

## Supplementary Information

# Magnetically reusable Ce-MOF/GO/Fe<sub>3</sub>O<sub>4</sub> composite for effectively photocatalytic degradation of chlortetracycline

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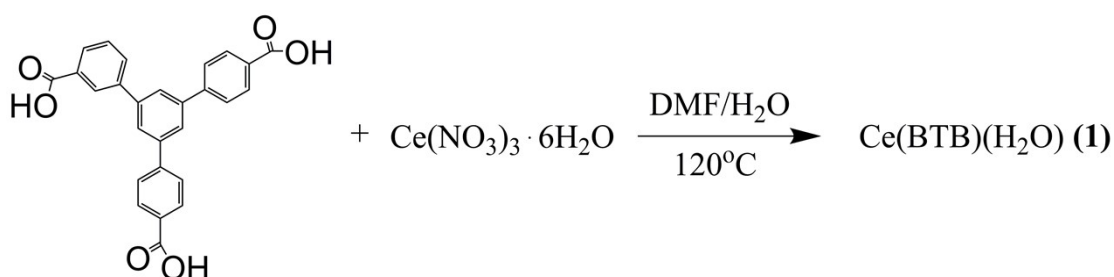
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## Experimental

### Preparation of photocatalysts

#### Preparation of MOF-1

**MOF-1** was prepared according to the reported literature.<sup>1</sup> The reaction route of **MOF-1** is shown in **Scheme S1**.  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.434 g, 1 mmol),  $\text{H}_3\text{BTB}$  (0.438 g, 1 mmol) and 20 mL *N,N'*-dimethylformamide (DMF) were placed in a 25 mL Teflon-lined steel autoclave, and the mixture was stirred at room temperature until all the solids were dissolved. One drop of triethylamine was added to the solution and kept stirring until the sediment disappears. The autoclave was sealed, heated up to 120°C and kept at this temperature for 3 days. Needle-shaped light yellow crystals were obtained.



**Scheme S1.** Synthesis route of **MOF-1**.

#### Preparation of 1/GO/Fe<sub>3</sub>O<sub>4</sub>

The GO and Fe<sub>3</sub>O<sub>4</sub> were prepared according to a method reported in references.<sup>2,3</sup>

A two-step process was developed for preparing the 1/GO/Fe<sub>3</sub>O<sub>4</sub> composite. Firstly, the 1/GO composite was prepared by treating the ethanol dispersion of **MOF-1** (100 mg) and GO (12 mg) under sonication for 15 minutes, respectively, then, mixing the dispersion and maintaining reflux at 90 °C for 4 hours. The second step was to mix the obtained 1/GO (5 mg) with Fe<sub>3</sub>O<sub>4</sub> (6 mg) into ethanol and ultrasound for 1 hour to achieve the self-assembly of three components. Finally, the powder in the suspension was collected via a centrifugal process, dried at 60°C, and denoted as 1/GO/Fe<sub>3</sub>O<sub>4</sub>-5. The other composites of 1/GO/Fe<sub>3</sub>O<sub>4</sub>-9, 1/GO/Fe<sub>3</sub>O<sub>4</sub>-15, and 1/GO/Fe<sub>3</sub>O<sub>4</sub>-22 were prepared using the same procedure just with the weight ratio of 4:1, 8:3, and 1:1 (**MOF-1:GO**) respectively.

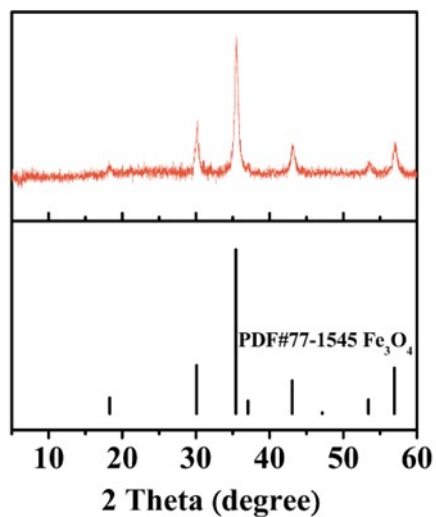
## **Materials Characterization**

The phase composition of the composite photocatalyst was measured on a Bruker D8 Advance X-ray diffractometer employing Cu-K $\alpha$  radiation with a  $2\theta$  value ranging from 5 to 60°. The Fourier transform infrared spectroscopy (FTIR) spectra were carried out using a BRUKER TENSOR27 spectrometer with KBr disks in the range of 400 to 4000 cm<sup>-1</sup>. The surface morphology and particle dimension of the prepared samples were observed by a field emission scanning electron microscope (FE-SEM) (Caisi Sigma 300). The optical properties were analyzed by UV-Vis spectrophotometer (TU-1950) using fine BaSO<sub>4</sub> powder as the reference standard. The identification of the elemental composition and chemical state in the composite was carried out by an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha+) with an Al K $\alpha$  X-ray source at 1486.6 eV. The amount of •OH and •O<sub>2</sub><sup>-</sup> produced by

