Electronic Supplementary Information

Photocatalytic transformation of climbazole and 4-chlorophenol formation using a floral array of chromium-substituted magnetite nanoparticles activated with peroxymonosulfate

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References

Text A.1. The synthetic processes of $Fe_{3-x}Cr_xO_4$, ($0<x<1$).

Polyethylene glycol, with an average molecular weight of 600 (PEG-600), was employed as a soft template. In brief, 2.0 mL glacial acetic acid and 10 mL of PEG-600 were added to 60 mL aqueous solution of $FeSO_4 \cdot 7H_2O$ and $CrCl_3 \cdot 6H_2O$ (the total moles of Fe and Cr ions was 6.0 mmol). The solution was stirred with a continuous N_2 flow. Then, another 60 mL of lye solution containing NaOH, $NaNO_3$ and a few drops of hydrazine hydrate was added dropwise to the above solution. After that, the reflux reaction was proceeded with a microwave reactor at 98.0±2.0 ^oC for 15-60 min with an output power of 600 W. The black precipitate was collected and washed several times, and then freeze-dried in vacuum.

Text A. 2. The characterization details of the prepared chromium-magnetite samples. Powder X-ray diffraction (PXRD) patterns were recorded between 10^{o} to 80^{o} (2θ) at a step of 4^{o} min^{-1} on a Bruker D8 advance diffractometer equipped with Cu $K\alpha$ radiation (40 kV and 40 mA) at room temperature.

BET specific surface area was measured by nitrogen physisorption on a Quantachrome Instruments Quadrasorb SI surface area and pore size analyzer, after degassed at 110 ^{o}C for 12 h. Pore size distribution was also tested and analyzed by the adsorption branch (BJH model).

X-ray photoelectron spectrometer (XPS) was performed on a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer, equipped with monochromatic Al $K\alpha$ (hv =1486.6 eV) radiation. The curve fitting was carried out by XPSPEAK4.1 software using a Gaussian-Lorentz peak shape and Shirley background function. The binding energies of Fe2p and O1s were determined, and the carbon signal (C1s) at 284.8 eV was taken as a reference for binding energy calibration.

Scanning transmission electron microscopy [1] was observed on Hitachi 8020 using 2 kV accelerating voltage. High resolution transmission electron microscopy (HRTEM) was observed on a FEI Tecnai G2 F20 S-Twin operating at 200 kV. Nanocrystal morphology, size distributions and lattice fringes were scrutinized with Gatan software Digital Micrograph (TM) 3.7.4.

The Raman spectrum was performed at room temperature with a Renishaw in Via Laser Raman Spectrometer by employing 514.5 nm line of Ar ion laser. A wavelength band of

100- 900 nm was collected with a spectral resolution of 6 cm^{-1}.

The ESR spin-trapped signals of radicals was conducted on a Bruker E500 spectrometer with 0.2 g L^{-1} magnetite sample and 50 mmol DMPO under UVA irradiation (λ=365 nm). The detections of $^{\bullet}OH$ and $SO_4^{\bullet-}$ were carried out in deionized water. The ESR was processed with the center field at 323 mT, microwave frequency of 9.057 GHz, power of 0.998 mW, sweep width of 5 mT, sweep time of 1.0 min and time constant of 0.03 s.

At the end of the catalytic test, the leaching Fe ions concentration was determined using a Flame Atomic Absorption Spectrophotometer (FAAS) Hitachi Z-2000 at 248.3 nm, with a hollow-cathode lamps operating at 30 mA and an acetylene air-flame.

The supernatant solution after reaction was analyzed by total organic carbon (TOC) using a TOC analyzer (Shimadzu, TOC-VPV) using the nonpurgeable organic carbon method.

Text A.3. The conditions of HPLC for the determination of CBZ.

CBZ was analyzed using a Waters e2695 High Performance Liquid Chromatography (HPLC) quipped with a diode array detector (DAD). The column was a Waters XBridge C18 column (250 × 4.6 mm, 5 μm). The mobile phase consists of water and methanol (35:65, v/v) at a flow rate of 1 mL min^{-1} under an isocratic condition. The sample injection, detection wavelength of DAD, and column temperature were 100 μL, 222 nm, and 40 ^{o}C, respectively. The retention time of CBZ was 9.9 min.

Text A.4. The detailed procedures of solid phase extraction and pre-column derivation.

Solid phase extraction

The reaction solution (100 mL, pH ≈ 3) was loaded at a flow rate of 10 mL min^{-1} on the Oasis HLB cartridge (500 mg, 6 mL), which has been previously preconditioned by 2 × 5 mL methanol and 2 × 5 mL acidic Milli-Q water (pH = 3) in sequence. The cartridge was then dried under vacuum for 2 h. The potential intermediate products were consecutively eluted with 2 × 1.5 mL dichloromethane, 2 × 2.5 mL ethyl acetate and 2 × 2.5 mL methanol. These three eluates were combined, dried under a gentle nitrogen stream, redissolved in 0.5 mL methanol into a 2 mL amber glass vial, and stored at -20 °C.

Pre-column derivation

Pre-column derivation is necessary to be performed for the detection of 4-CP by GC-MS. The above 50 μL of extracts was dried under a gentle nitrogen stream, after which the residue was dissolved in 100 μL BSTFA pyridine solution (1:1, *v*/*v*). The resultant mixture was vigorously vortexed, incubated at 60 °C for 1 h, dried under a gentle nitrogen stream, redissolved in 50 μL methyl *tert*-butyl ether (MTBE), and then analyzed by GC-MS. The derivation of 4-CP standards was conducted as the above proceudre.

