

Supporting Information

Synthesis of Iron Phthalocyanine/CeO₂ Z-scheme nanocomposites as efficient photocatalysts for degradation of 2, 4-dichlorophenol

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1. Experimental details

1.1 Hydroxyl radical measurements (FS)

0.05 g of samples was dispersed in 50 mL coumarin aqueous solution (0.001 M) in a beaker. Prior to irradiation, the reactor was magnetically stirred for 10 min to attain an adsorption-desorption equilibrium in dark. After irradiation for 1 h with a 150 W Xenon lamp (GYZ220 made in China), the mixed liquor was centrifuged at 4000 rpm for 15 min, and then a certain volume of solution was transferred into a glass cell for the fluorescence measurement of 7-hydroxycoumarin at 332 nm excitation wavelength with an emission peak wavelength at 460 nm through the above-mentioned spectrofluorometer.

1.2 Evaluation for O₂ temperature-programmed desorption (O₂-TPD)

The temperature-programmed desorption (TPD) curves of O₂ were measured with a home-built flow apparatus. The typical method is as follows. About 50 mg of the samples were preheated to 100 °C for 0.5 h to remove any moisture and then were cooled to room temperature under an ultra-high-purity He stream with a flow rate of 30 mL·min⁻¹. After that, the system was cooled to room temperature and then the sample was blown continuously with O₂ for 60 min at 30 °C. The excess weakly adsorbed O₂ was removed by exposure to ultra-high pure He. Then the temperature was increased to 400 °C with a heating rate of 10 °C min⁻¹ under pure He.

1.3 Photoelectrochemical (PEC) and electrochemical (EC) experiments

The PEC experiments were performed in a three-electrode cell with a Platinum plate (99.9%) as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode on a LK2006 A workstation. The working electrode (the illumination area is about 1 cm²) was positioned in 0.5 M Na₂SO₄ electrolyte with the obtained sample. High purity O₂ was used to bubble through the electrolyte before and during the electrochemical O₂ reduction experiments. Electrochemical impedance spectra (EIS) were measured using the same three-electrode configuration with the Princeton Applied Research Versa STAT 3 and carried out over the frequency range from 102 to 105 Hz with amplitude of 10 mV (RMS) in a 0.5 M Na₂SO₄ solution. The electrodes were illuminated with a 150 W Xenon lamp.

1.4 Photocatalytic performance measurements

The photocatalytic activities of the as prepared samples were evaluated by degrading 2,4-DCP as model pollutants. A 150 W Xenon lamp was used as a light source. 0.02 g photocatalyst was dispersed in 50 mL of 20 mg L⁻¹ 2,4-DCP aqueous solution. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium. The aqueous solutions were mixed by stirring for 1 h in an open glass reactor under light irradiation and the concentration of 2,4-DCP was analyzed by UV spectrometer.

1.5 The active species trapping experiment

Tiny amount of scavenger including disodium ethylenediaminetetraacetate (EDTA), triethanolamine (TEA), 1,4-benzoquinone (BQ), isopropyl alcohol (IPA) was added in the photocatalytic system, to find out the effects of the corresponding active species on the photocatalytic reaction. Additionally, the EDTA (for water system) is applied as h^+ scavenger, BQ as $\bullet O_2^-$ radical scavenger and IPA as $\bullet OH$ radical scavenger.

1.6 Analysis of intermediates and chlorine ions

The various intermediates during 2, 4-DCP photodegradation were obtained by using a typical experiment. Adsorption-desorption equilibrium and photocatalytic degradation process were same with the above photocatalytic activities experiment. After that, a certain volume liquid was taken out for measurement at regular interval during the photocatalytic degradation process. The intermediates were detected with LC-MS/MS (liquid chromatography tandem mass spectrometry) (Xevo TQD, USA) technique. The fragments of the main reaction intermediate were analyzed through scan mode.

1.7 In situ irradiation XPS measurement

The in situ irradiation XPS was carried out on VG ESCALAB. In a typical test, the dark environment binding energy was characterized with all lights turned off in the SAC chamber. and the test was conducted. Then the irradiation light source was turned on, the wavelength was set to 400-800 nm, and repeat the test.

