CTC-HCl was measured by HPLC.

The continues flow reaction performance of the $\text{g-C}_3\text{N}_4/\text{TiO}_2$, $\text{g-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT-5}$, $\text{g-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT-10}$, and $\text{g-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT-15}$ were evaluated by removing CTC-HCl in seawater (10 mg/L), which conducted in a self-made reactor. A peristaltic pump (Longer Precision Pump Co., Ltd. BT100-2J) was used to provide fresh solution and control the solution flow rate (2 mL/min). A 300 W xenon lamp with a 420 nm cut-off filter was placed above the reactor (15 cm) as the visible light source. 0.1 g photocatalysts were packed into the reactor. The reactor can contained about 10 mL solution. At the beginning of the photocatalytic experiment, the peristaltic pump and

xenon lamp were opened at the same time. 2 mL of the solution was collected at the given time intervals. The CTC-HCl concentration was analyzed by HPLC.

1.5 The detection experiments of active species

The active species of the g-C₃N₄/TiO₂, g-C₃N₄/TiO₂/CNOT-5, g-C₃N₄/TiO₂/CNOT-10, and g-C₃N₄/TiO₂/CNOT-15 samples were investigated by employing various scavengers into the CTC-HCl solution under visible light irradiation. The experimental process was similar to the static degradation experiment. Naturally, the static degradation experiment of CTC-HCl was repeated by adding 1 mmol benzoquinone (BQ) as a superoxide radical scavenger ($\cdot\text{O}_2^-$), 1 mmol tert-butyl alcohol (TBA) as a hydroxyl radical scavenger ($\cdot\text{OH}$) and 1 mmol formic acid as a hole (h^+) scavenger.

1.6 Photoelectrochemical measurements

The CHI-660B electrochemical workstation was used to measure the photocurrent performance under visible light based on the standard three-electrode electrochemical system. The working electrode was prepared by a dipping coating method. The 2 mg as-prepared samples were dispersed into 1 mL of deionized water to form a uniform slurry after 30 min of ultrasonic processing. The slurry was dip-coated on a piece of ITO glass (2 cm × 4 cm), then dried at room temperature for 24 h. ITO glass deposited with photocatalyst, platinum wire, and saturated calomel were respectively used as working electrode, a counter electrode and reference electrode. The electrolyte solution was the 0.1 M Na₂SO₄ aqueous solution.

2. The supplement of characterization analysis

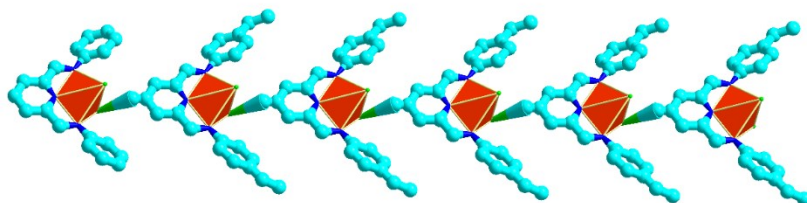


Figure S1. 1D chain structure of MOC.

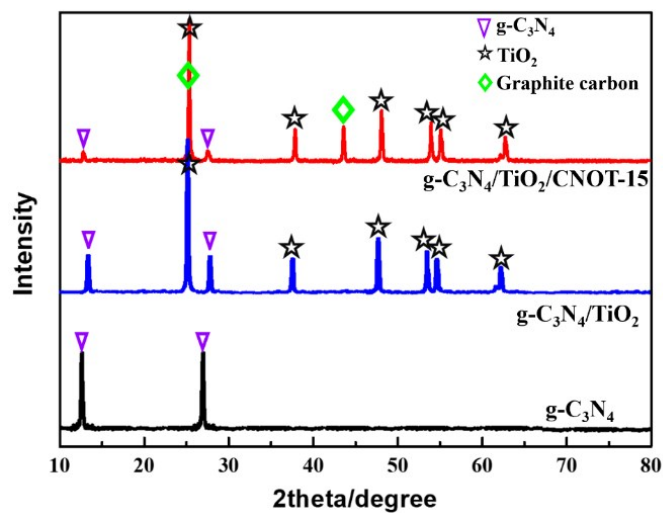


Figure S2. XRD patterns of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4/\text{TiO}_2$ and $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT-15}$.

