

Supplementary materials

Novel Fenton-like Catalyst HKUST-1(Cu)/MoS₂-3-C with Non-Equilibrium-State Surface for Selective Degradation of Phenolic Contaminants: Synergistic Effects of σ -Cu-Ligand and $\equiv\text{Mo}-\text{OOSO}_3^-$ Complex

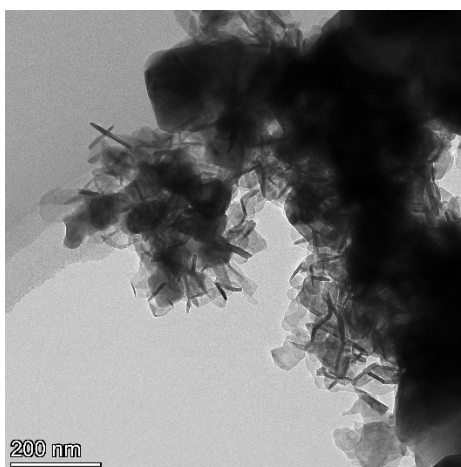


Figure S1 TEM image of HKUST/MoS₂-3-C

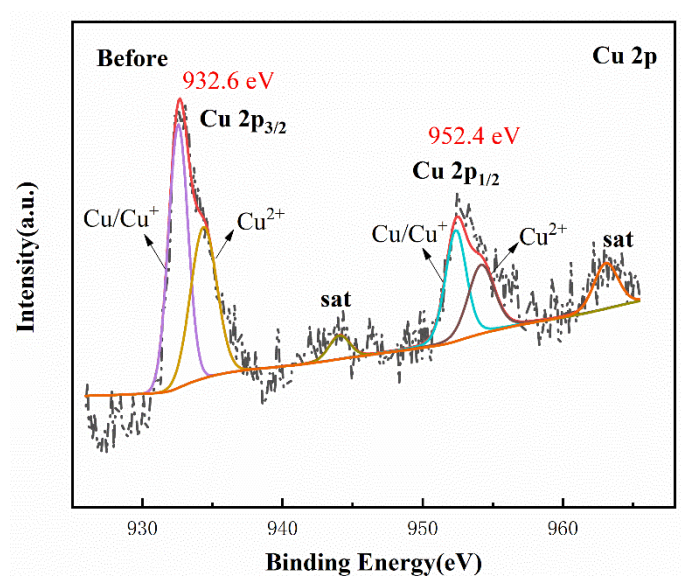


Figure S2 High-resolution XPS spectra of Cu 2p for HKUST-1(Cu)-C.

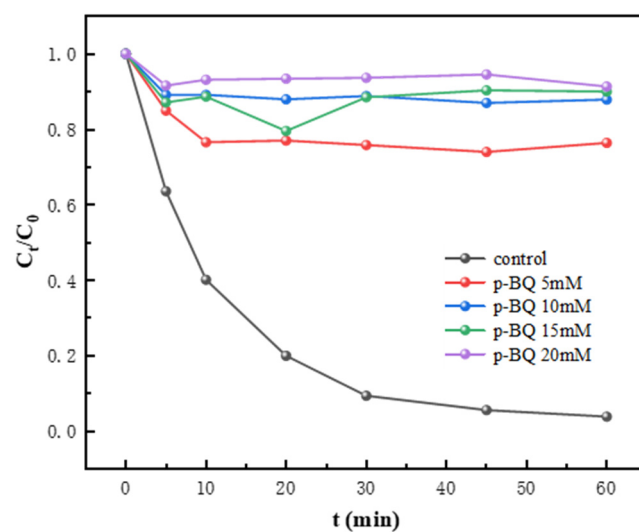


Figure S3 Degradation efficiency of BPA under different quenching conditions (p-BQ concentration = 5, 10, 15, 20 mM)