2. Supplementary Figures

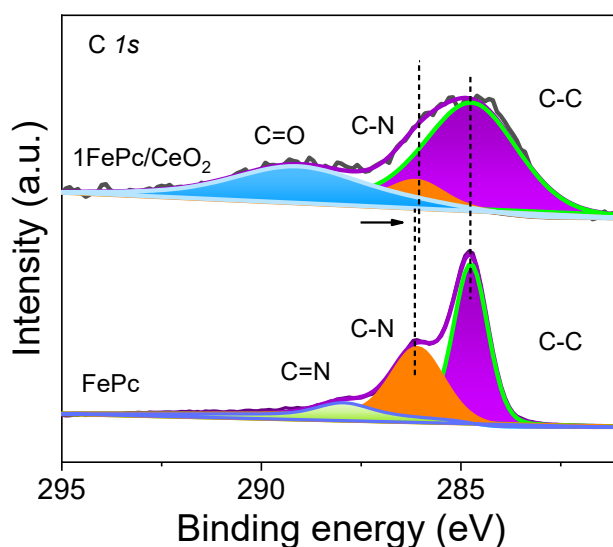


Figure S1 C *1s* XPS spectra of FePc and 1FePc/ CeO₂.

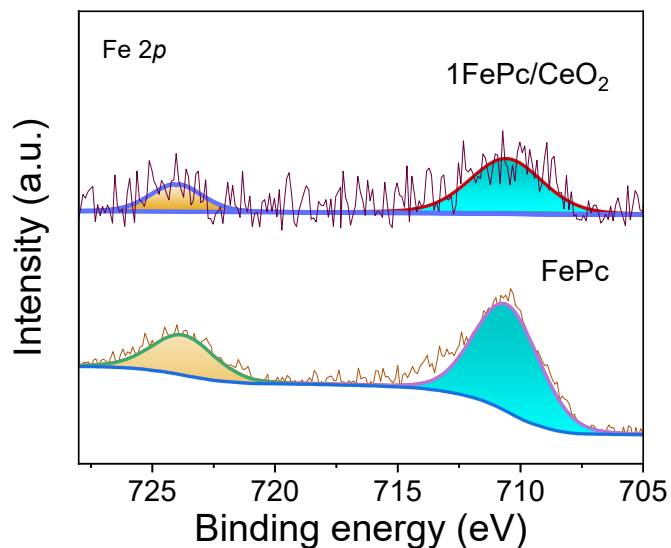


Figure S2 Fe 2p XPS spectra of FePc and 1FePc/CeO₂.

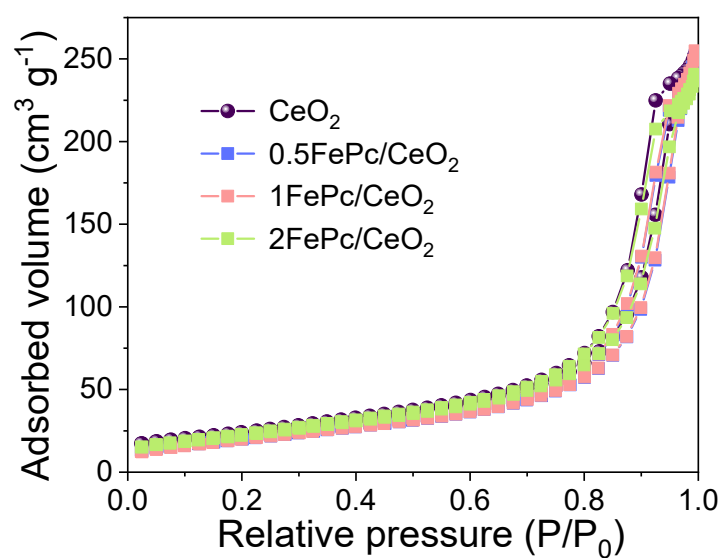


Figure S3 Comparison of nitrogen sorption curves of XFePc/CeO₂.

