

**Trimetallic MOF₁@MOF₂ heterostructure derived Co-NC@CuM-C
for enhanced photothermal catalysis in styrene epoxidation**

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1 Materials and Instruments.

All chemicals were purchased from Energy Chemical and used without further purification: acetonitrile ($\geq 99.9\%$), styrene (99.5%), methanol (99.5%), isobutyraldehyde (98.5%), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99.0\%$), 2-methylimidazole (98%), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%), dimethyl sulfoxide (99.7%), 1,3,5-benzenetricarboxylate (98%), silver nitrate (AgNO_3 , 99.8%), Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, ~38% Pt basis), Potassium chloropalladite (K_2PdCl_4).

Power X-ray diffraction (PXRD) were carried out on a Rigaku Saturn 70 diffractometer at 113 K with Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at 77 K. Scanning electron microscopy (SEM) images were acquired on a JEOL JSM-7800F at an acceleration voltage of 10 kV. The transmission electron microscopy (TEM) was acquired on JEOL-2010, and elemental mapping was measured on JEOL ARM-200F with an electron acceleration energy of 200 kV. The metal contents samples were analyzed by an Agilent ICP-OES 730 inductively coupled plasma atomic emission spectrometer (ICP-AES). X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250 high-performance electron spectrometer using monochromatized AlK α ($h\nu = 1486.7 \text{ eV}$) as the excitation source. Catalytic reaction products were analyzed and identified by gas chromatography (GC, Shimadzu 2030

Plus). The UV-Vis diffuse reflectance spectroscopy (DRS) spectra of catalysts were measured using BaSO_4 as a reference on an Agilent Instruments Cary5000 Spectrophotometer.

2 Preparation of catalysts.

2.1 Preparation of BMZIF: Typically, 1.4 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.274 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 80 mL of methanol; then 2-methylimidazole (3.7 g) in 80 mL of methanol was added into above solution. The mixture was vigorously stirred for 24 h at room temperature. The product was collected by centrifugation, washed several times with methanol, and dried overnight at room temperature prior to use.

2.2 Preparation of HKUST-1 precursor solution: Typically, a mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.22 g) and 1,3,5-benzenetricarboxylate (0.58 g) were dissolved in 4.5 mL of dimethyl sulfoxide (DMSO) to obtain the blue precursor solution.

2.3 Preparation of BMZIF@HKUST-1: The as-synthesized BMZIF (0.0414 g) was dispersed in 10 mL of methanol solution. A proper amount of DMSO, $\text{Cu}(\text{NO}_3)_2$, and 1,3,5- H_3BTC were dropped slowly with intensive stirring. In this process, the drop rate was very important. 50-1000 μL HKUST-1 precursor solution was added to adjust different core/shell metal ratios. Whereafter, the solution was stirred at room temperature for 5-30 minutes. Finally, the bluish purple powder was collected by centrifugation, and dried overnight at room temperature.

2.4 Preparation of Co-C@Cu-C: The obtained BMZIF@HKUST-1 was heated directly to 800 °C at the heating rate of 5 °C/min and kept for 2 h under 20% H₂/Ar atmosphere. Then the final sample was cooled naturally to room temperature.

2.5 Preparation of Co-C@CuAg-C: The prepared Co-C@Cu-C (0.05 g) was dispersed in a 20 mL methanol solution. Then AgNO₃ solution (100 μL/200 μL/400 μL, 50 mg/mL) was added into above solution under vigorously stirred for 4 h at 50 °C. The resulting sample was collected by centrifugation, washed several times with methanol and water, and dried overnight at room temperature.

2.6 Preparation of Co-C@Cu₂Opt-C: Similar to the synthetic procedure of Co-C@CuAg-C, the Co-C@Cu-C (0.05 g) was dispersed in 20 mL of water. Then H₂PtCl₆·6H₂O (520 μL/1050 μL, 4.76 mg/mL) was added into above solution under vigorously stirred for 4 h at 50 °C. The resulting sample was collected by centrifugation, washed several times with water, and dried overnight at room temperature.