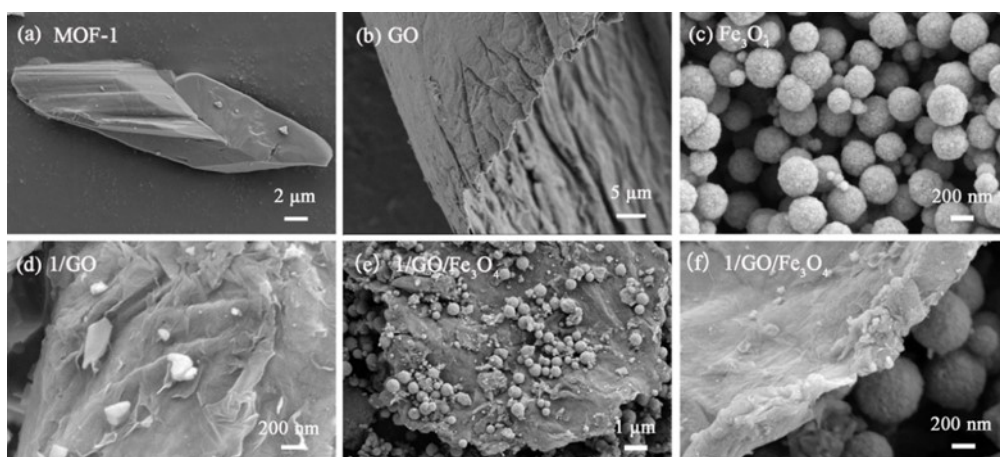
the composite in the presence of 5,5-dimethyl-1-pyrroline Noxide (DMPO) was measured by electron spin resonance (ESR). The electrochemical properties of 1/GO/Fe<sub>3</sub>O<sub>4</sub> including electrochemical impedance spectroscopy (EIS), Transient photocurrent responses (I-t), Circulating Volan Curves (CV), and Mott-Schottky spectra (M-S) were measured over an electrochemical workstation (RST5200F) with a three-electrode system. Furthermore, The intermediates during CTC photodegradation were detected with liquid chromatography-mass spectrometry (LC-MS, Thermo Scientific Q Exactive).

### **Evaluation of photocatalytic activity**

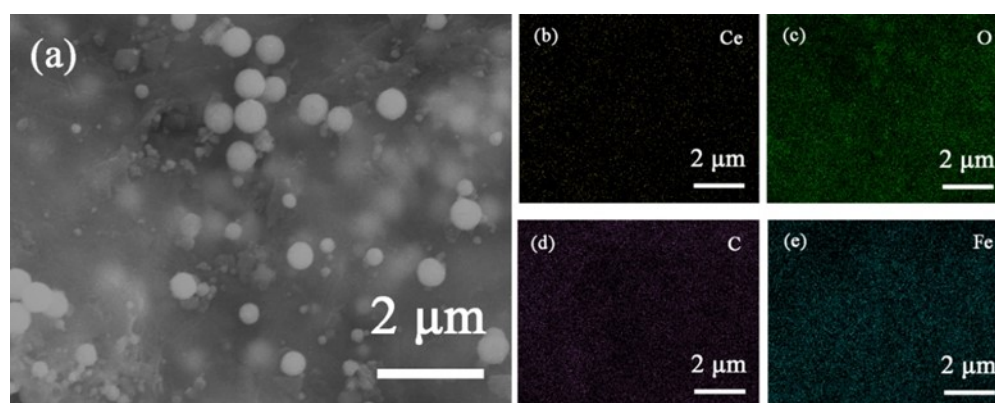
The photocatalytic activity of 1/GO/Fe<sub>3</sub>O<sub>4</sub> composite was assessed by using CTC as a target pollutant in aqueous solution under irradiation by a solar simulator (300 W Xenon lamp). The as-prepared photocatalyst was dispersed into 20 mL of 20 mg L<sup>-1</sup> CTC solution. Before the irradiation, the suspension was magnetically stirred in the dark for 30 min to achieve adsorption-desorption equilibrium. When equilibrium is established, the suspension is illuminated under visible light, followed by adding H<sub>2</sub>O<sub>2</sub> to the mixed solution. During the photoreaction process, 2 mL solution was taken out every 30 min and transferred for UV analysis. The absorbance value at the maximum absorption wavelength of 365 nm was measured using the UV spectrophotometer to calculate the CTC concentration in the degraded solution.



**Fig. S1** The experimental PXRD pattern and the JCPDS card of Fe<sub>3</sub>O<sub>4</sub>.



**Fig.S2.** SEM images of MOF-1 (a), GO (b), Fe<sub>3</sub>O<sub>4</sub> (c), 1/GO (d), and 1/GO/Fe<sub>3</sub>O<sub>4</sub> (e and f).



**Fig.S3.** The corresponding SEM elemental mapping images of elements Ce, O, C, and Fe in the selected area (a-e) of 1/GO/Fe<sub>3</sub>O<sub>4</sub>.

