Supporting Information For

Peroxymonosulfate Activation by a Nitrogen-Doped Multilayer Graphene Catalyst Derived from Cotton for Enhanced Flurbiprofen Degradationn

Rui Sun[1*], Yanfei Chen[2], Limeng Yang[3], Zhi Zhu[1], Zhaohua Zheng[1] and Li Sun[1*]

[1] *Department of Digestive Surgery, Honghui Hospital, Xi'an Jiaotong University, Xi'an 710054, P. R. China*

[2] *Department of Spine Surgery, Honghui Hospital, Xi'an Jiaotong University, Xi'an 710054, P. R. China*

[3] *School of Textile Science & Engineering, Xi'an Polytechnic University, Xi′an, Shaanxi, 710048, China*

[*] *Correspondence information:*

E-mail: hhsl_11@163.com

Mailing address: Department of Digestive Surgery, Honghui Hospital, Xi'an Jiaotong University, 555 Youyi East Road, Beilin District, Xi'an 710054, P. R. China

Text

Text S1. Analytical methods of HPLC-MS

A C18 column (5 μm, 4.6 × 150 mm) was used to extract the pollutant degradation products. Agilent MassHunter program was used to retrieve the detector signal. There were two solutions in the mobile phase: A:B=60:40 (V/V). Solution A was prepared with aqueous solution of 0.10% formic acid, while solution B was generated with acetonitrile. The elution applied a drift rate of 0.30 mL/min and a 10-μliter injection volume. The time-of-flight mass spectrometer was used with the gradient HPLC extraction (Agilent 6530TOF). An electrospray ionization (ESI) source was installed in the mass spectrometer. The ESI conditions were: 3500 V capillary voltage, 135 V fragmentor, 65 V skimmer, 10 L/min drying gas flow, and 350 °C drying temperature. The mass ranged between 70 and 700 m/z.

Text S2. Electrochemical analysis tests

(1) Chronopotentiometry

Firstly, 2.0 $g \cdot L^{-1}$ INC_{II} catalyst (denoted as cat.) was added into an isopropanol solution containing 1% Nafion perfluorinated resin. After sonicating the mixed solution to a homogenously dispersed ink, 10 μL of the ink was syringed onto the disk of the glassy carbon electrode (GCE, 0.07065 cm^2), which was then left to dry in air under an infrared heat lamp. Herein, a INC_{II}-10:5:1-900 catalyst-coated glassy carbon electrode (denoted as cat.-GCE) was prepared. The cat.-GCE was dipped in 20 mM phosphate buffer solution (PBS) overnight maintaining a stable potential before the electrochemical analysis. Then the open circuit potential of cat.-GCE was monitored by chronopotentiometry analysis using saturated calomel electrode (SCE) as the reference electrode, and platinum wire as the counter electrode. The system can also measure the potential variations at the electrode with the addition of PMS or/and flurbiprofen. The anodic current was set as 0.2 μA, and the anodic time was 1500 s.

(2) Chronoamperometry

Experiments were conducted in a mixture solution of 20 mM PBS and 0.2 mM MO in a three-electrode-cell configuration including a working electrode (bare GCE or cat.-GCE), a counter electrode (platinum electrode), and a reference electrode (SCE). The corresponding currents were recorded when an electrical potential was set at 0.50 or 0.78 V using the chronoamperometry (constant potential) measurement.

(3) Linear Sweep Voltammetry (LSV)

LSV was performed between -0.1 V and 1.0 V at a scan rate of 10 mV s^{-1} using an electrochemical workstation. The experiments were conducted in 20 mM PBS and 20 $mg \cdot L^{-1}$ flurbiprofen with a three-electrode-cell configuration including a working electrode (20 × 20 × 1 mm graphite plate), a counter electrode (platinum electrode), and a reference electrode (SCE).