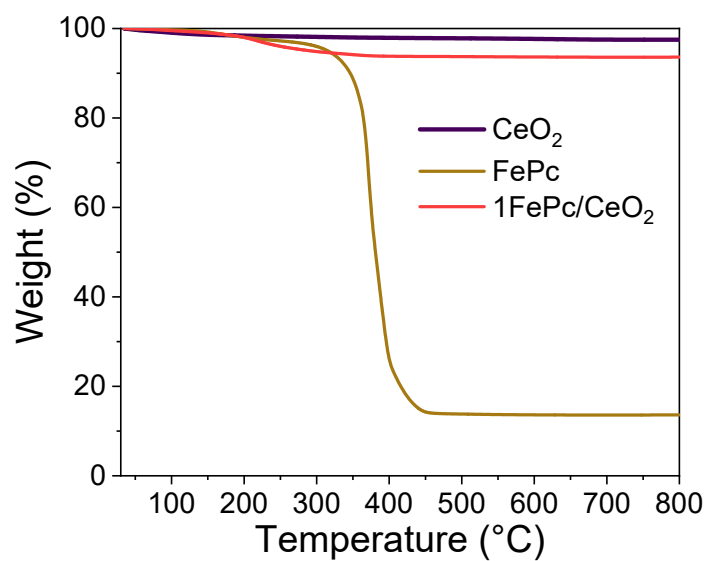


Figure S4 The TG curves for FePc, CeO₂ and 1FePc/CeO₂, respectively.

Table S1 Comparison of photocatalytic degradation of 2,4-dichlorophenol performance with literature reports.

Catalyst	Light source	Concentration	Efficiency	Rate, h ⁻¹	Refs
OV-HAp/GC	300 W Xe lamp ($\lambda > 400$ nm)	50 mL, 5 mg/L	49%, 4 h	0.107	1
TiO ₂ -CeO ₂	AM 1.5G filter solar simulator	100 ml, 100 mg/L	49%, 6 h		2
SA-TCPP	500 W Xe lamp ($\lambda > 420$ nm)	50 ml, 5 mg/L	82%, 4 h	0.371	3
7Cl/CN	150 W Xe lamp ($\lambda > 420$ nm)	60 ml, 10 mg/L	22%, 1 h		4
MC-450-R1	500 W Xe lamp ($\lambda > 420$ nm)	100 ml, 100 mg/L	87.65%, 7 h		5
15%CeO/CN	300 W Xe lamp ($\lambda > 400$ nm)	40 ml, 10 mg/L	32%, 1 h		6
AgCoTC	500 W Xe lamp ($\lambda > 400$ nm)	100 ml, 40 mg/L	60%, 3 h		7
1FePc/CeO ₂	150 W Xe lamp ($\lambda > 420$ nm)	50 ml, 20 mg/L	82 %, 3 h 42%, 1 h	0.566	This work

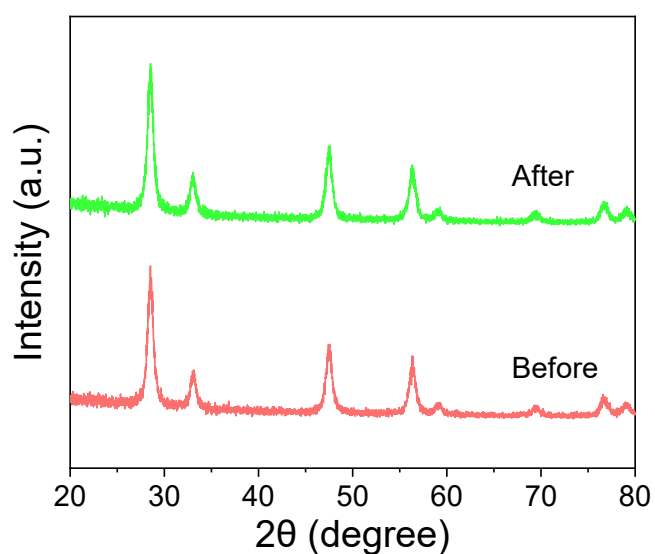


Figure S5 XRD patterns of 1FePc/CeO₂ before and after degradation.