2.7 Preparation of Co-C@CuOPd-C: Similarly, the Co-C@Cu-C (0.05g) was dispersed in 20 mL of water. Then K₂PdCl₄ (77 μL/192 μL/384 μL, 13 mg/mL) was added into above solution under vigorously stirred for 4 h at 50 °C. The resulting sample was collected by centrifugation, washed several times with water, and dried overnight at room temperature.

3 Catalytic Activity Evaluation.

3.1 Catalytic tests for styrene epoxidation: In a typical experiment, a mixture of 20 mg catalyst, 1.1 mmol styrene and 2.5 mmol isobutyraldehyde were dispersed in a

round-bottomed flask (25 mL) with 10 mL acetonitrile. The reaction was carried out at 80 °C and 1 atm O₂. The solution was regularly analyzed by gas chromatography.

3.2 Catalytic tests for styrene epoxidation under visible-light irradiation: In general, 20 mg of Co-NC@Cu-C, Co-NC@CuOPd(10%)-C, Co-NC@Cu₂OPt(10%)-C, Co-NC, and Cu-C was dispersed in 10 mL acetonitrile containing 0.1 mmol of styrene and 2 mmol of isobutyraldehyde. The mixture was stirred at oxygen atmosphere under visible-light irradiation for reaction. The reaction process was monitored by GC. For the recycling experiments, the samples were separated by centrifugation and washed with ethanol, and were reused in the subsequent reaction under the same reaction conditions.

3.3 Photothermal conversion efficiencies test: 20 mg of catalyst was dispersed into 10 mL water (room temperature = 25 °C). The solution was irradiated under visible light ($\lambda \geq 420$ nm). The temperature was monitored constantly using thermometer.

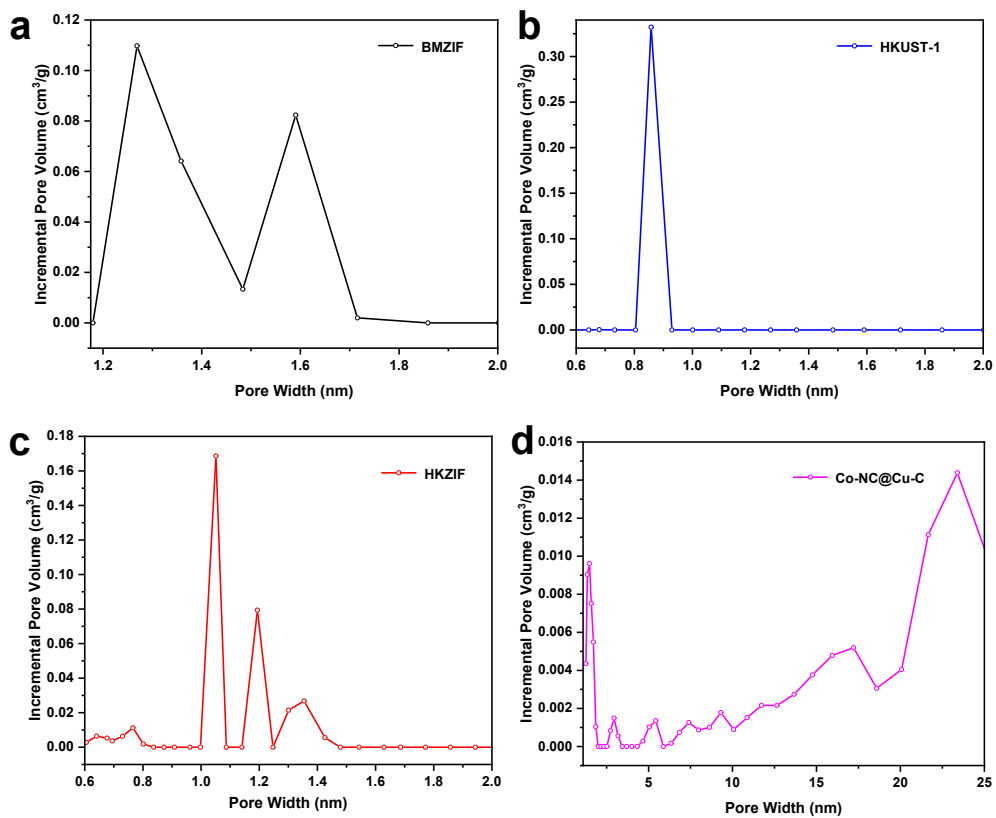


Fig. S1 (a-c) Pore size distribution of MOF precursors and (d) Co-NC@Cu-C.