Text A.5. The parameters of GC-MS and HPLC-HRMS for the analysis of 4-CP and other potential intermediate products.

GC-MS conditions for the identification and quantitation of 4-CP

The intermediate product 4-chlorophenol (4-CP) was identified and quantified by a Thermo TRACE™ 1300 gas chromatography connected to a TSQ 8000 Evo mass spectrometer (Waltham, MA, USA) with an electronic ionization (EI) source. A Thermo TG-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for chromatographic separation. Ultrapure helium (> 99.999%) was employed as carrier gas at a constant flow rate of 1 mL min^{-1}. The injection volume was 1 μL with a splitless inlet. The temperature of injector, ion source and transfer line were set at 280, 285 and 285 ^{o}C respectively. For the identification of 4-CP, the oven temperature was begun at 70 ^{o}C, held for 5 min, then raised with 7.5 ^{o}C min^{-1} to 285 ^{o}C, and held for 10 min. The scan range was set at *m*/*z* 50–450 under full scan mode.

For the quantitation of 4-CP, the oven temperature was initially held at 70 ^{o}C for 5 min, increased to 145 ^{o}C at a rate of 7.5 ^{o}C min^{-1}, then stepped to 285 ^{o}C at a rate of 20 ^{o}C min^{-1}, and held for 8 min. Quantitative analysis was conducted on selected ion monitoring (SIM) mode. Based on the peak intensity, the quantitative ion was selected as 185.1, while the qualitative ions were set at 187.1, 200.1 and 202.1. The retention time of 4-CP was 12.3 min.

HPLC-HRMS conditions for the identification of other potential intermediate products

The potential intermediate products were identified by a Thermo TRACE™ 1300 gas chromatography connected to a Dionex Ultimate 3000 ultra-high performance liquid

chromatographer (UHPLC) coupled to a Thermo Scientific Q Extractive Focus mass spectrometry (Thermo Scientific, USA). A Waters Acquity UPLC BEH C18 column (100 × 2.1 mm, 1.8 μm) was used for chromatographic separation. Table S1 shows the instrumental operating parameters of UHPLC-HRMS.

Under the positive mode, the retention time and molecular ion of climbazole were 28.07 min and *m*/*z* 293.1046. Under the negative mode, the retention time and molecular ion of climbazole were 28.05 min and *m*/*z* 291.0896.

Text A.6. The derivation of PNEC in this study.

Based on European Commission Technical Guidance Document, the median effective concentration (EC_{50}) or no observed effect concentration (NOEC) of a chemical was used to calculate the predicted no effect concentration (PNEC) for the acute or chronic effect [2]. The PNEC is commonly derived by an assessment factor approach. When sufficient toxicity data is available, a statistical extrapolation method for PNEC calculation is preferable. If using the assessment factor approach, the PNEC was calculated by dividing the lowest acute EC_{50} or chronic NOEC from the most sensitive species by an assessment factor (1000, 100, 50 or 10). If NOEC is absent, EC_{10} can be selected as an alternative. If using the statistical extrapolation methods, at least 10 NOEC values for different species containing at least eight taxonomic groups were necessary in this study to derive a PNEC value based on species sensitivity distribution (SSD). A log-logistic model with four fitting parameters (Eq. 1) is usually used to fit the toxicity data[3, 4]. HC_5 is a 5th percentile effect concentration based on the SSD, and expected to protect 95% of species at this concentration [2].

$$PNEC = HC_5/AF \quad (1)$$

where HC_5 is a 5th percentile effect concentration according to the SSD. The concentration high than HC_5 is considered as that 95% of species are safe, and AF is the assessment factor of 1.

Table S1 Instrumental operating parameters of UHPLC-HRMS

	Positive ionization mode	**Negative ionization mode**
UHPLC parameter		
Flow (mL/min)	0.3	
Column temperature (°C)	35	
Injection volume (μL)	5	
Mobile phase A	5 mM ammonium acetate and 0.05% formic acid in ultrapure water	
Mobile phase B	Methanol	
UHPLC gradient program	Time (min)	B (%)
	0	5
	10	5
	35	95
	50	95
	55	5
	60	5
MS parameter		
Ion source	HESI	HESI
Spray voltage (V)	3500	3000
Capillary temperature (°C)	350	300
Sheath gas flow rate	40	40
Aux gas flow rate	10	10
Scan range (m/z)	100-500	70-700