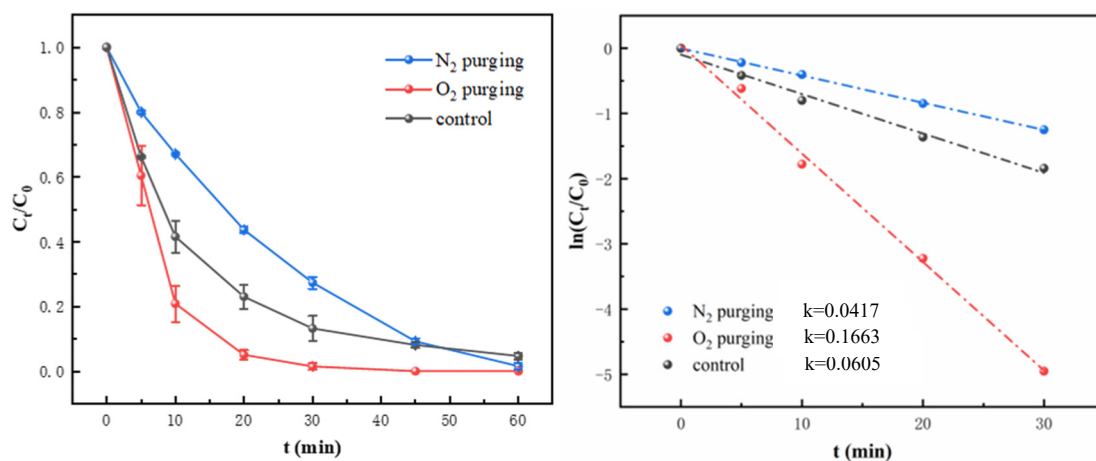


Figure S4 Degradation efficiency and kinetics of BPA under nitrogen/oxygen purging.

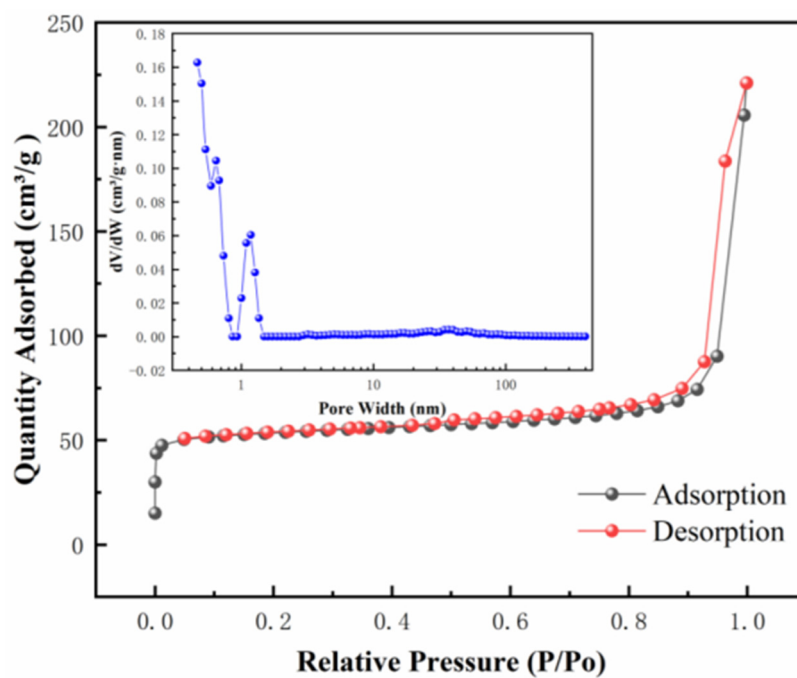


Figure S5 N_2 adsorption/desorption isotherms and pore-size distribution of HKUST-1(Cu)-C.

