

## SUPPORTING INFORMATION FOR

### **Atomically Dispersed Iron Sites on Multi-shelled Hollow Structure for**

### **Highly Efficient CO<sub>2</sub> Fixation**

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## S1. Experimental Details

**Reagents and Chemicals.** The chemical reagents mentioned in this article were purchased from commercial sources and used without further purification. Tetraethyl orthosilicate (Aladdin), zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sinopharm Chemicals), ferric nitrate nonahydrate (III) (Aladdin Biochemical Reagent Co., Ltd., 98%), 2-methylimidazole (MeIM, Aladdin), dopamine hydrochloride (Aladdin, 98%), hydrofluoric acid (Aladdin Biochemical Technology Co., Ltd.), cetyltrimethylammonium bromide (CTAB, Aladdin, purified with Millipore system), ammonia water (Sinopharm Chemical Reagent Co., Ltd., AR, 25.0%-28.0%), ethyl acetate (Sinopharm Chemicals Co., Ltd., AR, 99.5%), tetrabutyl ammonium bromide (TBAB) (Aladdin), absolute ethanol (Sinopharm Chemical Reagent Co., Ltd.) and deionized water (18.2 M $\Omega$ cm).

**Characterization.** The PXRD data were obtained from an X-ray diffractometer with a Smart Lab instrument model using Cu K $\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ). Transmission electron microscopy (TEM) images were obtained on a Hitachi HT7700 (accelerating voltage of 100 kV) instrument from Hitachi, Ltd., Japan. To obtain the morphology information of the sample, the catalyst was characterized using a scanning electron microscope (SEM) Hitachi 8100 with an acceleration voltage of 5 kV. High-resolution transmission electron microscopy (HR-TEM) and EDS measurements were performed on JEOL-2011. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) measurements were performed on JEM-ARM200F. Characterization of X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 Xi

X-ray photoelectron spectrometer, using Al K $\alpha$  radiation as the light source. Elemental analysis of iron in solid samples was quantified using an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). A Raman spectrometer with instrument model LABRAMHR was used to obtain Raman spectra using an argon laser with  $\lambda = 632$  nm as the excitation source. The specific surface area of the catalyst was analyzed using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution of the catalyst was based on N<sub>2</sub> adsorption under nitrogen adsorption conditions at 77 K. The product was analyzed and identified by gas-mass spectrometer (GC-MS).

### XAFS Characterization

X-ray absorption fine structure (XAFS) spectroscopy was carried out using the Rapid XAFS 1M (Anhui HeFei Absorption Spectroscopy Analysis Instrument Co., Ltd.) by transmission mode at 25 kV and 40 mA, and the Si (531) spherically bent crystal analyzer with a radius of curvature of 500 mm was used for Fe.

**Extended Data Table S1** | Structural parameters of Sample extracted from the EXAFS fitting. ( $S0^2=0.75$ )

sample	Scattering pair	CN	R (Å)	$\sigma^2$ ( $10^{-3}\text{Å}^2$ )	$\Delta E_0$ (eV)
Fe	Fe-N	6.2	1.95	10.0	-6.4
Fe-foil	Fe-Fe	12*	2.56	5.6	4.3

$S0^2$  is the amplitude reduction factor  $S0^2=0.75$ ; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms);  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static

disorder in absorber-scatterer distances);  $\Delta E_0$  is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model).

## **S2. Preparation of samples**

**ZIF-8-NC** : In a typical synthesis, 0.144 mL of 0.01 M CTAB aqueous solution and 1 mL of 1.32 M 2-MeIM aqueous solution were combined and labeled as solution A. The mixture was stirred for 10 minutes and then set aside. A separate 1 mL solution of  $24 \times 10^{-3}$  M  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in water was prepared and labeled as solution B. Subsequently, solution A and solution B were mixed and stirred for 5 minutes. The resulting mixture was transferred into a reaction vessel lined with polytetrafluoroethylene and heated at 120 °C for 6 hours. The synthesized product was subjected to centrifugation at 10,000 rpm for 6 minutes, followed by thorough washing with ethanol and deionized water. Subsequently, it was dried in an 80 °C oven for 12 hours to obtain pale yellow powdered ZIF-8-NC.

**ZIF-8-NC@SiO<sub>2</sub>** : Typically, the synthesized ZIF-8-NC is uniformly dissolved in a solution containing 10 mmol 2-Melm, 120 mL deionized water, and 80 mL ethanol. Then, add 2 mmol of CTAB and 2 mL of ethyl orthosilicate, continue stirring for 24 hours, centrifuge to obtain precipitate, and dry overnight in a vacuum oven at 60 ° C. The obtained white powdery substance ZIF-8-NC@SiO<sub>2</sub>.