Table S2. Toxicity data of 4-CP to the most sensitive aquatic species

No.	Phylum	Species	Duration (d)	Effect	Endpoint	Conc. (mg/L)	Reference
Chronic toxicity							
1	Proteobacteria	*Vibrio fischeri*	0.9	Luminescence intensity	NOEC	1	5
2	Angiosperms	*Lemna gibba*	7	Number of fronds	EC10	4.37	6
3	Cnidaria	*Hydra vulgaris* (pink hydra)	0.0833	Tentacle Clubbing	NOEC	5.7	7
4	Cnidaria	*Hydra viridissima* (green hydra)	6	Population growth	NOEC	10.3	7
5	Cnidaria	*Hydra viridissima* (green hydra)	0.0833	Tentacle Clubbing	NOEC	1.1	7
6	Rotifera	*Brachionus calyciflorus*	2	Progeny numbers	NOEC	30	5
7	Chlorophyta	*Scenedesmus subspicatus*	3	Biomass	EC10	1.9	8
8	Chlorophyta	*Scenedesmus subspicatus*	2	Population changes, general	EC10	5.5	8
9	Chlorophyta	*Pseudokirchneriella subcapitata*	2	Dissolved oxygen production	NOEC	5	9
10	Chlorophyta	*Pseudokirchneriella subcapitata*	2	Growth rate	NOEC	5	9
11	Chlorophyta	*Chlorella pyrenoidosa*	3	Chlorophyll	NOEC	10	10
12	Arthropoda	*Daphnia magna*	21	Biomass	NOEC	0.63	8
13	Arthropoda	*Daphnia magna*	9-11	Mortality	NOEC	2.6	11
14	Arthropoda	*Daphnia magna*	9-11	Total progeny	NOEC	0.6	11
15	Arthropoda	*Daphnia magna*	9-11	Number of broods	NOEC	2.6	11

16	Arthropoda	*Daphnia magna*	9-11	Mean brood size	NOEC	0.3	11
17	Arthropoda	*Daphnia magna*	21	Reproduction	NOEC	0.63	12
18	Arthropoda	*Daphnia magna*	2	Mortality	NOEC	1.1	13
19	Arthropoda	*Ceriodaphnia dubia*	7-10	Total progeny	NOEC	1.6	11
20	Arthropoda	*Ceriodaphnia dubia*	7-10	Number of broods	NOEC	1.6	11
21	Arthropoda	*Ceriodaphnia dubia*	7-10	Mean brood size	NOEC	1.6	11
22	Arthropoda	*Ceriodaphnia dubia*	7-10	Mortality	NOEC	0.2	11
23	Chordata	*Cyprinodon variegatus*	4	Mortality	NOEC	3.2	14
24	Chordata	*Carassius auratus* (Fish scale cell line, GFS)	1	Disruption of cell membranes	IC10	32 [a]	15
Acute toxicity							
1	Proteobacteria	*Vibrio fischeri*	0.9	Luminescence intensity	EC50	3.23	5
2	Angiosperms	*Lemna minor*	7	Dry weight	EC50	26 [a]	16
3	Angiosperms	*Lemna minor*	7	Number of fronds	EC50	33.2 [a]	16
4	Angiosperms	*Lemna minor*	7	Number of plants	EC50	36.1 [a]	16
5	Angiosperms	*Lemna gibba*	7	Dry weight	EC50	54	16
6	Angiosperms	*Lemna gibba*	7	Number of plants	EC50	56	16
7	Angiosperms	*Lemna gibba*	7	Number of fronds	EC50	36.0 [a]	6, 16
8	Cnidaria	*Hydra vulgaris* (pink hydra)	4	Mortality	LC50	32	7
9	Cnidaria	*Hydra vulgaris* (pink hydra)	0.0417	Tentacle Clubbing	EC50	43	7
10	Cnidaria	*Hydra viridissima* (green hydra)	4	Mortality	LC50	45	7

11	Cnidaria	*Hydra viridissima* (green hydra)	0.0833	Tentacle Clubbing	EC50	7.8	7
12	Ciliophora	*Tetrahymena thermophila*	2	Cell density	EC50	1.54	17
13	Ciliophora	*Tetrahymena pyriformis*	2	Population growth rate	IC50	36.7	18
14	Rotifera	*Brachionus calyciflorus*	2	Progeny numbers	EC50	38.2	5
15	Chlorophyta	*Scenedesmus subspicatus*	4	Biomass	EC50	8	8
16	Chlorophyta	*Scenedesmus subspicatus*	3	Population changes, general	EC50	17	8
17	Chlorophyta	*Pseudokirchneriella subcapitata*	2	Dissolved oxygen production	EC50	20.88	9
18	Chlorophyta	*Pseudokirchneriella subcapitata*	2	Growth rate	EC50	14.75	9
19	Chlorophyta	*Chlorella vulgaris*	4	Growth inhibition	EC50	29	19
20	Ochrophyta	*Skeletonema costatum*	5	Total cell count	EC50	13.8	20
21	Ochrophyta	*Skeletonema costatum*	5	Total cell volume	EC50	11.6	20
22	Arthropoda	*Saduria entomon*	14	Mortality	LC50	36.8	21
23	Arthropoda	*Tisbe battagliai*	1	Mortality	LC50	21	22
24	Arthropoda	*Crangon septemspinosa*	4	Mortality	LC50	4.6	23
25	Arthropoda	*Nitocra spinipes*	4	Mortality	LC50	21	24
26	Arthropoda	*Daphnia magna*	9-11	Total progeny	EC50	3	11
27	Arthropoda	*Daphnia magna*	9-11	Number of broods	EC50	4	11
28	Arthropoda	*Daphnia magna*	9-11	Mean brood size	EC50	3	11
29	Arthropoda	*Daphnia magna*	7	Mortality	LC50	2.31	25