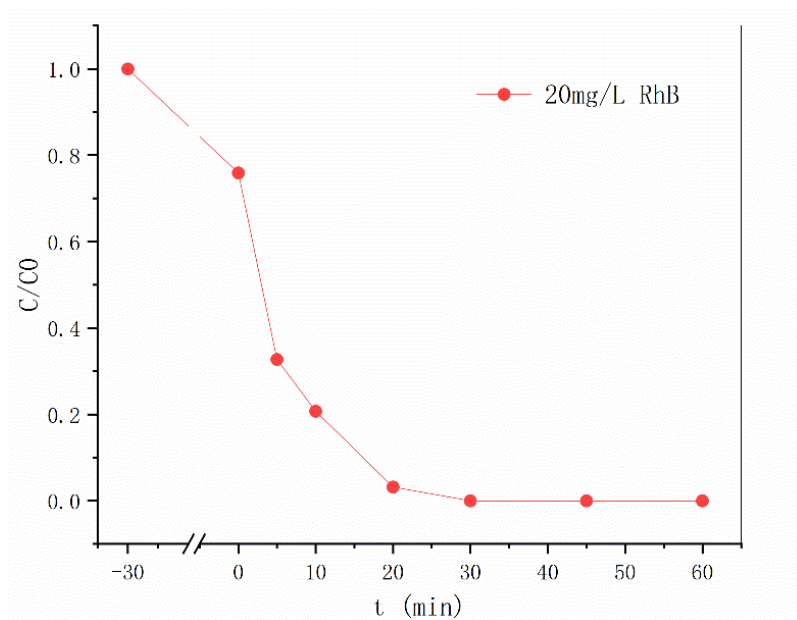


Figure S6 Degradation of RhB in HKUST-1(Cu)/MoS₂-3-C system. Reaction conditions: [RhB] = 20 mg/L, [PMS] = 1 mM, [Catalysts] = 0.3 g/L.

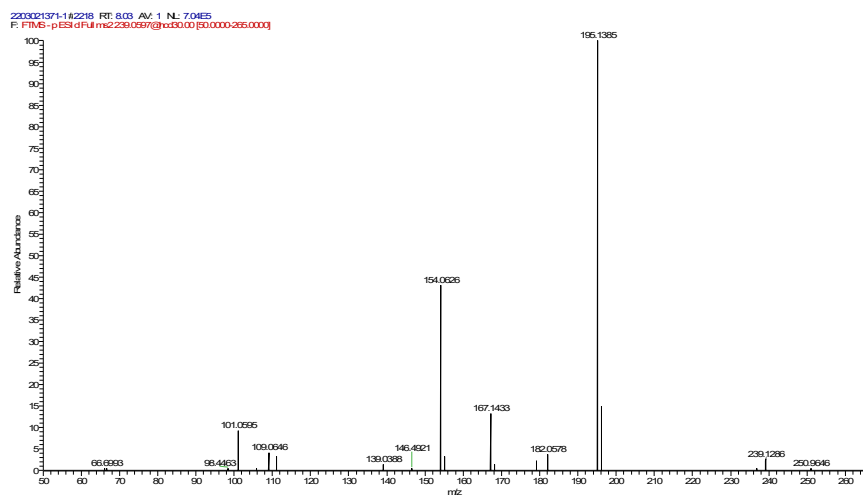
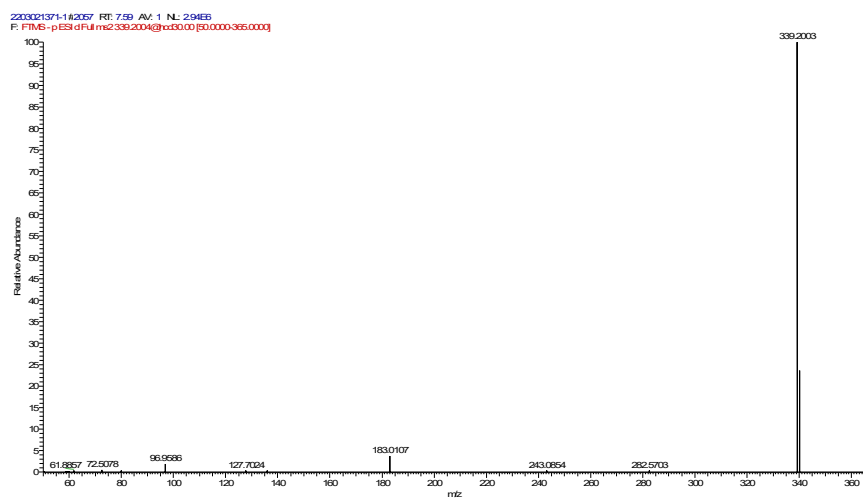
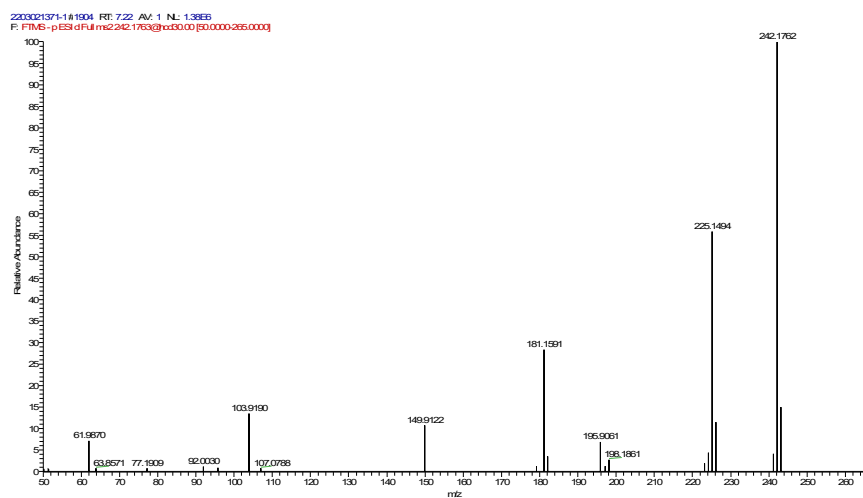


Figure S7 ESI-MS spectra of BPA (sampling time: 10 min).

