

Electronic Supplementary Information

Facile and Efficient Photocatalyst for Degradation of Chlortetracycline Promoted by H₂O₂

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Section 1. Experimental section

Materials and Methods

1,3,5-tris(4-carboxyphenoxy)benzene was purchased from Jinan Henghua Sci. & Tec. Co. Ltd. of China. All of the solvents and other reagents were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) measurements were measured on a Bruker D8 Advance X-ray diffractometer employing Cu-K α radiation with a 2θ value ranging from 5 to 60°. Thermogravimetric analysis (TGA) and DTA were carried out using a DuPont thermal analyzer from room temperature to 800° with a heating rate of 10 K min⁻¹ in a flowing nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were recorded on a BRUKER TENSOR27 spectrometer with KBr disks in the range of 400 to 4000 cm⁻¹. The morphology was measured on a ZEISS EVO 18, a field emission scanning electron microscope (FE-SEM). The Brunauer-Emmett-Teller (BET) surface area test was measured by a Quantachrome-AUTOSORB IQ instrument. The light absorption spectra were recorded on a TU-1950 UV-vis spectrophotometer using fine BaSO₄ powder as the reference standard. The photoluminescence spectra for samples were obtained on a FluoroMax-4 spectrophotometer. The electrochemical impedance spectra (EIS), Mott-Schottky curves, and Transient photocurrent responses were measured on an electrochemical workstation. The measurement was performed in a conventional three-electrode system, with a photocatalysts-coated FTO electrode as the working electrode, Pt plate as the counter electrode, and Ag/AgCl electrode as the reference electrode, respectively. Ultraviolet Photoelectron Spectroscopy was performed on an Thermo ESCALAB 250XI. Liquid chromatography-mass spectrometry (LC-MS, Thermo Scientific Q Exactive) was used to detect the intermediates of chlortetracycline in photocatalytic degradation.

Synthesis of MOF [Ce₂(tcpb)₂(DMF)(H₂O)]_n (MOF-1 or 1)

Ce(NO₃)₃·6H₂O (35.3mg, 0.1mmol), H₃tcpb (48.6 mg, 0.1 mmol), distilled water (2.0 mL), C₂H₅OH (3.0 mL), and *N,N*-dimethylformamide (DMF) (2.0 mL) were stirred for 30 min, and the mixture was subjected to solvothermal conditions in a Teflon-lined stainless-steel autoclave for 72 h at 120°C. After cooling to room temperature, colorless block-shaped

crystals were obtained. The product was washed with distilled water and dried in the air, with a 42% yield based on H₃tcpb. Analysis calculated for [Ce₂(tcpb)₂(DMF)(H₂O)]_n: C 51.30, H 3.12, N 2.03; found: C 51.23, H 3.08, N 1.98. IR (KBr, ν/cm^{-1} ; s = strong, m = medium, and w = weak): 3427m, 1935w, 1651s, 1600s, 1538s, 1505s, 1452m, 1410s, 1350m, 1230s, 1170s, 1113w, 1007w, 785s, 711m, 623w, 437w (Fig. 2b).

X-ray Crystallography

Crystallographic data for [Ce₂(tcpb)₂(DMF)(H₂O)]_n were collected on a Bruker SMART with a CCD area detector using Mo-K α ($\lambda=0.71073$ Å) as the radiation source. SADABS¹ was applied for absorption corrections. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the *SHELXTL*-2014.² In the processes of the refinements for **MOF-1**, coordinated DMF and H₂O molecules were found to be severely disordered, and they were refined with some occupancies based on the diffraction data and the report of element analyzes. Seriously disordered atoms and relevant distances were constrained by ISOR and DFIX instructions. Attempting to locate H atoms to the disordered H₂O molecule of **MOF-1** was unsuccessful. Therefore, H atoms of some disordered O atoms belong to an unknown or inconsistent label in CHECKCIF, but their contributions were also included in the overall formula. The topological analyzes were performed on the Topos program. Crystallographic data in CIF format are deposited on the Cambridge Crystallographic Data Center as CCDC 2094467 for **MOF-1**. Crystallographic and structure refinement data of **MOF-1** are summarized in Table S1. Selected distances and angles for **MOF-1** are given in Table S2.

Table S1. Crystal data and structure refinement parameters for **MOF-1**.