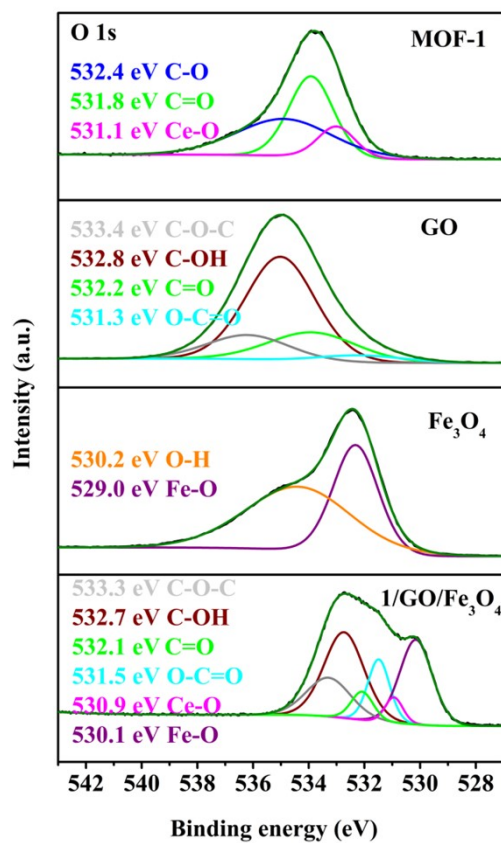


Fig. S4. The high-resolution XPS spectra of O1s.

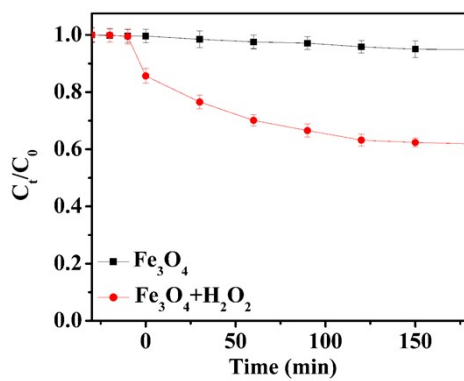


Fig. S5. The photocatalytic performance of Fe<sub>3</sub>O<sub>4</sub>.

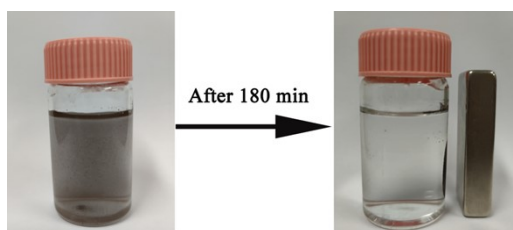
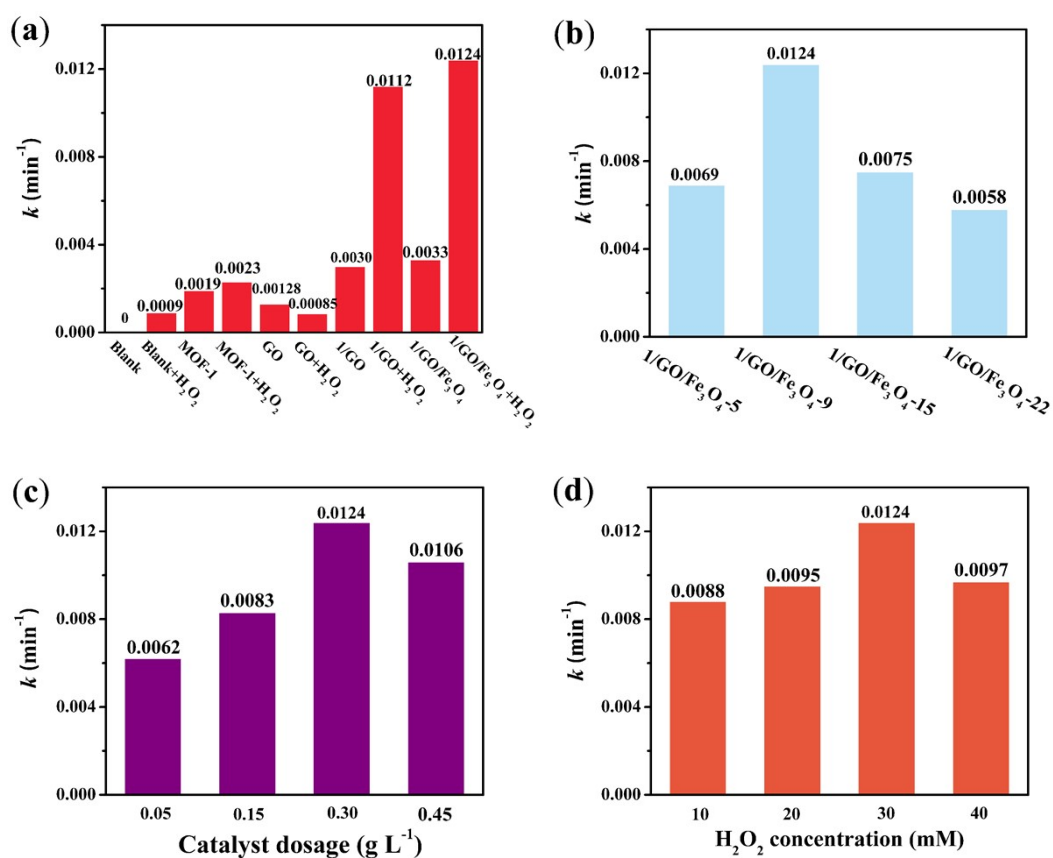


Fig. S6. Photographic image of CTC before and after degradation by 1/GO/Fe<sub>3</sub>O<sub>4</sub> and recovery of the catalysts under an external magnetic field.