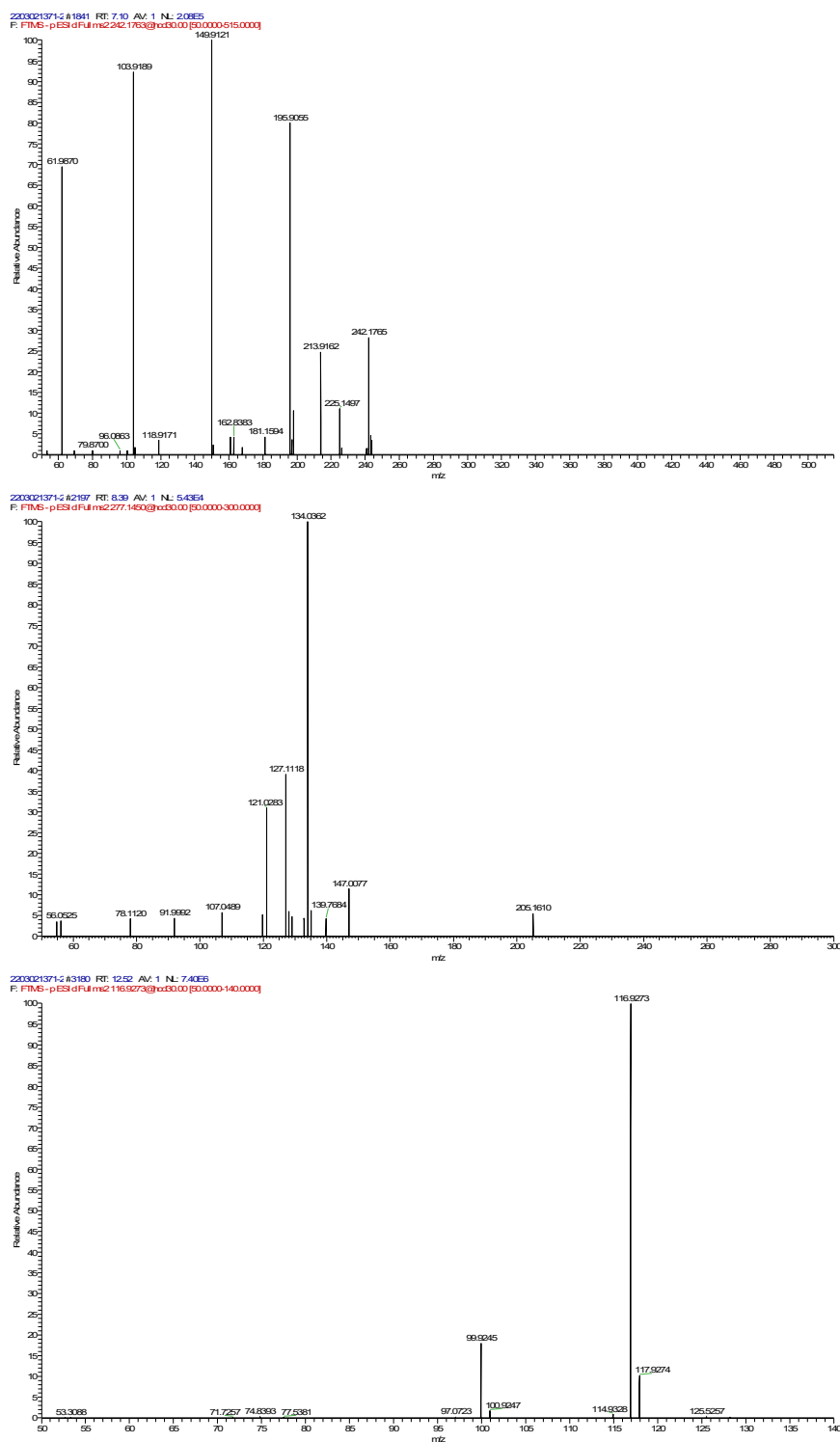


Figure S8 ESI-MS spectra of BPA (sampling time: 30 min).