Compound	MOF-1
CCDC	2094467
Formula	C ₅₇ H ₃₉ Ce ₂ NO ₂₀
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	5.5405 (2)
<i>b</i> /Å	13.7558 (6)
<i>c</i> /Å	18.1753 (8)
α /°	72.622 (1)

$\beta/^\circ$	85.278 (1)
$\gamma/^\circ$	80.859 (1)
$V/\text{\AA}^3$	1304.30 (9)
T/K	296
Z	1
R_{int}	0.053
GOF	1.01
$F(000)$	664
ρ_{calcd} (mg/m ³)	1.704
μ , mm ⁻¹	1.81
R_1/wR_2 ($I > 2\sigma(I)$) ^a	0.0431/0.1096
R_1/wR_2 (all data) ^b	0.0559/0.1171
$\rho_{max,min}$, e(e \AA^{-3})	1.319/-0.575

$${}^a R_1 = \sum \left| |F_o| - |F_c| \right| / \sum |F_o| \quad {}^b wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$$

Table S2. Selected distances (Å) and angles (°) for MOF-1.

O10—Ce1	2.527 (10)	Ce1—O6 ⁱ	2.411 (4)	Ce1—O7 ^{iv}	2.514 (4)
O11—Ce1	2.517 (9)	Ce1—O2 ⁱⁱ	2.449 (4)	Ce1—O7 ^v	2.576 (4)
Ce1—O1	2.366 (4)	Ce1—O8 ⁱⁱⁱ	2.482 (5)	Ce1—O9 ⁱⁱⁱ	2.687 (5)
O1—Ce1—O6 ⁱ	165.19(15)	O6 ⁱ —Ce1—O11	111.8 (3)	O2 ⁱⁱ —Ce1—O7 ^v	73.89 (13)
O1—Ce1—O2 ⁱⁱ	90.07 (14)	O2 ⁱⁱ —Ce1—O11	68.8 (2)	O8 ⁱⁱⁱ —Ce1—O7 ^v	139.77 (17)
O6 ⁱ —Ce1—O2 ⁱⁱ	85.16 (14)	O8 ⁱⁱⁱ —Ce1—O11	81.3 (3)	O7 ^{iv} —Ce1—O7 ^v	65.86 (13)
O1—Ce1—O8 ⁱⁱⁱ	121.08 (16)	O7 ^{iv} —Ce1—O11	147.2 (3)	O11—Ce1—O7 ^v	138.0 (3)
O6 ⁱ —Ce1—O8 ⁱⁱⁱ	71.69 (15)	O1—Ce1—O10	106.6 (3)	O10—Ce1—O7 ^v	143.6 (2)
O2 ⁱⁱ —Ce1—O8 ⁱⁱⁱ	131.88 (18)	O6 ⁱ —Ce1—O10	85.1 (3)	O1—Ce1—O9 ⁱⁱⁱ	72.04 (15)
O1—Ce1—O7 ^{iv}	84.30 (14)	O2 ⁱⁱ —Ce1—O10	71.0 (3)	O6 ⁱ —Ce1—O9 ⁱⁱⁱ	120.41 (13)
O6 ⁱ —Ce1—O7 ^{iv}	90.29 (13)	O8 ⁱⁱⁱ —Ce1—O10	65.7 (3)	O2 ⁱⁱ —Ce1—O9 ⁱⁱⁱ	136.97 (15)
O2 ⁱⁱ —Ce1—O7 ^{iv}	139.75 (13)	O7 ^{iv} —Ce1—O10	148.5 (3)	O8 ⁱⁱⁱ —Ce1—O9 ⁱⁱⁱ	49.06 (15)
O8 ⁱⁱⁱ —Ce1—O7 ^{iv}	83.31 (18)	O1—Ce1—O7 ^v	82.40 (14)	O7 ^{iv} —Ce1—O9 ⁱⁱⁱ	78.51 (14)
O1—Ce1—O11	79.2 (3)	O6 ⁱ —Ce1—O7 ^v	82.80 (13)	O11—Ce1—O9 ⁱⁱⁱ	69.5 (3)
O10—Ce1—O9 ⁱⁱⁱ	77.1 (3)	O7 ^v —Ce1—O9 ⁱⁱⁱ	137.87 (14)	O1—Ce1—C27 ⁱⁱⁱ	96.90 (16)

Symmetry codes: (i) $x, y, z+1$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+2$; (iv) $x-1, y, z+1$; (v) $-x+2, -y+2, -z+1$; (vi) $x-1, y, z$; (vii) $x, y, z-1$; (viii) $x+1, y, z-1$.