Figure

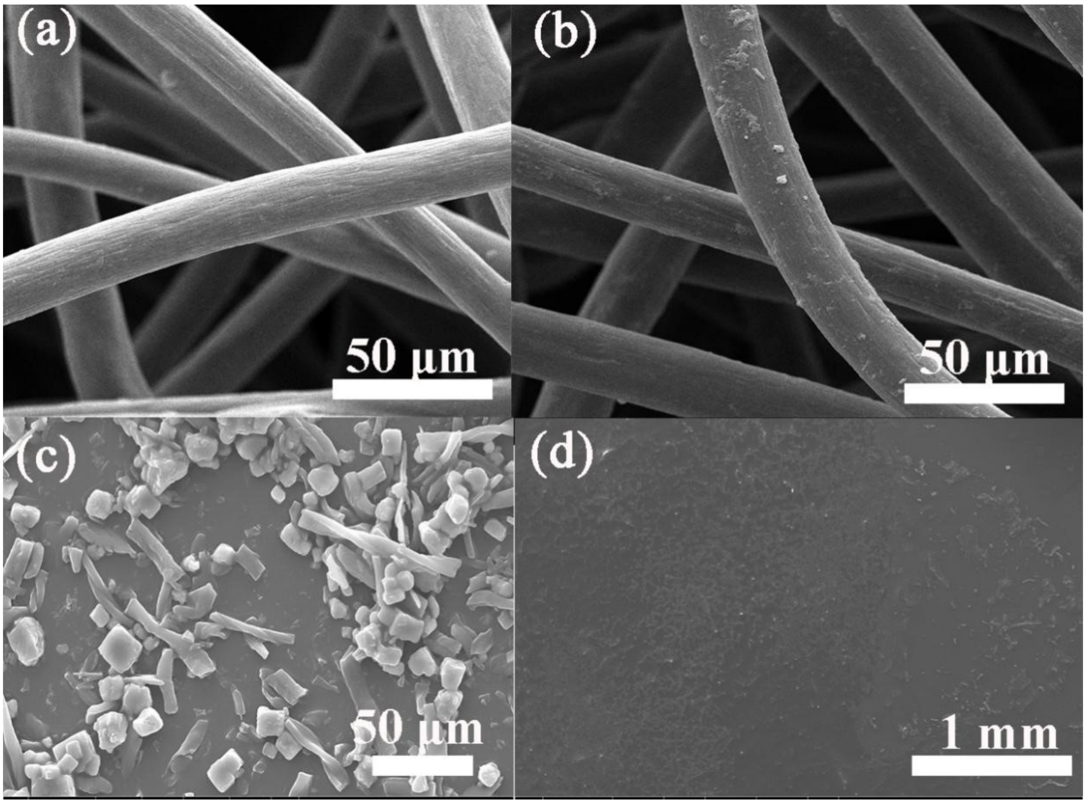


Fig. S1 SEM images of two different cotton fibers: C-I (a), C-II (b), the dried mixture of carbonized C-II and NaCl (c), the precursor of ionic liquid ([EMIm][$N(CN)_2$]) and carbonized C-II and NaCl mixture (d).

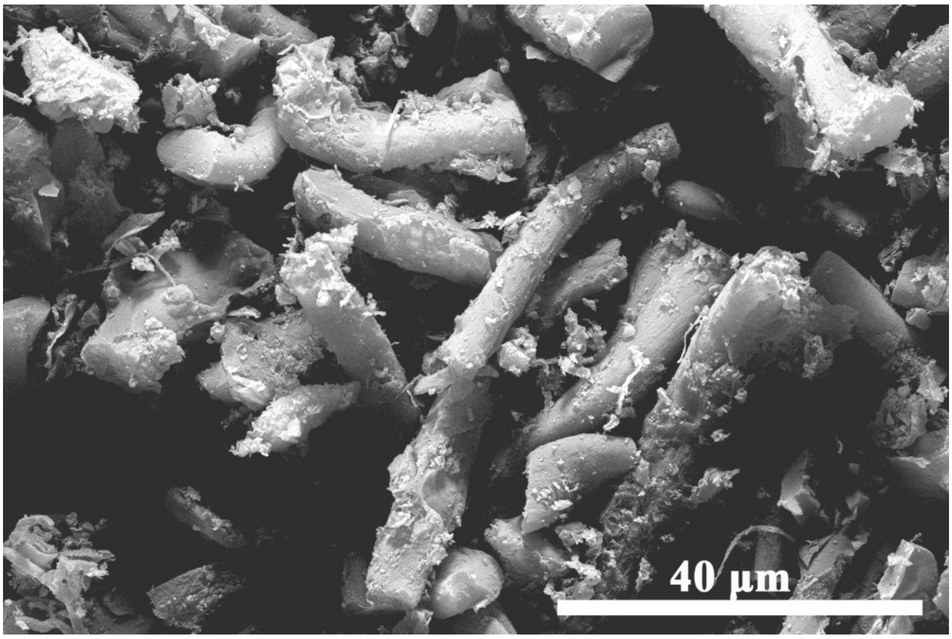


Fig. S2 SEM image of INC_{II} catalyst.