**ZIF-8-NC@SiO<sub>2</sub>@Fe-PDA** : Firstly, 300 mg was synthesized by ultrasound ZIF-8-NC@SiO<sub>2</sub> evenly disperse in a mixture of 50 mL deionized water, 50 mL ethanol, and 1 mL ammonia solution, labeled as solution A; Dissolve 20 mg of ferric nitrate (III) trihydrate and 40 mg of dopamine hydrochloride (DA) in a mixture of 10 mL of ethanol

and deionized water (volume ratio 2:3), labeled as solution B. After stirring at room temperature for 60 minutes, add solution B to solution A in sequence after stirring for 10 hours. Finally, collect the sediment by centrifugation. Wash three times with ethanol and deionized water, and dry overnight in a vacuum drying oven at 80°C. After complete drying, record the brown black powder sample as ZIF-8-NC@SiO<sub>2</sub>@Fe-PDA.

**Fe-HNC@SiO<sub>2</sub>:** 300 mg of ZIF-8-NC@SiO<sub>2</sub>@Fe-PDA was placed in a tube furnace. Adjust the flow rate to 60 mL/min in an argon atmosphere. Heating rate is 5°C/min, maintain the calcination condition at 900 ° C for 3 hours, then naturally anneal to room temperature to obtain a carbon black powder like solid Fe-HNC@SiO<sub>2</sub>.

**Fe/NC:** The synthesis according our previous report.<sup>1</sup>

**MHS:** The preparation process of MHS was like that of Fe/MHS, with the only difference being that no iron source is added during the modification of the precursor.

**Fe/NC:** The difference between the synthesis method of Fe/HNC and Fe/MHS lies in the absence of SiO<sub>2</sub> coating.

### **Catalytic cycloaddition reaction of carbon dioxide with epoxides**

**Cycloaddition:** Typically, a mixture of 5 mg of catalyst (for the compared catalysts, the dosage of the catalyst based on the Fe content), 0.1 mmol of TBAB, 3 mL of MeCN, and 0.22 mmol of epoxide was introduced into an autoclave and filled three times with CO<sub>2</sub> to remove the air allowing the reaction to be carried out in an atmosphere of pure CO<sub>2</sub>. The catalytic cycloaddition reaction was carried out at a pressure of 4 bar and a temperature of 90 °C for 4 h. After completion of the reaction, the mixture was

centrifuged and 2 mL of the supernatant was added to 2 mL of ethyl acetate. The mixture was then shaken well and waited for the two phases to separate. The organic phase was collected and 2 mL of supernatant was added to 2 mL of anhydrous ethanol. 1.5 mL of the organic phase was extracted using a medical syringe and analyzed by GC-MS with *n*-dodecane as internal standard.

### **Density Functional Theory calculations (DFT)**

The DFT method employed in all calculations is based on the PBE0-D3 (BJ) function using the Gaussian 09 program. The basis group used for the compound of FeN<sub>6</sub> in this work is Lan12TZ/6-31G\*, where Lan12TZ is used to describe the Fe atoms and the remaining atoms (C, N, O, Br and H) are described by 6-31G\*. Electron Density Differences (EDD) were extracted from Multiwfn for lattice data and visualized using VMD.

**TableS2. ICP-AES and element analysis results for the contents of Fe in catalysts**

Catalyst	The content of Fe (wt%)
Fe/MHS	7.8%
Fe-HNC@SiO <sub>2</sub>	6.7%

### **Turnover Frequency Calculation (TOF)**

Loading capacity: 7.8 %

Catalyst amount: 5 mg

Substrate amount: 0.22 mmol

Catalysis time: 20 min

Conversion percent: 34%

TOF=N/(M\*Time)

N: The conversion of substrates in 20 min.

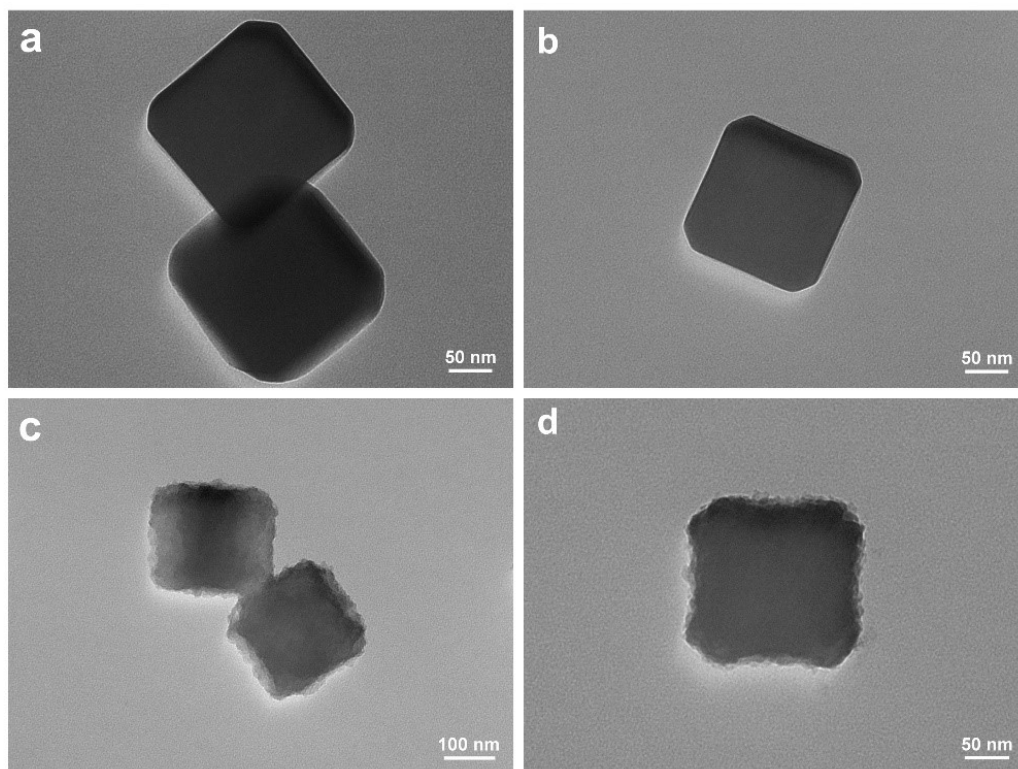
M: The number of iron atoms on the catalyst surface