**Table S1.** Comparison of photocatalytic performance of 1/GO/Fe<sub>3</sub>O<sub>4</sub> composite with some reported photocatalysts for the degradation of CTC.

Entry	[Photocatalyst] (g/L)	C <sub>CTC</sub> (mg/L)	Light Source	$\eta_{CTC}$ (%)	Time (min)	Recycling method	Ref.
1	Ce/Bi <sub>2</sub> WO <sub>6</sub> (0.5)	CTC (25)	UV-Vis light	100.0	201	–	4
2	g-C <sub>3</sub> N <sub>4</sub> nanosheets /schwertmannite (0.2)	CTC (50)	Visible light	98.7	120	Filtration	5
3	BiVO <sub>4</sub> (1.5)	CTC (10)	Visible light	88.0	120	Filtration	6
4	1/GO/Fe <sub>3</sub> O <sub>4</sub> (0.3)	CTC (20)	UV-Vis light	88.0	180	Magnetic separation	<b>This work</b>
5	Ag <sub>3</sub> PO <sub>4</sub> /MIL-53(Fe) (0.5)	CTC (20)	Visible light	85.5	60	Centrifugation	7
6	CuO/ZnO (0.7)	CTC (10)	UV-Vis light	91.1	210	–	8
7	BiOCl/TiO <sub>2</sub> (0.5)	CTC (20)	Visible light	75.1	120	Filtration	9
8	Zn <sub>0.75</sub> Mn <sub>0.75</sub> Fe <sub>1.5</sub> O <sub>4</sub> /ZnFe <sub>2</sub> O <sub>4</sub> /ZnO (0.7)	CTC (10)	Visible light	73.0	240	Centrifugation	10
9	Cu <sub>3</sub> P-ZnSnO <sub>3</sub> -g-C <sub>3</sub> N <sub>4</sub> (1.0)	CTC (10)	Visible light	63.5	60	Centrifugation	11



**Fig. S7.** The  $k$  values for CTC degradation over 1/GO/Fe<sub>3</sub>O<sub>4</sub> with various reaction parameters: (a) catalyst type, (b) loading amount of GO, (c) catalyst dosage, and (d) H<sub>2</sub>O<sub>2</sub> concentration. Except for the investigated parameter, other parameters were set as follows: CTC concentration = 20 mg L<sup>-1</sup>, catalyst dosage = 0.3 g L<sup>-1</sup>, and H<sub>2</sub>O<sub>2</sub> concentration = 30 mM.

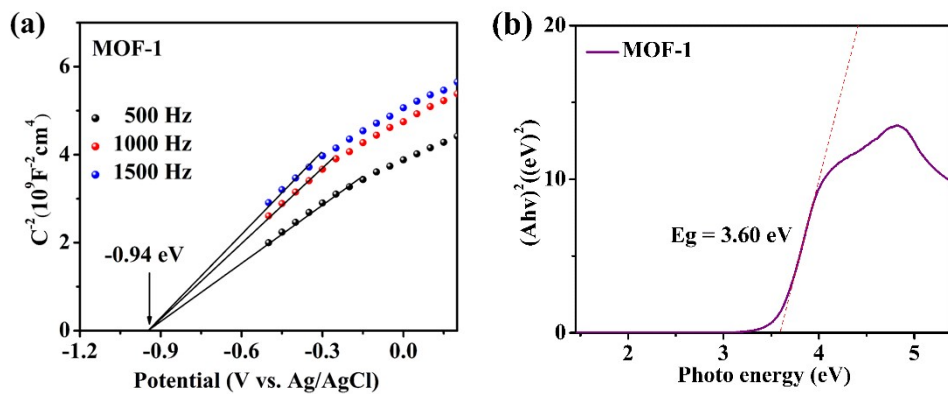
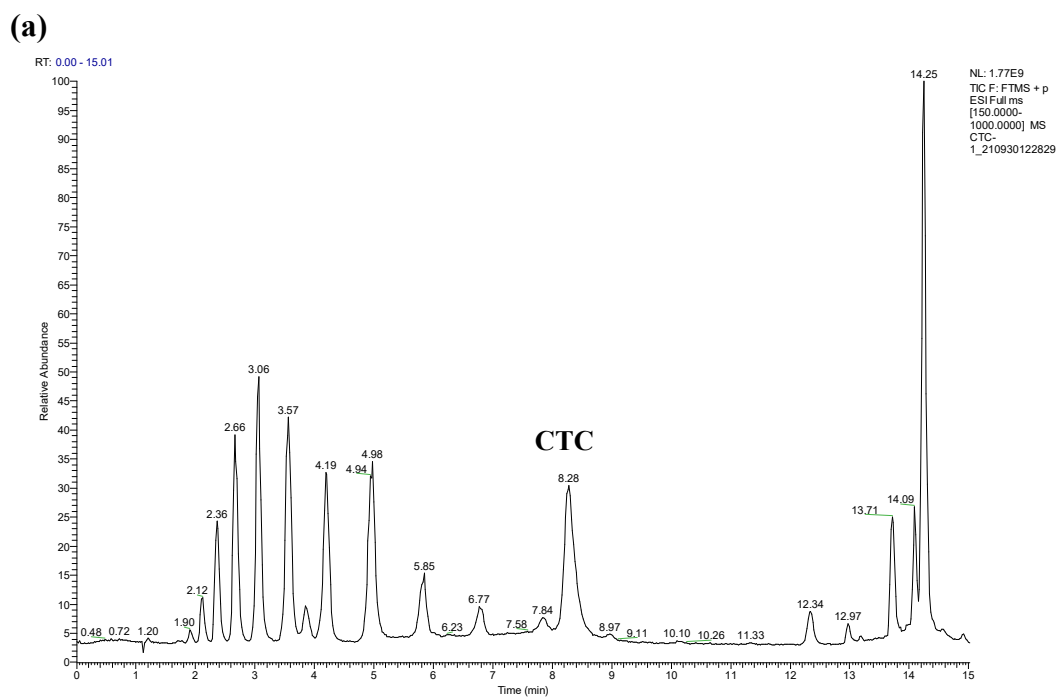


