Supporting Data

Defect modulation of MIL-53(Fe) by Ce doping for PMS activation on the

degradation of tetracycline: Singlet oxygen and electron transfer

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Test.S1 Chemical and materials

Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), cerous nitrate (Ce(NO$_3$)$_3$·6H$_2$O), terephthalic acid (H$_2$BDC, C$_8$H$_6$O$_4$), N,N-dimethylformamide (DMF, C$_3$H$_7$NO), peroxymonosulfate (PMS, KHSO$_5$·0.5KHSO$_4$·0.5K$_2$SO$_4$) and furfuryl alcohol (FFA, C$_5$H$_6$O$_2$) were obtained from Aladdin (Shanghai, China). Tetracycline (TC, C$_{22}$H$_{24}$N$_2$O$_8$·HCl), tert-butanol (TBA, C$_4$H$_9$OH), p-Benzoquinone (p-BQ, C$_6$H$_4$O$_2$) and potassium iodide (KI) were purchased from Macklin (Shanghai, China). Ethyl alcohol (C$_2$H$_5$OH), methanol (CH$_3$OH), salicylic acid (C$_7$H$_6$O$_3$), sodium hydroxide (NaOH), and sulfuric acid (H$_2$SO$_4$) were purchased from Guangzhou Chemical Reagent Factory. All chemicals were analytical grade and did not require further purification. Nafion solution (5% wt) was purchased from DuPont Co., Ltd (United States). Ultrapure water with a resistivity of 18.2 MΩ•cm was used for all experiments.

Test.S2 Characterization

The morphology and elemental composition of the electrode surface were observed by scanning electron microscope (SEM, Carl Zeiss Microscopy, GmbH, Germany) and energy dispersive spectrometer (EDS, Carl Zeiss Microscopy, GmbH, Germany). Using Cu Kα radiation (λ= 1.5405Å) in the 2θ range of 5-90° at a scan step of 5° min^{-1} to study the crystalline phase of MIL-53(Fe) and MIL-53(Fe$_{1-x}$Ce$_x$) via powder X-ray diffractometer (XRD, Bruker D8, Germany). Use X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha, United States) to know the surface chemical composition of materials. Fourier transforms infrared (FTIR, Nicolet 5700, United States) spectroscopy can obtain the functional groups and chemical bonds. Raman spectroscopy analysis was carried out using a Horiba LabRAM HR Evolution Raman spectrometer. The BET results of surface areas, pore volume, and pore size were calculated using an ASAP 2460 Micromeritics at 77 K.

Test.S3 Analytical methods

The concentrations of TC were analyzed via high-performance liquid chromatography (HPLC, Waters 2695, United States) system equipped with a C18 column (4.6 nm × 250 nm, 5 μm, Agilent) and a UV-Vis detector. A solution of iodide (KI, 0.5 M) with bicarbonate buffer (NaHCO$_3$, 0.05 M) was prepared to determine the PMS

concentration, then mixed 0.1 mL filtered sample into the above solution (4.9 mL). After 20 min complete reaction, the chromogenic sample was detected at $\lambda = 352$ nm[1]. A UV-Vis spectrophotometer (HACH DR 5000, United States) equipped with quartz cuvettes of 1 cm light path was used for the absorption measurements. The point of zero electric charges (pHpzc) was determined by a Zetasizer Nano analyzer (ZetaPALS, Malvern, UK). The concentrations of dissolved iron were measured by inductively coupled plasma-mass spectrometry (ICP-MS, PerkinElmer NexlON 300X, USA). Electron paramagnetic resonance (EPR, Bruker A300, Germany) spectroscopy was used for in situ detection of ROS using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TEMP) as the spin-trapping agent. TC degradation intermediates were studied using an Agilent 1290 ultrahigh performance liquid chromatography-mass spectrometry system (UHPLC-MS, Bruker maXis impact, German) with a Zorbax Rx-C18 column. Gradient elution was employed, with eluent A comprising 0.1% formic acid and eluent B consisting of acetonitrile.

Open circuit potential-time (OCPT) were carried out on a three-electrode cell system in 0.1 mM Na_2SO_4 electrolyte solution by the electrochemical workstation (Chenhua Instruments CHI 760E, China). The working electrode was prepared by the commercial glassy carbon electrode (GCE). 5 g·L^{-1} catalysts (MIL-53 or MIL-53(Fe$_{1-x}$Ce$_x$)) were added into a methanol solution containing 5% Nafion and then dispersed ultrasonically for 30 min. 9 μL slurry was dropped on the surface of the GCE by pipette. Hg/Hg_2SO_4 and platinum electrodes work as the reference and counter electrodes.