$$M = (5/1000) * 0.078/56 = 6.96 * 10^{-6}$$

$$N = (0.22/1000) * 0.34 = 0.75 * 10^{-4}$$

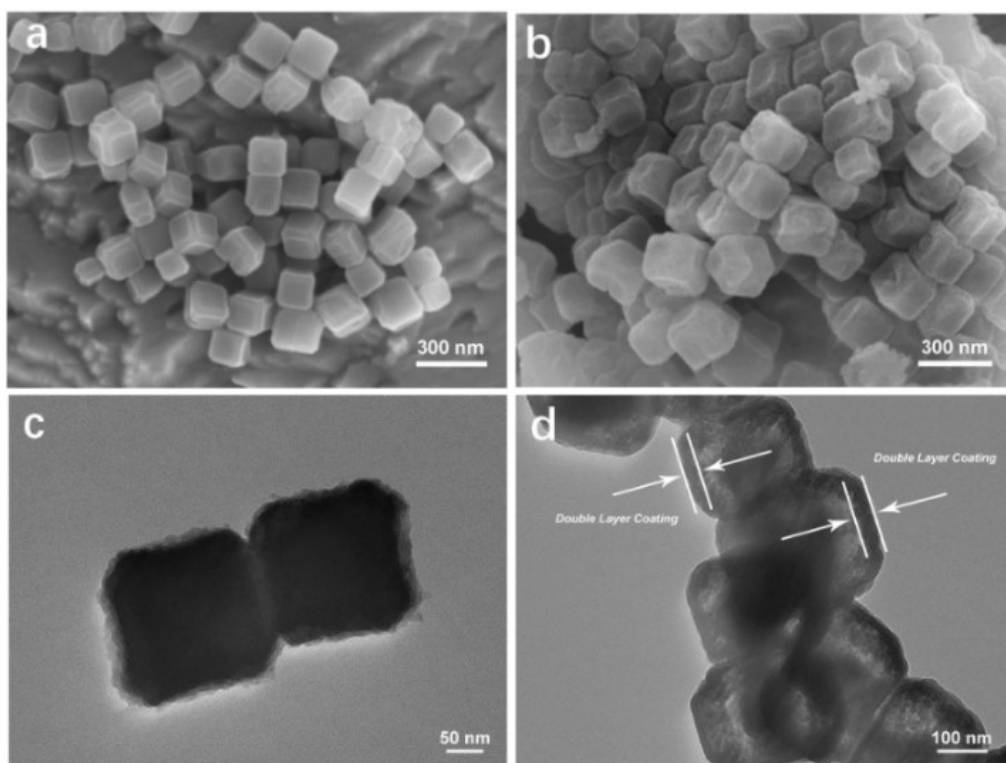
$$\text{TOF} = N/(M * \text{Time}) = 0.75 * 10^{-4} / (6.96 * 10^{-6} * 20) = 0.5605 \text{ min}^{-1} = 33.63 \text{ h}^{-1}$$

### S3. Characterizations



**Figure S1.** (a, b) TEM images of ZIF-8-NC, (c, d) TEM images of ZIF-8-NC@SiO<sub>2</sub>





**Figure S2.** SEM diagram (a) ZIF-8-NC; (b) ZIF-8-NC@SiO<sub>2</sub>; TEM diagram (c) ZIF-8-NC@SiO<sub>2</sub>; (d) ZIF-8-NC@SiO<sub>2</sub>@Fe-PDA