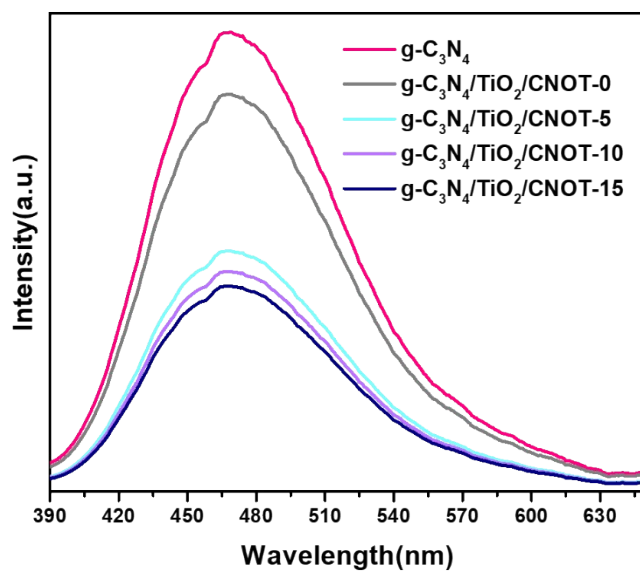


Figure S3. Photoluminescence (PL) spectra of the $g\text{-C}_3\text{N}_4/\text{TiO}_2$ and $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT}$.

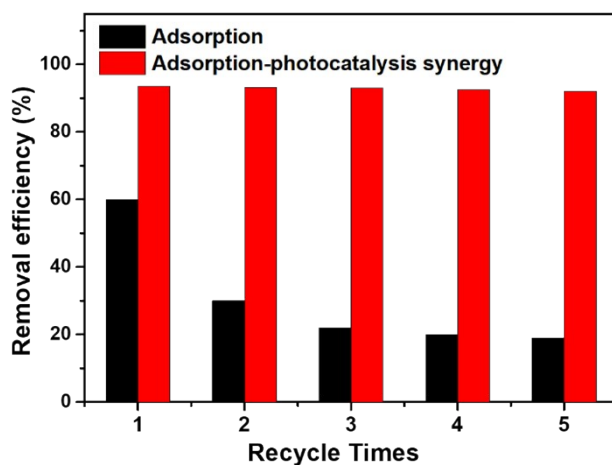


Figure S4. Recycling runs of the $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT-15}$ in removing CTC-HCl.

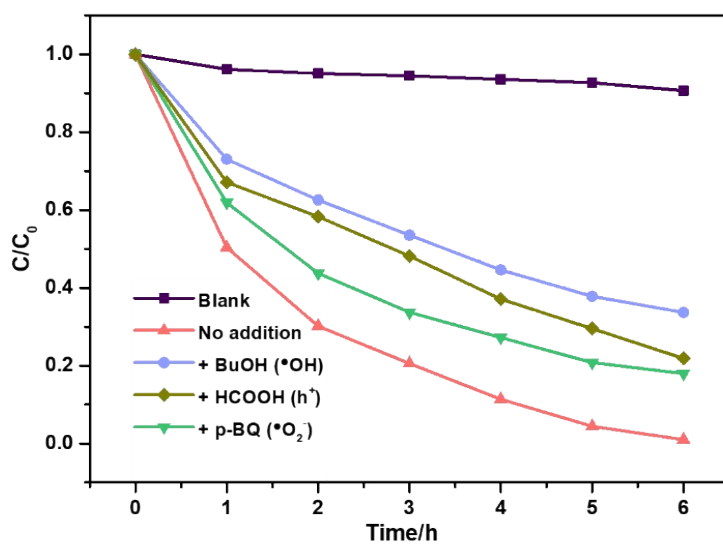


Figure S5. Radical trapping experiments of $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT-15}$.