Synthesis of 1/GO/Fe₃O₄

The graphene oxide (GO) and Fe₃O₄ nanoparticles were synthesized according to the method reported in references^{3,4}. Firstly, **MOF-1** (100 mg) and graphene oxide (12 mg) were dispersed in ethanol respectively and treated by ultrasonication for 15 minutes. Then, **MOF-1** dispersion (3.0 mL) and graphene oxide dispersion (10.0 mL) were mixed under reflux condition for 4 hours. Then **1/GO** can be obtained by rotating evaporation. Finally, **1/GO** (5 mg) and Fe₃O₄ (6 mg) were mixed in ethanol and treated by ultrasonication for 1 hour, and after rotating evaporation **1/GO/Fe₃O₄-5** composite was successfully synthesized. The other composites of **1/GO/Fe₃O₄-9**, **1/GO/Fe₃O₄-15** and **1/GO/Fe₃O₄-22** were prepared using the same procedure just with the weight ratio of 4:1, 8:3 and 1:1 (**MOF-1** : graphene oxide) respectively.

Evaluation of photocatalytic activity

The photocatalytic degradation of the chlortetracycline was carried out under irradiation by a solar simulator (300 W Xenon lamp) with wavelengths in the range of 320 - 780 nm and the reaction temperature was kept at 24 ± 1°C. The solution pH was adjusted with HCl or NaOH. Typically, photocatalyst was dispersed into a 20 mL chlortetracycline aqueous solution with a concentration of 20 mg L⁻¹. Before irradiation, the resultant solution was stirred magnetically in the dark for 30 minutes to establish the adsorption-desorption equilibrium between the chlortetracycline and the photocatalyst. As the equilibrium was set up, the suspension was illuminated under the solar simulator, followed by adding a known concentration of hydrogen peroxide (H₂O₂) to the mixture solution. During the photoreaction, 2 mL of the sample solution was extracted every 30 minutes and transferred for UV-analysis. Simultaneously, the same experiment was carried out without any catalyst to monitor the self-degradation of chlortetracycline. After the photocatalytic reaction, the photocatalyst was easily recovered by a magnetic field and washed with distilled water for the next cycle.

Section 2. Supplemental figures

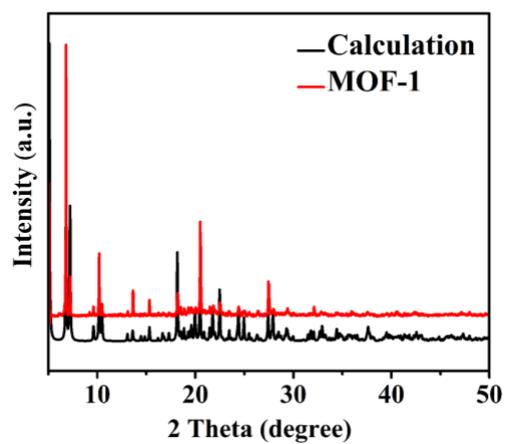


Fig. S1 PXR D patterns of **MOF-1** (calculation and experiment) at room temperature.

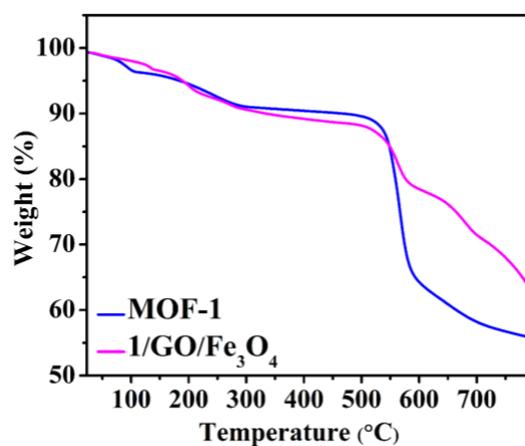


Fig. S2 TGA plots of **MOF-1** and **1/GO/Fe₃O₄**.

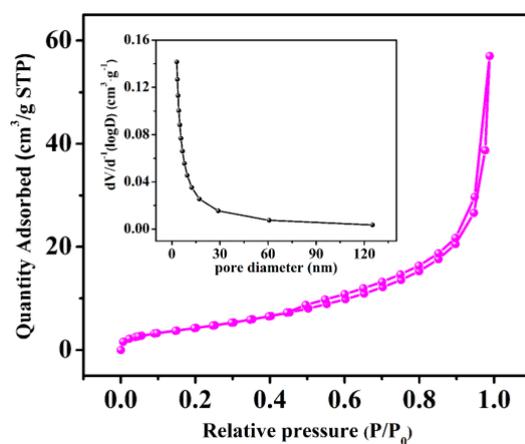


Fig. S3 N₂ adsorption-desorption isotherms and pore size distribution plots of **1/GO/Fe₃O₄**.