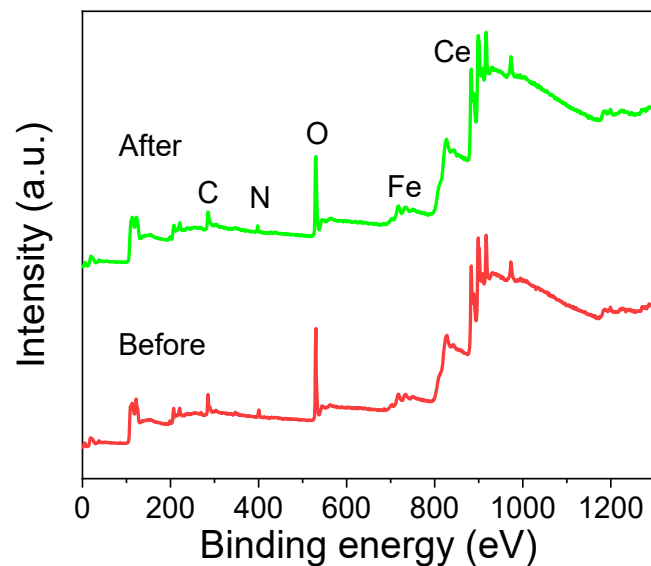


Figure S6 Survey scan XPS profiles of 1FePc/CeO₂ before and after degradation.

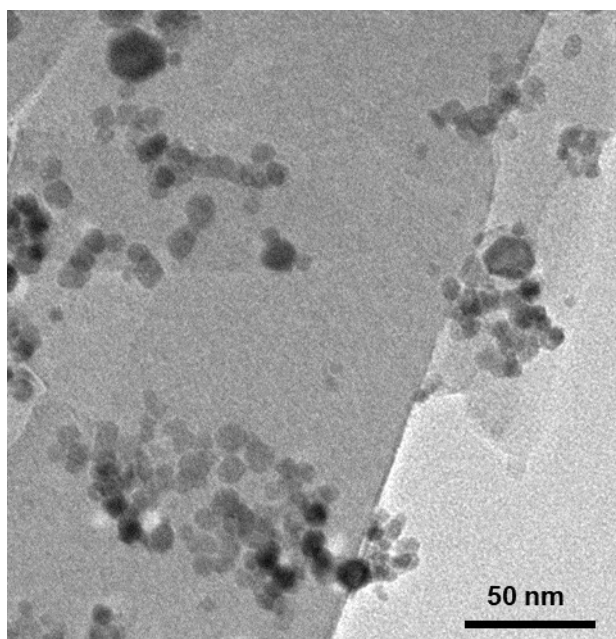


Figure S7 TEM image of 1FePc/CeO₂ after degradation.

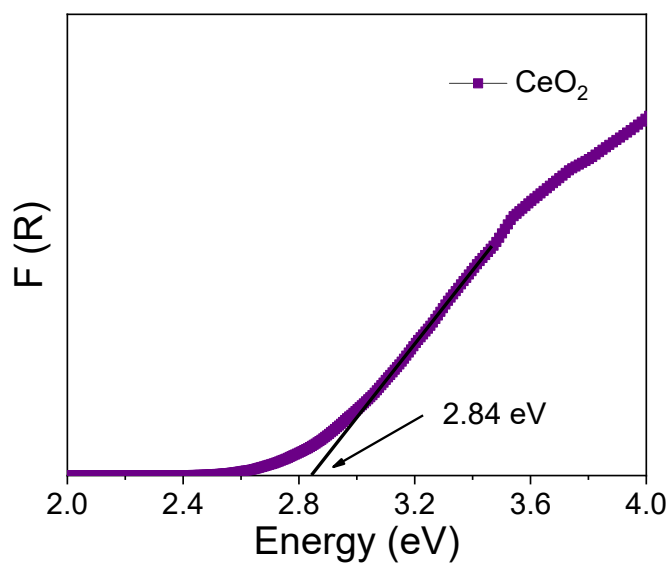


Figure S8 Tauc plot of CeO₂ for band gap calculation.

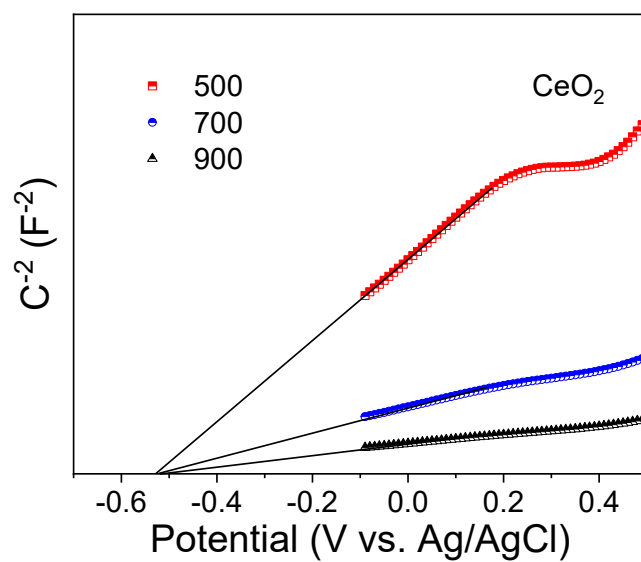


Figure S9 Mott-Schottky plots of CeO_2 .