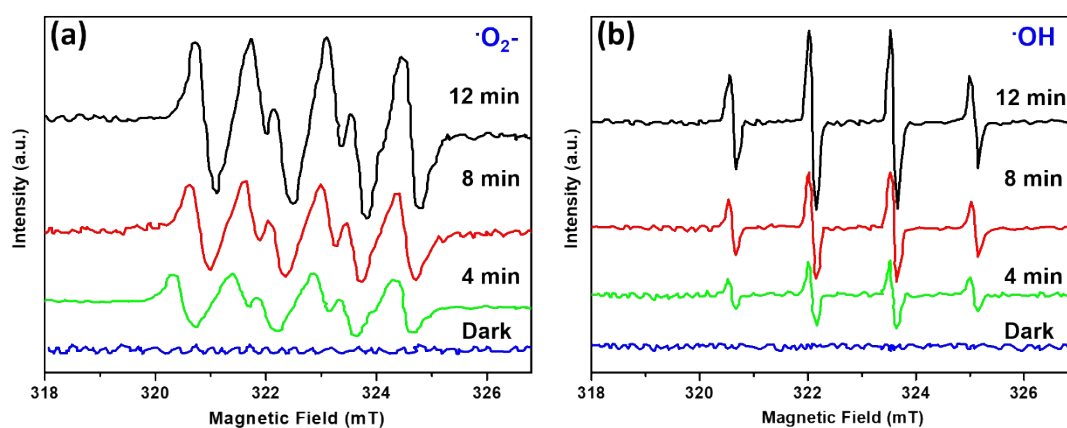


Figure S6. Electron spin resonance spectroscopy spectra of the $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{CNOT-15}$. (a) Signal intensity of $\text{DMPO}\cdot\text{O}_2^-$. (b) Signal intensity of $\text{MPO}\cdot\text{OH}$.

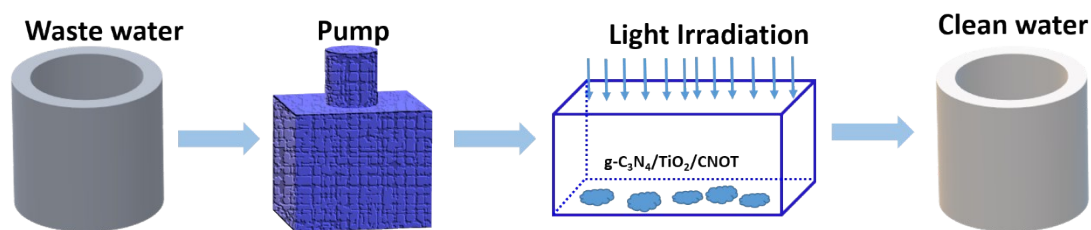


Figure S7. Synergy effect of adsorption pre-concentration and subsequent photocatalytic degradation through g-C₃N₄/TiO₂/CNOT samples.

Table S1. Crystallographic and structural data for MOC.

	MOC
CCDC No.	2023896
Formula	C ₂₅ H ₃₃ ZnCl ₂ N ₅ O ₂
<i>Mr</i>	571.83
Crystal system	Triclinic
Space group	'C2/c'
<i>a</i> [Å]	11.749(3)
<i>b</i> [Å]	8.961(2)
<i>c</i> [Å]	25.585(6)
α [°]	90
β [°]	101.49(3)
γ [°]	90
Volume [Å ³]	2639.7(11)
<i>Z</i>	4
<i>D</i> _c [g·cm ⁻³]	1.439
μ [mm ⁻¹]	1.165
<i>F</i> (000)	1192
Θ range [°]	2.88–32.70
<i>h</i> range	-15 ≤ <i>h</i> ≤ 17
<i>k</i> range	-13 ≤ <i>k</i> ≤ 12
<i>l</i> range	-36 ≤ <i>l</i> ≤ 36
data/restraints/params	4474 / 0 / 162
GOF	0.950
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0467, 0.1068
<i>R</i> ₁ , <i>wR</i> ₂ [all data] ^a	0.0928, 0.1358
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ [e·Å ⁻³]	0.690, -0.821

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (°) for MOC.