The biotoxicity of degraded TC solution was evaluated. The biotoxicity of the degraded TC solution was assessed using Escherichia coli (E. coli) as indicator bacteria. The bacteria were first incubated for one day at 37 °C in Luria-Bertani medium (LB broth: tryptone 10 g/L, NaCl 10 g/L, yeast extract g/L, pH 7.4). They were then washed by centrifugation with distilled water at 3000 rpm. The bacteria were then resuspended in sterilised aqueous solution and diluted to $1*10^4$ CFU/mL. The experimental conditions for the toxicity test were as follows: 0.6 mL of the original TC solution or the post-reaction solution was mixed with 5.4 mL of the bacterial solution and incubated in a thermostatic incubator at 230 rpm for 12 h. Then 0.1 mL of the mixture was homogeneously distributed on an agar plate. The plates were incubated at 37°C for 24 hours.
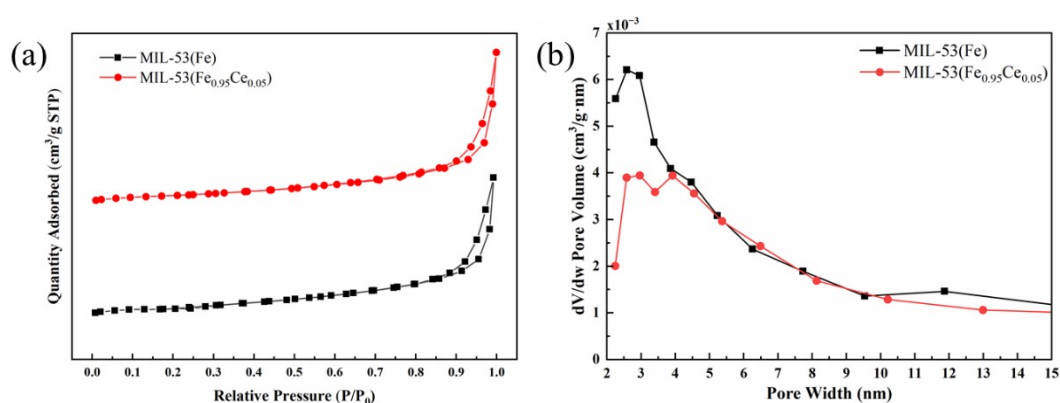

Fig. S1. N_2 adsorption-desorption isotherm (a) and Pore size distribution(b) of MIL-53(Fe) and MIL-53(Fe$_{0.95}$Ce$_{0.05}$).

Table S1 Average pore diameter and total pore volume of catalysts

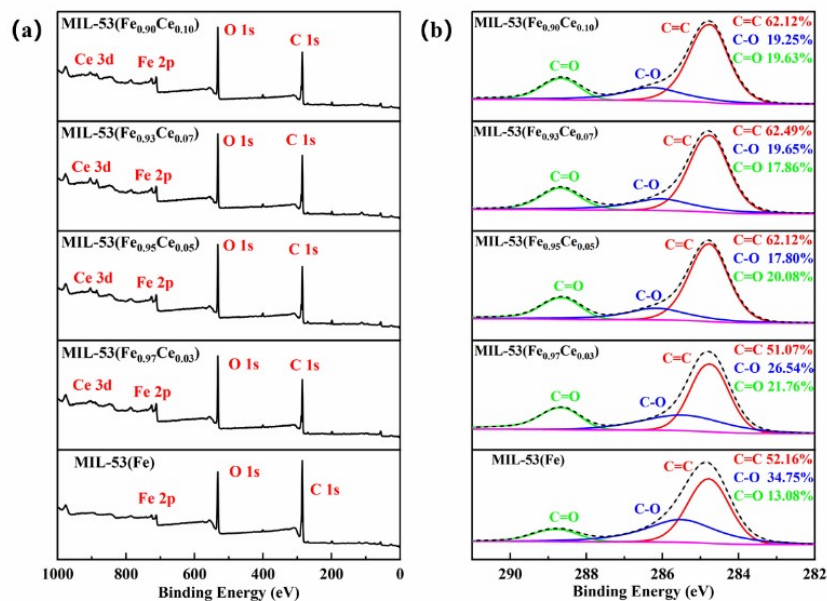| Sample	S_{BET} (m^2·g^{-1})	Average pore diameter (nm)	Total pore volume (cm^3·g^{-1})
MIL-53(Fe)	19.7792	19.2707	0.101833
MIL-53(Fe$_{0.95}$Ce$_{0.05}$)	17.4271	17.7322	0.0962009