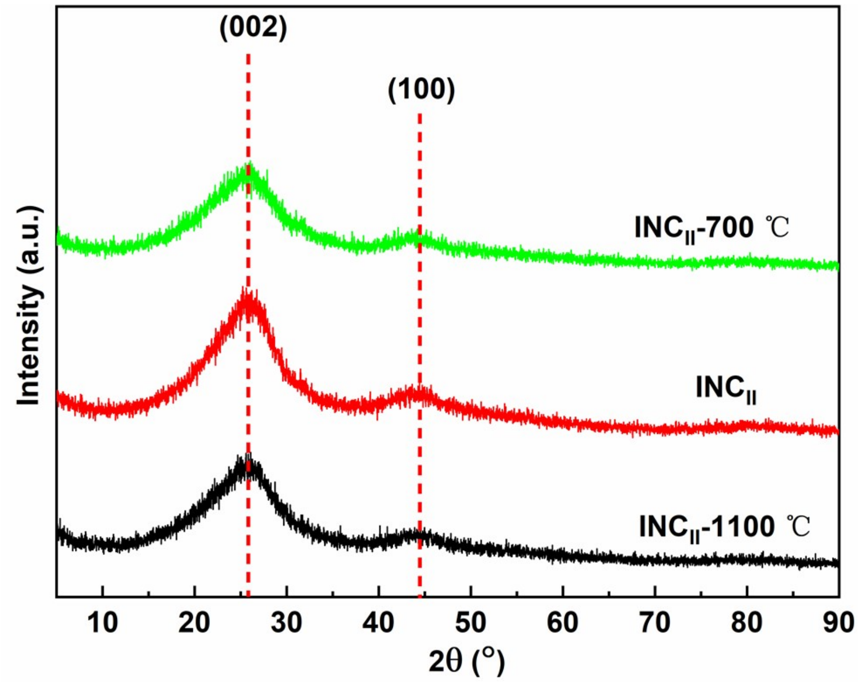


Fig. S3 XRD patterns of INC$_{II}$-700℃, INC$_{II}$, INC$_{II}$-1100℃

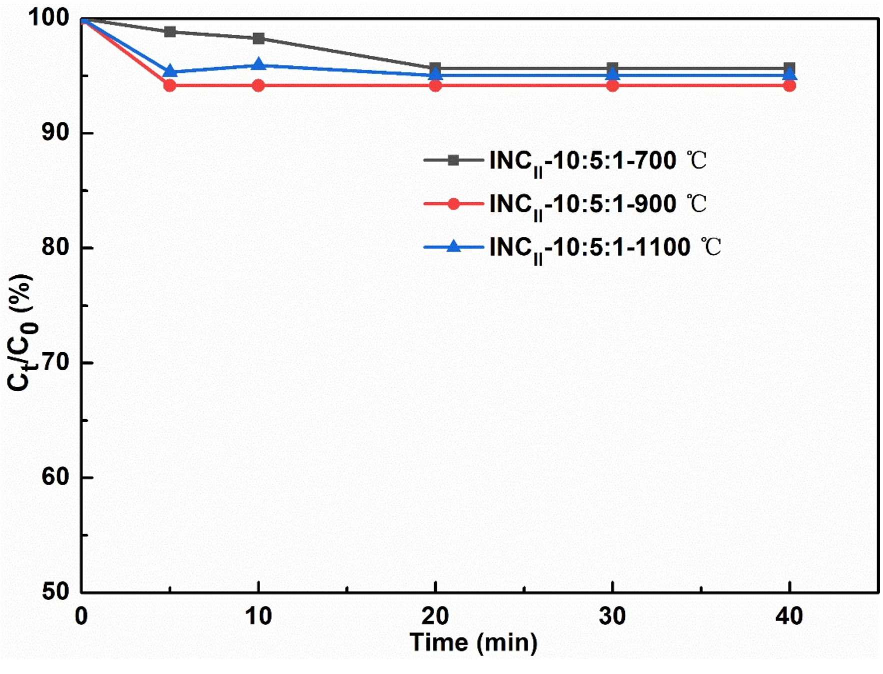


Fig. S4 The adsorption removal of three catalysts with various pyrolysis temperature