MOC			
Parameter		Parameter	
Zn(1)-N(3)	2.036(3)	N(3)-Zn(1)-Cl(1)#1	120.20(2)
Zn(1)-Cl(1)#1	2.2239(9)	N(3)-Zn(1)-Cl(1)	120.20(2)
Zn(1)-Cl(1)	2.2239(9)	Cl(1)#1-Zn(1)-Cl(1)	119.61(4)
Zn(1)-N(2)#1	2.303(2)	N(3)-Zn(1)-N(2)#1	74.55(5)
Zn(1)-N(2)	2.303(2)	Cl(1)#1-Zn(1)-N(2)#1	94.81(6)
O(1)-C(2)	1.350(3)	Cl(1)-Zn(1)-N(2)#1	100.62(6)
O(1)-C(1)	1.416(4)	N(3)-Zn(1)-N(2)	74.55(5)
N(2)-C(8)	1.269(3)	Cl(1)#1-Zn(1)-N(2)	100.62(6)
N(2)-C(5)	1.408(3)	Cl(1)-Zn(1)-N(2)	94.81(6)
N(3)-C(9)#1	1.327(3)	N(2)#1-Zn(1)-N(2)	149.10(10)
N(3)-C(9)	1.327(3)	C(2)-O(1)-C(1)	118.1(2)
C(8)-N(2)-C(5)	119.6(2)	C(9)#1-N(3)-Zn(1)	120.09(14)
C(8)-N(2)-Zn(1)	111.33(17)	C(9)-N(3)-Zn(1)	120.09(14)
C(5)-N(2)-Zn(1)	128.37(15)	O(1)-C(1)-H(1A)	109.5
C(9)#1-N(3)-C(9)	119.8(3)	O(1)-C(1)-H(1B)	109.5

Table S3. The geometrical parameters noncovalent bonding for MOC.

	X-H...Y	X-H/Å	H...Y/Å	X...Y/Å	dimension	topology	point symbol
MOC	C7-H7...Cl2	0.9300	2.8915	3.8188	3D	<i>dia</i>	{6 ⁶ }
	C11-H11...Cl2	0.9302	2.8782	3.6242			
	C3-H3...O1	0.9286	2.5915	3.4322			

^a Between the phenanthroline ring and benzene ring; C_{gt} = phenanthroline ring.

Table S4. Pore parameters of prepared photocatalysts from N₂ adsorption

Samples	S_{BET} ^a	S_{mic} ^b	V_t ^c	V_{mic} ^d	$V_{meso-macro}$ ^e	D^f
	(m ² g ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(nm)
g-C ₃ N ₄ /TiO ₂ /CNOT-0	182.1	131.3	0.152	0.069	0.083	3.33
g-C ₃ N ₄ /TiO ₂ /CNOT-5	1111.6	897.0	1.036	0.471	0.565	3.73
g-C ₃ N ₄ /TiO ₂ /CNOT-10	1518.8	1081.7	1.376	0.680	0.696	3.62
g-C ₃ N ₄ /TiO ₂ /CNOT-15	1644.1	1370.8	1.607	0.776	0.831	3.91

^a Calculated by the BET model from the adsorption branches of the isotherms.

^b Calculated from t-plot method.

^c Calculated from adsorption data at P/P₀ = 0.982.

^d Calculated from t-plot method.

^e Calculated by c minus d.

^f Calculated from $4 V_t / S_{BET}$.