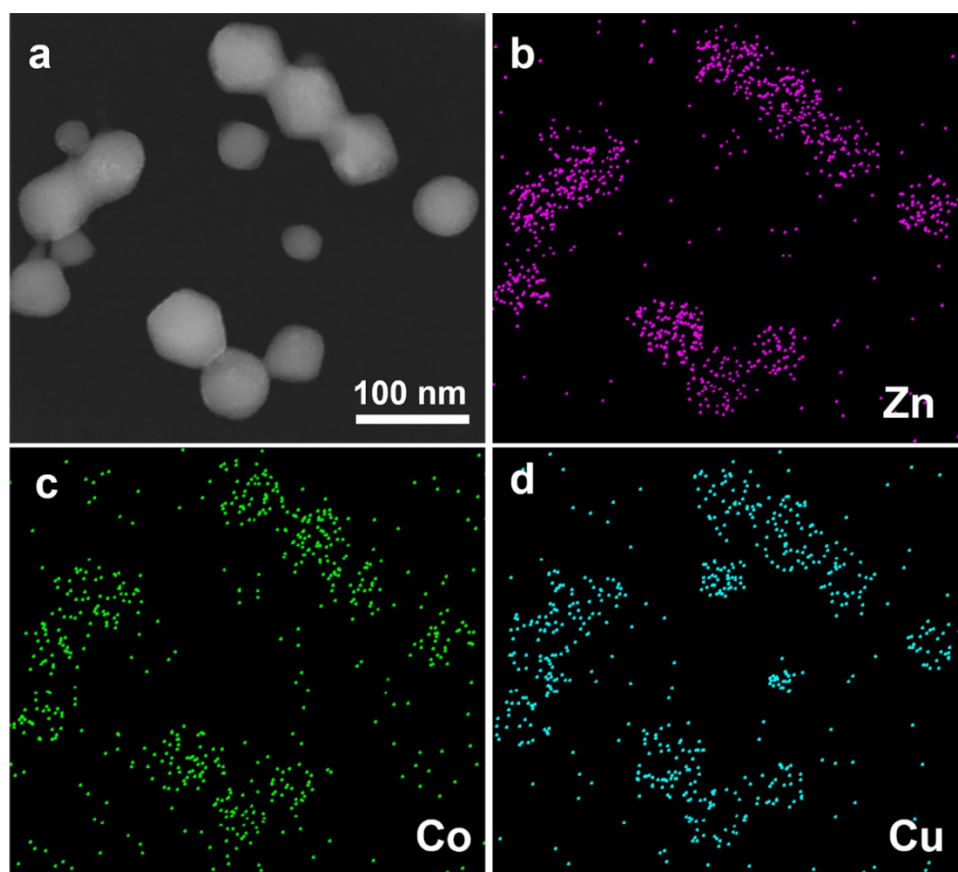


Fig. S2 (a-d) HAADF-STEM images and corresponding EDS elemental (Zn, Co, Cu) mapping of HKZIF.