Fig. S4 Photographic images of the MOF-1, 1/GO, 1/GO/Fe₃O₄.

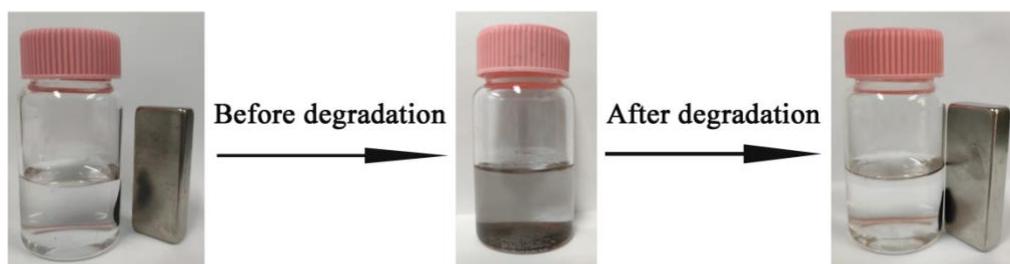


Fig. S5 Photographic images of the recovery of 1/GO/Fe₃O₄ catalyst by the magnetic field before and after degradation.

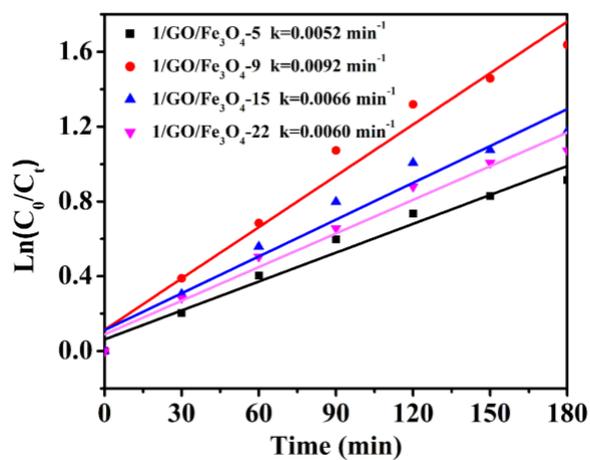


Fig. S6 First-order kinetics plots for the photodegradation of chlortetracycline by 1/GO/Fe₃O₄ under the irradiation of visible light.

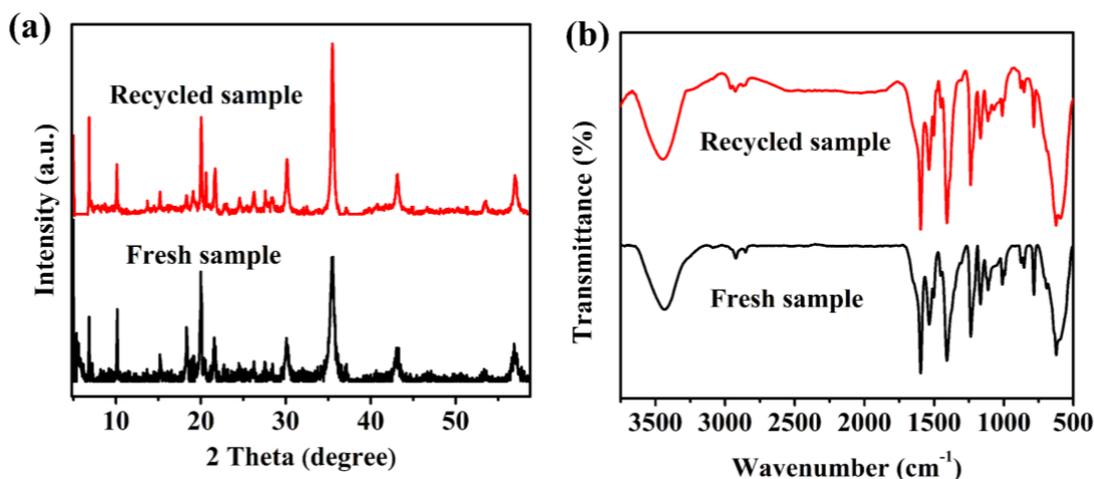


Fig. S7 (a) PXRD patterns and (b) FT-IR spectra of 1/GO/Fe₃O₄ before and after the photocatalytic reaction (solid, temperature: 25 °C).