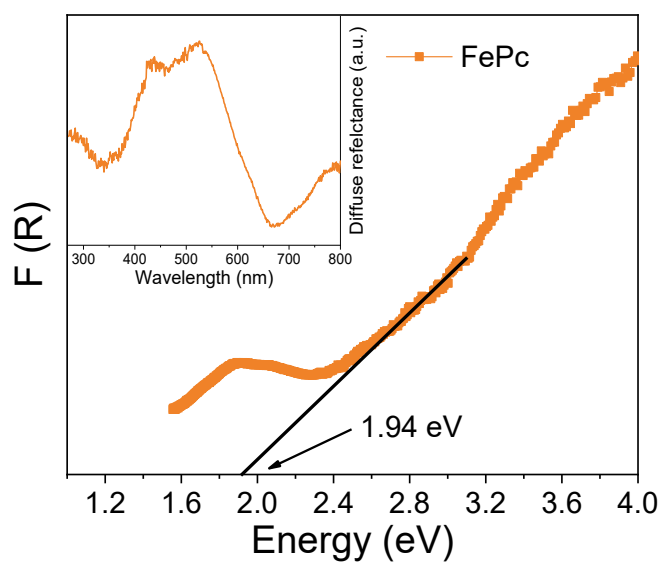


Figure S10 Tauc plot of FePc for band gap calculation.

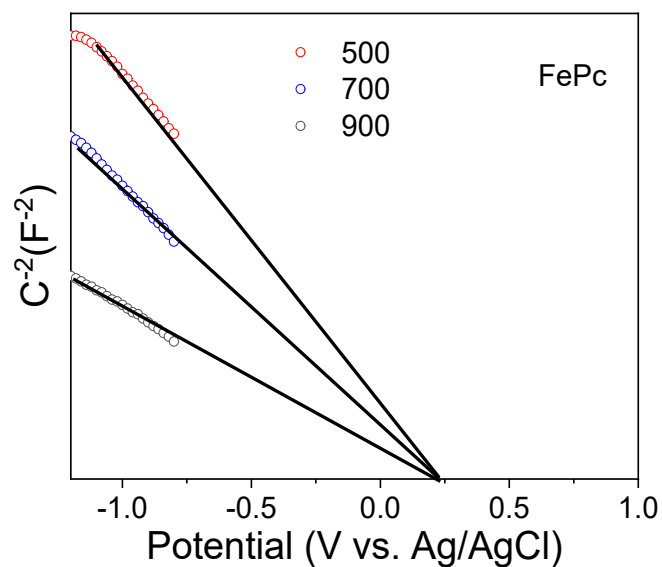


Figure S11 Mott-Schottky plots of FePc.

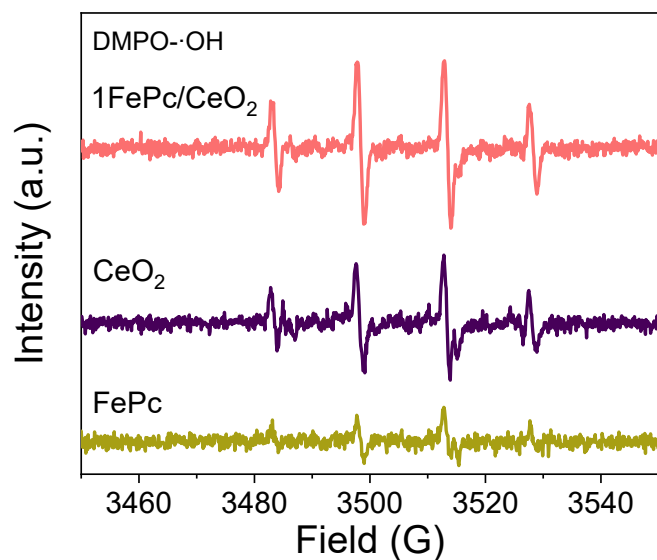


Figure S12 DMPO spin-trapping EPR spectra recorded for •OH radicals under visible-light irradiation of FePc, CeO₂ and 1FePc/CeO₂.