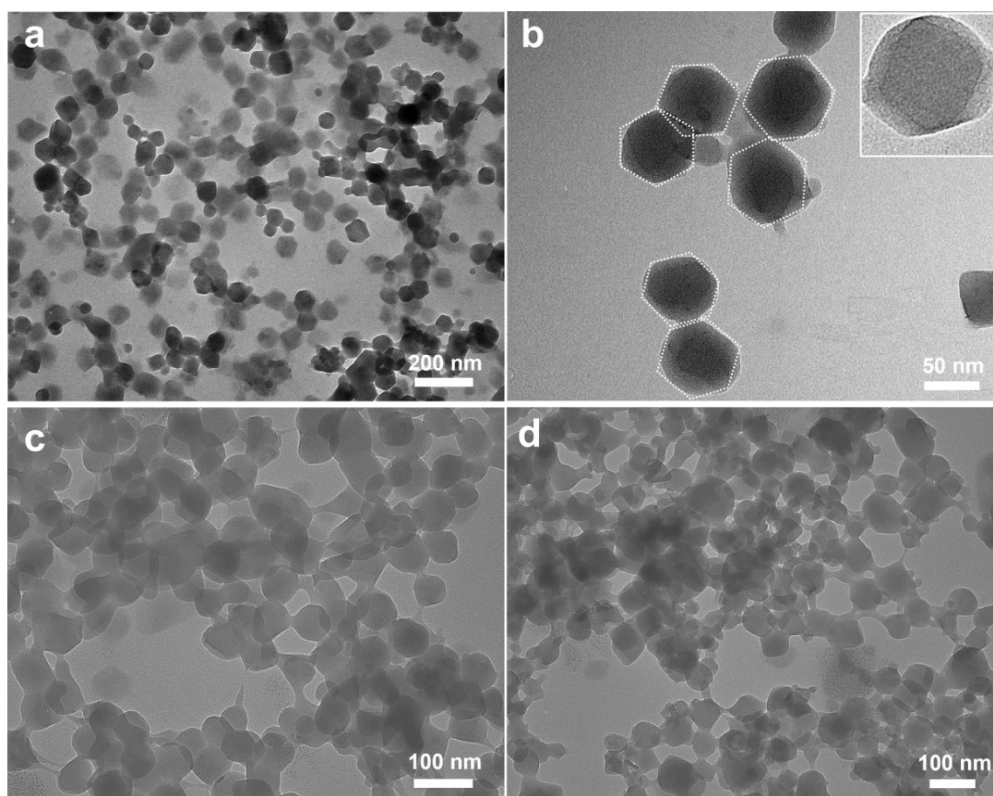


Fig. S3 SEM images of HKZIF at different growth times, (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min.

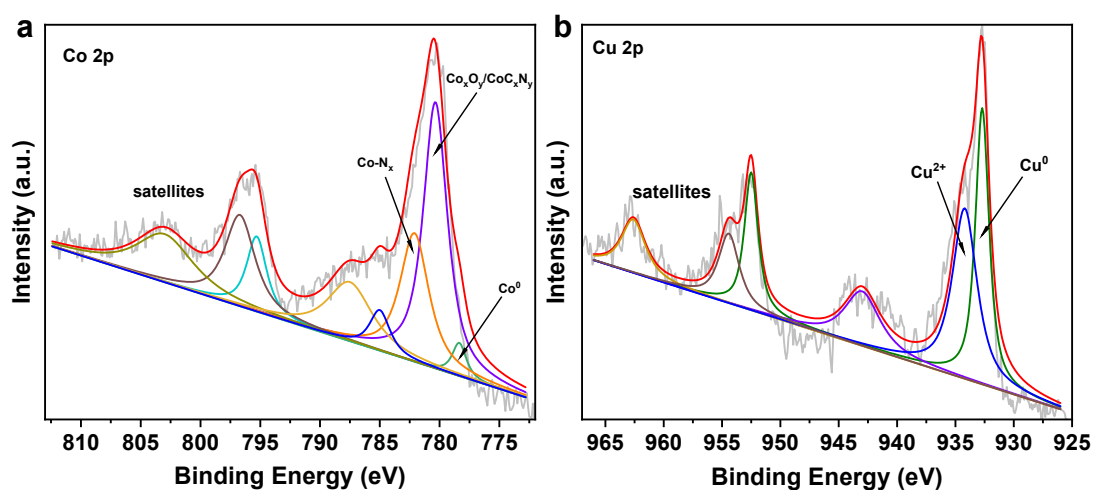


Fig. S4 X-ray photoelectron spectroscopy (XPS) spectra of (a) Co 2p and (b) Cu 2p for as-synthesized Co-NC@Cu-C.