([flurbiprofen]=20 mg • L^{-1}, [catalyst]=0.5 g • L^{-1}, [PMS]=6 mM)

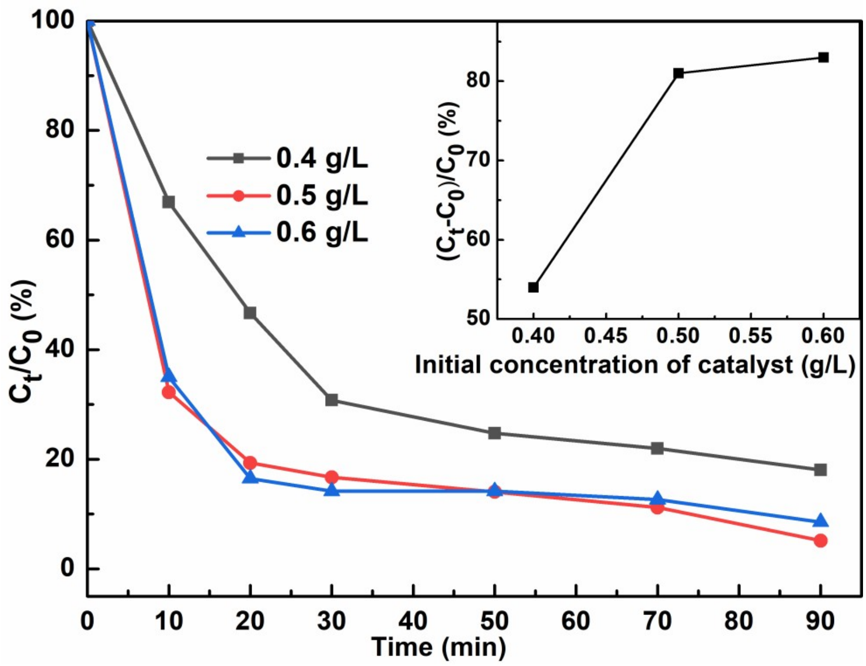


Fig. S5 Comparison of catalytic performance of INC_{II} in different concentrations and correlation of the initial concentration of catalysts versus the conversion of flurbiprofen for 20 minutes (inset) ([flurbiprofen]=20 mg・L^{-1}, [PMS]=6 mM, pH=7.0)