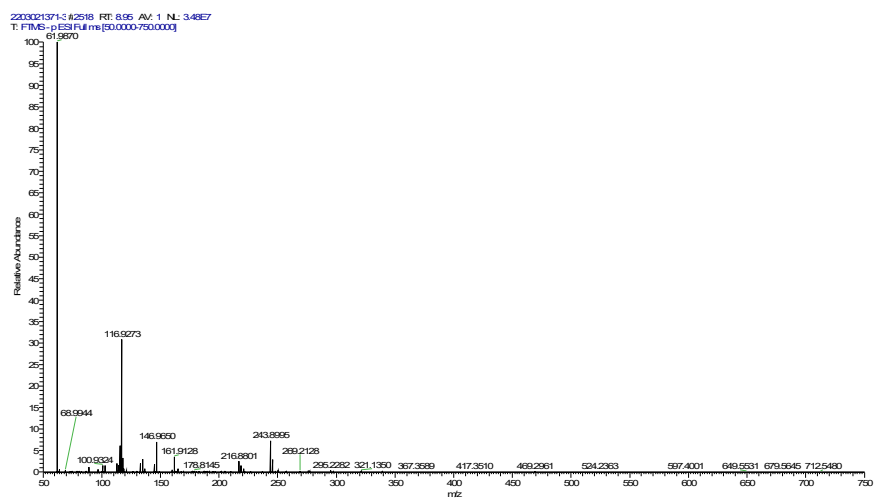
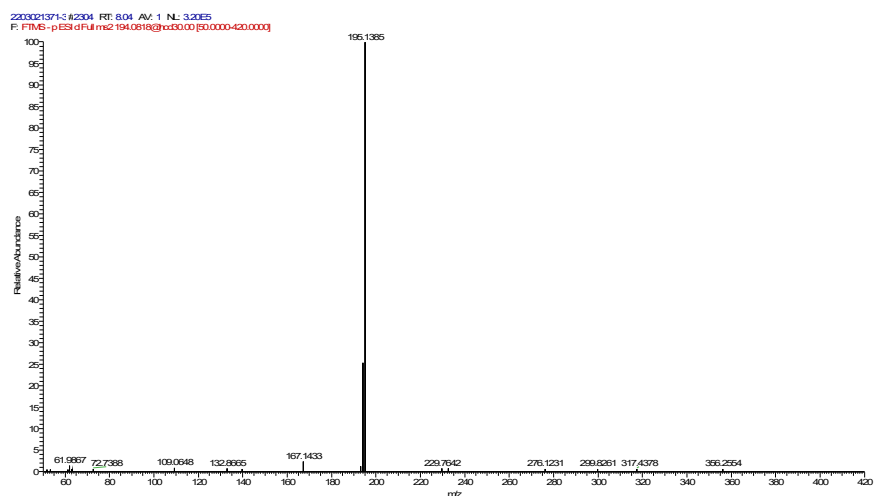
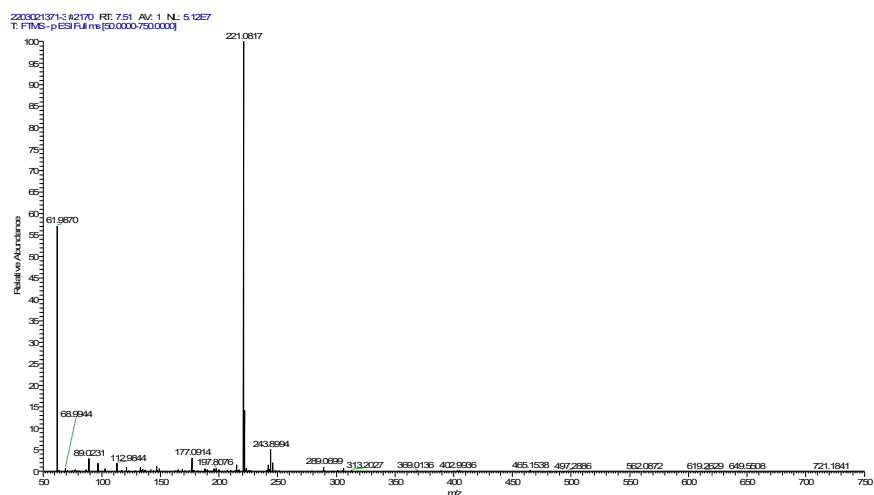


Figure S9 ESI-MS spectra of BPA (sampling time: 60 min).