30	Arthropoda	*Daphnia magna*	1	Change in direct movement	EC50	6.8	26
31	Arthropoda	*Ceriodaphnia dubia*	7-10	Total progeny	EC50	2	11
32	Arthropoda	*Ceriodaphnia dubia*	7-10	Number of broods	EC50	2	11
33	Arthropoda	*Ceriodaphnia dubia*	7-10	Mean brood size	EC50	2	11
34	Arthropoda	*Ceriodaphnia dubia*	9	Mortality	LC50	6	11
35	Mollusca	*Crassostrea rhizophorae*	1	Abnormal	EC50	20.6 [a]	27
36	Chordata	*Platichthys flesus*	4	Mortality	LC50	5	22
37	Chordata	*Poeciliopsis lucida* (Fish Hepatoma cell line, PLHC-1)	1	Membrane damage	EC50	398.54	28
38	Chordata	*Poeciliopsis lucida* (Fish Hepatoma cell line, PLHC-2)	1	Mitochondrial metabolic function	EC50	308.55	28
39	Chordata	*Tilapia zillii*	2	Mortality	LC50	4.49	29
40	Chordata	*Lepomis macrochirus* (Fish cell line, BF-2)	1.1388	Membrane damage	EC50	201.84	30
41	Chordata	*Pimephales promelas*	4	Mortality	LC50	4	31
42	Chordata	*Pimephales promelas*	4	Mortality	LC50	3.8	31
43	Chordata	*Pimephales promelas*	4	Mortality	LC50	5	31
44	Chordata	*Cyprinodon variegatus*	2	Mortality	LC50	5.4	14
45	Chordata	*Poecilia reticulata*	4	Mortality	LC50	6.3	32
46	Chordata	*Lepomis macrochirus*	4	Mortality	LC50	3.8	33

47	Chordata	*Oncorhynchus mykiss* (Fish Gonadal cell line, RTG-2)	1	Cell Viability	EC50	1208	34
48	Chordata	*Oncorhynchus mykiss* (Fish Liver cell line, R1)	1	Cell Viability	EC50	166	35
49	Chordata	*Oncorhynchus mykiss*	4	Mortality	LC50	1.9	36
50	Chordata	*Carassius auratus* (Fish scale cell line, GFS)	1	Mitochondrial metabolic function	IC50	168	15
51	Chordata	*Carassius auratus* (Fish scale cell line, GFS)	1	Disruption of cell membranes	IC50	140 [a]	15
52	Chordata	*Carassius auratus*	1	Mortality	LC50	9	37