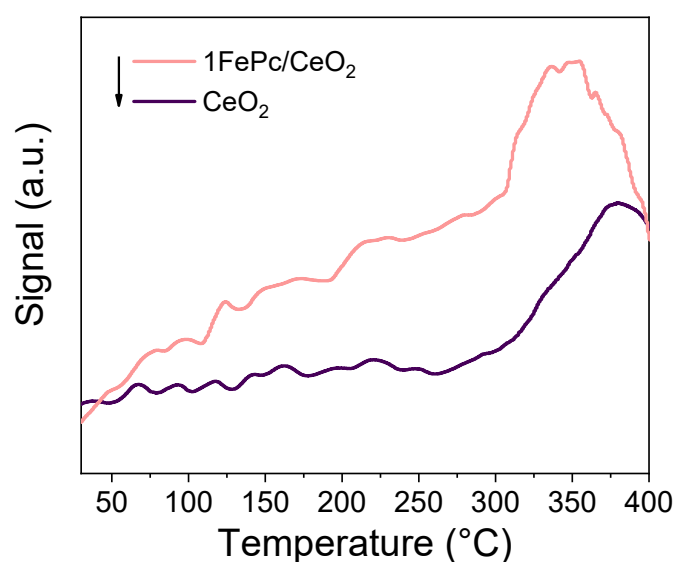


Figure S13 The O₂ temperature-programmed desorption (O₂-TPD) curves of CeO₂, 1FePc/ CeO₂.

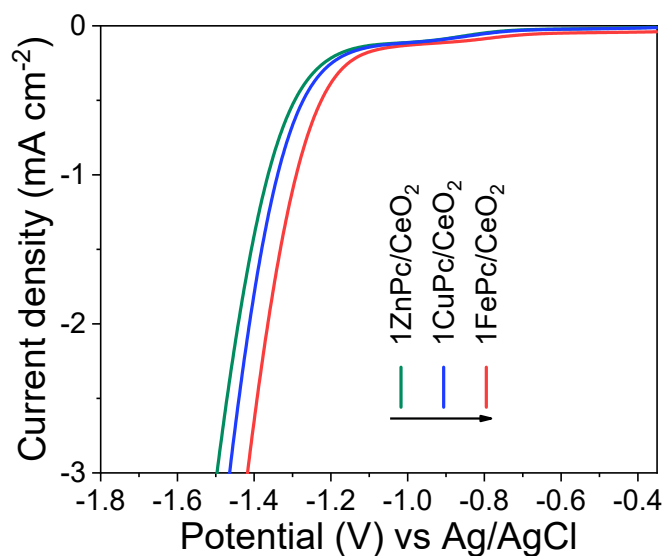


Figure S14 The I–V curves with O₂-bubbled of 1ZnPc/CeO₂, 1CuPc/CeO₂ and 1FePc/CeO₂.