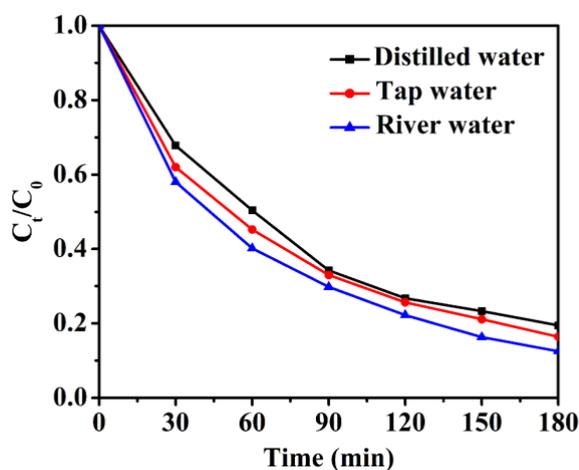


Fig. S8 Degradability of chlortetracycline by 1/GO/Fe₃O₄ in distilled water, tap water and river water. (Experimental conditions: 20 mg/L chlortetracycline, 0.45 g/L 1/GO/Fe₃O₄, and 10 mM H₂O₂).

Table S3. Water quality parameters of tap water in Shanxi University and river water in Fenhe River

Sample	Cr(VI)	Mn	Fe	Cu	Zn	As	Se	Cd	Hg	Nitrate	Sulfate
(mgL ⁻¹)											
tap	0.004	<	<	0.00076	0.0037	<	<	<	<	2.34	37.4
water		0.0005	0.010			0.0005	0.0005	0.0005	0.00005		
river	0.004	0.008	0.016	0.008	0.006	0.0003	0.0004	0.000015	0.00004	9.40	980
water											

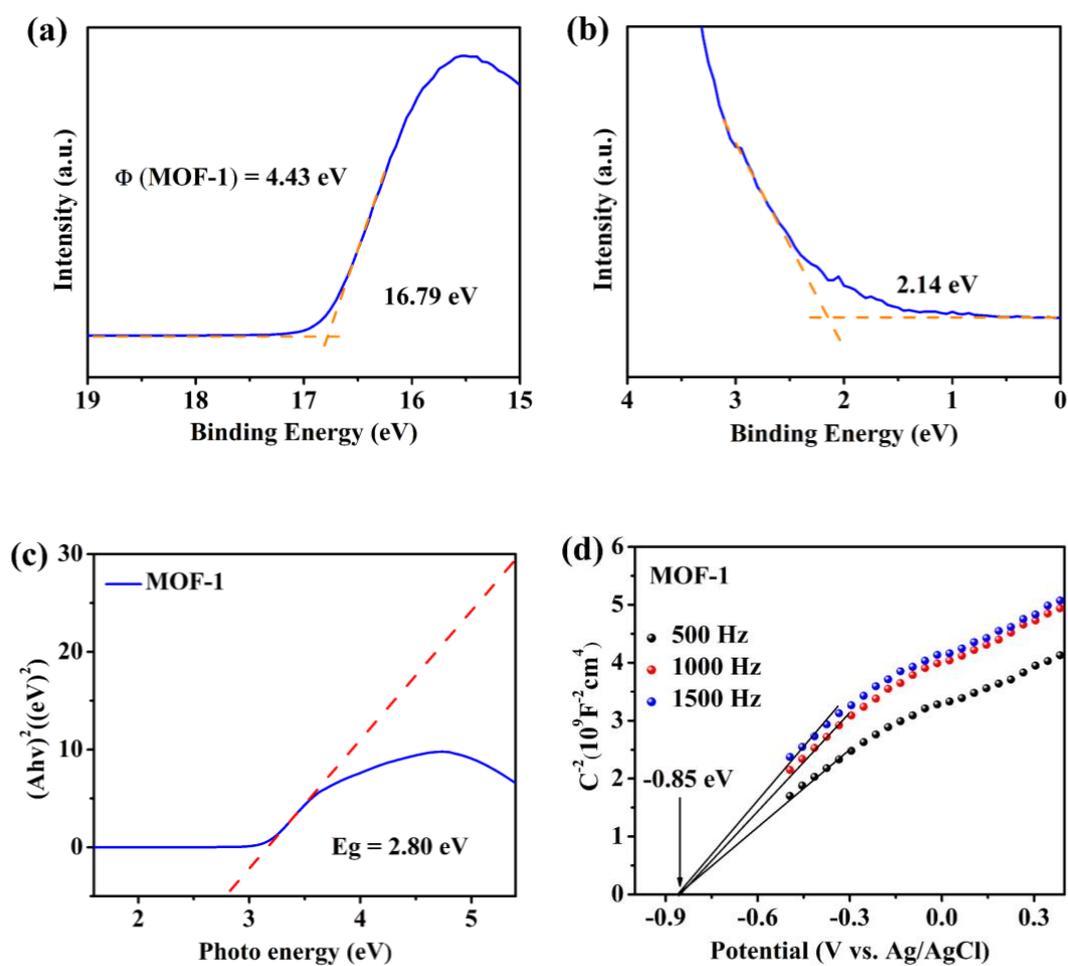


Fig. S9 (a, b) Ultraviolet photoelectron spectroscopy, (c) the band-gap, and (d) Mott-Schottky plots of MOF-1.