[a] The value is a geometrical mean value

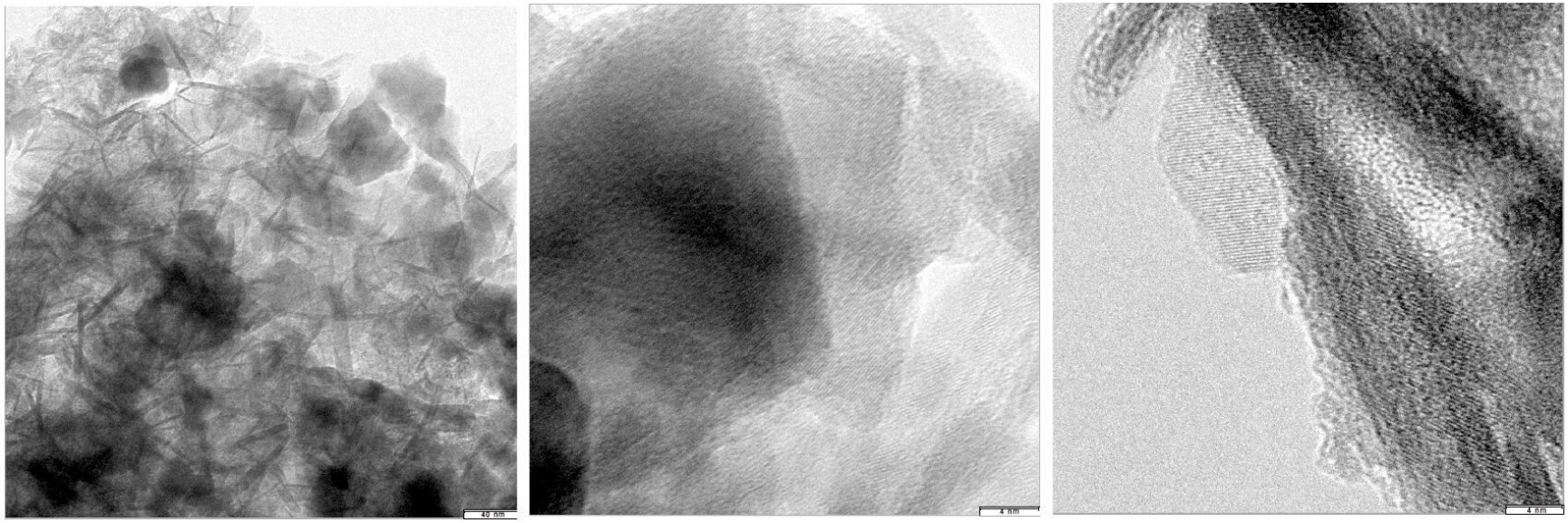
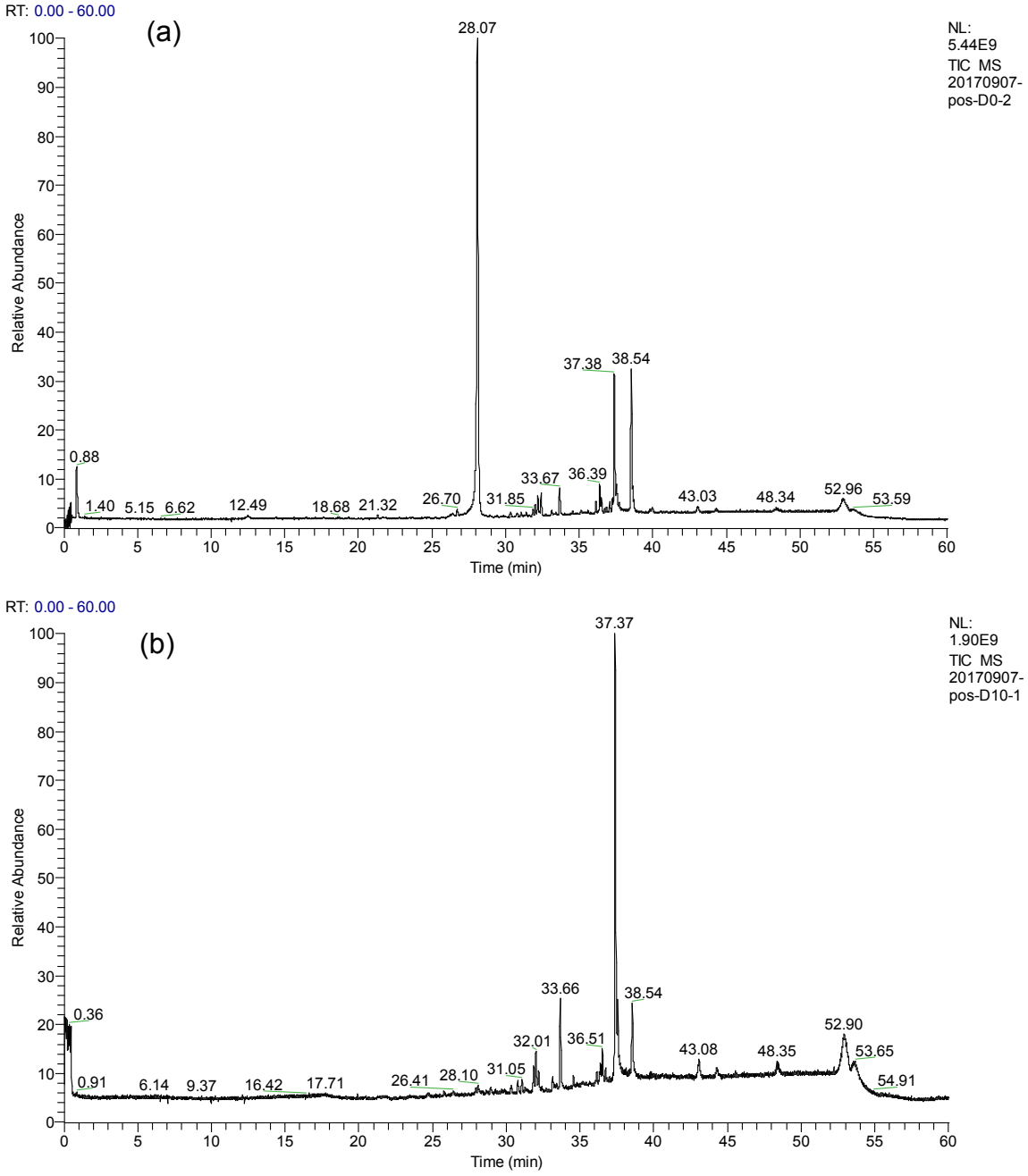