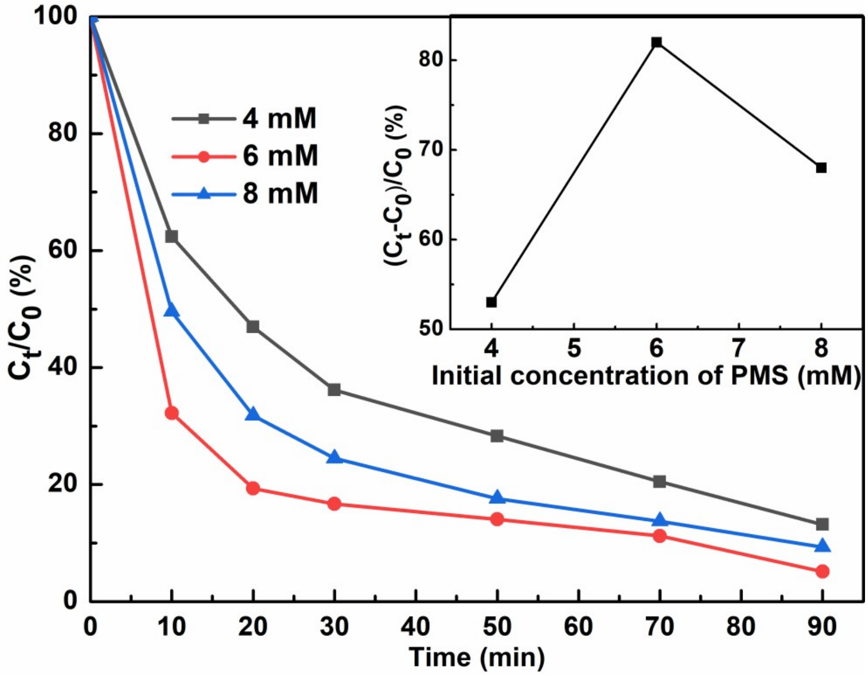
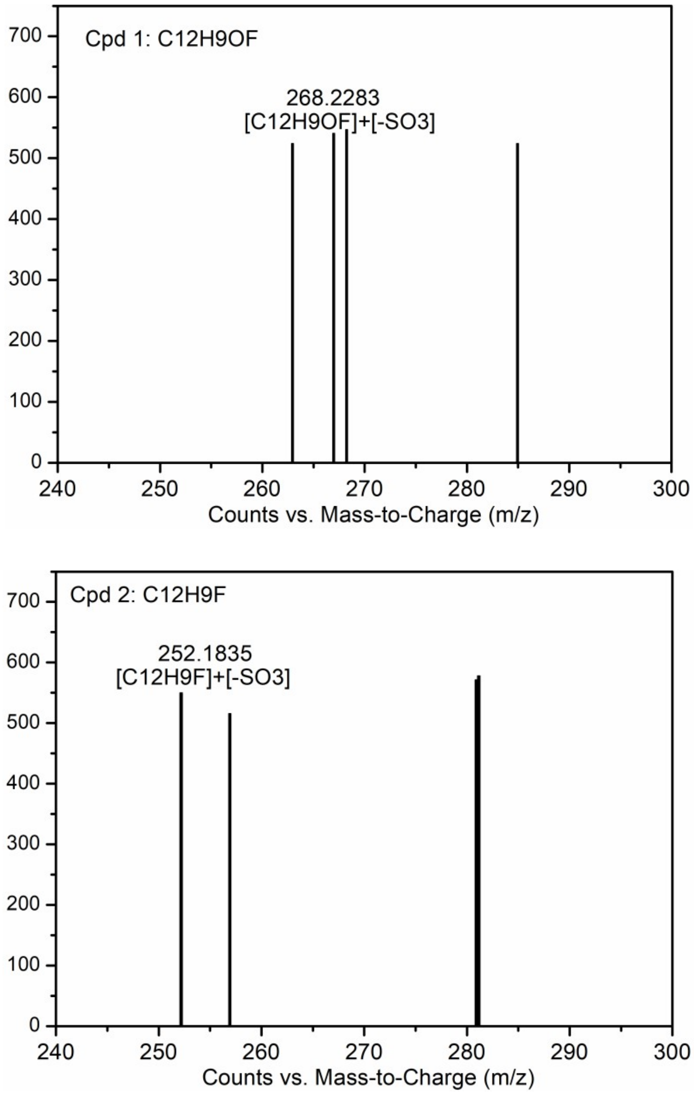
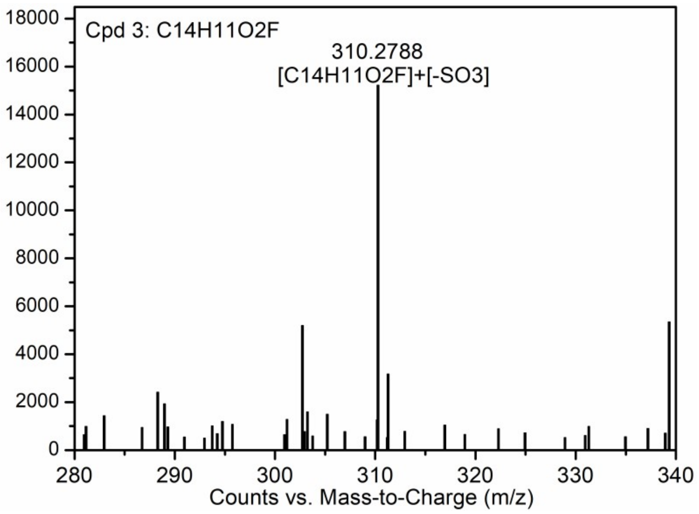
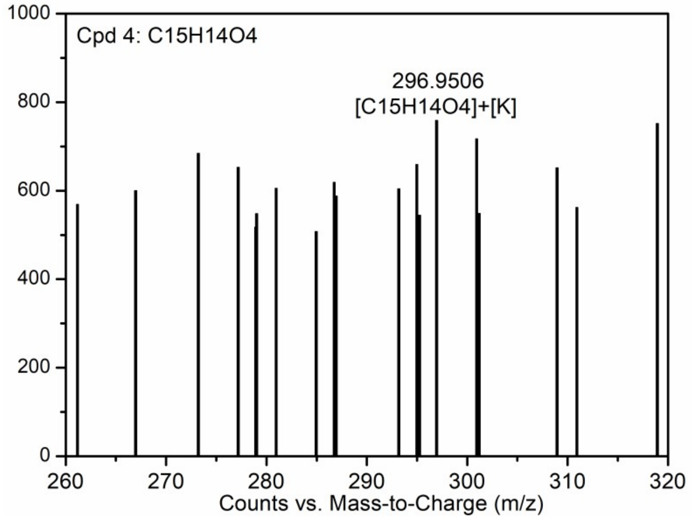
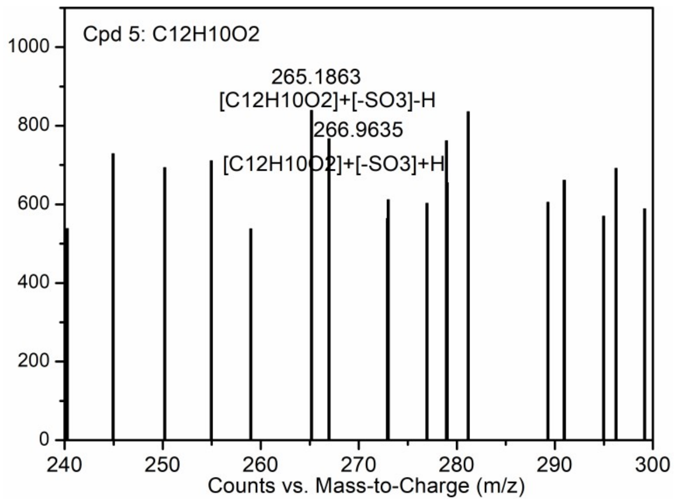