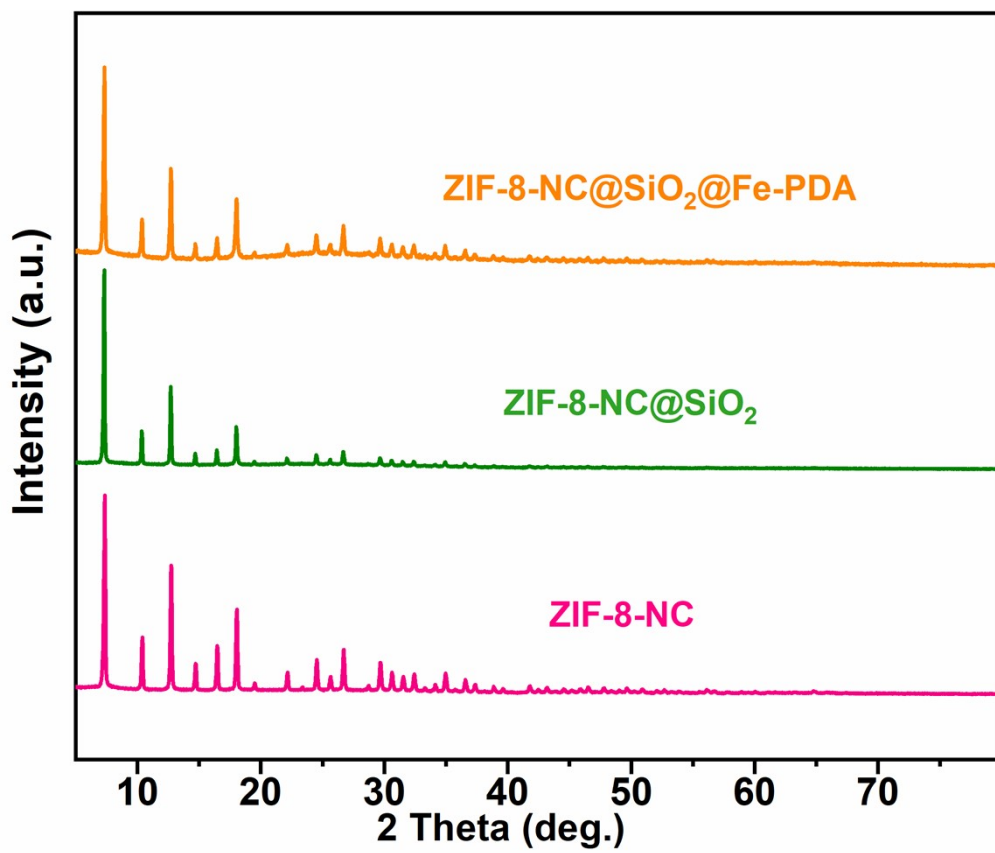


Figure S3. PXRD characterization diagram of the precursors.