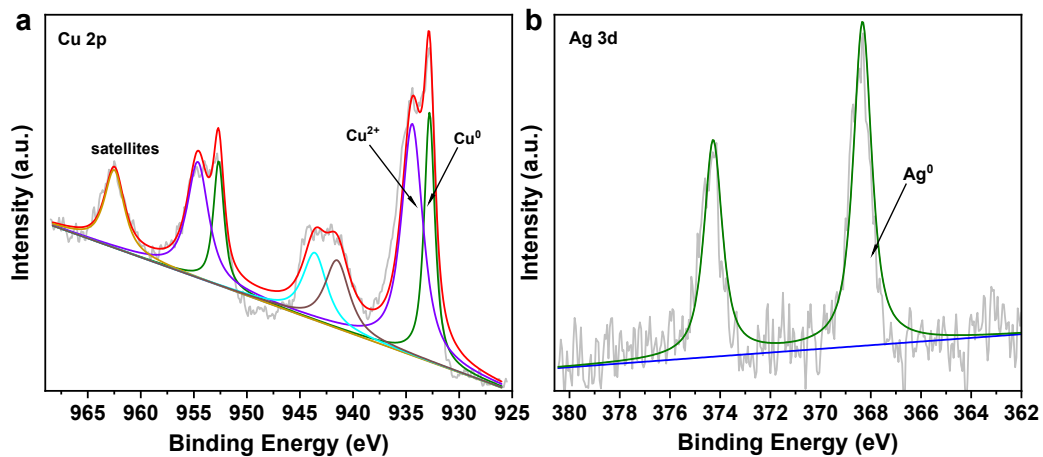


Fig. S5 X-ray photoelectron spectroscopy (XPS) spectra of (a) Cu 2p and (b) Ag 3d for as-synthesized Co-NC@CuAg-C.

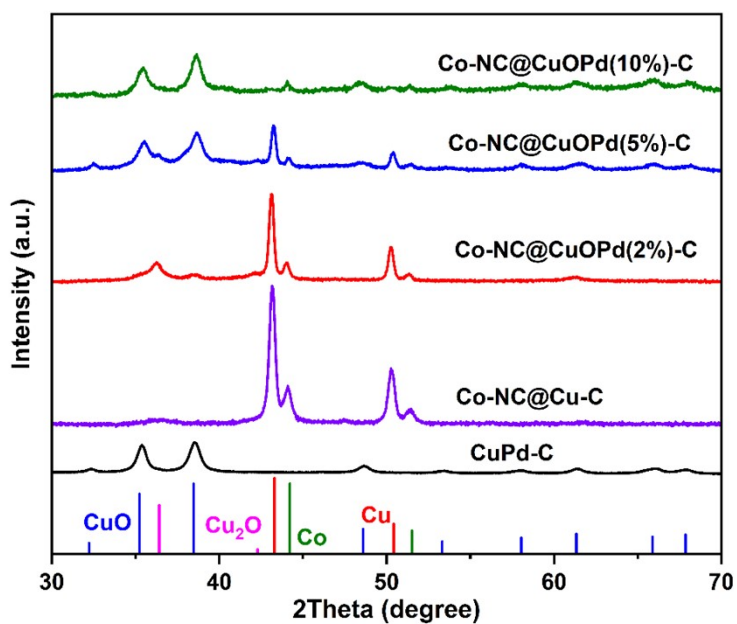


Fig. S6 XRD patterns of CuPd-C, Co-NC@Cu-C and Co-NC@CuOPd(2%, 5%, 10%)-C.

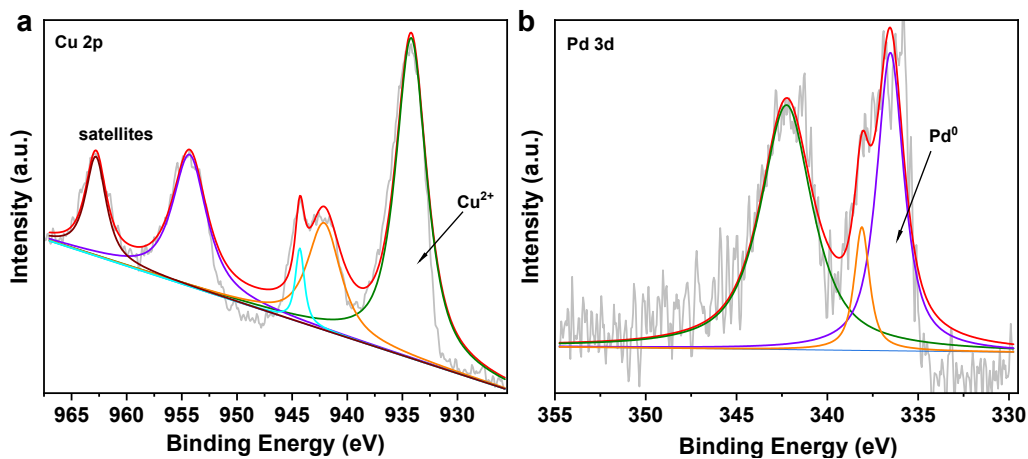


Fig. S7 X-ray photoelectron spectroscopy (XPS) spectra of (a) Cu 2p and (b) Pd 3d for as-synthesized Co-NC@CuOPd-C.