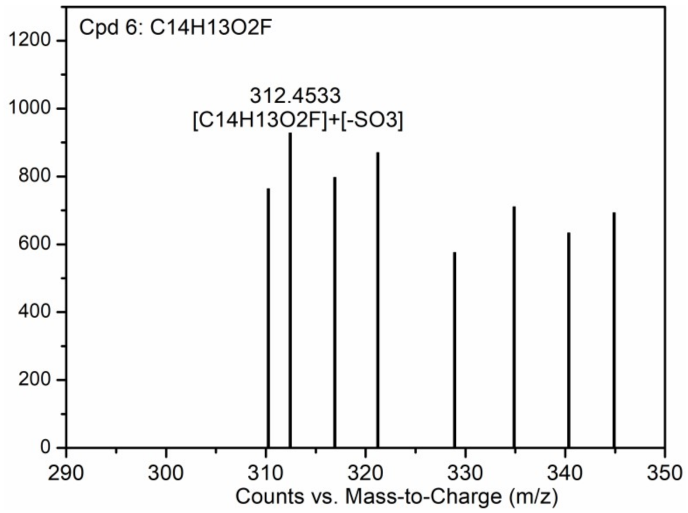
Fig. S6 Comparison of catalytic performance of INC_{II} at the presence of different concentrations of PMS and correlation of the initial concentration of PMS versus the conversion of flurbiprofen for 20 minutes (inset) ([flurbiprofen]=20 mg • L^{-1}, [catalyst]=0.5 g • L^{-1}, pH=7.0)