Fig. S8. Mott-Schottky plots (a) and the band gaps (b) of MOF-1.

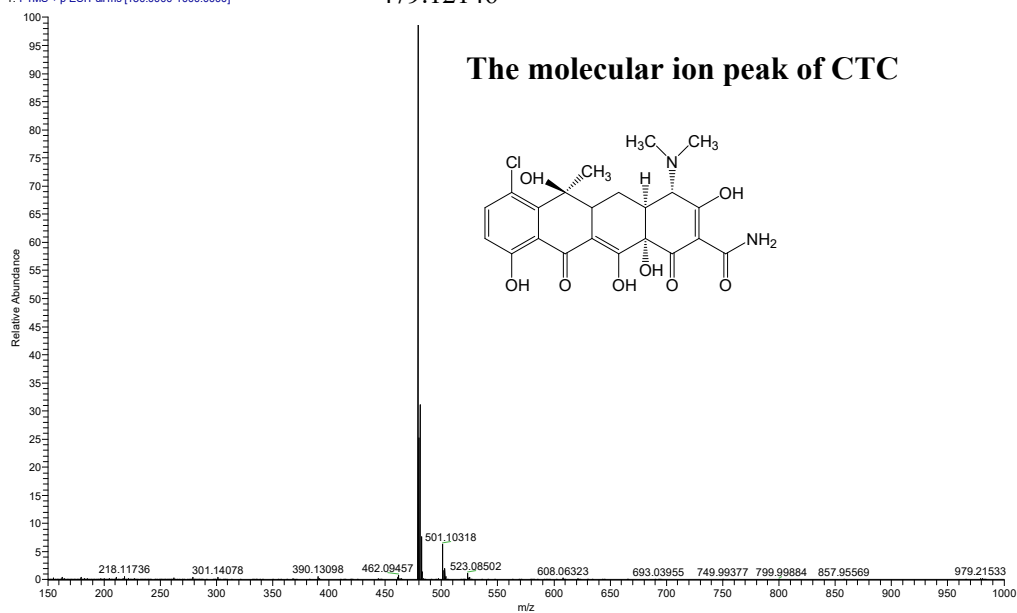




(b)

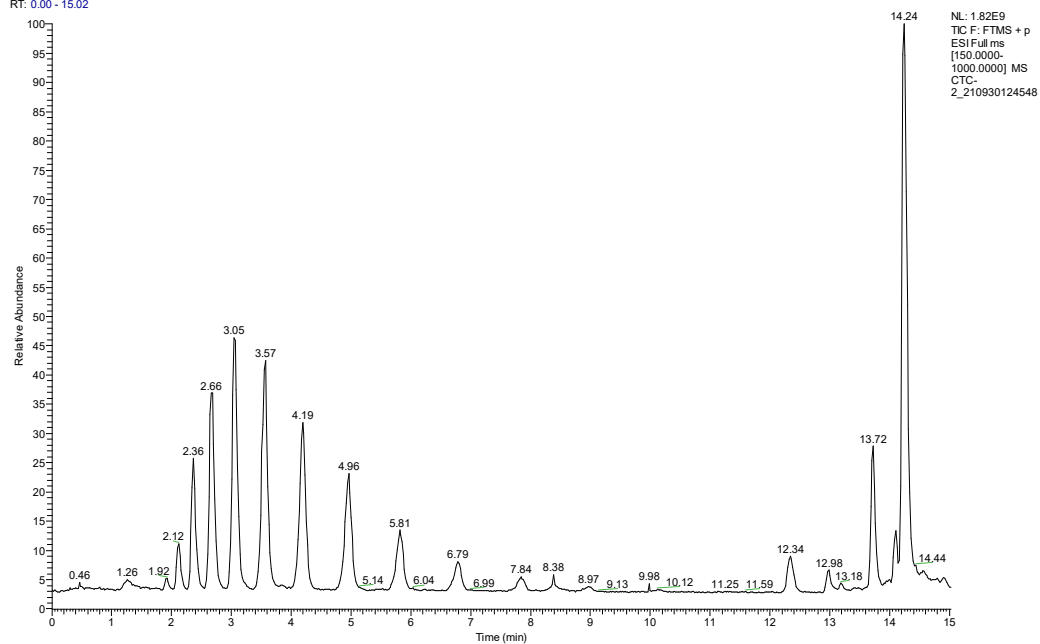
CTC-1\_210930122829 #821 RT: 8.26 AV: 1 NL: 2.56E8  
T: FTMS + p ESI Full ms [150.0000-1000.0000]