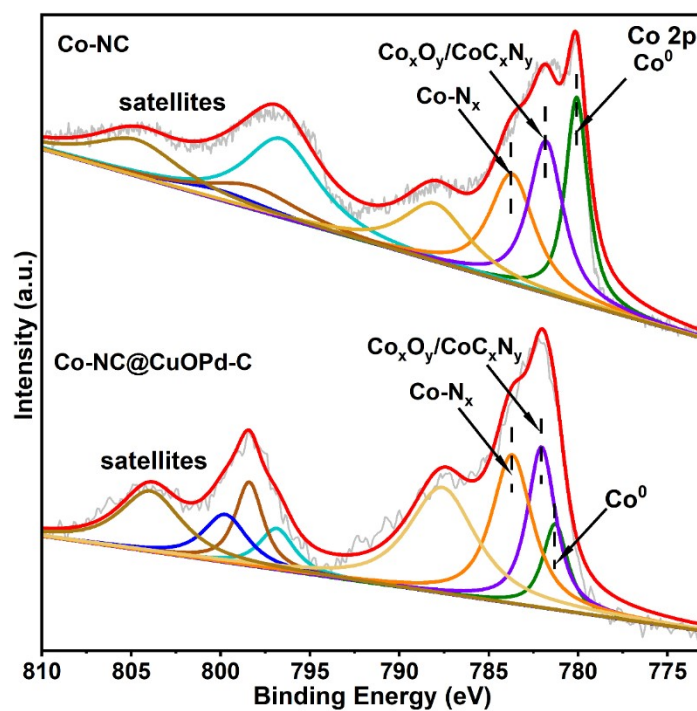


Fig. S8 X-ray photoelectron spectroscopy (XPS) spectra of Co-NC and Co-NC@CuOPd-C.

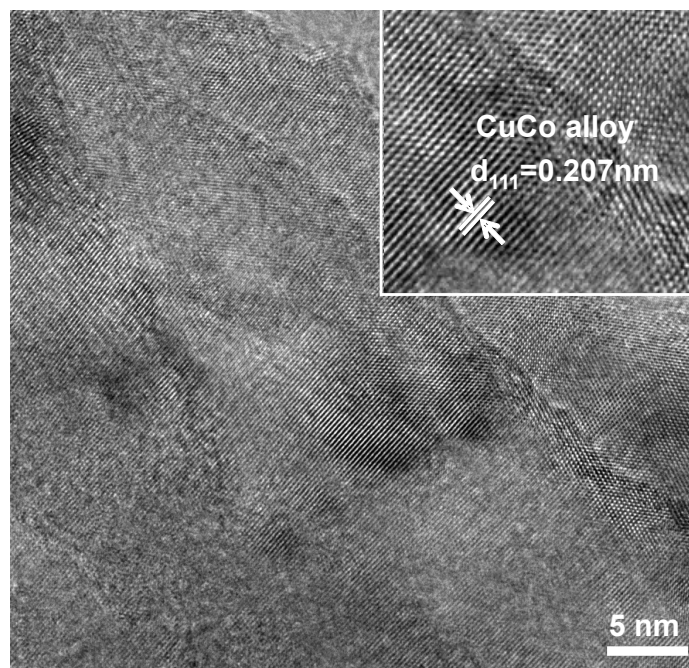


Fig. S9 HRTEM image of CoCu@NC.