Figure S1. HRTEM images of the synthetic $Fe_{2.76}Cr_{0.24}O_4$ sample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12.49
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31.85
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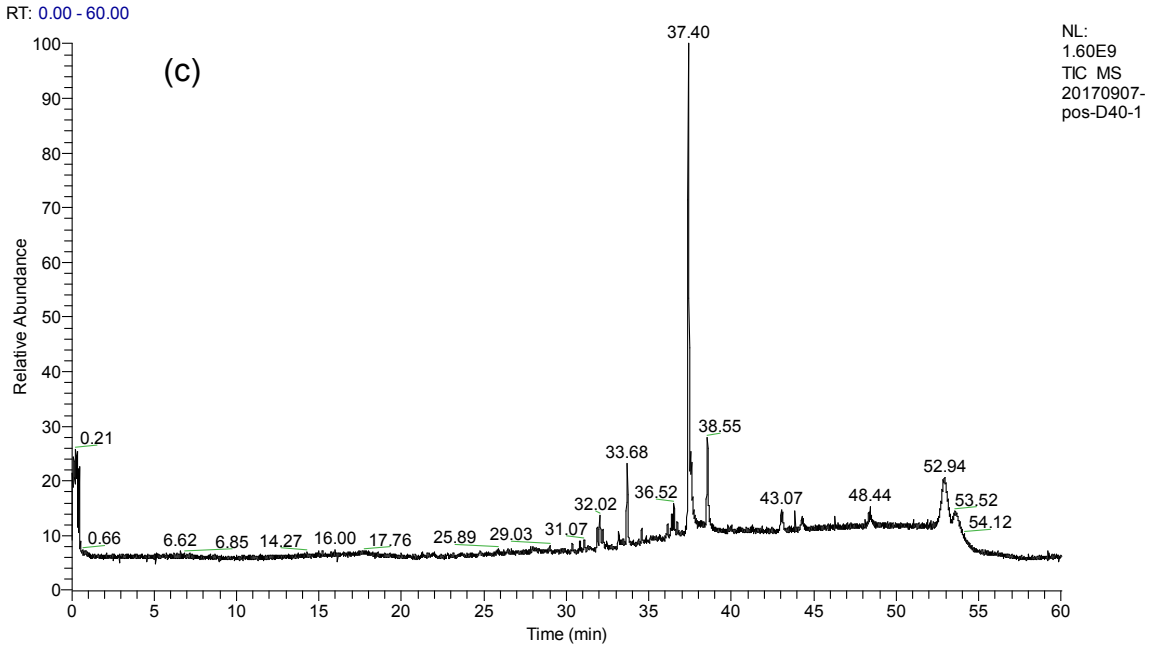
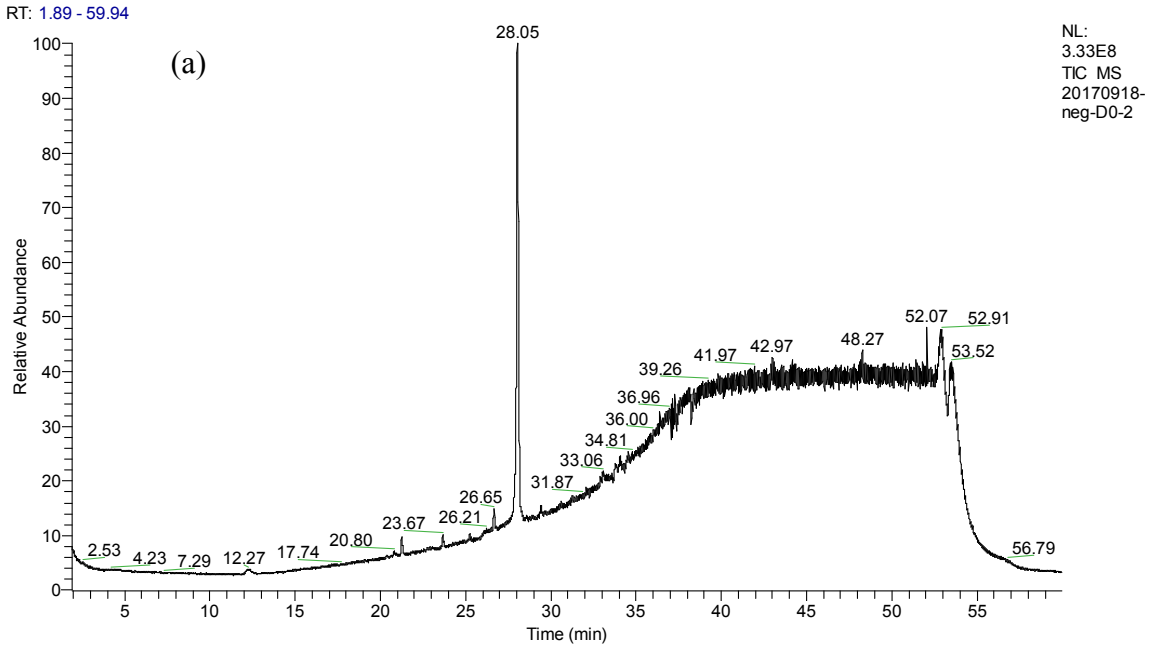


Figure S2. The total ion chromatogram of the D0 (a), D10 (b), and D40 (c) via UHPLC-HRMS analysis with positive ionization mode at different degradation reaction times.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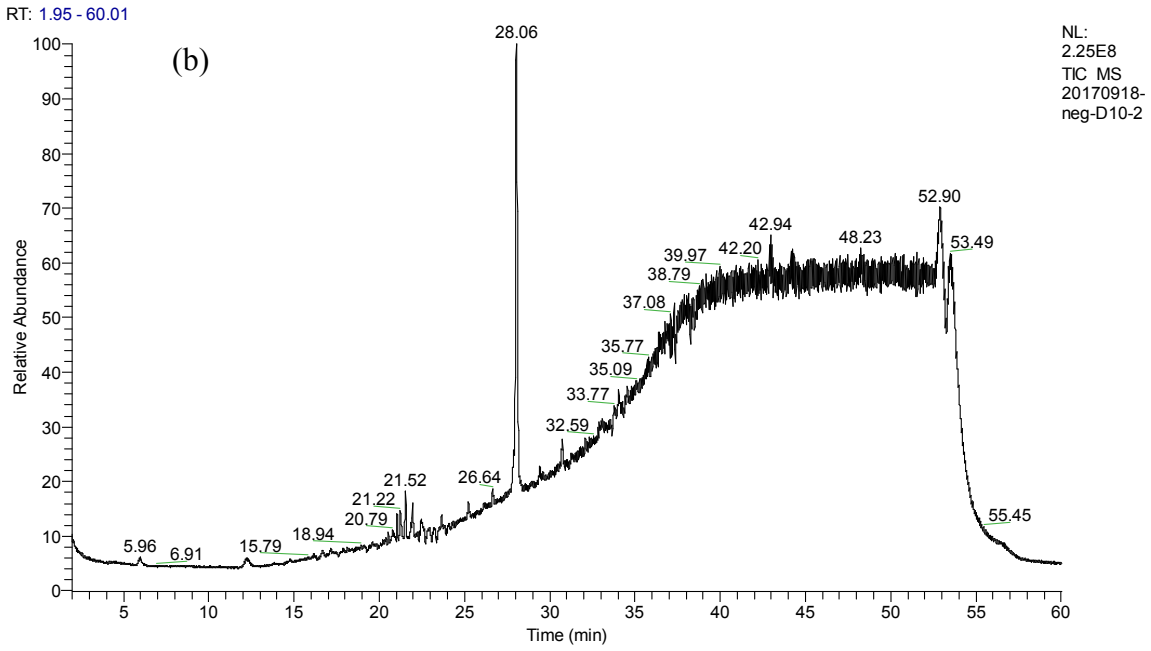
2.53
56.79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53.49
42.20
39.97
38.79
37.08
35.77
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55.45