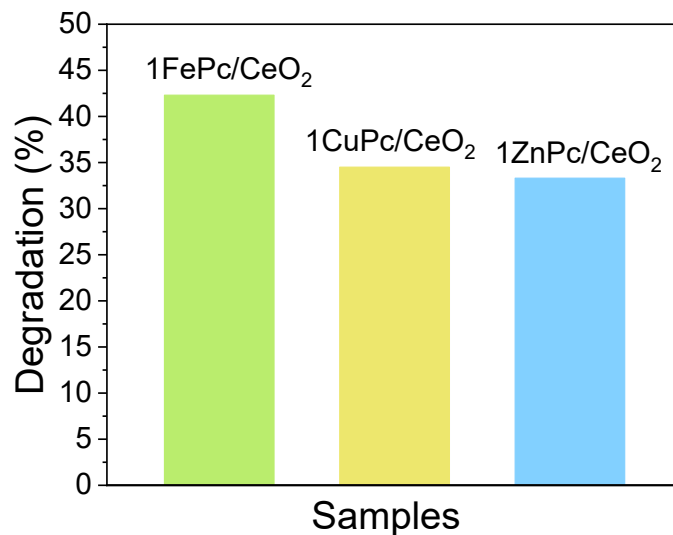
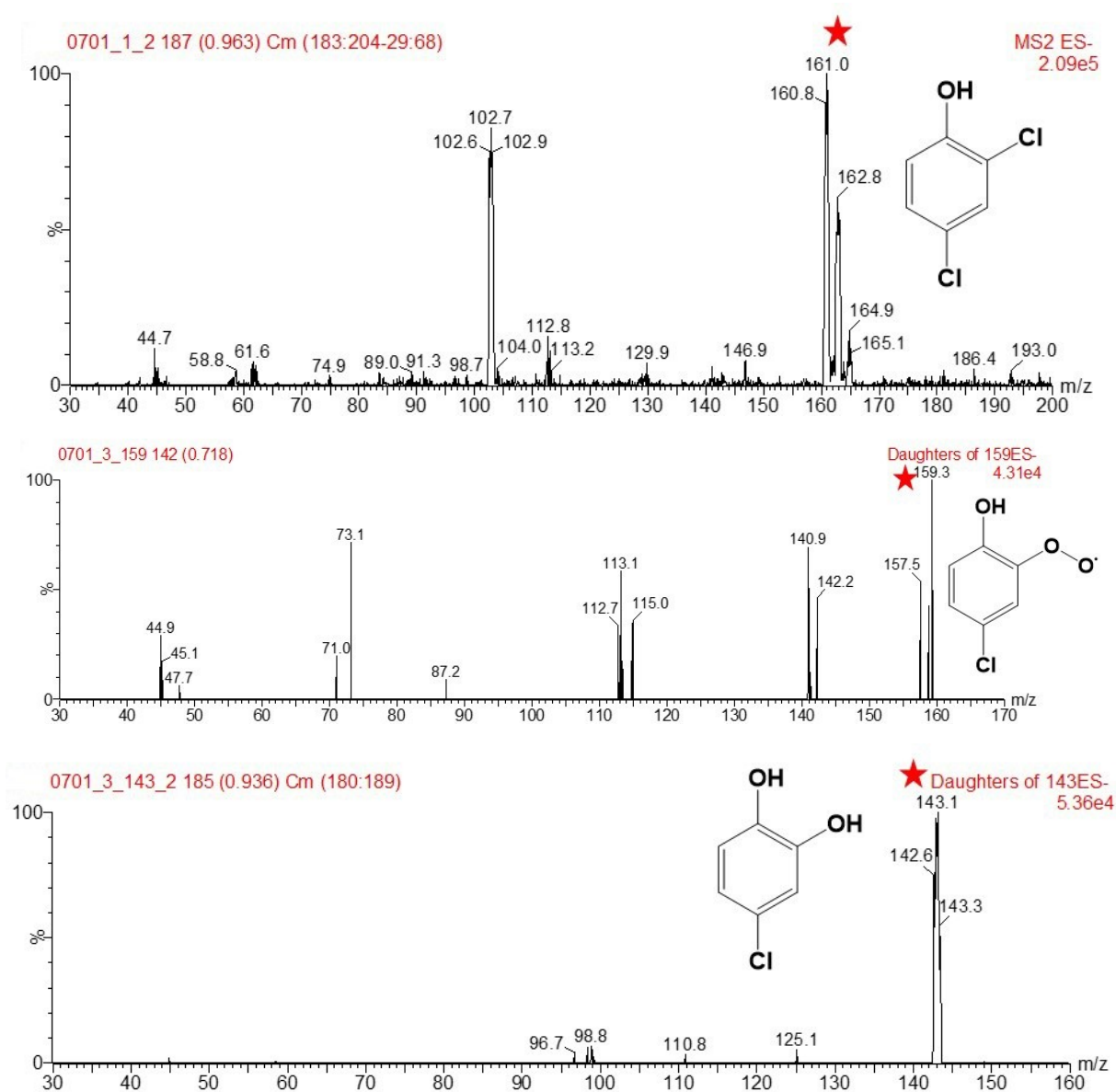


Figure S15 Photocatalytic activities for 2,4-DCP degradation of 1ZnPc/CeO₂, 1CuPc/CeO₂ and 1FePc/CeO₂ under visible-light irradiation.