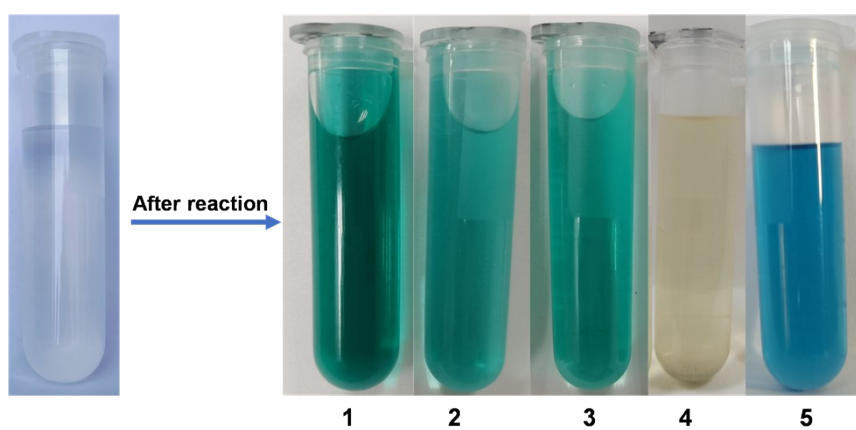
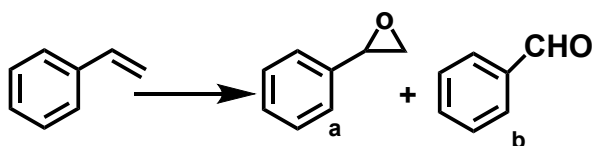


Fig. S10 Solution color change during catalysis of (1) Co-NC@Cu-C, (2) Co-NC@CuAg-C, (3) Co-NC@Cu₂OPt-C, (4) Co-NC@CuOPd-C, (5) CoCu-NC, respectively.

Table S1. Metal contents of the synthesized Co-NC@CuM (M = Ag, Pd, Pt)-C before and after catalysis.

Sample	Substance (wt%)				
	Co	Cu	Ag	Pt	Pd
Co-NC@Cu-C	16.3	47.9	---	---	---
Co-NC@Cu-C(1 st run)	57.7	2.64	---	---	---
Co-NC@CuAg (20%)-C	16.3	28.3	16	---	---
Co-NC@CuAg (20%)-C(1 st run)	52.1	2.98	9.4	---	---
Co-NC@CuOPd (5%)-C	12.8	36.3	---	---	3.7
Co-NC@CuOPd (5%)-C(1 st run)	12.24	36.24	---	---	3.64
Co-NC@Cu ₂ OPt (5%)-C	15.8	30.5	---	3.7	---
Co-NC@Cu ₂ OPt (5%)-C (1 st run)	15.6	30.35	---	3.1	---

Table S2. Comparison of different catalysts for styrene epoxidation.



Catalyst	Time	Solvent	Conditions	Conv. (%)	Select. of a (%)	Refs.
Co-NC@CuOPd(5%)-C	30 min	CH ₃ CN	2 mmol IBA, 300 W Xe lamp, room temperature	99	92.9	This work
Co-NC@Cu ₂ OPt(5%)-C	30 min	CH ₃ CN	2 mmol IBA, 300 W Xe lamp, room temperature	>99	94.5	This work
Cu _{0.25} -Co _{0.75} -MOF	8 h	CH ₃ CN	30 mmol TBHP, 80 °C	97.8	83.04	1
CuO/CoAl-HT	6 h	CH ₃ CN	3 mmol TBHP, 85 °C	99.5	72	2

Fe ₃ O ₄	4 h	DMF	O ₂ flux 3 mL/min, 100 °C	38.0	56.5	3
BaMST	3 h	CH ₃ CN	60 mmol H ₂ O ₂ , 60 °C	63.3	77.8	4
S-8CoYZr	8 h	DMF	O ₂ flux 7 ml/min, 120 °C	61.0	80	5
CuO-0.2CeO ₂ /CoAl-HT	6 h	CH ₃ CN	3 mmol TBHP, 85 °C	99.6	79.5	6
SAS-Fe	3 h	DMF	1 atm O ₂ , 140 °C	64.0	89	7
CuCdCo PBA	6 h	CH ₃ CN	0.75 mmol TBHP, 72 °C	95.0	62	8
CoFe ₂ O ₄	8 h	CH ₃ CN	45 mmol TBHP, urea, 80 °C	96.4	82.7	9
35CoOx /SBA-15	6 h	CH ₃ CN	15 mmol TBHP, 80 °C	88.0	61	10
Cu/Co-Co PBA- 250	7 h	CH ₃ CN	1 mmol TBHP, 72 °C	99.0	73	11
LZAC	9 h	CH ₃ CN	1 mL TBHP, 140 °C	93.8	66.8	12
0.2CuMn-MS	12 h	CH ₃ CN	3 mmol TBHP, 80 °C	95.3	72.4	13
Ag NPs/CNFs	8 h	C ₃ H ₈ O	5 mL TBHP, 82 °C	59.8	46.7	14