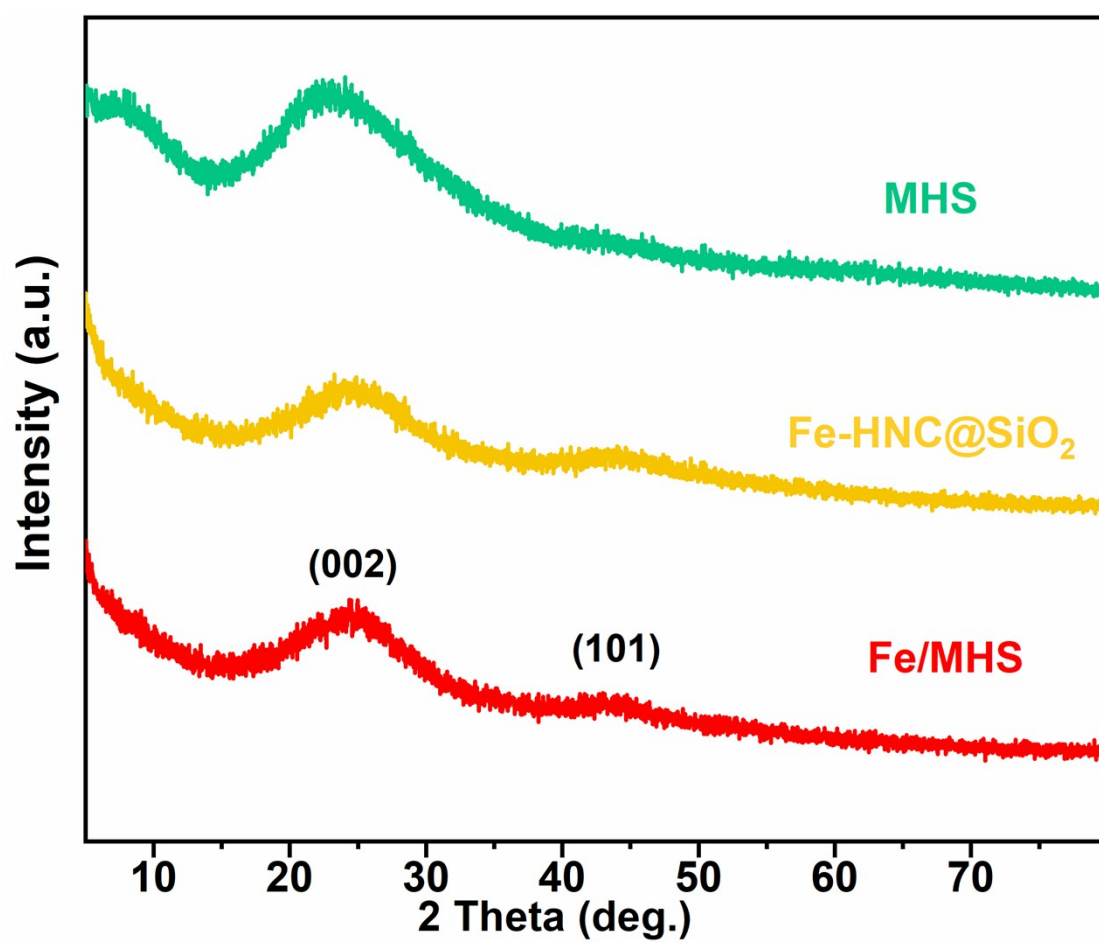
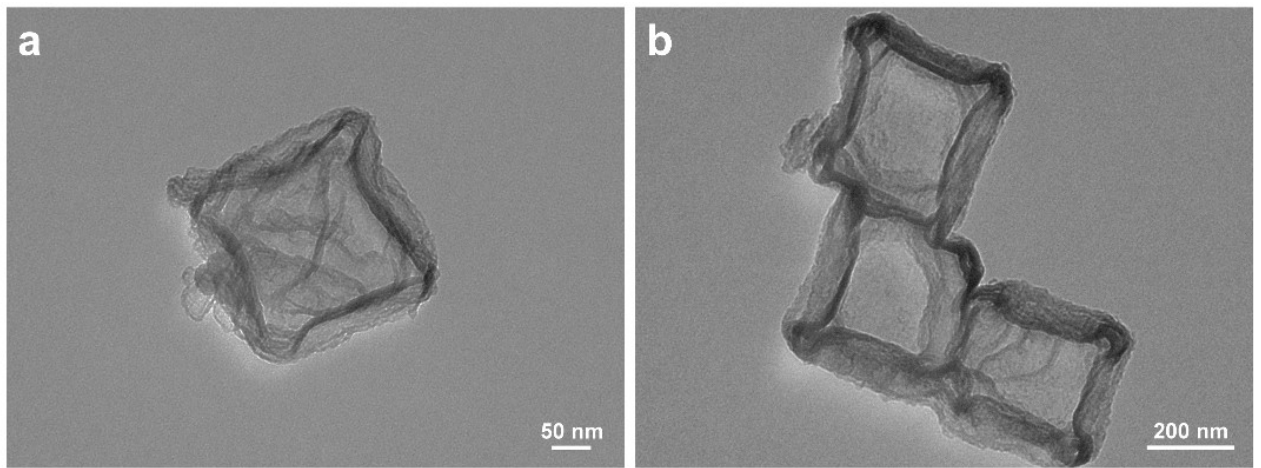
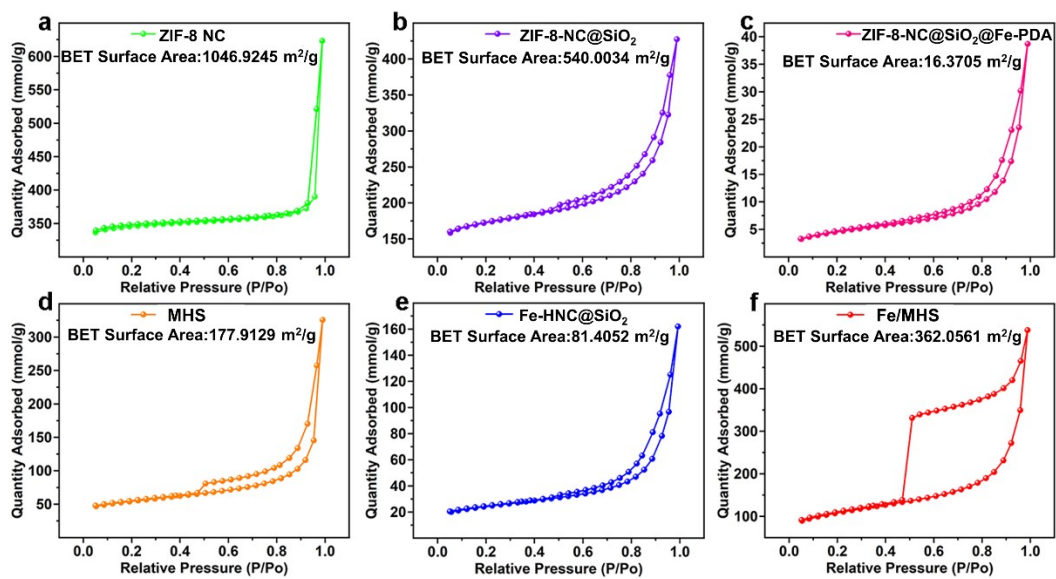


Figure S4. PXRD characterization diagram of the samples.