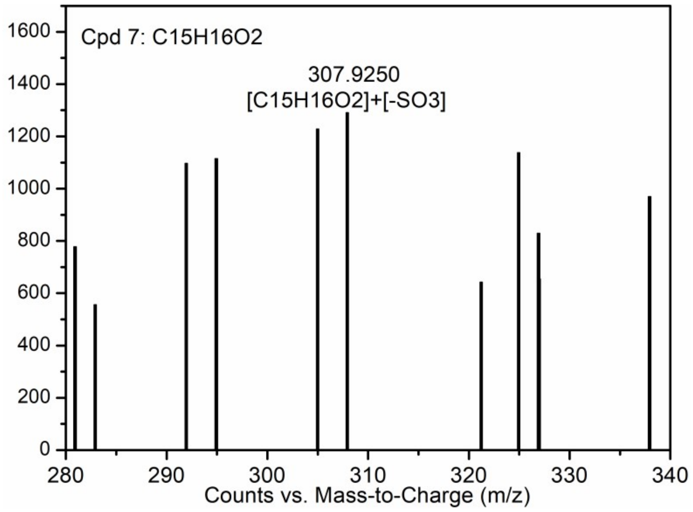


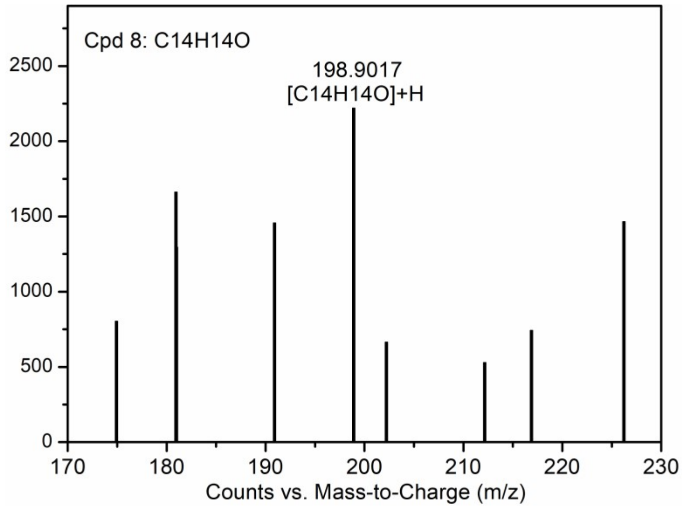

Cpd 3: C14H11O2F
310.2788
[C14H11O2F]+[-SO3]
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
280
290
300
310
320
330
340
Counts vs. Mass-to-Charge (m/z)


Cpd 4: C15H14O4
296.9506
[C15H14O4]+[K]
1000
800
600
400
200
0
260
270
280
290
300
310
320
Counts vs. Mass-to-Charge (m/z)


Cpd 5: C12H10O2
265.1863
[C12H10O2]+[-SO3]-H
266.9635
[C12H10O2]+[-SO3]+H
1000
800
600
400
200
0
240
250
260
270
280
290
300
Counts vs. Mass-to-Charge (m/z)


Cpd 6: C14H13O2F
312.4533
[C14H13O2F]+[-SO3]
1200
1000
800
600
400
200
0
290
300
310
320
330
340
350
Counts vs. Mass-to-Charge (m/z)


Cpd 7: C15H16O2
307.9250
[C15H16O2]+[-SO3]
1600
1400
1200
1000
800
600
400
200
0
280
290
300
310
320
330
340
Counts vs. Mass-to-Charge (m/z)


Cpd 8: C14H14O
198.9017
[C14H14O]+H
2500
2000
1500
1000
500
0
170
180
190
200
210
220
230
Counts vs. Mass-to-Charge (m/z)