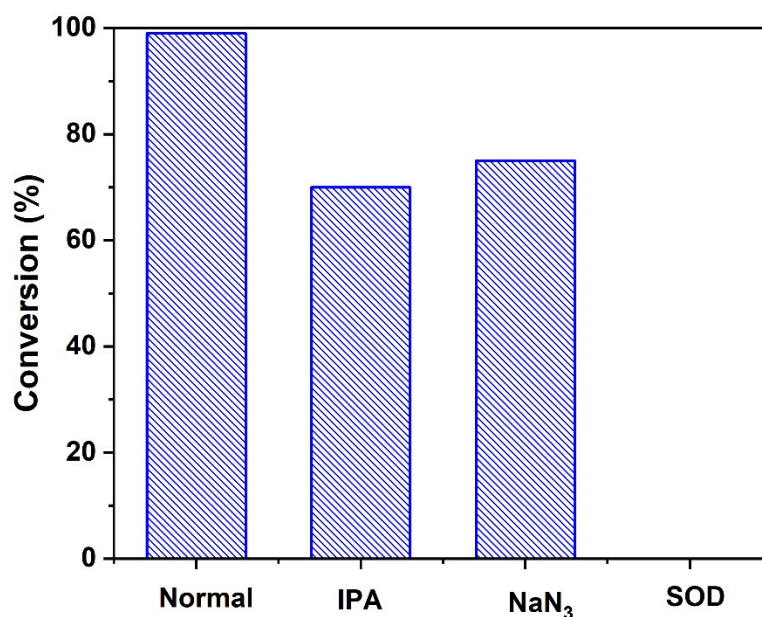
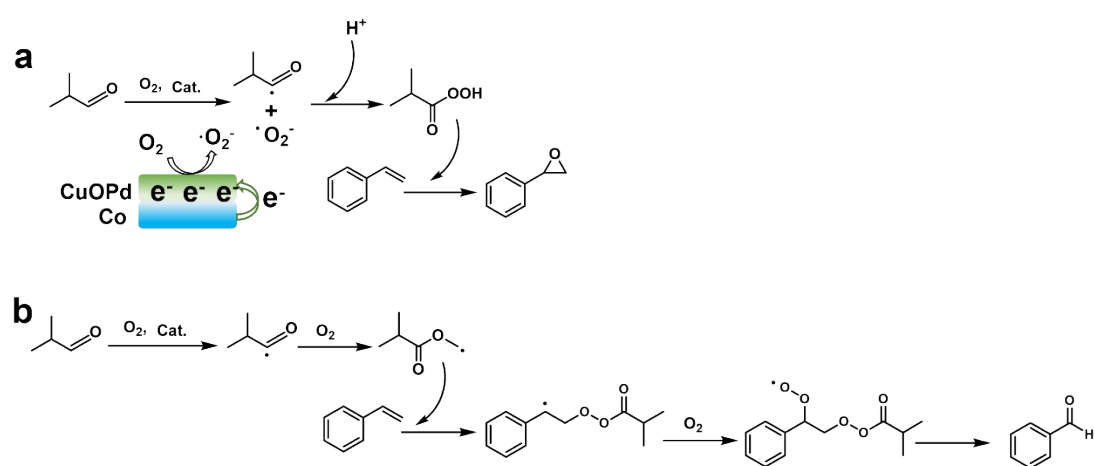


Fig. S11 Styrene conversion over Co-NC@CuOPd-C in the presence of the different trapping species.



Scheme S1. The mechanism reaction pathways to (a) styrene oxide and (b) benzaldehyde.

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