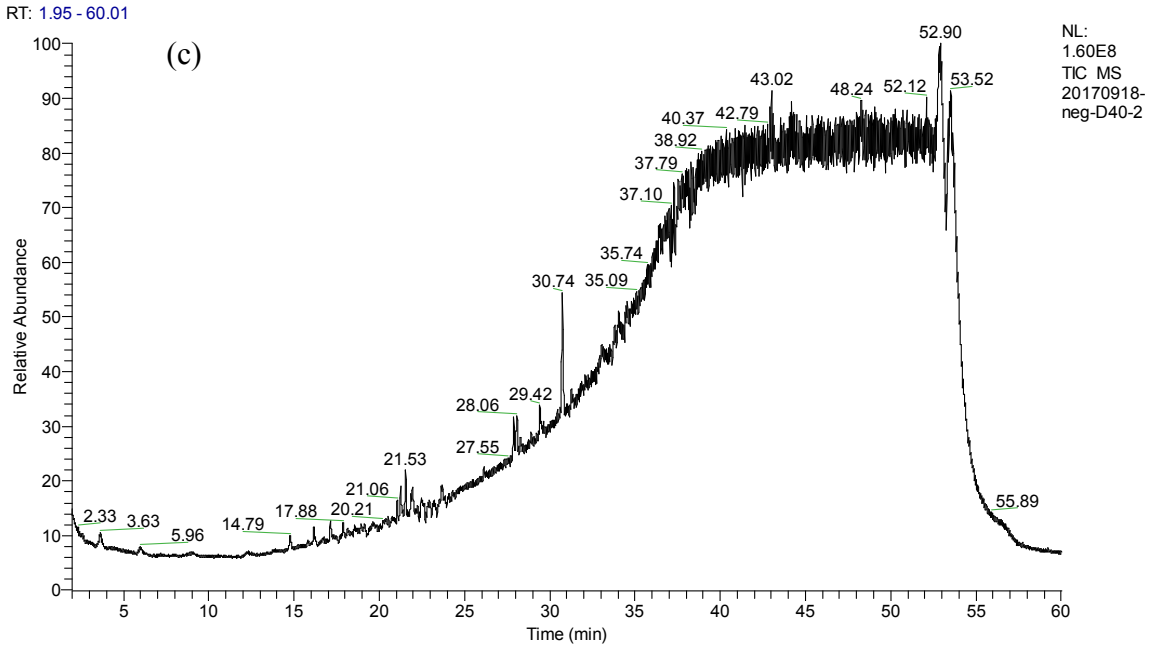

Figure S3. The total ion chromatogram of the D0 (a), D10 (b), and D40 (c) via UHPLC-HRMS analysis with negative ionization mode at different degradation reaction times.