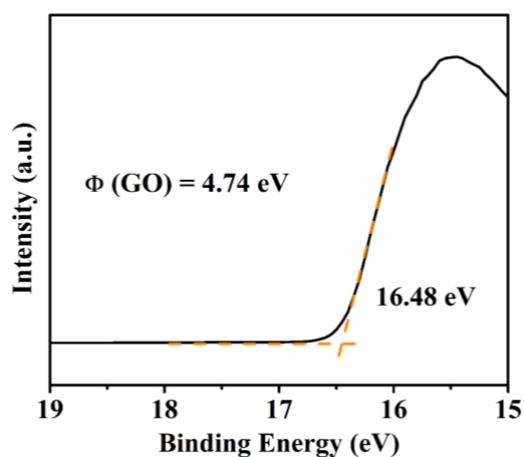
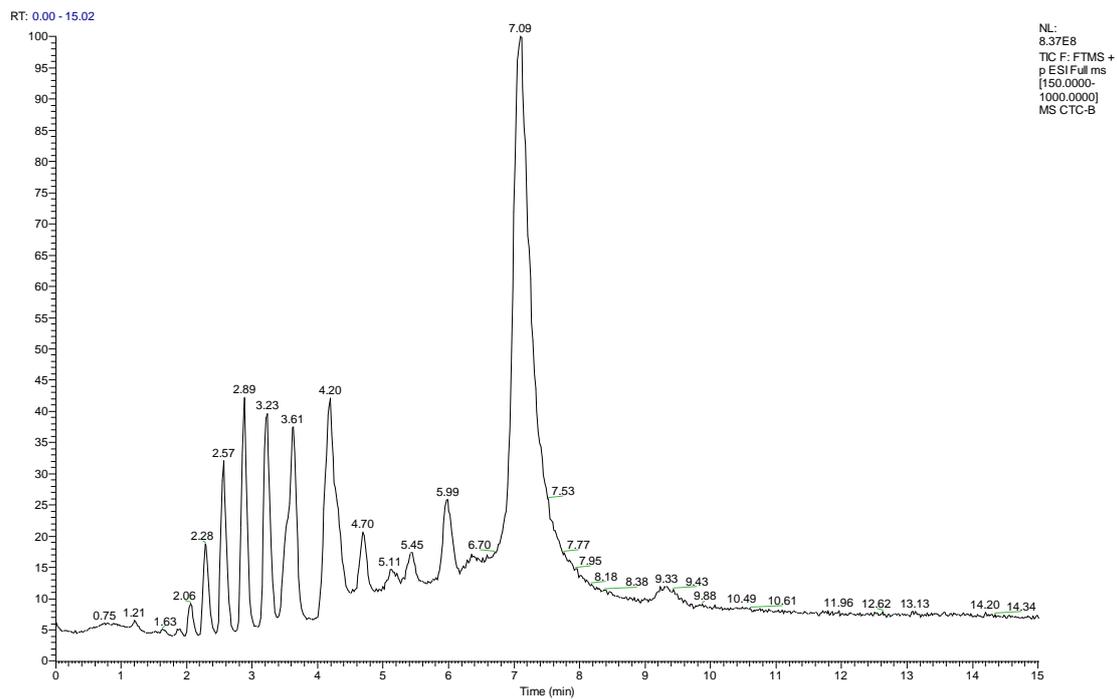
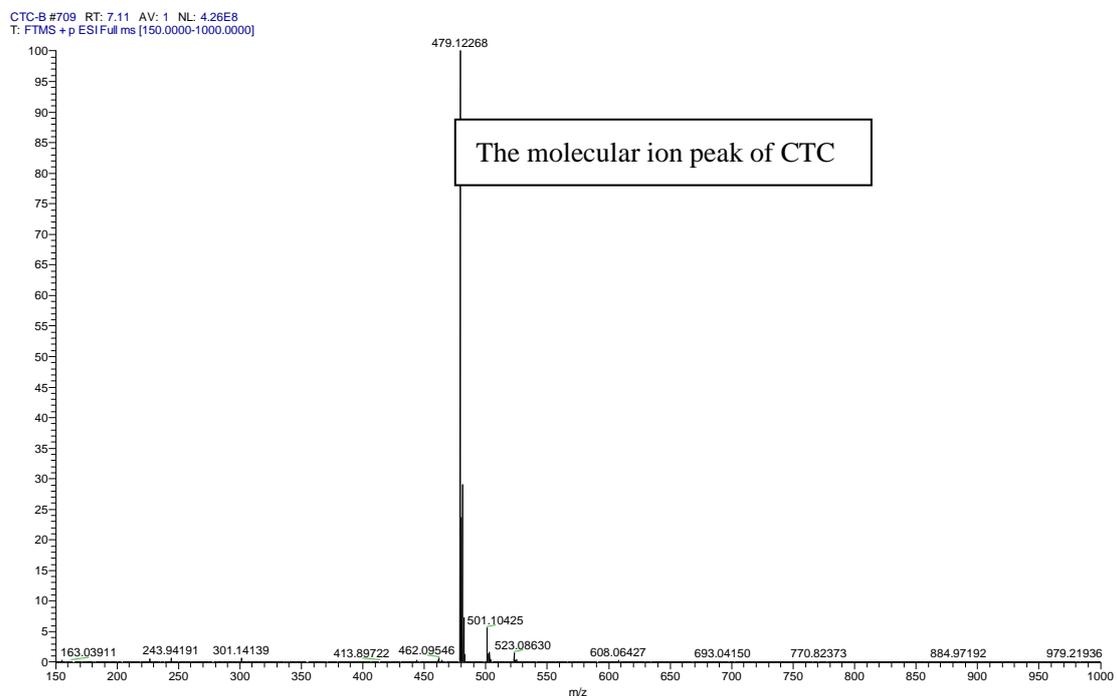