**Figure S5.** TEM image of catalyst Fe/MHS



**Figure S6.** Nitrogen adsorption isotherm curve of the sample

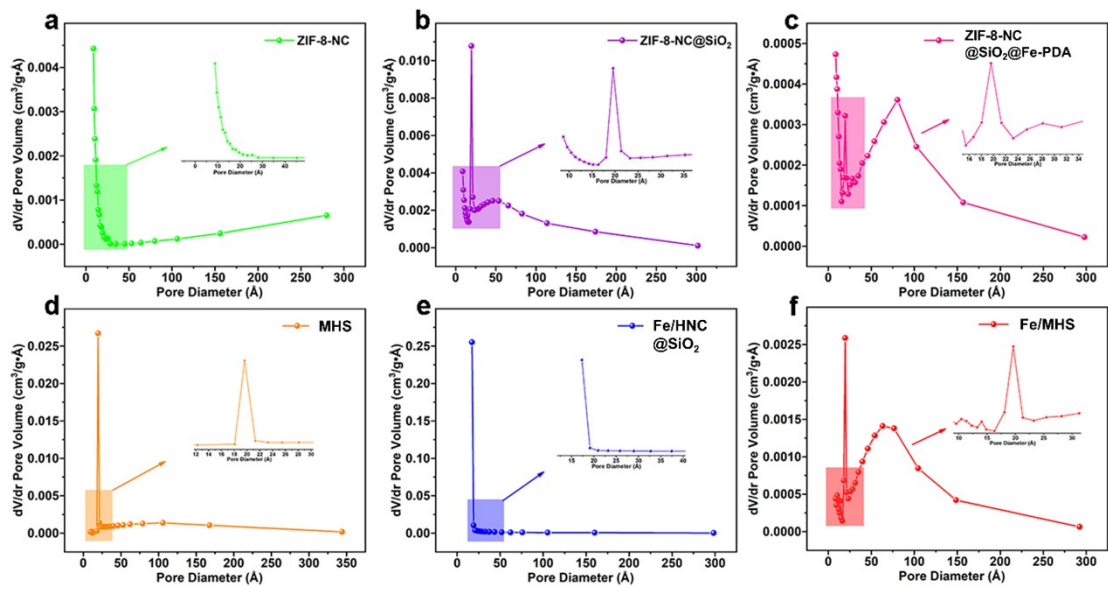
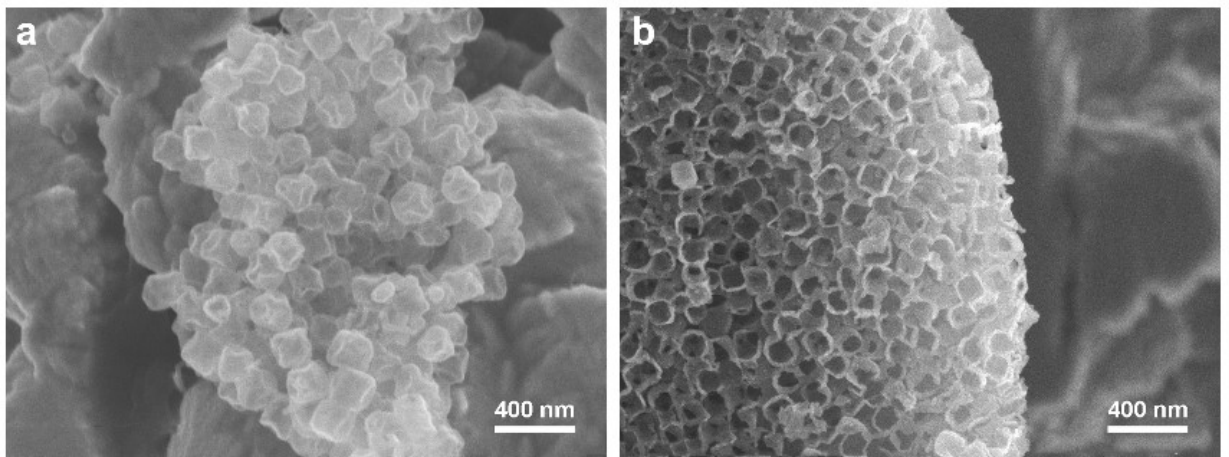