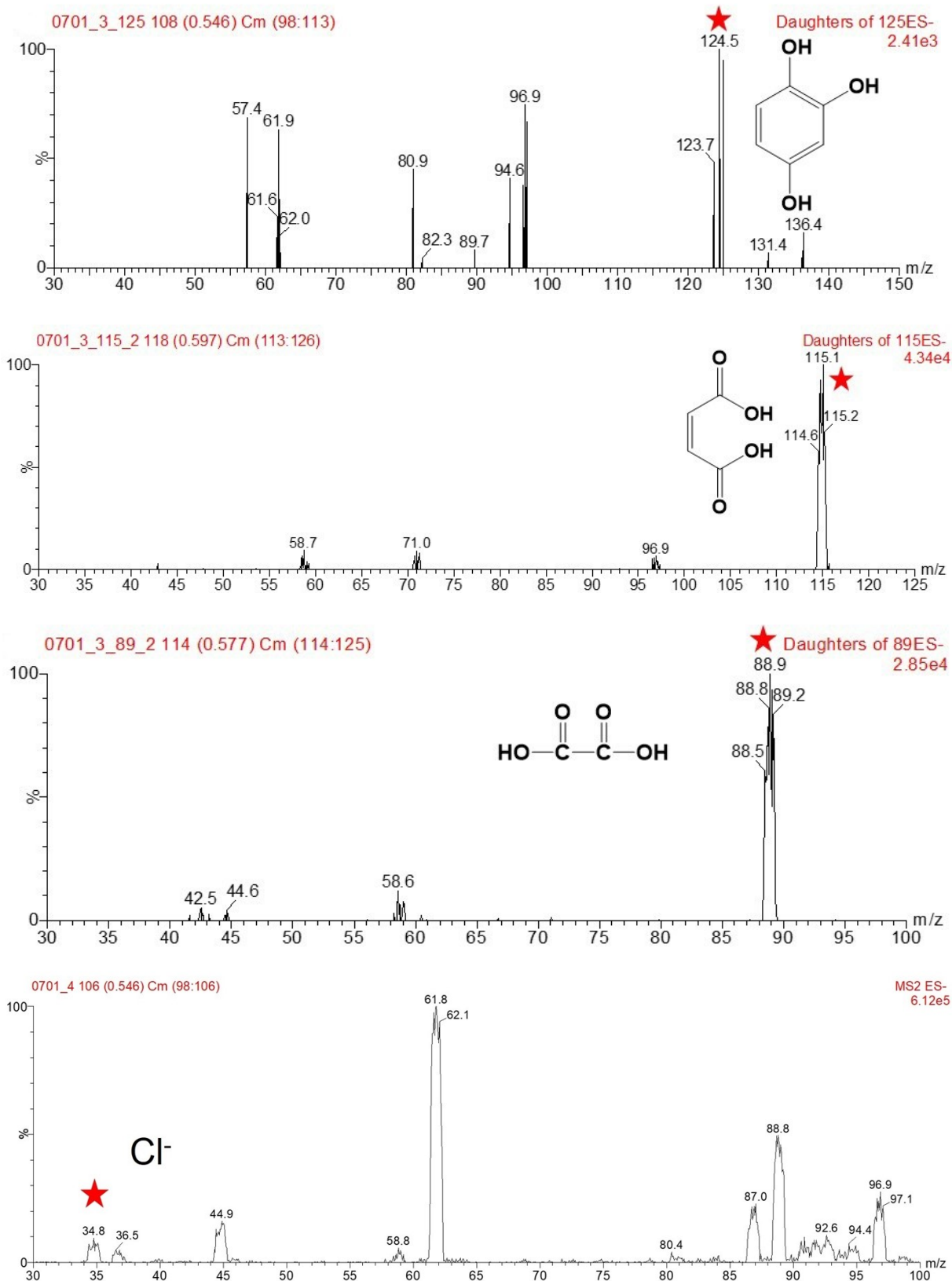


Figure S16 Liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) analyses of reaction intermediates for the degradation of 2,4-DCP over 1FePcCeO₂.

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