Table S1 The effectiveness of PMS utilization for BPA (20 mg/L) degradation during the Fenton-like reaction.

Catalyst	Time (min)	$\Delta n[\text{BPA}]$ (mmol)	$\Delta n[\text{PMS}]$ (mmol)	PMS stoichiometric efficiency
HKUST-1(Cu)-C	60	0.00261	0.0294	0.09
MoS ₂ -C	60	0.00252	0.0230	0.11
HKUST-1(Cu)/ MoS ₂ -C	60	0.00438	0.0307	0.14

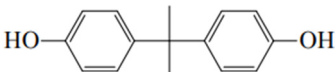
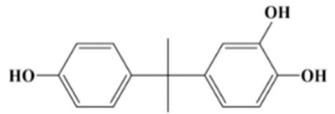
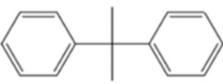
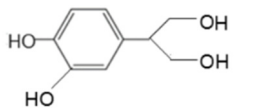
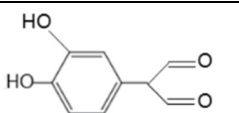
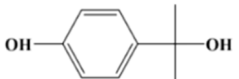
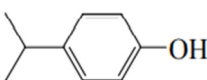
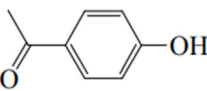
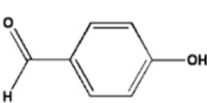
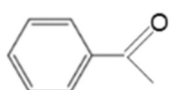
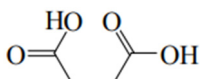
$$\text{stoichiometric efficiency} = \frac{\Delta n[\text{BPA}]}{\Delta n[\text{PMS}]}$$

stoichiometric efficiency is defined as the ratio of the number of moles of BPA oxidized ($\Delta n[\text{BPA}]$) to the number of moles of PMS consumed ($\Delta n[\text{PMS}]$).

Table S2 The chemical formulas and fragments (m/z) of intermediate products during BPA degradation.

Entry	Formula	<i>m/z</i>	detected
1	C ₉ H ₁₂ O	135.1	Yes
2	C ₈ H ₈ O ₂	135.0	Yes
3	C ₇ H ₈ O ₂	123.0	No
4	C ₆ H ₆ O ₂	109.0	Yes
5	C ₆ H ₆ O	93.0	Yes

Table S3 The molecular structure and fragments (m/z) of intermediate products during BPA degradation.

Compound	Structure	Formula	ESI Negative mode(m/z)
bisphenol A		C ₁₅ H ₁₆ O ₂	227.0
monohydroxylated BPA		C ₁₅ H ₁₆ O ₃	243.9
2,2-diphenylpropane		C ₁₅ H ₁₆	195.1
P1		C ₉ H ₁₂ O ₄	183.0
P2		C ₈ H ₈ O ₄	181.2
4-(2-hydroxypropan- 2-yl)phenol		C ₉ H ₁₂ O ₂	149.9
4-isopropylphenol		C ₉ H ₁₂ O	135.1
4- hydroxyacetophenone		C ₈ H ₈ O ₂	135.0
p- hydroxybenzaldehyde		C ₇ H ₆ O ₂	121.0
acetophenone		C ₈ H ₈ O	117.9
maleic acid		C ₄ H ₄ O ₄	116.9



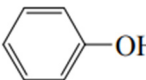
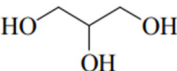
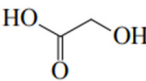
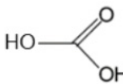
Compound	Structure	Formula	ESI Negative mode(m/z)
hydroquinone		C ₆ H ₆ O ₂	109.0
1,4-benzoquinone		C ₆ H ₄ O ₂	107.0
phenol		C ₆ H ₆ O	93.0
glycerol		C ₃ H ₈ O ₃	92.0
glycolic acid		C ₂ H ₄ O ₃	77.0
carbonic acid		H ₂ CO ₃	62.0

Table S4 Operation parameters of ESI-MS

Time (min)	Flow rate	A (%)	B (%)
	(mL/min)		
00.00	0.20	80	20
03.00	0.20	80	20
06.00	0.20	10	90
09.00	0.20	10	90
12.00	0.20	80	20
15.00	0.20	80	20