Fig. S10 Ultraviolet photoelectron spectroscopy of graphene oxide.

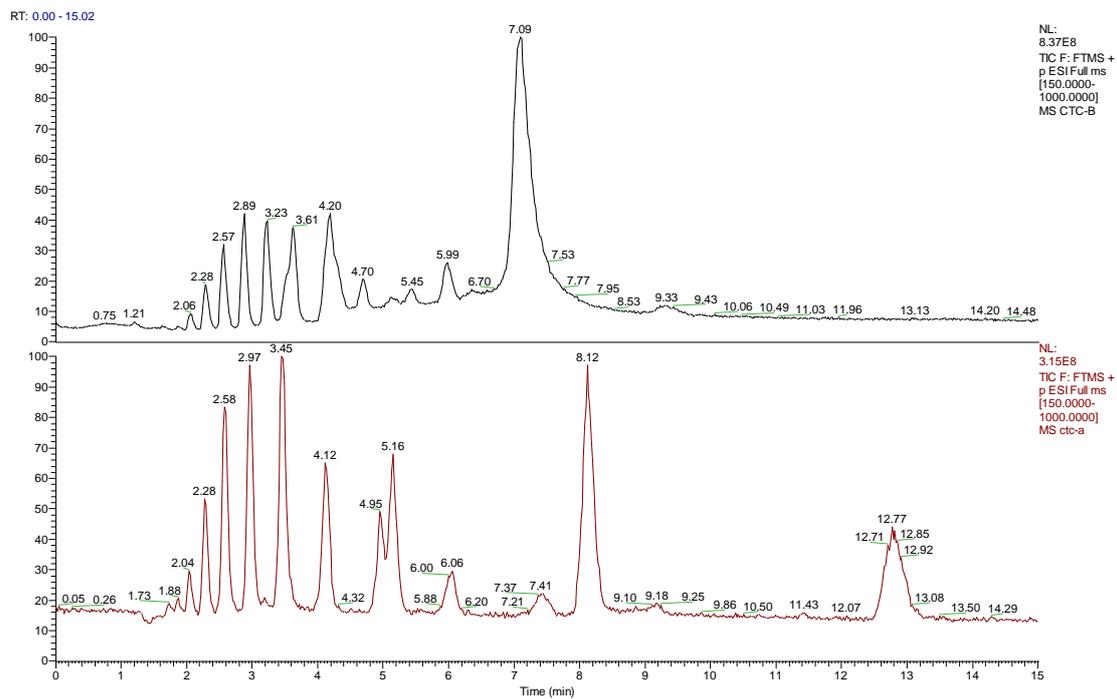
(a)



(b)