Fig. S2. XPS spectra of MIL-53(Fe) and MIL-53(Fe$_{1-x}$Ce$_x$): (a) Survey, (b) C 1s.
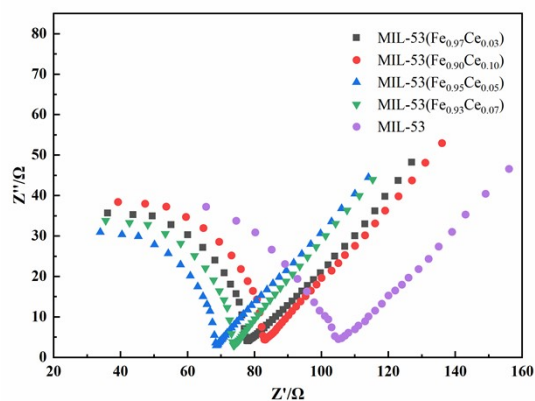

Fig. S3. EIS spectra for MIL-53(Fe) and MIL-53(Fe$_{1-x}$Ce$_x$).

Table S2. XPS fitting results for different catalysts.

Sample	C 1s			O 1s			Fe 2p		Ce 3d	
	C=C(%)	C-O(%)	C=O(%)	O$_{H2O}$(%)	O$_V$(%)	O$_L$(%)	Fe^{2+}(%)	Fe^{3+}(%)	Ce^{3+}(%)	Ce^{4+}(%)
MIL-53	52.16	34.75	13.08	34.74	51.75	13.51	59.34	40.66	—	—
MIL-53(Fe$_{0.97}$Ce$_{0.03}$)	51.07	26.54	21.76	23.78	54.37	21.85	65.47	34.53	35.96	64.04
MIL-53(Fe$_{0.95}$Ce$_{0.05}$)	62.12	17.80	20.08	20.46	57.38	22.16	65.68	34.32	41.99	58.01
MIL-53(Fe$_{0.93}$Ce$_{0.07}$)	62.49	19.65	17.86	25.77	59.16	15.07	65.47	34.53	37.73	62.27
MIL-53(Fe$_{0.90}$Ce$_{0.10}$)	62.12	19.25	19.63	17.89	61.37	20.74	64.66	35.34	32.30	67.70
Used MIL-53(Fe$_{0.95}$Ce$_{0.05}$)	63.28	11.50	25.23	29.44	40.41	20.15	51.48	48.52	34.94	63.06

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Table S3. Comparison of In2O3/Co3O4 with other catalysts on the degradation of TC.

| Catalysts	C catalysts	C_{TC}	C_{PMS}	Degradation performance	Degradation time	Ref.
MIL-53(Fe$_{0.95}$Ce$_{0.05}$)	**0.1 g/L**	**20 mg/L**	**0.1 mM**	**94%**	**7 min**	**Present work**
Mn-MIL-53(Fe)-0.3	0.2 g/L	30 mg/L	0.3 g/L	93.2%	60 min	[2]
MIL-53(Fe)@AC	0.2 g/L	20 mg/L	2.0 g/L	92.14%	120 min	[3]
25% Co-MIL-53(Al)	0.2 g/L	30 mg/L	0.3 g/L	94%	120 min	[4]
ZIF-67@Ce-MOF-600	0.2 g/L	20 mg/L	0.5 g/L	99.2%	30 min	[5]
CoCu-MOF	0.1 g/L	20 mg/L	3 Mm	98.17%	30 min	[6]
FeCo−MOF	0.1 g/L	20 mg/L	0.1 mM	91%	5 min	[7]
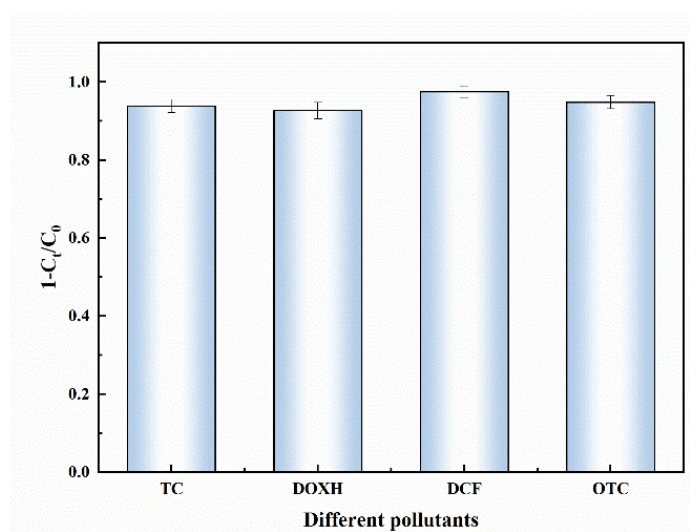
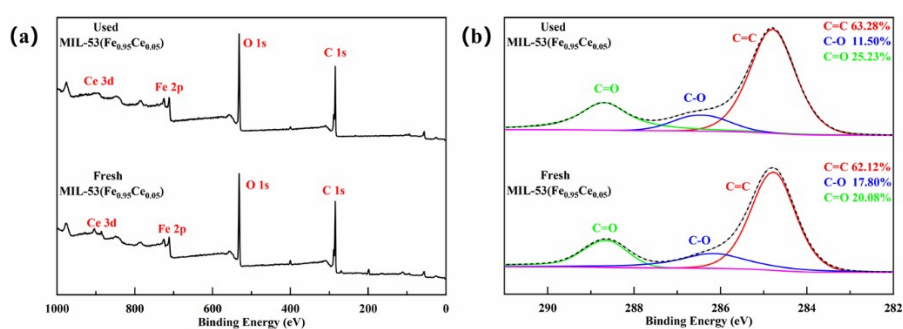Fig.S4. Degradation of different pollutants by the MIL-53(Fe0.95Ce0.05)/PMS system