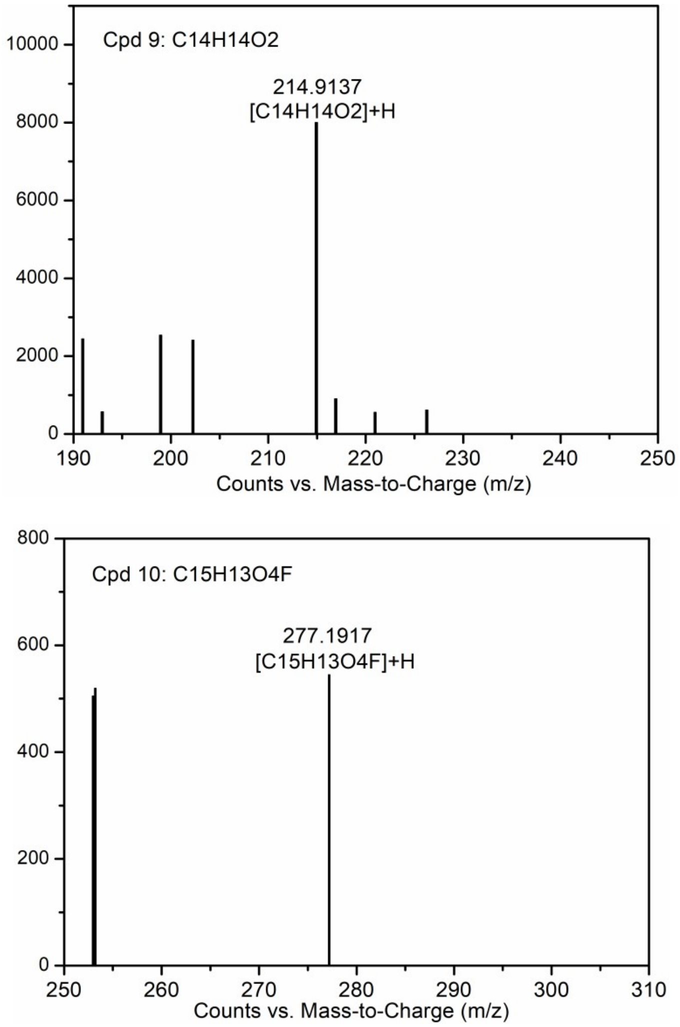


Fig. S7 Mass spectra of partial intermediates during the reaction.

Table

Tab. S1 The surface area and pore volume of different catalysts.

Catalysts	**BET surface area(m^{2}g^{-1})**	**Total Pore volume(cc/g)**
INC$_{II}$-10:5:1-900℃	88.37	——
INC$_{II}$-10:0:1-900℃	36.04	0.222
C$_{II}$-900℃	49.30	1.029

Tab. S2 The TOC and COD removal of INC$_{II}$-10:5:1-900℃/PMS/ flurbiprofen system after 90 min of degradation.

Catalysts	**INC$_{II}$-10:5:1-900℃**
TOC before degradation (mg/L)	909.2
TOC after degradation (mg/L)	511.0
TOC removal rate (%)	43.8
COD before degradation (mg/L)	$2.93*10^3$
COD after degradation (mg/L)	$1.67*10^3$
COD removal rate (%)	43.0

Tab. S3 Element composition of different catalysts (at%).

Catalysts	C（%）	N（%）	O（%）
IC$_{II}$	80.05	11.45	8.50
INC$_{II-UC}$	69.68	12.01	18.31
IN	66.18	8.70	25.11
Regenerated INC$_{II}$	75.99	16.05	7.96
INC$_{II}$	77.44	16.37	6.19

Tab. S4 The comparison with previous works.

Catalysts	**Pollutant concentration (mg·L^{-1})**	**PMS dosage (mM)**	**Degradation time (min)**	**Reference**
$Co_{0.5}Cu_{0.5}Fe_2O_4$	5	1	40	[1]
$FeCo_2O_4$	10	2	60	[2]
$MnSnO_2$@$CsPbBr_3$	10	1	70	[3]
This work	20	6	30	

Tab. S5 Percentage of different N species in each catalyst.

Catalysts	Pyridinic N	Pyrrolic N	Graphitic N	Oxidized N
IC_{II}	43.7%	18.0%	29.0%	9.3%
INC_{II-UC}	34.3%	17.6%	38.1%	10.0%
IN	36.2%	16.0%	34.4%	13.4%
Regenerated INC_{II}	48.6%	19.3%	26.4%	5.7%
INC_{II}	51.1%	11.3%	30.1%	7.4%

Tab. S6 Percentage of different O species in each catalyst.

Catalysts	O-C=O	C-O-C	-C-OH	C=O
IC_{II}	15.7%	1.9%	68.5%	13.9%
INC_{II-UC}	8.7%	4.5%	74.2%	12.6%
IN	6.5%	1.9%	80.8%	10.7%
Regenerated INC_{II}	18.0%	3.9%	60.1%	18.0%
INC_{II}	18.9%	3.8%	55.2%	22.0%

References

[1] Chen Junyu, Rasool Raqiqa Tur, Ashraf Ghulam Abbas, et al. The stimulation of peroxymonosulfate via novel $Co_{0.5}Cu_{0.5}Fe_2O_4$ heterogeneous photocatalyst in aqueous solution for organic contaminants removal, Materials Science in Semiconductor Processing, 157 (2023) 107321.

[2] Ding C, Lei J, Cai Z, et al. Catalytic oxidation activation of peroxymonosulfate over Fe-Co bimetallic oxides for flurbiprofen degradation, Environmental Science and Pollution Research, 30 (2023) 53355-53369.

[3] Rasool Raqiqa Tur, Ashraf Ghulam Abbas, Pasha Mohsin, et al. Nanoscaled $MnSnO_2$@$CsPbBr_3$ quantum dots heterostructure photocatalyst as efficient organic pollutants degradation by peroxymonosulfate; DFT calculation, Journal of Materials Science & Technology, 153 (2023) 41-55.