Figure S7. Pore size distribution profile of the sample



**Figure S8.** SEM images of Fe/NC and MHS

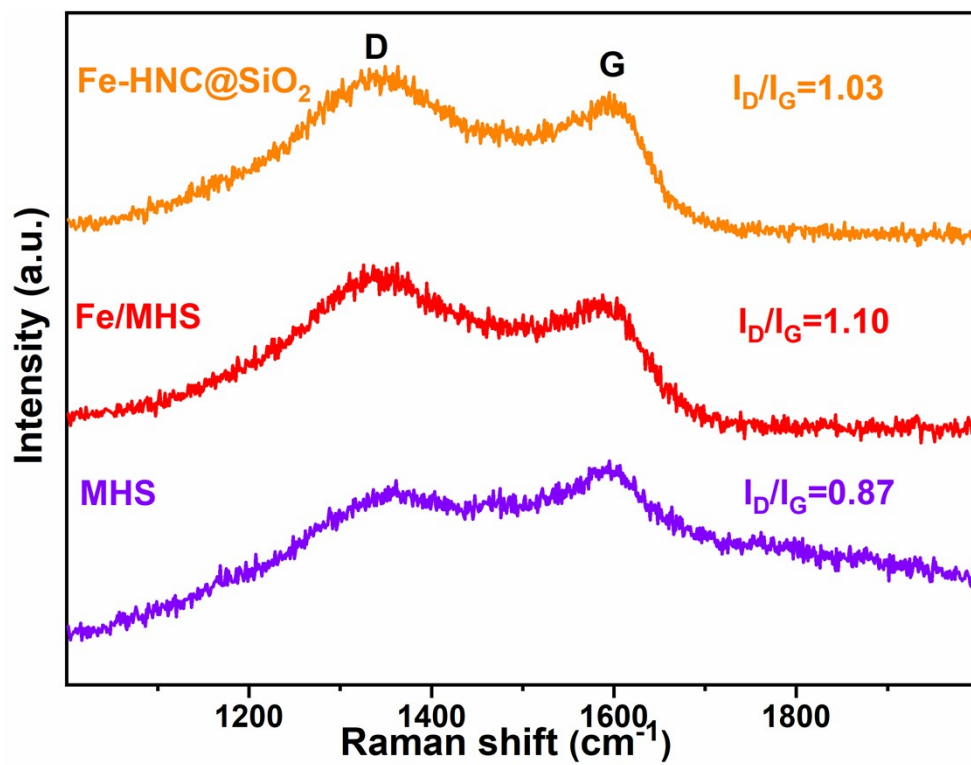
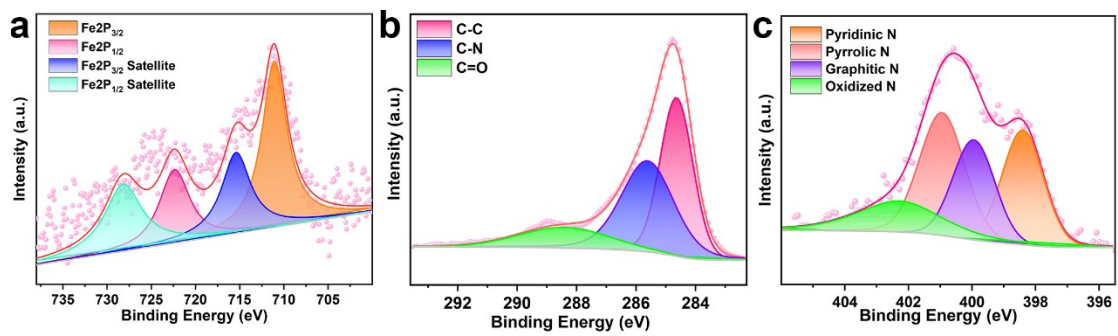
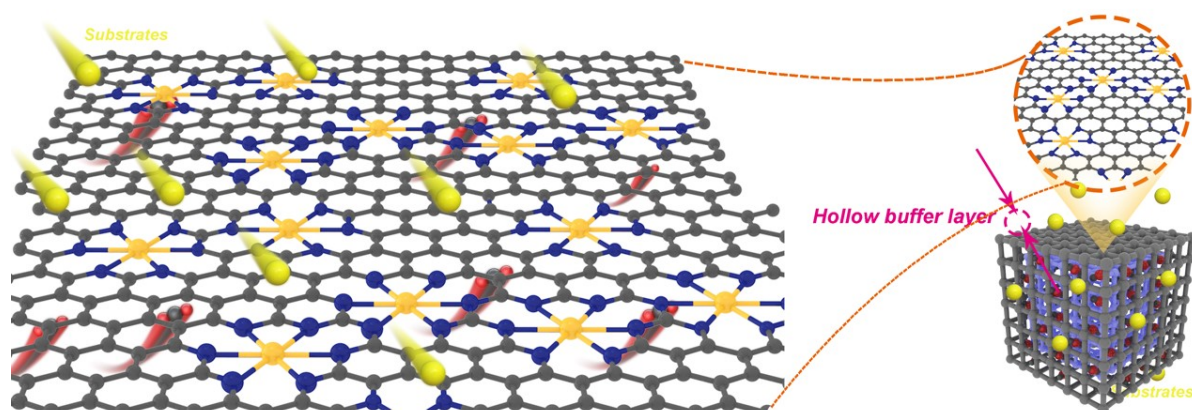


Figure S9. The Raman spectrum of the relative catalysts





**Figure S10.** XPS spectra of Fe/MHS.



**Figure S11.** The schematically demonstrate the accessible active sites of Fe/MHS and the dispersed epoxides and CO<sub>2</sub>.