Fig.S5. XPS spectra of MIL-53(Fe$_{1-x}$Ce$_x$) before and after reaction (a) Survey, (b) C 1s.

Table S4 The information of the intermediate products for TC degradation via LC/MS

Compounds	Formula	m/z	Proposed structure
TC	$C_{22}H_{24}N_2O_8$	444	
P1	$C_{20}H_{20}N_2O_8$	417	
P2	$C_{20}H_{20}O_6$	359	
P3	$C_{22}H_{26}N_2O_{11}$	495	
P4	$C_{19}H_{24}O_8$	381	
P5	$C_{15}H_{16}O_3$	245	
P6	$C_{19}H_{21}NO_9$	407	
P7	$C_{10}H_{18}O_5$	218	
P8	$C_9H_{16}O_2$	157	
P9	$C_{15}H_{14}O_6$	291	
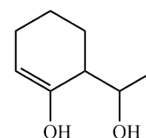
P10	$C_8H_{14}O_2$	143	
P11	$C_6H_{10}O_2$	114	

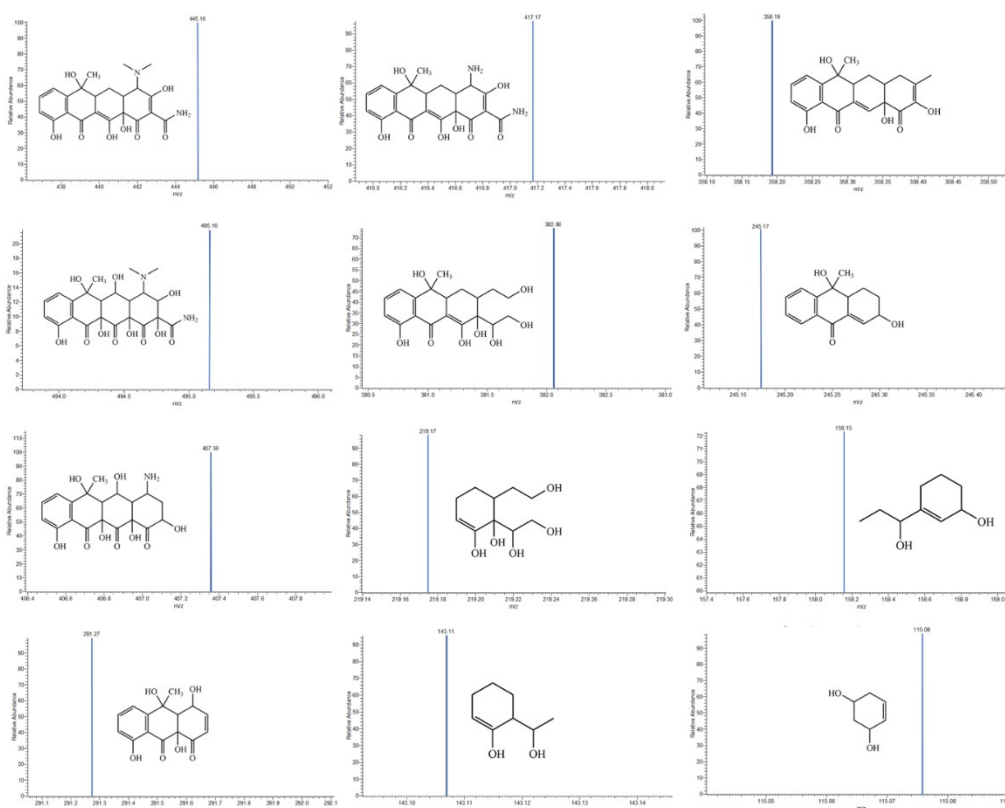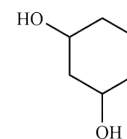
Fig.S6. LC/MS spectral fragments of TC and its intermediates

Reference：

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