479.12146



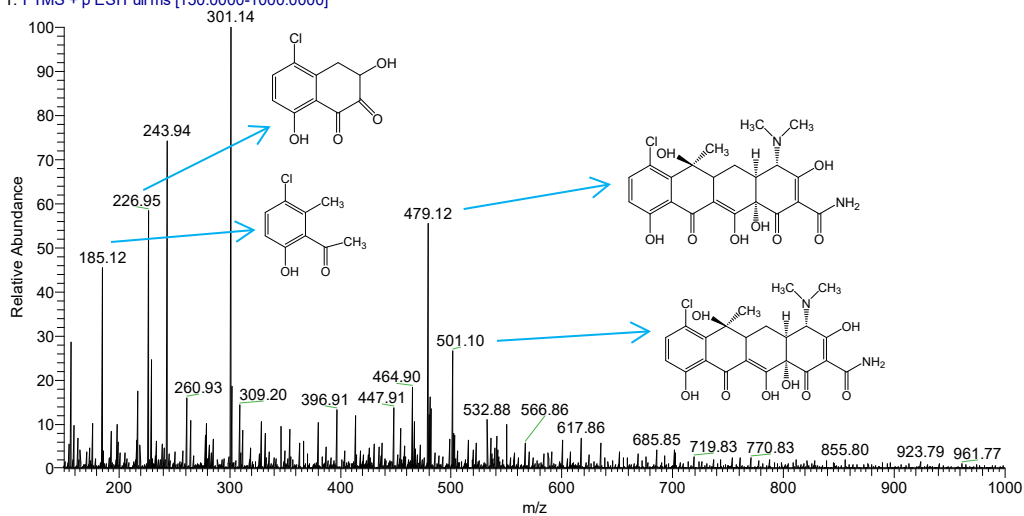
(c)

RT: 0.00 - 15.02



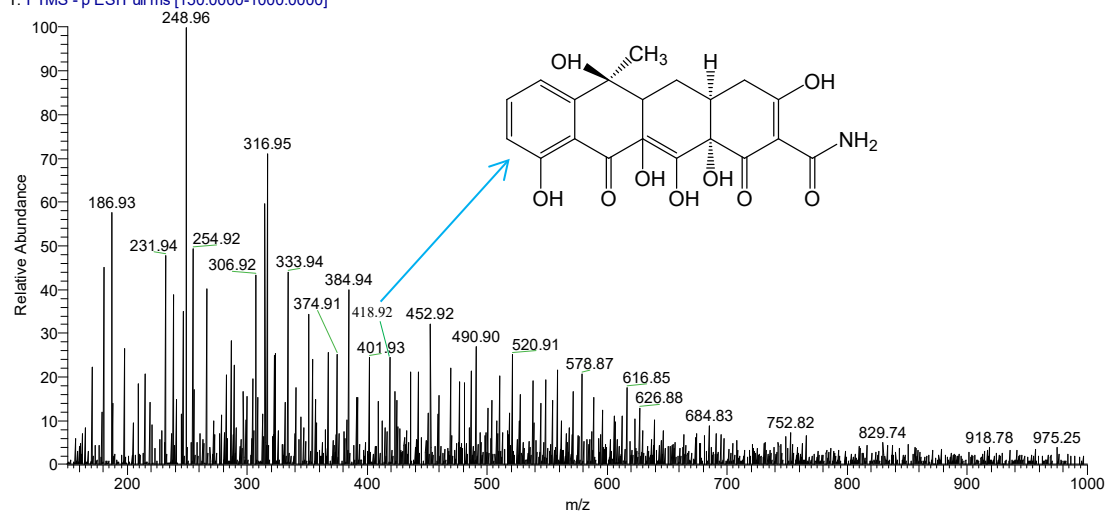
(d)