Mobile phase: A (Ultrapure water with 0.1%formic acid), B (acetonitrile)

Table S5 HPLC operating conditions for the detection of BPA

Mobile phase	A (methanol)
	B (Ultrapure water)
	Mobile phase of mixture (A:B=70:30)
Chromatographic column	Eclipse XBD-C18, 4.5 × 150 mm, 5 μm
Flow rate	1.0 ml/min
Detector temperature	303 K
Detector wavelength	λ=225 nm

Table S6 The leached concentration of Mo and Cu ions after BPA degradation

Metal ions	Mo	Cu
Concentration (mg/L)	0.7196	0.1565

Text.S1 Synthesis of comparative catalysts.

MoS₂ was prepared by solvothermal treatment method. A certain amount of Na₂MoO₄•2H₂O and CH₅N₂S (the molar mass of Na₂MoO₄•2H₂O and CH₅N₂S was about 1:2) were dissolved in 40 mL of ultrapure water with continuously stirring for 30 minutes, and ultrasonicated for 2 h. Afterward the mixture was transferred to a stainless steel lined Teflon autoclave reactor and heated at 200 °C for 24 h. Then the precipitate was collected through centrifugation and washed with ultrapure water and ethanol several times. After drying in a vacuum oven at 60 °C for 12 h, MoS₂ was obtained.

MoS₂-C was prepared by calcining MoS₂ at 800 °C for 2 h in tube furnace under an argon atmosphere.

Text.S2 Preparation of working electrode for EIS.

The working electrode was prepared as follows: 0.03 g catalyst was dispersed into a mixture solution comprised of 1mL Ethanol and 30 µL Nafion. Then the mixture was ultrasonicated for 30 min to form a stable uniform suspension solution. After that, the suspension was slowly dropped onto a glassy electrode and dried at 60 °C. Then a catalyst film can be formed on the glassy electrode.

Text.S3 Raman analysis procedures for in situ characterization of the catalyst surface during catalytic PMS decomposition.

Catalysts were pressed into slice of about 1 mm in thickness and 13 mm in diameter. PMS solution (100 mM, 2 mL) was dropped onto the slice. Then the slice was scanned from 100 to 2000 cm⁻¹. The irradiation did not cause PMS decomposition in the solution.

Text.S4 ABTS method for measuring PMS.

PMS was quantified using 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) as a colorimetric agent. 0.125 mL of freshly prepared ABTS solution (50 mM) and 2.25 mL of phosphate buffer solution (50 mM, pH 7) was mixed in 5 mL centrifugal tube. Then 0.125 mL of water sample or standard solution containing PMS was added to the tube. After stirring the reaction magnetically for 10 min at room temperature, the mixture was immediately transferred into quartz cells to measure the absorbance (wavelength=415 nm).

Phosphate buffer solution (50 mM, pH 7) was using 50 mM K_2HPO_4 and 50 mM KH_2PO_4 mixed in the ration of 61:39.

Text.S5 EPR analysis procedures for detecting radical signals.

Detecting method of $\cdot OH/SO_4^{\cdot -}$: DMPO-trapped EPR signals were detected in different air-saturated aqueous dispersions of the corresponding samples. Typically, 0.01 g prepared sample was added into 1 mL ultrapure water and 1 mL BPA solution (20 mg/L), respectively. Then, 100 mmol/L DMPO solution and 100 mmol/L PMS solution were both added in these two suspensions. After different reaction time, the solution was detected and EPR spectra were recorded.

Detecting method of $O_2^{\cdot -}$: DMPO-trapped EPR signals were detected in different air-saturated aqueous dispersions of the corresponding samples. Typically, 0.01 g prepared sample was added into 1 mL methanol and 1 mL BPA methanol solution (20 mg/L), respectively. Then, 100 mmol/L DMPO solution and 100 mmol/L PMS solution were both added in these two suspensions. After different reaction time, the solution was detected and EPR spectra were recorded.

Detecting method of 1O_2 : TEMP-trapped EPR signals were detected in different air-saturated

aqueous dispersions of the corresponding samples. Typically, 0.01 g prepared sample was added into 1 mL ultrapure water and 1 mL BPA solution (20 mg/L), respectively. Then, 100 mmol/L TEMP solution and 100 mmol/L PMS solution were both added in these two suspensions. After different reaction time, the solution was detected and EPR spectra were recorded.