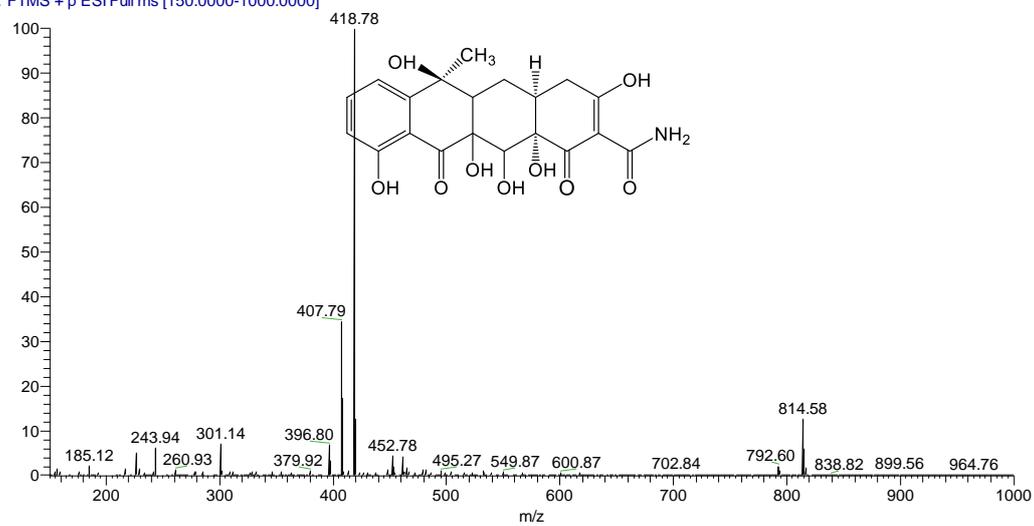


(c)



(d)

CTC-A #1249 RT: 12.77 AV: 1 NL: 3.36E7
T: FTMS + p ESI Full ms [150.0000-1000.0000]



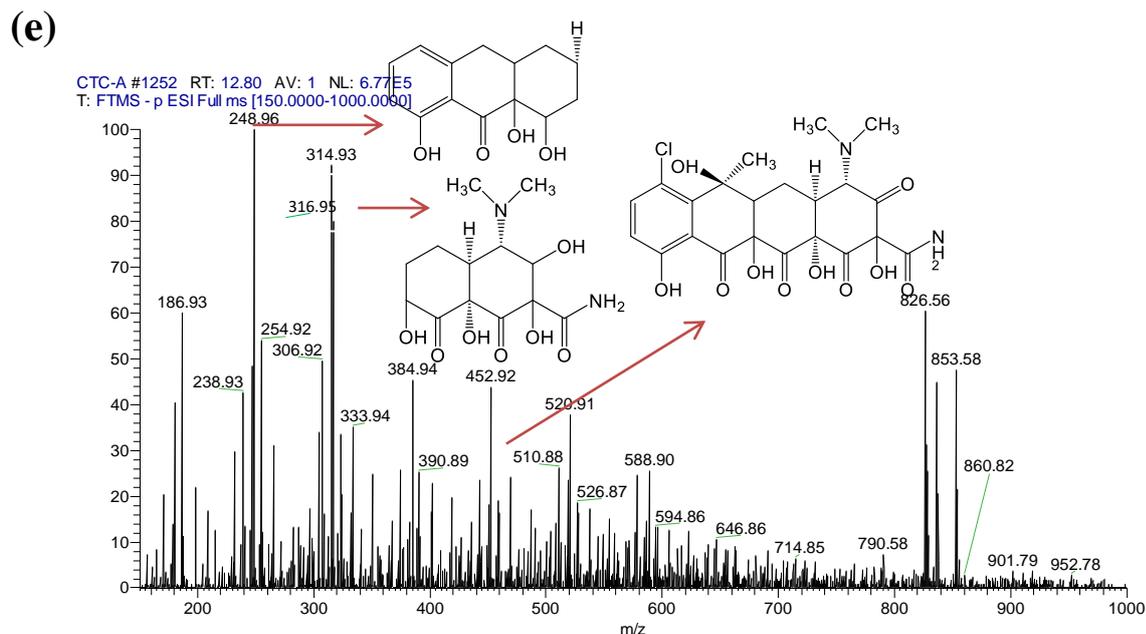


Fig. S11 (a) LC of chlortetracycline aqueous solution without the catalyst. (b) MS corresponding to the chlortetracycline (CTC) aqueous solution without the catalyst at a retention time of 7.09 min in LC. (c) LC after photocatalytic degradation of chlortetracycline aqueous solution by **1**/GO/Fe₃O₄. (d,e) MS corresponding to the degradation of chlortetracycline at a retention time of 12.77 and 12.80 min in LC respectively.

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