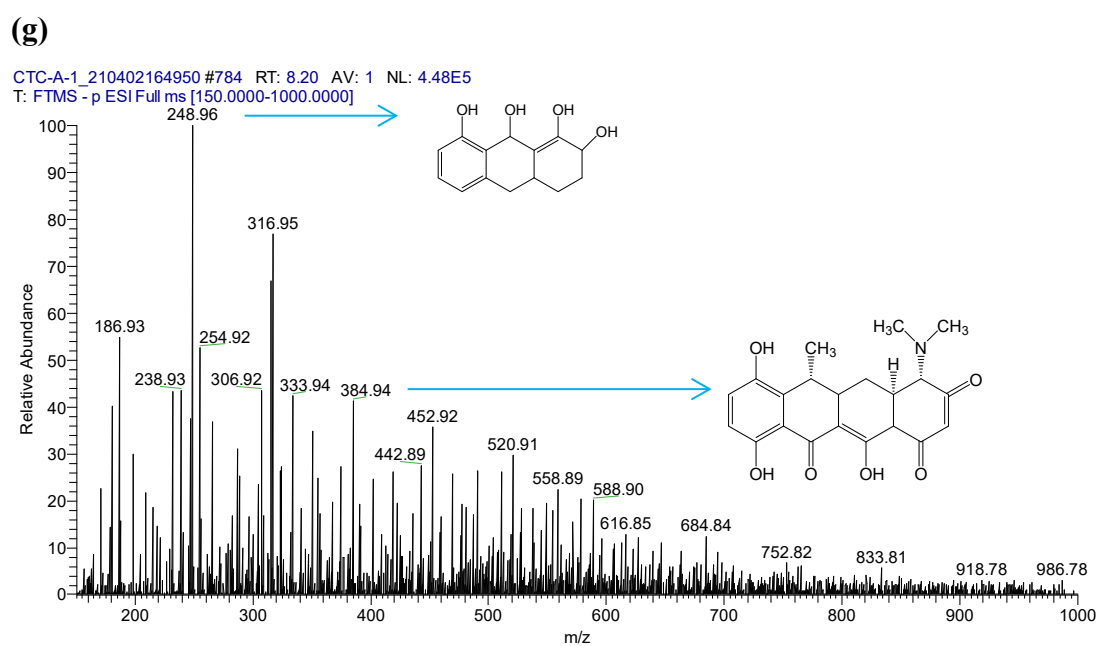
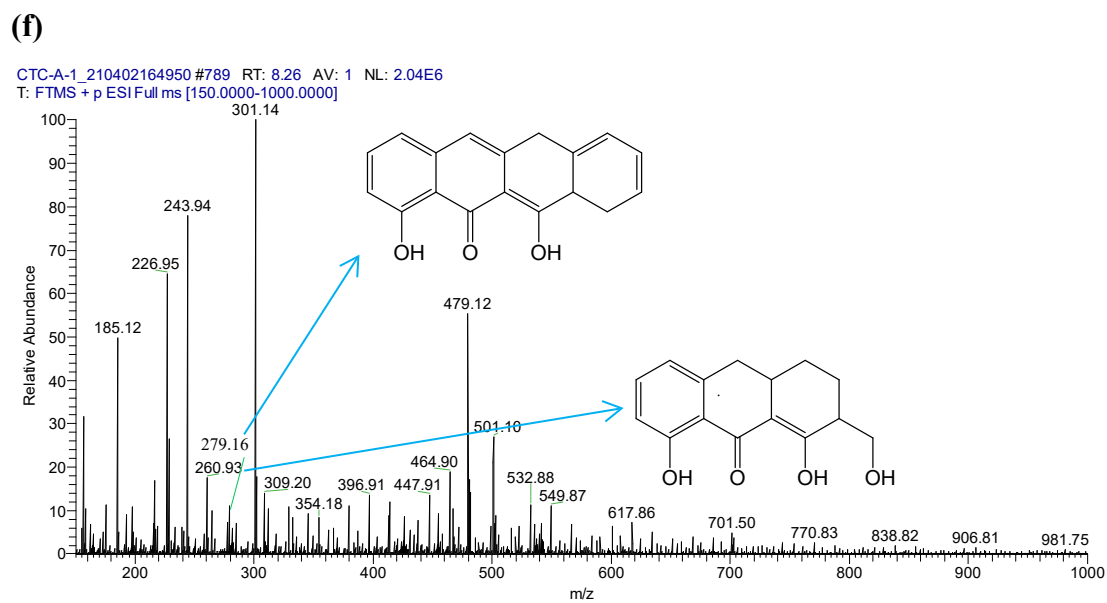
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(e)

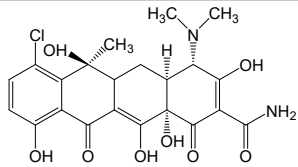
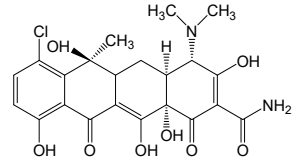
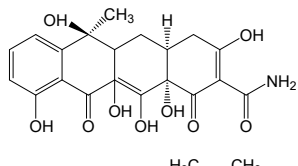
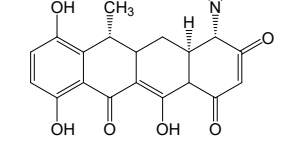
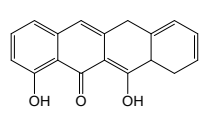
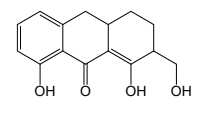
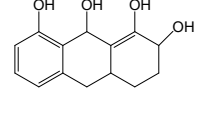
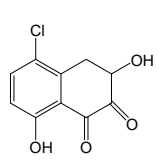
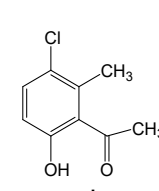
CTC-A-1\_210402164950 #790 RT: 8.27 AV: 1 NL: 4.35E5  
T: FTMS - p ESI Full ms [150.0000-1000.0000]