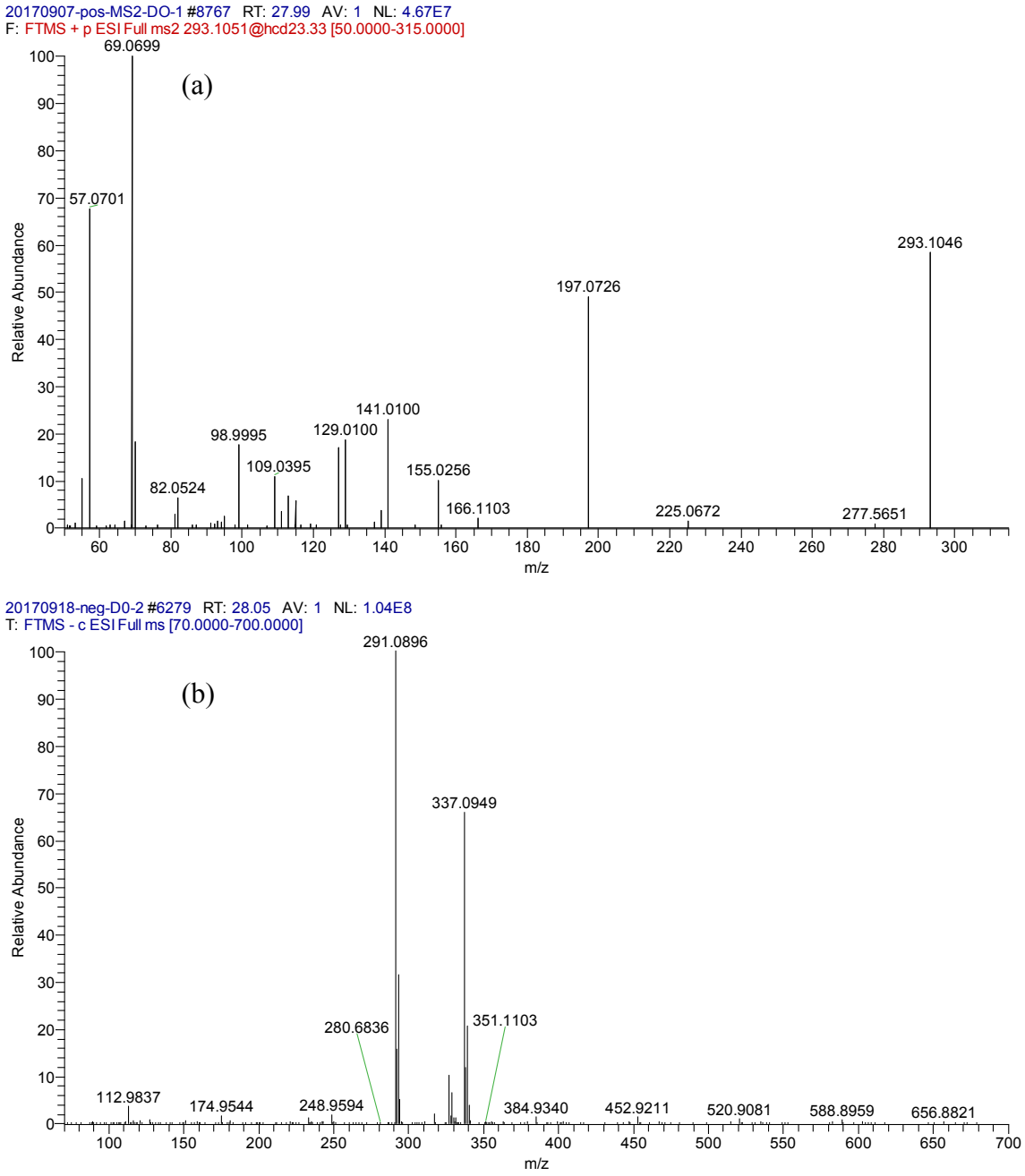

Figure S4. MS spectrums of climbazole in positive and negative mode. MS^2 spectrum of 293.1046 at 27.99 min (a); MS spectrum at 28.05 min (b).

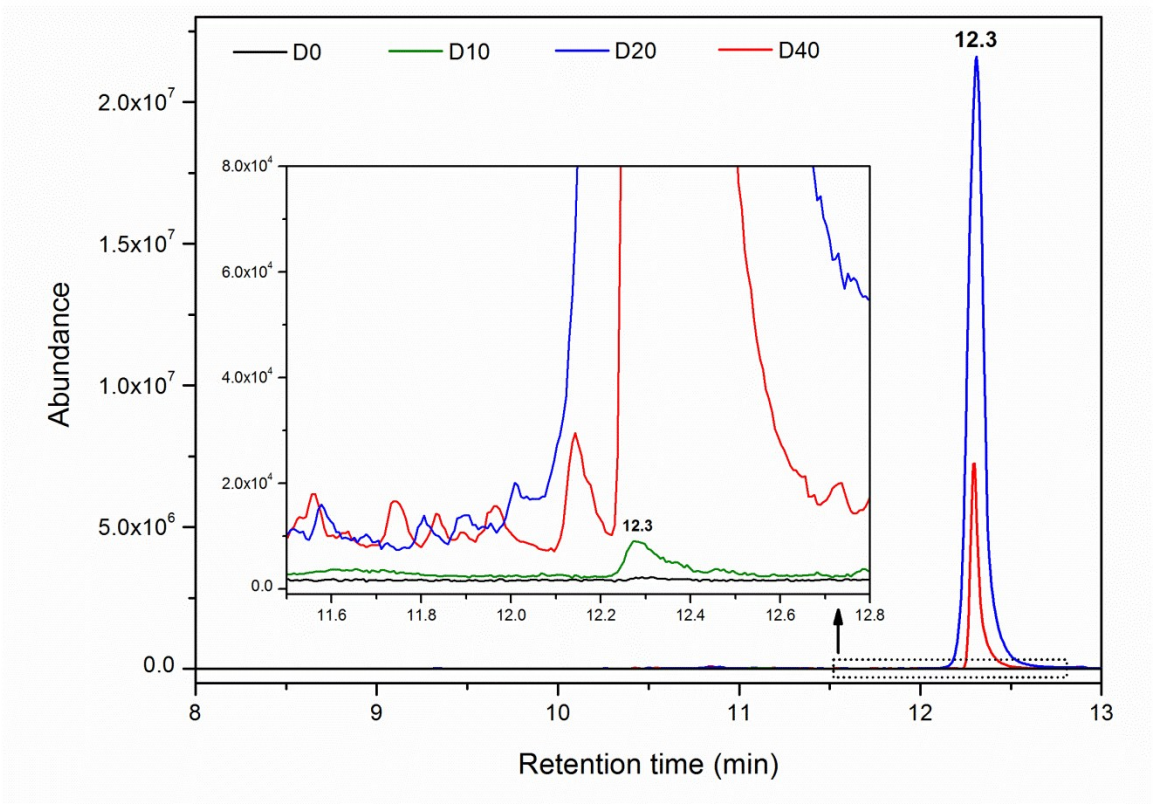

Figure S5. The total ion chromatogram of the samples (D0, D10, D20 and D40) via GC-MS analysis at different degradation reaction times.

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