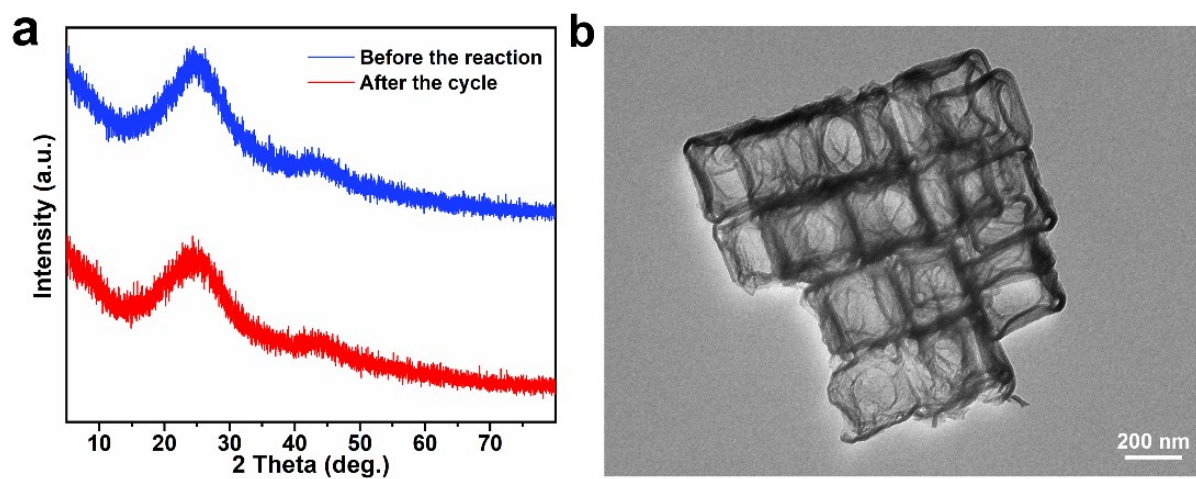


Figure S12. PXR D and TEM images after Fe/MHS recycling.

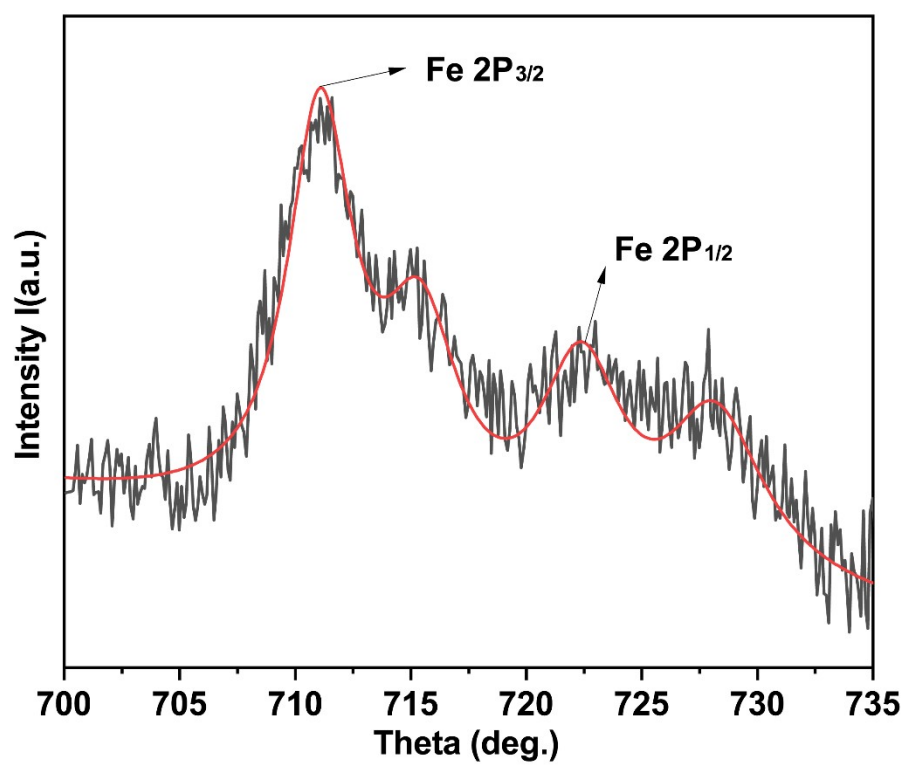


Figure S13. XPS spectrum of Fe 2p of Fe/MHS after recycling test.

**Table S3.** Comparison of cycloaddition catalytic performance of catalysts from different literature

Entry	Catalyst	Pres./ MPa	Temp./ °C	Time/ h	Conv. /%	Ref.
1	Fe/MHS	0.4	90	4	98	This work
2	Fe/NC	0.4	90	4	85	This work
3	MHS	0.4	90	4	41	This work
4	ZIF-8-NC@SiO <sub>2</sub> @Fe-PDA	0.4	90	4	43	This work
5	PIL-diz-RhMOP	1.5	75	6	91	2
8	ZIF-67@ZIF-8	0.7	140	8	84	3
9	HC-FSD	0.3	100	7	92	4
10	PTC-282	0.1	30	24	84	5
11	CuTOS	0.1	90	6	91	6
12	g-C <sub>3</sub> N <sub>4</sub> /SBA-15g	3.5	150	1.5	90	7

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