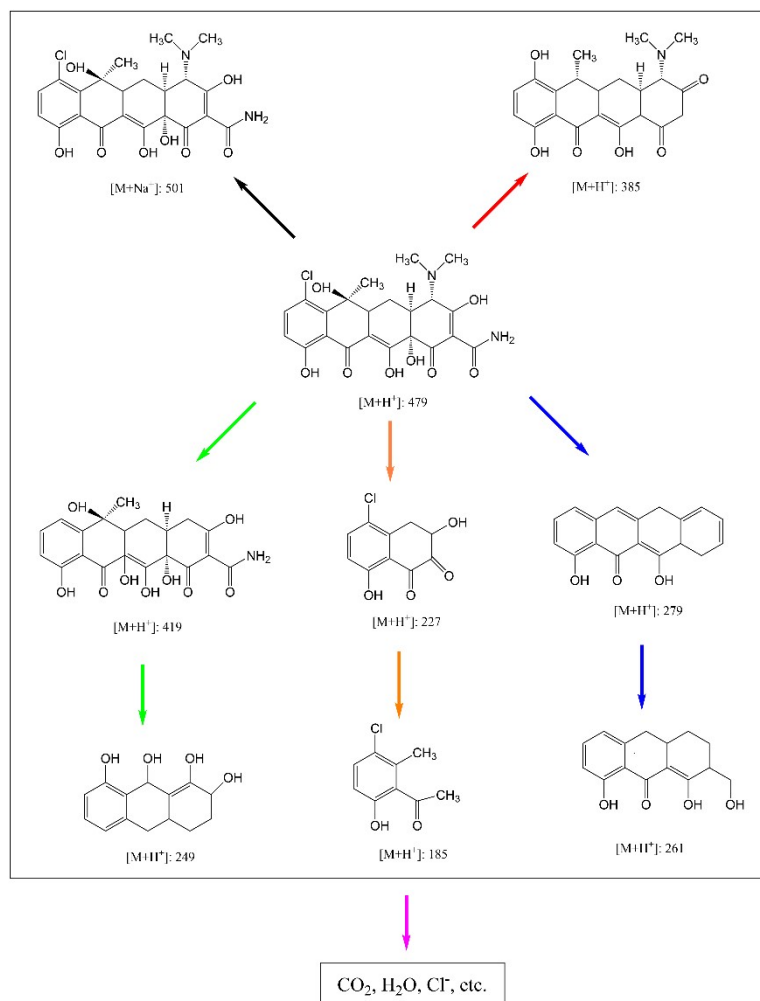




**Fig. S9.** (a) LC of CTC aqueous solution without catalyst. (b) MS corresponding to the CTC aqueous solution without catalyst at a retention time of 8.28 min in LC. (c) LC after photocatalytic degradation of CTC aqueous solution by 1/GO/Fe<sub>3</sub>O<sub>4</sub>. (d-g) MS corresponding to the degradation of CTC at a retention time of 8.20 - 8.30 min in LC, respectively.

**Table S2.** The structural information of the possible intermediates products.

Compounds	RT (min)	Formula	<i>m/z</i>	Proposed structures
CTC	8.30	C <sub>22</sub> H <sub>23</sub> ClN <sub>2</sub> O <sub>8</sub>	[M+H <sup>+</sup> ]: 479	
CTC <sub>1</sub>	8.30	C <sub>22</sub> H <sub>23</sub> ClN <sub>2</sub> O <sub>8</sub>	[M+Na <sup>+</sup> ]: 501	
CTC <sub>2</sub>	8.27	C <sub>21</sub> H <sub>20</sub> NO <sub>9</sub>	[M+H <sup>+</sup> ]: 419	
CTC <sub>3</sub>	8.20	C <sub>21</sub> H <sub>23</sub> NO <sub>6</sub>	[M+H <sup>+</sup> ]: 385	
CTC <sub>4</sub>	8.26	C <sub>18</sub> H <sub>14</sub> O <sub>3</sub>	[M+H <sup>+</sup> ]: 279	
CTC <sub>5</sub>	8.26	C <sub>15</sub> H <sub>16</sub> O <sub>4</sub>	[M+H <sup>+</sup> ]: 261	
CTC <sub>6</sub>	8.20	C <sub>14</sub> H <sub>13</sub> ClO <sub>2</sub>	[M+H <sup>+</sup> ]: 249	
CTC <sub>7</sub>	8.30	C <sub>10</sub> H <sub>7</sub> ClO <sub>4</sub>	[M+H <sup>+</sup> ]: 227	
CTC <sub>8</sub>	8.30	C <sub>9</sub> H <sub>9</sub> ClO <sub>2</sub>	[M+H <sup>+</sup> ]: 185	
⋮				
CTC <sub>n</sub>				⋮ CO <sub>2</sub> , H <sub>2</sub> O, Cl <sup>-</sup> .....



**Scheme S2.** Proposed degradation paths of CTC by 1/GO/Fe<sub>3</sub>O<sub>4</sub> under visible light irradiation.

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